MIXED HALO/HEXAMETHYLPHOSPHORAMIDE COMPLEXES OF INDIUM(III). ¹¹⁵In, ³¹P, ¹⁹F AND ¹H NMR STUDIES OF INDIUM(III) SPECIES IN HEXAMETHYLPHOSPHORAMIDE SOLUTION. X-RAY STRUCTURE OF *TRANS*-DIIODOTETRAKIS(HEXAMETHYLPHOSPHORAMIDE)INDIUM(III) IODIDE

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Abstract—¹¹⁵In NMR studies are reported for InX_3 (X = Cl, Br, I) solutions in hexamethylphosphoramide (HMPA). The resonances of InX_4^- anions are observed for tribromide and triiodide solutions. Mixed $InBr_{4-n}I_n^-$ anions may be obtained for the mixtures of InI_3 and $InBr_3$. A trigonal-bipyramidal complex, $InCl_3(HMPA)_2$, is formed from $InCl_3^-$ HMPA solutions. Diiodotetrakis(hexamethylphosphoramide)indium(III) iodide has been prepared from an InI_3 -HMPA system and fully characterized by elemental analysis, IR and NMR spectroscopy and X-ray crystallography. The cation is *trans*-octahedral. ¹⁹F NMR spectra of $In(NO_3)_3$ -F⁻-HMPA systems demonstrate the formation of sixcoordinate mixed $InF_n(HMPA)_m(H_2O)_{6-n-m}^{3-n}$ species.

The high donor number ($DN_{SbCl_s} = 38.8$) of hexamethylphosphoramide (HMPA) makes it a strong ionizing solvent. Besides this, the shape and dimensions of the HMPA molecule cause different steric interactions in the adducts solvated by it and so complexes with unusual stereochemistry may be formed.

The coordination chemistry of indium(III) halide compounds with HMPA has not been studied intensively. There are no data on solution chemistry of indium species in HMPA and only two works are devoted to the solid-state chemistry of indium adducts with HMPA.^{2.3} When studying coordination compounds of aminophosphine oxides Bolster obtained a number of indium(III) halide adducts with HMPA-InX₃(HMPA)₂ (X = Cl⁻, Br⁻, I⁻).² Based on the data of vibrational spectroscopy Bolster proposed a dimeric structure for these compounds, $[InX_2(HMPA)_4]^+[InX_4]^-$ with *trans*-geometry of the cation. Later, a chloride complex with the same composition was characterized by X-ray crystallography.³ Indium was shown to be in a trigonal-bipyramidal arrangement with hexamethylphosphoramide molecules in axial positions and three chloride ions in equatorial positions.

The present paper concerns the investigation of a number of complexes formed from InX_3 -HMPA (X = Cl⁻, Br⁻, I⁻) and $In(NO_3)_3$ -F⁻-HMPA-H₂O systems, both in solution and in the solid state, and also continues the consideration of the stereochemical aspects and mutual influence of ligands in mixed halo species of indium(III).

EXPERIMENTAL

Materials

Indium trichloride was prepared by chlorination of indium(III) oxide with CCl₄ at *ca* 450°C. Indium triiodide was obtained according to the literature procedures.^{4,5} (C₄H₉)₄NInX₄ salts were prepared as insoluble precipitates when mixing aqueous solutions of InX₃ and (C₄H₉)₄NX and their subsequent

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recrystallization was achieved from acetonitrile followed by drying *in vacuo*. Indium trinitrate was obtained by dissolving indium(III) oxide of a stoichiometric quantity of nitric acid.

The salts of $InBr_3$, $InF_3 \cdot 3H_2O$, NH_4F and $(CH_3)_4NF$ were obtained from commercial sources without further purification.

Hexamethylphosphoramide was rigorously dried and distilled by standard methods and was used as a solvent for preparing the solutions. All operations with InX_3 (X = Cl⁻, Br⁻, I⁻) salts and HMPA were performed under nitrogen.

