

1160. Co-ordination Compounds of Indium. Part I. Some Cationic Complexes of Indium(III).

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Indium(III) perchlorate hydrate reacts with a variety of donor ligands to give products containing perchlorate anion and a complex cation. The complexes are formulated as six-co-ordinate species when the donor ligand is 2,2'-bipyridyl, 1,10-phenanthroline, ethylenediamine, 2,2',2''-terpyridyl, urea, dimethyl sulphoxide, *NN*-dimethylacetamide, and thiourea, but are four-co-ordinate with triphenylphosphine, triphenylarsine, triphenylphosphine oxide, and 1,2-bis(diphenylphosphino)ethane. Possible reasons for the existence of two series of complexes are discussed.

In the III oxidation state, indium may have co-ordination numbers of either four or six.¹ The present paper is concerned with the preparation of cationic indium(III) complexes, and with the co-ordination number of the metal in such species; anionic halide complexes are discussed in Part II.²

There are a number of neutral indium(III) complexes, of which $\text{In X}_3 \text{py}_3$ ($\text{X} = \text{Cl, Br}$; $\text{py} = \text{pyridine}$ ³) is typical, and chelated species such as the trisacetylacetonate⁴ and trisoxinate⁵ are known, but comparatively little work has been done on cationic complexes. Sutton⁶ has reported the preparation of $[\text{In en}_3]\text{Cl}_3$ and $[\text{In en}_2\text{Cl}_2]\text{Cl}$ ($\text{en} = \text{ethylenediamine}$), and the corresponding six-co-ordinate compounds with 1,10-phenanthroline and 2,2'-bipyridyl. In addition, there is evidence of the complexing of the In^{3+} cation in aqueous solution, which involves displacement of water from the first hydration sphere of the cation.

The solid that crystallises from a perchloric acid solution of indium(III) is $\text{In}(\text{ClO}_4)_3 \cdot 8\text{H}_2\text{O}$ and, since the cationic species in dilute perchloric acid⁷ is $[\text{In}(\text{H}_2\text{O})_6]^{3+}$, the solid is presumably $[\text{In}(\text{H}_2\text{O})_6](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$. We have used this as the starting material for the preparation of salts, in which the perchlorate is anionic (as shown by their infrared spectra), and In^{3+} is complexed by various donor ligands. Since the perchlorate is non-ligating in these compounds, the co-ordination number follows from the stoicheiometry. The most important features of these complexes are discussed in terms of the donor atom concerned.

Nitrogen Donors.—With bipyridyl, 1,10-phenanthroline, and ethylenediamine, the reaction of indium perchlorate with ligand in a polar non-aqueous solvent (*e.g.* ethanol) gave products of the type $[\text{In}(\text{bipy})_3](\text{ClO}_4)_3$. Infrared measurements showed in each case (and with all the compounds subsequently discussed) that the perchlorate absorption is a single strong band centred at 1100 cm.^{-1} , characteristic of ionic perchlorate; no band at 920 cm.^{-1} , associated with ligand perchlorate,⁸ or splitting of the main 1100 cm.^{-1} band, was observed.

Changes were observed in the infrared spectra of the ligand when it was complexed with In^{3+} . Thus with 2,2'-bipyridyl, the 760 cm.^{-1} band (out-of-plane bending of C-H bonds) is higher by $10\text{--}15 \text{ cm.}^{-1}$, and medium bands at 1585 and 1610 replace those at 1558 and 1600 cm.^{-1} in the pure ligand; in addition, a new band of medium strength appears at 1540 cm.^{-1} . Similar changes have been reported for other bipyridyl complexes.⁹ In the phenanthroline complex, little change ($\sim 5 \text{ cm.}^{-1}$) is seen in the C-H bending frequencies ($737, 850 \text{ cm.}^{-1}$),

¹ Bradley, *Progr. Stereochem.*, 1963, **3**, 1.

² Tuck and Woodhouse, following paper.

³ Renz, *Z. anorg. Chem.*, 1901, **36**, 101; *Ber.*, 1904, **37**, 2110.

