1317. *The Preparation and Characterisation of Complexes of Rodium*(III) *and Iridium*(III) *with Di-2-pyridylamine*

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Simple preparations of the following complexes of rhodium(III) and iridium(III) are given: *trans*-[Rh(dipyam)$_2$X$_2$]X, [Rh(dipyam)$_3$]Cl$_3$,3H$_2$O, [Ir(dipyam)$_3$]X$_3$,3H$_2$O where X = Cl, Br, or I, and dipyam = di-2-pyridylamine. Physical data, including the far-infrared spectra, are given for these compounds as well as for some 2,2'-bipyridyl and 1,10-phenanthroline complexes of rhodium(III) and iridium(III). The detailed stereochemistry of *trans*-[Rh(dipyam)$_2$X$_2$]X is discussed.

We are currently investigating the reaction of a wide variety of reducing agents with complexes of rhodium(III) and iridium(III) containing various bidentate 2-substituted pyridines as ligands.[1] We report in this Paper the preparation of some new complexes of rhodium and iridium which were required as starting materials for the above work.

Experimental

Spectra.—Solution spectra (35,000—4000 cm.$^{-1}$) were measured using a Unicam S.P. 700 spectrophotometer. Infrared spectra were taken for Nujol mulls using Perkin-Elmer 237 (4000—625 cm.$^{-1}$) and Grubb–Parsons DM4 (667—222 cm.$^{-1}$) spectrophotometers.

Halide Analysis.—We have developed the following method of halide analysis to overcome the difficulties experienced in obtaining reliable data for bromo- and iodo-complexes of rhodium and iridium. An intimate mixture of the complex (0·1—0·15 g.) and sodium carbonate (1·0 g.) was heated in a platinum crucible at 1000° for 1—2 hr. The fusion mixture was extracted with dilute nitric acid and filtered; the halide in the filtrate was determined as the silver salt.

Magnetic measurements were by the Gouy method at room temperature, solution conductivities were measured with a Doran conductivity bridge at 25°. All solvents were purified by literature methods.

trans-*Dichlorobis(di-2-pyridylamine)rhodium*(III) *Chloride.*—Rhodium trichloride trihydrate (0·26 g.) in absolute ethanol (30 ml.) was treated with an acetone (5 ml.) solution of di-2-pyridylamine (0·47 g.) and refluxed for 15 min. The colour of the solution changed from brownish yellow through red-brown to orange-yellow. The volume was reduced to 20 ml. and yellow crystals deposited on cooling. The *complex* (0·27 g.) (Table 1) was recrystallised from 20% aqueous ethanol.

trans-*Dibromo- and Di-iodobis-(di-2-pyridylamine)rhodium*(III) *Halide.*—Rhodium trichloride trihydrate (0·26 g.) together with a ten-fold excess of potassium bromide (or iodide) was dissolved in water (10 ml.) and treated with an ethanolic (5 ml.) solution of di-2-pyridylamine. The resulting solution was refluxed for 30 min. and then cooled. The *complexes* (Table 1) were recrystallised from dimethylformamide–carbon tetrachloride (yields: bromide, 0·4 g.; iodide, 0·45 g.).

Tris(di-2-pyridylamine)rhodium(III) *Trichloride Trihydrate.*—An intimate mixture of rhodium trichloride trihydrate (0·26 g.) and di-2-pyridylamine (1·7 g.) was heated in an oven at 212° for 14 hr. The mixture was extracted with water (250 ml.) after cooling and filtered, the residue being unreacted ligand. Fractional crystallisation of the filtrate yielded first *trans*-[Rh(dipyam)$_2$Cl$_2$]Cl and secondly the *tris-complex trihydrate* (0·35 g.). The complex could be dehydrated by heating for 6 hr. at 137°/0·1 mm. The complex could also be isolated from the filtrate of any preparation of *trans*-[Rh(dipyam)$_2$Cl$_2$]Cl.

Tris(di-2-pyridylamine)iridium(III) *Trihalide Trihydrate.*—Potassium chloroiridite (0·32 g.) in water (10 ml.) was treated with an ethanolic solution (5 ml.) of di-2-pyridylamine (0·37 g.) and heated under reflux for 30 min. The solution was cooled to yield crystals of the *complex* (Table 1) which was recrystallised from dimethylformamide–carbon tetrachloride. The bromide and iodide were obtained by adding potassium bromide or iodide (yields: chloride, 0·27 g.; bromide, 0·46 g.; iodide, 0·57 g.).

