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ONE-STEP SYNTHESIS OF DITHIOCARBAMATES FROM METAL POWDERS

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ABSTRACT

Neutral metal dithiocarbamate complexes ($M(NR_2CS_2)_x$) are well-known precursors to metal sulfides, a class of materials with numerous technological applications. We are involved in a research effort to prepare new precursors to metal sulfides using simple, reproducible synthetic procedures. We describe the results of our synthetic and characterization studies for $M = Fe, Co, Ni, Cu,$ and In . For example, treatment of metallic indium with tetramethylthiuramdisulfide (tmtdd) in 4-methylpyridine (4-Mepy) at 25 °C produces a new homoleptic indium (III) dithiocarbamate, $In(N(CH_3)_2CS_2)_3$ (**I**), in yields of over 60%. The indium (III) dithiocarbamate was characterized by X-ray crystallography; (**I**) exists in the solid state as discrete distorted-octahedral molecules. Compound (**I**) crystallizes in the $P1\bar{6}$ (No. 2) space group with lattice parameters: $a = 9.282(1)$ Å, $b = 10.081(1)$ Å, $c = 12.502$ Å, $\alpha = 73.91(1)^\circ$, $\beta = 70.21(1)^\circ$, $\gamma = 85.84(1)^\circ$, and $Z = 2$. X-ray diffraction and mass spectral data were used to characterize the products of the analogous reactions with Fe, Co, Ni, and Cu. We discuss both use of dithiocarbamates as precursors and our approach to their preparation.

INTRODUCTION

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

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

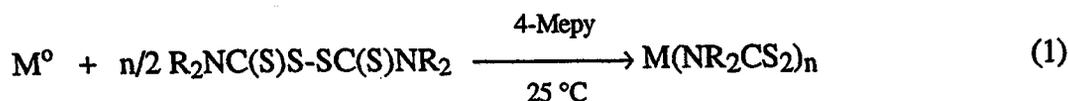
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EXPERIMENTAL

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

RESULTS AND DISCUSSION

Metal dithiocarbamates were typically prepared by reaction of metal powder (M = Fe, Co, Ni, Cu, and In) (0.50 g) and stoichiometric amounts of tetraalkylthiuramdisulfides (for R = Me, tntd; 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.



