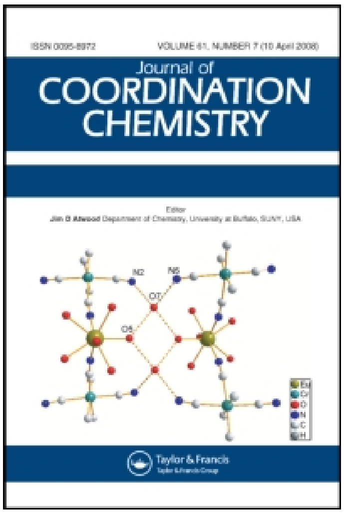

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and Structural Characterization of a Novel Indium Mercapto Derivative $[ClIn(SCH_2(CO)O)_2]^{2-}[(4\text{-}MepyH)_2]^{2+}$

Kulbinder K. Banger[a][b]; Stan A. Duraj[c]; Philip E. Fanwick[d]; David G. Hehemann[b][c]; Aloysius F. Hepp[b]; Robert A. Martuch[c]
[a] Ohio Aerospace Institute, Cleveland, OH, USA [b] Glenn Research Center, National Aeronautics and Space Administration, (NASA), Cleveland, OH, USA [c] Department of Chemistry, Cleveland State University, Cleveland, OH, USA [d] Department of Chemistry, Purdue University, West Lafayette, IN, USA

To cite this Article Banger, Kulbinder K. , Duraj, Stan A. , Fanwick, Philip E. , Hehemann, David G. , Hepp, Aloysius F. and Martuch, Robert A.(2002) 'Synthesis and Structural Characterization of a Novel Indium Mercapto Derivative $[ClIn(SCH_2(CO)O)_2]^{2-}[(4\text{-}MepyH)_2]^{2+}$', Journal of Coordination Chemistry, 55: 12, 1427 — 1431
To link to this Article: DOI: 10.1080/0095897021000058817
URL: http://dx.doi.org/10.1080/0095897021000058817

J. Coord. Chem., 2002, Vol. 55, No. 12, pp. 1427–1431

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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF A NOVEL INDIUM MERCAPTO DERIVATIVE $[ClIn(SCH_2(CO)O)_2]^{2-}[(4\text{-}MepyH)_2]^{2+}$

KULBINDER K. BANGER[a,d,*], STAN A. DURAJ[b,†], PHILIP E. FANWICK[c,‡], DAVID G. HEHEMANN[b,d], ALOYSIUS F. HEPP[d,**] and ROBERT A. MARTUCH[b]

[a]*Ohio Aerospace Institute, 22800 Cedar Point Road, Cleveland, OH, 44142, USA;* [b]*Department of Chemistry, Cleveland State University, Cleveland, OH 44115, USA;* [c]*Department of Chemistry, Purdue University, West Lafayette, IN, 47907, USA;* [d]*National Aeronautics and Space Administration, (NASA), Glenn Research Center, MS 302-1, 21000 Brookpark Road, Cleveland, OH, 44135, USA*

(Received 30 October 2001; Revised 14 February 2002; In final form 13 June 2002)

The synthesis and structural characterization of a novel In(III) complex is described. The reaction between $InCl_3$ with sodium mercapto-acetic acid ($NaSCH_2(CO)OH$) in 4-methylpyridine ($CH_3(C_5H_5N)$, (4-Mepy)) at 25°C affords $[ClIn(SCH_2(CO)O)_2]^{2-}[(4\text{-}MepyH)_2]^{2+}$ **(1)**. X-ray diffraction studies of **(1)** show it to have a distorted square-pyramidal geometry with the $[(^{-}SCH_2(CO)CO^{-})]$ ligands in a *trans* conformation. The compound crystallizes in the $P\bar{1}$ (No. 2) space group with $a = 7.8624(6)$ Å, $b = 9.950(1)$ Å, $c = 13.793(2)$ Å, $\alpha = 107.60(1)^\circ$, $\beta = 90.336(8)^\circ$, $\gamma = 98.983(9)^\circ$, $V = 1014.3(4)$ Å^3, $R(F^\circ) = 0.037$ and $R_w = 0.048$.

