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

Final Report

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Period Covered: 1/16/90 to 3/31/94

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Grant Number: NCC 3-162
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Received October 7, 1991

We report the synthesis and structural characterization of the first main group oxo-centered, trinuclear carboxylato-bridged species, namely, [Ga3(μ3-O)(μ2-O2CC6H5)(4-Mepy)3]GaCl4-4-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 [M3(μ3-O)(μ2-O2CR)L3]1-, previously observed only for transition metals.12

Compound 1 was prepared in the following manner. Under argon, a solution of Ga2Cl4 (1.25 g, 4.44 mmol) and C6CO2Na (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 [Ga3(μ3-O)(μ2-O2CC6H5)(4-Mepy)3]GaCl4-4-Mepy over a period of 1 week.4

Figure 1. ORTEP drawing of the complex cation [Ga3(μ3-O)(μ2-O2CC6H5)(4-Mepy)3]GaCl4-4-Mepy, 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-O, 120.0 (9); O-C-O, 126 (1); O-B-Ga-N, 177.6 (9); O-C-C, 117 (2).

Figure 2. Ga3(μ3-O)(μ2-O2C)3N3 core of 1 showing the coordination sphere around the gallium atoms.

1 This work was done while the author held a National Research Council-NASA Research Associateship.
2 NASA Lewis Research Center.
3 Cleveland State University.
4 Purdue University.

3) Analytical results calculated (found) for C27H23GaCl3N3O4: C, 49.95 (49.58); H, 3.56 (3.78); C, 9.83 (9.6). A single crystal (0.5 x 0.4 x 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 monochromated Mo Kα radiation (λ = 0.71073 Å). A total of 5378 independent reflections with 2θ = 4-45° were collected. Crystal data: monoclinic, space group P21; a = 14.398 (2) Å, b = 17.638 (3) Å, c = 16.215 (2) Å, β = 113.15 (1); V = 3786 (2) Å3; Z = 2; Dc = 1.347 g/cm3; μ(Mo Kα) = 16.01 cm-1; R = 0.057 (Rw = 0.067) for 3776 reflections with I > 3σ(I); GOF = 1.15.
The solid-state molecular structure of the complex cation is shown in Figure 1. The central Ga₂O 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-O atom is equidistant from the three gallium atoms; the average Ga-O(B) distance is 1.874 (3) Å. Each edge of the Ga₂O core is bridged by two C7H₇CO₂⁻ 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. The six bridging benzoato groups are equivalent as demonstrated by ¹H and ¹³C NMR spectroscopy. Within the benzoato groups, the average bond distances and angles are in accord with values reported for related complexes.

As evidenced by Figure 1, there is a distinct difference in the orientation of the three axial 4-methylpyridine ligands around the Ga₂O core. Two of the 4-methylpyridine planes are approximately parallel to the Ga₂O 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. Two sets of signals, in a 1:2 ratio, are observed for each of the three types of protons in the 4-methylpyridine ligands. 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 of 1, between 800 and 4000 cm⁻¹, is dominated by bands attributable to the organic constituents of the cation. We tentatively assign the strong bands at 1602, 1556, and 1495 cm⁻¹ to bridging benzoato groups. Several IR bands below 800 cm⁻¹ may be assigned by analogy to other [M₃(μ₃-O)(μ₂-O₂CR)₃L₂]⁺ complexes. These include an asymmetric stretch at 655 cm⁻¹ of the central M₂O unit and the ν₄ mode at 500 and 479 cm⁻¹ of the MO₃ units. The band at 550 cm⁻¹ occurs in almost all trimeric carboxylates and is assigned to a carboxylate mode.

In conclusion, we have observed a new reactivity pattern for Ga₂Cl₄. This simple one-step reaction demonstrates the accessibility of main group carboxylates of the general formula, [M₃(μ₃-O)(μ₂-O₂CR)₃L₂]⁺, and constitutes a starting point in the discovery of related complexes. Investigations into the synthesis, 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.

(5) Individual Ga-O(B) and Ga-Ga bond distances: Ga(1)-O(1B) 1.890 (9), Ga(2)-O(1B) 1.866 (9), Ga(3)-O(1B) 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.


(12) 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), 1229 (m), 1315 (m), 1109 (m), 1233 (m), 1215 (m), 1178 (s), 1070 (s), 1026 (s), 724 (vs), 688 (s), 683 (vs), 655 (vs), 350 (m), 500 (s), 479 (vs).


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 CuInSe₂ (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.5-9 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 preclude 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 process11 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 CuInSe₂ solar cells.

EXPERIMENTAL

All operations of moisture- and air-sensitive...
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. 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 Kα 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 (Cp3In: 0.17 g, 0.548 mmol) and cuprous selenide (Cu2Se: 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. The Cu:In ratio for samples produced is a function of the Cp3In:Cu2Se 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 CuInSe2 (with an Ni X-ray standard) and a sample produced at room temperature (sample R9) from Cu2Se and Cp3In 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 CuInSe₂ 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. 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) or reaction of H₂Se with deposited thin films of metals (450 °C). Other methods using simple oxide or sulphate precursors include spray pyrolysis (250 °C) and electrodeposition (25 °C). Recently described preparative methods with chemical precursors include decomposition of a single-molecule precursor (350 °C for CuInS₂), reaction of a mixture of Cu and In polyselenides with alkylphosphines or KCN (65–185 °C) and decomposition of a combination of Cu and In polyselenides (450 °C). 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.
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 stoichiometry 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:

$$\text{Cp}_3\text{In} + 2\text{Cu}_2\text{Se} + 3\text{L} \rightarrow \text{CuInSe}_2 + 3\text{CpCu(L)}$$

This metathesis reaction should produce insoluble CuInSe$_2$ a soluble complex 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 $\text{Cp}_3\text{In}:\text{Cu}_2\text{Se}$ ratio. Finally, the Cu:In ratio in the product can vary and appears to be a function of the reactants' ratio; at this point we have not determined an optimal $\text{Cp}_3\text{In}:\text{Cu}_2\text{Se}$ 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 and solid-state halides and chalcogenides and is an important route to precursors to solid-state materials. 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. Interestingly, we obtained the same CuS precursor as Rauchfuss et al. by reaction of S$_8$ with Cu$_2$S. 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$_2$Se and Cp$_3$In in 4-methylpyridine. Characterisation of the material produced shows it to be platelet-shaped crystals 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 compound 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**

Support from NASA Lewis Research Center cooperative agreement NCC3-162 (S.A.D.), a National Research Council/NASA Lewis Research Center Associateship (M.T.A.) and the NASA Lewis Research Center Director's Discretionary Fund for independent research (A.F.H.) are gratefully acknowledged. We thank Ms. Ruth Cipcic (XRD) for technical assistance. We thank Professor Mercouri Kanatzidis of the Chemistry Department, Michigan State University and Dr. Bulent Basol, International Solar Electric Technology (ISET) for helpful discussions and preprints of their work.

