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Mössbauer and electronic spectral studies of iron(III) complexes of oximes

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Abstract

The hydroxo-bridge complexes of the type $[Fe_2(ligand{-}H)_4(OH)_2]$ with bidentate nitrogen–oxygen donor ligands, viz. 2-hydroxynaphthaldehydeoxime $[hnoH_2]$, 2-hydroxyacetphenoneoxime $[haoH_2]$, salicylaldooxime $[SalH_2]$, 2-hydroxypropiophenoneoxime $[hnoH_2]$ have been prepared. All the complexes have been characterized by elemental analysis, magnetic moments, electronic and Mössbauer spectral studies. Mössbauer parameters of the complexes clearly suggest high spin configuration of Fe(III) showing lower magnetic moment to that of the spin only value, i.e. 5.92 BM. It may be due to the antiferromagnetic interaction between Fe(III) centers.

Keywords: Fe(III); Oximes; Mössbauer; Magnetic moment; Electronic spectra

1. Introduction

The metal complexes of *o*-hydroxyoximes received considerable attention due to their structural features which are of general interest [1–5]. These features include short intramolecular hydrogen bonds and a packing configuration, which gives rise to unusual optical properties. Hydroxyoximes are playing an important role as commercial reagents in extractive metallurgy in both solvent extraction and froth flotation [6,7]. Oximes are also applicable as biochemical [8,9] models and as semi-conducting materials [10,11]. The dioxime and *o*-hydroxyoximes have also been used as analytical reagent [12–17] for the detection and determination of metal ions.

In this paper, we report the synthesis and characterization of Fe(III) complexes of oximes, viz. 2-hydroxynaphthaldehydeoxime $[hnoH_2]$ L_1, 2-hydroxyacetphenoneoxime $[haoH_2]$ L_2, salicylaldooxime $[SalH_2]$ L_3, 2-hydroxypropiophenoneoxime $[hnoH_2]$ L_4.

2. Experimental

All the chemicals used were of AnalaR grade. All the solvents used were distilled before use.

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2.1. Preparation of the ligands

A general method for the preparation of ligands has been used. The ligands were prepared by treating 0.05 mol of an ethanolic solution (20 ml) of particular aldehyde or ketone with an ethanolic solution (20 ml) of hydroxylamine hydrochloride (0.1 mol, 6.95 g) containing an aqueous solution (20 ml) of sodium acetate (0.15 mol, 12.30 g). The solution was heated on water bath for about 2–4 h with constant stirring. On cooling the contents at 5 °C, ligands were precipitated out. They were filtered, washed with ethanol and dried under vacuum over P_4O_{10}.

2.2. Preparation of the complexes

A hot aqueous solution (20 ml) of ferric perchlorate (0.1 mol) was mixed with the hot ethanolic solution (20 ml) of the corresponding ligand (0.2 mol). In the case of 2-hydroxynaphthaldehyde, aqueous solution of sodium hydroxide was added dropwise until dark brown colour complexes precipitated out. But in the case of salicylaldehyde and 2-hydroxyacetophenone, aqueous NH_3 solution (1:1) was added dropwise until the brown-coloured complexes precipitated out. The coloured precipitate was filtered, washed with absolute ethanol and dried under vacuum over P_4O_{10}.

