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Transition Metal Chemistry of Oxime Containing Ligands, VII.

Electronic and Structural Properties of Iron(II) and Chromium(III) Complexes Containing Pyridine-2-aldoxime

Madan Mohan*, **Shri G. Mittal**, **Harish C. Khera**,
and **Anant K. Sirivastava**

Department of Chemistry, N.R.E.C. College, Khurja (U.P.) 203131, India

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Complexes of pyridine-2-aldoxime (H*pox*) with iron(II) and chromium(III) of type, $[Fe(Hpox)_2X_2]$ (X = Cl, Br, I or NCS); $[Cr(Hpox)_3]Cl_3 \cdot 3\,H_2O$; $[Cr(Hpox)_2X_2]ClO_4$ (X = F, Cl or Br) and $[Cr(Hpox)_2(H_2O)_2]Br_3 \cdot H_2O$ were prepared and characterized by analytical X-ray powder diffraction, magnetism, vibrational (conventional and far-infrared) and electronic spectroscopy techniques. X-ray and electronic spectral data indicate that all the complexes except $[Cr(Hpox)_3]Cl_3 \cdot 3\,H_2O$ have *trans*-pseudo-octahedral microsymmetry around the metal ion. Infrared spectral data indicate that the ligand, H*pox*, behaves like a neutral ligand and coordinates to the metal ion through pyridine nitrogen atom and oxime nitrogen atom in all these complexes. The magnetic susceptibilities of chromium(III) complexes, measured over a temperature range 300-78 K, are independent of temperature whereas the magnetic moments of iron(II) complexes over a temperature range 300-20 K are dependent of temperature. The observed temperature dependence of magnetic moments of iron(II) complexes was used to evaluate the magnitude of orbital reduction factor, k, the low-symmetry distortion parameter, Δ, and the extent of reduction in spin-orbital coupling, λ. In all these iron(II) complexes the magnetic results indicate the presence of an orbitally non-degenerate, $^5B_{2g}$, ground state. Magnetically unperturbed and perturbed *Mössbauer* spectra of iron(II) complexes at various temperatures have also been reported. Magnetically perturbed *Mössbauer* spectra of iron(II) complexes at 4.2 K in an axial field of 60 kGauss indicate that the principal component of electric field gradient tensor is positive and consistent with $^5B_{2g}$ ground electronic state in a tetragonal (D_{4h}) local site symmetry.

[Keywords: Chromium(III)complexes; Iron(II)complexes; Magnetic susceptibility measurements; Mössbauer spectra]

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Übergangsmetallkomplexe mit Oxim-enthaltenden Liganden, VII. Elektronische und strukturelle Eigenschaften von Fe(II)- *und* Cr(III)-*Komplexen mit Pyridin-2-aldoxim*

Es wurden Komplexe von Pyridin-2-aldoxim (H*pox*) mit Fe(II) und Cr(III) vom Typ [Fe(H*pox*)$_2X_2$] (X = Cl, Br, I, NCS), [Cr(H*pox*)$_3$]Cl$_3 \cdot 3\,H_2O$, [Cr(H*pox*)$_2X_2$]ClO$_4$ (X = F, Cl, Br) und [Cr(H*pox*)$_2$(H$_2$O)$_2$]Br$_3 \cdot H_2O$ hergestellt. Charakterisierung und Diskussion von Geometrie und Bindungsverhalten in den Komplexen erfolgte auf Grund von analytischen Daten, Röntgen-Pulveraufnahmen, Elektronenanregungsspektroskopie, Infrarotspektroskopie, magnetischen Messungen und *Mössbauer*-Spektroskopie.

Introduction

Aromatic aldehyde oximes are well known for their high coordinating abilities, but little is known of pyridine-2-aldoxime (H*pox*). *Underhill et al.*[1,2] have reported the spectral properties of several copper(II) complexes of H*pox* and nickel(II) complexes with several aromatic aldehyde oximes. In continuation of our earlier work on H*pox* complexes of bivalent transition metals[3–8], we are reporting here the results of our studies on complexes of iron(II) and chromium(III) with H*pox*. Although, the preparation and some of the properties of iron(II) complexes have been reported earlier[5], detailed studies of iron(II) and chromium(III) complexes with H*pox* are to be reported here.

Experimental

Materials: Iron(II) and chromium(III) salts, ammonium thiocyanate, sodium perchlorate (all reagent grade) and pyridine-2-aldoxime (K & K Laboratories, New York) were used without further purification.

Preparation of the Complexes

Iron(II) complexes of type [Fe(H*pox*)$_2X_2$] (X = Cl, Br, I *or* NCS): Prepared by previously reported procedures[5] under inert atmosphere.

Tris(pyridine-2-aldoxime)chromium(III) trichloride 3-hydrate; [Cr(H*pox*)$_3$]Cl$_3 \cdot 3\,H_2O$: This complex was prepared from Cr(*Urea*)$_6$Cl$_3 \cdot 3\,H_2O$, which was prepared by the method of *Brauer*[9] except that ethanol was used as solvent instead of water. Cr(*Urea*)$_6$Cl$_3 \cdot 3\,H_2O$ (0.22 mol) and H*pox* (1.32 mol) in ethanol were heated over the steam bath until conversion into a yellow-brown solid was complete ($\sim$ 2–3.5 h). The crude product which contained an excess of ligand was recrystallized from ethanol.

Dihalogeno-bis(pyridine-2-aldoxime)chromium(III) mono-perchlorate [Cr(H*pox*)$_2X_2$]ClO$_4$ (X = F, Cl, or Br): An ethanolic solution of chromium(III) halide (0.005 mol) was added to an ethanolic solution of ligand (0.11 mol). After the addition of an aqueous solution of sodium perchlorate, the mixture was heated on steam bath for 30 min. The green precipitate which formed was filtered off, washed with ethanol and dried in a vacuum desiccator over P_4O_{10}.

