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Synthesis and Magnetic Properties of SOD Mimics – Two Copper(II) Binuclear Complexes Bridged by Oxamido-N,N′-diacetic Acid and Acetate Anion

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It is well known that SOD (superoxide dismutase) plays a critical role in organism. However, as a kind of protein, SOD itself has certain limits in the field of application. As a result, the SOD-mimetic complexes which may better SOD-activity to a certain extent can be of much importance. Two SOD mimics which are novel μ-oxamidato binuclear unit complexes with 1D structure have been synthesized, namely $\{Na[Cu_2(oxaa)L_2OAc]\}_n$, where oxaa is oxamido-N,N′-diacetic acid tetraanion and L denotes 1,10-phenanthroline or 5-nitro-1,10-phenanthroline. The temperature dependence of the magnetic susceptibilities of $\{Na[Cu_2(oxaa)(1,10\text{-}phen)_2OAc]\}_n$ has been investigated in the 4.99–299 K range, giving the exchange parameter $J = -309.0\ cm^{-1}$. This result is commensurate with antiferromagnetic interaction between the adjacent metal ions.

Key words: SOD mimic, oxamidato bridge, acetate bridge, Cu(II)–Cu(II) binuclear complex, magnetic properties

The synthesis and magnetic investigations of binuclear transition-metal complexes propagated by multi-atom bridges are of current interest, not only for gaining some insight into the pathways of electron transfers in biological system [1], but also for obtaining information about designing and synthesizing SOD mimics and molecule-based magnets [2], and for investigating the spin-exchange mechanism between paramagnetic metal ions [3]. N-Substituted and N,N′-disubstituted oxamidos such as I have been playing a key role in the design of polymetallic systems. The versatility of these ligands, which is based on (a) their easy cis-trans conformational change affording symmetric and asymmetric oxamidato bridges [4–5] and (b) the bidentate character of the mononuclear metal-oxamidato complex allows the formation of di- [6–7], tri- [8–9] and tetranuclear [10–11] complexes. The effective bridging function of μ-oxamido has been revealed by X-ray analysis for some of the complexes [12–16]. In order to provide more examples of oxamidato-bridges binuclear complexes to investigate further the structural variation effects upon spin-coupling and SOD-like activity, and meanwhile to gain a structure which is more similar to the active center of SOD (superoxide dismutase), in this paper, two new copper(II) complexes have been synthesized by using oxamido-N,N′-diacetic acid [abbreviated as $H_4(oxaa)$] as bridg-

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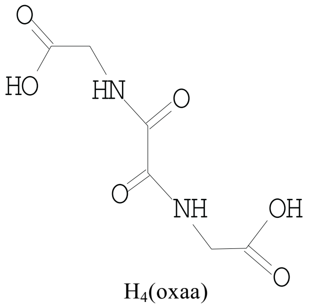

H_4(oxaa)
I

ing ligand and acetic salt as the metal atom supplier and ligand bridging binuclear units. Magnetic properties of the complex, $\{Na[Cu_2(oxaa)(1,10\text{-}phen)_2OAc]\}_n$, have also been studied.

EXPERIMENTAL

All chemicals were of analytical grade and were purchased from Peking Chemical Company. The ligand oxamido-N,N′-diacetic acid was synthesized by the following general procedure reported in [17]. A 20 mmol amount of glycine dissolved in about 25 cm^3 of water was neutralized with equivalent NaOH, and 10 mmol of diethyl oxalate in 25 cm^3 of ethanol was added to the aqueous solution. After the mixture was heated at 60°C with stirring, an excess of HCl (pH = 1) was added for precipitation of white microcrystals of free H_4(oxaa). The product was filtered off, washed with cold water, ethanol and ether and dried *in vacuo*.

Preparation of $\{Na[Cu_2(oxaa)(1,10\text{-}phen)_2OAc]\}_n$: To H_4(oxaa) (204.1 mg, 1.0 mmol) and 1,10-phen (396.4 mg, 2.0 mmol) stirred in absolute ethanol (10 cm^3), NaOH (4.0 mmol, methanol solution) was added dropwisely, then a solution of $Cu(OAc)_2$ H_2O (399.3 mg, 2.0 mmol) in absolute methanol (10 cm^3) was added. After stirring for 5 h, yellow green microcrystalline product formed immediately. Microcrystals were washed several times with absolute methanol and ether and dried *in vacuo*. (Found: C, 49.5; H, 3.0; N, 10.7. $C_{32}H_{23}N_6O_8Cu_2Na$ calcd: C, 49.5; H, 3.0; N, 10.9%).

