Monatshefte für Chemie 111, 1273–1285 (1980)

Monatshefte für Chemie

Transition Metal Chemistry of Oxime-Containing Ligands, IX.

Spectral and Magnetic Studies of Manganese(II) and Iron(III) Complexes of Pyridine-2-aldoxime and 6-Methylpyridine-2-aldoxime

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(Received 29 September 1978. Accepted 25 May 1979)

The vibrational (conventional and far-infrared) and diffuse-reflectance spectra in conjunction with magnetic susceptibility measurements over a temperature range down to liquid nitrogen temperature are reported and discussed for the complexes; $[Mn(HPOX)_2X_2]$; $[Mn(HMPX)_2X_2]$; $[Fe(HPOX)(POX)X_2]$ and $[Fe(HMPX)(MPX)X_2]$ (where $HPOX$ = pyridine-2-aldoxime ($C_6H_6N_2O$); $POX = C_6H_5N_2O$; $HMPX$ = 6-Methylpyridine-2-aldoxime ($C_7H_8N_2O$); $MPX = C_7H_7N_2O$; X = Cl, Br, I, NO_3, NCS, or OAc and $X_2 = SO_4$). On the basis of these physical studies a six-coordinated structure is suggested for the manganese(II) and iron(III) complexes. *Mössbauer* spectra, measured at room-temperature and liquid nitrogen temperature also indicated a six-coordinate geometry for iron(III) complexes.

[Keywords: Diffuse-reflectance spectra; Iron(III) complexes; Magnetic susceptibility; Manganese(II) complexes; Vibrational spectra]

Übergangsmetallkomplexe mit Oxim-enthaltenden Liganden, IX. Spektroskopische und magnetische Untersuchungen von Mn(II)- und Fe(II)-Komplexen mit Pyridin-2-aldoxim und 6-Methylpyridin-2-aldoxim

Es wurden Komplexe von Pyridin-2-aldoxim (H*POX*) und 6-Methylpyridin-2-aldoxim (H*MPX*) vom Typ $[Mn(HPOX)_2X_2]$, $[Mn(HMPX)_2X_2]$, $[Fe(HPOX)(POX)X_2]$ und $[Fe(HMPX)(MPX)X_2]$ (X = Cl, Br, I, NO_3, NCS, OAc; $X_2 = SO_4$) dargestellt. Die Diskussion erfolgt basierend auf Infrarotspektroskopie (inklusive fernes IR), Messungen der magnetischen Suszeptibilität (Temp. bis zu fl. N_2) und *Mössbauer*-Spektroskopie.

Introduction

Although aliphatic aldo- or keto-oximes transition metal complexes have been studied extensively[1] the complexes formed by aromatic aldoxime such as pyridine-2-aldoxime (H*POX*) and 6-methylpyridine-2-aldoxime (H*MPX*), have received relatively little attention. In continuation of our previous reports[2–9] on iron(II), cobalt(II), nickel(II), copper(II) and chromium(III) complexes of H*POX* and H*MPX*, we report in this paper the results of our investigation on the isolation and characterization of Manganese(II) and iron(III) complexes of H*POX* and H*MPX*.

Experimental

Materials: Manganese(II) and iron(III) salts, sodium iodide, ammonium thiocyanate (all reagent grade), pyridine-2-aldoxime and 6-methylpyridine-2-aldoxime (K&K Laboratories: Inc., New York) were used without further purification.

Synthesis of Complexes

Dihalogeno-bis (pyridine-2-aldoxime) manganese(II) and Dihalogeno-bis (6-methylpyridine-2-aldoxime) manganese(II): $Mn(L)_2X_2$ (L = H*POX* or H*MPX* and X = Cl or Br): Stoichiometric quantities of $MnX_2 \cdot 4\,H_2O$ (0.0025 mol) and ligand H*POX* or H*MPX* (0.005 mol) were dissolved in ethanol and solutions were mixed while hot. A yellow precipitate formed immediately. It was filtered, washed with ethanol and diethylether and dried in a vacuum desiccator over P_4O_{10}.

Diiodo-bis (pyridine-2-aldoxime) manganese(II) and Diiodo-bis (6-methylpyridine-2-aldoxime) manganese(II): $Mn(L)_2I_2$ (L = H*POX* or H*MPX*): These complexes were prepared as described above, except that MnI_2 was formed *in situ* by the double decomposition of $MnCl_2 \cdot 4\,H_2O$ and NaI in ethanol. The precipitated NaCl was filtered and the solution of MnI_2 was used as in the preparation of $Mn(L)_2X_2$.

