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A Mössbauer Spectroscopy Investigation of Iron Chromophore Equivalence in Three Tetrairon Clusters

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The temperature dependence (1.6 to 300 K) of the zero field Mössbauer spectra of a series of tetrametal clusters demonstrates that the local iron environments are equivalent. Compounds investigated include the cubane-like $Fe_4(NO)_4(\mu_3\text{-}S)_4$, $Fe_4(NO)_4(\mu_3\text{-}S)_2(\mu_3\text{-}NC(CH_3)_3)_2$ *and the extensively studied black Roussin's salt,* $NH_4[Fe_4(NO)_7(\mu_3\text{-}S)_3]$. *Two types of iron environments can be distinguished from the X-ray structures of the latter two compounds, leading to an expectation of four line Mössbauer spectra. However, least-squares analyses of the high resolution, zero-field spectra for all three compounds result in a single quadrupole doublet with isomer shifts ranging from 0.05 to 0.15 mm/sec and quadrupole splittings (at 78 K) of 1.46, 1.30 and 0.91 mm/sec, respectively. High field (0 to 60 kG) spectra of the three compounds are indicative of diamagnetic species. The iron environments in the first two clusters exhibit axial symmetry* (η = 0) *with* V_{zz} *negative while for Roussin's salt* $\eta \sim 1$.

Introduction

Numerous compounds have been synthesized and introduced as possible model systems for the study of electronic behavior in the 4Fe–4S ferredoxin proteins. Common to these compounds is a cubane-like chromophore in various oxidation levels for which all of the iron sites have been shown to be equivalent by Mössbauer spectroscopy [1–4]. The ligation in these tetrairon clusters involves "non-innocent" species such as nitrosyl, carbonyl, *etc.* with identical metal–ligand chromophores at each metal site. However, there has been evidence presented for one of the naturally occurring proteins, the oxidized form of the high potential iron protein from *Chromatium*, that an inequivalence between two pairs of iron atoms may exist [5, 6]. Mössbauer spectroscopy has been used successfully to clarify structures of multinuclear iron carbonyl compounds [7, 8] which possess iron atoms in different coordination environments.

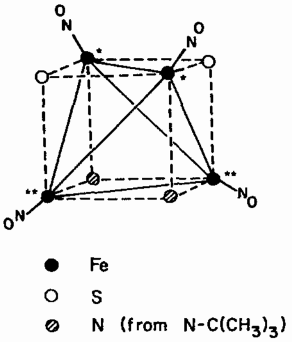

Fig. 1. Schematic representation of $Fe_4(NO)_4(\mu_3\text{-}S)_2(\mu_3\text{-}NC(CH_3)_3)_2$ * = $FeS_2N'N$ Chromophore, ** = $FeSN'_2N$ Chromophore.

As part of a further study of metal atom equivalence *versus* inequivalence in clusters containing non-innocent ligands, we present below zero and high field Mössbauer spectra for some related iron–sulfur–nitrosyl tetrametal clusters, two of which contain formally different metal–ligand chromophores.

Two of the clusters investigated are the recently prepared [9] $Fe_4(NO)_4(\mu_3\text{-}S)_4$ and $Fe_4(NO)_4(\mu_3\text{-}S)_2(\mu_3\text{-}NC(CH_3)_3)_2$ (Fig. 1), hereafter designated Fe_4S_4 and $Fe_4N_2S_2$ respectively. While the four iron positions in Fe_4S_4 are chemically identical (each iron is bonded to three triply bridging sulfur atoms and one nitrosyl group), two distinct iron chromophores can be seen in the second complex. Two of the iron atoms in $Fe_4N_2S_2$ are each bonded to two triply bridging sulfur atoms, a triply bridging nitrogen atom from the t-butyl amine function and one nitrosyl group ($FeS_2N'N$)* while the other two iron atoms are bonded to one sulfur, two amine nitrogens and one nitrosyl ($FeSN'_2N$)**. X-ray structure determinations [9] reveal that the Fe–S bond lengths are essentially identical in both clusters (2.219 ± 0.007 Å). The Fe–N′ bond lengths are significantly shorter (1.910 ± 0.007 Å), suggesting that the two types of iron chromophores in the amine modified cluster experience different electronic environments, a difference possibly observable via Mössbauer spectroscopy.

