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Complexes of Chromium(II) and Iron(II) with Hexamethylphosphoramide

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Abstract

The chromium(II) complexes $CrX_2(HMPA)_2$, in which X = Cl or Br and HMPA is hexamethylphosphoramide, and $Cr(HMPA)_4(BF_4)_2$ have been prepared. The effective magnetic moments show little deviation from the value expected for high spin chromium(II) from room temperature to liquid nitrogen temperature. The diffuse reflectance spectra suggest that the chromium ions are in a strongly distorted six coordinate environment. The iron(II) complexes, $FeX_2(HMPA)_2$, X = Br or I, and $[Fe(HMPA)_4](BF_4)_2$, from their magnetic behaviour and Mössbauer and electronic spectra, contain tetrahedral iron(II). The isomer shift of the last complex is the most positive so far reported for a tetrahedral iron(II) complex.

Introduction

A number of complexes of hexamethylphosphoramide (HMPA) with metals of the first transition series are known [1, 2]. With bivalent metal ions they are of the types $MX_2(HMPA)_2$ and $[M(HMPA)_4](ClO_4)_2$; in the former the anions X (halide, NO_3^-, NCO^- or NCS^-) are coordinated to give pseudo-tetrahedral molecules, and in the latter the presence of weakly coordinating perchlorate permits the production of tetrahedral cations. Hexamethylphosphoramide forms tetrahedral complexes with metal ions which are more commonly found in octahedral environments. No complexes of this ligand with chromium(II) are known and some have been synthesised in unsuccessful attempts to prepare well-established tetrahedral chromium(II) complexes for the first time. In addition, some iron(II) complexes have been prepared in order to extend Mössbauer investigations to tetrahedral complexes of O-donor ligands. Mössbauer data for tetrahedral iron(II) are restricted to complexes of N- and S-donors and halides [3, 4].

Experimental

All complexes were handled under nitrogen because of their air sensitivity. Diffuse reflectance spectra were recorded on a Unicam SP 700C spectrophotometer with a reflectance attachment, and LiF as reference. Infrared spectra of Nujol mulls were recorded on a Perkin-Elmer 577 spectrophotometer. Magnetic susceptibility measurements were carried out by the Gouy method over the temperature range 85–300 K.

To determine chromium the complex was boiled with dilute nitric acid, and the metal precipitated as the hydroxide by adding concentrated ammonia until the solution was alkaline to methyl red. The hydroxide was then filtered off and ignited to Cr_2O_3. Halides were determined in the filtrate as the silver salt or CaF_2 [5]. Iron was determined as the oxinate. Analyses are given in Table I.

Preparation of Chromium(II) Complexes

To prepare $CrCl_2(HMPA)_2$, water was removed from hydrated chromium(II) chloride [6] (6.0 g) by heating it with an excess of 2,2-dimethoxypropane (50 cm^3) for 2 h at 60 °C with stirring. After the light green solution had been concentrated to one third volume, hexamethylphosphoramide in excess (15 cm^3) was added. The solution became blue, and after further stirring for 2 h, five volumes of anhydrous ether were added and a pale violet solid crystallised. It was washed well with ether to remove traces of HMPA. The pale blue bromide was similarly obtained. Both complexes rapidly turned green in air.

To obtain $Cr(HMPA)_4(BF_4)_2$, chromium(II) tetrafluoroborate hexahydrate was first prepared as follows. Chromium metal (2.56 g) was added to a mixture of fluoroboric acid (3.90 cm^3, 40% acid by weight) and water (15 cm^3) and heated at 60–80 °C. After the reaction had ceased, the deep blue solution was allowed to cool, the excess of chromium filtered off, and the solution concentrated to dryness under reduced pressure. The water was difficult to

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TABLE I. Analytical Data and Infrared Spectra