Dinitrato-bis (pyridine-2-aldoxime) manganese(II) and Dinitrato-bis (6-methylpyridine-2-aldoxime) Manganese(II) $Mn(L)_2\ (NO_3)_2$ (L = H*POX* or H*MPX*): $Mn(NO_3)_2 \cdot 4\,H_2O$ (0.0025 mol) was dissolved in ethanol and added slowly to hot ethanolic solution of ligand H*POX* or H*MPX*. The solution, which immediately turned dark yellow, was stirred for several hours, the dark yellow solid was filtered and washed with copious amounts of diethylether and dried in a vacuum desiccator over P_4O_{10}.

Diisothiocyanato-bis (pyridine-2-aldoxime) manganese(II) and Diisothiocyanato-bis (6-methylpyridine-2-aldoxime) manganese(II): $Mn(L)_2(NCS)_2$ (L = H*POX* or H*MPX*): An ethanolic solution of manganese thiocyanate (0.002 mol), prepared from $MnCl_2 \cdot 4\,H_2O$ and NH_4SCN, was filtered into a solution of H*POX* or H*MPX* (0.005 mol), in hot ethanol. The mixture was gently boiled for 30 min. The solid product was collected by filtration and washed with ethanol and diethylether and dried in a vacuum desiccator over P_4O_{10}.

Diacetato-bis(pyridine-2-aldoxime) manganese(II) and Diacetato-bis(6-methylpyridine-2-aldoxime) manganese(II) $Mn(L)_2OAc_2$ (L = H*POX* or H*MPX*): $Mn(OAc)_2 \cdot H_2O$ (0.002 mol) was dissolved in minimum amount of water and ligand H*POX* or H*MPX* (0.0045 mol) dissolved in hot ethanol was added. The resulting solution was refluxed for 30 min. On cooling the solution a light yellow precipitate was obtained immediately. The solid was filtered and washed well with water and then with ethanol and diethylether and dried in a vacuum desiccator over P_4O_{10}.

Monosulphato-bis (pyridine-2-aldoxime) manganese(II) and Monosulphato-bis(6-methylpyridine-2-aldoxime) manganese(II): $\mathrm{Mn}(L)_2\mathrm{SO}_4$ ($L = \mathrm{H}POX$ or $\mathrm{H}MPX$): $\mathrm{MnSO_4 \cdot H_2O}$ (0.001 mol) was dissolved in water and refluxed for 15 min. The ligand H*POX* or H*MPX* was dissolved in hot ethanol and added dropwise with continuous stirring to the hot metal salt solution. Crystallization occurred almost immediately. A light yellow solid was collected by filtration washed with water and then with ethanol and diethylether and dried in a vacuum desiccator over $\mathrm{P_4O_{10}}$.

Dihalogeno-monohydrogen bis-(pyridine-2-aldoxime) iron(III) and Dihalogeno-monohydrogen bis-(6-methylpyridine-2-aldoxime) iron(III): $\mathrm{Fe}(\mathrm{H}POX)(POX)X_2$ and $\mathrm{Fe}(\mathrm{H}MPX)(MPX)X_2$ (X = Cl, Br or I): A solution of $\mathrm{Fe}X_3 \cdot 6\,\mathrm{H_2O}$ (0.004 mol) in 50 ml of absolute ethanol was prepared and refluxed for 30 min. A solution of ligand H*POX* or H*MPX* (0.008 mol) in 70 ml of absolute ethanol were prepared by heating and added very slowly to the metal salt solution. A red colour formed immediately, and a precipitate formed within minutes. The mixture was allowed to stand for 30 min and then heated to boiling and filtered hot via suction through a sintered glass. The precipitate was dried in a vacuum desiccator over $\mathrm{P_4O_{10}}$.

Dinitrato-monohydrogen bis-(pyridine-2-aldoxime) iron(III) and Dinitrato-monohydrogen bis-(6-methylpyridine-2-aldoxime) iron(III): $\mathrm{Fe}(\mathrm{H}POX)(POX)(\mathrm{NO_3})_2$ and $\mathrm{Fe}(\mathrm{H}MPX)(MPX)(\mathrm{NO_3})_2$: $\mathrm{Fe(NO_3)_2 \cdot 6\,H_2O}$ (0.005 mol) was dissolved in ethanol and added to an hot ethanolic solution of ligand H*POX* or H*MPX* (0.01 mol) and left in the freezer overnight. A negligible amount of fine red precipitate came down and was filtered off. The filtrate was slowly evaporated on a steam bath, giving red crystals. The solid product was filtered, washed with small amount of ethanol and diethylether and dried in a vacuum desiccator over $\mathrm{P_4O_{10}}$.

