

Copper(II) Oxyanion Complexes Derived from Sparteine Copper(II) Dinitrate: Synthesis and Characterization of 4- and 5-Coordinate Copper(II) Complexes

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Nine copper(II) oxyanion, and mixed oxyanion complexes that have four- or five-coordinate geometries around copper(II) centers were derived from sparteine copper(II) dinitrate precursor $[\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)_2]$. The precursor complex undergoes an anion exchange with various oxyanions, and an interchange reaction with other sparteine copper(II) complexes. The $[\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{CH}_3\text{CO}_2)_2]$ also undergoes "halogen atom abstraction" reaction with CCl_4 to produce the mixed anion complex $[\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{CH}_3\text{CO}_2)\text{Cl}]$. The whole set of prepared complexes has been used for the comparative electrochemical and spectroscopic studies.

Keywords : (–)-Sparteine, Oxyanion, Copper(II), Interchange reaction.

Introduction

There has been considerable interest in the coordination chemistry of 4- or 5-coordinate copper(II) compounds that mimic the aspects of the properties of copper in protein.¹ Among these properties that have drawn the attraction of bioinorganic chemists have been the unusually positive reduction potentials and the small hyperfine coupling constants A_{\parallel} in the ESR spectrum of type I copper(II) protein.¹⁻⁶ These extraordinary properties are known to be related to the copper coordination geometry in the metalloprotein.

The lack of enough redox and spectral data relating to the CuN_3S_2 center of azurin² and the CuN_2S_2 center of plastocyanin⁵ make it useful to deduce parallels between these systems and others such as CuN_4 , CuN_5 , CuN_2O_2 , CuN_2O_3 or CuN_2X_2 ($\text{X} = \text{halide}$) centers.⁷⁻¹⁰ Central to such research is the existence of a series of both structurally and spectroscopically well-characterized model complexes that allow comparisons to be made with each other.

Several studies of the transition metal complexes of the (–)-*l*-sparteine ($\text{C}_{15}\text{H}_{26}\text{N}_2$) have been reported,¹¹⁻²⁰ and the crystal structures of sparteine copper(II) complexes with nitrate,²¹ nitrite²² and acetate²³ have been determined previously in our laboratory. The copper(II) centers in these complexes are found to have a distorted tetrahedral or distorted square-pyramidal geometry (See Figure 1).

In this study we attempted to prepare a series of four- and five-coordinate oxyanion complexes derived from precursor $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)_2$, **1** because the nitrate ligand in **1** is substitutionally very labile, and complex **1** easily undergoes ligand exchanges with various anions.²² The lability of nitrate ligand and the steric bulk of sparteine ligand permit the preparation of a variety of 4- and 5-coordinate copper(II) oxyanion complexes of the types $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{L}_2$, $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{LL}'$, and binuclear $\text{Cu}_2(\text{C}_{15}\text{H}_{26}\text{N}_2)_2(\mu\text{-C}_2\text{O}_4)(\text{NO}_3)_2$ from **1**.

This paper describes the detail of synthetic methods, and

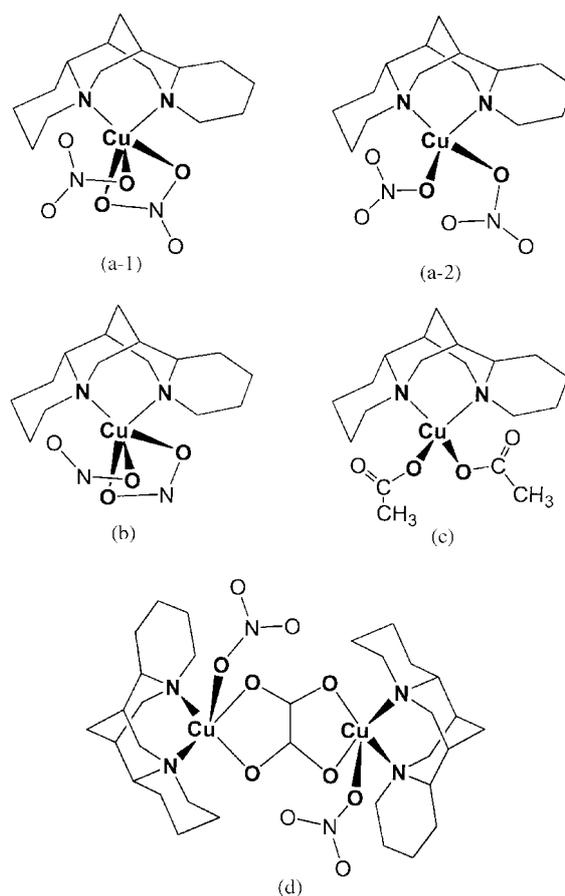


Figure 1. The coordination structures of (–)-sparteine copper(II) complexes with various oxyanions. Central copper(II) ion and coordinated donor atoms are printed in boldface. The depicted structures are referenced from references 21-24.

the characterization and the redox/spectral properties of a series of 4- and 5-coordinate oxyanion complexes of copper (II).

Experimental Section

Materials. All reagents and solvents were obtained commercially either from Sigma chemical company or Aldrich chemicals, and were used without further purification except where noted. Anhydrous ethanol was distilled from calcium hydride and stored under argon. The (–)-sparteine was purchased from Sigma chemical company. All sodium salts (NaNO_2 , NaCl , NaBr , NaCH_3CO_2 , NaOCN , NaN_3 , and $\text{Na}_2\text{C}_2\text{O}_4$) were purified by recrystallization. The anhydrous copper nitrate and sodium salts were dried under vacuum at 60 °C for 12 h before use.

Synthesis of the Complexes

$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)_2$, **1, $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{Cl}_2$, and $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{Br}_2$.** The precursor complex **1**, $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{Cl}_2$ and $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{Br}_2$ were prepared according to the published procedures.^{12,19}

$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{OCN})_2$, **2, $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$, **3**, $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{CH}_3\text{CO}_2)_2$, **4**, and $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{N}_3)_2$.** The complexes **2-4** and $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{N}_3)_2$ were prepared by the anion exchange reaction of precursor complex **1** with stoichiometric amounts of NaOCN (**2**), NaNO_2 (**3**), NaCH_3CO_2 (**4**), and NaN_3 respectively; the complex **1** (1.00 g, 2.37 mmol) was dissolved in 50 mL of ethanol-triethylorthoformate mixture solvent at 60 °C for 2 h. Then, to this solution the corresponding sodium salts in amount of 4.75 mmol was added and stirred vigorously for 6-10 h. Sodium salts produced were removed by filtration and the filtrate was evaporated in a rotary evaporator until the precipitates start to form, and then polycrystalline precipitates formed were isolated and dried under vacuum. The products were purified by recrystallization in dichloromethane-triethylorthoformate mixture solvent (5 : 1 v/v). The $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{N}_3)_2$ was prepared as a precursor for the synthesis of complex **10**. The yield of the complexes **2-4** and copper(II) azide derivative prepared were 0.71 g (80.7%), 0.81 g (87.8%), 0.80 g (81.3%) and 0.77 g (85.3%), respectively.

