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Isolation and Properties of the Copper(II)–Thiolate Complexes

NOBUO AOI, GEN-ETSU MATSUBAYASHI and TOSHIO TANAKA*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565, Japan

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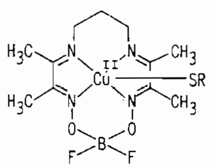
Abstract

Copper(II)–thiolate complexes of the CuN_4S type were synthesized: (1,1-difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetraaza-2,14-dioxocyclotetradeca-3,5,10,12-tetraenato)(SR)copper(II) (R = $(C_6H_5)_3C$, 4-ClC_6H_4, and 2-$C_{10}H_7$), (1,1-difluoro-4,5,12,13-tetramethyl-1-bora-3,6,11,14-tetraaza-2,15-dioxocyclopentadeca-3,5,11,13-tetraenato)(triphenylmethanethiolato)copper(II), and (2-oximino-10-oximinato-3,9-dimethyl-4,8-diazaundeca-3,8-diene)(triphenylmethanethiolato)copper(II). These complexes exhibit an absorption band assignable to the thiolate sulfur-to-copper charge transfer (c.t.) transition in the 340–420 nm region in methanol; the band maximum is shifted to low frequencies with increasing of not only the electron-donating ability of the thiolate ligand but also the electron-accepting ability of the CuN_4 moiety. The cyclic voltammetry of the complexes in dichloromethane shows a quasi-reversible redox couple at $E_{1/2}$ of –0.38 to –0.54 V *vs.* s.c.e. which is more negative than that of the corresponding CuN_4 complex without thiolate ligand. The $|A_\parallel|$ values ($(193–201) \times 10^{-4}$ cm^{-1}) observed in the ESR spectra of the CuN_4S complexes are relatively smaller than those of the corresponding CuN_4 complexes. Thus, the negative shift of $E_{1/2}$ and the decrease of $|A_\parallel|$ upon coordination of the thiolate ligand to the CuN_4 moiety may be due to electron donation from the thiolate ligand.

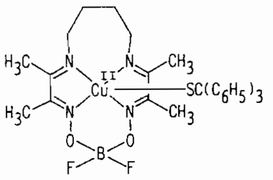
Introduction

Blue (type 1) copper proteins exhibit unusual spectral and electrochemical properties, being different from copper(II) complexes with low molecular weights; the proteins show an intense absorption band near 600 nm (ϵ = 3500–11300 dm^3 mol^{-1} cm^{-1}), a small electron–copper nucleus hyperfine coupling constant ($|A_\parallel| = (30–90) \times 10^{-4}$ cm^{-1}), and a relatively high redox potential ($E_{1/2}$ = 0 to +0.6 V *vs.* s.c.e.) [1]. Recent single-crystal X-ray diffraction studies on Cu(II) *Poplar plastocyanin* and *Pseudomonas aeruginosa azurin* demonstrated that the copper(II) ion in the active site is placed in a distorted tetrahedral geometry formed by two imidazole nitrogen atoms of histidine residue and two sulfur atoms of methionine thioether and cysteinate thiolate [2]. It seems to be of importance to investigate copper(II) complexes involving alkyl thiolate ligands for further understanding of the properties of blue copper proteins. The copper(II) ion or its complexes are readily reduced by alkyl and aryl thiolate anions [3–6]. Thus, the limited number of simple copper(II)–thiolate complexes has been isolated so far [7–12]. This paper reports the isolation of some copper(II) complexes (**1a–1c**, **2**, and **3**) containing alkyl and aryl thiolate ligands and their properties in comparison with the corresponding copper(II) complexes without thiolate ligand.