Diisothiocyanato-monohydrogen bis-(pyridine-2-aldoxime) iron(III) and Diisothiocyanato-monohydrogen bis-(6-methylpyridine-2-aldoxime) iron(III): $\mathrm{Fe}(\mathrm{H}POX)(POX)(\mathrm{NCS})_2$ and $\mathrm{Fe}(\mathrm{H}MPX)(MPX)(\mathrm{NCS})_2$: A suspension of $\mathrm{Fe}(\mathrm{H}POX)(POX)(\mathrm{NO_3})_2$ or $\mathrm{Fe}(\mathrm{H}MPX)(MPX)(\mathrm{NO_3})_2$ (0.01 mol) in absolute ethanol was treated with $\mathrm{NH_4SCN}$ (0.02 mol). The red solid turned into dark reddish-green on shaking the mixture. The product was filtered, washed with ethanol and diethylether and dried in a vacuum desiccator over $\mathrm{P_4O_{10}}$.

Diacetato-monohydrogen bis-(pyridine-2-aldoxime) iron(III) and Diacetato-monohydrogen bis-(6-methylpyridine-2-aldoxime) iron(III): $\mathrm{Fe}(\mathrm{H}POX)(POX)\mathrm{O}Ac_2$ and $\mathrm{Fe}(\mathrm{H}MPX)(MPX)\mathrm{O}Ac_2$: $\mathrm{Fe}(\mathrm{O}Ac)_3 \cdot 6\,\mathrm{H_2O}$ (0.001 mol) was dissolved in a minimum amount of water and added to a ethanolic solution of ligand H*POX* or H*MPX* (0.002 mol). The solution was then left in the freezer overnight. This yielded a thin dark film on the sides of the flask. The solution was filtered and filtrate left in the freezer for another week, giving well formed, dark red crystals. These crystals were collected, washed with small amount of ethanol and diethylether and dried in a vacuum desiccator over $\mathrm{P_4O_{10}}$.

Monosulphato-monohydrogen bis-(pyridine-2-aldoxime) iron(III) and Monosulphato-monohydrogen bis (6-methylpyridine-2-aldoxime) iron(III): $\mathrm{Fe}(\mathrm{H}POX)(POX)\mathrm{SO_4}$ and $\mathrm{Fe}(\mathrm{H}MPX)(MPX)\mathrm{SO_4}$: Ligand H*POX* or H*MPX* (0.005 mol) in hot ethanol was added slowly to a solution of ferric sulphate hexahydrate (0.0025 mol) in 10 ml of water with constant stirring. A deep red solution was formed. The resulting solution was refluxed for 30 min, giving red crystals. The crystals were filtered, washed with water and then with ethanol and diethylether and dried in a vacuum desiccator over $\mathrm{P_4O_{10}}$.

Physical Measurements

All magnetic susceptibility measurements at various temperatures were made on polycrystalline samples on a standard *Gouy* balance. The susceptibility standard was $HgCo(NCS)_4$ and the sample temperature was measured with a copper-constant thermocouple. Diamagnetic corrections were made by using tables of *Pascal*'s constants[10]. The error limits for the reported magnetic moments are ± 0.05 μ_{eff} B.M.

Diffuse-reflectance spectra at room temperature were recorded by using Cary-14 spectrophotometer equipped with a diffuse reflectance accessory, using MgO as a reference. The infrared spectra in the range 4,000-200 cm^{-1} were recorded on a Perkin-Elmer 180 spectrophotometer on samples in Nujol mulls and CsI disks.

Iron *Mössbauer* spectra were obtained on a polycrystalline samples by using a constant acceleration *Mössbauer* spectrometer which was calibrated with natural iron foil. The source was $^{57}Co(Pd)$ and was at room-temperature for all experiments. The low temperature results were measured in a vacuum cryostat with a sample holder which protected the sample from the cryostat vacuum. The *Mössbauer* results were determined by inspection with a accuracy of ± 0.01 mm/s.

All metal analyses were performed in this laboratory. Metals were analyzed by *EDTA* titrimetry[11] by using Erichrome Black T as an indicator[12] after decomposition of the complexes by a mixture of sulphuric acid and nitric acid. Halides were determined by *Volhard*'s method while nitrate was determined as its nitron salt[13]. The microanalyses of carbon, hydrogen and nitrogen was obtained through the kind courtesy of Micro-analytical Division of Aligarh Muslim University, Aligarh.