$\text{Cu}_2(\text{C}_{15}\text{H}_{26}\text{N}_2)_2(\text{C}_2\text{O}_4)(\text{NO}_3)_2$, **5.** Complex **5** was prepared according to a published procedure.²⁴

$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)\text{Cl}$, **6.** To a CH_2Cl_2 solution (15 mL) of $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{Cl}_2$, (0.875 g, 2.37 mmol) was added a CH_2Cl_2 solution of **1** (1.00 g, 2.37 mmol). The mixture was stirred for 3 h at room temperature and set aside until a light green precipitate appeared. It was filtered off, washed with cold ethanol and purified by recrystallization in 50 mL of dichloromethane-triethylorthoformate mixture solvent (5 : 1 v/v). The yield of the light green product was 1.34 g (71.8 %).

$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)\text{Br}$, **7.** To a CH_2Cl_2 solution (15 mL) of $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{Br}_2$, (1.09 g, 2.38 mmol) was added a CH_2Cl_2 solution of **1** (1.00 g, 2.37 mmol). The mixture was stirred for 5 h at room temperature and set aside until a olive green precipitate appeared. It was filtered off, washed with cold ethanol and purified by recrystallization in 50 mL of dichloromethane-triethylorthoformate mixture solvent (5 : 1 v/v). The yield of the product was 1.72 g (82.5%).

$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)(\text{OCN})$, **8.** To a CH_2Cl_2 solution (15

mL) of **2** (0.906 g, 2.37 mmol) was added a CH_2Cl_2 solution of **1** (1.00 g, 2.37 mmol). The mixture was allowed to react with stirring for 4 h at room temperature and set aside until a greenish blue precipitate appeared. It was filtered off, washed with cold ethanol and purified by recrystallization in 50 mL of dichloromethane-triethylorthoformate mixture solvent (5 : 1 v/v). The yield of the product was 1.44 g (75.6%).

$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)(\text{NO}_2)$, **9.** To a CH_2Cl_2 solution (15 mL) of **3** (0.925 g, 2.37 mmol) was added a CH_2Cl_2 solution of **1** (1.00 g, 2.37 mmol). Then 50 mL of triethylorthoformate was added into the mixture solution. The mixture was allowed to react with stirring at room temperature for 3 h until green precipitate appeared. It was filtered off, washed with cold ethanol and purified by recrystallization in 50 mL of dichloromethane-triethylorthoformate mixture solvent (5 : 1 v/v). The yield of the product was 1.36 g (70.7%).

$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)(\text{N}_3)$, **10.** To a CH_2Cl_2 solution (15 mL) of $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{N}_3)_2$ (0.906 g, 2.37 mmol) was added a CH_2Cl_2 solution of **1** (1.00 g, 2.37 mmol). Then 60 mL of triethylorthoformate was added into the mixture solution. The mixture was allowed to react with stirring for 6 h at room temperature, and set aside until dark green precipitate appeared. It was filtered off, washed with cold ethanol, and purified by recrystallization in 50 mL of dichloromethane-triethylorthoformate mixture solvent (5 : 1 v/v). The yield of the product was 1.48 g (77.7%).

$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{CH}_3\text{CO}_2)\text{Cl}$, **11.** **Method 1;** to a CH_2Cl_2 solution (15 mL) of $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{CH}_3\text{CO}_2)_2$, **4** (1.00 g, 2.40 mmol) was added a CH_2Cl_2 solution of $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{Cl}_2$, (0.886 g, 2.40 mmol). The mixture was stirred for 4 h at room temperature and set aside until a green precipitate appeared. It was filtered off, washed with cold absolute ethanol and purified by recrystallization in 50 mL of dichloromethane-triethylorthoformate mixture solvent (5 : 1 v/v). The yield of the product was 1.36 g (72.1%). **Method 2;** to degassed CCl_4 solution (30 mL) was added $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{CH}_3\text{CO}_2)_2$, **4** (2.00 g, 4.80 mmol) in CH_2Cl_2 solution. Most of **4** were suspended in CH_2Cl_2 due to the poor solubility of **4** in CCl_4 . The mixture was vigorously stirred for about 10 h until the blue color of **4** changed completely to a light green precipitate. It was collected by filtration and dried under vacuum. The product was purified by recrystallization in 50 mL of dichloromethane-triethylorthoformate mixture solvent (5 : 1 v/v). The yield of the product was 0.46 g (24.3%).

Physical Measurements. Electronic absorption spectra (600-1600 nm) were recorded on a Shimadzu UV-3101PC spectrophotometer. Infrared spectra (4000-400 cm^{-1}) were obtained by using KBr pellets with a Mattson Polaris FTIR spectrometer. Mass spectra were obtained on a JOEL JMS-DX 300 mass spectrometer in FAB mode.

ESR spectra were acquired at approximately 9 GHz (X-band) and at 77 K by using a 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 Quantum Design MPMS7-SQUID susceptometer. The data was corrected for the diamagnetism of the constituent atoms with Pascal's

constant.

Electrochemical experiments were performed using a conventional three electrode with a Pt disk of 1.6 mm in diameter. All solutions were freshly prepared with HPLC grade solvent and deoxygenated with nitrogen gas before the electrochemical experiments were carried out. A Pt wire was used as an auxiliary electrode. The cell solution was made from 0.1 M TBAP/CH₃CN, where TBAP was used as a supporting electrolyte.

Kinetic measurements on the rates of formation and disappearance of the mixed anion complex Cu(C₁₅H₂₆N₂)(CH₃CO₂)Cl were carried out using a Shimadzu 265 UV-visible spectrometer equipped with a temperature controlled cell holder.

