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Transition Metal Chemistry of Oxime-Containing Ligands, VI:

Magnetic and Structural Properties of Mono (pyridine-2-aldoxime) dithiocyanato iron(II) and Mono (6-methylpyridine-2-aldoxime) dithiocyanato iron(II) Complexes

By

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With 2 Figures

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The complexes of pyridine-2-aldoxime (H*POX*) and 6-methylpyridine-2-aldoxime (H*MPX*) with iron(II) thiocyanate of the type $[Fe(L)(NCS)_2]$ (L = H*POX* and H*MPX*) have been prepared and characterized. A study of X-ray, magnetic, vibrational spectra (conventional and far-infrared), electronic spectra and *Mössbauer* spectra has indicated that these complexes have polymeric, pseudo octahedral, coordination geometry with linear bridging thiocyanate ligands. The electronic spectra of mono complexes show a larger, low symmetry, ligand field than that present in $[Fe(L)_2(NCS)_2]$ complexes. Unperturbed *Mössbauer* spectra show a large quadrupole splitting, ΔE_Q, and smaller isomer shift values in these iron(II) thiocyanate complexes. The magnetically perturbed *Mössbauer* spectra of these iron(II) thiocyanate complexes at room temperature show that the principal component of the electric field gradient tensor is positive and corresponds to a d_{xy} ($^5B_2$) ground state.

Introduction

The metal complexes of aromatic aldehyde oximes, particularly, those of H*POX* and H*MPX* have not been studied extensively so far, although they present many structural features worth investigating.

Krause et al.[1–4] have reported on the preparation and some of the properties of nickel(II), platinum(II), and palladium(II) complexes of H*POX*, H*MPX*, and 4,6-dimethyl-s-triazine-2-aldoxime. *Hanania* and *Irving*[5] reported the stabilities of some iron(II), cobalt(II) and nickel(II) complexes of H*POX*, *Liu*, and *Liu*[6] have isolated $[Cu(HPOX)_2SO_4] \cdot 3\,H_2O$ and a number of copper(II) complexes containing two molecules of H*POX*

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in which one oxime hydrogen is lost to give compounds of the type [Cu(H*POX*)(*POX*)*X*] (X = Cl, Br, I, or NO_3). *Green* and *Svasti*[7] studied a few complexes of this type and also prepared [Cu(H*POX*)Cl_2] and a number of salts of the polynuclear cation [Cu_3(*POX*)$_3OH^{2+}$. *Underhill* et al.[8, 9] have studied the spectral properties of several copper(II) complexes with H*POX* of the above type and nickel(II) complexes with several oxime-containing ligands. *Mohan* et al.[10–14] have described the structural and magnetic properties of several iron(II), cobalt(II), nickel(II), and copper(II) complexes formed by H*POX* and H*MPX*.

In the present paper, we report the results of our investigation on the isolation and characterization of mono-(pyridine-2-aldoxime)-dithiocyanato-iron(II) and mono-(6-methylpyridine-2-aldoxime)-dithiocyanato-iron(II) complexes.

Experimental Section

Materials

Iron(II) thiocyanate, pyridine-2-aldoxime and 6-methylpyridine-2-aldoxime were obtained from K & K Laboriatores; Inc., New York, and used as received.

Syntheses of Complexes

The complexes [Fe(H*POX*)$_2$(NCS)$_2$] and [Fe(H*MPX*)$_2$(NCS)$_2$] were prepared by the same general procedure under inert atmosphere as previously reported[12].

The mono complexes of iron(II) thiocyanate with H*POX* and H*MPX* were prepared by the following general procedure:

All reactions were performed under strictly anhydrous conditions. All transfers and measurements were carried in a dry box which was constantly flushed with dry N_2 gas. Equimolar solutions of iron(II) thiocyanate and ligand in deoxygenated absolute ethanol were mixed while hot and stirred while being allowed to cool: pale brown crystals, recrystallized by deoxygenated absolute ethanol.

$FeC_8H_6N_4OS_2$:	C 32.64,	H 2.04,	N 19.04,	S 21.76,	Fe 19.04.
Found:	C 32.65,	H 2.04,	N 19.07,	S 21.78,	Fe 19.09.
$FeC_9H_8N_4OS_2$:	C 35.06,	H 2.59,	N 18.18,	S 20.77,	Fe 18.18.
Found:	C 35.06,	H 2.60,	N 18.20,	S 20.78,	Fe 18.21.

