= 3. However, the value of n may be obtained from the general equation from the ratio of intercept and the slope, i.e., $(n - 1)^2[Cr_T]/n$ since $a = [Cr_T]/n$. The actual results show that $n = 3.1 \pm 0.2$ which points only to $Cr_3Cl_{10}^{4-}$.

(14) D. M. Gruen and R. L. McBeth, *Pure Appl. Chem.*, **6**, 23 (1963).

(15) L. F. Larkworthy, J. K. Trigg, and A. Yavari, *J. Chem. Soc., Dalton Trans.*, 1879 (1975).

(16) See, for example, the energy level diagram given by A. B. P. Lever, "Inorganic Electronic Spectroscopy", American Elsevier, New York, N.Y., 1968, p 154.

Contribution from the Department of Chemistry,
University of Windsor, Windsor, Ontario, N9B 3P4, Canada

Coordination Compounds of Indium. 32. Preparation and Properties of Hexahalogenatodiindate(II) Anions

BRIAN H. FREELAND, J. LAWRENCE HENCHER, DENNIS G. TUCK,* and J. GUILLERMO CONTRERAS

Received February 18, 1976 AIC601277

The salts $(Bu_4N)_2[In_2X_6]$ (X = Cl, Br, I) have been prepared by the reaction of Bu_4NX and InX_2 in xylene. The vibrational spectra lead to the formulation of the anions as $[X_3In-InX_3]^{2-}$ species, so that these are the first unambiguous indium(II) complexes to be prepared. Force constant calculations support the vibrational assignments. A possible reaction scheme for the preparation is discussed. The reaction of $(Me_2bpy)InX_3$ (Me_2bpy^{2+} = *N,N*-dimethyl-4,4′-bipyridinium cation) with InX_3 yields a lattice of $Me_2bpy^{2+} + InX_2^- + InX_4^-$; the reasons for the difference between this reaction and that giving $(Bu_4N)_2[In_2X_6]$ are discussed.

Introduction

The coordination chemistry of indium(III) is now reasonably well understood, and there have been some encouraging recent developments in our knowledge of indium(I) complexes,[1] but information on indium(II) remains sparse. The only well-established compounds whose stoichiometry implies indium in the +II state are the dihalides InX_2 (X = F, Cl, Br, I), whose structure in the solid and liquid states has been the subject of considerable discussion, reviewed elsewhere.[1-3] A brief summary of the situation is that these InX_2 compounds, and other indium subhalides, are mixed oxidation state compounds, for which ionic formulations (e.g., $In[InX_4]$, $In_3[InX_6]$) represent the structure within the very considerable limits of present information. More importantly, such compounds are apparently not genuine indium(II) species, and earlier suggestions of a dimeric indium–indium bonded structure for InX_2 can therefore be discounted. We may also note that the polarographic reduction of indium(III) chelate[5-7] complexes yields indium(II) species, but none of these reduction products has been isolated. Monomeric indium(II) species would, of course, contain an unpaired electron, and might be expected to be highly reactive.

We recently reported[8] a simple synthesis of indium dihalides involving the reduction of indium(III) halide by the metal in aromatic solvents, in which the InX_2 products are reasonably soluble. It has now been found that these compounds react in such solvents with tetrabutylammonium halides to yield $(Bu_4N)_2[In_2X_6]$ salts (X = Cl, Br, I). Spectroscopic measurements and force constant calculations establish that the anions are correctly formulated as $[X_3In-InX_3]^{2-}$, analogous to a group of gallium(II) compounds[9-11] whose structure has been confirmed by an x-ray study[12] of $(Et_4N)_2[Cl_3Ga-GaCl_3]$. The $[In_2X_6]^{2-}$ anion has been postulated in discussions of the structure of In_2X_3 (X = Cl, Br) which are held to be $(In^I)_2[In_2X_6]$ compounds[13,14] (cf. previous paragraph).

The present work also leads to an understanding of earlier studies of the reaction of $InCl_3^{2-}$, a potential electron pair donor,[15] with $InCl_3$; this reaction is believed to involve halide transfer and rearrangement following adduct formation, eventually yielding InX_2^- and InX_4^-.