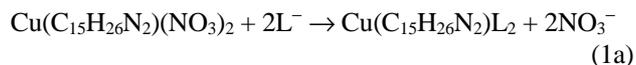
The C, H, N elemental analyses for the prepared complexes were carried out by using a Carlo Erba Instruments EA-1108 Elemental Analyzer at the Korean Basic Science Institute (Seoul Branch) or a Profile HV-3 Elemental Analyzer System (Germany) at Korean Basic Science Institute (Pusan Branch).

Results and Discussion

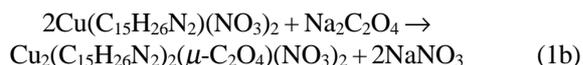
Synthesis and Characterization of the Complexes. Four mononuclear copper(II) oxyanion complexes **1-4**, a binuclear copper(II) oxyanion complex **5**, and six copper(II) mixed-anion complexes **6-11** were prepared. For the synthesis of copper(II) mixed-anion complexes **6-11**, Cu(C₁₅H₂₆N₂)Cl₂, Cu(C₁₅H₂₆N₂)Br₂, and Cu(C₁₅H₂₆N₂)(N₃)₂ were also prepared as precursors. Synthetic schemes for the eleven complexes are shown in Figure 2.

The reaction between precursor compound **1** and the corresponding sodium salts (NaOCN, NaNO₂, NaCH₃CO₂, Na₂C₂O₄, and NaN₃) in ethanol readily results in complexes **2-5** and Cu(C₁₅H₂₆N₂)(N₃)₂ in high yield (72-83%), in

accordance with general equation 1a.



However, in the reaction of compound **1** with oxalate, the dimeric species **5** was obtained²⁴ instead of a monomer, as shown in equation 1b. This result is unique because all other potential bridging ligands such as acetate, sulfate, and nitrite do produce monomers.



The precursor compound **1** interacts with other sparteine copper(II) complexes of the type Cu(C₁₅H₂₆N₂)L₂ (L = Cl⁻, Br⁻, OCN⁻, NO₂⁻, and N₃⁻) to undergo an interchange reaction in CH₂Cl₂ to produce the mixed anionic complexes **6-11**, in accordance with equation 2.



The reaction 2 is believed to proceed *via* the 4-center mechanism in which two complexes simultaneously exchange ligands. This type of interaction would be expected for the reaction because both NO₃⁻ and other anionic ligands in these complexes are labile, and copper(II) centers are able to expand their coordination number from four to five.²² The four-center structure needed for this mechanism correspond, in fact, to a quite stable bridged complex and an example would be a binuclear complex **5**.²⁴

The mixed anion complex Cu(C₁₅H₂₆N₂)(CH₃CO₂)Cl, **11** can be prepared similarly as in equation 2 *via* the interchange reaction between complex **4** and Cu(C₁₅H₂₆N₂)Cl₂ in CH₂Cl₂. However, in the course of the crystal growing of **4**, we found a striking side reaction occurs, and the reaction can be described by equation 3a. Complex **11** reacts further with

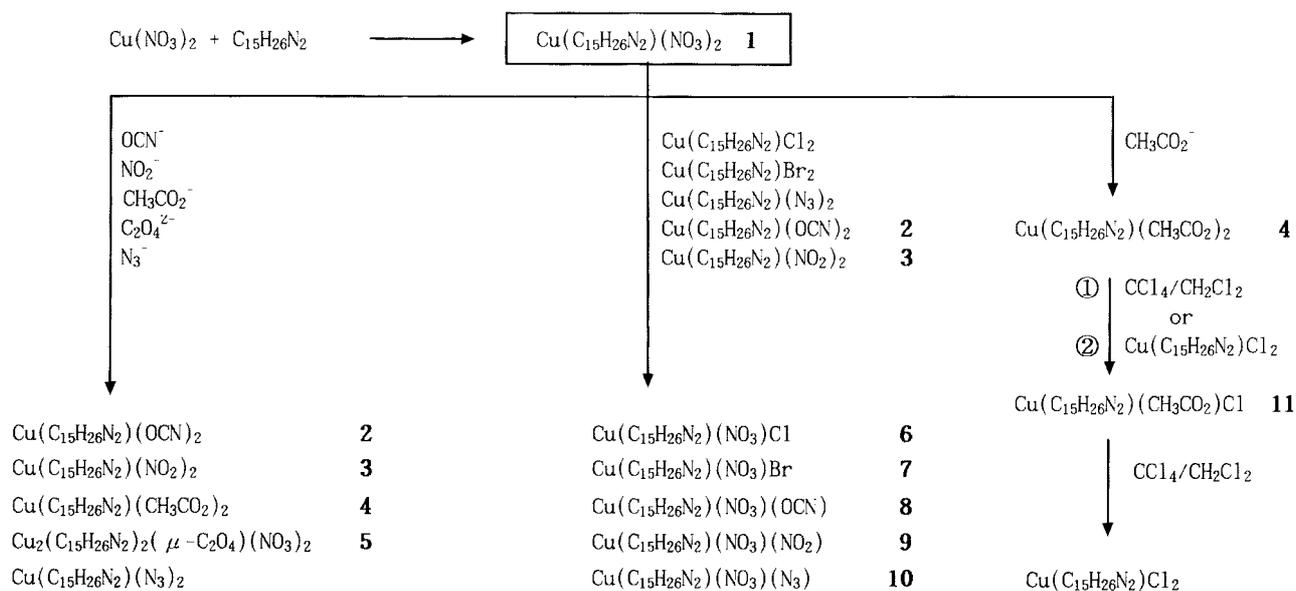
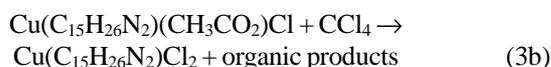
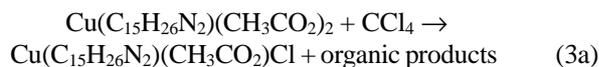


Figure 2. Scheme showing the synthesis of mono- and binuclear copper(II) oxyanion complexes **2-11** from the precursor complex Cu(C₁₅H₂₆N₂)(NO₃)₂, **1**. The ethanol-triethylorthoformate (5 : 1 v/v) mixture solvent was used in all synthetic processes.

CCl₄ until the formation of Cu(C₁₅H₂₆N₂)Cl₂ is completed.



