*Inorganica Chimica Acta*, 25 (1977) 91–96
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# Electronic Structure and Magnetic Properties of a Synthetic Molecular Oxygen Carrier: Spin-Only Triplet Behavior for Divalent Iron(II)

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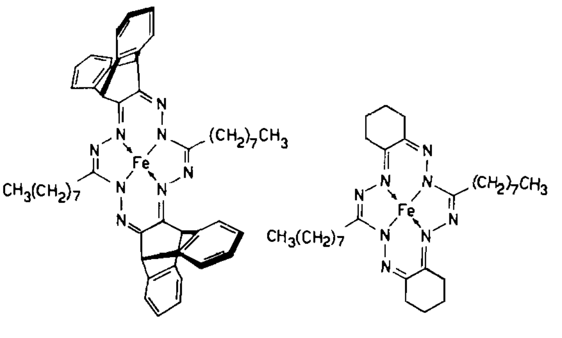
Received March 29, 1977

*The magnetic susceptibility of a four coordinate, approximately square planar iron(II) complex of a substituted octa-aza[14]annulene of known structure has been studied over the range 1.6 to 300 K. The compound contains an* $FeN_4$ *chromophore and exhibits essentially spin-only magnetic behavior* ($\mu_{eff}$ = 2.94 $\mu_\beta$ *at 300 K) to as low as 25 K. Below this temperature zero-field splitting is evident, D* ~ *14* $cm^{-1}$, *with the effective moment decreasing to 1.34* $\mu_\beta$ *at 1.6 K. Zero-field Mössbauer spectra have been measured over the range 300–4.2 K and this system as well as another less hindered analogue are found to have the largest quadrupole interactions (~4 mm/sec) yet reported for triplet iron(II) complexes. The Mössbauer spectra also suggest temperature dependence of the recoil free fraction (Goldanskii–Karyagin effect). The large quadrupole effect is consistent with either a* $^3B$ *or* $^3E$ *ground term (based on* $^3T_{2g}$ *of* $O_h$*) with negligible reduction of the electric field gradient by covalency effects. A reevaluation of the current use of Mössbauer spectroscopy data in distinguishing spin-triplet* versus *singlet iron(II) is made.*

## Introduction

There has been considerable interest in synthetic molecular oxygen carriers in an attempt to arrive at chemically viable models for hemoglobin. Some of these iron complexes have the ability to undergo reversible oxygenation both in the solid state and solution at ambient temperature. A good example of this kind of system is the so called "picket-fence" [1–5] tetraphenylporphinato iron(II). Other models have been capable of reversibly binding di-oxygen only in solution and at low temperatures. A complex of the latter type has been synthesized by Huff and Baldwin [6] and its molecular structure recently [7] determined by single crystal X-ray diffraction. The complex (I) as well as a less hindered analogue (II) are shown in Figure 1. These compounds are approximate square-planar iron(II) macrocycles based on octa-aza(14)annulene. In I, a deep (~4.5 Å) hydrophobic pocket [7] is formed by the steric hindrance provided by the n-octyl and 9,10-dihydroanthryl substituents. The less hindered II presumably more readily undergoes irreversible oxidation via the reaction:



I II

Figure 1. Schematic drawing of the substituted octa-aza[14]-annulene (I) and the less hindred analogue (II).

$$Fe(II) + O_2 \rightarrow Fe(II)O_2 + Fe(II) \rightarrow Fe(II)O{-}OFe(II) \rightarrow 2Fe(III)$$

where Fe(II) is the iron(II) macrocycle and the resulting ferric species are often thought to be oxo-bridged binuclear systems.

A common feature of the foregoing model systems is that they contain S = 1 iron(II) when there is no axial ligation. This is an unusual spin state for iron(II) and it has received little previous detailed characterization except for the cases of ferrous phthalocyanine and [8–10] certain pseudo-octahedral α-di-imine complexes such [11–13] as $Fe(phenanthroline)_2F_2 \cdot 4H_2O$. These compounds as well as other presumably spin triplet iron(II) systems in the literature are problematical in that their magnetic moments are considerably greater than the expected spin-only value, $\sqrt{8}$. For example $\mu_{eff}$ = 3.71 $\mu_\beta$ at 298K for ferrous phthalocyanine while for Fe(phenanthroline)$_2$F$_2$$\cdot$4H$_2$O $\mu_{eff}$ = 5.20 $\mu_\beta$ at 77K and 3.71 $\mu_\beta$ at 0.97K. For the latter compound, the moment at 77K is quite reasonable for a spin-quintet ground state although its Mössbauer parameters are clearly consistent with a $^3$A ground term. Complex I of this work is interesting in that it exhibits a room temperature magnetic moment close to the spin-only value for S = 1. In this article we present magnetic susceptibility and Mössbauer spectroscopy data bearing on the nature of its electronic ground state.