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TABLE I. Temperature Dependence of Zero Field Mössbauer Spectra.

Compound	T (K)	δ^a (mm/sec)	ΔE (mm/sec)	Linewidth^b (mm/sec)
$Fe_4(NO)_4(\mu_3\text{-}S)_4$	300	0.092	1.448	0.321
	195	0.117	1.461	0.316
	78	0.150	1.473	0.334
	4.2^c		1.461	
$Fe_4(NO)_4(\mu_3\text{-}S)_2\,\mu_3\text{-}NC(CH_3)_2$	300	0.093	1.307	0.285
	195	0.116	1.316	0.297
	78	0.141	1.326	0.321
	4.2^c		1.311	

^{a}Relative to natural iron metal. ^{b}Average value for two peaks. ^{c}Determined from near zero field spectra run at the Francis Bitter National Magnet Laboratory (see Fig. 4a + 5a). The remnant field of the Nb_3Sn solenoid causes some linewidth broadening.

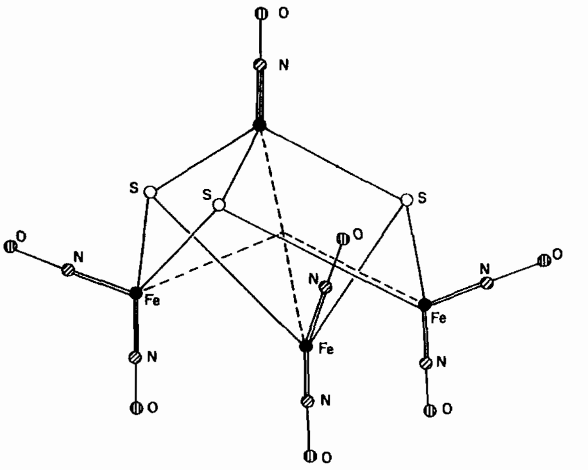

Fig. 2. Schematic representation of Roussin's black salt. $NH_4[Fe_4(NO)_7(\mu_3\text{-}S)_3]$.

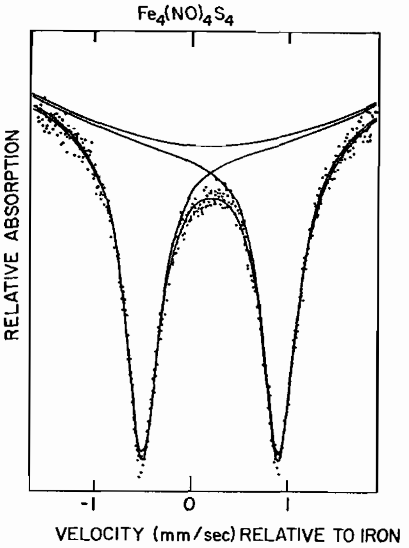

Fig. 3. Zero field Mössbauer spectrum of $Fe_4(NO)_4(\mu_3\text{-}S)_4$ at 78 K.

Work with the preceding compounds prompted us to reinvestigate Roussin's black salt, $NH_4[Fe_4(NO)_7(\mu_3\text{-}S)_3]$ (Fig. 2), which possesses similar iron chromophores. This monoanion has been the subject of many publications since its formulation in 1882 by Pawel [10] including two X-ray structure determinations [11, 12] and two Mössbauer studies [13, 14] and is, in fact, the product obtained upon sodium/mercury amalgam reduction of the present Fe_4S_4 system [12]. *Roussin's salt contains an apical iron atom in an environment formally identical to that found in Fe_4S_4 and provides an obvious basis of comparison to the present work.* This comparison is further warranted since one of the previous Mössbauer studies [14] claims to have distinguished the apical (Fe_A) and basal (Fe_B) iron atoms in the salt, although the initial Mössbauer study [13] does not claim to distinguish these environments. The results of our zero and high field Mössbauer spectroscopy for $NH_4[Fe_4(NO)_7(\mu_3\text{-}S)_3]$ are included below.