The reactions 3a and 3b are different from other halogen abstraction reactions in that copper(II) retains the +2 oxidation state during the reaction. Brown *et al.*²⁵ reported that an efficient halogen abstraction is also facilitated by the presence of redox-active ligands. One possible explanation for the formation of complex **11** via equation 3 is the one-electron oxidation of a coordinated acetate ligand by a chlorine radical produced from CCl₄ at the initial step; the alkoxy radical CH₃CO₂[•] and chloride ion Cl⁻ will be generated. The Cl⁻ will coordinate to the copper(II) center, and the CH₃CO₂[•] will easily undergo the usual decarboxylation.²⁶ The reaction will result in other products derived from the coupling of the radicals.

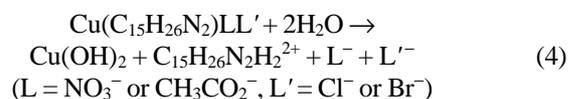
The mixed anion complex **11** could be isolated as an intermediate of reaction 3, in which Cu(C₁₅H₂₆N₂)Cl₂ is the final product. The isolation of **11** was possible because the rate of 3a is much faster than that of 3b; preliminary studies on the rates of the formation and disappearance of **11** in CH₂Cl₂/CCl₄ mixture solvent in equations 3a and 3b were conducted by monitoring the absorbance change at 700 nm. The second-order rate constants evaluated were 4.6 × 10⁻⁴ M⁻¹sec⁻¹ for 3a and 1.1 × 10⁻⁵ M⁻¹sec⁻¹ for 3b at 30 °C.

We conducted elemental analysis on the prepared complexes and the results are summarized in Table 1. The mixed anion complexes **6-10** exhibit the IR bands attributable to the presence of nitrate and other ligands in the complexes. The characteristic IR frequencies are summarized in Table 2. Because complex **11** was prepared from the halogen abstraction reaction of **4** with CCl₄ and the redox process is involved, the dehydrogenation or oxygenation of a

coordinated sparteine ligand was suspected. For further characterization of complex **11**, we obtained the FAB-mass spectrum of this complex; FAB-mass spectrum of **11** exhibits [Cu(C₁₅H₂₆N₂)]⁺ and other (-)-sparteine fragment ion peaks as **4** did. However, two different fragmentations, [Cu(C₁₅H₂₆N₂)(CH₃CO₂)]⁺ (356 m/e), and [Cu(C₁₅H₂₆N₂)Cl]⁺ (332 m/e) were also observed. These results, in addition to the IR data and the elemental analysis results, support the formulation of [Cu(C₁₅H₂₆N₂)(CH₃CO₂)Cl] for **11**.

The magnetic susceptibility data of copper(II) mixed oxyanion complexes were collected from 300 K down to 5 K, and the effective magnetic moments of six complexes were evaluated from the relationship $\mu_{\text{eff}} = 2.828(\chi_M \times T)^{1/2}$. The effective magnetic moments and the Curie-Weiss parameters of these complexes are summarized in Table 2. The plot of the effective magnetic moments vs. the temperature of the mixed anion complex **6** is compared with those of the binuclear complex **5**,²⁴ as shown in Figure 3. All prepared mixed oxyanion complexes exhibit effective magnetic moment values in the range 1.9-2.1 BM at 300 K, and the temperature dependency of magnetic moments clearly indicate that no magnetic super-exchange between Cu(II) centers are present and all the mixed anion complexes **6-11** are monomeric.

The halide ion analysis for the hydrolysis products of **6**, **7**, and **11** was also conducted. The determination of the Cl⁻ or Br⁻ produced from the hydrolysis of complexes **6**, **7**, and **11** was conducted by the use of a standard AgNO₃ solution. A quantitative amount of the halide ion expected from the stoichiometry of the hydrolysis reaction 4 was detected.



Structural Features and Electronic Spectral Properties of the Complexes. The molecular and crystal structures of some sparteine copper(II) complexes have been determined

Table 1. Elemental analysis results and color of sparteine copper(II) complexes

Compound	Found (Calcd.) (%)			Color
	C	H	N	
Cu(C ₁₅ H ₂₆ N ₂)(NO ₃) ₂	42.60(42.70)	6.34(6.21)	13.32(13.28)	Blue
Cu(C ₁₅ H ₂₆ N ₂)Cl ₂	48.50(48.85)	7.09(7.11)	7.30 (7.60)	Greenish Yellow
Cu(C ₁₅ H ₂₆ N ₂)Br ₂	39.01(39.36)	5.70(5.72)	6.01 (6.12)	Orange
Cu(C ₁₅ H ₂₆ N ₂)(N ₃) ₂	47.83(47.17)	6.91(6.86)	29.59(29.34)	Dark Brown
Cu(C ₁₅ H ₂₆ N ₂)(OCN) ₂	53.20(53.46)	6.99(6.86)	14.60(14.67)	Green
Cu(C ₁₅ H ₂₆ N ₂)(NO ₂) ₂	46.51(46.20)	6.74(6.72)	14.27(14.37)	Dark Green
Cu(C ₁₅ H ₂₆ N ₂)(CH ₃ CO ₂) ₂	54.80(54.86)	7.82(7.75)	6.65 (6.73)	Blue
Cu ₂ (C ₁₅ H ₂₆ N ₂) ₂ (μ-C ₂ O ₄)(NO ₃) ₂	47.10(47.57)	6.41(6.49)	10.19(10.40)	Light Green
Cu(C ₁₅ H ₂₆ N ₂)(NO ₃)Cl	45.46(45.57)	6.60(6.63)	10.61(10.63)	Light Green
Cu(C ₁₅ H ₂₆ N ₂)(NO ₃)Br	40.91(40.96)	5.94(5.96)	9.32 (9.55)	Olive Green
Cu(C ₁₅ H ₂₆ N ₂)(NO ₃)(N ₃)	45.25(44.82)	6.21(6.52)	20.70(20.91)	Deep Green
Cu(C ₁₅ H ₂₆ N ₂)(NO ₃)(NO ₂)	44.24(44.38)	6.42(6.46)	13.24(13.80)	Green
Cu(C ₁₅ H ₂₆ N ₂)(NO ₃)(OCN)	47.50(47.81)	6.66(6.51)	13.68(13.94)	Greenish Blue
Cu(C ₁₅ H ₂₆ N ₂)(CH ₃ CO ₂)Cl ^a	51.70(52.03)	7.31(7.45)	6.99 (7.14)	Pale Green

^aThe complex was prepared by method **2** which is described in experimental part.

