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The Crystal and Molecular Structures of Tris(*O*-ethylxanthato)-gallium(III) and indium(III)

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The crystal structures of the title compounds, $Ga(S_2COEt)_3$ (1) and $In(S_2COEt)_3$ (2) have been determined by three dimensional X-ray diffraction methods. Both compounds crystallize in the trigonal space group $R\bar{3}$ with $Z = 6$. Cell dimensions for (1) are a_{hex} 15.065(1) and c_{hex} 13.421(1) Å and for (2) 15.319(3) and 13.522(4) Å. Final R and R_w values 0.044 and 0.049 for (1) and 0.040 and 0.037 for (2) for 668 and 1153 statistically significant reflections respectively.

The complexes are isostructural. The metal centres are in a distorted octahedral environment, the distortion arising from the restricted bite distance of the xanthate ligands. For each compound, each xanthate moiety chelates the metal atom with similar M–S bonds.

Introduction

The chemistry of the xanthate complexes involving Group III elements is not well known [1]. The tris(xanthato) complexes of Ga [2], In [2–4], and Tl [5] have been prepared but as yet no structure determination of any of these compounds has been reported. So far there is only one Group III xanthate for which a X-ray crystal structure analysis has been reported, namely the organothallium compound, $(CH_3)_2Tl(S_2COCH_3)$, in which the Tl atom is seven coordinate [6]. We report here the results of our X-ray structure determinations of $M(exa)_3$, where M = Ga(III) and In(III) and exa is *O*-ethylxanthato.

Experimental

Ga(exa)$_3$

Gallium metal (2 g) was dissolved in a minimum of warm HCl to yield $GaCl_3$. The acidic solution was diluted and potassium ethylxanthate (11 g) added. The suspension was stirred briefly and $Ga(exa)_3$ was quickly extracted with benzene to minimize decomposition by the acid. The benzene was removed under reduced pressure and the product was recrystallized from a benzene/petroleum spirit (60–80 °C) solution. Characteristic infrared absorptions in the C–O, C–S and M–S regions were observed at 1275, 1250; 1061, 1040, 1030, 1005; and 455, 405 cm^{-1} respectively. The hydrogen-1 NMR spectrum in $CDCl_3$ shows the expected triplet and quartet due to the xanthate ligand protons: δCH_3 1.48, δCH_2 4.52 ppm, $^3J(H–H)$ 7.1 Hz. The carbon-13 NMR spectrum in $CDCl_3$ shows three resonances; $\delta C(1)$ 226.5, $\delta C(2)$ 74.7, and $\delta C(3)$ 14.0 ppm; see Fig. 1 for numbering scheme.

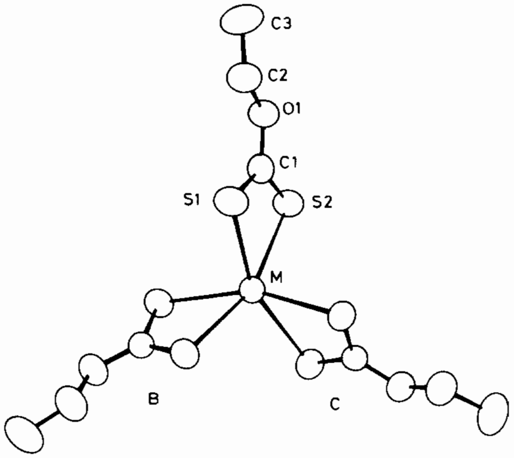

Fig. 1. Numbering scheme for $M(exa)_3$. Ligands B and C are related by the symmetry operations y, x – y, z and y – x, $\bar{x}$, z respectively.

In(exa)$_3$

$In(exa)_3$ was prepared as described previously [3]. Characteristic C–O, C–S and M–S infrared absorptions: 1270, 1245; 1035, 1020, 1002; and 450, 402 cm^{-1} respectively. NMR measurements in $CDCl_3$: ^1H δCH_3 1.50, δCH_2 4.52 ppm, $^3J(H–H)$ 7.1 Hz. ^{13}C $\delta C(1)$ 229.9, $\delta C(2)$ 76.2, and $\delta C(3)$ 14.1 ppm.

