Pergamon

0277-5387(94)00261-4

Polyhedron Vol. 14, No. 3, pp. 373–376, 1995

0277-5387/95 \$9.50+0.00

SYNTHESIS AND MAGNETIC PROPERTIES OF NOVEL OXAMIDO HETEROTRINUCLEAR COMPLEXES Cu^{II}–M^{II}–Cu^{II} (M = Mn AND Cu)

SHU-LIN MA
Tianjin College of Commerce, Tianjin, 300400, P. R. China

and

ZONG-HUI JIANG, DAI-ZHENG LIAO, SHI-PING YAN and GENG-LIN WANG*
Department of Chemistry, Nankai University, Tianjin, 300071, P. R. China

(*Received* 17 *December* 1993; *accepted* 12 *July* 1994)

Abstract—Two novel trinuclear complexes have been synthesized, namely $[Cu_2(oxae)_2(H_2O)_2Mn](ClO_4)_2$ (**1**) and $[Cu_2(oxae)_2Cu](ClO_4)_2$ (**2**), where oxae denotes the *N*,*N'*-bis(2-aminoethyl)oxamido dianion. Based on IR, elemental analyses, conductivity measurements and electronic spectra, the complexes are proposed to have extended oxamido-bridged structures. The magnetic susceptibility of the complex **1** has been studied in the 4–300 K range and the observed data were fit by least-squares to a susceptibility equation derived from the spin Hamiltonian, $\hat{H} = -2J(\hat{S}_1\hat{S}_2+\hat{S}_2\hat{S}_3)-2J'\hat{S}_1\hat{S}_3$. The exchange integrals, J and J', were found to be equal to -18 and -0.38 cm^{-1}. This procedure indicates the existence of an antiferromagnetic spin-exchange interaction between the adjacent metal ions. The powder ESR spectrum of complex **1** has been obtained and discussed.

The area of polynuclear complexes with extended bridges has attracted the attention of many chemists.[1–3] Their work has attempted to mimic the active sites and functions of biological substances and to design and synthesize molecular magnets. In comparison to a number of studies dealing with binuclear systems, relatively few studies dealing with magnetic trinuclear systems have been reported, especially for heterotrinuclear complexes.

Based on the bridging function of the oxamido group, Kahn *et al.*[4,5] and our laboratory[6–11] utilized *N*,*N'*-bis(3-aminopropyl)oxamidocopper(II) [Cu(oxpn)] as a bidentate mononuclear fragment to prepare binuclear and a few trinuclear complexes, and their magnetic properties and some crystal structures were studied. Recently, complexes of this kind with *N*,*N'*-bis(2-aminoethyl)oxamido have been synthesized and characterized in our laboratory.[12] As an extension of the above investigation, this paper deals with the synthesis and magnetic and ESR properties of the two novel trinuclear complexes, $[Cu_2(oxae)_2(H_2O)_2Mn](ClO_4)_2$ and $[Cu_2(oxae)_2Cu](ClO_4)_2 \cdot H_2O$, [where oxae = *N*,*N'*-bis(2-aminoethyl)oxamido dianion].

EXPERIMENTAL

Materials

All of the reagents used in the synthesis were analytical grade and were purchased from Peking Chemical Company. Cu(oxae) was synthesized as described previously.[12,13]

Preparation of $[Cu_2(oxae)_2(H_2O)_2Mn](ClO_4)_2$ (1)

To Cu(oxae) (188.4 mg, 0.8 mmol) stirred in absolute ethanol (15 cm^3) was added a solution of $Mn(ClO_4)_2 \cdot 6H_2O$ (144.8 mg, 0.4 mmol) in absolute

---

*Author to whom correspondence should be addressed.

ethanol (10 cm^3). The stirring was continued for a further 5 h to give red microcrystals which were separated, washed with absolute ethanol and diethyl ether several times and dried *in vacuo*. Found: C, 19.0; H, 3.7; N, 14.4; Cu, 16.7; Mn, 7.0. Calc. for $C_{12}H_{28}N_8O_{14}Cl_2Cu_2Mn$: C, 18.8; H, 3.7; N, 14.6; Cu, 16.7; Mn, 7.2%.