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[1] B. Martin, W. R. McWhinnie, and G. M. Waind, *J. Inorg. Nuclear Chem.*, 1961, **23**, 207.

TABLE 1

Preparation of the complexes

No.	Complex	Colour	Ref.
1	*trans*-[Rh(dipyam)$_2$Cl$_2$]Cl	Yellow	This work
2	*trans*-[Rh(dipyam)$_2$Br$_2$]Br	Orange-brown	,,
3	*trans*-[Rh(dipyam)$_2$I$_2$]I	Brown	,,
4	[Rh(dipyam)$_3$]Cl$_3$,3H$_2$O	Pale yellow	,,
5	[Rh(dipyam)$_3$]Cl$_3$	Orange-yellow	,,
6	[Ir(dipyam)$_3$]Cl$_3$,3H$_2$O	Orange	,,
7	[Ir(dipyam)$_3$]Br$_3$,3H$_2$O	Brown-yellow	,,
8	[Ir(dipyam)$_3$]I$_3$,3H$_2$O	Brown	,,
9	*trans*-[Rh(bipy)$_2$Cl$_2$]NO$_3$		2
10	*trans*-[Rh(bipy)$_2$Cl$_2$]Cl,2H$_2$O		3
11	*trans*-[Rh(bipy)$_2$Br$_2$]Br,2H$_2$O		3
12	*cis*-[Ir(phen)$_2$Cl$_2$]Cl,3H$_2$O		4
13	*trans*-[Ir(phen)$_2$Cl$_2$]Cl,3H$_2$O		4
14	*trans*-[Rh(phen)$_2$Cl$_2$]Cl,2H$_2$O		*

Analytical data

	Found (%)					Formula	Required (%)				
No.	C	H	M	N	X		C	H	M	N	X
1	43·5	3·9	18·9	14·8	18·9	$C_{20}H_{18}Cl_3N_6Rh$	43·5	3·3	18·7	15·5	19·1
2	35·9	3·1	15·1	11·6	34·6	$C_{20}H_{18}Br_3N_6Rh$	35·1	2·7	15·2	12·3	35·0
3	28·1	2·8	12·4	—	45·7	$C_{20}H_{18}I_3N_6Rh$	29·1	2·3	12·5	—	46·1
4	—	—	—	—	13·4	$C_{30}H_{33}Cl_3N_9O_3Rh$	—	—	—	—	13·7
5	—	—	—	—	14·2	$C_{30}H_{27}Cl_3N_9Rh$	—	—	—	—	14·2
6	—	—	22·8	—	12·3	$C_{30}H_{33}Cl_3IrN_9O_3$	—	—	22·3	—	12·5
7	—	—	20·1	—	23·9	$C_{30}H_{33}Br_3IrN_9O_3$	—	—	19·3	—	23·9
8	33·3	3·1	—	11·3	32·9	$C_{30}H_{33}I_3IrN_9O_3$	31·6	2·9	—	11·1	33·4

* Prepared by a method similar to one recently published.[3]

Adduct Formation with Hydrochloric Acid.—It was recently shown [5] that *trans*-dihalogeno-complexes of rhodium(III) form adducts containing the ion $H_5O_2^{2+}$, with halogen acids which may be identified by a characteristic infrared spectrum. We have prepared the adducts tabulated below and have analysed them by recording the weight loss under the following conditions:

$$[\mathrm{M(chelate)_2Cl_2}]\mathrm{Cl,2H_2O,HCl} \xrightarrow{137^\circ/0{\cdot}1\ \mathrm{mm.}} [\mathrm{M(chelate)_2Cl_2}]\mathrm{Cl}$$

	Weight loss	
	Found	Calculated
[Rh(dipyam)$_2$Cl$_2$]Cl,2H$_2$O,HCl	11·7	11·6
[Rh(phen)$_2$Cl$_2$]Cl,2H$_2$O,HCl	10·6	11·3
[Ir(phen)$_2$Cl$_2$]Cl,2H$_2$O,HCl	10·0	11·0

The adducts gave satisfactory infrared spectra. The compound reported [4] to be *cis*-[Ir(phen)$_2$Cl$_2$]Cl,3H$_2$O did not give an adduct with hydrochloric acid.

