

On the Nature of the Spin Ground State of Iron(II) in $\text{Fe}(2,9\text{-di-CH}_3\text{-phenanthroline})_2(\text{NCS})_2$

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The temperature dependence of the zero field Mössbauer spectrum and magnetic susceptibility of $\text{Fe}(2,9\text{-di-CH}_3\text{-phenanthroline})_2(\text{NCS})_2$ over the range 1.8 to 300 K show that the complex contains spin quintet iron(II) at all temperatures. The ligand is apparently to the weak field side of the 'crossover point' and contrary to the results of a previous study there is no evidence of a transition to a lower multiplicity (triplet or singlet) ground state. The observed decrease of the magnetic moment ($4.81 \mu_B$ at 302 K to $3.48 \mu_B$ at 1.82 K) is consistent with zero field splitting ($|D| \sim 5 \text{ cm}^{-1}$) of the ground spin manifold.

Introduction

Bargeron and Drickamer [1] reported the pressure dependence of the Mössbauer spectrum of $\text{Fe}(2,9\text{-di-CH}_3\text{-phenanthroline})_2(\text{NCS})_2$ at room temperature. Their high pressure cell required the use of micro samples which were further diluted in boron, seven: one. Hence in their study, they used samples enriched in iron-57 in order to obtain spectra of acceptable signal to noise. At ambient temperature and pressure, they obtained a spectrum consisting of two sets of transitions. One set was attributed to a high spin ($S = 2$) doublet, while the second doublet was thought to correspond to a lower spin ($S = 0$ or $S = 1$) iron(II) phase. The values of the Mössbauer parameters that they obtained (relative to iron metal) are: most intense doublet, $\delta = 1.04 \text{ mm/sec}$, $\Delta E = 1.28 \text{ mm/sec}$; less intense 'lower spin' doublet, $\delta = 0.33 \text{ mm/sec}$, $\Delta E = 0.75 \text{ mm/sec}$. The parameters of the former are clearly indicative of high spin iron(II). However, those of the latter doublet are not unreasonable for $S = 5/2$ iron(III) as well as $S = 0$ or $S = 1$ iron (II). To our knowledge, there have been no previous magnetic susceptibility studies of $\text{Fe}(2,9\text{-di-CH}_3\text{-phenanthroline})_2(\text{NCS})_2$. In the present study, we present both susceptibility and Mössbauer spectroscopy results bearing on the temperature dependence

of conversion (if any) of $\text{Fe}(2,9\text{-di-CH}_3\text{-phenanthroline})_2(\text{NCS})_2$ from a high to low spin phase.

Experimental

The sample of $\text{Fe}(2,9\text{-di-CH}_3\text{-phenanthroline})_2(\text{NCS})_2$ studied was prepared by the method of Bargeron and Drickamer [1] using the stoichiometric ratio of natural iron and ligand, 2,9-di- CH_3 -phenanthroline (hereafter 2,9-dmp). The result of chemical analysis of the product is %C = 61.22, %H = 4.11, %N = 14.28 (calculated); %C = 61.07, %H = 4.17, %N = 13.67 (observed). Mössbauer spectra at 300 and 78 K were obtained with base line count $>6 \times 10^6$ ensuring adequate signal to noise and 'good' statistics for Lorentzian fitting (Figs. 1(a) and 1(b)). The source was 100 milli-Curie ^{57}Co on rhodium metal. Further details of the magnetic susceptibility and zero field Mössbauer spectroscopy measurements have been published elsewhere [2]. All temperature measurements and control were based on silicon ($H_0 = 0$) or gallium arsenide diode ($H_0 \neq 0$) thermometry.

Results and Discussion

As can be seen in Figs. 1a and 1b, only one quadrupole doublet is seen at both 300 and 77 K. The values of δ and ΔE measured in this work (see Table I) correspond to high spin ($S = 2$), pseudooctahedral iron(II) at 300 and 77 K, and no spin state change ($S = 2 \rightarrow S = 1$, $S = 2 \rightarrow S = 0$, or $S = 1 \rightarrow S = 0$) appears to occur in this temperature range. Our parameters agree well with those for the most intense ($S = 2$) doublet of Bargeron's and Drickamer's Mössbauer spectrum of $\text{Fe}(2,9\text{-dmp})_2(\text{NCS})_2$ at 300 K. These authors did not report the parameters for their spectrum at 77 K.

In an effort to see if any of the preceding spin state changes occur at even lower temperatures, zero field Mössbauer spectra were determined at 4.2 and $\sim 1.8 \text{ K}$ (Figs. 1c and 1d). The parameters are given in Table I. Clearly, there is still no evidence of a spin

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TABLE I. Mössbauer Parameters for $\text{Fe}(2,9\text{-dmp})_2(\text{NCS})_2$.

