

Synthesis and magnetism of tetrachlorophthalato-bridged manganese(II) binuclear complexes

Yu-Qing Qi, Ming-Ming Miao, Xian-Ru Sun, Zong-Hui Jiang*, Dai-Zheng Liao and Geng-Lin Wang

Department of Chemistry, Nankai University, Tianjin, 300071, Peoples Republic of China

Summary

Four novel manganese(II) binuclear complexes have been prepared and characterized, namely $[\text{Mn}_2(\text{TCPHTA})(\text{L})_4](\text{ClO}_4)_2$ [where L is 2,2'-bipyridyl (bipy), 1,10-phenanthroline (phen), 4,4'-dimethyl-2,2'-bipyridyl (Me_2bipy) or 5-nitro-1,10-phenanthroline ($\text{NO}_2\text{-phen}$) and TCPHTA is the tetrachlorophthalate dianion]. Based on i.r. spectra, elemental analyses, conductivity measurements, extended tetrachlorophthalato-bridged structures consisting of two manganese(II) ions in which each manganese(II) ion has a distorted octahedral environment are proposed for these structures. The temperature dependence of the magnetic susceptibility for $[\text{Mn}_2(\text{TCPHTA})(\text{phen})_4](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ was measured over the 4–300 K range and the observed data were successfully simulated by an equation based on the spin Hamiltonian operator ($\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$), giving the exchange integral $J = -1.05 \text{ cm}^{-1}$. This result is indication of a weak antiferromagnetic spin exchange interaction between the metal ions.

Introduction

Polynuclear complexes with extended bridges have received much attention^(1,2), and interest in this area stems from attempts to mimic the structural and functional properties of biological systems and to design molecular magnets. In view of the effective bridging function of the terephthalato (TPHA) and phthalato (PHTH) dianions, many binuclear complexes containing TPHA and PHTH bridges were synthesized and their magnetic properties were studied^(3–16). It has been revealed by X-ray diffraction analyses and variable temperature magnetic susceptibility investigation that long-range magnetic coupling can occur between two paramagnetic centres bridged by TPHA or PHTH. However, to the authors' knowledge, so far no tetrachlorophthalato-bridged complexes have been reported. In this paper, four novel binuclear manganese(II) complexes, $[\text{Mn}_2(\text{TCPHTA})(\text{L})_4](\text{ClO}_4)_2$, were prepared and characterized [where TCPHTA is the tetrachlorophthalate dianion and L is 2,2'-bipyridyl (bipy), 4,4'-dimethyl-2,2'-bipyridyl (Me_2bipy), 1,10-phenanthroline (phen) or 5-nitro-1,10-phenanthroline ($\text{NO}_2\text{-phen}$)], in which each manganese(II) ion has a distorted octahedral environment.

Experimental

Syntheses – general

All reagents used in the synthesis were of analytical grade. The hydrated manganese perchlorates were prepared by a general method⁽¹⁷⁾. Tetrachlorophthalic acid was purchased from Aldrich. Piperidinium tetrachlorophthalate was synthesized by the literature method⁽⁴⁾.

Preparation of $[\text{Mn}_2(\text{TCPHTA})(\text{bipy})_4](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (1)

To a solution of piperidinium tetrachlorophthalate (98.4 mg, 0.2 mmol) and $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (144.8 mg, 0.4 mmol) in EtOH (15 cm³) was added an EtOH solution (10 cm³) of 2,2'-bipy (124.8 mg, 0.8 mmol) in EtOH (10 cm³). After the mixture was further stirred for 4 h at room temperature, the yellow microcrystals thus obtained were removed by filtration, washed with EtOH and Et₂O several times, and dried *in vacuo*. (Found: C, 45.6; H, 2.5; Mn, 8.7; N, 8.6; $\text{C}_{48}\text{H}_{36}\text{Cl}_6\text{Mn}_2\text{N}_6\text{O}_{14}$ calcd.: C, 45.4; H, 2.8; Mn, 8.6; N, 8.8%.)

Preparation of $[\text{Mn}_2(\text{TCPHTA})(\text{Me}_2\text{bipy})_4](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (2)

The complex was obtained as yellow microcrystals by the same procedure as above but by using Me_2bipy instead of bipy. (Found: C, 48.7; H, 3.8; Mn, 8.0; N, 8.1; $\text{C}_{56}\text{H}_{52}\text{Cl}_6\text{Mn}_2\text{N}_8\text{O}_{14}$ calcd.: C, 48.6; H, 3.7; Mn, 7.9; N, 8.1%.)

