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Structural Features of Group VA Xanthates. The Crystal and Molecular Structures of Tris(*O*-isopropylxanthato–Arsenic(III), –Antimony(III) and –Bismuth(III)

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Abstract

The crystal structures of the title compounds, $M(S_2CO^iC_3H_7)_3$, M = As(III), (1); Sb(III), (2); and Bi(III), (3) have been determined by three dimensional X-ray diffraction techniques and refined by a least squares method. Crystals of (1) and (2) are isomorphous and both crystallize in the rhombohedral space group $R\bar{3}$, with unit cell parameters for (1) a_{hex} = 11.559(2), c_{hex} = 28.131(3) Å and for (2) a_{hex} = 11.696(2) and c_{hex} = 28.135(2) Å, $Z = 6$. The central metal atom in both (1) and (2) is coordinated by three asymmetrically chelating xanthate ligands [As–S 2.305(2) and 2.978(2) Å and Sb–S 2.508(1) and 3.006(1) Å] which form a distorted octahedral environment consistent with the presence of a stereochemically active lone pair of electrons. Crystals of (3) are orthorhombic, space group *Pnma*, $Z = 4$ with cell dimensions a = 11.003(3), b = 20.833(4) and c = 9.428(2) Å. The environment of the bismuth atom in (3) is seven coordinate and is comprised of six sulphur atoms, derived from three asymmetrically coordinating xanthate ligands, and a bridging sulphur atom from a neighbouring molecule which results in the formation a polymeric array. For (1) final R and R_w 0.050 and 0.047 respectively for 936 reflections [$I \geqslant 3\sigma(I)$]; (2) R 0.040, R_w 0.040 for 1455 reflections [$I \geqslant 2\sigma(I)$]; and (3) R 0.042, R_w 0.039 for 1796 reflections [$I \geqslant 2\sigma(I)$].

Introduction

Structural studies of tris(*O*-ethylxanthato)–arsenic(III) and antimony(III) [1–4] have indicated considerable asymmetry in the mode of coordination of the exa ligands (where exa is *O*-ethylxanthato), the asymmetry being the more pronounced in $As(exa)_3$ [1, 2]. The crystal structure of $[NEt_4][Bi(exa)_4]$ [5] showed that the bismuth atom in the anion is coordinated by a total of eight sulphur atoms, two from each of the exa ligands, with three of the ligands showing relatively minor asymmetry in their coordination. Structural features of $Bi(exa)_3$ are so far not available due to the lack of suitable crystals for X-ray diffraction studies. For the tris(*o*-isopropylxanthato)–bismuth(III) complex, $Bi(iprxa)_3$, suitable crystals were now obtained and hence we have determined its structure**. The crystal structures of the related $As(iprxa)_3$ and $Sb(iprxa)_3$ complexes have also been determined to enable a valid comparison between the modes of coordination of the iprxa ligand in this series.

Experimental

Instrumentation

Infrared spectra were obtained as KBr discs on a Perkin-Elmer 457 spectrophotometer. NMR spectra were recorded on a JEOL FX100 spectrometer: hydrogen-1 at 100 MHz and carbon-13 using internal deuterium lock and both referenced against internal TMS. High frequency positive notation used.

Preparations

$As(iprxa)_3$ was prepared in an analogous manner to that described for $As(exa)_3$ [4]; M.P. 151–152 °C. In the C–O and C–S regions of the infrared spectrum characteristic absorptions are observed at 1240 and 1020 cm^{-1} respectively. In the hydrogen-1 NMR spectrum in $CDCl_3$ solution: δCH_3 1.43 (d), δCH 5.67 ppm (sept), ^3J(H–H) 6.10 Hz. The carbon-13 NMR spectrum in $CDCl_3$ solution shows three resonances; δC_α 216.1, δC_β 80.0 and δC_γ 21.4 ppm where the carbon atoms are labelled as follows: $S_2C_\alpha OC_\beta H(C_\gamma H_3)_2$.

