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Synthesis and Characterization of the First Main Group Oxo-Centered Trinuclear Carboxylate

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Synthesis and Characterization of the First Main Group Oxo-Centered Trinuclear Carboxylate

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We report the synthesis and structural characterization of the first main group oxo-centered, trinuclear carboxylato-bridged species, namely, $[Ga_3(\mu_3\text{-}O)(\mu\text{-}O_2CC_6H_5)_6(4\text{-Mepy})_3]GaCl_4\cdot 4\text{-Mepy}$ (**1**); 4-Mepy is 4-methylpyridine. Compound **1** is a main group example of a well-established class of complexes, referred to as "basic carboxylates" of the general formula $[M_3(\mu_3\text{-}O)(\mu\text{-}O_2CR)_6L_3]^+$, previously observed only for transition metals.[1,2]

Compound **1** was prepared in the following manner. Under argon, a solution of Ga_2Cl_4 (1.25 g, 4.44 mmol) and $C_6H_5CO_2Na$ (1.28 g, 8.88 mmol) in 35 mL of 4-methylpyridine was stirred for 3 days at 25 °C. The mixture was filtered; the resulting light gray residue was washed with hexanes and recrystallized from 4-methylpyridine/hexanes to produce white microcrystalline **1** in 80% yield.[3] Colorless, prismatic crystallographic-quality crystals were obtained by diffusion of hexanes into a 4-methylpyridine solution of $[Ga_3(\mu_3\text{-}O)(\mu\text{-}O_2CC_6H_5)_6(4\text{-Mepy})_3]GaCl_4\cdot 4\text{-Mepy}$ over a period of 1 week.[4]

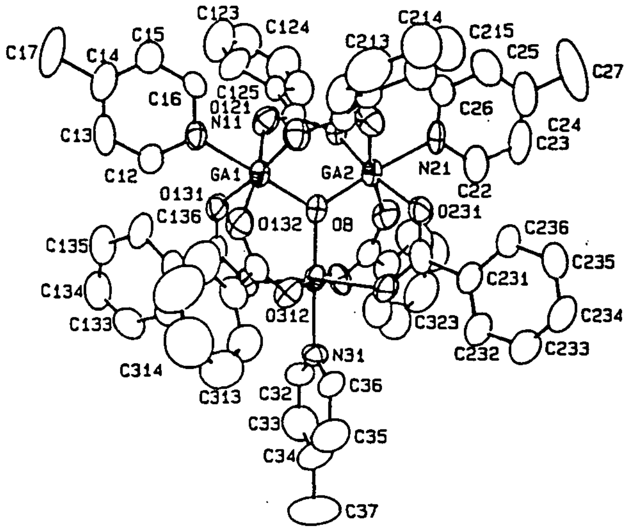

Figure 1. ORTEP drawing of the complex cation $[Ga_3(\mu_3\text{-}O)(\mu\text{-}O_2CC_6H_5)_6(4\text{-Mepy})_3]^+$, showing 50% thermal ellipsoids and the atomic-labeling scheme. Pertinent average bond distances (Å) and angles (deg) are as follows: Ga–O(B), 1.874 (8); Ga–O(benzoates), 1.985 (6); Ga–N, 2.08 (0); Ga⋯Ga, 3.246 (9); C–C, 1.37 (2) Å; C–O, 1.25 (2); Ga–Ga–Ga, 60.0 (3); Ga–Ga–O(B), 30.0 (3); Ga–O(B)–Ga, 120.0 (9); O–C–O, 126 (1); O(B)–Ga–N, 177.6 (9); O–C–C, 117 (2).

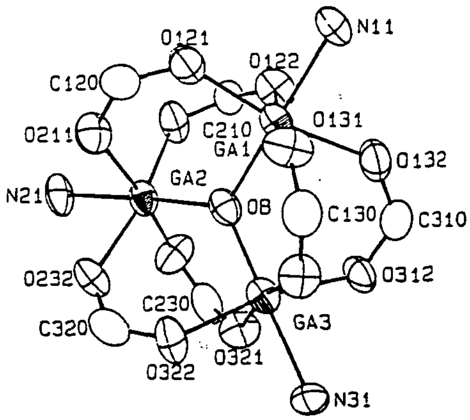

Figure 2. $Ga_3(\mu_3\text{-}O)(\mu\text{-}O_2C)_6N_3$ core of **1** showing the coordination sphere around the gallium atoms.

[†] This work was done while the author held a National Research Council–NASA Research Associateship.

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(3) Analytical results calculated (found) for $C_{60}H_{51}Cl_4Ga_4N_5O_{13}$: C, 49.95 (49.58); H, 3.56 (3.78); Cl, 9.83 (9.6).

(4) A single crystal (0.5 × 0.4 × 0.38 mm) of **1** was sealed in a glass capillary for data collection. Diffraction data were collected at 20 °C on an Enraf-Nonius CAD-4 diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). A total of 5137 independent reflections with $2\theta = 4\text{–}45°$ were collected. Crystal data: monoclinic, space group $P2_1$; $a = 14.398$ (2) Å, $b = 17.638$ (3) Å, $c = 16.215$ (2) Å, $\beta = 113.15$ (1)°; $V = 3786$ (2) Å^3; $Z = 2$; $D_c = 1.347$ g/cm^3; μ(Mo Kα = 16.01 cm^{-1}); $R = 0.057$ ($R_w = 0.067$) for 3776 reflections with $I > 3\sigma(I_o)$; GOF = 1.15.

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The solid-state molecular structure of the complex cation is shown in Figure 1. The central Ga_3O moiety consists of a planar, oxo-centered triangular arrangement of gallium(III) atoms; see Figure 2. The average Ga–Ga–Ga, Ga–Ga–O(B), and Ga–O(B)–Ga angles (see Figure 1) are within experimental error of the angles of an equilateral triangle. The μ_3-O atom is equidistant from the three gallium atoms; the average Ga–O(B) distance is 1.874 (3) Å.[5] Each edge of the Ga_3O core is bridged by two $C_6H_5CO_2^-$ ligands; the three axial positions are occupied by 4-methylpyridine molecules. Thus, each gallium(III) center possesses a slightly distorted octahedral coordination sphere.

The peripheral Ga–O distances range from 1.959 (5) to 2.006 (9) Å, with an average distance of 1.985 (6) Å. The observed distances are comparable to the average Ga–O distances found in other octahedrally-coordinated gallium(III) compounds.[6] The six bridging benzoato groups are equivalent as demonstrated by ^1H and ^{13}C NMR spectroscopy.[7] Within the benzoate groups, the average bond distances and angles are in accord with values reported for related complexes.[8]

As evidenced by Figure 1, there is a distinct difference in the orientation of the three axial 4-methylpyridine ligands around the Ga_3O core. Two of the 4-methylpyridine planes are approximately parallel to the Ga_3O plane; the dihedral angle is 10°. The plane of the third 4-methylpyridine is perpendicular to the plane; the dihedral angle is 90.1°.

Variable-temperature ^1H NMR studies of 1 indicate a rapid interconversion between the two orientations of the axial 4-methylpyridine ligands. At 34 °C, the ^1H NMR spectrum of 1 in solution is consistent with the solid-state structure shown in Figure 1.[7] Two sets of signals, in a 1:2 ratio, are observed for each of the three types of protons in the 4-methylpyridine ligands.[9] Increasing the temperature to 50 °C results in coalescence for each 4-methylpyridine (methyl and α and β ring: 2.63, 9.06, and 7.54 ppm, respectively) proton signal. Finally, as the probe is returned to ambient conditions, the original ^1H NMR spectrum is obtained.

The infrared spectrum[10] of 1, between 800 and 4000 cm^{-1}, is dominated by bands attributable to the organic constituents of the cation.[11] We tentatively assign the strong bands at 1602, 1556, and 1420 cm^{-1} to bridging benzoate groups.[8a] Several IR bands below 800 cm^{-1} may be assigned by analogy to other $[M_3(\mu_3\text{-}O)(\mu\text{-}O_2CR)_6L_3]^+$ complexes.[11] These include an asymmetric stretch at 655 cm^{-1} of the central M_3O unit and the ν_d mode at 500 and 479 cm^{-1} of the MO_4 units. The band at 550 cm^{-1} occurs in almost all trimeric carboxylates and is assigned to a carboxylate mode.[1b,11]

In conclusion, we have observed a new reactivity pattern for Ga_2Cl_4. This simple one-step reaction demonstrates the accessibility of main group carboxylates of the general formula, $[M_3(\mu_3\text{-}O)(\mu\text{-}O_2CR)_6L_3]^+$, and constitutes a starting point in the discovery of related complexes. Investigations into the syntheses, characterization, and applications of related main group carboxylates are currently underway.

Acknowledgment. M.T.A. (Postdoctoral Fellowship, National Research Council/NASA Lewis Research Center), S.A.D. (NASA grant NCC3-162), and A.F.H. (Director's Discretionary Fund) acknowledge support from NASA Lewis Research Center. We thank Dr. David G. Hehemann and Mr. Frederick K. Oplinger of Cleveland State University for the NMR studies of 1.

Supplementary Material Available: Tables of positional parameters, thermal parameters, and bond distances and angles (21 pages); tables of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page. Similar information is also available from A.F.H. at NASA Lewis Research Center.

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(5) Individual Ga–O(B) and Ga–Ga bond distances: Ga(1)–O(B) 1.890 (9), Ga(2)–O(B) 1.866 (9), Ga(3)–O(B) 1.867 (9), Ga(1)–Ga(2) 3.228 (2), Ga(2)–Ga(3) 3.259 (2), and Ga(3)–Ga(1) 3.251 (2) Å.

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(7) NMR data in $CDCl_3$: ^1H δ (ppm) 2.35 (s, 3 H, Me′), 2.67 (s, 6 H, Me), 7.12 (d, 2 H, β'), 7.35 (t, 12 H, meta), 7.48 (t, 6 H, para), 7.61 (d, 4 H, β), 7.84 (d, 12 H, ortho), 8.47 (d, 2 H, α'), 9.09 (d, 4 H, α); ^{13}C δ (ppm) 21.1, 21.7, 124.8, 125.4, 128.4, 130, 132.9, 133, 148.1, 149, 153, 173.5. The unique 4-methylpyridine ligand is indicated by (′).

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(9) The ^1H NMR spectrum of $[Co_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_5(OH)(py)_3]PF_6$ shows similar behavior; see: Sumner, C. E., Jr.; Steinmetz, G. R. *J. Am. Chem. Soc.* **1985**, *107*, 6124–6126.

(10) Infrared data (KBr, cm^{-1}): 3067 (m), 1664 (s), 1625 (vs, br), 1602 (vs, br), 1575 (vs), 1556 (s), 1551 (s), 1546 (s), 1536 (m), 1509 (m), 1495 (s), 1420 (vs, br), 1340 (m), 1329 (m), 1315 (m), 1309 (m), 1233 (m), 1215 (m), 1178 (s), 1070 (s), 1026 (s), 724 (vs), 688 (s), 683 (vs), 655 (vs), 550 (m), 500 (s), 479 (vs).

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ADVANCED MATERIALS FOR OPTICS AND ELECTRONICS, VOL 1, 99–103 (1992)

Room Temperature Synthesis of Copper Indium Diselenide in Non-aqueous Solution Using an Organoindium Reagent

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Reaction of triscyclopentadienylindium with cuprous selenide in 4-methylpyridine at 25 °C produces polycrystalline copper indium diselenide.

KEYWORDS Copper compound Copper indium diselenide Indium compound Low-temperature synthesis Photovoltaic materials Selenides

INTRODUCTION

The very high radiation tolerance,[1] high absorption coefficient and low cost of deposition of polycrystalline $CuInSe_2$ (CIS) and related chalcopyrite semiconductors make this class of materials ideal for thin-film solar cell arrays.[2–4] Another important variable to consider for space applications is the total array mass or power-to-weight ratio.[5] Indeed, the potential for low-cost, high-power-to-weight-ratio, radiation-resistant solar arrays has led to a renewed interest in chalcopyrite semiconductors.[6–9] While considerable savings can be achieved by using thin films for the energy conversion portion of a solar cell, a significant fraction of the mass of a solar cell array is taken up by the substrate. At this point the state-of-the-art CIS solar cell is deposited on Mo-coated glass substrates.[2,6,7] Therefore, to progress further in the achievement of higher power-to-weight ratios, it is essential to consider other substrates.

Potentially useful substrates for CIS solar cells are polymers such as polyimides. The high temperatures of physical deposition techniques precludes the use of polymers in conventional processing. To this end we have embarked on a research program to produce films of CIS at low temperatures using chemical precursors. Because stoichiometry control is very important in producing high-quality devices,[10] a molecular engineering approach should allow for greater control in the synthesis of a desired stoichiometry. Added benefits from this process include use of less hazardous materials in the production process[11] and a simple manufacturing process that may prove important in future *in situ* manufacturing of power systems for space applications.[12] This communication reports preliminary results on a two-phase room temperature synthesis of the chalcogenide CIS that we have discovered recently in the course of our research. We also discuss the impact of our results on the design of potential precursors for thin-film $CuInSe_2$ solar cells.

EXPERIMENTAL

All operations of moisture- and air-sensitive

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materials were performed under an inert atmosphere using a double-manifold vacuum line and standard Schlenk techniques. Solids were manipulated in a Vacuum Atmospheres Co. dry-box equipped with an He-493 dri-train. Solvents were freshly distilled from benzophenone ketyl prior to use. Solutions were transferred via stainless steel cannulae and/or syringes. Copper(I) selenide was purchased from Alfa Products (Danvers, MA) and used without further purification. Triscyclopentadienylindium was prepared according to literature methods.[13] Elemental analysis was conducted by Galbraith Analytical Laboratory (Knoxville, TN). Scanning electron microscopy was done on a Hitachi S 800 microscope. X-ray diffraction (XRD) data were collected using monochromated Cu K_α radiation on a Scintag PAD V and a Philips APD diffractometer.

RESULTS AND DISCUSSION

A typical synthetic procedure is as follows. A mixture of triscyclopentadienylindium (Cp_3In: 0.17 g, 0.548 mmol) and cuprous selenide (Cu_2Se: 0.20 g, 0.9706 mmol) in 15 mL of 4-methylpyridine was stirred for 5 days at 25 °C. During this time the solution gradually changed from faint pink to dark purple. The mixture was filtered and the resulting black solid was dried under vacuum for 14 h to yield 0.07 g of product. Elemental analysis showed the material to have less than 2% carbon and hydrogen.[14] The Cu:In ratio for samples produced is a function of the Cp_3In:Cu_2Se ratio; this is currently under study and will be reported in a full paper.

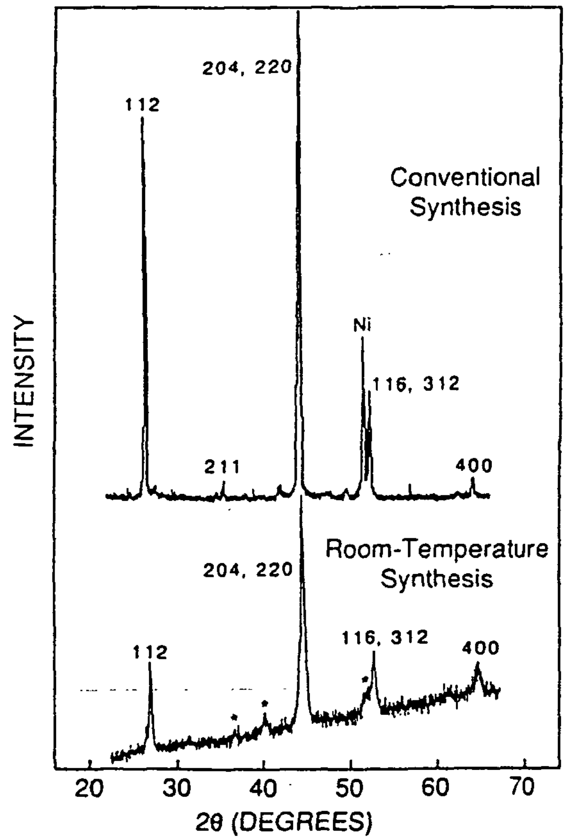

Fig. 1. Comparison of X-ray diffraction powder patterns for a reference sample of $CuInSe_2$ (with an Ni X-ray standard) and a sample produced at room temperature (sample R9) from Cu_2Se and Cp_3In in 4-methylpyridine. Peaks marked with an asterisk could not be matched to any known copper- or indium-containing powder pattern

A comparison between an XRD powder pattern of the material obtained at 25 °C and a reference sample obtained from Johnson-Matthey is shown in Fig. 1. The main points of interest are (1) the low level of crystalline impurity(ies) detected by XRD, (2) the presence of all the major diffraction peaks found for a reference sample of $CuInSe_2$ and (3) the polycrystalline nature of the material produced at 25 °C. Our XRD data are consistent with the chalcopyrite phase, the phase used for electronic devices.[2] Typical morphology of the material is seen in scanning electron micrographs (Fig. 2). The crystallites have a range of size from 5 to 20 μm with a mode of ~ 10 μm. Another feature of the material is the platelet morphology of the particles; this may account for the difference in the intensity ratio of the diffraction peaks in Fig. 1 as compared to the reference sample with more isotropic crystallites. It is not clear from our data whether the particles are single crystals; since XRD detects only crystalline material, amorphous impurities would be undetected. Current efforts are being directed to a more exhaustive chemical analysis of product materials and will be included in a future report.

As mentioned in the Introduction, conventional bulk synthesis or thin-film processing typically occurs at temperatures above 400 °C; examples include direct reaction of the elements (1150 °C)[15] or reaction of H_2Se with deposited thin films of metals (450 °C).[2,6,7] Other methods using simple oxide or sulphate precursors include spray pyrolysis (250 °C)[16] and electrodeposition (25 °C).[17] Recently described preparative methods with chemical precursors include decomposition of a single-molecule precursor (350 °C for $CuInS_2$),[18] reaction of a mixture of Cu and In polyselenides with alkylphosphines or KCN (65–185 °C)[19] and decomposition of a combination of Cu and In polyselenides (450 °C).[20] These methods are inadequate for preparation of space solar cell arrays on polymer substrates because of the temperature regimes required, lack of stoichiometry control or use of chemically corrosive environments.

