Co-ordination Compounds of Indium. Part XVIII.[1] Anionic Thiocyanato-complexes of Indium(III)

By **J. J. Habeeb** and **D. G. Tuck**,* † Department of Chemistry, Simon Fraser University Burnaby 2, British Columbia, Canada

Salts of the anion $[In(NCS)_6]^{3-}$ have been prepared with the cations Me_4N^+, Et_3NH^+ and $Bu^n{}_4N^+$; with the cation Ph_4As^+ and $B_2Ph_3P^+$, the anion is $[In(NCS)_5]^{2-}$. Vibrational spectra show that in each case, the ligand is *N*-bonded, in agreement with earlier studies of neutral adducts of indium(III) thiocyanate. The co-ordination numbers of five and six in these anions are discussed in terms of previous work on anionic halide complexes of indium(III).

ONE of the interesting features of indium(III) is the range of co-ordination numbers found in its complexes. The neutral trihalides, for example, are three-co-ordinate as the monomer in the gas phase, although bridged dimers have also been detected,[2] while in the solid state the iodide [3] is the four-co-ordinate dimer $I_2InI_2InI_2$, but the chloride and bromide form polymeric lattices in which indium is six-co-ordinate.[4] Similarly, anionic halide complexes [5] have been prepared with four-, five-, and six-co-ordinate indium(III). As with the neutral compounds, the co-ordination number in these species does not exceed four with iodide as ligand, but four and six co-ordinate species are found with chloride and bromide. In addition, the mononuclear five-co-ordinate

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† *Present address:* Deparment of Chemistry, University of Windsor, Windsor 11, Ontario.

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$InCl_5^{2-}$ is known.[5-7] The co-ordination number of indium in a salt of the type $(\text{cation})_nInX_{n+3}^{n-}$ depends then in part on the nature of the halide involved. Possible reasons for this effect, which also shows up in the neutral adducts of the indium trihalides,[8] have been discussed in terms of ligand size, electronegativity, and polarisibility, and the possible importance of π-donation from ligand to metal.[8,9]

We have now carried out preparative and spectroscopic studies of anionic complexes of indium(III) with the pseudohalide thiocyanate ligand. The parent compound, indium(III) thiocyanate [10,11] is a polymeric solid, but monomeric adducts with neutral donor ligands have been prepared. In these adducts, the thiocyanate group is bonded through the hard, electronegative, nitrogen atom, and in keeping with earlier studies the co-ordination number of the metal in these species was found to be six in all cases.[10,12] The present results show that five- and six-co-ordinate anionic thiocyanate complexes can be prepared, and this is discussed in terms of the previous results.

	Analytical data/% [a]				Vibrational spectra [b]					
					ν(CN)		ν(CS)	δ(NCS)	ν(In–N)	Other
Compound	C	H	N	In	I.r. (all vs,br)	Raman	I.r.	I.r.	Raman	Raman
$(Ph_4As)_2[In(NCS)_5]$	54·3 (54·3)	3·7 (3·4)	5·5 (6·0)	9·9(9·8)	2065	2108m 2072s	[c]	480m,sh	269m, 242s	193vs
$(Ph_3PCH_2Ph)_2[In(NCS)_5]$	61·6 (61·1)	4·4 (4·1)	6·0 (6·4)	10·6 (10·6)	2090 2072	2117w 2076vs	[c]	480m	285w, 260m, 240s	197vs
$(Me_4N)_3[In(NCS)_6]$	31·3 (31·5)	5·3 (5·3)	17·9 (18·3)	16·7 (16·8)	2090 2075 2035m	2124w 2078s 2043w	820w	478m	250vw	195m
$(Et_3NH)_3[In(NCS)_6]$	36·9 (37·5)	5·8 (6·2)	16·2 (16·3)	14·9 (15·0)	2062	2122w 2072s	810sh	480s	252w	194s
$(Et_4N)_3[In(NCS)_6]$	42·1 (42·2)	7·1 (7·0)	14·3 (14·8)	13·5 (13·5)	2070	2116w 2076s	820sh	481s	[c]	193s
$(Bu^n{}_4N)_3[In(NCS)_6]$	54·3 (54·5)	9·1 (9·1)	10·5 (10·6)	9·7 (9·7)	2085	2122m 2077s	820sh	478s	260m, 251m	189s

[a] Calculated values in parentheses. [b] Estimated accuracy ±2 cm^{-1}, except ±5 cm^{-1} on ν (CN) i.r. [c] Not detected.