Experimental Section

General Data. Experimental methods in general were similar to those reported in ref 8. Raman spectra were recorded over the range 100–500 cm^{-1} on a Spectrophysics Model 700 spectrometer in conjunction with a Model 164 argon ion laser and Model 265 exciter unit. Power output was typically 100–300 mW with the 20 492-cm^{-1} exciting frequency. The infrared spectra, kindly provided by Professor A. J. Carty (University of Waterloo), were obtained as Nujol mulls between polythene plates on a Perkin-Elmer 180 spectrophotometer.

Magnetic susceptibilities were determined on a conventional Gouy balance. Conductivity measurements were as in earlier work.[3]

Preparative Data. Indium diiodide (1.6 g, 2.17 mmol, calculated as In_2I_4) was suspended in xylene (75 ml), and tetrabutylammonium iodide (1.6 g, 4.34 mmol) was added. The suspension was warmed, with stirring, and finally heated to reflux; the formation of a yellow oil was apparent at this stage. After 10 min, the reaction mixture was allowed to cool to room temperature, whereupon the oil yielded a yellow solid. Solvent was removed by decantation, and the solid was washed with diethyl ether (100 ml) and then triturated with more ether. The final solid was again washed with diethyl ether and dried in vacuo; analysis showed this solid to be $(Bu_4N)_2[In_2I_6]$; yield 2.53 g (79%). The preparations of the $In_2Cl_6^{2-}$ and $In_2Br_6^{2-}$ salts were essentially identical. Anal. Calcd for $(Bu_4N)_2[In_2Cl_6]$: C, 41.4; H, 7.8; N, 3.0; Cl, 23.0. Found: C, 42.3; H, 7.9; N, 3.9; Cl, 22.0. Calcd for $(Bu_4N)_2[In_2Br_6]$: C, 32.2; H, 6.0; N, 2.4; Br, 40.2. Found: C, 32.2; H, 6.0; N, 2.5; Br, 40.2. Calcd for $(Bu_4N)_2[In_2I_6]$: C, 26.0; H, 4.9; N, 1.9; I, 51.6. Found: C, 25.9; H, 4.9; N, 1.7; I, 50.7. The chloride complex gave relatively poor analytical results, which is no doubt connected with the fact that the reaction of $InCl_2$ and Bu_4NCl was the least satisfactory of the preparations, since $InCl_2$ is the least soluble of the indium dihalides in xylene.[8] We were unable to find a satisfactory solvent for the recrystallization of $(Bu_4N)_2[In_2Cl_6]$.

Rapid decomposition in solvents such as acetonitrile prevented any conductometric studies of these compounds in solution.

Reaction between InX_3^{2-} and InX_3. Indium(III) halides dissolved in dry methanol were added to the corresponding $(Me_2bpy)In^IX_3$ salts (Me_2bpy^{2+} = *N,N*-dimethyl-4,4′-bipyridinium cation) prepared by the method described earlier,[3] and the mixture was refluxed for 10 h. The resultant solids (colorless for X = Cl or Br, orange for X = I) were collected, washed with methanol, and dried in vacuo. Each analyzed as the compound $(Me_2bpy)In_2X_6$. Anal. Calcd for $C_{12}H_{14}N_2In_2Cl_6$: C, 22.9; H, 2.2; N, 4.5; Cl, 33.9; In, 36.5. Found: C, 22.3; H, 2.1; N, 4.3; Cl, 33.4; In, 36.4. Calcd for $C_{12}H_{14}N_2In_2Br_6$: C, 16.5; H, 1.6; N, 3.2; Br, 54.8; In, 26.2. Found: C, 14.2; H, 1.7; N, 3.6; Br, 54.8; In, 26.1. Calcd for $C_{12}H_{14}N_2In_2I_6$: C, 12.2; H, 1.2; N, 2.4; I, 64.7; In, 19.6. Found: C, 12.6; H, 1.5; N, 2.2; I, 64.3; In, 19.4. These compounds are sufficiently soluble in acetonitrile for conductivity studies (see below).

