

Review of crystallographic and molecular structures of complexes formed between N,N'-dialkyloxamides, N,N'-dialkyldithio-oxamides, N,N'-dialkylmalonamides, N,N'-dialkyldithiomalonmides, N,N'-dialkylsuccinamides, and toluene, 3,4-dithiol with Group VB and Group IV metal halides*

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Our interest in the synthesis of possible chemotherapeutic agents against schistosomiasis led us to investigate compounds formed between antimony (III) chloride and thiourea as well as the title compounds [1,2]. The crystal structures of the metal halides with the ligands N,N'-dialkyloxamides, N,N'-dialkyldithio-oxamides, N,N'-dialkyldithiomalonamides, N,N'-dialkylsuccinamides and toluene-3,4-dithiol were determined [3–9].

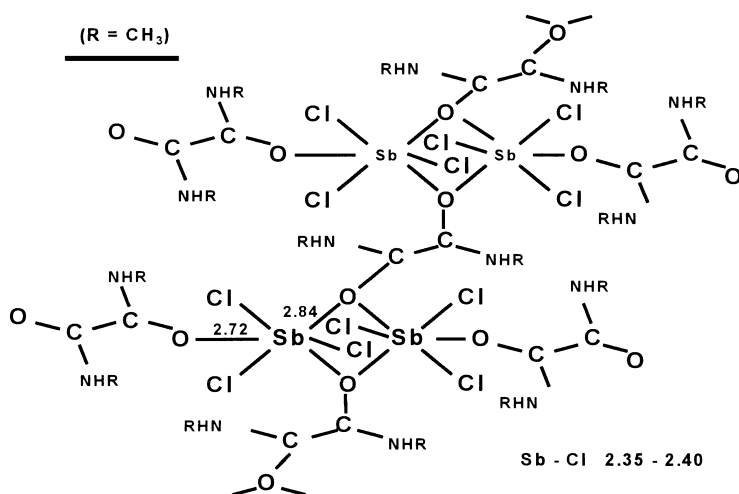


Fig. 1 Crystal and molecular structure of N,N'-dimethyloxamide and SbCl₃ L.

The crystal and molecular structure of N,N'-dimethyloxamide antimony (III) chloride shows the O,O' ligand bridging the metals in a *trans* position as well as in a centrosymmetric Sb(μ-O)₂Sb mode resulting in a polymeric molecular structure. There are strong SbCl bonds and the SbCl₃ remains as a unit. The transbridging Sb-O bond lengths are shorter than the double bridging oxygen-antimony bond lengths. The symmetry around Sb(III) atom is octahedral with no evidence for stereochemically active lone pair distortion (Fig. 1).

The N,N'-dialkyldithio-oxamides, [where the alkyls are methyl, ethyl and isopropyl], form 1:1.5 complexes with SbCl₃ where the crystal and molecular structure of the complex exhibits each antimony

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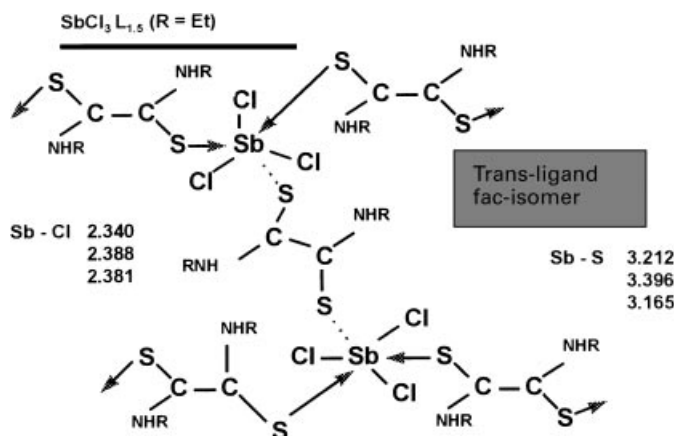


Fig. 2 Crystal and molecular structure of N,N' -Di-isopropylthio-oxamide and $\text{SbCl}_3(\text{L}^3) 1.5$.