Crystallography

Ga(exa)$_3$

Crystals suitable for the X-ray diffraction study were grown by the slow evaporation of a benzene/

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petroleum spirit (40–60 °C) solution of the compound. Preliminary oscillation and equi-inclination Weissenberg photographs revealed the space groups to be either R3 and R3 [7a]; subsequent solution and refinement of the structure indicated R$\bar{3}$ was the true space group. A crystal was mounted with its *c*-axis coincident with the Φ-axis of a Siemens single crystal diffractometer. Accurate cell parameters together with their estimated standard deviations were derived by a least squares procedure [8] from the 2θ values obtained for eleven carefully centred, well resolved, near axial reflections, each having a 2θ value $\geqslant 110°$. Intensity measurements for 2544 reflections were made by means of a 'five value' θ–2θ scan method [9] using CuKα (nickel filtered) radiation (λ 1.5418 Å) to a maximum Bragg angle of 70°. The net intensity of a check reflection, monitored after every twenty intensity measurements indicated that the crystal had decomposed somewhat during the data collection even though the crystal had been coated with shellac as a precautionary measure; accordingly the intensity data were placed on a common arbitrary scale. The structure amplitudes were corrected for Lorentz and polarization effects and for absorption [7b, 10].

Crystal Data $C_9H_{15}O_3S_6Ga$, $M = 433.3$, trigonal, R$\bar{3}$ (C_{3i}^2, No. 148), $a_{hex} = 15.065(1)$, $c_{hex} = 13.421(1)$ Å, $U = 2637.9$ Å^3, $D_m = 1.63$ (flotation, aqueous zinc bromide solution), $Z = 6$, $D_{calc} = 1.63$ M gm^{-3}, F(000) = 1323, $\mu = 86.26$ cm^{-1}, Siemens diffractometer, absorption corrections applied.

There were 668 unique reflections satisfying the $I \geqslant 3\sigma(I)$ criterion which were used to derive a Patterson synthesis which readily revealed the position of the Ga atom to be on a site of symmetry 3. All non-hydrogen atoms were located in a subsequent difference map and refined isotropically, minimizing the function $\Sigma w\Delta^2$ [11], where $\Delta = ||F_o| - |F_c||$, yielding *R* 0.089. A weighting scheme was applied of the type $w = (a|F_o|^2 + b|F_o| + c)^{-1}$ according to the criterion of Cruickshank [12]. The coefficients a, b, and c were determined by a least squares method from a plot of $\Sigma\Delta^2/n$ for ranges of $|F_o|$ against $\langle|F_o|\rangle$ (a = 0.0042, b = 0.3525 and c = 74.0442). Refinement was continued with anisotropic thermal parameters. All hydrogen atoms were located in a subsequent difference map and when included in the model, refinement converged with *R* 0.044 and R_w 0.049, where $R_w = [\Sigma w\Delta^2/\Sigma|F_o|^2]^{1/2}$. A final difference map revealed no peaks with heights greater than 0.4 eÅ^3.

The atomic scattering factors used for Ga and S were those calculated by Cromer and Waber [13], and were corrected for the real and imaginery parts of anomalous dispersion [14]. Values for H, C, and O were those from reference [7c].

In(exa)$_3$

Suitable crystals for X-ray analysis were grown by the slow evaporation of a benzene solution of the compound. Preliminary photographic and diffractometer studies indicated that In(exa)$_3$ was isomorphous with Ga(exa)$_3$.

Intensity data were collected in an Enraf-Nonius four circle CAD-4F diffractometer controlled by a PDP8/A computer using CuKα radiation (graphite monochromatized) λ 1.5418 Å. The ω: 2θ scan technique was employed to measure the intensity profiles for 4456 reflections for which $1° \leqslant \theta \leqslant 75°$. Using the $I \geqslant 2\sigma(I)$ criterion of observability on 1262 unique reflections there were 1153 reflections remaining. No significant decomposition of the crystal occurred during the data collection and correction was made for Lorentz and polarization effects and for absorption [7d].

Crystal Data $C_9H_{15}O_3S_6In$, M = 487.4, trigonal, R$\bar{3}$ (C_{3i}^2, No. 148), $a_{hex} = 15.319(4)$, $c_{hex} = 13.522(3)$ Å, $U = 2748.1$ Å^3, $D_m = 1.75$ (flotation, aqueous zinc bromide solution), Z = 6, $D_{calc} = 1.734$ M gm^{-3}, F(000) = 1428, $\mu = 167.46$ cm^{-1}, Enraf-Nonius CAD-4F diffractometer, absorption corrections applied.

