Co-ordination Compounds of Indium. Part 38.[1] Complexes of Indium(I) and Indium(III) with Macrocyclic Ligands

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The macrocycles 6,7,9,10,17,18,20,21-octahydrodibenzo[*b,k*][1,4,7,10,13,16]hexaoxacyclo-octadecin (dibenzo-18-crown-6) and 1,4,8,11-tetra-azacyclotetradecane (cyclam) form adducts with InX_2 and InX_3, but not with InX (X = Cl, Br, or I). Vibrational spectroscopy shows that the product In_2X_4L (L = macrocycle) should be formulated as $[InL][InX_4]$. With InX_3 and dibenzo-18-crown-6, the spectra reveal the presence of InX_4^- anions and linear InX_2^+ species, which may be part of either a mononuclear or polynuclear complex cation. The reaction of cyclam and InX_3 yields products formulated as $[In(cyclam)_2][InX_4]_3$.

THE chemistry of the lower oxidation states of indium has been the subject of recent research in this laboratory. For indium(I), both neutral[2] and anionic[3,4] species have been prepared, while for indium(II) the metal–metal bonded $In_2X_6^{2-}$ anions have been characterised,[5] as have a number of apparently analogous neutral compounds such as $In_2I_4{\cdot}2PEt_3$ and $In_2Br_4{\cdot}2(tmen)$[6] (tmen = *NNN'N'*-tetramethylethylenediamine).

Cationic complexes have been proposed in compounds formulated as $[In(aniline)_4]X$ and $[In(morpholine)_2]X$ (X = Cl, Br, or I),[7] and the presence of the indium(I) cation has been presumed in indium dihalides, for which the structure $In^I[InX_4]$ (X = Br or I) has been suggested on the basis of the vibrational spectra.[3] Russian work[8] on the preparation of compounds of the type $In_2I_4{\cdot}2(bipy){\cdot}4NH_2Et$ (bipy = 2,2'-bipyridyl) *etc.* has not unfortunately been followed by definitive structural studies.

We have now investigated the interaction of a variety of indium halides with macrocyclic ligands, in an attempt to stabilise the indium(I) cation by complexation. The only previous work in this area refers to porphyrin species,[9] although there has been a detailed preparative study of the complexes formed by thallium(I) salts and a number of crown ethers.[10] Our work has been concerned with the reactions between the polyether 6,7,9,10,17,18,20,21-octahydrodibenzo[*b,k*][1,4,7,10,13,16]hexaoxacyclo-octadecin (dibenzo-18-crown-6) or the nitrogen donor 1,4,8,11-tetra-azacyclotetradecane (cyclam) with indium mono-, di-, and tri-halides (X = Cl, Br, or I), and certain organoindium halides. The structures of the products, which include the first unambiguous cationic indium(I) species, were elucidated by vibrational spectroscopy.

EXPERIMENTAL

General.—The indium halide and organohalide starting materials were prepared by previously reported methods;[3,11-14] $In[AlCl_4]$, first described by Clark *et al.*,[15] was prepared by refluxing equimolar quantities (typically 10 mmol) of InCl and $AlCl_3$ in mixed xylenes (50 cm³). After 10 h, the insoluble material was removed by filtration, the filtrate evaporated down to 10 cm³, and light petroleum (30 cm³) (b.p. 37–60 °C) added; the resultant solid was collected, washed with light petroleum, and dried (m.p. 268 °C).

Cyclam was prepared by the reaction of 1,3-dibromopropane with ethylenediamine;[16] dibenzo-18-crown-6 (Alfa) was used as supplied. Solvents were dried before use. All operations were carried out under dry nitrogen.

Infrared spectra were recorded on Perkin-Elmer 180 or Beckman IR-12 instruments, and Raman spectra on a Spectra-Physics model 700 spectrometer using argon ion excitation. Hydrogen-1 n.m.r. spectra were recorded on a JEOL C60 HL instrument.

Indium and halogen analyses were performed by methods described earlier.[11] It proved necessary to destroy the compounds by boiling in concentrated H_2SO_4 to ensure complete dissolution.

