A Structural Study on Indium Tris-thiocarbamates
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Z. Naturforsch. 49b, 193–198 (1994); received August 2, 1993

Indium Tris-thiocarbamates, \(^1\)H NMR Spectra

Indium tris(thiocarbamates) In(S\(_2\)CN'Pr\(_2\))\(_3\) (1), In(SOCN'Pr\(_2\))\(_3\) (2) and In(SNC=C\(_6\)H\(_4\))\(_3\) (3) have been synthesized and characterized. Variable temperature \(^1\)H NMR spectra of 1 and 2 are reported. The X-ray molecular structures of 1 and 3 are found to be quite similar; the symmetry of the In(S\(_2\)C)\(_3\) unit in 3 is close to point group D\(_3\) with small asymmetry in the In–S bonds.

Introduction

Considerable interest in metal tris-chelates with MO\(_3\) and MS\(_8\) cores has developed due to structural and mechanistic aspects of intramolecular rearrangements and their interrelationship. The problem of structural and electronic features responsible for a particular rearrangement pathway is quite vexing at present [1–4]. The metal tris-chelates with a MO\(_3\) core obtainable from asymmetrical sulfur ligands [5, 6] such as thiocarbamates may be of special relevance in this context. Our efforts to synthesize and characterize such tris-chelates derived from the asymmetrical ligand benzyolithiobenzoylmethane (LH) with group 15 elements has led to diverging results. The bismuth complex [7], BiL\(_3\), turns out to be a loosely held dimer in the solid state while a thermally unstable arsenic analogue [8], AsL\(_3\), decomposes to an arsenic sulfide, AsS(L), and an organic sulfide, S(PhC:CHCOPh)\(_2\). The attempted reaction of antimony trichloride [9] with LH always led to a thermally unstable product which so far could not be characterized. The synthesis of the corresponding tris-thiocarbamates of these elements [10] gives the expected tris-ligand complexes. Amongst the heavier group 13 elements which exhibit class "b" behaviour the crystallographically characterizable tris(benzylthiobenzoylmethanato-O,S)indium has been described earlier [11]. Here, we report the synthesis and structure including the single crystal X-ray analysis and variable temperature \(^1\)H NMR spectra of tris(N,N-diisopropylthiocarbamate), In(S\(_2\)CN'Pr\(_2\))\(_3\) 1, as well as tris(N,N-diisopropylthiocarbamate), In(SOCN'Pr\(_2\))\(_3\) 2. These include a diastereotopic probe in the molecular frame of the ligand. Also, the tris(pyrrolyldithiocarbamate) In(SNC=C\(_6\)H\(_4\))\(_3\) 3 has been synthesized and examined for its crystal and molecular structure.

Experimental

Experimental manipulations were carried out under a nitrogen atmosphere. Solvents were purified and dried by standard methods. N,N-diisopropylthiocarbamate [12] and thiocarbamate [13] were obtained as sodium and lithium salts, respectively, by the literature procedure. Potassium pyrrolyldithiocarbamate was prepared as reported [14]. Indium(III) chloride (Alfa-Chemie) was used without further purification. Sulfur was estimated by Messenger's method. Carbon, hydrogen and nitrogen analyses were carried out on a Perkin-Elmer 240 C model analyzer. IR: Perkin-Elmer 783 model instrument, 4000–200 cm\(^{-1}\), Nujol mulls, CsI plates. NMR: JEOL-FX-90Q (\(^1\)H and \(^{13}\)C) recorded at 25 °C; CDC\(_3\) (1 and 3) and CD\(_3\)OD (2) using TMS as an internal standard. MS: Kratos 32 IS model at 70 eV and a source temperature of 25 °C. Single crystal X-ray diffraction: Nicolet R 3 diffractometer, SHELXTL Plus and SHELXTL PC software.
Indium tris(N,N-diisopropylthiocarbamate),
\(\text{In}(S_2CNPr_2)_3\) (1)

A solution of sodium N,N-diisopropylthiocarbamate (2.31 g) in water (~30 ml) was added to the solution of indium(III) chloride tetrahydrate (1.11 g) in water (~15 ml) with continuous stirring at room temperature (31 °C). After 2 h the white precipitate was separated by filtration and dried in vacuum for 8 h at 0.1 mm Hg. The product was crystallized from a dichloromethane/n-hexane mixture to yield 1.95 g (80%) of yellow solid 1; m.p. 270 °C dec., IR (cm\(^{-1}\)): \(v(C=N) 1480\) s; \(v(NC_2) 1144\) s; \(v(C-S) 941\) w; \(v(In-S) 405\) w.

\[\text{Analysis for } C_{21}H_{42}N_3S_6In (643.8)\]

Calcd C 39.2 H 6.82 N 6.52 S 29.9%, Found C 39.4 H 6.67 N 6.30 S 30.2%.

