Inorganica Chimica Acta, *120* (1986) 61–76

On the Existence of Tris 2,2′-biquinoline Complexes of First Transition Series Metal Ions in the Solid State. Spectra and Magnetic Characterization of $[Fe(II)(2,2'\text{-biquinoline})_3](NCS)_2$ and some Related Pseudo-tetrahedral Ferrous Compounds

BRUCE W. DOCKUM and WILLIAM MICHAEL REIFF*

Department of Chemistry, Northeastern University, Boston, Mass. 02115, U.S.A.

(Received April 28, 1986)

Abstract

Double benzo substitution *cis* to the nitrogen atoms of 2,2′-bipyridine results in 2,2′-biquinoline, hereafter, biq. Numerous examples of tris 2,2′-bipyridine metal species are known, but to our knowledge, there have been no previous reports of tris biq metal species. Herein, we report the first isolation of what appears to be a tris biq species, $Fe(biq)_3(NCS)_2$, in the solid state obtained from a water–acetone solution as an analytically pure, pale blue–gray solid. Zero and high field Mössbauer, optical (near infrared-visible), and infrared spectra as well as cryomagnetic data clearly show that $Fe(biq)_3(NCS)_2$ contains a pseudo-octahedral high spin iron(II) chromophore. Several possibilities are proposed for the structure of $Fe(biq)_3(NCS)_2$ including some with unidentate biq. The weak field, highly hindered environment of the complex is such that it readily undergoes facile loss of two moles of ligand simply on mixing the solid complex with a variety of organic solvents. The resulting neutral buff-colored iron(II) complex, $Fe(biq)(NCS)_2$, is a pseudo-tetrahedral monomer which can also be prepared by the direct reaction of an ethanolic solution of $Fe(NCS)_2$ with a benzene solution of biq in a 1:1 stoichiometry. The spectral and cryomagnetic properties of $Fe(biq)(NCS)_2$ as well as those for the related pseudo-tetrahedral compounds $Fe(biq)Cl_2$, $Fe(2,9\text{-dimethyl-}1,10\text{-phenanthroline})X_2$ ($X = Cl^-$, Br^-, I^-, NCS^-) and $Fe(2,9\text{-dimethyl-}4,7\text{-di-phenyl-}1,10\text{-phenanthroline})Cl_2$, are reported as well. In particular, the latter pseudo-tetrahedral systems are found to exhibit a novel, complex range of slow paramagnetic behavior depending on T, H_0 and specific coordinated anion. This behavior correlates with low temperature susceptibility data.

Introduction

The diimine ligands, 2,2′-bipyridine and 1,10-phenanthroline (known hereafter as bipy and phen), readily form tris-complex cations having the formulae $M(bipy)_3^{2+}$ or $M(phen)_3^{2+}$ with first series transition metal divalent cations (M^{2+}), such as iron [1, 2]. In each of the complex cations, the diimine acts as an *endo*-bidentate ligand forming a pseudo-octahedral coordination environment, MN_6, of D_3 symmetry. The counter anions associated with the tris-cation are not directly coordinated to the metal center. In the case of divalent iron, the compounds are often low spin ($S = 0$), and diamagnetic. The intense optical spectra of these iron compounds are basically charge transfer in nature. However, if substituent groups are placed near the coordinating imine nitrogen atoms in each of the parent ligands, bipy or phen, steric crowding can cause significant changes in the metal-chelating properties of the substituted diimine ligands as compared with bipy and phen precursors and result in considerable differences in the chemistry, structural, electronic, and magnetic properties among the new diimine compounds. For example, there have been extensive studies of first series transition metal compounds formed by the phen derivative 2,9-dimethyl-1,10-phenanthroline (known hereafter as 2,9-dmp) (see Fig. 1). This diimine ligand generally forms mono-diimine compounds with first series metal divalent cations with the empirical formula $M(2,9\text{-dmp})X_2$ ($X = Cl^-$, Br^-, I^-, $\tfrac{1}{2}SO_4^{2-}$) [3–5]. With iron, the halo-anions generally form pseudo-tetrahedral, high spin ($S = 2$) compounds, e.g. $Fe(2,9\text{-dmp})Cl_2$ has high spin iron(II) in a pseudo-tetrahedral (C_{2v} symmetry) coordination environment with terminal chloro-groups [4, 6]. In contrast, the compounds formed by the sulfato-groups are polymers with bridging groups connecting the metal centers in a chain. This is best exemplified by $Fe(2,9\text{-dmp})SO_4$ [5] which contains high spin iron(II). The low temperature magnetic properties of Fe(2,9-dmp)-

---

*Author to whom correspondence should be addressed.

0020-1693/86/3.50

SO_4 are dominated by antiferromagnetic interactions within the polymer chains ordering 3-dimensionally at ~3.25 K [7]. The ligand 2,9-dmp may also form bis-complexes as well, but they are not as numerous. One example is $Fe(2,9\text{-dmp})_2(NCS)_2$, a six-coordinate monomer with terminal *N*-bonded thiocyanate groups. In an initial study [8] of this compound, it was believed that the iron underwent a spin state change from high spin ($S = 2$) to low spin ($S = 0$) with decreasing temperature. However, a later study [9] indicates that $Fe(2,9\text{-dmp})_2(NCS)_2$ remains high spin to as low as 4.2 K. To our knowledge no tris ligated complexes of 2,9-dmp have ever been reported.

Other sterically hindered diimine ligands may be constructed using 2,2′-bipyridine as the parent molecule. One such ligand is 2,2′-biquinoline (Fig. 1), which is formed by double benzo substitution *cis* to the imine nitrogen atoms of 2,2′-bipyridine. Harris *et al.* [10] studied the properties of biq and noted through the use of molecular models that it is unlikely (owing to steric hindrance) for biq to act as a planar bidentate ligand with more than one other ligand atom in the same plane as the biq molecule and the metal atom. During this study, they synthesized two mono-biquinoline complexes, $Fe(biq)Cl_2$ and $Fe(biq)Br_2$, and a bis-complex $Fe(biq)_2(ClO_4)_2 \cdot 2.5H_2O$. Using a series of spectral, magnetic and solution conductivity measurements, they concluded that each of the above compounds had a four-coordinate iron center with either a FeN_2X_2 chromophore (N = diimine nitrogen and X = halo-anion) for the mono-biq compounds or a FeN_4 chromophore for $Fe(biq)_2(ClO_4)_2 \cdot 2.5H_2O$. Each compound was reported to have high spin ($S = 2$) iron(II). They did not report the existence of a $Fe(biq)_3X_2$ species though they did try to synthesize them.

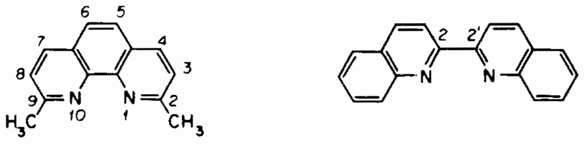

Fig. 1. Schematic diagrams of the ligands 2,9-di-methyl-phenanthroline and 2,2′-biquinoline.

Our initial interest in mono-diimine complexes containing biq and 2,9-dmp was stimulated by the need to characterize the structures of mono-bipyridyl compounds, e.g. $Fe(bipy)(NCS)_2$ [11]. Since stable iron compounds containing the foregoing ligands are generally four-coordinate, we were able to perform a series of comparative spectral and magnetic measurements with compounds for which the iron coordination number was known. During this work, we have further characterized $Fe(biq)Cl_2$ and prepared two additional new iron compounds, $Fe(biq)(NCS)_2$ and $Fe(2,9\text{-dmp})(NCS)_2$. As well as being an aid in the characterization of $Fe(bipy)(NCS)_2$, these compounds have interesting properties in their own right. For instance, in a previous article [12], we reported the low temperature (~2 K) Mössbauer spectroscopy and magnetic behavior of $Fe(2,9\text{-dmp})(NCS)_2$ which showed that it underwent slow paramagnetic relaxation and hyperfine splitting of its zero field Mössbauer spectra, phenomena not previously observed for monomeric pseudo-tetrahedral high spin iron(II) complexes. We now report details of the synthesis and properties of $Fe(biq)_3(NCS)_2$ and related diimine compounds.

Experimental

Syntheses

All the metal salts used in this work were reagent grade. The ligand 2,2′-biquinoline was obtained from Columbia Organic Chemical Co., while the source for 2,9-dimethyl-1,10-phenanthroline hemihydrate was Aldrich Chemical Co. The metal salts and the ligands were used in the synthesis without further purification. The compounds were analyzed by Galbraith Laboratories, Knoxville, Tenn. 37921, U.S.A.

$Fe(biq)_3(NCS)_2$

$Fe(biq)_3(NCS)_2$ was obtained quite unexpectedly during the first attempted synthesis of $Fe(biq)(NCS)_2$. The method of preparation is given below.

100 ml of a 2,2′-biquinoline solution, made by dissolving 0.4329 g (1.689 mmol) of 2,2′-biquinoline in warm acetone, was added slowly to 60 ml of a freshly prepared aqueous ferrous thiocyanate, ($Fe(NCS)_2$), solution. This latter solution was made by mixing together 30 ml aqueous solutions of $FeSO_4 \cdot 7H_2O$ (2,4562 g, 8.835 mmol) and $Ba(NCS)_2 \cdot 2H_2O$ (2.7675 g, 9.175 mmol) under nitrogen and filtering out the $BaSO_4$ precipitate. Upon vigorous stirring of the ferrous-biquinoline mixture, a pale blue–gray precipitate formed. After filtering the product, it was washed with distilled water only and dried under vacuum. Initially, two washing steps were planned, one with acetone and the second with distilled water. However, the product dissolved completely in acetone, and the washing step with acetone was discontinued. The results of the elemental analysis of the initial preparation are reported in Table I as $Fe(biq)_3(NCS)_2$ (a). This batch of the compound was used for the spectroscopic and magnetic characterization of $Fe(biq)_3(NCS)_2$. Another batch was also prepared to test the reproducibility of the method and to obtain material for subsequent solubility studies. The analysis results of this latter batch are given in Table I as $Fe(biq)_3(NCS)_2$ (b).