Results and Discussion

The analytical data for the present manganese(II) and iron(III) complexes were found satisfactory and reveal 1:2 (metal:ligand) stoichiometry for both manganese(II) and iron(III) complexes. All the present complexes were easily recrystallized from simple solvents but it was found that in general such recrystallization was not necessary and did not improve product purity. Likewise, the present complexes could be recovered unchanged after solution in specific solvents, such as acetone, acetonitrile and nitromethane. Small variations in reactant stochiometry ratios had no effect upon the product isolated. All complexes are stable at room-temperature and soluble in most common organic solvents except manganese(II) and iron(III) acetate and sulphate complexes but decomposes in aqueous solutions.

The magnetic susceptibilities for manganese(II) and iron(III) complexes have been measured over a temperature range down to liquid nitrogen temperature. The μ_{eff} B.M. values of the present complexes at room-temperature are in the range 5.80-5.90 (B.M.) expected for spin-only value for five-unpaired electrons, irrespective of whether the symmetry is octahedral, tetrahedral or lower[14]. Since manganese(II) and iron(III) complexes have orbitally non-degenerate ^6S ground term spin-only magnetic of 5.92 (B.M.) independent of temperature are expected[15]. The magnetic susceptibilities of manganese(II) and iron(III) complexes over a temperature range down to liquid nitrogen temperature obey the *Curie-Weiss* law with relatively small value of θ, ruling out the possibility of antiferromagnetic interaction and contributions from terms other then the ground term $^6A_{1g}/(t^3_{2g}e_g^2)$.

The *Mössbauer* spectrum of each of the iron(III) complexes has been measured at room and liquid nitrogen temperatures and exhibit the *Mössbauer* isomer shift ca. 0.64 mm/s^{-1} at room temperature and ca. 0.71 mm/s^{-1} at liquid nitrogen temperature. The high spin character of the present iron(III) complexes as evidenced by the magnetic data is further supported by these high values of the *Mössbauer* isomer-shift[16, 17] and as expected show slight increase with decreasing temperature. The isomer-shift values are surprisingly constant from one compound to the next and indicate that a change in the anion group has little effect upon the s-electron density at the surface of the iron nucleus.

The diffuse-reflectance spectra of manganese(II) and iron(III) complexes have been measured at room-temperature and detailed spectral data and assignments are presented in Table 1. Assignments are reasonable for high-spin complexes in octahedral environment[18]. The crystal field parameters and nephelauxetic parameters (Dq, B, C and β), calculated using the methods described by *Lever*[18], are recorded in Table 2, which confirms the octahedral environment of these complexes.

The infrared spectra of pyridine-2-aldoxime (H*POX*) and 6-methylpyridine-2-aldoxime (H*MPX*) differ from those of the common oximes, which show a ν_{OH} broad band at 3,250 cm^{-1}. This ν_{OH} broad band is replaced by multiple bands between 3,194 and 2,791 cm^{-1} in H*POX* and H*MPX*, the strongest of these lying around 2,791 cm^{-1}. This implies a much stronger hydrogen bonding in H*POX* and H*MPX* than in other oximes. The band assigned to $\nu C=N$ (acyclic) at 1,520 cm^{-1} in H*POX* and H*MPX* is considerably lower than normal. This lowering is attributed to the structure of type (I) in which the oxime proton is partially ionised. This lowering effect is further verified by a study of potassium salts of these ligands, where the $\nu C=N$ (acyclic band) was observed at ca. 1,517 cm^{-1}. The infrared spectra of H*POX* and H*MPX* exhibit four ring-stretching frequencies in between 1,600–1,400 cm^{-1}; the ring-breathing mode at ca. 980 cm^{-1}; the $\nu N—O$ stretching frequency at ca. 950 cm^{-1}; an out-of-place CH deformation at ca. 810 cm^{-1}, a skeletol mode at ca. 730 cm^{-1} and an out-of-plane deformation band at ca. 400 cm^{-1}.

Table 1. *Electronic absorption spectra of* Mn^{2+} *and* Fe^{3+}

Assignment	Mn(H*POX*)$_2$Cl$_2$	Mn(H*POX*)$_2$Br$_2$	Mn(H*POX*)$_2$I$_2$
$^6A_{1g} \rightarrow {}^4T_{1g}(G)$	16,600	16,240	16,125
$\rightarrow {}^4T_{2g}(G)$	21,060	20,760	20,657
$\rightarrow {}^4A_{1g}, {}^4E_g(G)$	23,290	23,095	
	24,680	24,398	24,410
$\rightarrow {}^4T_{2g}(D)$	27,835	27,591	27,566
$\rightarrow {}^4E_g(D)$	28,980	28,736	28,740
		33,557 CT*	33,602 CT*
		34,557 CT*	
	35,890 CT*		
		36,965 CT*	37,020 CT
	40,890 CT*	41,495 CT*	42,020 CT*

