

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 $[\text{Zn}(\text{MNT})_2]^{2-}$ (MNT^{2-} = maleo-nitriledithiolate 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 $[\text{In}(\text{MNT})_2]^-$ or $[\text{In}(\text{MNT})_3]^{3-}$, depending on the $\text{In}:\text{MNT}^{2-}$ mole ratio used in the preparation. Treatment of $[\text{In}(\text{MNT})_2]^-$ with neutral bidentate donor ligands in alcohol gave anionic complexes of the type $[\text{In}(\text{MNT})_2\text{L}]^-$ [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; $\text{Et}_4\text{N}[\text{In}(\text{MNT})_2]$ is a 1:1 electrolyte, and $(\text{Et}_4\text{N})_3[\text{In}(\text{MNT})_3]$ a 3:1 electrolyte in this solvent. No reaction of $[\text{In}(\text{MNT})_2]^-$ was detected either chemically or spectroscopically with monodentate donors (pyridine, ammonia, urea, Ph_3P) other than *NN'*-dimethylacetamide (dma), which gave an unstable adduct $\text{Et}_4\text{N}[\text{In}(\text{MNT})_2(\text{dma})_2]$ (decomp. $\sim 60^\circ$). From similar reactions involving indium chloride and TDT^{2-} (TDT^{2-} = toluene-3,4-dithiolate anion) we obtained the 1:1 electrolytes $\text{Et}_4\text{N}[\text{In}(\text{TDT})_2]$ and $[\text{In}(\text{TDT})_2\text{L}]^-$ (L = bipy, phen), and the 3:1 electrolyte $(\text{Et}_4\text{N})_3[\text{In}(\text{TDT})_3]$. The acceptor ability of the $[\text{In}(\text{MNT})_2]^-$ and $[\text{In}(\text{TDT})_2]^-$ complexes, while in keeping with the ability of the metal in this oxidation state to form $[\text{InCl}_4\text{L}_2]^-$ 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 $\text{In}^{\text{III}} \rightarrow \text{In}^{\text{II}} \rightarrow \text{In}^{\text{I}} \rightarrow \text{In}^0$. This behaviour is in sharp contrast to the usual aqueous phase $\text{In}^{\text{III}} \rightarrow \text{In}^0$ polarographic reduction,⁶ and represents the first identification of a formally In^{II} complex, although this oxidation state has been reported⁷ in a matrix of frozen aqueous sulphuric acid irradiated with γ -rays at -77° . In view of earlier work¹, 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 $(\text{Et}_4\text{N})_3[\text{In}(\text{MNT})_3]$ 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 $[\text{In}(\text{MNT})_3]^{3-}$ 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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