TABLE I. Elemental Analysis of Iron 2,2′-biquinoline and 2,9-dimethyl-1,10-phenanthroline Compounds

Compound		Calculated (%)			Found (%)		
		C	H	N	C	H	N
Fe(biq)$_3$(NCS)$_2$	(a)[a]	71.48	3.86	11.91	72.59	3.98	11.55
	(b)				68.80	3.79	11.84
Fe(biq)(NCS)$_2$	(a)[b]	56.08	2.82	13.08	56.01	2.75	12.18
	(b)				58.07	2.70	12.19
Fe(biq)Cl$_2$		56.44	3.16	7.31	56.20	3.13	7.21
Fe(2,9-dmp)(NCS)$_2$		50.54	3.18	14.73	50.49	2.99	14.46

[a] (a) = first preparation, (b) = second preparation. [b] (a) = prepared directly, (b) = prepared by decomposition of Fe(biq)$_3$(NCS)$_2$ (b) preparation.

Fe(biq)(NCS)$_2$ and Fe(2,9-dmp)(NCS)$_2$

Each of these compounds was prepared by reacting together a ten-to-one molar ratio of freshly prepared Fe(NCS)$_2$ to the corresponding ligand. To prevent the formation of undesired products, the synthesis was done under anhydrous conditions: anhydrous metal salts and solvents and the use of the dehydrating agent, 2,2-dimethoxypropane, known hereafter as DMOP, to remove traces of water from the solutions. For each synthesis the materials and solvents used are as follows. Fe(biq)(NCS)$_2$: 2.6384 g (20.81 mmol) anhydrous FeCl$_2$ in 50 ml of absolute ethanol and 14 ml DMOP. 0.5014 g (1.956 mmol) 2,2′-biquinoline in 45 ml of benzene. 3.4829 g (42.96 mmol) NaNCS in 60 ml of absolute ethanol. Fe(2,9-dmp)(NCS)$_2$: 2.1821 g (17.21 mmol) anhydrous FeCl$_2$ in 35 ml of absolute ethanol and 10 ml DMOP. 0.3697 g (1.702 mmol) 2,9-dimethyl-1,10-phenanthroline: hemihydrate in 15 ml of absolute ethanol. 3.5501 g (36.53 mmol) KNCS in 20 ml of absolute ethanol. The details of the method are given below.

The Fe(NCS)$_2$ solution for the above preparations was made by mixing together a filtered solution of anhydrous FeCl$_2$ in absolute ethanol and DMOP with an absolute ethanol solution of either KNCS or NaNCS. The resulting red solution was filtered into a 300 ml round-bottom flask to remove the KCl or NaCl precipitate and was used as soon as it was prepared. The solution of the ligand was slowly added via a dropping funnel to the Fe(NCS)$_2$ solution. A yellow (buff) or yellow–green product (Fe(biq)(NCS)$_2$ or Fe(2,9-dmp)(NCS)$_2$, respectively, formed immediately and was washed several times with absolute ethanol after being filtered. The product was dried in a vacuum desiccator. The results of analysis for each compound are given in Table I; the Fe(biq)(NCS)$_2$ prepared by this method is designated as Fe(biq)(NCS)$_2$ (a).

Fe(biq)Cl$_2$

This compound was prepared by the method of Harris *et al.* [10]. In the preparation, 0.2227 g (1.757 mmol) anhydrous FeCl$_2$ in methanol and 0.4475 g (1.745 mmol) biquinoline in benzene were used. The product obtained gave the expected analysis (see Table I). We have been unable to obtain the perchlorate, Fe(biq)$_2$(ClO$_4$)$_2$·2.5H$_2$O, via the reported [10] preparation or modifications of our own.

Physical Measurements

The details of the physical (Faraday susceptibility and zero field Mössbauer spectroscopy) measurements reported within this paper have been discussed elsewhere [13]. Applied field Mössbauer spectroscopy experiments were performed using a niobium-tin superconducting solenoid in longitudinal geometry ($H_0 \| E_\gamma$). Depending on previous use history, the remenant field for this particular solenoid at zero current is estimated as high as ~5 kG.

Solubility of Fe(biq)$_3$(NCS)$_2$

From our experience, the choice of substance to be used as a reaction medium and as a washing solvent is a major factor as to whether Fe(biq)$_3$(NCS)$_2$ is obtained as the product when Fe(NCS)$_2$ and 2,2′-biquinoline are reacted together. We have already pointed out that Fe(biq)$_3$(NCS)$_2$ is insoluble in water and dissolves readily in acetone. It was decided to study the solubility of Fe(biq)$_3$(NCS)$_2$ in organic solvents of various polarities. The solvents chosen were the ‘polar’ solvent absolute ethanol and the nonpolar solvents: acetone, benzene, toluene and carbon tetrachloride. The results of these studies are given below.

If Fe(biq)$_3$(NCS)$_2$ is mixed with each of the aforementioned solvents, a pale blue suspension is initially formed. However, this suspension does not remain stable in nonpolar solvents. In acetone, Fe(biq)$_3$(NCS)$_2$ dissolves completely to form a red solution. When this solution was evaporated to dryness, small colorless needles of the ligand 2,2′-biquinoline, and two solids, one red and the other yellow, of uncertain composition were deposited. In benzene or toluene, the blue suspension changed to a yellow one after

TABLE II. Mössbauer Parameters for $Fe(biq)_3(NCS)_2$ and Related Compounds

Compound	T (K)	δ^a (mm s^{-1})	ΔE_Q (mm s^{-1})	$\Gamma_1{}^b$ (mm s^{-1})	$\Gamma_2{}^b$ (mm s^{-1})	$\Gamma_1/\Gamma_2{}^b$	$A_1/A_2{}^b$	References
$Fe(biq)_3(NCS)_2$	300	1.05	2.06	0.26	0.28	0.94	1.04	d
	4.2	1.06	2.41	0.40	0.33	1.23	1.30	
$Fe(biq)(NCS)_2{}^c$ (a)	300	0.78	2.40	0.33	0.36	0.89	1.04	d
	78	0.87	2.50	0.34	0.34	0.99	1.04	
	4.2	0.92	2.44	0.35	0.36	0.96	1.12	
	1.6	0.93	2.45	0.35	0.39	0.91	1.08	
$Fe(biq)(NCS)_2{}^c$ (b)	300	0.79	2.40					d
	78	0.84	2.50					d
$Fe(biq)Cl_2$	300	0.78	2.76	0.29	0.30	0.96	0.89	d
	78	0.88	2.85	0.33	0.32	1.02	0.92	
	4.2	0.93	2.84	0.33	0.35	0.96	0.91	
	1.84	0.93	2.84	0.31	0.34	0.92	0.92	
$Fe(2,9\text{-dmp})(NCS)_2$	300	0.79	2.47	0.29	0.35	0.83	0.87	d
	78	0.89	2.55	0.40	0.39	1.02	1.01	
	20	0.99	2.31	0.48	0.42	1.02	1.02	
$Fe(2,9\text{-dmp})Cl_2$	300	0.80	2.66					20
	78	0.91	2.77					
	4.2	0.93	2.76					20

[a] Relative to iron foil at 300 K. [b] Subscript 1 refers to peak at lower energy; subscript 2 to higher energy peak. [c] (a) prepared directly; (b) prepared from $Fe(biq)_3(NCS)_2$ decomposition. [d] This work.

~15 min at room temperature. If carbon tetrachloride is the solvent, no color change was observed at room temperature after 2 h. However, if the mixture was heated, the color change, blue to yellow, did occur. In the more polar medium, absolute ethanol, $Fe(biq)_3(NCS)_2$ did not change color.

To check the identity of the yellow material, a larger sample of $Fe(biq)_3(NCS)_2$ (0.5195 g) was refluxed in 150 ml benzene for one hour. The product was filtered into a preweighed glass filter, washed five times with fresh benzene, and dried under vacuum in the filter. The amount of yellow product obtained was 0.2511 g which is reasonable when compared to the theoretical yield (0.2232 g) of $Fe(biq)(NCS)_2$ obtained from the following reaction:

$$Fe(biq)_3(NCS)_2(s) \xrightarrow[\Delta]{\text{benzene}} Fe(biq)(NCS)_2(s) + 2biq(solution)$$

The results of the elemental analysis for the yellow compound is given in Table I as $Fe(biq)(NCS)_2$ (b). The difference found between the actual yield and the theoretical yield indicates that a small amount of $Fe(biq)_3(NCS)_2$ did not decompose; however, the analysis was not greatly affected. Both forms of $Fe(biq)(NCS)_2$ (a) and (b) give identical Mössbauer spectra, a single quadrupole doublet with similar isomer shift and quadrupole splitting values (see Table II). Thus, $Fe(biq)_3(NCS)_2$ appears to undergo facile loss of one or two moles of 2,2′-biquinoline consistent with high steric hindrance and/or weak ligation operative in the tris biquinoline complex. Additional discussion of the lability of $Fe(biq)_3(NCS)_2$ and its structure is given in a later section of this paper.