Assignment	Mn(H*MPX*)$_2$Cl$_2$	Mn(H*MPX*)$_2$Br$_2$	Mn(H*MPX*)$_2$I$_2$
$^6A_{1g} \rightarrow {}^4T_{1g}(G)$	16,619	16,225	15,940
$\rightarrow {}^4T_{2g}(G)$	21,300	20,942	20,647
$\rightarrow {}^4A_{1g}, {}^4E_g(G)$	23,625	23,420	24,308
	24,530	24,272	
$\rightarrow {}^4T_{2g}(D)$	26,460	26,210	26,244
$\rightarrow {}^4E_g(D)$	29,040	28,818	28,826
		33,557 CT	33,608 CT
	35,820 CT	35,714 CT	36,776 CT
	40,890 CT	41,322 CT	42,080 CT
	45,980 CT	47,619 CT	46,890 CT

Assignment	Fe(H*POX*)(*POX*)Cl$_2$	Fe(H*POX*)(*POX*)Br$_2$	Fe(H*POX*)(*POX*)I$_2$
$^6A_{1g} \rightarrow {}^4T_{1g}(G)$	13,635	13,700	13,674
$\rightarrow {}^4T_{2g}(G)$	18,695	18,870	18,872
$\rightarrow {}^4A_{1g}, {}^4E_g(G)$	25,350	25,460	25,500
$\rightarrow {}^4T_{2g}(D)$	28,594	28,810	28,870
$\rightarrow {}^4E_g(D)$	30,110	30,330	30,400
		32,000 CT	32,051 CT
	35,980 CT	36,380 CT	36,364 CT
			37,736 CT
	40,795 CT	38,040 CT	
		45,980 CT	44,643 CT

complexes (all values in cm^{-1}; CT = *Charge Transfer band)*

$\mathrm{Mn}(\mathrm{H}POX)_2(\mathrm{NO}_3)_2$	$\mathrm{Mn}(\mathrm{H}POX)_2(\mathrm{NCS})_2$	$\mathrm{Mn}(\mathrm{H}POX)_2\mathrm{O}Ac_2$	$\mathrm{Mn}(\mathrm{H}POX)_2\mathrm{SO}_4$
16,300	16,610	18,285	17,050
20,870	21,286	22,620	21,395
24,741	25,187	25,926	24,895
26,610	27,100	27,695	26,670
29,100	29,660	30,060	29,036
34,080 CT	35,715 CT		32,026 CT
38,040 CT	39,685 CT	38,880 CT	37,092 CT
40,090 CT	40,486 CT	40,996 CT	39,892 CT
42,040 CT		42,260 CT	41,190 CT
45,900 CT	45,870 CT	45,920 CT	46,020 CT

$\mathrm{Mn}(\mathrm{H}MPX)_2(\mathrm{NO}_3)_2$	$\mathrm{Mn}(\mathrm{H}MPX)_2(\mathrm{NCS})_2$	$\mathrm{Mn}(\mathrm{H}MPX)_2\mathrm{O}Ac_2$	$\mathrm{Mn}(\mathrm{H}MPX)_2\mathrm{SO}_4$
16,198	16,142	16,652	16,754
20,950	20,950	21,070	21,196
24,595	24,788	24,233	24,298
26,552	26,764	26,051	26,125
29,159	29,399	28,473	28,566
34,107 CT	35,695 CT		35,700 CT
37,805 CT	38,970 CT	38,598 CT	37,600 CT
40,055 CT	40,550 CT	40,980 CT	39,992 CT
40,126 CT	44,082 CT		
46,798 CT	46,626 CT	47,020 CT	46,982 CT

$\mathrm{Fe}(\mathrm{H}POX)(POX)(\mathrm{NO}_3)_2$	$\mathrm{Fe}(\mathrm{H}POX)(POX)(\mathrm{NCS})_2$	$\mathrm{Fe}(\mathrm{H}POX)(POX)\mathrm{O}Ac_2$	$\mathrm{Fe}(\mathrm{H}POX)(POX)\mathrm{SO}_4$
13,814	13,924	13,680	13,657
19,185	19,393	18,666	18,628
25,825	26,105	25,190	25,130
29,350	29,700	28,384	28,316
30,900	31,270	29,880	29,806
31,980 CT		32,051 CT	32,162 CT
36,400 CT	36,418 CT	36,101 CT	35,987 CT
37,980 CT	38,126 CT		
45,480 CT	45,328 CT	44,248 CT	44,210 CT

Table 1 (continued)

