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Mössbauer and Magnetic Study of Mononuclear and Oxo-bridged Binuclear Iron(III) Complexes of 1,10-Phenanthroline and 2,2′-Bipyridine

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The oxo-bridged binuclear iron(III) complexes $[L_2(NCS)Fe–O–Fe(NCS)L_2]^{2+}$ (L=1,10-phenanthroline or 2,2′-bipyridine) were prepared recently in spite of the earlier report that they could not be prepared. The unperturbed and perturbed Mössbauer spectral and magnetic susceptibility data on these compounds are reported here and compared with those for the well characterized oxo-bridged compounds $[L_2XFe–O–FeXL_2]^{2+}$ (X=Cl^-, Br^-, SO_4^{2-},/2 or NO_3^-). The effect of Fe–X bond (X=Cl^-, Br^-, $SO_4^{2-}/2$, NO_3^-, or NCS^-) on the Mössbauer parameters was investigated, and the results are discussed in terms of the bonding properties of these anionic ligands. The data indicate that the electronegativity of the X ligands has no significant effect on the Mössbauer parameters. Another system, the mononuclear iron(III) complexes $[FeL_2(NCS)_2](NCS)$, investigated in this work showed no Mössbauer resonance at or above 223 K and below this temperature the unperturbed spectra exhibited a broad asymmetric singlet. Magnetic susceptibilities and magnetically perturbed Mössbauer spectra indicated that iron(III) ion in these mononuclear complexes was paramagnetic with $S=5/2$.

The Mössbauer parameters of isomer shift (*I.S.*) and quadrupole splitting (*Q.S.*) have been utilized in elucidating the structure and bonding in a large series of organometallic and coordination compounds.[1–6] Mössbauer studies have indicated that *I.S.* values are an approximate additive property of the type and number of ligands, and Erickson[7] has suggested a relative covalency scale. The *Q.S.* values provide complementary information on the nature of σ- and π-bonding in low-spin and high-spin compounds.

Binuclear complex of iron(III) with 1,10-phenanthroline (phen) or 2,2′-bipyridine (bipy), $[Fe_2L_4OCl_2]Cl_2$ (L=phen or bipy) has been of considerable interest since its first isolation by Gains *et al.*[8] It is now established that these complexes contain a linear Fe–O–Fe bridge[9–12]. Mössbauer studies on binuclear complexes $[Fe_2(phen)_4OX_2]X_2 \cdot YH_2O$ (X=Cl^-, Br^- or $SO_4^{2-}/2$; Y=2—7) have been reported[4,10,12] while only one bipy complex, $Fe_2(bipy)_4O(SO_4)_2 \cdot 9H_2O$ has received attention[4,10].

The exchange of Cl^- ligands in $[Fe_2L_4OCl_2]^{2+}$ by SO_4^{2-}, ClO_4^-, and Br^- to form $[Fe_2L_4X_2]^{2+}$ (where X=$SO_4^{2-}/2$, ClO_4^-, or Br^-) has been described.[9,13a,14] But it was reported by Driver and Walker[14] that an attempt to prepare $[Fe_2(phen)_4O(NCS)_2]^{2+}$ by analogous procedure resulted in the reduction product $Fe(II)(phen)_2(NCS)_2$. David[13] recently investigated in detail the reaction between $[Fe_2L_4OCl_2]^{2+}$ and NCS^- and reported that the observations of Driver and Walker were incorrect. David[13] prepared the binuclear complexes $[Fe_2L_4O(NCS)_2](NCS)_2$. We report here the Mössbauer spectral and magnetic susceptibility data on these compounds. The present data are in firm support of the conclusions reached earlier by David[13] based on electronic and infrared spectral data, and conductivity studies. Further, the Mössbauer spectral and magnetic susceptibility data for these compounds are in fair agreement with those reported for similar oxo-bridged binuclear compounds.

The effect of the anionic ligand X^- on the Mössbauer spectra of the binuclear complexes $[Fe_2L_4OX_2]X_2$ (where X=Cl^-, Br^-, $SO_4^{2-}/2$, NO_3^-, or NCS^-) are also presented here. Preparations of these anhydrous compounds have been reported recently. Even though Mössbauer investigation on a few of these complexes has been carried out,[4,10,12] there has been no systematic study to decide on the effect of the bonding properties of these anionic ligands on the Mössbauer parameters.