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

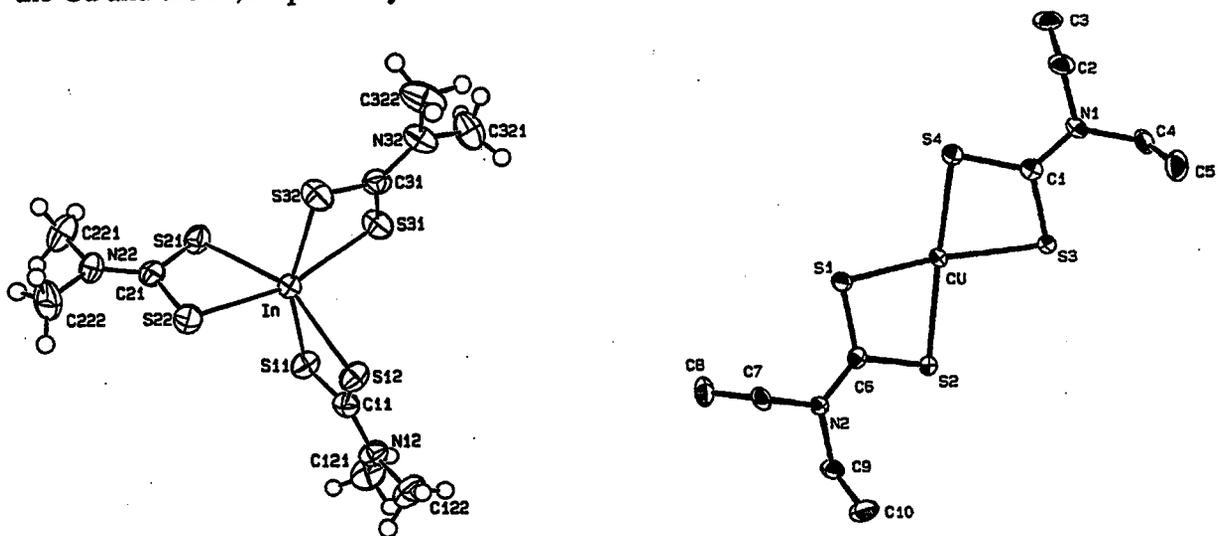


Figure 1. - ORTEP drawings of $In(N(CH_3)_2CS_2)_3$ and $Cu(N(C_2H_5)_2CS_2)_2$ with key atoms labelled. The thermal ellipsoids enclose 50 % of electron density.

Table 1.

MASS SPECTRA OF METAL DIMETHYLDITHIOCARBAMATES

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

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

It was previously reported that room-temperature reaction of copper and nickel powders with sodium dithiocarbamates and photochemical reaction of copper powder with tetraalkylthiuramdisulfides (tatsd) in CHCl_3 produce metal dithiocarbamates [11,12]. We and others have discovered that in strong basic, coordinating solvents such as 4-MePy, species such as S_8 , REER (R = alkyl or aryl, E = S or Se) and $(\text{C}_6\text{H}_5\text{CO})_2\text{O}_2$ will oxidize metal powders [15-19]. The advantage of reaction (1) is the lack of by-products. Production of dithiocarbamates via oxidation of metal powders results in a much greater control of impurities, first by the use of metal powders as a starting material and second by simplicity in the chemistry that results in only one product.

The dithiocarbamates prepared for M = Fe, Co, Ni, and Cu were examined by mass spectrometry. A diagram of the instrument used in these studies is shown in figure 2. A summary of relevant mass spectral data is given in table 1. All of the metal complexes show characteristic peaks corresponding to breakdown of the dimethyldithiocarbamate residues. Each compound gives an ion at m/z 120 corresponding to the dimethyldithiocarbamate residue itself. Each spectrum has as its base peak, m/z 88 with 100 %, consistent with loss of a sulfur atom, $(\text{CH}_3)_2\text{NCS}]^+$. 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.

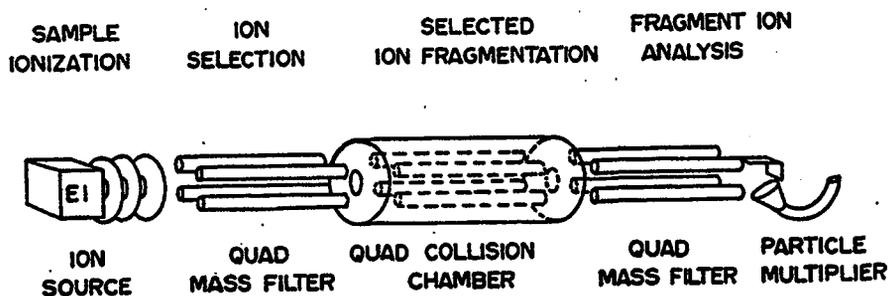


Figure 2. - Schematic diagram of Finnigan TSQ-45 mass spectrometer used in this study.

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

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

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

CONCLUSIONS

We have described a simple one-step synthesis to metal 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 $\text{In}(\text{N}(\text{CH}_3)_2\text{CS}_2)_3$, a distorted octahedron and only the second structurally-characterized indium dithiocarbamate, was briefly described. Mass spectral data on Fe, Co, Ni, and Cu dimethyldithiocarbamate indicate that all four are reasonably volatile. Both the divalent and trivalent compounds had fairly intense ML_2^+ ion peaks, the M^+ and MS_2^+ (for Cu, Ni, and Co) though weaker, were present. The mass spectral data demonstrates the key attributes of dithiocarbamates: volatility, relative stability in the gas phase, and ample decomposition pathways for clean production of metal sulfide.

