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On the Highly Varied Magnetic Behavior in a Series of Mono(α-diimine)dichloroiron(II) Complexes.
Strong High-Temperature One-Dimensional Ferromagnetic Exchange in Fe(phen)Cl_2

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Mössbauer spectroscopy and magnetization measurements have been used to characterize the one-dimensional ferromagnetism of the polymeric, six-coordinate complexes Fe(phen)Cl_2 and Fe(4-CH_3-phen)Cl_2, the one-dimensional antiferromagnetism of the related complex Fe(5-CH_3-phen)Cl_2, and the single-ion, zero-field splitting and rapidly relaxing paramagnetism of the polymeric, five-coordinate complex Fe(3,4,7,8-tetra-CH_3-phen)Cl_2. The ferromagnetism of Fe(phen)Cl_2 is described in detail; the magnetic behaviors of the other complexes are summarized.

Introduction

The red complex Fe(phen)Cl_2 (phen = 1,10-phenanthroline) is unusual because it orders ferromagnetically at low temperatures (Curie temperature $T_{Curie} \cong 5.0$ K); this aspect was emphasized in a previous report [1]. In later and more detailed studies, we have found novel, one-dimensional (*1-D*) ferromagnetism at high temperatures (>20 T_{Curie}), and we report these results herein.

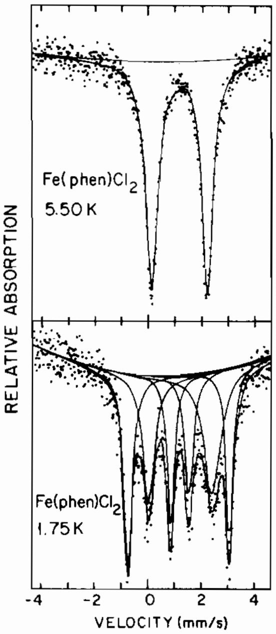

Fig. 1. Mössbauer spectra of Fe(phen)Cl_2.

Experimental

The magnetism of Fe(phen)Cl_2 was examined by Mössbauer spectroscopy [2], Faraday balance magnetometry [2], and vibrating sample magnetometry [3]. We prepared this complex both by following the Broomhead-Dwyer synthesis [4] and by adding with heating and stirring under nitrogen gas a deoxygenated ethanol solution of 1,10-phenanthroline to a deoxygenated ethanol solution of freshly prepared $FeCl_2$ (stoichiometric ratio: Fe/phen = 10/1). The product from either method is a fine, rose-red powder. Elemental analyses by Galbraith Laboratories, Inc., Knoxville, Tennessee 37921, U.S.A., agree with our molecular formula (calculated for $C_{18}H_8Cl_2FeN_2$: 46.95% C, 2.63% H, 9.13% N; found in a typical analysis: 46.88% C, 2.75% H, 9.09% N).

Results

Mössbauer Spectroscopy

Fe(phen)Cl_2 at 296 K has a chemical shift (δ) and a quadrupole splitting (ΔE_Q) characteristic of

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TABLE I. Magnetic Moments *vs.* Temperature for Fe(phen)Cl_2; Applied Field = 1.1 kG.

T, K	Moment, μ_β
1.68	4.27
3.73	8.90
4.20	10.61
5.62	11.16
8.50	9.75
10.60	8.83
15.00	7.71
22.25	7.07
30.60	6.74
39.73	6.50
55.90	6.20
79.70	5.95
88.40	5.98
97.16	5.92

TABLE II. Magnetic Moments *vs.* Temperature for Fe(5-CH_3-phen)Cl_2; Applied Field = 1.7 kG.

T, K	Moment, μ_β
1.78	0.94
4.20	1.33
12.72	2.19
30.03	3.23
50.90	4.02
103.63	4.97
167.88	5.36
264.88	5.60
293.36	5.60

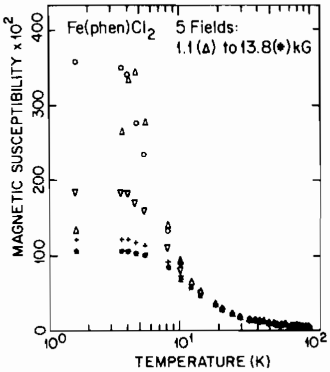

Fig. 2. Field dependence of the magnetic susceptibility χ'_m of Fe(phen)Cl_2.

