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Complexes of 2,9-Dimethyl-1,10-phenanthroline with Rhodium(III) and Iridium(III) Halides

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The preparation and properties of the complexes M-(2,9-dimethyl phenanthroline) X_3 *(where M = Rhodium(III) or iridium(III) and X = Cl, Br or I) are reported. The stereochemistry of the complex* [*Rh-(dmp)*Cl_3] *is discussed in terms of penta co-ordination and the other trihalogeno complexes are found to be isomorphous. Solid state reaction of* $RhCl_3 . 3H_2O$ *with dmp yields a chloroform soluble low valent rhodium complex, the exact nature of which is uncertain.*

Introduction

The steric effects of the methyl groups of the rigid bidentate ligands 2,9-dimethylphenanthroline(dmp) would primarily determine the stereochemistry of complexes formed with metal salts.[1] The *bis*-chelate compounds of the type $[M(dmp)_2X_2]$ (where X = halogen) would be *cis*-complexes. An alternative behaviour would be similar to that of the parent ligands 1,10-phenanthroline (phen) producing *either* the [phen H]-$[M(phen)X_4]$ (X = halogen) complex which in the case of iridium(III) undergoes photocatalytic aquation reaction to yield the neutral species $[Ir(phen)X_3 . H_2O]$[2] or the *cis*–$[M(phen)_2X_2]^+$ complex with rhodium(III)[3,4] and iridium(III)[5] halides.

Preston and Kennard recently reported five co-ordinate complexes of dmp with nickel(II) and copper(II) chlorides.[6] This paper describes some complexes of dmp with rhodium(III) and iridium(III)-halides.

Experimental Section

Preparation of Complexes. Trichloro- mono 2,9-dimethylphenanthroline Rhodium(III). A *warm* methanolic solution of $RhCl_3 . 3H_2O$ 0.26 g in 10 ml was mixed with a *warm* methanolic solution (5 ml) of dmp (0.25 g) and 5 ml of 2,2′-dimethoxypropane. The mixture was refluxed for 30 min, the solution was cooled and the resulting orange-brown crystals were dried over P_4O_{10} and recrystallised from an acetonitrile-carbon tetrachloride mixture. Yield: 0.45 g; *Anal.* Found: C, 40.4, H, 3.0; N, 6.6; $C_{14}H_{12}Cl_3N_2Rh$ requires C, 40.3; H, 2.9; N, 6.7. Molecular weight in nitromethanes (0.25% of solution) 435 (vapour pressure osmometer). Required 417.6; Λ_M chloroform ~0 Mhos cm^{-1} mole^{-1}.

The Aquo-disolvato adduct of chloride [*Rh*(*dmp*)-$Cl_3 . H_2O$]. *2ROH* (*R = methyl, ethyl*). The preparation of the chloro complex made by refluxing a mixture of the *cold* ethanolic or methanolic solutions of the reactants results in the formation of a creamy yellow solid. Recrystallised from a chloroform/carbon tetrachloride mixture (50%). *Anal.* (Found (for the methanol adduct): C, 38.8; H, 4.1; N, 5.6; Cl, 21.3; $C_{16}H_{22}Cl_3N_2RhO_3$ requires: C, 38.5; H, 4.0; N, 5.6; Cl, 21.3. (Λ_M in $CHCl_3$ ~0 mhos cm^{-1} mole^{-1}).

The yellow complex on heating at 140° for 12 hours lost the solvent molecules yielding the anhydrous brown complex. Thermogravimetric assay and mass spectral measurements indicated the presence of methanol and water in the yellow complex. Losses of the water molecules and methanol in T.G.A. occur at 60-80° and 120-140° respectively.

Tri-bromo mono-2,9-dimethylphenanthroline Rhodium(III). $RhCl_3 . 3H_2O$ (0.26 g) and rhodium bromide (1 g) dissolved in *warm* methanol (20 ml) was mixed with a *warm* methanolic solution (10 ml) of dmp (0.22 g). On refluxing for 30 min the creamy orange solid initially formed dissolved and the solution deposited a chocolate brown solid. Yield 0.4 g. Recrystallised from DMF/CCl_4 mixture (10%) (DMF = Dimethylformamide). *Anal.* Found: C, 30.6; H, 2.9; N, 5.1; $C_{14}H_{12}Br_3N_2Rh$ requires: C, 30.6; H, 2.2; N, 5.1. (Λ_M in CH_3CN = 8 mhos cm^{-1} mole^{-1}).

