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Crystal and Molecular Structures of $[Cu_2(taec)X](ClO_4)_3 \cdot nH_2O$ (taec= *N,N',N'',N'''*-Tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane; X=I, F, NO_2, and CH_3COO; n=0, 1, or 2). Effect of Incorporation of an Anion X on the Structure of the Complex Cation

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The crystal structures of four binuclear copper(II) complexes of *N,N',N'',N'''*-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (taec), $[Cu_2(taec)I](ClO_4)_3$ (**1**), $[Cu_2(taec)F](ClO_4)_3 \cdot H_2O$ (**2**), $[Cu_2(taec)(NO_2)](ClO_4)_3$ (**3**), and $[Cu_2(taec)(CH_3COO)](ClO_4)_3 \cdot 2H_2O$ (**4**), were determined by single-crystal X-ray analysis. In all the complexes, each copper is coordinated by two ring- and two pendant-nitrogen atoms. All the complexes except for **4** adopt similar structures, where I^-, F^-, or NO_2^- is incorporated into the "cavity" of $[Cu_2(taec)]^{4+}$ as a bridging group. The structure of **4** is different from those of **1**, **2**, and **3**. In **4**, one of the oxygen atoms of acetate ion coordinates to one of the copper ions at the apical site and the other oxygen occupies an in-plane coordination site of the other copper ion. The structural effect of incorporation of an anion, X, into $[Cu_2(taec)]^{4+}$ was discussed on the basis of the crystal structures.

Recently we have prepared an octadentate ligand, *N,N',N'',N'''*-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (abbreviated as taec) and its metal complexes.[1-5] So far, all the complexes isolated are 2:1 (metal:taec) binuclear complexes where each metal ion is coordinated by two cyclam-ring nitrogens and two pendant amino nitrogens. Two types of binuclear structures are known for these complexes. One is the chair form (Fig. 1(A)) where the cyclam ring adopts the trans III form [6] as found for $[M_2(taec)](ClO_4)_4$ (M=Cu, Ni).[1,2] The other is the boat form (Fig. 1(B)) where the cyclam ring adopts the trans I form,[6] as found for $[Cu_2(taec)X](ClO_4)_3$ (X=Br, N_3, NCO).[2,5] In the latter case, the two coordination planes face to each other forming a space or cavity in the molecule to accommodate an anion which bridges the two copper ions. Owing to this property, we obtained a series of $[Cu_2(taec)X](ClO_4)_3$ complexes (X=F, Br, I, N_3, NCO, NO_2, CH_3COO) as single crystals.[3] Further ligation of X^- to $[Cu_2(taec)]^{4+}$ was investigated by potentiometric and spectrophotometric methods.[3,7] The stabilities of halogeno-copper linkage in aqueous solution are greatly enhanced compared to those of ordinary halogeno copper complexes. Such a high stability should be ascribed not only to the binding to both copper ions but rather to the incorporation of X^- into the "cavity" of $[Cu_2(taec)]^{4+}$. It is expected that the size and shape of the anion, X^-, may affect the structure of $[Cu_2(taec)]^{4+}$, i.e., the size of the "cavity" and the coordination mode of taec. Therefore, we have carried out the X-ray structure analyses of the title complexes and compared their structures with the previous data of the bromo, azido, and cyanato complexes in order to examine the relationship between the anion, X, and the structure of taec in the $[Cu_2(taec)X](ClO_4)_3$ complexes.

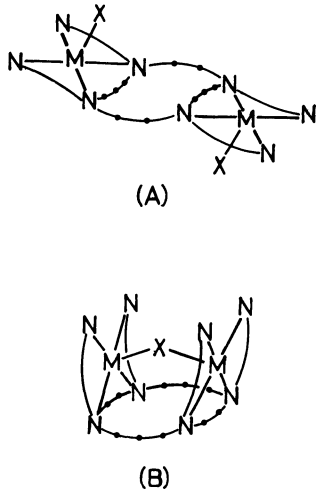

Fig. 1 Coordination modes of taec.

