Studies of Dioxamide and Dithio-oxamide Metal Complexes. Part 3.[1] Confirmation of *NN'*-Disubstituted Dithio-oxamides as *SS'*-Bidentate Chelating Ligands. Crystal and Molecular Structures of the Six-co-ordinate Tin(IV) Complex $SnBr_4L^1$ (L^1 = *NN'*-Di-n-butyldithio-oxamide) and the Seven-co-ordinate Bismuth(III) Complex $BiCl_3(L^2)_2$ (L^2 = *NN'*-Diethyldithio-oxamide) *

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Crystal structures of two metal complexes with *NN'*-disubstituted dithio-oxamides as bidentate chelating ligands have been determined. $SnBr_4L^1\cdot0.33C_6H_6$ (1 ; L^1 = *NN'*-di-n-butyldithio-oxamide) is monoclinic, space group $C2/c$, with a = 20.766(15), b = 21.245(15), c = 14.835(9) Å, β = 91.4(1)°, and Z = 12. $BiCl_3(L^2)_2\cdot Me_2CO$ (2; L^2 = *NN'*-diethyldithio-oxamide) is monoclinic, space group $P2_1/c$, with a = 10.568(9), b = 8.780(9), c = 30.086(15) Å, β = 101.2(1)°, and Z = 4. 1 247 [For (1)] and 2 341 [for (2)] independent reflections above background were collected and the structures refined to R 0.10 and 0.08, respectively. Complex (1) has two equivalent molecules in the asymmetric unit, one with imposed C_2 symmetry. The tin atoms are six-co-ordinate octahedral, being bonded to four bromine atoms [2.527(11)—2.625(13) Å] and to a bidentate dithio-oxamide ligand through sulphur [Sn–S 2.551(25)—2.609(25) Å]. In (2), the bismuth atom is seven-co-ordinate with a pentagonal bipyramidal geometry. Chlorine atoms occupy the axial sites [2.635(10) and 2.717(10) Å] while the equatorial girdle is occupied by two bidentate ligands [Bi–S 2.818(13)—3.042(12) Å] and another chlorine atom [2.651(12) Å]. In both structures all the ligand –NH groups are hydrogen bonded for the most part to halogen atoms but also in (2) to the acetone solvent molecule. This intermolecular hydrogen bonding is a direct cause of ring puckering in the chelates.

In Part 2 [1] various metal complexes of a series of *NN'*-disubstituted dithio-oxamides [RNHC(S)C(S)NHR, L] were reported, complete with spectroscopic characterisation.

For complexes of the type $MX_3L_{1.5}$ (where M = Group 5B element and X = halogen) structural characterisation of two such examples shows a consistent *SS'*-bidentate bridging ligand attachment to separate pseudo-octahedral M^{III} metal centres.[1,2] The structures are polymeric. This is taken to be the norm for such species.

For complexes of the type MX_4L (where M = Group 4A or 4B element and X = halogen), all the spectral indications (and chemical intuition) point to ligand binding in terms of *SS'*-bidentate chelation with a mononuclear formulation. Such chelation has been invoked previously for related metal complexes.[3–7] This prediction is now confirmed for the first time in the *X*-ray analysis of a tin(IV) bromide complex of *NN'*-di-n-butyldithio-oxamide (L^1), details of which are presented and discussed herein.

Quite by chance we find that the 1 : 2 adduct of bismuth(III) chloride with *NN'*-diethyldithio-oxamide (L^2) [1] also embodies *SS'*-bidentate chelation. An *X*-ray crystallographic investigation of this particular compound reveals, furthermore, that the bismuth atom is seven-co-ordinate with two chlorines occupying the *trans*-axial positions of an almost regular pentagonal bipyramid. The ramifications of this surprising yet not totally unexpected result are discussed against the known background of stereochemical involvement of the lone pair of electrons associated with Bi^{III}.[8–12]

Experimental

Crystals of $SnBr_4L^1\cdot0.33C_6H_6$ (1) and $BiCl_3(L^2)_2\cdot Me_2CO$ (2) were prepared as described in the previous paper [1] from solutions of nitromethane–benzene [for (1)] and acetone [for (2)].