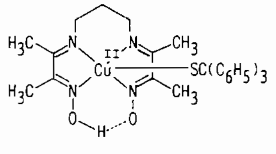
1

$[CuN_4^{(1)}(SR)]$
R = $C(C_6H_5)_3$ (**1a**)
C_6H_4Cl-4 (**1b**)
$C_{10}H_7$-2 (**1c**)



2

$[CuN_4^{(2)}(SC(C_6H_5)_3)]$



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$[CuN_4^{(3)}(SC(C_6H_5)_3)]$

Experimental

Materials

(1,1-Difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetraaza-2,14-dioxocyclotetradeca-3,5,10,12-tetra-

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*Author to whom correspondence should be addressed.

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TABLE I. Properties and Analyses of the Copper(II)–Thiolate Complexes

	Complex[a]	Color	Decomposition temperature (°C)	Analysis (found (calc.))		
				%C	%H	%N
1a	$[CuN_4^{(1)}(SC(C_6H_5)_3)]$	dark green	>105	57.25	5.42	8.68
				(57.56)	(5.31)	(8.95)
1b	$[CuN_4^{(1)}(SC_6H_4Cl\text{-}4)]$	brown	>142	41.93	4.74	11.31
				(41.31)	(4.49)	(11.34)
1c	$[CuN_4^{(1)}(SC_{10}H_7\text{-}2)]$	brown	>124	49.14	5.17	10.78
				(49.47)	(4.94)	(10.99)
2	$[CuN_4^{(2)}(SC(C_6H_5)_3)]$	brown	>111	58.17	5.73	8.36
				(58.18)	(5.51)	(8.75)
3	$[CuN_4^{(3)}(SC(C_6H_5)_3)]$	dark green	>109	62.32	5.93	9.69
				(62.28)	(6.06)	(9.53)

[a] $N_4^{(1)}$ = 1,1-difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetraaza-2,14-dioxocyclotetradeca-3,5,10,12-tetraenate, $N_4^{(2)}$ = 1,1-difluoro-4,5,12,13-tetramethyl-1-bora-3,6,11,14-tetraaza-2,15-dioxocyclopentadeca-3,5,11,13-tetraenate and $N_4^{(3)}$ = 2-oximino-10-oximinate-3,9-dimethyl-4,8-diazaundeca-3,8-diene.

enato)copper(II) perchlorate hydrate, $[CuN_4^{(1)}][ClO_4]\cdot H_2O$ [13], (1,1-difluoro-4,5,12,13-tetramethyl-1-bora-3,6,11,14-tetraaza-2,15-dioxocyclopentadeca-3,5,11,13-tetraenato)copper(II) perchlorate 0.5 dioxane, $[CuN_4^{(2)}][ClO_4]\cdot 0.5C_4H_8O_2$ [14], and (2-oximino-10-oximinato-3,9-dimethyl-4,8-diazaundeca-3,8-diene)copper(II) perchlorate dihydrate, $[CuN_4^{(3)}][ClO_4]\cdot 2H_2O$ [13] were prepared according to the literature methods. Commercially available triphenylmethanethiol, 4-chlorobenzenethiol, and 2-naphthalenethiol were used for the preparations of the copper(II)–thiolate complexes without further purification. All the solvents used in this experiment were purified by the usual methods [15].

Preparation of the Copper(II)–Thiolate Complexes

Under the nitrogen atmosphere, a methanol (20 cm^3) solution containing equimolar amounts (0.25 mmol) of $(C_6H_5)_3CSH$ (69 mg) and CH_3ONa (*ca.* 14 mg *in situ*) was added dropwise to a cooled (ice bath) methanol (20 cm^3) solution of $[CuN_4^{(1)}][ClO_4]\cdot H_2O$ (100 mg, 0.25 mmol). The solution was allowed to stand overnight at –15 °C to afford dark green crystals of $[CuN_4^{(1)}(SC(C_6H_5)_3)]$ (**1a**), which were collected by filtration and dried *in vacuo*, 62% yield. $[CuN_4^{(1)}(SC_6H_4Cl\text{-}4)]$ (**1b**) and $[CuN_4^{(1)}(SC_{10}H_7\text{-}2)]$ (**1c**) were obtained by the reactions of $[CuN_4^{(1)}][ClO_4]\cdot H_2O$ with five-fold excess amounts of $4\text{-}ClC_6H_4SNa$ and $2\text{-}C_{10}H_7SNa$ in 43% and 54% yields, respectively. $[CuN_4^{(2)}(SC(C_6H_5)_3)]$ (**2**) and $[CuN_4^{(3)}(SC(C_6H_5)_3)]$ (**3**) were prepared similarly by the reactions of the corresponding CuN_4 complexes with the appropriate thiolate ligand and crystallized at –15 °C and –70 °C, respectively; both were obtained in 43% yields. Although all the complexes obtained are stable to air in the solid state, they decompose gradually in solution at room temperature. Elemental analyses and properties of the complexes are summarized in Table I.