Keywords: Indium; MOCVD; Photovoltaics; Coordination; Thioglycolic acid; Mercapto-acetic acid

INTRODUCTION

The synthesis of suitable single source Metal Organic Chemical Vapor Deposition (MOCVD), precursors for the preparation of binary compounds of group 13/16 (IIIB/VIB), has been the recent subject of investigation by a number of groups [1–7]. Thin films of metal chalcogenides In_xS_y or Ga_xS_y *i.e.* "midbandgap" semiconductors [8] (*e.g.*, $InS = 2.44$ eV and β-$In_2S_3 = 2.07$ eV) display properties suitable for use in a large array of optoelectronic devices [9]. The mechanism for decomposition yields metal sulfide type moieties which can be incorporated into thin-film coatings during fabrication *e.g.*, Scheme 1 [10]. Therefore, the facile synthesis of this group of

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*Tel.: 440 962 3000. Fax: 440 962 3057. E-mail: KulbinderBanger@oai.org

†Tel.: 216 687 2451. Fax: 216 687 906. E-mail: s.duraj@csuohio.edu

‡Tel.: 765 494 445725. Fax: 765 494 0239. E-mail: fanwick@xray.chem.purdue.edu

**Corresponding author. Tel.: 216 433 3835. Fax: 216 433 6106; E-mail: Aloysius.F.Hepp@grc.nasa.gov

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/0095897021000058817

compounds, which readily decompose to afford the desired semiconductors with the correct stoichiometry, are highly desirable.

$$M(S_2NEt_2)_2 \longrightarrow MS + EtNCS + Et_2NCS_2Et$$

$$Et_2NCS_2Et \longrightarrow Et_2NH + CS_2 + C_2H_4$$

SCHEME 1 Suggested decomposition pathway of metal chalcogenides.

In continuing the development of binary single source precursors, we have investigated the preparation of In(III) compounds containing auxiliary oxygen and sulfur donor ligands. An apparent limitation of these complexes is the possibility of oxygen incorporation during thin film growth. However, recent reports in literature demonstrate thin film fabrication using *mono*-thio-oxygen derivatives by MOCVD, which show no oxygen contamination [11–13].

Recently we synthesized a novel gallium(III) mercapto derivative [7]. Further to this series, we now report the facile preparation and structural characterization of $[ClIn(SCH_2(CO)O)_2]^{2-}[(4\text{-MepyH})_2]^{2+}$ **(1)**.

EXPERIMENTAL

General

Air and moisture-sensitive materials were handled under anaerobic conditions using standard Schlenk line techniques, in flame-dried glassware. Solids were manipulated in a Vacuum Atmospheres dry box equipped with a HE-493 dri-train. Heptane and 4-methylpyridine were distilled from CaH_2 under a dinitrogen atmosphere prior to use. Anhydrous indium(III)chloride and $[NaSCH_2(CO)OH]$ were purchased from Aldrich Chemical Co. (Milwaukee, Wl) and used without further purification.

Preparation of $[ClIn(SCH_2(CO)O)]^{5-}[(4\text{-MepyH})_2]^{2+}$

Sodium mercapto-acetic acid, $(NaSCH_2(CO)OH)$ (0.64 g, 5.651 mmol) and $InCl_3$, (0.50 g, 2.261 mmol) were reacted in 50 mL of 4-methylpyridine in a Schlenk tube, at ambient temperature under argon for 7 days. The reaction mixture was then filtered and the collected filtrate layered with 100 mL of heptane. Controlled evaporation, at room temperature subsequently afforded colorless white needles suitable for single crystal analysis.