Experimental

The preparative methods for all the complexes were reported in the preceding paper.[3]

A Rigaku AFC-5 automated four-circle diffractometer was used for all measurements at 21±1 °C. Crystal data and details of the data collection are given in Table. 1. Lattice constants were determined by least-squares refinement based on 40 reflections with $20<2\theta<30°$. The intensity data were corrected for Lorentz-polarization effects, but not for absorption. The structures were solved by the direct methods. Refinements were carried out by the block-diagonal least-squares methods. In the course of the refinement it became apparent that the carbon atom, C(3), is

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Table 1. Crystal Data and Data Collection Details[a)]

Complex	$[Cu_2(taec)I](ClO_4)_3$	$[Cu_2(taec)F](ClO_4)_3 \cdot H_2O$	$[Cu_2(taec)(NO_2)](ClO_4)_2$	$[Cu_2(taec)(CH_3COO)](ClO_4)_3 \cdot 2H_2O$
Formula	$C_{18}H_{44}Cl_3Cu_2IN_8O_{12}$	$C_{18}H_{46}Cl_3Cu_2FN_8O_{13}$	$C_{18}H_{44}Cl_3Cu_2N_9O_{14}$	$C_{20}H_{51}Cl_3Cu_2N_8O_{16}$
F.W.	924.95	835.06	844.05	893.12
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$Pca2_1$	$Pmn2_1$	$Pmn2_1$	$P2_1/n$
a/Å	15.612(8)	8.925(6)	8.928(4)	13.138(6)
b/Å	14.511(9)	8.124(5)	7.886(2)	28.695(13)
c/Å	14.633(4)	21.560(6)	22.074(5)	9.452(2)
β/°				93.73(3)
V/Å^3	3315.0(27)	1563.2(15)	1554.1(8)	3555.8(23)
Z	4	2	2	4
D_c/gcm^{-3}	1.85	1.77	1.80	1.67
D_m/gcm^{-3}	1.80	1.71	1.78	1.66
$F(000)$	1864	864	872	1856
μ(Mo $K\alpha$)/cm^{-1}	25.16	16.99	17.08	15.02
Crystal dimensions (mm)	0.17×0.32×0.44	0.30×0.36×0.45	0.26×0.35×0.45	0.13×0.25×0.30
2θ range/°	2.5—64.0	1.5—66.0	1.5—68.0	1.0—50.0
Total no. of observed reflections	6354	3368	3611	6714
No. of unique reflections with $\|F_o\| > 3\sigma(\|F_o\|)$	3059	2493	2588	3817
Final no. of variables	390	281	299	443
Final residuals				
R	0.078	0.056	0.061	0.070
R'	0.097	0.068	0.072	0.076
Largest peak in final diff Fourier (e/Å^3)	1.20	0.93	0.88	0.71

a) Common data: graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å), scan type θ—2θ, scan speed 3° min^{-1}, scan width $(1.4+0.5\tan\theta)$°.

Table 2. Fractional Positional Parameters(×10^4) and Thermal Parameters of Non-Hydrogen Atoms with Their Estimated Standard Deviations in Parentheses[a)]

Atom	x	y	z	B_{eq} or B_{iso}/Å^2
(1) $[Cu_2(taec)I](ClO_4)_3$				
I	4935(1)	3667(1)	1853(2)	5.3
Cu(1)	5665(1)	1817(1)	1785(2)	3.3
Cu(2)	3923(2)	4099(2)	247(2)	3.6
Cl(1)	7135(3)	-293(4)	3545(4)	4.0
Cl(2)	2468(4)	6288(4)	3776(4)	5.0
Cl(3)	4872(4)	7370(4)	952(6)	6.5
O(1)	6497(11)	-84(15)	4187(11)	7.6
O(2)	7837(10)	-716(11)	4014(12)	6.1
O(3)	6793(14)	-847(14)	2877(15)	8.9
O(4)	7424(12)	517(11)	3154(13)	7.6
O(5)	2818(13)	6209(16)	4676(14)	9.5
O(6)	1627(15)	6252(21)	3819(22)	14.3
O(7)	2599(16)	7327(13)	3581(16)	11.2
O(8)	2822(18)	5901(26)	3294(22)	16.6
O(9)	4995(19)	6610(23)	1309(24)	14.7(10)*
O(10)[a)]	4383(28)	8047(29)	1788(41)	10.0(11)*
O(11)[a)]	5538(29)	7871(31)	1503(31)	9.9(13)*