Preparation of the compounds

X-ray quality crystals of I and II were grown by slow evaporation of $InCl_3$ and InI_3 solutions, respectively, in HMPA in a vacuum desiccator. The crystals were washed with a small amount of CCl_4 to remove the excess HMPA. The crystals of both I and II are colourless and transparent. The crystals of II are very unstable and completely decompose in air in a few minutes.

Spectra

IR spectra of samples I and II were run on a Specord 715 IR spectrometer between 400 and 4000 cm⁻¹. ¹¹⁵In, ³¹P, ¹⁹F and ¹H NMR spectra were obtained with a Bruker AC-200 P spectrometer. All samples were run as solutions. The main experimental conditions are given in Table 1.

X-ray structure determinations

An Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo- K_{α} radiation was used for structure determinations.

The unit cell parameters of crystals of I indicated absolute similarity with the penta-coordinated complex $InCl_3(HMPA)_2$ described in ref. 3.

For preserving, a single crystal of **II** was cemented to a glass fibre and mounted into a sealed Pyrex capillary (under nitrogen) and was then examined on a diffractometer. Data were collected at 200(2) K for $2\theta_{max} = 50^{\circ}$. The crystals of II belong to the triclinic space group $P\overline{I}$. The unit cell parameters and other crystal data for II are: a = 14.053(3), b = 17.621(3), c = 20.920(4) Å; $\alpha = 73.89(1)$, $\beta = 89.25(2)$, $\gamma = 80.05(2)^{\circ}$; V = 4899(2) Å³; Z = 4, $\mu = 25.1$ cm⁻¹. A total of 8104 independent reflections were measured, of which 6213 with $I \ge 2\sigma$ were used for calculation.

The positions of indium and iodine atoms were derived from the heavy-atom procedure; the positions of the remaining non-hydrogen atoms were revealed by a sequence of the difference-Fourier syntheses. The coordinates of the hydrogen atoms were determined for geometrically idealized positions (C—H, 1 Å). Block-diagonal least-squares anisotropic refinement for all non-hydrogen atoms (866 refined parameters) with regard to the hydrogen atoms ($U_{eq} = 0.06 \text{ Å}^2$) converged to values of R = 0.057, $R_w = 0.056$, GOOF = 1.97, $w = (\sigma^2(F_0) + 0.0001F_0^2)^{-1}$.

RESULTS AND DISCUSSION

The ¹¹⁵In NMR spectra of InX₃ (X = Br⁻, I⁻) solutions in HMPA show bands almost identical in frequencies to those found for the corresponding InX_{4}^{-} anions (Table 2). A similar situation has been observed when dealing with acetonitrile solutions of indium trihalides also displaying resonances of InX_4^- (X = Cl⁻, Br⁻, I⁻) species (Table 2).⁶ This was interpreted as being a result of a disproportionation reaction which leads to mixed sixcoordinate cationic complexes that share the same anion InX_4^- . As for acetonitrile solutions, no bands for the cationic complexes were observed for InX_{3} -HMPA systems. It seems reasonable that lowering of the symmetry of the cations causes large quadrupole broadening⁷ and thus they are undetectable in ¹¹⁵In NMR. Therefore, it might be assumed that the balance between the ionic charges of the species in solutions of HMPA is reached by forming only unsymmetrical InX_n (HMPA) $_{6-n}^{(3-n)+}$ $(X = Br^{-}, I^{-}; n = 1, 2)$ cationic species because $In(HMPA)_{6}^{3+}$ could be detected as $In(H_2O)_{6}^{3+}$.⁸

Table 1. Experimental conditions of running NMR spectra

	'H	¹⁹ F	³¹ P	¹¹⁵ In
Frequence (MHz)	200.00	188.31	81.01	43.86
Lock	(CD ₃) ₂ CO	(CD ₃) ₂ CO	(CD ₃) ₂ CO	D ₂ O
Tube (o.d.)	5	5	5	10
Standard	(CH ₃) ₄ Si	SiF ₆ ²⁻	H ₃ PO ₄	(C ₄ H ₉) ₄ NInCl ₄
Temperature (K)	298	253-298	298	298

		δ (ppm) ($\Delta H_{1/2}$, Hz)	
x	HMPA InX ₃	InX ⁶ ₃	$\frac{CH_{3}CN}{[(C_{4}H_{9})_{4}N]InX_{4}^{6}}$	RInX ^{7,a}
Cl		8 (1300)	0 (290)	0±2 (310)
Br	-279(1500)	-254 (580)	-261(220)	-258 (180)
I	-1021 (730)	- 999 (430)	-1007 (240)	-989 (250)

Table 2. ¹¹⁵In NMR resonances in HMPA solution of indium salts (0.1 M)

" $R = (C_6H_5)_4P$ for $InCl_4^-$ and $InBr_4^-$; $(C_4H_9)_4N$ for InI_4^- .