Experimental

Preparation of $Fe_4(NO)_4(\mu_3\text{-}S)_4$ and $Fe_4(NO)_4(\mu_3\text{-}NC(CH_3)_3)_2$

Both cluster compounds were prepared by the method of Gall, *et al.* [9]. Identification of the products was confirmed by infrared spectra (KBr pellet) consisting of a single nitrosyl band at 1780 cm^{-1} (s) for Fe_4S_4 and three nitrosyl bands at 1745(s), 1760(vs) and 1792 cm^{-1} (w) for $Fe_4N_2S_2$ as found previously [9]. The proton NMR spectrum of $Fe_4N_2S_2$ contained the expected sharp singlet at 1.47 ppm (*vs.* TMS). Mössbauer spectroscopy parameters of multiple preparations of both compounds were reproducible.

Preparation of $NH_4[Fe_4(NO)_7(\mu_3\text{-}S)_3]$

Roussin's black salt was prepared by the method of Brauer [15]. Infrared spectra (KBr pellet) containing three nitrosyl bands at 1708 (sh.w), 1745(s) and 1800 cm^{-1} (sh.w.) agreed with a published spectrum [12].

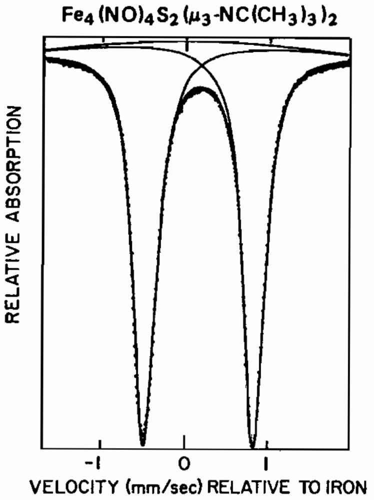

Fig. 4. Zero field Mössbauer spectrum of $Fe_4(NO)_4(\mu_3\text{-}NC(CH_3)_3)_2$ at 78 K. The continuous curves are least-squares fits assuming Lorentzian peak shapes.

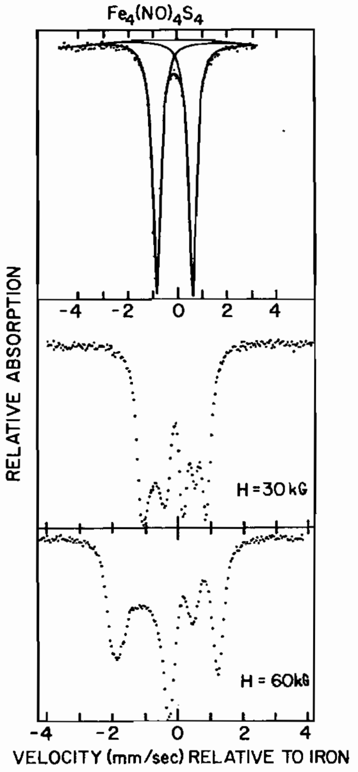

Fig. 5. Mössbauer spectra of $Fe_4(NO)_4(\mu_3\text{-}S)_4$ at 4.2 K in longitudinal magnetic fields of (a) ~0 kG, (b) 30 kG and (c) 60 kG.

Physical Methods

The details of the techniques and apparatus used for zero and high field Mössbauer spectroscopy and cryogenic susceptibility measurements have been reported previously [16].

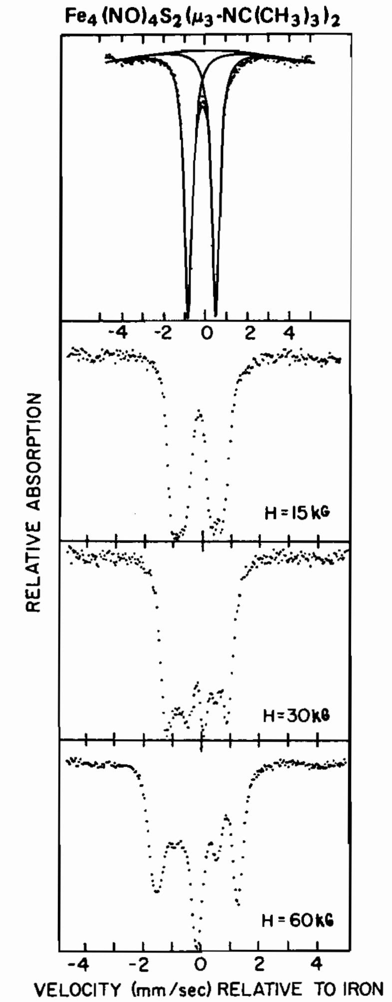

Fig. 6. Mössbauer spectra of $Fe_4(NO)_4(\mu_3\text{-}S)_2$ $(\mu_3\text{-}NC(CH_3)_3)_2$ at 4.2 K in longitudinal magnetic fields of (a) ~0 kG, (b) 15 kG, (c) 30 kG and (d) 60 kG.