Table 2. (Continued)

Atom	*x*	*y*	*z*	B_{eq} or B_{iso}/Å^2
O(12)[a]	4407(33)	8272(36)	646(36)	11.3(14)*
O(13)[a]	5577(38)	8054(42)	731(41)	13.7(18)*
O(14)[a]	5287(22)	7236(25)	20(27)	7.2(9)*
O(15)[a]	4272(31)	7517(34)	393(38)	11.2(14)*
N(1)	4622(9)	915(10)	1932(11)	3.4
N(2)	5932(9)	1130(10)	583(11)	3.4
N(3)	4178(13)	3410(14)	-968(11)	5.7
N(4)	2856(10)	3232(11)	358(12)	4.3
N(5)	5695(13)	1778(13)	3218(12)	5.3
N(6)	6885(12)	2231(12)	1694(18)	7.1
N(7)	4794(15)	5031(18)	-120(14)	7.4
N(8)	3215(14)	5066(14)	1016(12)	5.9
C(1)	4772(13)	191(12)	1222(15)	3.9
C(2)	5675(14)	194(14)	895(14)	4.5
C(3)	5494(17)	1304(16)	-298(15)	5.3
C(4)	5378(15)	2318(15)	-478(14)	4.6
C(5)	4494(17)	2474(14)	-1039(14)	5.3
C(6)	3236(20)	3296(20)	-1256(19)	8.4
C(7)	2741(15)	2784(17)	-566(17)	5.9
C(8)	2838(15)	2476(15)	1090(17)	5.6
C(9)	3592(12)	1799(14)	944(14)	3.7
C(10)	3737(11)	1277(13)	1841(17)	3.9
C(11)	4716(15)	515(14)	2837(13)	4.4
C(12)	4886(16)	1165(18)	3510(17)	6.3
C(13)	6845(15)	1138(16)	425(22)	6.4
C(14)	7251(22)	1388(29)	1090(28)	12.8
C(15)	4627(19)	4061(20)	-1509(18)	6.9
C(16)	5173(18)	4686(25)	-953(22)	10.4
C(17)	2155(16)	3913(17)	589(21)	6.6
C(18)	2410(18)	4534(20)	1300(22)	8.1
(2) $[Cu_2(taec)F](ClO_4)_3 \cdot H_2O$				
Cu(1)[a]	0	6402(1)	3151(1)	1.9
Cu(2)[a]	0	6401(1)	5112(1)	1.9
Cl(1)[a]	0	8913(3)	6973(1)	3.4
Cl(2)[a]	0	8907(3)	1290(1)	2.7
Cl(3)[a]	0	10722(3)	-863(3)	3.6
F[a]	0	7002(5)	4162(5)	3.1
O(1)[a]	0	10036(10)	6436(4)	4.4
O(2)[a]	0	7347(12)	6707(6)	10.4
O(3)	1288(7)	9126(10)	7355(4)	6.8
O(4)[a]	0	10030(12)	1752(5)	7.5
O(5)[a]	0	7206(10)	1524(4)	6.9
O(6)	1306(8)	9134(9)	939(4)	7.3
O(7)[a]	0	9140(18)	-739(12)	20.7
O(8)[a]	547(22)	10909(32)	-1418(7)	15.0
O(9)[a]	549(19)	11672(25)	-368(12)	14.1
O(10)[a]	1474(16)	10609(30)	-639(11)	13.1
OW[a]	657(13)	10102(10)	4187(12)	7.1
N(1)	1611(5)	4548(7)	3038(2)	2.5
N(2)	1544(6)	4577(6)	5264(2)	2.4