The solution and refinement of the In(exa)$_3$ crystal structure was as for Ga(exa)$_3$. Refinement of all atomic positions and isotropic thermal parameters for the non-hydrogen atoms yielded *R* 0.092. Anisotropic thermal parameters were introduced and a subsequent difference map indicated the positions of all the hydrogen atoms, which were then included in the model but not refined. The weighting scheme $w = [\sigma^2(F) + 0.001|F_o|^2]^{-1}$ was applied and the refinement continued until convergence; the values of *R* and R_w were 0.040 and 0.037 respectively.

A final difference map revealed an electron density peak of 0.28 eÅ^{-3}. The scattering factors used for H, C, O and S were those collected by Sheldrick [15], while the scattering factors and anomalous dispersion terms for neutral indium were those listed in ref. 7e and 7f.

Fractional atomic coordinates and their estimated standard deviations are given in Table I and all relevant interatomic parameters are listed in Tables II and III. The numbering scheme used is illustrated in Fig. 1. Materials deposited with the editors: anisotropic thermal parameters, hydrogen atom parameters and the observed and calculated structure factor tables.

Instrumentation

Infrared spectra were obtained from KBr discs on a Jasco-A-302 spectrophotometer. NMR spectra were recorded on a JEOL FX100 spectrometer: hydrogen-1 at 100 MHz internal deuterium lock; carbon-13 at 25.0 MHz using internal 2H lock. Hydrogen-1

TABLE I. Fractional Atomic Coordinates for M(exa)$_3$. Estimated Standard Deviations in Parentheses.

Atom	M = Ga			M = In		
	x/a	*y/b*	*z/c*	*x/a*	*y/b*	*z/c*
M	0.0	0.0	0.1984(1)	0.0	0.0	0.19479(3)
S(1)	0.0445(1)	−0.1094(1)	0.2984(1)	0.0412(1)	−0.1198(1)	0.2980(1)
S(2)	−0.0648(1)	−0.1589(1)	0.1091(1)	−0.0626(1)	−0.1683(1)	0.1033(1)
C(1)	−0.0127(4)	−0.1924(4)	0.2045(6)	−0.0116(3)	−0.1983(3)	0.2005(3)
O(1)	−0.0189(3)	−0.2817(3)	0.1962(4)	−0.0154(2)	−0.2854(2)	0.1919(2)
C(2)	0.0181(7)	−0.3199(6)	0.2773(8)	0.0199(4)	−0.3235(4)	0.2733(3)
C(3)	0.0279(9)	−0.4066(7)	0.2370(10)	0.0279(5)	−0.4092(4)	0.2327(4)

TABLE II. Bond Distances (Å) for M(exa)$_3$. Estimated Standard Deviations in Parentheses.[a]

	M = Ga	M = In
M–S(1)	2.465(2)	2.622(1)
M–S(2)	2.405(2)	2.574(1)
S(1)–C(1)	1.678(7)	1.693(4)
S(2)–C(1)	1.704(7)	1.705(4)
C(1)–O(1)	1.305(7)	1.311(5)
O(1)–C(2)	1.46(1)	1.470(5)
C(2)–C(3)	1.48(1)	1.484(8)
S(2)–S(2)′	3.598(4)	3.592(2)

[a] S(2)′ is related by the symmetry operation x − y, x, −z.

TABLE III. Bond Angles (°) for M(exa)$_3$. Estimated Standard Deviations in Parentheses.[a]

	M = Ga	M = In
S(1)–M–S(2)	73.50(6)	69.77(4)
S(1)–M–S(2)′	162.90(5)	158.94(4)
S(2)–M–S(1)′	98.13(5)	100.38(4)
S(1)–M–S(1)′	93.19(8)	94.29(4)
S(2)–M–S(2)′	97.34(8)	98.83(4)
M–S(1)–C(1)	83.0(2)	83.5(2)
M–S(2)–C(1)	84.4(2)	84.7(1)
S(1)–C(1)–S(2)	118.9(3)	121.9(2)
S(1)–C(1)–O(1)	125.2(5)	123.7(3)
S(2)–C(1)–O(1)	115.7(5)	114.4(3)
C(1)–O(1)–C(2)	119.8(6)	120.0(3)
O(1)–C(2)–C(3)	107.4(8)	106.5(4)

[a] The atoms S(1)′ and S(2)′ are related by the symmetry operation x − y, x, −z.

and carbon-13 referenced against internal TMS, high frequency positive notation used.