⁴ Morgan and Drew, *J.*, 1921, **119**, 1058.

⁵ Moeller, *Ind. Eng. Chem. Analyt.*, 1943, **15**, 270, 346; Moeller and Cohen, *Analyt. Chem.*, 1950, **22**, 686.

⁶ Sutton, *Austral. Chem. Inst. J. and Proc.*, 1948, **15**, 356; *Austral. J. Sci. Res.*, 1951, **A4**, 651.

⁷ Celeda and Tuck, unpublished work.

⁸ Hathaway and Underhill, *J.*, 1961, 3091.

⁹ Schilt and Taylor, *J. Inorg. Nuclear Chem.*, 1959, **9**, 211.

but the ring vibration at 1500 cm.^{-1} moves to 1525 cm.^{-1} ; this is again similar to previous results.⁹ With ethylenediamine, the principal changes are: (i) the 900 cm.^{-1} band in anhydrous ethylenediamine is replaced by a strong absorption at 700 cm.^{-1} ; (ii) the broad 1610 cm.^{-1} band is resolved into a strong doublet at 1610 and 1570 cm.^{-1} ; (iii) the 3400 cm.^{-1} band is replaced by a doublet at 3200 and 3500 cm.^{-1} (cf. Nakamoto¹⁰).

The reaction between indium perchlorate and 2,2',2''-terpyridyl gave $[\text{In}(\text{terpy})_2](\text{ClO}_4)_3$. Infrared spectra showed the presence of ionic perchlorate; strong bands in the pure ligand at 760 , 1457 , and 1580 cm.^{-1} were replaced by bands at 780 , 1422 , 1470 , 1537 , and 1610 cm.^{-1} in the complex. There appears to be no report in the literature on the infrared spectra of analogous compounds.

Although pyridine adducts of indium trihalides are known,³ attempts to prepare $(\text{In py}_n)^{3+}$ cationic species were unsuccessful. Addition of pyridine to an alcoholic solution of indium perchlorate gave only pyridinium perchlorate and indium hydroxide (both identified by infrared spectra after separation). Refluxing pyridine with $[\text{In}(\text{urea})_6](\text{ClO}_4)_3$ (see below) gave the unchanged starting products. Although some reaction seemed to occur on adding pyridine to indium perchlorate dehydrated with 2,2-dimethoxypropane¹¹ in alcoholic solution, it was not possible to isolate a pure product from the reaction mixture. We also failed to prepare $[\text{In}(\text{NH}_3)_x]^{3+}$ perchlorate; the method used involved repeated condensation of ammonia on to indium perchlorate hydrate that had been pumped dry *in vacuo*, but infrared examination of the final product showed an almost complete absence of NH_3 vibrations.

Oxygen Donors.—The reaction between indium perchlorate hydrate and excess of urea in 50:50 aqueous alcohol gave, on evaporation, crystalline $[\text{In}(\text{urea})_6](\text{ClO}_4)_3$. Infrared spectra showed that the NH_2 stretching and rocking frequencies of urea (3400 and 1170 cm.^{-1}) are unchanged in the complex, whereas the bands at 1603 and 1683 cm.^{-1} (mixed C=O stretching and NH_2 bending frequencies) give way to bands at 1510 and 1550 cm.^{-1} , showing clearly that the bonding to indium is through oxygen.¹² A similar reaction with dimethyl sulphoxide gave $[\text{In}(\text{dmsO})_6](\text{ClO}_4)_3$, in which the S=O stretching frequency was at 950 cm.^{-1} , a reduction of 110 cm.^{-1} from the uncomplexed ligand (1060 vs cm.^{-1}), so that here again oxygen is the donor element.¹³ Following Bagnall,¹⁴ and Bull, Madan, and Willis,¹⁵ we also studied the reaction with *NN*-dimethylacetamide, in which indium perchlorate hydrate is soluble. The white product obtained after extensive washing with dry ether was extremely deliquescent, although the freshly prepared material contained no water (from infrared spectra). The C=O stretching mode, at 1650 cm.^{-1} in the ligand, is at 1610 cm.^{-1} in the complex, indicating complexing *via* oxygen.

