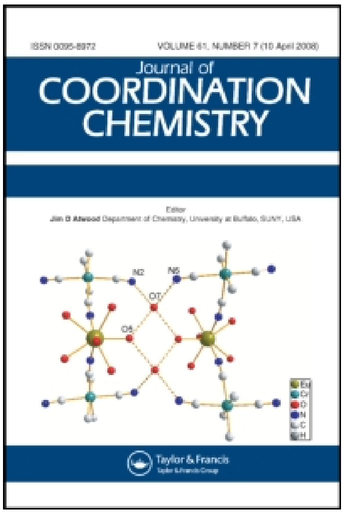

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Bo, Liu , Hong, Zhou , Zhi-Quan, Pan , You, Song , Cheng-Gang, Wang , Han-Ping, Zhang , Jing-Dong, Hu and Ru-An, Chi(2006) 'Synthesis, characterization, magnetic and electrochemical studies of an asymmetric heterodinuclear macrocyclic complex', Journal of Coordination Chemistry, 59: 11, 1271 — 1280

To link to this Article: DOI: 10.1080/00958970500490947

URL: http://dx.doi.org/10.1080/00958970500490947

Journal of Coordination Chemistry
Vol. 59, No. 11, 20 July 2006, 1271–1280

Synthesis, characterization, magnetic and electrochemical studies of an asymmetric heterodinuclear macrocyclic complex

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(*Received in final form 14 September 2005*)

A macrocyclic heterodinuclear complex $[Cu(II)Mn(II)L(H_2O)_2](ClO_4)_2$ was synthesized by cyclo-condensation of *N*,*N*′-bis(3-formyl-5-*n*-butylsalicylidene)-ethylenediimine and diethylenetriamine in the presence of Cu^{2+} and Mn^{2+}. The crystal structure of the complex was determined. Variable-temperature magnetic susceptibilities and cyclic voltammograms of the complex were measured. $[Cu(II)Mn(II)L(H_2O)_2](ClO_4)_2$ displays very strong antiferromagnetic exchange and undergoes a one-electron transfer process.

Keywords: Macrocycle; *N*,*N*′-bis(3-formyl-5-*n*-butylsalicylidene)ethylenediimine; Diethylenetriamine; Copper; Manganese; Crystal structure; Magnetic properties; Cyclic voltammetry

1. Introducion

Polynuclear complexes, particularly heterometallic systems [1–3], are of special interest due to their relevance to different branches of physics, chemistry and biology. Enzymes containing copper(II) and magnesium(II) are involved in many biological processes [4, 5], such as superoxide dismutase and hydrogen peroxide decomposition. The active sites in biological enzymes are metal sites in many cases, e.g., dicopper sites in hemocyanin and tyrosinase, dirron(III) sites in methemerythrin and ribonucleotide reductase, and heterobimetallic sites involving Fe(III) and Cu(II) in respiratory

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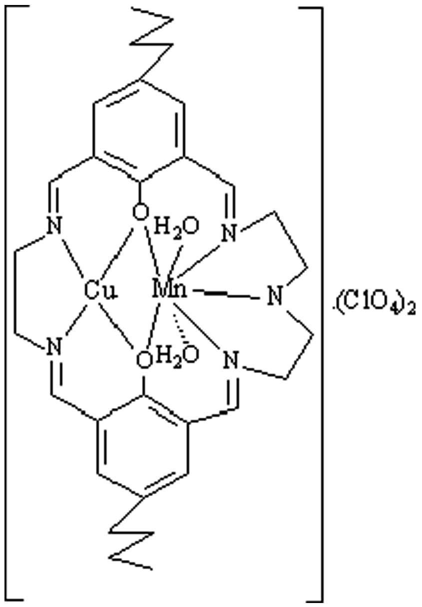
ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970500490947



Scheme 1. The chemical structure of the complex $[CuMnL(H_2O)_2](ClO_4)_2$.