Assignment	Fe(H*MPX*)(*MPX*)Cl$_2$	Fe(H*MPX*)(*MPX*)Br$_2$	Fe(H*MPX*)(*MPX*)I$_2$
$^6A_{1g} \rightarrow {}^4T_{1g}(G)$	13,865	13,825	13,965
$\rightarrow {}^4T_{2g}(G)$	19,188	19,150	19,350
$\rightarrow {}^4A_{1g}, {}^4E_g(G)$	25,340	25,325	25,460
$\rightarrow {}^4T_{2g}(D)$	28,890	28,874	29,000
$\rightarrow {}^4E_g(D)$	30.380	30.365	30.570
			36,380 CT
			38,556 CT
	42,200 CT	42,132 CT	42,132 CT
		46,272 CT	46,272 CT

Table 2. *Crystal field parameters of* Mn^{2+} *and* Fe^{3+} *complexes of* H*POX and* H*MPX (all values in* cm^{-1}*)*

Compound	*Dq*	*B*	*C*	β*
Mn(H*POX*)$_2$Cl$_2$	1092.9	614.2	3707.4	0.6397
Mn(H*POX*)$_2$Br$_2$	1092.6	616.8	3650.0	0.6425
Mn(H*POX*)$_2$I$_2$	1102.8	618.5	3645.0	0.6442
Mn(H*POX*)$_2$(NO$_3$)$_2$	1124.6	623.0	3702.0	0.6489
Mn(H*POX*)$_2$(NCS)$_2$	1141.2	638.7	3760.0	0.6653
Mn(H*POX*)$_2$O*Ac*$_2$	1070.8	590.0	4004.0	0.6152
Mn(H*POX*)$_2$SO$_4$	1080.0	592.0	3795.0	0.6166
Mn(H*MPX*)$_2$Cl$_2$	1050.0	644.2	3617.5	0.671
Mn(H*MPX*)$_2$Br$_2$	1056.0	649.2	3555.0	0.676
Mn(H*MPX*)$_2$I$_2$	1095.0	645.4	3570.8	0.672
Mn(H*MPX*)$_2$(NO$_3$)$_2$	1100.8	652.0	3615.0	0.679
Mn(H*MPX*)$_2$(NCS)$_2$	1128.7	658.8	3640.0	0.686
Mn(H*MPX*)$_2$O*Ac*$_2$	1028.9	605.8	3635.0	0.631
Mn(H*MPX*)$_2$SO$_4$	1024.0	609.8	3640.0	0.635
Fe(H*POX*)$_2$(*POX*)Cl$_2$	1460.2	680.0	3710.0	0.523
Fe(H*POX*)(*POX*)Br$_2$	1460.0	696.2	3700.0	0.535
Fe(H*POX*)(*POX*)I$_2$	1465.8	700.0	3700.0	0.538
Fe(H*POX*)(*POX*)(NO$_3$)$_2$	1480.4	725.0	3715.0	0.557
Fe(H*POX*)(*POX*)(NCS)$_2$	1498.2	738.2	3745.0	0.567
Fe(H*POX*)(*POX*)O*Ac*$_2$	1440.0	670.2	3698.0	0.515
Fe(H*POX*)(*POX*)SO$_4$	1435.5	668.0	3690.0	0.513
Fe(H*MPX*)(*MPX*)Cl$_2$	1415.4	720.4	3628.0	0.554
Fe(H*MPX*)(*MPX*)Br$_2$	1418.0	720.6	3625.0	0.554
Fe(H*MPX*)(*MPX*)I$_2$	1415.0	730.0	3632.0	0.561
Fe(H*MPX*)(*MPX*)(NO$_3$)$_2$	1448.9	750.8	3656.0	0.577
Fe(H*MPX*)(*MPX*)(NCS)$_2$	1462.0	758.2	3659.0	0.583
Fe(H*MPX*)(*MPX*)O*Ac*$_2$	1400.00	700.0	3610.0	0.538
Fe(H*MPX*)(*MPX*)SO$_4$	1396.7	695.0	3600.0	0.534

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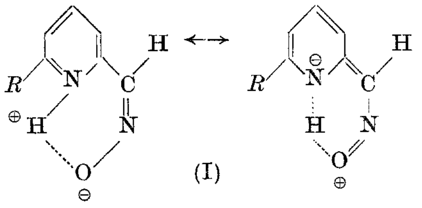
* Free ion B_0 value taken in Mn^{2+} = 960 cm^{-1} and in Fe^{3+} = 1,300 cm^{-1}

