Crystal Structures of Tris(diethyldithiocarbamato)-gallium(III) and -indium(III)

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The crystal structures of the isostructural title compounds, $[Ga(S_2C{\cdot}NEt_2)_3]$ (I) and $[In(S_2C{\cdot}NEt_2)_3]$ (II), have been determined by direct methods from *X*-ray diffraction data and refined by full-matrix least-squares to *R* 0.034 and 0.037 for 1 119 (I) and 2 054 (II) observed diffractometer reflections. Crystals are monoclinic, space group *A*2/*a*, ($Z = 4$), with unit-cell dimensions: (I): $a = 14.862(3)$, $b = 10.244(2)$, $c = 17.863(2)$ Å, $\beta = 117.49(1)°$; (II): $a = 14.826(5)$, $b = 10.396(5)$, $c = 18.139(3)$ Å, $\beta = 117.88(3)°$. The array of discrete molecules represent a new structural type among the $[M(S_2C{\cdot}NEt_2)_3]$ derivatives. The three ligands within each molecule are *quasi*-symmetric bidentate with an overall approximate D_3 molecular symmetry (mean Ga–S 2.436, In–S 2.597 Å).

In studies of dithiocarbamate derivatives, the diethyl-substituted derivative is usually taken as the representative member and made the subject of any more specific investigation unless there are compelling reasons to the contrary. The reasons for this are probably (i) tradition, (ii) the ready availability of the sodium salt, $Na[S_2C{\cdot}NEt_2]{\cdot}3\,H_2O$, and (iii) the usually convenient solubility properties which permit ready recrystallization from organic solvents.

Among the simple tris-ligand derivatives $[M(S_2C{\cdot}$

$NEt_2)_3]$ so far studied, an unusually wide range of crystallographic and molecular types has been recorded, in contrast to the acetylacetonate derivatives $M(acac)_3$, for example, which tend to be much more closely related. While in a few cases there are obvious and good electronic reasons for the presence of considerable intramolecular distortion which might influence the crystal packing, in other cases the origin of the differences is more subtle, and may originate in factors such as molecular lability on the crystallization time-scale, the metal–sulphur distance, and the extent of the twist about the ML_3 true or pseudo-three-fold axis, and solvent interaction. In view of the desirability of accurate structural data on these important systems as a basis for solid-state electronic studies, it was considered desirable to examine these variations in more detail. We now describe the structure determination of one discrete structural type, observed with gallium and indium; in addition, it was considered of interest to examine this system because of the scarcity of data available on Group III sulphur complexes. We describe the results of two independent studies on these complexes, which have yielded results which are not significantly different and accordingly the observations reported represent one set of measurements only.

EXPERIMENTAL

Colourless crystals were obtained by recrystallization from benzene; the derivatives were prepared by the reaction of aqueous solutions of gallium(III) and indium(III) chlorides and the sodium salt of the ligand.

In the determination of the crystal structure conditions used for the gallium derivative are described, with those for the indium compound in parentheses, where different.

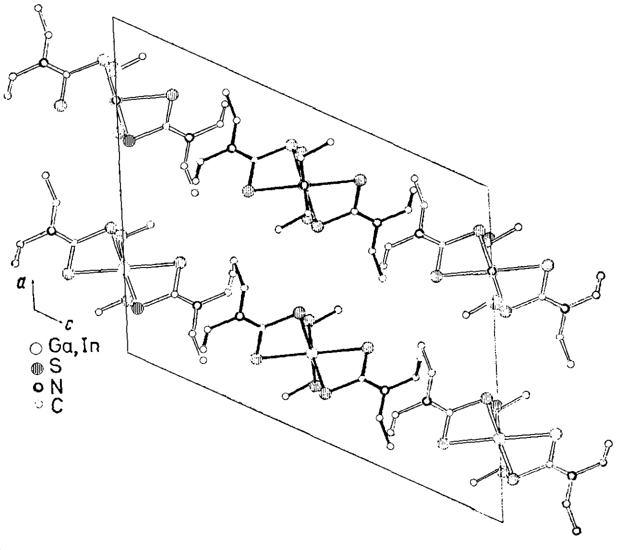

FIGURE 1 Projection of the unit cell of $[Ga,In(S_2C{\cdot}NEt_2)_3]$ down *b*. Molecules with solid bonds are centred at *y ca.* 0.5