Compound	Colour	Analysis (%)[a]					Infrared spectra (cm^{-1})		
		Cr/Fe	X	C	H	N	ν(PO)	ν(MO)	ν(MX)
$CrCl_2(HMPA)_2$	light violet	11.12 (10.80)	14.45 (14.74)	30.13 (29.95)	7.80 (7.54)	17.22 (17.45)	1190	475	330
$CrBr_2(HMPA)_2$	light blue	9.30 (9.10)	27.91 (28.02)	25.50 (25.28)	6.56 (6.36)	15.07 (14.73)	1190	470	265
$Cr(HMPA)_4(BF_4)_2$	pale green	5.96 (5.52)	16.29 (16.13)	29.77 (30.59)	7.68 (7.70)	17.47 (17.84)	1189[b]	480	
$FeBr_2(HMPA)_2$	white	9.80 (9.72)	28.13 (27.86)	25.23 (25.08)	6.47 (6.27)	14.56 (14.63)	1191	480	240
$FeI_2(HMPA)_2$	light grey	8.42 (8.36)	38.34 (37.99)	21.55 (21.57)	5.58 (5.43)	12.59 (12.58)	1188	480	
$[Fe(HMPA)_4](BF_4)_2$	cream	5.89 (5.90)	16.29 (16.06)	30.24 (30.46)	7.80 (7.67)	17.55 (17.76)	1190[b]	480	

[a] Calculated values are given in parentheses. [b] BF_4^- absorption bands: ν_3, 1050.

remove and it was necessary to heat for several hours at 75–80 °C. A sky blue solid was obtained.

The hydrated tetrafluoroborate (3.27 g) was heated with an excess of 2,2-dimethoxypropane (25 cm^3) as in the preparations of the halides above. After concentration, hexamethylphosphoramide in excess (10 cm^3) was added to the light green solution. The deep green solution obtained was stirred for 2 h and a large quantity of anhydrous ether added. A solid slowly separated and the suspension was left for 48 h with occasional shaking. After filtration etc. as above a pale green powder was obtained.

Attempts to isolate the iodide by similar procedures were unsuccessful.

Preparation of Iron(II) Complexes

The bromide $FeBr_2(HMPA)_2$ was prepared from iron(II) bromide hexamethanolate which was first obtained as follows. Iron wire (5 g) was heated with a mixture of concentrated hydrobromic acid (23 cm^3) and methanol (50 cm^3). When the reaction was complete the greenish-grey solution was filtered into another vessel, and concentrated under vacuum at 100 °C to give the pale yellow hexamethanolate [7]. This was heated for about 2 h at 60 °C with an excess of hexamethylphosphoramide (15 cm^3) in the presence of 2,2-dimethoxypropane (30 cm^3) to remove traces of water. The mixture was cooled, and anhydrous ether added in large quantity to separate the colourless bromide which was filtered off, washed well with ether and dried.

The light grey iodide $FeI_2(HMPA)_2$ was obtained from the deep red hexamethanolate of iron(II) iodide, both complexes being prepared by analogous procedures to the bromides. Attempts to prepare $FeCl_2(HMPA)_2$ by adding HMPA in excess in acetone to the solution obtained by heating $FeCl_2 \cdot 4H_2O$ in ethanol/2,2-dimethoxypropane were unsuccessful. Neither the addition of ether in excess nor the passage of HCl gas induced crystallisation.

To obtain the tetrafluoroborate, $[Fe(HMPA)_4](BF_4)_2$, iron(II) tetrafluoroborate hexamethanolate was prepared by heating iron wire (6.72 g) for 4 h at 50 °C under nitrogen with a mixture of fluoroboric acid (40% by weight, 12 cm^3) and methanol (50 cm^3). When the reaction was complete, the colourless solution was filtered into another vessel, and concentrated at 100 °C *in vacuo*. The solid obtained was heated at 60 °C for 1 h with an excess of HMPA (15 cm^3) dissolved in 2,2-dimethoxypropane (30 cm^3). The pale brown solution was cooled and shaken, but the solid did not separate until a large amount of anhydrous ether was added. The cream-coloured solid was filtered off, washed well with anhydrous ether, and dried for 3 h *in vacuo*.