$Fe(HMPX)(MPX)(NO_3)_2$	$Fe(HMPX)(MPX)(NCS)_2$	$Fe(HMPX)(MPX)OAc_2$	$Fe(HMPX)(MPX)SO_4$
13,945	13,895	13,750	13,685
19,485	19,490	18,930	18,830
25,780	25,870	25,000	24,950
29,500	29,635	28,480	28,350
31,000	31,180	29,950	29,815
36,370 CT	36,364 CT	35,714 CT	35,628 CT
38,425 CT	28,023 CT	38,023 CT	38,040 CT
42,128 CT		42,016 CT	42,182 CT
46,268 CT	45,249 CT		45,300 CT



(I)

[R = H or CH_3]

Krause et al.[19] have extensively investigated transition metal complexes of pyridine-2-aldoxime in νC=N (acyclic) and νN—O regions and postulated that complexes containing unionized oxime proton have νC=N (acyclic) and νN—O stretching frequencies in the range 1,654-1,614 cm^{-1} and 1,069-1,036 cm^{-1}; respectively. Whereas the complexes containing ionized oxime proton (the oxime may or may not be hydrogen bonded) have νC=N (acyclic) and νN—O stretching frequencies in the range 1,556-1,526 cm^{-1} and 1,150-1,041 cm^{-1}, respectively. The present manganese(II) complexes of H*POX* and H*MPX* exhibit the bands at ca. 3,250; ca. 1,660 and ca. 1,074 cm^{-1} which can be assigned to νOH, νC=N (acyclic) and νN—O stretching frequencies, respectively. These data in manganese(II) complexes show that oxime proton is unionized and there is a contribution from the —C=N—OH groups. Whereas the iron(III) complexes of H*POX* and H*MPX* possess the νC=N (acyclic) band at ca. 1,550 cm^{-1} and the νN—O band at ca. 1,130 cm^{-1}. No νOH stretching band is observed in these iron(III) complexes. These results indicate that oxime proton of one H*POX* or H*MPX* is heterolysed and there is a contribution from —C=N—$\overset{\circ}{O}$ . . . HO—N=C-grouping in these iron(III) complexes.

The infrared spectra of dihydrogen (containing —C=N—OH-groups) and monohydrogen (containing—C=N—O - - - HO—N=C-groups) metal complexes have weak absorption bands at ca. 1,700 and ca. 1,600 cm^{-1}, respectively. These bands are assigned to OH stretching of the intramolecularly hydrogen bonded oxime OH groups[20].

The infrared spectra of the present complexes exhibit the four $\nu(C=C)$, $\nu(C=N)$, skeletal frequencies in the following ranges; Band I; 1,620-1,600 cm^{-1}; Band II; 1,575-1,565 cm^{-1}; Band III; 1,490-1,482 cm^{-1} and Band IV; 1,440-1,430 cm^{-1}. Band I shows a significant increase in frequency from its free ligand value of ca. 1,570 cm^{-1}, an indication of pyridine coordination to metal atom[21]. The ring-breathing mode observed at ca. 980 cm^{-1} in the free ligands disappears in the complexes and is replaced by a band at ca. 1,020 cm^{-1}. This shift is also an indication of pyridine coordination to metal atom[22, 23].

Two strong bands are observed in the spectrum of free ligands H*POX* and H*MPX* at ca. 810 and ca. 730 cm^{-1}, which may be assigned to γ(C—H) and (C—C), respectively[24]. The ca. 730 cm^{-1} bond splits into two components lying between 718 and 752 cm^{-1}. This splitting is also believed to be an indication of pyridine-coordination to metal atom[23, 25]. The band observed at ca. 810 cm^{-1} in free H*POX* and H*MPX* ligands disappears in their manganese(II) and iron(III) complexes and is observed as a single band lying between 780 and 824 cm^{-1} in the complexes.

The free ligands, H*POX* and H*MPX*, exhibit a band at ca. 400 cm^{-1} assigned to the C—C out-of-plane deformation[24, 25], while all the present complexes exhibit a single band at ca. 412 cm^{-1}. An increase in frequency upon coordination of pyridine to metal atom is to be expected[26].

These data leave little doubt that in the present manganese(II) and iron(III) complexes the ligands H*POX* and H*MPX* are coordinated to the metal ion via pyridine nitrogen and oxime nitrogen atoms.