Structure Determination.—Precession photographs established preliminary cell constants and space groups. The crystals were then transferred to a Stoe STADI-2 diffractometer equipped with a graphite monochromator. The crystals were aligned by *X*-ray counter methods and precise determinations of lattice constants were carried out from the accurate setting angles of a number of axial reflections. Data were taken *via* ω scans of width (1.5 + 0.5 sinμ/tanθ). The scan speed was 0.033° s^{-1} and the background was measured at the ends of the ω scan for 20 s. Measurement of standard reflections showed no deterioration. Details of cell constants, data collection, and refinement details are given in Table 1. Absorption corrections for both (1) and (2) were carried out using SHELX 76.[13]

The positions of the heavy atoms in (1) were determined by direct methods; those in (2) from the Patterson function. Fourier methods were used to locate all the remaining atoms. Both molecules in structure (1) showed considerable signs of disorder in the butyl ligands. After many unsuccessful attempts at refinement of disordered models, we refined an ordered model but with C–N, C–C bond lengths, and C ··· N, C ··· C distances (between atoms bonded to the same atom) constrained to be equivalent. These atoms were given isotropic thermal parameters which were refined independently. The Sn, Br, and S atoms were refined anisotropically. The only hydrogen atoms included in the refinement were those bonded to the nitrogen atoms.

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* *Supplementary data available* (No. SUP 23946, 26 pp.): thermal parameters, H-atom co-ordinates, remaining dimensions, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Crystal data and refinement details

Compound	(1)	(2)
Formula	$SnBr_4L^1 \cdot 0.33C_6H_6$ $C_{12}H_{22}Br_4N_2S_2Sn$	$BiCl_3(L^2)_2 \cdot Me_2CO$ $C_{15}H_{30}BiCl_3N_4OS_4$
M	696.4	725.8
Crystal class	Monoclinic	Monoclinic
Space group	*C*2/*c*	*P*2$_1$/*c*
Absences	$hkl; h + k = 2n + 1$ $h0l; l = 2n + 1$ $0k0; k = 2n + 1$	$h0l; l = 2n + 1$ $0k0; k = 2n + 1$
a/Å	20.766(15)	10.568(9)
b/Å	21.245(15)	8.780(9)
c/Å	14.835(9)	30.086(15)
β/°	91.4(1)	101.2(1)
U/Å^3	6 542.9	2 737.9
F(000)	3 792	1 416
Z	12	4
D_m/g cm^{-3}	2.09	1.76
D_c/g cm^{-3}	2.12	1.76
μ/cm^{-1}	91.1	67.2
λ/Å	0.7107	0.7107
Crystal size/mm	0.5 × 0.65 × 0.5	0.6 × 0.6 × 0.5
Rotation axis	*a*	(110)
$2\theta_{max.}$/°	40	50
No. of data measured	3 210	8 687 (2 quadrants)
No. of data used in refinement	1 247	2 341
Criterion for data inclusion	$I > 2\sigma(I)$	$I > 3\sigma(I)$
R	0.10	0.08