cytochrome oxidase which catalyses the 4e reduction of dioxygen to water in the mitochondria of eukaryotic cells. Active sites involving more than one metal centre in metalloproteins have elicited the interest of bioinorganic chemists in such interactions. Studies on the intimate relationship between spin coupling and molecular structure have developed understanding of molecular magnetism [6–8]. Phenol-based macrocyclic compounds having two dissimilar N_2O_2 cavies can bond different metals to form heterodinuclear complexes [9–11]. Although many Cu(II)–Zn(II) and Cu(II)–Mn(II) model complexes have been synthesized to mimic superoxide dismutase (SOD)-like activity [12, 13], macrocyclic complexes having two dissimilar cavies, N_2O_2 and N_3O_2, have not been synthesized. In order to understand the effects of cavies on properties of complexes, the heterodinuclear complex (scheme 1) derived from *N*,*N*′-bis(3-formyl-5-*n*-butylsalicylidene)ethylenediimine and diethylenetriamine in the presence of Cu^{2+} and Mn^{2+} was synthesized by cyclocondensation, and electrical, redox and magnetic properties have been studied.

2. Experimental

2.1. *Materials*

N,*N*′-bis(3-formyl-5-*n*-butylsalicylidene)ethylenediimine, was prepared according to the literature [14].

Safety note: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with caution.

2.2. *Physical measurements*

IR spectra were measured (KBr discs) on a Vector 22 FTIR spectrophotometer. Elemental analyses were determined with a Perkin-Elmer 240 instrument. Electrospray mass spectra (ES-MS) were obtained using a Finnigan LCQ ES-MS mass spectrograph with methanol as mobile phrase and a sample concentration of about 1.0 mmol dm^{-3}. Magnetic susceptibilities of a powder sample were measured on a MPMS-XL7 SQUID magnetometer in the temperature range 2.0–300 K, and diamagnetic corrections were made according to Pascal's constants. Cyclic voltammograms were run on a CHI model 750B electrochemical analyzer in DMF solution containing tetra(*n*-butyl)ammonium perchlorate (TBAP) as supporting electrolyte. A three-electrode cell equipped with a glassy carbon-working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode was used. Scanning speeds around 50–200 mV s^{-1} were employed. The solution was deaerated for about 15 min before measurement. Half-wave potentials were calculated approximately from $(E_{pa} + E_{pc})/2$, and the measured error was ±2 mV. Unless otherwise stated, all potentials reported are referenced to the Ag/AgCl electrode.

2.3. *Crystal structure*

Intensity data were collected on a SMART-CCD area-detector diffractometer at 293 K using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Data reduction and cell refinement were performed by SMART and SAINT programs [15]. The structure was solved by direct methods (Bruker SHELXTL) and refined on F^2 by full-matrix least-squares techniques (Bruker SHELXTL) using all unique data [16]. The non-H atoms in the structure were treated anisotropically. All hydrogen atoms were placed in calculated positions, assigned fixed isotropic thermal parameter at 1.2 times the equivalent isotropic U of the atoms to which they were attached (1.5 times for methyl groups) and allowed to ride on their respective parent atoms. The contribution of these hydrogen atoms was included in the structure factor calculations.

2.4. *Synthesis*

An absolute methanol solution (10 cm^3) of diethylenetriamine (0.051 g, 0.5 mmol) and a methanol solution (10 cm^3) of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.181 g, 0.5 mmol) were added stepwise to an absolute methanol solution (30 cm^3) containing *N*,*N'*-bis(3-formyl-5-*n*-butylsalicylidene)ethylenediimine (0.218 g, 0.5 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.1 g, 0.5 mmol) and triethylamine (two drops). The mixture was stirred at room temperature for 10 h, and a brown solid obtained by filtration. It was washed with ether and dried in air with a yield of 0.16 g (39.1%). Brown cubic crystals of $[CuMnL(H_2O)_2](ClO_4)_2$ suitable for X-ray diffraction were obtained by slow diffusion of diethylether into a MeCN solution of the product over one week. Anal. Calcd for $C_{30}H_{42}N_5O_{12}Cl_2CuMn$ (%): C, 42.18; H, 4.96; N, 8.20. Found: C, 42.27; H, 4.99; N, 8.29. IR ν(cm^{-1}): 3502, 3452 (O–H), 2956, 2926, 2859 (C–H), 1643 (C=N), 1600 (C=C) and 1090, 626 (ClO_4^-).