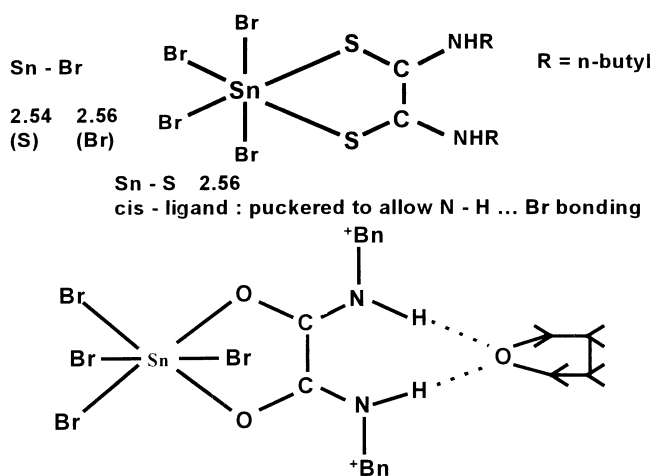


Fig. 3 The molecular structure of $\text{BiCl}_3(\text{L}^2)_2(2)$.

octahedrally bonded to the ligand in a *trans*-bridging position. The lone pair is not stereochemically active, however, there are two types of Sb-S bonds with the axial bond length being longer than the equatorial. The SbCl_3 remains as a unit (Fig. 2).

On the other hand the dioxamides and dithio-oxamides act as O,O' and S,S' -bidentate chelates when reacted to SnBr_4 and BiCl_3 . The $\text{Sn}(\text{IV})$ complex exhibits an octahedral symmetry as the compound crystallizes with one mole of solvent molecule attached through hydrogen bonding (Fig. 3). The $\text{Bi}(\text{III})$ complex is however, seven coordinate with a molecular structure having one role of solvent coordinated through hydrogen bonding. The differences between the bonding modes of the ligands with $\text{Sb}(\text{III})$, $\text{Sn}(\text{IV})$ and $\text{Bi}(\text{III})$ are attributable to the differences in ionic radius size, the stability of the chelate ring structure and preference of hard-hard, soft-soft Lewis acid, Lewis bases. There is no evidence of the role of the metal lone pair influencing the stereochemistry of the chelates (Fig. 4).

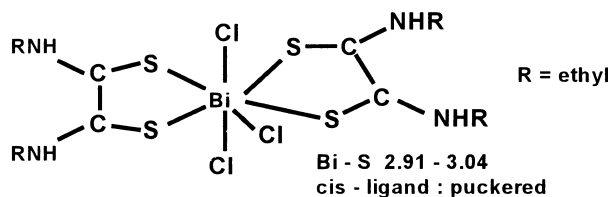


Fig. 4 The molecular structure of $\text{SnBr}_4\text{L}^1(1)$.

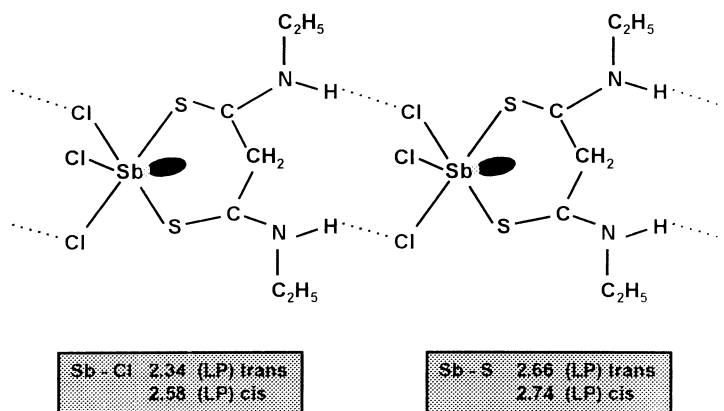


Fig. 5 The molecular structure of N,N-dialkyldithiomalonamide with Antimony (III).

On increasing the size of the chelate ring, from five to six as with dithiomalonamide ligands Sb(III) forms a six coordinate complex with the lone pair occupying the axial position. The geometry is a slightly distorted octahedron to allow room for the lone pair as explained by VSEPR (valence shell electron pair repulsion) theory (Fig. 5).

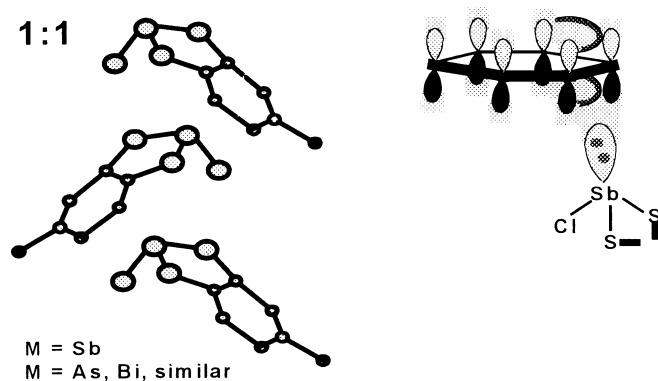


Fig. 6 The packing of the SbCl(tdt) molecules along the b axis.