Results and Discussion

The temperature dependence of the zero field Mössbauer spectra of $Fe_4N_2S_2$ has been determined over the range of 1.6 to 300 K and from 4.2 to 300 K for Fe_4S_4. Spectral parameters are reported in Table I. The 78 K zero field spectra shown in Figs. 3 and 4 are representative of these cubane-like tetrametal clusters. The spectra of Fe_4S_4 and $Fe_4N_2S_2$ are markedly similar (compare isomer shifts and quadrupole splittings), with each exhibiting a single, symmetric quadrupole doublet throughout the temperature range. Attempts to least-squares computer fit the spectra of $Fe_4N_2S_2$ assuming overlap of two quadrupole doublets have failed. In addition the absolute magnitudes of the linewidths and their temperature dependence are in no way remarkable. These results lead us to conclude that the iron sites in $Fe_4N_2S_2$ are, in fact, equivalent on a Mössbauer time scale and must be very similar in nature to those in the Fe_4S_4 cluster.

TABLE II. Mössbauer Parameters Obtained by Least Squares Analysis of 78 K Spectra of $NH_4[Fe_4NO)_7(\mu_3\text{-}S)_3]$.

Fitting Procedure	Iron Site[a]	δ^b (mm/sec)	ΔE (mm/sec)	Peak Area Ratio[c]	Text Designation
2 line fit, unconstrained	–	0.157	0.917	1.11:1	I
4 line fit, unconstrained	Fe_A	0.153	1.051	1.97:1	II
	Fe_B	0.162	0.835		
4 line fit, areas constrained in 3:1 ratio	Fe_A	0.243	0.889	3.00:1	III
	Fe_B	0.127	0.921		
Kostiner fit	Fe_A	0.265	0.802	3.03:1	IV
	Fe_B	0.126	0.895		
Kerler fit[d]	–	0.125	0.895		

[a] Fe_A: apical iron atom; Fe_B: basal iron atoms. [b] Relative to natural iron metal. [c] Area of Fe_B quadrupole doublet: area of Fe_A doublet. [d] Parameters listed are for the sodium salt at 150 K (ref. 13).

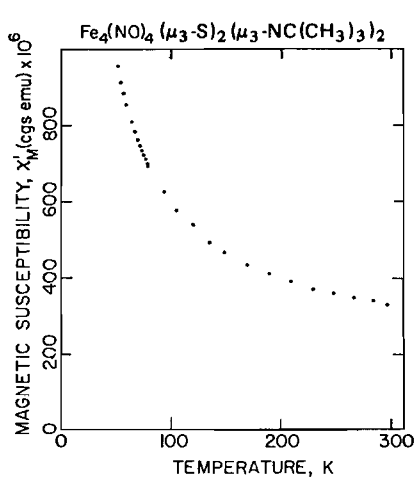

Fig. 7. χ'_M *vs.* T for $Fe_4(NO)_4(\mu_3\text{-}S)_2(\mu_3\text{-}NC(CH_3)_3)_2$ at 5 kG.

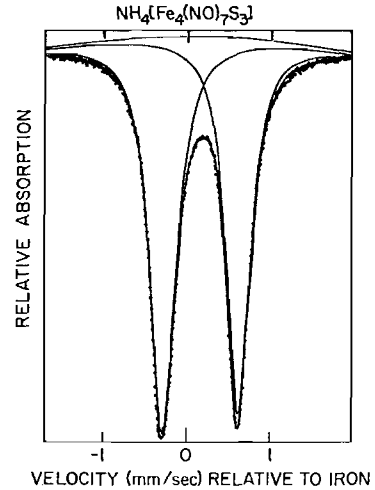

Fig. 8. Zero field Mössbauer spectrum of $NH_4[Fe_4(NO)_7(\eta_3\text{-}S)_3]$ at 78 K.