Indium tris(N,N-diisopropylthiocarbamate),
\(\text{In}(SCN)NPr_2\) (2)

A solution of lithium N,N-diisopropylthiocarbamate (1.07 g) in methanol (~20 ml) was slowly dropped into the solution of indium(III) chloride (0.73 g) in methanol (~30 ml) with continuous stirring at room temperature (30 °C). After 3 h an almost negligible quantity of suspended particles was removed by filtration. The solvent was then evaporated from the solution under reduced pressure, the white residue extracted with acetone (20 ml) and the insoluble material separated by filtration. After evaporation of the solvent the pasty residue was treated with 10 ml of diethyl ether and then dried for 4 h at 30 °C/0.1 mm Hg. Yield: 0.75 g of 2 as a white solid (61%); m.p. 135–138 °C. IR (cm\(^{-1}\)): \(v(C-O) 1630\) s; \(v(ON) 1474\) s; \(v(NC_2) 1151\) m; \(v(C-S) 967\) w, \(v(COS) 668\) w, \(v(In-O) 668\) w, \(v(In-S) 375\) w. NMR (< 5 ppm): 1.40 (d, CH3), 200.75 (CS).

\[\text{Analysis for } C_{21}H_{42}N_3S_6In (643.8)\]

Calcd C 42.8 H 7.05 N 6.75 S 17.2%, Found C 42.8 H 6.98 N 7.05 S 17.2%.

Indium tris(pyrolyldithiocarbamate),
\(\text{In}(S,NCN,H_2)\) (3)

A solution of potassium pyrolyldithiocarbamate (1.79 g) in methanol (~25 ml) was added to a solution of indium(III) chloride (0.73 g) in methanol (~30 ml) with continuous stirring at room temperature (30 °C) under nitrogen atmosphere. After 5 h the yellow insoluble solid was separated by filtration and then dried for 6 h at 30 °C/0.1 mm Hg. Crystallization from dichloromethane/n-hexane gave 1.47 g of 3 (82%); m.p. 190–192 °C. IR (cm\(^{-1}\)): \(v(C=W) 1325\) s; \(v(C-S) 992\) m, \(v(In-S) 355\) w. \(^1\)H NMR (δ, ppm): 6.20 (t, \(\beta-H\)), 7.42 (t, \(\alpha-H\)), \(^{13}\)C NMR(δ, ppm): 116.20 (β-C), 122.68 (α-C), 212.68 (CS).

\[\text{Analysis for } C_{15}H_{22}N_3S_6In (541.5)\]

Calcd C 33.3 H 2.21 N 7.76 S 33.5%, Found C 33.7 H 2.19 N 7.77 S 33.7%.

X-ray structure determinations [15]

Selected single crystals were mounted in glass capillaries. Determination of crystallographic data and data collection were performed at 20 °C using a graphite monochromator and MoK\(_\alpha\) radiation. Parameters of non-hydrogen atoms were refined anisotropically while H atoms were placed in calculated positions and refined with a riding model and fixed isotropic \(U_\text{eq} = 1.2U_{\text{eq}}(C)\).

1: \(C_{15}H_{22}N_3S_6In\), \(M_r = 643.8\), crystal size = 0.20 \times 0.25 \times 0.55 mm, \(a = 17.585(5)\), \(b = 11.810(5)\), \(c = 15.681(4)\) Å, \(\beta = 108.242(2)°\), \(V = 3093(2)\) Å\(^3\), \(Z = 4\), \(d_{\text{calc}} = 1.382\) mg/m\(^3\), \(\mu = 1.155\) mm\(^{-1}\), monoclinic, space group C2/c (No. 15), F(000) = 1336. – Data collection: 2θ = 3–48° in 0 < h < 20, 0 < k < 14, \(-18 < l < 17\), \(\omega\)-scans, scan range = 1°, scan speed = 1.8–29.3/min, reflections: 2921 measured, 2637 unique (\(R_{\text{int}} = 0.037\)), 2244 observed (4σ limit), semi-empirical absorption correction, max./min. transmission: 0.750/0.645. – Structure solution and refinement: Patterson method, \(R = 0.0484\), \(R_w = 0.0618\), GOF 0.92, 151 variables, largest difference peak = 0.46 e/Å\(^3\).