Toluene-3,4-dithiol (H_2tdt) reacts with Group VB metal halides to form $[MCl(tdt)]$ $M = As, Sb$ and $Bi(m)$, $M[(Htdt)(tdt)]$, $M = Sb$; $[NEt_3H] Bi(tdt)_2$; and $[(Y)Sb(tdt)_3]$ ($Y = Net_4$ or PPh_4). The crystal structure of $[AsCl(tdt)]$ has As bonded to two sulfur atoms and one chlorine atom in a tetrahedral symmetry with the lone pair occupying the fourth position (Fig. 6).

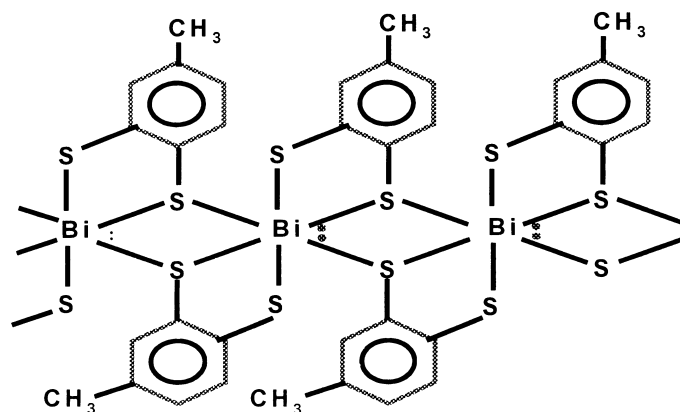


Fig. 7 The molecular structure of $Bi(tdt)_2$ complex.

The crystal structures of $M[(\text{Htdt})(\text{tdt})]$ shows the central Sb(III) as a trigonal bipyramidal with lone pair occupying the axial position (Fig. 8) while the Bi(III) complex $[\text{NEt}_3\text{H}]\text{Bi}(\text{tdt})_2$ is polymeric with each metal in an octahedral geometry with double bridging $\text{Bi}(\mu\text{-S})_2\text{Bi}$ bond and single Bi-S bond. The Bi(III) lone pair of electrons is stereochemically active (Fig. 8).

1:2 $M = \text{As}$ \times

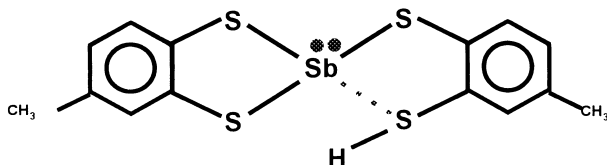
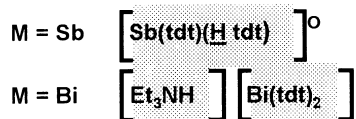


Fig. 8 The structure of $\text{Sb}(\text{tdt})(\text{Htdt})$.

The Sb(III) 1:2 addition complexes retain the thiol S-H bond which is only removed by addition of base (Fig. 8). The addition of base results in the formation of $[\text{Sb}^{\text{V}}(\text{tdt})_3]^-$ complex rather than the $[\text{Sb}^{\text{III}}(\text{tdt})_2]$ compound.

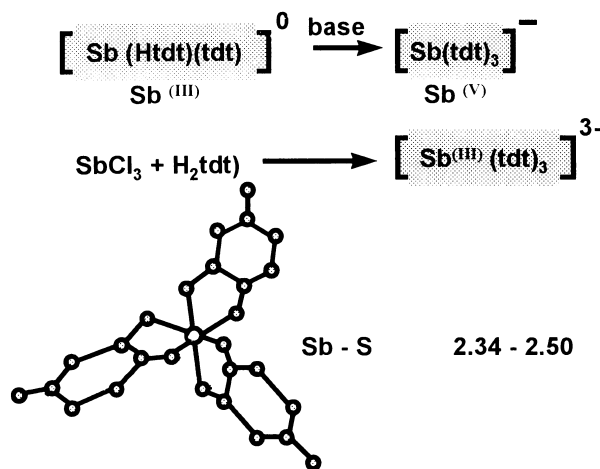


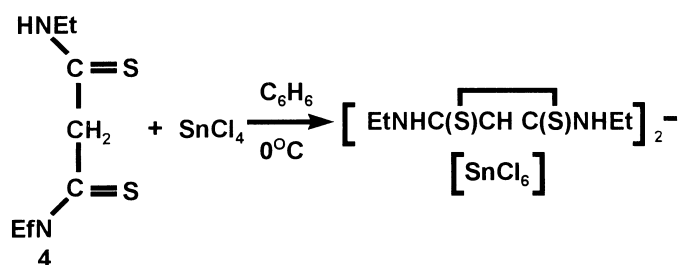
Fig. 9 The molecular structure of $[\text{Sb}(\text{tdt})_3]^{3-}$.