**REFERENCES**


14. Combustion analysis performed by Galbraith Laboratories, Inc., Knoxville, TN. Found: C (1.23); H (<0.5).


Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic thermal parameters (Å²)

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

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

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Fig. 1. Molecular structure with atom numbering.

References


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

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(Received 30 March 1992; accepted 9 June 1992)

Abstract. Bromobis(4-methylpyridine)copper(I), [CuBr(C₆H₅N)₂], $M_r = 329.71$, triclinic, $P1$, $a = 9.254 (7)$, $b = 9.736 (3)$, $c = 7.955 (3)$ Å, $\alpha = 102.34 (3)$, $\beta = 112.33 (3)$, $\gamma = 95.09 (4)$°, $V = 636.2 (6)$ Å³, $Z = 1$, $D_m = 1.8$, $D_e = 1.721$ g cm⁻³, $\lambda(Mo K\alpha) = 0.710696$ Å, $\mu = 50.84$ cm⁻¹, $F(000) = 0108-2701/93/030536-03$ © 1993 International Union of Crystallography
using an Enraf-Nonius CAD-4 automated diffractometer. Intensity data were collected with ω-2θ scans at room temperature in the range 4 < 2θ < 50°. The scan rate varied from 2 to 10° min⁻¹ with ω-scan width (1.00 + 0.35θ tanθ)°. 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 Fc = Fc/(1 + gΔ2) was also applied, with g = 1.459 × 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 ≤ h ≤ 11, −11 ≤ k ≤ 11, −9 ≤ l ≤ 9), of which 1517 had I > 3σ(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 = 0.088, for 1517 independent observed [I > 3σ(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.

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

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

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328, T = 293 K, R = 0.057, wR = 0.088, for 1517 independent observed [I > 3σ(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 [CuBr2(S(CH3)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 tetrahydrofuran.

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 < θ < 22.78°, using an Enraf–Nonius CAD-4 automated diffractometer (Mo Kα radiation and graphite monochromator).
0.088 \{w = 4(Fo)^2/[sigma(Fo)^2]\} and quality of fit indicator S = 2.967. All shifts of 146 refined parameters were found to be smaller than 0.001\sigma. 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 ORTEPII (Johnson, 1976) drawing and the atomic labeling scheme are shown in Fig. 1. A packing diagram is presented in Fig. 2.

* 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]

References


NADALAK (NASA grant NCC3-162) and AFH (Director's Discretionary Fund) acknowledge support from NASA Lewis Research Center.

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

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(Received 30 March 1992; accepted 9 June 1992)

Abstract. [Cu(C6H5O3)2(C11H21N)4], M, = 694.29, monoclinic, C2/c, a = 15.180 (6), b = 14.431 (5), c = 15.269 (6) Å, \(\beta = 96.38(4)^\circ\), \(V = 3324(2) Å^3\), \(Z = 4\), \(D_x = 1.388 \text{ g cm}^{-3}\), \(\lambda(\text{Mo }K\alpha) = 0.71073 Å\), \(\mu = 8.54 \text{ cm}^{-1}\), \(F(000) = 1436\), \(T = 295 \text{ K}\), \(R = 0.067\), \(wR = 0.087\) for 1141 independent reflections with \(I \geq 3\sigma(I)\) and 207 variables. The [Cu(\text{O}-SC}_{11}H_{21}N)_{2}(\text{C}_6\text{H}_{5}O_{3})_{2} 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:

- \text{Cu–O1} 2.471 (8), S–\text{Cl} 1.785 (10) Å, \text{Cu–O1–S} 154.1 (6), \text{O1–S–O2} 112.3 (5), \text{O1–S–O3} 111.5 (5)°.

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).

* Authors to whom correspondence should be addressed.

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

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

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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, C3D, C3B 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 \( w = 4(Fo)^2/(σ(Fo)^2) \) 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(O~SC6H4)2(NC6H4)] (Birker, Crisp & Moore, 1977), [Cu(O~SCF3)2(C6H5N)] (Al Sarraj, Gouteron, Jeannin & Jeannin, 1987), [Cu(O~SCF3)2(C6H5N)] (Haynes, Rettg, Sams, Trotter &...
Structure of an Allotropic Form of [Bis(trimethylsilyl)amido]dichloro-\((η^5\text{-cyclopentadienyl})\)titanium

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(Received 12 March 1992: accepted 3 July 1992)