Diaquo-bis(pyridine-2-aldoxime)chromium(III)tribromide-1-hydrate [Cr(H*pox*)$_2$(H$_2$O)$_2$]Br$_3 \cdot H_2O$: This complex was obtained by adding

$[Cr(Hpox)_2Br_2]ClO_4$ to 50 ml of 1:1 (by volume) 47 percent HBr and H_2O and adding a few drops of acetone. The mixture was gently heated on water bath until solution was complete. On cooling the solution in a refrigerator for 36 h, a light green crystalline solid was obtained. The complex was filtered and washed with a small amount of ethanol and diethylether.

Physical Measurements

Room temperature magnetic susceptibility measurements were made on a standard *Gouy* balance. All low-temperature susceptibility measurements were made on a *Faraday* balance which was calibrated with $Hg[Co(NCS)_4]$ and the sample temperatures was measured with a platinum resistance thermometer. All the magnetic measurements were made at three different field strengths. None of the compounds exhibited any field dependence in the magnetic moment. The error limits for the reported magnetic moments are $\pm$ 0.05 B.M.

Diffuse reflectance spectra at room temperature and at liquid N_2 temperature were recorded by using Cary-14 spectrophotometer equipped with a reflectance accessory, using magnesium oxide as a reference.

The infrared spectra in the range 4,000–400 cm^{-1} were recorded in KBr pellets by using Perkin-Elmer infracord spectrophotometer, Model 180. In the 800–200 cm^{-1} range a Beckman IR-12 spectrophotometer and freshly dried CsI were used.

X-ray powder diffraction patterns were taken with a Philips X-ray generator using CuK_α radiation and *Debye-Scherrer* type powder camera.

Mössbauer spectra were recorded with a constant acceleration spectrometer using an electromechanical transducer and a multichannel analyser in the time mode. The spectrometer was equipped with a copper matrix source which was maintained at room temperature and was calibrated with natural iron foil. The low-temperature results were obtained with a liquid nitrogen cryostat that has a sample holder which protects the polycrystalline sample from the cryostat vacuum. The unperturbed *Mössbauer* results were determined by inspection with an accuracy of $\pm$ 0.01 mm/s. The low-temperature magnetically perturbed *Mössbauer* results were determined by means of a conventional constant acceleration spectrometer. The magnetic field was generated by using Nb—Sn superconducting magnet which operated in the persistent mode up to fields of 80 kGauss. The polarization direction was longitudinal and both a source and the absorber were at 4.2 K.

All elemental analysis were performed by Microanalytical Laboratories, I.I.T., Kanpur-16. Metals were analysed by standard techniques[10] after decomposition of the complexes with H_2O_2 and conc. H_2SO_4. Halide analyses were carried by potentiometric titration with $AgNO_3$, after decomposition of the complexes by sodium fusion. The analytical data of the complexes are given in Table 1.

Results and Discussion

X-Ray Powder Diffraction Spectra

The X-ray powder diffraction patterns for each of the new complexes under study and $[Fe(py)_4(NCS)_2]$ (where py = pyridine) were measured and compared for any indications of isomorphism. The results indicate that except $Cr(Hpox)_3^{3+}$ these complexes, in most instances, have almost identical powder patterns. Hence, they are probably isostructural and have slightly different unit cell parameters. Therefore, in analogy of the known structure[11] of $[\mathrm{Fe}(py)_4(\mathrm{NCS})_2]$ complex, the present complexes may have *trans*-octahedral geometry around the metal ion.

Infrared Spectra

The infrared absorption spectrum of H*pox* differs from the conventional oximes, which show a broad band at $\sim$ 3,250 cm^{-1}. This band is replaced by multiple bands between 3,194 and 2,791 cm^{-1} in H*pox*, the strongest of which lies at 2,791 cm^{-1}. This implies much stronger hydrogen bonding in H*pox* than in other oximes. The band assigned to $\nu\mathrm{C{=}N}$ (acyclic) stretch at 1,520 cm^{-1} is considerably lower than the normal. This lowering is attributed to a structure in which the oxime proton is partially ionized. This lowering is further verified by a study of the potassium salt of H*pox* where it was observed at $\sim$ 1,517 cm^{-1}. The infrared spectrum of H*pox* exhibits four-ring stretching frequencies in between 1,600–1,400 cm^{-1}; the ring-breathing mode at 980 cm^{-1}; the $\nu\mathrm{N{-}O}$ stretching frequency at 950 cm^{-1}, an out-of-plane CH deformation at 810 cm^{-1} a skeletal mode at 730 cm^{-1} and an out-of-plane deformation band at 400 cm^{-1}.

Krause et al.[12] have investigated extensively transition metal complexes of pyridine-2-aldoxime in $\nu\mathrm{C{=}N}$ (acyclic) and $\nu\mathrm{N{-}O}$ regions and postulated that compounds containing $\mathrm{{-}C{=}N{-}OH}$ groups have $\nu\mathrm{C{=}N}$ and $\nu\mathrm{N{-}O}$ stretching frequencies in the range 1,654–1,614 and 1,069–1,036 cm^{-1}, respectively. Whereas the compounds containing $\mathrm{{-}C{=}N{-}}\overset{\ominus}{\mathrm{O}}\mathrm{\cdots HO{-}N{=}C{-}}$ (the compounds may or may not be hydrogen bonded) groups have $\nu\mathrm{C{=}N}$ and $\nu\mathrm{N{-}O}$ stretching frequencies in the range 1,556–1,526 and 1,150–1,041 cm^{-1}; respectively. However, the present complexes of H*pox* exhibit the bands in the regions 3,250–3,015; $\sim$ 1,660 and $\sim$ 1,074 cm^{-1}, which can be assigned to $\nu\mathrm{OH}$; $\nu\mathrm{C{=}N}$ and $\nu\mathrm{N{-}O}$ stretching frequencies, respectively. These data indicate that oxime proton is not hydrolysed and there is a contribution from the $\mathrm{{-}C{=}N{-}OH}$ groups in these complexes.