Each of these three products involves six-co-ordinate indium(III), but the product obtained with triphenylphosphine oxide was $[\text{In}(\text{Ph}_3\text{PO})_4](\text{ClO}_4)_3$. The P–O stretching frequency in this complex occurs at 1148 cm.^{-1} , a lowering of $\sim 50\text{ cm.}^{-1}$ from the 1190 cm.^{-1} of the starting material, as found in other cases of co-ordination of this ligand *via* oxygen.^{16, 17}

Phosphorus and Arsenic Donors.—The 4-co-ordinate complex $[\text{In}(\text{Ph}_3\text{P})_4](\text{ClO}_4)_3$ was obtained by refluxing triphenylphosphine with indium perchlorate hydrate in a mixture of ethanol and carbon tetrachloride, followed by precipitation of the crystalline salt. In addition to the strong ionic perchlorate band, the only significant change in the infrared spectrum (compared with the uncomplexed ligand) is a new band at 900 cm.^{-1} . Under similar reaction conditions, tributylphosphine gave a white gelatinous product, which could

¹⁰ Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, 1963, p. 186.

¹¹ Franz, *J. Inorg. Nuclear Chem.*, 1963, **25**, 737.

¹² Penland, Mizushima, Curran, and Quagliano, *J. Amer. Chem. Soc.*, 1957, **79**, 1575.

¹³ Cotton and Francis, *J. Amer. Chem. Soc.* 1960, **82**, 2986.

¹⁴ Bagnall, Deane, Markin, Robinson, and Stewart, *J.*, 1961, 1611; Bagnall, Brown, and Deane, *J.*, 1962, 1655.

¹⁵ Bull, Madan, and Willis, *Inorg. Chem.*, 1963, **2**, 303.

¹⁶ Cotton, Barnes, and Bannister, *J.*, 1960, 2199.

¹⁷ Frazer, Gerrard, and Twaits, *J. Inorg. Nuclear Chem.*, 1963, **25**, 637.

not be crystallised, and whose infrared spectrum showed the presence of ionic perchlorate. A complex was also produced by reaction with 1,2-bisdiphenylphosphino)ethane (= diphos), shown to be $[\text{In}(\text{diphos})_2](\text{ClO}_4)_3$; the infrared spectrum was very similar to that of 1,2-bis(diphenylphosphino)ethane.

Triphenylarsine did not react readily with indium perchlorate hydrate, and no product was obtained by any of the solution techniques used previously. Reaction occurred when the two were heated in a sealed evacuated tube, and purification gave $[\text{In}(\text{Ph}_3\text{As})_4](\text{ClO}_4)_3$; as with triphenylphosphine, a new band (850 cm.^{-1}) was the only significant feature of the infrared spectrum.

Sulphur Donors.—Thiourea gave a deliquescent crystalline solid, $[\text{In}(\text{thiourea})_6](\text{ClO}_4)_3$. The principal changes in the infrared spectrum of the ligand are (i) a new band appears at 1510 and 1520 cm.^{-1} (doublet) probably the N-C-N stretching mode moving to higher frequency;¹⁸ (ii) the C-S stretching frequency at 1100 cm.^{-1} broadens and weakens in intensity. No changes occur in the N-H stretching and rocking frequencies. These observations are in keeping with thiourea bonded to indium through sulphur (cf. ref. 18).

Fairbrother and Flitcroft¹⁹ reported that dimethyl and diethyl sulphides form adducts with indium trichloride, but although the former dissolves indium perchlorate hydrate, the salt was recovered unchanged even after long refluxing. Equally, none of the methods successful with other ligands gave any reaction with diphenyl sulphide.

Factors Affecting the Co-ordination Number of In^{3+} .—The preparative work described shows that In^{3+} has a co-ordination number of six with nitrogen, oxygen, and sulphur (except in the case of triphenylphosphine oxide), in keeping with the observation that main group elements readily exceed the octet (inert gas) configuration with highly electronegative elements.²⁰ With both phosphorus donors, with triphenylarsine, and with triphenylphosphine oxide, however, the co-ordination number is four, and the inclusion of the last-named ligand in this group shows clearly that atomic electronegativities cannot be the only factor involved.