Abstract. \([\text{TiCl_2(C_5H_5NSi_2)(C_5H_5)}], M_r = 344.3,\) triclinic, \(a = 8.831(4), b = 14.270(8), c = 6.774(8) \text{ Å}, \alpha = 91.98(8), \beta = 99.33(9), \gamma = 85.13(5)\)°, \(V = 839.2(8) \text{ Å}^3, Z = 2, D_x = 1.36 \text{ Mg m}^{-3}, \lambda(\text{Mo }K_α) = 0.71069 \text{ Å}, \mu = 0.95 \text{ mm}^{-1}, (F(000)) = 360, T = 185 \text{ K}.\) Full-matrix least-squares refinement based on 1583 reflections led to \(R(F_0) = \text{ 0.042, } \omega R(F_0) = \text{ 0.053, } S = 1.45,\) for 154 variables. The room-temperature unit cell is also triclinic with consistent parameters. This triclinic form is an allotropic modification of the monoclinic \([\text{CpTiCl_2(N(SiMe_3)_2)}]\) [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. \([\text{CpTiCl_2(N(SiMe_3)_2)}]\) from LiN\(_2\) (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 \(\times 0.20 \times 0.05 \text{ mm}\) 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 Kα radiation. Cell dimensions were determined from setting angles of 25 reflections having \(3.5 < \theta < 14.1°\). 2277 reflections were measured using \(\omega/2\theta\) scans with \(2 \theta\) from 3 to 44° (\(9 < h < 9, -15 \leq k \leq 15, 0 \leq l \leq 7\) and scan width \(0.90 + 0.35\tan \theta)\)°, with variable scan speed \(0.97–8.24\) min\(^{-1}\). Intensities of three reflections (101, 141, 011) 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 \(\psi\) scans (North, Phillips & Mathews, 1968); minimum and maximum relative transmission 0.83 and 0.99, respectively. 1925 reflections were unique; \(R_{int} = 0.019\) for averaging redundant \(h \pm k 0\) reflections. Direct methods followed by Fourier and least-squares techniques using 1583 reflections having \(F_2 > 3\sigma(F_2)^{2}\) based on counting statistics, were used to solve the structure. Full-matrix least-squares refinement was based on \(F_0\) minimizing \(\Sigma w[F_0^2 - |F_0|^2]\), with anisotropic thermal parameters for non-H atoms. All H atoms were located by \(\Delta F\) map and included with constrained geometry (\(C^-H = 0.97 \text{ Å}\)) and with isotropic \(U_H\) kept fixed to 0.05 Å\(^2\). Final \(R = 0.042, \omega R = 0.053, S = 1.45,\) for 154 variables, and with unit weights.† Maximum parameter

† 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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References


Structure of 4-Methylpyridinium Bromide

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(Received 9 December 1991; accepted 25 June 1992)

Abstract. γ-Picolinium bromide, [C₆H₇NH]Br, Mᵣ = 174.05, monoclinic, Cm, a = 8.785 (4), b = 8.318 (3),
c = 4.920 (1) Å, β = 103.62 (3)°, V = 349.4 (4) Å³, Z = 2, Dᵣ = 1.654 g cm⁻³, λ(Mo Kα) = 0.71073 Å, µ = 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 C₆H₇NH⁺ 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
copper(I) bromide dimethyl sulfide \([\text{CuBr-S(C}_2\text{H}_5])\) (0.62 g, 3 mmol) and tetraethylthiram disulfide \([\text{(C}_4\text{H}_9)_2\text{NCS}_2]\) (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 \(\times 0.31 \times 0.22\) 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 \(\omega-2\theta\) scan technique in the range 4 < \(2\theta\) < 55°. The scan rate varied from 2 to 16° min \(^{-1}\) with \(\omega\)-scan width = (0.96 + 0.350tan\(\theta\))º. Intensities were corrected for Lorentz and polarization effects, and for absorption effects based on the empirical method of Walker & Stuart (1983); relative \(T_{\text{min}}\) = 0.446, \(T_{\text{max}}\) = 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, \(F^2 > 3\sigma(F^2)\). 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 \(w [(F_o^2 - |F_e|^2)^2\) and the weight, \(w\), defined by the Kilean & 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 \((\Delta/\sigma)_{\text{max}} = 0.00\). The maximum residual peak in the final difference Fourier map was 0.52 e \(\text{Å}^{-3}\). All other absolute structure refinements were refined under identical conditions, and the structure leading to the lower residual value 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 \(F_o\) (Ibers & Hamilton, 1964); the values for \(f^\prime\) and \(f^\prime\prime\) were those of Cromer (1974). Plots of \(w [(F_o^2 - |F_e|^2)\) versus \(|F_e|^2\), 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 \textit{MolEN} (Enraf–Nonius, 1990). Final positional parameters and equivalent isotropic thermal parameters are listed in Table 1.* Bond

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

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<th>Atom</th>
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<td>6.8(1)</td>
<td>0.213</td>
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<td>0.520</td>
</tr>
</tbody>
</table>

* 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: HH90618]

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

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

| Bond     | d(Å) | \(|\sigma(d)|\) | \(|\sigma(\alpha)|\) |
|----------|------|----------------|-----------------|
| Br—N(1)  | 3.12(1) | 0.0033 | 0.0043 |
| C(1)—C(2) | 1.34(1) | 0.0015 | 0.0016 |
| C(2)—C(3) | 1.49(2) | 0.0020 | 0.0020 |
| \(\alpha_{\text{N}(1)-C(2)}\) | 119.2(5) | 0.213 | 0.121 |
| \(\alpha_{\text{C}(2)-C(3)}\) | 121.4(9) | 0.327 | 0.213 |
| \(\alpha_{\text{N}(1)-C(2)-C(3)}\) | 120.4(7) | 0.402 | 0.278 |

\[ \text{Bond distances (Å) and angles (°) with e.s.d.'s in parentheses} \]

* Bond

Fig. 1. ORTEP (Johnson, 1965) drawing depicting the stereochemistry of the \([\text{C}_5\text{H}_5\text{N}]\text{Br}\) 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.


MTA gratefully acknowledges a postdoctoral fellowship from the National Research Council–NASA Lewis Research Center. AFH acknowledges support from the Director’s Discretionary Fund at NASA Lewis. SAD acknowledges partial support from NASA grant NCC3-162.

MTA gratefully acknowledges a postdoctoral fellowship from the National Research Council–NASA Lewis Research Center. AFH acknowledges support from the Director’s Discretionary Fund at NASA Lewis. SAD acknowledges partial support from NASA grant NCC3-162.
Structure of Diphenyl Carbonate

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(Received 11 February 1992; accepted 13 July 1992)

Abstract. Phenyl phenoxyfonnate, C\textsubscript{13}H\textsubscript{10}O\textsubscript{3}, \(M_r = 214.2\), orthorhombic, \(P2_12_12_1\), \(a = 6.062\) (2), \(b = 7.242\) (1), \(c = 23.375\) (4) \(\text{Å}\), \(V = 1026.2\) \(\text{Å}^3\), \(Z = 4\), \(D_x = 1.387\) \(\text{g cm}^{-3}\), \(\mu = 0.92\) \(\text{cm}^{-1}\), \(F(000) = 448\), \(T = 164\) 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\textsubscript{carbonyl} bond lengths are 1.345 (2) and 1.337 (2) \(\text{Å}\). The O—C bond length of the carbonyl moiety is 1.191 (3) \(\text{Å}\). The two C\textsubscript{aryl}—O—C\textsubscript{carbonyl} angles are 118.4 (2) and 118.8 (2)°, while the two O—C\textsubscript{carbonyl}—O\textsubscript{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 benzene ring and the carbonate plane are 52.7 (2) and 57.7 (2)°.