The infrared spectra of the present complexes have a weak absorption band at $\sim$ 1,710 cm^{-1}. This band is assigned to O—H stretching of the intramolecularly hydrogen-bonded oxime OH group[13].

All the present complexes exhibit the four ring stretching frequencies in the following ranges: band I, 1,620–1,618; band II, 1,580–1,570; band III, 1,490–1,485 and band IV, 1,440–1,438 cm^{-1}. Band I is increased significantly in frequency from the free ligand value of 1,570 cm^{-1}, an indication of the coordination of pyridine to a metal atom[15]. The ring-breathing mode observed at 980 cm^{-1} in the free ligand disappears in these iron(II) and chromium(III) complexes and is

Table 1. *Analytical data* [a]

Compound	Found (calc.)%				
	C	H	N	M	X [b]
$[Cr(C_6H_6N_2O)_3]Cl_3 \cdot 3\,H_2O$	37.40 (37.35)	4.13 (4.15)	14.60 (14.52)	9.04 (8.99)	18.51 (18.41)
$[Cr(C_6H_6N_2O)_2F_2]ClO_4$	33.18 (33.17)	2.79 (2.76)	12.95 (12.91)	12.10 (12.00)	8.72 (8.74)
$[Cr(C_6H_6N_2O)_2Cl_2]ClO_4$	30.90 (30.86)	2.60 (2.56)	12.09 (12.00)	11.16 (11.13)	15.26 (15.21)
$[Cr(C_6H_6N_2O)_2Br_2]ClO_4$	25.92 (25.90)	2.17 (2.15)	10.05 (10.07)	9.38 (9.35)	28.80 (28.77)
$[Cr(C_6H_6N_2O)_2(H_2O)_2]Br_3 \cdot H_2O$	24.43 (24.40)	3.00 (3.05)	9.46 (9.49)	8.85 (8.81)	40.72 (40.68)

[a] For iron(II) complexes see ref. no. 5.

[b] X = anion.

Table 2. *Far-Infrared spectra results (cm^{-1})*

Compound	Ligand Absorption	$\nu\,M\text{—}X$	$\nu\,M\text{—N}$
H*pox*	400 (s), 380 (m), 298 (m), 217 (m)	—	
[Fe(H*pox*)$_2$Cl$_2$]	398 (s), 390 (s), 385 (m), 330 (m)	264 (vs)	250 (vs), 217 (s, sh)
[Fe(H*pox*)$_2$Br$_2$	398 (s), 390 (s), 385 (m), 330 (m)	< 200	245 (vs), 220 (w, sh)
[Fe(H*pox*)$_2$I$_2$	398 (s), 389 (m), 385 (s), 330 (m)	< 200	248 (vs), 215 (s, sh)
[Fe(H*pox*)$_2$(NCS)$_2$]	400 (s), 392 (m), 385 (m), 330 (m)	267 (s)	240 (vs), 215 (s, sh)
[Cr(H*pox*)$_3$]Cl$_3$ · 3 H$_2$O	400 (s), 385 (s), 380 (m), 330 (m)	—	360 (vs), 345 (w), 320 (s, sh)
[Cr(H*pox*)$_2$F$_2$]ClO$_4$	400 (s), 385 (s), 390 (m), 382 (sh), 330 (m)	—	375 (m), 370 (sh)
[Cr(H*pox*)$_2$Cl$_2$]ClO$_4$	400 (s), 395 (m), 389 (s), 382 (sh), 330 (m)	280 (vs)	377 (m), 370 (sh)
[Cr(H*pox*)$_2$Br$_2$]ClO$_4$	400 (s), 395 (m), 389 (s), 382 (sh), 330 (m)	298 (vs)	380 (m), 317 (sh)
[Cr(H*pox*)$_2$(H$_2$O)$_2$]Br$_3$ · H$_2$O	400 (s), 395 (m), 389 (s), 382 (sh), 330 (m)	—	380 (m), 365 (sh)

replaced by a band at ~ 1,020 cm^{-1}. This shift is also indicative of pyridine coordination[16,17] to metal atom.

Two strong bands are observed in the spectrum of free ligand at 730 and 810 cm^{-1}. These bands are assigned to φ(C—C) and γ(C—H), respectively. The 730 cm^{-1} bands splits into two components lying between 718 and 752 cm^{-1}. This splitting is also believed to be an indication of pyridine to metal coordination[16,18]. The band observed at 810 cm^{-1} in the free H*pox* is observed as a single band between 780 and 825 cm^{-1}.

The uncoordinated ligand exhibits a band at 400 cm^{-1} assigned to C—C out-of-plane deformation[17,19] while all the complexes exhibit a single band around 412 cm^{-1}. An increase in frequency upon coordination is to be expected[20].

These data leave little doubt that in all the present complexes, the ligand, H*pox*, is coordinated to the metal atom via pyridine nitrogen and oxime nitrogen atom.

The appearence of the strong bands at 2,045 cm^{-1} and a weak band at 805 cm^{-1} in the infrared spectrum of $[\mathrm{Fe}(\mathrm{H}pox)_2(\mathrm{NCS})_2]$ complex, due to ν_1 and ν_3 vibrations, characterizes the N-bonded thiocyanate group in this complex[21].

The appearence of two strong bands at ~ 1,115 and ~ 630 cm^{-1} due to the ν_3 and ν_4 vibrations, in $[\mathrm{Cr}(\mathrm{H}pox)X_2]\mathrm{ClO}_4$ complexes indicate the presence of ionic ($\mathrm{T_d}$) perchlorate group in these complexes[22].

