Co-ordination Compounds of Indium. Part VIII.[1] Studies of Indium(III) Cyanate Systems

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Attempted preparations of indium(III) cyanate were unsuccessful, and probable reasons for this are discussed. Addition compounds of the type $In(NCO)_3L_3$ (L = unidenate ligand) and $In(NCO)_3L^{II}_{1.5}$ (L^{II} = 2,2'-bipyridyl or 1,10-phenanthroline) were obtained from the corresponding indium(III) halide complexes. The properties of these adducts are compared with those of the analogous halide and pseudohalide compounds.

In previous papers we have described the preparation and properties of the addition compounds formed by indium(III) chloride, bromide, iodide,[2] and thiocyanate [3] with various unidentate and bidentate donor ligands. As a continuation of the studies of indium pseudohalides and their adducts, we attempted to prepare indium(III) cyanate under various conditions. While none of these attempts was successful, information was obtained on the probable route by which the hypothetical 'indium(III) cyanate' decomposes. A number of addition compounds were obtained from analogous indium halide adducts by ligand exchange, and the properties and structure of these species have been studied.

Attempted Preparation of Indium(III) *Cyanate.*—Aqueous phase reaction of barium cyanate and indium(III) sulphate (analogous to the method successfully used in the preparation of indium thiocyanate [3]) gave rise to a filtrate from which indium carbonate slowly precipitated, suggesting hydrolysis of any indium cyanate formed. Reaction of an indium halide and silver cyanate in benzene was ineffective because of the low solubility of both reactants in this solvent, but in methanol, ethanol, or propan-2-ol solution, quantitative precipita-

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[1] Part VII, R. C. Ferguson, P. Dobud, and D. G. Tuck, *J. Chem. Soc.* (*A*), 1968, 1058.

[2] A. J. Carty and D. G. Tuck, *J. Chem. Soc.* (*A*), 1966, 1081.

[3] S. J. Patel, D. B. Sowerby, and D. G. Tuck, *J. Chem. Soc.* (*A*), 1967, 1187.

tion of silver iodide occurred, suggesting that the reaction

$$InI_3 + 3AgCNO \xrightarrow{ROH} 3AgI + In/3NCO \qquad (1)$$

had gone to completion. Removal of solvent gave in each case a product (A) which would not redissolve in the alcohol, or indeed in any other solvent, and which did not correspond analytically to indium(III) cyanate or any of its simple derivatives. Infrared spectra showed the presence of C≡N, C=O, NH_2, and alkyl groups in this material. On heating *in vacuo* to about 50°, (A) yielded a white sublimate (B) which was shown by analytical and spectroscopic methods to be the alkyl urethane containing the alkyl group of the solvent. The residue (C) remaining after an exhaustive sublimation of (A) again showed no simple stoicheiometry, and had an infrared spectrum qualitatively similar to that of (A) save for the absence of urethane bands.

Our interpretation of these results is that indium iodide, probably strongly solvated by alcohol molecules, reacts with silver cyanate to give solvated indium cyanate in solution, and this then reacts with further alcohol to give the alkyl urethane. These reactions apparently do not go to completion under the conditions used, so that product (A) is a mixture of this urethane plus product (C) and possibly some undecomposed indium cyanate. Heating *in vacuo* drives off the urethane and leaves (C), which probably involves the polymeric decomposition products of ' indium cyanate ', and which resists further formation of urethane because of the lack of an excess of ROH (cf. Lappert and Pyszora [4]); there may be In–OR groups in (C).

The reaction of indium halide and silver cyanate was also carried out in both acetone and acetonitrile solution, but the properties of the products obtained on evaporation of the excess of solvent (after removal of the quantitatively precipitated silver iodide) indicated that ' indium(III) cyanate ' had decomposed, again presumably by reaction with an excess of solvent. These systems were not investigated further.

Preparation of Indium(III) *Cyanate Adducts.*—Despite the failure to isolate indium(III) cyanate, a number of addition compounds were prepared by the reaction of a corresponding indium(III) halide adduct with silver cyanate, or of indium halide plus free ligand with silver cyanate. With pyridine and dimethyl sulphoxide InX_3L_3 adducts were obtained; triphenylphosphine oxide gave InX_3L_2 or InX_3L_3, depending on the stoicheiometry of the reaction mixture; and 2,2′-bipyridyl and 1,10-phenanthroline yielded $InX_3L_{1.5}$ species (where X = CNO). The complexes have molar conductivities in nitromethane in the range 10—50% of those reported for 1 : 1 electrolytes in this solvent (cf. ref. 2).