The infrared spectra of nitrato complexes of manganese(II) and iron(III) with H*POX* and H*MPX* exhibit bands at ca. 1,290; ca. 1,020; ca. 740; ca. 1,430; ca. 720 and ca. 820 cm^{-1} which can be assigned[27–29] to NO_2 symmetric stretching (ν_1); N—O stretching (ν_2); NO_2 symmetric banding (ν_3); NO_2 asymmetric stretching (ν_4); NO_2 asymmetric bending (ν_5) and out-of-plane rocking; respectively. These frequencies are compatible with monodentately coordinated nitrate groups. The infrared spectra of these complexes also shows weak bands at ca. 1,730; 1,750; and at ca. 2,295 and ca. 2,410 cm^{-1} which can be assigned to the combination bands of ($\nu_1 + \nu_4$) and ($\nu_1 + \nu_3$)[27]; respectively. The energy separation of the frequencies of ($\nu_1 + \nu_4$) is ca. 22 cm^{-1} and that of ($\nu_1 + \nu_3$) is ca. 125 cm^{-1}, which also confirms the monodentate nature of the nitrate group[27, 28].

The thiocyanato complexes show bands at ca. 2,045; ca. 485; and ca. 810 cm^{-1} assignable[30] to C—N stretching (ν_1); NCS bending (ν_2) and C—S stretching (ν_3), respectively. These frequencies corroborates the presence of N-bonded thiocyanate[30] group in the present thiocyanato complexes.

The acetato complexes of manganese(II) and iron(III) complexes exhibit two bands at ca. 1,650 and ca. 1,390 cm^{-1} which can be assigned[31–33] to νCOO asymmetric and νCOO symmetric vibrations, respectively. These vibrational band values are intermediate between those observed for purely ionic and covalent acetate molecules[34,35], indicating the metal-oxygen bond is moderately covalent[31–33].

In the infrared spectra of sulphato complexes bands are observed at ca. 1,135; ca. 1,100; ca. 1,050; ca. 900; ca. 680; ca. 600; and ca. 450 cm^{-1} which may be assigned to coordinated sulphate group[36,37]. The occurrence of H*POX* and H*MPX* ligand vibrational bands in these regions allows only tentatively assignment of individual bands to sulphate vibrations. The νS—O band, however, occurs in a region of the spectrum free of organic ligand bands and can therefore be assigned with certainty. In these sulphato complexes this band occurs at ca. 990 cm^{-1} which suggests[37] bidentate as opposed to monodentate coordination of sulphate group in the present complexes.

The free ligands exhibit the medium to strong far-infrared absorption bands at ca. 400; ca. 385; ca. 300 and ca. 220 cm^{-1}. Whereas all the present complexes have bands of varying intensity at ca. 400; ca. 380; ca. 300 and ca. 220 cm^{-1}, which corresponds to medium to strong bands in this region in the free ligand spectrum.

The far-infrared spectra of manganese(II) complexes of H*POX* and H*MPX* exhibit a strong band at ca. 250 cm^{-1} and a shoulder at ca. 215 cm^{-1} which can be assigned to *M*—N vibrations[32–42] for manganese(II) complexes. For iron(III) complexes similar ν*M*—N vibrations[38–42] are observed at ca. 375 and ca. 364 cm^{-1}. The bands occurring at ca. 320 and ca. 350 cm^{-1} are assigned to ν*M*—O in nitrato- and acetato-complexes of manganese(II) complexes.

The bands appearing at ca. 270 and ca. 260 cm^{-1} are assigned to ν*M*—Cl and ν*M*—NCS vibrations, respectively, in manganese(II) complexes. No ν*M*—Br and ν*M*—I vibrations are observed down to 200 cm^{-1} in manganese(II) complexes, indicating that these vibrations occur below 200 cm^{-1}. The ν*M*—Cl, ν*M*—Br, ν*M*—I and ν*M*—NCS vibrations in iron(III) complexes are observed at ca. 380; ca. 300; ca. 230 and ca. 341 cm^{-1} respectively. The stereochemistry of a large number of four- and six-coordinate complexes has been assigned[38] on the basis of the metal-ligand (particularly metal halide) stretching frequencies. The M—X_2 complexes can conform either to C_{2v} or D_{4h}

point group symmetry. In C_{2v} symmetry, two $\nu M—X$ vibrations are expected while in D_{4h} point only one $\nu M—X$ vibrations are observed[43,44]. The present manganese(II) and iron(III) complexes exhibit only one $\nu M—X$ vibration indicating that anions are present in *trans*-position[45] to each other in D_{4h} point group symmetry.

Acknowledgement

We are thankful to Dr. *P. C. Gupta*, Principal, N.R.E.C. College, Khurja for providing laboratory facilities and Prof. Dr. *K. P. Gopinathan*, Materials Science Laboratory, Reactor Research Centre, Kalpakkam, Tamilnadu for *Mössbauer* spectral measurements. Financial support to *R. Dutt* by U.G.C. New Delhi is gratefully acknowledged.

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