The structure of $[\text{Sb}^{\text{V}}(\text{tdt})_3]^-$, is octahedral with Sb-S mean bond distance of 2.44 \AA , varying only by 0.10 \AA . The five-membered ring ligand confers an octahedral geometry around Sb(V) and not Sb(III) (Fig. 9).

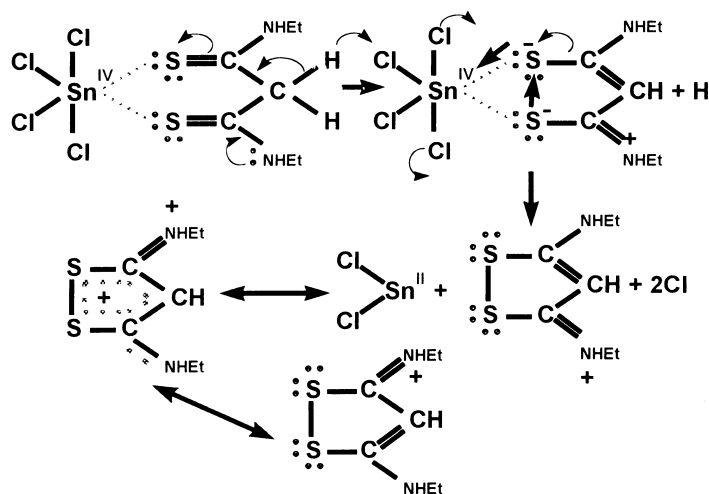
Reaction of N,N' -diethyldithiomalonamide with SnCl_4 gave unexpected cyclisation to yield a dithiolyllium ion salt $[\text{EtNHC}(\text{S})\text{CHC}(\text{S})\text{NHET}]_2\text{SnCl}_6$. The crystal structure shows the octahedral structure of SnCl_6^- with chlorine hydrogen bonding attached to each N-H proton. The cyclisation mechanism is as shown in Schemes 1, 2 and 3.

Finally, N,N' -dimethylsuccinamide reacts with SnBr_4 to form a six coordinate complex with a seven membered ring. The compound crystallizes with one mole of tetrahydrofuran. The five and six membered ring ligands exhibited puckered structures with extensive hydrogen bonding. Extension of the ligand ring size allows formation of O,O' chelation with less puckering as confirmed in the succinamide complex (Fig. 10).

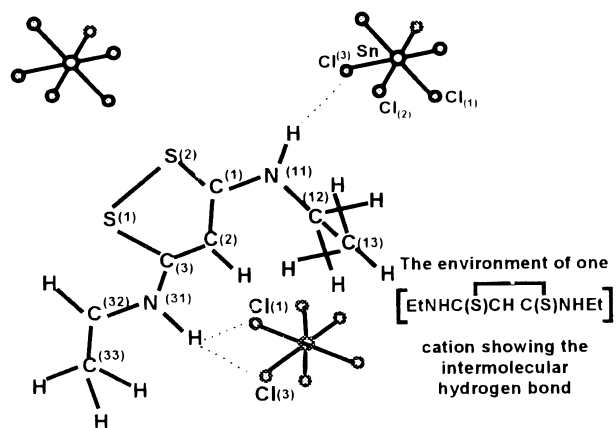
Reaction



Scheme 1 Cyclisation of N,N'-diethylidithiomalonamide.



Scheme 2



Scheme 3

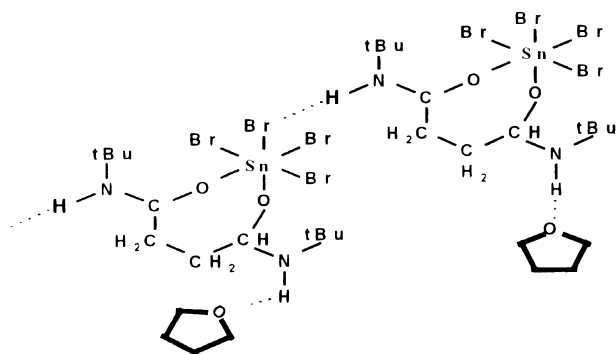


Fig. 10 The structure of $\text{SnBr}_4\text{L}(1)$. Thf with hydrogen bonds shown as dotted lines.

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