These molar conductivities are of the same order as, but lower than, those previously reported for the corresponding indium(III) halide and thiocyanate compounds,[2,3] and, as before, the structural implication of these results is of a neutral solid-state adduct which undergoes rearrangement and/or dissociation into ionic species in solution.

TABLE 1

Molar conductivity of indium(III) cyanate adducts in nitromethane (10^{-3}M concn.) at 25°

	Molar cond. (ohm^{-1} cm.^{2})
$In(NCO)_3\,py_3$	20
$In(NCO)_3(Me_2SO)_3$	8
$In(NCO)_3(Ph_3PO)_2$	17
$In(NCO)_3(Ph_3PO)_3$	11
$In(NCO)_3\,bipy_{1.5}$	28
$In(NCO)_3\,phen_{1.5}$	45

py = Pyridine; bipy = 2,2′-bipyridyl; phen = 1,10-phenanthroline.

It is worth noting that the instability of the cyanate group in ' indium(III) cyanate ' is not found in the adducts; for example, acetone was safely used as a reaction medium in the preparation of the bis(triphenylphosphine oxide) adduct from $InCl_3(Ph_3PO)_2$. This behaviour confirms the view (see above) that the presence of solvent molecules strongly bound to the indium species is in part responsible for the decomposition of the ' indium cyanate ' initially formed in reaction (1).

Structure of the Addition Compounds.—Absorption bands in the sodum chloride region of the infrared spectrum due to the donor ligand show that the bonding of the latter in the complexes is in each case essentially identical with that found for the corresponding indium halide [2] and thiocyanate [3] adducts.

The question of the bonding of the cyanate group in co-ordination complexes (*i.e.* –NCO or –OCN) has been discussed by a number of authors. Frequencies in the region 2273 ± 30 cm.$^{-1}$ have been reported for ν_{as} (*i.e.* essentially the C≡N stretch of NCO group) in a series of ioscyanate–boranes [4] and related compounds.[5] Because of the many infrared absorption bands due to the presence of organic groups, only this vibration could be identified with certainty in the spectrum of the complexes. The frequencies found are shown in Table 2.

TABLE 2

C≡N stretching frequencies (cm.$^{-1}$) in indium(III) cyanate addition compounds

	C≡N stretch (all strong)	
Compound (X = CNO)	Nujol	$MeNO_2$ soln.
$InX_3\,py_3$	2210, 2190sh	2205
$InX_3(Me_2SO)_3$	2180, 2220sh	2215
$InX_3(Ph_3PO)_2$	2195br	—
$InX_3(Ph_3PO)_3$	2220br	2195, 2215
$InX_3\,bipy_{1.5}$	2205br	2195, 2220
$InX_3\,phen_{1.5}$	2195, 2230	—

The cyanate groups in those Group IIIB and IVB compounds whose structures have been investigated are nitrogen-bonded,[4] and, in view of the similarity of the C≡N stretching frequencies in these and the indium compounds, we formulate the above adducts as $In(NCO)_3L_3$, etc.

In theory, the number of ν(C≡N) absorptions should

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[4] M. F. Lappert and H. Pyszora, *Adv. Inorg. Chem. Radiochem.*, 1966, **9**, 160.

[5] M. F. Lappert and H. Pyszora, *J. Chem. Soc.* (*A*), **1967**, 854.

give information on the stereochemistry of the adducts, but in both Nujol mulls and nitromethane solution the bands are too broad for such analysis, although splitting is observed in some cases. The solubilities in non-polar solvents are too low for spectral studies. The number of ν(In–N) and ν(In–ligand) bands is more useful. The Sn–N stretching mode [6] in $[Sn(NCO)_6]^{2-}$ is at 383 cm.$^{-1}$, so that the analogous ν(In–NCO) should be in the 300—350 cm.$^{-1}$ region. With donor ligands such as pyridine [7] and 2,2′-bipyridyl,[8] ν(In–N) is at 200—235 cm.$^{-1}$, and ν(In–O) is at 430—470 cm.$^{-1}$ in $[InL_6]^{3+}$ and InX_3L_3 (X = Cl, Br) species.[7,8] In $In(NCO)_3(Me_2SO)_3$, there are two bands at 455s and 439s cm.$^{-1}$, assigned to ν(In–O), and two at 343s and 331s cm.$^{-1}$ [ν(In–NCO)], which is compatible with a *cis*-$In(NCO)_3(Me_2SO)_3$ structure.[7] In the pyridine adduct, two bands at 334m and 309m are assigned to ν(In–NCO), and one at 215s to ν(In–py); this too suggests that we are dealing with a *cis*-isomer, although the failure to identify more than one ν(In–py), probably because of instrumental limitations, leaves this conclusion uncertain. The spectra of $In(NCO)_3(Ph_3PO)_2$ and $In(NCO)_3(Ph_3PO)_3$ are essentially identical in the 500—200 cm.$^{-1}$ region, and contain a number of donor-ligand bands which prevent proper interpretation. The structure and spectra of $In(NCO)_3bipy_{1·5}$ and $In(NCO)_3phen_{1·5}$ will be discussed elsewhere.

