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Syntheses and Properties of Copper(II) Triperchlorates with *N,N′,N″,N‴*-Tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane and an Anion

Sigeo Kida,* Ichiro Murase, Chizu Harada, Liao Daizeng, and Masahiro Mikuriya
Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashi-ku, Fukuoka 812
Laboratory of Chemistry, College of General Education, Kyushu University 01, Ropponmatsu, Fukuoka 810

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Copper complexes of the title ligand (taec) of the general formula $Cu_2(taec)X(ClO_4)_3$ (X=F, Cl, Br, I, HCOO, CH_3COO, NO_2) were prepared and characterized. The formation constants for $[Cu_2(taec)]^{4+}+X^-=[Cu_2(taec)X]^{3+}$(X=F, Cl, Br, I) were determined spectrophotometrically in aqueous solution. The stabilities of the halogen-copper bonds were greatly enhanced relative to those of ordinary halogenocopper complexes, the order of the formation constants being Cl>Br>I>F. This result can be explained as that the anion is trapped in a cavity formed by two copper ions and the methylene chains of taec molecule, thereby the stability of the bound anion is enhanced and the fitness of the size of anion to the cavity is the most important factor for the formation constant.

A number of tetraazamacrocycles with pendant arms on the nitrogen atoms were synthesized and characterized in recent several years because of their specific complexation behavior and structural interest of their metal complexes.[1–6] In the preceding papers,[7,8] we reported the synthesis and characterization of dicopper(II) complexes of taec(*N,N′,N″,N‴*-tetrakis(2-aminoethyl)cyclam). The crystal structure analyses revealed that in $Cu_2(taec)(ClO_4)_4$ and $Cu_2(taec)Br(ClO_4)_3$ each copper ion is coordinated by the two ring nitrogens and the two pendant nitrogens forming a nearly square planar coordination entity, but the coordination modes of ligand are entirely different between these complexes as depicted in Fig. 1. In both cases one of the axial sites is open for coordination on each copper, but the other site is hindered with ligand methylene groups. In $Cu_2(taec)(ClO_4)_4$ both axial coordination sites are open toward the outside of the molecule in opposite direction so that perchlorate oxygen weakly coordinates to each copper, whereas in $Cu_2(taec)Br(ClO_4)_3$ the axial coordination sites face to each other allowing the bromide ion to be bound by both coppers. This structure is in good harmony with the facts that the addition of excess sodium perchlorate to a concentrated solution of $Cu_2(taec)Br_4$ does not yield the tetrakis(perchlorate) but invariably precipitated the bromide tris(perchlorate) and the Cu–Br bond is very stable toward hydrolysis relative to ordinary Cu–Br bonds. Being interested in these results, in this study we have newly prepared a series of complexes of the formula, $Cu_2(taec)X(ClO_4)_3$ (X=F, Cl, I, HCOO, CH_3COO, NO_2), and discussed the nature of Cu–X bonds in terms of stability constants and electronic spectra.

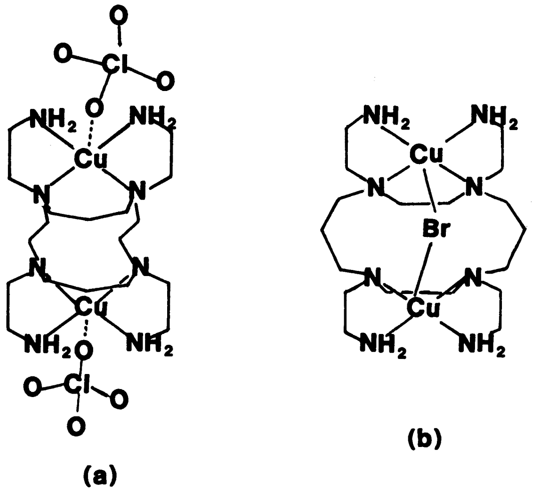

Fig. 1. Schematic drawing of the molecular structures of (a) $Cu_2(taec)(ClO_4)_4$ and (b) $Cu_2(taec)Br(ClO_4)_3$, where uncoordinated perchlorate ions are omitted.