$Sb(iprxa)_3$ was prepared in an analogous manner to that for $Sb(exa)_3$ [1]; M.P. 144–145 °C. In the infrared spectrum characteristic C–O and C–S absorptions are observed at 1235 and 1015 cm^{-1}, respectively. ^1H NMR in $CDCl_3$: δCH_3 1.43 (d), δCH 5.59 ppm (sept), ^3J(H–H) 6.10 Hz. ^{13}C NMR in $CDCl_3$: δC_α 221.6, δC_β 80.7, and δC_γ 21.4 ppm.

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**A preliminary account of the structure determination has been published, see ref. [6].

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$Bi(iprxa)_3$ was prepared by stirring $BiCl_3$ (2 g) in ethanol solution containing the stoichiometric amount of potassium isopropylxanthate. After one minute stirring the pale yellow product, $Bi(iprxa)_3$, was filtered off and recrystallized from dichloromethane; M.P. 169 °C (dec.). In the infrared spectrum; C–O region: 1210, 1220(sh), 1245(sh) and C–S region: 1015, 1025(sh) cm^{-1}. ^1H NMR in $CDCl_3$: δCH_3 1.49 (d), δCH 5.73 ppm (sept), ^3J-(H–H) 6.35 Hz. ^{13}C NMR in $CDCl_3$: δC_α 224.9, δC_β 80.3 and δC_γ 21.5 ppm.

For each compound, suitable crystals for X-ray diffraction studies were grown by the slow evaporation of benzene/petroleum spirit (60–80 °C) solutions.

Crystallography

Preliminary Work

Preliminary photographic and diffractometer studies revealed that crystals of $As(iprxa)_3$ and $Sb(iprxa)_3$ were isomorphous and that they belonged to the trigonal space group $R\bar{3}$ [7a]. Subsequent solution and refinement of the structures were achieved in the hexagonal settings of the $R\bar{3}$ space group. Oscillation and Weissenberg photographs showed that $Bi(iprxa)_3$ crystallizes in the orthorhombic crystal class. The systematic absences as determined from the data collection were consistent with the non-centrosymmetric space group $Pna2_1$ ($C_{2v}{}^9$, No. 33) and the centrosymmetric $Pnma$ ($D_{2h}{}^{16}$, No. 62). The densities of the crystals were measured by flotation using aqueous zinc bromide solution.

Data Collection

For each of the compounds $M(iprxa)_3$, M = As, Sb, and Bi, intensity data were collected on an Enraf-Nonius CAD-4F four circle diffractometer controlled by a PDP8/A computer using the ω:2θ scan technique. Accurate cell parameters and an orientation matrix were obtained by a least squares refinement of the setting angles for 25 reflections obtained from the Enraf-Nonius procedure SEARCH. CuKα (nickel filtered) radiation λ 1.5418 Å was used for the As and Sb compounds and MoKα (graphite monochromator) radiation λ 0.71069 Å for $Bi(iprxa)_3$. No significant decomposition of any of the crystals occurred during its respective data collection. The raw intensity data were corrected for Lorentz and polarization effects and for absorption [7b]. Each data set of N reflections were amalgamated, yielding N_0 unique reflections of which only those which satisfied the criterion of observability were used in the subsequent solution and refinement of the structures. Relevant crystal data are listed in Table I.

Solution and Refinement

$As(iprxa)_3$

The three dimensional Patterson synthesis revealed the position of the As atom to be on a site of symmetry 3. Subsequent difference maps based on this position enabled the location of all non-hydrogen atoms. The structure was refined using a full-matrix least squares method in which the function $\Sigma w\Delta^2$ was minimized; where w was the weight assigned to each reflection and $\Delta = ||F_o| - |F_c||$. Refinement of all atomic positions and individual isotropic thermal parameters converged with R 0.139 where $R = \Sigma\Delta/\Sigma|F_o|$. Anisotropic thermal parameters were introduced and refined. Hydrogen atoms were also included in the model at their calculated positions which were not refined. A weighting scheme for which w was modified according to the expression $w = [\sigma^2(F) + 0.0001|F|^2]^{-1}$; refinement converged with final R 0.050 and R_w 0.047 where $R_w = [\Sigma w\Delta^2/\Sigma w|F_o|^2]^{1/2}$. The analysis of variance showed no special features indicating a satisfactory weighting scheme had been used. A final difference map revealed a maximum residual electron density peak of 0.39 $eÅ^{-3}$.