One measure of the utility of a chemical approach may be made by comparison with a recently reported rapid thermal processing technique using deposited thin films of In, Cu and Se. In this process, the ternary compound was formed at temperatures between 500 and 700 °C; during deposition, the substrate was maintained at a temperature above the melting point of indium

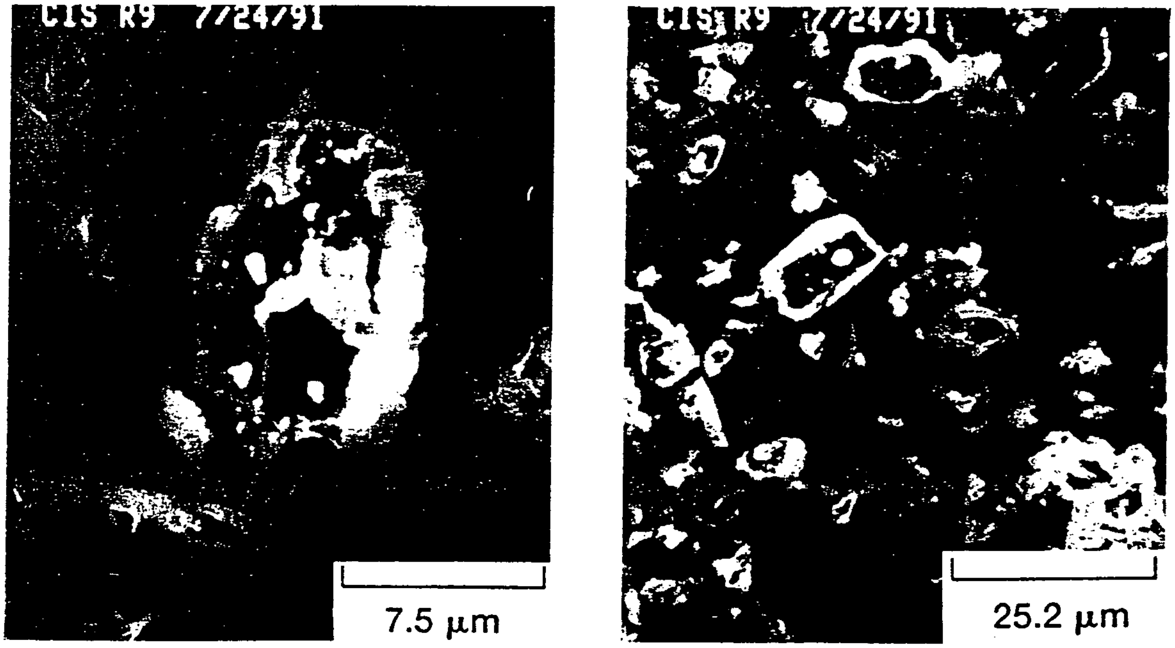

Fig. 2. Scanning electron micrographs of sample R9 at two levels of magnification, showing the range of grain sizes and the morphology of a typical platelet-shape grain

(225 °C).[9] Since this process maintains a low substrate temperature during deposition using only the elements as precursors, a competing chemical approach must be able to produce the ternary at lower temperatures, below the decomposition temperature of a substrate with minimum impurity and maximum metal stoichoimetry and phase control.

At this point the mechanism and byproducts of this reaction are not known. It is possible to write a balanced equation for the reaction:

$$Cp_3In + 2Cu_2Se + 3L \rightarrow CuInSe_2 + 3CpCu(L) \quad 1$$

This metathesis reaction should produce insoluble $CuInSe_2$ a soluble complex[21-23] of the general formula CpCuL, where L is a two-electron donor. There are several difficulties with such a reaction. First, we have not isolated the brown byproduct. Second, as discussed above, the $CuInSe_2$ yield is a function of the Cp_3In:Cu_2Se ratio. Finally, the Cu:In ratio in the product can vary[2] and appears to be a function of the reactants' ratio; at this point we have not determined an optimal Cp_3In:Cu_2Se ratio. We also have not determined the generality of this reaction for other organoindium or gallium compounds.

An alternative mechanism may be the dissolution of the selenide in the coordinating solvent and subsequent reaction with the organoindium compound. This chemistry has been observed for the dissolution of metals[24,25] and solid-state halides and chalcogenides[26] and is an important route to precursors to solid-state materials.[24] Another reaction byproduct may contain all the elements needed to produce $CuInSe_2$ by analogy with the production of CuS from a copper sulphur precursor.[24] Interestingly, we obtained the same CuS precursor as Rauchfuss *et al.*[24] by reaction of S_8 with Cu_2S.[27] Our current efforts are focused on a complete elucidation of the products of this reaction, its mechanism and generality, and the possible isolation of a precursor molecule that produces $CuInSe_2$ at low temperature.

CONCLUSIONS

We have discovered a novel two-phase synthesis of $CuInSe_2$ at 25 °C from Cu_2Se and Cp_3In in 4-methylpyridine. Characterisation of the material produced shows it to be platelet-shaped crystallites with an average particle size of 10 μm, less than 2% C and H, with a small amount of unidentified crystalline impurity. Our results demonstrate that it is possible to produce from solution a material that is ordinarily synthesized in bulk or films at much higher temperatures or using extraneous reagents and/or electrons. A further point of interest is the use of a solid-state reagent as a starting material which is converted to another solid-state comound by an organometallic reagent. This chemistry has tremendous potential to produce precursors for a wide range of solid-state materials of interest to the electronics, defense and aerospace communities. Our results are significant not only for the potential low-temperature production of solid-state materials and use of such materials in chemical synthesis, but also because they stimulate the search for low-temperature precursors to an important class of electronic materials.

ACKNOWLEDGEMENTS

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Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic thermal parameters* (Å^2)

H atoms were refined isotropically. For non-H atoms U_{eq} is defined as one third of the trace of orthogonalized U_{ij} matrix.

	x	y	z	U_{eq}
Ni	0	0	0	0.0403 (2)
S	0.3578 (1)	0	−0.6817 (2)	0.0579 (3)
C	0.2378 (2)	0	−0.4544 (5)	0.0379 (9)
N	0.1510 (2)	0	−0.3003 (5)	0.0529 (10)
N1	0.0835 (2)	0.1862 (3)	0.1599 (4)	0.0527 (8)
H1	0.123 (2)	0.256 (4)	0.054 (5)	0.10 (1)
H2	0.038 (2)	0.252 (4)	0.259 (5)	0.11 (1)
H3	0.128 (2)	0.152 (4)	0.238 (5)	0.10 (1)

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

Ni—N	2.079 (3)	N—C	1.136 (3)
Ni—N1	2.103 (3)	C—S	1.615 (3)
N1—H1	0.86 (3)	N1—H3	0.80 (3)
N1—H2	0.85 (3)		
N—Ni—N1	88.7 (1)	Ni—N—C	175.8 (3)
N—C—S	177.6 (3)		

kina, Dickareva & Jukhnov (1957), but refined structural data were necessary for a study of structure correlations (Jóna, Valach, Gažo, Fendrych & Šramko, 1983), for reactivity studies of solid nickel-(II) complexes (Jóna, Šramko & Gažo, 1975) and for comparison with related [Ni(NCS)$_2L_x$] complexes [L is an N-donor ligand such as ammonia, piperidine (pip) or pyridine (py)], *e.g.* [Ni(NCS)$_2$(pip)$_4$] (Koman, Handlovič, Ďurčanská & Gažo, 1983), [Ni(NCS)$_2$(py)$_4$] (Valach, Sivý & Koreň, 1984) and [Ni(NCS)$_2$(3-ethylpy)$_4$] (Ďurčanská, Jamnický, Koman, Wnęk & Głowiak, 1986), for $x = 4$.

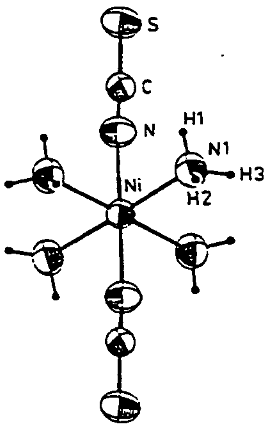

Fig. 1. Molecular structure with atom numbering.

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Acta Cryst. (1993). C49, 536–538

Structure of Bis(4-methylpyridine-*N*)copper(I) Bromide

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Abstract. Bromobis(4-methylpyridine)copper(I), [CuBr(C$_6$H$_7$N)$_2$], $M_r = 329.71$, triclinic, $P\bar{1}$, $a = 9.254$ (7), $b = 9.736$ (3), $c = 7.955$ (3) Å, $\alpha = 102.34$ (3), $\beta = 112.33$ (3), $\gamma = 95.09$ (4)°, $V = 636.2$ (6) Å^3, $Z = 2$, $D_m = 1.8$, $D_x = 1.721$ g cm^{-3}, λ(Mo $K\alpha$) = 0.710326 Å, $\mu = 50.84$ cm^{-1}, $F(000) =$

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0108-2701/93/030536-03$06.00

Table 1. *Positional parameters and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = \tfrac{1}{3}\Sigma_i \Sigma_j B_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	B_{eq}
Br	0.2138 (1)	0.2461 (1)	0.2934 (2)	4.76 (3)
Cu	0.4557 (1)	0.3860 (1)	0.3107 (2)	4.49 (3)
N1*B*	0.4030 (8)	0.5347 (8)	0.179 (1)	3.7 (2)
N1*A*	0.6431 (8)	0.3045 (7)	0.4349 (9)	3.2 (2)
C2*B*	0.513 (1)	0.645 (1)	0.200 (1)	3.8 (2)
C2*A*	0.623 (1)	0.1745 (9)	0.466 (1)	3.7 (2)
C3*A*	0.753 (1)	0.1170 (9)	0.558 (1)	3.8 (2)
C3*B*	0.472 (1)	0.755 (1)	0.124 (1)	4.4 (3)
C4*B*	0.317 (1)	0.7624 (9)	0.024 (1)	3.5 (2)
C4*AA*	1.048 (1)	0.130 (1)	0.722 (1)	4.8 (3)
C4*A*	0.907 (1)	0.190 (1)	0.619 (1)	3.7 (2)
C4*BB*	0.272 (1)	0.890 (1)	−0.050 (1)	5.2 (3)
C5*A*	0.923 (1)	0.319 (1)	0.582 (1)	4.5 (3)
C5*B*	0.204 (1)	0.648 (1)	−0.002 (1)	3.7 (2)
C6*A*	0.790 (1)	0.373 (1)	0.488 (1)	4.3 (2)
C6*B*	0.251 (1)	0.541 (1)	0.078 (1)	4.4 (2)

Table 2. *Bond distances* (Å) *and angles* (°)

Br—Cu	2.455 (2)	C3*A*—C4*A*	1.387 (13)
Cu—N1*B*	1.956 (8)	C3*B*—C4*B*	1.367 (13)
Cu—N1*A*	1.973 (7)	C4*B*—C4*BB*	1.509 (15)
N1*A*—C2*B*	1.349 (12)	C4*B*—C5*B*	1.384 (13)
N1*B*—C6*B*	1.345 (12)	C4*AA*—C4*A*	1.493 (14)
N1*A*—C2*A*	1.353 (12)	C4*A*—C5*A*	1.361 (15)
N1*A*—C6*A*	1.327 (12)	C5*A*—C6*A*	1.389 (14)
C2*B*—C3*B*	1.352 (15)	C5*B*—C6*B*	1.353 (15)
C2*A*—C3*A*	1.388 (13)		
Br—Cu—N1*B*	110.6 (2)	C2*A*—C3*A*—C4*A*	121.4 (9)
Br—Cu—N1*A*	110.4 (2)	C2*B*—C3—CB4	122.2 (9)
N1*B*—Cu—N1*A*	138.7 (3)	C3*B*—C4*B*—C4*BB*	121.8 (9)
Cu—N1*B*—C2*B*	122.8 (6)	C3*B*—C4*B*—C5*B*	116.2 (9)
Cu—N1*B*—C6*B*	120.9 (7)	C4*BB*—C4*B*—C5*B*	122.0 (8)
C2*B*—N1*B*—C6*B*	115.9 (8)	C3*A*—C4*A*—C5*A*	116.3 (8)
Cu—N1*A*—C2*A*	119.7 (6)	C4*AA*—C4*A*—C5*A*	122.3 (9)
Cu—N1*A*—C6*A*	121.8 (6)	C4*A*—C5*A*—C6*A*	121.0 (9)
C2*A*—N1*A*—C6*A*	118.5 (8)	C4*B*—C5*B*—C6*B*	119.4 (8)
N1*B*—C2*B*—C3*B*	121.9 (8)	N1*A*—C6*A*—C5*A*	122.2 (9)
N1*A*—C2*A*—C3*A*	120.5 (8)	N1*B*—C6*B*—C5*B*	124.3 (9)

328, $T = 293$ K, $R = 0.057$, $wR = 0.088$, for 1517 independent observed $[I > 3\sigma(I)]$ reflections. An interesting structural feature of this compound is a distance between Cu atoms of 3.101 (2) Å within the same unit cell compared to a distance of 6.124 (2) Å between Cu atoms of different unit cells.

Experimental. All reactions were performed in a dry box or on a vacuum line under inert atmosphere using standard Schlenk techniques. The title compound was prepared by the reaction of copper(I) bromide–dimethyl sulfide complex with 4-methylpyridine. A solution of copper(I) bromide–dimethyl sulfide [$CuBr{\cdot}S(CH_3)_2$, 0.62 g, 3 mmol] in 25 ml of 4-methylpyridine was stirred for 3 d at 293 K under argon. Filtration and layering of the 4-methylpyridine solution with 30 ml of hexanes produced colorless crystals of the title compound. Density was measured by flotation in dichloromethane and tetrabromoethane.

A single crystal of dimensions 0.37 × 0.31 × 0.23 mm was sealed inside a glass capillary. The determination of the unit cell was accomplished by collecting 25 reflections having $11.62 < \theta < 22.78°$, using an Enraf–Nonius CAD-4 automated diffractometer (Mo $K\alpha$ radiation and graphite monochromator). Intensity data were collected with ω–2θ scans at room temperature in the range $4 < 2\theta < 50°$. The scan rate varied from 2 to 10° min^{-1} with ω-scan width $(1.00 + 0.350\tan\theta)°$. Intensities were corrected for Lorentz–polarization effects and for absorption (North, Phillips & Mathews, 1968), the latter ranging from 0.795 to 1.000; a secondary-extinction correction of the form $F_c = F_c/(1 + gI_c)$ was also applied, with $g = 1.459 \times 10^{-6}$. Three standard reflections, monitored every 60 min, showed 2.6% variation in intensity; decay correction applied. A total of 2381 independent reflections were measured $(0 \le h \le 11, -11 \le k \le 11, -9 \le l \le 9)$, of which 1517 had $I > 3\sigma(I)$ and were used to solve the structure. Positions of Br and Cu atoms were determined by solving a Patterson map. All remaining non-H atoms and most of the H atoms were found by analysis of difference electron density maps and least-squares refinements (on F). The few remaining H atoms were calculated assuming reasonable bond distances and angles. All non-H atoms were refined anisotropically. H atoms had fixed positional and displacement parameters throughout the refinements. The entire structure was refined to convergence to give reliability factors $R = 0.057$, $wR =$

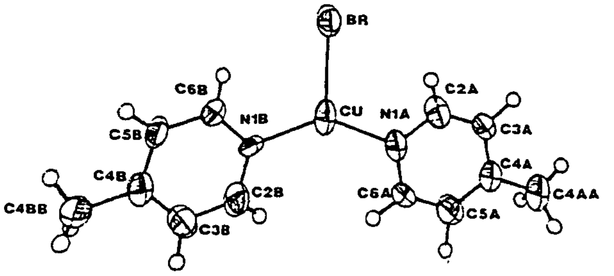

Fig. 1. *ORTEP*II (Johnson, 1976) drawing depicting the stereochemistry of the [$CuBr(C_6H_7N)_2$] complex and the atomic labeling scheme. Thermal ellipsoids are drawn at the 50% probability level. Isotropic H-atom displacement parameters are represented by spheres of arbitrary size.

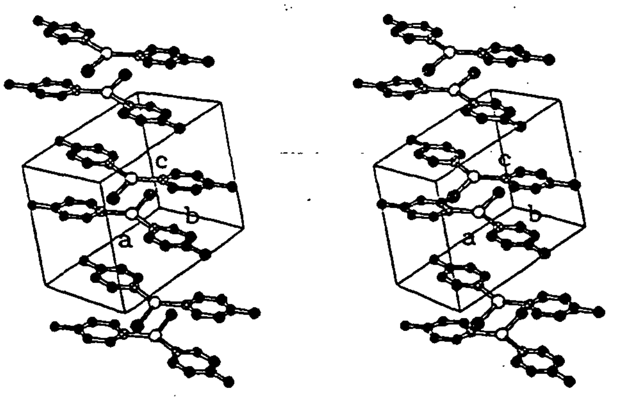

Fig. 2. Stereoview of the packing diagram of the [$CuBr(C_6H_7N)_2$] complex.

0.088 {$w = 4(F_o)^2/[\sigma(F_o)^2]^2$} and quality of fit indicator $S = 2.967$. All shifts of 146 refined parameters were found to be smaller than 0.001σ. The highest peaks remaining on the resulting electron density map, measuring from 0.825 to 0.500 e Å^{-3}, were in the immediate vicinity of the Cu and Br atoms. Atomic scattering factors were taken from Cromer & Waber (1974). All calculations were performed utilizing a PDP-11/60 minicomputer and Enraf–Nonius (1983) *SDP-Plus* software.

Final positional parameters and equivalent isotropic displacement parameters are listed in Table 1. Bond distances and angles between atoms are listed in Table 2.* An *ORTEP*II (Johnson, 1976) drawing and the atomic labeling scheme are shown in Fig. 1. A packing diagram is presented in Fig. 2.

Related literature. X-ray structures of the following two adducts were recently determined: copper(I) bromide with 2-bromopyridine and copper(I) chloride with 2-benzylpyridine (Healy, Kildea, Skelton, Waters & White, 1991).

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* Lists of structure factors, complete bond distances and angles, anisotropic displacement parameters, and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55497 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SP1000]

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Structure of Bis(benzenesulfonato-*O*)tetrakis(pyridine-*N*)copper(II)

3

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Abstract. [Cu($C_6H_5O_3S$)$_2$(C_5H_5N)$_4$], $M_r = 694.29$, monoclinic, $C2/c$, $a = 15.180$ (6), $b = 14.431$ (5), $c = 15.269$ (6) Å, $\beta = 96.38$ (4)°, $V = 3324$ (2) Å^3, $Z = 4$, $D_x = 1.388$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 8.54$ cm^{-1}, $F(000) = 1436$, $T = 295$ K, $R = 0.067$, $wR = 0.087$ for 1141 independent reflections with $I \geq 3\sigma(I)$ and 207 variables. The [Cu($O_3SC_6H_5$)$_2$(C_5H_5N)$_4$] complex has a distorted *trans* octahedral stereochemistry. The bond angles about the Cu atom are consistent with this structure type. The important bond distances and angles are: Cu—O1 2.471 (8), S—C1 1.785 (10) Å, Cu—O1—S 154.1 (6), O1—S—O2 112.3 (5), O1—S—O3 111.5 (5)°.