Table 2. (Continued)

Atom	x	y	z	B_{eq} or B_{iso}/Å^2
N(3)	1679(7)	7901(8)	2893(3)	3.6
N(4)	1650(6)	7973(6)	5389(3)	2.9
C(1)	879(8)	3596(8)	2563(3)	3.2
C(2)	2250(10)	3749(11)	3566(4)	5.2
C(3A)[a]	1639(11)	3619(12)	4146(12)	2.6
C(3B)[a]	2600(12)	4542(13)	4178(11)	2.5
C(4)	2433(9)	3808(12)	4734(3)	4.7
C(5)	627(7)	3072(8)	5494(3)	3.1
C(6)	2977(8)	5474(9)	2770(4)	3.5
C(7)	2671(10)	7018(12)	2504(6)	6.3
C(8)	2411(7)	5160(10)	5794(3)	3.3
C(9)	2908(10)	6902(11)	5697(5)	5.2
(3) $[Cu_2(taec)(NO_2)](ClO_4)_3$				
Cu(1)[a]	0	6476(1)	3386(1)	1.8
Cu(2)[a]	0	6502(1)	5407(1)	1.9
Cl(1)[a]	0	8867(3)	7234(1)	2.6
Cl(2)[a]	0	8860(3)	1573(1)	2.2
Cl(3)[a]	0	10719(2)	-596(3)	2.7
O(1)[a]	0	10023(12)	6765(5)	6.0
O(2)[a]	0	7167(10)	7030(4)	5.1
O(3)	1338(8)	9079(9)	7580(4)	6.3
O(4)[a]	0	10137(10)	2055(4)	4.4
O(5)[a]	0	7196(10)	1881(4)	6.2
O(6)	-1236(9)	9040(9)	1207(5)	7.2
O(7)[a]	0	9017(14)	-675(12)	13.0
O(8)[a]	669(19)	11284(23)	-74(6)	8.9
O(9)[a]	566(18)	11652(29)	-1099(12)	12.6
O(10)[a]	1554(16)	10951(23)	-665(11)	7.8
O(11)[a]	0	7455(6)	4420(7)	2.7
O(12A)[b]	0	9938(16)	4044(6)	3.9
O(12B)[b]	0	9895(22)	4698(9)	4.5
N(1)	1600(7)	4590(6)	3304(2)	2.3
N(2)	1577(6)	4536(6)	5497(3)	2.1
N(3)	1719(6)	7979(6)	3128(3)	2.3
N(4)	1642(7)	8066(7)	5701(3)	2.8
N(5)[a]	0	9062(9)	4298(6)	3.8
C(1)	688(8)	3069(8)	3075(4)	3.0
C(2)	2123(9)	3407(8)	3835(3)	2.7
C(3A)[a]	1603(12)	3838(12)	4393(12)	2.4
C(3B)[a]	2546(13)	4444(13)	4386(12)	2.3
C(4)	2482(8)	4215(9)	4971(3)	3.1
C(5)	862(9)	3521(9)	5960(3)	3.1
C(6)	3024(8)	5331(9)	3054(3)	2.9
C(7)	2844(11)	6930(13)	2800(5)	5.2
C(8)	2426(8)	5256(9)	6026(3)	2.9
C(9)	2806(10)	7014(9)	6007(6)	5.1
(4) $[Cu_2(taec)(CH_3COO)](ClO_4)_3 \cdot 2H_2O$				
Cu(1)	9464(1)	1243(1)	7867(1)	2.5
Cu(2)	5900(1)	942(1)	7808(1)	2.7

Table 2. (Continued)