3: \(C_{15}H_{22}N_3S_6In\), \(M_r = 541.5\), crystal size = 0.32 \times 0.18 \times 0.55 mm, \(a = 14.184(4)\), \(b = 9.596(2)\), \(c = 14.907(7)\) Å, \(\beta = 91.87(3)°\), \(V = 2061(1)\) Å\(^3\), \(Z = 4\), \(d_{\text{calc}} = 1.745\) mg/m\(^3\), \(\mu = 1.718\) mm\(^{-1}\), monoclinic, space group P2\(_1\)/c (No. 14), F(000) = 1072. – Data collection: 2θ = 3–50° in \(-4 < h < 17\), \(-11 < k < 11\), \(-17 < l < 17\), \(\omega\)-scans, scan range = 0.8°, scan speed = 2–29.3/min, reflections: 4052 collected, 3647 unique and 3218 observed (3σ level), semi-empirical absorption correction, max./min. transmission: 0.4848/0.3836. – Structure solution and refinement: Direct methods, 226 variables, \(R = 0.0308\), \(R_w = 0.0704\), GOF 0.38, largest difference peak = 0.41 e/Å\(^3\).

Results and Discussion

Indium tris(N,N-diisopropylthiocarbamate), 1, indium tris(N,N-diisopropylthiocarbamate), 2, and indium tris(pyrolyldithiocarbamate), 3, have been...
synthesized in good yields by the following reactions (M = Na, K).

\[ \text{InCl}_3 + 3 \text{M}[\text{S}_2\text{CNR}_2] \rightarrow 3\text{MCl} + \text{In}(\text{S}_2\text{CNR}_2)_3 \quad (1) \]

\[ \text{InCl}_3 + 3 \text{Li}[\text{S(O)CN'Pr}_2] \rightarrow 3\text{LiCl} + \text{In}[\text{S(O)CN'Pr}_2]_3 \quad (2) \]

The complexes 1 and 3 are yellow crystalline solids soluble in common organic solvents, whereas 2 is a white solid soluble in alcohols.

The IR spectra of 1 and 2 show a band at 1480 and 1474 cm\(^{-1}\), respectively, due to \(v(\text{C-N})\) [16-18], whereas in 3 the corresponding band is observed at 1325 cm\(^{-1}\). The higher frequency in 1 and 2 can be attributed to the partial double bond between carbon and nitrogen atoms due to a comparatively greater contribution of structure A. In the aromatic dithiocarbamates this resonance form is assumed to be less important because aromaticity in the heterocyclic ring system would otherwise be disrupted by positive charge built up on the nitrogen atom. Consequently the CS bonds should have a higher bond order in 3 as compared to 1. This is further supported by CS bond distances (see Fig. 1 and 2).

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* Equivalent isotropic U defined as one third of the trace of the orthogonalized \(U_{ij}\) tensor.

isopropyl resonances in all dithiocarbamate and thio­carbamate complexes have been interpreted in terms of hindered rotation about the isopropyl nitrogen (N\(=\)C) bonds [1-4, 12]. However, complex 2 with its InO_3S_3 core shows a different behaviour. The isopropyl groups remain equivalent over the temperature range of +50 to −50 °C. Therefore, the barrier to rotation appears to be lower than in the previous example. The \(^1\text{H} \) NMR spectrum of 3 at room temperature shows two “triplets” for the pyrrole protons.

The \(^{13}\text{C} \) NMR spectra of the complexes 1-3 show the correct number of signals and also confirm the fact that the thiocarbon atom of complex 1 resonates at higher field (200.8 ppm) as compared to that in 3 where the corresponding absorption is observed at 212.6 ppm.

The mass spectrum of 3 also supports the formula. 3 undergoes fragmentation according to Scheme 1.

In this case subsequent loss of ligands S_2CNCY_4H_4 from the \([\text{In}(\text{S}_2\text{CNCY_4H_4})_3]\) unit to \([\text{In}(\text{S}_2\text{CNCY_4H_4})_2]\) (m/e 399) and \([\text{In}(\text{S}_2\text{CNCY_4H_4})_3]^+\) (m/e 257) and fragmentation of the ligand by proton attachment in the form of HS_2CNCY_4H_4 (m/e 143) was observed as low intensity peaks. The base peak at m/e 110 is due to the \([\text{S}=\text{C}═\text{NCY_4H_4}]^+\) fragment.

Although vibrational and NMR data reveal part of the structural features of the complexes under
investigation an X-ray structure determination of the compounds was essential for determining the geometry of the InS₆ and InO₃S₃ cores. Its results would also help in an unambiguous assignment of spectral data. Crystals of complexes 1 and 3 were obtained from dichloromethane/n-hexane. However, attempts to crystallize 2 failed due to the decomposition of 2 in MeOH solution.