Preparative.—Equimolar amounts (typically 5 mmol, all species calculated as monomers) of the appropriate indium compound and the macrocyclic ligand were refluxed in benzene (50 cm³). In all cases, signs of reaction were evident after the first 2 h, but experience showed that the materials isolated at this point were not analytically acceptable, so that as a general rule reflux was continued for at least another 10 h, and in some cases for 24 h, after which the resulting suspension was filtered hot and the collected solids washed with 50—100 cm³ of hot benzene. Approximately one half of the original quantity of ligand was recovered from the mother- and wash-liquors. The solid products were dried overnight *in vacuo* at 105 °C. Analytical results are given in Table 1; here and elsewhere, the macrocyclic ligands are abbreviated as ' crown ' and ' cyclam ' respectively. The products are off-white powders except for the In_2I_4–cyclam (red) and In_2Br_4–cyclam (orange) derivatives.

TABLE 1

Analytical results for indium complexes with macrocyclic ligands, expressed as found (calc.)/%

	In	Halogen
$[In(crown)][InCl_4]$	31.9 (31.5)	19.5 (19.4)
$[In(crown)][InBr_4]$	24.7 (25.3)	35.0 (35.2)
$[In(crown)][InI_4]$	20.3 (20.9)	45.9 (46.3)
$[In(crown)][AlCl_4]$	18.0 (17.9)	22.3 (22.0)
$[InCl_2(crown)][InCl_4]$ [a]	28.8 (28.6)	27.5 (26.6)
$[InBr_2(crown)][InBr_4]$	21.0 (21.5)	44.3 (44.9)
$[InI_2(crown)][InI_4]$	16.6 (17.0)	55.8 (56.4)
$[In(CH_3)_2(crown)][InI_4]$	20.9 (20.4)	44.5 (45.1)
$[In(cyclam)][InCl_4]$	40.7 (40.2)	25.0 (24.8)
$[In(cyclam)][InBr_4]$	31.5 (30.7)	43.0 (42.7)
$[In(cyclam)][InI_4]$	24.3 (24.5)	54.7 (54.2)
$[In(cyclam)][AlCl_4]$	22.8 (23.8)	28.9 (29.3)
$In_2Cl_6(cyclam)$ [b]	35.7 (35.8)	33.0 (33.2)
$In_2Br_6(cyclam)$	52.8 (52.7)	25.2 (25.3)
$In_2I_6(cyclam)$	19.4 (19.3)	63.9 (63.7)

[a] Found (calc.): C, 29.3 (29.9); H, 3.2 (3.0)%. [b] Found (calc.): C, 17.9 (18.7); H, 3.9 (3.7); N, 8.5 (8.7)%.

All the compounds are insoluble in aromatic and aliphatic hydrocarbons. Attempts to recrystallise the products from basic solvents (acetone, acetonitrile) or chloroform lead to decomposition, with release of the free ligand (see ^{1}H n.m.r. results below), and the deposition of solids which in the case of the In_2X_4 derivatives were identified as indium(I) halides.

RESULTS AND DISCUSSION

Ligand Complexation.—Before moving to a discussion of the structural assignments, it seems appropriate to review the evidence for complexing by the crown and cyclam ligands in the products isolated.

Three bands in the i.r. spectrum of the free crown ether can be associated with C–O stretching vibrations, namely those at 1 133, 1 262, and 1 236 cm^{-1}. In a typical system, such as In_2I_6(crown) the band at 1 133 cm^{-1} is split into three components at 1 075, 1 108, and 1 138 cm^{-1}, while the remaining pair moves to 1 216 and 1 267 cm^{-1}. Similar features are observed in the other crown ether derivatives. Unfortunately the complexity of the spectrum prevents a detailed analysis of these features. The ^{1}H n.m.r. spectrum ([$^2H_6$]acetone solution) confirms the alteration of the electron density around the oxygen atoms on complexation. The aromatic signal at 6.90 p.p.m. from external $SiMe_4$ in the free ligand shifts to 7.10 p.p.m. upon complexation, while the A_2B_2 multiplet centered at 3.95 p.p.m. appears at 4.25 p.p.m. in the complexes. The pattern of the multiplet does not change as a result of complex formation, suggesting that at least in this solvent either the mode of donation is symmetric, or that the sites of co-ordination are exchanging quickly on the n.m.r. time scale. The spectrum of a freshly prepared solution of a crown ether–indium complex changed within 5—10 min, and the resonance pattern of the free ligand was eventually the only observable feature.