Physical Measurements

All magnetic measurements at various temperatures were made on a standard Gouy balance. The tube was calibrated using Hg[CO(NCS)$_4$] and the sample temperature was measured with a copper—constantan thermocouple. The error limits for the reported magnetic moments are ± 0.05 μ_B.

Diffuse reflectance spectra, at room temperature and at liquid nitrogen 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 4000–400 cm^{-1} were recorded in KBr pellets by using Perkin-Elmer infracord spectrophotometer, Model 180. The far infrared spectrophotometer both as Nujol mulls and as solids in a diamond cell.

X-ray powder photographs were obtained on Philips "Hungary" X-ray generator using nickel filtered copper radiation and a Debye Scherrer type powder camera.

A conventional constant-acceleration *Mössbauer* spectrometer was used to obtain the magnetically unperturbed spectral results. The spectrometer was equipped with a copper matrix source which was maintained at room temperature and was calibrated with natural iron foil. All the samples were measured in a vacuum cryostat with a sample holder which protected the sample from the cryostat vacuum. The unperturbed *Mössbauer* spectral results were determined by inspection with an accuracy of ± 0.01 mm/sec. The longitudinal magnetically perturbed *Mössbauer* spectra at ambient temperature were recorded with a conventional constant-acceleration spectrometer. The magnetic field was generated by using a Westinghouse Nb—Ti super conducting magnet. The source consisted of 100 mCi of ^{57}Co in a rhodium matrix.

All elemental analysis were performed by Microanalytical laboratories of I.I.T., Kanpur-16. Iron metal was analysed by standard technique[15] after decomposition of the complexes.

Results and Discussion

The X-ray powder diffraction pattern for each of the new complexes, $[Fe(L)(NCS)_2]$ and $[Fe(L)_2(NCS)_2]$ (L = H*POX* and H*MPX*) and $[Co(py)_2(NCS)_2]$ (*py* = pyridine) have been measured and crystal *d* spacings are presented in Table 1. The comparison of the results for these complexes suggests that mono- and bis-complexes of H*POX* and H*MPX* with iron(II) thiocyanate are not isomorphous and the mono-complexes, within the limits of X-ray analysis, are not contaminated with any residual bis-complexes, $[Fe(L)_2(NCS)_2]$. The mono-complexes of H*POX* and H*MPX* and bis-complexes of pyridine, $[Co(py)_2(NCS)_2]$ are isomorphous, hence, the mono-complexes are assigned the polymeric, pseudo octahedral, coordination geometry, having linear-bridged thiocyanate groups[16].

The magnetic susceptibilities of $[Fe(L)(NCS)_2]$ and $[Fe(L)_2(NCS)_2]$ complexes have been measured as a function of temperature. The magnetic moment values are essentially independent of temperature between 102 and 298 K. The magnitude (5.4 μ_{eff} B.M.) and temperature independence of the magnetic moments are reasonable for tetragonally distorted, octahedral, high-spin iron(II) complexes[17].

The infrared spectra of H*POX* and H*MPX* ligands differ from the conventional oximes, which show a band at ca. 3250 cm^{-1}. This band is replaced by multipole bands between 3194 and 2791 cm^{-1} in H*POX* and H*MPX* ligands, the strongest of which lies at ca. 2791 cm^{-1}. This implies much stronger hydrogen bonding than in other oximes. The ν C=N (acyclic) stretching mode in H*POX* and H*MPX* occurs at ca. 1520 cm^{-1} and is in the range observed by *Krause* et al.[3] in their study of oxime compounds. The ring stretching frequencies, ring breathing mode, N—O stretching frequency, out-of-plane CH deformation, a skeletal mode, and an out-of-plane deformation bands appear at 1620–1425; ca. 1000; ca. 950; ca. 800; ca. 740 and ca. 400 cm^{-1}, resp., in H*POX* and H*MPX* ligands.