The formation of InX_4^- anions in InX_3 -HMPA (X = Br⁻, I⁻) systems allowed us to obtain InBr_nI_{4-n} species when mixing InBr₃ and InI₃ solutions. The case of an equimolar mixture of InBr₃ and InI₃ solutions illustrates well these findings; the spectrum consists of five distinct lines with chemical shifts (-278, -439, -619, -813 and -1018 ppm) corresponding to the ¹¹⁵In NMR frequencies in InBr_nI_{4-n} anions.^{6,7}

In view of the much better electron donor properties of HMPA compared with acetonitrile $(DN_{SbCl_s} = 38.8 \text{ and } 14.1, \text{ respectively})$ it is somewhat surprising that no ¹¹⁵In NMR resonances are observed for InCl₃ solutions in HMPA in contrast to CH₃CN (Table 2). It is apparent that, in this case, interaction between indium trichloride and the solvent does not lead to salt disproportionation to $InCl_n(HMPA)_{6-n}^{(3-n)+}$ and $InCl_4^-$ complex ions. We can assume that some uncharged mixed InCl₃(HMPA)_n solvates, with thermodynamic stabilities appreciably greater than the ionic complexes, are formed. Taking into account the tendency of indium(III) to form complexes with high coordination numbers with oxygen-donor ligands species with n = 2 and 3 seem to be preferred.

This was indeed confirmed when compound I was prepared from InCl₃-HMPA solution. Elemental analyses (Table 3), IR spectrum and X-ray diffraction of sample I indicated it to be the penta-coordinated complex trans-InCl₃(HMPA)₂.³ Thus, in spite of the difference in preparative techniques (ours and ref. 3) only one product from the interaction of InCl3 and HMPA is formed. Usually small changes in preparative conditions cause the formation of different products because of the lability complexes. The case of indium(III) of $InCl_3(HMPA)_2$ is an exception to this rule. The trigonal-bipyramidal arrangement of ligands with three halide atoms in equatorial positions is not rare for indium(III) chemistry. Compounds with this type of structure InX_3L_2 , where $L = (CH_3)_3 N_5^9 (CH_3)_4 N_2 CO_{10} \{ (CH_3)_2 N \}_3 PO_{10}^3$ (CH₃)₄N₂CS,¹⁰ (CH₃)₃PS, (CH₃)₃AsS,¹¹ (CH₃)₃P,

 $Ph_2P(CH_2)_2PPh_2^{12}$ and $(C_6H_5)_3P_1^{13}$ are known. Among a total of 11 complexes, eight are chlorides. Moreover, a comparison of the bond lengths between indium and atoms in the axial positions for complexes with different X indicates that the distances for chloride species are significantly shorter. Considering all these facts we must assume that $InCl_3L_2$ species are more stable compared with other halides, which can circumstantially explain the formation of $InX_3(HMPA)_2$ only for the $InCl_3-$ HMPA system.

¹¹⁵In NMR resonances of InX_4^- species for indium tribromide and triiodide solutions in HMPA, together with the data indicating an ionic dimeric structure of $InX_3(HMPA)_2$ adducts,² led us to expect the formation of $[InX_2(HMPA)_4]^+$ $[InX_4]^-$ complexes from InX_3 -HMPA (X = Br⁻, I⁻) systems.

No crystal phase was yielded from InBr₃ solution in HMPA due to glass formation.

Crystals of **II** were obtained from the InI_{3^-} HMPA system. Table 3 indicates that the elemental analysis of this compound differs from that expected for $InI_3(HMPA)_2$.