Yet another purpose of this article is to present data on Mössbauer spectra and magnetic susceptibility on the mononuclear iron(III) complexes $[FeL_2(NCS)_2]NCS$. The preparations of these compounds were reported recently by David and were characterized to be iron(III) compounds based on electronic and infrared spectral data and conductivity studies. Our Mössbauer and magnetic susceptibility data confirmed the conclusions of David while proving to be incorrect the earlier report of Driver and Walker that reduction of iron(III) to iron(II) occured during the attempted preparation of $[FeL_2(NCS)_2]^+$.

Experimental

Preparations. The following binuclear and mononuclear complexes were prepared by literature procedures: $Fe_2(phen)_4OCl_4$,[8] $Fe_2(phen)_4OBr_4$,[14] $Fe_2(phen)_4O(SO_4)_2$,[14] $Fe_2(phen)_4O(NO_3)_4$,[9] $Fe_2(phen)_4O(NCS)_4$,[13] $Fe_2(bipy)_4OCl_4$,[13] $Fe_2(bipy)_4OBr_4$,[13] $Fe_2(bipy)_4O(SO_4)_2$,[14] $Fe_2(bipy)_4O(NCS)_4$,[13] $Fe(phen)_2(NCS)_3$,[13] and $Fe(bipy)_2(NCS)_3$.[13] All these complexes were dried at room temperature in a vacuum desiccator for 3—5 days to effect complete removal of water of hydration.

The compound $Fe_2(bipy)_4O(NO_3)_4$ was prepared by a modification of the method used for the corresponding phen complex. In this procedure 2.34 g (0.015 mol) of 2,2′-bipyridine was added to a solution containing 3.03 g of $Fe(NO_3)_3 \cdot 9H_2O$ (0.0075 mol) in 20 ml of water. The resulting dark brown solution was nearly saturated with sodium nitrate. The solution was filtered and the filtrate cooled in a refrigerator for 2—3 days, during which time dark brown crystals of $Fe_2(bipy)_4O(NO_3)_4$ separated out. The crystals were collected by filtration, washed with small quantities of ice-cold water followed by *n*-hexane, and dried at room temperature in a vacuum desiccator.

Found: C, 47.40; H, 3.22; N, 16.60; Fe, 10.88%. Calcd for $Fe_2O(C_{40}N_8H_{32})(NO_3)_4$: C, 47.27; H, 3.17; N, 16.53; Fe, 10.98%.

Methods. The Mössbauer spectra were recorded in the standard transmission geometry with a constant acceleration Doppler velocity transducer, ^{57}Co in copper, and Ar–CH_4 filled proportional counter, and a 400 channel analyser. The data were least square fitted. To avoid possible corrections of solid angle, fairly small distance of detector-to-absorber, and large distance of source-to-absorber of the order of four times the window for detection were used. The velocity scale of the spectrometer was calibrated using an enriched iron foil. For calibration of temperature a copper-constantan thermocouple was used. For low temperature spectra in external magnetic field a Westinghouse superconducting solenoid with a stainless steel cryostat was used.

Magnetic susceptibility measurements were made with a torsion balance type magnetometer, Shimadzu MB-2, equipped with cryostatic arrangements for low temperature measurements.

Infrared spectra were recorded using a Perkin-Elmer 237 grating spectrophotometer. The samples were in the form of Nujol mulls. The potassium bromide disk method was considered but rejected owing to the possibility of exchange of the anionic ligands with Br^- which may lead to ambiguous results.

Results and Discussion

Binuclear Complexes. The binuclear oxygen-bridged complexes I—X (Table 1) are octahedral, the oxygen sharing the two octahedra. The presence of an oxygen bridge has been supported by infrared spectra.[10,15] It is known that in the solid phase $Fe_2L_4OX_4$ ($X=Cl^-$, NO_3^-, or $SO_4^{2-}/2$) exhibits an effective paramagnetic moment of the order of 1.5 B.M. per iron indicating the ground state multiplicities of iron(III) ions to be either $S=5/2$ corresponding to the d^5 high-spin configuration in the octahedral symmetry or $S=3/2$ corresponding to an electronic configuration $t_{2g}^4\,e_g^1$ in octahedral symmetry.[9,10] Simple magnetic data do not clearly indicate the spin state $S=3/2$ or

