

Anionic Halide Complexes of Indium(I)

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Summary Stable crystalline compounds containing the $\text{In}^{\text{I}}\text{X}_3^{2-}$ anion (X = Cl, Br, or I) have been prepared for the first time; the Raman spectra are in agreement with the predicted trigonal pyramidal structure.

Few co-ordination compounds of indium(I) have been reported, although the existence of the M^{I} state is an

important feature of the chemistry of Group IIIA. Indium monobromide and monoiodide react with ammonia under pressure to give complexes of the type $\text{InX}_2\cdot 2\text{NH}_3$ (X = Br or I).¹ The 1:1 electrolytes, $\text{In}(\text{aniline})_4\text{X}$ and $\text{In}(\text{morpholine})_2\text{X}$, have been prepared from the monohalides (X = Cl, Br, or I).² More recently, the preparation and redox stability of aqueous solutions of In^{I} have been investigated.³

We now report that the stable crystalline anionic InX_3^{2-} complexes ($X = \text{Cl}, \text{Br}, \text{or I}$) can be readily prepared. Powdered indium monohalide was suspended in a methanolic solution of *NN'*-dimethyl-4,4'-bipyridinium halide ($\text{Me}_2\text{-bipy}^{2+}\text{X}_2^-$), with the salt:InX mole ratio of 1:1. After 2–3 h stirring *in vacuo* at room temperature, removal of solvent gave a residue of $(\text{Me}_2\text{bipy})^{2+}[\text{InX}_3]^{2-}$.† The molar conductivity of $(\text{Me}_2\text{bipy})[\text{InI}_3]$ in nitrobenzene was $25 \text{ ohm}^{-1} \text{ cm}^2$, in agreement with values reported for 1:1 electrolytes in this solvent.⁴ The chloro- and bromo-complexes are insoluble in solvents normally used in conductivity measurements. The compounds are diamagnetic and air-stable.

The InX_3^{2-} anion is isoelectronic with both $\text{Sn}^{\text{II}}\text{X}_3^-$ and $\text{Sb}^{\text{III}}\text{X}_3$, for which C_{3v} molecular symmetry has been demonstrated by vibrational spectroscopy.^{5,6} The Raman spectra of the InX_3^{2-} anions (Table) are similar to those of

TABLE. Raman frequencies of $(\text{Me}_2\text{bipy})(\text{InX}_3)/\text{cm}^{-1}$

			X		
			Cl	Br	I
ν_1	252	177	136
ν_2	185	149	110
ν_3	102	74	78
ν_4	97		

the analogous Sn^{II} and Sb^{III} trihalides, but different from those of the indium monohalides. On the basis of the structural analogies just noted, these emissions were assumed to be ν_1 , ν_3 , ν_2 and ν_4 of anions of C_{3v} symmetry. Force constant calculations have confirmed these assignments.

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† Satisfactory total analyses were obtained in each case.

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