The field dependence of the spectra of Fe_4S_4 and $Fe_4N_2S_2$ (Figs. 5 and 6) provides further evidence that the four iron atoms in each cluster are experiencing equivalent environments. Again, it is seen that the high field spectra of Fe_4S_4 are essentially identical to those of $Fe_4N_2S_2$. In an applied field of 30 kG, the Mössbauer spectra (Figs. 5b and 6c) are resolved into the doublet–triplet pattern expected for a diamagnetic species with axial symmetry ($\eta = 0$). Because the triplet occurs at a higher energy (velocity) than the doublet, the sign of the principal component of the electric field gradient (V_{zz}) is *negative* [17]. A zero asymmetry parameter is readily predicted from the C_{3v} local iron site symmetry in Fe_4S_4. However, the iron site symmetry in $Fe_4N_2S_2$ is nominally C_S, producing an η of unity. *Therefore the t-butyl nitrogen and sulfur ligands are apparently sufficiently similar to produce comparable ligand fields at the iron nucleus,* resulting in $\eta = 0$ and essential metal atom equivalence for all sites in the $Fe_4N_2S_2$ cluster. The internal hyperfine field at the iron nucleus as determined from the splitting of the triplet [18] is zero for both tetrametal clusters, as expected for diamagnetic ground states. The small magnetic moment per metal atom measured over a temperature range of 300 to 50 K for both compounds is also consistent with a diamagnetic ground state. In Fe_4S_4 the moment per iron drops from 0.76 to 0.52 μ_B and in $Fe_4N_2S_2$ the moment decreases from 0.89 to 0.62 μ_B. However, both clusters exhibit a small degree of paramagnetic character as indicated by the increase in molar susceptibility with decreasing temperature (Fig. 7) rather than remaining strictly constant as expected for pure diamagnetism.

The zero field Mössbauer parameters for Roussin's black salt (Fig. 8) are presented in Table II. This table also lists the conflicting results of previously published Mössbauer studies. While the authors of the initial study [13] interpreted their results in terms of equivalent sites, Kostiner *et al.* [14] suggested that the Roussinate spectrum consisted of two overlapping quadrupole doublets arising from the differing apical and basal iron atoms. To justify this assumption, Kostiner, *et al.* noted that the linewidths of the absorption peaks reported by Kerler, *et al.* [13] increased (0.297 to 0.360 mm/sec) over a decreasing temperature range (298 to 150 K). This linewidth increase becomes somewhat less dramatic (and is not even monotonic) when one considers the full temperature range actually reported by Kerler, *et al.*: 0.312 to 0.36 mm/sec over a 341 to 150K range or an increase of 4.2×10^{-4} mm/sec K. This variation is still larger than that obtained by us of 1.9×10^{-4} mm/sec K [19].

We have redetermined the temperature dependence of the Mössbauer spectra for multiple preparations of Roussin's black salt in a cryostat with totally iron free (mylar) windows and employing a higher spectral sensitivity (fewer mm/sec/memory channel) than used previously. Kostiner, *et al.* had to account for background absorption of iron in their cryostat windows when computer fitting their spectral data [14]. Least squares analyses based upon a single quadrupole doublet in the Mössbauer spectra of multiple preparations of the ammonium salt gave consistently good fits (Table II, I). Attempts to fit the data as a four line spectrum resulted in either a divergent fit or a spectral fit whose parameters bore little resemblance to those values reported by Kostiner, *et al.* (Table II, II). A peak area ratio of 2:1 was obtained for this unconstrained fit. Only when the peak areas were constrained to have a 3:1 ratio (Table II, III) was it possible to reproduce the Kostiner parameters.

The increased isomer shift of the apical *versus* basal iron sites (Table II, IV) was justified by Kostiner, *et al.* on the basis of an earlier crystallographic (film) study [11] which found that the Fe_A–N bond was 0.10 Å shorter than the average Fe_B–N bond. The stronger Fe_A–N bond was considered indicative of $d\pi(Fe) \rightarrow \pi^*(NO)$ back donation, thus decreasing the s-election density at the apical iron nucleus relative to the basal iron nucleus. However, a more recent, higher resolution X-ray diffraction analysis [12] has shown that all seven Fe–N bond lengths in Roussin's black salt are identical within the mean reported (1.64 ± 0.02 Å), thus invalidating the preceding basis for a difference in isomer shifts between the presumed inequivalent iron chromophores. Perturbed Mössbauer spectra were obtained in the present study in an attempt to further clarify this situation.