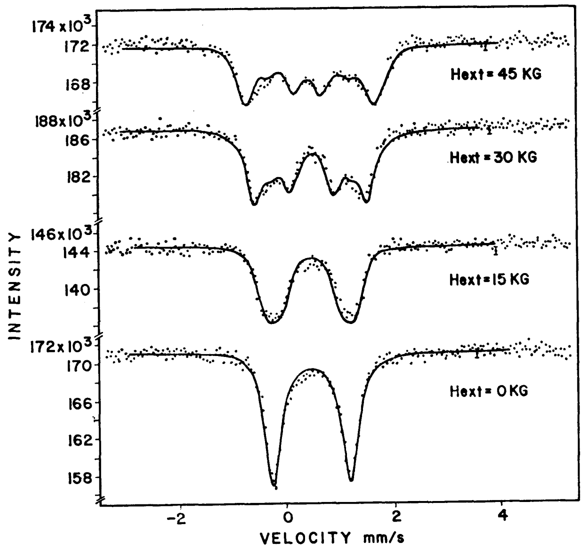

Fig. 1. Mössbauer spectra of $Fe_2(bipy)_4O(NCS)_4$ in externally applied magnetic fields at 4.2 K. The solid lines are the theoretical best fit curve for $\eta=1.0$ and $H_{ext}=H_{int}$.

TABLE 1. MÖSSBAUER PARAMETERS

	Compound	Temperature (K)	*I.S.*/Fe (mm/s)	*Q.S.* (mm/s)	Γ (mm/s)
I	$Fe_2(phen)_4O(NCS)_4$	77	0.50±0.03	1.43±0.04	0.65
		4.2	0.81±0.14	1.52±0.14	
II	$Fe_2(phen)_4OCl_4$	300	0.36±0.02	1.65±0.02	0.24
		77	0.46±0.02	1.70±0.02	0.27
III	$Fe_2(phen)_4OBr_4$	300	0.43±0.02	1.62±0.02	
		77	0.50±0.02	1.62±0.02	
IV	$Fe_2(phen)_4O(SO_4)_2$	300	0.40±0.02	1.52±0.02	
		77	0.52±0.02	1.60±0.02	
V	$Fe_2(phen)_4O(NO_3)_4$	300	0.36±0.02	1.45±0.24	
		77	0.47±0.02	1.48±0.24	
VI	$Fe_2(bipy)_4O(NCS)_4$	77	0.50±0.02	1.23±0.02	0.36
		4.2	0.60±0.02	1.67±0.02	0.44
VII	$Fe_2(bipy)_4OCl_4$	300	0.37±0.02	1.48±0.02	
		77	0.47±0.02	1.52±0.02	
VIII	$Fe_2(bipy)_4OBr_4$	300	0.36±0.02	1.60±0.02	
		77	0.51±0.02	1.60±0.02	
IX	$Fe_2(bipy)_4O(SO_4)_2$	300	0.41±0.02	1.31±0.02	
		77	0.49±0.02	1.45±0.02	
X	$Fe_2(bipy)_4O(NO_3)_4$	300	0.37±0.02	1.48±0.02	
		77	0.48±0.02	1.50±0.02	
XI	$Fe(phen)_2(NCS)_3$	77	0.55±0.03		0.62
		4.2	0.55±0.02		0.80
		1.3	0.52±0.20		0.60
XII	$Fe(bipy)_2(NCS)_3$	77	0.34±0.02		0.72
		4.2	0.55±0.01		0.80
		1.3	0.46±0.01		0.60

$S=5/2$. But recent NMR contact shift,[13] Mössbauer,[10,16,17] and ESR[18] data have been interpreted to support that both iron(III) ions in the binuclear complexes are high-spin ($S=5/2$). The two $S=5/2$ ground state ions couple, through the intramolecular π-bonding interaction of the two oxygen p-orbitals and the metal d_{xz} and d_{yz} orbitals, to form a singlet ground state ($S=0$) for the complex as a whole. Our Mössbauer results in external magnetic field give further support to this singlet ground state (see below).

The effect of an external magnetic field on the Mössbauer spectra of the binuclear complex VI is shown in Fig. 1. All other binuclear complexes investigated in the present study shows similar effects in an external magnetic field. Similar study on [$Fe_2(salen)_2O$], a compound similar to those investigated in our work, was carried out by Okamura *et al.*[19] They assigned a positive electric field gradient to their compound conforming to the observation that the quadrupole split lines underwent further splitting in the external field, one at the low velocity into a triplet and the other at the higher velocity into a doublet. In our oxo-bridged compounds the low velocity and the high velocity peaks split further into doublets in the external magnetic fields (Fig. 1) giving rise to a nearly symmetrical spectrum. Hence, the assignment of the sign to the electric field is not feasible. The nearly symmetrical spectrum may arise from the large asymmetry parameter.[20] The least square fit curves assuming $\eta=1.0$ and $H_{\text{ext}}=H_{\text{int}}$ closely approximate the experimental points, thus conforming to the asymmetry parameter close to 1.0.