Table 1. *X-Ray Powder Data*, d Spacings (Å)*

$Fe(L)(NCS)_2$	$Co(py)_2(NCS)_2$	$Fe(L)_2(NCS)_2$
		8.14 vs
7.33 vs	7.33 vs	7.03 w
		6.73 w
5.24 m	5.24 m	
5.11 m	5.11 m	
		4.41 m
4.25 m	4.25 m	4.30 w
		4.05 w
		4.00 w
3.90 m	3.92 m	3.90 m
		3.81 s
3.65 s	3.65 s	3.56 m
		2.95 s
		2.88 m
2.84 m	2.84 s	
2.76 m	2.76 m	2.68 w
2.64 m	2.64 m	
2.43 w	2.43 w	2.48 w
2.38 w	2.38 w	2.39 w
2.36 w	2.36 w	
2.25 w	2.25 w	
2.24 w	2.24 w	
		2.21 w
		2.16 w
		2.08 w
1.85 w	1.85 w	
	1.84 w	
1.80 w	1.80 w	

* L = H*POX*, H*MPX*, *py* = pyridine.

Krause et al.[3] have extensively investigated transition metal complexes of H*POX* in ν C=N (acyclic) and ν N—O stretching vibration regions and postulated that compounds containing C=N—OH groupings have ν C=N and ν N—O stretching vibrations in the range 1654 to 1614 and 1069–1036 cm^{-1}, respectively. However, the mono-complexes, [Fe(L)(NCS)$_2$], show bands in the regions 3260–3015 cm^{-1}, 1640 to 1630 cm^{-1}, and 1074–1050 cm^{-1}, which can be assigned to OH, C=N, and N—O stretching frequencies, resp. From these data one can suppose that the oxime proton is not removed and there is a contribution from the C=N—OH groupings in these mono-complexes.

The mono-complexes, [Fe(*L*)(NCS)$_2$], exhibit the four ring stretching vibrations in the following ranges; band I, 1620–1612 cm^{-1}; Band II, 1580–1574 cm^{-1}; Band III, 1490–1477 cm^{-1} and Band IV, 1440 to 1425 cm^{-1}. Band I is increased significantly in frequency from the free ligand value of ca. 1570 cm^{-1}; an indication of pyridine coordination to the iron(II) atom[18]. The ring breathing mode observed at ca. 1000 cm^{-1} in free H*POX* and H*MPX* ligands disappears in their iron(II) mono-complexes and is replaced by a band at 1005–1020 cm^{-1}. This shift[19] is also indicative of pyridine coordination to iron(II) atom.

Two strong bands are observed in the spectrum of free ligands, H*POX* and H*MPX*, at ca. 798 and ca. 740 cm^{-1}. These bands are assigned[20] to ν (C—H) and ϕ (C—C), resp. The ca. 740 cm^{-1} band splits into two components lying between 718 and 752 cm^{-1}. This splitting is also believed to be an indication of *py* to iron(II) coordination[20, 21]. The band observed at ca. 798 cm^{-1} in the free ligands is observed as a single band lying between 780 and 824 cm^{-1}.

The uncoordinated ligands, H*POX* and H*MPX*, exhibit a band at ca. 400 cm^{-1} assigned to the C—C out-of-plane deformation[20, 22] while mono-complexes exhibit a single band between 405 and 412 cm^{-1}. An increase in frequency upon coordination is to be expected[23].

The infrared spectrum of thiocyanate group has been studied by many workers and reviewed by *Burmeister*[24]. Thiocyanate can coordinate through the nitrogen or sulfur or act as a bridge. Infrared data may be used to distinguish the modes of bonding of the thiocyanate group according to the assignments (cm^{-1}) given below which should however be used with some caution. The position of ν_1 frequency is the least reliable guide to the nature of the bonding. The wide separation in the ν_3 stretching frequencies for N-bonded, S-bonded and bridged thiocyanate makes ν_3 a much more reliable guide when the band can be unequivocally assigned. Table 2 lists bands observed in mono- and bis-complexes of iron(II) thiocyanate with H*POX* and H*MPX*. It should be noted that both ν_2 and ν_3 are found at higher energies in the bis-complexes than in the mono-complexes; however, the energy dif-

	ν_1 (C—N str.)	ν_2 (N—C—S bending)	ν_3 (C—S str.)
N-bonded thiocyanate	2040–2100	450–490	780–860
S-bonded thiocyanate	2080–2120	410–470	690–720
Bridged thiocyanate	2075–2150	–	775–790

ference is much smaller than that found for terminal nitrogen and terminal sulfur bonded thiocyanate ligands[25]. This smaller difference can be understood on the basis of the slightly smaller carbon—sulfur bond order in the bridging thiocyanate ligand as compared with the terminal nitrogen bonded thiocyanate. The difference in the carbon—sulfur bond order is, of course, larger for the two possible terminal bonded ligands[27]. The assignments of ν_1 and ν_3 bands are in excellent agreement with the previous work of *Clark* and *Williams*[27] and will related work by *Konig* et al.[28] and *Nelson* and *Rodgers*[29].