## Experimental

Complexes I and II were synthesized as previously described [6]. Owing to their extreme aerial instability, all manipulations were carried out in an inert atmosphere or under vacuum for polycrystalline powders. Near infrared–visible optical spectra were measured on a Cary-14 spectrometer for fluorinated hydrocarbon mulls. Mössbauer spectra were determined on a conventional constant acceleration spectrometer, operated in the time mode, using a 100 mC $^{57}$Co source in a rhodium metal matrix. These spectra were fit using a National Bureau of Standards program [14] to Lorentzian line shapes.

Variable temperature magnetic susceptibility measurements were made at Northeastern University on a Faraday balance composed of a Cahn RG electrobalance, a Varian model 4000 electromagnet with four inch constant force pole caps and a Janis Super Vari-Temp cryostat over the range 1.5 to 300 K for ten fields between 1.6 and 5 kG. Temperature measurement and control was typically of the order ±0.01 K, or better and was achieved using a Leeds-Northrup K-5 potentiometer and a Lake Shore Cryotronics Model DT-500 C set point controller respectively, in conjunction with a calibrated silicon temperature sensor diode, a ten micro-amp constant current source and an uncalibrated gallium arsenide control diode. Final temperature equilibration and stability were continuously monitored on a Leeds-Northrup Speedomax-XL 600 millivolt recorder that was used to read the error signal of the calibrated silicon diode after cancellation by the K-5 potentiometer. Temperatures below 4.2K were measured *via* the vapor pressure of helium using Wallace-Tiernan models FA-160 and 61-050 absolute pressure gauges, while pumping was precisely controlled with an L. J. Engineering model 329 vacuum regulator valve. Temperatures below 78K and to as low as 50K were also achieved using liquid nitrogen by pumping (Welch 1397) to well below the triple point on solid nitrogen. Both the vapor pressure of nitrogen and a calibrated silicon diode were used to monitor the temperature. An F. W. Bell model 610 Gaussmeter with a transverse Hall probe was used for measurement of magnetic fields.

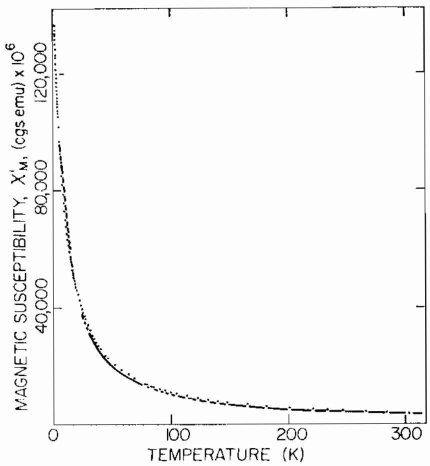


Figure 2. Temperature dependence of the molar susceptibility $\chi'_M$ for an applied field H$_0$ = 5.1 kG.

## Results

### *Magnetic Measurements*

Figure 2 shows the temperature dependence of the molar susceptibility ($\chi'_M$) of I over the range 300 to 1.6 K. The behavior is that expected for a simple paramagnet. No field dependence of $\chi'_M$ was observed for ten fields varying from 1.66 to 5.10 kG at 95 experimental temperatures. The curve super-imposed on the data points of Figure 2 is a best least squares fit to $\chi'_M$ for an axial zero field splitting D = +14 cm$^{-1}$, rhombic splitting parameter = 0.1 cm$^{-1}$, with g$_x$, g$_y$ and g$_z$ all close to 2.0 using the equation:

$$\chi_M = \frac{N\beta^2}{3\left\{1 + \exp\left(-\frac{D+E}{kT}\right) + \exp\left(-\frac{D-E}{kT}\right)\right\}} \times \left[\frac{g_z^2}{E} \times \left\{\exp\left(-\frac{D-E}{kT}\right) - \exp\left(-\frac{D+E}{kT}\right)\right\} + \frac{2g_x^2}{D+E}\left\{1 - \exp\left(-\frac{D+E}{kT}\right)\right\} + \frac{2g_y^2}{D-E}\left\{1 - \exp\left(-\frac{D-E}{kT}\right)\right\}\right] \quad (1)$$

The foregoing equation was derived by Birker [15] *et al.*, using the energy expressions given by Ballhausen [16].