3. Physical measurements

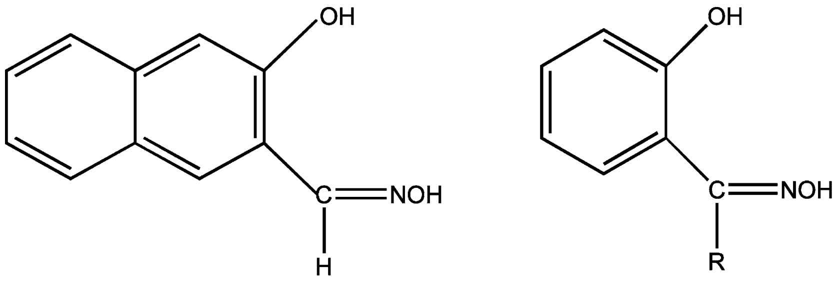
Magnetic susceptibility on the solid complexes were made at room temperature by Gouy method using $Hg[Co(CNS)_4]$ ($\chi_g = 16.44 \times 10^{-6}$ cgs units) as the calibrating agent. Electronic spectra in Nujol mull were recorded on Perkin-Elmer 137. IR spectra were recorded on a Perkin-Elmer 621 automatic recording spectrophotometer in Nujol mull. Microanalyses of C, H and N were performed at the Microanalytical Laboratory, CDRI, Lucknow. Mössbauer measurements were carried out on a multichannel (512 channels) analyzer in constant acceleration mode. Source (NEN) used is Co^{57} in Pd matrix (15 mc) and was held at room temperature. Sufficient counts were stored in each channel and the data from multichannel analyzer were reduced by means of a least-square-fitting programme run on IBM 360 computer.

4. Results and discussion

All the complexes were found to have general composition $[Fe_2(ligand{-}H)_4(OH)_2]$ where the ligands are of 2-hydroxynaphthaldehydeoxime $[hnoH_2]$ L_1, 2-hydroxyacetophenoneoxime $[haoH_2]$ L_2 (Ia), salicylaldooxime $[SalH_2]$ L_3, 2-hydroxypropiophenoneoxime $[hnoH_2]$ L_4 (Ib) (Fig. 1). All the complexes are stable in air and moisture. The analytical data of complexes with the stoichiometries proposed are summarized in Table 1.

5. Magnetic moments

These complexes show magnetic moment in the range 4.0–4.3 BM which is lower than the spin only value, i.e. 5.92 BM. Fe(III) d^5 case, under weak fields of O_h symmetry, the ground state is $^6A_{1g}(t_{2g}^3, e_g^2)$ with $S = 5/2$ (high spin). Such system exhibits magnetic moments close to spin only value, i.e. 5.92 BM. In the presence of strong field of O_h symmetry, the ground state is [2] $T_{2g}(t_{2g}^5, e_g^0)$ with $S = 1/2$ (low spin); in this case, the magnetic moments are close to 2.0 BM. Deviation from the spin only value of 1.73 BM is due to the small contribution from the non-zero value of the orbital angular momentum in the t_{2g}^5 configuration. The magnetic moment is intermediate to high or low spin values due arise when the ligand field strength is comparable with the mean electronic pairing energy of the d^5 configuration. In such a case, the two possible ground states $^6A_{1g}$ and $^2T_{2g}$ are in thermal equilibrium resulting in temperature-dependent variation of magnetic moments between the limiting values of 5.92–2.0 BM. This has also been confirmed by Mössbauer quadrupole splitting.



Ia

Ib

R = CH_3, H & C_2H_5

Fig. 1. Structure of ligands.

6. IR spectra

The most important bands in the IR spectra of the ligands and their metal complexes are presented in Table 2 along with their tentative assignments.

In the IR spectra of ligands, a strong band at 3450–3475 cm^{-1} is assigned to ν(OH) of the oxime or phenolic group. The absence of this band in the spectra of the metal complexes of these ligands suggests coordination through the oxygen of the phenolic group [18–20]. Another strong band in the IR spectra of the ligands assignable to ν(C=N) appears at 1580–1590 cm^{-1} and is shifted to lower frequency (~25 cm^{-1}) in the spectra of the complexes, suggesting involvement of this group in chelation [21]. Some new bands also appeared in the IR spectra of the complexes at 460–475 and 398–393 cm^{-1} which may be due to the formation of ν(M–O) and ν(M–N) bonds [22,23].