Table 2. Effective magnetic moments, Curie-Weiss parameters, and selected infrared spectral features and their assignments for sparteine copper(II) mixed anion complexes

Complexes	μ_{eff}^a (B.M.)	Curie-Weiss Parameters		Characteristic IR frequencies in cm^{-1}
		C^b	θ^b	
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)\text{Cl}$, 6	2.01	0.50	-0.67	$\nu_s(\text{NO}_3)$ at 1384(vs), $\nu_a(\text{NO}_3)$ at 1283(vs)
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)\text{Br}$, 7	2.07	0.51	-0.95	$\nu_s(\text{NO}_3)$ at 1384(vs), $\nu_a(\text{NO}_3)$ at 1284(vs)
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)(\text{OCN})$, 8	2.07	0.47	0.12	$\nu_s(\text{NO}_3)$ at 1384(vs), $\nu_a(\text{NO}_3)$ at 1288(vs) $\nu_a(\text{OCN})$ at 2217(vs), $\nu_s(\text{OCN})$ at 1343(m)
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)(\text{NO}_2)$, 9	1.97	0.50	-0.14	$\nu_s(\text{NO}_3)$ at 1384(vs), $\nu_a(\text{NO}_3)$ at 1287(s) $\nu_a(\text{NO}_2)$ at 1272(s), $\nu_s(\text{NO}_2)$ at 1143(m)
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)(\text{N}_3)$, 10	1.99	0.47	-0.47	$\nu_s(\text{NO}_3)$ at 1384(vs), $\nu_a(\text{NO}_3)$ at 1281(s) $\nu_a(\text{NNN})$ at 2042(vs)

^aThe effective magnetic moment was calculated by $\mu_{\text{eff}} = 2.828(\chi_M \times T)^{1/2}$ at 300 K. ^bCurie-Weiss parameters were obtained by $\chi_M = C/(T-\theta)$. The susceptibility data for the calculation were obtained in the range 5 K-300 K.

in several studies.^{17,20-23} It was found that the Cu(II) centers in most of the complexes adopt four-coordinate and distorted-tetrahedral geometries. However, the nitrite and nitrate oxyanions can coordinate to Cu(II) either in a monodentate or bidentate fashion, and the Cu(II) center in $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$, **3** adopts a five-coordinate and distorted square-pyramidal geometry.²² Whereas, the molecules of $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)_2$, **1** are mixed four- and five-coordinate in one crystalline phase and only four-coordinate in others.²¹ However, based on the ESR studies, the coordination structure of **1** has been suggested to be mainly four-coordinate in the CH_2Cl_2 solution.²¹ And the Cu(II) center in the binuclear complex **5** is also speculated to have a distorted trigonal-bipyramidal geometry.²⁴

Except for the complexes **3**, **5**, and **9**, the Cu(II) centers in the complexes prepared in this study are expected to adopt four-coordinate and distorted tetrahedral geometries in a solution. Although X-ray structures are not available for the mixed anion complexes **6-11**, it is amply evident that nitrate and acetate act as a monodentate ligand in these complexes.

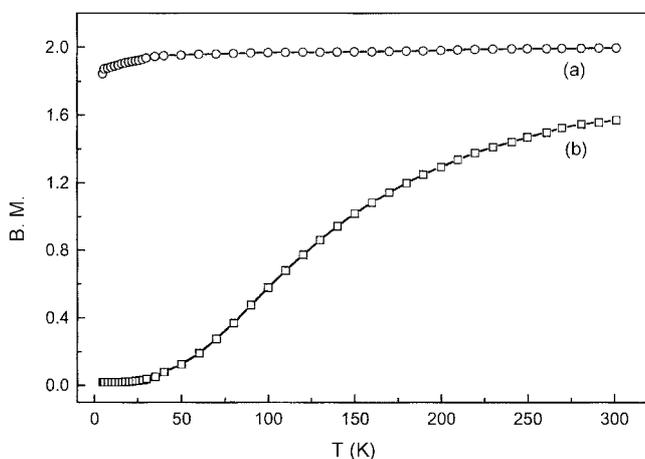


Figure 3. Thermal variation of effective magnetic moments for (a) $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)\text{Cl}$, **6** compared with those for (b) $\text{Cu}_2(\text{C}_{15}\text{H}_{26}\text{N}_2)(\mu\text{-C}_2\text{O}_4)(\text{NO}_3)_2$, **5**.²⁴

The Vis/NIR spectra of the complexes were recorded at room temperature in CH_2Cl_2 . All complexes exhibit spectra having a broad unsymmetrical envelope in the region 600-1600 nm, which consists of at least three overlapping bands. The absorption envelope could be resolved into three Gaussian components by using the PeakFit (version 4.0) program of Microcal Software Inc. Some observed absorption spectra and their Gaussian resolutions are shown in Figure 4, and the results are summarized in Table 3. The absorption in this region is assigned to ligand field transitions. The strong intensities of these absorption bands are attributable both to the metal centered "d-p" mixing expected for nonsymmetric complexes, and the covalency effects.^{26,27}

For the interpretation of electronic spectra of complexes **1**, **2**, **4**, and other precursor complexes, $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{Cl}_2$, $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{Br}_2$, and $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{N}_3)_2$, the $d_{x^2-y^2}$ is chosen to be ground state. Three bands (ν_1 , ν_2 , and ν_3) obtained by Gaussian resolutions are tentatively assigned to $d_{x^2-y^2} (^2B_2) \rightarrow d_{xz}, d_{yz} (^2E)$, $d_{x^2-y^2} (^2B_2) \rightarrow d_{xy} (^2B_1)$ and $d_{x^2-y^2} (^2B_2) \rightarrow d_{z^2} (^2A_1)$, respectively. These results are well expected when planar copper(II) complexes are twisted toward the distorted tetrahedral structure of D_{2d} or C_{2v} symmetry.²⁷ The transition energies of the acetate complex **4** are lower than those of the nitrate complex **1**. Although both complexes **1** and **4** have distorted-tetrahedral geometries around Cu(II) centers, the dihedral angles between the N_2Cu and O_2Cu planes are 31.7° for **1** and 45.8° for **4**, respectively.^{21,23} The greater dihedral angle for **4** by 14.1° reflects a greater degree of distortion toward the tetrahedral from the planar geometry and will cause a red-shift of transitions by $70\text{-}230\text{ cm}^{-1}$.

