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Far Infrared Spectra of Some Halo-Amine Complexes of Cobalt(III), Rhodium(III) and Iridium(III)

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Far infrared spectra of halopentammine, trans-*dihalobisethylenediamine and some* cis *or* trans *dihalotriethylenetetramine complexes of cobalt(III), rhodium(III) and iridium(III) have been measured and assignments made for the metal-halogen stretching vibration and nitrogen metal nitrogen deformation bands.*

Introduction

This paper reports the far infrared spectra of several cobalt(III), rhodium(III) and iridium(III) amine complexes. The data presented have been used to characterise some of the complexes used in our other work.[1-3]

Modern instruments and techniques have made measurements down to 30 cm^{-1} possible thus making metal ligand vibrations observable. It is with two of these vibrations, namely the nitrogen-metal deformation (δNMN) and the metal-halogen stretching vibration (νM–X) that this paper is mainly concerned.

Several papers have reported the far infrared spectra of $[Co(NH_3)_5X]^{2+}$ complexes,[4-6] where X=Cl or Br, and assignments have now been agreed. No far infrared spectra of the corresponding rhodium and iridium complexes have been reported. Nakagawa and Shimanouchi[6] and Hughes and McWhinnie[7] have both carried out far infrared measurements on *trans*-$[Coen_2Cl_2]Cl$ and agree closely on their assignments. There is disagreement between Adams[8] and Nakamoto[9] on the assignment of the metal-chlorine stretching vibration in *trans*–$[Rhen_2Cl_2]Cl$. It is only very recently that data have been published on the far infrared spectra of *trans*–$[Iren_2Cl_2]Cl$[10] but until this paper no data have been published on $[MtrienX_2]^+$ complexes where M=Co, Rh and Ir.

In this investigation we have measured the far infrared spectra of all the chloro complexes of the type $[M(X)Cly]^{(3-y)+}$ where M is either Co^{III}, Rh^{III} or Ir^{III} and X is either NH_3, en or trien (en=ethylenediamine, trien=triethylenetetramine). The spectra of the corresponding bromo complexes have also been measured in many cases, enabling us to assign with certainty the metal-halogen frequencies.

Experimental Section

In most cases the complexes studied were prepared by standard methods or modifications thereof. Where modifications have been made this is indicated below. All the complexes prepared gave satisfactory elemental analyses.

$[Co(NH_3)_5Cl]Cl_2$, G. G. Schlessinger[11]; $[Co(NH_3)_5Br]Br_2$, H. Diehl *et al.*;[12] $[Rh(NH_3)_5Cl]Cl_2$, F. Basolo and S. A. Johnson[13]; $[Rh(NH_3)_5Br]Br_2$, this complex was prepared as for the chloro complex[13] by substituting rhodium tribromide for rhodium trichloride and ammonium bromide for ammonium chloride in the correct molar quantities.

$[Ir(NH_3)_5Cl]Cl_2$, E. R. Gardner *et al.*[1]; *trans*–$[Coen_2Cl_2]Cl$, J. C. Bailar[14]; [*trans*–$[Coen_2Br_2]Br$, this complex was prepared as for the chloro complex[14] by substituting cobalt(III) bromide for cobalt chloride and hydrobromic acid for hydrocloric acid in the correct molar quantities. *trans*–$[Rhen_2Cl_2]Cl$ and *trans*–$[Rhen_2Br_2]Br$; F. Basolo and S. A. Johnson.[13] The nitrates prepared by this method were converted to the halide form by ion exchange.

trans–$[Iren_2Cl_2]Cl$; R. A. Bauer and F. Basolo[15] *trans*–$[Iren_2Br_2]Br$; 1 g of *trans*–$[Iren_2Cl_2]Cl$ was refluxed with 30 cm^3 of 40% HBr for 10 hours. The solvent was then removed by vacuum distillation and the procedure repeated a further two times. The complex was recrystallised from water.

cis–$[Iren_2Cl_2]Cl$, I. B. Baranovskii *et al.*[16]; *cis*–$[Iren_2Br_2]Br$, the method of Baranovskii *et al.*[16] was followed but was found to give an impure product. The impure product was boiled under reflux with further quantities of KBr in order to obtain pure *cis*–$[Iren_2Br_2]Br$.