RESULTS

The solubility of the complexes in water and ethanol decrease as the size of the halide anion increases. Dimethylformamide was the only solvent of those investigated which dissolved appreciable amounts of all the complexes and we therefore report solution spectra and molar conductivities taken in this solvent, together with magnetic data, in Table 2. The infrared spectra (4000—625 cm.$^{-1}$) are unremarkable and are not tabulated. The far-infrared spectra are presented in Table 3.

DISCUSSION

The simple preparations of the complexes reported in this Paper are undoubtedly achieved because of the catalytic behaviour of ethanol as recently demonstrated by Wilkinson and his associates.[3]

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[2] B. Martin and G. M. Waind, *J.*, 1958, 4284.

[3] R. D. Gillard, J. A. Osborn, and G. Wilkinson, *J.*, 1965, 1951.

[4] B. Chiswell and S. E. Livingstone, *J. Inorg. Nuclear Chem.*, 1964, **26**, 47.

[5] R. D. Gillard and G. Wilkinson, *J.*, 1964, 1640.

TABLE 2

Solution spectra (in DMF, $\nu_{max.}$ in cm.$^{-1}$, $\varepsilon \times 10^{-3}$ in parentheses), molar conductivities (in DMF), and magnetic moments of the solids at 291°K

		Conductivity (mhos)			
Complex	$\nu_{max.}$	10^3M	10^{-4}M	10^{-5}M	μ_{eff} (B.M.
trans-[Rh(dipyam)$_2$Cl$_2$]Cl	33,600(14), 29,800(8·7), 24,800(1·98)	45			0
trans-[Rh(dipyam)$_2$Cl$_2$]Cl *	34,100(14), 30,350(9·0)	—			
trans-[Rh(dipyam)$_2$Br$_2$]Br	34,200(15·6), 30,300(10·5), 24,550(3·9)	33			0 †
trans-[Rh(dipyam)$_2$I$_2$]I	34,600(31·2), 29,400(9·8), 24,800(4·9)	92			0·65
trans-[Rh(bipy)$_2$Cl$_2$]NO$_3$		78			
trans-[Rh(phen)$_2$Cl$_2$]Cl,2H$_2$O	34,600(21·7), 30,400(4·9), 27,300(2·9)	—			
[Rh(dipyam)$_3$]Cl$_3$,3H$_2$O	32,500(44·4), 29,600(17·3), 23,900(13·0)	‡	287		0
[Ir(dipyam)$_3$]Cl$_3$,3H$_2$O	32,700(33·3), 30,000(26·9), 26,500(6·7)	40		200	0
[Ir(dipyam)$_3$]Br$_3$,3H$_2$O	33,000(33·9), 30,100(24·8), 26,700(8·5)	69	112	298	0
[Ir(dipyam)$_3$]I$_3$,3H$_2$O	33,000(34·9), 30,400(22·8), 26,800(7·1)	72	122	298	0

* In aqueous solution. † At 292°K. ‡ Insufficiently soluble.

TABLE 3

Far-infrared spectra (column headings refer to Table 1)

1	2	3	4	6	7	8	Assignment
649m	649m	645m	649m	645m	649sh		
606m	606w	606w	604w	602s	621m	602w	α(CCC)
					599w-m		
578w	588w	576w	563w	555w	585w-m	575w	
535m	535m	532m	535m	538m-s	533m	532m	X-sens.
465m	465m	465m	468m	468m	459w	461w	
445m	444m	439m	443m-w	444w-m	431w	435w	ϕ-(CC)
395w	395w	391m, sh	392m	401w	408w	408w	
374m	377m-s	375m	382m	383m	375w	392w	X-sens.
368w-m	370m	364m	355m	367m	350w	350w	
350m-s	339m	338m	337m-s	325s	325s	327m	X-sens.
				315s	302s	302m	
331vs							ν_{as}Rh–Cl
300m	295m	300m					Rh–N
287m-s	288m	276m					
270s	265m-s	262m					
249m-s	247m	248m-s					
	222sh, s						ν_{as}Rh–Br
			300sh				
			294m		293m-s		
			289m	285w		289m-w	Rh–N$^+$
			275s	279s	278m	278m	
			267m	265w-m	260m	252m	H$_2$O
			244m	243m	246m	245m-w	H$_2$O