Results and Discussion

Iron(II) Complexes

The iron(II) complexes have magnetic moments which are essentially temperature-independent (Table II, θ values $\simeq 0°$), and somewhat greater than the spin-only value (4.90 BM) as expected for pseudo-tetrahedral or tetrahedral high-spin iron(II) complexes [8]. The moment of 5.0 BM for $[Fe(HMPA)_4](BF_4)_2$ is close to that (5.2 BM) for $[Fe(HMPA)_4](ClO_4)_2$. The presence of high-spin iron(II) is confirmed by the isomer shifts δ (Table II) which are within the range 0.7–1.5 mm s^{-1} relative to iron metal found for a large number of high-spin iron

TABLE II. Magnetic Properties and Mössbauer Parameters at 78 K

Compound	Temperature (K)	Magnetic properties			Mössbauer parameters	
		μ_{eff}[a] (BM)	θ[a] (°)	$10^6 \times \chi_L$[b] (c.g.s.)	δ[c] (mm s^{-1})	ΔE[c] (mm s^{-1})
$CrCl_2(HMPA)_2$	295	4.89	0	283		
	90	4.90				
$CrBr_2(HMPA)_2$	295	5.03	4	304		
	90	4.96				
$Cr(HMPA)_4(BF_4)_2$	295	4.72	10	537		
	90	4.55				
$FeBr_2(HMPA)_2$	295	5.38	2	304	1.289	2.884
	90	5.34				
$FeI_2(HMPA)_2$	295	5.40	5	332	0.951	2.559
	90	5.30				
$[Fe(HMPA)_4](BF_4)_2$	295	5.05	3	537	1.395	2.627
	90	5.00				

[a] Calculated from $\mu_{eff} = 2.828(\chi_A T)^{1/2}$ BM and $\chi_A^{-1} \alpha (T + \theta)$. [b] χ_L = diamagnetic correction. [c] Isomer shift δ with respect to natural iron; ΔE = quadrupole splitting.

TABLE III. Reflectance Spectra

Compound	Assignment	Absorption maxima (cm^{-1})	
		RT[a]	LNT[a]
$CrCl_2(HMPA)_2$[b]		25200vw	25200vw
	${}^5B_{1g} \rightarrow {}^5B_{2g}, {}^5E_g$	17800s	17800s
	${}^5B_{1g} \rightarrow {}^5A_{1g}$	12000s,vb	12000s,vb
$CrBr_2(HMPA)_2$	${}^5B_{1g} \rightarrow {}^5B_{2g}, {}^5E_g$	16800s,vb	17400m
	${}^5B_{1g} \rightarrow {}^5A_{1g}$	12000m	15500w,sh
			12200m
$Cr(HMPA)_4(BF_4)_2$	${}^5B_{1g} \rightarrow {}^5B_{2g}, {}^5E_g$	21000s,vb	21300s,vb
	${}^5B_{1g} \rightarrow {}^5A_{1g}$	14000s,vb	14300s,vb
$FeBr_2(HMPA)_2$		28500s	28600s
		26700w	26700w
		25300m	25400m
		22800w	23600w
		21700vw	22800w
		20500vw	21600w
		18900vw	20800w
		1800vw,sh	18600w
		16500w	18200w
		14500w,sh	16500m
			14400m
	${}^5E \rightarrow {}^4T_2$	6000vs	5500vs
$FeI_2(HMPA)_2$		28000s	28000s
		24900m	25000m
		23300vw	23500w
		21100m	21100s
		19400w	19400m
		18000vw	18000w
		16200m	16300s
		14300w	14100m
	${}^5E \rightarrow {}^5T_2$	6200s,vb	5500vs

(continued)

TABLE III. *(continued)*

Compound	Assignment	Absorption maxima (cm^{-1})	
		RT[a]	LNT[a]
$[Fe(HMPA)_4](BF_4)_2$			21400vw
			18900vw
			17000vw
	$^5E \rightarrow {^5T_2}$	6800s,vb	7250s,vb

[a] RT is room temperature, LNT liquid nitrogen temperature.

[b] Usually for chromium(II) complexes the lower frequency band is weaker; the opposite is found with the HMPA complexes.

complexes [3]. However, the isomer shifts for the tetrafluoroborate and the bromide are much larger than reported [3] for $FeBr_4^{2-}$ or $FeCl_4^{2-}$, presumably because of the greater ionic character of the iron(II)–oxygen bond, and for pseudotetrahedral complexes of the type $FeL_2(halide)_2$, where L is the bidentate N-donor ligand di-2-pyridylamine, quinoline or sparteine [4]. The tetrafluoroborate has the largest isomer shift so far reported for a tetrahedral iron(II) complex. The isomer shifts decrease $BF_4^- > Br^- > I^-$ in line with increasing covalency.