TABLE 2

The vibrational spectra (cm^{-1}) of In_2X_4L and [In(crown)][$AlCl_4$] below 500 cm^{-1} (X = Cl, Br, or I; L = crown or cyclam)

		InX_4^-					
	Cation	$\nu_3(F_2)$		$\nu_1(A_1)$		$\nu_4(F_2)$	Unassigned
Compound	ν(In–L) I.r.	I.r.	Raman	I.r. [a]	Raman	I.r.	I.r.
[In(crown)][$InCl_4$]	351m [b]	297s 312vs 342m			322m	110m 120w	169w
[In(crown)][$InBr_4$]	340w	205s 215vs 220s	230vw	188w	194s	masked	
[In(crown)][InI_4]	336m	184s 193s	188w	135w	139s	60m [c]	75m
[In(crown)][$AlCl_4$]	334w	486vs 494s			357s [d]	135 [d,e]	
[In(cyclam)][$InBr_4$]	403w	242m 230m		190m			
[In(cyclam)][InI_4]		176vs 188s	186w		139s	56w	210w

[a] Breakdown of selection rules by symmetry lower than T_d in the solid. [b] Weak Raman feature at 359 cm^{-1} [c] Medium intensity Raman line at 56 cm^{-1}. [d] Vibrations of $AlCl_4^-$. [e] Raman spectrum.

In the cyclam systems the broad i.r. band at 1 140 cm^{-1}, assigned to a general ' C–N stretching ' mode, does not change appreciably upon co-ordination. Clearer evidence is obtained from the ν(N–H) region of the spectrum, where bands at 3 270 and 3 200 cm^{-1} in free cyclam are shifted to 3 320 and 3 240 cm^{-1} respectively, with a significant increase in intensity. The proton n.m.r. spectrum of cyclam in $CDCl_3$ includes, amongst others, a broad singlet (2.30 p.p.m. from external $SiMe_4$) which disappears in D_2O solution and is therefore assigned to the N–H proton. This resonance sharpens and moves to 2.50 p.p.m. on complex formation; the other resonances are unchanged.

The spectral changes summarised above were detected in all the compounds prepared, and thus confirm the existence of complexes of these ligands. The subsequent discussion focuses on the use of In–X vibrations in the further characterisation of these complexes.

Indium Monohalides.—Repeated attempts at reacting indium monohalides with crown or cyclam were unsuccessful. This is somewhat surprising, given that complexes of thallium(I) with various crown ethers (including dibenzo-18-crown-6) have been reported,[10] and the formation of indium(I) cationic complexes in other work (see below); the low reactivity of indium(I) halides, which has been remarked upon previously, may be at the root of this problem.

Indium Dihalides.—The reactions of InX_2 (X = Cl, Br, or I) with both crown and cyclam lead to compounds of stoicheiometry In_2X_4L. The species most easily identified from the vibrational spectra of these products are the InX_4^- anions (see Table 2), save for the $InCl_2$–cyclam system discussed below. The assignments are readily made on the basis of earlier work on solid state [17] and solution [18-20] spectra. The ν_1 modes are detected in the Raman spectra, which also demonstrate the absence of molecules with an In–In bond. The splitting of ν_3, and the detection of ν_1 as a weak feature of the i.r. spectrum, are ascribed to a lowering of the T_d symmetry in the solid state, and interaction between InX_4^- and the cation may be the cause of this distortion.

