The *X*-Ray Crystal Structure of the Indium(III) Iodide–Bis(dimethyl sulphoxide) Adduct

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Summary The addition compound of stoicheiometry $InI_3(Me_2SO)_2$ is shown to be an ionic dimer $[InI_2(Me_2SO)_4][InI_4]$ in the solid state: the iodine atoms in the cation are in the *cis*-configuration.

ADDITION compounds of Group IIIA trihalides with neutral monodentate ligands are known with the stoicheiometries MX_3L, MX_3L_2, and MX_3L_3 (M = Al, Ga, In; X = Cl, Br, I; L = donor ligand). All three stoicheiometries have been reported for indium(III) halides.[1] With L = dimethyl sulphoxide, indium(III) chloride and bromide both yield $InX_3(Me_2SO)_3$, which have been shown[2] to be neutral mononuclear species, but the iodide adduct has the stoicheiometry $InI_3(Me_2SO)_2$. The only reported *X*-ray structure determination for an indium(III) halide adduct refers to $InCl_3(Ph_3P)_2$, which Veidis and Palenik[3] find to have an axially substituted trigonal-bipyramidal structure, in agreement with earlier work.[2]

We now report the results of a crystallographic study of the compound of stoicheiometry $InI_3,(Me_2SO)_2$, which we find to have the molecular formula $[InI_2(Me_2SO)_4][InI_4]$ in the solid state. Crystals of $[InI_2(Me_2SO)_4][InI_4]$ crystallize in the monoclinic space group $C2/c$, with cell dimensions $a = 39{\cdot}86$, $b = 8{\cdot}048$, $c = 27{\cdot}70$ Å, and $\beta = 129{\cdot}15°$. There is one formula unit in the asymmetric unit; neither ion has any crystallographic symmetry. An *X*-ray crystal structure determination using scintillation counter data (1133 observed reflexions) gives an agreement of $R = 0{\cdot}098$ based on full-matrix least-squares refinement of all co-ordinate and isotropic thermal parameters for non-hydrogen atoms.

The anion has an almost regular tetrahedral symmetry, with an average In–I bond length of 2·71 ± 0·01 Å. The cation has the iodine atom in a *cis*-arrangement, subtending an angle of 98° at the indium atom; the indium–iodine bond lengths of 2·79 and 2·81 Å are longer than in the anion. The increase is close to that predicted for a change in co-ordination number from four to six. In the similar case of $[GaCl_2(bipy)_2][GaCl_4]$ (bipy = 2,2′-bipyridyl), the Ga–Cl bond lengths in cation and anion are 2·264 and 2·166 Å, respectively.[4] The dimethyl sulphoxide ligands in $[InI_2(Me_2SO)_4]^+$ are all oxygen-bonded, with In–O distances ranging between 2·15 and 2·20 Å.

The In–I bond in $[InI_4]^-$ is longer than in the isoelectronic molecule SnI_4 (Sn–I 2·64 ± 0·04 Å),[5] but similar to that in In_2I_6 (average 2·76 Å).[6] The most interesting feature of the structure of the cation is the *cis*-configuration of the two iodine atoms. At present, it is not possible to say with certainty whether this is the unique stable stereoisomer of $[InI_2(Me_2SO)_4]^+$, or whether the stabilisation of this form is a function of the anion present in the lattice. The $[GaCl_2(bipy)_2]^+$ ion also has the *cis*-configuration, which has been discussed in terms of a stabilising *trans*-effect in d^{10} complexes.[7] The electronic interpretation of such an effect is not yet clear, but in any case the effect does not appear to be significant in the $[InI_2(Me_2SO)_4]^+$ structure. In contrast to the Ga–Cl situation, the difference in the In–I and In–O bond lengths is 0·63 Å, very close to the difference in the single-bond covalent radii of iodine and oxygen (0·67 Å), so that there is apparently little or no shortening of In–I bond, as would be required by a *trans*-effect of the type invoked to explain the different Ga–Cl bond lengths in $[GaCl_2(bipy)_2]^+$ and in $GaCl_3$(2,2′,2″-terpyridyl).[4,7]

The existence of two different structures with the stoicheiometry InX_3L_2 is of considerable interest. The structure of $InI_3(Me_2SO)_2$ could not be established by i.r. studies alone,[2] but the Raman spectrum shows emissions at 138vs, and 180w, br (cm^{-1}), readily assigned to the $[InI_4]^-$ anion.[8] The type of structure found is apparently not peculiar to the dimethyl sulphoxide adduct, since $InI_3(Ph_3PO)_2$ also has a strong Raman band at 139 cm^{-1}.

Both $InCl_3(Ph_3P)_2$ and $[InI_2(Me_2SO)_4][InI_4]$ have conductivities typical of weak electrolytes in polar organic solvents,[1] so that considerable rearrangement of the solid state structures must occur in such solutions. The isolation of $[InI_2(Me_2SO)_4][InI_4]$, rather than the mononuclear $InI_3(Me_2SO)_2$, in the solid state, may be due in part to the stability of the $[InI_4]^-$ anion, which is the only anionic indium(III) complex halogeno-anion identified in salts with a wide variety of cations.[9]

This work was supported in part by the National Research Council of Canada.

(*Received, July 23rd,* 1970; *Com.* 1223.)

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