

단 신

다리 리간드로 연결되고 구리(II)를 포함하는 금속 이합체 화합물 $\text{Cu}_2(\text{C}_{15}\text{H}_{26}\text{N}_2)_2(\mu\text{-C}_2\text{O}_4)(\text{NO}_3)_2$ 의 합성 및 자기적 성질

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Synthesis and Magnetic Properties of Binuclear Copper(II) Complex with a Bridging Oxalate, $\text{Cu}_2(\text{C}_{15}\text{H}_{26}\text{N}_2)_2(\mu\text{-C}_2\text{O}_4)(\text{NO}_3)_2$

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Many studies of copper(II) complexes of the neutral alkaloid (-)-sparteine ($\text{C}_{15}\text{H}_{26}\text{N}_2$) (Fig. 1) have been reported.¹⁻⁶ It has been recognized that, without an exception, the prepared copper(II) sparteine complexes of the type $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{X}_2$ are always monomeric, and the role of anions (X) in these compounds is important in the ultimate molecular structure.⁴⁻⁶

However, in our previous studies^{4,5}, we found that the coordinated nitrate ligands in $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)_2$ is very labile with respect to nucleophilic substitution.

By utilizing the lability of the nitrate ligand and introducing the oxalate as a bridging ligand, we prepared a new binuclear copper(II) sparteine complex with a bridging oxalate.

Polymetallic complexes with bridged structures have been the research concerns of many workers primarily due to spin-exchange between metal ions and the role of metal ions in metalloenzymes.⁷ The μ -oxalate ligand provides an efficient superexchange pathway to give anti-ferromagnetism of varying extents in these types of molecules.⁸⁻¹³

Hoffma¹⁴ and Kahn¹⁵ have independently shown that there is a correlation between coordination geometry around a Cu(II) center and the magnitude of the singlet-triplet separation, $-2J$. Magnetostructural data concerning

the oxalate-bridged Cu(II) complexes also revealed that the magnetic coupling J is strongly dependent on the nature of terminal ligands L and L' in $\text{LCuC}_2\text{O}_4\text{CuL}'$ unit.¹⁵

In this work, we characterized the prepared title complex and conducted a magnetic study of this compound.

EXPERIMENTAL

Preparation. $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)_2$ as a precursor compound was prepared by literature method,⁴ and was purified by recrystallization in dichloromethane/triethyl-orthoformate (5:1 by volume) mixture.

A solution of 1.00 g (2.37 mmol) of $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)_2$, dissolved in a mixture of absolute ethanol (40 mL) and triethylorthoformate (5 mL), was refluxed for 2

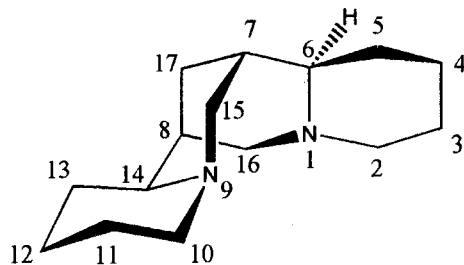
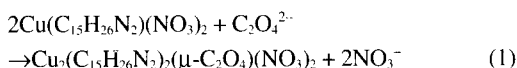


Fig. 1. (-)-sparteine (6R, 7S, 8S, 14S).

hrs in order to remove water. Then 0.32 g (2.37 mmol) of sodium oxalate was added into the solution. The mixture was allowed to react for about 2 days at 50. The solution become turbid as the sodium nitrate is produced from the reaction. Sodium nitrate was removed from the solution by filtration. The filtrate was concentrated by evaporation in a rotary evaporator, and the light green product precipitated was isolated. The overall reaction can be described by equation 1.



The yield of $\text{Cu}_2(\text{C}_{15}\text{H}_{26}\text{N}_2)_2(\mu\text{-C}_2\text{O}_4)(\text{NO}_3)_2$ was 0.69 g (72.3%). Element analysis was performed at Korea Research Institute of Chemical Technology, Taejeon, Korea. Anal. Calcd. for $\text{Cu}_2(\text{C}_{15}\text{H}_{26}\text{N}_2)_2(\mu\text{-C}_2\text{O}_4)(\text{NO}_3)_2$: C, 47.57; H, 6.49; N, 10.40. Found: C, 47.10; H, 6.41; N, 10.19.