Results and Discussion

Zero Field Mössbauer Spectra

Zero field Mössbauer spectra for $Fe(biq)_3(NCS)_2$ were measured between 300 K and 4.2 K, and the results of these measurements are given in Table II. The spectrum at each temperature is a single quadrupole doublet which shows that $Fe(biq)_3(NCS)_2$ is a simple, rapidly relaxing paramagnet to 4.2 K. There is no evidence of any structural or magnetic phase transitions in the entire temperature range. The isomer shift values at 300 K (δ = 1.053 mm/s) and lower temperatures are clearly characteristic for high spin ($S = 2$) iron(II) (at all T) with a six-coordinate iron center [14–17]. The observed increase in the value of the isomer shift with decreasing temperature is the typical magnitude for the second order Doppler shift [18], an effect involving

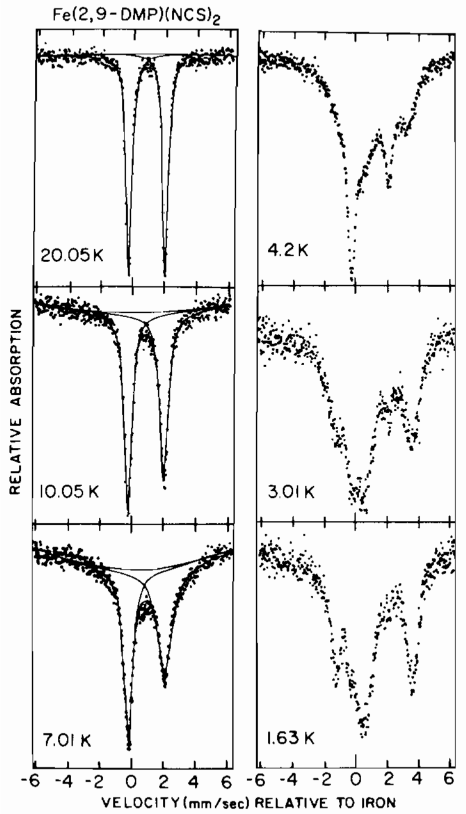

Fig. 2. Temperature dependence of the Mössbauer spectrum of Fe(2,9-dmp)(NCS)$_2$ over the range 20 to 1.6 K.

the temperature and not changes in the iron coordination number, etc. The relatively large quadrupole splitting is indicative of a large axial or rhombic splitting of the low lying T_{2g} ground state in O_h symmetry. As observed in the data, there is a substantial increase in the quadrupole splitting with decreasing temperature. This is the result of thermal depopulation of the lower lying excited states rather than any phase transition which results from a change of symmetry of the iron coordination environment as observed, e.g. in the NCS-bridged polymer Fe(2,2'-bipyridine)(NCS)$_2$ [11, 19]

Zero field Mössbauer spectra data are also presented for Fe(biq)(NCS)$_2$, Fe(biq)Cl$_2$, and Fe(2,9-dmp)(NCS)$_2$ for the temperature range 300 K to 1.6 K. The room temperature isomer shifts for each compound are all near ~0.80 mm/s (see Table II), which is similar to that reported for Fe(2,9-dmp)-Cl$_2$ (Table II) [20], a well known pseudo-tetrahedral monomer containing high spin ($S = 2$) iron(II) with a FeN$_2$Cl$_2$ chromophore of C_{2v} symmetry [4, 6]. The observed increase in the isomer shift for each of these compounds with decreasing temperature is again an effect of the second order Doppler shift while the increasing value of the quadrupole splitting observed at lower temperatures is the result of thermal depopulation of the higher lying component of a nominal ^{5}E ground term in T_d symmetry split in a crystal field of C_{2v} symmetry. If the isomer shifts for Fe(biq)-(NCS)$_2$ are compared to those for Fe(biq)$_3$(NCS)$_2$, the values for the latter are significantly larger at all temperatures. This behavior is in accord with well established systematics of the iron coordination number *vs.* isomer shift (δ) while maintaining the oxidation state, spin state and ligand types constant. That is, everything else being equal, higher isomer shifts imply higher coordination numbers with δ values ~0.8, ~0.9 and $\gtrsim$1.0 mm/s corresponding to four, five and six coordination.

The Mössbauer spectra for each of the monodiimine compounds were determined from 78 K to ~1.6 K. The behavior for Fe(2,9-dmp)(NCS)$_2$ is unusual. In a previous preliminary report, it has been interpreted as the onset of slow spin–lattice relaxation below 20 K [12] leading to partially resolved paramagnetic hyperfine splitting of its zero field Mössbauer spectra. A complete series of spectra showing this phenomenon is given in Fig. 2. In contrast, the spectra for Fe(biq)Cl$_2$ and Fe(biq)(NCS)$_2$ in this entire temperature range remain as a single, near symmetric, unbroadened quadrupole doublet. A similar result (rapid relaxation) is found for Fe(2,9-dmp)Cl$_2$, as well as the corresponding bromide, iodide and the more highly substituted Fe(4,7-diphenyl-2,9-di-CH$_3$-phen)Cl$_2$ in the same temperature range. Over the entire temperature range studied (300 K to 1.6 K), Fe(biq)Cl$_2$, Fe(biq)(NCS)$_2$ and the dmp halide systems are rapidly relaxing, pseudo-tetrahedral paramagnetic species in zero applied magnetic fields. Thus, it seems likely on the basis of zero field Mössbauer spectra that in the series Fe(2,9-di-CH$_3$-phen)X$_2$, (X = Cl$^-$, Br$^-$, I$^-$, NCS$^-$, D (the zero field splitting parameter, Fig. 3)) is positive for the cases of Cl$^-$, Br$^-$, I$^-$ and negative for NCS$^-$. The former leads to a non-magnetic singlet ($m_s = 0$) ground state while the latter results in a slowly relaxing $m_s = \pm 2$ ground Kramers doublet.

High Field Mössbauer Spectra

The Mössbauer spectra of Fe(biq)Cl$_2$, Fe(biq)-(NCS)$_2$ Fe(2,9-dmp)Cl$_2$ and [Fe(biq)$_3$](NCS)$_2$ were measured at 4.2 K using applied magnetic fields between 2 and 60 kG. Under conditions in which these compounds act as rapidly relaxing paramagnets, their magnetically perturbed spectra should be similar to that found for Fe(2,9-dmp)Cl$_2$ at ambient temperature, where Fe(2,9-dmp)Cl$_2$ is clearly expected to act as a rapidly relaxing paramagnet [21]. In transverse ($H_0 \perp E_\gamma$) magnetic fields up to ~26 kG obtained from a laboratory electromagnet, the room temperature spectra exhibit a triplet at lower energies relative to the doublet. This signifies a positive electric quadrupole coupling constant (e^2Qq) where Q is the quadrupole moment (for the ^{57}Fe nuclear excited state, $I = 3/2$ and Q is positive [22]

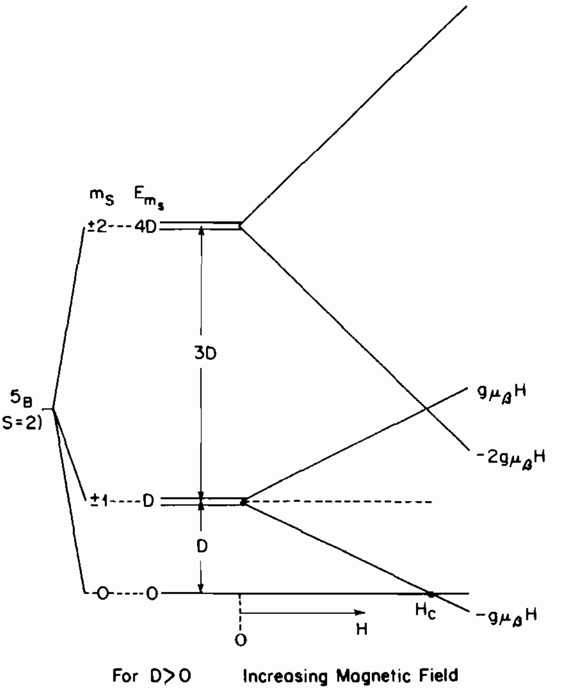

Fig. 3. Energy level diagram for a spin quintet ground state, $D > 0, H_0 = 0$ (left), $D > 0, H_0 \neq 0$ (right).

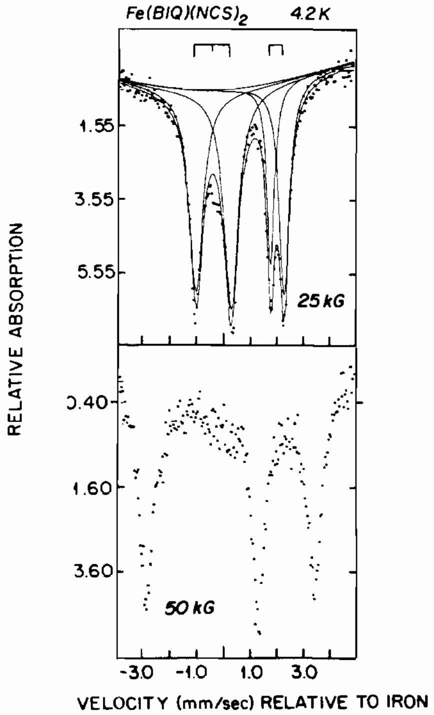

Fig. 4. Mössbauer spectra of Fe(biq)(NCS)$_2$ at 4.2 K, H_0 = 25 kG and 50 kG.

and eq = V_{zz}, the principal component of the electric field gradient tensor. Hence, for Fe(2,9-dmp)Cl$_2$, V_{zz} is positive, and the ground electronic energy level is described as the $|x^2 - y^2\rangle$ orbital or a linear combination of $|x^2 - y^2\rangle$ and $|z^2\rangle$ weighted primarily with the former wavefunction giving an orbital singlet, ^{5}B, ground state. This corresponds to an elongation of the FeN$_2$Cl$_2$ chromophore relative to its C_2 axis leading to destabilization of the "d_{z^2}" orbital. Such an elongation is the result of an N–M–N bite angle significantly <90°, *e.g.* 82° for Zn(2,9-dmp)Cl$_2$. This type of distortion is suggested in X-ray structure determinations for Zn(2,9-dmp)Cl$_2$ and Ni(2,9-dmp)Cl$_2$ (purple tetrahedral (β) form) to which the iron(II) analogue is isomorphous. The results, given below (using longitudinal fields, $H_0 \parallel E_\gamma$) at 4.2 K, for Fe(biq)Cl$_2$ and Fe(biq)(NCS)$_2$ indicate that V_{zz} is positive for these materials as well as Fe(2,9-dmp)Cl$_2$ and that there is a considerable range of hyperfine effects depending on the specific complex.