Experimental. The title compound was prepared by reaction of metallic copper powder with diphenyl disulfide in pyridine solution. Slow diffusion of hexanes into the reaction solution afforded regular prismatic blue crystals at room temperature. A suitable single crystal for X-ray crystallography (0.26 × 0.34 × 0.31 mm) was mounted inside a glass capillary using fast drying epoxy glue. The unit-cell parameters were determined from 25 reflections with $12.78 < \theta < 24.16°$. A total number of 2919 unique reflections with $2 < \theta < 25°$ ($0 \leq h \leq 19$, $0 \leq k \leq 19$, $-19 \leq l \leq 19$) were collected (ω–2θ scans) using an Enraf–Nonius X-ray automated diffractometer with Mo $K\alpha$ radiation and graphite monochromator. Three standard reflections, monitored every 60 min, showed 3.3% variation in intensity; decay correction

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Table 1. *Positional parameters and equivalent isotropic displacement parameters* (Å²)

$$B_{eq} = \tfrac{1}{3}\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cu	0.500	0.2706 (1)	0.750	3.52 (4)
S	0.2518 (2)	0.3020 (2)	0.7643 (2)	3.94 (6)
O1	0.3429 (5)	0.2709 (5)	0.7785 (5)	5.0 (2)
O2	0.2349 (5)	0.3600 (4)	0.6864 (4)	4.9 (2)
O3	0.1913 (6)	0.2266 (5)	0.7668 (6)	7.9 (2)
N1	0.500	0.4106 (6)	0.750	2.7 (2)
N2	0.4680 (6)	0.2701 (5)	0.6180 (5)	3.4 (2)
N3	0.500	0.1316 (6)	0.750	2.8 (2)
C1	0.2396 (7)	0.3728 (7)	0.8581 (6)	4.1 (3)
C1*A*	0.2633 (9)	0.4627 (8)	0.8574 (8)	7.0 (3)
C1*B*	0.4406 (8)	0.0841 (6)	0.7888 (7)	4.4 (3)
C1*D*	0.4281 (7)	0.4577 (6)	0.7073 (7)	4.2 (2)
C1*C*	0.5163 (8)	0.3181 (8)	0.5666 (7)	5.3 (3)
C2*D*	0.4285 (8)	0.5534 (6)	0.7128 (7)	4.9 (3)
C2*A*	0.260 (1)	0.5136 (9)	0.936 (1)	8.7 (5)
C2*B*	0.443 (1)	−0.0117 (7)	0.7952 (9)	6.7 (3)
C2*C*	0.493 (1)	0.318 (1)	0.4764 (8)	8.3 (4)
C3*D*	0.500	0.6016 (8)	0.750	4.7 (4)
C3*C*	0.4253 (9)	0.268 (1)	0.4383 (7)	6.8 (4)
C3*B*	0.500	−0.0582 (9)	0.750	6.2 (5)
C3*A*	0.226 (1)	0.475 (1)	1.001 (1)	12.0 (6)
C4*C*	0.3743 (8)	0.2242 (8)	0.4905 (7)	4.8 (3)
C4*A*	0.199 (2)	0.389 (1)	0.998 (1)	18.5 (7)
C5*C*	0.3976 (7)	0.2263 (7)	0.5799 (6)	4.0 (2)
C5*A*	0.205 (1)	0.3358 (9)	0.9250 (8)	11.3 (5)

Table 2. *Bond distances* (Å) *and angles* (°)

Cu—O1	2.471 (8)	C1—C5*A*	1.31 (2)
Cu—N1	2.020 (9)	C1*A*—C2*A*	1.41 (2)
Cu—N2	2.020 (7)	C1*B*—C2*B*	1.387 (14)
Cu—N3	2.006 (9)	C1*D*—C2*D*	1.384 (13)
S—O1	1.448 (8)	C1*C*—C2*C*	1.38 (2)
S—O2	1.455 (7)	C2*D*—C3*D*	1.359 (12)
S—O3	1.427 (9)	C2*A*—C3*A*	1.30 (3)
S—C1	1.785 (10)	C2*B*—C3*B*	1.35 (2)
N1—C1*D*	1.386 (11)	C2*C*—C3*C*	1.34 (2)
N2—C1*C*	1.327 (14)	C3*C*—C4*C*	1.34 (2)
N2—C5*C*	1.320 (13)	C3*A*—C4*A*	1.30 (3)
N3—C1*B*	1.324 (12)	C4*C*—C5*C*	1.371 (14)
C1—C1*A*	1.346 (15)	C4*A*—C5*A*	1.37 (2)
O1—Cu—O1	180.0 (8)	Cu—N3—C1*B*	121.1 (5)
O1—Cu—N1	89.9 (2)	C1*B*—N3—C1*B*	117.7 (9)
O1—Cu—N2	92.6 (3)	S—C1—C1*A*	119.6 (9)
O1—Cu—N2	87.4 (3)	S—C1—C5*A*	118.5 (9)
O1—Cu—N3	90.1 (2)	C1*A*—C1—C5*A*	122.0 (1)
N1—Cu—N2	90.2 (2)	C1—C1*A*—C2*A*	118.0 (1)
N1—Cu—N3	180.00 (0)	N3—C1*B*—C2*B*	122.0 (1)
N2—Cu—N2	179.6 (3)	N1—C1*D*—C2*D*	117.5 (9)
N2—Cu—N3	89.8 (2)	N2—C1*C*—C2*C*	120.0 (1)
O1—S—O2	112.3 (5)	C1*D*—C2*D*—C3*D*	122.0 (1)
O1—S—O3	111.5 (5)	C1*A*—C2*A*—C3*A*	119.0 (1)
O1—S—C1	103.9 (5)	C1*B*—C2*B*—C3*B*	118.0 (1)
O2—S—O3	113.9 (5)	C1*C*—C2*C*—C3*C*	122.0 (1)
O2—S—C1	107.6 (4)	C2*D*—C3*D*—C2*D*	118.0 (1)
O3—S—C1	106.9 (5)	C2*C*—C3*C*—C4*C*	118.0 (1)
Cu—O1—S	154.1 (6)	C2*B*—C3*B*—C2*B*	120.0 (1)
Cu—N1—C1*D*	119.3 (5)	C2*A*—C3*A*—C4*A*	122.0 (2)
C1*D*—N1—C1*D*	121.3 (9)	C3*C*—C4*C*—C5*C*	119.0 (1)
Cu—N2—C1*C*	120.0 (7)	C3*A*—C4*A*—C5*A*	121.0 (2)
Cu—N2—C5*C*	122.3 (7)	N2—C5*C*—C4*C*	124.0 (1)
C1*C*—N2—C5*C*	117.6 (8)	C1—C5*A*—C4*A*	118.0 (1)

applied. Experimental absorption corrections ranging from 1.00 to 0.98 (North, Phillips & Mathews, 1968) and a secondary-extinction correction of the form $F_c = F_c/(1 + gF_c)$, with $g = 1.511 \times 10^{-10}$, were applied. F_o were corrected for Lorentz and polarization effects. Atomic scattering factors were taken from Cromer & Waber (1974). The structure was solved by the heavy-atom method for the positions of Cu and S atoms. All calculations were performed on a PDP-11 minicomputer utilizing Enraf–Nonius (1983) *SDP-Plus* software. Positions of remaining non-H atoms were determined by least-squares refinements (on F) and difference electron density map analysis. Some H atoms were also found by this procedure; the remaining H-atom positions were calculated assuming standard geometry. The non-H atoms were refined anisotropically; H atoms were not refined. The asymmetric unit contains one half of the structural unit. The atoms N1, N3, C3*D*, C3*B* and the Cu atom reside on a twofold rotation axis in the cell which generates the full structure. The structure was refined to convergence giving $R = 0.067$ and $wR = 0.087$ $\{w = 4(F_o)^2/[\sigma(F_o)^2]^2\}$ with quality of fit indicator $S = 1.893$. All shifts were smaller than 0.001σ. The three largest peaks still evident on the difference electron density map were located in the vicinity of the Cu and S atoms and were less than 0.414 e Å^{-3}. The most negative peak was −0.457 e Å^{-3}. Final positional parameters and equivalent isotropic displacement parameters are supplied in Table 1. Important bond distances and angles are given in Table 2.[*] Fig. 1 shows an *ORTEP* representation (Johnson, 1976) of the whole molecule and also depicts the atomic labeling scheme.

Related literature. X-ray structures of the following copper(II) complexes were recently determined: $[Cu(OSO_2OC_{12}H_{25})_2(N_2C_2H_8)_2]$ (Birker, Crisp & Moore, 1977), $[Cu(O_3SCF_3)_2(C_9H_7N)_4]$ (Al Sarraj, Gouteron, Jeannin & Jeannin, 1987), $[Cu(O_3SCF_3)_2(C_5H_5N)_4]$ (Haynes, Rettig, Sams, Trotter &

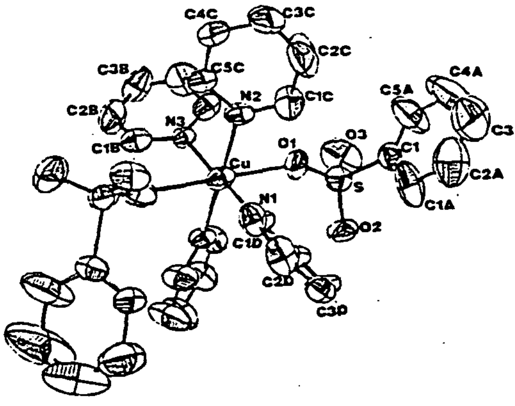

Fig. 1. *ORTEP*II representation (Johnson, 1976) of the *trans*-$[Cu(O_3SC_6H_5)_2(C_5H_5N)_4]$ complex. The ellipsoids are drawn at the 50% probability level.

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[*] Lists of structure factors, complete bond distances and angles, and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55496 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SP1001]

Thompson, 1988) and $[Cu(O_4S)(C_5H_5N)_4]\cdot H_2O$ (Kožíšek, Hricov & Langfelderová, 1989).

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Acta Cryst. (1993). C49, 540–542

Structure of an Allotropic Form of [Bis(trimethylsilyl)amido]dichloro-(η^5-cyclopentadienyl)titanium

4

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Abstract. $[TiCl_2(C_6H_{18}NSi_2)(C_5H_5)]$, $M_r = 344.3$, triclinic, $P\bar{1}$, $a = 8.831\ (4)$, $b = 14.270\ (8)$, $c = 6.774\ (8)$ Å, $\alpha = 91.98\ (8)$, $\beta = 99.33\ (9)$, $\gamma = 85.13\ (5)^\circ$, $V = 839.2\ (8)$ Å^3, $Z = 2$, $D_x = 1.36$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.95$ mm^{-1}, $F(000) = 360$, $T = 185$ K. Full-matrix least-squares refinement based on 1583 reflections led to $R(F_o)$ and $wR(F_o)$ values of 0.042 and 0.053, respectively. The room-temperature unit cell is also triclinic with consistent parameters. This triclinic form is an allotropic modification of the monoclinic $[CpTiCl_2\{N(SiMe_3)_2\}]$ [Bai, Roesky & Noltemeyer (1991). *Z. Anorg. Allg. Chem.* 595, 21–26]. No significant difference is observed in the molecular structure of both forms, characterized by a tetrahedral environment of the Ti atom and a noticeably short [1.881 (6) Å] Ti—N bond.

Experimental. $[CpTiCl_2\{N(SiMe_3)_2\}]$ from $LiN(SiMe_3)_2$ and $CpTiCl_3$ in toluene under nitrogen, recrystallized from toluene solution at 255 K. A moisture-sensitive orange crystal of dimensions 0.40 × 0.20 × 0.05 mm was protected by a film of mineral oil, stuck with Apiezon grease and quickly transferred to the nitrogen gas flow of a cooling device. Intensity data were recorded at 185 K on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Cell dimensions were determined from setting angles of 25 reflections having $3.5 < \theta < 14.1^\circ$. 2277 reflections were measured using $\omega/2\theta$ scans with 2θ from 3 to 44° ($-9 \leq h \leq 9$, $-15 \leq k \leq 15$, $0 \leq l \leq 7$) and scan width $(0.90 + 0.35\tan\theta)^\circ$, with variable scan speed 0.97–8.24° min^{-1}. Intensities of three reflections ($\bar{1}01$, 141, $0\bar{1}\bar{1}$) measured every 2 h showed 3.4% decay, for which correction was made. Corrections were applied for Lp effects, as well as for absorption by ψ scans (North, Phillips & Mathews, 1968); minimum and maximum relative transmission 0.83 and 0.99, respectively. 1925 reflections were unique; $R_{\text{int}} = 0.019$ for averaging redundant $\pm h \pm k\ 0$ reflections. Direct methods followed by Fourier and least-squares techniques using 1583 reflections having $F_o^2 > 3\sigma(F_o^2)$ based on counting statistics, were used to solve the structure. Full-matrix least-squares refinement was based on F_o, minimizing $\sum w(|F_o| - |F_c|)^2$, with anisotropic thermal parameters for non-H atoms. All H atoms were located by ΔF map and included with constrained geometry (C—H = 0.97 Å) and with isotropic U_H kept fixed to 0.05 Å^2. Final $R = 0.042$, $wR = 0.053$, $S = 1.45$, for 154 variables, and with unit weights.† Maximum parameter

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† Lists of structure factors, H-atom parameters and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55570 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1006]

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N atom {[*N*-methyl and 3-(*p*-chlorophenyl)]-3,4-dihydro-1*H*-2,3-benzothiazine 2,2-dioxide, 1.634 (6) and 1.641 (4) Å, respectively (Rivero, Bianchet & Bravo, 1991*b*, 1993)}. The S—N length is considerably shorter than the normal single-bond value of 1.67–1.68 Å, which indicates electron delocalization within the SN group. A search of the July 1991 edition of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) showed that no other 2,3-benzothiazine structures have been reported. However, 1,2-benzothiazines are relatively common (Kojić-Prodić & Ružić-Toroš, 1982; Norris, Berke & Lombardino, 1985; Golič & Leban, 1987).

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Acta Cryst. (1993). C49, 548–550

Structure of 4-Methylpyridinium Bromide

5

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(*Received* 9 *December* 1991; *accepted* 25 *June* 1992)

Abstract. γ-Picolinium bromide, $[C_6H_7NH]Br$, $M_r = 174.05$, monoclinic, Cm, $a = 8.785$ (4), $b = 8.318$ (3), $c = 4.920$ (1) Å, $\beta = 103.62$ (3)°, $V = 349.4$ (4) Å^3, $Z = 2$, $D_x = 1.654$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 57.23$ cm^{-1}, $F(000) = 172$, $T = 293$ K, $R = 0.033$ for 415 reflections with $F_o^2 > 3\sigma(F_o^2)$ and 41 variables. The compound consists of $C_6H_7NH^+$ cations and Br^- anions. Both species reside on crystallographic mirror planes defined by the Br, N(1), C(4), C(7) and H(71) atoms. The Br—N distance is 3.12 (1) Å.

Experimental. The title compound was prepared in the following manner. Under argon, a solution of

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* This work was performed while the author held a National Research Council–NASA Research Associateship.

† Address correspondence to these authors.

copper(I) bromide dimethyl sulfide [$CuBr{\cdot}S(CH_3)_2$] (0.62 g, 3 mmol) and tetraethylthiuram disulfide [$(C_2H_5)_2NCS_2$]$_2$ (0.89 g, 3 mmol) in 25 ml of 4-methylpyridine was stirred for three days at 293 K. Filtration and layering of the 4-methylpyridine solution with 30 ml of hexane afforded colorless crystals of the title compound. A crystal of dimensions 0.52 × 0.31 × 0.22 mm was sealed inside a glass capillary. Cell constants were determined from least-squares refinement of 22 reflections having $18 < \theta < 22°$, using an Enraf–Nonius CAD-4 diffractometer. Intensity data were collected with the ω–2θ scan technique in the range $4 < 2\theta < 55°$. The scan rate varied from 2 to $16° \min^{-1}$ with ω-scan width = $(0.96 + 0.350\tan\theta)°$. Intensities were corrected for Lorentz and polarization effects, and for absorption effects based on the empirical method of Walker & Stuart (1983); relative $T_{\min} = 0.446$, $T_{\max} = 1.000$. Within the index ranges, $0 \leq h \leq 11$, $0 \leq k \leq 10$, $-6 \leq l \leq 6$, 430 unique reflections were collected of which 415 are classified as observed, $F_o^2 > 3\sigma(F_o)^2$. The structure was solved using the Patterson function which revealed the position of the Br atom. The remaining non-H atoms were located and refined, with anisotropic temperature factors, by a series of difference Fourier maps and least-squares refinements on F. The function minimized was $w(|F_o| - |F_c|)^2$ and the weight, w, defined by the Killean & Lawrence (1969) method with terms of 0.020 and 0.1. The H atoms were located from a difference Fourier map and added to the structure-factor calculations, but their positions were not refined. The final refinement parameters are: $R = 0.033$, $wR = 0.043$, $S = 1.540$ and $(\Delta/\sigma)_{\max} = 0.00$. The maximum residual peak in the final difference Fourier map was $0.52\ \mathrm{e}\ \text{Å}^{-3}$. Both absolute structures were refined under identical conditions, and the structure leading to the lower residual values is reported here. The final refinement parameters for the other absolute structure are: $R = 0.035$, $wR = 0.043$ and $S = 1.570$. Atomic scattering factors were taken from Cromer & Waber (1974). Anomalous-dispersion effects were included in F_c (Ibers & Hamilton, 1964); the values for f' and f'' were those of Cromer (1974). Plots of $w(|F_o| - |F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. All calculations were performed on a VAX computer using Enraf–Nonius *MolEN* (Enraf–Nonius, 1990). Final positional parameters and equivalent isotropic thermal parameters are listed in Table 1.* Bond distances and angles are listed in Table 2. The stereochemistry of the molecule is illustrated in the *ORTEP* (Johnson, 1965) drawing in Fig. 1.