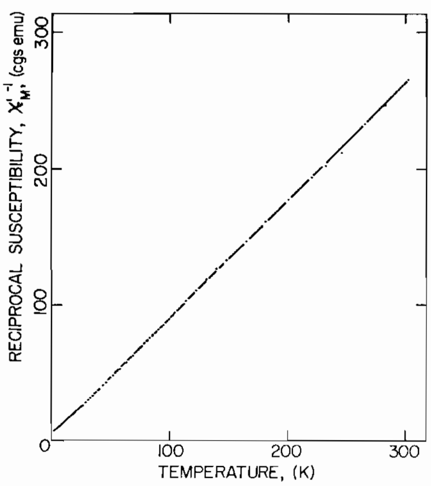


Figure 3. Temperature dependence of the reciprocal molar susceptibility, $\chi'^{-1}_M$.

Fits for negative values of D were rejected on the basis of what seem to be unrealistic values of $g_i$ and E, *e.g.* for $D = -11.5\ cm^{-1}$, $g_x = 2.77$, $g_y = 1.24$, $g_z = 1.61$ and $E = 2\ cm^{-1}$. This point will be discussed in greater detail subsequently.

In Figure 3, a plot of the reciprocal susceptibility shows that the material obeys a Curie–Weiss law. The straight line is a least squares fit of $\chi'^{-1}_M$ *versus* T for a Curie constant C = 1.16 emu/mol, $\mu_{eff} = 3.05$ $\mu_\beta$ and a paramagnetic Curie temperature $\theta = -5.97$. The small value of $\theta$ and agreement of the moment with that derived from solution measurements of the susceptibility (Evans NMR method) at ambient temperature are consistent with negligible intermolecular magnetic interaction. This is reasonable in view of the dilute nature of the compound and in particular the shielded environment of the metal ion, *i.e.* a pocket ~4.5 Å and large metal–metal distance [7].

The foregoing value of D is large and the effects of zero-field splitting are evident in the temperature dependence of $\mu_{eff}$, Figure 4 and some sample moment data, Table I. The room temperature moment is quite close to $\sqrt{8} \sim 2.83$ $\mu_\beta$, *i.e.* a simple spin triplet with apparently little or no orbital contribution. As the temperature is decreased there is a decrease in the moment corresponding to depopulation of the excited $m_s = \pm 1$ Kramers doublet assuming D is in fact positive.

### *Mössbauer Spectra*

Mössbauer spectra with Lorentzian fits for compound I are given in Figure 5 with the pertinent parameters in Table II. The most striking feature of these spectra is the very large, essentially temperature independent quadrupole splitting. This is the largest value of quadrupole splitting yet reported for an S = 1 iron(II) compound and its probable origin will be discussed subsequently. At 4.2 K, the quadrupole splitting

TABLE I. Sample Magnetic Moments.

| T(K) | $\mu_{eff}$ ($\mu_\beta$) |
|---|---|
| 302.90 | 2.97 |
| 265.69 | 3.01 |
| 220.59 | 3.01 |
| 164.72 | 2.99 |
| 131.21 | 2.97 |
| 104.80 | 2.97 |
| 90.64 | 2.95 |
| 78.56 | 2.94 |
| 52.04 | 2.92 |
| 38.06 | 2.88 |
| 27.24 | 2.81 |
| 19.92 | 2.71 |
| 14.49 | 2.58 |
| 11.63 | 2.46 |
| 8.42 | 2.30 |
| 6.02 | 2.11 |
| 4.25 | 1.90 |
| 3.63 | 1.79 |
| 2.87 | 1.65 |
| 2.37 | 1.54 |
| 2.14 | 1.48 |
| 1.93 | 1.43 |
| 1.84 | 1.40 |
| 1.74 | 1.37 |
| 1.63 | 1.34 |

TABLE II. Mössbauer Parameters[a].

| T | $\delta$ | $\Delta E$ | $\Gamma_1$ | $\Gamma_2$ | $H_1/H_2$ | $A_1/A_2$ |
|---|---|---|---|---|---|---|
| 300 | 0.11 | 4.04 | 0.26 | 0.26 | 1.13 | 1.10 |
| 78 | 0.19 | 4.13 | 0.28 | 0.28 | 0.98 | 0.97 |

[a] The Mössbauer parameters are given in mm/sec with $\delta$ relative to natural iron foil.