The IR spectrum of sample II contains characteristic bands due to coordinated HMPA molecules and indicates that coordination occurs via the oxygen atom (Table 4).^{2,3}

The structure of **II** involves the complex cations $[InI_2(OP\{N(CH_3)_2\}_3)_4]^+$ and I^- anions. The two crystallographically independent cations (a and b) have the same configuration, which is illustrated in Fig. 1. The indium atoms are hexa-coordinated to four HMPA molecules via oxygen and to two *trans*-

Table 3. Elemental analysis of samples I and II

	$InCl_3(HMPA)_2$ (I)		InI ₃ (HMPA) ₄ (II)	
	Found	Calc.	Found	Calc.
N	14.1	14.5	13.2	13.9
С	25.3	24.9	23.9	23.8
Н	5.7	6.3	6.0	5.9

	Species	Frequency $(cm^{-1})^a$		
Mode description		HMPA, liquid	$InI_3(HMPA)_4$	
PO stretch	a_1	1218	1190	
PN stretch	a_1	740	740	
PN stretch	e	982	980	
PO bend	е	481	475	
CN stretch	<i>a</i> ″	1150, 1174	1130	

Table 4. IR spectral data

arranged iodine atoms in an octahedral geometry (Fig. 1, Table 5). The packing of **II** is extraordinarily loose; for one non-hydrogen atom there is a value of 25.5 Å³. The shortest contacts are $I \cdots I = 7.20$, $I \cdots C = 3.45$, $C \cdots C = 3.45$ Å.

Careful analyses of the solid phase from InI_{3} -HMPA solution demonstrates that compound II is the only product formed in this system. We can, therefore, conclude that despite the unequivocal formation of the InI_{4} anion in solution the balance between the ionic charges in the solid is reached by iodide ions which are displaced by HMPA molecules from the inner coordination shell of indium.

To date all known ionic structures containing the six-coordinate indium cation $InX_2L_4^+$, where $L = Me_3PO$ for $X = Cl^-$, Br^- ; Ph_2MePO for $X = Br^-$; Ph_3PO for $X = Cl^-$, Br^- ; Ph_3AsO for $X = Cl^{-14}$ and Me_2SO for X = I, ¹⁵ have InX_4^-

species as an anion and thus compound II is the first example of mixed indium(III) complexes containing an acido ligand in the outer coordination sphere.

Previous authors¹⁴ have tried to analyse reasons for the appearance of ionic structures and assumed preferential formation of ionic derivatives by a heavier halogen and the structure of $InI_3(HMPA)_4$ verifies this assumption.

One more interesting feature of the structure of $InI_3(HMPA)_4$ is the *trans* configuration of the cation. Recently we analysed the stereochemical features of pseudo-octahedral complexes of indium(III) halides.¹⁶ Both VSEPR (valence-shell electron-pair repulsion)¹⁷ and electronic-vibrational¹⁸ concepts predict stabilization of the *trans* isomer for InX_2L_4 species when the difference between the electronegativity and geometrical parameters of donor atoms X and L are significant.



Fig. 1. The $[InI_2(OP{N(CH_3)_2}_3)_4]^+$ cation of II.

Table 5. Selected bond lengths (Å) and angles (°) for complex cations of II

		willieule 0
In—I(1)	2.812(2)	2.794(2)
In-I(2)	2.811(2)	2.803(2)
In—O(1)	2.16(1)	2.15(1)
In	2.18(1)	2.17(1)
In—O(3)	2.16(2)	2.16(1)
In	2.09(2)	2.14(1)
I(1)—In—I(2)	179.71(9)	179.19(8)
I(1)—In— $O(1)$	89.1(4)	90.5(4)
I(1) - In - O(2)	89.2(4)	90.1(4)
I(1)—In—O(3)	88.9(4)	89.2(4)
I(1)—In—O(4)	91.0(4)	88.0(4)
I(2)—In— $O(1)$	90.8(4)	89.6(4)
I(2)—In— $O(2)$	90.8(4)	89.8(4)
I(2)—In—O(3)	90.8(4)	91.6(4)
I(2)—In—O(4)	89.2(4)	91.2(4)
O(1)—In— $O(2)$	178.1(5)	179.3(5)
O(1) - In - O(3)	88.2(5)	90.1(5)
O(1)—In— $O(4)$	90.1(5)	90.8(5)
O(2)—In— $O(3)$	92.6(5)	89.6(5)
O(2)—In—O(4)	89.1(5)	89.5(5)
O(3)—In—O(4)	178.3(6)	177.1(5)
In— $O(1)$ — $P(1)$	169.2(9)	159.3(9)
In-O(2)-P(2)	161.1(9)	166.2(9)
In-O(3)-P(3)	167(1)	162.6(9)
In— $O(4)$ — $P(4)$	163(1)	161.2(9)