Table 2. Atomic co-ordinates (× 10^4 for Sn, Br, S; × 10^3 for N, C) for $SnBr_4L^1 \cdot 0.33C_6H_6$ (1) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Sn(1A)	4 468(3)	3 024(3)	3 546(4)
Br(1A)	4 079(5)	2 641(5)	5 051(6)
Br(2A)	3 402(5)	2 727(5)	2 747(7)
Br(3A)	5 576(6)	3 310(6)	4 332(7)
Br(4A)	4 119(6)	4 172(5)	3 559(7)
S(1A)	4 854(14)	1 899(12)	3 238(16)
S(8A)	4 972(14)	3 249(11)	2 031(15)
Sn(1B)	−2 500	3 946(4)	7 500
Br(1B)	−1 704(6)	3 977(5)	8 885(7)
Br(2B)	−1 747(5)	3 198(5)	6 700(7)
S(1B)	−3 092(12)	4 879(11)	8 290(16)
C(2A)	510(4)	195(3)	228(5)
N(3A)	521(3)	144(3)	171(4)
C(4A)	494(5)	84(3)	196(6)
C(5A)	446(8)	67(7)	116(10)
C(6A)	389(10)	18(8)	145(11)
C(7A)	419(8)	−25(6)	225(9)
C(9A)	534(3)	256(3)	189(4)
N(10A)	588(3)	248(3)	136(4)
C(11A)	618(4)	305(4)	102(5)
C(12A)	687(4)	305(4)	140(7)
C(13A)	737(4)	352(5)	102(8)
C(14A)	730(7)	422(5)	127(9)
C(1B)	−271(3)	547(3)	800(4)
N(3B)	−270(4)	607(3)	841(4)
C(4B)	−299(3)	612(3)	927(5)
C(5B)	−239(4)	623(5)	994(5)
C(6B)	−258(5)	633(6)	1 094(5)
C(7B)	−319(4)	597(4)	1 122(5)
C(41)	−595(6)	529(5)	570(8)
C(42)	6(9)	434(7)	490(11)
C(43)	−41(5)	454(5)	572(7)

The positions of all the C and N atoms in the tin complex were constrained in the refinement (see text).

Table 3. Atomic co-ordinates (× 10^4) for $BiCl_3(L^2)_2 \cdot Me_2CO$ (2) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Bi	10(1)	1 894(2)	3 726(0)
Cl(1)	−1 291(12)	2 056(18)	4 388(4)
Cl(2)	1 387(11)	1 673(17)	3 054(3)
Cl(3)	—1 620(13)	−214(15)	3 327(4)
S(4)	2 323(12)	2 722(14)	4 458(4)
S(5)	1 124(13)	−838(16)	4 109(4)
S(6)	−2 050(11)	3 465(13)	3 114(4)
S(7)	561(10)	5 221(12)	3 786(3)
C(41)	2 031(34)	1 239(46)	4 779(12)
N(42)	1 718(33)	1 363(41)	5 178(10)
C(43)	1 490(61)	2 772(59)	5 362(18)
C(44)	2 573(55)	3 293(72)	5 747(20)
C(51)	2 097(35)	−339(50)	4 618(12)
N(52)	2 885(38)	−1 223(46)	4 833(12)
C(53)	3 014(55)	−2 901(65)	4 727(15)
C(54)	4 187(98)	−3 279(116)	4 650(52)
C(61)	−1 615(33)	5 191(46)	3 096(10)
N(62)	−2 352(31)	6 327(40)	2 977(10)
C(63)	−3 720(41)	6 168(62)	2 811(21)
C(64)	−4 306(44)	7 542(65)	2 539(21)
C(71)	−224(37)	5 636(50)	3 255(11)
N(72)	262(30)	6 422(43)	2 966(12)
C(73)	1 640(54)	7 046(69)	3 057(16)
C(74)	2 468(60)	5 861(63)	2 960(18)
O(1)	5 446(31)	305(46)	4 349(11)
C(81)	5 079(50)	922(103)	3 966(19)
C(82)	5 192(77)	2 576(83)	3 867(23)
C(83)	4 662(74)	−130(99)	3 611(26)

In (2) all atoms except hydrogen were included with anisotropic thermal parameters. Hydrogen atoms were placed in trigonal or tetrahedral positions at 0.95 Å from the C or N atom to which they were bonded. Their thermal parameters were refined, although those of atoms bonded to the same atom were constrained to be the same. Scattering factors and dispersion corrections were taken from ref. 14. Both (1) and (2) were refined by full-matrix least squares. In the final cycles of refinement no shift was greater than 0.1σ. Calculations were carried out using SHELX 76 [13] at the University of Manchester Computer Centre. The final *R* values for (1) and (2) were 0.10 and 0.08 respectively. Atomic parameters are given in Tables 2 and 3, bond lengths and angles in Table 4.

Discussion

The structures of $SnBr_4L^1$ (1) and $BiCl_3(L^2)_2$ (2) are shown in Figures 1 and 2 respectively, together with the atomic numbering scheme. Both structures contain discrete monomers together with solvent [benzene in (1), acetone in (2)].