Compound	T	$\delta^{a,b}$	ΔE_Q	Γ_1	Γ_2	Γ_1/Γ_2	A_1/A_2	χ^2 (chisquare)
$\text{Fe}(2,9\text{-dmp})_2(\text{NCS})_2$	300	1.033	1.237	0.293	0.299	0.979	1.031	262.14
	78	1.152	1.560	0.354	0.343	1.032	1.031	134.68
	4.20	1.177	1.678	0.403	0.414	0.9734	0.986	189.47
	1.80	1.176	1.678	0.469	0.485	0.9670	1.011	180.74

^aRelative to iron foil at 300 K. ^bSubscript 1 refers to peak at lower energy, subscript 2 refers to peak at higher energy.

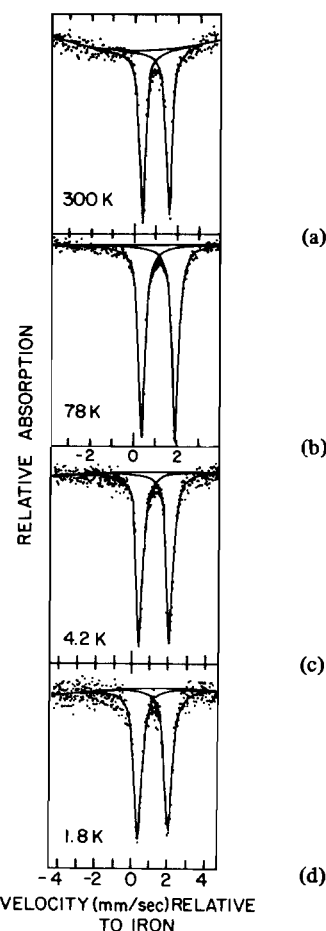


Fig. 1. a) Mössbauer spectrum of $\text{Fe}(2,9\text{-Di-CH}_3\text{-Phen})_2(\text{NCS})_2$ at 300 K. b) Mössbauer spectrum of $\text{Fe}(2,9\text{-Di-CH}_3\text{-Phen})_2(\text{NCS})_2$ at 77 K. c) Mössbauer spectrum of $\text{Fe}(2,9\text{-Di-CH}_3\text{-Phen})_2(\text{NCS})_2$ at 4.20 K. d) Mössbauer spectrum of $\text{Fe}(2,9\text{-Di-CH}_3\text{-Phen})_2(\text{NCS})_2$ at 1.80 K.

state change in accord with magnetic susceptibility results to be discussed subsequently. Unlike $\text{Fe}(4,7\text{-dimethyl-1,10-phenanthroline})_2(\text{NCS})_2$ [3, 4] and $\text{Fe}(4\text{-methyl-1,10-phenanthroline})_2(\text{NCS})_2$ [5] or $\text{Fe}(\text{phenanthroline})_2(\text{NCS})_2$ as well as the corresponding bipyridine analog [7], no evidence of a change in metal ion spin multiplicity with temperature is found

TABLE II. Sample Moment Data.

T(K)	$\mu(\mu_B)$	T(K)	$\mu(\mu_B)$
302.82	4.80	27.67	4.58
265.51	4.78	23.80	4.54
188.47	4.76	21.58	4.50
104.32	4.77	20.37	4.49
99.73	4.76	19.49	4.47
94.97	4.76	18.32	4.46
90.19	4.76	17.11	4.44
85.08	4.76	15.63	4.39
79.98	4.76	14.46	4.38
74.65	4.75	13.05	4.36
69.38	4.74	11.38	4.28
66.74	4.75	10.48	4.26
63.94	4.75	9.09	4.23
61.14	4.74	7.87	4.23
55.24	4.72	6.84	4.27
53.91	4.55	5.38	4.18
52.27	4.70	4.20	4.03
49.49	4.73	4.00	4.02
46.60	4.68	3.76	4.00
44.32	4.68	3.51	3.96
42.15	4.66	3.25	3.93
39.87	4.65	3.00	3.88
37.58	4.65	2.73	3.84
35.26	4.62	2.49	3.72
33.13	4.59	2.25	3.66
30.89	4.59	2.04	3.59
29.34	4.59	1.82	3.48
29.18	4.84		

for $\text{Fe}(2,9\text{-dmp})_2(\text{NCS})_2$. For the preceding complexes, such transformations are generally evident and often near complete for $T \gtrsim 100$ K on Mössbauer spectroscopy and magnetic susceptibility time scales. The results of Barger and Drickamer can be explained as either (a) due to trace impurities whose presence is enhanced in the iron-57 enriched sample spectra, or (b) the existence of a structural polymorph of $\text{Fe}(2,9\text{-dmp})_2(\text{NCS})_2$ that does exhibit a spin state change. We believe that explanation (a) is favored, although (b) cannot be unequivocally ruled out from the results of the present work. It appears that owing to steric hindrance effects, the ligand 2,9-