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 KSM/1 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 (Micro-VAX II) program package (Sheldrick, 1988). H atoms were placed in idealized positions and constrained to have C—H = 0.96 \(\text{Å}\) and isotropic thermal parameters, \(U = 0.08\) \(\text{Å}^2\). 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

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Synthesis, Characterization, and Decomposition of the First Mononuclear Eight-Coordinate Indium(III) Benzoate, In(η²-O₂CC₆H₅)₃(4-Mepy)₂

Maria T. Andras, Aloysius F. Hepp, Stan A. Duraj, Eric B. Clark, Daniel A. Scheiman, David G. Hehemann, and Phillip E. Fanwick

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Reprinted from INORG. CHEM., Volume 32, Number 19, Pages 4150–4152

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Synthesis, Characterization, and Decomposition of the First Mononuclear Eight-Coordinate Indium(III) Benzoate, In\(\left(\text{C}_7\text{H}_6\text{O}_2\right)\text{C}_6\text{H}_{5}\text{CH}_3\)\(\left(4\text{-Mepy}\right)\)_2

Maria T. Andras, Aloysius F. Hepp, Stan A. Duraj, Eric B. Clark, Daniel A. Scheiman, David G. Hehemann, and Phillip E. Fanwick

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Received May 15, 1992

Introduction

The existence of indium and gallium carboxylates is well documented. Numerous homoleptic polynuclear indium(III) carboxylates, \([\text{In}(\text{O},\text{CR})_2]_n\) (R = H, CH\(_3\), C\(_6\text{H}_{5}\), n-C\(_3\text{H}_{7}\), CH\(_3\text{CH}=\text{CH}_2\)-CH, (CH\(_3\))\(_2\)), as well as polynuclear organoindium(III) carboxylates, \([\text{R}_2\text{In}(\text{O},\text{CR})_2(\text{H})]_n\) (R = CH\(_3\), C\(_6\text{H}_{5}\), R'[H] = CH\(_3\), C\(_6\text{H}_{5}\), R = n-C\(_3\text{H}_{7}\), R'[H] = CH\(_3\)) are known; however, there is a void in the literature on analogous indium(III) benzoates. To the best of our knowledge, \(\text{Cl}_2\text{In}(\text{O},\text{C},\text{C}_6\text{H}_{5})_2(pyy)\) (py = pyridine), a six-coordinate mononuclear species, is the only structurally characterized indium(III) benzoate to date.

In this note we report the synthesis and full characterization of the first eight-coordinate mononuclear indium(III) benzoate complex, namely, \(\text{In}(\text{O},\text{C},\text{C}_6\text{H}_{5})_2(4\text{-Mepy})_2\), from the reaction of indium metal with benzoyl peroxide in 4-methylpyridine at 25 °C. The preparation of this indium(III) benzoate is significant of the first eight-coordinate mononuclear indium(III) benzoato complex to date.

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. Indium metal (99.99%), benzoyl peroxide (99%), and 4-methylpyridine (Aldrich) were used without additional purification. Benzoyl peroxide was degassed under vacuum at room temperature. Elemental analyses were performed by Galin Microanalytical Laboratories, Inc., Knoxville, TN. NMR spectra were recorded on a Bruker AC300F magnetic resonance spectrometer. The infrared spectrum was obtained from a KB 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 Ka radiation on a Scintag PAD V and a Phillips APD diffractometer.

Preparation of \(\text{In}(\text{O},\text{C},\text{C}_6\text{H}_{5})_2(4\text{-Mepy})_2\). 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 (1/4/40) and dried under vacuum for 18 h. Yield: 53-60%.

Analytical Caled (found) for C\(_{36}\)H\(_{25}\)InO\(_4\)N\(_2\)C\(_2\): C, 64.0 (64.3); H, 3.6 (3.8); N, 4.5 (4.5).

1H-NMR (DMSO-d\(_6\)) \(\delta\): 2.33 (6, Me, 6), 7.28 (d, 4H, p), 7.46 (s, 6H, meta), 7.56 (t, 3H, para), 8.00 (d, 6H, ortho), 8.50 (d, 4H, a).

13C-NMR (DMSO-d\(_6\)) \(\delta\): 20.5, 124.8, 128.2, 129.9, 131.9, 148.9, 149.1, 171.1. (KBr disk, cm\(^{-1}\)): 3091 (m), 3069 (s), 3058 (m), 3048 (m), 3031 (m), 2926 (m), 1654 (m), 1623 (vs, sh), 1611 (vs), 1600 (vs), 1566 (vs), 1543 (vs), 1507 (vs), 1496 (vs), 1418 (vs, bre), 1347 (vs, sh), 1314 (vs), 1306 (s), 1234 (vs), 1220 (m), 1175 (s), 1068 (s), 1021 (vs), 968 (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 \(\text{In}(\text{O},\text{C},\text{C}_6\text{H}_{5})_2(4\text{-Mepy})_2\). 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 ≤ 0 ≤ 23°. Intensity data were collected in the range 4 ≤ θ ≤ 45° by the ω-2θ scan technique. Within index ranges (12 ≤ θ ≤ 12, 0 ≤ k ≤ 0, 0 ≤ l ≤ 27), 2449 unique reflections were collected, of which 2067 were considered observed, \(F_0^2 > 3σ(F_0)\). 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 MoIEN.\(^4\) 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(100) and O(200) 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 \(R(F) = 0.059\) and \(R_w(F) = 0.079\) 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 benzophenone ketyl prior to use. Solutions were transferred via stainless steel cannulae and/or syringes. Indium powder (Alrich) was used without additional purification. Benzoyl peroxide was degassed under vacuum at room temperature. Elemental analyses were performed by Galin Microanalytical Laboratories, Inc., Knoxville, TN. NMR spectra were recorded on a Bruker AC300F magnetic resonance spectrometer. The infrared spectrum was obtained from a KB 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 Ka radiation on a Scintag PAD V and a Phillips APD diffractometer.