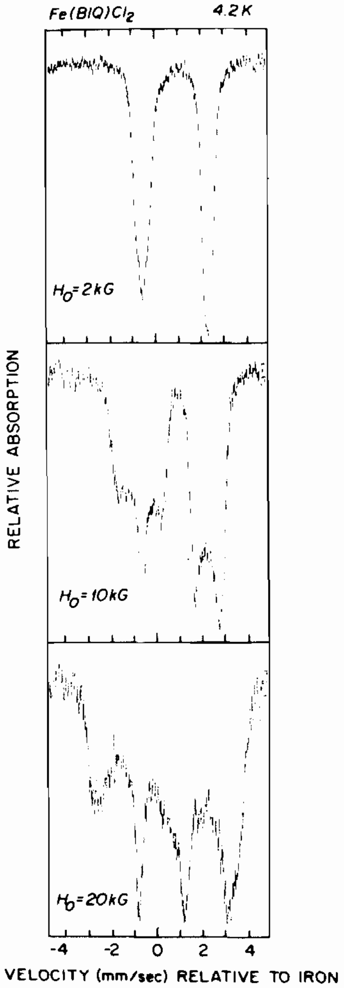

Fig. 5. Mössbauer spectra of Fe(biq)Cl$_2$ at 4.2 K, H_0 = 2 kG, 10 kG and 20 kG.

Fe(biq)(NCS)$_2$

The Mössbauer spectra for Fe(biq)(NCS)$_2$ were measured using applied magnetic fields of 25 and 50 kG (see Fig. 4). In the 25 kG spectrum, a triplet–doublet (the triplet transitions at lower energy relative to the doublet) pattern can just barely be seen. In the 50 kG spectrum, the pattern has expanded so that the peaks from the triplet have overlapped those of the doublet. The middle transition of the triplet in the latter spectrum is poorly resolved. These results imply a positive sign for V_{zz}.

Fe(biq)Cl$_2$

The Mössbauer spectra for Fe(biq)Cl$_2$ were measured using applied magnetic fields at 4.2 K between 2 and 60 kG and are shown in Figs. 5 and 6. In the region 2 to 10 kG, the spectra reveal a triplet–doublet pattern similar to that found for Fe(2,9-dmp)Cl$_2$ (see Fig. 7). The spectrum at 2 kG is slightly broadened, while at 10 kG, the triplet pattern is more resolved. In each case, V_{zz} is positive indicating that the $|x^2 - y^2\rangle$ orbital lies lowest in energy. In this low field regime, a rough estimate of values of the effective magnetic field at the iron-57 nucleus, H_{eff}, may be obtained using the following equation [23]:

$$H_{\mathrm{eff}} = 39.29\ \Delta_{\mathrm{T}} \tag{1}$$

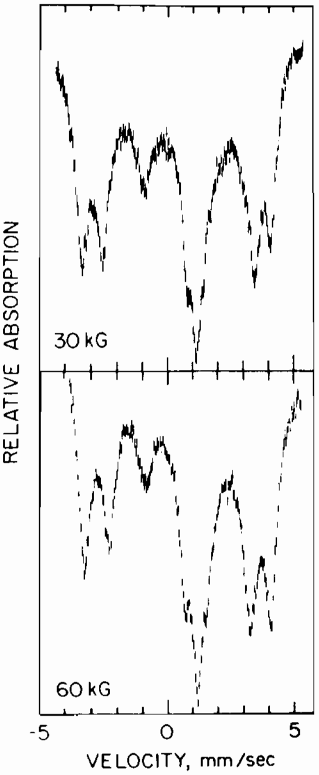

Fig. 6. Mössbauer spectra of Fe(biq)Cl$_2$ at 4.2 K, H_0 = 30 kG and 60 kG.

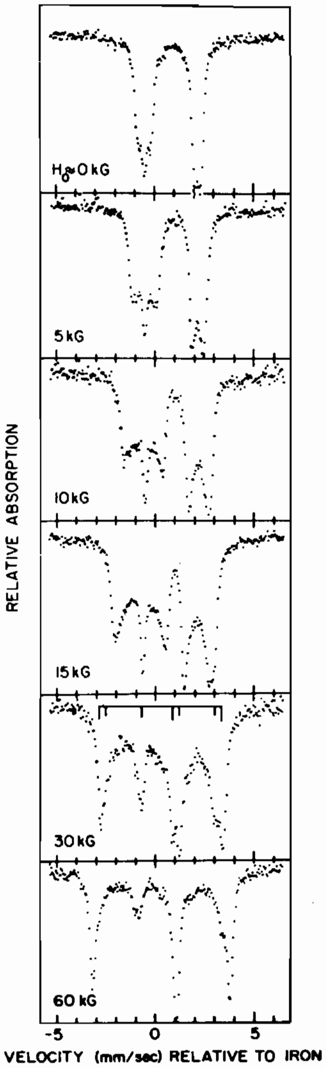

Fig. 7. Mössbauer spectra of Fe(2,9-dmp)Cl$_2$ at 4.2 K, H_0 varying from ≈0 to 60 kG.

where Δ_{T} is the observed triplet splitting (in mm/s). The effective magnetic field is made up of two contributions: the applied field H_0 and an internal hyperfine field, H_{n}, or

$$H_{\mathrm{eff}} = H_0 + H_{\mathrm{n}} \tag{2}$$

Using eqn. (1), H_{eff} has been estimated to be 18.5 and 74 kG for the 2 and 10 kG spectra, respectively. These greater induced effective fields are the consequence of the increased magnetization with applied field at low temperatures. For ambient temperature spectra $H_{\mathrm{eff}} = H_0$, *i.e.* the magnetization of the sample is much smaller at small values of H_0/T. In the range up to ~20 kG at 4.2 K, Fe(biq)Cl$_2$ still acts as a rapidly relaxing paramagnet with the quadrupole interaction being a greater perturbation than the magnetic hyperfine interaction ($e^2Qq/2 \gg \mu H_n$).

When the applied field increases to 20 kG, the resulting spectrum becomes more complicated (see Fig. 6). The triplet–doublet pattern broadens, and new transitions start appearing. Therefore, the magnetic hyperfine interactions, which were small in the 2 kG spectrum and grew in magnitude in the 10 kG spectrum, are starting to become the dominant features in the spectra for $H_o > 20$ kG, *i.e.* $\mu H \gtrsim e^2Qq/2$. The spectra determined with applied fields of 30 and 60 kG show eight transitions which are the result of the six usually allowed $\Delta m_I = 0, \pm 1$ and two normally forbidden $\Delta m_I = \pm 2$ transitions between the iron-57 ground and excited nuclear Zeeman states. We note that similar 'eight' transition Mössbauer spectra have been observed [24] in the field dependence of the Mössbauer spectrum of reduced Ch. ethylica rubredoxin at 4.2 K. This form of rubredoxin contains tetrahedral FeII in a highly distorted environment ($\Delta E = 3.16$ mm/s at 77 K) corresponding to an FeS_4 chromophore.

Fe(2,9-dmp)Cl$_2$

The field dependence of the Mössbauer spectrum of Fe(2,9-dmp)Cl$_2$ at 4.2 K is also included (Fig. 7). This is done for completeness and particularly since its structure is known with greater certainty in view of its isomorphism to Zn(2,9-dmp)Cl$_2$ whose structure has been determined in a single crystal X-ray study [6]. Generally the spectral behavior is very similar to that of Fe(biq)Cl$_2$ in the low field range. In higher fields, its transitions are not as well resolved. In addition at higher fields there are obvious complex sample polarization-field dependent intensity effects.

The change in the character of the perturbed Mössbauer spectra of Fe(biq)Cl$_2$ and to a lesser extent those of Fe(2,9-dmp)Cl$_2$ with increasing magnetic field results from a change in the character of the electronic ground state from the nonmagnetic state $|m_s = 0\rangle$ to a paramagnetic one $|m_s = -1\rangle$ (see Fig. 3). It is possible to estimate the zero field splitting for Fe(biq)Cl$_2$ by noting that at particular field, H_c, the $|m_s = 0\rangle$ and $|m_s = -1\rangle$ electronic states are degenerate, and the following relation is true:

$$D = g\mu_\beta H_c$$

where D is the zero field splitting, and μ_β is the Bohr magneton for the electron. Assuming that $g = 2$, and $H_c \simeq 20$ kG, a rough lower limit of the value of D is estimated as ~2 cm^{-1}, a value fairly typical of distorted tetrahedral ferrous.

[Fe(biq)$_3$](NCS)$_2$

The field dependence of the Mössbauer spectrum of [Fe(biq)$_3$](NCS)$_2$ is shown in Fig. 8, where the limiting spectrum at $H_o = 60$ kG is exactly as expected for a rapidly relaxing paramagnet. That is, hyperfine splitting-magnetization effects are substantially less for this material as compared to the previously discussed pseudotetrahedral systems. The spectra indicate that V_{zz} is positive and that the electric field gradient tensor is axially symmetric, *i.e.* the asymmetry parameter $\eta = V_{xx} - V_{yy}/V_{zz}$ is zero. A positive electric quadrupole coupling constant correlates with either a ^5B ground state based on d_{xy} in tetragonally distorted (compression) O_h symmetry or ^5E based on the pair $t_{2g}^{+} = (2/3)^{1/2}(d_{x^2-y^2} - (1/3)^{1/2}d_{xz}$, $t_{2g}^{-} = (2/3)^{1/2}d_{xy} + (1/3)^{1/2}d_{yz}$ in trigonally distorted (elongation) O_h symmetry [25].

