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Magnetic Characterization of the Linear Chain Polymer Bis Hydrazine Ferrous Chloride $Fe(N_2H_4)_2Cl_2$

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Cryomagnetic studies of the linear chain polymer bis hydrazine ferrous chloride, $Fe(N_2H_4)_2Cl_2$, indicate little if any magnetic interaction between Fe(II) centers. The exchange pathways, two N–N bridge groups are apparently too long. Significant zero field splitting of the single ion ground spin quintet is however evident in the low temperature moment data.

Introduction

The bis-hydrazine metal(II) halides, $M(N_2H_4)_2Cl_2$, were first prepared in 1908 by Franzen and von Mayer [1]. Little further work was reported until 1962 when Braibante, Ferrari and Lanfredi [2] identified these complexes as linear chain polymers with *bridging bidentate hydrazine molecules*, via X-ray diffraction. In systematic infrared studies of hydrazine complexes, Sacconi and Sabatini [3] confirmed the bridging hydrazine structure.

The detailed crystal structure of the zinc isomorph was performed by Ferrari, Bagliardi, and Bigliardi [4]. In this system, the four nitrogens of the hydrazine molecules are coplanar with the metal. The halogen atoms lie in the plane normal to that of the nitrogen atoms, trans to each other. Figure 1 shows the local structure including bond angles and distances, while Fig. 2 shows articulation of the local

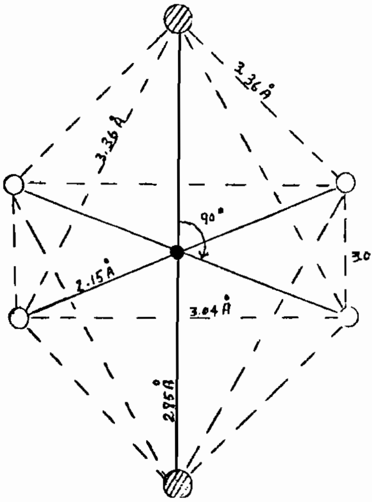

Fig. 1. Local coordination of the ZnN_4Cl_2 chromophore of $Zn(N_2H_4)_2Cl_2$; ●, Zn; ○, N; ⊜, Cl.

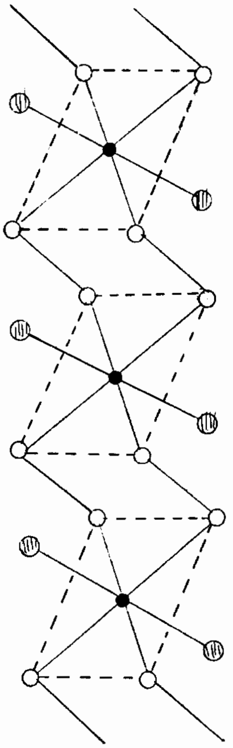

Fig. 2. Schematic representation of the linear chain polymer, $[M(N_2H_4)_2X_2]_n$; ●, metal; ○, N; ⊜, Cl.

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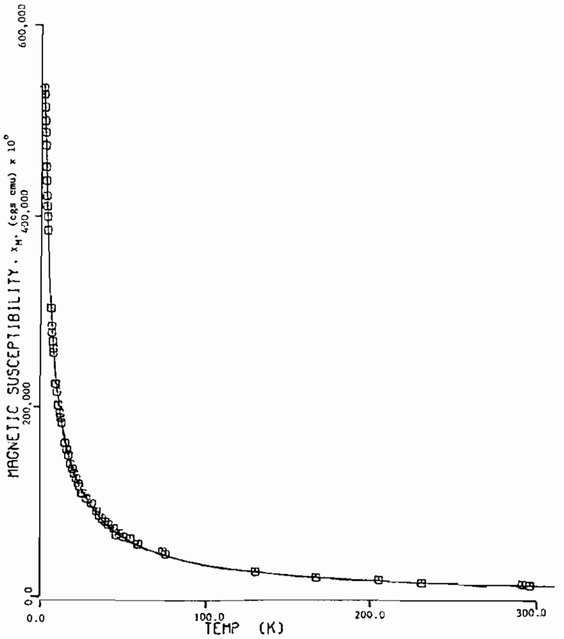

Fig. 3. Magnetic susceptibility *versus* temperature for $Fe(N_2H_4)_2Cl_2$. Solid curve represents least squares fit for zero field splitting with the parameters shown; D = 4.22 cm^{-1}, gx = 1.16, gz = 3.06.