In both cases *pseudo*-spherical crystals 0.30 mm in diameter were used, and cell dimensions obtained by a least-squares fit of the angular parameters of 15 reflections centred in the counter aperture of a Syntex P$\bar{1}$ four-circle diffractometer. Unique data sets were collected by a conventional 2θ—θ scan within the limits $2\theta < 100°$ (50°) by use of Ni-filtered Cu(K_α) radiation, $\lambda = 1.5418$ Å (monochromatic Mo-K_α radiation, $\lambda = 0.710\,69$ Å) yielding 1 225 (2 252) independent reflections, of which 1 199 (2 054) having $I > \sigma(I)$ were considered 'observed' and used in the structure solution and refinement. A spherical absorption correction was applied to the data of (I).

Crystal Data.—$C_{15}H_{30}GaN_3S_6$ ($C_{15}H_{30}InN_3S_6$), $M = 514.5$ (559.6), Monoclinic, Space group $A2/a$ (C^6_{2h}, No. 15), $a = 14.862(3)$ [14.826(5)], $b = 10.244(2)$ [10.396(5)], $c = 17.863(2)$ [18.139(3)] Å, $\beta = 117.49(1)$ [117.88(3)°], $U = 2\,412.6(7)$ [2 469(1)] Å^3, $D_m = 1.42(1)$ [1.51(1)], $Z = 4$, $D_c = 1.46$ (1.50) g cm^{-3}, $F(000) = 1\,072$ (1 144). Scattering factors for the neutral atoms,[1,2] those for Ga (In) and S being corrected for the effects of anomalous dispersion ($\Delta f'$, $\Delta f''$).[3] μ(Cu-K_α) = 63.4 (I), μ(Mo-K_α) = 14.4 cm^{-1} (II).

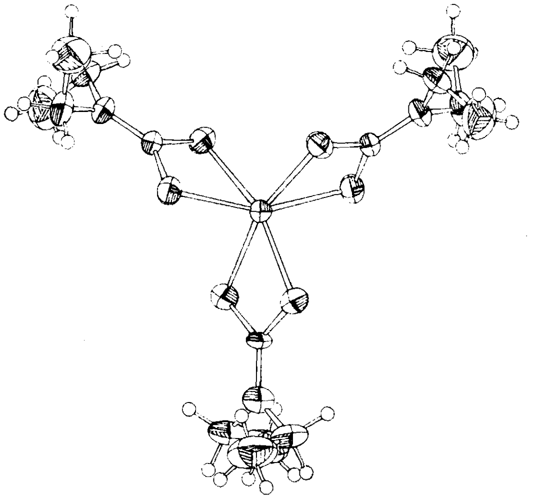

FIGURE 2 Projection of the (II) molecules down the *pseudo*-three-fold axis, showing ligand substituent disposition and 50% thermal ellipsoids (H atoms are given an arbitrary radius of 0.10 Å). Note the three-fold symmetry of the terminal methyl substituents with respect to the three-fold axis

The structures were solved by direct methods, the final stages of refinement being carried out by full-matrix least-squares using anisotropic thermal parameters of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hl\,a^*c^* + 2U_{23}kl\,b^*c^*)]$; hydrogen atoms were located and their positional parameters included in the refinement, thermal parameters being fixed isotropically at U 0.10 Å^2. In the final least-squares cycle no parameter shift exceeded 0.20σ. Final R values were 0.034 (0.037), and $R' = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$ 0.053 (0.042); weighting schemes of the form $w = (\sigma^2(F_o) + n \times 10^{-4}(F_o)^2)^{-1}$ were used, values of $n = 0$ (4) being found appropriate.