9	10(xH$_2$O) *	11(xH$_2$O) *	14	13	13(xH$_2$O) *	Assignment
649m	645w	640w	608w	617m-w	615m-w	Ligand
526w	568m		520w	535w	534w-m	
		515b	508w	522w	524w-m	
	478m	478m	495w	510w	510w-m	
465w	463m	463m		462m	463m	
457w	455m	452m	444m	442m	437m	
417s	417s	415s	412w	421w-m	421w	
		368m	406w	410w-m	410w	
		351m	396w	400w-m	398w	
349vs	352vs		347vs			
	348vs		342vs	339s	339s	M–Cl
		318s				M–Br(?)
276s	276s	282m-s	308s	313sh	313sh	M–N
266m	266m	267m-s	294m	303s	304vs	
			276m-s	290s	290m-s	
			255m-s	249m-s		
	246m	245w	246m	245m-s	247m	H$_2$O
			235m	235m	236vs	

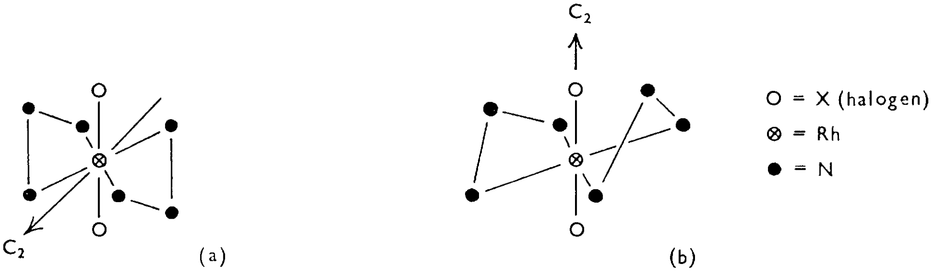
s = strong, m = medium, w = weak (relative intensities of bands within a spectrum).

* These compounds were heated at 196°/0·1 mm. for 6 hr. before measuring the spectrum, but could not be completely dehydrated.

Solution Spectra and Conductivity Data.—The spectra of [Rh(dipyam)$_2$X$_2$]X (X = Cl, Br, or I) strongly suggest that the three cations have the same stereochemistry, also they are not untypical of other *trans*-dihalogeno-complexes of rhodium(III),[3] thus supporting the assignment of stereochemistry suggested by the ability of the chloro-complex to form an adduct with hydrochloric acid. The conductivity data characterise the bisdipyridylamine complexes as 1 : 1 electrolytes,[6] cf. [Rh(bipy)$_2$Cl$_2$]NO$_3$.[2] The tris-complexes gave low molar conductivities in 10^{-3}M-solutions (because of ion-pairing[7] in dimethylformamide).

Infrared Spectra (667—222 cm.$^{-1}$).—The assignments of the first half of Table 3 are based on previous work with various halogeno-complexes[8] and with other di-2-pyridylamine complexes.[9] It is possible to assign only one strong band as $\nu_{\text{Rh-Cl}}$ for [Rh(dipyam)$_2$Cl$_2$]Cl, thus suporting the *trans*-stereochemistry of the cation. The region assigned to metal–nitrogen[9] is complex, but this is also true of other dipyridylamine complexes. However, the fact that the absorptions are faithfully reproduced in the spectra of the bromo- and iodo-complexes does strengthen the conclusions drawn from the solution spectra that all three bisdipyridylamine complexes have the same stereochemistry.

Any description of the stereochemistry of the *trans*-dihalogenobis(dipyridylamine)-rhodium(III) cations must consider the relative disposition of the two co-ordinated dipyridylamine molecules which are pyramidal about the imino-nitrogen atom. The two possible structures are shown schematically in the Figure. Molecular models indicate that the *true* molecular symmetries are C_{2h} (a) and C_{2v} (b). It can be shown that the two metal-halogen stretching vibrations span the irreducible representations A_g (Raman) + B_u (i.r.) of C_{2h} or $2A_1$ (Raman, i.r.) of C_{2v}; thus, it is possible in theory to distinguish the two possible structures. In practice we feel it would be too bold to regard our failure to observe a second (weak) Rh–Cl band as conclusive proof of the C_{2h} structure.



Schematic representation of *trans*-[Rh(dipyam)$_2$X$_2$]X

The compounds which crystallise as hydrates give complex spectra below 300 cm.$^{-1}$ which it would be premature to discuss. The assignments in the second half of Table 3 are very tentative and based on previous work with 2,2′-bipyridyl[10,11] and 1,10-phenanthroline[10] complexes.

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