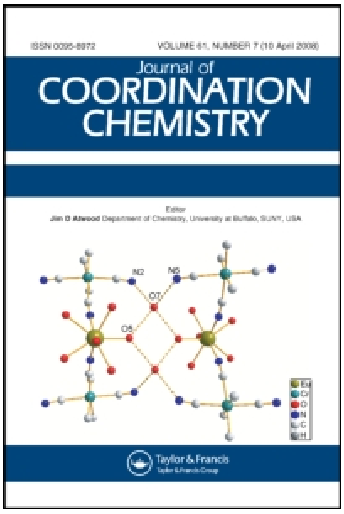

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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF TRIS(DIMETHYLDITHIOCARBAMATE) INDIUM(III), $In[S_2CN(CH_3)_2]_3$

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The synthesis and structure of the indium dithiocarbamate, $In[S_2CN(CH_3)_2]_3 \bullet (1/2)$ 4-mepy (4-mepy = 4-methylpyridine), is described. Indium metal was oxidized by tetramethylthiuram disulfide in 4-methylpyridine at 25°C to form a new, homoleptic indium(III) dithiocarbamate in yields exceeding 60%. $In[S_2CN(CH_3)_2]_3$ exists as a discrete molecule with a distorted-octahedral geometry. The compound crystallizes in the $P\bar{1}$ (No. 2) space group with $a = 9.282(1)$ Å, $b = 10.081(1)$ Å, $c = 12.502$ Å, $\alpha = 73.91(1)°$, $\beta = 70.21(1)°$, $\gamma = 85.84(1)°$, $Z = 2$, $V(Å^3) = 1057.3(3)$, $R = 0.046$ and $R_w = 0.061$.

Keywords: Indium; Dithiocarbamate; Tetralkylthiuram disulfide; Tetraalkyldithiocarbamate; Photovoltaics; MOCVD

INTRODUCTION

Numerous applications demonstrate the significance of metal chalcogenide semiconductors. Photoelectrical or electrical properties of these materials are important in electronic devices such as solar cells, infrared detectors,

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light-emitting diodes, and transistors [*e.g.*, CdE (E = S, Se, or Te), GaS, CuInQ_2 (Q = S or Se)] [1–5]. Often these films are grown by metalorganic chemical vapor deposition, MOCVD, at high temperatures using highly-toxic and pyrophoric precursors. There is great interest in discovering new routes for growing thin films of these materials at relatively low temperatures to reduce cost and allow deposition on a broader variety of substrates (*e.g.*, flexible plastics). It can also be beneficial if two or more of the desired elements are contained in the same precursor [1, 2, 5]. Therefore, compounds are needed which will readily decompose to form the desired semiconductors with the proper stoichiometry.

Metal dithiocarbamates are under investigation as MOCVD precursors to metal sulfides [9, 10]. These compounds contain metal-sulfur bonds which are incorporated into thin-film semiconductors upon precursor decomposition and sublimation of the new materials onto a substrate.

Many homoleptic, metal dithiocarbamates, $M(S_2CNR_2)_n$, have been studied [6] and several synthetic routes have been devised for their preparation. A few such examples include the reaction of CS_2 with metal amide complexes ($M(NR_2)_n$), the reaction of metal chlorides with CS_2 in the presence of amines, and the direct reaction of metal halides with sodium dithiocarbamate salts [7]. Additionally, reactions with metal powders offer a simple and more direct approach.

Metal thiocarbamates have been prepared from metal powders and sodium dithiocarbamate in organic solvents such as chloroform, dimethyl sulfoxide (DMSO) and ethanol [8]. However, previous attempts to react the metals directly with tetralkylthiuram disulfide have been unsuccessful, with one exception. Bis(dibutyldithiocarbamate)copper(II) was synthesized through the combination of tetrabutylthiuram disulfide and copper powder in chloroform, but this reaction proceeded through a photochemical pathway [9]. By utilizing the strongly basic, coordinating solvent, 4-methylpyridine, we have been able to prepare both divalent (M = Ni and Cu) and trivalent (M = Fe, Co, and In) metal dithiocarbamates [10] at room temperature by non-photochemical means. The previously unreported $In(S_2CN(CH_3)_2)_3$ is described herein.

EXPERIMENTAL

General

Air and moisture-sensitive materials were handled under inert atmospheres employing standard Schlenk techniques and a double-manifold vacuum line.

Solids were manipulated in a Vacuum Atmospheres drybox equipped with an HE-493 dri-train. Solvents were freshly distilled from sodium benzophenone ketyl prior to use. Solutions were transferred *via* stainless steel cannula and/or syringes. The indium metal powder was obtained from Strem Chemicals (Newburyport, MA), while the tetramethylthiuram disulfide was purchased from Aldrich Chemical Co. (Milwaukee, WI). Both were used without further purification.