The far-infrared spectral results of free-ligand, H*pox*, and its metal complexes are presented in Table 2. The free ligand exhibits the absorption bands at 400 (s), 380 (m), 298 (m) and 217 (m) cm^{-1}. Whereas all the complexes have bands of varying intensity at ~ 400; ~ 390; ~ 380 and ~ 330 cm^{-1}, which corresponds to the sharp and medium bands in this region in the free ligand absorption. The relatively high energy of these bands and their lack of sensitivity towards change, either of halogen or of metal ion would seem to preclude their assignment as metal ligand vibrations.

Geometrically, H*pox* ligand is very close similar to that of bipyridyl, because it contains both an aromatic pyridine nitrogen atom and an oxime nitrogen atom at its alpha position for coordination to the metal ion. Therefore, it seems to be reasonable to compare and assign the far-infrared spectral results, observed in H*pox* complexes, with that of bipyridyl complexes. The far-infrared spectra of iron(II) complexes exhibit a sharp band at ~ 250 cm^{-1} and a shoulder at ~ 220 cm^{-1}. These bands lie in the general region expected for metal-nitrogen vibrations[23–25]. However, metal-nitrogen (bipyridyl) vibrations are not observed in this region[26], casting some doubt on this assignment. *Clark* and *Williams*[26] have suggested that bands observed in bipyridyl-metal(II) complexes berween 300 and 260 cm^{-1} and assigned as metal-nitrogen (bipyridyl) vibrations[27] are ligand bands activated by coordination to the metal ion. This assignment is based on the observation that although the bands disappear when the metal ion is trivalent or spin-paired divalent, they are apparently not replaced by a new band at high energy. In chromium(III) complexes additional bands are observed between 400 and 300 cm^{-1}, which could be Cr—N (H*pox*) vibrations. Thus, the assignment of the bands ~ 250 (vs) and ~ 220 (sh), in the spectra of iron(II) complexes of the above type to Fe—N (H*pox*), as shown in Table 2, is reasonable. The metal-nitrogen vibrations are likely to be extensively coupled together, the multiplicity of the bands being due to the lowsymmetry of the complexes.

Magnetic Properties

The magnetic properties for the iron(II) complexes of the type [Fe(H*pox*)$_2X_2$] (X = Cl, Br, I or NCS) have been studied over a temperature range of 300 to 20 K and the numerical results are presented in Fig. 1. For the complexes [Fe(H*pox*)$_2$Cl$_2$] and [Fe(H*pox*)$_2$(NCS)$_2$], rather unusual magnetic properties were observed at low temperatures. Several different methods were used to carefully repeat the preparation of these complexes but all these preparations produced similar results at low temperature.

Because high spin iron(II) in a pure octahedral ligand field possesses at $^5T_{2g}$ ground state, the results shown in Fig. 1 were interpreted with the approach developed by *Figgis et al.*[28] where theoretical values of magnetic susceptibilities are calculated in terms of the parameters, ν, k and λ. The parameters were adjusted and the resulting best-fit parameters are presented in Table 3.

Inspection of the parameters presented in Table 3 for [Fe(H*pox*)$_2$Br$_2$] and [Fe(H*pox*)$_2$I$_2$] reveals several interesting points. The values of λ are confined to a range which extends from —70 to —85 cm^{-1}. This indicates a reduction in λ i.e. λ/λ_0 of approximately 0.8 which is in good agreement with the reduction of about 0.8 observed in B (the interelectronic repulsion parameter) for some analogous nickel(II) complexes[5]. For these complexes there is also a good correlation between λ/λ_0 and k. The reduction in k for these complexes is certainly reasonable because H*pox* can be expected to enter into extensive Λ-bonding with the metal t_{2g} orbitals. The values of Δ are all positive which indicate a non-degenerate $^5B_{2g}$ ground state.

The magnetic moments of chromium(III) complexes were measured as a function of temperature and the detailed magnetic moments are shown in Fig. 1. These chromium(III) complexes have magnetic mo-