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Table I. Observed band frequencies for a series of halopentammine complexes

	νM–Br		νM–Cl	δNMN
$[Co(NH_3)_5Cl]^{2+}$		204 mb	278, 284 sb	325 sb
$[Co(NH_3)_5Br]^{2+}$	203 sb			324 sb
$[Rh(NH_3)_5Cl]^{2+}$			274, 282 sb	296 sb
$[Rh(NH_3)_5Br]^{2+}$	207 sb			292 sb
$[Ir(NH_3)_5Cl]^{2+}$			266, 276 svb	282 svb

s, strong; m, medium; w, weak; refer to the relative heights of peaks. vb, very broad; b, broad; m, medium; sh, sharp refer to the relative widths of peaks. Coding lists peak heights before peak widths.

Table II. Observed band frequencies for a series of *trans*-dihalobisethylenediamine complexes

	νM–Br			νM–Br		δNMN	νM–Cl
$[Coen_2Cl_2]^+$			214 mm		235 wm	283, 287, 296*sb	349, 363*wm
$[Coen_2Br_2]^+$	188, 196 mb		214 mm		235 wm	287, 298 sb	
$[Rhen_2Cl_2]^+$		198 mm				278, 280 sb	350 s, sh
$[Rhen_2Br_2]^+$		198 mm		221 sb		262, 273, 280 sb	

The irididum data is shown in Table III. * Reference 7.

cis–$[CotrienCl_2]Cl$, F. Basolo[14]; *cis*– and *trans*–$[CotrienBr_2]Br$, J. C. Bailar Jr and J. Selbin[18]; *cis*–$[RhtrienCl_2]Cl$, F. Basolo and S. A. Johnson[13] *cis*–$[RhtrienBr_2]Br$.

The method for preparing the chloro complex by Johnson and Basolo[13] was modified as follows.

To 1g of rhodium tribromide in 50 mls of water was added a solution containing 0.715 g trien, 3.48 g 48% w.w. H. Br and 1.11 g KOH.

The solution was boiled under reflux for twenty minutes, filtered and then transferred to a steam bath until the volume had been reduced to 10 mls. The solution was then cooled in an ice bath where upon the yellow powder of the complex resulted. The complex was filtered off and recrystallised from water.

trans–$[IrtrienCl_2]Cl$. The method of Basolo[19] was modified as follows: 5 g of K_2IrCl_6 were placed in 50 ml hot water and reduced with 0.955 g of $K_2C_2O_4$ by heating at 80°C for a few minutes. A solution of 6 ml triethylenetetramine in 15 ml H_2O was neutralised with conc. HCl and added to the reaction solution. The solution was heated to boiling and 0.05 g KH_2PO_2 was added followed by 10 ml conc HCl. The solution was then boiled for a half an hour before a further 6 ml of triethylenetetramine were added. The solution was then boiled under reflux for twenty four hours, allowed to cool and then neutralised with $HClO_4$. The solution was then transferred to a steam bath and evaporated to one third its original volume. The solution was then left to cool overnight in a refrigerator whereupon a yellow powder of the complex resulted. The complex was recrystallised from water and converted to the chloride form by ion exchange.

trans–$[CotrienCl_2]Cl$; R. D. Gillard and G. Wilkinson.[21]

Infrared spectra were measurd as wax discs on a RIIC Interferrometer type No. F. S. 720 coupled with a wave analyser. The measurements were carried out at the P.C.M.U., U.K.A.E.A., Harwell and a resolution of less than 0.5 cm^{-1} was obtained. Computer resolved spectra were also run in a number of cases but the results showed no advantages over those run using a coupled wave analyser.