The presence of InX_4^- implies the existence of [In(crown)]$^+$ and [In(cyclam)]$^+$ cations, and again the vibrational spectra support this formulation. Indium–oxygen stretching vibrations have been observed in a number of relevant compounds. The band at 444 cm^{-1} in the Raman spectrum of [In(acac)$_3$] (acac = acetylacetonate) has been assigned[21] as ν(In–O), and a similar assignment has been made for an i.r. feature at 454 cm^{-1} in the adducts $InX_3 \cdot 2Et_2O$ (X = Cl or Br),[22,23] for which group theory predicts one i.r.-active mode (A''_2) in D_{3h} symmetry. Similarly, Carty and Patel[24] have identified strong bands between 400 and 460 cm^{-1} in the spectra of a series of In–dmso complexes (dmso = dimethyl sulphoxide) as In–O stretching modes. Table 2 shows that each of the crown ether compounds absorbs in the 340 cm^{-1} region, and we tentatively assign these vibrations as ν(In–O), with reduction in frequency from the values just noted ascribed to the formation of In–O bonds involving the heavy cyclic ligand. This argument is supported by that given below for indium(III) derivatives; the spectra of the latter show that some additional weak features in the spectra of the InX_2–crown products arise from contamination by In_2X_6–crown species.

TABLE 3

The vibrational spectra (cm^{-1}) of In_2X_6L below 500 cm^{-1} (X = Cl, Br,or I; L = crown or cyclam; all combinations)

	Cation						InX_4^-						
	ν(In-L)	ν_{asym}(In-X_2)		ν_{sym}(In-X_2)		δ(InX_2)	$\nu_3(F_2)$		$\nu_1(A_1)$		$\nu_4(F_2)$	Unassigned	
Compound	I.r.	I.r.	Raman	I.r.	Raman	I.r.	I.r.	Raman	I.r. [a]	Raman	I.r.	I.r.	Raman
[$InCl_2$(crown)][$InCl_4$]	masked	406m	405w	masked	332m	190w	334vs 342 (sh)	masked	320 (sh)	322m	114m	90w	
[$InBr_2$(crown)][$InBr_4$]	316m 346w	307m		206vw	206m	164vw	228s 235s	230w	194w	196s	80w		
[InI_2(crown)][InI_4]	340w [b]	256w	260w	148w	150s		184vs 194s	188w	136w	138s	58m [c]		
In_2Cl_6(cyclam) [d]	410w						336vs 342s				122m	286m 250w	
In_2Br_6(cyclam)	404w			206w	206w		229 (sh) 236vs 243 (sh)	236vw	190m	194w	80w	90w	118w 110w
In_2I_6(cyclam)	397m						178s 185s 192s	188m	148m	139s		360w	

[a] Breakdown of selection rules by symmetry lower than T_d in the solid. [b] Weak Raman feature at 320 cm^{-1}. [c] Medium intensity Raman counterpart at 57 cm^{-1}. [d] Sample strongly fluorescent; Raman results not available.

For the cyclam systems, the most relevant vibrational spectrum is for the dimer [{$InMe_2(NMe_2)$}$_2$], for which a series of bands in the range 420—490 cm^{-1} are assigned to In–N stretching modes in the In_2N_2 ring.[25] We have found similar absorptions in In–tmen complexes. Tables 2 and 3 show that the cyclam derivatives have weak absorptions at 397—400 cm^{-1}, which by the argument given above for crown complexes can reasonably be identified as In–N stretching modes.

Since the complexes decompose in solution, we were unable to measure the molar conductivity, or to prepare salts of InL$^+$ with large anions by way of structural confirmation. We did however carry out the reaction between In[$AlCl_4$] and crown to obtain a compound with the indium-free anion $AlCl_4^-$, whose vibrational spectrum is clearly observed (see Table 2 and ref. 26). The corresponding cyclam analogue could not be isolated, since decomposition with evolution of HCl was evident during the reaction; the disappearance of the N–H stretching features and other skeletal changes in the i.r. spectrum of cyclam were also observed. The spectral results then are consistent with the formulation of these compounds as salts of [In(crown)]$^+$ and [In(cyclam)]$^+$ cations, which are the first examples of indium(I) cationic complexes. One exception to this conclusion is the product of the reaction between $InCl_2$ and cyclam; the analytical results for this compound do not fit the [In(cyclam)][$InCl_4$] formulation particularly well, and the grey appearance is similar to that often associated in this laboratory with the presence of indium metal, implying disproportionation of indium(II). The identification of [In(crown)]$^+$ in the ether complexes is supported by the work of Herber and Smelkinson,[27] who prepared tin(II) derivatives of dibenzo-18-crown-6 and 18-crown-6 and confirmed the presence of complexed Sn^{2+} cation by means of Mössbauer spectroscopy.