Structure of (1).—There are two independent molecules of (1) in the structure; molecule A in a general position and molecule B in a special position with the metal atom sitting on a two-fold axis which passes through the metal atom itself and the midpoint of the chelate C–C bond.

In both molecules, the tin environment is octahedral and the Sn–Br bond lengths *trans* to sulphur are shorter [A, 2.527(11) and 2.545(12); B, 2.544(11) Å] than those *trans* to bromine [A, 2.565(12) and 2.625(13); B, 2.605(11) Å]. The Sn–S bond lengths are equivalent within experimental error [2.565(28), 2.551(25), and 2.609(25) Å].

The bite of the bidentate dithio-oxamide ligand is sufficiently large not to distort the octahedron by much, the S–Sn–S

Table 4. Bond lengths (Å) and angles (°)

(*a*) For (1)

Sn(1A)–Br(1A)	2.527(11)
Sn(1A)–Br(2A)	2.565(12)
Sn(1A)–Br(3A)	2.625(13)
Sn(1A)–Br(4A)	2.545(12)
Sn(1A)–S(1A)	2.565(28)
Sn(1A)–S(8A)	2.551(25)
Sn(1B)–Br(1B)	2.605(11)
Sn(1B)–Br(2B)	2.544(11)
Sn(1B)–S(1B)	2.609(25)
Br(1A)–Sn(1A)–Br(2A)	92.2(4)
Br(1A)–Sn(1A)–Br(3A)	88.7(3)
Br(2A)–Sn(1A)–Br(3A)	178.5(4)
Br(1A)–Sn(1A)–Br(4A)	101.8(4)
Br(2A)–Sn(1A)–Br(4A)	89.8(4)
Br(3A)–Sn(1A)–Br(4A)	91.3(4)
Br(1A)–Sn(1A)–S(1A)	88.0(5)
Br(2A)–Sn(1A)–S(1A)	87.6(7)
Br(3A)–Sn(1A)–S(1A)	91.2(7)
Br(4A)–Sn(1A)–S(1A)	170.0(6)
Br(1A)–Sn(1A)–S(8A)	171.1(6)
Br(2A)–Sn(1A)–S(8A)	90.5(7)
Br(3A)–Sn(1A)–S(8A)	88.4(7)
Br(4A)–Sn(1A)–S(8A)	86.7(6)
S(1A)–Sn(1A)–S(8A)	83.6(7)
Br(1B)–Sn(1B)–Br(2B)	89.9(3)
Br(1B)–Sn(1B)–S(1B)	85.6(6)
Br(2B)–Sn(1B)–S(1B)	168.9(6)
Br(1B)–Sn(1B)–Br(2B *)	91.9(3)
Br(2B)–Sn(1B)–Br(2B *)	102.7(5)
Br(1B)–Sn(1B)–Br(1B *)	177.1(6)
Br(1B *)–Sn(1B)–S(1B)	92.2(6)
Br(2B *)–Sn(1B)–S(1B)	87.6(5)
S(1B)–Sn(1B)–S(1B *)	82.5(7)

* Refers to the symmetry element $-0.5 - x, y, 1.5 - z$.

(*b*) For (2)

Bi–Cl(1)	2.635(10)
Bi–Cl(2)	2.717(10)
Bi–Cl(3)	2.651(12)
Bi–S(4)	3.042(12)
Bi–S(5)	2.818(13)
Bi–S(6)	2.910(12)
Bi–S(7)	2.977(10)
Cl(1)–Bi–Cl(2)	178.6(4)
Cl(1)–Bi–Cl(3)	89.5(4)
Cl(2)–Bi–Cl(3)	90.5(4)
Cl(1)–Bi–S(4)	84.5(3)
Cl(2)–Bi–S(4)	94.8(3)
Cl(3)–Bi–S(4)	148.7(3)
Cl(1)–Bi–S(5)	88.5(4)
Cl(2)–Bi–S(5)	90.1(3)
Cl(3)–Bi–S(5)	76.9(4)
S(4)–Bi–S(5)	72.2(3)
Cl(1)–Bi–S(6)	90.9(3)
Cl(2)–Bi–S(6)	90.4(3)
Cl(3)–Bi–S(6)	72.8(3)
S(4)–Bi–S(6)	137.8(3)
S(5)–Bi–S(6)	149.8(3)
Cl(1)–Bi–S(7)	91.5(4)
Cl(2)–Bi–S(7)	89.3(3)
Cl(3)–Bi–S(7)	144.5(3)
S(4)–Bi–S(7)	66.5(3)
S(5)–Bi–S(7)	138.5(3)
S(6)–Bi–S(7)	71.7(3)