Physical Measurements

Electronic absorption spectra were measured with a Union SM-401 spectrophotometer at 25 °C, immediately after the complex was dissolved in an appropriate solvent. ESR spectra were recorded on a JEOL ME-2X spectrometer calibrated with diphenylpicrylhydrazyl ($g = 2.0037$), for methanol/ethanol (1:4 v/v) solutions of **1a**–**1c** and **3** and for an acetone/nitromethane (1:1 v/v) solution of **2** at 77 K under the nitrogen atmosphere; the solution prepared at *ca.* –88 °C was transfered rapidly into an ESR tube and then immediately frozen by liquid nitrogen for the measurements. Cyclic voltammetry was measured with a Hokuto Denko HA-301 potentiostat, a Hokuto Denko HB-107A function generator, and a Watanabe WX1000 recorder. The measurement was performed in a conventional cell equipped with a glassy carbon (working electrode), a platinum wire (counter electrode), and saturated calomel reference electrode (s.c.e.), using $[Bu_4{}^nN][BF_4]$ (0.1 mol dm^{-3}) as a supporting electrolyte.

Results and Discussion

All the complexes of the CuN_4S type may assume a penta-coordinate square-pyramidal configuration, being similar to $[CuN_4^{(3)}(SR)]$ ($R = C_6H_5$ and $C_6H_4Cl\text{-}4$), whose molecular structures have been determined by the X-ray analysis [9]. Figure 1 shows the absorption spectrum of **1a** in methanol at 25 °C. The strong absorption band at 398 nm can be attributed to the thiolate sulfur-to-copper(II) charge transfer (c.t.) transition, since neither $[CuN_4^{(1)}]$-

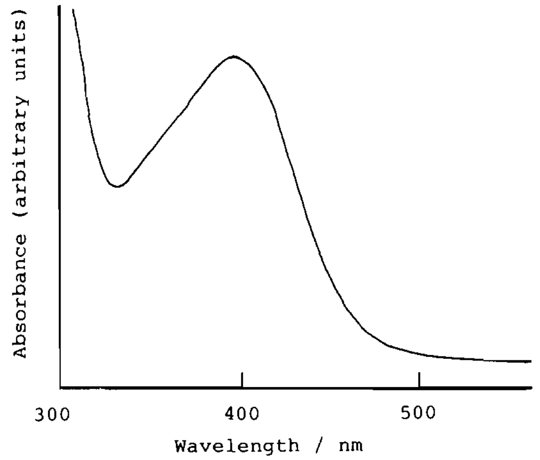

Fig. 1. The electronic absorption spectrum of $[CuN_4^{(1)}(SC(C_6H_5)_3)]$ (**1a**) in methanol at 25 °C.

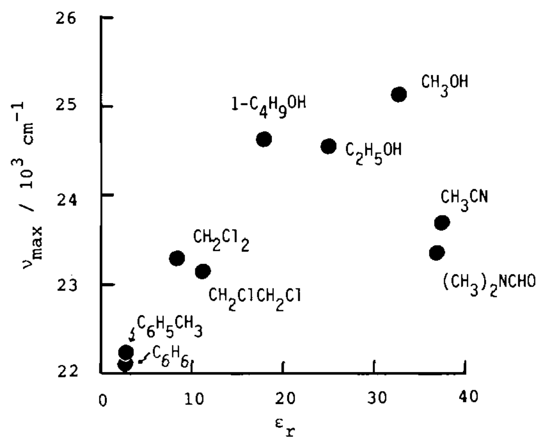

Fig. 2. A plot of the wavenumber of the c.t. band maximum for $[CuN_4^{(1)}(SC(C_6H_5)_3)]$ (**1a**) against the dielectric constant of solvents.