Preparation of $In[S_2CN(CH_3)_2]_3$

The dialkyldithiocarbamate was typically prepared through oxidation of indium metal powder (0.50 g, 4.3 mmol) by stochiometric amounts of tetramethylthiuram disulfide in 35 mL of 4-methylpyridine at ambient temperature for several days, under argon [10]. The dark brown or black precipitate was filtered and washed with 150 mL of hexane. Yields exceeded 60% of crude product.

X-ray Crystal Data Collection

A chunk of $InC_{12}H_{18}N_3S_6$, having dimensions of 0.50 × 0.38 × 0.34 mm, was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with a Mo K_α radiation source ($\lambda = 0.71073$ Å) on an Enraf–Nonius CAD 4 computer-controlled kappa axis diffractometer equipped with a graphite crystal, incident beam monochromator.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement (See Tab. I), using the setting angles of 25 reflections in the range $21° < \theta < 23°$, measured by the computer controlled diagonal slit method of centering. Data support an empirical formula of $InS_6N_{3.5}C_{12}H_{21.5}$. The calculated volume for the triclinic cell was $V = 1057.3$ Å. For $Z = 2$ and $F.\ W. = 514.53$, the calculated density is 1.62 g/cm^3. As a check on crystal quality, omega scans of several intense reflections were measured; the width at half-height was 0.72° with a take-off angle of 3.0° indicating moderate crystal quality. There were no systematic absences; the space group was determined to be $P\ \bar{1}$ (No. 2).

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 16.7 cm^{-1} for Mo K_α radiation. An empirical absorption correction based on the method of Walker and Stuart [11] was applied. Relative transmission coefficients ranged from 0.811 to 1.000 with an average value of 0.938.

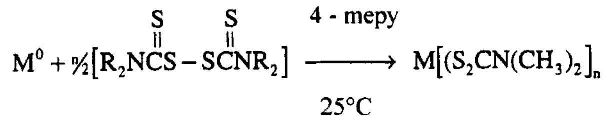
TABLE I Crystallographic data for $In[S_2CN(CH_3)_2]_3$

Molecular formula	$InS_6N_{3.5}C_{12}H_{21.5}$
Formula weight	522.03
Crystal size (mm)	0.50 × 0.38 × 0.34
Space group (No.)	$P\bar{1}$ (2)
a (Å)	9.282(1)
b (Å)	10.081(1)
c (Å)	12.502(2)
α (°)	73.91(1)
β (°)	70.21(1)
γ (°)	85.84(1)
V(Å^3)	1057.3(3)
Z	2
d_{calc} (g cm^{-3})	1.64
μ (cm^{-1})	16.52
Transmission coefficient	1.000-0.811
2θ Range (°)	4.00-45.00
Scan method	$\omega - 2\theta$
No. unique data	2757
No. observed data ($1 > 3\sigma(I)$)	2373
R^a	0.046
R^b_w	0.061
GOF	2.191
Largest shift/e. s. d. final cycle	0.09

Calculations were performed on a VAX computer. Refinement was done using Enraf-MolEN [12]. The crystal structure was solved with the structure solution program SHELX-86 [13]. Using the Patterson heavy-atom method, the position of the In atom was revealed. The remaining atoms were found in succeeding difference Fourier syntheses. Hydrogen atoms were added to the structure factor calculations but their positions were not refined.

RESULTS AND DISCUSSION

This group has successfully reacted tetraalkylthiuram disulfides to form homoleptic dithiocarbamates with Fe, Co, Ni, Cu and In metal powders (See Scheme 1).



$$M^0 + {}^n\!/_2[R_2N\overset{\overset{S}{\|}}{C}S - S\overset{\overset{S}{\|}}{C}NR_2] \xrightarrow[25°C]{4\text{ - mepy}} M[(S_2CN(CH_3)_2]_n$$

SCHEME 1

Synthesis of the title compound is straightforward and offers a high degree of control over the introduction of impurities, since only metal powders and the tetralkylthiuram disulfide are used.

The unit cell of the title compound consists of an In^{3+} cation ligated by three dithiocarbamate molecules and one half a formula weight of 4-methylpyridine (See Fig. 1).

In[S$_2$CN(CH$_3$)$_2$]$_3$ has a distorted octahedral geometry. Selected bond distances and angles for this compound appear in Table II.

