# 1,2-Dithiolate Complexes of Antimony and Bismuth

By **G. Hunter**, Department of Chemistry, The University, Dundee DD1 4HN

The syntheses of dicyanoethylene-1,2-dithiolate (' maleonitriledithiolate ' mnt) and toluene-3,4-dithiolate (tdt) complexes of antimony(III) and bismuth(III) are described. Isolated were the series of complexes, $[Sb(mnt)_2]^-$, $[Sb_2(tdt)_3]^\circ$, $[Bi_2(mnt)_2X_4]^{2-}$, $[Bi_2(mnt)_3X_2]^{2-}$, $[Bi_2(mnt)_5]^{4-}$ and $[Bi_2(tdt)_3]^\circ$ (X = Cl, Br, I). The bismuth–mnt complexes are considered to be dinuclear with respect to the metal and proposed for them are structures which have the two bismuth atoms bridged by two dithiolate ligands.

ALTHOUGH dithiolate † complexes of transition metals have been extensively studied in recent years,[1-3] post-transition-metal dithiolate complexes are only now receiving detailed attention. Recently reported have been complexes of Group IIB,[4] IIIB,[5-8] and IVB [9] metals and, as part of a general investigation of the chemistry of post-transition metal dithiolate complexes, this paper describes the reactions of the anionic ligands toluene-3,4-dithiolate (tdt) and dicyanoethylene-1,2-dithiolate (mnt) with antimony(III) and bismuth(III) halides.

Powell [10] has already reported a purple, highly polymeric complex of stoicheiometry $[Bi(tdt)Cl]_n^\circ$ formed from bismuth trichloride and tdt. The present author found that with an excess of tdt, bismuth trihalides formed only the orange, neutral complex $[Bi_2(tdt)_3]^\circ$ and antimony trihalides only the yellow complex $[Sb_2(tdt)_3]^\circ$. Both these complexes were soluble in chloroform but only the antimony complex was sufficiently so for a molecular-weight determination. In this solvent, although the experimental molecular weight of 840 was appreciably higher than the expected value of 705·5, it showed that the complex was not highly polymeric.

With $Na_2$mnt, $SbX_3$ ‡ gave only the bis-complex $[Sb(mnt)_2]^-$, obtained as the yellow, crystalline tetraethylammonium salt which slowly decomposed on exposure to air. However, the reactions of bismuth trihalides with $Na_2$mnt were more complicated. In addition to various, unidentified mixed halogeno-complexes, from the reaction mixtures were isolated three series of formally $Bi^{III}$ complexes of stoicheiometries, $[Bi(mnt)X_2]^-$, $[Bi_2(mnt)_3X_2]^{2-}$ and $[Bi_2(mnt)_5]^{4-}$, all being obtained as their tetraethylammonium salts. Whatever the mole ratios of bismuth halide to $Na_2$mnt used, mixtures of the three series of dithiolate complexes were always obtained and separation by repeated fractional crystallisation from ethanol was necessary. All the complexes of the $Et_4N[Bi(mnt)X_2]$ series were obtained as well formed crystals, as was $(Et_4N)_4[Bi_2(mnt)_5]$. However, complexes of composition $(Et_4N)_2[Bi_2(mnt)_3X_2]$ could only be isolated as dark-red, microcrystalline powders.

As the $[Bi_2(tdt)_3]^\circ$, $[Bi_2(mnt)_3X_2]^{2-}$, and $[Bi_2(mnt)_5]^{4-}$ series of complexes were all at least dinuclear with respect to the metal atom, logic suggests that the $[Bi(mnt)X_2]^-$ series also existed in a dimeric form. However, owing to the numerous ions present in solution, molecular-weight determinations in ethanol did not unambiguously indicate the state of aggregation in this last series of complexes. No more indicative were the molar conductivities measured in acetonitrile since the values determined using a monomeric formulation fall within the range expected for 1 : 1 electrolytes, whilst those based on a dimeric formulation fall within the range expected for 1 : 2 electrolytes.