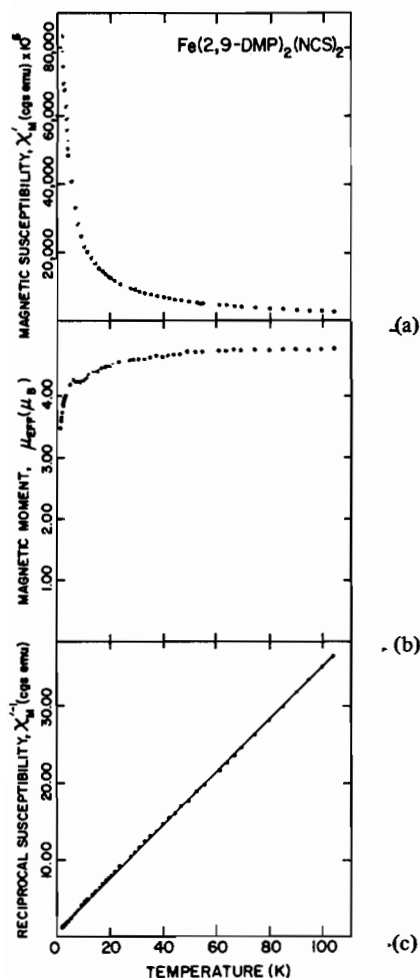


Fig. 2. a) Magnetic susceptibility vs. $T(K)$ for $\text{Fe}(2,9\text{-dmp})_2(\text{NCS})_2$, $H_0 = 5.10$ kG. b) Magnetic moment vs. $T(K)$ for $\text{Fe}(2,9\text{-dmp})_2(\text{NCS})_2$, $H_0 = 5.10$ kG. c) Reciprocal magnetic susceptibility vs. $T(K)$ for $\text{Fe}(2,9\text{-dmp})_2(\text{NCS})_2$, $H_0 = 5.10$ kG, solid line is a least squares computer fit for the Curie Law given in the text.

dimethyl-1,10-phenanthroline is sufficiently far away from the spin crossover point toward the weak ligand field region as to result in a ground spin quintet at all temperatures.

The foregoing conclusion based on Mössbauer spectroscopy is further supported by the results of a study of the temperature dependence of the molar susceptibility. The magnetic susceptibility was determined over the field range 1.60 to 5.10 kG. Some sample moment data for $H_0 = 5.10$ kG are given in Table II. The susceptibility and moment behavior (Figs 2a and 2b) are unremarkable and give no evidence of a change in spin state. The material obeys a Curie-Weiss law (Fig. 2c), with least squares computer fit of χ_M^{-1} yielding a Curie constant, $C = 2.90$ emu/mol, $\mu_{\text{eff}} = 4.82$ and $\theta = -2.39$ K. The observed decrease in magnetic moment at very low

temperatures ($< \sim 30$ K) can be explained in terms of zero field ($|D| \sim 2$ to 5 cm^{-1}) splitting of the ground spin quintet.

Di-methyl substitution of phenanthroline at the 2,9 positions is expected to increase the ligand's sigma donation basicity through positive (electron releasing) inductive and resonance effects. This should increase the spin pairing ability of the ligand from the point of view of increased ligand field strength, *i.e.* value of $10Dq$ relative to average spin pairing energy. This increased basicity is supported via pK_a measurements [8]. On the other hand, 2,9 substitution is expected to have the maximum steric effect on the Fe-N ligation, increasing this distance and decreasing π delocalization and spin pairing ability. The present investigation suggests that the latter steric effect dominates at all temperatures for ambient pressure in the case of $\text{Fe}(2,9\text{-dmp})_2(\text{NCS})_2$.

To conclude, we mention that the small limiting ($T \rightarrow 0$ K) value of the quadrupole splitting is indicative of an orbital doublet ground state, *i.e.*, 5E ground term. This situation is somewhat less common than the usual observation of a non degenerate, 5A or 5B ground term. Thus for example [3], the quadrupole splitting of $\text{Fe}(4,7\text{-dmp})_2(\text{NCS})_2$ at 121 K is 3.14 mm/sec undoubtedly corresponding to one of the latter non degenerate ground terms. We are currently further investigating the nature of the ground state of $\text{Fe}(2,9\text{-dmp})_2(\text{NCS})_2$ via Mössbauer spectroscopy in applied fields and the results of this work will be the subject of future publication.

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