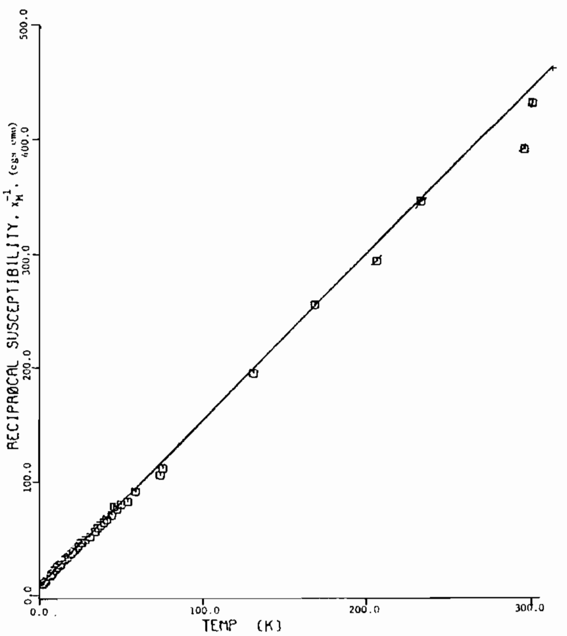

Fig. 4. Reciprocal molar susceptibility *versus* temperature for $Fe(N_2H_4)_2Cl_2$; D = 4.22 cm^{-1}, gx = 1.16, gz = 3.06.

coordination to a linear chain polymer. The local symmetry of the metal ligand coordination is D_{4h}. The linear chain structure suggests the possibility of low dimensionality magnetic exchange interactions at low temperatures. In this note, the low temperature magnetic behavior of bis-hydrazine ferrous chloride and Mössbauer spectroscopy characeterization of the corresponding thiocyanate complex are presented.

Experimental

Preparation of $Fe(N_2H_4)_2Cl_2$

A slight excess of 0.1 *M* hydrochloric acid was added to 0.01 moles iron powder, heated to dissolution and then evaporated to dryness. The resulting pale green $FeCl_2 \cdot 4H_2O$ was dissolved in deaerated, absolute ethanol. Then, 0.02 mol of anhydrous hydrazine was added dropwise. An off-white precipitate formed immediately. The mixture was stirred for twenty minutes to insure complete reaction. The solid was filtered, washed with ethanol and dried *in vacuo*. *Anal.*: Calculated for $Fe(N_2H_4)_2Cl_2$: N: 29.36, H: 4.19. Found: N: 27.86, H: 4.40.

Preparation of $Fe(N_2H_4)_2(NCS)_2$

$Fe(NCS)_2$ was prepared by adding 0.02 mol potassium thiocyanate to a freshly prepared solution of ferrous chloride hydrate in ethanol. The mixture was filtered to remove KCl. Anhydrous hydrazine (0.02 mol) was added dropwise to the solution of $Fe(NCS)_2$. A precipitate formed immediately. The mixture was stirred for twenty minutes to insure

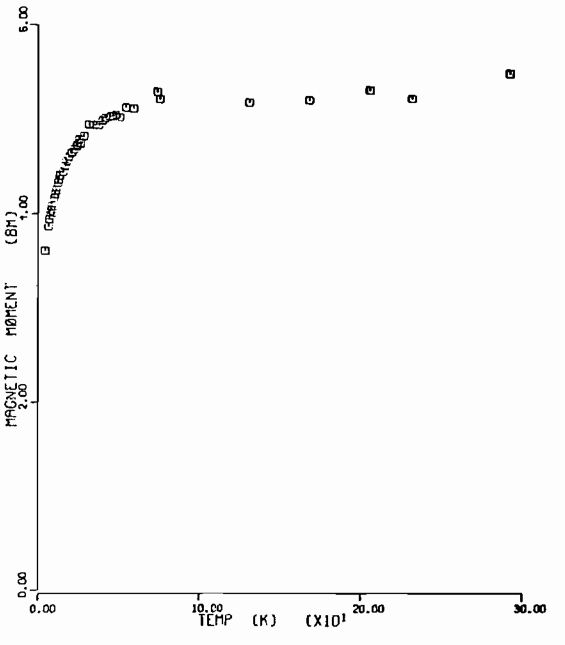

Fig. 5. Magnetic moment *versus* temperature for $Fe(N_2H_4)_2Cl_2$.

TABLE I. Sample Magnetic Moment Data for $Fe(N_2H_4)_2Cl_2$.