Even in the absence of conclusive structural data, reasonable speculation is still possible on the structures of the dinuclear bismuth complexes. $[Bi_2(mnt)_5]^{4-}$ may well have a similar structure to $[Mo_2(tdt)_5]^\circ$, reported by Butcher and Mitchell,[11] on n.m.r. evidence, as having the molybdenum atoms bridged by two dithiolate ligands. Dimeric bis-dithiolate complexes are well known [12,13] with structures usually based on two tetragonal pyramids sharing a common edge. Additionally, Corbett [14] has shown that the $Bi_2Cl_8^{2-}$ ion has a structure based in two distorted tetragonal, pyramids or two octahedra, each with an atom removed and the vacant position occupied by a non-bonding pair of electrons. The structures of $[Bi_2(mnt)_2X_4]^{2-}$ and $[Bi_2(mnt)_3X_2]^{2-}$ are likely to be based on such units and not unreasonable structural predictions for the three series of bismuth–mnt complexes are shown in the Figure. Single crystal *X*-ray studies have begun in an attempt to obtain more definite structural information.

It has already been noted [5] that stereochemistry does not appear to be a critical test of the involvement or otherwise of metal π-orbitals and ligand π-orbitals. In the i.r. spectra of the antimony and bismuth com-

---

† In the present paper, both free ligands and the complexes are referred to as dithiolates without regard to their detailed electronic structures.

‡ Throughout this paper X, refers to Cl, Br, and I.

[1] H. B. Gray, *Transition Metal Chem.*, 1965, **1**, 239.

[2] G. N. Schrauzer, *Transition Metal Chem.*, 1968, **4**, 299.

[3] J. A. McCleverty, *Progr. Inorg. Chem.*, 1968, **10**, 49.

[4] H. B. Gray, R. Williams, I. Bernal, and E. Billig, *J. Amer. Chem. Soc.*, 1962, **84**, 3596.

[5] D. G. Tuck and M. K. Yang, *J. Chem. Soc.* (*A*), 1971, 214.

[6] A. Berniaz, G. Hunter, and D. G. Tuck, *J. Chem. Soc.* (*A*), 1971, 3254.

[7] G. Hunter and B. C. Williams, *J. Chem. Soc.* (*A*), 1971, 2254.

[8] R. O. Fields, T. J. Bergendahl, and J. H. Waters, *Inorg. Chem.*, 1971, 2805.

[9] E. S. Bretschneider, C. W. Allen, and J. H. Waters, *J. Chem. Soc.* (*A*), 1971, 500.

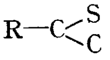
[10] P. Powell, *J. Chem. Soc.* (*A*), 1968, 2587.

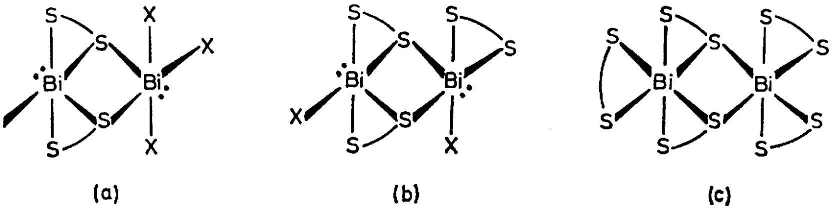
[11] A. Butcher and P. C. H. Mitchell, *Chem. Comm.*, 1967, 176.

[12] J. H. Enermark and W. N. Lipscomp, *Inorg. Chem.*, 1967, **6**, 458.

[13] W. C. Hamilton and I. Bernal, *Inorg. Chem.*, 1967, **6**, 2003.

[14] J. D. Corbett and A. Hershaft, *Inorg. Chem.*, 1963, **2**, 979.

plexes, the perturbed 'C=C' stretching mode ($\nu_1$), which in all the mnt complexes appears as a doublet is close to that observed in the free ligand,[15] at a frequency which implies some delocalisation of the $\pi$ electrons out of the C=C bond. In agreement with this, the 'C–S' and  $R{-}C\langle^{S}_{C}$ stretching modes ($\nu_2$ and $\nu_3$) are at similar frequencies to those reported for transition metal complexes, where there is other evidence of electron delocalisation in the $MS_2C_2$ ring.[2,3]



Proposed structures: (a) $[Bi_2(mnt)_2X_4]^{2-}$, (b) $[Bi_2(mnt)_3X_2]^{2-}$, (c) $[Bi_2(mnt)_5]^{4-}$