Table 1. *Positional and equivalent isotropic thermal parameters and with e.s.d.'s in parentheses*

$$B_{eq} = (1/3)\textstyle\sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Br	0.9	1	−0.2	3.68 (1)
N(1)	0.626 (1)	1	0.106 (2)	3.5 (2)
C(2)	0.5724 (9)	0.8595 (9)	0.178 (2)	4.0 (1)
C(3)	0.4635 (8)	0.8566 (9)	0.329 (2)	3.9 (1)
C(4)	0.402 (1)	1	0.412 (2)	3.3 (2)
C(7)	0.278 (2)	1	0.572 (3)	5.2 (3)
H(21)	0.613	0.763	0.121	5.1†
H(31)	0.427	0.756	0.382	5.0†
H(71)	0.32 (3)	1.000	0.76 (4)	7 (6)†
H(72)	0.213	0.907	0.520	6.8†

† H atoms were included in the structure-factor calculations but were not refined; B(H) = 1.3 × B(C).

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Br—N(1)	3.12 (1)	C(3)—C(4)	1.41 (1)
N(1)—C(2)	1.34 (1)	C(4)—C(7)	1.49 (2)
C(2)—C(3)	1.34 (1)		

Br—N(1)—C(2)	119.2 (5)	C(2)—C(3)—C(4)	121.1 (7)
Br—N(1)—C(2')	119.2 (5)	C(3)—C(4)—C(3')	115.8 (9)
C(2)—N(1)—C(2')	121.4 (9)	C(3)—C(4)—C(7)	122.1 (5)
N(1)—C(2)—C(3)	120.4 (7)		

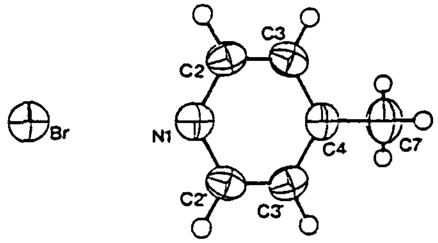

Fig. 1. *ORTEP* (Johnson, 1965) drawing depicting the stereochemistry of the [C_6H_7NH]Br molecule and the atom-labeling scheme. Thermal ellipsoids are drawn at the 50% probability level. Isotropic H-atom thermal parameters are represented by spheres of arbitrary size.

Related literature. ^{1}H NMR spectrum, viscosity and conductance measurements of 4-methylpyridinium bromide (Newman, Tillack, Morgan & Wan, 1977). X-ray structural characterization of piperidinium chloride (Gaudet, Zaworotko & White, 1989).

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* Lists of structure factors, anisotropic thermal parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55540 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0618]

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Acta Cryst. (1993). C49, 550–551

6

Structure of Diphenyl Carbonate

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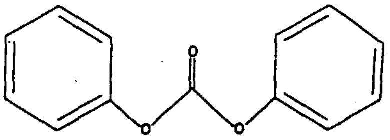
Abstract. Phenyl phenoxyformate, $C_{13}H_{10}O_3$, $M_r = 214.2$, orthorhombic, $P2_12_12_1$, $a = 6.062\,(2)$, $b = 7.242\,(1)$, $c = 23.375\,(4)$ Å, $V = 1026.2$ Å^3, $Z = 4$, $D_x = 1.387$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.92$ cm^{-1}, $F(000) = 448$, $T = 164$ K, $R = 0.0384$ for 1375 unique reflections with $I > 2\sigma(I)$. Diphenyl carbonate constitutes the simplest congener in the aromatic polycarbonate family. The two O—C_{carbonyl} bond lengths are 1.345 (2) and 1.337 (2) Å. The O—C bond length of the carbonyl moiety is 1.191 (3) Å. The two C_{aryl}—O—C_{carbonyl} angles are 118.4 (2) and 118.8 (2)°, while the two O—C_{carbonyl}—O_{carbonyl} angles are 127.5 (2) and 127.8 (2)°. The two benzene rings are canted relative to the plane defined by the carbonate group. The dihedral angles between each benezene ring and the carbonate plane are 52.7 (2) and 57.7 (2)°.



(1)

Experimental. Compound (1), obtained by reaction of phosgene with phenol and triethylamine in methylene chloride, recrystallized from anhydrous ethanol at 298 K. A crystal was sealed in a glass capillary for low-temperature data collection on a Siemens *R3m/V* upgrade of a Nicolet *P3F* automated diffractometer, using Wyckoff scans of variable scan speed. The structure was solved by direct methods and refined on F using the *SHELXTL-Plus* (MicroVAX II) program package (Sheldrick, 1988). H atoms were placed in idealized positions and constrained to have C—H = 0.96 Å and isotropic thermal parameters, $U = 0.08$ Å^2. All non-H atoms were treated as anisotropic. No absorption correction was applied. A correction for secondary extinction of the type described by Zachariasen (1967) refined in the later stages with a maximum correction of 25% for the 041 reflection. There were no apparent groups of

Table 1. *Experimental details*

Crystal	
Habit	Hexagonal rod
Size (mm)	0.52 × 0.24 × 0.24
Lattice-parameters determination	
No. of reflections	22
2θ range (°)	14.8–26.7
Reflection range	
h	−7 to 7
k	−9 to 2
l	−7 to 30
Maximum $\sin\theta/\lambda$ (Å^{-1})	0.650
Check reflections	$\bar{0}1\bar{6}$, $1\bar{1}\bar{3}$
Variation (%)	6, 5
Reflections	
Collected	1495
Unique observed	1375
R_{int}	0.0161
Observed criterion	$I > 2\sigma(I)$
No. of parameters	146
R	0.0384
wR	0.0418
S	1.75
Secondary-extinction parameters, χ, in $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$	0.0032 (5)
Weighting factor, g, in $w^{-1} = \sigma^2(F) + gF^2$	0.0002
Difference Fourier peaks	
Minimum (e Å^{-3})	−0.20
Maximum (e Å^{-3})	0.28
Maximum (Δ/σ)	0.005

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Synthesis, Characterization, and Decomposition of the First Mononuclear Eight-Coordinate Indium(III) Benzoate, $In(\eta^2\text{-}O_2CC_6H_5)_3(4\text{-}Mepy)_2$

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Synthesis, Characterization, and Decomposition of the First Mononuclear Eight-Coordinate Indium(III) Benzoate, $In(\eta^2\text{-}O_2CC_6H_5)_3(4\text{-}Mepy)_2$

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Introduction

The existence of indium and gallium carboxylates is well documented.[1] Numerous homoleptic polynuclear indium(III) carboxylates, $[In(O_2CR)_3]_x$ ($R = H, CH_3, C_2H_5, n\text{-}C_3H_7, (CH_3)_2CH, (CH_3)_3C$),[2] as well as polynuclear organoindium(III) carboxylates, $[R_2In(O_2CR'[Hl])]_x$ ($R = CH_3, C_2H_5$, $R'[Hl] = CH_3, C_2H_5$; $R = n\text{-}C_4H_9$, $R'[Hl] = C_2H_5$)[3] are known; however, there is a void in the literature on analogous indium(III) benzoates. To the best of our knowledge, $Cl_2In(\eta^2\text{-}O_2CC_6H_5)(py)_2$ (py = pyridine), a six-coordinate mononucler species, is the only structurally characterized indium(III) benzoato complex to date.[4]

In this note we report the synthesis and full characterization of the first eight-coordinate mononuclear indium(III) benzoato complex, namely, $In(\eta^2\text{-}O_2CC_6H_5)_3(4\text{-}Mepy)_2$ from the reaction of indium metal with benzoyl peroxide in 4-methylpyridine at 25 °C. The preparation of this indium(III) benzoate is significant in the development of indium(III) carboxylato chemistry since the occurrence of eight-coordinate *mononuclear* indium(III) carboxylates is rare.[5]

Experimental Section

Materials and General Procedures. All operations involving moisture- and air-sensitive materials were performed under an inert atmosphere using standard Schlenk techniques and a double-manifold vacuum line. Solids were manipulated in a Vacuum Atmospheres Co. drybox equipped with a HE-493 Dri-Train. Solvents were freshly distilled from sodium benzophenone ketyl prior to use. Solutions were transferred via stainless steel cannulae and/or syringes. Indium powder (Aldrich) was used without additional purification. Benzoyl peroxide was deareated under vacuum at room temperature. Elemental analyses were performed by Galbraith Microanalytical Laboratories, Inc., Knoxville, TN. NMR spectra were recorded on a Bruker AC300F magnetic resonance spectrometer. The infrared spectrum was obtained from a KBr pellet using a Galaxy FT-IR 4020 spectrophotometer. Thermogravimetric analyses were performed under an atmosphere of nitrogen using a Perkin-Elmer TGS-II. Powder X-ray diffraction (XRD) data were collected using monochromated Cu Kα radiation on a Scintag PAD V and a Phillips APD diffractometer.

Preparation of $In(\eta^2\text{-}O_2CC_6H_5)_3(4\text{-}Mepy)_2$. A mixture of 150-mesh indium powder (0.50 g, 4.35 mmol) and benzoyl peroxide (1.58 g, 6.52 mmol) in 35 mL of 4-methylpyridine was stirred at ambient temperature for 6 days. The mixture was filtered, and the resulting off-white solid was washed with three 25-mL aliquots of hexanes and dried under vacuum for 2 h. Hexane, 150 mL, was added to the bright yellow filtrate to further precipitate the white solid. The supernatant was decanted, and the white solid was washed with two 25-mL aliquots of hexanes and dried under vacuum for 2 h. The solids were combined, recrystallized from 4-methylpyridine/hexanes (v/v 40/70) and dried under vacuum for 18 h. Yield: 53–60%.

Anal. Calcd (found) for $C_{33}H_{29}InO_6N_2$: C, 59.66 (59.34); H, 4.4 (4.52). ^{1}H-NMR (DMSO-d_6): δ 2.33 (s, 6H, Me), 7.28 (d, 4H, β), 7.46 (t, 6H, meta), 7.56 (t, 3H, para), 8.00 (d, 6H, ortho), 8.50 (d, 4H, α). ^{13}C-NMR (DMSO-d_6): δ 20.5, 124.8, 128.2, 129.9, 131.9, 148.0, 149.1, 171.1. IR (KBr disk, cm^{-1}): 3091 (m), 3069 (s), 3058 (m), 3048 (m), 3031 (m), 2926 (m), 1654 (m), 1623 (vs), 1611 (vs), 1600 (vs), 1566 (vs), 1543 (vs), 1507 (vs), 1496 (vs), 1418 (vs, br), 1347 (vs, sh), 1314 (s), 1306 (s), 1234 (vs), 1220 (m), 1175 (s), 1068 (s), 1021 (vs), 868 (vs), 814 (vs), 810 (vs), 721 (vs), 716 (vs), 690 (vs), 642 (m), 542 (m), 492 (vs).

X-ray Crystallography. Colorless single crystals, suitable for X-ray diffraction studies, were grown by slow interdiffusion of hexanes into a 4-methylpyridine solution of $In(\eta^2\text{-}O_2CC_6H_5)_3(4\text{-}Mepy)_2$. Pertinent crystallographic data are summarized in Table I. X-ray diffraction data were collected at 20 ± 1 °C on a 0.38 × 0.38 × 0.31 mm crystal using an Enraf-Nonius CAD-4 diffractometer. Unit cell parameters were determined from least-squares refinement using the setting angles of 25 reflections in the range $20 < \theta < 23°$. Intensity data were collected in the range $4 \leq 2\theta \leq 45°$ by the ω–2θ scan technique. Within index ranges ($-12 \leq h \leq 12$, $0 \leq k \leq 12$, $0 \leq l \leq 27$), 2449 unique reflections were collected, of which 2067 were considered observed, $F_o^2 > 3\sigma(F_o)^2$. Intensities were corrected for Lorentz, polarization, and absorption effects. Systematic monitoring of three representative reflections at regular intervals showed no changes in diffraction intensity.

All calculations were performed on a VAX computer using Enraf-Nonius MolEN.[6] The In atom was located using the Patterson function and was found to reside on a 2-fold rotation axis. The positions of the remaining non-hydrogen atoms were located and refined through a series of difference Fourier maps and full-matrix least-squares refinements. Thermal parameters for all of the non-hydrogen atoms except O(W100) and O(W200) were refined anisotropically. Hydrogen atoms (except water hydrogens) were located from a difference Fourier map and included in the structure factor calculations without refinement. Atomic scattering factors were taken from ref 7. Least-squares refinement of 200 parameters resulted in residuals $R(F_o) = 0.059$ and $R_w(F_o) = 0.079$ and in a quality-of-fit of 2.6. Final positional and thermal parameters are listed in Table II.

Results and Discussion

Oxidation of indium metal by benzoyl peroxide in 4-methylpyridine produces the mononuclear indium(III) benzoate in

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Table I. Crystallographic Data for $In(\eta^2\text{-}O_2CC_6H_5)_3(4\text{-Mepy})_2\text{-}4H_2O$

chem formula $InO_{10}N_2C_{33}H_{37}$	space group $C2/c$ (No. 15)
fw 736.49	$T = 20$ °C
$a = 11.7195(8)$ Å	$\lambda = 0.710\,73$ Å
$b = 11.995(1)$ Å	$\rho_{calc} = 1.373$ g cm^{-3}
$c = 25.407(2)$ Å	$\mu(\text{Mo K}\alpha) = 7.04$ cm^{-1}
$\beta = 94.177(6)°$	$R(F_o)^a = 0.059$
$V = 3562.0(8)$ Å^3	$R_w(F_o)^b = 0.079$
$Z = 4$	

[a] $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F_o) = [\sum w|F_o| - |F_c|]^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Table II. Positional Parameters and Their Estimated Standard Deviations for $In(\mu\text{-}O_2CC_6H_5)_3(4\text{-Mepy})_2\text{-}4H_2O$

atom	x	y	z	B,[a] Å²
In	0	0.10564(5)	1/4	2.52(1)
O(10)	0.0705(4)	0.2736(4)	0.2248(2)	3.6(1)
O(21)	0.1192(5)	0.1312(4)	0.3212(2)	4.0(1)
O(22)	−0.0841(4)	−0.0438(4)	0.1967(2)	3:8(1)
N(31)	0.1466(5)	0.0444(5)	0.1996(2)	3.3(1)
C(10)	0	0.3261(8)	1/4	3.3(2)
C(11)	0	0.4501(8)	1/4	3.0(2)
C(12)	−0.0792(6)	0.5077(6)	0.2769(3)	3.8(2)
C(13)	−0.0790(8)	0.6223(7)	0.2770(5)	5.8(2)
C(14)	0	0.679(1)	1/4	8.9(5)
C(20)	0.1329(6)	0.0289(6)	0.3322(3)	3.2(1)
C(21)	0.2045(6)	−0.0057(6)	0.3801(3)	3.2(1)
C(22)	0.2620(7)	0.0741(7)	0.4122(3)	4.3(2)
C(23)	0.3257(8)	0.0405(9)	0.4568(4)	5.6(2)
C(24)	0.3316(9)	−0.071(1)	0.4698(4)	6.2(2)
C(25)	0.2776(9)	−0.1494(8)	0.4381(4)	5.7(2)
C(26)	0.2139(8)	−0.1161(7)	0.3938(3)	4.4(2)
C(32)	0.2081(7)	0.1106(6)	0.1719(3)	4.1(2)
C(33)	0.2937(8)	0.0699(7)	0.1413(3)	4.9(2)
C(34)	0.3172(7)	−0.0400(7)	0.1392(3)	3.9(2)
C(35)	0.2518(7)	−0.1083(6)	0.1685(3)	3.9(2)
C(36)	0.1688(6)	−0.0645(6)	0.1973(3)	3.5(1)
C(37)	0.4099(9)	−0.0849(9)	0.1084(4)	5.7(2)
O(W100)	0.456(2)	0.330(2)	0.4959(9)	18.6(6)*
O(W200)	0.030(1)	0.001(2)	0.0365(6)	17.3(5)*

[a] Starred values indicate that atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

yields of up to 60% (eq 1). $In(\eta^2\text{-}O_2CC_6H_5)_3(4\text{-Mepy})_2$ can be

$$2In^0 + 3(C_6H_5CO)_2O_2 \xrightarrow[25\,°C]{4\text{-Mepy}} 2In(\eta^2\text{-}O_2CC_6H_5)_3(4\text{-Mepy})_2 \qquad (1)$$

stored under an inert atmosphere at room temperature for extended periods of time. TGA studies show that it is thermally stable up to 100 °C; at this temperature loss of 4-methylpyridine occurs. In contrast, pyridine adducts of indium(III) acetate and formate are unstable, losing pyridine slowly at room temperature.[8]

Single-crystal X-ray diffraction analysis reveals that $In(\eta^2\text{-}O_2CC_6H_5)_3(4\text{-Mepy})_2\text{-}4H_2O$ is composed of an ordered array of discrete mononuclear eight-coordinate molecules positioned on a crystallographic 2-fold rotation axis. Interatomic bond distances and angles are presented in Table III. The solid-state molecular structure of $In(\eta^2\text{-}O_2CC_6H_5)_3(4\text{-Mepy})_2$ is shown in Figure 1.

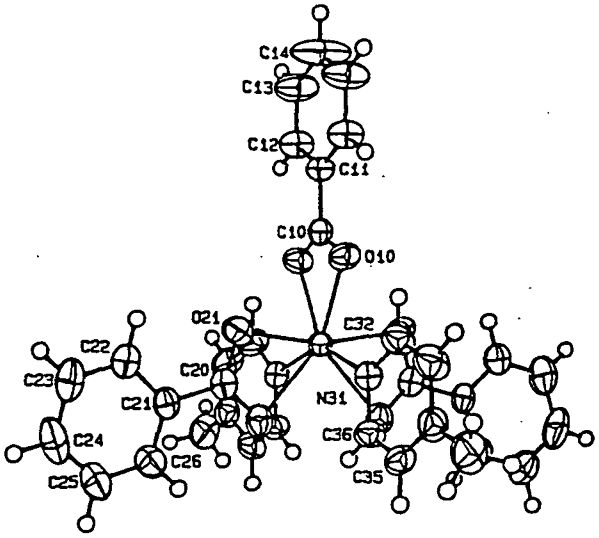

Figure 1. ORTEP drawing of the $In(\eta^2\text{-}O_2CC_6H_5)_3(4\text{-Mepy})_2$ molecule showing 50% thermal ellipsoids and the atomic labeling scheme.

