Complexes of Indium with Unsaturated Bidentate Sulphur-donor Ligands

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THERE is an extensive literature on the chemistry of transition-metal complexes with unsaturated bidentate ligands in which sulphur is the donor atom,[1] but, of the main-group elements, only zinc(II) and tin(IV) compounds have been reported. The structure of $[Zn(MNT)_2]^{2-}$ (MNT^{2-} = maleonitriledithiolate anion) is not known;[2] the tin(IV) complexes are polymeric unless aryl groups are also bonded to the metal.[3]

We find that the reaction of indium(III) chloride with MNT^{2-} gives rise to the anionic complexes $[In(MNT)_2]^-$ or $[In(MNT)_3]^{3-}$, depending on the In : MNT^{2-} mole ratio used in the preparation. Treatment of $[In(MNT)_2]^-$ with neutral bidentate donor ligands in alcohol gave anionic complexes of the type $[In(MNT)_2L]^-$ [L = 2,2′-bipyridyl, 1,10-phenanthroline, 8-hydroxyquinoline, ethylenediamine, or 1,2-bis(diphenylphosphino)ethane]. The Et_4N^+ salts of all of these anions are yellow; salts of the adduct species are 1 : 1 electrolytes in acetonitrile, except that the 8-hydroxyquinoline adduct has a conductivity *ca.* 50% lower than expected; $Et_4N[In(MNT)_2]$ is a 1 : 1 electrolyte, and $(Et_4N)_3[In(MNT)_3]$ a 3 : 1 electrolyte in this solvent. No reaction of $[In(MNT)_2]^-$ was detected either chemically or spectroscopically with monodentate donors (pyridine, ammonia, urea, Ph_3P) other than *NN′*-dimethylacetamide (dma), which gave an unstable adduct $Et_4N[In(MNT)_2(dma)_2]$ (decomp. ~ 60°). From similar reactions involving indium chloride and TDT^{2-} (TDT^{2-} = toluene-3,4-dithiolate anion) we obtained the 1 : 1 electrolytes $Et_4N[In(TDT)_2]$ and $[In(TDT)_2L]$ (L = bipy, phen), and the 3 : 1 electrolyte $(Et_4N)_3[In(TDT)_3]$. The acceptor ability of the $[In(MNT)_2]^-$ and $[In(TDT)_2]^-$ complexes, while in keeping with the ability of the metal in this oxidation state to form $[InCl_4L_2]^-$ species,[4] is markedly different from the behaviour of the complexes of transition-metal ions other than cobalt(III) with di-sulphur ligands.[1,5]

Polarographic reduction of these complexes in aqueous or absolute methanol showed in almost each case a series of reversible one-electron changes, formally $In^{III} \rightarrow In^{II} \rightarrow In^{I} \rightarrow In^{0}$. This behaviour is in sharp contrast to the usual aqueous phase $In^{III} \rightarrow In^{0}$ polarographic reduction,[6] and represents the first identification of a formally In^{II} complex, although this oxidation state has been reported[7] in a matrix of frozen aqueous sulphuric acid irradiated with γ-rays at −77°. In view of earlier work[1], however, it seems highly probable that the added electrons are associated with the metal–ligand ring system rather than being in purely metal orbitals.

In those analogous transition-metal complexes for which structure determinations have been reported,[8] the MS_6 co-ordination is either a precise or distorted trigonal prismatic arrangement. An *X*-ray structure determination on $(Et_4N)_3[In(MNT)_3]$ shows that the InS_6 kernel in this anion has a distorted octahedral structure, with the In–S bond length 2·59 Å. The S–In–S angle within the chelate ring is 80°, and the S–S distance in the ring 3·39 Å. A three-dimensional electron-density difference map shows the positions of all the remaining non-hydrogen atoms; refinement by block-diagonal least-squares method is presently being undertaken with the 25 atoms of the anion (R = 0·24 for 1866 reflexions). The $[In(MNT)_3]^{3-}$ anion is thus the first example of a di-sulphur ligand complex with the "classical" distorted octahedral symmetry associated with tris(bidentate ligand) co-ordination, yet showing the stabilization of unusual formal oxidation states.

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