Preparation of $[Cu_2(oxae)_2Cu](ClO_4)_2 \cdot H_2O$ (**2**)

This complex was obtained as blue–green microcrystals by the same procedure but using $Cu(ClO_4)_2 \cdot 6H_2O$ (148.2 mg, 0.4 mmol) instead of $Mn(ClO_4)_2 \cdot 6H_2O$. Found: C, 19.2; H, 3.4; N, 14.8; Cu, 25.3. Calc. for $C_{12}H_{24}N_8O_{12}Cl_2Cu_3H_2O$: C, 19.2; H, 3.5; N, 14.9; Cu, 25.4%.

Measurements

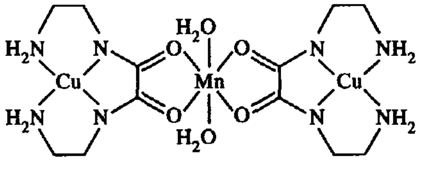
Elemental analyses of carbon, hydrogen and nitrogen were carried out with a Perkin–Elmer elemental analyser, Model 240. Metal contents were determined by EDTA titration. IR spectra were measured on a Shimadzu IR spectrophotometer. Model 408, using KBr pellets, and the electronic spectra (DMF solution) were measured on a Hitachi-240 spectrophotometer. The molar conductances were measured with a DDS-11A conductometer. Variable temperature magnetic susceptibilities were carried out at the Institute of Physics, Chinese Academy of Sciences using a vibrating sample magnetometer, Model CF-1. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms, and the magnetic moments were calculated using the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$. The ESR spectra were measured with a JES-FEIXG ESR-apparatus using the X-band.

RESULTS AND DISCUSSION

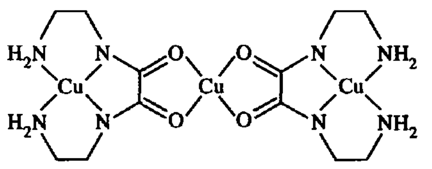
Elemental analyses have indicated that the reaction of Cu(oxae) with $Mn(ClO_4)_2 \cdot 6H_2O$ or $Cu(ClO_4)_2 \cdot 6H_2O$ yielded the trinuclear complexes. For all complexes, the molar conductance values (see Table 1) fall in the expected range for 1 : 2 electrolytes,[14] indicating that the perchlorate anions are situated outside the metal coordination sphere. The significant bands from the IR spectra for the complexes are given in Table 1. It is noted that the carbonyl stretching vibration at 1615 cm^{-1} for the mononuclear fragment Cu(oxae) was considerably shifted towards higher frequencies (20 cm^{-1} for **1** and 45 cm^{-1} for **2** in their trinuclear complexes. It is likely that the bond order of C═O in the trinuclear complexes is higher than in its corresponding mononuclear complex. This shift has often been used as definite proof of an oxamido bridge.[15] On the other hand, the —NH_2 vibration at 3250 cm^{-1} for Cu(oxae) was present for all complexes and a broad, intense band was observed at 1085 cm^{-1}, which is typical for a non-coordinated perchlorate ion.[16] This is consistent with the measured conductance data. The electronic absorption spectral data for Cu^{II}–Mn^{II}–Cu^{II} complexes (MeCN solution) showed a broad band in the visible range at 19.0×10^3 cm^{-1}, which may be attributed to the *d*–*d* transition of copper(II). A strong absorption in the short wavelength range (at 28.6×10^3 cm^{-1}) may be attributed to the charge-transfer band. Further investigation on these and similar systems is still required in order to get a detailed assignment for charge-transfer. 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 ${}^6A_{1g}$. Because *d*–*d* transitions of manganese(II) (${}^6A_{1g} \rightarrow {}^4T_{1g}(G), {}^4T_{2g}(G), {}^4A_{1g}$, etc.) are spin forbidden, in the spectra of Cu^{II}–Mn^{II}–Cu^{II} complex no characteristic band of manganese(II) was found. The electronic absorption spectrum for the Cu^{II}–Cu^{II}–Cu^{II} complex (DMF solution) shows a strong absorption in the ultraviolet range at 29.9×10^3 cm^{-1} and only a weak absorption in the visible range at 16.1×10^3 cm^{-1} can be observed. The former may be attributed to the charge-transfer