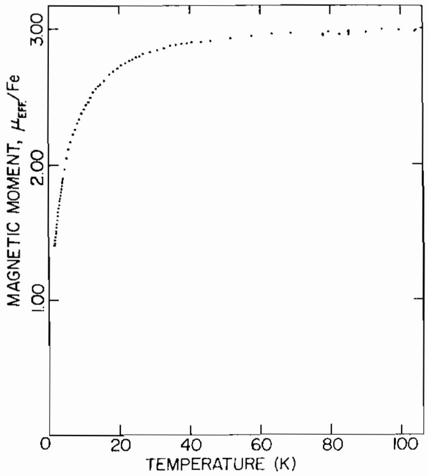


Figure 4. Temperature dependence of the effective magnetic moment, $\mu_{eff}$ ($\mu_\beta$).

TABLE III. Magnetic Moments and Zero-Field Splittings of Some Triplet ($d^6$) Complexes.

| Compound | T(K) | $\mu_{eff}$ ($\mu_\beta$) | D | Reference |
|---|---|---|---|---|
| Ferrous Phthalocyanine | 1.25 | 0.64 | 64–70 | 8, 10 |
| $KCo(3\text{-prbi})_2 \cdot 2H_2O$ | 1.68 | 0.69 | 54 | 15, 20 |
| Complex I | 1.63 | 1.34 | 15 | This Work |
| $Fe(di\text{-}imine)_2X_2 \cdot nH_2O$ | 1.40 | 2.99–4.09 | 2–3 | 13 |

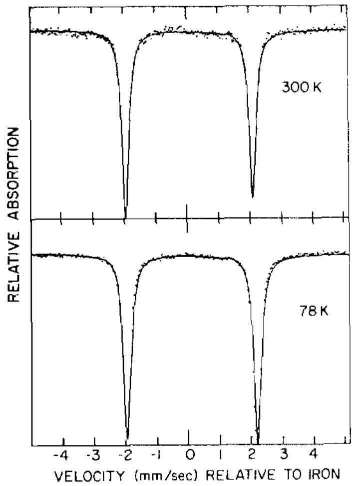


Figure 5. Zero-field Mössbauer spectrum of Complex (I) at 300 and 78 K.

of I is 4.11 mm/sec while that of the less hindered analog II, is comparable at 3.76 mm/sec. The isomer shift values in conjunction with the foregoing magnetic moment data clearly demonstrate the spin triplet nature of compound I. However, it should be emphasized that these data taken separately do not unequivocally show S = 1 and we will consider this problem in relation to other triplet ferrous systems.

The spectral line widths (Γ) are nearly equal and relatively narrow. There is no evidence of relaxation broadening or hyperfine splitting at low temperatures. The behavior is that expected of a rapidly relaxing paramagnet. Further inspection of the spectra of Figure 5 and Table II shows amplitude asymmetry at room temperature that approaches unity at *ca.* 78 K. This type of temperature dependence suggests anisotropy of the recoil free fraction (Goldanskii–Karyagin effect) [17]. The intensity ratio approaches one as the lowest energy (symmetric) vibrational state is populated at low temperatures. Vibrational anisotropy is not unexpected for a square-planar environment which in the present case corresponds to four in-plane nitrogen atoms and of course no axial ligands. The Fe–N distances [7] (1.826 Å and 1.846 Å) of the present S = 1 system are considerably shorter than those (1.893 to 2.166) observed for a number of spin-singlet, octahedral ferrous complexes. This is consistent with very strong in-plane bonding and vibrational anisotropy.

## Discussion

The temperature independence of the quadrupole splitting for compound I can be rationalized as follows. The energy separation, Δ, between the ground and first excited state of the complex is approximately related to the zero field splitting parameter D by the equation, $D = \lambda^2/_\Delta$. As in the case of ferrous phthalocyanine [8], we assume $\lambda_o = 200$ $cm^{-1}$ for a ‘free” spin-triplet ferrous ion and of the order 25% reduction in the complex ($\lambda \sim 150$ $cm^{-1}$). Then for a D value of ~15 $cm^{-1}$, Δ ~1500 $cm^{-1}$ or a relatively large orbital separation leading to an essentially temperature independent quadrupole splitting.