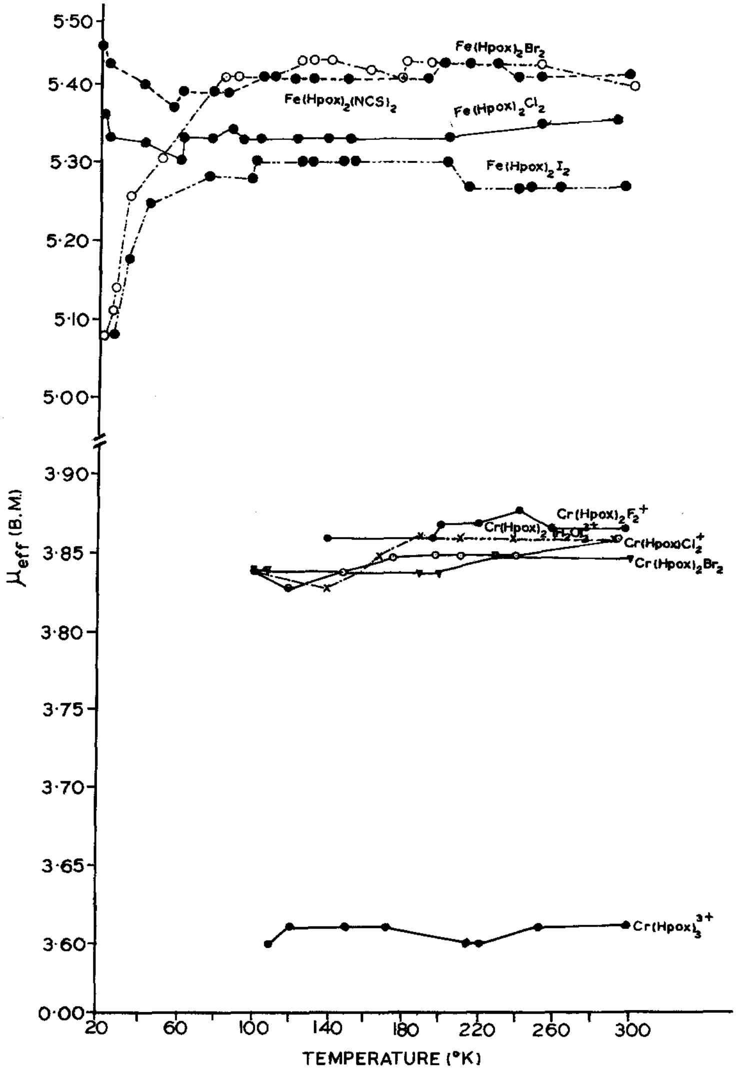

Fig. 1. Plot of μ_{eff} vs temperature for iron(II) and chromium(III) complexes

Table 3. *Best-fit parameters for some iron(II) complexes* (cm^{-1})

Compound	k	ν	λ	λ/λ_0	Δ
[Fe(H*pox*)$_2$Br$_2$]	0.85	—4.00	—85	0.85	348
[Fe(H*pox*)$_2$I$_2$]	0.70	—3.76	—65	0.65	247

ments at room temperature in agreement with the theoretical spin-only value of 3.87 B.M. The possibility of high-magnetic moments for these chromium(III) complexes due to distorted octahedral environment around chromium(III) ion, may also not be ignored. The temperature independent magnetic moments observed for these complexes are consistent with non-degenerate A ground term.

Table 4. *Mössbauer spectral parameters*

Compound	T °K	δ[a] mm/s	ΔE_Q mm/s	Γ_1[a] mm/s	Γ_2[b] mm/s
[Fe(H*pox*)$_2$Cl$_2$	78	1.16	2.00	0.29	0.32
	RT	1.06	1.54	0.26	0.27
[Fe(H*pox*)$_2$Br$_2$]	78	1.14	2.00	0.28	0.32
	RT	1.05	1.54	0.26	0.26
[Fe(H*pox*)$_2$I$_2$]	78	1.16	1.96	0.26	0.25
	RT	1.05	1.50	0.25	0.25
[Fe(H*pox*)$_2$(NCS)$_2$]	78	1.12	2.00	0.26	0.24
	RT	1.00	1.49	0.24	0.25

[a] Relative to natural iron foil.

[b] Full width at half maximum for low velocity line Γ_1, and high velocity line Γ_2.

Mössbauer Spectra

The *Mössbauer* spectrum of each of the iron(II) complexes, has been measured at room and liquid nitrogen temperature. The resulting spectral and line shape parameters are presented in Table 4. The error limits for the values of quadrupole splitting, ΔE_Q and isomer shift δ are better than or equal to ± 0.01 mm/s. The isomer shift values, presented in Table 4 are of the magnitude expected for high-spin iron(II) complexes[29, 30] and show as expected a slight decrease with decreasing temperature. These values are surprisingly constant from chloride to thiocyanate and indicate that a change in the anion has little effect upon the s-electron density at the surface of the iron(II) nucleus. The magnitude of the quadrupole splitting, ΔE_Q, reported in Table 4 is also that which is expected for pseudooctahedral, high-spin, iron(II) nucleus containing nitrogen donor ligands[31]. It is interesting to note that the temperature dependence of the quadrupole splitting is large. This temperature dependence of the quadrupole splitting is an indication of an electric field gradient which is a thermal average of the gradients resulting from the occupation of two or more orbital states. Then, as a consequence, the similar temperature dependence may indicate a comparable splitting of the ground state, t_{2g} orbitals, in these complexes. Under a tetragonal distortion $^5T_{2g}$ state is split into $^5B_{2g}$ and ^5E_g states. The magnitude of the contributions to ΔE_Q from a d-electron in

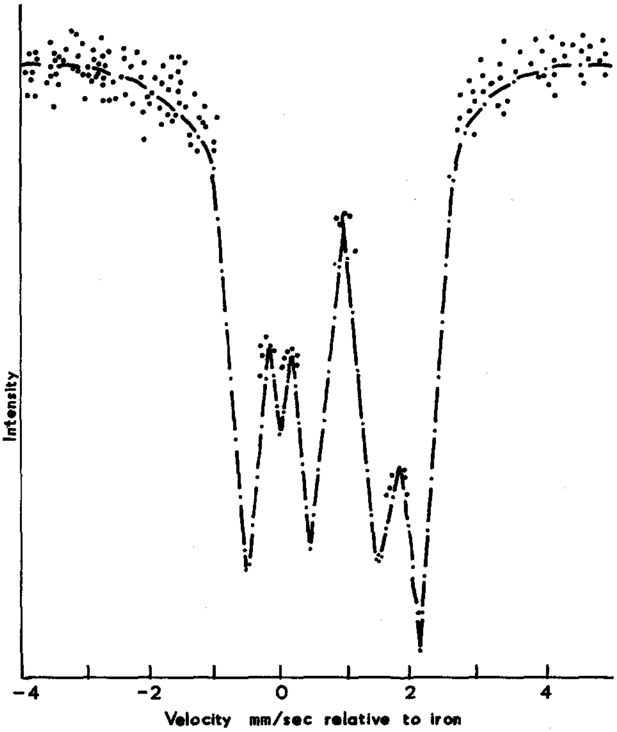

Fig. 2. *Mössbauer* spectrum of [Fe(H*pox*)$_2$Br$_2$] at 4.2 K and *H*app = 60 kGauss

either of a $^5B_{2g}$ and ^5E_g ground state are equal but the electric field gradient tensor, V_{zz}, associated with two states are of opposite sign.