Experimental

Preparation. The preparative methods for taec and $Cu_2(taec)Br(ClO_4)_3$ were already reported in the preceding papers.[7,8]

Complexes, $Cu_2(taec)X(CLO_4)_3$ (X=F, Cl, I, HCOO, CH_3COO, NO_2), were prepared by similar procedures from $Cu(ClO_4)_2\cdot 6H_2O$, taec, and NaX. The procedure for $Cu_2(taec)F(ClO_4)_3\cdot 2H_2O$ is shown below as an example.

$Cu_2(taec)F(ClO_4)_3\cdot 2H_2O$. To an aqueous solution of $Cu(ClO_4)_2\cdot 6H_2O$ (185 mg, 0.5 mmol) and taec (93 mg, 0.25 mmol) was added NaF (82 mg, 2 mmol), and the mixture was heated at 80 °C for 20 min. The resulting blue solution was filtered. When the filtrate was allowed to stand for about 6 h, blue needles were separated. Leaving the mixture for longer period may result in contamination of purple crystals ($Cu_2(taec)(ClO_4)_4$). The crude product was recrystallized from aqueous solution by adding NaF (≈ 50 mg). The crystals were collected, washed with methanol, and desiccated over P_2O_5. Yield; 175 mg (85%). Found: C, 25.60; H, 5.73; N, 13.23; Cu, 14.87%. Calcd for $C_{18}H_{48}N_8O_{14}Cl_3FCu_2$: C, 25.35; H, 5.67; N, 13.14; Cu, 14.90%

$Cu_2(taec)Cl(ClO_4)_3\cdot H_2O$. Blue fine crystals. Yield; 177 mg (85%). Found: C, 25.37; H, 5.25; N, 13.25; Cu, 14.87%. Calcd for $C_{18}H_{46}N_8O_{13}Cl_4Cu_2$: C, 25.39; H, 5.44; N, 13.16; Cu, 14.93%.

$Cu_2(taec)I(ClO_4)_3$. Violet needles. Yield; 210 mg (91%). Found: C, 23.32; H, 4.69; N, 11.95; Cu, 13.48%. Calcd for $C_{18}H_{44}N_8O_{12}Cl_3ICu_2$: C, 23.37; H, 4.79; N, 12.11; Cu, 13.74%.

$Cu_2(taec)(HCOO)(ClO_4)_3$. Blue needles. Yield; 196 mg (93%). Found: C, 26.73; H, 5.43; N, 13.15; Cu, 15.07%. Calcd for

Table 1. Magnetic, Spectral, and Stability Data

Compounds	μ_{eff}		θ/K	$\nu_{max}/10^3\,cm^{-1}$		log$K$
	(290K)	(88K)		Nujol	H_2O (ε)	
$Cu_2(taec)F(ClO_4)_3\cdot 2H_2O$	1.85	1.78	−10	15.3	16.9(160)	3.93±0.13
$Cu_2(taec)Cl(ClO_4)_3\cdot H_2O$	1.76	1.70	−8	16.1	16.3(220)	5.14±0.08
$Cu_2(taec)Br(ClO_4)_3$	1.80	1.77	−5	16.2	16.3(230)	4.78±0.12
$Cu_2(taec)I(ClO_4)_3$	1.75	1.71	−4	16.2	16.3(230)	4.46±0.17
$Cu_2(taec)(NO_2)(ClO_4)_3$	1.79	1.77	−3	16.7	17.0(170)	
$Cu_2(taec)(HCOO)(ClO_4)_3$	1.78	1.75	−4	15.9	17.3(150)	
$Cu_2(taec)(CH_3COO)(ClO_4)_3\cdot 2H_2O$	1.78	1.74	−5	15.7	17.4(150)	
$Cu_2(taec)(ClO_4)_4$	1.81	1.67	−20	19.2	17.7(165)	

$K=[Cu_2(taec)X^{3+}]/[Cu_2(taec)^{4+}][X^-]$ at 30 °C in the presence of 0.01 M $NaClO_4$.