$[ClO_4]\cdot H_2O$ nor the thiolate ligand has shown any strong bands in this region. The c.t. band undergoes an appreciable solvent effect, as shown in Fig. 2, which seems to indicate that there are two different factors influencing the position of the absorption maximum; one is a negative solvatochromic effect, which may cause high frequency shifts of the c.t. transition with increasing of the dielectric constants of solvents including alcohols. This trend may be interpreted by the assumption that the electronic transition may reduce an electric dipole of the complex in the ground state; the ground state with markedly dipolar ($Cu(II)^{\delta+}$–$S^{\delta-}$) may be stabilized in a solvent with a higher dielectric constant, while an excited state with much less dipole may be destabilized. Another factor may be displayed by the solvents with electron-donating abilities (acetonitrile and *N,N*-dimethylformamide in Fig. 2) which shift the c.t. band to a frequency lower than would be expected from the dielectric constants. This is suggestive of the coordination of a solvent molecule (D) to the penta-coordinated CuN_4S complex, resulting in the formation of a hexa-coordinate configuration of the $CuN_4S(D)$ type in solution. Such a solvation may decrease the $Cu(II)^{\delta+}$–$S^{\delta-}$ polarity to cause a lower frequency shift of the c.t. band. Complexes **1b** and **1c** similarly display single c.t. bands which undergo a solvent effect analogous to **1a**.

On the other hand, two c.t. bands, one of which is a shoulder, were observed for **2** and **3** in methanol and in dichloromethane, which display similar solvent effects (see Table II). The electronic spectra of

TABLE II. Sulfur-to-copper c.t. Band Maxima of the Copper(II)–Thiolate Complexes at 25 °C

Complex	λ_{max} (nm)	
	In methanol	In dichloromethane
1a	398	430
1b	408	426
1c	419	436
2	[a]	394sh 424
3	342sh 386	422

[a] Not determined because of the extremely low solubility.

$[CuN_4^{(3)}(SR)]$ (R = C_6H_5 and C_6H_4Cl-4), which are analogues of **3**, were reported to show two similar c.t. bands in the visible region: λ_{max} = 355 and 428 nm for R = C_6H_5, λ_{max} = 354 and 428 nm for R = C_6H_4Cl-4; these were assigned to the Cu ← S(σ) and Cu ← S(π) c.t. transitions, respectively [9]. The latter wavenumber for each complex is close to those of c.t. bands observed in **1a**–**1c** and **3** (in dichloromethane); this wavenumber is presumably attributed to the Cu ← S(π) c.t. transition. Intensities of the c.t. bands of **1a**–**1c**, **2** and **3** in solution are gradually decreased on standing at room temperature, presumably because of the reduction of the copper(II)-center by the thiolate ligands.

Table III summarizes the electrochemical parameters obtained from the cyclic voltammetry of **1a**–**1c** and **3** as well as $[CuN_4^{(1)}][ClO_4]\cdot H_2O$ and $[CuN_4^{(3)}][ClO_4]\cdot 2H_2O$ in dichloromethane at 25 °C. Complexes **1a**–**1c** and **3** exhibit a quasi-reversible couple with the cathodic and anodic peak separation of 110–320 mV, while complex **2** decomposed too quickly to be measured. The redox potentials ($E_{1/2} = (E_{pc} + E_{pa})/2$) fall in the range −0.38 to −0.54 V *vs.* s.c.e., which is somewhat negative compared to those for the CuN_4 complexes, suggesting that ligation of the thiolate anion may stabilize the copper(II)-state in the present complexes. On the