$Sb(iprxa)_3$

The structure was solved and refined as for $As(iprxa)_3$. Refinement of positional and invidual isotropic thermal parameters yielded R 0.103. Anisotropic thermal parameters, with the inclusion of hydrogen atoms, and a weighting scheme [as for $As(iprxa)_3$] resulted in R 0.040 and R_w 0.040 at convergence; the maximum residual electron density peak was 0.38 $eÅ^{-3}$ and the analysis of variance showed no special features.

$Bi(iprxa)_3$

The structure was solved initially in both $Pna2_1$ and $Pnma$. The position of the Bi atom was determined from the three dimensional Patterson synthesis. All non-hydrogen atoms were located in subsequent maps and the structures were refined as for $As(iprxa)_3$. After the introduction of anisotropic thermal parameters and a weighting scheme, $w = [\sigma^2(F) + 0.001|F_o|^2]^{-1}$, refinement was continued for both models. The non-centrosymmetric solution was discarded because of marked correlation effects which inhibited the convergence of the refinement. The centrosymmetric solution converged with R 0.042 and R_w 0.039. The analysis of variance showed no significant features and the maximum residual electron density peak in the final difference map of 1.8 $eÅ^{-3}$ was located near the bismuth atom.

Neutral atom scattering factors for C, H, O and S were those listed in SHELX-76 [8] while those for As, Sb, and Bi were those from ref. [7c] the values being corrected for anomalous dispersion [7d]. Material deposited with the Editors: Tables of aniso-

TABLE I. Summary of Crystal Data for $M(iprxa)_3$, M = As, Sb, and Bi.

Complex	$As(iprxa)_3$	$Sb(iprxa)_3$	$Bi(iprxa)_3$
Molecular formula	$C_{12}H_{21}O_3S_6As$	$C_{12}H_{21}O_3S_6Sb$	$C_{12}H_{21}O_3S_6Bi$
Formula weight	480.57	527.40	614.63
Systematic absences	$-h + k + l = 3n$	$-h + k + l = 3n$	$0kl: k + l = 2n$ $hk0: h = 2n$
Space group	$R\bar{3}$ hex. setting $(C_{3i}^2$, No. 148)	$R\bar{3}$ hex. setting $(C_{3i}^2$, No. 148)	*Pnma* $(D_{2h}^{16}$, No. 62)
a, Å	11.559(2)	11.696(2)	11.003(3)
b, Å	11.559(2)	11.696(2)	20.833(4)
c, Å	28.131(3)	28.135(2)	9.428(2)
V, Å^3	3255	3333	2161
ρ_{meas}, Mg m^{-3}	1.46	1.55	1.86
ρ_{calc}, Mg m^{-3}	1.475	1.576	1.889
Z	6	6	4
Radiation	CuKα	CuKα	MoKα
λ, Å	1.5418	1.5418	0.71069
μ, mm^{-1}	7.41	15.23	16.81
$F(000)$	1476	1584	1184
Reflections meas., N	3203	5796	6758
Unique reflections, N_0	1498	1545	2545
Criterion of obs.	$I \geqslant 3\sigma(I)$	$I \geqslant 2\sigma(I)$	$I \geqslant 2\sigma(I)$
Reflections used	936	1455	1796
No. of parameters	67	67	109
Final R	0.050	0.040	0.042
Final R_w	0.047	0.040	0.039

TABLE II. Fractional Atomic Coordinates for $M(iprxa)_3$, M = As, Sb. (Estimated standard deviations are in parentheses in this and all subsequent tables).