Indium Trihalides.—The products of the reaction between indium(III) halides and crown or cyclam are a group of 'In_2X_6L' species. The presence of the InX_4^- anion is again evident from the vibrational spectra (Table 3) of the crown ether derivatives, leading to the formulation [InX_2L][InX_4]. A number of related structures have been suggested for indium(III) halide adducts.[9] The $\nu_1(A_1)$, $\nu_3(F_2)$, and $\nu_4(F_2)$ modes of the InX_4^- anion were observed in each case; splitting of ν_3 occurs, but is less pronounced than in the In_2X_4 series. There is a sharp distinction between the crown ether and cyclam complexes of InX_3, in that the spectra imply a completely different structure for the latter (see below).

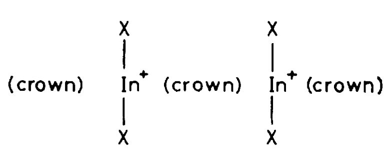
The structure of the cationic moiety is more difficult to determine, but the vibrational spectra give some guidance. We first note that bands observed at *ca.* 330 cm^{-1} in the crown complexes are tentatively assigned as ν(In–O), following the argument above for the indium(I) species, showing that there is little change in this frequency with oxidation state. The ν(In–X) bands are more informative. Group theory predicts one In–X stretching mode in the i.r. if the X–In–X moiety is linear, with a non-coincident Raman mode, while two bands are expected in each case for a bent InX_2 skeleton. The better fit to the spectral results is obtained with the second possibility. Raman modes at 150 and 206 cm^{-1} are observed for the I– and Br–crown systems respectively, with weak coincident i.r. features. The spectra of ' In_2Cl_6(crown) ' are less easily assigned, since the relevant frequency range is overlapped by ν(In–O) and by ν_3 of $InCl_4^-$, but a Raman band at 332 cm^{-1} is reasonably attributed to ν_{sym}(In–Cl) of $[InCl_2(crown)]^+$. The i.r. spectra show bands at 256, 307, and 406 cm^{-1} for I, Br, and Cl species respectively, assigned to ν_{asym}(In–X). The corresponding Raman emissions are weak, but quite detectable in the iodide case. It is noteworthy that the i.r. spectra also have bands attributable to the bending modes of InX_2 (Table 3). The large frequency separation between the symmetric and antisymmetric stretching modes, together with the weak intensity of the ν_{sym}(In–X) bands in the i.r., and of ν_{asym}(In–X) in the Raman, suggests that the $X–In–X^+$ unit may be close to linear in the solid state. The breakdown of the mutual exclusion rule for a linear MX_2 species may be the result of interactions between anion and cation in the solid state, in keeping with the splitting observed for the ν_3 vibration of the InX_4^- anion. Before discussing the structural implications of a linear $X–In–X^+$ unit, it is worth noting the close similarity between the frequencies assigned above, and the corresponding values for the iso-electronic CdX_2 molecules. Raman studies [28] of CdX_2 in solution lead to identification of ν_1 for the linear, solvated species, while the i.r. spectra [29] of CdX_2 molecules in the gas phase lead to values for ν_{asym}(Cd–X). The difference in phase raises some questions, but the comparison between these results and the present values is striking (see Table 4).

