Inorganica Chimica, 41 (1980) 227–228
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

A Low Temperature Magnetic Susceptibility Study of Phenanthrolinium Pentachloro Manganate(III): [PhenH$_2$] [MnCl$_5$]

E. H. WITTEN and W. M. REIFF*

Department of Chemistry, Northeastern University, Boston, Mass. 02115, U.S.A.

Received January 17, 1980

The temperature and field dependence of the magnetic susceptibility of [PhenH$_2$] [MnCl$_5$] have been determined over the range 300 K to 1.43 K. The complex behaves as a simple Curie paramagnet over this temperature interval with no evidence of either significant intermolecular exchange, single ion zero field splitting or spin-orbit effects in the magnetic behavior. These results are considered in terms of the known electronic and molecular structure of the complex.

Introduction

Considerable recent effort in our laboratory has been devoted to the study of magnetic interactions between relatively isolated metal–ligand polyhedra of high symmetry. In particular, we have recently synthesized and determined the molecular structure [2,9-di-CH$_3$-PhenH] [FeCl$_4$] [1] and find that it three dimensionally orders antiferromagnetically at T ~ 2.2 K. In addition, we have also found that a well known complex such as Co(1,2-propanediamine)$_3$ [FeCl$_6$] [1] also order with Néel temperatures of ~9.6 K. Since there are no direct metal–metal or indirect bridging ligand (superexchange) pathways for the preceding systems, the surprising fact that they order is probably the result of exchange through short (~3.7 Å) nonbonded (Cl-------Cl) contact interactions between the complex anion polyhedra. Hydrogen bonding interactions may also be involved. However, since the hydrogen atom positions are usually not known that well one can usually only speculate on their role in the exchange.

In an attempt to extend our study to other metal ion systems, we now present our results for [PhenH$_2$] [MnCl$_5$]. This complex as well as the 2,2'-bipyridine analogue was first reported by Goodwin and Sylva [2] and on the basis of a variety of indirect evidence postulated to contain MnCl$_5^{2-}$ anions. This was subsequently confirmed in X-ray studies [3, 4] that showed Mn(III) present in square pyramidal (C_{4v}) coordination of five chloride anions.

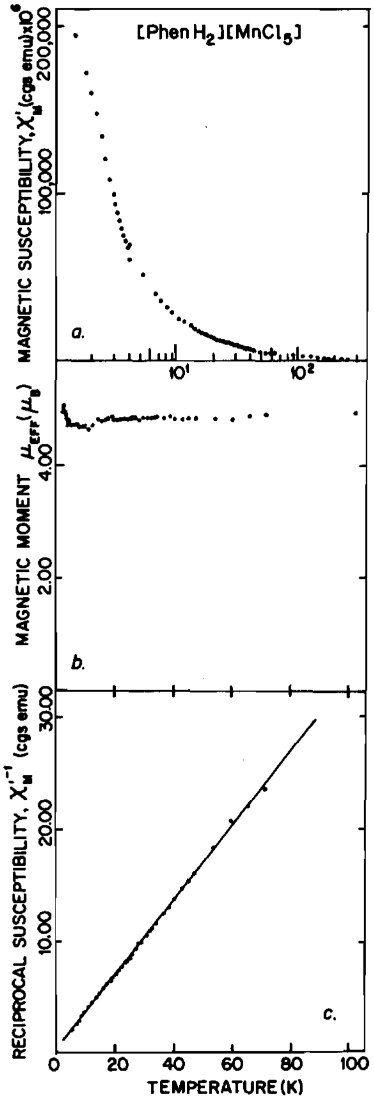

Fig. 1. a, Magnetic susceptibility *vs.* log temperature; b, Magnetic moment *vs.* temperature; c, Reciprocal susceptility *vs.* temperature.

The samples of [PhenH$_2$] [MnCl$_5$] investigated were prepared [2] as previously described and their susceptibility determined soon thereafter to avoid

---

*Author to whom correspondence should be addressed.

TABLE I. Sample Moment Data.