Physical measurement. Infrared spectral data were obtained by standard KBr pelleting techniques in conjunction with a Mattson Instruments Polaris FT-IR spectrometer operated at 4 cm^{-1} resolution. The FAB-mass spectrum of the prepared complex dissolved in DMSO/4-nitrobenzyl alcohol was obtained with a Jeol Instruments JMS-DX300 mass spectrometer.

Frozen glass ESR spectra of Cu(II) complexes were acquired at X-band frequency (9.45 GHz) and at 77 K by the use of Bruker Instruments ESP-300S ESR spectrometer.

Magnetic susceptibility measurements were made on a powdered polycrystalline sample over the temperature range of 5 K to 300 K with a SQUID magnetometer (Quantum Design). The data was corrected for the diamagnetism of the constituent atoms with Pascal's constants.

RESULTS AND DISCUSSION

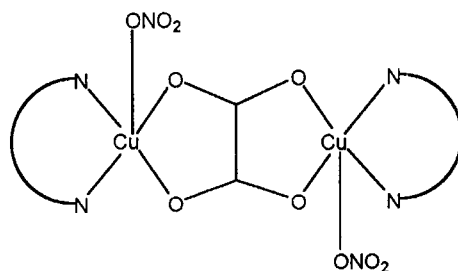
The characterization of the prepared complexes was made by conducting elemental analysis, the use of IR spectroscopy and FAB-mass. Elemental analysis results of the prepared complex strongly suggest that this compound can be formulated as $\text{Cu}_2(\text{C}_{15}\text{H}_{26}\text{N}_2)_2(\mu\text{-C}_2\text{O}_4)(\text{NO}_3)_2$. The IR spectrum of this complex exhibits several bands originated from the oxalate and nitrate ligands: $\nu_a(\text{NO}_3^-)$ at 1466 cm^{-1} , $\nu_s(\text{NO}_3^-)$ at 1420 cm^{-1} , $\nu_a(\text{C}=\text{O})$ at 1650 cm^{-1} , and $\nu_s(\text{C}=\text{O})$ at 986 cm^{-1} . The values are con-

sistent with the presence of a bridging tetradentate oxalate^{16,17} and a monodentate nitrate in this compound. The FAB-mass spectrum of $\text{Cu}_2(\text{C}_{15}\text{H}_{26}\text{N}_2)_2(\mu\text{-C}_2\text{O}_4)(\text{NO}_3)_2$ does not exhibit parent peak but shows $[\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)]^+$ ion peak at $m/e=359$. The fragmentation patterns and the ratio of Cu^{63} and Cu^{65} ($m:m+2:m+4=54:39:7$) clearly indicate that this compound contains two copper atoms in a molecule.

The ESR spectrum of $\text{Cu}_2(\text{C}_{15}\text{H}_{26}\text{N}_2)_2(\mu\text{-C}_2\text{O}_4)(\text{NO}_3)_2$ ($g_{\parallel}=2.262$, $g_{\perp}=2.054$, $A_{\parallel}=141\times 10^{-4}\text{ cm}^{-1}$) is quite similar to that of $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)_2$ ($g_{\parallel}=2.259$, $g_{\perp}=2.047$, $A_{\parallel}=144\times 10^{-4}\text{ cm}^{-1}$) except that the signal intensity of the spectrum is greatly reduced. The reduction in signal intensity is attributable to the antiferromagnetic coupling between two Cu(II) centers in the complex. All the experimental results described above are consistent with the oxalate-bridged dimeric structure for the molecule.

We have attempted several times to prepare single crystals of this compound to determine the crystal structure but failed. This compound is either insoluble or quite unstable in most organic solvents.

However, deduced from the reported crystallographic data of $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)_2$,⁴ and our experimental results, the geometry around two Cu(II) centers is expected to maintain a five-coordinate geometry; the bridged oxalate ligand provides two oxygen donor atoms to each Cu(II) center, and each nitrate ligand coordinates to each Cu(II) center in monodentate fashion. The remaining coordination sites are occupied by the two nitrogen atoms of (-)-sparteine(N^{\sim}N).



A magnetochemical study of the complex has been made in the temperature range of 2–300 K. The complex exhibits very strong antiferromagnetism, and the data follow the Bleaney-Bowers equation.¹⁸ Dependency of magnetic susceptibility on temperature is shown in Fig. 2, which exhibits characteristic strong antiferromagnetic interaction with the maximal susceptibility at 150 K.