Results and Discussion

Crystals of Ga(exa)$_3$ and In(exa)$_3$ are isomorphous and consist of enantiomorphous pairs of discrete molecules of M(exa)$_3$ which are separated at distances commensurate with those predicted from van der Waals radii. The only significant intermolecular contact is the S(2)---S(2)′ interaction of 3.598(4) Å for Ga(exa)$_3$ and 3.592(2) Å for In(exa)$_3$ [where S(2)′ is related by the symmetry operation x − y, x, −z] which occurs between the enantiomorphic pair centred about the site of symmetry $\bar{3}$ at (0, 0, 0). This close approach of the two molecules is similar to that observed in the complexes, As(mexa)$_3$ (where mexa is *O*-methylxanthato) [16] and As(exa)$_3$ [17], both of which have been described as loosely associated dimers in the solid state [16]. A projection of half the unit cell contents is shown in Fig. 2.

Each molecule has a three-fold axis of symmetry, the sulphur atoms forming two parallel equilateral triangles separated by 2.540(3) Å for Ga(exa)$_3$ and 2.633(2) Å for In(exa)$_3$, with one triangle rotated 40.27(7)° (46.43(5)°) relative to the other. This

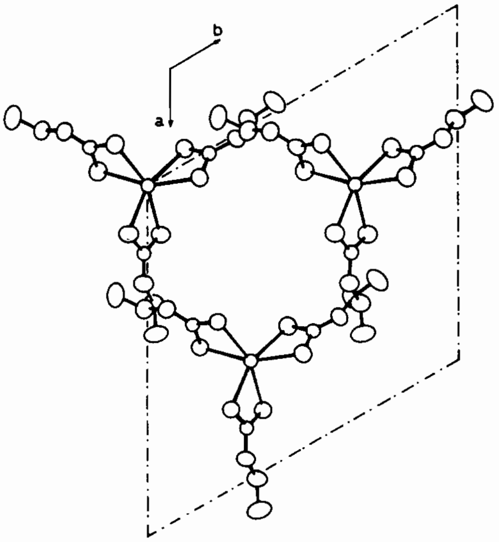

Fig. 2. Projection of half the unit cell contents of M(exa)$_3$ viewed down the [001] direction illustrating the three-fold symmetry of both the individual molecules and the crystal lattice.

geometry is intermediate between trigonal prismatic and octahedral. The six sulphur atoms in each molecule may be considered to be arranged in a distorted octahedron about the central metal atom; the distortion arising as a result of the steric requirements imposed by the restrictive chelate bite of the xanthate ligands. As a result the normal octahedral angle of 90° is reduced to a value of 73.50(6)° for $Ga(exa)_3$ and 69.77(4)° for In $(exa)_3$ for the S(1)–M–(2) angle, and as a consequence, there is a trigonal twist of the two parallel triangular planes away from the ideal value of 60° resulting in a reduction in the distance between these planes.

The xanthate moieties in these complexes chelate the metal centres almost symmetrically with M–S bonds of 2.465(2) and 2.405(2) Å (2.622(1) and 2.574(1) Å), the M–S bonds being comparable to those distances observed in other 1,1 dithiolate derivatives [18–20]. The near equivalence of the M–S bonds is also reflected in the equality (within esds) of the corresponding C–S bonds as would be expected.

Finally, it is interesting to note that the almost symmetrical coordination environment found for the Ga and In compounds reported here resembles more closely the situation found for the corresponding transition metal derivatives, such as $M(exa)_3$ where M = Cr [21], Fe [22] and Co [23], than that found for other main group systems such as for example $A(exa)_3$, where A = As [17] and Sb [24] for which an asymmetric environment has been noted. These observations add weight to the suggestion [17] that the lone pair on the central atom in the As and Sb compounds plays an important role in the determination of the adopted coordination polyhedra.

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