Results and Discussion

Table I lists the observed band frequencies for the series of halopentammine complexes. Our values for the cobalt complexes are in agreement with those of Watt and Klett,[4] Sacconi *et al.*[5] and Nakagawa and Shimanouchi.[6] The assignment for the iridium complex followed from a comparison with the analogous cobalt and rhodium complexes.

Table II lists the observed band frequencies for the series of dihalobisethylenediamine complexes. In our spectrum of the cobalt complex, the bands assigned to νM–Cl Hughes and McWhinnie[7] are of very low intensity. This is in complete contrast to those of the rhodium and iridium complexes. In addition it appears that the strong, broad band at 283-296 cm^{-1} may contain a shoulder at 280 cm^{-1} as the intensity of this band is reduced in the corresponding *trans*–$[Coen_2Br_2]Br$ spectrum. Hughes and McWhinnie[7] assigned the νM–Br at approximately 230 cm^{-1}, and although we observed a band at 235 cm^{-1} it is of weak intensity and may have been masked by the strong broad peak in the chloro spectrum. The strong, broad band at 188-196 cm^{-1} is typical of metal bromine stretching vibration bands found in other bromine containing complexes discussed in this paper and hence we have assigned this band to νM–Br for *trans*–$[Coen_2Br_2]Br$. However this assignment gives a lower νCo–Br: νCo–Cl ratio than one would expect and in addition it does not give the increase in νCo–Br expected when comparing the bisethylenediamine and pentammine complexes.

For the dichloro rhodium complex our results support the findings of Adams.[8] Our values for the *cis* and *trans*–$[Iren_2Cl_2]Cl$ complexes show similarity

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Table III. Observed band frequencies for *cis-* and *trans-*dihalobisethylenediamine iridium(III) ions

		νM—Br	δN—Ir—N	νIr—Cl	Reference
trans—[Iren$_2$Cl$_2$]$^+$			278	327	[a]
			267 mb	321 mb	[b]
trans—[Iren$_2$Br$_2$]$^+$	215 mb	218 sb	266 sb		[b]
cis—[Iren$_2$Cl$_2$]$^+$			250	290, 303	[a]
			258 sb	295 sh 311 sm	[b]
cis—[Iren$_2$Br$_2$]$^+$		210 sb	256 sb		[b]

[a] See reference 10. [b] This paper.

Table IV. Observed band frequencies for some dihalotriethylenetetramine complexes

	νM—Br			νM—Cl	δNMN	νM—Cl	
cis—[CotrienCl$_2$]$^+$			240 mb	275 m	298 sb		337 wsh
cis—[CotrienBr$_2$]$^+$	193, 203 m		240 mb		294 mb		337 wsh
trans—[CotrienCl$_2$]$^+$					292, 304 svb	316 sm	
trans—[CotrienBr$_2$]$^+$	202 sb		240 mb		288, 306 mb		
cis—[RhtrienCl$_2$]$^+$		218 wm		274 sb	286 sb		344 wsh
cis—[RhtrienBr$_2$]$^+$	195, 211 sm	218 wm			284 mm		

to those obtained by Baranovskii *et al.*[10] (see Table III).

The observed band frequencies for some triethylenetetramine complexes are reported in Table IV.

Assignments for *trans*—[IrtrienCl$_2$]Cl presents difficulty due to preparative problems with the corresponding bromo complex. The dichloro complex spectrum shows five distinct peaks at 198 sm, 240 sm 275 sm, 303 sm and 327 sm.

Differences in the near infrared spectra of *cis*—α and *cis*—β—[CotrienCl$_2$]Cl were reported by Buckingham and Jones.[20] We have noticed corresponding differences in the far infrared in the region 160-200 cm^{-1} for both the cobalt and rhodium complexes.

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