As(III)				Sb(III)			
Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
As	0.0	0.0	0.07286(4)	Sb	0.0	0.0	0.06636(1)
S(1)	0.1886(2)	0.0796(2)	0.1195(1)	S(1)	0.1983(1)	0.0859(1)	0.11943(4)
S(2)	0.1840(2)	−0.0950(2)	0.0410(1)	S(2)	0.1922(1)	−0.0903(1)	0.04158(5)
C(1)	0.2599(6)	0.0065(6)	0.0856(2)	C(1)	0.2680(4)	0.0115(4)	0.0864(2)
O(1)	0.3817(5)	0.0445(5)	0.1020(2)	O(1)	0.3862(3)	0.0466(4)	0.1018(1)
C(2)	0.4660(9)	−0.0045(11)	0.0799(3)	C(2)	0.4685(6)	−0.0031(8)	0.0806(3)
C(3)	0.5898(12)	0.1108(12)	0.0642(4)	C(3)	0.5913(10)	0.1103(13)	0.0646(4)
C(4)	0.4900(13)	−0.0813(12)	0.1161(5)	C(4)	0.4868(11)	−0.0820(11)	0.1170(4)

tropic thermal parameters, hydrogen atom parameters and the observed and calculated structure factors for each compound. Structure solution and refinement were performed by the SHELX-76 [8] program using the University of Melbourne's CYBER 175-760 computer system. Fractional atomic coordinates for $As(iprxa)_3$ and $Sb(iprxa)_3$ are given in Table II and those for $Bi(iprxa)_3$ in Table III, the numbering schemes used are shown in Figs. 1 and 2.

Results and Discussion

As(iprxa)$_3$ and Sb(iprxa)$_3$

Interatomic distances and angles for $As(iprxa)_3$ and $Sb(iprxa)_3$ are listed in Tables IV and V. Crystals of $As(iprxa)_3$ and $Sb(iprxa)_3$ are isomorphous and the geometrical features of their structures are very similar to the compounds, $As(exa)_3$ [1, 2] and $Sb(exa)_3$ [3, 4].

TABLE III. Fractional Atomic Coordinates for $[Bi(iprxa)_3]_n$.

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Bi	0.42068(3)	0.25	0.62080(4)	S(3)	0.3270(2)	0.3360(1)	0.4395(2)
S(1)	0.6309(3)	0.25	0.4488(3)	S(4)	0.4175(3)	0.3836(1)	0.7164(3)
S(2)	0.6846(2)	0.25	0.7570(3)	C(4)	0.3423(8)	0.3943(4)	0.5660(10)
C(1)	0.7282(10)	0.25	0.5821(10)	O(2)	0.2880(7)	0.4483(3)	0.5296(7)
O(1)	0.8467(7)	0.25	0.5662(9)	C(5)	0.2759(13)	0.5018(4)	0.6351(13)
C(2)	0.9062(10)	0.25	0.4345(13)	C(6)	0.1417(16)	0.5171(7)	0.6360(19)
C(3)	0.9821(13)	0.1900(6)	0.4203(12)	C(7)	0.3475(15)	0.5540(7)	0.5796(22)

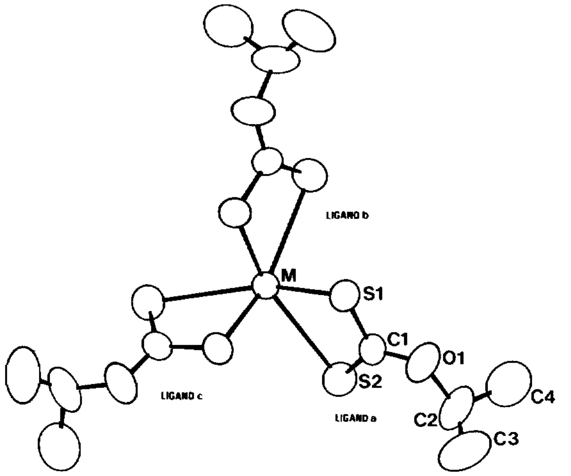

Fig. 1. The numbering scheme used for $M(iprxa)_3$ [M = As(III) and Sb(III)] where ligands b and c are related to ligand a by the symmetry operations $\bar{x}$, x − y, z and y − x, $\bar{y}$, z respectively.