Preparation of \(\text{In}(\text{O},\text{C},\text{C}_6\text{H}_{5})_2(4\text{-Mepy})_2\). 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 (1/4/40) and dried under vacuum for 18 h. Yield: 53-60%.


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The In-O(22) bond length, 2.413(5) Å, is slightly longer (by 0.19 Å) than the In-O(21) bond length, 2.35(6) Å. Unsym-}

pendent benzoato ligand, the In-O bond lengths are not equivalent. The indium(III) atom is best described as a pseudo square pyramid CC«H5)3(4-Mepy)

and angles are presented in Table III. The solid-state molecular 

crystallographic 2-fold rotation axis. Interatomic bond distances 

occurs. In contrast, pyridine adducts of indium(m) acetate and 

yields of up to 60% (eq 1). In(\(\eta^2\)-OCC,H\(\text{H}_2\))\(\text{Me}\)_2 can be 

\(\text{II}^n + 3(\text{C}_2\text{H}_5\text{CO}_2)\text{O} \rightarrow \text{II}(\eta^2\text{OCC}_2\text{H}_4)\(\text{Me}\)_2\(\text{H}_2\text{O}\)\(\text{eq} 1\)

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.

Single-crystal X-ray diffraction analysis reveals that In(\(\eta^2\)-OCC,H\(\text{H}_2\))\(\text{Me}\)_2H\(\text{O}\) 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(\(\eta^2\)-OCC,H\(\text{H}_2\))\(\text{Me}\)_2 is shown in Figure 1.

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) bidentate 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. Unsym-
lengths differ significantly, i.e., 2.14 and 2.87 Å. 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 benzene 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(O2CCMe)2L (L = bipy, 2.325(6) Å; L = phen, 2.335(3) Å)9 and is significantly longer than values reported for six-coordinate CtIn(O2CPPh)(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.3,8,11 In the case of indium(III) carboxylates (of which In(η2-O2CCMe)2(4-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 chains. In In(η2-O2CCMe)3(4-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) benzoate species.

Thermal decomposition of In(η2-O2CCMe)3(4-Mepy)2 was followed by TGA, and the composition of the final pyrolysatae 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(η2-O2CCMe)3(4-Mepy)2 to In2O3, as demonstrated by the X-ray powder diffraction pattern (Table IV).13,14 The material is more than 90% crystalline In2O3, consistent with scanning electron microscopy, X-ray powder data, and thermal analysis.

Concluding Remarks

In summary, we have demonstrated a simple and direct one-step route to In(η2-O2CCMe)3(4-Mepy)2, the first mononuclear eight-coordinate indium(III) benzene and precursor to indium(III) oxide. Our approach to the synthesis of indium(III) carboxylates differs significantly from previously reported methods.1-11 The presence of 4-methylpyridine at the initial stages of reaction precludes In(O2CR)3 polymerization by coordinatively saturating the indium(III) center as it is formed. In addition, we have established that In(η2-O2CCMe)3(4-Mepy)2 is a stable inorganic precursor to indium oxide. A thorough discussion of material and thin-film preparation and characterization is forthcoming.

Acknowledgement. M.T.A. (Postdoctoral Fellowship, National Research Council/NASA Lewis Research Center), A.F.H. (Director's Discretionary Fund), and S.A.D. (NASA Grant NCC-162) acknowledge support from the NASA Lewis Research Center. We thank Ms. Ruth Cipic (XRD) and Mr. Frederick K. Oplinger for technical assistance.

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

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, Cu4S10(4-methylpyridine)4 (4-MePy), was prepared by three routes: reaction of Cu2S, reaction of CuBr·SMe2 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 (H2NC(S)NH2) in 4-methylpyridine to produce thiocyanate (NCS-) complexes. Three isolated and characterized compounds are: Cu(NCS)(4-MePy)2, a polymer, [4-MePy]2[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-Melm) resulted in the synthesis of a Cu-containing polymer, Cu(SO4)(N-Melm). 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 CuInO2 (Q = S or Se) [13,14] for thin-film photovoltaics; rare-earth, bismuth, and thallium ceramic superconductors, such as YBa2Cu3O7-x, Bi2Sr2Ca2Cu2O8, and Tl2Ba2Ca2Cu3O10 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.
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 (H₂NC(S)NH₂) and sulfur (Aldrich), and CuBr·SMe₂ (Alfa) were used without additional purification. The synthesis of ((CH₃)₃C₂Ga(μ-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 S₈ in pyridine (C₅H₅N,Py), (1), produces the cluster Cu₄S₁₀(Py)₄·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 Cu₄S₁₀(4-methylpyridine)₄·4-methylpyridine (4-MePy) (1) whose Cu₄S₁₀ 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 Cu₂S with excess sulfur in 4-methylpyridine as shown in equation (2). It has also been prepared according to equation (3) in which CuBr·SMe₂ reacts with S₈. The structure 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 S₄ approximate symmetry. The structure of (1) is shown in figure 1. Selected structural parameters are given in table 1.

\[
\begin{align*}
\text{Cu}^{0} + S_{8} & \xrightarrow{25 \degree C} Cu_{4}S_{10}(4-\text{MePy})_{4} \tag{1} \\
Cu_{2}S + S_{8} & \xrightarrow{25 \degree C} Cu_{4}S_{10}(4-\text{MePy})_{4} \tag{2} \\
CuBr·SMe_{2} + S_{8} & \xrightarrow{25 \degree C} Cu_{4}S_{10}(4-\text{MePy})_{4} \tag{3}
\end{align*}
\]

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 298 K in 4-methylpyridine when swept at 20 mV/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 S₂ 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-Melm)₆]S₈ for M = Mg, Mn, Fe, and Ni, (N-Melm) = N-methylimidazole (N(CH₃)NC₃H₃) [22]. However, Cu₄S also served as a starting material for the production of the N-Melm 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 S₂⁻ to form CuS.
under an inert line. Solids were tri-train. Copper, were used without bed in [18]. The

line (C₅H₅N,Py), in the solid-state line produces the S₁0 cluster unit is r (1) can also be tion of Cu₂S with pared according to ) was determined and consists of two pyridine and has selected structural