The electronic spectra of five-coordinate complexes **3** and **5** also exhibit similar absorption envelopes but the transition energies of the nitrite complex are higher than those of the binuclear complex **5**. This might be ascribed to the greater field strength of the NO_2^- ligand than the $\text{C}_2\text{O}_4^{2-}$ or NO_3^- ligand, but may also be caused by the structural difference between **3** and **5**; the Cu(II) in **3** adopts the distorted square pyramidal (SP) structure while the Cu(II) in **5** adopts a near-regular trigonal bipyramidal (TBP) structure.²⁴

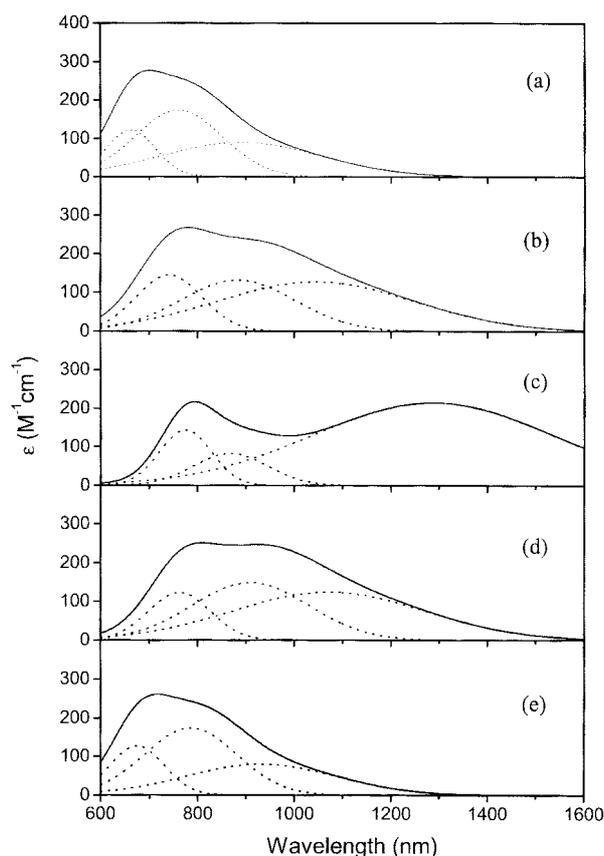


Figure 4. Electronic absorption spectra (—) and transition analysis spectra (---) of (a) $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)_2$, **1** (b) $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)\text{Cl}$, **6**, (c) $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{Cl}_2$, (d) $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{CH}_3\text{CO}_2)\text{Cl}$, **11** and (e) $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{CH}_3\text{CO}_2)_2$, **4** in CH_2Cl_2 solution.

The transition energies of mixed anion complexes of the type $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{LL}'$ are in between those of $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{L}_2$ and those of $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{L}'_2$. The electronic spectra of complexes **1**, **4**, **6**, **11**, and $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{Cl}_2$ are shown and

compared with each other in Figure 4.

Electrochemical Behavior of the Complexes. Cyclic voltammetry measurements on complexes **1-5** in CH_3CN are summarized in Table 5. In the potential range $-1.00 \sim +0.50$ V vs. Ag/AgCl , the only process that could be ascribed to reduction of the metal center, $\text{Cu}(\text{II}) + e^- \rightarrow \text{Cu}(\text{I})$, was observed and no oxidation of the metal center of either $\text{Cu}(\text{II}) \rightarrow \text{Cu}(\text{III}) + e^-$ or the oxidation of the ligands was apparent. The reduction of $\text{Cu}(\text{I})$ to $\text{Cu}(\text{0})$ was not observable, presumably because this occurs at a more negative potential where the reduction of free ligand (–)-sparteine occurs (See Figure 5a and 5b). The cyclic voltammograms were well-behaved in all cases, except for the binuclear complex **5**, which showed an evidence of adsorption of the $\text{Cu}(\text{I})$ species on the electrode surface. A reversal of the

Table 4. Cyclic voltammetric data^a for sparteine copper(II) complexes

Complexes	$E_{\text{pc}}(\text{V})$	$E_{1/2}(\text{V})$	$E_{\text{pa}}(\text{V})$	$\Delta E_{\text{p}}^b(\text{V})$
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)_2$	-0.105	-0.056	-0.006	0.099
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{Cl}_2$	-0.530	-0.390	-0.250	0.280
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{Br}_2$	-0.050	+0.030	+0.100	0.150
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{N}_3)_2$	-0.459	-0.344	-0.238	0.221
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{OCN})_2$	-0.286	-0.235	-0.183	0.103
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$	-0.400	-0.325	-0.250	0.150
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{CH}_3\text{CO}_2)_2$	-0.672	-0.545	-0.418	0.254
$\text{Cu}_2(\text{C}_{15}\text{H}_{26}\text{N}_2)_2(\text{C}_2\text{O}_4)(\text{NO}_3)_2$	-0.342	-0.202	-0.061	0.281
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)\text{Cl}$	-0.365	-0.255	-0.145	0.255
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)\text{Br}$	-0.205	-0.140	-0.076	0.129
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)(\text{OCN})$	-0.240	-0.145	-0.050	0.190
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)\text{N}_3$	-0.215	-0.125	-0.035	0.180

^aWorking electrode: Pt disk ($\phi = 1.6$ mm). Reference electrode: Ag/Ag^+ electrode. Concentration: 0.5 mM. Supporting electrolyte: 0.1 M TBAP in CH_3CN . Scan rate: 100 mV/s. $E_{1/2}$ for the ferrocium/ferrocene couple is at +0.47 V vs Ag/AgCl under experimental conditions. ^b ΔE_{p} is defined as $E_{\text{pa}} - E_{\text{pc}}$.

Table 3. Electronic absorption spectral data for sparteine copper(II) complexes in CH_2Cl_2 solution

Complexes and Chromophores		Ligand field transition band		
		λ_1 , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$)	λ_2 , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$)	λ_3 , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$)
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)_2$	CuN_2O_2	663(137)	768(173)	905(90)
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{Cl}_2$	CuN_2Cl_2	775(143)	868(83)	1288(214)
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{Br}_2$	CuN_2Br_2	806(266)	924(131)	1361(267)
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{N}_3)_2$	CuN_4	695(365)	840(285)	1063(209)
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{OCN})_2$	CuN_4	722(105)	881(121)	1171(135)
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$	CuN_2O_3	654(121)	755(179)	881(67)
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{CH}_3\text{CO}_2)_2$	CuN_2O_2	675(127)	786(174)	932(80)
$\text{Cu}_2(\text{C}_{15}\text{H}_{26}\text{N}_2)_2(\text{C}_2\text{O}_4)(\text{NO}_3)_2$	CuN_2O_3	701(149)	809(235)	948(195)
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)\text{Cl}$	CuN_2OCl	741(145)	886(134)	1049(127)
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)\text{Br}$	CuN_2OBr	770(200)	944(197)	1211(95)
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)(\text{OCN})$	CuN_3O	694	791	919
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)(\text{NO}_2)$	CuN_2O_3	658	752	867
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)(\text{N}_3)$	CuN_3O	669	760	878
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{CH}_3\text{CO}_2)\text{Cl}$	CuN_2OCl	765(137)	922(157)	1092(113)