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REFERENCES

1. L.L. Kazmerski and S. Wagner, in *Current Topics in Photovoltaics*, edited by T. J. Coutts and J. D. Meakin (Academic Press, London, 1985) pp. 41-109.
2. A.N. MacInnes, M.B. Power, A.R. Barron, P.P. Jenkins, and A.F. Hepp, *Appl. Phys. Lett.* **62**, 711 (1993).
3. R. Chevrel and M. Sargent, *Topp. Curr. Phys.* **32**, 25 (1982).
4. O. Weisser and S. Landa, *Sulfide Catalysts, Their Properties and Applications* (Pergamon Press, New York, 1973).
5. D.A. Pitt, M.L. Rachu, and M.R.V. Sayhun, *Photogr. Sci Eng.* **25**, 57 (1981).
6. F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed. (John Wiley and Sons, New York, 1988).
7. W. Hirpo, S. Dhingra, A. Sutorik, and M.G. Kanatzidis, *J. Am. Chem. Soc.* **115**, 1597 (1993).

8. B.M. Basol, V.K. Kapur, A. Halani, and C. Leidholm, *Solar Energy Materials and Solar Cells* **29**, 163 (1993).
9. M. Tabib-Azar, S. Kang, A.N. MacInnes, M.B. Power, A.R. Barron, P.P. Jenkins, and A.F. Hepp, *Appl. Phys. Lett.* **63**, 625 (1993).
10. See the following extensive reviews: D. Coucouvanis, *Prog. Inorg. Chem.* **11**, 233 (1970); D. Coucouvanis, *Prog. Inorg. Chem.* **26**, 301 (1979).
11. T. Tetsumi, M. Sumi, M. Tanaka, and T. Shano, *Polyhedron* **4**, 707 (1985).
12. T. Tetsumi, M. Sumi, M. Tanaka, and T. Shano, *Polyhedron* **5**, 707 (1986).
13. K. Dymock, G.J. Palenik, J. Slezak, C.L. Raston, and A.H. White, *J. Chem. Soc., Dalton Trans.*, 28 (1976).
14. B.H. O'Connor and E.N. Maslen, *Acta. Cryst.* **21**, 828 (1966).
15. R. Kumar, H.E. Mabrouk, and D.G. Tuck, *J. Chem. Soc., Dalton Trans.*, 1045 (1988).
16. G. Speier and V. Fulop, *J. Chem. Soc., Dalton Trans.*, 2331 (1989).
17. E. Ramli, T.B. Rauchfuss, and C.L. Stern, *J. Am. Chem. Soc.* **112**, 4043 (1990).
18. S. Dev, E. Ramli, T.B. Rauchfuss, and S.R. Wilson, *Inorg. Chem.* **30**, 2514 (1991).
19. M.T. Andras, A.F. Hepp, S.A. Duraj, E.B. Clark, D.A. Scheiman, D.G. Hehemann, and P.E. Fanwick, *Inorg. Chem.* **32**, 4150 (1993).
20. *Handbook of Chemistry and Physics*, edited by R.C. Weast, 55th ed. (Chemical Rubber Company Press, Cleveland, OH, 1974).
21. I.R. Gelling, *Rubber Chemistry and Technology* **46**, 524 (1973).
22. D.M. Frigo, O.F.Z. Khan, and P. O'Brien, *J. Cryst. Growth* **96**, 989 (1989).
23. M.B. Hursthouse, M.A. Malik, M. Motevalli, and P. O'Brien, *Polyhedron* **11**, 45 (1992).
24. M.B. Hursthouse, M.A. Malik, M. Motevalli, and P. O'Brien, *Organometallics* **10**, 730 (1991).
25. M.A. Malik and P. O'Brien, *Chem. Mater.* **3**, 999 (1991).
26. M.A. Malik, M. Motevalli, J.R. Walsh, and P. O'Brien, *Organometallics* **11**, 3136 (1992).
27. Q. Powell, A. Gurav, T.T. Kudas, M.J. Hampden-Smith, D. Zeng, and M.L. Wang, submitted.
28. D. Zeng, M.J. Hampden-Smith, T.M. Alam, and A.L. Rheingold, submitted.
29. R. Nomura, S. Seki, and H. Matsuda, *J. Mater. Chem.* **2**, 765 (1992).



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