EXPERIMENTAL

General.—Materials, and analytical, spectroscopic, and conductometric methods were essentially as in previous work. No reliable method was found for cyanate determination, and we therefore rely on metal and C, H, and N analysis throughout.

Anhydrous silver cyanate was obtained from City Chemical Corporation, New York (Found: Ag, 71·8. Calc. for AgCNO: Ag, 72·0%).

Spectroscopic grade methanol, ethanol, and propan-2-ol were distilled from calcium metal before use. All preparative work was carried out in a dry-box over P_2O_5.

Attempted Preparation of Indium(III) *Cyanate*.—(*a*) A slurry of indium(III) iodide and silver cyanate (1: 3 mole ratio) in benzene was stirred at room temperature for 2 weeks, after which the supernatant liquor was decanted off and evaporated to dryness. The traces of residue showed no CN bands in the infrared spectrum.

(*b*) A solution of indium(III) iodate (4·95 g.) and silver cyanate (4·49 g.) in methanol (150 ml.) was stirred for 3 days at room temperature. After filtration, the dried silver iodide collected weighed 7·00 g.; complete reaction of InL_3 + 3 AgCNO requires 7·04 g. of AgI. The filtrate was evaporated to dryness *in vacuo* at room temperature, yielding a white solid (C, 13·3; H, 3·6; N, 9·1; In 39·7%); this material (A) (R = Me), which darkened at approx. 180°, did not redissolve in methanol even on refluxing, and was insoluble in a wide variety of organic solvents, and in water; dilute aqueous mineral acid gave carbon dioxide, and boiling conc. aqueous sodium hydroxide released ammonia. The infrared spectrum had bands at 3300s,br, 2220s, 1705s, 1610m, 1460s, 1370s, 1430m, 1395m, 1350s, 1085s,br, 875w, 805m, and 690vw cm.$^{-1}$.

Product (A) (R = Me) was exhaustively sublimed *in vacuo* at 50°, yielding a white crystalline compound (B) (R = Me), m. p. 54°. The infrared and n.m.r. spectra, and solubilities of this material were identical with those of an authentic sample of methyl urethane (lit., m.p. 54°) (Found: C, 32·0; H, 6·9; N, 18·5; OMe, 41·3. Calc. for $C_2H_5NO_2$: C, 32·0; H, 6·7; N, 18·7; OMe, 41·3%). The residue (C) (R = Me) remaining after vacuum-sublimation had similar physical and spectral properties to (A) (Found: C, 8·6; H, 2·8; N, 7·6; OMe, 25·7; In, 49·4%).

(*c*) Repetition of the above reaction in ethanol gave the theoretical yield of silver iodide. The material (A) (R = Et) had C, 19·1; H, 3·9; N, 7·4; In, 39·3%. No product could be sublimed out of this material, but a chloroform extract yielded ethyl urethane (Found: C, 40·3; H, 8·0; N, 15·5. Calc. for $C_3H_7NO_2$: C, 40·4; H, 7·9; N, 15·7%); a residue (Found: C, 6·3; H, 2·4; N, 6·0; In, 55·0%) remained after this chloroform extraction. Ethyl urethane was also found in a trap used to collect ethanol distilled *in vacuo* from the original reaction mixture. The infrared spectra of (A) (R = Et) and the residue were essentially identical with those found in the methanol case.

The product obtained from a reaction in propan-2-ol was the analogue of (A) (In, 33·9%), which yielded as sublimate isopropyl urethane, m.p. 93° (Found: C, 46·6; H, 8·8; N, 13·8. Calc. for $C_4H_9NO_2$: C, 46·6; H, 8·8; N, 13·6%), and a residue (Found: In, 52·7%). The infrared spectra were identical with those in the methanol case, except for the urethane.

(*d*) Reaction of silver cyanate and indium(III) iodide in acetone yielded silver iodide (98·5%); removal of solvent as described above gave a pink solid, soluble in acetone, methanol, ethanol, acetonitrile, and water, but insoluble in other organic solvents. The solid (Found: C, 19·5; H, 3·3; N, 12·8; In, 41·2%) decomposed at approx, 170°; no sublimate was obtained on heating *in vacuo*. An involatile solid (Found: In, 38·4%) was also obtained from reaction in acetonitrile. In both cases, the infrared spectra indicated the presence of CN and CO groups in the solid.