Preparation of $[\text{Mn}_2(\text{TCPHTA})(\text{phen})_4](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (3)

This complex was obtained as yellow microcrystals by the same procedure as above but by using phen instead of bipy and MeOH instead of EtOH. (Found: C, 49.5; H, 2.6; Mn, 8.1; N, 8.1; $\text{C}_{56}\text{H}_{34}\text{Cl}_6\text{Mn}_2\text{N}_8\text{O}_{13}$ calcd.: C, 49.9; H, 2.5; Mn, 8.1; N, 8.3%.)

Preparation of $[\text{Mn}_2(\text{TCPHTA})(\text{NO}_2\text{-phen})_4](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (4)

This complex was obtained as yellow microcrystals by the same procedure as above but by using $\text{NO}_2\text{-phen}$ instead of bipy and MeOH instead of EtOH. (Found: C, 43.9; H, 1.9; Mn, 7.3; N, 10.9; $\text{C}_{56}\text{H}_{30}\text{Cl}_6\text{Mn}_2\text{N}_{12}\text{O}_{21}$ calcd.: C, 44.0; H, 2.0; Mn, 7.2; N, 11.0%.)

Physical measurements

C, H, N analyses were carried out on a Perkin-Elmer analyser, model 240. Metal contents were determined by EDTA titration. The i.r. spectra were recorded with an IR-408 spectrophotometer using KBr discs. Molar conductances were measured with a DDS-11A conductometer. Variable temperature magnetic susceptibilities were measured at the Institute of Physics, Chinese Academy of Sciences, using a vibrating sample magnetometer, model CF-1 (sensitivity $m = 10^{-4}$ emu). Diamagnetic corrections were made with Pascal's constant⁽¹⁸⁾ for all the constituent atoms and the magnetic moments were calculated by the equation $\mu_{\text{eff}} = 2.828(\chi T)^{1/2}$.

* Author to whom all correspondence should be directed.

Table 1. Physical data for the complexes

Complex	I.r. (cm ⁻¹)		$\Delta(\nu_{as} - \nu_s)$	$\nu(\text{ClO}_4^-)$	Λ_M ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)	U.v. (cm ⁻¹)
	$\nu_{as}(\text{CO}_2)$	$\nu_s(\text{CO}_2)$				
(1)	1600	1440	160	1100	142	34483
(2)	1600	1410	190	1100	139	34490
(3)	1600	1430	170	1100	131	34468
(4)	1600	1410	190	1100	135	34472

(1), [Mn₂(TCPHTA)(bipy)₄](ClO₄)₂·2H₂O; (2), [Mn₂(TCPHTA)(Me₂bipy)₄](ClO₄)₂·2H₂O; (3), [Mn₂(TCPHTA)(phen)₄](ClO₄)₂·H₂O; (4), [Mn₂(TCPHTA)(NO₂-phen)₄](ClO₄)₂·H₂O.

Results and discussion

General characterization

Elemental analyses indicate that reaction occurs between TCPHTA with Mn(ClO₄)₄·6H₂O and bipy, Me₂bipy, phen or NO₂-phen. Based on conductance measurements, spectroscopic and magnetic data (*vide infra*) the complexes are presumed to have the coordination environment as shown in Figure 1. For all four, the molar conductances in DMF solution (Table 1) fall in the expected range for 1:2 electrolytes⁽¹⁹⁾, indicating that the two perchlorate anions are outside the coordination sphere. The most relevant i.r. absorption bands for the complexes, together with their assignments, are shown in Table 1. All complexes exhibited the two characteristic strong and broad $\nu_{as}(\text{COO}^-)$ (*ca* 1600 cm⁻¹) and $\nu_s(\text{COO}^-)$ (*ca* 1420 cm⁻¹) absorption bands. According to the literature⁽²⁰⁾, the carboxylato group coordination modes have often been determined by the separation between $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$; i.e. bidentate carboxylate groups show a separation < 200 cm⁻¹, whereas unidentate carboxylato groups show a separation > 200 cm⁻¹. Thus, the separation for the present complexes ($\nu_{as} - \nu_s = \text{ca } 180 \text{ cm}^{-1}$) indicated a bidentate bonding mode for both carboxylato groups of the TCPHTA ligand. In addition, the —N=C— stretching vibration at *ca* 1560 cm⁻¹ for a terminal ligand (bipy, Me₂bipy, phen or NO₂-phen) and the ClO₄⁻ group vibration at 1100 cm⁻¹, which is typical for a non-coordinated perchlorate ion⁽²¹⁾, were present in all complexes. The electronic spectra absorb strongly at *ca* 34480 cm⁻¹ ($\epsilon > 10^4 \text{ M}^{-1} \text{cm}^{-1}$), and may be assigned to the charge transfer transition. Failure to observe the manganese(II) d–d band may be due to the weakness of absorption. The coordination environment of manganese(II) in the complex is a distorted octahedron. Thus, according to ligand field theory, and assuming *O_h* symmetry, the ground state of manganese(II) is ⁶A_{1g}. The d–d transitions of manganese(II) (⁶A_{1g} → ⁴T_{1g}(G), ⁴T_{2g}(G), ⁴A_{1g}, ...) are spin-forbidden; in the spectra of Mn^{II}–Mn^{II} complexes no characteristic manganese(II) band was found. Based on