Atom	*x*	*y*	*z*	B_{eq} or B_{iso}/Å^2
Cl(1)	7477(2)	2461(1)	2739(3)	3.8
Cl(2)	7466(2)	-1490(1)	7573(3)	4.7
Cl(3)	1822(2)	-282(1)	7960(3)	4.2
O(1)	8110(5)	783(2)	7954(7)	3.7
O(2)	6703(4)	369(2)	7480(7)	3.3
O(3)	7282(6)	2800(3)	1651(9)	6.4
O(4)	8459(6)	2267(3)	2657(8)	6.5
O(5)	7392(7)	2679(4)	4068(9)	8.0
O(6)	6741(7)	2104(3)	2583(10)	7.3
O(7)	6513(7)	-1674(4)	7762(11)	9.1
O(8)	7459(8)	-1253(5)	6298(11)	11.5
O(9)	8189(8)	-1843(4)	7642(13)	10.3
O(10)	7736(11)	-1166(4)	8684(13)	13.0
O(11)	1886(12)	-150(4)	6594(10)	13.7
O(12)	2110(6)	-751(3)	8222(9)	6.6
O(13)	822(8)	-236(4)	8308(18)	16.0
O(14)	2408(11)	19(4)	8815(13)	13.3
OW(1)	2651(6)	-3737(3)	6600(10)	7.1
OW(2)	5900(7)	-420(4)	8823(11)	8.3
N(1)	9363(5)	1483(3)	5802(7)	3.0
N(2)	9178(5)	1929(3)	8437(8)	2.7
N(3)	5490(6)	1609(3)	8213(8)	3.2
N(4)	5668(6)	1111(3)	5670(8)	3.4
N(5)	10496(6)	780(3)	7215(9)	4.0
N(6)	9829(6)	1133(3)	9946(8)	3.9
N(7)	5911(6)	840(3)	9922(8)	3.2
N(8)	4381(6)	553(3)	7382(9)	4.6
C(1)	9381(7)	2003(4)	5871(10)	3.8
C(2)	9775(7)	2170(3)	7344(10)	3.3
C(3)	8147(7)	2150(4)	8417(11)	3.7
C(4)	7331(6)	1845(3)	9004(10)	2.8
C(5)	6286(7)	1984(3)	8285(12)	3.8
C(6)	4721(7)	1713(4)	6999(12)	4.1
C(7)	5156(7)	1566(5)	5573(11)	4.8
C(8)	6618(7)	1106(4)	4852(10)	4.0
C(9)	7441(7)	1433(4)	5459(10)	3.0
C(10)	8468(7)	1299(4)	4896(9)	3.9
C(11)	10344(7)	1309(4)	5241(10)	4.1
C(12)	10523(8)	811(4)	5660(12)	4.8
C(13)	9728(8)	1979(4)	9864(11)	4.3
C(14)	9538(8)	1550(4)	10735(10)	4.0
C(15)	4973(8)	1565(4)	9580(11)	4.3
C(16)	5616(7)	1278(3)	10621(10)	3.3
C(17)	4985(8)	737(4)	5048(11)	4.3
C(18)	4036(8)	652(5)	5899(12)	5.5
C(19)	7678(7)	411(3)	7619(10)	3.1
C(20)	8283(8)	-23(4)	7375(14)	5.0

a) Atoms refined with occupancy factors of 0.5. b) Atoms refined with occupancy factors of 0.25. c) Starred values are for atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $4/3[a^2B_{11}+b^2B_{22}+c^2B_{33}+ab(\cos\gamma)B_{12}+ac(\cos\beta)B_{13}+bc(\cos\alpha)B_{23}]$.