3. Results and discussion

3.1. *Synthesis and characterization*

When *N*,*N*′-bis(3-formyl-5-*n*-salicylidene)ethylenediimine reacted with diethylenetriamine in the presence of Cu^{2+}, followed by adding Mn^{2+}, a strong band at $1680\,cm^{-1}$ disappeared, and a sharp C=N stretch corresponding to imine groups was observed at about $1643\,cm^{-1}$, indicating that the macrocyclic complex was formed; in addition, a very strong broad band centred at 1090, and a sharp band at $626\,cm^{-1}$ could be ascribed to ν_3 and ν_4 of ionic ClO_4^-. The ES-MS spectrum of complex in MeOH solution is shown in figure 1. It shows that the peak at m/z 309.8 (100%) corresponding to $[CuMnL]^{2+}$ is dominant. The peak at m/z 345.9 (49%) can be assigned to $[CuMnL(H_2O)_4]^{2+}$ and that at 718.3 (14%) to $[CuMnL(ClO_4)]^+$. All species in the ES-MS spectrum contain $[CuMnL]^{2+}$, indicating that the macrocyclic cation is stable in methanol solution. The theoretical and experimental isotope distributions of the dominant peak of the complex are shown in figure 1. It reveals good agreement between observed and calculated data for the dominant peak.

3.2. *Crystal structure*

A perspective view of the complex is shown in figure 2, together with the atom numbering scheme. Crystallographic data and details concerning data collection are given in table 1. Selected bond distances and angles relevant to the copper(II) and manganese(II) coordination spheres are listed in table 2. The complex consists of one macrocyclic ligand, one Cu(II) ion, one Mn(II) ion, two perchlorate anions and two water molecules. The two perchlorate ions do not participate in coordination and sit in the lattice. Cu(II) and Mn(II) ions are bridged by the two endogenous phenolic oxygens of L with a Cu(1)–Mn(1) separation of 3.244 Å. The Mn(II)–O(1)–Cu(II) and Mn(II)–O(2)–Cu(II) angles are 100.13(10) and 101.59(10)°, respectively. Cu(II) lies in

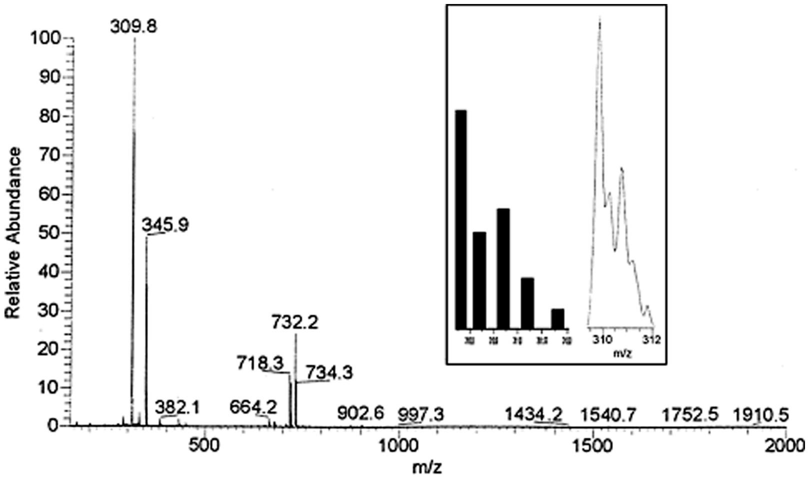


Figure 1. The ES-MS spectrum of $[CuMnL(H_2O)_2](ClO_4)_2$ (inset the isotopic distribution of the peak at $m/z = 309.8$; left: calculated pattern; right: experimental pattern).