TABLE III. Electrochemical Parameters for the Copper(II)–Thiolate Complexes[a]

Complex	$E_{1/2}$ (V)	$\lvert E_{pc} - E_{pa}\rvert$ (V)
1a $[CuN_4^{(1)}(SC(C_6H_5)_3)]$	−0.46	0.17
1b $[CuN_4^{(1)}(SC(C_6H_4Cl\text{-}4))]$	−0.38	0.32
1c $[CuN_4^{(1)}(SC_{10}H_7\text{-}2)]$	−0.39	0.32
3 $[CuN_4^{(3)}(SC(C_6H_5)_3)]$	−0.54	0.11
$[CuN_4^{(1)}][ClO_4]\cdot H_2O$	−0.16	0.13
$[CuN_4^{(3)}][ClO_4]\cdot 2H_2O$	−0.43	0.17

[a] Measured in dichloromethane containing $[Bu_4{}^nN][BF_4]$ (0.1 mol dm^{-3}) as a supporting electrolyte with the sweep rate 0.1 V s^{-1} at 25 °C; complex **2** has not been measured owing to the instability in solution at 25 °C.

other hand, the $E_{1/2}$ value of **3** is about 0.3 V more positive than those of its analogues $[CuN_4^{(3)}(SR)]$ (R = C_6H_5 and C_6H_4Cl-4) ($E_{1/2}$ = −0.85 and −0.86 V *vs.* s.c.e. in dichloromethane, respectively) [9]; complex **3** is less stabilized than the analogues. Table IV summarizes the oxidation peak potentials (E_p) of sodium thiolates and $E_{1/2}$ of the Cu(II)N_4 complexes in methanol at 25 °C. The E_p values of the thiolate anions may be taken as their electron-donating abilities and the $E_{1/2}$ values of the CuN_4 complexes as their electron-accepting powers. Plots of the wavenumber of the c.t. band maxima of **1a**–**1c** and **3** in methanol *vs.* $E_p - E_{1/2}$ values give an approximate linear relation, as depicted in Fig. 3. Thus, the stronger ligation of the thiolate anions to the CuN_4 moieties causes the low-frequency shift of the c.t. bands of the copper(II)–thiolate complexes.

Figure 4 shows an ESR spectrum of **1a** in methanol/ethanol (1:4 v/v) at 77 K. The spectral patterns not only of **1a** but also of **1b**, **1c**, **2**, and **3** are all very similar to that of the CuN_4 complexes without the thiolate ligand. Table V summarizes the ESR parameters for the complexes prepared here together with those for the CuN_4 complexes. The $\lvert A_\parallel\rvert$ values of **1a**–**1c**, **2** and **3** are smaller than those of the CuN_4 complexes without thiolate ligands, while the $g_\parallel$ and $g_\perp$ values of the former complexes are close to or somewhat larger than those of latter complexes. These observations may result from the electron-donation to the copper(II)-center from the thiolate sulfur atom which is located on the axial position in the penta-coordinate CuN_4S configuration. The same tendency was observed in the ESR parameters

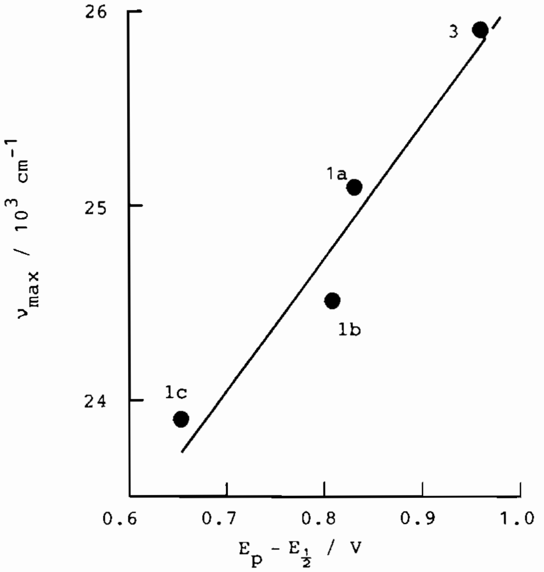

Fig. 3. A plot of the wavenumber of the c.t. band maxima for the copper(II)–thiolate complexes (**1a**–**1c** and **3**) in methanol against the value of $E_p - E_{1/2}$ in methanol at 25 °C; E_p and the $E_{1/2}$ are defined in the text.