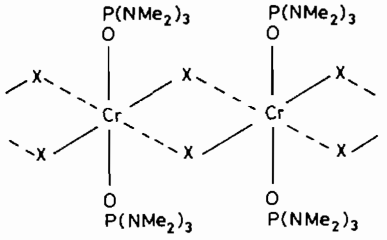
The iron(II) complexes exhibit the single broad absorption band in the near infrared expected for tetrahedral complexes. This band is assigned to the $^5E \rightarrow {^5T_2}$ transition (Table III). The spectra, especially of the lower symmetry bromo- and iodo-complexes, contain many weak absorptions which can be assigned to spin forbidden transitions.

Infrared Spectra

Coordination of HMPA through oxygen is shown by the lowering of the P–O stretching frequency (Table I) by about 12 cm^{-1} from the value in the free ligand (1200 cm^{-1}); the many other absorption bands of HMPA are present in the spectra of the complexes with only minor shifts in wave number. The spectrum of $[Fe(HMPA)_4](BF_4)_2$ exhibits additional strong and broad absorption, with fine structure and a maximum at 1050 cm^{-1}, which can be assigned to the ν_3 vibration of the tetrahedral BF_4^- ion [9]. There are absorptions at *ca.* 480 and 520 cm^{-1} in the spectra of all three iron(II) complexes obscuring the region where ν_4, the other infrared active absorption of BF_4^-, is expected. Complexities arise in the spectrum of BF_4^- through isotope doubling as well as through interactions of the ion with fields of lower than tetrahedral symmetry [9]. This, in addition to the difficulty in distinguishing HMPA and BF_4^- bands, means that whether BF_4^- is ionic or coordinated cannot be determined from the spectra. However, the magnetic, Mössbauer and reflectance data clearly indicate tetrahedral $[Fe(HMPA)_4]^{2+}$ and therefore uncoordinated BF_4^-.

Chromium(II) Complexes

It is more difficult to assign structures to the chromium(II) complexes. They have magnetic moments close to the value (4.90 BM) expected for high-spin chromium(II) which vary little with temperature. The reflectance spectra of the complexes $CrCl_2(HMPA)_2$ and $CrBr_2(HMPA)_2$ contain broad bands at 17 800 and 16 800 cm^{-1} respectively, and a weaker band near 12 000 cm^{-1}. This is the usual pattern for high-spin, distorted six coordinate chromium(II) complexes. The assignments are given in Table III. The bands are to higher wave number than expected for a CrO_2X_4 chromophore [10] suggesting that, as in structure I, there is an essentially planar CrO_2X_2 unit with the axial (bridging) halides interacting only weakly with the metal. This is consistent with the absence of antiferromagnetic interaction indicated



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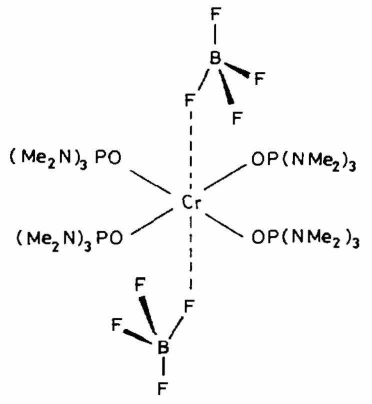

II

by the temperature-independent magnetic moments. Unfortunately, no crystals suitable for X-ray investigation have been obtained.

In the spectrum of $Cr(HMPA)_4(BF_4)_2$ the bands are to higher wave number than for the halide complexes consistent with a planar CrO_4 chromophore and axial BF_4^- as in structure **II**. The infrared spectrum contains a broad absorption band at 1050 cm^{-1} due to $\nu_3(BF_4^-)$, and, as discussed for the iron(II) complex, it is not possible to tell whether the anion is ionic or coordinated. Tetrafluoroborate is not expected to coordinate strongly, but in $Cu(en)_2(BF_4)_2$, where en is 1,2-diaminoethane, there is a planar CuN_4 unit [11] with axial 'semi-coordinated' BF_4^- groups analogous to **II**. High-spin chromium(II) complexes are often structurally similar to copper(II) complexes.

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