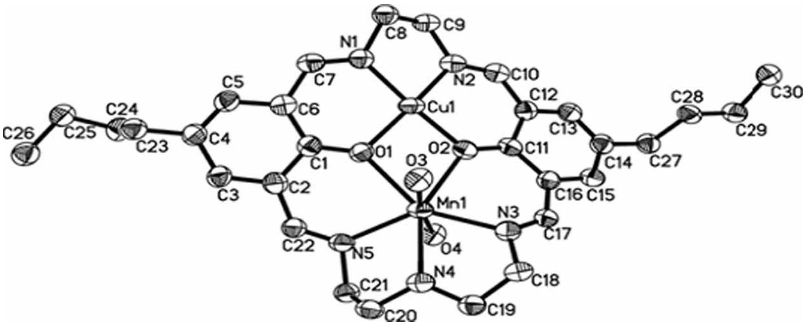


Figure 2. X-ray crystal structure of the complex cation, showing the atom numbering scheme. Hydrogen atoms are omitted for simplicity.

Table 1. Crystal data and refinement details for $[CuMnL(H_2O)_2](ClO_4)_2$.

Empirical formula	$C_{30}H_{42}Cl_2CuMnN_5O_{12}$
Formula weight	854.07
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	17.084(4)
b (Å)	12.323(3)
c (Å)	17.416(5)
β (°)	91.372(5)
Volume (Å^3)	3665.5(16)
Z	4
$D_{(\mathrm{Calcd})}$ (g cm^{-3})	1.548
μ (Mo-Kα) (mm^3)	1.137
F (000)	1764
Crystal size (mm^3)	$0.22 \times 0.23 \times 0.31$
Temp. (K)	293
Mo-Kα radiation (Å^3)	0.71073
θ range (°)	2.0–26.5
Limiting indices	$-19 \le h \le 21$; $-15 \le k \le 9$; $-21 \le l \le 21$
Tot., uniq. data R(int)	19972, 7557, 0.036
Observed data [$I > 2.0\sigma(I)$]	6076
Nref, Npar	7557, 462
W^{-1}	$1/[\sigma^2(F_o^2) + (0.07P)^2 + 1.99P]$; $P = (F_o^2 + 2F_c^2)/3$
R, wR_2, S	0.0539, 0.1304, 1.04
Min. and max. resd. dens. (e Å^{-3})	−0.60, 0.44

the N_2O_2 coordination site and assumes a nearly planar geometry (the mean plane deviation 0.031 Å), a situation which is different from its analogues [17]. The deviation of the Cu(II) from the N_2O_2 plane is 0.0813 Å. In-plane bond distances range from 1.907 to 1.920 Å. The Mn(II) ion resides at the N_3O_2 site and assumes a pentagonal bipyramidal geometry together with two water oxygen atoms, O(3) and O(4). The Mn(II) coordination sphere is somewhat distorted from a regular pentagonal dipyramid as judged from bond distances and angles (see table 2). Mn–O(1) and Mn–O(2) bond distances (2.299(3) and 2.281(2) Å, respectively) and the Mn(1)–N(3), Mn(1)–N(4) and Mn(1)–N(5) bond distances (2.243(4), 2.427(4) and 2.214(3) Å, respectively) are somewhat longer than usual [18, 19]. The Mn(1)–O(3) and Mn(1)–O(4) bond distances are shorter (2.172(2) and 2.228(2) Å, respectively) than in-plane bond distances. Mn(II) is situated in an N_3O_2 plane (the mean plane deviation is 0.3089 Å) with a deviation

Table 2. Selected bond distances (Å) and angles (°) for $[CuMnL(H_2O)_2](ClO_4)_2$.