In order to correctly determine the ground state for these iron(II) complexes, magnetic perturbation technique was applied[32]. The magnetically perturbed *Mössbauer* spectra of [Fe(H*pox*)$_2X_2$] complexes have been measured at 4.2 K in an axial field of 60 kGauss. A typical spectrum is shown in Fig. 2. It is clear from the Fig. 2 that triplet occurs at negative velocity relative to doublet, which is at the more positive velocity. The tripletdoublet pattern (triplet at lower velocity) is that expected for a rapidly relaxing paramagnet and corresponds to a positive principal component of the electric field gradient tensor, V_{zz}, and because the quadrupole moment of the iron-57 excited nuclear state is positive, the results also indicate a positive ΔE_Q and a small asymmetry parameter, η. The external applied and internal effective magnetic fields are, however, not equal (e.g. at an applied field of ~ 60 kGauss, the effective field is ~ 42 kGauss) suggesting both some degree of anisotropy in the magnetic susceptibility at 4.2 K and a negative internal hyperfine field. The positive value of ΔE_Q is consistent with additive contribution from covalence anisotropy and a $^5B_2$ group state, corresponding to an electron in the d_{xy} orbital of D_{4h} symmetry.

These results may be understood in terms of the relative bonding ability of the two anions and four nitrogen atoms of ligand molecules bonded to the central iron(II) ion. The crystal structure[11] of $[Fe(py)_4(NCS)_2]$ indicates a tetragonal compression along the *trans*-thiocyanate nitrogen axis with Fe—NCS bond distance of 2.09 Å. The equitorial Fe—N (pyridine) bond distance are considerably longer (2.24 and 2.27 Å) and all the bond angles are ~ 90°. The X-ray powder diffraction patterns of $[Fe(Hpox)_2X_2]$ complexes are isomophous with $[Fe(py)_4(NCS)_2]$ complex, it is therefore reasonable to assume Fe—X shorter than Fe—N (ligand) bond lengths in iron(II) complexes. Thus in $[Fe(Hpox)_2X_2]$ complexes the local symmetry of the coordination sphere around the iron(II) ion is approximately D_{4h}. From a crystal point of view, the tetragonal compression of the octahedral ligand field by the trans anions destabilizes the d_{xz} and d_{yz} orbitals relative to d_{xy} orbital; which becomes the ground state orbital. For this ground state orbital, a positive quadrupole splitting is expected, and is observed for these complexes under investigation.

A perhaps more reasonable approach is the semi-empirical molecular orbital method of *McClure*[33, 34]. This approach also predicts a $^5B_{2g}$ ground state as follows.

In $[Fe(Hpox)_2(NCS)_2]$ complexes, the energy difference involved is $E_{xz,yz} — E_{xy} = 2\,d_\Lambda$ where $d_\Lambda = \Lambda_N(NCS) — \Lambda_N(Hpox)$ is the difference in the pi bonding interactions of the H*pox* and NCS ligands. We make the assumptions that: (a) $\Lambda_N(Hpox) < 0$, i.e. the H*pox* ligand has a stabilizing π bonding effect as opposed to a destabilizing ($\Lambda > 0$) effect; (b) $|\Lambda_{N(Hpox)}| > |\Lambda_{N(NCS)}$. Then it follows that, $E_{xz,yz} — E_{xy}$, as is required for a $^5B_{2g}$ ground electronic configuration and the observed positive ΔE_Q. In the case of iron(II) halide complexes, $\Lambda_X > 0$, $\Lambda_{N(Hpox)} < 0$ and $E_{xz,yz} — E_{xy} > 0$ giving the $^5B_{2g}$ ground state in D_{4h} symmetry.

Reflectance Spectra

The diffuse reflectance spectra of iron(II) complexes are similar to one another, band positions and assignments are presented in Table 5.

The reflectance spectra of iron(II) complexes [Fe(H*pox*)$_2X_2$], exhibit two broad, partially resolved bands at ~ 10.0 kcal and ~ 12.0 kcal at room temperature and ~ 10.2 kcal and ~ 12.2 kcal at liquid nitrogen temperature. On the basis of D_{4h} symmetry (as indicated by magnetic and *Mössbauer* studies discussed above), these two absorption bands are assigned to the transitions form the ground state $^5B_{2g}$ to the $^5A_{1g}$ and $^5B_{1g}$ states, respectively[35]. The small increase in the energy of the electronic transitions at liquid nitrogen temperature is most likely as a result of an increase in the ligand field strength with decreasing temperature which arises from a slight contraction of the unit cell volume at low temperature.

Table 5. *Reflectance spectra of iron(II) complexes (cm^{-1})*

Compound	Temperature	$^5B_{2g} \rightarrow {^5A_{1g}}$	$^5B_{2g} \rightarrow {^5B_{1g}}$	Charge transfer $(t_{2g}—\Lambda^*)$	d_σ
[Fe(H*pox*)$_2$Cl$_2$]	RT	9,950	11,590	18,000	—615
	78	10,200	11,790	18,000	—596
[Fe(H*pox*)$_2$Br$_2$]	RT	9,980	11,590	18,000	—604
	78	10,200	11,790	18,000	—596
[Fe(H*pox*)$_2$I$_2$]	RT	10,050	11,610	18,000	—585
	78	10,210	11,800	18,000	—596
[Fe(H*pox*)$_2$(NCS)$_2$]	RT	10,000	11,600	17,890	—600
	78	10,190	11,800	17,980	—604

The reflectance spectra of these iron(II) complexes show a strong and broad band at ~ 18 kcal, which may be due to a chargetransfer band from metal to ligand ($t_{2g} \rightarrow \Lambda^*$).

