Reaction of Indium(III) and Gallium(III) Halides with Transition-metal Ion Schiff-base Complexes

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The planar transition-metal chelates *NN'*-ethylenebis(salicylideneaminato)metal(II) [M''(saen)] where the metal ion is cobalt(II), nickel(II), or copper(II) react with the halides InX_3 (where X = Cl or Br) to form 1 : 1 adducts in which planarity about the transition metal is retained. Structures are suggested for these adducts. The reaction of Ni^{II}(saen) with the halides GaX_3 (where X = Cl or Br) results in the formation of a 1 : 1 adduct whose structure, it is suggested, is best represented as $GaX_2[Ni^{II}(saen)]_2{}^+GaCl_4$. The reaction of indium(III) and gallium(III) halides with $Fe^{III}(saen)_2O$ in the majority of cases leads to products arising from halide exchange reactions However, in the reaction of $InBr_3$ with $Fe^{III}(saen)_2O$ a product formulated as $Fe^{III}(saen)OInBr_2$ has been isolated.

It has been shown that the planar transition-metal ion compounds *NN'*-ethylenebis(salicylideneaminato)metal-(II) [M''(saen)] where the metal ion is cobalt(II), nickel(II), or copper(II) react with the halides SnX_4 and SnX_2 (where X = Cl or Br) to form 1 : 1 adducts.[1] Characterisation of these adducts indicated a retention of planarity about the transition-metal ion. The present investigation deals with the ability of indium(III) halides and gallium(III) halides to form adducts with M^{II}(saen) complexes. In addition the reaction of the halides with the oxo-bridged iron(III) Schiff-base complex has been studied.

Thus reaction of indium(III) halides with M^{II}(saen) complexes (M = Co, Ni, Cu) leads to the formation of 1 : 1 adducts. The elemental analyses and room-temperature magnetic moments of these adducts are outlined in the Table. The magnetic properties of the adducts are consistent with a retention of planarity of the metal Schiff-base moiety. The far-i.r. spectra of the indium(III) halide adducts are almost superimposable on those of the tin(IV) halide adducts reported previously.[1] The adducts formed by reaction of the gallium(III) with Ni^{II}(saen) were also prepared, the magnetic and i.r. data being consistent with the behaviour of Ni^{II}(saen) as a neutral ligand.

In dealing with structural considerations of the 1 : 1 adducts formed, it is recalled that the co-ordination number of indium(III) may take values and appropriate stereochemical forms of four,[2] five, and six.[3-6] Thus

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[1] M. D. Hobday and T. D. Smith, *J. Chem. Soc.* (*A*), 1971, 1453.

[2] (*a*) L. A. Woodward and G. H. Singer, *J. Chem. Soc.*, 1958, 716; (*b*) L. A. Woodward and M. J. Taylor, *ibid.*, 1960, 4473; (*c*) L. A. Woodward and P. T. Bill, *ibid.*, 1955, 1699.

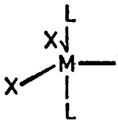
[3] R. A. Walton, *J. Chem. Soc.* (*A*), 1967, 1485.

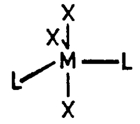
[4] D. M. Adams, A. J. Carty, P. Carty, and D. G. Tuck, *J. Chem. Soc.* (*A*), 1968, 162.

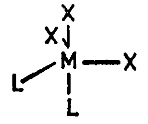
[5] T. Barrowcliffe, I. R. Beattie, P. Day, and K. Livingston, *J. Chem. Soc.* (*A*), 1967, 1810.

[6] M. Veidis and G. J. Palenik, *Chem. Comm.* 1969, 586.

the adduct may possess a pentaco-ordinate structure involving *cis*- or *trans*-forms, $M^{II}(saen)InCl_3$, comparable with previously reported cases or an ionic structure of the type $InX_2(M^{II}saen)InX_4$ involving both four and six co-ordination [structures (1)—(3)]. However the experimental evidence available at present does not allow an unambiguous distinction between these structures to be made.