Cu1–O1	1.920(3)	Mn1–O3	2.172(2)
Cu1–O2	1.893(3)	Mn1–O4	2.228(2)
Cu1–N1	1.907(4)	Mn1–N3	2.243(4)
Cu1–N2	1.915(3)	Mn1–N4	2.427(4)
Mn1–O1	2.299(3)	Mn1–N5	2.214(3)
Mn–O2	2.281(2)	Cu1–Mn1	3.244
O1–Cu1–N1	95.79(12)	N4–Mn1–N5	71.90(12)
O1–Cu1–N2	164.45(12)	O2–Cu1–O21	94.96(9)
O2–Cu1–N1	173.99(12)	O2–Cu1–N2	95.76(13)
O21–Cu1–N1	79.52(11)	O21–Cu1–N2	102.61(11)
N1–Cu1–N2	83.27(14)	O1–Mn1–O2	69.73(9)
O1–Mn1–O3	81.41(9)	O1–Mn1–O4	101.80(9)
O1–Mn–N3	46.55(10)	O1–Mn1–N4	137.67(10)
O1–Mn1–N5	75.52(11)	Cu1–O1–C1	123.2(2)
O2–Mn1–O3	90.97(9)	Cu1–O1–Mn1	100.13(10)
O2–Mn1–O4	83.31(9)	Mn1–O1–C1	136.2(2)
O2–Mn1–N3	77.68(10)	Cu1–O2–Mn1	101.59(10)
O2–Mn1–N4	149.61(10)	Cu1–O2–C11	126.0(2)
O2–Mn1–N5	137.83(11)	Mn1–O2–C11	131.4(2)
O3–Mn1–O4	171.92(10)	Cu1–O21–Cl2	155.79(17)
O3–Mn1–N3	92.03(10)	O3–Mn1–N4	82.97(10)
O3–Mn1–N5	06.94(10)	O4–Mn1–N3	81.21(10)
O4–Mn1–N4	99.10(10)	O4–Mn–N5	81.10(10)

of 0.0241 Å. Two water molecules coordinated to the Mn(II) ion are *trans* to each other, and each water molecule is disposed to the open face above the Cu(II) ion. The macrocycle is not planar because of N(3), N(4) and N(5) coordination to Mn(II) ion and is bent at the O(1) and O(2) edge; the dihedral angle between the least-squares plane defined by N(1), N(2), O(1) and O(2), and the plane defined by O(1), O(2), N(3), N(4) and N(5) is 23.0°. The ethylene chain in a five-membered chelate ring involving Cu(1), N(1) and N(2) adopts a skew conformation. The bite angle between the N(1)–C(8) and N(2)–C(9) bonds with respect to the C(8)–C(9) axis is 51.9°. The NH-diethylene chain in the two five-membered chelate rings (involving Mn(1), N(3) and N(4) and involving Mn(1), N(4) and N(5)) adopts an S-form conformation, and the angle between the C(19)–C(18) and C(21)–C(22) is 97.1°. Each moiety composed of phenyloxide, and two C=N groups assumes a near planar configuration with angles between phenyl and C=N less than 2.7°. The sum of bond angles around O(1) and O(2) are 359.5(8) and 359.2(2)°, respectively. The angle between the O(1)–C(1)–C(4)–C(23) axis of one phenolic moiety and the O(2)–C(11)–C(14)–C(27) axis of the other phenolic moiety is 31.1°, which indicates that the macrocycle are bent. The two phenyl planes are not parallel, with a dihedral angle of 35.1°.

3.3. *Magnetic properties*

The temperature dependence of magnetic susceptibility from 2 to 300 K is shown in figure 3 in the forms of χ_M and $\chi_M T$ *versus* T. At room temperature, $\chi_M T$ is 4.36 emu K mol^{-1}, which is slightly lower than the theoretical value 4.75 emu K mol^{-1} based on the CuMn unit ($S_{Cu} = 1/2$, $S_{Mn} = 5/2$ and assuming $g_{average} = 2$) without any interaction between ions. As the temperature is lowered, $\chi_M T$ continuously decreases to 3.03 emu K mol^{-1} at 30 K and a plateau with $\chi_M T = 3$ emu K mol^{-1} between 30 and 6 K