Table III. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $In(\eta^2\text{-}O_2CC_6H_5)_3(4\text{-Mepy})_2\text{-}4H_2O$

In–O(10)	2.286(5)	C(20)–C(21)	1.49(1)
In–O(21)	2.225(6)	C(21)–C(22)	1.40(1)
In–O(22)	2.413(5)	C(21)–C(26)	1.37(1)
In–N(31)	2.335(6)	C(22)–C(23)	1.37(1)
O(10)–C(10)	1.252(7)	C(23)–C(24)	1.37(2)
O(21)–C(20)	1.266(9)	C(24)–C(25)	1.37(2)
O(22)–C(20)	1.252(9)	C(25)–C(26)	1.36(1)
N(31)–C(32)	1.31(1)	C(32)–C(33)	1.40(1)
N(31)–C(36)	1.33(1)	C(33)–C(34)	1.35(1)
C(10)–C(11)	1.49(1)	C(34)–C(35)	1.38(1)
C(11)–C(12)	1.379(9)	C(34)–C(37)	1.49(1)
C(12)–C(13)	1.37(1)	C(35)–C(36)	1.36(1)
C(13)–C(14)	1.37(1)		
O(10)–In–O(10)	56.5(3)	N(31)–In–N(31)	143.3(3)
O(10)–In–O(21)	83.5(2)	N(31)–C(36)–C(35)	123.4(7)
O(10)–In–O(21)	82.5(2)	In–O(10)–C(10)	92.0(5)
O(10)–In–O(22)	129.7(2)	In–O(21)–C(20)	96.2(4)
O(10)–In–O(22)	132.1(2)	In–O(22)–C(20)	87.9(4)
O(10)–In–N(31)	80.1(2)	In–N(31)–C(32)	124.0(5)
O(10)–In–N(31)	136.6(2)	In–N(31)–C(36)	119.1(5)
O(21)–In–O(21)	164.1(3)	C(32)–N(31)–C(36)	116.9(7)
O(21)–In–O(22)	139.9(2)	O(10)–C(10)–O(10)	119 (1)
O(21)–In–O(22)	55.9(2)	O(10)–C(10)–C(11)	120.3(5)
O(21)–In–N(31)	92.6(2)	O(21)–C(20)–O(22)	120.0(7)
O(21)–In–N(31)	92.4(2)	O(21)–C(20)–C(21)	120.5(7)
O(22)–In–O(22)	84.1 (3)	O(22)–C(20)–C(21)	119.5(7)
O(22)–In–N(31)	75.2(2)	N(31)–C(32)–C(33)	122.0(7)
O(22)–In–N(31)	77.7(2)		

The immediate coordination sphere around the central indium(III) atom is best described as a pseudo square pyramid with each bidentate benzoate assuming a single position. The In atom is bound to six oxygen atoms from three equivalent (vide infra) bidendate benzoate groups. The In–O bond distances range from 2.225(6) to 2.413(5) Å. Within the symmetrically independent benzoato ligand, the In–O bond lengths are not equivalent. The In–O(22) bond length, 2.413(5) Å, is slightly longer (by 0.19 Å) than the In–O(21) bond length, 2.225(6) Å. Unsymmetrical bonding of chelating carboxylate groups to an indium(III) center is not unusual. Slight deviations within bidentate carboxylato In–O bond distances are reported for the eight-coordinate complex $In(O_2CMe)_3L$ [L = phen: In–O(21) = 2.370(7) Å and In–O(22) = 2.213(6) Å; In–O(31) = 2.422(7) Å and In–O(32) = 2.224(7) Å. L = bipy: In–O(11) = 2.394(6) Å and In–O(12) = 2.222(6) Å].[5] More pronounced unsymmetrical bonding is found in (acetato)(porphyrinato)indium(III), $(OEP)In(CO_2CH_3)\cdot 2CHCl_3$ (OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinate(2−)). The central indium atom is bound to the acetato group through both oxygen atoms; In–O(1) is 2.60(2) Å and In–O(2) is 2.14(1) Å.[9] Also, in the dimeric μ-oxo-bridged neutral complex $[L_2In_2(CH_3CO_2)_4(\mu\text{-}O)]\cdot 2NaClO_4$ (L = 1,4,7-triazacyclononane), each indium(III) atom is bound to one monodentate and one bidentate acetate group. The two chelating In–O bond

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lengths differ significantly, i.e., 2.14 and 2.87 Å.[10] It should be noted that, in most indium(III) bidentate carboxylato complexes, the In–O bond distances are equivalent within experimental error.[3,4,9] Within the benzoate groups, the bond distances and angles are in accordance with values reported for similar complexes.[4,11]

The central indium(III) atom is also coordinated to two symmetrically equivalent 4-methylpyridine ligands by their N-donor atoms. The In–N(31) bond distance of 2.335(6) Å is comparable to distances found in $In(O_2CMe)_3L$ (L = bipy, 2.325(6) Å; L = phen, 2.335(3) Å)[5] and is significantly longer than values reported for six-coordinate $Cl_2In(O_2CPh)(py)_2$, 2.28(2) Å.[4] Within the 4-methylpyridine ligands, the bond distances and angles are comparable to values reported for related complexes.[4]

The equivalency of the three chelating benzoates and the two 4-methylpyridine ligands is expected for a fluxional pseudo-square pyramidal arrangement. At room temperature, the ^1H-NMR spectrum shows a single pattern for the benzoate groups and 4-methylpyridine ligands (cf. Experimental Section).

A common reactivity/bonding characteristic of indium(III) complexes is the expansion of the indium(III) atom coordination sphere through polymerization or adduct formation.[2,3,8,12] In the case of indium(III) carboxylates (of which $In(\eta^2\text{-}O_2CC_6H_5)_3(4\text{-}Mepy)_2$ is an example), the coordination number of the indium(III) atom generally increases to 6 or 8 via polymerization of the $[In(OOCR)_3]$ units—oxygen atoms from adjacent carboxylate molecules bridge the units, creating infinite $[In(OOCR)_3]_n$ chains. In $In(\eta^2\text{-}O_2CC_6H_5)_3(4\text{-}Mepy)_2$ the presence of the two methylpyridine ligands prevents such polymerization by coordinatively saturating the indium(III) atom, resulting in the formation of a mononuclear eight-coordinate indium(III) benzoato species.

Thermal decomposition of $In(\eta^2\text{-}O_2CC_6H_5)_3(4\text{-}Mepy)_2$ was followed by TGA, and the composition of the final pyrolysate was determined by XRD. No attempt was made to identify the intermediate pyrolysates produced during this analysis. The first two steps in the thermogram (see Figure 2) correspond to the sequential loss of the two 4-methylpyridine ligands. The final weight loss corresponds to complete decomposition of $In(\eta^2\text{-}O_2CC_6H_5)_3(4\text{-}Mepy)_2$ to In_2O_3, as demonstrated by the X-ray powder diffraction pattern (Table IV).[13,14] The material is more than 90% crystalline In_2O_3, consistent with scanning electron microscopy, X-ray powder data, and thermal analysis.

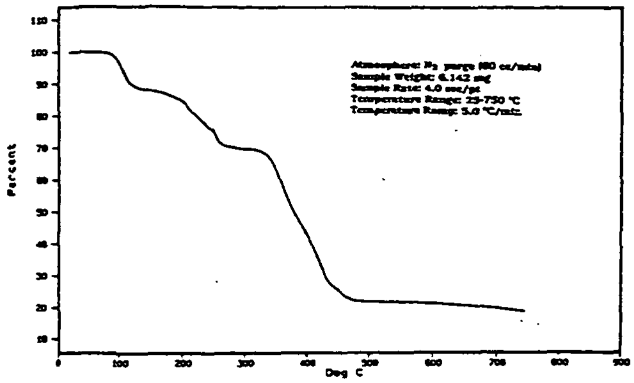

Figure 2. Thermogravimetric analysis of $In(\eta^2\text{-}O_2CC_6H_5)_3(4\text{-}Mepy)_2$ under an atmosphere of nitrogen. Theoretical values for weight changes: 86%, $[In(O_2CC_6H_5)_3(4\text{-}Mepy)_2 - (4\text{-}Mepy)]$; 72%, $[In(O_2CC_6H_5)_3(4\text{-}Mepy)_2 - 2(4\text{-}Mepy)]$; 21%, $In_2O_3/In(O_2CC_6H_5)_3(4\text{-}Mepy)_2$.

Table IV. X-ray Diffraction (XRD) Powder Pattern for Pyrolysate, In_2O_3, between 1.20 and 5.00 Å

angle, 2θ, deg	d, Å	I/I_{max}, %	angle, 2θ, deg	d, Å	I/I_{max}, %
21.522	4.126	1.18	59.200	1.56	8.30
30.750	2.905	100.00	60.675	1.525	58.17
35.510	2.53	35.19	52.222	1.491	13.16
37.725	2.383	3.48	63.700	1.46	12.67
41.895	2.155	11.72	65.198	1.43	4.85
45.710	1.983	6.64	68.030	1.377	8.11
49.302	1.847	3.11	69.475	1.351	5.16
51.115	1.786	65.64	73.745	1.284	5.63
52.745	1.734	2.99	75.102	1.264	8.50
56.075	1.638	7.54	76.272	1.247	7.92

Concluding Remarks

In summary, we have demonstrated a simple and direct one-step route to $In(\eta^2\text{-}O_2CC_6H_5)_3(4\text{-}Mepy)_2$, the first mononuclear eight-coordinate indium(III) benzoate and precursor to indium(III) oxide. Our approach to the synthesis of indium(III) carboxylates differs significantly from previously reported methods.[1-12] The presence of 4-methylpyridine at the initial stages of reaction precludes $In(O_2CR)_3$ polymerization by coordinatively saturating the indium(III) center as it is formed. In addition, we have established that $In(\eta^2\text{-}O_2CC_6H_5)_3(4\text{-}Mepy)_2$ is a stable inorganic precursor to indium oxide. A thorough discussion of material and thin-film preparation and characterization is forthcoming.

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, complete bond lengths and angles, anisotropic thermal parameters, torsion angles, and hydrogen atom locations (6 pages). Ordering information is given on any current masthead page. Supplementary material may also be obtained from A.F.H. of the NASA Lewis Research Center.

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[13] The diffraction pattern was matched with that of In_2O_3 in the JCPDS International Centre for Diffraction Data, 1989: Powder Diffraction File No. 6-0416.

[14] Chemical analysis showed total C, H, and N content below the detection limit.

8

Copper-Containing Ceramic Precursor Synthesis: Solid-State Transformations and Materials Technology

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COPPER-CONTAINING CERAMIC PRECURSOR SYNTHESIS: SOLID-STATE TRANSFORMATIONS AND MATERIALS TECHNOLOGY

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ABSTRACT

Three copper systems with relevance to materials technology are discussed. In the first, a CuS precursor, Cu_4S_{10}(4-methylpyridine)$_4$ (4-MePy), was prepared by three routes: reaction of Cu_2S, reaction of CuBr•SMe_2 and oxidation of copper powder with excess sulfur in 4-methylpyridine by sulfur. In the second, copper powder was found to react with excess thiourea ($H_2NC(S)NH_2$) in 4-methylpyridine to produce thiocyanate (NCS^-) complexes. Three isolated and characterized compounds are: Cu(NCS)(4-MePy)$_2$, a polymer, [4-MePy•H][Cu(NCS)$_3$(4-MePy)$_2$], a salt, and t-Cu(NCS)$_2$(4-MePy)$_4$. Finally, an attempt to produce a mixed-metal sulfide precursor of Cu and Ga in N-methylimidazole (N-MeIm) resulted in the synthesis of a Cu-containing polymer, Cu(SO_4)(N-MeIm). The structures are presented; the chemistry will be briefly discussed in the context of preparation and processing of copper-containing materials for aerospace applications.

INTRODUCTION

The chemical and physical properties of copper have resulted in its use going back to ancient times [1]. Current technological applications include thin-films of the metal in electronics [2], use of sulfides and mixed-metal chalcogenides in photovoltaics [3], and as a component of the recently-discovered high-temperature ceramic superconductors [4]. All three of these technologies offer research opportunities for chemists and materials scientists involved in materials fabrication and processing.

Due to the critical importance of copper as an interconnect metal in microelectronics, there has been an international effort to produce selective chemical vapor deposition (CVD) precursors [5-8]. Also, the lack of a simple, effective dry etch for copper has resulted in a large effort to understand mechanisms for copper etching in heterogeneous systems [9-12]. Other areas of active chemical research relevant to copper include: the search for precursors for copper-containing materials such as $CuInQ_2$ (Q = S or Se) [13,14] for thin-film photovoltaics; rare-earth, bismuth, and thallium ceramic superconductors, such as $YBa_2Cu_3O_{7-x}$, $Bi_2Sr_2Ca_2Cu_2O_8$, and $Tl_2Ba_2Ca_2Cu_3O_{10}$ and related metal-doped compounds for numerous applications [15,16]; and the synthesis of catalysts for the chemical and petroleum industries [17]. In our efforts to prepare new copper-containing precursors for aerospace applications, we have discovered a number of new compounds and new chemistry. We highlight selected reaction chemistry and the relevant structures.

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EXPERIMENTAL

All operations of moisture- and air-sensitive materials were performed under an inert atmosphere using standard Schlenk techniques and a double-manifold vacuum line. Solids were manipulated in a Vacuum Atmospheres Co. drybox equipped with an HE-493 dri-train. Copper, thiourea ($H_2NC(S)NH_2$) and sulfur (Aldrich), and $CuBr{\bullet}SMe_2$ (Alfa) were used without additional purification. The synthesis of $[((CH_3)_3C)_2Ga(\mu\text{-}SH)]_2$ is described in [18]. The instrumental details are given in [18].

RESULTS AND DISCUSSION

In 1990, Rauchfuss et. al. reported that the reaction of Cu with S_8 in pyridine (C_5H_5N,Py), (1), produces the cluster $Cu_4S_{10}(Py)_4{\bullet}Py$, where Py is a solvent of crystallization in the solid-state structure[20]. We report here that carrying out the reaction in 4-methylpyridine produces the cluster Cu_4S_{10}(4-methylpyridine)$_4{\bullet}$4-methylpyridine (4-MePy) (1) whose Cu_4S_{10} cluster unit is the same as that of the Rauchfuss compound. The 4-methylpyridine cluster (1) can also be prepared by other routes. In fact, compound (1) was first produced by the reaction of Cu_2S with excess sulfur in 4-methylpyridine as shown in equation (2). It has also been prepared according to equation (3) in which $CuBr{\bullet}SMe_2$ reacts with S_8. The stucture of compound (1) was determined by x-ray crystallography. The structure determination shows that this compound consists of two pentasulfide chains linking four Cu(I) ions each with a coordinating 4-methylpyridine and has approximate S_4 symmetry. The structure of (1) is shown in figure 1. Selected structural parameters are given in table 1.

$$Cu^0 + S_8 \xrightarrow[25\ ^\circ C]{4\text{-Mepy}} Cu_4S_{10}(4\text{-MePy})_4 \qquad (1)$$

$$Cu_2S + S_8 \xrightarrow[25\ ^\circ C]{4\text{-Mepy}} Cu_4S_{10}(4\text{-MePy})_4 \qquad (2)$$

$$CuBr{\bullet}SMe_2 + S_8 \xrightarrow[25\ ^\circ C]{4\text{-Mepy}} Cu_4S_{10}(4\text{-MePy})_4 \qquad (3)$$

Computer enhancement of a featureless electronic absorption spectrum yielded a single peak in the near ultraviolet (λ = 334 nm, ε= 10,000), most likely an intraligand transition [21]. Cyclic voltammetry indicates that (1) undergoes an irreversible oxidation and reduction at -0.25 and -0.58 V vs. SCE, respectively, at 298K in 4-methylpyridine when swept at 20mV/sec. It is logical to conclude that oxidation takes place at the copper atoms, destabilizing tetrahedral geometry, leading to decomposition. Reduction is most likely to occur at the polysulfide ligands, leading to the decomposition of the cluster through the production of smaller S_x^{2-} units.

The compound seems to form quite readily in systems of Cu(I)-polysulfide chemistry. Similar reaction conditions with other metals did not produce analogs of (1), but instead produced $[M(N\text{-}MeIm)_6]S_8$ for M = Mg, Mn, Fe, and Ni, (N-MeIm) = N-methylimidazole ($N(CH_3)NC_3H_3$) [22]. However, Cu_2S also served as a starting material for the production of the N-MeIm analog of (1), (2) [22]. The pyridine analog of compound (1) was found to produce CuS quite readily at 200 °C by Rauchfuss et al. [20]. Its facile formation but ease of decomposition seems to be a result of the metastability of Cu(I); even moderate temperatures, by solid-state processing standards drives the redox chemistry of Cu^+ and S_x^{2-} to form CuS.

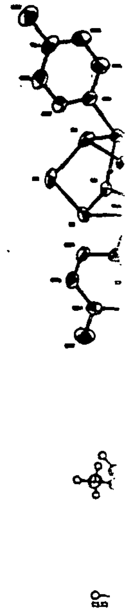

Figure 1. - (

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Compound

a, Å

b, Å

c, Å

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β

γ

V, Å^3

Z

form. weigh

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λ

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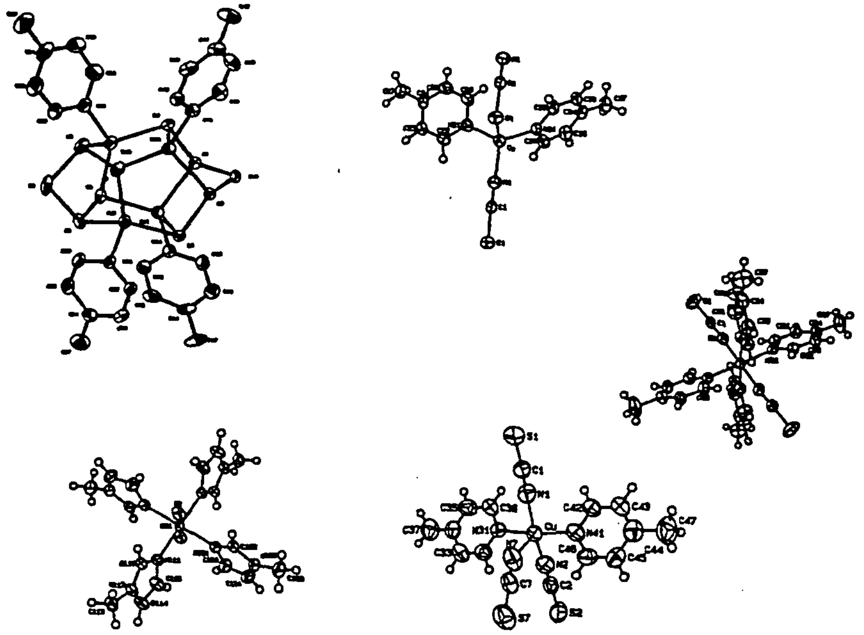

Figure 1. - ORTEP drawings of compounds (1) - (5). The thermal ellipsoids enclose 50 % of electron density. Compounds are shown clockwise with (1) in upper left-hand corner.