Temperature (K)	Moment (μ_β)	Temperature (K)	Moment (μ_β)
1.74	2.710	52.82	5.236
2.22	2.980	60.54	5.279
2.99	3.286	72.11	5.329
3.49	3.431	121.94	5.413
4.00	3.575	228.74	5.442
6.15	3.860	303.28	5.425
6.93	3.927		
7.59	4.036		
7.98	4.047		
8.91	3.996		
9.62	4.153		
10.75	4.162		
12.44	4.331		
15.14	4.428		
17.33	4.546		
20.85	4.645		
25.21	4.684		
31.09	4.928		
35.70	4.921		
41.42	4.996		
44.49	5.029		

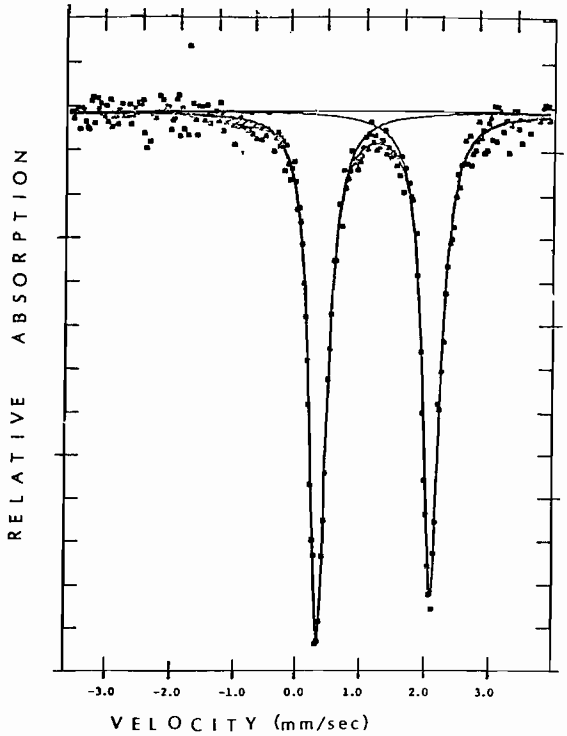

Fig. 6. Zero field Mössbauer spectrum of $Fe(N_2H_4)_2Cl_2$ at 300 K.

complete reaction, filtered, washed with ethanol and dried *in vacuo.*

Mössbauer spectroscopy was used to confirm the gross purity of the resulting products. Note that both of these compounds are extremely air sensitive, oxidizing to dark brown solids, in some cases pyrophorically. Therefore, manipulation in the air was kept to a minimum and complexes were prepared immediately prior to magnetic measurements.

Results

Magnetic Susceptibility

The magnetic susceptibility, reciprocal susceptibility, and magnetic moment behavior of $Fe(N_2H_4)_2Cl_2$ is presented in Figs. 3, 4 and 5 respectively, and Table I. No magnetic study of the thiocyanate complex was undertaken because of its extremely rapid air oxidation. The effective moment of $Fe(N_2H_4)_2Cl_2$ is consistent with high spin ferrous ion with a distorted ^5T ground term. A least squares fit of χ_M^{-1} *vs.* T shows that the reciprocal susceptibility follows a Curie–Weiss law with a small paramagnetic Curie temperature, $\theta = -5.7$ K and a Curie constant, C = 3.72 emu/mol. The susceptibility is unremarkable and no maximum was observed at low temperatures, indicating the ***absence of significant antiferromagnetic exchange interactions.*** There is, however, a sharp decrease in moment below 15 K that is undoubtedly due to single ion zero field splitting.

TABLE II. Mössbauer Parameters* for Ferrous Hydrazine Complexes.

Complex	Temp. K	Isomer Shift	Quadrupole Splitting	Γ_1	Γ_2	Γ_1/Γ_2	A_1/A_2	χ^2
$Fe(N_2H_4)_2Cl_2$	300	1.205	1.345	0.312	0.322	0.968	1.064	208
	78	1.336	1.996	0.519	0.492	1.054	1.137	577
$Fe(N_2H_4)_2(NCS)_2$	300	1.106	1.461	0.375	0.350	1.069	1.223	243
	78	1.325	1.759	0.527	0.392	1.344	1.22	564

*MM/sec relative to natural iron metal foil.