The simplest explanation would ascribe the lowering of the co-ordination number to steric effects, and this cannot be ignored. An alternative hypothesis is that 4-co-ordination of In^{3+} only occurs with ligands that can form both σ - and π -bonds with the metal. The factors governing this type of bonding in transition-metal carbonyls and related compounds have been discussed by Craig and Doggett,²⁰ who conclude that the inert-gas rule is unlikely to hold in highly positively charged ions, since the charge causes contraction of the d -orbitals, and in this way reduces overlap with the ligand acceptor orbitals. The application of these concepts to main group elements and their complexes is hindered by a lack of detailed information on the bonding orbitals involved (cf. Nyholm²¹). Qualitatively, however, it is clear that strongly electronegative ligands do not easily transfer negative charge to the positive ion in complex formation, so that with such ligands the charge on the central ion remains highly positive, and π -bonding involving d -orbitals is unlikely. With less electronegative ligands, the reduction of the positive charge is more probable, so that the d -orbitals will be less contracted than previously and π -bonding becomes possible. This is only possible with weakly electronegative ligands that can also π -bond; the former qualification probably explains why ligands such as bipyridyl, normally regarded as favouring π -bond formation,²² give six-co-ordinate complexes with In^{3+} . To the extent that this argument parallels that which holds for transition-metal complexes, it supports the view that d -orbitals are involved in the bonding in 4-co-ordinate complexes. The π -overlap may be between unfilled $5d$ -orbitals of indium and filled p -orbitals of the ligand donor atom, or filled $4d$ -orbitals of indium and empty d -orbitals of phosphorus or arsenic.

¹⁸ Yamaguchi, Penland, Mizushima, Lane, Curran, and Quagliano, *J. Amer. Chem. Soc.*, 1958, **80**, 527.

¹⁹ Fairbrother and Flitcroft, *J. Less Common Metals*, 1962, **4**, 504.

²⁰ Craig and Doggett, *J.*, 1963, 4189.

²¹ Nyholm, *Proc. Chem. Soc.*, 1961, 273.

²² Orgel "An Introduction to Transition Metal Chemistry," Methuen, London, 1960, p. 144.

EXPERIMENTAL

General.—Indium(III) perchlorate hydrate was obtained by dissolving the metal in hot aqueous perchloric acid, reducing the volume of the solution by evaporation, and allowing the white deliquescent solid to crystallise. Excess of water and acid were removed *in vacuo*; approx. 1 g. of this dried material was used in each preparation.

Ligand reagents were generally reagent grade materials, and were recrystallised or redistilled as appropriate before use. Triphenylphosphine, triphenylphosphine oxide, and 2,2'-bipyridyl were recrystallised from ethanol. Triphenylarsine was made by treating arsenic trichloride or tri-iodide with phenyl-lithium; the product was crystallised from ethanol.

Indium was determined by titration with e.d.t.a., pyridine-2-azo-4-resorcinol being used as indicator.²³ Complexes were generally dissolved in 6M-aqueous hydrochloric acid, and the pH of the solution adjusted to 8—10; precipitated indium hydroxide was dissolved by adding 1M-sodium potassium tartrate. The colour change of the indicator, normally rather slow, could be accelerated by heating the solution to 60°. Other analyses were made by conventional micro-methods, except that carbon was determined by the wet oxidation method because of the explosive nature of the complex perchlorates.

Infrared spectra were obtained with a Unicam SP 200 spectrophotometer over the range 4000—650 cm.⁻¹.