The energies of the bands can be formulated in terms of three unknown parameters[35] D_{qxy}, D_s and D_t, and since only two items of information are available, it is not possible to solve for these three parameters. It may be assumed that the ground state is $^5B_{2g}$, then the transition to $^5B_{1g}$ level is equal as always to $10\,D_{qxy}$. For the ground state to be $^5B_{2g}$ it is necessary that d_Λ be negative and on the basis of Λ bonding capabilities of the various ligands listed in Table 5, it is clear that d_Λ is positive in all the cases listed. Hence the ground state should be ^5E_g. It is interesting to note that magnetic and *Mössbauer* experiments (as discussed above) suggest the ground state is non-degenerate $^5B_{2g}$. The Table 5 also contains the value of d_σ whose sign is chosen on the basis of whether the in-plane or out-of-plane ligands are regarded as having the stronger base strength.

Table 6. *Orbital angular overlap data from assignments I and II*

Compound	I $^4E_g > {}^4A_{2g}$		II $^4A_{2g} > {}^4E_g$	
	e_σ	e_Λ	e_σ	e_Λ
$[Cr(H$*pox*$)_2F_2]ClO_4$	7383 (H*pox*) 4969 (F)	0 (H*pox*) 320 (F)	7383 (H*pox*) 7935 (F)	0 (H*pox*) 2020 (F)
$[Cr(H$*pox*$)_2Cl_2]ClO_4$	7483 (H*pox*) 6021 (Cl)	0 (H*pox*) 880 (Cl)	7483 (H*pox*) 6490 (Cl)	0 (H*pox*) 1565 (Cl)
$[Cr(H$*pox*$)_2Br_2]ClO_4$	7716 (H*pox*) 5219 (Br)	0 (H*pox*) 1003 (Br)	7716 (H*pox*) 6567 (Br)	0 (H*pox*) 2002 (Br)
$[Cr(H$*pox*$)_2(H_2O)_2]Br_3 \cdot H_2O$	7640 (H*pox*) 5895 (H_2O)	0 (H*pox*) 105 (H_2O)	7640 (H*pox*) 7609 (H_2O)	0 (H*pox*) 1371 (H_2O)

Table 7. *Reflectance spectra of chromium(III) complexes (cm^{-1})*

Compound	$^4B_{1g} \rightarrow$ $^4E_g[^4T_{2g}(F)]$	$^4B_{1g} \rightarrow$ $^4B_{2g}[^4T_{2g}(F)]$	$^4B_{1g} \rightarrow$ $^4A_{2g}[^4T_{1g}(F)]$	$^4B_{1g} \rightarrow$ $^4E_g[^4T_{1g}(F)]$
$[Cr(H$*pox*$)_3]Cl_3 \cdot 3\,H_2O$		22,300	28,820	
$Cr(H$*pox*$)_2F_2]ClO_4$	18,940	22,150	29,750	25,750
$[Cr(H$*pox*$)_2]ClO_4$	17,750	22,450	25,750	26,950
$[Cr(H$*pox*$)_2Br_2]ClO_4$	17,405	23,150	24,655	26,418
$[Cr(H$*pox*$)_2(H_2O)_2]Br_3 \cdot H_2O$	20,128	22,920	30,117	27,920

In an octahedral ligand field three spin-allowed d-d transitions corresponding to $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ (ν_2) and $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) are expected in chromium(III) complexes; but ν_3 is generally submerged under charge-transfer and inter-ligand transitions in the near UV spectra[36]. The first spin-allowed transitions (ν_1) whose energy is assumed to be equal to $10\,D_q$ was observed at 22.3 kcal in the $[Cr(H$*pox*$)_3]^{3+}$ complex. The second spin-allowed transition (ν_2) has been assigned to transition peak observed at 28.82 kcal. Both ν_1 and ν_2 bands are broader and do not show any sign of splitting.

Assignment of ν_1 and ν_2 make it possible to extract only two ligand field parameters, $10\,Dq$ and B. *Racah*'s parameter of electronic repulsion, B, has been calculated by susing the equation[37]

$$B = (2\,\nu_1 - \nu_2)(\nu_2 - \nu_1)/(27\,\nu_1 - 15\,\nu_2)$$

The value of β ($B_{\text{complex}}/B_{\text{free ion}}$) has been calculated from the free ion value of $920\,\text{cm}^{-1}$ for chromium(III) gaseous ion. The parameters values are given in Table 8.

Table 8. *Ligand field parameters (cm^{-1}) of the*

Compound	D_s	D_t	Δ_1	Δ_3	$e_{\Lambda\,\mathrm{H}pox}$
$[\mathrm{Cr(H}pox)_2\mathrm{F_2]ClO_4}$	—735	365	—4040	—1115	0
$[\mathrm{Cr(H}pox)_2\mathrm{Cl_2]ClO_4}$	263	510	—1760	3602	0
$[\mathrm{Cr(H}pox)_2\mathrm{Br_2]ClO_4}$	350	610	—2007	4450	0
$[\mathrm{Cr(H}pox)_2\mathrm{(H_2O)_2]Br_3 \cdot H_2O}$	—383	319	—2743	—63	0
$[\mathrm{Cr(H}pox)_3\mathrm{]Cl_3 \cdot 3\,H_2O}$	—	—	—	—	—

The transition arising from the ν_3 spin-allowed band is obscured by very intense charge-transfer band in the spectra of $[\mathrm{Cr(H}pox)_3]^{3+}$ complexes.

The diffuse reflectance spectra of $[\mathrm{Cr(H}pox)_2X_2]^+$ complexes at room temperature exhibit the features associated with *trans*-pseudo-octahedral chromium(III) complexes[37] (Table 7). Therefore the band maxima observed at ~ 32.0 kcal can be assigned to $^4B_{1g} \rightarrow {}^4B_{2g}$ transition and the shoulder on the low energy side to the $^4B_{1g} \rightarrow {}^4E_g$ transition, all of which arise from the splitting of the ν_1 band (O_h symmetry) when the symmetry is lowered to D_{4h}. The band system at ~ 27.0 kcal can be assigned to $^4B_{1g} \rightarrow {}^4A_{2g}$, ^4E_g transitions which arise from the ν_2 band (O_h symmetry). The transition arise from the ν_3 band are obscured by very intense charge-transfer bands in these chromium(III) complexes.