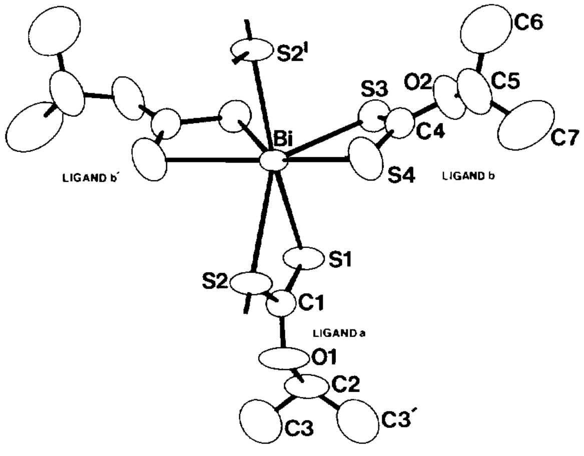

Fig. 2. The numbering scheme used for $[Bi(iprxa)_3]_n$. Ligands b and b' are related to each other across the mirror plane. $S(2)^{I}$ is related by the symmetry operation 0.5 + x, 0.5 − y, 0.5 − z.

TABLE IV. Interatomic Distances (Å) for $M(iprxa)_3$, M = As, Sb.

Atoms[a]	As(III) Distance	Sb(III) Distance
M–S(1)	2.305(2)	2.508(1)
M–S(2)	2.978(2)	3.006(1)
S(1)–C(1)	1.732(6)	1.731(5)
S(2)–C(1)	1.640(6)	1.655(5)
C(1)–O(1)	1.330(8)	1.304(5)
O(1)–C(2)	1.49(1)	1.477(7)
C(2)–C(3)	1.45(2)	1.46(1)
C(2)–C(4)	1.47(2)	1.46(1)
$M\cdots M^{I}$	4.099(2)	3.7341(4)
$S(2)\cdots S(2)^{II}$	3.659(3)	3.745(2)

[a] Superscript I refers to the symmetry operation $\bar{x}$, $\bar{y}$, $\bar{z}$ and II refers to y, y − x, $\bar{z}$.

TABLE V. Bond Angles (°) in $M(iprxa)_3$, M = As, Sb.

Atoms[a]	As(III) Angle	Sb(III) Angle
S(1)–M–S(2)	67.12(7)	64.80(3)
$S(1)–M–S(1)^{I}$	90.81(9)	88.19(4)
$S(1)–M–S(2)^{I}$	88.62(7)	87.21(3)
$S(1)–M–S(2)^{II}$	157.91(8)	152.71(4)
$S(2)–M–S(2)^{I}$	111.35(6)	114.79(3)
M–S(1)–C(1)	94.5(2)	93.0(2)
M–S(2)–C(1)	74.4(2)	78.2(2)
S(1)–C(1)–S(2)	123.7(4)	123.6(3)
S(1)–C(1)–O(1)	109.3(4)	110.8(4)
S(2)–C(1)–O(1)	126.9(5)	125.6(4)
C(1)–O(1)–C(2)	121.1(6)	122.6(4)
O(1)–C(2)–C(3)	108.1(9)	107.9(7)
O(1)–C(2)–C(4)	107.4(8)	107.2(7)
C(3)–C(2)–C(4)	111.6(9)	113.7(7)

[a] Superscript I refers to the symmetry operation $\bar{y}$, x − y, z and II refers to y − x, $\bar{x}$, z.

