Contribution from the Department of Chemistry,
University of New Hampshire, Durham, New Hampshire 03824, U.S.A.

The Reaction of Ammonia with Indium Bromide in Methanol. Indium Bromide Ammines

R. Ochoa and H. M. Haendler[1]

Received April 1, 1969

Indium(III) bromide reacts with ammonia in methanol to form a series of ammine complexes. In the presence of excess ammonia the product is pentaammineindium(III) bromide, from which lower ammines can be formed by thermal decomposition. Conductivity and spectral data indicate that both ammonia and bromine are coordinated, and it is suggested that the two principal complexes, pentaammineindium(III) bromide, and triammineindium(III) bromide should be represented as $[In(NH_3)_5Br]Br_2$ *and* $[In(NH_3)_3Br]Br_2$*, respectively.*

Introduction

Recent interest in the coordination chemistry of indium has led to the isolation and characterization of complexes with a variety of ligands.[2,3] Attempts to prepare ammine indium perchlorates by direct reaction of gaseous ammonia with the perchlorate were unsuccessful.[4] Kochetkova and Gilyarov[5] did succeed in preparing hexaammineindium(III) bromide and iodide by reaction of the halides with ammonia at an ultimate pressure of 6-8 atm. Thermal decomposition led to formation of lower ammines.

Reactions in nonaqueous solvents often result in inorganic compounds not otherwise obtainable. Solutions of indium bromide can readily be prepared by bromination of indium in methanol,[6] and these solutions react readily with solutions of ammonia in the same solvent.

Experimental Section

Preparation of Compounds. $InBr_3 . 5NH_3$. Indium turnings (11.5 g, 0.1 mole; Electronic Space Products, Inc., Los Angeles, Cal.) were suspended in 100 ml of methanol (dried by refluxing with activated magnesium). Reagent grade bromine (24 g, 0.15 mole) was added in small amounts, with stirring and mild heating, to dissolve the indium. The resultant solution was colorless; the presence of a slight excess of bromine gave a permanent yellow color.

Dry ammonia gas was bubbled through a sintered glass disc into methanol, at a controlled temperature, to prepare a solution of the desired concentration. A saturated ammonia solution in methanol had a concentration of about 4 *M* at 22°, 7 *M* at 14°, and 10 *M* at 0°, as determined by titration with hydrochloric acid.

The 1 *M* solution of indium bromide in methanol was mixed with twice the volume of an approximately 7 *M* ammonia solution, both being first cooled to 0°. A white precipitate formed immediately; this was filtered, washed with dilute ammonia-methanol and methanol, and dried *in vacuo* over silica gel.

Anal. Calcd. for $InBr_3 . 5NH_3$: In, 26.11; Br, 54.52; N, 15.91. Found: In, 26.1; Br, 54.3; N, 15.5.

$InBr_3 . 3NH_3$. The pentaammine was heated at 105° to constant weight.

Anal. Calcd. for $InBr_3 . 3NH_3$: In, 28.30; Br, 59.10; N, 10.35. Found: In, 28.7; Br, 59.1; N, 9.9. Calcd. weight loss: 7.74%. Found: 7.49.

$InBr_3 . NH_3$. Decomposition of $InBr_3 . 3NH_3$ at 105° was extremely slow, but the compound lost further ammonia rapidly at temperatures near 200°.

Anal. Calcd. for $InBr_3 . NH_3$: In, 30.90; Br, 64.52; N, 3.76. Found: In, 31.1; Br, 63.9; N, 2.9.

Mixtures of methanol solutions of ammonia and indium bromide in $NH_3 : InBr_3$ ratios of less than 6:1 gave products whose analysis and X-Ray patterns indicate they are probably mixtures of the above complexes. The solubility of the compounds in polar solvents increases as the ammonia content decreases.

Apparatus. A Fisher Model 260 differential thermal analyzer was used, along with a thermogravimetric balance constructed by David Kingston, to study thermal decompositions. Conductances were measured with a conventional Wheatstone bridge circuit, using approximately 10^{-3} *M* solutions in methanol. Infrared spectra in the range 4000-500 cm^{-1} were recorded on a Perkin-Elmer 337 spectrophotometer, using halocarbon and Nujol mulls; in the range 800-100 cm^{-1} a Beckman IR-11 spectrophotometer was employed, with Nujol mulls on polyethylene plates. The mass spectra

---

(1) To whom communications should be addressed.
(2) D. G. Tuck, *Coord. Chem. Rev.*, *1*, 286 (1966).
(3) D. M. Adams, A. J. Carty, P. Carty, and D. G. Tuck, *J. Chem. Soc.*, *A* 162 (1968).
(4) A. J. Carty and D. G. Tuck, *J. Chem. Soc.*, 6012 (1964).
(5) A. P. Kochetkova and O. N. Gilyarov, *Zh. Neorg. Khim.*, *12*, 2858 (1967); *Russ. J. Inorg. Chem.*, *12*, 1510 (1967).
(6) H. M. Haendler, F. A. Johnson, and D. S. Crocket, *J. Am. Chem. Soc.*, *80*, 2662 (1958).

Table I. Molar Conductances in Methanol (ohm^{-1} cm^2 $mole^{-1}$).