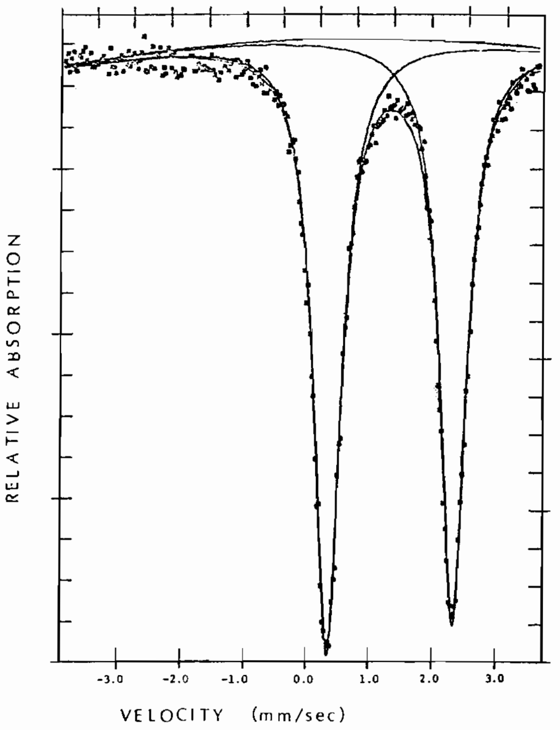

Fig. 7. Zero field Mössbauer spectrum of $Fe(N_2H_4)_2Cl_2$ at 78 K.

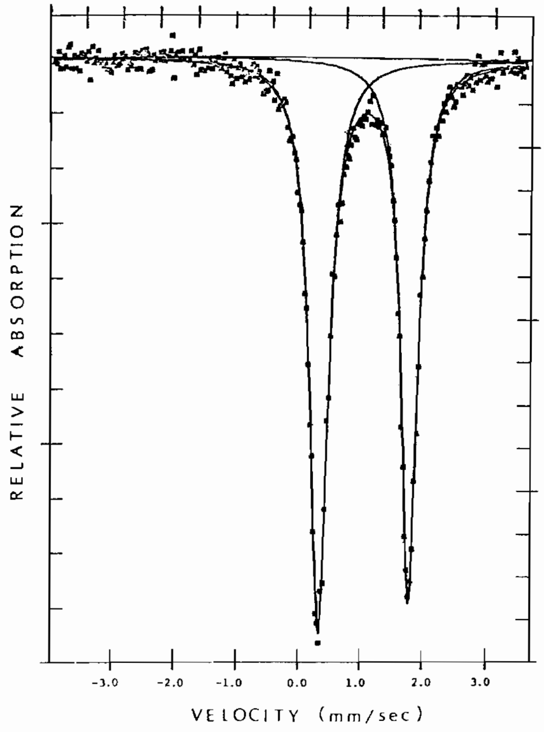

Fig. 8. Zero field Mössbauer spectrum of $Fe(N_2H_4)_2(NCS)_2$ at 300 K.

Mössbauer Spectroscopy

Mössbauer spectroscopy behavior of $Fe(N_2H_4)_2Cl_2$ and $Fe(N_2H_4)_2(NCS)_2$ taken at 300 K and 78 K is shown in Figs. 6–8 and Table II. The isomer shifts of ~1.2 mm/sec are consistent with the nitrogen and chlorine ligation in a pseudo-octahedral high spin $Fe(II)N_4Cl_2$ chromophore. An asymmetric well-resolved quadrupole doublet was observed at all temperatures, in agreement with the results of Staradub [6].

Discussion

Significant antiferromagnetic exchange interactions were not observed in the magnetic susceptibility behavior of $Fe(N_2H_4)_2Cl_2$. Both super and direct exchange pathways are apparently too long for significant exchange to be observed. This is not surprising since in the zinc isomorph the M–N–N–M distance is 5.76 Å and direct metal– metal distance is about 5 Å. Thus, the sharp decrease in moment is the result of single ion zero field splitting. The zero field splitting parameter, D, was determined from a least squares fit of χ_M *vs.* T to the following equation used by Edwards for high spin ferrous monomers [7].

$$\chi_M = \frac{2N\beta^2 g_\parallel^2}{3kT}\,\frac{X}{A} + \frac{4N\beta^2 g_\perp^2}{9D}\,\frac{Y}{A}$$

$$A = 1 + 2e^{-2x} + 4e^{-4x}$$

$$X = e^{-x} + 4e^{-4x}$$

$$Y = 9 - 7e^{-x} - 2e^{-4x} \qquad x = D/kT$$

where D is the zero field splitting parameter and the other variables have their usual significance. The best fit was obtained for $D = 4.22\ cm^{-1}$, $g_\parallel = 1.46$ and $g_\perp = 3.06$ shown as the solid curve in Fig. 3. These parameters are similar to those reported by Hodges [5] for the square pyramidal high spin ferrous complexes, $[Fe(TMC)(NCS)]BF_4$ and $[Fe(TMC)Br]Br$. For these complexes $D \approx 5.5\ cm^{-1}$, $g_\parallel \approx 2.5$ and $g_\perp \sim 1.96$. We have found similar D values for other four, five and six coordinate high-spin ferrous systems [8]. D values at least ~5 cm^{-1} appear common for ferrous systems having limiting quadrupole splittings ~2.0 mm/sec or greater.

Acknowledgements

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