Table 2. *Thiocyanate Group Infrared Frequencies* (cm^{-1})

Complex	ν_1	ν_2	ν_3
$Fe(L)(NCS)_2$	2145 sh 2088 vs 2050 w	474 m	780 m
$Fe(L)_2(NCS)_2$	2095 sh 2045 vs 2016 vw	480 m	805 m

In the region 400–300 cm^{-1} H*POX* and H*MPX* exhibit the absorption bands at ca. 375 (m), ca. 370 (s), ca. 355 (m), ca. 335 (s), ca. 322 (s) and ca. 310 (s) cm^{-1}. Whereas mono-complexes, $[Fe(L)(NCS)_2]$ have bands of varying intensity between 390–320 cm^{-1} which correspond to the sharp and medium bands in this region in the spectrum of free ligands. The relatively high energy of these bands would seem to preclude their assignments as metal — ligand vibrations.

The infrared spectra of $[Fe(L)(NCS)_2]$ complexes in the region 300–160 cm^{-1} exhibit the bands at ca. 261 (2), ca. 208 (m), ca. 186 (m) and ca. 165 (m) cm^{-1}. *Forster* and *Goodgame*[30] studied the infrared spectra of bridging thiocyanate ligands in the 400–200 cm^{-1} region and concluded that metal—sulfur stretching vibration must occur below 200 cm^{-1}. Therefore, the band observed at ca. 186 cm^{-1} has been assigned to the iron—sulfur stretching vibration: no similar band is observed in bis-complexes, $[Fe(L)_2(NCS)_2]$, of H*POX* and H*MPX*. It is tempting to assign the band at ca. 165 cm^{-1} in $[Fe(L)(NCS)_2]$ to a bending vibration associated with the Fe—NCS—Fe group[31], however, this assignment would be unlikely in view of the similar band at ca. 167 cm^{-1} in the $[Fe(L)_2(NCS)_2]$ complexes. The bands at ca. 261 and ca. 208 cm^{-1} are in the same general region expected for metal—nitrogen (ligand) vibrations[32]. *Clark* and *Williams*[33] have suggested that bands observed in bipyridyl—metal(II) complexes between 300 and 260 cm^{-1} and assigned as metal—nitrogen (bipyridin) vibrations[34] are ligand vibrations activated by coordination to the metal ion. Therefore, the bands at ca. 261 and ca. 208 cm^{-1} have been assigned as iron(II)—nitrogen (thiocyanate) and iron(II)—nitrogen (ligand) in $[Fe(L)(NCS)_2]$ complexes, resp.

The diffuse reflectance spectra of bis-complexes $[Fe(L)(_2NCS)_2]$ have been reported previously[12] and consists of a broad partially resolved band extending from ca. 9.0 to 12.0 kK at room temperature and ca. 9.2 to 12.2 kK at liquid nitrogen temperature. These two absorption bands are assigned to transitions from the ground state to the $^5A_{1g}$ state and to the $^5B_{1g}$ state derived from the splitting of the ^5E_g spectroscopic excited state in tetragonal ligand field. In contrast the diffuse reflectance spectra of mono-complexes exhibit two well resolved bands at ca. 7.2 and 13.2 kK at room temperature. On the basis of the *Mössbauer* spectral results (presented below) which show that d_{xy} ($^5B_{2g}$) orbital is the ground state orbital, we assign the ca. 7.2 kK band to the transition from the $^5B_{2g}$ ground state (component of the $^5T_{2g}$ state in O_h symmetry) to the $^5B_{1g}$ state and the band ca. 13.2 kK to $^5A_{1g}$ state (components of ^5E_g excited state in O_h symmetry). It is apparent that in these mono-complexes the low-symmetry splitting of ^5E_g excited is of the order of ca. 6 kK, while the separation of $^5B_{1g}$ and $^5A_{1g}$ stated in bis-complexes is of the order of ca. 3.0 kK. This result indicates a much more highly distorted ligand field in the mono-complexes than the bis-complexes. This situation is clearly consistent with the structures of these mono- and bis-complexes. The bonded sulfur atoms in the mono-complexes are believed to provide a substantially smaller crystal field than the four coordinated nitrogen atoms about the iron(II) atom. The distortion is, as a result, greater than in the bis-complexes where six nitrogen atoms make up the coordination sphere. This greater distortion is also clearly observed in the *Mössbauer* spectra of the two type complexes. The small increase in the energy of the electronic transitions in mono- and bis-complexes at liquid nitrogen temperature is most likely a result of an increase in ligand field strength which arises from the contraction of unit cell volume at low temperature.