Concentration	10^{-4} *M*	5×10^{-4}	10^{-3} *M*	2×10^{-3} *M*	10^{-2} *M*
$InBr_3$	68	—	68	62	54
$InBr_3 . 3NH_3$	267	240	220	—	—
$InBr_3 . 5NH_3$	348	280	260	245	—
1:2 Electrolyte[9]	—	—	210	—	—
1:1 Electrolyte[9,10]	—	—	90-105	—	—
Nonelectrolyte[10]	—	—	13-32	—	—

Table II. Vibrational Frequencies of the Ammine Complexes (cm^{-1})

Compound	$\nu(NH_3)$ [a]	$\delta_d(NH_3)$ [b]	$\delta_s(NH_3)$ [c]	$\rho_r(NH_3)$ [d]	ν(M—N) [e]	δ(NMN) [e]	Other bands
$InBr_3 . 5NH_3$	3300	1600	1250	720	480 [f]	330 [f]	420, 240 [f], 185 [g]
$InBr_3 . 3NH_3$	3250	1600	1280	670	—	—	490 [f], 380 430, 280, 200 [g]
$[Co(NH_3)_6]Br_3$	3120	1578	1318	797	~460	322	—
$[Co(NH_3)_5Br]Br_2$	—	—	—	—	~480	322	205 [h]

[a] Stretching; [b] Degenerate deformation; [c] Symmetric deformation; [d] Rocking; [e] Tentative assignments; [f] Broad bands; [g] Sharp, intense doublet; [h] ν(Co—Br)

were taken with a Hitachi RMU-6F instrument. X-Ray powder data were obtained with a 57.3 mm camera, using Ni-filtered Cu Kα radiation (λ = 1.5418 Å).

Analyses. Indium was determined by precipitation with 8-quinolinol from acetic acid-acetate solution.[7] Bromine was determined by Volhard titration after dissolving the ammine in nitric acid. Nitrogen was determined with a Coleman Model 29 nitrogen analyzer.

Results and Discussion

The reaction of ammonia and indium(III) bromide in methanol produces white, crystalline ammine complexes of different compositions. In the presence of a large excess of ammonia, pentaammineindium(III) bromide is formed. Differential thermal analysis shows two consecutive decompositions, leading to the triammine and the monoammine, confirming an earlier report.[5] Thermogravimetric analysis, however, suggests that kinetic factors are significant and care must be taken to insure that decomposition occurs at a temperature low enough to preclude rapid decomposition in the next step. Isothermal decomposition of the pentaammine at 105° leads to the triammine; subsequent formation of the monoammine can be controlled at about 200°. Compositions were confirmed by weight loss and analysis, and the presence of ammonia, as such, confirmed by mass spectral analysis.

The compounds were not sufficiently soluble in solvents of low dielectric constant to permit conductance measurements, so methanol was used. The results are summarized in Table I, and comparison are shown with values reported for various electrolytes in the same solvent. The data indicate that the pentaammine and the triammine are 1:2 electrolytes in methanol and that the bromide is a nonelectrolyte which undergoes extensive solvolysis or some dissociation. The latter view is consistent with the conclusions of Greenwood, *et al.*[8] who postulate a polymeric, 6-coordinate structure for indium(III) bromide.

The infrared spectra are consistent with coordination of both ammonia and bromine and are shown in Table II. The stretching frequencies associated with complexed ammonia lie between those of free ammonia and the ammonium ion.[11] Four infrared active vibrations have often been associated with coordinated ammonia, as shown in Table II. Adams[12] has also discussed these assignments and has clarified earlier confusion about the metal-nitrogen frequencies. In general, the stretching frequency, ν(M—N), lies between 400 and 500 cm^{-1}, and the bending frequency, δ(NMN), lies between 240 and 330 cm^{-1} for hexaammines of trivalent metals, tetraammines of divalent metals, and for the few $[M(NH_3)_5X]X_2$ compounds studied. There are a few reports of indium-bromine frequencies, with ν(In—Br) values of 200 and 183 cm^{-1} in $InBr_3 . py_3$[3] and 243 and 202 cm^{-1} in $InBr_3 . 2Me_3N$.[13] Both the triammine and the pentaammine exhibit strong absorption in these regions, but the data do not permit unequivocal assignment of structure.

Acknowledgment. This work was supported in part by the U.S. Atomic Energy Commission and is taken from the M.S. Thesis of R.O., who gratefully acknowledges the support of the University of San Marcos, Lima, Peru, and the Ford Foundation.

---

(7) A. I. Busev, « The Analytical Chemistry of Indium », The Macmillan Co., New York, N. Y., 1962, p. 144.
(8) N. N. Greenwood, D. J. Prince, and B. P. Straughan, *J. Chem. Soc., A*, 1694 (1968).
(9) L. V. Interrante, *Inorg. Chem.*, *7*, 943 (1968).
(10) R. A. Krause and D. H. Busch, *J. Am. Chem. Soc.*, *82*, 4830 (1960).
(11) K. Nakamoto, « Infrared Spectra of Inorganic and Coordination Compounds », John Wiley and Sons, Inc., New York, N. Y., 1963, pp. 143-150.
(12) D. M. Adams, « Metal-Ligand and Related Vibrations », Edward Arnold (Publishers) Ltd. London, 1967, pp. 274-277.
(13) I. R. Beattie, T. Gilson, and G. A. Ozin, *J. Chem. Soc., A*, 1092 (1968).