Table 5. Electron spin Hamiltonian parameters for sparteine copper(II) complexes

Compound	g_o^a	$g_{ }^b$	$A_{ }(\times 10^4 \text{ cm}^{-1})$
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)_2$	2.134	2.259	144
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{Cl}_2$	2.158	2.290	116
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{Br}_2$	2.136	2.276	117
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{N}_3)_2$	2.112	2.230	135
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{OCN})_2$	2.134	2.294	124
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$	2.103	2.257	168
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{CH}_3\text{CO}_2)_2$	2.130	2.279	158
$\text{Cu}_2(\text{C}_{15}\text{H}_{26}\text{N}_2)_2(\mu\text{-C}_2\text{O}_4)(\text{NO}_3)_2$	2.123	2.262	141
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)(\text{N}_3)$	2.124	2.252	133
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)(\text{OCN})$	2.139	2.380	135
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)(\text{NO}_2)$	2.130	2.259	147
$\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{CH}_3\text{CO}_2)\text{Cl}$	2.131	2.268	124

^aAmbient temperature, $\text{CH}_2\text{Cl}_2/\text{DMF}$ (1 : 1 v/v) solvent mixture. ^bFrozen glass spectra at 77 K, $\text{CH}_2\text{Cl}_2/\text{DMF}$ (1 : 1 v/v) solvent mixture. Coordination by solvent molecules was checked by using toluene or CH_2Cl_2 /toluene solutions.

potential scan just after the first reduction process results in a quasi-reversible one-electron reduction $\text{Cu}(\text{II}) \rightarrow \text{Cu}(\text{I})$, with $E_{1/2}$ value in the range -0.05~-0.55 V vs. Ag/AgCl for the prepared oxyanion complexes. The anodic and cathodic peak potential differences ($\Delta E_p = 100\text{-}250$ mV) are much larger than that expected for a fully reversible process, as often found in nonaqueous solvents.²⁸ We conducted a bulk electrolysis with coulometry to count the number of electrons involved in this process and found that only one electron is involved ($n = 0.86$ for complex **1**, 1.1 for complex **2**, and 0.90 for complex **5**).

Among five sparteine copper(II) oxyanion complexes, $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)_2$, **1** has the largest $E_{1/2}$ value (smallest negative value) whereas $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{CH}_3\text{CO}_2)_2$, **4** has the smallest value (largest negative value). The reason why **1** exhibits the largest $E_{1/2}$ value among the tested complexes is not certain at present time. However, one plausible explanation is the flexibility of the coordination sphere of **1**. The coordination structure of **1** is much less constrained than those of **3** or **4** due to the structural flexibility attributable to the ambidentate characteristics of the NO_3^- ligand.²¹ Because of the larger flexibility of the coordination sphere, $\text{Cu}(\text{II})$ center will require the least reorganization energy upon reduction, and $\text{Cu}(\text{I})$ can be stabilized comparably to the way it is in the complexes containing other oxyanions such as NO_2^- , CH_3CO_2^- , or $\text{C}_2\text{O}_4^{2-}$.

The smallest $E_{1/2}$ value of -0.545 V observed for $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{CH}_3\text{CO}_2)_2$, **4** is unpredictable if only the geometric factor is considered. The $\text{Cu}(\text{II})\text{N}_2\text{O}_2$ chromophore of **4** is highly distorted toward tetrahedral geometry,²³ and this condition is expected to stabilize $\text{Cu}(\text{I})$ state upon reduction of $\text{Cu}(\text{II})$. This unexpected result might be attributable to the strong Lewis basicity of acetate ligand which can stabilize the higher oxidation state of copper center.

The cyclic voltammogram of dimeric $\text{Cu}_2(\text{C}_{15}\text{H}_{26}\text{N}_2)_2(\mu\text{-C}_2\text{O}_4)(\text{NO}_3)_2$, **5** is unique among the tested compounds. As mentioned earlier, this dimeric compound exhibits an ad-

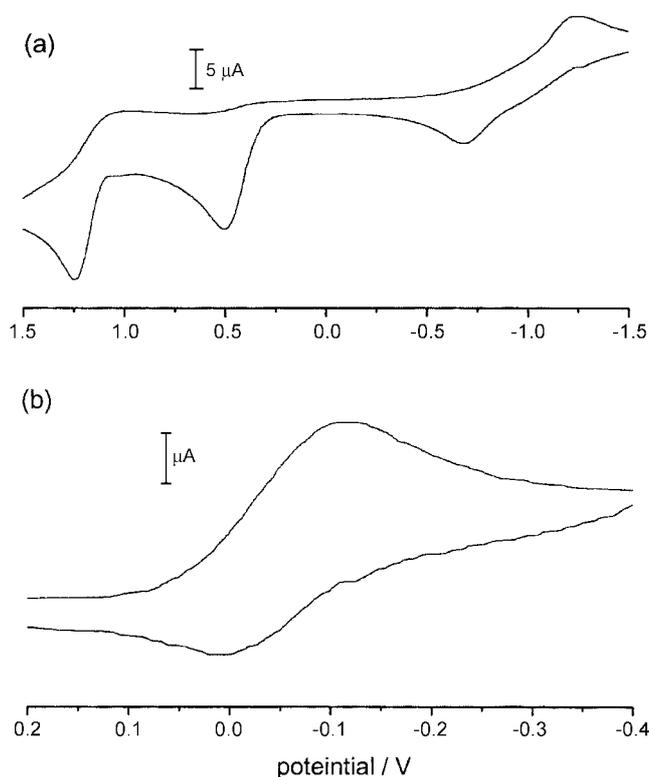
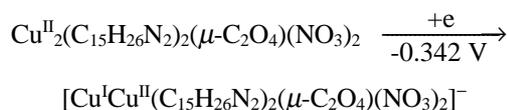


Figure 5. Cyclic voltammograms for (a) free (–)sparteine ($\text{C}_{15}\text{H}_{26}\text{N}_2$) and (b) $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_3)_2$, **1**, in acetonitrile at room temperature (Reference electrode: Ag/Ag^+ Supporting electrolyte: 0.1 M TBAP).