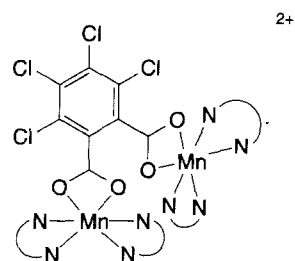


Figure 1. Coordination environment of the complexes (N–N = phen, NO₂-phen, bipy or Me₂bipy).

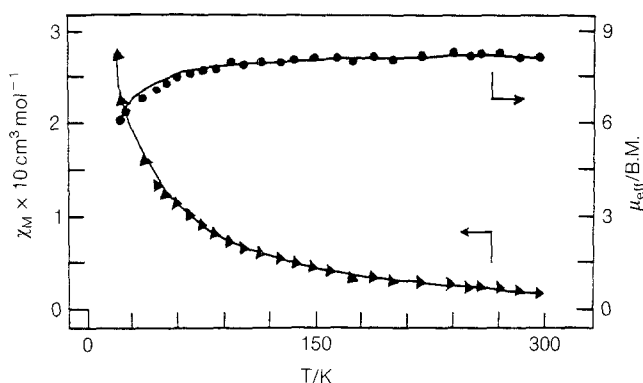


Figure 2. Variable temperature magnetic susceptibility and magnetic moment for [Mn₂(TCPHTA)(phen)₄](ClO₄)₂·H₂O.

the above discussion, it is reasonable to suppose that each manganese(II) ion in [Mn₂(TCPHTA)(L)₄](ClO₄)₂ has an octahedral coordinated environment.

Magnetic properties of [Mn₂(TCPHTA)(phen)₄](ClO₄)₂·H₂O

The observed magnetic moment per binuclear manganese(II) complex at room temperature is 8.25 μ_B for complex (3), which is slightly less than the spin-only value (8.36 μ_B). The result suggests the presence of an antiferromagnetic spin-exchange interaction in the complexes⁽²²⁾. In order to understand quantitatively the magnitudes of spin-exchange interaction, the temperature dependence of magnetic susceptibility and magnetic moment for [Mn₂(TCPHTA)(phen)₄](ClO₄)₂·H₂O were measured and are shown in Figure 2. The magnetic analysis was carried out with the susceptibility equation based on the Heisenberg spin-exchange operator $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, where the exchange integral *J* is negative for antiferromagnetic and positive for a ferromagnetic interaction. The mole susceptibility of the Mn^{II}–Mn^{II} (*S*₁ = *S*₂ = 5/2) system is given in Equation 1:

$$\chi_M = (2Ng^2\beta^2/kT)(A/B) \quad (1)$$

$A = 55 + 30 \exp(-10J/kT) + 14 \exp(-18J/kT) + 5 \exp(-24J/kT) + \exp(-28J/kT)$; $B = 11 + 95 \exp(-10J/kT) + 7 \exp(-18J/kT) + 5 \exp(-24J/kT) + 3 \exp(-28J/kT) + \exp(-30J/kT)$. χ_M is the mol susceptibility per binuclear complex and the other symbols have their usual meanings. As shown in Figure 2, good fits with the experimental data are obtained for $J = -1.05 \text{ cm}^{-1}$ and $g = 2.01$. The agreement factor, $F = \sum[(\chi_M)_{\text{obs.}} - (\chi_M)_{\text{calc.}}]^2 / \sum(\chi_M)_{\text{obs.}}$, is 2.86×10^{-3} . The result (small and negative *J* value) indicates a very weak antiferromagnetic spin-exchange interaction between manganese(II) and manganese(II) ions.