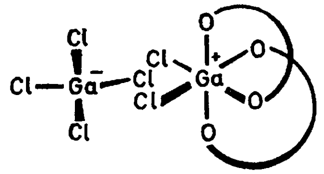

D_{3h} (1)


C_{2v} (2)


C_s (3)

The 1 : 1 adduct of gallium(III) chloride with $Ni^{II}(saen)$ possesses two absorptions assignable to gallium–chlorine vibrations (374 cm^{-1} and 318 cm^{-1}). The gallium(III) chloride complex with 2,2′-bipyridyl (bipy) was found to possess gallium–chlorine absorptions in those i.r. regions, and was formulated as $[GaCl_2(bipy)_2]^+(GaCl_4]^-$,[7] a structure which was confirmed by *X*-ray crystallography.[8] Analogous 1,10-phenanthroline adducts have also been isolated and assigned a similar ionic structure.[9] Likewise the absorption at 270 cm^{-1} observed in the 1 : 1 adduct of gallium(III) bromide with $Ni^{II}(saen)$ is similar to that observed in systems containing the anion $GaBr_4^-$.[10,11] Thus it is suggested that the structure of gallium(III) halide adducts of $Ni^{II}(saen)$ is $\{GaX_2[Ni(saen)_2]\}^+[GaX_4]^-$ (where X = Cl and Br) [structure (4)].

Exchange Reactions.—The $Co^{II}(saen)$ adducts of the indium trihalides, unlike their tin(IV) halide counterparts, do not undergo metal halide exchange when refluxed in co-ordinating solvents.[1] The indium Schiff-base complexes $In^{III}(saen)$ X (X = Cl or Br) can however be synthesised by alternative means. The indium Schiff-base compounds are insoluble in all but co-ordinating solvents, such as dimethylformamide, dimethyl sulphoxide, and pyridine. This is usually indicative of hexaco-ordination.[8] The ability of these compounds to achieve six-co-ordination about the central metal is illustrated by the isolation of the pyridine adduct In(saen)Br,py (pyridine = py; Table).



(4)

Compound	Colour	μ_{eff}/B.M.	Analyses (calc., found)/% C	H	N	X
$Co(saen)InCl_3$	Yellow-brown	2·25	35·15, 34·95	2·6, 2·85	5·13, 4·6	19·5, 19·9
$Co(saen)InBr_3$	Red-brown	2·28	28·25, 28·2	2·1, 2·1	4·1, 3·95	35·3, 35·0
$Ni(saen)InCl_3$	Orange	dia.	35·2, 34·95	2·6, 2·6	5·15, 4·9	19·5, 19·7
$Ni(saen)InBr_3$	Orange	dia.	28·3, 28·05	2·1, 2·0	4·1, 3·95	35·3, 3·95
$Ni(saen)GaCl_3$	Orange	dia.	38·35, 37·9	2·8, 2·85	5·6, 4·9	21·2, 22·6
$Ni(saen)GaBr_3$	Orange	dia.	30·3, 28·95	2·2, 2·2	4·4, 4·1	37·8, 38·9
$Cu(saen)InCl_3$	Pink	1·82	34·9, 35·95	2·55, 3·35	5·1, 5·75	19·3, 21·9
$Cu(saen)InBr_3$	Pink	1·85	28·1, 27·15	2·05, 2·1	4·1, 3·6	35·0, 34·3
In(saen)Cl	Off-white	dia.	46·15, 45·9	3·4, 3·35	6·75, 6·85	8·5, 8·9
In(saen)Br	Off-white	dia.	41·7, 42·0	3·05, 3·2	6·1, 6·05	17·3, 17·5
In(saen)Br,py	White	dia.	46·7, 46·1	3·55, 3·45	7·8, 7·5	14·8, 15·2
$Fe(saen)OInBr_2$	Purple					
(1 : 2) A		5·98	31·35, 31·9	2·3, 2·6	4·55, 4·5	26·1, 26·1
(1 : 1) B			31·35, 32·8	2·3, 2·95	4·55, 4·4	26·1, 27·3
Fe(saen)Cl	Purple		53·75, 53·5	3·95, 3·85	7·85, 7·85	9·9, 10·2
$Fe(saen)BrCHCl_3$	Black		40·05, 39·9	3·4, 2·95	5·55, 5·2	15·9, 15·7 (Br) 21·0, 19·0 (Cl)

Reactions of $[Fe^{III}(saen)]_2O$ *with Indium*(III) *and Gallium*(III) *Halides.*—Although the neutral ligand properties of the $M^{II}(saen)$ complexes have been studied to some extent,[1] there has been no published account of attempts to involve the oxygen-bridged iron compound $[Fe^{III}(saen)]_2O$ in adduct formation. Reaction of the halides of indium(III) and gallium(III) with $[Fe^{III}(saen)]_2O$ resulted in rapid halide exchange in most cases. Only the iron Schiff-base complex was isolated from the reaction mixture. In one instance, however, exchange was only partial, resulting in the precipitation of a compound with an analysis consistent with the formulation $Fe(saen)OInBr_2$ (Table). This complex was isolated independently of the ratio of the reactants and is obtained in almost 100% yield according to equation (1).

$$[Fe^{III}(saen)]_2O + InBr_3 \longrightarrow Fe^{III}(saen)OInBr_2 + Fe^{III}(saen)Br \quad (1)$$

$Fe^{III}(saen)Br$ was isolated as the solvate. The complex

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[7] A. J. Carty, *Canad. J. Chem.*, 1968, **46**, 3779.