Triiodo mono 2,9-dimethylphenanthroline rhodium(III). The preparation was as for the bromide using sodium iodide (2 g) and aqueous methanol as the solvent. Yield 0.5 g. *Anal.* Found: C, 23.8; H, 1.8; N, 3.9. $C_{14}H_{12}I_3N_2Rh$ requires: C, 24.3; H, 1.8; N, 4.1. The complex was insufficiently soluble in nitromethane and acetonitrile for conductivity measurements. Λ_M in DMF = 10.2 mhos cm^{-3} mole^{-1}.

Solid state reaction of rhodium trichloride and 2,9-dimethylphenanthroline. An intimate mixture of

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(1) D. B. Fox, J. R. Hall, and R. A. Plowman, *Austral. J. Chem.*, *15*, 235 (1962).

(2) I. A. Broomhead and W. Grumley, *Chem. Comm.*, 1211 (1968).

(3) G. C Kulasingam, W. R. McWhinnie, and J. D. Miller, *J. Chem. Soc.*, (A), 521 (1969).

(4) R. D. Gillard and B. T. Heaton, *J. Chem. Soc.* (A), 451 (1969). E. D. McKenzie and R. A. Plowman, *J. Inorg. Nucl. Chem.*, 32, 199 (1970).

(5) G. C. Kulasingam and W. R. McWhinnie, *J. Less Common Metals*, *17*, 47 (1969).

(6) H. S. Preston and C. H. L. Kennard, *J. Chem. Soc.* (A), 2955 (1969).

$RhCl_3 . 3H_2O$ and dmp (0.26 g and 0.22 g respectively) was heated in a jacket of nitrobenzene for 12 hours. The product was extracted with purified chloroform and the solvent evaporated. An intense purple diamagnetic solid was obtained (0.3 g). This product was recrystallised from a 10% solution of CCl_4 in chloroform, the only solvent of those investigated with which no apparent reaction occurred. However since it proved virtually impossible to obtain consistent analytical data for a large number of independently prepared specimens it is possible that some reaction occurs with these chlorinated solvents. The data obtained suggested a rhodium to ligand ratio of 1:1. The chloride analysis varied considerably, thus giving some support for the above suggestion of reaction with the solvent.

Although the problem of purification could not be satisfactorily overcome the visible absorption spectrum of a chloroform solution (λ_{max}, 17,800 cm^{-1}, $\varepsilon \simeq 10{,}000$) is suggestive of a rhodium(I) complex comparable with those suggested for those of 2,2′-dipyridyl.[7] The brown trichlororhodium(III) dmp complex also decomposes when heated above 250° for 12 hours to yield this purple low valent species. During the breakdown of the trichloro system HCl is one of the main products obtained. This purple compound is not discussed further in this paper.

Trichloro mono 2,9-Dimethylphenanthroline Iridium(III). Potassium chloroiridate (0.5 g) dissolved in water (10 ml) was added to a warm ethanolic solution of dmp (0.22 g in 5 ml). A grey solid was formed on mixing and on refluxing dissolved; the yellow solution changed colour to orange-brown and deposited orange crystals after 30 minutes. Solid dried over P_4O_{10}. Yield: 0.45 g. *Anal.* Found: C, 393.3; N, 5.5; H, 2.4. $C_{14}H_{12}IrCl_3N_2$ requires: C, 33.2; H, 2.4; N, 5.5; solid insufficiently soluble in nitromethane for conductivity and molecular weight determinations. Λ_M (10^{-3} *M* in acetonitrile) 9.2 mhos cm^{-3} $mole^{-1}$.