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>
<thead>
<tr>
<th>Compound</th>
<th>a, Å</th>
<th>b, Å</th>
<th>c, Å</th>
<th>α, °</th>
<th>β, °</th>
<th>γ, °</th>
<th>V, Å³</th>
<th>Z</th>
<th>form. weight</th>
<th>space group</th>
<th>T, °C</th>
<th>μ(Mo Kα)</th>
<th>R(Fo)</th>
<th>Rw(Fo)</th>
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<td>(1)</td>
<td>13.983 (2)</td>
<td>15.384 (2)</td>
<td>9.660 (1)</td>
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<td>93.38 (1)°</td>
<td>99.78 (1)°</td>
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<td>1040.42 g</td>
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<td>16.070 (1)</td>
<td>9.0754 (6)</td>
<td>5</td>
<td>3038.0 (1)</td>
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<td>114.153 (5)°</td>
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<td>3</td>
<td>620.31 g</td>
<td>Cc (#9)</td>
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TABLE 1. X-RAY DATA SUMMARY FOR COPPER COMPOUNDS

\[ R(F_o) = \sum |F_o| - |F_c|/\sum |F_o|; \quad \text{Rw}(F_o) = [\sum w(F_o)^2]/\sum w(F_o)^2]^{1/2}; \quad w = 1/\sigma^2(F_o). \]
Other copper and sulfur containing compounds were obtained when thiourea (H₂NC(S)NH₂) instead of S₂ 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-MePy)₂ (2), t-Cu(NCS)₂(4-MePy)₄(4-MePy)₂(H₂O)₁/₃ (3), and [4-MePy-H][Cu(NCS)₂(4-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).

The first step in this reaction may be attack of thiourea of Cu° (6) to produce hydrogen where thiourea acts like an acid on copper. The H₂NC(S)NH⁻ species can then rearrange to produce NCS⁻ and NH₃. 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 NH₃ 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).

While (6) and (7) are reasonable proposed reactions, we have not as yet obtained direct evidence of hydrogen or NH₃ 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•SMe₂ and ((CH₃)₂C₆Ga(μ-SH))₂in N-methylimidazole (N-MeIm), reaction (8), resulted in the synthesis of a Cu-containing polymer, Cu(SO₄)(N-MeIm)₄ (5), figure 1 and table 1.

ACKNOWLEDGMENTS


REFERENCES

1. F.A. Son
2. S.P. Pres
3. L.L. and
4. K.A Leu
5. A.E Leu
6. D.B
7. H.K Che
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(C6H5SO3)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(SO4)(Py)4*H2O 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 CuIn(Qz (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.

ACKNOWLEDGEMENT


REFERENCES

Redetermination of Piperidinium Hydrogen Sulfide Structure

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April 1994
Redetermination of Piperidinium Hydrogen Sulfide Structure

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ABSTRACT

The presence of adventitious water in a reaction between dicyclopentamethylenethiuramdisulfide \((\text{C}_5\text{H}_{10}\text{NCS}_2)_2\) and a picoline solution of tricyclopentadienylium(III) \((\text{C}_5\text{H}_2)_3\text{In}\) resulted in the formation of piperidinium hydrogen sulfide \((\text{C}_5\text{H}_{13}\text{NS})\). 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 \((\text{MW} = 119.23 \text{ g/mol})\) has an orthorhombic \((\text{Pbcm})\) unit cell whose parameters are: \(a = 9.818 \text{ (2)}, b = 7.3720 \text{ (1)}, c = 9.754 \text{ (1)} \text{ Å}, V = 706.0 \text{ (3)} \text{ Å}^3, Z = 4\). \(\text{Dx} = 1.122 \text{ g \ cm}^{-3}\), \(\text{Mo K\(\alpha\)} (\lambda = 0.71073\text{Å}), \mu = 3.36 \text{ cm}^{-1}, \text{F}(000) = 264.0, T = 293 \text{ K}, R = 0.036\) for 343 reflections with \(F_o^2 > 3\sigma(F_o^2)\) and 65 variables. The compound consists of \([\text{C}_5\text{H}_{10}\text{NH}_2]^+\) cations and \([\text{SH}]^-\) anions with both species residing on crystallographic mirror planes. \(\text{N-H \cdots S}\) hydrogen bonding contributes to the interconnection of neighboring piperidinium components of the compound.

\(^{1}\text{National Research Council–NASA Resident Research Associate at Lewis Research Center.}\)
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.

\[
\text{C}_2\text{H}_{10}\text{NH} + \text{HX} \rightarrow \left[\text{C}_5\text{H}_{10}\text{NH}_2\right]^+\text{X}^- \quad (1)
\]

For example, reacting tetraethylthiuram disulfide \([(\text{C}_2\text{H}_5)_2\text{NCS}_2]_2\) with a picoline (\(\text{C}_6\text{H}_7\text{N}\)) solution of copper(I) bromide dimethylsulfide [\(\text{CuBr} \cdot \text{S(CH}_3)_2\)] in the absence of rigorous drying produces picolinium bromide (Andras et. al., 1993). In a similar vein, we now report that reacting dicyclopentamethylenethiuram disulfide \((\text{C}_5\text{H}_{10}\text{NCS}_2)_2\) with a picoline solution of tricyclopentadienylindium(n) \([(\text{C}_5\text{H}_5)_3\text{In}]\) in the absence of rigorous drying gives piperidinium hydrogen sulfide \([\text{C}_5\text{H}_{10}\text{NH}_2]\text{HS}\). 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 crystals were prepared in the following manner. Under argon, a solution of tricyclopentadienylindium(n), \((\text{C}_5\text{H}_5)_3\text{In}\) (0.25 g, 0.806 mmol) and dicyclopentamethylenethiuram disulfide, \((\text{C}_5\text{H}_{10}\text{NCS}_2)_2\) (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°. Intensity data were collected with the \(\omega-2\theta\) scan technique with 4 < \(2\theta\) < 45°; the scan rate varied from 1 to 16° 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 ≤ \(h\) ≤ 10, 0 ≤ \(k\) ≤ 10, 0 ≤ \(l\) ≤ 7), 572 unique reflections were collected of which 343 are classified as observed, \(F_\text{o}^2 > 3\sigma(F_\text{o}^2)\). 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
\[ \sum w(\mid F_o \mid - \mid F_c \mid )^2. \]  
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: \( R = 0.036, wR = 0.044, S = 1.364, (\Delta/\sigma)_{\text{max}} = 0.06. \) 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 \( w(\mid F_o \mid - \mid F_c \mid )^2 \) versus \( \mid F_o \mid \) reflection order in data collection, sin \( \theta/\lambda \) 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 \( \cdots \) 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 dicyclopentamethylenethiuram 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): \( Pmab, a = 9.77 \ (1), b = 7.30 \ (2), c = 9.84 \ (1) \ \text{Å}, \ R = 0.075 \) 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.