Bond distances and angles for In[S$_2$CN(CH$_3$)$_2$]$_3$ are very similar to those reported for the ethyl analog of this compound [14]. On average, the N(12)—C(11), N(22)—C(21) and N(32)—C(31) bond lengths of the methyl compound are slightly shorter at 1.319 Å than the comparable N—C bonds of the ethyl compound, 1.329 Å. The rest of the values for similar structure components are comparable between both analogs within statistical deviation of their calculated values.

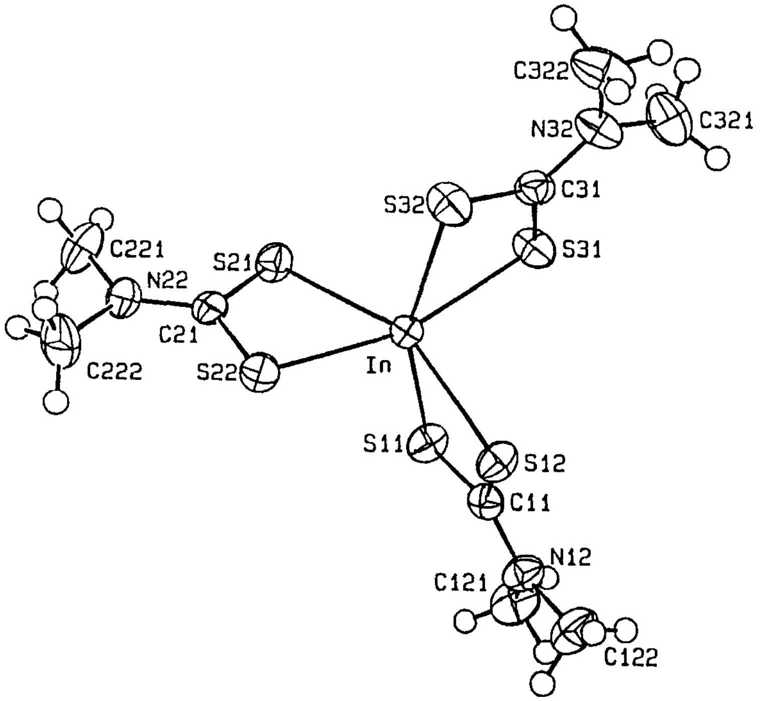


FIGURE 1 ORTEP drawing of In[S$_2$CN(CH$_3$)$_2$]$_3$ with key atoms labeled. The thermal ellipsoids enclose 50% of electron density.

TABLE II Selected bond distances (Å) and angles (°) for $In[S_2CN(CH_3)_2]_3$

Bond	*Distance*	*Atoms*	*Angle*
In—S(11)	2.602(2)	S(11)—In—S(12)	69.62(6)
In—S(12)	2.583(2)	S(11)—In—S(21)	96.15(6)
In—S(21)	2.582(2)	S(11)—In—S(22)	105.88(7)
In—S(22)	2.590(2)	S(11)—In—S(31)	91.63(6)
In—S(31)	2.600(2)	S(11)—In—S(32)	157.88(7)
In—S(32)	2.608(2)	S(12)—In—S(21)	154.94(7)
N(12)—C(11)	1.319(9)	S(21)—In—S(22)	69.67(6)
N(22)—C(21)	1.308(9)	S(22)—In—S(31)	161.87(7)
N(32)—C(31)	1.33(1)	S(31)—In—S(32)	68.91(6)
S(11)—C(11)	1.727(7)	In—S(11)—C(11)	85.6(2)
S(12)—C(11)	1.720(7)	In—S(12)—C(11)	86.4(2)
S(21)—C(21)	1.724(7)	S(11)—C(11)—N(12)	120.7(6)
S(22)—C(21)	1.723(7)	S(11)—C(11)—S(12)	118.4(4)
S(31)—C(31)	1.725(8)	C(11)—N(12)—C(21)	121.8(7)
S(32)—C(31)	1.713(8)		

Sulfur to metal bond angles around the pseudo-octahedral metal center fit into three general categories. The bidentate, ligand to metal bite angles range from S(31)—In—S(32) = 68.91(6)° to S(21)—In—S(22) = 69.67(6)°. The *cis*, sulfur to metal bond angles deviate from 90° over the range of S(11)—In—S(31) = 91.63(6)° to S(11)—In—S(22) = 105.88(7)°. Bond angles for sulfurs arranged *trans* to one another with respect to the metal deviate from 180° over the range of S(12)—In—S(21) = 154.94(7)° to S(22)—In—S(31) = 161.87(7)°.

CONCLUSION

We have described a simple one-step synthesis to a metal dithiocarbamate by oxidation of indium powder with tetramethylthiuram disulfide 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 $In[S_2CN(CH_3)_2]_3$, a distorted octahedron and only the second structurally-characterized homoleptic indium dithiocarbamate, was described in detail herein.

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