A Structural Study on Indium Tris-thiocarbamates

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Indium Tris-thiocarbamates, ^{1}H NMR Spectra

Indium tris(thiocarbamates) $In(S_2CN^iPr_2)_3$ (**1**), $In(SOCN^iPr_2)_3$ (**2**) and $In(S_2CNC_4H_4)_3$ (**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 $In(S_2C)_3$ 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_6 and MS_6 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_3S_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 benzoylthiobenzoylmethane (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(benzoylthiobenzoylmethanato-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-diisopropyldithiocarbamate), $In(S_2CN^iPr_2)_3$ **1**, as well as tris(N,N-diisopropylthiocarbamate), $In(SOCN^iPr_2)_3$ **2**. These include a diastereotopic probe in the molecular frame of the ligand. Also, the tris(pyrrolyldithiocarbamate) $In(S_2CNC_4H_4)_3$ **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-diisopropyldithiocarbamate [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-90 Q (^{1}H and ^{13}C) recorded at 25 °C; CDCl$_3$ (**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-diisopropyldithiocarbamate),
In(S$_2$CN^{i}Pr$_2$)$_3$ (**1**)

A solution of sodium N,N-diisopropyldithio-carbamate (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}): ν(C=N) 1480 s; ν(NC$_2$) 1144 s; ν(C–S) 941 w; ν(In–S) 405 w. ^{1}H NMR (δ, ppm): 1.42 (s, CH$_3$), 3.7, 4.2 (b, CH); ^{13}C NMR (δ, ppm): 19.89 (CH$_3$), 200.75 (CS).

Analysis for C$_{21}$H$_{42}$N$_3$S$_6$In (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),
In(SOCN^{i}Pr$_2$)$_3$ (**2**)

A solution of lithium N,N-diisopropylthiocarba-mate (1.07 g) in methanol (~20 ml) was slowly dropped into the solution of indium(III) chloride (0.46 g) in methanol (~20 ml) with continuous stir-ring 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 pres-sure, the white residue extracted with acetone (20 ml) and the insoluble material separated by fil-tration. After evaporation of the solvent the pasty residue was treated with 10 ml of diethylether 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}): ν(C=O) 1630 s; ν(C=N) 1474 s; ν(NC$_2$) 1151 m; ν(C–S) 967 w, δ(COS) 668 w, ν(In–O) 501 w, ν(In–S) 375 w. ^{1}H NMR (δ, ppm): 1.40 (d, CH$_3$), 3.43 (sept. CH).

Analysis for C$_{21}$H$_{42}$N$_3$O$_3$S$_3$In (595.56)
    Calcd   C 42.3   H 7.05   N 7.05   S 16.1%,
    Found   C 42.8   H 6.98   N 7.25   S 17.2%.

Indium tris(pyrrolyldithiocarbamate),
In(S$_2$CNC$_4$H$_4$)$_3$, (**3**)

A solution of potassium pyrrolyldithiocarbamate (1.79 g) in methanol (~25 ml) was added to a solu-tion of indium(III) chloride (0.73 g) in methanol (~30 ml) with continuous stirring at room tem-perature (30 °C) under nitrogen atmosphere. After 5 h the yellow insoluble solid was separated by fil-tration and then dried for 6 h at 30 °C/0.1 mm Hg.

Crystallization from dichloromethane/*n*-hexane gave 1.47 g **3** (82%); m.p. 190–192 °C. IR (cm^{-1}): ν(C=N) 1325 s, ν(C–S) 992 m, ν(In–S) 355 w. ^{1}H NMR (δ, ppm): 6.20 (t, β-H), 7.42 (t, α-H). ^{13}C NMR(δ, ppm): 116.20 (β-C), 122.68 (α-C), 212.68 (CS).

Analysis for C$_{15}$H$_{12}$N$_3$S$_6$In (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 cal-culated positions and refined with a riding model and fixed isotropic U$_i$ ≈1.2 U$_{eq}$(C).