The transition $^4B_{1g} \rightarrow {}^4B_{2g}$ is equal to $10\,D_{qxy}$ and is approximately constant in these chromium(III) complexes. It can, therefore, be easily identified in the spectra of these complexes. The separation between $^4B_{1g} \rightarrow {}^4B_{2g}$ and $^4B_{1g} \rightarrow {}^4E_g$ transition is, to first order, $35/4\,D_t$ and D_t is related to the in-plane and out-of-plane field strength via[35]

$$D_t = 4/7\,(D_{qxy} - D_{qz}) \tag{1}$$

where D_{qxy} = In-plane (xy) ligand-field strength and

D_{qz} = Out-of-plane (z) ligand field strength.

Since the first order energy of $^4B_{1g} \rightarrow {}^4E_g$ is $10\,D_q - 35/4\,D_t$ and the sign of D_t is generally identificable through Equ. (1); assignment of $^4B_{1g} \rightarrow {}^4E_g$ to the band on the low or high-energy side of $^4B_{1g} \rightarrow {}^4B_{2g}$ is generally unambiguous.

In order to distinguish the transitions to $^4A_{2g}$ and ^4E_g (components of $^4T_{1g}$(F)) states, the values of parameters e_σ and e_Λ for both ligand and anions were calculated from the both assignments (I $^4E_g > {}^4A_{2g}$ and *chromium(III) complexes* (e_Λ H*pox* assumed 0)

e_σ H*pox*	e_Λ	e_σ	d_Λ	d_σ	*B*	$D_{q\mathrm{H}pox}$	D_{qx}	β
7383	2020	7935	2020	414	670	2215	1600	0.728
7483	880	6021	880	—1344	643	2245	1352	0.698
7716	1003	5219	1003	—1865	530	2315	1250	0.576
7640	1371	7609	1371	—23	714	2292	1734	0.776
—	—	—	—	—	616	2230	—	0.669

II $^4E_g < {}^4A_{2g}$) and the values are given in Table 6. Assignment II is preferred for fluoride and aquo complexes of chromium(III) because it is conceivable that flouride and water be a Λ acceptor to chromium(III), assignment is therefore accepted, this implies that the F^- and H_2O is a better Λ donor towards chromium(III). Assignment I is preferred for the chloride and bromide ions, since these ions are expected to be Λ donor. Moreover assignment II requires Cl^- and Br^- to be a better σ donors towards chromium(III) which in view of the hardness of this metal ion is not expected.

The various parameters calculated from the spectral data (Table 7) assuming these transitions are given in Table 8.

From the calculated values of e_σ and e_Λ, the variation of the parameter e_Λ may be written

$$\mathrm{H}pox < Cl^- < Br^- < H_2O < F^- \tag{2}$$

and the variation in e_σ

$$Br^- \simeq Cl^- < \mathrm{H}pox \simeq H_2O < F^-$$

These results confirm the work of *Glerup* and *Schaffer*[38] who derived the values for *trans*- $[Cr(NH_3)_4X_2]^+$ (X = F, Cl, Br, H_2O and OH) from a systematic study of their solution spectra.

It is evident from these results that chromium(III) interacts much more strongly with the H_2O ligand and the F^- ion than it does with the H*pox* ligand or the heavier halogens. This indicates strong class A behaviour for the chromium(III) ion as expected. The high position of the F^- ion in the σ-bonding series should not, be too surprising. Its high position in the Λ-bonding series is however, puzzling at first sight.

To clarify this point a plot was made of the splitting of the t_{2g} (Δ_1) and e_g (Δ_3) levels (in O_h symmetry) by tetragonal field and is shown in Fig. 3. As *Yamatera* showed[39] in terms of molecular orbital theory the splitting of the cubic t_{2g} orbital is due to the difference in the Λ-antibonding character of the equatorial ligand (XY) and the axial ligand (ZX, YZ). Similarly the splitting of the e_g orbital arises due to the difference in the σ-antibonding character of the equatorial ligand (X^2—Y^2) and the axial ligand (Z^2). The energy of the d_{xy} orbital was arbitararily set at zero in all the complexes, since its energy, to first order, should be unaffected by changes in axial ligand. From this Fig. 3 it is clear that as the splitting of the t_{2g} level decreases, the splitting of the e_g level also decreases and changes in sign in the center of the diagram. This diagram reinforces the view evident from the series 2 and 3 that the strongly σ-bonding ligands are also the strongly Λ-bonding ligands.

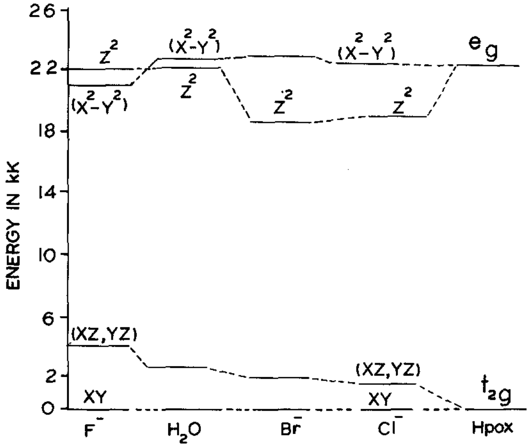

Fig. 3. One electron d orbital energy levels in the complexes $[Cr(Hpox)_2X_2]^{n+}$; where X = F, Cl, Br or X_2 = H*pox*

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