Table 2
Infrared spectral bands in cm^{-1} and their assignments

Complexes	ν(OH)	ν(C=N)	ν(M–O)	ν(N–O)
[hnoH$_2$]	3460s	1560m	–	–
[Fe$_2$(hnoH–H)$_4$(OH)$_2$]	–	1579m	471m	398w
[haoH$_2$]	3475s	1560m	–	–
[Fe$_2$(haoH–H)$_4$(OH)$_2$]	–	1580m	469m	393w
[hSalH$_2$]	3450	1564m	–	–
[Fe$_2$(SalH–H)$_4$(OH)$_2$]	–	1590m	470m	398w
[hmpH$_2$]	3470s	1575m	–	–
[Fe$_2$(hmpH–H)$_4$(OH)$_2$]	–	1590m	467m	397w

Table 1
Colour melting point and composition of iron(III) complexes of oximes

Complexes	Colour	Melting point (°C)	Yield (%)	Elemental analysis calculated (found) (%)		
				M	C	H
[Fe$_2$(hnoH–H)$_4$(OH)$_2$] $Fe_2C_{44}H_{34}N_4O_{10}$	Dark brown	270	60	12.54 (12.14)	59.34 (59.11)	3.85 (3.42)
[Fe$_2$(haoH–H)$_4$(OH)$_2$] $Fe_2C_{32}H_{34}N_4O_{10}$	Dark brown	250	75	14.96 (14.44)	51.49 (51.14)	4.59 (4.12)
[Fe$_2$(SalH–H)$_4$(OH)$_2$] $Fe_2C_{28}H_{26}N_4O_{10}$	Dark reddish-brown	255	67	16.18 (16.38)	48.73 (48.23)	3.79 (3.32)
[Fe$_2$(hnoH–H)$_4$(OH)$_2$] $Fe_2C_{36}H_{42}N_4O_{10}$	Dark reddish-brown	265	64	13.75 (13.33)	53.22 (52.84)	5.21 (5.56)

7. Electronic spectra

The electronic spectra of the Fe(III) complexes exhibit a number of fairly broad bands rather than the series of narrow bands as expected [24]. The complexes under study show three bands of varying intensities at 16 320–20 879, 19 570–26 900 and 28 560 cm^{-1}, respectively. These transitions may be assigned, respectively, to the following transitions: $^6A_{1g}\rightarrow{}^4T_{1g}$, $^6A_{1g}\rightarrow{}^4T_{2g}$ and $^6A_{1g}\rightarrow{}^4T_{1g},{}^4E_g$.

Table 3
Electronic spectral bands and magnetic moment data in BM for iron(III) complexes

Complexes	λ_{max} (cm^{-1})	μ_{eff} (BM)
[Fe_2(hnoH–H)$_4$(OH)$_2$]	10 125, 20 879, 21 690, 28 650	4.13
[Fe_2(haoH–H)$_4$(OH)$_2$]	15 650, 16 320, 19 570, 21 690	4.09
[Fe_2(SalH–H)$_4$(OH)$_2$]	10 130, 16 360, 18 629	4.18
[Fe_2(hmpH–H)$_4$(OH)$_2$	11 013, 18 621, 29 062	4.30

8. Mössbauer spectra

Mössbauer parameters of the complexes are clearly suggestive of high spin Fe(III) observed lower magnetic moments as against 5.92 BM may arise due to antiferromagnetic interaction between Fe(III) centers. The alternative possibility of spin-state equilibrium should lead to temperature-dependent Mössbauer quadrupole splitting [25], while the complexes under study show remarkably temperature-independent QS values. Keeping in view the composition of the complexes and bidentate nature of the ligands, the following dihydroxybridged structure may be considered (Fig. 2).

Dihydroxybridging of this type may give rise to moderate antiferromagnetic exchange interaction causing only small lowering in the magnetic moment value as observed in these complexes in Table 3. The characteristics Fe–O–Fe antisymmetric vibrations in such complexes are known to absorb at ~950 cm^{-1} in the IR spectra. [Fe_2(SalH)$_4$(OH)$_2$] show medium non-ligand bands at 960 cm^{-1} while the spectrum of other complexes contains strong ligand bands at this position.