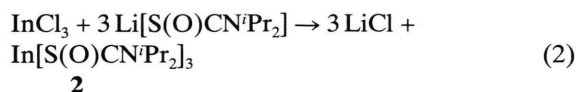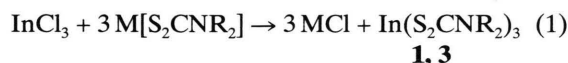**1:** C$_{21}$H$_{42}$N$_3$S$_6$In, M$_r$ = 643.8, crystal size = 0.20 × 0.25 × 0.55 mm, a = 17.585(5), b = 11.810(5), c = 15.681(4) Å , β = 108.24(2)°, V = 3093(2) Å^3, Z = 4, d$_{calc}$ = 1.382 mg/m^3, μ = 1.155 mm^{-1}, mono-clinic, space group C2/c (No. 15), F(000) = 1336. – *Data collection:* 2θ = 3–48° in 0 < h < 20, 0 < k < 14, –18 < l < 17, ω-scans, scan range = 1°, scan speed = 1.8–29.3°/min, reflections: 2921 measured, 2637 unique (R_{int} = 0.037), 2244 observed (4 σ limit), semi-empirical absorption correction, max./min. trans-mission: 0.750/0.645. – *Structure solution and refine-ment:* 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$_{12}$N$_3$S$_6$In, M$_r$ = 541.5, crystal size = 0.32 × 0.18 × 0.55 mm, a = 14.418(4), b = 9.596(2), c = 14.907(7) Å , β = 91.87(3)°, V = 2061(1) Å^3, Z = 4, d$_{calc}$ = 1.745 mg/m^3, μ = 1.718 mm^{-1}, monoclinic, space group P2$_1$/c (No. 14), F(000) = 1072. – *Data collection:* 2θ range = 2–50° in –4 < h < 17, –11 < k < 11, –17 < l < 17, ω-scans, scan range = 0.80°, scan speed = 2–29.3°/min, reflections: 4052 collected, 3647 unique and 3218 observed (3 σ level), semi-empirical absorption correction, max./min. transmission: 0.4848/0.3836. – *Structure solution and refinement:* Direct methods, 226 varia-bles, 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-diisopropyldithiocarbamate), **1,** indium tris(N,N-diisopropylthiocarbamate), **2,** and indium tris(pyrrolyldithiocarbamate), **3,** have been

synthesized in good yields by the following reactions (M = Na, K).

$$InCl_3 + 3\,M[S_2CNR_2] \rightarrow 3\,MCl + In(S_2CNR_2)_3 \quad (1)$$
$$\mathbf{1, 3}$$

$$InCl_3 + 3\,Li[S(O)CN^iPr_2] \rightarrow 3\,LiCl +$$
$$In[S(O)CN^iPr_2]_3 \quad (2)$$
$$\mathbf{2}$$

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 $\nu(C{\doteq}N)$ [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). In the far infrared region the indium-sulfur absorption band $\nu_s InS_2$ occurs at 405 cm⁻¹ in **1**, and at 355 cm⁻¹ in **3**. In complex **2**, $\nu(In-O)$ is displayed at 501 cm⁻¹ and $\nu(In-S)$ at 375 cm⁻¹.

A   B   C
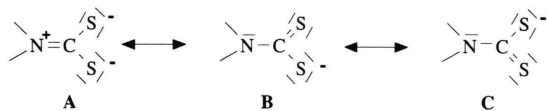
The low temperature ¹H NMR spectrum of **1** at −20 °C shows absorptions for the gem dimethyl and methine protons as two equally intense isopropyl methyl doublets and two equally intense methine septets. On increasing the temperature the lines get broad enough to obscure the spin coupling. On further increasing the temperature coalescence of methyl resonances has been noted at +23 °C and at +50 °C. The methyl H-atoms then appear as a singlet. However, if the spectrum is recorded in deuterated pyridine, a single sharp doublet can be seen at ~60 °C.

The coalescence temperature of +23 °C of complex **1** is found to be somewhat different from an earlier report (−8 °C) [12]. The coalescence of the

Table I. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$).

	x	y	z	U_{eq}
In	5000	2115(1)	7500	52(1)
S(1)	6515(1)	1562(1)	8131(1)	60(1)
S(2)	5282(1)	888(1)	8929(1)	77(1)
S(3)	4684(1)	3935(1)	8260(1)	75(1)
C(1)	6278(2)	881(3)	8987(3)	53(1)
N(1)	6823(2)	372(3)	9664(3)	58(1)
C(2)	7682(3)	205(4)	9708(4)	75(2)
C(3)	8181(4)	1246(5)	9874(5)	103(3)
C(4)	7765(4)	−586(5)	8996(5)	97(3)
C(5)	6601(3)	−98(4)	10447(3)	78(2)
C(6)	7009(6)	509(6)	11291(4)	132(4)
C(7)	6669(4)	−1332(4)	10528(5)	102(3)
N(2)	5000	5822(5)	7500	85(3)
C(8)	5000	4705(5)	7500	63(2)
C(12)	4897(6)	6799(9)	6077(6)	169(6)
C(11)	6149(6)	6792(10)	7335(8)	223(8)
C(10*)	5521(10)	6358(11)	6885(9)	86(4)
C(10+)	5263(8)	6610(11)	6990(9)	78(3)