According to these approaches the arrangement of iodide ions in $[InI_2(HMPA)_4]^+$ should also be *trans*. It should, however, be noted that the same composition of donor atoms in the coordination sphere (I and O) gives the *cis* isomer for the cation in $[InI_2]$ $(Me_2SO)_4]^+[InI_4]^{-1.5}$ Authors¹⁹ have assumed the dominant role of steric effects of ligands. Calculations of the steric angles of donor iodine and oxygen atoms (based on average bond lengths In-I 2.80 and In—O 2.18 Å) give values of 91° and 80° . respectively. Sums of the steric angles show that the trans isomer is destabilized since two of three octahedral planes, in contrast to one for cis, contain the larger iodine atoms. In-I and In-O distances in $[InI_2(HMPA)_4]^+$ (Table 5) are almost the same and so the values of the steric angles are equal, but the configuration is trans nevertheless. There seems to be two reasons influencing the geometry of the cation, notably (1) that the stabilization of the isomer is a function of the anion present in the lattice $(I^- \text{ or } InI_4^-)$ and (2) that, as was pointed out in ref. 19, steric stabilization of the cis species may disappear for bulky ligands where L-L non-bonded repulsions become predominant and trans-ML₂X₄ species may become favoured. HMPA should be undoubtedly considered as a bulky ligand due to the downwards-spreading umbrella geometry of the ${(CH_3)_2N}_3PO$ molecule, which invalidates the above arguments by producing an effective steric angle greater than that of the monatomic donor.

The arrangement of four bulky HMPA molecules in one plane and thus the contribution to the cation stability is enabled by an increase in the P—O—In angles, to *ca* 164° in InI₂(HMPA)₄⁺ compared with 153° for InCl₃(HMPA)₂.³ This oxygen angle value is the greatest for known oxo ligands coordinated to indium and even larger than that for *trans*-[InCl₂(Ph₃PO)₄]⁺ (160°) with a ligand as large as triphenylphosphine oxide,¹⁴ which indicates the more ionic nature of the indium–oxygen linkage in the adduct with HMPA.

The last assumption can be circumstantially confirmed by ¹H and ³¹P NMR values. The coordination of HMPA molecules to indium [benzene solution of InI₃(HMPA)₄ was analysed] causes a small high-field shift of the NMR lines of both ¹H [1.38 ppm, J(H-H) = 9.5 Hz compared with 1.44 ppm and 9.3 Hz, respectively, for HMPA-C₆H₆ solution] and ³¹P (22.86 ppm compared to 24.49 ppm for HMPA-C₆H₆ solution). This sharply contrasts with ³¹P lines of phosphine oxide¹⁴ and phosphate²⁰ molecules in indium complexes, which are usually shifted downfield by *ca* 5–13 ppm.

In a number of recent papers concerning complex fluorides of group III(13) metals—aluminium, gallium and indium—with various O- and N-donor molecular ligands we have suggested some relation between shielding of the ¹⁹F nucleus and the electronegativity of an atom in the *trans* position to fluorine.^{21,22} It has been shown that oxygen causes greater transfer of electron density than nitrogen from the ligand donor atom through metal to fluorine, leading to a high-field shift. A similar situation seems to be observed for $InI_3(HMPA)_4$ because the complex cation comprises oxygen atoms in O—In—O fragments, which results in a strong *trans* effect and an increase in electron density on all atoms of the HMPA molecule.