Tris(*pyridine*)*indium*(III) *Isocyanate*.—Anhydrous indium(III) iodide (5·49 g.), silver cyanate (5·0 g.), and pyridine (60 ml.) were stirred mechanically for 3 days at room temperature. Silver iodide (Found, 7·80 g.; theoretical yield, 7·81 g.) was removed, and the filtrate evaporated *in vacuo* at room temperature, to yield a white *solid*, which was extracted with acetone and dried *in vacuo* [Found: C, 45·0; H, 3·0; N, 17·6; In, 24·0. $In(NCO)_3(C_5H_5N)_3$ requires C, 45·2; H, 3·2; N, 17·6; In, 24·0%]. The complex, which darkens at ~260°, but does not melt below 300°, is soluble in lower alcohols, acetone, nitromethane, and acetonitrile, and insoluble in water, ether, methylene dichloride, chloroform, benzene, ethyl acetate, and cyclohexane.

An unsuccessful attempt was made to obtain indium cyanate by removing pyridine from $In(NCO)_3py_3$ by reaction with tungsten hexacarbonyl.[9] No production of the yellow $W(CO)_5py$ was detected after refluxing for some hours in acetone. (We are grateful to Dr. N. Flitcroft for suggesting this reaction to us.)

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[6] D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 1965, 1286.

[7] D. M. Adams, A. J. Carty, P. Carty, and D. G. Tuck, *J. Chem. Soc.* (*A*), 1968, 162.

[8] A. J. Carty, S. J. Patel, and D. G. Tuck, *Canad. J. Chem.*, in the press.

[9] C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, 1963, **3**, 533.

Tris(dimethyl Sulphoxide)indium(III) *Isocyanate.*—The preparative method was analogous to that used for the pyridine complex. The *dimethyl sulphoxide complex*, m.p. 80°, has similar solubilities to those listed above, but in addition is soluble in water [Found: C, 22·7; H, 3·6; N, 8·9; In, 24·0. $In(NCO)_3(C_2H_6SO)_3$ requires C, 22·7; H, 3·8; N, 8·8; In, 24·2%).

Bis- and Tris-(triphenylphosphine Oxide)indium(III) *Isocyanate.*—Bis(triphenylphosphine oxide)indium(III) chloride and the stoicheiometric quantity of silver cyanate were stirred mechanically in acetone for 4 days at room temperature. After removal of the quantitative yield of silver chloride, the *complex* (m.p. 84°) was purified in the usual way [Found: C, 59·0; H, 4·0; N, 5·3; In, 14·4. $In(NCO)_3(C_{18}H_{15}PO)_2$ requires C, 58·7; H, 3·8; N, 5·3; In, 14·4%]. When the above reaction was carried out in the presence of a further mole equivalent of triphenylphosphine oxide, the product was *tris(triphenylphosphine oxide)-indium*(III) *isocyanate*, m.p. 62° [Found: C, 63·4; H, 4·4; N, 3·7; In, 10·5. $In(NCO)_3(C_{18}H_{15}PO)_3$ requires C, 63·6; H, 4·2; N, 3·9; In, 10·7%]. Both of these compounds had solubilities similar to those of the pyridine complex, but in addition were soluble in methylene dichloride and chloroform.

2,2'-*Bipyridyl- and* 1,10-*Phenanthroline-indium*(III) *Isocyanate.*—The product of the reaction of 2,2'-bipyridyl-indium(III) iodide and silver cyanate in nitromethane was a white crystalline *solid*, m.p. above 300° [Found: C, 45·5; H, 2·4; N, 17·5; In, 24·1. $In(NCO)_3(C_{10}H_8N_2)_{1\cdot5}$ requires C, 45·5; H, 2·5; N, 17·7; In, 24·1%]. A similar reaction with 1,10-phenanthrolineindium(III) bromide and an excess of 1,10-phenanthroline monohydrate gave 1,10-*phenanthroline indium isocyanate*, m.p. above 300° [Found: C, 50·0; H, 2·7; N, 16·4; In, 22·3. $In(NCO)_3(C_{12}H_8N_2)_{1\cdot5}$ requires C, 49·3; H, 2·4; N, 16·4; In, 22·5%]. Both of these compounds are soluble in acetone, methanol, nitromethane, and nitrobenzene, but insoluble in water, ethanol, and other organic solvents.

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

[8/199 *Received, February* 12*th*, 1968]