The only significant intermolecular contact between the enantiomorphic pairs centred about the site of symmetry $\bar{3}$ at (0, 0, 0) is that of the $S(2)\cdots S(2)^{II}$ contact of 3.659(3) Å for $As(iprxa)_3$ and 3.745(2) Å for $Sb(iprxa)_3$ [where $S(2)^{II}$ is related by the symmetry operation y, y − x, $\bar{z}$]. Similar contacts are observed in $As(mexa)_3$ (where mexa is *O*-methylxanthato) [9], $M(exa)_3$, where M = Ga(III) [10], In(III) [10], As(III) [1, 2], Sb(III) [3, 4], and M(exa)$_2$ where M = S(II) [11], and Se(II) [11]. It is interesting to note that the M$\cdots$M$^{\mathrm{I}}$ [where superscript I refers to the symmetry operation $\bar{x}$, $\bar{y}$, $\bar{z}$] separation in As(iprxa)$_3$ is 4.099(2) Å while that for Sb(iprxa)$_3$ is only 3.741(4) Å. Although the As$\cdots$As$^{\mathrm{I}}$ separation in As(iprxa)$_3$ is shorter than that observed in As(exa)$_3$ (4.4123(4) Å) [2], the distance is comparable to that observed in As(mexa)$_3$ [8] of 4.110(4) Å. In all cases, however, the As$\cdots$As$^{\mathrm{I}}$ separations are longer than twice the value of the van der Waals radius of arsenic *viz.* 3.8 Å [12]. However, the Sb$\cdots$Sb$^{\mathrm{I}}$ distance in Sb(exa)$_3$ of 3.855(1) Å [4] and that of Sb(iprxa)$_3$ are not only shorter than the corresponding distances in the analogous arsenic compounds but are also well within 4.4 Å, which is twice the value of the van der Waals radius of antimony [12]. Although the intermolecular S(2)$\cdots$S(2) contacts are of similar strength in both the arsenic and antimony xanthates mentioned above, the M$\cdots$M$^{\mathrm{I}}$ contacts are shorter in Sb(exa)$_3$ and Sb(iprxa)$_3$ in comparison with those of the corresponding arsenic(III) compounds it is suggested that there are notable but weak Sb$\cdots$Sb$^{\mathrm{I}}$ interactions in Sb(exa)$_3$ and Sb(iprxa)$_3$.

TABLE VI. Interatomic distances (Å) for [Bi(iprxa)$_3$]$_n$.

Atoms	Distance	Atoms	Distance
Bi–S(1)	2.825(3)	Bi–S(3)	2.682(2)
Bi–S(2)	3.175(2)	Bi–S(4)	2.926(2)
S(1)–C(1)	1.65(1)	S(3)–C(4)	1.711(9)
S(2)–C(1)	1.72(1)	S(4)–C(4)	1.66(1)
C(1)–O(1)	1.31(1)	C(4)–O(2)	1.32(1)
O(1)–C(2)	1.40(2)	O(2)–C(5)	1.50(2)
C(2)–C(3)	1.51(2)	C(5)–C(6)	1.51(2)
Bi–S(2)$^{\mathrm{Ia}}$	2.842(2)	C(5)–C(7)	1.44(2)

[a] S(2)$^{\mathrm{I}}$ is related by 0.5 + x, 0.5 – y, 0.5 – z.

The iprxa ligands chelate the metal centres with unequal M–S distances, see Table IV, and this asymmetry is reflected in the associated C–S distances. The asymmetric environment about the arsenic and antimony atoms is comparable to that observed in corresponding M(exa)$_3$ [1–4] compounds. Clearly, the substitution of the ethyl group in the xanthate ligand by the isopropyl group has not altered the geometry of the central atom's immediate environment. It has been noted earlier [13] that the asymmetry observed in these compounds may arise as a result of the presence of a stereochemically active lone pair of electrons which protrudes along the three fold axis, through the triangular face formed by the sulphur atoms involved in the long M–S interactions.

[Bi(iprxa)$_3$]$_n$

Relevant interatomic dimensions for [Bi(iprxa)$_3$]$_n$ are given in Tables VI and VII. The bismuth atom and one iprxa group (ligand a) are situated on a crystallographic mirror plane while the remaining iprxa ligands are on either side of this plane. The coordination sphere of the bismuth atom consists of the six sulphur atoms of the three asymmetrically chelating iprxa ligands and an additional sulphur atom from an adjacent molecule, S(2)$^{\mathrm{I}}$, related by the symmetry operation 0.5 + x, 0.5 – y, 0.5 – z. The coordination of the seven sulphur atoms results in a linear polymeric structure through –Bi–S–Bi– and Bi–S–C–S–Bi bridges, Figs. 3 and 4. The Bi–S distances associated with the iprxa ligand which lies in the mirror plane (Bi–S(1) 2.825(3) and Bi–S(2) 3.175(2) Å) are substantially longer than the corresponding

TABLE VII. Bond Angles (°) for [Bi(iprxa)$_3$]$_n$.