The studies [5] of the anionic halide complexes of indium(III) revealed that the size of the balancing cation also plays an important part in determining the co-ordination number, with the larger cations being associated with complexes of lower co-ordination number. The same effect is found in the present work, but to a lesser extent, in that large cations, such as tetraphenylarsonium, give rise to five-co-ordinate indium(III) complexes, rather than the InX_4^- (X = Cl, Br, or I) anions of the halide series.

EXPERIMENTAL

Spectroscopic and analytical methods were those described in previous publications,[5,10] except that indium analysis was by atomic absorption spectroscopy, using a Perkin-Elmer 305 instrument, rather than by EDTA titration. Vibrational spectra of finely ground solid samples were recorded with Cary 81 (Raman) or Beckman IR 12 spectrometers.

The Table shows the compounds prepared in this work, and the analytical results obtained. A total thiocyanate determination was carried out (by titration against silver nitrate) in one case, that of $(Et_4N)_3[In(NCS)_6]$, and confirmed the elemental analysis (Found: NCS^- 40·3; required 40·8%).

Although polymeric anhydrous indium(III) thiocyanate is insoluble in organic solvents,[10] mixing ethanol solutions of indium trichloride and sodium thiocyanate (1 : 3 mole ratio) gives a solution suitable for preparative work; the precipitation of sodium chloride was shown to be quantitative. Similarly, solutions of tetra-alkylammonium chloride and sodium thiocyanate precipitate sodium chloride on mixing. The reaction of solutions of indium(III) thiocyanate and tetra-alkylammonium thiocyanate (1 : 3 mole ratio in all cases) gave pale pink crystals on standing at room temperature; these were collected, washed and dried *in vacuo*. This procedure worked satisfactorily for the compounds listed in the Table. In three cases, with the cations $MeNH_3^+$, $Me_2NH_2^+$, and $Et_2NH_2^+$, no precipitate appeared when the solution of the substituted ammonium thiocyanate was mixed with the indium thiocyanate solution. Changes of solvent, temperature, *etc.* did not have any effect, and we were unable to isolate complexes with those cations. Similar problems were observed with certain cations in the work on the preparation of anionic halide complexes.[5]

RESULTS AND DISCUSSION

Bonding of the Thiocyanato-group.—The Table lists bands in the i.r. and Raman spectra identified as ν(CN), ν(CS), and δ(NCS). The frequencies are similar to those reported [10] for adducts of indium(III) isothiocyanate, and we conclude that the anionic species are also isothiocyanato-complexes, in keeping with the general preference of A-type metals to *N*-bond to this ligand.

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Stereochemistry.—Two series of anionic complexes of formulae $[In(NCS)_6]^{3-}$ and $[In(NCS)_5]^{2-}$ have been prepared. The Table gives Raman bands in the ν(In–NCS) region, following the identification of ν(M–NCS) in the 220—370 cm^{-1} region for anionic transition metal isothiocyanate complexes.[13,14] By analogy with $InCl_6^{3-}$, the In–N_6 kernel of $[In(NCS)_6]^{3-}$ should have O_h symmetry, in which case the band *ca.* 250 cm^{-1} is presumably the symmetrical breathing mode. For a salt $(cation)_2[In(NCS)_5]$, the anion may either be mononuclear (D_{3h} or C_{4v}), or a bridged dimer $[In_2(CNS)_{10}]^{4-}$. The highest frequency ν(In–N) band in both $[In(NCS)_5]^{2-}$ complexes is *ca.* 20 cm^{-1} higher than in the In–N_6 species, suggesting a monomeric anion, since ν_1 generally decreases with increasing co-ordination number.[5] The vibrational spectra in the ν(CN) region supports this, since there is no evidence for more than one type of thiocyanate group. The strong Raman emission at 190—195 cm^{-1} is assigned as δ(MCNS), by analogy with i.r. bands *ca.* 170 cm^{-1} in anionic transition metal isothiocyanate complexes.[13,14a]

Thus, in these isothiocyanato-indate(III) species, co-ordination numbers of six and five predominate for indium(III) complexes with small electronegative ligands in keeping with earlier studies.[5,8,9] The effect of the nature of the cation on the stoicheiometry is also clearly similar to that in the anionic halide complexes.[5]

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