TABLE 1

Molar conductivities and half-wave potentials[a] of antimony(III) and bismuth(III) dithiolate complexes

| Compound | $\Lambda/\Omega^{-1}$ cm$^2$ (for mM soln.) | Half-wave potentials/v $E_{\frac{1}{2}}^{I}$ | $E_{\frac{1}{2}}^{II}$ | $E_{\frac{1}{2}}^{III}$ |
|---|---|---|---|---|
| $[Sb_2](tdt)_3]^\circ$ | 15 | | −0·19 | *b* |
| $[Bi_2(tdt)_3]^\circ$ | 12 | | −0·62 | *b* |
| $Et_4N[Sn(mnt)_2]$ | 139 | −0·02 | −0·57 | −1·51 |
| $(Et_4N)_2[Bi_2(mnt)_2Cl_4]$ | 257 | | −0·63 | −1·51 |
| $(Et_4N)_2[Bi_2(mnt)_2Br_4]$ | 262 | | −0·60 | −1·46 |
| $(Et_4N)_2[Bi(mnt)_2I_4]$ | 260 | | −0·60 | −1·48 |
| $(Et_4N)_2[Bi_2(mnt)_3Cl_2]$ | 251 | | −0·55 | −1·52 |
| $(Et_4N)_2[Bi_2(mnt)_3Br_2]$ | 256 | | −0·57 | −1·47 |
| $(Et_4N)_2[Bi_2(mnt)_3I_2]$ | 261 | | −0·57 | −1·48 |
| $(Et_4N)_4[Bi(mnt)_5]$ | 473 | | −0·54 | −1·51 |

[a] Supporting electrolyte 0·1M-$Et_4NCl$ in MeCN. The half-wave potentials were measured against a saturated calomel electrode. [b] This reduction step not clearly observed in the polarogram.

TABLE 3

Analytical results for antimony(III) and bismuth(III) complexes

| | Found (%) | | | | | Required (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Compound | C | H | N | Halogen | S | C | H | N | Halogen | S |
| $[Sb_2(tdt)_3]^\circ$ | 35·6 | 2·7 | | | | 35·7 | 2·6 | | | |
| $[Bi_2(tdt)_3]^\circ$ | 28·5 | 2·5 | | | | 28·7 | 2·1 | | | |
| $Et_4N[Sb(mnt)_2]$ | 36·1 | 3·6 | 12·9 | | | 36·1 | 3·8 | 13·2 | | |
| $(Et_4N)_2[Bi_2(mnt)_2Cl_4]$ | 26·0 | 3·6 | 7·2 | 11·9 | 12·2 | 26·2 | 3·6 | 7·6 | 12·9 | 11·7 |
| $(Et_4N)_2[Bi_2(mnt)_2Br_4]$ | 22·6 | 2·9 | 6·4 | 24·7 | | 22·6 | 3·2 | 6·6 | 25·0 | |
| $(Et_4N)_2[Bi_2(mnt)_2I_4]$ | 19·4 | 2·5 | 5·7 | 34·3 | | 19·6 | 2·7 | 5·7 | 34·7 | |
| $(Et_4N)_2[Bi_2(mnt)_3Cl_2]$ | 28·7 | 3·1 | 9·5 | 6·1 | 16·7 | 28·8 | 3·6 | 9·6 | 6·1 | 16·5 |
| $(Et_4N)_2[Bi_2(mnt)_3Br_2]$ | 27·2 | 3·4 | 8·9 | 12·2 | | 26·7 | 3·2 | 8·9 | 12·7 | |
| $(Et_4N)_2[Bi_2(mnt)_3I_2$ | 25·2 | 2·8 | 8·3 | | | 24·9 | 3·0 | 8·4 | | |
| $(Et_4N)_4[Bi_2(mnt)_5]$ | 38·1 | 4·6 | 12·0 | | 18·2 | 38·1 | 4·9 | 12·0 | | 19·5 |

In common with their transition-metal analogues, antimony and bismuth dithiolate complexes undergo reversible electron-transfer reactions providing further evidence for $\pi$-electron delocalisation. Polarographic studies of the complexes in acetonitrile are recorded in Table 1. The value of $\alpha$, the polarographic reversibility in the polarographic wave equation[16] was also measured. Unit values of $\alpha$ (within experimental error) implying complete polarographic reversibility were found for all the reduction steps recorded in Table 1. For $Et_4N[Sb(mnt)_2]$, the wave at $E_{\frac{1}{2}} = -0{\cdot}02$ V explains the instability of this compound towards aerial oxidation.[17]