Atoms[a]	Angle	Atoms[a]	Angle
S(1)–Bi–S(2)	58.89(8)	S(1)–C(1)–S(2)	123.4(7)
S(1)–Bi–S(3)	87.07(7)	S(1)–C(1)–O(1)	123.9(8)
S(1)–Bi–S(4)	100.76(6)	S(2)–C(1)–O(1)	112.8(8)
S(1)–Bi–S(2)$^{\mathrm{I}}$	168.89(8)	C(1)–O(1)–C(2)	124.4(9)
S(2)–Bi–S(3)	127.53(4)	O(1)–C(2)–C(3)	109.7(7)
S(2)–Bi–S(4)	83.47(7)	C(3)–C(2)–C(3)$^{\mathrm{II}}$	112(1)
S(2)–Bi–S(2)$^{\mathrm{I}}$	132.23(8)	Bi–S(3)–C(4)	89.6(3)
S(3)–Bi–S(4)	63.66(7)	Bi–S(4)–C(4)	82.6(3)
S(3)–Bi–S(2)$^{\mathrm{I}}$	84.67(6)	S(3)–C(4)–S(4)	123.4(5)
S(3)–Bi–S(3)$^{\mathrm{II}}$	83.82(6)	S(3)–C(4)–O(2)	112.3(7)
S(3)–Bi–S(4)$^{\mathrm{II}}$	145.81(8)	S(4)–C(4)–O(2)	124.3(7)
S(4)–Bi–S(2)$^{\mathrm{I}}$	82.19(7)	C(4)–O(2)–C(5)	120.1(8)
S(4)–Bi–S(4)$^{\mathrm{II}}$	144.09(8)	O(2)–C(5)–C(6)	104(1)
Bi–S(1)–C(1)	95.4(4)	O(2)–C(5)–C(7)	106(1)
Bi–S(2)–C(1)	82.4(4)	C(6)–C(5)–C(7)	112(1)

[a] Superscript I refers to the symmetry operation 0.5 + x, 0.5 – y, 0.5 – z and II refers to x, 0.5 – y, z.

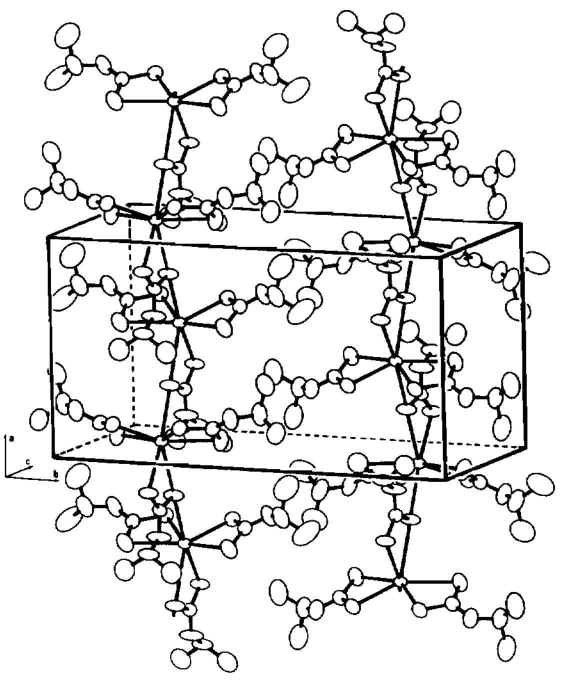

Fig. 3. Unit cell contents for $[Bi(iprxa)_3]_n$ highlighting the polymeric nature of the compound.