Results and Discussion

The ready availability of gram quantities of the indium dihalides and their solubility in aromatic solvents[8] has prompted the investigation of their mode of reaction in such

Table I. Vibrational Spectra of $In_2X_6^{2-}$ Anions (X = Cl, Br, I) as Bu_4N^+ Salts (in cm^{-1})

$In_2Cl_6^{2-}$	$In_2Br_6^{2-}$	$In_2I_6^{2-}$	Assignment[c]	Description
		Infrared		
332 m 284 sh [a]	235 s 207 s [b]	186 m	E_u	ν(In–X)
292 s	185 s	164 vs	A_{2u}	ν(In–X)
		Raman		
325 m	244 w	210 w	E_g	ν(In–X)
289 m	202 w	152 w	A_g	ν(In–X)
174 s	139 vs	108 vs	A_g	ν(In–In)

[a] Fermi resonance from fundamental at 308 cm^{-1}. [b] Fermi resonance from fundamental at 221 cm^{-1}. [c] Based on D_{3d} symmetry (see text).

Table II. Stretching Force Constant Data in $In_2X_6^{2-}$ Anions

	Force constants,[a] 10^5 dyn cm^{-1}		
	$In_2Cl_6^{2-}$	$In_2Br_6^{2-}$	$In_2I_6^{2-}$
K_{In-In}	0.63 (8)	0.69 (6)	0.24 (1)
K_{In-X}	1.45 (2)	1.19 (2)	1.09 (1)
$f_{In-In/In-X}$	0.02 (4)	0.04 (1)	0.07 (4)
$f_{In-X/In-X}$	0.05 (1)	0.02 (1)	0.08 (5)

	Frequencies, cm^{-1}					
	$In_2Cl_6^{2-}$		$In_2Br_6^{2-}$		$In_2I_6^{2-}$	
	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
A_g	290	289	204	202	157	159
	175	174	140	139	108	108
E_g	318	325	239	244	211	210
A_{2u}	289	292	187	185	162	164
E_u[b]	312	308	224	221	190	186

	Potential energy distribution[c]		
	$In_2Cl_6^{2-}$	$In_2Br_6^{2-}$	$In_2I_6^{2-}$
A_g ν(In–In)	39(1) + 4(2) + 55(3)	30(1) + 40(2) + 22(3)	22(1) + 21(2) + 40(3)
ν(In–X)	100(2)	32(1) + 57(2) + 17(3)	18(1) + 71(2) + 24(3)

[a] Figures in parentheses denote limits of uncertainty. [b] Note that observed values for Cl and Br are means of experimentally observed doublets. [c] Figures in parentheses imply $1 = K_{In-In}$, $2 = K_{In-X}$, and $3 = H_{In-X}$.

media. In the reaction of indium diiodide with tetrabutylammonium iodide in warm xylenes, the deep red color which initially appears is consistent with the formation of indium monoiodide, which reacts further, ultimately yielding the isolated materials. The bromide and chloride react analogously to form white powders.

The following reaction scheme is suggested to account for the initial formation of InX.

$$In_2X_4 + Bu_4NX \rightarrow InX + Bu_4N[InX_4] \quad (1)$$

$$InX + Bu_4NX \rightarrow Bu_4N[InX_2] \quad (2)$$

$$Bu_4N[InX_4] + Bu_4N[InX_2] \rightarrow (Bu_4N)_2[In_2X_6] \quad (3)$$

The obvious alternative, that involving successive addition of halide ion to In_2X_4, does not explain the elimination of InX. We return to eq 3 in later discussion.

Vibrational Spectra of $(Bu_4N)_2[In_2X_6]$ Salts. The infrared and Raman spectra of the $[In_2X_6]^{2-}$ anions (as the tetra-*n*-butylammonium salts) are shown in Table I. The lack of coincidences between infrared and Raman modes immediately identifies the molecules as centrosymmetric and hence rules out structures such as $X_3In^{III}\leftarrow[In^IX_3]^{2-}$. Instrument limitations prevent the observation of some low-frequency bands, especially in the spectra of $In_2Br_6^{2-}$ and $In_2I_6^{2-}$, and we therefore restrict the discussion to the stretching modes.