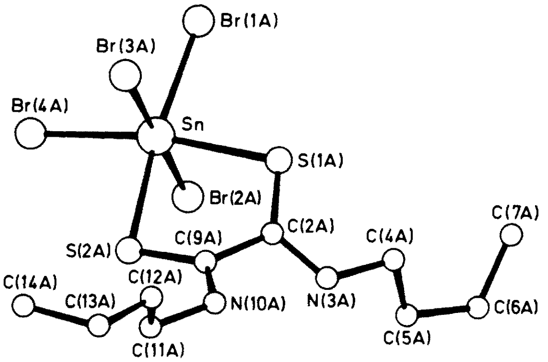

Figure 1. The molecular structure of $SnBr_4L^1$ (1)

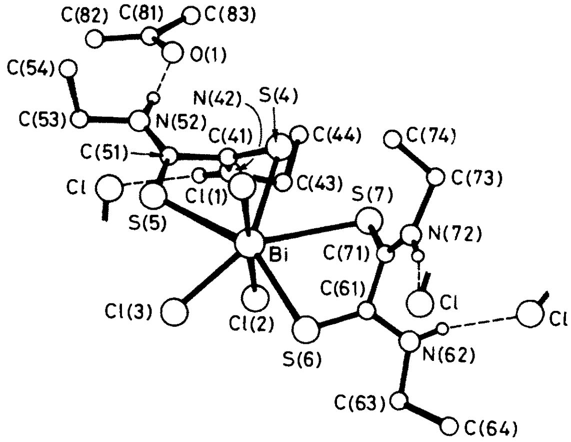

Figure 2. The molecular structure of $BiCl_3(L^2)_2$ (2). Hydrogen bonds between the –NH groups and the acetone solvent and three chlorine atoms from other molecules are shown as dashed lines

angles varying from 82.5(7) to 83.6(7)°. The angle Br(1A)–Sn–Br(4A) (*i.e.* the angle subtended by the bromines *trans* to sulphur) is 101.8(4)° in A and the equivalent angle [Br(2B)–Sn–Br(2B)*] in B is 102.7(5)°. This angle is clearly extended to compensate for the chelate angle.

The ligands are puckered in that the two S–C–C–S torsion angles are −44.3 and −40.7°. This is somewhat surprising as the two carbon atoms maintain their sp^2 character, the three angles subtended at the carbon adding up to *ca.* 360°. This ring puckering contrasts with the planar conformation observed in the complexes $MX_3L_{1.5}$, where the ligand forms a weak *S*-bonded link between metal atoms.[1,2] It is possible that the puckering increases the distance between the two hydrogen atoms on the nitrogen and thus permits the formation of intermolecular hydrogen bonds. If there was no puckering it would be impossible to form such bonds because of steric hindrance. All the N–H bonds are involved in hydrogen bonding to Br atoms, *viz.* Br(3A) ··· N(3A) ($x, \frac{1}{2} - y, \frac{1}{2} + z$) 3.66, Br(2A) ··· N(3B) ($1 - x, 1 - y, -z$) 3.40, and Br(1B) ··· N(10A) ($\frac{1}{2} - x, \frac{1}{2} - y, -z$) 3.56 Å. Using the calculated hydrogen positions, we calculate the Br ··· H–N angles to be 155, 165, and 156° respectively.

The structure of (1) can be compared with that of the 1 : 2 adduct $SnCl_4L_2$ (L = 1,3-diethylthiourea) where the monodentate ligands are *cis* octahedral and where the ligands are bonded to the metal through sulphur rather than through nitrogen.[15]

Apart from the distances mentioned above, there are no close contacts less than the sum of van der Waals radii involving the benzene ring and/or the tin complex.