Acknowledgements

M.T.A. gratefully acknowledges a postdoctoral fellowship from the National Research Council - NASA Lewis Research Center. A.F.H. acknowledges support from the Director’s Discretionary Fund at NASA Lewis. S.A.D. acknowledges partial support from NASA grant NCC3-162.
References


TABLE 1

Positional and Equivalent Isotropic Thermal Parameters with e.s.d.'s for \([\text{CsH}_x\text{NH}_2][\text{SH}]\).

\[
B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i^* a_j^* \cdot a_i \cdot a_j.
\]

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* Refined isotropically
TABLE 2

Bond lengths (Å) and angles (°) with e.s.d's for $[\text{C}_5\text{H}_{10}\text{NH}_2][\text{SH}]$. 

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$^{*}$ C(1)-C(2)-H(21) 106(2)  
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C(3)-C(2)-H(21) 113(2)  
C(3)-C(2)-H(22) 108(3)  
H(21)-C(2)-H(22) 113(3)  
C(2)-C(3)-C(2)' 110.6(6)  
C(2)-C(3)-H(31) 110(2)  
C(2)-C(3)-H(32) 115(3)  
H(31)-C(3)-H(32) 94(7)  
S-H(1)-N 177(5)  
S-H(N)-N 171(5)
FIGURE 1

ORTEP (Johnson, 1965) drawing of the \([C_5H_{10}NH_2][SH]\) compound 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$_5$H$_{10}$NH$_2$][SH].

10*F$_{obs}$ and 10*F$_{calc}$ for (NC$_5$H$_{12}$)(H$_2$)

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Page 1
Supplemental data from the structural determination of \([\text{C}_5\text{H}_{10}\text{NH}_2][\text{SH}]\).

10\(^*\)\(F_{\text{obs}}\) and 10\(^*\)\(F_{\text{calc}}\)

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Supplemental data from the structural determination of [C₃H₁₀NH₂][SH].

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Appendix A (cont.)

Supplemental data from the structural determination of [C$_5$H$_{10}$NH$_2$][SH].

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Redetermination of Piperidinium Hydrogen Sulfide Structure

Maria T. Andras, Aloysius F. Hepp, Phillip E. Fanwick, Stan A. Duraj, and Edward M. Gordon

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135–3191

National Aeronautics and Space Administration
Washington, D.C. 20546–0001

Maria T. Andras, National Research Council-NASA Research Associate at Lewis Research Center; Aloysius F. Hepp, NASA Lewis Research Center; Phillip E. Fanwick, Purdue University, Department of Chemistry, West Lafayette, Indiana 47907 (work funded by NASA Contract NCC3-246); Stan A. Duraj, Cleveland State University, Department of Chemistry, Cleveland, Ohio 44115 (work funded by NASA Contract NCC3-162); and Edward M. Gordon, Wilberforce University, Wilberforce, Ohio 45384 (work funded by NASA Contract NCC3-281). Responsible person, Aloysius F. Hepp, organization code 5410. (216) 433-3835.

The presence of adventitious water in a reaction between dicyclopentamethylenethiuram-disulfide (C₅H₁₀NCS₂)₂ and a picoline solution of tricyclopentadienylindium(III) (C₅H₅)₃In resulted in the formation of piperidinium hydrogen sulfide (C₅H₁₃NS). 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 (Pbcn) unit cell whose parameters are: a = 9.818(2), b = 7.3720(1), c = 9.754(1) Å, V = 706.0(3) Å³, Z = 4, Dₐ = 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 F₀ > 3σ(F₀) and 65 variables. The compound consists of [C₅H₁₀NH₂⁺]⁺ 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.
One-Step Synthesis of Dithiocarbamates from Metal Powders

ONE-STEP SYNTHESIS OF DITHIOCARBAMATES FROM METAL POWDERS

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*NASA Lewis Research Center, M.S. 302-1, Cleveland, OH 44135
**School of Technology, Kent State University, Kent, OH 44242
†Department of Chemistry, Cleveland State University, Cleveland, OH 44115
††Department of Chemistry, Purdue University, West Lafayette, IN 47907

ABSTRACT

Neutral metal dithiocarbamate complexes (M(NR₂CS₂)₃) 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 tetramethylthiuram disulfide (tmtd) in 4-methylpyridine (4-Mepy) at 25 °C produces a new homoleptic indium (II) dithiocarbamate, In(N(CH₃)₂CS₂)₃ (I), in yields of over 60%. The indium (II) dithiocarbamate was characterized by X-ray crystallography; (I) exists in the solid state as discrete distorted-octahedral molecules. Compound (I) crystallizes in the Pibar (No. 2) space group with 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. 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 CuInS₂) [1,2]. Chevrel phases are superconducting, for example PbMo₆S₈ has a T_c of 21 K [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 H₂ from crude oil, this allows efficient or environmentally sound use of "dirtier" feedstocks [4]. Chemical sensitization to form AgAu₃S₄ 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(NR₂CS₂)₃ [10]. There are several typical synthetic routes to these compounds including reaction of CS₂ with metal amide complexes (M(NR₂)₃), reaction of metal chlorides with CS₂ 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(CH₃)₂CS₂)₃ (I). We also discuss mass spectral data on several transition metal complexes and relate it to their potential use as precursors in chemical vapor deposition (CVD) and other deposition technologies.

† - Senior Research Fellow/NASA Lewis Research Center Resident Research Associate.
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 S99B 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.

\[
M^0 + \frac{n}{2} R_2NC(S)S-SC(S)NR_2 \xrightarrow{25 \, ^\circ C} M(NR_2CS_2)_n
\]

For example, treatment of metallic indium with tmtd in 4-Mepy at 25 °C produces In(N(CH3)2CS2)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(C2H5)2CS2)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(CH3)2CS2)3 and Cu(N(C2H5)2CS2)2 with key atoms labelled. The thermal ellipsoids enclose 50 % of electron density.