The field dependence of the Mössbauer spectra of $NH_4[Fe_4(NO)_7(\mu_3\text{-}S)_3]$ is shown in Fig. 9. At 60 kG (Fig. 9d), the spectrum is resolved into the near symmetric, though overlapped, triplet–triplet form typical of an asymmetry parameter approaching

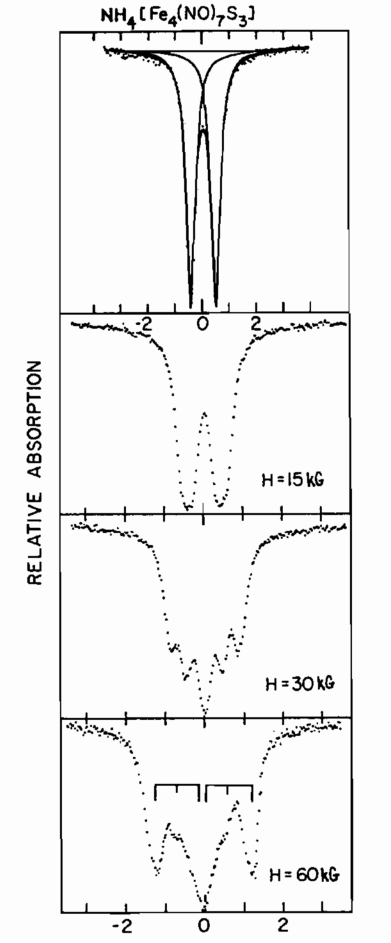

Fig. 9. Mössbauer spectra of $NH_4[Fe_4(NO)_7(\mu_3\text{-}S)_3]$ at 4.2 K in longitudinal magnetic fields of (a) ~0 kG, (b) 15 kG, (c) 30 kG and (d) 60 kG.

1.0 ($V_{zz} = -V_{yy}$, $V_{xx} = 0$). One interpretation is that the spectrum is indicative of a single iron environment with a large η value, *i.e.* 4 equivalent iron atoms. On the other hand, consideration of the Fe_A C_{3v} local symmetry predicts an $\eta = 0$ which would result in a perturbed spectrum identical to that shown in Fig. 5b assuming V_{zz} is negative (a reasonable assumption since the Fe_A chromophore is in the same ligand field environment as the iron chromophore in the Fe_4S_4 cluster). The $(NO)_2(\mu_3\text{-}S)_2$ ligation of the remaining three Fe_B atoms is expected, on a point charge basis, to result in $\eta \sim 1$ at these sites. Inequivalent iron sites in the Roussinate monoanion can then result in a perturbed spectrum similar to that of Fig. 9d, but with increased intensity at the middle line of the higher energy triplet arising from the overlap of $\eta \sim 1$ (times 3) with $\eta \sim 0$, $V_{zz} < 0$ (times 1) spectrum. We believe that the observed magnetically perturbed Mössbauer spectra do not allow for a clear cut choice between these two possibilities, especially in view of the high degree of overlap near zero velocity.

Conclusions

It appears that attempts to unequivocably observe iron site inequivalence in *non-innocent ligand* tetrametal clusters which contain iron atoms in formally different environments have proven unsuccessful *vis à vis* Mössbauer spectroscopy. While a simple electronegativity difference argument, supported by observed bond length data for $Fe_4N_2S_2$, suggests that sulfur and t-butyl nitrogen would produce ligand fields of different strengths and local symmetries, this is not observed to be the case in the $Fe_4N_2S_2$ cluster. The work of this laboratory, coupled with the most recent X-ray data, demonstrates that this same phenomenon occurs in Roussin's salt. Variant nitrosyl and sulfur ligation does not produce iron environments in the case of the Roussinate anion that are readily distinguishable via Mössbauer spectroscopy.

Acknowledgments

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17 The sign of V_{zz} was inadvertently and incorrectly reported to be positive in a recent abstract (*ACS National Convention, Miami Beach,* 1978).
18 $H_{effective} = H_{applied} + H_{internal}$; where H_{eff} can be calculated from the triplet splitting ($H_{eff} = 39.29\ \Delta_t$). Since $H_{eff} = H_{appl}$ as determined experimentally, $H_{int} = 0$.
19 Value reported is the average linewidth increase observed when four separate preparations of $NH_4[Fe_4(NO)_7(\mu_3\text{-}S)_3]$ were run between 300 and 78 K.