[8] R. Restivo and G. Palenik, *Chem. Comm.* 1969, 867.

[9] C. D. Schmulbach and I. Y. Ahmed, *Inorg. Chem.*, 1971, **10**, 1902.

[10] A. J. Carty, *Canad. J. Chem.*, 1967, **45**, 3187.

[11] A. J. Carty, *Co-ordination Chem. Rev.*, 1969, **4**, 29.

$Fe^{III}(saen)OInBr_2$ appears to undergo further exchange in the presence of other solvents such as acetonitrile.

$$Fe^{III}(saen)OInBr_2 \longrightarrow Fe^{III}(saen)Br + (InOBr) \quad (2)$$

Equation (2) suggests that complexes of this type are possibly intermediates in the halide exchange reactions. The partial exchange complex $Fe^{III}(saen)OInBr_2$ possesses a room-temperature magnetic moment consistent with high-spin iron(III), *i.e.*, 5·98 B.M., unlike the parent compound $[Fe^{III}(saen)]_2O$ where a reduced moment is observed (1·89 B.M.).[12] This indicates that magnetic exchange, as observed in the parent compound $[Fe^{III}(saen)]_2O$, is either absent or negligible in the indium bromide reaction product. The i.r. absorption at 1531 cm^{-1} in $[Fe^{III}(saen)]_2O$ itself remains at this frequency in $Fe^{III}(saen)OInBr_2$ indicating that the metal Schiff-base is not behaving as a donor ligand.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer model 521 spectrophotometer with sodium chloride and caesium iodide optics, the samples being prepared as Nujol mulls. Magnetic measurements were made at room temperature by the Gouy method with a glass tube calibrated for diamagnetism. ^1H N.m.r. measurements were made with a Varian A100 spectrometer with trimethylsilane as the internal standard.

Indium(III) chloride and gallium(III) chloride were used as obtained commercially. The bromides were prepared as described by Brauer.

Preparation of $In^{III}(saen)X$ ($X = Cl$ *and* Br).—The Schiff-base ligand $H_2(saen)$ (1·34 g) was dissolved in chloroform (150 ml) and indium(III) halide added under a stream of nitrogen (1·10 g and 1·77 g for $X = Cl$ and Br respectively). A slight excess of triethylamine (1·2 g) was added slowly and the mixture refluxed for 2 h. The resulting pale yellow precipitate was filtered off, washed with ethanol, and purified by dissolution in the minimum of dimethylformamide and addition of this solution to a mixture of acetone and light petroleum (1 : 3 v/v). The ^1H n.m.r. spectrum recorded in $[^2H_6]$dimethyl sulphoxide possesses resonances at 8·44 p.p.m. (CH=N, singlet); 7·3—7·1 and 6·8—6·5 p.p.m. (both complex patterns due to phenyl protons); and 3·25 p.p.m. [singlet due to $(CH_2)_2$] for both chloride and bromide. The mass spectrum of $In^{III}(saen)Cl$ possessed a strong parent ion peak at *m/e* 416 owing to the molecular ion $In^{III}(saen)Cl^+$ but a corresponding parent ion peak was not observed for $In^{III}(saen)Br$.

Preparation of $M^{II}(saen)InX_3$ *and* $Ni^{II}(saen)GaX_3$ *Adducts*.—The procedure described previously was used to isolate these adducts with the modification that the solvent employed was chloroform instead of methylene dichloride.[1]

Preparation of $Fe^{III}(saen)OInBr_2$.—$[Fe^{III}(saen)]_2O$ (0·66 g) was dissolved in refluxing chloroform and a solution of $InBr_3$ (0·70 g) in chloroform added under nitrogen. The reaction mixture was refluxed for 30 min and the resulting purple precipitate which is the product filtered off under nitrogen. The other product of this reaction, $Fe^{III}(saen)Br,CHCl_3$, was obtained by removing the bulk of the solvent from the filtrate and allowing crystallisation to take place.

[2/634 *Received*, 20*th March*, 1972]

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[12] J. Lewis, F. E. Mabbs, and A. Richards, *J. Chem. Soc.*, (*A*), 1967, 1014.