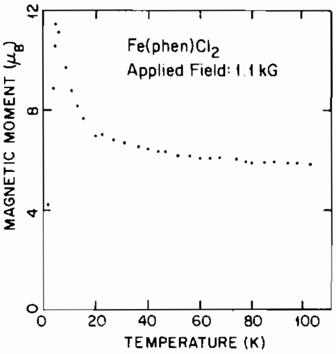

Fig. 3. Temperature dependence of the magnetic moment μ of Fe(phen)Cl_2.

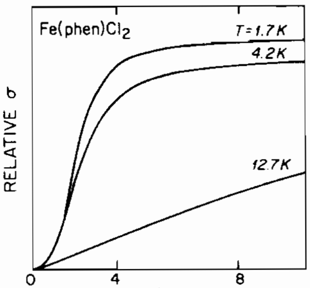

Fig. 4. Field dependence of the magnetization σ of Fe(phen)Cl_2.

six-coordinate, high-spin Fe(II): δ = 1.02 mm/sec, $\Delta E_Q \cong$ 1.43 mm/sec (spectrometer was calibrated with Fe foil). Mössbauer spectroscopy reveals also that this complex orders at $T_{Curie} \cong$ 5.0 K (Fig. 1; the solid curves in each plot result from the computer fit [2]).

Magnetic Susceptibility

Least-squares fits of the Curie–Weiss law to data gathered between 70 K and 300 K yield the following magnetic constants: $\theta \cong$ +10 K, C = 3.7 emu·K/mol, and μ_{eff} = 5.45.

Vibrating sample magnetometry reveals that below ~7.5 K, Fe(phen)Cl_2 orders ferromagnetically. The susceptibility χ'_m is dependent on the applied field (Fig. 2), and the moment μ rises to ~11μ_β (Fig. 3). Furthermore, below T_{Curie}, the magnetization σ depends on the applied field H in a non-Brillouin manner (Fig. 4) typical of a three-dimensional (*3-D*) ferromagnet. The *3-D*, cooperative, ferromagnetic ordering observed here is rare for insulating systems [5].

More remarkable, however, is the fact that at temperatures as high as 20T_{Curie} ($T_{Curie} \cong$ 5.0 K), the moment (~5.9 μ_β at T ≅ 97 K, Table I) is far too large for a high-spin Fe(II) complex, even one with a typical orbital contribution.

These results, which we have not previously emphasized, are reproducible by either Faraday

TABLE III. Magnetic Moment *vs.* Temperature for Fe-3,4,7,8-tetra-CH_3-phen)Cl_2; Applied Field = 1.7 kG.

T, K	Moment, μ_β
1.77	4.02
2.51	4.29
3.48	4.48
4.20	4.57
7.53	4.92
13.13	5.14
18.30	5.22
24.94	5.24
31.44	5.23
34.41	5.26
38.80	5.25
43.27	5.21
63.68	5.23
84.94	5.29
104.16	5.23

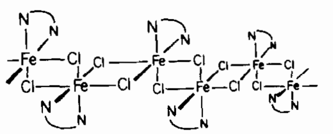

Fig. 5. Polymer of six-coordinate Fe(II) ions linked together by twin chloro-bridges.

balance or vibrating sample magnetometry and confirm the existence of a novel, strong, *1-D*, ferromagnetic correlation at high temperatures in a polymer that orders ferromagnetically three-dimensionally at low temperatures*.

Discussion

X-ray powder diffraction patterns have shown that Fe(phen)Cl_2 is isomorphous with α-Co(2,2'-bipyridine)Cl_2. An X-ray crystallographic analysis have revealed that the latter compound consists of stepped, zig-zag chains of six-coordinate Co(II) ions linked together by twin chloro-bridges (Co–Cl–Co angle 97.04° and Cl–Co–Cl angle 82.95°) (Fig. 5) [6]. Above the Curie temperature, the chloro-bridges in Fe(phen)Cl_2 can serve as the paths along which the observed, *1-D*, ferromagnetic interactions occur. Below T_{Curie}, these bridges and the *interleaving* [6] of 1,10-phenanthroline ligands on adjacent chains are the paths by which the cooperative, *3-D*, ferromagnetic ordering occurs.

We conclude by pointing out that in studying related complexes, we have uncovered a rich variety of magnetic behavior. The red, six-coordinate, poly-

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*Large moments are also observed at still higher temperatures; Broomhead and Dwyer recorded a magnetic moment of 5.79 μ_β for analytically pure Fe(phen)Cl_2 at ambient temperature [4], and we measured moments of ~5.55 μ_β at T ≅ 297 K.

TABLE IV. Structures and Magnetic Behaviors of FeLCl_2 Complexes.