Tris-(2,2'-bipyridyl)indium(III) Perchlorate.—Indium perchlorate hydrate (1 g.) in dry ethanol was added to a solution of 2,2'-bipyridyl (5 ml.) in the same solvent; the white flocculent product was washed with ether, dried *in vacuo*, and then crystallised from methanol-acetone; it had m. p. 318° (decomp.) [Found C, 39.3; H, 2.9; N, 9.09; In, 13.0. In(ClO₄)₃.3C₁₀H₈N₂ requires C, 40.7; H, 2.7; N, 9.53; In, 13.0%]. 2,2'-Bipyridyl was extracted with chloroform from an alkaline solution of the complex, and then determined spectrophotometrically²⁴ at 283 mμ [Found: bipy, 52.7%. Calc.: 53.6%]. The compound is insoluble in most organic solvents, and decomposes in aqueous acid or alkali.

Tris-(1,10-phenanthroline)indium(III) Perchlorate.—Reaction of 1,10-phenanthroline monohydrate with indium(III) perchlorate under the conditions used for the bipyridyl complex gave a product containing water. The 1,10-phenanthroline was dehydrated *in vacuo* at 100° for 4 hr. (absence of water confirmed by infrared spectrum), and the product material gave the anhydrous complex [Found: In, 12.0. In(ClO₄)₃.3C₁₂H₈N₂ requires In, 12.0%]. 1,10-Phenanthroline was determined spectroscopically in the same way as 2,2'-bipyridyl, the absorption band at 270 mμ being used [Found: phen, 57.6%. Calc.: 56.5%] (experimental In:phen ratio 1:3.06). The solubility of this compound was very similar to that reported above for the 2,2'-bipyridyl complex. The compound as freshly precipitated was white, but almost immediately became pale pink; no reason for this behaviour, which was quite reproducible, is obvious. This compound has recently been reported by Sutton.²⁵

Tris(ethylenediamine)indium(III) Perchlorate.—An ethanolic solution of indium(III) perchlorate was added dropwise to an excess of anhydrous ethylenediamine, giving a white flocculent precipitate, which was washed with dry ether and dry ethanol, and was crystallised from methanol-acetone. The complex, which exploded at approx. 200°, is non-deliquescent, slightly soluble in acetone, ethanol, and 1,4-dioxan, and insoluble in benzene and carbon tetrachloride [Found C, 12.4; H, 4.7; N, 14.0; In, 18.5. In(ClO₄)₃.3C₂H₈N₂ requires C, 12.1; H, 4.0; N, 14.2; In, 19.3%].

Bis-(2,2''-terpyridyl)indium(III) Perchlorate.—The preparative technique was essentially that used for the bipyridyl complex. The terpyridyl complex was obtained in only small quantities and its 2,2''-terpyridyl content was determined spectroscopically, by using the broad absorption band^{24a} centred at 280 mμ; for this purpose, the complex was decomposed with aqueous sodium hydroxide and the terpyridyl extracted into chloroform, in which its absorption was measured [Found: terpy, 54.3, In, 13.9. In(terpy)₂(ClO₄)₃ requires terpy, 53.0; In, 13.1%].

Hexaureaindium(III) Perchlorate.—Indium(III) perchlorate (1 g.) and urea (3 g.) were refluxed in 50% (v/v) aqueous ethanol for 6 hr.; slow evaporation of the resultant solution produced colourless crystals, which were washed with ether, and crystallised from ethanol. The complex (m. p. 220°) was soluble in ethanol, but insoluble in ether and acetone [Found: C, 8.8; H, 2.9; N, 21.4; In, 14.8. In(ClO₄)₃.6CH₄N₂O requires C, 9.3; H, 3.1; N, 21.6; In, 14.8%].

Hexa(dimethyl sulphoxide)indium(III) Perchlorate.—Addition of an ethanolic solution of

²³ Sommer and Hnilickova, *Naturwiss.*, 1958, **45**, 544.

²⁴ (a) Nakamoto, *J. Phys. Chem.*, 1960, **64**, 1420; (b) Mitchell, private communication.

²⁵ Sutton, *Austral. J. Chem.*, 1963, **16**, 278.

indium(III) perchlorate to dimethyl sulphoxide (purified and dried as recommended by Cotton and Francis¹³) gave a white solid, which was washed several times with ether and dried for 2 days *in vacuo* [Found: C, 16.2; H, 3.8; S, 21.6; In, 12.6. $\text{In}(\text{ClO}_4)_3 \cdot 6\text{C}_2\text{H}_6\text{SO}$ requires C, 16.3; H, 4.1; S, 21.7; In, 13.0%].