Table 3. Selected Interatomic Distances (l/Å) and Angles (ϕ/°) with Their Estimated Standard Deviations in Parentheses

(1) $[Cu_2(taec)I](ClO_4)_3$			
Cu(1)-Cu(2)	4.841(3)	Cu(1)-N(6)	2.001(19)
Cu(1)-I	2.919(3)	Cu(2)-N(3)	2.078(17)
Cu(2)-I	2.901(3)	Cu(2)-N(4)	2.095(16)
Cu(1)-N(1)	2.101(14)	Cu(2)-N(7)	1.992(25)
Cu(1)-N(2)	2.064(16)	Cu(2)-N(8)	2.111(20)
Cu(1)-N(5)	2.098(18)		
Cu(1)-I-Cu(2)	112.6(1)	N(3)-Cu(2)-N(4)	86.0(7)
N(1)-Cu(1)-N(2)	86.7(6)	N(3)-Cu(2)-N(7)	88.0(8)
N(1)-Cu(1)-N(5)	84.1(7)	N(4)-Cu(2)-N(8)	86.6(7)
N(2)-Cu(1)-N(6)	84.1(8)	N(7)-Cu(2)-N(8)	92.9(9)
N(5)-Cu(1)-N(6)	93.1(10)	I-Cu(2)-N(3)	119.0(5)
I-Cu(1)-N(1)	105.4(4)	I-Cu(2)-N(4)	103.9(5)
I-Cu(1)-N(2)	123.5(4)	I-Cu(2)-N(7)	89.6(6)
I-Cu(1)-N(5)	89.9(5)	I-Cu(2)-N(8)	89.8(5)
I-Cu(1)-N(6)	95.6(5)		
(2) $[Cu_2(taec)F](ClO_4)_3 \cdot H_2O$[a]			
Cu(1)-Cu(2)	4.229(2)	Cu(1)-N(3)	2.009(6)
Cu(1)-F	2.234(10)	Cu(2)-N(2)	2.050(5)
Cu(2)-F	2.106(10)	Cu(2)-N(4)	2.039(6)
Cu(1)-N(1)	2.097(5)		
Cu(1)-F-Cu(2)	154.0(2)	N(2)-Cu(2)-N(2)^i	84.5(2)
N(1)-Cu(1)-N(1)^i	86.6(2)	N(2)-Cu(2)-N(4)	85.4(2)
N(1)-Cu(1)-N(3)	83.8(2)	N(4)-Cu(2)-N(4)^i	92.5(2)
N(3)-Cu(1)-N(3)^i	96.5(3)	F-Cu(2)-N(2)	108.9(2)
F-Cu(1)-N(1)	105.7(2)	F-Cu(2)-N(4)	98.1(2)
F-Cu(1)-N(3)	97.9(2)		
(3) $[Cu_2(taec)(NO_2)](ClO_4)_3$[a]			
Cu(1)-Cu(2)	4.462(2)	Cu(2)-N(2)	2.104(5)
Cu(1)-O(11)	2.411(15)	Cu(2)-N(4)	2.022(6)
Cu(2)-O(11)	2.304(15)	N(5)-O(11)	1.296(10)
Cu(1)-N(1)	2.070(6)	N(5)-O(12A)	0.889(17)
Cu(1)-N(3)	2.021(5)	N(5)-O(12B)	1.102(22)
Cu(1)-O(11)-Cu(2)	142.3(2)	N(2)-Cu(2)-N(2)^i	84.0(2)
Cu(1)-O(11)-N(5)	96.6(10)	N(2)-Cu(2)-N(4)	86.2(2)
Cu(2)-O(11)-N(5)	121.1(10)	N(4)-Cu(2)-N(4)^i	92.9(2)
N(1)-Cu(1)-N(1)^i	87.3(2)	O(11)-Cu(2)-N(2)	109.2(2)
N(1)-Cu(1)-N(3)	82.7(2)	O(11)-Cu(2)-N(4)	96.0(2)
N(3)-Cu(1)-N(3)^i	98.9(2)	O(11)-N(5)-O(12A)	153.1(17)
O(11)-Cu(1)-N(1)	108.2(2)	O(11)-N(5)-O(12B)	114.6(15)
O(11)-Cu(1)-N(3)	94.5(2)	O(12A)-N(5)-O(12B)	92.4(14)
(4) $[Cu_2(taec)(CH_3COO)](ClO_4)_3 \cdot 2H_2O$			
Cu(1)-Cu(2)	4.758(2)	Cu(2)-N(3)	2.031(8)
Cu(1)-N(1)	2.066(7)	Cu(2)-N(4)	2.081(8)
Cu(1)-N(2)	2.083(8)	Cu(2)-N(7)	2.018(8)
Cu(1)-N(5)	2.023(9)	Cu(2)-N(8)	2.301(9)
Cu(1)-N(6)	2.017(8)	C(19)-O(1)	1.240(11)
Cu(1)-O(1)	2.222(6)	C(19)-O(2)	1.284(11)