Figure 2. - Sc...
It was previously reported that room-temperature reaction of copper and nickel powders with sodium dithiocarbamates and photochemical reaction of copper powder with tetraalkylthiuramdisulfides (ttd) in CHCl₃ produce metal dithiocarbamates \([11,12]\). We and others have discovered that in strong basic, coordinating solvents such as 4-MePy, species such as SG, REER (R = alkyl or aryl, E = S or Se) and \((\text{CH}_3\text{H}_2\text{CO})_2\text{O}\) 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 results in only one product.

\(\text{C}_2\text{H}_4\text{Ni} \cong \text{Fe}, \text{Co}, \text{Ni}, \text{Cu} \text{ 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, \((\text{CH}_3)_2\text{NCS}\). Finally, each compound has a peak 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.}

\[
\text{Fe}^{2+}, \text{Cu}^{2+} \text{m/z 303 for the } \text{Cu}^{63} \text{ isotope and a m/z 298 peak for the } \text{Ni}^{58} \text{ 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 CH₃S 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 MS₂⁺ 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 ML₂⁺ (Co: 299, Fe: 296) of both Fe and Co are much more intense than the corresponding parent ions and the analogous Ni and Cu species ML⁺. The rationale for the intensity of these ions is two-fold: the stability of Fe²⁺ and Co²⁺ relative to monovalent Ni and Cu and the greater volatility of a lower-mass fragment. The stability argument is born out by the relative weakness of the FeI⁺ and CoI⁺ 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 MS₂⁺ 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.

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<td>$[\text{CH}_3\text{NCS}]^+$</td>
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</tr>
<tr>
<td>$[\text{CH}_3\text{NCS}]^+$</td>
<td>88 (100)</td>
</tr>
<tr>
<td>$[\text{CH}_3\text{NCS}]^+$</td>
<td>120 (10.2)</td>
</tr>
<tr>
<td>$\text{MS}_2^+$</td>
<td>127,129 (2.9, 1.5)</td>
</tr>
<tr>
<td>$[\text{MS}_2\text{CNCH}_3]^-$</td>
<td>136,138 (14.3, 7.1)</td>
</tr>
<tr>
<td>$[\text{MS}_2\text{CNCH}_3]^-$</td>
<td>183,185 (28.8, 15.9)</td>
</tr>
<tr>
<td>$[\text{MS}_2\text{CNCH}_3]^-$</td>
<td>303,305 (74.0, 56.8)</td>
</tr>
<tr>
<td>$[\text{MS}_2\text{CNCH}_3]^-$</td>
<td>423,425 (-,-)</td>
</tr>
</tbody>
</table>
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-butyl dithiocarbamate to prepare a single-molecule precursor to CuInS2 [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 dithiocarbamates 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(CH3)2CS2)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 ML2+ ion peaks, the M+ and MS2* (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.

ACKNOWLEDGEMENTS

A.F.H. (Director's Discretionary Fund), D.G.H (NASA Cooperative Agreement NCC3-318), S.A.JD. (NASA Cooperative Agreement NCC3-162) and P.E.F. (NASA Cooperative Agreement NCC3-246) acknowledge support from NASA Lewis Research Center. We thank Profs. Andrew Barron of Harvard University, Mercouri Kanatzidis of Michigan State University, and Mark Hampden-Smith of the Univ. of New Mexico for pre-prints of their work.

REFERENCES


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**Table: Mass spectral data**

<table>
<thead>
<tr>
<th>Compound</th>
<th>m/z (relative intensity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[M(N(CH3)2CS2)+1]</td>
<td>136,138 (14.37)</td>
</tr>
<tr>
<td>[M(N(CH3)2CS2)+1]+</td>
<td>132 (3.0)</td>
</tr>
<tr>
<td>[M(N(CH3)2CS2)+1]</td>
<td>176 (15.2)</td>
</tr>
<tr>
<td>[M(N(CH3)2CS2)+1]</td>
<td>299 (49.7)</td>
</tr>
<tr>
<td>[M(N(CH3)2CS2)+1]</td>
<td>419 (13.9)</td>
</tr>
<tr>
<td>[MS2(N(CH3)2CS2)+2]+</td>
<td>303,305 (74.56)</td>
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<tr>
<td>[MS2(N(CH3)2CS2)+2]+</td>
<td>423 (6.7)</td>
</tr>
<tr>
<td>[MS2(N(CH3)2CS2)+2]+</td>
<td>418 (6.7)</td>
</tr>
<tr>
<td>[M(N(CH3)2CS2)+1]</td>
<td>136,138 (14.37)</td>
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<tr>
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</tr>
</tbody>
</table>

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(Received 12 June 1992; accepted 1 January 1993)

Abstract

The structure of trans-bis(acetato-O)bis(4-methylpyridine-N)copper(II), $[\text{Cu(C}_2\text{H}_5\text{ClO}_2)_2\text{C}_6\text{H}_7\text{N}]$ 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).

$\text{(I)}$

$\text{Cu}^\text{II}$

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, 1971a,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, 1971a,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 $[\text{Cu}_2\text{(C}_2\text{H}_5\text{ClO}_2)_2\text{C}_6\text{H}_7\text{N}]$ (Davey & Stephens, 1970). All angles and bonds within the 4-methylpyridine rings are as expected.
Experimental

Crystal data
[Cu(C2H3O2)2(H2N2)]

\[ M_{r} = 367.89 \]

Monoclinic

\[ a = 6.194 (2) \text{ Å} \]
\[ b = 16.474 (6) \text{ Å} \]
\[ c = 8.270 (3) \text{ Å} \]
\[ \beta = 92.02 (3)^{\circ} \]
\[ V = 843.5 (9) \text{ Å}^3 \]

Z = 2

\[ D_{x} = 1.448 \text{ Mg m}^{-3} \]

Data collection
Enraf-Nonius CAD-4

\[ \text{w-20 scans} \]

\[ \text{Absorption correction: empirical } \psi \text{ scans} \]

(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.

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.

Reference

References


