Bistetraethylammonium Chlorobis-(1,2-dicyanoethylene-1,2-dithiolato)-tellurium(III): a Paramagnetic Tellurium Complex

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Summary The preparation is reported of a paramagnetic ($\mu_{eff} = 1{\cdot}5 \pm 0{\cdot}1$ B.M.) formally tellurium(III) complex of stoicheiometry $[Te(mnt)_2Cl][Et_4N]_2$ (mnt = 1,2-dicyanoethylene-1,2-dithiolate).

The recent increase in interest in post-transition-metal complexes of dithiolate ligands has resulted in the preparation of a large number of complexes which exhibit a variety of co-ordination numbers and geometries.[1] In contrast with their transition-metal analogues, however, dithiolato-complexes of the post-transition elements have not been reported where the formal oxidation state of the central metal atom has value other than those accepted as being usual for the element. Tellurium tetrachloride and tetrabromide readily form red, microcrystalline complexes of stoicheiometry $[Te(mnt)_2X][Et_4N]$† on reaction with $Na_2(mnt)$ and Et_4NCl. Reaction of tellurium tetraiodide with $Na_2(mnt)$ and Et_4NCl under the same conditions did not give the expected $[Te(mnt)_2I][Et_4N]$ but instead a red tar from which, after repeated crystallisation from ethanol, were isolated small amounts of the dark red, crystalline, formally Te^{III}, complex $[Te(mnt)_2Cl][Et_4N]_2$ and the orange-red tetraethylammonium salt of the first oxidation product of mnt^{2-}, bis-(2-sulphido-1,2-dicyanovinyl) disulphide, $(C_8N_4S_4)^{2-}$.[2] Other products of the reaction could not be identified. Attempts to prepare $[Te(mnt)_2X]^{2-}$ by reduction of $[Te(mnt)_2X]^-$ were unsuccessful, the only products being intractable dark red tars.

$[Te(mnt)_2Cl][Et_4N]_2$ was insoluble in water but sparingly soluble in ethanol and acetonitrile and in the latter solvent its molar conductance of 289 Ω^{-1} cm^2 mol^{-1} was within the range expected[3] for uni-bivalent electrolytes. Magnetic susceptibility measurements (obtained on solid samples by the Faraday method) gave a value for its effective magnetic moment at 18 °C of $1{\cdot}5 \pm 0{\cdot}1$ B.M., indicating the presence of one unpaired electron. A more accurate value for the magnetic moment was unobtainable because of the difficulty in accurately estimating the large diamagnetic correction for this weakly paramagnetic complex of high molecular weight. This correction was in fact estimated by summing the measured magnetic susceptibilities of Et_4NCl and the diamagnetic Te^{IV} complex $[Te(mnt)_2Cl]Et_4N$ and subtracting the Pascal constant for Cl^-.

Although for dithiolato-complexes it is unwise to attempt

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† Satisfactory elemental analyses have been obtained for all new compounds.

to assign integral numbers of electrons to the central metal atom and hence determine its true as compared with its formal oxidation state, some evidence does exist that for indium complexes at least the formal oxidation state does approximate to the true situation.[4] This may well be true for the dithiolato-complexes of other post-transition metals including tellurium and work is in progress to determine whether or not this is the case.

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[1] See, for example, C. W. Allen, R. O. Fields, and E. S. Bretschneider, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1951.
[2] H. E. Simmons, D. C. Blomstrom, and R. D. Vest, *J. Amer. Chem. Soc.*, 1962, **84**, 4756.
[3] D. G. Tuck and M. K. Yang, *J. Chem. Soc.* (*A*), 1971, 214.
[4] A. F. Berniaz, G. Hunter, and D. G. Tuck, *J. Chem. Soc.* (*A*), 1971, 3254.