Hexa-(NN-dimethylacetamide)indium(III) Perchlorate.—Vacuum-dried indium(III) perchlorate was dissolved in excess of *NN*-dimethylacetamide, the solution heated to 40°, and excess of solvent pumped off; the resultant viscous oil was digested with dry ether and gave a white, extremely deliquescent solid [Found: C, 28.9; N, 9.3; In, 11.7. $\text{In}(\text{ClO}_4)_3 \cdot 6\text{C}_4\text{H}_9\text{NO}$ requires C, 30.7; N, 9.5; In, 12.2%]. The low analytical results are probably due to absorption of water; the C:In ratio is 24.7, compared with the theoretical value of 24.

Hexathiourea-indium(III) Perchlorate.—Indium(III) perchlorate and excess of thiourea were refluxed in methanol for 6 hr., and the resultant solution allowed to evaporate over phosphorus pentoxide. The colourless crystals produced were recrystallised from ethanol; the product is deliquescent [Found: C, 8.3; H, 3.2; N, 18.7; S, 20.1; In, 12.3. $\text{In}(\text{ClO}_4)_3 \cdot 6\text{CH}_4\text{N}_2\text{S}$ requires C, 8.3; H, 2.8; N, 19.3; S, 22.0; In, 13.2%].

Tetra(triphenylphosphine)indium(III) Perchlorate.—No reaction occurred when ethanolic solutions of indium(III) perchlorate and triphenylphosphine were mixed; when, however, an ethanolic solution of the ligand and triphenylphosphine was refluxed for 12 hr., and diethyl ether or cyclohexane added, white crystals, m. p. 159°, were obtained. The complex could also be prepared by the dropwise mixing of solutions of the two reactants in ethyl acetate, when the crystalline product was precipitated immediately. The compound is soluble in acetone, ethanol, and *NN*-dimethylformamide.

Determination of indium by titration with e.d.t.a. proved unsuccessful, apparently because phosphorus oxyanions present (after decomposition with *aqua regia*, or fusion with sodium hydroxide) obscured the end-point; check titrations with standard indium solutions gave low results in the presence of phosphate ion. The *triphenylphosphine complex* was therefore dissolved in ethanol, and the tris-(2,2'-bipyridyl)indium(III) perchlorate complex precipitated, dried, and weighed (see above); the results for indium obtained in this way were reproducible within approx. $\pm 3\%$ [Found: C, 60.1; H, 4.4; In, 7.5%; *M* (Rast, in camphor), 1550. $\text{In}(\text{ClO}_4)_3 \cdot 4(\text{C}_6\text{H}_5)_3\text{P}$ requires C, 59.4; H, 4.1; In, 7.8%; *M*, 1465].

Tetra(triphenylarsine)indium(III) Perchlorate.—No product was obtained from indium(III) perchlorate and triphenylarsine when the various solution techniques described above were used. Finally, vacuum-dried indium(III) perchlorate (2 g.) and excess of triphenylarsine were heated in a sealed tube at 120° for 6 hr. The reaction mixture was washed several times with both acetone and benzene to remove unchanged starting material; the residual white powder, which was insoluble in water, acetone, benzene, and 1,4-dioxan, was the required *complex* [Found: C, 52.1; In, 7.2. $\text{In}(\text{ClO}_4)_3 \cdot 4(\text{C}_6\text{H}_5)_3\text{As}$ requires C, 53.0; In, 7.0%].

Tetra(triphenylphosphine oxide)indium(III) Perchlorate.—Triphenylphosphine oxide (2 g.) and indium(III) perchlorate (1 g.) were refluxed in methanol-carbon tetrachloride; addition of diethyl ether precipitated a white solid, which was washed with benzene and methanol and dried; it had m. p. 289°. The *compound* was insoluble in acetone, ether, and water [Found: C, 56.0; H, 4.6; In, 6.1—8.8. $\text{In}(\text{ClO}_4)_3 \cdot 4(\text{C}_6\text{H}_5)_3\text{PO}$ requires C, 56.7; H, 3.9; In, 7.5%]. Indium determinations were again complicated by the presence of phosphorus.