Possible molecular symmetries for $In_2X_6^{2-}$ species are D_{3d}, C_{2h}, and D_{2h}. The most probable of these is D_{3d} (ethanelike, staggered configuration), especially since x-ray studies[12] have shown that this is the symmetry of the $Ga_2Cl_6^{2-}$ anion. A D_{3d} A_2B_6 species should have two infrared-active (ν(In–X) (E_u and A_{2u})) and three Raman-active vibrations (ν(In–In) (A_g) and two ν(In–X) (E_g and A_g)). The results in Table I agree well with these predictions. For $In_2I_6^{2-}$, the highest frequency vibration (210 cm^{-1}) is assigned to the asymmetric E_g mode. The band at 108 cm^{-1} is then ν(In–In), so that the 152-cm^{-1} vibration is identified as the A_g ν(In–X), close in frequency to the 164-cm^{-1} infrared mode. The remaining infrared band at 186 cm^{-1} is assigned as E_u(In–X). The argument for the bromide and chloride is similar, except that in both cases we observe three infrared bands rather than the two predicted for D_{3d} symmetry. For $In_2Br_6^{2-}$, the two bands at 235 and 207 cm^{-1} have approximately identical intensities and we believe these to be a Fermi doublet; the unshifted ν(In–X) fundamental would then be at the arithmetic mean of 221 cm^{-1}. Similarly, in $In_2Cl_6^{2-}$, the two bands at 332 + 284 cm^{-1} are identified as arising from a fundamental at 308 cm^{-1}. It does not appear possible to account for the presence of three infrared bands by a lowering of the molecular symmetry, since this would not agree with the presence of only two Raman emissions. From these arguments, we conclude that the anions in each of the $(Bu_4N)_2[In_2X_6]$ salts have D_{3d} symmetry and are of the form $[X_3In-InX_3]^{2-}$, being genuine indium(II) complexes. Magnetic susceptibility measurements show that the salts are diamagnetic, in keeping with this structural formulation of the anion.

Force Constant Calculations. Although the above vibrational assignments (Table I) appear well-founded, it seemed worthwhile to carry out force constant calculations in order to provide further evidence for the structures proposed. We have therefore performed modified valence force field calculations for each anion. The structural parameters assumed in common are the In–In bond length of 300 pm and all X–In–X and In–In–X angles of 109.5°. The assumed In–X bond lengths are for Cl 240 pm, for Br 260 pm, and for I 280 pm, values which are derived from the covalent radii of the atoms in question and from known structural results for indium(I) and -(III) halide complexes.[1] We restrict the calculation to the stretching modes, but this does not obviate the need for information on the force constants for the bending modes of the molecules (H_{AB}). In view of the other assumptions involved in these calculations, we feel justified in assuming that $H_{XInX} = H_{InXIn} = 0.1$ (cf. ref 15 for similar values in indium(III) and indium(I) species). Table II shows the results of such calculations, the good agreement between observed and calculated frequencies, and the potential energy distribution in the In–In and In–X (A_g) stretching modes. Although the bending force constants do in fact contribute significantly, the assumed constant values do not apparently distort the calculations appreciably.

Within the very real limits of the calculation, the assignments in Table I are completely supported. The calculations also show that the A_g mode described in Table I as ν(In–In) is far from pure, which explains in part the strong ligand dependence of the frequency (see Table I). The force constants show that the In–In bond is in fact significantly weaker in $In_2I_6^{2-}$ than in either $In_2Cl_6^{2-}$ or $In_2Br_6^{2-}$, in which K_{In-In} is constant within the limits of the calculation. The ν(In–X) force constants show the same monotonic change from chloride to iodide found in both indium(I) and indium(III) anions.[15] The corresponding values for K_{In-X} in InX_4^- and InX_3^{2-}, which provide the closest structural comparison with $In_2X_6^{2-}$, are as follows: $InCl_4^-$, 1.865; $InBr_4^-$, 1.598; InI_4^-, 1.199; $InCl_3^{2-}$, 0.760; $InBr_3^{2-}$, 0.750; InI_3^{2-}, 0.625. For a given halogen ligand, the values for $In_2X_6^{2-}$ are close to the mean of the results for InX_4^- and InX_3^{2-}. It has been argued elsewhere[15,16] that the dependence of stretching force constant upon the oxidation state and coordination number of the metal in such species is evidence of ionic bonding. The present results therefore indicate a very similar situation for the $In_2X_6^{2-}$ anions.