Preparation of $\{Na[Cu_2(oxaa)(5\text{-}NO_2\text{-}1,10\text{-}phen)_2OAc]H_2O\}_n$: This complex was prepared in the same way as above by replacing 1,10-phen with 5-NO_2-1,10-phen. Blue green microcrystals were obtained. (Found: C, 44.0; H, 2.5; N, 12.9. $C_{32}H_{19}N_8O_{13}Cu_2Na$ calcd: C, 44.0; H, 2.2; N, 12.8%).

Physical measurements: Elemental analyses of carbon, hydrogen and nitrogen were carried out with a Perkin-Elmer elemental analyzer, Model 240. The IR spectra were measured on a Perkin Elmer 983G, using KBr pellets. Variable temperature magnetic susceptibilities (4.99–299 K) were performed at the Institute of Physics, Chinese Academy of Science, China, using a Superconducting Quantum Interference Device (SQVID) Magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms, and the magnetic moments were calculated using the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$.

RESULTS AND DISCUSSION

General characterization: Elemental analyses indicate that the reaction of H_4(oxaa) with $Cu(OAc)_2$ H_2O and 1,10-phen or 5-NO_2-1,10-phen yielded the binuclear copper(II)-copper(II) complexes.

Selected IR bands of the complexes are given in Table 1. The amide I band is located at 1621 cm^{-1} and 1624 cm^{-1} for 1,10-phen and 5-NO_2-1, 10-phen, respectively.

Since for free H_4(oxaa) the absorption occurs at 1640 cm^{-1}, the shift to lower wave numbers of the amide I band is consistent with the presence of a bridging oxamidato ligand [18]. In addition, the stretching vibrations of carboxylate groups, $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$, appear as strong absorptions for the studied complexes (see Table 1).

Table 1. Physical data of the complexes.

Complex	Color	IR(cm^{-1})			$\mu_{eff}(\mu B)$
		ν(C=O)	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	Room Temp.
1	yellow green	1621	1650	1371	1.40
2	blue green	1624	1639	1380	–

1. $\{Na[Cu_2(oxaa)(1,10\text{-}phen)_2OAc]\}_n$; 2. $\{Na[Cu_2(oxaa)(5\text{-}N\text{-}1,10\text{-}phen)_2OAc]H_2O\}_n$.

Based on the composition of these complexes and their IR spectra, the complexes are proposed to have an oxamidato-bridged structure and consist of two copper(II) ions in an octahedron environment, as shown in Figure 1.

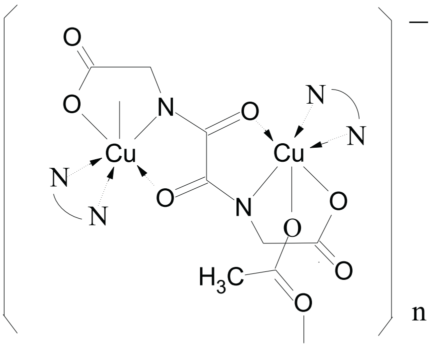

Figure 1. Supposed structure of $\{Na[Cu_2(oxaa)L_2OAc]\}_n$ (L = 1,10-phenanthroline or 5-nitro-1,10-phenanthroline, n is a casual natural number).