Bis-(1,2-bisdiphenylphosphinoethane)indium(III) Perchlorate.—The ligand was prepared by the method of Hewertson and Watson.²⁶ Stoichiometric quantities of the ligand and indium(III) perchlorate were refluxed in methanol-carbon tetrachloride for 4 days; addition of ether precipitated a white solid. The complex can also be prepared by mixing solutions of the two reactants in ethyl acetate. The *complex* is soluble in ethanol and acetone, and insoluble in benzene, ether, and water [Found, C, 52.2; H, 4.5; In, 9.8. $\text{In}(\text{ClO}_4)_3 \cdot 2\text{C}_{26}\text{H}_{24}\text{P}_2$ requires C, 51.3; H, 4.0; In, 9.5%]. Indium analyses were carried out by precipitation of the terpyridyl complex from ethanolic solution (no reaction occurred with 2,2'-bipyridyl).

Conductivities.—The conductivities of a number of the compounds prepared were measured in nitromethane. The solvent was purified by storage over calcium chloride for 1 week, followed by distillation from Linde molecular sieves, substantial head and tail fractions being rejected; the final product had a conductivity of 10^{-6} ohm.⁻¹. The molar conductivities (ohm.⁻¹ cm.²) of 0.001*M*-solutions (except of the trisethylenediamine complex, which was relatively insoluble in nitromethane, and for which a 0.0005*M*-solution was used) were: $\text{In}(\text{dipy})_3(\text{ClO}_4)_3$, 259;

²⁶ Hewertson and Watson, *J.*, 1962, 1490; Chatt and Hart, *J.*, 1960, 1378.

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$\text{In}(\text{phen})_3(\text{ClO}_4)_3$, 235; $\text{In}(\text{en})_3(\text{ClO}_4)_3$, 209; $\text{In}(\text{dmsO})_6(\text{ClO}_4)_3$, 237; $\text{In}(\text{dimac})_6(\text{ClO}_4)_3$, 224; $\text{In}(\text{Ph}_3\text{P})_4(\text{ClO}_4)_3$, 365; $\text{In}(\text{Ph}_3\text{PO})_4(\text{ClO}_4)_3$, 225; $\text{In}(\text{diphos})_2(\text{ClO}_4)_3$, 310 [where bipy = 2,2'-bipyridyl, phen = 1,10-phenanthroline, en = ethylenediamine, dmsO = dimethyl sulphoxide, dimac = *NN*-dimethylacetamide, and diphos = 1,2-bis(diphenylphosphino)ethane]. The hexaurea complex was not sufficiently soluble for conductivity measurements to be carried out.

It is difficult to interpret these results in detail, beyond noting that the compounds concerned are electrolytes in nitromethane, which confirms the cationic formulation of the complexes. It has been reported²⁷ that 1:3 electrolytes in nitromethane have molar conductivities of approx. $390 \text{ ohm}^{-1} \text{ cm.}^{-2}$, and it may be that the lower values observed are due to decomposition in solution, since the two phosphorus compounds, which we believe to be the most stable, give the highest values, and there is a gradual decrease on going to the six-co-ordinate compounds (although the phosphine oxide complex does not fit into this argument). It is worth noting that Sutton²⁸ has reported molar conductivities of 180—190 $\text{ohm}^{-1} \text{ cm.}^{-2}$ for $\text{In}(\text{en})_3\text{I}_3$ and $\text{In}(\text{pic})_3\text{I}_3$ (pic = picolylamine), so that such low conductivities may be a general feature of nitromethane solutions of indium complexes.

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²⁷ Ferguson and Nyholm, *Nature*, 1959, **183**, 1039; Nyholm and Parrish, *Chem. and Ind.*, 1956, 470.

²⁸ Sutton, *Austral. J. Chem.*, 1961, **14**, 33, 37.