Computation was carried out on a CDC 6200 machine with the '*X*-Ray' program system.[4] Structure factors are deposited as Supplementary Publication No. SUP 21509 (7 pp., 1 microfiche).*

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

[1] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[2] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

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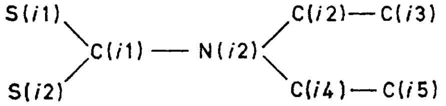
Labelling of atoms within ligand nos. $i = 1$ or 2 is as shown [because of its orientation about a two-fold axis,



only the top half is relevant for ligand (1), comprising S(1) C(1) N(1) C(2) C(3)] H(*ijk*), *k* = *a*,*b*,*c*, are attached to C(*ij*). C(3) and C(5) are disposed on either side of the ligand plane. Results are shown in Tables 1—3 and Figures 1 and 2.

DISCUSSION

Both structures are composed of discrete molecules of $[M(S_2C{\cdot}NEt_2)_3]$; the two complexes are isostructural, each molecule containing three *quasi*-symmetrically co-ordinated bidentate ligands and located on a two-fold

TABLE 1

Atomic fractional cell co-ordinates (× 10^4, for H × 10^3) and thermal parameters (× 10^3 Å^2). Values for (II) are beneath those for (I). Least-squares estimated standard deviations are given in parentheses