Regarding ³¹P NMR spectroscopy of indium complexes it should be noted that in contrast to aluminium, for which $Al(HMPA)_4^{3+}$ displays a sharp quintet by ²⁷Al NMR and a sextet for ³¹P showing clear evidence for a tetrahedral arrangement of four HMPA ligands around Al^{3+} , ²³ it is not possible to observe couplings between ¹¹⁵In and ³¹P nuclei. Line broadening must be attributed in the first place to quadrupolar relaxation of the metallic nucleus and then to the low symmetry of the complex.

We have not managed to prepare adducts of InF_3 with HMPA due to the insolubility of $InF_3 \cdot 3H_2O$ in this solvent. In spite of this some interesting information about indium complexes with such ligands as F^- and HMPA may be obtained when investigating the $In(NO_3)_3-F^-(NH_4F,$ $(CH_3)_4NF)$ -HMPA-H₂O systems using ¹⁹F NMR spectroscopy.

Fast exchange between various indium fluoride species slowed down only at ca 258 K, allowing the observation of the separate ¹⁹F lines (40-80 Hz) of individual complexes. Varying the HMPA/In(NO₃)₃ molar ratio over the range 6-10 when $F^{-}/In(NO_3)_3$ was kept close to 1 allowed us to detect eight resonances of mixed-fluoro/HMPA/aqua species. We have no direct evidence for the coordination number of indium in these complexes, but the number of bands observed together with the results we obtained when dealing with ¹⁹F NMR spectra of $In^{3+}-F^{-}-L-H_2O$ [L = Cl⁻, Br⁻, I⁻, NCO⁻, NCS^{-} ,²⁴ (NH₂)₂CO, NH₂CH₃CO, (NH₂)₂CS and $NH_2CH_3CS^{25}$] systems allowed us to consider the interval of chemical shifts (-150 to -175 ppm)corresponding to the six-coordinate species. The assignment of lines (Table 6) was performed in accordance with both the tendency of the ligands to cause deshielding of ¹⁹F nuclei in the complex and the dependence of the integration curves on HMPA concentration. Chemical shifts (δ) of the complexes show the additivity of δ when substituting water molecules in $InF_n(H_2O)_{6-n}^{3-n}$ by HMPA (ca 2.5 ppm per substitution). The corresponding values for acido ligands (17, Cl⁻; 15, Br⁻; 7, NCS⁻) are significantly higher and demonstrate a stronger influence of ionic ligands compared with neutral molecules on coordinated fluoride.

The consideration of interactions of various indium halide salts with hexamethylphosphoramide leads to several conclusions, notably: HMPA molecules can be combined with atoms of all halides (from F to I) in the coordination sphere of indium(III).

The coordination numbers of indium in mixedhalide complexes with HMPA differ. The same pre-

Table 6. ¹⁹F resonances for mixed InF_n(HMPA)_m(H₂O)³⁻ⁿ_{6-n-m} species in aqueous solution

Complex	$-\delta$ (ppm)
InF(HMPA)(H ₂ O) ₄ ²⁺	174.2
$InF(HMPA)_{2}(H_{2}O)_{3}^{2+}$	171.4
$InF(HMPA)_{3}(H_{2}O)_{2}^{2+}$	169.2
InF(HMPA) ₄ (H ₂ O) ²⁺	167.0
$InF(HMPA)_{5}^{2+}$	164.7
$InF_{2}(HMPA)(H_{2}O)_{3}^{+}$	163.6
$InF_{2}(HMPA)_{2}(H_{2}O)_{2}^{+}$	160.6
$InF_2(HMPA)_3(H_2O)^+$	157.3

parative technique leads to five-coordinate chloride species, whereas the coordination number for the iodide complex cation is six. This result is rather unexpected because the opposite situation should be more likely. The reasons for the preference of trigonal-bipyramidal chloride structure has been discussed earlier. It can be assumed that the formation of similar iodide species is hindered by the arrangement of three large iodine atoms in the equatorial plane. The systematic discussion of this observation needs more structural information and quantitative thermodynamic data on mixed indium complexes. Work on this is proceeding.

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