Acknowledgement

This project was supported by the National Nature Science Foundation of China.

References

- (1) R. D. Willett, D. Gatteschi and O. Kahn (Eds.), *Magneto-Structural Correlations in Exchange Coupled Systems*, NATO ASI Series C 140, Reidel, Dordrecht, Holland, 1985.
- (2) D. Gatteschi, O. Kahn, J. S. Miller and F. Palacio (Eds.), *Molecular Magnetic Materials*, NATO AST Series, Kluwer, Dordrecht, 1991.
- (3) L. C. Francesconi, D. R. Corlbin, A. W. Clauss and D. N. Stucky, *Inorg. Chem.*, **20**, 2078 (1981).
- (4) M. Verdaguer, J. Gouteron, S. Jeannin, Y. Jeannin and O. Kahn, *Inorg. Chem.*, **23**, 4291 (1984).
- (5) E. G. Bakalbassis, J. Mrozinski and C. A. Tsipis, *Inorg. Chem.*, **24**, 4231 (1985).
- (6) E. G. Bakalbassis, J. Mrozinski and C. A. Tsipis, *Inorg. Chem.*, **25**, 3684 (1986).
- (7) F. Tiniti, M. Verdaguer, O. Kahn and J. M. Savariault, *Inorg. Chem.*, **26**, 2380 (1987).
- (8) M. Ilve, M. Verdaguer and E. Gutierrez-Puebla, *Inorg. Chem.*, **26**, 3250 (1987).
- (9) E. G. Bakalbassis, A. P. Bozopoulos, J. Mrozinski, J. P. Rentzeperis and C. A. Tsipis, *Inorg. Chem.*, **27**, 529 (1988).
- (10) P. Chaudhuri, O. Karen, K. Wiegardt, S. Gehring, W. Haase, B. Nuber and J. Wess, *J. Am. Chem. Soc.*, **10**, 3657 (1988).
- (11) E. Bakalbassis, C. A. Tsipis, A. Bozopoulos, W. Dreissig, H. Hartl and J. Mrozinski, *Inorg. Chim. Acta*, **186**, 118 (1991).
- (12) Z. L. Deng, J. Shi, Z. H. Jiang, D. Z. Liao, S. P. Yan, G. L. Wang, H. G. Wang and R. J. Wang, *Polyhedron*, **11**, 885 (1992).
- (13) S. L. Ma, Z. H. Jiang, S. P. Yan, D. Z. Liao and G. L. Wang, *Chinese J. Struct. Chem.*, **12**, 142 (1993).
- (14) S. L. Ma, D. Z. Liao, Z. H. Jiang, S. P. Yan and G. L. Wang, *Synth. React. Inorg. Met-Org. Chem.*, **23**, 239 (1993).
- (15) S. K. Shakhathreh, E. G. Bakalbassis, I. Brudgam, H. Hartl, J. Mrozinski and C. A. Tsipis, *Inorg. Chem.*, **30**, 2801 (1991).
- (16) Z. H. Jiang, S. L. Ma, D. Z. Liao, S. P. Yan and G. L. Wang, *J. Chem. Soc. Commun.*, **745** (1993).
- (17) J. R. Bethrendt and S. K. Madan, *J. Inorg. Nucl. Chem.*, **20**, 195 (1950).
- (18) P. W. Selwood, *Magnetochemistry*, Interscience, New York, 1956, p. 78.
- (19) W. Geary, *J. Coord. Chem. Rev.*, **7**, 81 (1971).
- (20) G. B. Deacon and R. Philips, *Coord. Chem. Rev.*, **88**, 227 (1980).
- (21) W. Radecka-Paryzek, *Inorg. Chim. Acta*, **34**, 5 (1979).
- (22) H. Okawa, Y. Imada and M. Tanaka, *Inorg. Chim. Acta*, **129**, 173 (1987).

(Received 21 June 1994)

TMC 3304