The observed field in all our binuclear complexes is equal to the externally applied one within the experimental error of ± 5.0 KG. Even if the moment for each iron(III) ion is 1 B.M., the internal field would be observable when the external field is close to 45 KG at 4.2 K. Hence, this is a clear evidence for the singlet ground state in these binuclear complexes, in agreement with the previous studies.[9,10,12]

In the solid phase the binuclear complexes have the structure $[L_2XFe\text{-}O\text{-}FeXL_2]^{2+}$ ($X=Cl^-$, NO_3^-, $SO_4^{2-}/2$, or NCS^-). The evidence for the coordination of these X ligands to iron(III) is obtained from the infrared spectral data. Khedekar *et al.*[9] observed the Fe–Cl stretching vibrations at 253 cm^{-1} in the infrared spectrum of $Fe_2(phen)_4OCl_4$, while our results in Table 2 prove the existence of coordination between iron(III) and the anionic ligands NO_3^-, SO_4^{2-}, and NCS^-. Our results are in fair agreement with the literature results for compounds containing coordinated NO_3^-, SO_4^{2-}, or NCS^- to metal.[21–24] There is no experimental evidence for the coordination of Br^- to iron(III) in the binuclear compound $Fe_2L_4OBr_4$. But considering the coordination of weak ligands like NO_3^- to iron(III) we tend to believe that Br^- is also coordinated.

Table 2. Infrared vibrartional frequencies of the anionic ligands

Compound	Anionic Ligand	$\bar{\nu}$, cm^{-1}
$Fe_2(phen)_4O(SO_4)_2$	SO_4^{2-}	1173(s), 1035(s), 975(s)[a]
$Fe_2(bipy)_4O(SO_4)_2$	SO_4^{2-}	1160(s), 1039(s), 930(s)[a]
$Fe_2(phen)_4O(NO_3)_4$	NO_3^-	1280(s, b), 1030(v, s)[a]
$Fe_2(bipy)_4O(NO_3)_4$	NO_3^-	1500(s),[a],[b] 1282(s, b), 1010(v, s)[a]
$Fe_2(phen)_4O(NCS)_4$	NCS^-	2080(s, sh),[a] 2040(s)
$Fe_2(bipy)_4O(NCS)_4$	NCS^-	2080(s, sh),[a] 2040(s)

s=strong, v=very, b=broad, sh=shoulder

a) These peaks clearly indicate the presence of coordination of these anionic ligands to iron(III). b) This peak was partially obscured by the Nujol peaks.

The Mössbauer parameters for the binuclear complexes in which the anionic ligands are Cl^-, Br^-, NO_3^-, SO_4^{2-}, or NCS^- are depicted in Table 1. Within the experimental uncertainty the *I.S.* values do not show any appreciable change with the variation of the anionic ligands. By virtue of the strong antiferromagnetic coupling through the π-bonding interaction of the metal d-orbitals and the p-orbitals of O^{2-} the change in bonding properties, if any, of the X ligands may not have any significant effect on the Mössbauer parameters. The bonding is influenced by the combined effects of the electronegativity and the resonance of the X ligands concerned. While the electronegativity may fall in the order $Cl^- > Br^- > SO_4^{2-} > NO_3^- > NCS^-$, the last named three ligands can withdraw electrons away from the coordination site by virtue of the resonance effects. The failure of these ligands to influence the *I.S.* values to any appreciable extent suggests that the electron density at the metal due to the ($L \rightarrow M$) σ-donation is essentially identical.