Tribromo 2,9-dimethylphenanthroline. Potassium chloroiridate (0.5 g) and sodium bromide (1.2 g) dissolved in water (10 ml) was mixed with an ethanolic solution of dmp (0.22 g in 5 ml) and refluxed for 30 minutes. A deep brown complex deposited on cooling. The complex dried over P_4O_{10}. Yield 0.5 g. Found: C, 26.00; H, 1.85; N, 4.35. $C_{14}H_{12}Br_3IrN_2$ requires: C, 26.30; H, 1.90; N, 4.38. Complex insufficiently soluble in nitromethane. $\Lambda_M = 8.0$ mhos (10^{-3} *M* in acetonitrile).

Physical measurements. Infrared spectra were measured using a Perkin Elmer 225 spectrometer and with a RIIC FS interferometer between 400 and 50 cm^{-1}. Diffuse reflectance spectra were determined using a Unicam Sp700 spectrophotometer incorporating a standard reflectance attachment. Molar conductivities were measured with a Wayne Kerr bridge. Mass spectra and thermogravimetric analysis were measured with an A.E.I. MS9 and DuPont 950 thermogravimetric analyser respectively. X-ray measurements were made by using CuKα radiation. Vapour pressure osmometer Mechrolab model 301 A was used for molecular weight determinations (accuracy within ±5%).

Results and Discussion

In order to prepare the *cis*[$M(dmp)_2X_2$] cationic complex, the metal to ligand ratio was varied and different preparative routes used including the use of hydrazine as a reducing agent. However, the products of the reaction of dmp with halides of rhodium(III) and iridium(III) were found to be 1:1 complexes. Rhodium trichloride reacts with dmp in methanol or ethanol to give a yellow complex and elemental analysis, mass spectrum and thermogravimetric assay indicate the presence of a water molecule and alcohol in this compound. Support for formulating this non-electrolyte as the octahedral complex [$Rh(dmp)Cl_3 . H_2O$] . 2ROH (R = methyl or ethyl) is found in the infrared spectrum (Table I and Figure1). On heating at 140° for 12 hours this complex loses the solvent molecules to yield a brownish compound The latter could also be made by reacting rhodium trichloride and dmp in methanol in the presence of 2.2′-dimethoxypropane. On the basis of elemental analysis the composition corresponds to « $Rh(dmp)Cl_3$ » and the complex is a non-electrolyte. The molecular weight determination in nitromethane (vapour pressure osmometry) gave a value of 435 (calculated 417) which although marginally high for a monomer is still within the range of accuracy of the technique (±5%) but does not unambiguously distinguish it from bridged dimeric octahedral species (Figure 2) which may be cleaved by the weakly donating nitromethane molecules.

Table I. Far infra red spectra[a] (metal-halogen bands only).

Complex	ν in Cm^{-1}
[$Rh(dmp)Cl_3 . H_2O$] . $2CH_3O$	345s, 336s, 323s, 309ms
[$Rh(dmp)Cl_3$]	357s, 343s, 320s
[$Ir(dmp)Cl_3$]	339ms, 320sh, 314s

[a] As nujol mulls between CsI plates. - s = strong, m = medium, sh = shoulder.

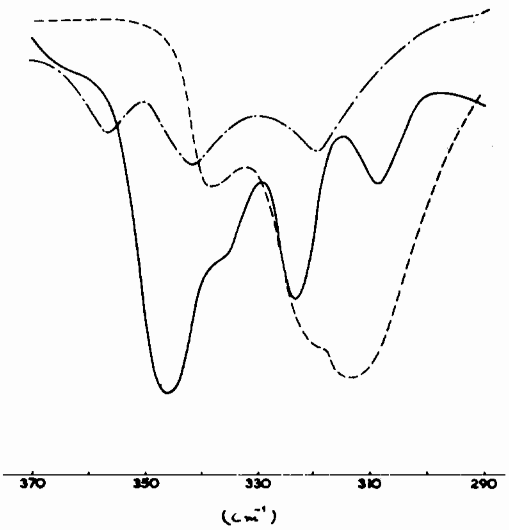

Figure 1. Far-infrared spectra (metalhalogen bands only) of 1. [$Rh(dmp)Cl_3 . H_2O$]. $2CH_3OH$. (————). 2. [$Rh(dmp)Cl_3$] (—— — ——) 3. [$Ir(dmp)Cl_3$] (— — — —).