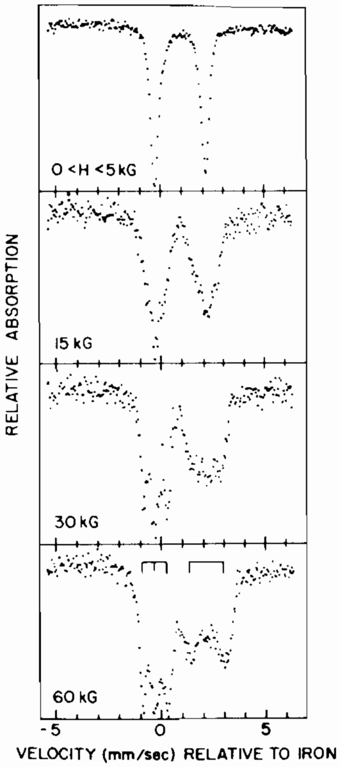

Fig. 8. Mössbauer spectra of [Fe(biq)$_3$](NCS)$_2$ at 4.2 K, H_o varying from ≈0 to 60 kG.

Fe(2,9-dmp)(NCS)$_2$

We conclude this section by showing a few applied field spectra (Fig. 9) for Fe(2,9-dmp)(NCS)$_2$ which as discussed previously exhibits slow relaxation in zero field (Fig. 2). In general the effect of the applied field is to induce even slower relaxation at a given temperature. Compare, for instance, the spectrum at $T = 4.2$ K, $H_o \approx 5$ kG to that at $H_o = 0$, $T = 3.01$ K or $H_o = 20$ kG, $T = 4.2$ K to $H_o = 0$, $T = 1.63$ K (right side of Fig. 2).

Optical Spectra

The ligand field d–d transitions for the optical spectra of the monodiimine complexes Fe(2,9-dmp)-

TABLE III. Optical Spectra Band Maxima for Fe(biq)$_3$(NCS)$_2$ and Related Compounds at Room Temperature

Compound	Band maxima (in cm^{-1}) and related intensities^a	References
Fe(biq)$_3$(NCS)$_2$	~6700(w)	b
Fe(biq)(NCS)$_2$	6000(sh); 6900(vs); 17600(sh), 18700(sh)	b
Fe(biq)Cl$_2$	6000(s,sh); 7100(vs); 17000	b, 10
Fe(2,9-dmp)(NCS)$_2$	5600(w,sh); 6940(vs); 19200(s,sh)	b
Fe(2,9-dmp)Cl$_2$	6800(s)	20

^{a}w = weak vs = very strong m = medium, sh = shoulder, s = strong. ^{b}= this work.

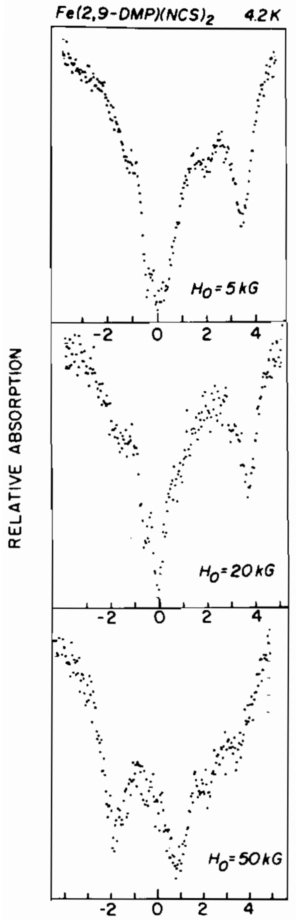

Fig. 9. Mössbauer spectra of Fe(2,9-dmp)(NCS)$_2$ at 4.2 K, H_0 varying from 5 kG to 50 kG.

(NCS)$_2$, Fe(biq)Cl$_2$ and Fe(biq)(NCS)$_2$ are tabulated in Table III. Each compound clearly exhibits an intense band around ~7000 cm^{-1} corresponding to the $^5E \rightarrow {}^5T$ transition found in Fe(2,9-dmp)Cl$_2$ [20] (see Table III). Broadening and low symmetry splitting of this transition are evident. For Fe(biq)Cl$_2$, this is the first reported low energy optical spectrum. Harris *et al.* [10] reported only a charge transfer band at ~17000 cm^{-1} and from Fig. 10 a charge transfer band does probably appear at that point as well as the one near ~7000 cm^{-1}. Unlike the spectrum for Fe(biq)Cl$_2$, the spectrum for Fe(biq)(NCS)$_2$ and Fe(2,9-dmp)(NCS)$_2$ show high intensity shoulders between 17000 and 19000 cm^{-1} These bands are probably spin forbidden in nature, but because of the close proximity of an intense charge transfer band above ~20000 cm^{-1}, they steal from the charge transfer band and appear as high intensity shoulders. The strong similarity of the optical spectra of these three compounds to that for Fe(2,9-dmp)Cl$_2$ plus the Mössbauer data support the assumption that each compound has a pseudotetrahedral structure containing high spin (S = 2) iron(II).

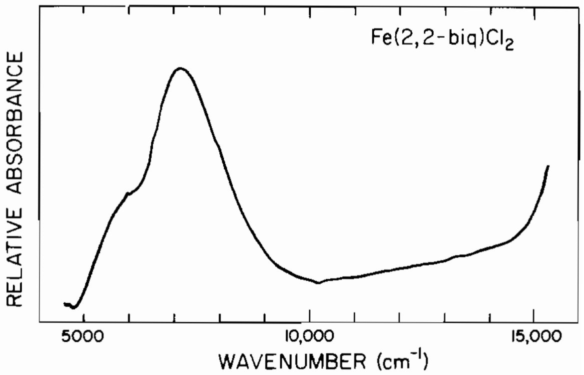

Fig. 10. Near infrared visible optical spectrum of Fe(biq)Cl$_2$ from 5000 cm^{-1} to 15 000 cm^{-1}

Surprisingly, Fe(biq)$_3$(NCS)$_2$ exhibits only one weak, broad band at approximately 6700 cm^{-1} (Table III). At higher energies, a charge transfer band centered above 800 nm (12500 cm^{-1}) is seen. At first site, the position of the band implies a spectrum similar to those of the pseudotetrahedral compounds mentioned above. However, the relative intensity of the band for Fe(biq)$_3$(NCS)$_2$ was significantly less than that of the corresponding band in the pseudotetrahedral complexes where it is of course Laporte allowed, since the inversion center is absent in C_{2v} symmetry. This further eliminates the possibility of four coordinate iron(II) in Fe(biq)$_3$(NCS)$_2$. An assignment for the transition is $^5T_2 \rightarrow {}^5E$ in nominal O_h or D_3 symmetry. In iron(II) complexes of O_h symmetry, the energy of this transition

TABLE IV Room Temperature Infrared Spectra for Iron 2,2′-biquinoline and 2,9-dimethyl-1,10-phenanthroline Compounds

Band maxima (in cm^{-1})[a]			Assignment
$Fe(biq)_3(NCS)_2$	$Fe(biq)(NCS)_2$	$Fe(2,9\text{-dmp})(NCS)_2$	
		2120	
2075		2076	
2065		2044(center)	N–C stretch
2055	2020(vs)	2026	ν_1 (NCS)
	1998(sh)	1946	
	1968(sh)		
	1920(sh)		
		813(m)	C–S stretch (?)
	797	783(s)	
	791	775(w,sh)	ligand (?)
	782		
		548	ligand
	487	482	N–C–S band
	481	477	δ(N–C–S)
		443(sh)	
	394	436(s)	ligand
		414(m)	
	306(sh,s)	354(sh)	
	343(vs)	342(sh)	Fe–N (ligand) stretch
	338(sh)	329(vs)	
	306(s)	305	Fe–N (NCS) stretch
	290(sh)	291	
	278(sh)	278	
		266	

[a] s = strong; vs = very strong; m = medium; w = weak; sh = shoulder.

corresponds to 10 *D*q [25]. The present observations would then imply the lowest value of 10 *D*q reported for any six coordinate high spin iron(II) compound to date. For example, the latter transition occurs at ~9000 cm^{-1} for the $Fe(H_2O)_6{}^{2+}$ ion. This suggests that the bonding between 2,2′-biquinoline and the iron atom is indeed very weak. This weak bonding is undoubtedly the result of severe steric crowding caused by the benzo groups on 2,2′-biquinoline as these groups approach the metal center. These observations are entirely consistent with (1) the facile removal of one or two moles of biquinoline from $Fe(biq)_3(NCS)_2$ that is observed in various solvents and (2) the high-spin nature of the complex. The similar removal of one or especially two moles of bidentate ligand from less hindered tris-chelated, low spin, species such as $Fe(bipy)_3{}^{2+}$ typically requires exhaustive refluxing or soxhlet extraction in various solvents over periods of hours to days, or even more rigorous conditions such as high temperature thermolysis in inert gas environments or under vacuum. Alternatively, the band at ~6700 cm^{-1} may be interpreted as a transition between the ground state and a lower energy component of a highly split excited state with the transition to the higher energy component obscured by the charge transfer band. This latter possibility is rejected on the basis of the fact that the excited state ^5E splitting required would be extraordinarily large.