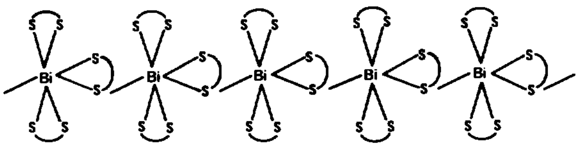

Fig. 4. A schematic representation of the $[Bi(iprxa)_3]_n$ polymer illustrating the unusual mode of coordination of the iprxa ligand bridging two Bi atoms while simultaneously chelating one of the Bi atoms.

Bi–S distances for the iprxa ligands related to each other by the mirror plane (Bi–S(3) 2.682(2) and Bi–S(4) 2.926(2) Å]. This lengthening of the Bi–S(2) bond is most likely the result of the additional bridging interaction (2.842(2) Å) of the S(2) atom with the bismuth atom from a neighbouring molecule.

The interpretation of the observed asymmetric chelation by the xanthate moieties in $As(iprxa)_3$ and $Sb(iprxa)_3$ as being due to the repulsion of the lone pair of electrons acting through an equilateral triangle of three sulphur atoms [13], is also applicable to $Bi(iprxa)_3$. In $Bi(iprxa)_3$ however, the two triangles are no longer equilateral as a result of the additional interaction by $S(2)^I$. The three sulphur atoms, S(1), S(3), and $S(3)^{II}$ (where $S(3)^{II}$ is related by the symmetry operation x, 0.5 – y, z) can be considered to form a triangular array and similarily S(2), S(4) and $S(4)^{II}$ to form a second triangle, approximately parallel (dihedral angle approximately 5°) to the first, through which it is believed that the lone pair is acting. The environment of the bismuth atom is best described as a distorted bicapped trigonal prism with $S(2)^I$ protruding through the approximate square face defined by S(3), S(4), $S(3)^{II}$ and $S(4)^{II}$.

The differences, between long and short M–S bonds (within a xanthate ligand) of approximately 0.7 Å for $As(iprxa)_3$, 0.5 Å for $Sb(iprxa)_3$, and 0.25 Å in $[Bi(iprxa)_3]_n$ for the iprxa ligands not involved in the intermolecular interactions show a definite trend, decreasing from As(III) to Bi(III), probably as a consequence of the increase in size of the central atom.

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References

1 C. Carrai and G. Gottardi, *Z. Kristallogr., 113,* 373 (1960).
2 B. F. Hoskins, P. M. Piko, E. R. T. Tiekink and G. Winter, *Inorg. Chim. Acta, 84,* L13 (1984).
3 G. Gottardi, *Z. Kristallogr., 115,* 451 (1961).
4 B. F. Hoskins, E. R. T. Tiekink and G. Winter, *Inorg. Chim. Acta, 97* (1985).
5 C. L. Raston, A. H. White and G. Winter, *Aust. J. Chem., 31,* 2207 (1978).
6 B. F. Hoskins, E. R. T. Tiekink and G. Winter, *Inorg. Chim. Acta, 81,* L33 (1984).
7 'International Tables for X-ray Crystallography', Kynoch Press, Birmingham, 1969, 1974, (a) Vol. 1; (b) Vol. 4, p. 58; (c) Vol. 4, p. 99; (d) Vol. 4, p. 149.
8 G. M. Sheldrick, 'SHELX-76', Program for Crystal Structure Determination, Cambridge, 1976.
9 T. Ito and H. Hishino, *Acta Crystallogr., Sect. C:, 39,* 448 (1983).
10 B. F. Hoskins, E. R. T. Tiekink, R. Vecchiet and G. Winter, *Inorg. Chim. Acta, 90,* 197 (1984).
11 N. J. Brondmo, S. Esperas and S. Husebye, *Acta Chem. Scand., Ser. A:, 29,* 93 (1975).
12 A. Bondi, *J. Phys. Chem., 68,* 441 (1964).
13 B. F. Hoskins and C. D. Pannan, *Aust. J. Chem., 29,* 2541 (1976).