X-ray Crystal Data Collection

Single crystal X-ray diffraction data were collected on an Enraf-Nonius CAD4 computer controlled kappa axis diffractometer equipped with a graphite crystal, incident beam monochromator. A colorless needle of $C_{16}H_{20}ClInN_2O_4S_2$ having approximate dimensions of $0.50 \times 0.17 \times 0.13$ mm was mounted on a glass fiber. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflection in the range $20 < \theta < 22°$, measured

TABLE I Crystallographic data for $C_{16}H_{20}ClInN_2O_4S_2$, (CCDC 170558)

Formula weight	518.75
Crystal size (mm)	$0.50 \times 0.17 \times 0.13$
Space group (No.)	$P\bar{1}$ (No. 2)
a (Å)	7.8624(6)
b (Å)	9.950(1)
c (Å)	13.793(2)
α (°)	107.60(1)
β (°)	90.336(9)
γ (°)	98.983(9)
V (Å^3)	1014.3(4)
Z	2
ρ_{calc} (g cm^{-3})	1.698
Temperature (K)	293
λ Radiation (wavelength)	Mo K_α (0.71073 Å)
μ (cm^{-1})	15.00
Transmission coeff.	1.000–0.426
Scan method	ω–2θ
$h, k, l,$	− 8–8, 0–18, 0–15
No. observed data	2665
No. unique data	2665
Largest shift/esd in final cycle	0.15
$R(F^o)$	0.037
R_w	0.048
F_{000}	520.0
Goodness of fit	1.473

by the computer-controlled diagonal slit method of centering. The triclinic cell parameters, calculated volume and density are shown in Table I. Crystal quality was determined by measuring several intense omega reflections, which displayed a half height width of 0.57° 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). A total of 2665 reflections were collected all of which were unique [14]. Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 17.0 cm^{-1} for Mo K_α radiation. An empirical absorption correction based on the method of Walker and Stuart was applied [15]. Relative transmission coefficients ranged from 0.769 to 1.000 with an average of 0.916.

The structure was solved using the solution program Mo1EN on a VAX computer [16]. Interpretation of a Patterson heavy atom method revealed the position of the In atom. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located and added to the structure factor calculations but not refined. The structure was refined in full-matrix least-squares where *w* is defined as per the Killean and Lawrence method with terms of 0.020 and 1.0 [17].

RESULTS AND DISCUSSION

The indium complex **(1)** was prepared by the stoichiometric reaction of indium(III)chloride and sodium mercapto-acetic acid ($NaSCH_2(CO)OH$), in 4-methyl-pyridine, which results in the concomitant deprotonation and ligation of the mercapto derivative. After 7 days, the organic phase is isolated from the grey precipitate and carefully layered with 100 mL of freshly distilled heptane. Slow evaporation at room temperature under inert conditions produced a large quantity of colorless crystals from which one was selected for analysis by single crystal X-ray diffraction. The product was elucidated as the ionic In(III) species $[\mathrm{ClIn(SCH_2(CO)O)}]^{2-}[(\text{4-MepyH})_2]^{2+}$ **(1)**, (Fig. 1, Table II).

Compound **(1)** is significant as it represents the first indium thioglycolic complex. The compound exists as a salt of 4-MepyH$^+$, which displays a distorted square-pyramidal geometry around the indium atom. The ligand–metal interactions are those of a indium(III) coordination sphere with negative charges on the bidentate ligand $[\mathrm{SCH_2(CO)O}]$ and on the chloride. The In–S and the In–O bond lengths are 2.407(2), 2.409(2) and 2.210(4), 2.233(4) Å, respectively, Table II. The thioglycolic derivatives $[^{-}\mathrm{SCH_2(CO)O}^{-}]$ are arranged in the expected *trans* geometry around the In(III) metal center. In addition, indium having an underlying d^{10} configuration allows it to take part in d_π–p_π and d_π–d_π back bonding with the thiogylcolic ligand. Hydrogen bonding is established between the carbonyl group of each mercapto derivative and the protonated amine with distances of 1.66(7) and 1.65(6) Å.