Infrared Spectra

The band maxima and their probable assignments for $Fe(2,9\text{-dmp})(NCS)_2$, $Fe(biq)(NCS)_2$ and $Fe(biq)_3(NCS)_2$ are presented in Table IV. Figure 11 shows the spectra in the region of the C–N stretching bands at ~2000 cm^{-1} for each compound. We concentrate on this region of the infrared spectrum because during our studies of $M(bipy)(NCS)_2$ type compounds, this band gave us much information concerning the nature of the metal–thiocyanate bonding, *i.e.* whether the thiocyanate anion bonds through the nitrogen atom, the sulfur atom, or both or is totally nonbonding, *i.e.* ionic. We now present the

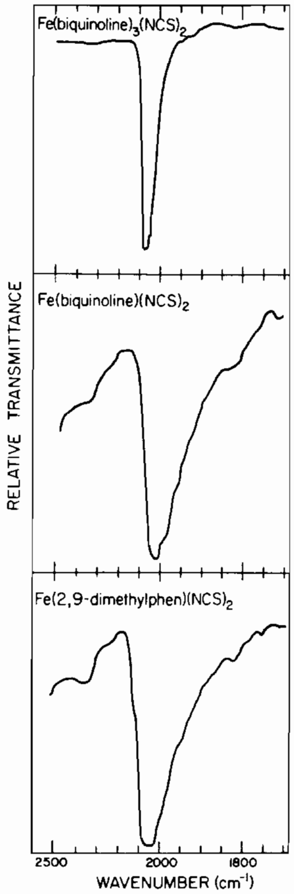

Fig. 11. Infrared spectra of Fe(2,9-dmp)(NCS)$_2$, Fe(biq)(NCS)$_2$ and Fe(biq)$_3$(NCS)$_2$ in the CN stretch region.

data for the monodiimine compounds of the present study.

Fe(2,9-dmp)(NCS)$_2$ and Fe(biq)(NCS)$_2$ show very broad bands centered about or below 2050 cm^{-1}, indicating nitrogen bonded thiocyanate anions in a low symmetry environment. It is assumed that as pseudotetrahedral compounds the local coordination environment has at most C_{2v} symmetry, and thus two C—N stretches are expected. The broadness of the band in each complex indicates both bands are present, but are not resolved. It should be pointed out that band maxima are lower in energy than those found for the six-coordinate, NCS bridged polymer, Fe(bipy)(NCS)$_2$ [11] or the famous 'high spin–low spin' monomer, Fe(bipy)$_2$(NCS)$_2$ [17]. Surprisingly, these bands are also lower in energy than the C—N stretching bands found in some other pseudotetrahedral compounds. For example, this band is found in the compounds, CoL$_2$(NCS)$_2$ where L is γ-picoline and β-picoline, at 2052 and 2060 cm^{-1}, respectively [26]. They are found at 2053 cm^{-1}, 2062 cm^{-1} and 2050 cm^{-1}, respectively. We assume that this reduction in the energy found in the monodiimine compounds is probably due to increased occupation of the C—N antibonding orbital of the thiocyanate anion as a result of increased back bonding by the metal to the thiocyanate ligand. In tetrahedral complexes, the fraction of d-electrons which can be backbonded would be expected to be greater than that for octahedral complexes.

The C—N stretching band for Fe(biq)$_3$(NCS)$_2$ is centered at 2070 cm^{-1} and strongly contrasts with the preceding pseudotetrahedral species. Its position, shape and relatively narrow width are clearly what is expected for ionic, nonbonded 'ionic' thiocyanate anions; e.g. for KNCS, the C—N stretch appears at 2053 cm^{-1} [27], while for NaNCS [28] this band occurs at 2060 cm^{-1}. This result, combined with the previous indication of six coordination based on Iron-57 Mössbauer spectra isomer shift data, strongly suggests that Fe(biq)$_3$(NCS)$_2$ is properly formulated as the cationic tris ligated species [Fe(biq)$_3$] (NCS)$_2$.

Magnetic Measurements

We report the results of the magnetic susceptibility measurements for the compounds [Fe(biq)$_3$] (NCS)$_2$, [Fe(biq)(NCS)$_2$] and [Fe(2,9-dmp)(NCS)$_2$] using powder samples and 10 different magnetic fields varying from 1.66 to 5.10 kG. Detailed susceptibility measurements were not made for [Fe(biq)Cl$_2$].

[Fe(biq)$_3$] (NCS)$_2$

The susceptibility data were measured between 50.66 and 303.45 K using a Faraday balance and are presented in Fig. 12. A Curie–Weiss fit of the data to the following equation was performed.

$$\chi_M = C/T - \theta \qquad (3)$$

Using the value of C obtained from the fits, the effective moment μ_{eff}, and an effective g-value, g_{eff}, are calculated from the following equations:

$$\mu_{eff} = 2.828\, C^{1/2} \qquad (4)$$

$$g_{eff} = 2.828 [C/S(S+1)]^{1/2} \qquad (5)$$

The quantity S in eqn. (5) is the electron spin, and for iron(II), $S = 2$. The results of the fits and calculations are reported in Table V. The magnetic moments for [Fe(biq)$_3$] (NCS)$_2$, uncorrected for TIP, and measured in a field of 5.10 kG, ranged

TABLE V. Results of Curie–Weiss Law Fits for [Fe(biq)$_3$] (NCS)$_2$ and [Fe(biq)(NCS)$_2$]

	[Fe(biq)$_3$] (NCS)$_2$	[Fe(biq)(NCS)$_2$
θ (in K)	−6.45	−2.16
C (in emu K^{-1} mol^{-1})	3.00	4.00
g_{eff}	2.00	2.31
μ_{eff}	4.90	5.65

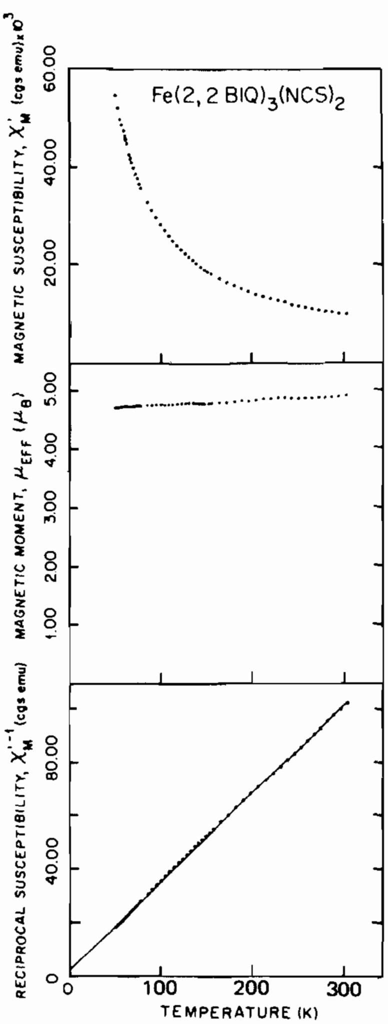

Fig. 12. Magnetic susceptibility (χ_M), moment (μ) and reciprocal susceptibility $\chi_M{}^{-1}$ for [Fe(biq)$_3$](NCS)$_2$ powder over the range 50 K to 300 K.

between 4.89 μ_β at 303.45 K down to 4.70 μ_β at 50.56 K. These values, especially the one at ~300 K, are very close to μ_{eff} derived from the fit, 4.90 μ_β. This is precisely the spin-only value for $S = 2$. The value of g_{eff} and μ_{eff} (2.00 and 4.90, respectively) indicate an orbital singlet ground state for [Fe(biq)$_3$](NCS)$_2$ caused by an axial or rhombic distortion of the local iron environment. The large negative value of θ is probably related to zero field splitting of the orbital singlet, which will result in an eventual decrease in the moment at very low temperatures ($\lesssim$20 K), and is probably not representative of significant intermolecular, antiferromagnetic exchange effects.

Fe(biq)(NCS)$_2$

Susceptbility measurements were taken between 1.55 and 302.61 K. A Curie–Weiss law is obeyed over most ($\gtrsim$20 K) of the temperature range. The results for 5.10 kG are presented in Table V along with values of μ_{eff} and g_{eff} calculated from eqns. (4) and (5). The value of μ_{eff} indicates an obvious orbital contribution. At 25 K, the moment is 5.55 μ_β. Below this temperature, there is a significant decrease in moment to a limiting value of ~3.5 μ_β at 1.55 K. On the other hand, the susceptibility exhibits no remarkable features. These observations signify a large single ion zero field splitting effect.

Edwards *et al.* [29] have derived the following equation which can be used to estimate the axial zero field splitting parameter, D, for $S = 2$ ions:

$$\chi_M = \frac{2N\mu_\beta 2 g_\parallel}{3kT}\left[\frac{e^{-x} + 4e^{-4x}}{1 + 2e^{-x} + 2e^{-4x}}\right] + \frac{4N\mu_\beta{}^2 g_\perp}{9D}\left[\frac{9 - 7e^{-x} - 2e^{-4x}}{1 + 2e^{-x} + 2e^{-2x}}\right] \tag{6}$$

where $\chi = D/\mathrm{k}T$, N is Avogadro's number; k is the Boltzmann constant; μ_β is the Bohr magneton; $g_\parallel$ is the g-value parallel to principal susceptibility axis, *i.e.* g_z; and $g_\perp$ is the g-value perpendicular to the principal susceptibility axis, *i.e.* g_x or g_y. From the powder susceptibility data of Fe(biq)(NCS)$_2$, only the absolute value of D may be obtained; its sign is generally unknown. As mentioned before, we have observed a single quadrupole doublet in the Mössbauer spectrum at 1.59 K in zero magnetic field, indicating the absence of slow paramagnetic relaxation broadening. This behavior is consistent with D positive. Since the mean powder susceptibility measures the overall properties of the polycrystalline powder, the principal g-values are not known beforehand in the absence of electron spin resonance or single crystal, magnetic anistropy data. Unfortunately, high spin ferrous does not typically exhibit measurable electron spin resonance spectra at ordinary temperatures. We used eqn. (6) in a nonlinear least squares fit of our powder susceptibility data. As initial estimates, we choose $g_\perp$ and $g_\parallel$ to be isotropic (= 2.0), and D to be a small positive number. Two fits were done: the first fit in which only D was allowed to vary, and in the second all three variables, D, $g_\perp$ and $g_\parallel$, were allowed to vary. The quality of the first fit, in which the final results were: $D = 3.67$ cm^{-1} and $g_\perp = g_\parallel = 2$, was not very good. This was perhaps not very surprising since there was a large deviation between g_{eff} obtained from the Curie–Weiss fit (= 2 31) and $g_\parallel$ and $g_\perp$ A better fit was obtained if all three variables were allowed to vary. The results of the fit are. $D = \sim 5$ cm^{-1} and $g_{average} = 2.30 = 1/3(g_\parallel + 2g_\perp)$ with $g_\parallel = 2.41$ and $g_\perp = 2.24$.