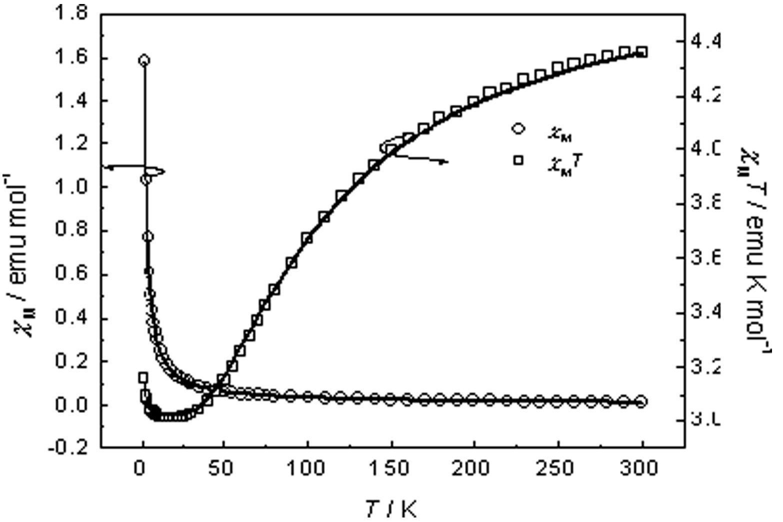


Figure 3. Plot of $\chi_M T$ *vs.* T for $[CuMnL(H_2O)_2](ClO_4)_2$.

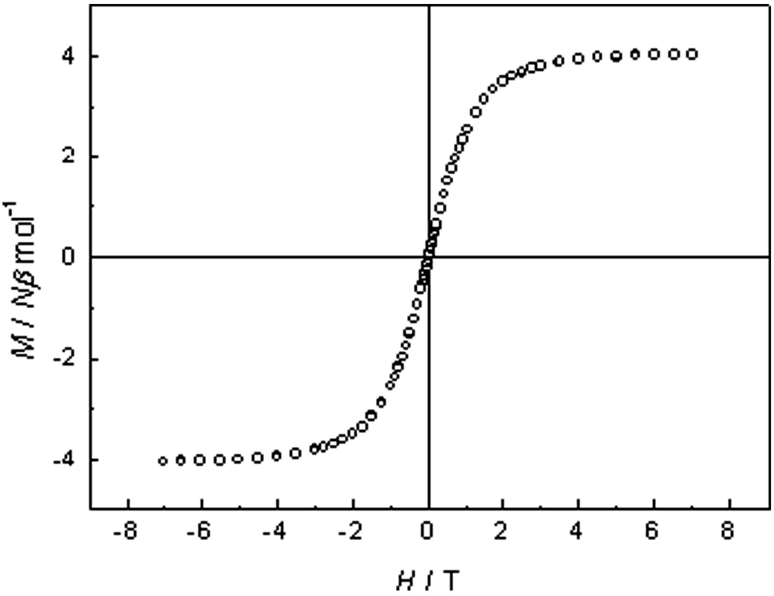


Figure 4. The relationship between the magnetic displacement and the magnetic field.

was observed, corresponding to a ground spin state $S = 2$, characteristic of antiferromagnetic coupling between magnetic centres. Below 6 K, $\chi_M T$ abruptly increases to 3.16 emu K mol^{-1} at 2 K, suggesting the presence of a weak intermolecular ferromagnetic interaction between net spins of the dimers. It is consistent with the field-dependence of magnetization at 1.8 K (figure 4), in which the saturation magnetization value of 4.03 $N\beta$ mol^{-1} exactly indicates the antiferromagnetic coupling between Cu^{II} and Mn^{II} ions based on the ground spin state $S = 5/2 - 1/2 = 2$. Lack of a hysteresis loop in M–H plot and a maximum in the out-of-phase AC magnetic measurements indicates that there is no long range magnetic ordering between the dimers.

According to this magnetic behaviour and the structure of the complex, the magnetostructure can be described by a traditional dinuclear CuMn model with Hamiltonian $\mathbf{H} = -2J\mathbf{S}_{\mathrm{Mn}}\mathbf{S}_{\mathrm{Cu}}$. Thus, the van Vleck equation can be written as follows [20–22].

$$\chi_{\mathrm{dimer}} = \frac{2Ng^2\beta^2}{kT}\frac{5 + 14\exp(6J/kT)}{5 + 7\exp(6J/kT)}$$

$$\chi_{\mathrm{M}} = \frac{\chi_{\mathrm{dimer}}}{1 - (2zj'/Ng^2\beta^2)\chi_{\mathrm{dimer}}}$$

The best fit result gives: $g = 2.001(1)$, $J = -18.4(1)\,\mathrm{cm}^{-1}$, $zj' = 0.015(1)\,\mathrm{cm}^{-1}$ and $R = 1.4 \times 10^{-4}$ ($R = \sum[(\chi_{\mathrm{M}}T)_{\mathrm{Calcd}} - (\chi_{\mathrm{M}}T)_{\mathrm{obs}}]^2/\sum(\chi_{\mathrm{M}}T)^2_{\mathrm{obs}}$), indicative of the relatively strong antiferromagnetic coupling between Mn(II) and Cu(II) ions and a very weak interdimer ferromagnetic interaction.