$(Me_2bpy)In_2X_6$. The reactions between $(Me_2bpy)InX_3$ and InX_3 species were originally intended to test the donor power of InX_3^{2-} toward the known acceptors InX_3. Since InX_3^{2-} is isoelectronic with $SnCl_3^-$, which is known as a ligand in complexes with transition metals,[17] some donor ability might be expected, although these indium(I) anions do not coordinate to the boron halides at room temperature.[18] The products of the reaction clearly correspond analytically to the predicted 1:1 adduct formulation (see Experimental Section), but their solution properties differ from those of the $(Bu_4N)_2[In_2X_6]$ salts in that they are soluble in acetonitrile. The molar conductivities for 1 mM solutions of $(Me_2bpy)In_2X_6$ are as follows: $X = Cl$, $\Lambda = 148\ \Omega^{-1}\ cm^2$; $X = Br$, $\Lambda = 138\ \Omega^{-1}\ cm^2$; $X = I$, $\Lambda = 143\ \Omega^{-1}\ cm^2$. These values are somewhat higher than those reported[3] for $(Me_2bpy)InX_3$ and other 1:1 indium salts[5] in the same solvent.

The Raman spectra of these compounds were of poor quality, with high background scattering, but the identifiable emissions are clearly not those of $[In_2X_6]^{2-}$ salts. For the compound $(Me_2bpy)In_2I_6$ a strong emission at 138 cm^{-1} indicates the presence of InI_4^-.[20] Together with a band at 182 (m) cm^{-1}, which is assigned to the InI_2^- anion,[21] this suggests that the solid state consists of $Me_2bpy^{2+} + InI_4^- + InI_2^-$. Similar structures have been observed previously; for example, the reaction of $(Me_2bpy)X_2$ with InX_2 yields compounds of stoichiometry $(Me_2bpy)InX_4$, shown[3] to be $2Me_2bpy^{2+} + InX_3^{2-} + InX_4^-$ for X = Br or I, and $2Me_2bpy^{2+} + InX_3^{2-} + InX_5^{2-}$ for X = Cl. Similarly, the compound $(Me_4N)_2InBr_5$ is actually $2Me_4N^+ + InBr_4^- + Br^-$ in the solid state.[20] In keeping with the proposal that $(Me_2bpy)In_2I_6$ is a lattice of two anions, the chlorine and bromine analogues have Raman emissions at 295 and 232 cm^{-1}, close to those observed[21] for $InCl_2^-$ (291 cm^{-1}) and $InBr_2^-$ (236 cm^{-1}).

Thus we tentatively conclude that the reaction of $(Me_2bpy)InX_3 + InX_3$ in methanol results in halide ion transfer to InX_3 from InX_3^{2-}, which need not involve prior coordination through an $In^I \rightarrow In^{III}$ bond. In view of the analogy suggested above between $InCl_3^{2-}$ and $SnCl_3^-$, it is worth noting that the reaction of the latter with BF_3 has also been shown[19] to result in halide transfer to yield $SnCl_2$ and BF_3Cl^-. There remains the difference between the halide-transfer reaction and the preparative reactions which lead to salts of the genuine $[X_3In-InX_3]^{2-}$ anions (eq 1–3). There are two obvious differences in the reaction conditions, namely, the cations and the solvents. Both factors are known to influence the stoichiometry and structure of anionic indium(III) halide complexes,[20] and there is evidence of analogous behavior in indium(I) chemistry.[21] It therefore seems reasonable to focus on eq 3 and suggest that this is in fact an equilibrium

$$InX_4^- + InX_2^- \rightleftharpoons In_2X_6^{2-} \tag{4}$$

in which the product distribution in solution depends upon the solvent and in the crystalline material depends upon solvent and cation. The conductivity results agree with the presence of more conducting species than would be found for a 2:2 electrolyte and hence support the proposed equilibrium. More work on this problem is planned.