Table 3. (Continued)

Cu(2)-O(2)	1.990(6)	C(19)-C(20)	1.502(14)
N(1)-Cu(1)-N(2)	85.8(3)	O(2)-Cu(2)-N(7)	93.7(3)
N(1)-Cu(1)-N(5)	86.2(3)	N(8)-Cu(2)-O(2)	91.9(3)
N(2)-Cu(1)-N(6)	86.0(3)	N(8)-Cu(2)-N(3)	104.7(3)
N(5)-Cu(1)-N(6)	94.2(4)	N(8)-Cu(2)-N(4)	82.6(3)
O(1)-Cu(1)-N(1)	103.3(3)	N(8)-Cu(2)-N(7)	93.0(3)
O(1)-Cu(1)-N(2)	113.2(3)	Cu(1)-O(1)-C(19)	148.9(6)
O(1)-Cu(1)-N(5)	100.1(3)	Cu(2)-O(2)-C(19)	116.2(6)
O(1)-Cu(1)-N(6)	90.7(3)	O(1)-C(19)-O(2)	122.9(9)
N(3)-Cu(2)-N(4)	86.6(3)	O(1)-C(19)-C(20)	120.9(9)
N(3)-Cu(2)-N(7)	86.3(3)	O(2)-C(19)-C(20)	116.1(8)
O(2)-Cu(2)-N(4)	94.9(3)		

a) Superscript i refers to the equivalent position $(-x, y, z)$.

subjected to disorder in $[Cu_2(taec)X](ClO_4)_3$ (X=F and NO_2). The carbon atom was divided into two positions with an occupancy factor 0.5 on the basis of a difference Fourier map. Hydrogen atoms were inserted in their calculated positions and fixed at their positions. The final discrepancy factors, $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R'=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, are listed in Table 1. The weighting scheme, $w=[\sigma_{count}^2+(0.015|F_o|)^2]^{-1}$, was employed.

The atomic scattering factors for all the atoms and the anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$, for all the non-hydrogen atoms were taken from Ref. 8. All the calculations were carried out on the HITAC M-680 H computer at the Computer Center of the Institute for Molecular Science using a local version of the MULTAN 78,[9] UNICS-III,[10] and ORTEP[11] programs. Atomic coordinates and thermal parameters of non-hydrogen atoms are listed in Table 2. The anisotropic thermal parameters of non-hydrogen atoms, the atomic coordinates and thermal parameters of hydrogen atoms, and the F_o—F_c tables have been deposited as a Document No. 8737 at the Office of the Editor.

Description of the Structures

$[Cu_2(taec)I](ClO_4)_3$. The crystal and molecular structure of $[Cu_2(taec)I](ClO_4)_3$ is similar to that of $[Cu_2(taec)Br](ClO_4)_3$[2]; they are isomorphous. A perspective drawing of the complex cation, $[Cu_2(taec)I]^{3+}$, and the numbering system are illustrated in Fig. 2. The cyclam ring assumes the trans I form. The taec ligand forms two 5-5-5 fused chelate ring systems with two copper ions. The coordination geometry of each copper ion is an elongated square pyramid. The basal plane is formed by two nitrogens of the cyclam ring and two pendant amino nitrogens. The deviations of the basal atoms from the mean plane are within ±0.15 Å, and Cu(1) and Cu(2) are displaced by 0.48 and 0.38 Å, respectively, from the mean planes toward the iodide ion. The iodide ion coordinates to both copper ions at the apical positions with Cu–I distances of 2.919(3) and 2.901(3) Å in the "cavity" of