Structure of (2).—The structure of (2) contains discrete molecules of $BiCl_3(L^2)_2$. The bismuth atoms are seven-co-ordinate, being bonded to three chlorine atoms and two bidentate dithio-oxamide ligands. The metal environment is almost ideal pentagonal bipyramidal with two chlorines in axial positions and with one chlorine and the two bidentate dithio-oxamides in the equatorial plane. The metal atom and the five donor atoms in the equatorial plane are closely planar [deviations: Bi −0.04, Cl(3) 0.04, S(4) 0.12, S(5) −0.08, S(6) 0.05, S(7) −0.10 Å]. The largest deviations, those of S(4) and S(7), are concomitant with the smallest equatorial angle, S(7)–Bi–S(4) 66.5(3)°, and are clearly necessary in order to increase the S(4) ··· S(7) non-bonded contact to a reasonable value. The Bi–S bonds for these atoms are longer [Bi–S(4) 3.042(12), Bi–S(7) 2.977(10) Å] than those for the sulphurs *cis* to Cl(3) [*viz.*, Bi–S(5) 2.818(13), Bi–S(6) 2.910(12) Å]. The Bi–S–C angles also fall into two groups, with Bi–S(4)–C(41), Bi–S(7)–C(71) considerably smaller at 91.1(12), 95.8(15)° than Bi–S(5)–C(51), Bi–S(6)–C(61), at 106.1(14), 106.8(12)°. These variations are all caused by steric strain in the pentagonal girdle.

The pentagonal bipyramidal geometry fits in well with predictions for seven-co-ordinate molecules [16] of type MA_3B_2 (A = monodentate, B = bidentate). This geometry is favoured for ligands with relatively large bites [defined as Y ··· Y/M–Y (Y = donor atom)] of *ca.* 1.15. This allows S–Bi–S angles of *ca.* 72° as required for the pentagonal bipyramid.

There is no vacancy in the bismuth(III) co-ordination sphere for a stereochemically active lone pair of electrons. It has been suggested [11] that this lone pair is active when the molecule contains 'hard' donor atoms and/or small bite bidentate ligands such as dithiocarbamates. Thus Bi^{III}–dithiophosphate systems [8,9] feature a stereochemically active lone pair, where the small bite bidentate ligands leave space in the co-ordination sphere. The resulting compounds are pseudo-seven-co-ordinate MB_3E (B = bidentate ligand, E = lone pair). On the other hand in μ_4-chloro-{tris[trichloro(thiosemicarbazide)-bismuth(III)]}[tris(thiosemicarbazide)bismuth(III)] hexachlorobismuthate(III) chloride [10] the ligands form five-membered rings with Bi^{III}; the metal atoms are both six- and seven-co-ordinate with no evidence for lone-pair spatial activity. The present structure therefore would not be considered likely to have an active lone pair on two grounds: the large bidentate bite and also the 'soft' nature of the donor sulphur atoms.

All four N–H groups are involved in hydrogen bonds: N(42) ··· Cl(1) $(-x, -y, 1 - z)$ 3.34, N(52) ··· O(1) $(1 - x, -y, 1 - z)$ 2.85, N(62) ··· Cl(3) $(x, 1 + y, z)$ 3.26, and N(72) ··· Cl(2) $(-x, \frac{1}{2} + y, \frac{1}{2} - z)$ 3.23 Å. The angles at hydrogen are 168, 171, 152, and 169°, respectively.

As discussed earlier with reference to the structure (1), the formation of intramolecular hydrogen bonding is probably a cause of ring puckering. In the bismuth structure the S–C–C–S torsion angles are −57.2 and −56.7°. The bonding around the carbon atoms retains its planar character. It may well be that the formation of hydrogen bonds also affects the Bi–Cl distances; for example, of the two axial chlorine atoms, that involved in the shorter contact to nitrogen forms the longer bond to the metal [Bi–Cl(2) 2.717(10) *vs.* Bi–Cl(1) 2.635(10) Å].

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