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ga	25 000(–)	03 661(7)	00 000(–)	69.0(7)	29.9(7)	39.7(7)		34.7(5)	
In	25 000(–)	04 211(3)	00 000(–)	63.5(3)	26.5(2)	38.2(2)		31.0(2)	
Ligand (1)									
S(1)	15 495(1)	2 272(1)	00 489(8)	79.9(9)	37.7(8)	61.1(9)	0.6(6)	45.7(7)	−2.4(5)
	15 274(9)	2 476(1)	00 412(7)	73.0(8)	35.9(5)	64.9(7)	2.5(5)	43.2(6)	−2.4(5)
C(1)	2 500(–)	3 161(6)	0 000(–)	80(4)	23(4)	42(4)		31(7)	
	2 500(–)	3 325(5)	0 000(–)	73(4)	31(3)	33(3)		23(3)	
N	2 500(–)	4 454(6)	0 0000(–)	83(4)	38(4)	60(4)		35(3)	
	2 500(–)	4 605(4)	0 000(–)	79(4)	29(3)	59(3)		26(3)	
C(2)	3 299(6)	5 208(6)	−0 063(5)	115(5)	32(3)	83(5)	−16(3)	49(4)	0(3)
	3 296(5)	5 343(5)	−0 075(4)	94(5)	36(3)	88(4)	−14(3)	35(3)	8(3)
C(3)	4 190(9)	5 532(9)	0 753(6)	132(7)	64(5)	102(7)	−27(5)	26(5)	−8(4)
	4 201(7)	5 660(7)	0 747(6)	99(6)	76(5)	118(6)	−27(6)	14(5)	−2(4)
H(2a) *	349(6)	473(8)	−046(6)						
	349(5)	494(6)	−046(4)						
H(2b)	310(6)	590(9)	−033(5)						
	300(4)	609(6)	−034(4)						
H(3a)	400(6)	606(9)	104(6)						
	398(5)	614(6)	111(4)						
H(3b)	443(7)	479(9)	098(6)						
	446(5)	491(6)	103(4)						
H(3c)	471(6)	624(9)	082(5)						
	474(4)	619(6)	065(4)						
Ligand (2)									
S(1)	14 545(9)	−1 115(1)	03 065(7)	66.4(8)	42.1(9)	41.5(9)	−9.2(5)	25.2(6)	1.1(5)
	13 653(8)	−1 068(1)	03 562(6)	58.3(7)	42.5(6)	41.6(6)	−10.0(5)	19.5(5)	3.8(4)
S(2)	34 337(9)	−0 094(1)	15 251(7)	65.0(9)	48.6(9)	41.4(9)	−10.2(6)	29.8(6)	−1.5(5)
	34 416(8)	−0 197(1)	15 790(6)	55.0(6)	49.5(6)	40.4(5)	−10.1(5)	24.1(5)	−1.3(5)
C(1)	2 408(3)	−1 092(4)	1 324(3)	65(3)	33(2)	32(2)	1(2)	28(2)	−1(2)
	2 362(3)	−1 107(3)	1 355(2)	54(2)	29(2)	41(2)	2(2)	28(2)	2(2)
N	2 369(3)	−1 795(4)	1 931(2)	69(2)	46(2)	42(2)	−7(2)	34(2)	3(2)
	2 302(3)	−1 805(3)	1 942(2)	60(2)	43(2)	42(2)	−4(2)	28(2)	8(2)
C(2)	1 440(5)	−2 539(6)	1 769(4)	96(4)	43(3)	65(4)	−12(3)	51(3)	4(2)
	1 358(4)	−2 500(5)	1 779(3)	77(3)	54(3)	63(3)	−14(3)	39(3)	10(2)
C(3)	0 749(7)	−1 786(10)	2 002(7)	94(5)	107(6)	102(6)	−25(6)	66(4)	−28(6)
	0 680(6)	−1 681(8)	1 994(5)	89(5)	115(6)	107(5)	−30(4)	70(5)	−19(4)
C(4)	3 201(5)	−1 855(7)	2 790(3)	88(4)	69(4)	44(3)	−8(3)	38(3)	5(3)
	3 150(4)	−1 906(5)	2 800(3)	75(3)	60(3)	44(2)	−4(3)	23(2)	11(2)
C(5)	3 839(6)	−3 044(9)	2 943(6)	93(5)	78(5)	80(5)	22(4)	23(4)	9(4)
	3 767(5)	−3 088(7)	2 919(5)	85(5)	84(4)	80(4)	18(4)	24(4)	23(4)
H(2a)	108(5)	−282(8)	117(6)						
	095(5)	−277(6)	121(4)						
H(2b)	168(5)	−328(10)	207(5)						
	158(4)	−323(6)	213(4)						
H(3a)	114(6)	−161(9)	256(4)						
	110(4)	−135(6)	258(4)						
H(3b)	073(8)	−115(10)	196(7)						
	055(5)	−092(6)	170(4)						
H(3c)	003(6)	−239(8)	170(5)						
	009(5)	−217(6)	187(4)						
H(4a)	367(6)	−121(9)	290(5)						
	357(4)	−117(4)	295(4)						
H(4b)	292(5)	−199(9)	315(5)						
	283(4)	−189(4)	318(4)						
H(5a)	348(5)	−395(10)	271(5)						
	335(5)	−379(7)	276(4)						
H(5b)	409(6)	−313(8)	246(5)						
	415(5)	−303(6)	260(4)						
H(5c)	435(6)	−298(9)	334(6)						
	429(5)	−313(6)	349(4)						

* See text.

axis so that only one half of the molecule is crystallographically independent. The S_2CNC_2 sections of the ligand are substantially planar, as usual; while the metal atom is coplanar with the ligand on the two-fold axis, a substantial deviation from the plane of ligand (2) is found in both (I) and (II). The terminal methyl groups in both ligands are disposed as usual, on alternate sides of the ligand plane. The dominant packing forces within the crystal are the expected weak S · · · H intermolecular interactions; however, these are few in number and unusually long, only one being <3.0 Å. The ligand geometries are normal; these are among the most accurate determinations of diethyldithiocarbamate geometry and establish the C–S distance as being close to 1.72 Å (but see later) while C–N is close to 1.327. The latter value is less susceptible to variation caused by changes in crystal packing, metal-atom geometry, or bonding. Neither has been corrected for the effects of thermal motion and both are therefore probably slightly underestimated.