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(7) B. Martin, W. R. McWhinnie, and G. M. Waind, *J. Inorg. Nucl. Chem.*, *23*, 207 (1961).

The diffuse reflectance spectrum of the brown « Rh(dmp)Cl_3 » complex is poorly resolved with intense ligand absorbtions partially masking the d↔d bands. However, the profile of the spectrum of the complex in nitromethane is similar to the diffuse reflectance spectrum, suggesting similar structures.

Table II. Diffuse reflectance spectra of M(dmp)X_3 Complexes Vs . MgO.

Complex	ν max (cm^{-1})
[Rh(dmp)Cl_3 . H_2O] . 2CH_3OH	26,800, 22,000 (s,b)
[Rh(dmp)Cl_3]	26,600, 21,800 (s,b) 18,600 (sh)
[Rh(dmp)Br_3]	26,400, 21,000 (sh) 17,800 (sh)
Rh(dmp)I_3	26,300 (sh), 20,600, 17,500 (sh)
Ir(dmp)Cl_3	27,000, 22,600 (sh), 20,000 (sh)
Ir(dmp)Br_3	26,000, 20,000(sh) 18,900 (sh)
«Rh^I Complex»	17,800 (solution spectrum in $CHCl_3$ ε ≃ 10,000)

s = strong, b = broad, sh = shoulder.

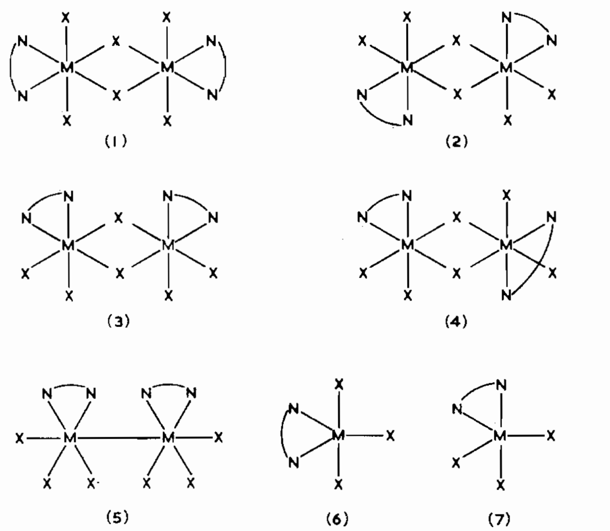

Figure 2. Possible structures for the complex «Rh dmp Cl_3».

The bromo- and iodo- complexes of rhodium(III) and the chloro- and bromo- complexes of iridium(III) also have the composition « M(dmp)X_3 ». The above four complexes and the brown « Rh(dmp)Cl_3 » complex gave similar X-ray powder photographs which are different from that of the hydrated yellow chlororhodium octahedral complex. Further the infra-red spectrum (4000-600 cm^{-1}) and the diffuse reflectance spectra (Table II) of the « RhdmpX_3 » (X = Cl, Br and I) complexes are alike and show the expected shifts of the d↔d bands to lower frequencies.

Far infrared spectra offer the possibility of distinguishing a five coordinate monomer from a six coordinate dimeric structure. Possible bridged dimeric and monomeric trigonal bipyramidal structures are given in Figure 2 Symmetry considerations would predict a minimum of four metal-halogen bands for the five coordinate monomers.[8] The appearance of only three bands (Table I and Figure 1) for the M(dmp)Cl_3 (M = Rh or Ir) complexes is strong evidence for 5-cordinate monomeric structures.

As noted elsewhere[9] a the bromo- complexes of rhodium(III) and iridium(III) with pyridyl ligands often give poorly resolved spectra in the region of the metal-halogen stretch. For the dmp complexes unambiguous assignments could not be made for more than one band (lack of Raman facilities).

A self consistent interpretation of the data presented in this paper can only be made in terms of five coordination for the complex [M(dmp)X_3]. However, although metal-halogen frequencies suggest this as a strong possibility, definitive proof is not available.

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(8) J. R. Hudman, M. Patel, and W. R. McWhinnie, *Inorg. Chim. Acta, 4,* 161 (1970).
(9) W. R. McWhinnie and I. Bhyat, unpublished Results