* 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 ($N{\doteq}C$) 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 ¹H NMR spectrum of **3** at room temperature shows two "triplets" for the pyrrole protons.

The ¹³C 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 $S_2CNC_4H_4$ from the $In(S_2CNC_4H_4)_3$ unit to $[In(S_2CNC_4H_4)_2^+]$ (m/e 399) and $[In(S_2CNC_4H_4)]^+$ (m/e 257) and fragmentation of the ligand by proton attachment in the form of $HS_2CNC_4H_4^+$ (m/e 143) was observed as low intensity peaks. The base peak at m/e 110 is due to the $[S=C=NC_4H_4]^+$ fragment.

Although vibrational and NMR data reveal part of the structural features of the complexes under
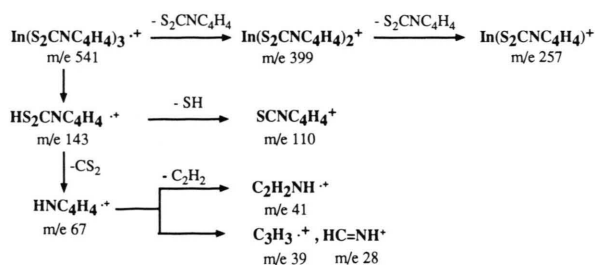
Scheme 1.

investigation an X-ray structure determination of the compounds was essential for determining the geometry of the InS_6 and InO_3S_3 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** inspite 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 InS_6 polyhedron shows lower symmetry than that of a trigonal antiprism. **1** actually possesses a crystallographic C_2 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 S_3 triangles $S_1S_3S_6/S_2S_4S_5$ 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 $S1S2AS3A/S2S3S1A$ 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, $Bi(S_2CO^iPr)_3$ [19, 20]. In **1** the two ligands which are correlated by the C_2 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.