TABLE 1. X-RAY DATA SUMMARY FOR COPPER COMPOUNDS

Compound	(1)	(2)	(3)	(4)	(5)
a, Å	13.983 (2)	8.4138 (8)	14.656 (1)	16.070 (1)	9.0754 (6)
b, Å	15.384 (2)	5.8127 (7)	15.635 (2)		9.9729 (7)
c, Å	9.660 (1)	14.459 (2)	14.390 (1)	16.070 (1)	12.745 (2)
α	93.87 (1)°				98.342 (9)°
β	93.38 (1)°	106.783 (9)°	112.886 (7)°		95.367 (9)°
γ	99.78 (1)°				114.153 (5)°
V, $Å^3$	2037.9 (9)	677.0 (3)	3038.0 (1)	2381 (2)	1026.3 (4)
Z	2	2	4	3	2
form. weight	1040.42 g	307.88 g	611.31 g	620.31 g	488.02 g
space group	P1bar (#2)	$P2_1$ (#4)	Cc (#9)	R3 bar (#148)	P1bar (#2)
T	-120 °C	-70 °C	20 °C	-70 °C	20 °C
λ	0.71069	0.71073	0.71073	0.71073	0.71073
ρ_{calc}, g/cm^3	1.695	1.510	1.337	1.297	1.579
μ(Mo Kα)	25.89 cm^{-1}	17.49 cm^{-1}	9.45 cm^{-1}	8.29 cm^{-1}	12.03 cm^{-1}
$R(F_o)^a$	0.026	0.028	0.043	0.071	0.031
$R_w(F_o)^b$	0.036	0.037	0.053	0.090	0.038

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[a] $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $R_w(F_o) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Other copper and sulfur containing compounds were obtained when thiourea ($H_2NC(S)NH_2$) instead of S_8 was reacted with copper metal. The reaction of copper powder with thiourea produced thiocyanate compounds, of which three were isolated and characterized. The three characterized products are: $Cu(NCS)(4\text{-}MePy)_2$ (2), $t\text{-}Cu(NCS)_2(4\text{-}MePy)_4{\bullet}(4\text{-}MePy)_{2/3}(H_2O)_{1/3}$ (3), and $[4\text{-}MePy{\bullet}H][Cu(NCS)_3(4\text{-}MePy)_2]$ (4) figure 1. Compound (2) has been previously structurally characterized [23]. The formation of these compounds is a function of the ratio of thiourea to metal. Compounds (2) and (3) were isolated for a ratio of 2:1, (4), while (4) was isolated in a reaction with an 5:1 ratio, equation (5).

$$Cu^0 + 2\,H_2NC(S)NH_2 \xrightarrow[140\ ^\circ C]{4\text{-}Mepy} (2) + \text{“O”} \xrightarrow[25\ ^\circ C]{4\text{-}Mepy} (3) \qquad (4)$$

$$Cu^0 + 5\,H_2NC(S)NH_2 \xrightarrow[140\ ^\circ C]{4\text{-}Mepy} [4\text{-}MePy{\bullet}H][Cu(NCS)_3(4\text{-}MePy)_2] \qquad (5)$$

The first step in this reaction may be attack of thiourea of Cu^0 (6) to produce hydrogen where thiourea acts like an acid on copper. The $H_2NC(S)NH^-$ species can then rearrange to produce NCS^- and NH_3. As discussed above, highly basic solvents promote the reaction of metals with sulfur. Another process that is likely is an acid/base reaction of thiourea with the solvent followed by rearrangement to produce NH_3 and NCS^- (7). The reaction does not occur at room temperature in 4-MePy or in boiling Py. The presence of both NCS^- and 4-MePy in the coordination sphere suggests a concerted reaction mechanism. A second oxidation step is indicated by the presence of two NCS^- ligands around the Cu(II) species, (3) and (4).

$$Cu^0 + H_2NC(S)NH_2 \xrightarrow[140\ ^\circ C]{4\text{-}Mepy} Cu^+ + 1/2\,H_2 + H_2NC(S)NH^- \qquad (6)$$

$$H_2NC(S)NH_2 \xrightarrow[140\ ^\circ C]{4\text{-}Mepy} [4\text{-}MePy{\bullet}H][NCS] + NH_3 \qquad (7)$$

While (6) and (7) are reasonable proposed reactions, we have not as yet obtained direct evidence of hydrogen or NH_3 formation. Work is currently underway to observe these by-products. It should be noted that acidic solutions of thiourea are used to remove copper encrustations from boilers by dissolution of the copper materials. In this case the mechanism is acid solubilization of copper species with stabilization of Cu(I) species by thiourea [24]. Dry etching of Cu remains a challenge; solution systems offer a low-cost alternative.

Finally, an attempt to produce a mixed-metal sulfide precursor of Cu and Ga by reaction of $CuBr{\bullet}SMe_2$ and $[((CH_3)_3C)_2Ga(\mu\text{-}SH)]_2$in N-methylimidazole (N-MeIm), reaction (8), resulted in the synthesis of a Cu-containing polymer, $Cu(SO_4)(N\text{-}MeIm)_4$ (5), figure 1 and table 1.

$$CuBr{\bullet}SMe_2 + [((CH_3)_3C)_2Ga(\mu\text{-}SH)]_2 + \text{“O”} \xrightarrow[25\ ^\circ C]{N\text{-}MeIm} Cu(SO_4)(N\text{-}MeIm)_4 \qquad (8)$$

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It is apparent that an oxidizing impurity led to the formation of the sulfate. Interestingly, this species has not been previously structurally characterized. We have previously observed similar chemistry. In an attempt to oxidize Cu powder with diphenyldisulfide in pyridine, the only isolable species that we characterized was $Cu(C_6H_5SO_3)_2(Py)_4$ (6) [25]. The presence of the phenyl ring in (6) precludes polymerization and results in isolated molecules in the solid-state structure. Compound (5) can also be compared to an analogous compound$Cu(SO_4)(Py)_4{\bullet}H_2O$ that is polymeric but linked through hydrogen bonds through the sulfate groups [26]. A one-dimensional structure such as (5) may have relevance for molecular magnets [27]. There are recent reports of In/Cu chalcogenide precursor molecules that were used to produce $CuInQ_2$ (Q = S or Se), a material used in thin-film solar cells [13,14].

CONCLUSIONS

In the process of investigating reactions of copper and its compounds with sources of sulfur for aerospace applications, we have observed some interesting new chemistry and obtained structural characterization of a number of the compounds produced. The structure determinations found that the nature and degree of linkage of the copper atoms of these precursor materials varies. One of the compounds has a cluster structure while another has a copper coordination unit linked in a polymeric chain. In a third compound, the Cu atoms of neighbors are associated through a weak CuNCS-Cu interaction. The remaining two compounds described have discrete molecular units containing a single Cu atom. The varying chemistries that we observed when reacting copper and low-valent copper compounds with sources of sulfur show that these systems are very sensitive to reaction conditions and are driven to produce Cu(II) species. This experience will hasten the discovery of useful materials precursors and processing for applications.

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Redetermination of Piperidinium Hydrogen Sulfide Structure

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ABSTRACT

The presence of adventitious water in a reaction between dicyclopentamethylenethiuram-disulfide $(C_5H_{10}NCS_2)_2$ and a picoline solution of tricyclopentadienylindium(III) $(C_5H_5)_3In$ resulted in the formation of piperidinium hydrogen sulfide ($C_5H_{13}NS$). The piperidinium hydrogen sulfide produced in this way was unambiguously characterized by X-ray crystallography. The structure determination showed that the piperidinium hydrogen sulfide crystal (MW = 119.23 g/mol) has an orthorhombic (*Pbcm*) unit cell whose parameters are: a = 9.818 (2), b = 7.3720 (1), c = 9.754 (1) Å, V = 706.0 (3) $Å^3$, Z = 4. $D\chi$ = 1.122 g cm^{-3}, Mo $K\alpha$(λ= 0.71073Å), μ= 3.36 cm^{-1}, F(000) = 264.0, T = 293 K, R = 0.036 for 343 reflections with $F_o^2 > 3\sigma(F_o^2)$ and 65 variables. The compound consists of $[C_5H_{10}NH_2]^+$ cations and $[SH]^-$ anions with both species residing on crystallographic mirror planes. N-H ··· S hydrogen bonding contributes to the interconnection of neighboring piperidinium components of the compound.

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Introduction

Pyridinium and piperidinium salts and their derivatives have been of interest for a number of years because of their physico-chemical properties. Of particular interest is their behavior as low temperature (sometimes even room temperature) melts. These compounds are most commonly prepared by treating a pyridine or piperidine derivative with the appropriate acid as is shown for piperidine in equation 1. In the course of carrying out reactions in pyridine and picoline (4-methylpyridine) solvent systems, we have observed the production of salts of this type through different routes.

$$C_2H_{10}NH + HX \rightarrow \left[C_5H_{10}NH_2\right]^+X^- \qquad (1)$$

For example, reacting tetraethylthiuram disulfide $[(C_2H_5)_2NCS_2]_2$ with a picoline (C_6H_7N) solution of copper(I) bromide dimethylsulfide $[CuBr \cdot S(CH_3)_2]$ in the absence of rigorous drying produces picolinium bromide (Andras et. al., 1993). In a similar vein, we now report that reacting dicyclopentamethylenethiuram disulfide $(C_5H_{10}NCS_2)_2$with a picoline solution of tricyclopentadienylindium(III) $[(C_5H_5)_3In]$ in the absence of rigorous drying gives piperidinium hydrogen sulfide $[C_5H_{10}NH_2]HS$. This product was unambiguously characterized by X-ray crystallography. This preparation and X-ray crystallographic analysis of piperidinium hydrogen sulfide are detailed in the following sections.

Experimental

Piperidinium hydrogen sulfide cystals were prepared in the following manner. Under argon, a solution of tricyclopentadienylindium(III), $(C_5H_5)_3In$, (0.25 g, 0.806 mmol) and dicyclopentamethylenethiuram disulfide, $(C_5H_{10}NCS_2)_2$ (0.62 g, 1.61 mmol) in 35 mL of 4-methylpyridine was stirred for six days at 20° C. Subsequent filtration and layering of the 4-methylpyridine solution with hexanes afforded colorless crystals of the piperidinium salt.

A crystal of dimensions 0.32 x 0.25 x 0.25 mm was sealed inside a glass capillary and mounted on an Enraf-Nonius CAD-4 diffractometer which produced graphite-monochromated Mo Kα radiation. Cell constants were determined from least-squares refinement of 25 reflections having $13 < \theta < 19^o$. Intensity data were collected with the ω-2θ scan technique with $4 < 2\theta < 45^o$; the scan rate varied from 1 to 16^o min^{-1}. Three standard reflections measured every 5000 sec. revealed no significant intensity loss. Intensities were corrected for Lorentz and polarization effects; an absorption correction was not applied. Within index ranges ($0 \leq h \leq 10$, $O \leq k \leq 10$, $O \leq l \leq 7$), 572 unique reflections were collected of which 343 are classified as observed, $F_o^2 > 3\sigma(F_o^2)$. Calculations were performed on a VAX computer using Enraf-Nonius *MolEN* (Enraf-Nonius,1990). All non- H atoms were located using SHELX-86 (Sheldrick, 1986). The H atoms were located from a difference map and refined isotropically.

The structure was refined by full-matrix least-squares on F and the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The weight, w, was defined by the Killean and Lawrence method with terms of 0.020 and 0.1 (Killean & Lawrence, 1969). The final refinement parameters are: R = 0.036, wR = 0.044, S = 1.364, $(\Delta/\sigma)_{max} = 0.06$. The maximum residual peak in the final difference Fourier map was 0.16 e $Å^{-3}$. Atomic scattering factors were taken from Cromer and Waber (1974). Anomalous dispersion effects were included in F_c (Ibers & Hamilton, 1964); the values for f' and f'' were those of Cromer (1974). Plots of $w(|F_o| - |F_c|)^2$ versus $|F_o|$ reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends.

Further details of the crystallographic analysis are given as supplemental material in Appendix A.

Results and Discussion

The crystallographic analysis of the product of the reaction between tricyclopentadienylindium(III) and dicyclopentamethylenethiuram disulfide produced the ORTEP (Johnson,1965) drawing of the piperidinium hydrogen sulfide molecule shown in Fig. 1. Final positional and equivalent isotropic thermal parameters are listed in Table 1. Bond distances and angles are listed in Table 2. The structure of piperidinium hydrogen sulfide consists of chains of piperidinium hydrogen sulfide connected by N-H • • • S hydrogen bonding. Both the cationic and anionic species of the compound reside on crystallographic mirror planes with the S, N, H(N), C(3), H(1), H(31) and H(32) atoms located in these planes. The piperidinium ring adopts the chair conformation in this structure. The structural data clearly indicates that the compound which was isolated from the reaction between tricyclopentadienylindium(III) and dicyclopentamethylene-thiuram disulfide is piperidinium hydrogen sulfide. Furthermore, the data is consistent with that for piperidinium hydrogen sulfide prepared by a different route (Smail & Sheldrick, 1973).

Conclusions

This technical memorandum describes the formation of piperidinium hydrogen sulfide in a reaction quite different from the reactions usually used to produce this type of compound. The piperidinium hydrogen sulfide product was characterized by X-ray crystallography. Although crystallographic data for the title compound were previously reported (Smail & Sheldrick, 1973): Pmab, a = 9.77 (1), b = 7.30 (2), c = 9.84 (1) A, R = 0.075 and wR = 0.078, we have included a description of the structure determination because it describes a more accurate determination of the structure of this compound.

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TABLE 1

Positional and Equivalent Isotropic Thermal Parameters with e.s.d.'s for $[C_5H_{10}NH_2][SH]$.

$$B_{eq} = (1/3)\Sigma_i\Sigma_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
S	0.1731(1)	0.0373(2)	1/4	3.96(2)
N	0.1358(4)	0.0446(6)	3/4	3.96(9)
C(1)	0.1941(4)	-0.0358(5)	0.6236(4)	5.30(9)
C(2)	0.3456(4)	-0.0071(5)	0.6229(5)	6.8(1)
C(3)	0.4090(6)	-0.0875(9)	3/4	8.5(2)
H(1)	0.153(5)	0.310(7)	1/4	8(1)*
H(N)	0.035(6)	0.033(7)	3/4	7(1)*
H(11)	0.146(4)	0.040(5)	0.547(4)	8(1)*
H(12)	0.168(3)	-0.184(5)	0.628(4)	7.2(9)*
H(21)	0.361(3)	0.143(5)	0.616(4)	7.3(9)*
H(22)	0.387(5)	-0.081(6)	0.532(4)	11(1)*
H(31)	0.397(6)	-0.233(9)	3/4	10(2)*
H(32)	0.499(8)	-0.09(1)	3/4	12(2)*

* Refined isotropically

TABLE 2

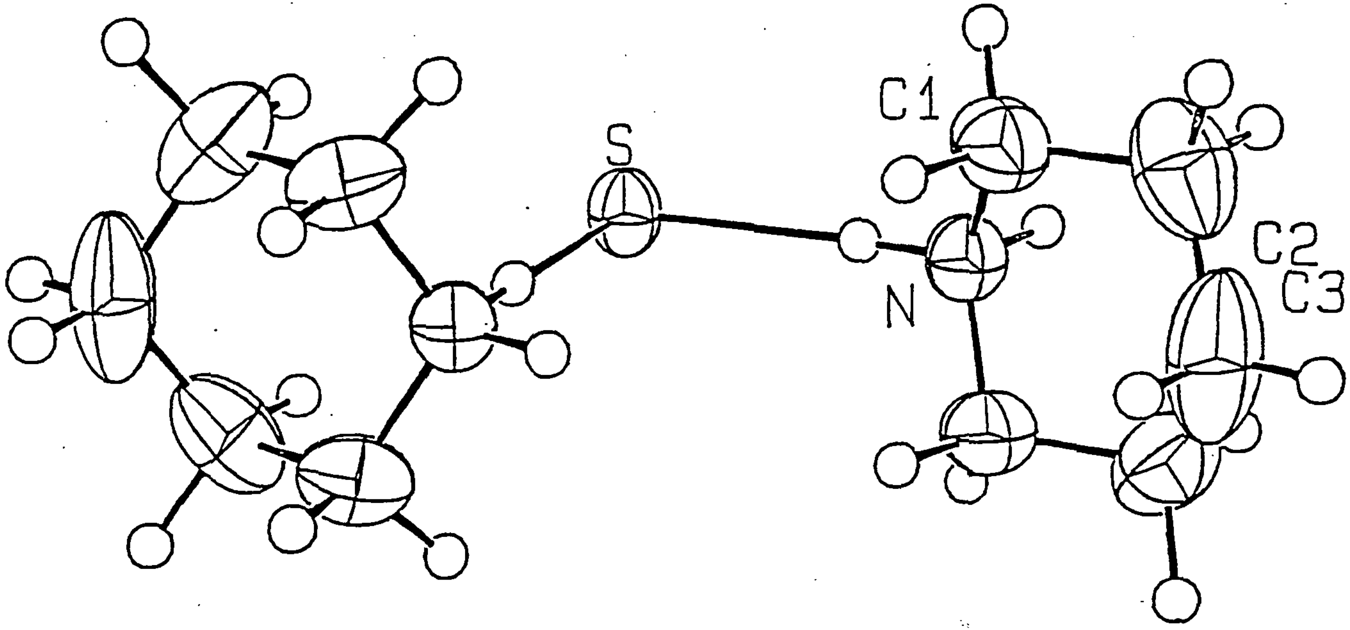
Bond lengths (Å) and angles (°) with e.s.d's
for $[C_5H_{10}NH_2][SH]$.