TABLE 2

Interatomic distances (Å) and angles (°) involving non-hydrogen atoms. Values for (II) follow those for (I)

(*a*) Metal environment	
M–S(11)	2.435(2), 2.597(2)
M–S(21)	2.408(2), 2.582(2)
M–S(22)	2.466(1), 2.611(2)
S(21)–M–S(21$^{\rm I}$)	101.93(5), 106.22(6)
S(21)–M–S(22$^{\rm I}$)	92.17(5), 92.92(5)
S(22)–M–S(22$^{\rm I}$)	157.98(5), 151.54(5)
S(11)–M–S(21)	92.92(5), 92.91(6)
S(11)–M–S(22)	98.83(5), 100.91(5)
S(11)–M–S(11$^{\rm I}$)	73.38(6), 69.40(7)
S(11)–M–S(21$^{\rm I}$)	163.53(5), 159.43(6)
S(11)–M–S(22$^{\rm I}$)	98.79(4), 102.42(5)
S(21)–M–S(22)	73.84(4), 69.75(5)
(*b*) Ligand (1)	
S(1)–C(1)	1.716(4), 1.723(3)
C(1)–N	1.324(9), 1.329(7)
N–C(2)	1.465(9), 1.468(8)
C(2)–C(3)	1.485(11), 1.502(9)
M–S(1)–C(1)	85.4(2), 86.1(2)
S(1)–C(1)–N	122.0(2), 120.8(2)
C(1)–N–C(2)	121.9(4), 121.5(3)
C(2)–N–C(2$^{\rm I}$)	116.3(6), 117.0(5)
N–C(2)–C 3)	115.4(8), 113.9(7)
S(1)–C(1)–S(1$^{\rm I}$)	115.9(4), 118.3(3)
S(1) · · · S(1$^{\rm I}$)	2.910(2), 2.959(2)
(*c*) Ligand (2)	
S(1)–C(1)	1.714(4), 1.719(4)
S(2)–C(1)	1.730(6), 1.736(5)
C(1)–N	1.325(7), 1.326(6)
N–C(2)	1.483(9), 1.476(7)
N–C(4)	1.461(6), 1.476(6)
C(2)–C(3)	1.49(1), 1.50(1)
C(4)–C(5)	1.49(1), 1.49(1)
S(1) · · · S(2)	2.928(2), 2.967(2)
S(1)–C(1)–N	122.3(3), 120.8(3)
S(2)–C(1)–N	121.3(3), 120.8(3)
C(1)–N–C(2)	120.5(4), 121.4(3)
C(1)–N–C(4)	123.1(5), 122.8(4)
C(2)–N–C(4)	116.3(5), 115.8(4)
N–C(2)–C(3)	112.3(6), 111.0(5)
N–C(4)–C(5)	112.8(6), 111.9(5)
S(1)–C(1)–S(2)	116.5(3), 118.4(3)
M–S(1)–C(1)	85.9(2), 86.6(2)
M–S(2)–C(1)	83.8(2), 85.3(1)

All C–H distances lie in the range 0.75—1.05 Å, σ *ca.* 0.09 Å. Transformations of the asymmetric unit: I $\frac{1}{2} - x, y, \bar{z}$. The only close intermolecular S · · · H contact is S(11) · · · H(23c) at $\bar{x}, \bar{y}, \bar{z}$ 2.92(7) Å.