The replacement of phen by bipy does not change the *I.S.* values and the π-back bonding of iron to both O^{2-} and bipy ligands (Table 1). Comparing the phen complex to the corresponding bipy complex, the *Q.S.* value is always greater for the phen complex although the same value of *I.S.* is obtained. This points out that the phen ligand is a better π-acceptor and/or a poorer σ-donor while the total σ-donor+π-acceptor ability is similar for both. In view of the lack of detailed information of the sign of *Q.S.* and the contribution from the lattice charge one cannot specifically refer to the d-orbitals which participate in the π-back

Table 3. Magnetic susceptibilities and magnetic moments

	Compound	Temperature (K)	$\chi\cdot 10^6$/Fe (cgs)[a]	μ_{eff}/Fe (B.M.)[b]
I	$Fe_2(phen)_4O(NCS)_4$	294	5413	1.79[c]
VI	$Fe_2(bipy)_4O(NCS)_4$	299	3583	1.49[c]
VII	$Fe_2(bipy)_4OCl_4$	295	4123	1.57
XI	$Fe(III)(phen)_2(NCS)_3$	9	432198	5.50
		80	48886	5.62
		293	13163	5.65
XII	$Fe(III)(bipy)_2(NCS)_3$	8	611870	6.28
		80	60817	6.23
		300	16266	6.28

a) The molar susceptibility after correction for diamagnetism. The diamagnetic corrections ($\times 10^6$ cgs/mol): Fe^{3+}, 13; bipy, 105; phen, 128; Cl^-, 23; NCS^-, 35; O^{2-}, 6 (Ref. 10). b) all ± 0.05 B.M. c) These are in fair agreement with the literature results for similar binuclear compounds (Refs. 8—10).

bonding.

The effect of temperature on the Mössbauer parameters (Table 1) is insignificant. The compounds $Fe_2L_4O(NCS)_4$ are remarkable for the absence of any detectable Mössbauer resonance at room temperature and slight absorption around 223 K, the absorption increasing as the temperature is decreased. It is considered that the absence of any resonance at temperatures above 223 K is a consequence of low Debye temperature for iron in these compounds.

Mononuclear Iron(III) Complexes. The magnetic susceptibility data indicate that iron(III) ion in $[FeL_2(NCS)_2]NCS$ is in the high-spin state with $S=5/2$ at room temperature and temperatures to about 8 K (Table 3). The Mössbauer parameters for these complexes are given in Table 1. Without any external magnetic field at temperatures below 223 K the spectrum has a broad asymmetric line, and no resonance at room temperature or down to around 223 K. This lack of absorption at temperatures above 223 K may be the result of low Debye temperature. The comparable results for the corresponding binuclear complexes $Fe_2L_4O(NCS)_4$ show the significant influence of NCS^- ligands on the Mössbauer spectra of these complexes. Very broad peaks for the compounds $[FeL_2(NCS)_2]NCS$ (compounds XI and XII) could possibly be due to spin-spin relaxation.

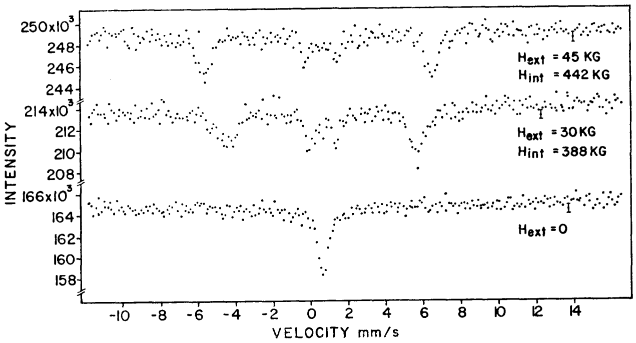

Fig. 2. Mössbauer spectra of $Fe(III)(bipy)_2(NCS)_3$ in externally applied magnetic fields at 4.2 K.

The Mössbauer spectra of $[Fe(bipy)_2(NCS)_2]NCS$ with the external magnetic fields are shown in Fig. 2. The compound $[Fe(phen)_2(NCS)_2]NCS$ shows identical effects. The results indicate that iron(III) ions in these complexes are in the high-spin state ($S=5/2$), in agreement with the magnetic susceptibility results. When the external field of 45 kG is applied the observed effective field is of the order of 442 kG. Because the sign of the internal field is negative, the induced field should be $442+45=487$ kG. Assuming purely paramagnetic case, the hyperfine field for $T \rightarrow 0$ and $H_{\mathrm{ext}} \rightarrow \infty$ can be calculated for a d^5 system using a Brillouin function, the calculated value being -550 kG.[25] This is the limiting value arising from the exchange polarization of 1s and 2s electron cores with the d-shell electrons. Since the iron(III) complexes have 3s as well as 4s electrons which are expected to produce a positive electric field, the actual internal field will be the difference between these negative and positive contributions. This may at least partially account for the low experimental value. Saturation core polarization fields of the order of 500 kG are common in iron(III) compounds.[26,27] Hence, this further supports the $S=5/2$ spin state for iron(III) in our mononuclear complexes.

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