Mössbauer parameters for all the complexes are given in Table 4. Representative spectra are shown in Fig. 3. The isomer shift value lie in the range 0.54–0.69 nm s^{-1} (300 K), which is indicative of an $S = 5/2$ iron(III) state [25]. Quadrupole splitting values lie in the range 0.70–0.97 nm s^{-1} for high spin iron(III) complexes. In iron(III) complexes, there is no valence contribution to the QS. The only source of QS, therefore, remains the lattice contribution arising mainly from the asymmetry of

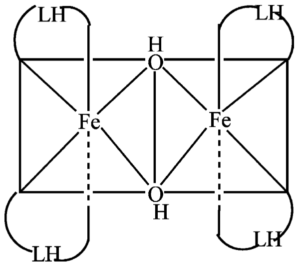
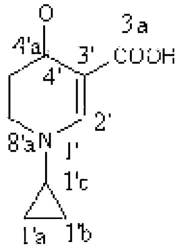


Fig. 2. Structure of Fe(III) complexes.



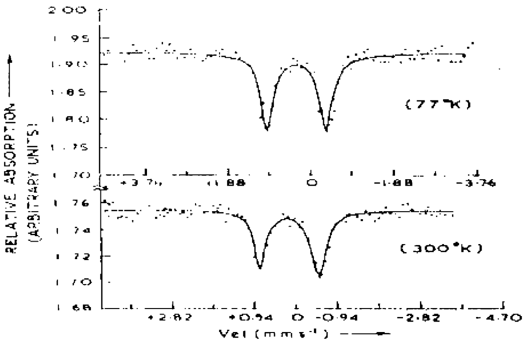


Fig. 3. Mössbauer spectra of (a) [Fe_2(SalH–H)$_4$(OH)$_2$] and (b) [Fe_2(haoH–H)$_4$(OH)$_2$].

Table 4
Mössbauer parameters for iron(III) complexes

Complexes	Temperature (K)	IS δ (mm s^{-1})	QS ΔE (mm s^{-1})	HW_h (mm s^{-1})	HW (mm s^{-1})	Hw/HW
$[Fe_2(hnoH{-}H)_4(OH)_2]$	300	0.65	0.98	0.58	0.48	1.20
	78	0.79	0.95	0.45	0.40	1.12
$[Fe_2(haoH{-}H)_4(OH)_2]$	300	0.51	0.86	0.75	0.57	1.31
	78	0.80	0.84	0.90	0.70	1.28
$[Fe_2(SalH{-})_4(OH)_2]$	300	0.63	0.97	0.64	0.57	1.12
	78	0.77	0.94	0.94	0.77	1.22
$[Fe_2(hmpH{-}H)_4(OH)_2$	300	0.62	1.33	0.31	0.41	0.76
	78	0.78	1.34	0.44	0.38	1.16

the ligand field, which is further supported by the temperature independence of the QS value.

All the complexes show asymmetry effect as expected for dimeric iron(III) compounds [26]. The half width ratios are temperature-independent for $[Fe_2(SalH_2)_4(OH)_2]$ and temperature-dependent for $[Fe_2(haoH{-}H)_4(OH)_2]$ and $[Fe_2(hnoH{-}H)_4(OH)_2]$. The asymmetry of the quadrupole doublet may be attributed to the interaction of the nucleus with fluctuating electronic and magnetic field. Fluctuations due to spin lattice relaxation cause a temperature-dependent and concentration-independent asymmetry and those due to spin–spin relaxation give temperature-independent asymmetry [27–29]. $[Fe_2(haoH{-}H)_4(OH)_2]$ and $[Fe_2(hnoH{-}H)_4(OH)_2]$ for which asymmetry is temperature-dependent, involve spin–lattice relaxation, since concentration dependence has not been studied, spin–spin relaxation also not to be ruled out. $[Fe_2(SalH_2)_4(OH)_2]$ shows temperature-independent asymmetry and hence involves spin–spin relaxation and not spin–lattice relaxation.

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