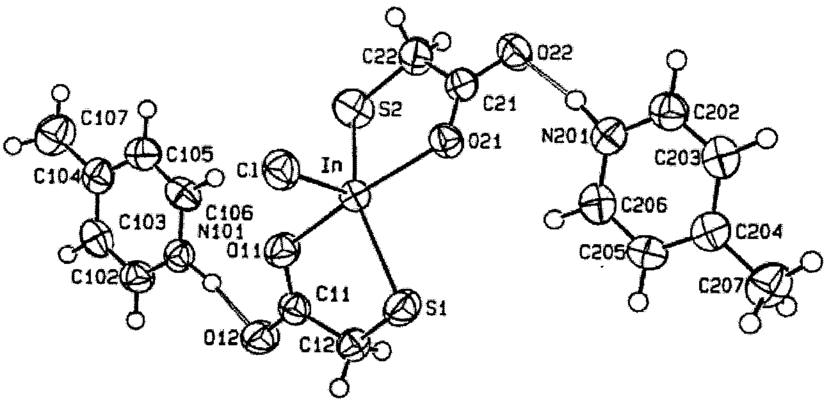

FIGURE 1 ORTEP drawing of $[\mathrm{ClIn(SCH_2(CO)O)_2}]^{2-}[(\text{4-MepyH})_2]^{2+}$,$(\text{4-Mepy}_2 = \mathrm{CH_3(C_5H_5N)})$; thermal ellipsoids enclose 50% of electron density.

TABLE II Selected bond distances (Å) and angles (°) for $\mathrm{C_{16}H_{20}ClInN_2O_4S_2}$

Bond	*Distance*/Å	*Atoms*	*Angle*/°
In–Cl	2.425(2)	Cl–In–S(1)	108.57(6)
In–S(1)	2.409(2)	Cl–In–S(2)	111.93(6)
In–S(2)	2.407(2)	Cl–In–O(11)	100.1(1)
In–O(11)	2.233(4)	Cl–In–O(21)	95.9(1)
In–O(21)	2.210(4)	S(1)–In–S(2)	139.46(7)
S(1)–C(21)	1.804(6)	S(1)–In–O(11)	82.3(1)
S(2)–C(22)	1.796(7)	S(1)–In–O(21)	95.1(1)
O(11)–C(11)	1.273(7)	S(2)–In–O(11)	88.9(1)
O(21)–C(21)	1.267(7)	S(2)–In–O(21)	82.7(1)
O(12)–C(11)	1.24(2)	O(11)–In–O(21)	163.8(2)
O(12)–H(1)	1.66(7)	In–S(1)–C(12)	97.4(2)
O(22)–H(2)	1.65(6)	In–S(2)–C(22)	97.3(2)
O(22)–C(21)	1.232(7)	In–O(11)–C(11)	119.3(4)
N(101)–H(1)	1.00(7)	In–O(21)–C(21)	119.9(3)
N(202)–H(2)	1.01(6)	O(12)–H(1)–N(101)	172(6)
		O(22)–H(2)–N(201)	172(5)

SUMMARY

In conclusion, the thiogylcolic ligand [$^{-}$SCH$_2$(CO)O^{-}] belongs to an interesting class of ligand that contains both soft and hard donor sites. Under neutral reaction conditions [$^{-}$SSCH$_2$(CO)OH] has been shown to be a 1e^{-} donor ligand binding through S^{-} [18]. However, under basic reaction conditions it is evident that the mercapto ligand undergoes deprotonation upon reaction with 4-Mepy (which exists in excess) thus generating the 2e^{-} ligand [$^{-}$SCH$_2$(CO)O^{-}]. In complex (**1**) bonding is through the soft and hard donor atoms, which account for the observed distorted square-pyramidal geometry. Preliminary studies for the use of complex (**1**) for the preparation of indium sulfide films is under investigation.

Acknowledgments

A.F.H (Director's Discretionary Fund), D.G.H. (NASA Cooperative Agreement NCC3-318), S.A.D. (NCC3-162), and P.E.F. (NCC3-246). We thank Profs. Andrew Barron of Rice University, and Paul O'Brien of Manchester University, UK, for preprints of their work.

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