TABLE 2

I.r. absorptions (in cm$^{-1}$) for antimony(III)- and bismuth(III)–mnt complexes

| Compound | $\nu_1$ | $\nu_2$ | $\nu_3$ |
|---|---|---|---|
| $Na_2mnt$ | 1453s | 1155s, 1115s | 860s |
| $(Et_4N)[Sb(mnt)_2]$ | 1483s, 1440s | 1171m, 1142s | 855m |
| $(Et_4N)_2[Bi_2(mnt)_2Cl_4]$ | 1485s, 1438s | 1165s, 1140s | 860m |
| $(Et_4N)_2[Bi_2(mnt)_2Br_4]$ | 1480s, 1140m | 1166s, 1135s | 850m |
| $(Et_4N)_2[Bi_2(mnt)_2I_4]$ | 1475s, 1448m | 1162m, 1130m | 845m |
| $(Et_4N)_2[Bi_2(mnt)_3Cl_2]$ | 1480s, 1440m | 1170s, 1140m | 863m |
| $(Et_4N)_2[Bi_2(mnt)_3Br_2]$ | 1480s, 1445m | 1165m, 1140m | 858m |
| $(Et_4N)_2[Bi_2(mnt)_3I_2]$ | 1475s, 1453m | 1166m, 1135m | 850m |
| $(Et_4N)_4[Bi_2(mnt)_5]$ | 1485m, 1445s | 1175m, 1140m | 860m |

## EXPERIMENTAL

*General.*—I.r. spectra were obtained using a Perkin-Elmer 521 grating i.r. spectrophotometer, and molar conductivities were measured using a Wayne–Kerr Universal Bridge B.221A. Polarographic studies were performed with a Cambridge General Purpose Polarograph.

Disodium dicyanoethylene-1,2-dithiolate was prepared by published procedures.[18]

*Tris(toluene-3,4-dithiolato)diantimony*(III) $[Sb_2(tdt)_3]^\circ$.—Antimony trichloride (0·37 g) was dissolved in acetone and

---

[15] D. M. Adams and J. B. Cornell, *J. Chem. Soc.* (*A*), 1967, 884.

[16] See, for example, L. Meites, 'Polarographic Techniques,' John Wiley, New York, 2nd edn., ch. 3 and 4.

[17] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, 1964, **3**, 814.

[18] G. Bahr and G. Schleitzer, *Ber.*, 1955, **88**, 1771; 1957, **90**, 438.

to the solution was added toluene-3,4-dithiol (0·50 g). Addition of distilled water to the solution precipitated the *complex* as a yellow solid. The product was crystallised methanol.

*Tris(toluene-3,4-dithiolato)dibismuth*(III) $[Bi_2(tdt)_3]^\circ$.—This complex was prepared from bismuth trichloride using a procedure analogous to that for $[Sb_2(tdt)_3]^\circ$. Crystallisation from methanol gave the *complex* as an orange-red microscrystalline powder.

*Tetraethylammonium Bis-(1,2-dicyanoethylene-1,2-dithiolato)antimony*(III).—Antimony trichloride (1·0 g) was reacted with $Na_2$mnt (1·65 g) in methanol. The reaction mixture was filtered into an aqueous solution of tetraethylammonium chloride (0·75) g when the *complex* was precipitated. The product was obtained as yellow crystals from methanol.

*1,2-Dicyanoethylene-1,2-dithiolatobismuth*(III) *Complexes.*—Typically, bismuth trihalide (10 mmol) and $Na_2$mnt (20 mmol) were treated in acetone. The dark red reaction mixture was filtered into an aqueous solution of tetraethylammonium chloride. The precipitate, consisted of a mixture of bismuth–halogeno-complexes and the three series of bismuth–mnt complexes which were separated by fractional crystallisation from ethanol. *Bistetraethylammonium tetrahalogenobis(1,2-dicyanoethylene-1,2-dithiolato)dibismuth*(III) complexes were the least soluble in this solvent. The *chloride* was obtained as orange-yellow needles, the *bromide*, as red needles, and the *iodide* as very dark red needles. *Bistetraethylammonium dihalogenotris-(1,2-dicyanoethylene-1,2-dithiolato)dibismuth*(III) complexes were the next least soluble in ethanol. The *chloride*, *bromide*, and *iodide* were all obtained as dark red, microcrystalline powders. The most soluble bismuth–mnt complex was *tetrakistetraethylammonium pentakis(1,2-dicyanoethylene-1,2-dithiolato)dibismuth*(III), obtained as dark-brown needles from ethanol.

I thank Mr. J. Armstrong for experimental help.

[2/210 *Received*, 1*st February*, 1972]

---