Fe(2,9-di-CH$_3$-phen)(NCS)$_2$

The Mössbauer results indicating $D < 0$ for Fe(2,9-dmp)(NCS)$_2$ and $D > 0$ for the correspond-

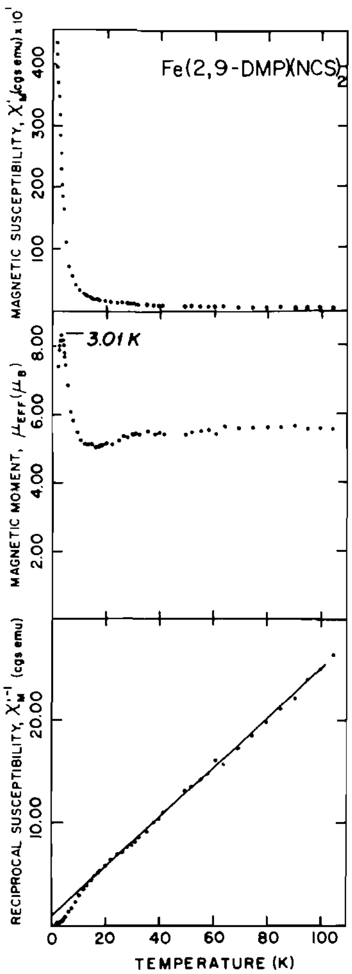

Fig. 13. Magnetic susceptibility (χ_M), moment (μ) and reciprocal susceptibility χ_M^{-1} for Fe(2,9-dmp)(NCS)$_2$ powder over the range 1.5 K to ~100 K, Faraday balance measurements.

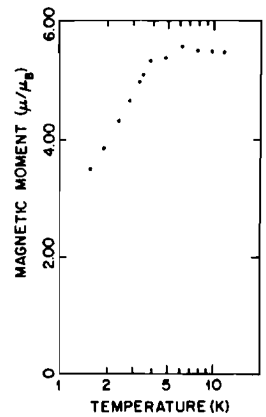

Fig. 14. Magnetic moment (μ) of Fe(2,9-dmp)(NCS)$_2$ powder over the range 1.5 K to 15 K, vibrating sample magnetometer measurements.

ing chloride, bromide and iodide are further supported in the temperature dependence of the effective moment of the thiocyanate (Fig. 13). Figure 13 shows μ_{eff} *versus* T for an applied field H_0 = 1.6 kG for the thiocyanate complex in powder form. The complex behaves as an oriented single crystal sample in our Faraday balance sample holder owing to large magnetic anisotropy and significant sample polarization and alignment in the field. We note that in the quartz sample holders used for these experiments, the polycrystal was packed quite loosely and thus quite free to move and align itself with the applied field. As expected, the temperature dependence of the molar susceptibility is unremarkable. However, the novel low temperature maximum and large value of μ are exactly as predicted [30, 31] for a single crystal with $\mu_\parallel > \mu_\perp$ implying $D < 0$ and large (~-2 to -5 cm^{-1}). It is found that Fe(2,9-dmp)(NCS)$_2$ has a μ value of 5.60 μ_β at 104 K that rises to a maximum of 8.10 μ_β at 3.01 K and then decreases to 6.94 μ_β at 1.5 K. Figure 14 shows the μ *versus* T variation below 10 K for the same Fe(2,9-dmp)(NCS)$_2$ polycrystals but now finely ground and very tightly packed. The measurements were taken using our vibrating sample magnetometer with H_0 ~ 2 kG. It is seen that the field alignment effect is now largely eliminated yielding the expected powder behavior.

Fe(2,9-dmp)Cl₂

For the case of $D > 0$ and for comparable $|D|$, one expects $\mu_\perp > \mu_\parallel$ and $|\mu_\perp - \mu_\parallel|$, *i.e.* the anisotropy to be somewhat smaller with the maximum value of μ smaller as well [31]. Powder samples of the latter type would then be expected to show less pronounced low temperature maxima in μ and field alignment effects if at all. Our study of μ *versus* T for a powder sample of Fe(2,9-dmp)Cl$_2$ over the range 300 K to 1.6 K shows essentially 'normal powder behavior,

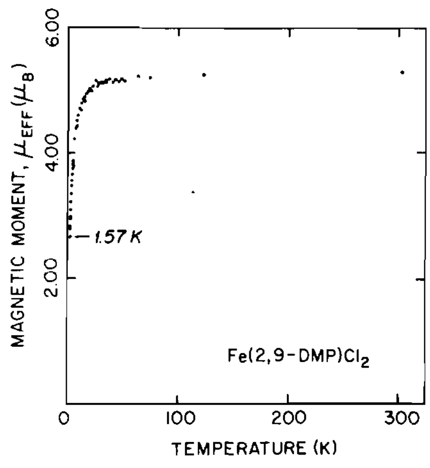

Fig. 15. Magnetic moment (μ) of Fe(2,9-dmp)Cl$_2$ powder over the range 1.6 K to 300 K.

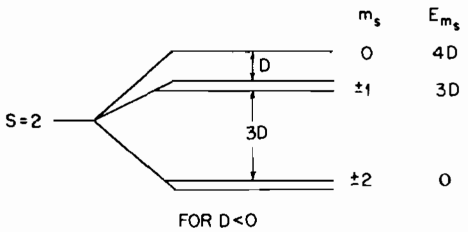

Fig. 16. Energy level diagram for $S = 2$ under negative zero field splitting.

i.e. no pronounced maximum in μ suggesting D positive in accord with the low temperature Mössbauer spectra. For the latter compound μ decreases from 5.07 μ_β at 302.78 K to 2.66 μ_β at 1.57 K, Fig. 15, a variation consistent [29] D ~+5 cm^{-1} as suggested for $[\mathrm{Fe(biq)(NCS)_2}]$. The D values refer to zero field splitting of the ground spin quintet of high spin ferrous such that for $D < 0$, the ground state is the Kramers doublet, $m_s = \pm 2$, with $m_s = \pm 1$ at $3|D|$ and $m_s = 0$ at $4|D|$, Fig. 16, or alternatively for $D > 0$, $m_s = 0$ is the ground state with $m_s = \pm 1$ at D and $m_s = \pm 2$ at $4D$, Fig. 3.

In summary, the magnetic susceptibility studies show $\mathrm{Fe(2,9\text{-}dmp(NCS)_2}$ and $\mathrm{Fe(2,9\text{-}dmp)Cl_2}$ to be Curie–Weiss paramagnets to low temperatures. The magnetic hyperfine splitting of the Mössbauer spectrum of the former is not due to an ordering process but to slow paramagnetic relaxation. We note in passing that there is precedent [32] for the observation of variation in the sign of D and thus the low temperature relaxation behavior in a closely related series of iron compounds. In particular, D is positive in the square pyramidal $S = 3/2$ iron(III) dithiocarbamate compounds $[\mathrm{Fe(III)(DTC)_2X}]$, when X = Cl, Br and negative for X = I.

Structure of the Compounds

No X-ray diffraction measurements were done on any of the compounds studied, because of the lack of suitable single crystals. However, we can propose structures for each compound based on the aforementioned spectral and magnetic data. Structure assignment of the monodiimine compounds is easier since the Mössbauer and optical spectral behavior for $\mathrm{Fe(biq)Cl_2}$, $\mathrm{Fe(biq)(NCS)_2}$ and $\mathrm{Fe(2,9\text{-}dmp)(NCS)_2}$ is similar to that for $\mathrm{Fe(2,9\text{-}dmp)Cl_2}$, a known pseudotetrahedral monomer. Zero field Mössbauer and optical spectral data clearly indicate that each compound has a four-coordinate, pseudotetrahedral iron(II) chromophore, $\mathrm{FeN_2X_2}$, of symmetry C_{2v}. The infrared data for the thiocyanate compounds indicate isothiocyanato bonding to the iron center. Furthermore, high field Mössbauer data indicate that the ground state for each compound, including $\mathrm{Fe(2,9\text{-}dmp)Cl_2}$, is based primarily on the $|x^2 - y^2\rangle$ orbital which corresponds to an elongation of the $\mathrm{FeN_2X_2}$ chromophore. This elongation is the consequence of the small 'bite' angle (N–Fe–N) between the imine nitrogen–iron bonds. From a single crystal X-ray structure study of $\mathrm{Zn(2.9\text{-}dmp)Cl_2}$ [6] which is isomorphous with $\mathrm{Fe(2,9\text{-}dmp)Cl_2}$ [4], the N–Zn–N 'bite' angle was determined to be 82°. It is expected that $\mathrm{Fe(biq)Cl_2}$, $\mathrm{Fe(biq)(NCS)_2}$ and $\mathrm{Fe(2,9\text{-}dmp)(NCS)_2}$ should have a similar structure to $\mathrm{Fe(2,9\text{-}dmp)Cl_2}$ with an N–Fe–N 'bite' angle of ~80° generated by the imine nitrogens of 2,2′-biquinoline or 2,9-dimethyl-1,10-phenanthroline. The proposed structures of the chloro- and thiocyanato compounds are simply as shown in Fig. 17.

Fig. 17. Structure schematic for some pseudotetrahedral ferrous species.