The molecular structures and numbering schemes for 1 and 3 are shown in Fig. 1 and 2. The unit cell of 3 contains discrete mononuclear molecules. However, there are intermolecular sulfur–sulfur contacts between two adjacent molecules as indicated by the dashed lines in Fig. 3. In contrast, no such interaction is noted in the crystal of 1 in spite of the similar core geometry of the molecules. Distances of intermolecular contacts are: S₅–S₂' 3.543, S₅–S₁' 3.815 and S₆–S₆' 3.899 Å. This is due to the much better steric shielding of the sulfur atoms in 1 by the bulky isopropyl groups. Selected bond lengths and bond angles are contained in the legends to Fig. 2 and 3. At first sight the molecular structures of the two complexes seem to be essentially similar. However, small variations in the C–N and other bond dimensions arise due to the difference in the electron donating abilities of the pyrrole and isopropyl groups. The coordination polyhedron around each indium atom consists of six sulfur neighbours. In both cases the InS₆ polyhedron shows lower symmetry than that of a trigonal antiprism. 1 actually possesses a crystallographic C₂ axis running through In, C₈ and N₂. The isopropyl group attached to atom N₂ is actually disordered. This is not only indicated by large thermal parameters for the carbon atoms of the methyl groups but more pronouncedly by split sites for the positions of the central C atoms of the isopropyl group. This C atom was refined only isotropically for two positions with equal occupancy. The C–C distances to C₈ arrived at in the final refinement were shorter and longer than fits a C–C single bond.

The two S₃ triangles S₃S₆/S₃S₆ in 3 are close to parallel with each other with an angle of 1.9° between the two planes. The same is true for the planes S₁S₂A S₃A/S₂S₃S₁A with 0.7° of the molecule 1. The deviation from ideal geometry could possibly arise due to the small bidentate ligand bite angle 68.5° (average) for 1 and 69.5° for 3 which is not sufficient to span the ideal octahedral angle. Other bond angles of the coordination polyhedron also deviate from the ideal octahedral angle of 90 °C (varying from 68.5° to a maximum of 118.8° in 1 and 69.2° to 103.5° in 3).

A similar structural feature as for 1 has been noted in a xanthate complex of bismuth, Bi(S₂CO₂Pr)₃ [19, 20]. In 1 the two ligands which are correlated by the C₂ operation display a small but significant asymmetry in their In–S bond lengths (2.617(2) and 2.583(2) Å). However, the In–S bonds of the S₃–S₃a–C₈–N₂ group are necessarily equal with a bonding distance of 2.601(2) Å.
This is almost the mean of the other two In–S bond lengths.

In the molecular structure of 3, comparable asymmetry is found in all three ligands, the In–S distances ranging from 2.577(1) to 2.612(1) Å. In this respect it is comparable to the structural features of the corresponding iron complex, Fe(S₂CNC₄H₄)₃ [21]. The average asymmetry in Fe–S bonds (0.022 Å) is similar to that in 3 (0.021 Å). However, this result is in sharp contrast to the observation in As(III) [22], Sb(III) [23] and Bi(III) [23] tris-dialkyldithiocarbamates, where the M–S distances are distinctly non-equivalent. The two C–S bond lengths in 3 (average 1.700(3) Å) differ little but significantly from those in 1 (average 1.723(5) Å). Nevertheless, they are consistent with the view that the pair of C–S electrons are delocalized in the CS₂ skeleton.

Different resonance structures make important contribution to the bonding of the dithiocarbamate ligand in all metal dithiocarbamate complexes. This is demonstrated by short C–N distances in 1 (1.331 to 1.318 Å) with double bond character. The corresponding distances in 3 are somewhat longer (1.360–1.384 Å) which reveals the effect of the substituents on the nitrogen over the electronic structure of the ligand moiety. Bond dimensions of the pyrrole ring in the complex are comparable to pyrrole whose structure has been determined by a microwave study [24]. The pyrrole ring itself is
slightly twisted versus the respective $S_2C$ plane (2.6, 6.9 and 7.1°).

**Conclusion**

Although no X-ray structure could be determined for 2 it is evident from this study that its indium center is hexacoordinated with an $InS_6$ core approaching a trigonal antiprism. This corresponds with the structures of $Ga(S_2CNCH_2)\{25\}$, $Ga(S_2CNEt_2)\{26\}$ and $Al[S_2CNNMe_2]_3\{27\}$. However, no hexacoordination is achieved for the lightest homologue in this series, $B(S_2CNMe_2)_3$. This molecule contains tetracoordinated boron atoms achieved by dimerization of the monomer $[28]$. Due to the larger $M-S$ distances in 1 and 3 as compared with the gallium dithiocarbamates a more acute bite angle results and as a consequence the distortion corresponds more with $Ti(S_2CNR_2)_3$ compounds $[29]$ than with Ga complexes.

The financial assistance from the Council of Scientific and Industrial Research, New Delhi (India) as Junior Research Fellowship to S. B. and Senior Research Fellowship to N. S. is gratefully acknowledged.