In both derivatives the metal symmetry is nearer D_3 rather than O_h, as is usual in symmetrically co-ordinated tris(dithiochelates) because of the small ligand bite. In (II), the InS_6 geometry closely parallels that found in the related [In{$S_2C·N(CH_2)_5$}$_3$];[5] in the latter the In–S distances lie in the range 2.588 ± 0.005 Å. In (II), however, considerable distortions are found, the In–S range being 2.58_2—2.61_1, mean 2.59_7 Å; such variations are typical of the 1 : 1 tris(dithiochelates) of indium,[6-8] *e.g.* [In{$S_2P(OEt)_2$}$_3$] 2.578 to 2.633 (mean 2.608 Å),[6] [In($S_2C·C_6H_8$)$_3$] 2.577 to 2.619 (mean 2.603 Å),[7] [In(dithiolene)$_3$] 2.585 to 2.626 (mean 2.604 Å).[8] In view of this variety of ligand types,[6-8] the overall variation among means is surprisingly and atypically small, especially considering the wide variation in crystal-field properties and bite of the ligands.[9-12] The reason for this is uncertain but may lie in the necessity for outer *d*-orbital participation in the bonding of the indium derivatives.

TABLE 3

Equations of least squares plane in the form $pX + qY + rZ = s$, where $X = ax + cz\cos\beta$, $Y = by$, and $Z = cz\sin\beta$. Deviations (Å) from the planes are given in square brackets. Values for (I) precede those for (II)

	10^4p	10^4q	10^4r	s	$10^3\sigma$(Å)	χ^2 *
Ligand (1): S(1), S(1$^{\rm I}$), C(1), N, C(2), C(2$^{\rm I}$)						
(I)	0 648	0 000	9 979	0.2408	016	18.9
(II)	0 720	0 051	9 974	0.2816	041	98.4
[S(1) −0.02, −0.04; S(1$^{\rm I}$) 0.02, 0.04; C(1) 0.00, 0.00; N 0.00, 0.01; C(2) −0.02, −0.05; C(3) 1.31, 1.37; M 0.00, 0.00]						
Ligand (2): S(1), S(2), C(1), N, C(2), C(4)						
(I)	5 892	−7 747	−2 297	1.8444	055	647
(II)	5 612	−7 885	−2 516	1.6707	036	132
[S(1) 0.05, 0.03; S(2) −0.06, −0.04; C(1) 0.01, 0.01; N 0.01, 0.01; C(2) −0.07, −0.05; C(4) 0.06, 0.03; C(3) −1.47, −1.49; C(5) 1.43, 1.45; M 0.05, 0.07]						

* Five degrees of freedom.

The mean gallium–sulphur distance in the GaS_6 core is 2.436 Å; the variation found, however, is much greater than that in the indium–sulphur distances in (II), ranging from 2.40 to 2.46 Å. The cause of these variations is not obvious; as observed earlier, these are no strong single interactions of hydrogen atoms with the sulphur atoms of the core, such as are usually responsible

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for distortions of this type. It is unlikely that the effect is electronic in origin, since the usual trend is to find distortions occurring with the heavier elements of the *p* block metals, and there are no metal-atom lone-pairs, as is the case with the arsenic analogue.[13] The most probable explanation is that of general pressure on the ligand systems due to packing forces; this is suggested by the appreciable deviation of the metal atom from the plane of ligand (2). No other structures of gallium–sulphur chelates are available for comparison.

While the effective ' bite ' of the ligand, as measured, for example, by the angle subtended at the metal, clearly decreases from (I) to (II), the intraligand S · · · S distance does not remain constant. In $[Co(S_2C{\cdot}NEt_2)_3]$ ⟨Co–S⟩ is 2.25_8, ⟨S · · · S⟩ 2.81, ⟨C–S⟩ 1.70_2 Å, and ⟨S–C–S⟩ is 111.6°. In (I) corresponding values are 2.43_6 2.92_8, 1.72_0 Å, and 116.1, and in (II) they are 2.59_7, 2.96_7, 1.72_5 Å, and 118.3°. This would suggest that as the size of the metal increases and the effective bite decreases, the ligand accommodates to some extent by increasing the S–C–S angle and at the same time increasing the C–S distances.

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[5/654 *Received, 8th April,* 1975]

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