A structure that we propose as a possibility for $\mathrm{Fe(biq)_3(NCS)_2}$ is a classical octahedral cation with the formula $\mathrm{Fe(biq)_3}^{2+}$ and for which the two thiocyanate counter anions are non-bonding. Each biquinoline molecule acts as a bidentate ligand in its bonding with the iron atom (see Fig. 18a). Because of strong steric interactions between biquinoline ligands, the Fe–N (imine) bonds within this structure are

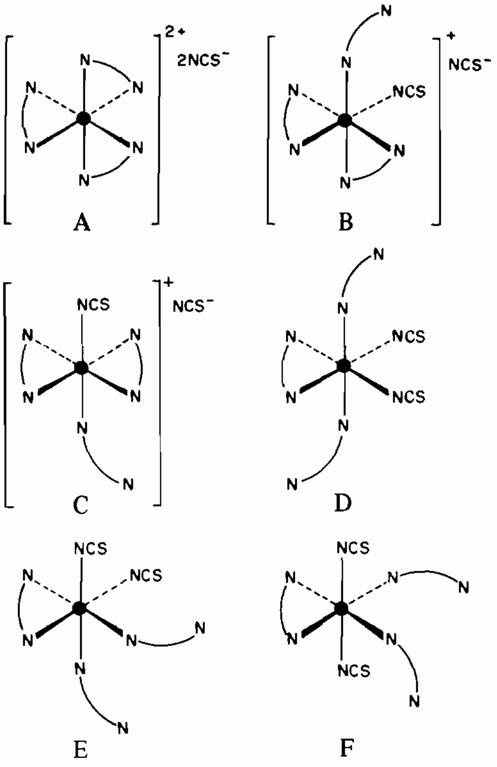

Fig. 18. Some structure possibilities for $\mathrm{Fe(biq)_3(NCS)_2}$.

expected to be substantially weaker and longer than those found in the corresponding 2,2′-bipyridine species, Fe(bipy)$_3^{2+}$. This leads to a weaker ligand field and results in a change in the iron ground state from the $S = 0$ found in Fe(bipy)$_3^{2+}$ to $S = 2$ as observed for [Fe(biq)$_3$] (NCS)$_2$ in the present work.

A number of other, some perhaps more bizarre, structure possibilities for Fe(biq)$_3$(NCS)$_2$ containing both uni- and bidentate biquinoline as well as both ionic and nitrogen coordinated thiocyanate anions come to mind and are pictured in Figs. 18b through 18f. We tend to reject b and c in that with two types of NCS$^-$ anions one would have expected a somewhat broader infrared spectrum in the C–N stretch region. Choice c is additionally strongly disfavored in view of its possessing two large diimine chelate ligands in the same plane. Molecular models clearly indicate that smaller unsubstituted diimines such as bipyridine and phenanthroline (much less biquinoline) are not likely to bond in the same plane owing to crowding of protons on different chelate rings. In accord with this, to our knowledge the published X-ray structure determinations of all [MII(bipy or phen)$_2$X$_2$] or [MIII(bipy or phen)$_2$X$_2^+$] species show *cis* 'X' groups. Structures d and e are also rejected in that since they contain *cis* NCS groups they are expected to exhibit a broader stretch region and possibly two C–N bands in strong contrast to the narrow infrared absorption observed herein. Finally, there is structure f, a choice not ruled out by the results of the present investigation. The trans NCS groups can lead to the C–N stretch behavior that we observe, a single narrow absorption. In addition the six-coordinate geometry pictured in f would seem to dispose the system to facile loss of 2 mol of biquinoline ligand and formation of a neutral pseudotetrahedral monomer with N-bonded thiocyanate groups. We conclude this section by stating that in consideration of all available data it is our opinion that structure possibilities.18a and 18f are the most viable. For the present, further discussion would be speculative.

Stability of [Fe(biq)$_3$] (NCS)$_2$

Stable compounds with the sterically hindered ligands 2,2′-biquinoline or 2,9-dimethyl-1,10-phenanthroline generally have four-coordinate metal chromophores. It is very rare that six-coordinate complexes with these ligands are formed. For example, during our study of Fe(2,9-dmp)(NCS)$_2$ [9], we prepared *cis*-Fe(2,9-dmp)$_2$(NCS)$_2$ in low yield. In contrast, tris-diimine iron complexes containing the diimines 2,2′-bipyridine or 1,10-phenanthroline are very stable. For example, to remove one mole of 2,2′-bipyridine from [Fe(bipy)$_3$] (NCS)$_2$ requires long term refluxing in a solvent or long term soxhlet extraction (usually several days) [17]. To remove the second mol of bipyridine, Fe(bipy)$_2$(NCS)$_2$ must be thermolyzed under vaccum at ~200 °C [11]. Our solubility studies of [Fe(biq)$_3$](NCS)$_2$ have shown that this system is very labile. 2 mol of the ligand can be easily extracted in organic solvents, such as benzene, by simply mixing the compound with solvent and allowing the mixture to stand at room temperature. Heating accelerates the reaction. Depending on the actual structure of [Fe(biq)$_3$] (NCS)$_2$, the steric crowding of three biquinoline molecules within the coordination sphere results in some metal–biquinoline bonds that are weak. The overall interactions between biquinoline and various organic solvents are apparently stronger than these weak metal–biquinoline bonds, and biquinoline is easily removed from Fe(biq)$_3$(NCS)$_2$. However, the situation is different with polar mixtures; in fact, [Fe(biq)$_3$] (NCS)$_2$ is isolated from a somewhat more polar mixture (water–acetone). The lack of specific interactions between polar solvents, such as water and biquinoline favors that biquinoline remains bonded to the metal center in spite of the strong steric interactions between the biquinoline molecules in the coordination sphere. It is expected that tris-biquinoline complexes with other transition metal ions will be isolated in the future.

Acknowledgements

We wish to acknowledge the support of the National Science Foundation, Division of Materials Research, Solid State Chemistry Programs, Grant No. DMR 8313710. We also thank G. A. Eisman for assistance in vibrating sample magnetometer measurements.

References

1 W. R. McWhinnie and J. D. Miller, *Adv. Inorg. Radiochem., 12* 135 (1969).
2 L. F. Lindoy and S. E. Livingstone, *Coord. Chem. Rev., 2,* 173 (1967).
3 D. B. Fox, J. R. Hall and R. A. Plowman, *Aust. J. Chem., 15,* 235 (1962).
4 H. S. Preston, C. H. L. Kennard and R. A. Plowman, *J. Inorg. Nucl. Chem., 30,* 1463 (1968).
5 J. R. Hall, C. H. L. Kennard and R. A. Plowman, *J. Inorg. Nucl. Chem., 28,* 467 (1966).
6 H. S. Preston and C. H. L. Kennard, *Chem. Commun.,* 708 (1967).
7 W. M. Reiff and B. W. Dockum, *J. Solid State Chem., 31,* 407 (1980).
8 C. B. Bargeron and H. G. Drickamer, *J. Chem. Phys., 55,* 3471 (1971).
9 B. W. Dockum and W. M. Reiff, *Inorg. Chim. Acta, 35,* 285 (1979).
10 C. M. Harris, S. Kokot, H. R. Patil, E. Sinn and H. Wong, *Aust. J. Chem., 25,* 1631 (1972).
11 B. W. Dockum and W. M. Reiff, *Inorg. Chem., 21,* 391 (1982).

12 W. M. Reiff, C. Nicolini and B. W. Dockum, *J. Phys. (Coll.), 40,* C2-230 (1979).

13 C. Cheng and W. M. Reiff, *Inorg. Chem., 16,* 2097 (1977).

14 N. N. Greenwood and T. C. Gibb, Mössbauer Spectroscopy', Chapman and Hall, London, 1971.

15 R. M. Golding, K. F. Mok and J. F. Duncan, *Inorg. Chem., 5,* 774 (1966).

16 C. D. Burbridge, D. M. L. Goodgame and M. Goodgame, *J. Chem. Soc. A,* 349 (1967).

17 E. Konig, K. Madeja and K. J. Watson, *J. Am. Chem. Soc., 90,* 1146 (1968).

18 N. N. Greenwood and T. C. Gibbs, 'Mössbauer Spectroscopy', Chapman and Hall, London, 1971, p. 50.

19 B. W. Dockum and W. M. Reiff, *Inorg. Chem., 21,* 1406 (1982).

20 W. M. Reiff, B. W. Dockum, M. A. Weber and R. B. Frankel, *Inorg. Chem., 14,* 800 (1975).

21 W. M. Reiff, *163rd National ACS Meeting, Inorganic Division,* Boston, Mass., 1972.

22 R. Ingalls, *Rev. Mod. Phys., 36,* 351 (1964).

23 W. M. Reiff, *Coord. Chem. Rev., 10,* 37 (1973).

24 K. K. Rao, M. C. W. Evans, R. Cammack, D. O. Hall, C. L. Thompson, P. J. Jackson and C. E. Johnson, *J. Biochem., 129,* 1063 (1972).

25 B. N. Figgis, 'Introduction to Ligand Fields', Interscience, New York, 1966; C. J. Balhausen, 'Intro to Ligand Field Theory', McGraw-Hill, New York, 1962.

26 D. Foster and D. M. L. Goodgame, *J. Chem. Soc.,* 268 (1965).

27 P. O. Kinell and B. Strandburg, *Acta Chem. Scand., 13,* 1607 (1959).

28 'Sadtler Handbook of Infrared Spectra, Sadtler Labs, Philadelphia, Pa. 1970.

29 P. R. Edwards, C. E. Johnson and R. J. P. Williams, *J. Chem. Phys., 47,* 2074 (1967).

30 A. K. Gregson and S. Mitra, *Chem. Phys. Lett., 3,* 528 (1969).

31 M. Gerloch, J. Lewis and R. C. Slade, *J. Chem. Soc. A,* 1422 (1969).

32 G. E. Chapps, S. W. McCann, H. H. Wickman and R. C. Sherwood, *J. Chem. Phys., 60,* 990 (1974).