Spin-exchange interaction of Cu(II)–Cu(II) complexes: The magnetic properties of the $\{Na[Cu_2(oxaa)(1,10\text{-}phen)_2OAc]\}_n$ in the solid state have been studied at 1.0 T, over the temperature range 4.99–299 K. The data obtained for the molar susceptibility and the effective magnetic moment are plotted in Fig. 2. At room temperature, the μ_{eff} value equals 1.40 μB, which is lower than the spin-only value of 2.45 μB for Cu(II)–Cu(II) system, and the μ_{eff} values decrease with decreasing temperature. This behavior indicates an antiferromagnetic coupling between the two copper(II) centers. The magnetic analysis was carried out with the modified Bleaney-Bowers equation based on the exchange Hamiltonian $\hat{H} = -2J\hat{S}_1\hat{S}_2$ with $S_1 = S_2 = 1/2$ and assuming that the integral between the binuclear units is zero. The molar susceptibility of copper(II)–copper(II) system is given by (1)

$$\chi_M = (2N\beta^2g^2/kT)[3 + \exp(-2J/kT)]^{-1}(1 - \rho) + N\beta^2g^2\rho/\,2kT + N_\alpha \qquad (1)$$

where χ_M denotes the susceptibility per binuclear complex, ρ the fraction of uncoupled copper(II) impurity, N_α the temperature independent paramagnetism (120×10^{6} cm^3mol^{-1}) and the other symbols have their usual meanings. As shown in Fig. 2, good least-squares fit to experimental data are attained with (1). The magnetic parameters thus determined are $J = -309.0\ cm^{-1}$, $g = 2.56$, $\rho = 0.019$ and $F = 4.36 \times 10^{-6}$ [$F = \Sigma[(\chi_M)_{obs.} - (\chi_M)_{calc.}]^2/\Sigma(\chi_M)_{obs.}$]. This result also indicates that the complex {$Na[Cu_2$(o-xaa)(1,10-phen)$_2$OAc]}$_n$ undergoes a strong antiferromagnetic spin-exchange interaction between the metal ions. This interaction gives a singlet ground state and a triplet excited state. The separation between the two states is equal to 618 cm^{-1}.

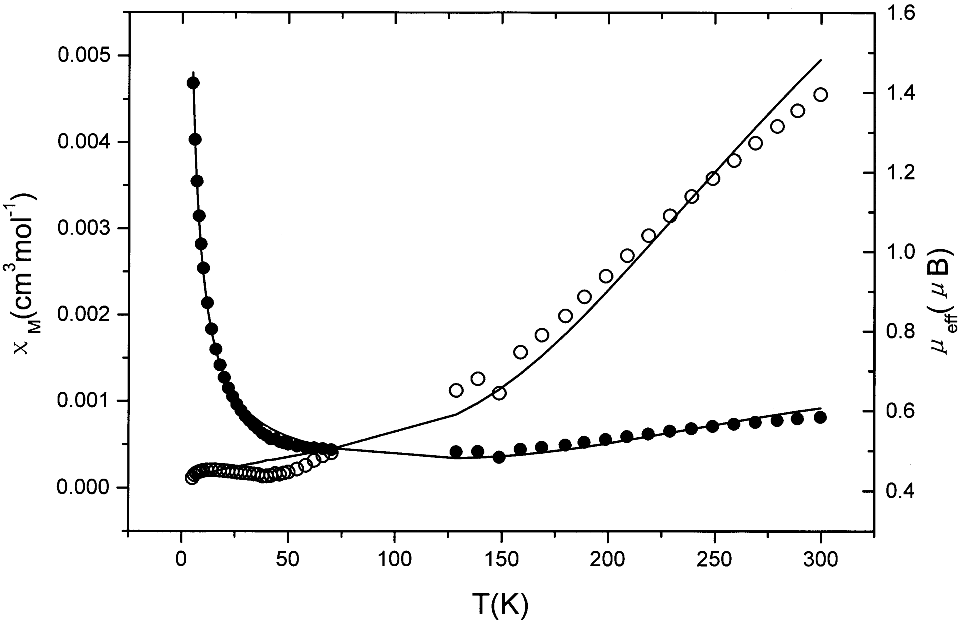

Figure 2. Temperature variation of the experimental and calculated magnetic susceptibility and magnetic moment of {$Na[Cu_2$(oxaa)(1,10-phen)$_2$OAc]}$_n$.