TABLE 4

Comparison of i.r. frequencies (cm^{-1}) for CdX_2 and InX_2^+

	CdX_2			InX_2^+		
	ν_{sym}	ν_{asym}	mean	ν_{sym}	ν_{asym}	mean
Cl	280	427	353	332	406	369
Br	186	315	250	206	407	257
I	144	265	205	150	256	203

In the light of this evidence, we believe the existence of linear $X–In–X^+$ units is well established. There are



then two structural formulations, either a mononuclear $[InX_2(crown)]^+$ species with *trans* halogeno-ligands, or a polymeric structure of the type shown above in which each In is co-ordinated by one or more O atoms from each of two crown ether molecules. Earlier work [30] on the co-ordination number of indium(III) suggests that a InX_2O_4 kernel is likely, requiring the donation from two pairs of oxygen atoms. The available evidence does not allow a clear choice to be made between the two proposed structures at the present time.

The results in Table 3 for the InX_3–cyclam systems do not lead to an analysis such as that given for the crown ether complexes. There are no In–X stretching modes other than those assignable to anionic indium(III) complexes, with the exception of a weak band at 206 cm^{-1} in the case of the bromide. The simplest explanation of these results is that the cyclam is a sufficiently strong ligand to displace halide completely from In^{3+}. The stoicheiometry of the products then requires the solid state to be $[In(cyclam)_2]^{3+} + 3InX_4^-$, with indium probably six-co-ordinate in the cation (*cf.* ref. 30). Further work on this problem is planned.

Organoindium(III) *Halides*.—In view of previous interest in the acceptor properties of organoindium(III) halides [13,14] we have briefly investigated the interaction of $In(CH_3)Cl_2$ and $In(CH_3)I_2$ with crown and cyclam. In the case of the latter ligand, it was not possible to identify the reaction products on the basis of the analytical results. The best characterised product has the stoicheiometry $In_2(CH_3)_2I_4$(crown), and in view of the structure of the starting material,[13] $[In(CH_3)_2][InI_4]$, and the work described above, the formulation $[In(CH_3)_2(crown)][InI_4]$ appeared most probable. In fact, the spectrum of this material below 500 cm^{-1} (and of the corresponding chloride analogue) clearly reveals the presence of the $In(CH_3)X_3^-$ anion, whose electrochemical preparation was recently reported [31] (See Table 5 for details). At the same time, a strong band at 184 cm^{-1} indicates that InI_4^- anions are also present. The ^1H n.m.r. spectrum equally identifies $In(CH_3)I_3^-$, and indicates the presence of a second $In–CH_3$ species in the solution. Finally, the presence of InX_4^- (X = Cl or I) in acetonitrile solution was confirmed by ^{115}In n.m.r. spectroscopy, with chemical shifts of 2 and 1 003 p.p.m. respectively from $[NBu_4][InCl_4]$; these values are identical within experimental error with those found for

TABLE 5

Hydrogen-1 n.m.r. and i.r. spectral data for some organoindium derivatives of dibenzo-18-crown-6

	^1H N.m.r. [a]	I.r. (cm^{-1})
$In_2(CH_3)_2I_4$(crown)	0.67 (s, 3 H), 0.60 (s, 3 H)	501m, 197s, 184s, 166s, 150m
$[NBu_4][In(CH_3)I_3]$ [b]	0.67 (s, 3 H)	496s, 165vs, 152m
$In(CH_3)Cl_2$(crown) [c]	0.20 (s), 0.07 (s) [d]	512m, 329, 294vs,br, 208m, 120s
$[NEt_4][In(CH_3)Cl_3]$	0.07 (s)	522s, 290vs,br, 206m, 120s

[a] All resonances in $[^2H_6]$acetone, in p.p.m. downfield from external $SiMe_4$. [b] Material made from $In(CH_3)I_2$ and $[NBu_4]I$. [c] Material not characterised by analysis. [d] Intensity of the signals varies after *ca.* 5 min.

authentic samples of $InCl_4^-$ and InI_4^- (see ref. 1 for details). From this evidence, it appears that we are dealing with a mixture of $[In(CH_3)_2(crown)][InI_4]$ and $[In(CH_3)I(crown)][In(CH_3)I_3]$ in both solid and solution phases. Attempts to separate the components were unsuccessful, and redistribution of ligands appears to occur rapidly in solution.

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