The reflectance spectra of mono-complexes show a very intense band at ca. 21.5 kK. The absorption spectrum of $[Fe(NCS)_6]^{3-}$ exhibits a strong band at ca. 20.0 kK[35]. Therefore, the band observed in mono-complexes is most likely due to the presence of some iron(III) impurity which in the presence of thiocyanate ligand shows a strong high intensity charge transfer band at ca. 21.5 kK. The amount of iron(III) impurity must be quite small, because it is not observed in any of the other physical properties of these mono-complexes.

Since, the unperturbed *Mössbauer* spectrum of $[Fe(HPOX)(NCS)_2]$ and $[Fe(HMPX)(NCS)_2]$ are similar at room temperature, the spectrum of $[Fe(HPOX)(NCS)_2]$ is shown in Fig. 1. The *Mössbauer* spectral parameters for mono- and bis-complexes are presented in Table 3. The chemical isomer shift, δ, relative to natural iron foil, which is sensitive to both the oxidation state and the spin-state of the iron, is found to lie in the range 0.96–1.06 mm/sec for several octahedral, high-spin iron(II) complexes containing nitrogen donor atoms[36, 37].

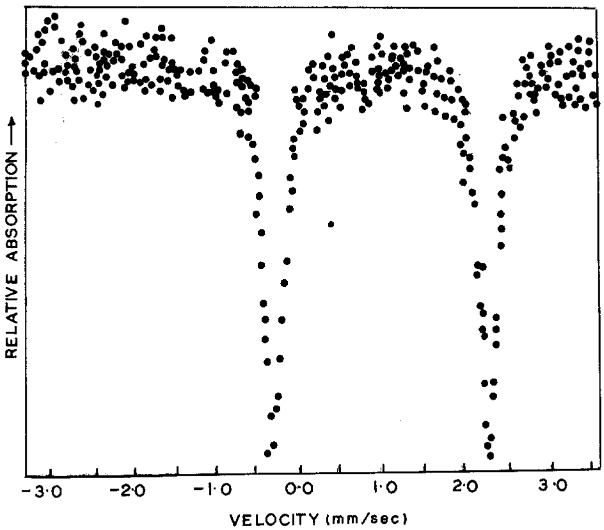

Fig. 1. *Mössbauer* spectrum of $Fe(HPOX)(NCS)_2$ at room temperature

The observed values for tetrahedral complexes of the same type lie in the range of 0.80–0.91 mm/sec[36]. The chemical isomer shift values, observed for both mono- and bis-complexes, were found to be in agreement with the structural assignments made on the basis of the X-ray, magnetic, electronic and infrared results. The small reduction in the chemical isomer shift in the mono-complexes as compared with the bis-complexes are believed to be due to the lower total electronegativity of the coordinated atoms in the mono-complexes. The lower sulfur electronegativity results in a higher S electron density in the vincinity of the iron nucleus in the mono-complexes and, consequently, in smaller chemical isomer shift in $[Fe(L)(NCS)_2]$ complexes.