At this stage, it is worthwhile to point out a rough correlation of the limiting low temperature value of $\mu_{eff}$ with $|D|$. A survey of the literature for all of the available low temperature magnetic data of triplet ground state $d^6$ complexes is given in Table III. The first three entries can be compared directly as they are square planar $MN_4$ complexes [7, 17, 18] while the last corresponds to pseudo-octahedral geometry. It is evident that $\mu_{eff}$ decreases with increasing $|D|$ although for the last entry the ground state apparently has a large g value resulting in even larger values of $\mu_{eff}$ through “mixing-in” of excited quintet levels [13]. It is important to realize that the sign of D is not unequivocably determined from various fits to powder susceptibility data. This requires single crystal anisotropy and/or fits to the temperature dependence of the esr spectrum (D/E) both of which were unavailable for the present work. Although our magnetic data suggest that a singlet level is lowest in energy, this may be either the $m_s = 0$ $(D > 0)$ or one of the components of $m_s = \pm 1$ $(D < 0)$. The removal of the degeneracy of the foregoing Kramers doublet requires an additional non-axial ligand field component, E. This could arise from deviation from local $D_{4h}$ symmetry with the unequal Fe–N bond lengths [7] (1.846 Å and 1.826 Å) and N–Fe–N bond angles (83.8° and 96.2°) of complex I clearly suggesting this possibility. In so far as bond distances and angles are used as criteria, ferrous phthalocyanine [19] and

TABLE IV. Mössbauer Parameters for Some S = 0 and S = 1 Ferrous Compounds.

| Compound | T(K) | $\delta^a$ | $\Delta E$ | Spin | Reference |
|---|---|---|---|---|---|
| Complex I | 300 | 0.11 | 4.04 | 1 | This Work |
|  | 78 | 0.19 | 4.13 |  |  |
| Fe(phthalocyanine) | 300 | 0.26 | 2.02 | 0 | 9 |
|  | 78 | 0.33 | 1.97 |  |  |
| Fe(phthalocyanine)(pyridine)$_2$ | 300 | 0.46 | 2.62 | 1 | 23 |
|  | 78 | 0.56 | 2.69 |  |  |
| Fe(tetra-phenylporphyrin)(pyridine)$_2$ | 78 | 0.41 | 1.15 | 0 | 24 |
| Fe(tetra-phenylporphyrin)(piperidine)$_2$ | 77 | 0.50 | 1.44 | 0 | 21 |
| Fe(tetra-phenylporphyrin) | 300 | 0.42 | 1.52 | 1 | 21 |
|  | 77 | 0.50 | 1.51 |  |  |
| [Fe(15-ane $N_4(NO_2)$)]$PF_6$ | 300 | 0.23 | 0.40 | 1 | 25 |
| [Fe(15-ane $N_4(CN)_2$] | 300 | 0.38 | 1.44 | 0 |  |
| [Fe(phenanthroline)$_3$] $(ClO_4)_2$ | 300 | 0.31 | 0.15 | 0 | 26 |
| [Fe(phenanthroline)$_2F_2$]$\cdot 4H_2O$ | 300 | 0.24 | 0.32 | 1 | 13 |
|  | 78 | 0.25 | 0.29 |  |  |
| Fe(phen-2-carbothioamide)$Cl_2 \cdot H_2O$ | 300 | 0.26 | 0.53 | 1 | 27 |
|  | 78 | 0.22 | 0.53 |  |  |
| Fe(phen-2-carbothioamide)$Cl_2 \cdot H_2O$ | 300 | 0.25 | 1.28 | 0 | 27 |
|  | 78 | 0.23 | 1.28 |  |  |

$^a$mm/sec, relative to natural iron.

ferrous tetraphenylporphyrin [21] have local environments that are much closer to $D_{4h}$ symmetry with metal ligand distances and angles of 1.927 Å (89.1° and 90.9°) and 1.972 Å (90.01°) respectively. Unfortunately, there are no detailed low temperature magnetic data available for the preceding tetraphenylporphyrin system.

The magnitude and sign of the quadrupole splitting is best considered in terms of the possibile ground terms for a triplet ferrous system in conjunction with the corresponding nonbonding electron populations and the respective expectation values for the principle component of the electric field gradient tensor. These are: $^3A_2$ based on $^3T_{1g}$ of $O_h$ ($\xi^2\eta^2\epsilon^1\rho^1$, $V_{zz} = 0$), $^3B_2$ based on $^3T_{2g}$ of $O_h$ ($\xi^2\eta^2\zeta^1\theta^1$, $V_{zz} = -8/7\ q\langle r^{-3}\rangle_{3d}$) and $^3E$ based on $^3T_{2g}$ of $O_h$ ($\theta^2(\eta\xi)^3\zeta^1$), $V_{zz} = -10/7\ q\langle r^{-3}\rangle_{3d}$ where $\xi = d_{yz}$, $\eta = d_{xz}$, $\zeta = d_{xy}$, $\theta = d_{z^2}$ and $\epsilon = d_{x^2-y^2}$, the real one-electron d orbitals.