$C_{19}H_{45}N_8O_{14}Cl_3Cu_2$: C, 27.07; H, 5.38; N, 13.29; Cu, 15.08%.

$Cu_2(taec)(CH_3COO)(ClO_4)_3\cdot 2H_2O$. Blue needles. Yield; 161 mg (89%). Found: C, 26.86; H, 5.78; N, 12.35; Cu, 14.82%. Calcd for $C_{20}H_{51}N_8O_{16}Cl_3Cu_2$: C, 26.90; H, 5.76; N, 12.55; Cu, 14.23%.

$Cu_2(taec)(NO_2)(ClO_4)_3$. Fine indigo-blue crystals. Yield; 200 mg (95%). Found: C, 26.86; H, 5.78; N, 12.35; Cu, 14.82%. Calcd for $C_{18}H_{44}N_9Cl_3O_{14}Cu_2$: C, 26.90; H, 5.76; N, 12.55; Cu, 14.23%.

Measurements. Electronic spectra were measured with a Shimazu MPS-5000 Multipurpose Spectrophotometer.

Infrared spectra were obtained with a Hitachi Grating Infrared Spectrophotometer Model 215 on KBr disk.

Magnetic susceptibilities were measured by the Faraday method. The apparatus was calibrated by use of $[Ni(en)_3]S_2O_3$. The susceptibilities were corrected for the diamagnetism of constituent atoms by use of Pascal's constants. Effective magnetic moments were calculated from the equation, $\mu_{eff}=2\sqrt{2(\chi-N\alpha)T}$, where χ is atomic magnetic susceptibility, and $N\alpha=60\times10^{-6}$ cgs emu.

Determination of stability constants. The equilibrium constants for $[Cu_2(taec)]^{4+}+X^- \rightleftarrows [Cu_2(taec)X]^{3+}$ (X=F, Cl, Br, I) were determined by a spectrophotometric method.[9] Absorbances of aqueous solutions containing $Cu_2(taec)X(ClO_4)_3$ (2×10^{-3}, 1×10^{-3}, 4×10^{-4}, 2×10^{-4}, 1×10^{-4}, and 5×10^{-5} M) and $NaClO_4$ (1×10^{-2} M) were measured in 1 cm or 10 cm cell at 30 °C, where M=mol dm^{-3}. The spectrum of $Cu_2(taec)(ClO_4)_4$ (1×10^{-3} M) was also measured to determine its molar extinction coefficients at the same condition as the above. The constants K were obtained by exploiting the relations,

$$\varepsilon_a(a-x) + \varepsilon_b x = D$$
$$(a-x)/x^2 = K,$$

where a and $a-x$ are initial and equilibrium concentrations of $[Cu_2(taec)X]^{3+}$, respectively; D is optical density of the solution; and ε_a and ε_b are molar extinction coefficients of $[Cu_2(taec)X]^{3+}$ and $[Cu_2(taec)]^{4+}$, respectively, the former of which were determined by measuring the absorbances of solutions containing $[Cu_2(taec)X]^{3+}$ (1×10^{-3} M) and the excess of X^- (10^{-2}—10^{-3}). Reasonable K values were obtained from the data in the range 600—640 nm, and those at 620 nm were chosen as the best values, which are listed in Table 1.

Results and Discussion

The binuclear structure of the present complexes is obvious judging from the elemental analyses and the crystal structures of $Cu_2(taec)Br(ClO_4)_3$ and $Cu_2(taec)(ClO_4)_4$.[8] However, as seen in Table 1 magnetic moments are not subnormal, and obey Curie-Weiss law in 80—300 K with very small negative Weiss constants, implying that there is no significant magnetic interaction between the copper ions.