S-H(1)	2.02(7)	C(1)-H(12)	1.12(4)
S-H(N)	2.11(7)	C(2)-C(3)	1.508(7)
N-C(1)	1.482(5)	C(2)-H(21)	1.12(5)
N-H(1)	1.09(7)	C(2)-H(22)	1.11(5)
N-H(N)	0.99(7)	C(3)-H(31)	1.08(8)
C(1)-C(2)	1.503(7)	C(3)-H(32)	0.9(1)
C(1)-H(11)	1.05(5)		

H(1)-S-H(N)	99(2)	C(11)-C(2)-H(21)	106(2)
C(1)-N-C(1)'	112.5(5)	C(1)-C(2)-H(22)	107(3)
C(1)-N-H(1)	110(1)	C(3)-C(2)-H(21)	113(2)
C(1)-N-H(N)	111(2)	C(3)-C(2)-H(22)	108(3)
H(1)-N-H(N)	104(4)	H(21)-C(2)-H(22)	113(3)
N-C(1)-C(2)	109.3(4)	C(2)-C(3)-C(2)'	110.6(6)
N-C(1)-H(11)	102(3)	C(2)-C(3)-H(31)	110(2)
N-C(1)-H(12)	106(2)	C(2)-C(3)-H(32)	115(3)
C(2)-C(1)-H(11)	112(3)	H(31)-C(3)-H(32)	94(7)
C(2)-C(1)-H(12)	111(2)	S-H(1)-N	177(5)
H(11)-C(1)-H(12)	116(3)	S-H(N)-N	171(5)
C(1)-C(2)-C(3)	110.4(5)		

FIGURE 1

ORTEP (Johnson, 1965) drawing of the $[C_5H_{10}NH_2][SH]$ compund showing the atomic-labeling scheme. Thermal ellipsoids are drawn at the 50% probability level while isotropic hydrogen *thermal parameters are represented by sphere of arbitrary size.*



Appendix A

Supplemental data from the structural determination of $[C_5H_{10}NH_2][SH]$. $10{*}F_{obs}$ and $10{*}F_{calc}$

```
     10*Fobs and 10*Fcalc for [NC5H12](HS)                                                               Page  1

 H K L  Fobs  Fcalc     H K L  Fobs  Fcalc     H K L  Fobs  Fcalc     H K L  Fobs  Fcalc     H K L  Fobs  Fcalc
 . . .  ----  -----     . . .  ----  -----     . . .  ----  -----     . . .  ----  -----     . . .  ----  -----

 0 2 0  1083   1322     8 4 0    64     64     1 2 2   238    233     1 2 3    89     92     1 7 4   161    155
 0 4 0   406    406     8 5 0    83     83     1 3 2   235    219     1 3 3   337    323     2 0 4    71     76
 0 6 0    64     65     9 0 0   114    109     1 4 2   127    124     1 5 3   141    142     2 1 4   201    211
 1 0 0   144    141     9 2 0    79     77     1 5 2   210    210     2 1 3   193    181     2 3 4   277    269
 1 2 0   194    194     0 2 1   382    359     1 7 2   143    141     2 3 3    91     90     2 5 4   199    205
 1 3 0   121    120     0 4 1   303    297     2 0 2   171    167     2 4 3    54     48     2 7 4   114    116
 1 4 0   123    127     0 6 1   183    179     2 1 2   226    224     2 6 3    49     54     3 0 4   386    381
 1 5 0   137    142     1 1 1   285    329     2 2 2   152    149     3 1 3   219    214     3 1 4    49     50
 1 7 0   104    111     1 2 1    82     85     2 3 2   324    304     3 2 3    27     27     3 2 4   303    306
 2 0 0   657    685     1 6 1    49     55     2 4 2    90     92     3 3 3    80     79     3 3 4    54     51
 2 1 0   215    218     2 1 1   400    376     2 5 2   233    234     3 4 3   106    104     3 4 4   153    152
 2 2 0   463    457     2 2 1   110    106     2 7 2   123    126     3 6 3    86     88     4 0 4   150    141
 2 3 0   347    357     2 3 1   178    169     3 0 2   550    538     4 1 3   245    238     4 1 4    86     85
 2 4 0   215    215     2 4 1   145    149     3 1 2    44     44     4 2 3    35     35     4 2 4    92     93
 2 5 0   250    244     2 6 1   123    124     3 2 2   404    376     4 3 3   168    165     4 3 4   164    161
 2 6 0    60     58     3 1 1   252    253     3 3 2    27     32     4 5 3    66     65     4 5 4   162    166
 2 7 0   125    115     3 2 1   167    163     3 4 2   166    166     5 1 3   240    236     4 6 4    37     32
 3 0 0   624    612     3 3 1    45     50     4 0 2   277    277     5 2 3    86     86     5 0 4    54     56
 3 1 0    36     36     3 4 1   173    169     4 1 2    46     48     5 3 3   145    146     5 1 4    64     70
 3 2 0   412    394     3 6 1   136    144     4 2 2   171    171     5 4 3    97     95     5 2 4    41     44
 3 4 0   158    161     4 1 1   167    167     4 3 2   130    129     5 5 3    62     68     5 3 4   135    138
 3 7 0    37     24     4 2 1    25     25     4 4 2    56     58     5 6 3    60     60     5 5 4   131    136
 4 0 0   584    601     4 3 1   184    178     4 5 2   149    153     6 1 3   164    163     6 0 4    69     71
 4 2 0   329    318     4 5 1    88     91     4 7 2   116    115     6 2 3    38     32     6 2 4    71     75
 4 3 0    61     61     5 2 1   201    202     5 0 2   227    226     6 3 3   102     99     6 4 4    41     41
 4 4 0   110    113     5 4 1   197    202     5 1 2    86     83     6 4 3    75     74     6 5 4    41     32
 4 5 0   113    113     5 6 1   124    124     5 2 2   144    150     6 5 3    43     36     7 0 4   183    186
 4 7 0    95     95     6 2 1    47     49     5 3 2   163    160     6 6 3    82     76     7 1 4    55     55
 5 0 0   404    413     6 4 1   103    104     5 4 2    41     56     7 1 3   263    265     7 2 4   133    139
 5 1 0    90     91     6 6 1   112    112     5 5 2   145    145     7 3 3   159    159     7 3 4   105    105
 5 2 0   242    243     7 1 1   165    173     6 0 2   196    194     7 5 3    57     54     7 4 4    64     58
 5 3 0   176    175     7 3 1    83     88     6 2 2   172    172     8 2 3    51     51     7 5 4    96     97
 5 4 0    84     76     8 1 1    85     90     6 4 2   109    109     8 4 3    79     73     8 3 4    33     29
 5 5 0   143    144     8 2 1    80     84     7 0 2   126    124     9 1 3    62     67     9 0 4   121    119
 6 0 0   407    396     8 3 1    84     88     7 1 2    59     57     9 2 3    49     57     9 2 4    92     95
 6 1 0    51     50     8 4 1   107    109     7 2 2    85     82     9 3 3    57     53     0 2 5    33     31
 6 2 0   325    319     8 5 1    50     51     7 3 2   109    110    10 1 3   108    109     0 4 5    55     54
 6 3 0    78     81     9 1 1    49     48     7 5 2   102     97     0 0 4   173    179     0 6 5    43     44
 6 4 0   201    200     9 2 1    63     63     8 0 2    69     70     0 2 4   126    121     1 1 5   291    294
 6 5 0    56     51     9 3 1    44     46     8 2 2    59     61     0 6 4    37     47     1 2 5    43     35
 6 6 0    79     73     9 4 1    74     77     8 3 2    45     46     1 0 4   239    233     1 3 5   197    196
 7 1 0    53     51    10 1 1   121    123     9 0 2   132    126     1 1 4   142    140     1 5 5    85     88
 7 3 0   100    104     0 0 2   876    940     9 2 2   103     97     1 2 4   221    214     2 1 5   117    117
 7 5 0    86     86     0 2 2   543    521     0 2 3   100     97     1 3 4   270    264     2 3 5    59     62
 8 0 0   125    129     0 4 2   171    171     0 4 3   110    104     1 4 4   118    117     2 5 5    31     13
 8 2 0   107    111     1 0 2   261    256     0 6 3    68     70     1 5 4   246    248     2 6 5    39     38
 8 3 0    59     62     1 1 2   107    103     1 1 3   579    572     1 6 4    39     37     3 1 5   135    125
```

Appendix A (cont.)

Supplemental data from the structural determination of $[C_5H_{10}NH_2][SH]$.
$10*F_{obs}$ and $10*F_{calc}$

```
10*Fobs and 10*Fcalc for [NC5H12](HS)                                                                          Page  2

H  K  L   Fobs  Fcalc     H  K  L   Fobs  Fcalc     H  K  L   Fobs  Fcalc     H  K  L   Fobs  Fcalc     H  K  L   Fobs  Fcalc
-  -  -   ----  -----     -  -  -   ----  -----     -  -  -   ----  -----     -  -  -   ----  -----     -  -  -   ----  -----

3  3  5     45     45     6  0  6    162    160     6  0  8    140    135
3  4  5     79     83     6  2  6    135    134     6  2  8    115    111
3  6  5     70     75     6  4  6     77     76     0  4  9     73     71
4  1  5    199    201     7  0  6     73     75     2  1  9     39     47
4  3  5    137    137     7  2  6     60     57     2  2  9     33     36
4  5  5     60     54     7  3  6     58     57     2  3  9     31     37
5  1  5    138    140     8  0  6     74     67     3  2  9     34     36
5  2  5     59     56     8  2  6     60     58     4  1  9     51     47
5  3  5    100     97     0  2  7     70     74     0  0 10    102    104
5  4  5     73     69     0  4  7     97    104     0  2 10     78     81
5  5  5     50     48     1  2  7     29     23     1  0 10     56     51
6  1  5    144    146     2  1  7     81     83     1  2 10     46     41
6  3  5     95     93     2  2  7     44     53     2  0 10     40     40
6  4  5     56     59     2  3  7     63     61     3  0 10     88     90
6  5  5     40     34     2  4  7     76     73
7  1  5    166    170     2  5  7     34     30
7  3  5    106    103     3  2  7     71     71
9  1  5     43     47     3  4  7     92     91
0  0  6    375    374     4  1  7    104     97
0  2  6    270    268     4  3  7     74     74
0  4  6    116    122     4  5  7     43     35
1  0  6    153    153     5  2  7     63     61
1  1  6     71     68     5  4  7     83     80
1  2  6    127    129     6  2  7     36     41
1  3  6    140    143     6  3  7     34     16
1  4  6     70     66     7  1  7     51     56
1  5  6    137    138     0  0  8    316    321
2  0  6    132    138     0  2  8    243    244
2  1  6     73     70     0  4  8    123    122
2  2  6    118    116     1  0  8     95     94
2  3  6    134    132     1  2  8     73     75
2  4  6     65     67     1  3  8     48     48
2  5  6    120    122     1  4  8     31     35
3  0  6    252    252     1  5  8     53     52
3  2  6    201    200     2  0  8    153    147
3  4  6     95     96     2  1  8     30     28
4  0  6    127    128     2  2  8    124    117
4  1  6     35     36     2  3  8     67     70
4  2  6     86     89     2  4  8     62     61
4  3  6     84     85     3  0  8    174    179
4  4  6     33     35     3  2  8    134    139
4  5  6     91     92     3  4  8     64     65
5  0  6     77     77     4  0  8     85     94
5  1  6     44     46     4  2  8     70     72
5  2  6     54     57     5  0  8    103    103
5  3  6     97     96     5  2  8     82     81
5  5  6     95     93     5  3  8     49     54
```

Appendix A (cont.)

Supplemental data from the structural determination of $[C_5H_{10}NH_2][SH]$.

Table of Atomic Multiplicities

Name	Multiplicity	Name	Multiplicity	Name	Multiplicity
S	1.000	N	1.000	C(1)	2.000
C(2)	2.000	C(3)	1.000	H(1)	1.000
H(N)	1.000	H(11)	2.000	H(12)	2.000
H(21)	2.000	H(22)	2.000	H(31)	1.000
H(32)	1.000				

Appendix A (cont.)

Supplemental data from the structural determination of $[C_5H_{10}NH_2][SH]$.

Table of Torsion Angles in Degrees

Atom 1	Atom 2	Atom 3	Atom 4	Angle
H(N)	N	C(1)	C(2)	176.77 (2.68)
H(N)	N	C(1)	H(11)	58.48 (3.44)
H(N)	N	C(1)	H(12)	-63.49 (3.18)
N	C(1)	C(2)	C(3)	56.92 (0.45)
N	C(1)	C(2)	H(21)	-65.11 (1.91)
N	C(1)	C(2)	H(22)	174.46 (2.43)
H(11)	C(1)	C(2)	C(3)	168.79 (2.22)
H(11)	C(1)	C(2)	H(21)	46.76 (2.91)
H(11)	C(1)	C(2)	H(22)	-73.68 (3.28)
H(12)	C(1)	C(2)	C(3)	-59.53 (1.96)
H(12)	C(1)	C(2)	H(21)	178.44 (2.69)
H(12)	C(1)	C(2)	H(22)	58.00 (3.11)
C(1)	C(2)	C(3)	H(31)	65.04 (3.02)
C(1)	C(2)	C(3)	H(32)	170.27 (4.93)
H(21)	C(2)	C(3)	H(31)	-177.19 (3.53)
H(21)	C(2)	C(3)	H(32)	-71.96 (5.28)
H(22)	C(2)	C(3)	H(31)	-51.92 (3.90)
H(22)	C(2)	C(3)	H(32)	53.31 (5.52)

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13. ABSTRACT ***(Maximum 200 words)***

The presence of adventitious water in a reaction between dicyclopentamethylenethiuram-disulfide $(C_5H_{10}NCS_2)_2$ and a picoline solution of tricyclopentadienylindium(III) $(C_5H_5)_3$ In resulted in the formation of piperidinium hydrogen sulfide ($C_5H_{13}NS$). The piperidinium hydrogen sulfide produced in this way was unambiguously characterized by X-ray crystallography. The structure determination showed that the piperidinium hydrogen sulfide crystal (MW = 119.23 g/mol) has an orthorhombic (*Pbcm*) unit cell whose parameters are: a = 9.818(2), b = 7.3720(1), c = 9.754(1) Å, V = 706.0(3) Å^3, Z = 4. D_x = 1.122 g cm^{-3}, Mo Kα (λ = 0.71073), μ = 3.36 cm^{-1}, F(000) = 264.0, T = 293 K, R = 0.036 for 343 reflections with $F_o^2 > 3\sigma(F_o^2)$ and 65 variables. The compound consists of $[C_5H_{10}NH_2]^+$ cations and $[SH]^-$ anions with both species residing on crystallographic mirror planes. N-H • • • S hydrogen bonding contributes to the interconnection of neighboring piperidinium components of the compound.

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ONE-STEP SYNTHESIS OF DITHIOCARBAMATES FROM METAL POWDERS

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ABSTRACT

Neutral metal dithiocarbamate complexes ($M(NR_2CS_2)_x$) are well-known precursors to metal sulfides, a class of materials with numerous technological applications. We are involved in a research effort to prepare new precursors to metal sulfides using simple, reproducible synthetic procedures. We describe the results of our synthetic and characterization studies for M = Fe, Co, Ni, Cu, and In. For example, treatment of metallic indium with tetramethylthiuramdisulfide (tmtd) in 4-methylpyridine (4-Mepy) at 25 °C produces a new homoleptic indium (III) dithiocarbamate, $In(N(CH_3)_2CS_2)_3$ (I), in yields of over 60%. The indium (III) dithiocarbamate was characterized by X-ray crystallography; (I) exists in the solid state as discrete distorted-octahedral molecules. Compound (I) crystallizes in the P1bar (No. 2) space group with lattice parameters: a = 9.282(1) Å, b = 10.081(1) Å, c = 12.502 Å, $\alpha = 73.91(1)°$, $\beta = 70.21(1)°$, $\gamma = 85.84(1)°$, and Z = 2. X-ray diffraction and mass spectral data were used to characterize the products of the analogous reactions with Fe, Co, Ni, and Cu. We discuss both use of dithiocarbamates as precursors and our approach to their preparation.

INTRODUCTION

Technological applications for metal sulfides are numerous. Many applications take advantage of the photoelectrical or electrical properties of these materials in electronic applications such as solar cells, infrared detectors, light-emitting diodes, and transistors (e.g. CdS, GaS, and $CuInS_2$) [1,2]. Chevrel phases are superconducting, for example $PbMo_6S_8$ has a T_c of 21K [3]. An example of a chemical application is the use of heterogeneous systems such as Co–promoted molybdenum sulfide (Ni or W are sometimes substituted for Co and Mo) on γ–alumina catalysts for metal and sulfur removal under H_2 from crude oil, this allows efficient or environmentally sound use of "dirtier" feedstocks [4]. Chemical sensitization to form $AgAu_xS_y$ clusters on silver halide grains is an integral step in producing photographic film [5]. It is also interesting to note that many enzymes and electron transfer proteins have metal–sulfide cluster active sites [6].

As part of an in-house and external effort to synthesize and use metal sulfides and selenides as precursors for photovoltaic and related optoelectronic applications [2,7-9], we are exploring synthetic aspects of metal calcogenide chemistry. One very well-studied class of compounds is neutral, homoleptic metal dithiocarbamates of the formula $M(NR_2CS_2)_x$ [10]. There are several typical synthetic routes to these compounds including reaction of CS_2 with metal amide complexes ($M(NR_2)_x$), reaction of metal chlorides with CS_2 in the presence of amines, and direct reaction of metal halides with the sodium dithiocarbamate salt [6]. Less typically discussed are reactions involving metal powders [11,12]. We have determined that a wide range of metals will react directly with tetraalkylthiuram disulfides to form homoleptic dithiocarbamates including Fe, Co, Ni, Cu, and In, in the case of In producing a new dithiocarbamate $In(N(CH_3)_2CS_2)_3$ (I). We also discuss mass spectral data on several transition metal complexes and relate it to their potential uses as precursors in chemical vapor deposition (CVD) and other deposition technologies.

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Mat. Res. Soc. Symp. Proc. Vol. 327.

EXPERIMENTAL

All manipulations of moisture and air-sensitive materials were done under an inert atmosphere by standard Schlenk techniques on a double-manifold vacuum line or in a Vacuum Atmospheres Co. glovebox equipped with a HE-493 dri-train. Solvents were freshly distilled from benzophenone ketyl prior to use. Metal powders were obtained from Strem Chemicals, Newburyport, MA. Sulfur compounds were obtained from Aldrich Chemical Co., Milwaukee, WI. Infrared spectra were recorded on a Perkin-Elmer 599B spectrophotometer. Electron impact mass spectra (25 and 70 eV, 150 °C) were recorded on a Finnigan TSQ-45 mass spectrometer. Single crystal X-ray analyses were done on an Enraf-Nonius CAD-4 diffractometer.