3.4. *Electrochemical properties*

Electrochemistry has been studied by means of cyclic voltammetry in DMF. A typical voltammogram is shown in figure 5. When scanning from −0.4 to −1.5 V, two anodic processes and one cathodic process were observed, and peaks appeared with half-wave potential ($E_{1/2}$) −0.787 for the complex, indicating that it exhibits a reversible

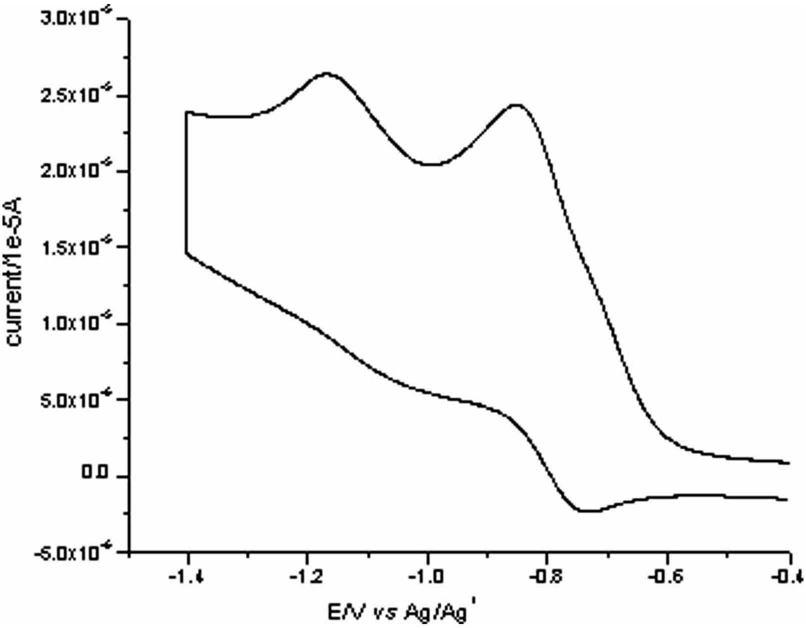


Figure 5. Cyclic voltammogram of $[\mathrm{CuMnL(H_2O)_2}](\mathrm{ClO_4})_2$ in DMF solution; concentration: $5 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$ (scan rate $100\,\mathrm{mV\,s^{-1}}$).

Cu(II)Mn(II)/Cu(I)Mn(II) and an irreversible Cu(I)Mn(II)/Cu(0)Mn(II) redox process. The two coupled redox processes can be expressed as follows (1).

$$[\mathrm{Cu(II)Mn(II)L}] \underset{-e}{\overset{e}{\rightleftharpoons}} [\mathrm{Cu(I)Mn(II)L}] \xrightarrow{e} [\mathrm{Cu(0)Mn(II)L}] \qquad (1)$$

No anodic process was observed when scanning the solution of the complex from −0.4 to 1.5 V, indicating that the complex is difficult to oxidize.

4. Conclusion

The heterodinuclear $[\mathrm{Mn(II)Cu(II)L(H_2O)_2}](\mathrm{ClO_4})_2$ complex has a rigid dinuclear core with Mn(II) in the N_3O_2 site and the Cu(II) in the N_2O_2 site. The coordination environments of Cu(II) and the Mn(II) can be described approximately as square planar and pentagonal bipyramidal, respectively. Very strong antiferromagnetic exchange occurs in the complex ($J = -18.4\,\mathrm{cm}^{-1}$), affording an $S_T = 2.001$ ground state. Electrochemical behaviour expresses two reduction processes.

Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 270758. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax +441223/336033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

Data concerning AC magnetic measurements are available from the authors at to zhiqpan@163.com.

Acknowledgements

The project was supported by the National Natural Science Foundation of China and the local Natural Science Foundation of Hubei, China.

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