The $^3A_2$ term is clearly incompatible with the large quadrupole splitting we observe. A $^3E$ can also arise from $^3T_{1g}$ of $O_h$ but it has been noted [13] that this will also result in zero contribution to the electric field gradient. One is then left with the two terms arising from $^3T_{2g}$ of $O_h$, both of which lead to a large *negative* electric field gradient. In the limit of very strong in-plane bonding one expects $^3B$ or possibly even the $^3E$ (the $d_{z^2}$ orbital lowest in energy). The very short Fe–N distances suggest this situation. Ferrous phthalocyanine is thought to have a ground state non-bonding electron configuration corresponding to a $^3B$ term. However, a *positive* quadrupole interaction is observed [9] presumably due to a positive covalence contribution from the in-plane bonding to the total electric field gradient. One is then left with the conclusion that for I either the ground term is $^3B$ as with ferrous phthalocyanine and covalency effects are less or the ground term is $^3E$ corresponding to an even larger negative nonbonding contribution which covalence effects do not outweigh. For a $^3B$ ground term, as many as six spin-allowed, single electron, ligand field (d–d) transitions are possible while for a genuine $^3E$ only five can occur. Our near-infrared–visible spectrum of a fluorocarbon mull of I showed only three of what are undoubtedly ligand field bands at 5260 cm$^{-1}$, 6450 cm$^{-1}$ and 7700 cm$^{-1}$ and strong charge transfer absorption above 8300 cm$^{-1}$ (1200 mu). Unfortunately, there is no easy way of determining whether these originate from a $^3B$ or $^3E$ ground term and little can be concluded from the spectrum. Hence, we summarize this section by stating that the ground term is a $^3B_2$ or a $^3E$ with the very large quadrupole splitting and extremely strong in-plane bonding of the system perhaps favoring the latter term.

In view of the results of this investigation and the fact that there are now a number of Mössbauer studies of S = 0 and S = 1 iron(II) systems in the literature, we conclude with some brief observations concerning the utility of Mössbauer spectroscopy in distinguishing the foregoing spin states of iron. It is usually easy to recognize high spin ferrous (S = 2) as opposed to low-spin (S = 0) in terms of the large difference in chemical isomer shift. This difference can vary from ~0.4 to ~1 mm/sec depending on the coordination number and the nature of the metal–ligand bond which will in turn depend on the specific ligands involved [22]. On the other hand the difference in $\delta$ is not nearly as large for singlet and triplet ferrous. In table IV we have assembled the isomer shifts ($\delta$) and quadrupole splittings ($\Delta E$) for a number of such systems. Inspection of the table brings out two important points. The first is that the value of $\Delta E$ can vary over a considerable range for *both* S = 0 and S = 1 iron(II). Of greater importance, it is seen that the isomer shifts for these two spin states are indeed quite similar or in a few cases $\delta$ of the S = 1 analogue is only slightly larger than that of the corresponding S = 0. On the basis of literature data available, a similar comment can be made concerning S = 3/2 *versus* S = 5/2 ferric. As noted previously, matters are further complicated by the fact that many triplet systems have effective moments considerably in excess of the spin only value. In addition, low spin iron(II) compounds can exhibit moments as high as ~1 $\mu_B$ from second order Zeeman contributions to $\chi'_M$. Thus the use of zero-field Mössbauer data in conjunction with ambient to liquid nitrogen temperature magnetic measurements does not allow for reliable, unequivocable ground state assignments in the case of singlet *versus* triplet ferrous. The preceding points seem to have been overlooked in the literature. We emphasize that very low temperature magnetic and Mössbauer spectroscopy measurements capable of discerning zero-field splitting effects are a necessity in this context.

## Acknowledgements

W. M. Reiff acknowledges the support of the National Science Foundation, Division of Materials Research, Solid State Chemistry Program, Grant No. DMR 75-13592A01. He also acknowledges the partial support of the Research Corporation and H. E. W. Grant No. RR 07143. Jack E. Baldwin acknowledges support by the National Science Foundation and the National Institutes of Health. Finally, the authors wish to express their appreciation to the Francis Bitter Magnet Lab. sponsored by the NSF for use of its high field Mössbauer spectroscopy facilities.

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