Table 1. Physical data of complexes

Complex	Colour	Λ_M ($\Omega^{-1}cm^2$ mol^{-1})	IR (cm^{-1})			UV (10^3 cm^{-1})	
			—NH_2	C═O	ClO_4^-	*d*–*d*	CT
Cu(oxae)	violet		3250	1615		18.7	
$[Cu_2(oxae)_2(H_2O)_2Mn](ClO_4)_2$	red	267 (MeCN)	3250	1635	1085	19.0	28.6
$[Cu_2(oxae)_2Cu](ClO_4)_2H_2O$	blue–green	133 (DMF)	3250	1660	1085	16.1	29.9



Complex (1)



Complex (2)

Fig. 1. Coordination environment of the complexes.

absorption band and the latter to the *d*–*d* transition. Based on the composition of these complexes, IR and electronic spectra and conductivity measurements, the complexes are proposed to have an oxamido-bridged structure, as shown in Fig. 1.

ESR spectra

The powder ESR spectrum for the trinuclear complex **1** has been studied at room temperature.

The ESR spectrum of the trinuclear complex **1** exhibits asymmetric broad bands with $g_{\parallel} = 2.31$, $g_{\perp} = 1.83$ and $\bar{g} = 1.99$, implying the existence of a magnetic spin-exchange interaction between the copper(II) ion and the manganese(II) ion in the trinuclear complex. Two copper(II) ions ($S_1 = S_3 = 1/2$) are coupled with the manganese(II) ion ($S_2 = 5/2$) to yield the total spin state $S_T = 7/2, 5/2, 5/2, 3/2$. On the basis of a Boltzmann distribution, some of the coupled states have a thermal population at room temperature owing to weaker interaction. Thus, the asymmetric broad peaks may be ascribed to these populated states in the complex.

Spin-exchange interaction of the complexes

The temperature dependences of the susceptibilities and magnetic moments for the complex **1** are shown in Fig. 2. The observed magnetic moment at room temperature for complex **1** is less than the spin-only value (6.40 B.M.) and decreases steadily with decreasing temperature, implying the existence of an antiferromagnetic spin-exchange interaction within each molecule.

In order to understand quantitatively the magnitudes of spin-exchange interaction, the magnetic analysis was carried out with the susceptibility equation based on the Heisenberg mode,[17] $\hat{H} = -2J(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3) - 2J'\hat{S}_1\hat{S}_3$. Assuming that the integral between the terminal copper ion is J', the molar susceptibility of Cu^{II}–Mn^{II}–Cu^{II} ($S_1 = S_3 = 1/2$, $S_2 = 5/2$) system is given in eq. (1):

$$\chi_M = \frac{Ng^2\beta^2}{4K(T-\theta)} \left[\frac{10\exp(-7J/kT) + 35\exp(-2J/kT) + 84\exp(-5J/kT) + 35\exp(-2J'/kT)}{2\exp(-7J/kT) + 3\exp(-2J/kT) + 4\exp(-5J/kT) + 3\exp(-2J'/kT)}\right], \quad (1)$$

where χ_M is the susceptibility per trinuclear complex, θ is the Curie–Weiss parameter and other symbols have their usual meanings. As shown in Fig. 2, a good least-squares fit to the experimental data was attained with eq. (1). The magnetic parameters thus determined are $J = -18$ cm^{-1},