sorption peak as a shoulder. As we reduced the concentration of **5** to 1×10^{-4} M, the shoulder peak disappeared. The presence of adsorption peak was further confirmed by conducting differential pulse voltammography. The observed quasi-reversible reduction wave at -0.342 V for **5** is assigned as a one-electron reduction process as described by the following;



Electron Spin Resonance Spectra of the Complexes. X-band ESR spectra of the $\text{CH}_2\text{Cl}_2/\text{DMF}$ (1 : 1 v/v) frozen glasses of the prepared complexes have been recorded at 77 K, and the ESR spectral parameters are summarized in Table 5. The ESR spectra of tetrahedrally distorted copper(II) complexes, $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{Cl}_2$, $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{Br}_2$, $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{OCN})_2$, **2**, $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{CH}_3\text{CO}_2)$, **4**, and $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{SO}_4$, exhibit axial symmetry with $g_{||} > g_{\perp} > 2.0023$, indicating that the copper(II) center has a $d_{x^2-y^2}$ ground state. However, the ESR spectra of five-coordinate copper(II) complex, $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{NO}_2)_2$, **3**, the binuclear copper(II) complex $\text{Cu}_2(\text{C}_{15}\text{H}_{26}\text{N}_2)_2(\mu\text{-C}_2\text{O}_4)(\text{NO}_3)_2$, **5**, and copper(II) mixed oxyanion complex $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{CH}_3\text{CO}_2)\text{Cl}$, **11** exhibit rhombic symmetry as shown in Figure 6(b). Furthermore, the five-coordinate and distorted square-pyramidal complex **3**

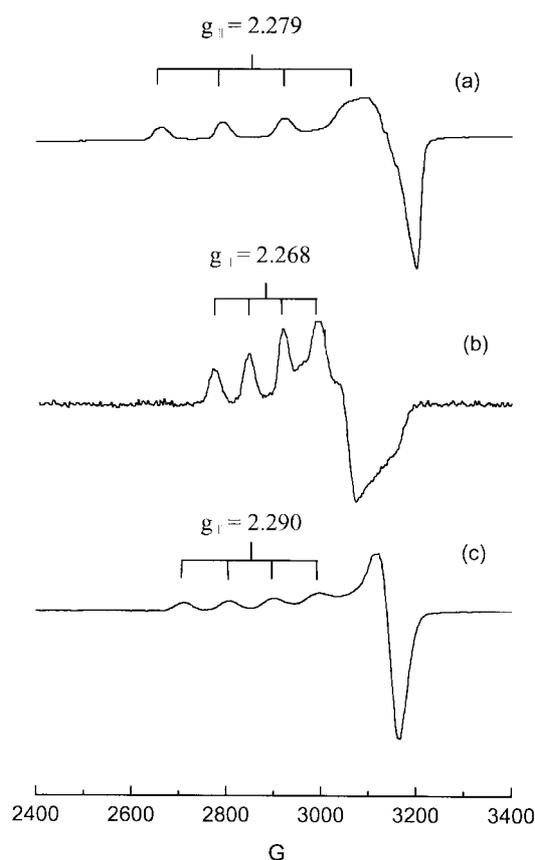


Figure 6. X-band ESR spectra of (a) $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{CH}_3\text{CO}_2)_2$, **4**, (b) $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{CH}_3\text{CO}_2)\text{Cl}$, **11** and (c) $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)\text{Cl}_2$ in a frozen glass of $\text{CH}_2\text{Cl}_2/\text{DMF}$ (1 : 1) solution at 77 K.

exhibits the largest A_{\parallel} value of $168 \times 10^{-4} \text{ cm}^{-1}$ while another five-coordinate but trigonal-bipyramidal complex **5** exhibit smaller A_{\parallel} value of $141 \times 10^{-4} \text{ cm}^{-1}$. It is well-known that distortion of square-pyramidal geometry toward a trigonal-bipyramidal geometry causes remarkable reduction in A_{\parallel} value,²⁹ and the difference in A_{\parallel} between **3** and **4** is believed to be originated from this structural factor.

The large A_{\parallel} value of $158 \times 10^{-4} \text{ cm}^{-1}$ observed for **4**, which also has a severely distorted tetrahedral geometry around Cu(II), may be attributable to the poor covalency of metal-oxygen bond in **4**. The $\text{Cu}(\text{C}_{15}\text{H}_{26}\text{N}_2)(\text{OCN})_2$ **2** exhibit the smallest A_{\parallel} value among the tested copper(II) oxyanion complexes, and this result strongly indicates that the cyanate ligands coordinate with Cu(II) via nitrogen atom as it has been suggested earlier in electronic spectral parts.

Summary and Conclusion

Nine copper(II) oxyanion, and mixed oxyanion complexes that have four- or five-coordinate geometries around copper (II) centers were prepared from sparteine copper(II) dinitrate precursor. The electronic transition energies of the three resolved ligand field bands in the region of 600-1600 nm are dependent upon both the geometry of the Cu(II) centers and the field strength of the ligands in the spectrochemical series. Among the tetrahedrally distorted compounds, one

with greater dihedral angle between the N-Cu-N and the L-Cu-L planes has the lower energies in the d-d transitions. The electronic spectra of five-coordinate complexes exhibit similar absorption envelopes but the transition energies of the distorted square-pyramidal compound are higher than those of the trigonal bipyramidal compound.

The electrochemical results of nine oxyanion copper(II) complexes indicate that the $E_{1/2}$ values for the process $\text{Cu}(\text{II}) + e^- \rightarrow \text{Cu}(\text{I})$ is greatly affected by the flexibility of the coordination sphere around the copper(II) center.

Except for **3** and **4**, the ESR A_{\parallel} values of the prepared complexes are in the range of $124\text{-}147 \times 10^{-4} \text{ cm}^{-1}$. Although A_{\parallel} values of the prepared complexes are larger by a factor 2-3 than the values reported for the type I copper site in metalloenzyme, these values are significantly smaller than those of other $\text{Cu}^{\text{II}}\text{N}_2\text{O}_2$ chromophore complexes ($A_{\parallel} = 150\text{-}220 \times 10^{-4} \text{ cm}^{-1}$).⁶ The geometric factor and the covalency of the metal-ligand bonding interaction seem to co-determine the A_{\parallel} values although the covalency of the metal-ligand bonding is more important than the geometric factors for a series of complexes prepared in this work.

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