Comparison with Previous Work. The $(Bu_4N)_2[In_2X_6]$ salts represent the first unambiguously identified indium(II) complex. As noted in the Introduction, the lower halides In_2Cl_3 and In_2Br_3 have been formulated as $(In^I)_2[In_2X_6]$ on the basis of Raman spectroscopy;[13,14] in particular the emission[14] at 170 cm^{-1} in In_2Cl_3 has been assigned to $\nu(In-In)$, a value in good agreement with the value of 170 cm^{-1} in $[In_2Cl_6]^{2-}$ (see Table I). Similarly, the Raman bands[13] at 139 (vs), 201 (m), and 241 (m) cm^{-1} in In_2Br_3 are in good agreement with those from $[In_2Br_6]^{2-}$. Thus the proposed ionic formulations for In_2X_3 are supported by the present work, given the obvious limitations of such spectroscopic techniques in elucidating solid-state structures; as in other work of this type, we have no knowledge as to the nature of the stereochemistry around the cation (cf. ref 3).

Acknowledgment. This work was supported in part by Operating Grants from the National Research Council of Canada.

Registry No. $(Bu_4N)_2[In_2Cl_6]$, 59643-22-0; $(Bu_4N)_2[In_2Br_6]$, 59643-24-2; $(Bu_4N)_2[In_2I_6]$, 59643-26-4; $(Me_2bpy)In_2Cl_6$, 59643-27-5; $(Me_2bpy)In_2Br_6$, 59643-28-6; $(Me_2bpy)In_2I_6$, 59643-29-7; In_2I_4, 53140-37-7.

References and Notes

(1) A. J. Carty and D. G. Tuck, *Prog. Inorg. Chem.*, **19**, 245 (1975).
(2) D. G. Tuck, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. Two*, **1**, 311 (1974).
(3) J. G. Contreras, J. S. Poland, and D. G. Tuck, *J. Chem. Soc., Dalton Trans.*, 922 (1973).
(4) A. P. Kotchetkova and O. N. Gilyarov, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **11**, 662 (1966).
(5) M. K. Yang and D. G. Tuck, *J. Chem. Soc. A*, 214 (1971).
(6) M. K. Yang and D. G. Tuck, *J. Chem. Soc. A*, 3100 (1971).
(7) J. B. Headridge and D. Fletcher, *Inorg. Nucl. Chem. Lett.*, **3**, 475 (1967).
(8) B. H. Freeland and D. G. Tuck, *Inorg. Chem.*, **15**, 475 (1976).
(9) L. A. Woodward and M. J. Taylor, *J. Inorg. Nucl. Chem.*, **27**, 737 (1965).
(10) C. A. Evans and M. J. Taylor, *Chem. Commun.*, 1201 (1969).
(11) C. A. Evans, K. H. Tan, S. P. Tapper, and M. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 988 (1973).
(12) K. L. Brown and D. Hall, *J. Chem. Soc., Dalton Trans.*, 1843 (1973).
(13) L. Waterworth and I. J. Worrall, *Inorg. Nucl. Chem. Lett.*, **8**, 123 (1972).
(14) J. H. R. Clarke and R. E. Hester, *Inorg. Chem.*, **8**, 1113 (1969).
(15) J. G. Contreras and D. G. Tuck, *Inorg. Chem.*, **11**, 2967 (1972).
(16) I. Wharf and D. F. Shriver, *Inorg. Chem.*, **8**, 914 (1969).
(17) J. F. Young, *Adv. Inorg. Chem. Radiochem.*, **11**, 92 (1968).
(18) J. G. Contreras and D. G. Tuck, *Inorg. Chem.*, **12**, 2596 (1973).
(19) I. Wharf and D. F. Shriver, *J. Inorg. Nucl. Chem.*, **32**, 1831 (1970).
(20) J. Gislason, M. H. Lloyd, and D. G. Tuck, *Inorg. Chem.*, **10**, 1907 (1971).
(21) J. J. Habeeb and D. G. Tuck, *J. Chem. Soc., Dalton Trans.*, 866 (1976).