L	Coordination Number	Magnetic Behavior[a]
1,10-phenanthroline[b]	6[d]	F
4-CH_3-1,10-phen	6	F
5-CH_3-1,10-phen	6	AF
5-NO_2-1,10-phen	6	RRP
5,6-di-CH_3-1,10phen[c]	6 5	F RRP
4,7-di-CH_3-1,10-phen	6	RRP
2,9-di-CH_3-1,10-phen	4[d]	RRP
3,4,7,8-tetra-CH_3-1,10-phen	5	RRP
5-Cl-1,10-phen	5	RRP
2,2'-bipyridine[b]	6	F
2,2'-bipyridine	5	SRP
4,4'-di-CH_3-2,2'-bipy	5	SRP
5,5'-di-CH_3-2,2-bipy	5	SRP
4,4'-diphenyl-2,2'-bipy	5	RRP

[a] Magnetic behavior: F = ferromagnetism; AF = antiferromagnetism; RRP = rapidly relaxing paramagnetism; SRP = slowly relaxing paramagnetism. [b] See reference [1]. [c] An approximately 1:1 mixture of the two types of polymers was obtained. [d] 6-coordinate = pseudooctahedral; 4-coordinate = pseudotetrahedral.

meric complex Fe(4-CH_3-phen)Cl_2 like Fe(phen)Cl_2 exhibits *1-D*, ferromagnetic interactions at high temperatures (moment $\cong$ 5.8 μ_β at T $\cong$ 93 K) and *3-D*, ferromagnetic ordering at low temperatures (T_{Curie} $\cong$ 3 K). In contrast, the six-coordinate, polymeric complex Fe(5-CH_3-phen)Cl_2 shows strong, *1-D*, antiferromagnetic interactions (Table II) with T (max χ, *1-D*) $\cong$ 30 K but does not order in zero field at any temperature between 300 K and 1.7 K. In fact, a very sharp rise in χ_m' below T $\cong$ 20 K suggests that this complex at low temperatures is a canted antiferromagnet.

In even greater contrast to Fe(phen)Cl_2, the orange complex Fe(3,4,7,8-tetra-CH_3-phen)Cl_2 contains *five-coordinate* Fe(II) (one bridging chloride and one *terminal* chloride per ferrous ion in Fig. 5; δ = 0.94 mm/sec, ΔE_Q $\cong$ 3.52 mm/sec) and is a rapidly relaxing paramagnet from 300 K to 1.7 K with single-ion, zero-field splitting evident for T < 25 K (Table III; the moment does not go below the expected, spin-only value of $\sqrt{24}$ until T < 7.5 K). In the five-coordinate Fe(II) complex, where single chloro-bridges link the Fe(II) ions weakly, the atomic orbitals overlap less effectively, and magnetic exchange interactions are not expected to be strong and are not detected. Strong magnetic interactions and magnetic ordering are expected and are observed, however, in the six-coordinate complexes Fe(phen)-Cl_2, Fe(4-CH_3-phen)Cl_2, and Fe(5-CH_3-phen)Cl_2, where double chloro-bridges hold the Fe(II) ions tightly and the atomic orbitals apparently overlap more effectively. Additional support for this argument comes from the observation that the five-coordinate Fe(II) complex Fe(3,4,7,8-tetra-CH_3-phen)Cl_2 with freer iron nuclei shows a weaker Mössbauer effect (a lower % absorption) than does the six-coordinate Fe(II) complex Fe(phen)Cl_2.

In Table IV, we summarize the results of our studies of a series of iron(II) complexes FeLCl_2. More details will be presented in future publications.

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References

1 W. M. Reiff and S. Foner, *J. Am. Chem. Soc., 95,* 260 (1973); see also W. M. Reiff, B. Dockum, M. A. Weber and R. B. Frankel, *Inorg. Chem., 14,* 800 (1975).

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

3 G. A. Eisman and W. M. Reiff, *Inorg. Chem., 20,* 3481 (1981);
S. Foner, *Rev. Sci. Instrum., 30,* 548 (1959).

4 J. A. Broomhead and F. P. Dwyer, *Aust. J. Chem., 14,* 250 (1961).

5 P. Day, *Acc. Chem. Res., 12,* 236 (1979).

6 G. A. Eisman, H. Wong, W. M. Reiff, W. Rode and B. Foxman, *Inorg. Paper No. 22, Abstracts, 179th National Meeting of the American Chemical Society,* Houston, Texas, U.S.A., March 1980.