RESULTS AND DISCUSSION

Metal dithiocarbamates were typically prepared by reaction of metal powder (M = Fe, Co, Ni, Cu, and In) (0.50 g) and stoichiometric amounts of tetraalkylthiuramdisulfides (for R = Me, tmtd; R = Et, tetd) in 35 mL of 4-methylpyridine at ambient temperature for several days, equation 1. The reaction was filtered, and the resulting solution was layered with hexanes. Hexanes, 150 mL, was added to the resulting dark brown or black material to further precipitate solid.

$$M^{o} + n/2\ R_2NC(S)S\text{-}SC(S)NR_2 \xrightarrow[25\ ^{\circ}C]{4\text{-}Mepy} M(NR_2CS_2)_n \qquad (1)$$

For example, treatment of metallic indium with tmtd in 4-Mepy at 25 °C produces $In(N(CH_3)_2CS_2)_3$ (I), in yields of over 60%. The indium (III) dithiocarbamate was characterized by X-ray crystallography; (I) exists in the solid state as discrete distorted-octahedral molecules, figure 1. *Compound (I) is only the second indium dithiocarbamate to be structurally characterized* [13]. Compound (I) crystallizes in space group P1bar (No. 2), lattice parameters: a = 9.282(1) Å, b = 10.081(1) Å, c = 12.502 Å, α = 73.91(1)°, β = 70.21(1)°, γ = 85.84(1)°, and Z = 2. Single crystal X-ray diffraction data were collected as well for $Cu(N(C_2H_5)_2CS_2)_2$, which has been previously structurally characterized [14]. The complexes that were isolated were both divalent (M = Ni and Cu) and trivalent (M = Fe, Co, and In) for R = Me and Et with structures analogous to the Cu and the In, respectively.

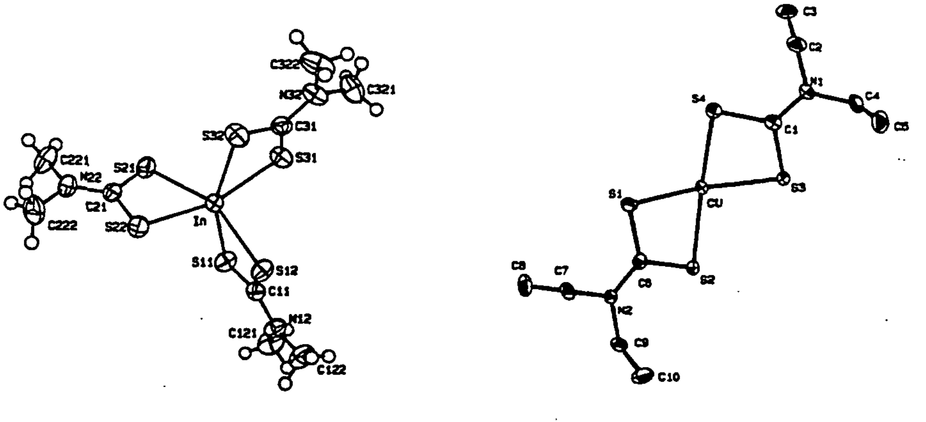

Figure 1. - ORTEP drawings of $In(N(CH_3)_2CS_2)_3$ and $Cu(N(C_2H_5)_2CS_2)_2$ with key atoms labelled. The thermal ellipsoids enclose 50 % of electron density.

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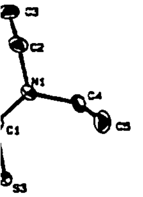

with key atoms

It was previously reported that room-temperature reaction of copper and nickel powders with sodium dithiocarbamates and photochemical reaction of copper powder with tetraalkylthiuramdisulfides (tatd) in $CHCl_3$ produce metal dithiocarbamates [11,12]. We and others have discovered that in strong basic, coordinating solvents such as 4-MePy, species such as S_8, REER (R = alkyl or aryl, E = S or Se) and $(C_6H_5CO)_2O_2$ will oxidize metal powders [15-19]. The advantage of reaction (1) is the lack of by-products. Production of dithiocarbamates via oxidation of metal powders results in a much greater control of impurities, first by the use of metal powders as a starting material and second by simplicity in the chemistry that resultis in only one product.

The dithiocarbamates prepared for M = Fe, Co, Ni, and Cu were examined by mass spectrometry. A diagram of the instrument used in these studies is shown in figure 2. A summary of relevant mass spectral data is given in table 1. All of the metal complexes show characteristic peaks corresponding to breakdown of the dimethyldithiocarbamate residues. Each compound gives an ion at m/z 120 corresponding to the dimethyldithiocarbamate residue itself. Each spectrum has as its base peak, m/z 88 with 100 %, consistent with loss of a sulfur atom, $(CH_3)_2NCS]^+$. Finally, each compound has apeak at m/z corresponding to the methyl isocyanate ion produced by the loss of a methyl and sulfide ion. The organic fragments for all metal complexes were of approximately the same intensity.

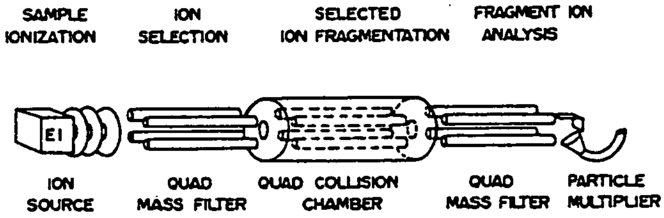

Figure 2. - Schematic diagram of Finnigan TSQ-45 mass spectrometer used in this study.

The divalent copper and nickel complex spectra contain a highest mass peak at m/z 303 for the ^{63}Cu isotope and a m/z 298 peak for the ^{58}Ni isotope. This peak indicates that the Cu or Ni atom is bound to two dimethyldithiocarbamate residues in the complex, the parent ion. This indicates that the complexes are fairly volatile and stable in the gas phase, an important attribute for a material precursor. In addition to this peak, these compounds display peaks corresponding to loss of one of the dimethyldithiocarbamate groups (Cu: 183; Ni: 178) and a lower intensity peak resulting from further loss of a CH_3S fragment to result in a metal methyl isocyanide fragment (Cu: 136; Ni: 131). Finally, both Cu and Ni have less intense peaks that correspond to M^+ and weak MS_2^+ peaks.

The parent ions of the trivalent Fe and Co occur at m/z 416 and 419, respectively. The parent ions of both trivalent complexes are less intense than for Cu and Ni, expected due to the highest molecular weights; a crude ordering of volatilities from this data is Cu>>Ni>Co~Fe. The dithiocarbamate-loss fragment ML_2^+ (Co: 299, Fe: 296) of both Fe and Co are much more intense than the corresponding parent ions and the analagous Ni and Cu species ML^+. The rationale for the intensity of these ions is two-fold: the stability of Fe^{2+} and Co^{2+} relative to monovalent Ni and Cu and the greater volatility of a lower-mass fragement. The stability argument is born out by the relative wekness of the FeL^+ and CoL^+ peaks. Finally, the M^+ peaks of Co and Fe are weak, Fe approximating Ni while Co is weakest, approximately following trends in the metals' boiling points [20]. The MS_2^+ ions for Fe and Co are essentially non-existent.

Table 1.

MASS SPECTRA OF METAL DIMETHYLDITHIOCARBAMATES

First numbers are m/z values. Numbers in brackets are relative intensities.

ION	METALS M			
	Cu	Co	Fe	Ni
M^+	63,65 (11.9,5.2)	59 (2.4)	56 (10.3)	58,60 (5.6,1.8)
$[CH_3NCS]^+$	73 (15.8)	73 (14.0)	73 (12.1)	73 (14.7)
$[(CH_3)_2NCS]^+$	88 (100)	88 (100)	88 (100)	88 (100)
$[(CH_3)_2NCS_2]^+$	120 (10.2)	120 (9.3)	120 (10.1)	120 (9.4)
MS_2^+	127,129 (2.9,1.5)	123 (.7)	120 (-)	122,124 (2.9,0.8)
$[MSCNCH_3]^+$	136,138 (14.3,7.1)	132 (2.0)	129 (3.0)	131,133 (4.7,2.1)
$[MS_2CN(CH_3)_2]^+$	183,185 (28.8,15.9)	179 (6.2)	176 (15.2)	178,180 (11.3,7.0)
$[M(S_2CN(CH_3)_2)_2]^+$	303,305 (74.0,56.8)	299 (49.7)	296 (84.7)	298,300 (37.5,20.7)
$[M(S_2CN(CH_3)_2)_3]^+$	423,425 (-,-)	419 (13.9)	416 (8.3)	418,420 (-,-)

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Metal dithiocarbamates have been shown to cleanly produce metal sulfides, both as bulk [21] and thin-film material [22,23]. Work by others is focused on producing dithiocarbamates with substituted or additional ligands to enhance volatility [24-26] and/or minimize dimerization that occurs with Zn diethyldithiocarbamate, for example [27,28]. For these complexes, the chemistry that we describe would be useful as a method to prepare a variety of dithiocarbamates for further reaction to the sulfide precursors. Another example of use of dithiocarbamates is the use of copper di-n-butyldithiocarbamate to prepare a single-molecule precursor to $CuInS_2$ [29]. Work is currently underway in our labs to exploit this chemistry to prepare precursors for binary and ternary sulfides.

CONCLUSIONS

We have described a simple one-step synthesis to metal dithiocarbamtes by oxidation of metal powders with dialkylthiuram disulfides in a basic coordinating solvent. Dithiocarbamates are excellent precursors to metal sulfides, an important class of materials for a number of applications. The structure of $In(N(CH_3)_2CS_2)_3$, a distorted octahedron and only the second structurally-characterized indium dithiocarbamate, was briefly described. Mass spectral data on Fe, Co, Ni, and Cu dimethyldithiocarbamate indicate that all four are reasonably volatile. Both the divalent and trivalent compounds had fairly intense ML_2^+ ion peaks, the M^+ and MS_2^+ (for Cu, Ni, and Co) though weaker, were present. The mass spectral data demonstrates the key attributes of dithiocarbamates: volatility, relative stability in the gas phase, and ample decomposition pathways for clean production of metal sulfide.

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Lists of structure factors, anisotropic displacement parameters and complete geometry of the non-H atoms have been deposited with the IUCr (Reference: BK1004). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-Bis(acetato-*O*)bis(4-methylpyridine-*N*)copper(II)

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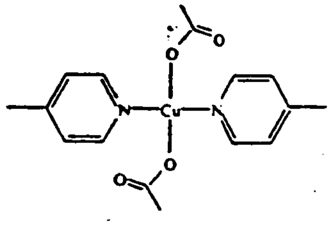
Abstract

The structure of *trans*-bis(acetato-*O*)bis(4-methylpyridine-*N*)copper(II), $[Cu(C_2H_3O_2)_2(C_6H_7N)_2]$, reported herein, represents a monomeric parent acetate complex with a distorted square-planar arrangement of acetate and 4-methylpyridine ligands around the Cu atom with the following distances and angles: Cu—N = 2.027 (4) and Cu—O1 = 1.950 (3) Å; O1—Cu—N = 89.1 (2) and O1—Cu—N′ = 90.9 (2)°. The Cu atom resides on a center of inversion. The most important dihedral angles are the angle between the 4-methylpyridine plane and the acetate plane (O1, O2, C21 and C22), 78.2°, and the angle between the 4-methylpyridine ring and the coordination plane (Cu, N, O1), 31.6°.

Comment

The title compound, (I), was prepared by the reaction of gallium sulfide with copper(I) acetate in 4-methylpyridine solution. A solution of copper(I) acetate (0.31 g, 2.4 mmol) and gallium sulfide (0.37 g, 3.6 mmol) in 25 ml of 4-methylpyridine was stirred for 3 days at 293 K under argon. All manipulations were performed in a drybox or on a vacuum line under an inert atmosphere using standard Schlenk techniques. Filtration and layering of the 4-methylpyridine solution with 30 ml of hexanes produced prismatic blue crystals of the title compound (I).



(I)

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X-ray structures of the two following copper(II) acetate complexes have been determined: *trans*-bis[(chloroacetato)(α-picoline)]copper(II) and *trans*-bis[(dichloroacetato)(α-picoline)]copper(II) (Davey & Stephens, 1971*a*,*b*). The complex reported herein represents the unchlorinated compound. The Cu atom is surrounded by four ligands in a virtually square-planar arrangement with an O atom (O2) of the acetate group efficiently blocking the two remaining axial sides of the Cu atom above and below the coordination plane defined by atoms Cu, O1, O1′, N and N′. The Cu—O2 distance of 2.623 (4) Å is indicative of a weak interaction between the two atoms. The two 4-methylpyridine rings, as well as the two acetato groups, are forced to be coplanar by a center of symmetry residing on the Cu atom. The dihedral angle between the 4-methylpyridine plane and the acetate plane is 78.2°. Steric interactions force the 4-methylpyridine ring to be skewed at an angle of 31.6° with respect to the coordination plane. The C21—O2 distance of 1.227 (7) Å is shorter than the C21—O1 distance of 1.279 (6) Å, which suggests more double-bond character for the C21—O2 bond (Davey & Stephens, 1971*a*,*b*). The O1—C21—O2 angle of 122.7 (5)° is significantly smaller than the O—C—O angles of 126.6 and 128.0° in the dimeric copper(II) acetate complex $[Cu_2(C_2H_2ClO_2)_4(C_6H_7N)_2]$ (Davey & Stephens, 1970). All angles and bonds within the 4-methylpyridine rings are as expected.

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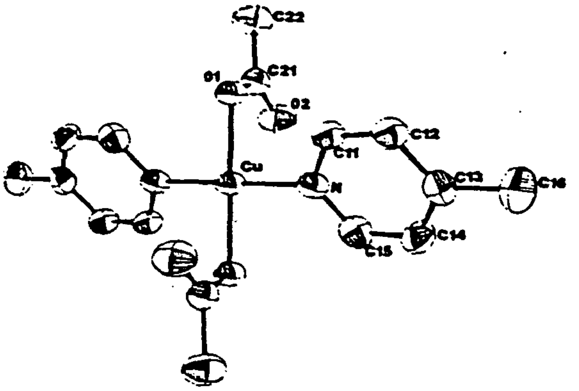

Fig. 1. *ORTEP* (Johnson, 1976) drawing representing the stereochemistry of the [$Cu(C_2H_3O_2)_2(C_6H_7N)_2$] molecule and the atomic labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

Crystal data

[$Cu(C_2H_3O_2)_2(C_6H_7N)_2$]
$M_r = 367.89$
Monoclinic
$P2_1/c$
$a = 6.194$ (2) Å
$b = 16.474$ (6) Å
$c = 8.270$ (3) Å
$\beta = 92.02$ (3)°
$V = 843.5$ (9) Å^3
$Z = 2$
$D_x = 1.448$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 2.44-15.8°$
$\mu = 1.295$ mm^{-1}
$T = 293$ K
Prism
0.34 × 0.32 × 0.30 mm
Blue

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.878$, $T_{max} = 0.999$
1689 measured reflections
1478 independent reflections

873 observed reflections [$I > 3\sigma(I)$]
$R_{int} = 0.39$
$\theta_{max} = 25°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 19$
$l = -9 \rightarrow 9$
3 standard reflections frequency: 60 min intensity variation: <5.1%

Refinement

Refinement on F
$R = 0.040$
$wR = 0.053$
$S = 1.142$
873 reflections
107 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.300$ e Å^{-3}
$\Delta\rho_{min} = -0.355$ e Å^{-3}
Extinction correction: $F_c = F_o/(1 + gI_c)$
Extinction coefficient: 2.1×10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (1/3)\Sigma_i\Sigma_j B_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cu	0	0	0	2.78 (1)
O1	0.1063 (6)	0.0795 (2)	−0.1527 (4)	3.13 (7)
O2	−0.1468 (7)	0.1486 (3)	−0.0336 (5)	4.78 (9)
N	0.2071 (7)	0.0459 (3)	0.1721 (4)	3.02 (9)
C11	0.1522 (8)	0.0462 (3)	0.3287 (6)	3.0 (1)
C12	0.2840 (9)	0.0783 (3)	0.4486 (6)	3.3 (1)
C13	0.4796 (9)	0.1142 (3)	0.4149 (6)	3.1 (1)
C14	0.5371 (8)	0.1127 (4)	0.2539 (7)	3.6 (1)
C15	0.3977 (8)	0.0798 (3)	0.1379 (6)	3.4 (1)
C16	0.626 (1)	0.1506 (4)	0.5428 (7)	4.6 (1)
C21	0.0045 (9)	0.1453 (3)	−0.1251 (6)	3.3 (1)
C22	0.080 (1)	0.2195 (4)	−0.2095 (7)	4.8 (1)

Table 2. *Selected geometric parameters* (Å, °)

Cu—N	2.027 (4)	N—C15	1.346 (7)
Cu—O1	1.950 (3)	C11—C12	1.367 (7)
Cu—O2	2.623 (4)	C12—C13	1.386 (8)
Cu—N	2.027 (4)	C13—C14	1.392 (8)
O1—C21	1.279 (6)	C13—C16	1.492 (8)
O2—C21	1.227 (7)	C14—C15	1.378 (7)
N—C11	1.351 (6)	C21—C22	1.492 (8)
O1—Cu—N	89.1 (2)	C11—C12—C13	121.5 (5)
O2—Cu—O1	55.2 (2)	C12—C13—C14	116.2 (5)
O2—Cu—N	93.8 (2)	C12—C13—C16	122.8 (5)
Cu—O1—C21	105.8 (3)	C14—C13—C16	121.0 (5)
Cu—N—C11	120.0 (3)	C13—C14—C15	119.8 (5)
Cu—N—C15	123.0 (3)	N—C15—C14	123.4 (5)
C11—N—C15	116.9 (4)	O1—C21—O2	122.7 (5)
N—C11—C12	122.2 (5)	O1—C21—C22	116.5 (5)
O2—C21—C22	120.8 (5)		

Profile analysis was performed on all reflections (Lehman & Larsen, 1974; Grant & Gabe, 1978). Intensities were corrected for Lorentz–polarization effects. Because of a center of inversion residing on the Cu atom, one formula unit is obtained from two asymmetric units. All calculations were performed using a PDP-11/60 microcomputer and the *SDP-Plus* (Enraf–Nonius, 1985) structure determination package.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and root-mean-squares data have been deposited with the IUCr (Reference: HH1030). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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