The second parameter listed is the quadrupole splitting, ΔE_Q. For transition metal complexes there are two factors which contribute to ΔE_Q, (a) the dissymmetry of the ligand field and the dissymmetry of the electron density around the nucleus. Hence, the more nonspherical the electron density and/or the greater the ligand field dissymmetry, the larger the quadrupole splitting, provided the two contributions have like sign[38]. For the mono- and bis-complexes characterization as six-coordinate high-spin iron(II) derivatives is confirmed by the ΔE_Q values. These are in the range 1.6–3.0 mm/sec which is characteristic of six-coordinate high-spin iron(II), as demonstrated for broad series of related complexes[39]. The large ΔE_Q values for the mono-complexes are assumed to be caused by the larger distortion of the crystal field in mono-complexes relative to bis-complexes which result in a larger electric field gradient. This difference as previously mentioned may be a direct result of the different atoms which comprise the coordination sphere of the two type of complexes. It is interesting to note, however, that the temperature dependence of the quadrupole splitting is large and of the same order of magnitude (ca. 0.4 mm/sec) in both the mono- and bis-complexes. This temperature dependence[40] is an indication of an electric field gradient which is the thermal average of the gradients resulting from the occupation of two or more orbital states. Then, as a consequence the similar temperature dependence of ΔE_Q may indicate a comparable splitting of the ground state t_{2g} orbital in mono- and bis-complexes. If this is the case, the difference in magnitude of the ΔE_Q could be explained on the basis of differing signs for the valence and ligand field contributions to the gradients experienced by the iron(II) nuclei in the mono- and bis-complexes.

Table 3. *Mössbauer Spectral Parameters*

Compound	*T*, K	δ* mm/sec	ΔE_Q mm/sec	Γ_1[a] mm/sec	Γ_2[a] mm/sec
$Fe(HPOX)(NCS)_2$	78	1.12	3.04	0.29	0.32
	RT	1.00	2.61	0.26	0.27
$Fe(HMPX)(NCS)_2$	78	1.13	3.03	0.28	0.32
	RT	1.00	2.61	0.26	0.26
$Fe(HPOX)_2(NCS)_2$	78	1.15	2.00	0.26	0.25
	RT	1.03	1.52	0.25	0.25
$Fe(HMPX)_2(NCS)_2$	78	1.14	1.98	0.26	0.24
	RT	1.03	1.52	0.24	0.25

* Relative to natural iron foil.

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

In order to correctly determine the ground state for mono-complexes, $[Fe(L)(NCS)_2]$, it is necessary to know the sign of the quadrupole splitting, ΔE_Q. This can be obtained for a polycrystalline sample by using magnetic perturbation technique[41]. Since, the magnetic perturbed *Mössbauer* spectra of mono-complexes with H*POX* and H*MPX* are similar at room temperature and $H_{\text{longitudinal}} = 40$ kK, the spectrum of [Fe(H*POX*)(NCS)$_2$] complex is shown in Fig. 2. It is clear from Fig. 2 that triplet occurs at negative velocity relative to doublet, which is at the more positive velocity. The triplet—doublet 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 ^{57}Fe excited nuclear state is positive, the latter result also indicates a positive quadrupole splitting. The latter is consistent with a $^5B_2$ ground state corresponding to an electron in the d_{xy} orbital. The spectrum presented in Fig. 2 can be fit reasonably with small values of the asymmetry parameter, η (up to values of ca. 0.4). This is consistent with the approximate D_{2h} symmetry of the complex and corresponds to the coordination geometry discussed above.

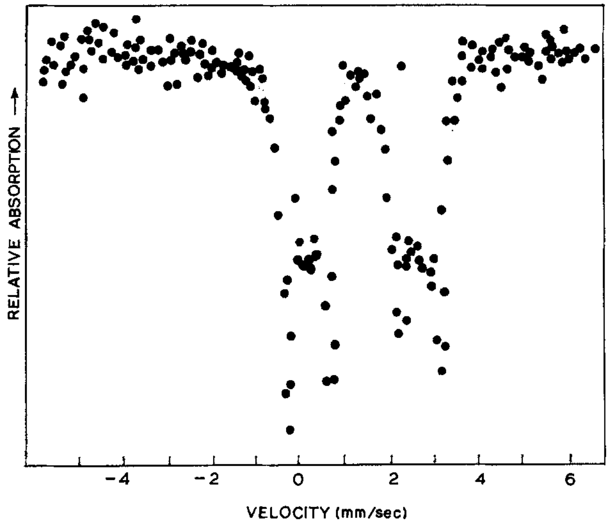

Fig. 2. *Mössbauer* spectrum of Fe(H*POX*)(NCS)$_2$ at room temperature with $H_{\text{longitudinal}} = 40$ kG

In conclusion, the magnetically perturbed *Mössbauer* spectra at room temperature and $H_l = 40$ kG indicate that mono-complexes [Fe(*L*)(NCS)$_2$] have $^5B_2$ ground state with D_{2h} coordination geometry around the iron(II) ion.

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