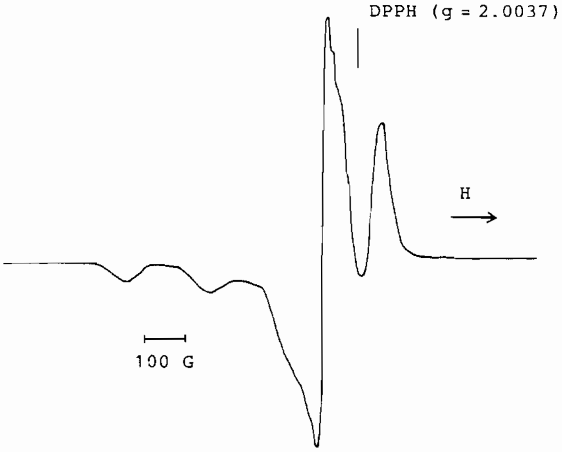

Fig. 4. The ESR spectrum of $[CuN_4^{(1)}(SC(C_6H_5)_3)]$ (**1a**) in methanol/ethanol (1:4 v/v) at 77 K.

TABLE IV. Oxidation Peak Potentials (E_p) of the Sodium Thiolates and Redox Potentials ($E_{1/2}$) of the CuN_4 Complexes[a]

Sodium thiolates	E_p (V)	CuN_4 complex	$E_{1/2}$ (V)
$Na[SC(C_6H_5)_3]$	+0.32	$[CuN_4^{(1)}][ClO_4]\cdot H_2O$	−0.51
$Na[SC_6H_4Cl\text{-}4]$	+0.30	$[CuN_4^{(3)}][ClO_4]\cdot 2H_2O$	−0.64
$Na[SC_{10}H_7\text{-}2]$	+0.14		

[a] In methanol containing $[Bu_4{}^nN][BF_4]$ (0.1 mol dm^{-3}) at 25 °C with the sweep rate 0.1 V s^{-1}.

TABLE V. ESR Parameters of the CuN_4S and CuN_4 Complexes[a]

Complex	$\lvert A_\parallel \rvert$ (10^{-4} cm^{-1})	$g_\parallel$	$g_\perp$
1a $[CuN_4^{(1)}(SC(C_6H_5)_3)]$	199	2.18	2.06
1b $[CuN_4^{(1)}(SC_6H_4Cl\text{-}4)]$	201	2.18	2.08
1c $[CuN_4^{(1)}(SC_{10}H_7\text{-}2)]$	195	2.17	2.07
2 $[CuN_4^{(2)}(SC(C_6H_5)_3)]$[b]	199	2.23	2.06
3 $[CuN_4^{(3)}(SC(C_6H_5)_3)]$	193	2.24	2.07
$[CuN_4^{(1)}][ClO_4]\cdot H_2O$	210	2.17	2.06
$[CuN_4^{(2)}][ClO_4]\cdot 0.5C_4H_8O_2$[b]	209	2.20	2.03
$[CuN_4^{(3)}][ClO_4]\cdot 2H_2O$	223	2.23	2.05

[a] Measured in methanol/ethanol (1:4 v/v) at 77 K, otherwise noted. [b] Measured in acetone/nitromethane (1:1 v/v) at 77 K.

for the penta-coordinated complexes of the $CuN_4(L)$ type, (2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene)(L)copper(II) hexafluorophosphate or dihexafluorophosphate (L = chloride, bromide, iodide, thiocyanate, and 1-methylimidazole) [16].

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