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

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

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ABSTRACT

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 $\overline{P}1$ (No. 2) space group with a = 7.8624(6) Å, b = 9.950(1) Å, c = 13.793(2) Å, α = 107.60(1)°, β = 90.336(8)°, γ = 98.983(9)°, V = 1014.3(4) Å^3, $R(F_\circ)$ = 0.037 and R_W = 0.048.

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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 sulphide type moieties which can be incorporated into thin-film coatings during fabrication, Scheme I.[10] Therefore, the facile synthesis of these group of 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 I. Suggested decomposition pathway of metal chalcogenides.

In continuing the development of these types of precursors, we have investigated the preparation of *mono*-thio-oxygen derivatives. An apparent limitation of these complexes is the possibility of oxygen incorporation during thin film growth. However, recent reports in literature successfully demonstrate thin film fabrication using *mono*-thio-oxygen derivatives by MOCVD, which show no oxygen contamination.[11–13]

Recently we have synthesized a novel gallium(III) mercapto derivative.[7] Further to this series, we now report the facile preparation and structural characterization of $[ClIn(SCH_2(CO)O)_2]^{2-}[(4\text{-mepyH})_2]^{2+}$, (4-$Mepy_2$ = $CH_3(C_5H_5N)$), (**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 Company (Milwaukee, WI) 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 an $InCl_3$, (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 by 0.17 by 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 reflections in the range $20 < \theta < 22°$, measured 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 $\overline{P}1$ (No. 2). A total off 2665 reflections were collected, of which 2665 were unique.[14] Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 17.0 cm^{-1} for Mo K 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.

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

Formula Weight	518.75
Crystal size (mm)	0.50 by 0.17 by 0.13
Space group (No.)	$\overline{P}$ 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–2 θ
h, k, l,	–8 to 8, 0 to 18, 0 to 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

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-methypyridine, 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 $[ClIn(SCH_2(CO)O)]^{2-}[(4\text{-}MepyH)_2]^{2+}$ (**1**), (Figure 1, Table II).

Table II. Selected bond distances (Å) and angles (°) for $C_{16}H_{20}ClInN_2O_4S_2$.

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)

Compound (**1)** is significant as it represents the first Indium thioglycol 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) co-ordination sphere with negative charge, (2e$^-$) on the bidentate ligand [$^-$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 thioglycollic derivatives [$^-$SCH$_2$(CO)O$^-$], are arranged in the expected *trans* geometry, binding preferentially through the soft donor, since In(III) behaves as a class b, (soft) acceptor. In addition, indium having an underlying d^{10} configuration allows it to take part in d_π-p_π back bonding with the thiogylcol ligand. In addition, ionic contacts are established between the carbonyl group of the mercapto derivative and the protonated amine, [4-MepyH]$^+$, 1.66(7) and 1.65(6) Å.

SUMMARY

In conclusion, the mercapto ligand, [$^-$SCH$_2$(CO)O$^-$] belongs to an interesting class of ligand that contains both soft and hard donors sites. Under neutral reaction conditions [$^-$SCH$_2$(CO)OH] has been shown to be a 1e$^-$ donor ligand binding through S$^-$.[18] However, under basic reaction conditions it is evident that mercapto ligand undergoes deprotonation with reaction with 4-Mepy, thus generating the 2e$^-$ ligand [$^-$SCH$_2$(CO)O$^-$]. Examination of the C-O bond lengths support these findings. 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.

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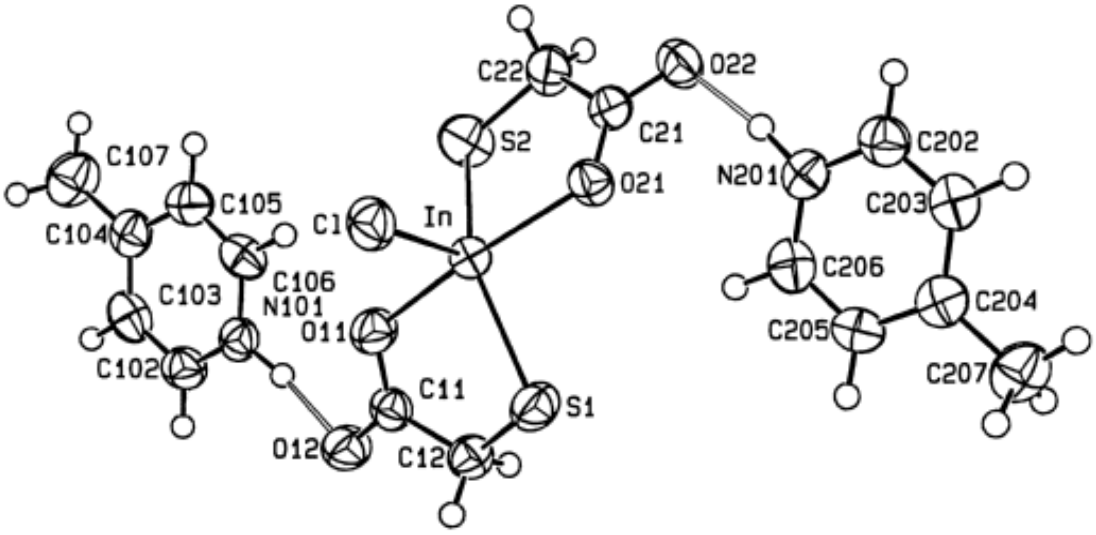

Figure 1. ORTEP drawing of $[ClIn(SCH_2(CO)O)]^{2-}[(4\text{-}MepyH)_2]^{2+}$, (4-$Mepy_2$ = $CH_3(C_5H_5N)$); thermal ellipsoids enclose 50% of electron density.

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