Infrared spectra of all the complexes showed bands at 3400—3200, 3000—2900, 1580—1500, and 1050—1150 cm^{-1} whcih can be assigned to the ν(NH), ν(CH), $\delta(NH_2)$, $\delta(CH_2)$, and $\nu(ClO_4^-)$, respectively,[10] and many small bands in the 1400—650 cm^{-1} region forming a complicated pattern. The spectra of the F^-, Cl^-, Br^-, and I^- complexes closely resemble each other, suggesting similar molecular structures. The spectra of the NO_2 and RCOO ($R=CH_3$, H) complexes differ from each other and from those of the halogeno complexes in detail in the 1400—650 cm^{-1} region, and the bands due to the axial ligands overlapped with those of the equatorial ligand (taec), hence no definite assignments were feasible.

As shown in Table 1 the ligand field bands of $Cu_2(taec)X(ClO_4)_3$ are generally lower in wave number than that of $Cu_2(taec)(ClO_4)_4$ in nujol mull spectra. When the complexes are dissolved in water, the bands of tris(perchlorate) complexes are blue-shifted in more or less degree, whereas that of the tetrakis(perchlorate) is red-shifted though it still maintains the highest ν_{max} values among those complexes. These shifts should be due to the hydrolysis of the axial ligands. Judging from the degree of the blue-shift, it seems that the halogeno complexes are hydrolyzed very little in spite of the general view that halogeno copper(II) complexes are readily hydrolized in water.[11] On the other hand, the other complexes of $Cu_2(taec)X(ClO_4)_3$ are considerably hydrolized. In the case of tetrakis(perchlorate) it is most likely that the weakly coordinated perchlorate ions in crystal[7] are fully replaced by water molecules.

In order to make the above view quantitative we have determined the formation constants K of the halogeno complexes spectrophotometrically, and the results are listed in Table 1.[12]

$$K = [Cu_2(taec)X^{3+}]/[Cu_2(taec)^{4+}][X^-]$$

Chung et al. determined the complexation constants between mononegative ions and some macrocyclic tetraamine copper(II) complexes, and found that they fell in the range of 1—10 for the cases of Cl^- and Br^- ions.[13] These values are comparable to the first formation constants (k_1) of Cl^- and Br^- ions with Cu^{2+} ($\log k_1=0.08$ and -0.055 respectively). Thus, the presently obtained K values are larger than those values by a factor of 10^4—10^5 (cf. Table 1). Such an amazing stability should be attributed to a special steric arrangement of the coordination site. In fact, the X-ray analysis of $Cu_2(taec)Br(ClO_4)_3$ demonstrated that the bromide ion is linked by the two copper ions and hedged by nondonating atoms of taec molecule like being trapped in a cavity.[8] Thus, the environment around the coordinated halide ion will become somewhat similar to that in a nonpolar solvent so that the copper-halide bond is greatly stabilized. It is also to be noted that the K values decrease in the order, Cl>Br>I>F. This can also be rationalized in terms of the fitness of the anion to the cavity. In the present case fluoride ion seems to be too small for the cavity to get the largest enhancement of stability. In view of the above results the present complexes may be a model for active sites of some metal enzymes possessing specific selectivity and reactivity which are not found in ordinary synthetic metal complexes.

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12) Although the interconversion between $[Cu_2(taec)]^{4+}+X^-$ and $[Cu_2(taec)X]^{3+}$ involves a substantial change in ligand configuration, we have confirmed that the solution readily reaches equilibrium under these experimental conditions. Because the spectra of the solutions were entirely time-independent, and $Cu_2(taec)(ClO_4)_4$ can be readily converted into $Cu_2(taec)X(ClO_4)_3$ in aqueous solution by adding NaX and vice versa by adding $AgClO_4$ instead of NaX.

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