Kahn [19] has proposed a molecular orbital model to rationalize the mechanism of the exchange interaction. In this model, the experimentally observed exchange parameter J is taken as the sum of a negative antiferromagnetic contribution and a positive ferromagnetic contribution J_{AF} and a positive ferromagnetic J_F, $J = J_{AF} + J_F$. It is usual to assume that the J_F value is much less than the J_{AF} value. Therefore, only when $J_{AF} = 0$, $J = J_F$, the system exhibits a ferromagnetic interaction, otherwise $J_{AF} \neq 0$, an antiferromagnetic interaction should be observed. J_{AF} depends on the overlap integral between two different magnetic centers, A and B, represented as $J_{AF} = -2\Delta S$, where $S = <\psi_A | \psi_B>$, Δ is the energy gap between the molecular orbitals built from two magnetic orbitals in the triplet state. ψ_A and ψ_B express one single occupied orbital in the two centers. In this case, no orthogonality could be involved according to the structure of the complexes. Thus, it is unreasonable to believe that the value of the overlap integral $<\psi_A|\psi_B>$ is zero. Actually, $J_{AF} \neq 0$, so an antiferromagnetic exchange interaction should be expected. Owing to the structure of the complexes, the two magnetic orbitals are easily located in the same plane of the oxamido bridge. Therefore, the interaction from out of the binuclear units should be rather strong. On the other hand, two magnetic orbitals are not easily located in the same plane of the acetic bridge between two binuclear units, consequently the interaction between two binuclear units is expected to be quite weak. Actually, we have assumed that the exchange interaction between binuclear units is zero.

A detailed characterization of the SOD-activity of the complexes is in progress.

REFERENCES

1. Arena F., Floriani C., Chiesi-Villa. and Guastini C., *Inorg. Chem*., **25**, 4589 (1986).
2. Willett R.D., Gatteschi D. and Kahn O. (Editors), *Magneto-Structural Correlation in Exchange-Coupled Systems*, NATO ASI Series. Reidel, Dordrecht, Holland, 1985.
3. Cairns C.J. and Busoh D.H., *Coord Chem. Rev*., **69**, 1 (1986).
4. Ma S.L., Liao D.Z., Jiang Z.H., Yan S.P. and Wang G.L., *Polyhedron*, **13**, 1647 (1994).
5. Jin C.Y., Ma S.L. and Liao D.Z., *Polyhedron*, **13**, 2881 (1994).
6. Pei Y., Kahn O. and Sletten J., *J. Am. Chem. Soc.*, **108**, 3143 (1986).
7. Nakatani K., Carriat J. Y., Journaux Y., Kahn O., Loret F., Renard J. P., Pei Y., Sletten J. and Verdaguer H., *J. Am. Chem. Soc*., **111**, 5739 (1989).
8. Pei Y., Journaux Y., Kahn O., Dei A. and Gatteschi D. J., *J. Chem. Soc*., *Chem. Commun.*, 1300 (1986).
9. Pei Y., Journaux Y. and Kahn O., *Inorg. Chem*., **27**, 399 (1988).
10. Okawa H., Kawahara Y., Mikuriya M. and Kida S., *Bull. Chem. Soc. Jpn.*, **53**, 549 (1980).
11. Lloret F., Journaux Y. and Julve M., *Inorg. Chem*., **29**, 3967 (1990).
12. Zhang Z.Y., Liao D.Z., Jiang Z.H., Hao S.Q., Yao X.K., Wang H.G. and Wang G.L., *Inorg. Chim. Acta*, **173**, 201 (1990).
13. Lloret F., Sletten J., Ruiz R., Julve M., Fans J. and Verdaguer M., *Inorg. Chem*., **31**, 778 (1992).
14. Mathoniere C., Kahn O., Daran J.C., Hilbig H. and Kohler F.H., *Inorg. Chem*., **32**, 4057 (1993).
15. Benelli C., Fabrett A. and Giusti A., *J. Chem. Soc*., *Dalton Trans*., **3**, 409 (1993).
16. Sanz J.L., Ruiz R., Gleizes A., Lloret F., Fans J., Julve M., Borras-Almenar J.J. and Journaux Y., *Inorg. Chem*., **35**, 7384 (1996).
17. Ojima H. and Yamada K., *Bull. Chem. Soc. Japan*, **43**, 1601 (1970).
18. Ojima H. and Nonoyama K., *Coord. Chem. Rev.*, **92**, 85 (1988).
19. Kahn O. and Charlot M.F., *Nouv. J. Chim*., **40**, 567 (1980).