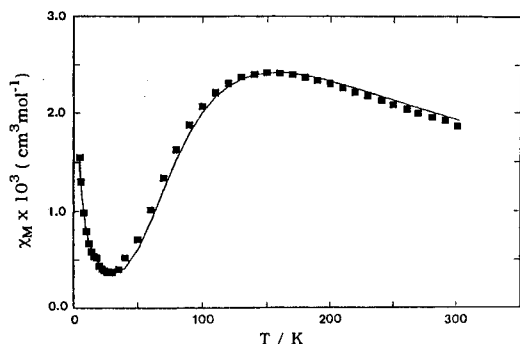


Fig. 2. Calculated (-) and experimental (■) magnetic data for $\text{Cu}_2(\text{C}_{15}\text{H}_{26}\text{N}_2)_2(\mu\text{-C}_2\text{O}_4)(\text{NO}_3)_2$. The equation of the calculated curve is $\chi_M = (2N\beta^2 g^2/kT)[3 + \exp(-J/kT)]^{-1}(1-\rho) + (N\beta^2 g^2/2kT)\rho + 2N\alpha$, with $J = -176.3 \text{ cm}^{-1}$, $g = 2.123$, $\rho = 0.00973$ and $N\alpha = 60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$.

$$\chi_M^{\text{exptl}} = \left(\frac{2N\beta^2 g^2}{kT} \right) \left\{ 3 + \exp\left(-\frac{J}{kT}\right) \right\}^{-1} (1-\rho) + \left(\frac{N\beta^2 g^2}{2kT} \right) \rho + 2N\alpha \quad (2)$$

The effective magnetic moment per Cu(II) ion varies from 0.01 B.M. at 5.0 K to 0.79 B.M. at 300 K. The temperature-independent paramagnetism $N\alpha$ was taken as $60 \times 10^{-6} \text{ cm}^3/\text{mol}$ per copper(II) ion. The average g value $\langle g \rangle$ was evaluated from the equation $\langle g \rangle = 1/3(g_{\parallel} + 2g_{\perp})$. The calculated $\langle g \rangle$ value of 2.123 was used to fit observed magnetic results. With the $\langle g \rangle$ value fixed at 2.123, the least-squares fittings of the data give J value of -176.3 cm^{-1} and ρ of 0.00973.

Kahn and coworkers have demonstrated five-coordinate μ -oxalatodicopper(II) complexes can be designed with J -values from approximately zero to 400 cm^{-1} by modifying the terminal ligand L in $[\text{LCuC}_2\text{O}_4\text{CuL}]^{n+}$ unit.^{19,20} The role of the terminal ligand is to realign the metal magnetic orbital relative to the oxalate σ orbital. If $[\text{LCuC}_2\text{O}_4\text{CuL}]^{n+}$ unit is entirely planar, the $d_{x^2-y^2}$ copper magnetic orbital will be ideally directed toward the oxalate σ orbitals, and the antiferromagnetic interaction will be maximized as in the square pyramidal binuclear complex. However, if the geometry at one of Cu(II) centers is such that its magnetic orbital does not overlap effectively with the oxalate σ orbital, the reduction in J -value will be observed.

For the system of $[\text{LCu}(\mu\text{-C}_2\text{O}_4)\text{CuL}]^{n+}$, Hendrickson *et al.*²¹ had shown that, with $L = 1,1,4,7,7$ -pentaethylene-

triamine (Et_5dien), J value is in the range -20 to -70 cm^{-1} depending on the nature of counteranion, and M. Julve *et al.*⁹ have shown that, with $L = 1,1,4,4$ -tetramethyl-ethylenediamine (tmen), J value is -385.4 cm^{-1} .

The structure of $[\text{Et}_5\text{dienCu}(\mu\text{-C}_2\text{O}_4)\text{CuEt}_5\text{dien}]^{2+}$ is reported to be distorted trigonal bipyramidal, and the structure of $[\text{tmen}(\text{H}_2\text{O})\text{Cu}(\mu\text{-C}_2\text{O}_4)\text{Cu}(\text{H}_2\text{O})\text{tmen}]^{2+}$ is known to have a distorted square pyramid.^{15,22}

From the observed J value of -176.3 cm^{-1} , it is plausible to speculate that the coordination structure around the Cu(II) centers in $\text{Cu}_2(\text{C}_{15}\text{H}_{26}\text{N}_2)_2(\mu\text{-C}_2\text{O}_4)(\text{NO}_3)_2$ adopt the intermediate structure between the trigonal bipyramid and the square pyramid. The chelated and bulky (-)-sparteine ligand might not permit the Cu(II) centers adopting the regular square pyramidal or trigonal bipyramidal structure.

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