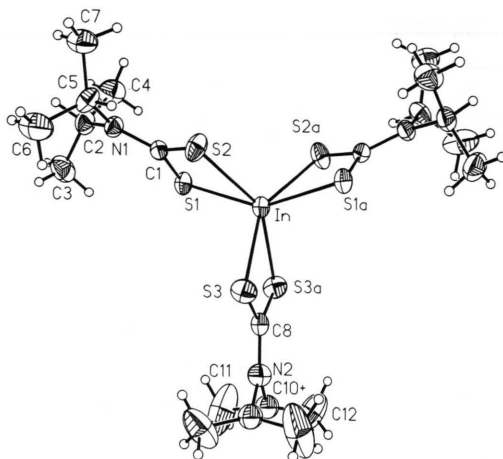Fig. 1. ORTEP representation of $In(S_2CN^iPr_2)_3$, **1**. Selected bond lengths (in Å): In–S1 2.617(2), In–S2 2.583(2), In–S3 2.601(2), S1–C1 1.724(5), S2–C1 1.724(5), S3–C8 1.724(4), N1–C1 1.331(5), N1–C2 1.502(7), N1–C5 1.507(7), N2–C8 1.319(9). – Selected bond angles (in °): S1–In–S2 68.6(1), S1–In–S3 111.8(1), S1–In–S2a 94.8(1), S1–In–S3a 92.4(1), S1–In–S1a 151.1(1), S2–In–S3 94.4(1), S2–In–S2a 111.8(1), S3–In–S5a 148.3(1), S3–In–S3a 68.5(1), S2–In–S3a 148.3(1), In–S1–C1 86.9(1), In–S2–C1 88.0(1), In–S3–C8 87.6(2), S1–C1–S2 116.5(2), S1–C1–N1 122.8(3), S2–C1–N1 120.7(4), C1–N1–C2 124.0(4), S3–C8–S3a 116.3(4), S3–C8–N2 121.9(2).
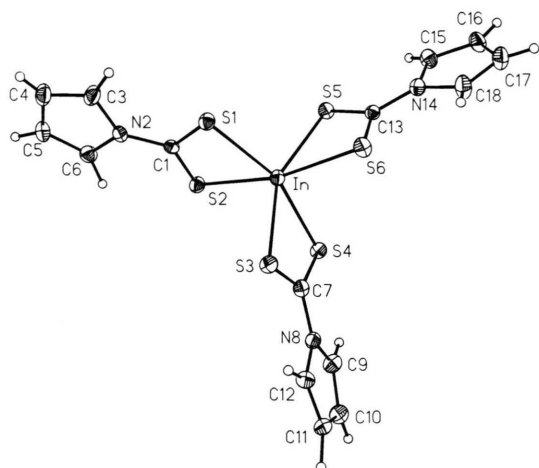
Fig. 2. ORTEP representation of a molecule of **3.** Selected bond distances (in Å): In–S1 2.597(2), In–S2 2.577(2), In–S3 2.607(2), In–S4 2.579(2), In–S5 2.612(2), In–S6 2.594(2), S1–C1 1.702(4), S2–C1 1.690(4), S3–C7 1.694(5), S4–C7 1.694(4), S5–C13 1.711(4), S6–C13 1.699(4), C1–N2 1.384(6), N2–C3 1.396(6), N2–C6 1.396(6), C7–N8 1.385(6), N8–C9 1.407(6), N8–C12 1.383(6), N14–C13 1.360(5), N14–C15 1.383(6), N14–C18 1.423(6). – Selected bond angles (in °): S1–In–S2 69.9(1), S1–In–S3 98.7(1), S1–In–S5 101.8(1), S1–In–S4 159.7(1), S1–In–S6 100.2(1), S2–In–S3 97.7(1), S2–In–S4 94.8(1), S2–In–S5 103.5(1), S2–In–S6 166.7(1), S3–In–S4 69.4(1), S3–In–S5 154.5(1), S3–In–S6 92.4(1), S4–In–S5 94.5(1), S4–In–S6 96.8(1), Sn5–In–S6 69.2(1), S1–C1–S2 121.8(3), S1–C1–N2 119.3(3), S3–C7–S4 121.3(3), S3–C7–N8 119.4(3), S5–C13–S6 129.3(2), S5–C13–N14 119.6(3).

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, $Fe(S_2CNC_4H_4)_3$ [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 CS_2 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
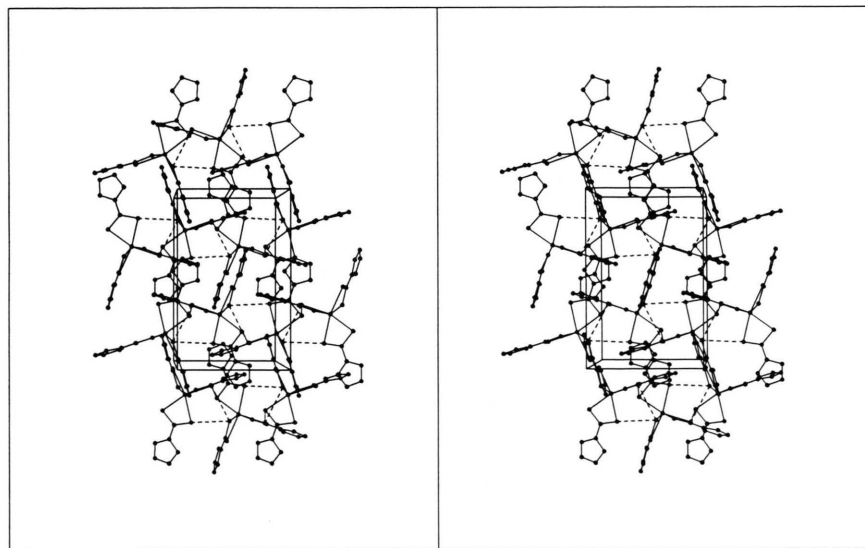

Fig. 3. Stereoplot of the unit cell of **3,** projection along the *a*-axis. Note the close contacts between sulfur atoms indicated by dashed lines. S···S contacts range from 3.543 to 3.899 Å.

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 $Ga(S_2CNC_4H_4)_3$ [25], $Ga(S_2CNEt_2)_3$ [26] and $Al[S_2CNMe_2]_3$ [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 $Tl(S_2CNR_2)_3$ compounds [29] than with Ga complexes.

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