T (K)	μ (μ_β)	T (K)	μ (μ_β)
302.14	5.03	10.96	4.65
264.91	4.98	9.51	4.70
207.69	4.95	8.67	4.70
167.03	5.08	7.68	4.69
124.69	5.03	6.91	4.72
71.26	4.90	5.42	4.73
59.91	4.81	4.20	4.50
47.22	4.84	4.00	4.64
42.65	4.82	3.81	4.66
38.47	4.87	3.69	4.71
34.43	4.88	3.56	4.74
31.98	4.86	3.43	4.79
29.19	4.87	3.30	4.84
27.33	4.85	3.15	4.87
25.10	4.88	3.03	4.90
23.49	4.84	2.81	4.93
21.19	4.84	2.56	4.97
19.19	4.83	2.38	5.05
17.43	4.83	2.16	5.06
14.99	4.79	1.95	5.00
14.04	4.82	1.77	4.94
12.13	4.72		

the effects of decomposition by loss of HCl or reaction with atmospheric water. Susceptibllities were determined (for ten fields varying from 1.6 to 5.1 kG) using a Faraday balance previously described. Temperature measurement and control were based on calibrated silicon and uncalibrated gallium arsenide diodes respectively.

Results

The temperature dependence of the magnetic moment (μ), the corrected molar susceptibility and the reciprocal molar susceptibility of [PhenH$_2$] [MnCl$_5$] are shown in Fig. 1. These data correspond to an applied field of 3.3 kG and are typical, *i.e.* χ'_M is field independent. The straight line through the data is a least squares computer fit to the expression $\chi'^{-1}_M = T - \theta/C$, *i.e.* a simple Curie–Weiss expression. The average values of the Curie–Weiss law parameters for fits at ten field values (sixty four temperatures/field) are: μ_{eff} = 4.95, C = 3.06 emu/mole, and the paramagnetic Curie temperature θ = –1.2 K. Sample moment data (H_o = 3.3 kG) are given in Table I. The values of χ'_M are plotted on $\log_{10}T$ scale for convenience relative to the following discussion.

Discussion

The small rise in μ at T < ~4K is attributed to sample alignment in the field and moment anisotropy. However, we find that the value of the magnetic moment (μ) never deviates significantly from the spin-only ($\sqrt{24}$ ~ 4.89 μ_β) expected for a high spin d^4 configuration. This is consistent with an orbitally non-degenerate, spin-quintet ground term in C_{4v} symmetry, see Fig. 1 and Table I. The previous susceptibility study [5] of this system corresponds to the range 336 to 79 K and at comparable temperatures generally agrees with results of the present work. Two imortant features are evident in the new data that we have obtained at lower temperatures. There is no evidence of significant magnetic exchange, *i.e.* χ'_M vs. T is unremarkable. Perhaps more surprising is the ***absence of zero field splitting.*** This is usually evident in a decrease in the magnetic moment to values well below the spin only at lowest temperatures. For example, in a recent study of the high spin d^4 complex, Mn(III) (acetylacetonate)$_3$, μ decreases from near the spin only value at ambient temperature to 3.8 μ_β at 1.5 K. This decrease is correlated with an axial zero field splitting, *D*, ~ +3.1 cm^{-1}.

The small value of θ ~ –1.2 K and relative temperature independence of μ suggest near Curie law behavior for the complex. Our value of θ is somewhat smaller than that (–20 K) originally reported by Goodwin and Sylva. This may be the result of a smaller data set (nine temperatures) and different temperature intervals (336 to 79 K) involved in their study.

We conclude by indicating that there is no evidence of low temperature magnetic ordering in [PhenH$_2$] [MnCl$_5$]. Although an X-ray structure determination of this compound has been made, complete details including atomic coordinates have not been published. Thus we do not have and cannot calculate accurate values of the smallest nonbonded inter $MnCl_5^{2-}$ anion Cl--------Cl contact distances. However, from the unit cell parameters and packing diagram that have been published, it appears that such distances are *closer to* ~4Å in this compound and apparently too large to result in magnetic exchange strong enough for three dimensional ordering above ~1.5 K.

Acknowledgments

The authors are pleased to acknowledge the support of the National Science Foundation, Division of Materials Research, Solid State Chemistry Program, Grant No. DMR-7712625.

References

1 W. M. Reiff *et al.*, to be published.
2 H. A. Goodwin, R. N. Sylva, *Aust. J. Chem.*, *18*, 1743 (1965).
3 I. Bernal, N. Elliot and R. LaLancette, *Chem. Commun.*, 803 (1971).
4 M. Matsui, S. Koda, S. Ooi, H. Kuroya and I. Bernal, *Chem. Letters*, 51 (1972).
5 H. A. Goodwin and R. N. Sylva, *Aust. J. Chem.*, *20*, 629 (1967).
6 A. K. Gregson, D. M. Doddrell and P. C. Healy, *Inorg. Chem.*, *17*, 1216 (1978).