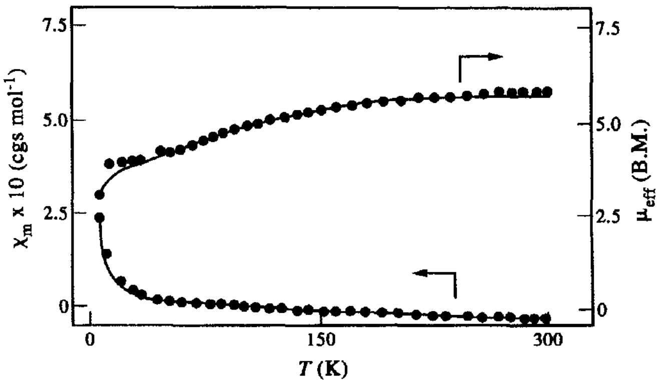


Fig. 2. Temperature variation of the magnetic susceptibility and magnetic moment of the $[Cu_2(oxae)_2(H_2O)_2Mn](ClO_4)_2$. The curves were calculated using eq. (1).

$J' = -0.38$ cm^{-1}, $g = 2.00$ and $\theta = -2.64$ K. The agreement factor F defined here as $F = \Sigma[(\chi_M)_{obs.} - (\chi_M)_{calc.}]^2/\Sigma(\chi_M)_{obs.}$ is then equal to 1.3×10^{-4}. This result also indicates that the complex **1** undergoes an antiferromagnetic spin-exchange interaction between the metal ions.

Acknowledgement—This project was supported by the National Natural Science Foundation of China.

REFERENCES

1. R. D. Willett, D. Gatteschi and O. Kahn (Eds), *Magneto-Structural Correlation in Exchange-Coupled Systems*, pp. 523–554. NATO ASI Series, Reidel, Dordrecht, Holland (1985).
2. O. Kahn, *Struct. Bond.* (*Berlin*) 1987, **68**, 89.
3. D. Gatteschi, O. Kahn, J. S. Miller and F. Palacio (Eds), *Molecular Magnetic Materials*. NATO, ASI Series. Kluwer, Dordrecht (1991).
4. Y. Journaux, J. Sletten and O. Kahn, *Inorg. Chem.* 1985, **24**, 4063.
5. Y. Journaux, J. Sletten and O. Kahn, *Inorg. Chem.* 1988, **25**, 399.
6. Z. M. Liu, Z. H. Jiang, D. Z. Liao, G. L. Wang, X. K. Yao and H. G. Wang, *Acta Chim. Sinica* 1991, **49**, 981.
7. Z. Y. Zhang, D. Z. Liao, Z. H. Jiang, S. Q. Hao, X. K. Yao, H. G. Wang and G. L. Wang, *Inorg. Chim. Acta* 1990, **173**, 201.
8. Z. M. Liu, D. Z. Liao, Z. H. Jiang and G. L. Wang, *Synth. React. Inorg. Met.-Org. Chem.* 1991, **21**, 289.
9. D. Z. Liao, Z. Y. Zhang and Z. H. Jiang, *J. Chin. Univ.* (*B*) 1990, **6**, 226.
10. Z. Y. Zhang, D. Z. Liao, Z. H. Jiang, S. Q. Hao, G. L. Wang, X. K. Yao and H. G. Wang, *Scientia Sinica* (*Ser. B*) 1990, **6**, 581.
11. Z. M. Liu, D. Z. Liao, Z. H. Jiang and G. L. Wang, *Chem. Res. Chin. Univ.* 1992, **8**, 138.
12. S. L. Ma, Z. H. Jiang, D. Z. Liao, S. P. Yan and G. L. Wang, *Polyhedron* 1993, **12**, 1523.
13. H. Ojima and K. Yamada, *Nippon Kagaku Kaishi* 1968, **89**, 490.
14. W. J. Geary, *Coord. Chem. Rev.* 1971, **7**, 81.
15. H. Ojima and K. Nonoyama, *Coord. Chem. Rev.* 1988, **92**, 85.
16. M. R. Rosenthal, *J. Chem. Educ.* 1973, **50**, 331.
17. E. Sinn and C. M. Harris, *Coord. Chem. Rev.* 1969, **4**, 391.