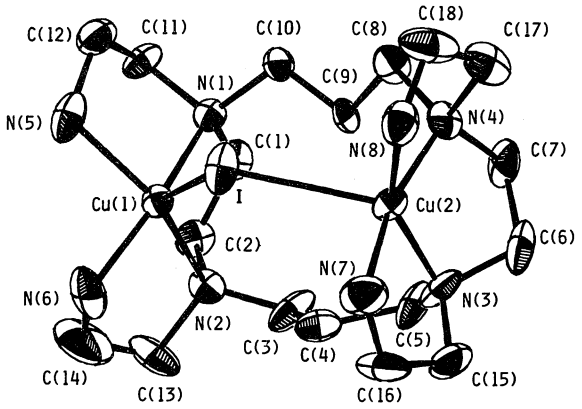

Fig. 2. ORTEP diagram of $[Cu_2(taec)I](ClO_4)_3$.

$[Cu_2(taec)]^{4+}$. The sixth coordination is not feasible because the other axial site of the copper ion is blocked by the CH_2 chains of taec. The pendant amino groups form hydrogen bonds with the iodide ion i.e., I···N(5) 3.593(19), I···N(6) 3.696(19), I···N(7) 3.507(22), I···N(8) 3.582(21) Å. These hydrogen bonds may contribute to the stabilization of the Cu–I bonds. The perchlorate ions are hydrogen-bonded to the pendant amino groups, e.g., O(4)···N(5) 3.262(27) Å.

$[Cu_2(taec)F](ClO_4)_3 \cdot H_2O$. A perspective drawing of the complex cation of $[Cu_2(taec)F](ClO_4)_3 \cdot H_2O$ is shown in Fig. 3. The complex cation has a mirror plane containing Cu(1), Cu(2), and F as required from the crystallographic symmetry. The coordination mode of taec is similar to that of $[Cu_2(taec)I](ClO_4)_3$. The coordination geometry of each copper ion is an elongated square pyramid. The basal planes are perfectly planar as required from the symmetry (the mirror plane) of the complex cation and the copper ions, Cu(1) and Cu(2), are displaced by 0.41 and 0.47 Å, respectively, from the planes toward the fluoride ion. The fluoride ion bridges the two copper

ions at the apical positions with Cu–F distances of 2.234(10) and 2.106(10) Å. The Cu(1)–Cu(2) separation (4.229(2) Å) is the shortest and the Cu(1)–F–Cu(2) angle (154.0 (2)°) is the largest among the $[Cu_2(taec)X](ClO_4)_3$ complexes. The oxygen atom of the water molecule, OW, (whose occupancy factor is 0.5) is located in a vicinity of the "cavity" of $[Cu_2(taec)]^{4+}$ forming a hydrogen bond with the fluoride ion (F···OW 2.587(10) Å).[12] The pendant amino groups form hydrogen bonds to the fluoride ion and perchlorate ions, e.g., F···N(3) 3.203(11), F···N(4) 3.129(11). O(2)···N(4) 3.240(13) Å.

$[Cu_2(taec)(NO_2)](ClO_4)_3$. The crystals of $[Cu_2(taec)(NO_2)](ClO_4)_3$ and $[Cu_2(taec)F](ClO_4)_3 \cdot H_2O$ are isomorphous. The complex cation, $[Cu_2(taec)(NO_2)]^{3+}$, has a mirror plane containing Cu(1), Cu(2), O(11), N(5), O(12A), and O(12B) (Fig. 4). The nitrite ion bridges the two copper ions with one of its oxygen atoms. The other oxygen atom of the nitrite ion is disordered in the ratio 1:1 (O(12A):O(12B)). Such disorder is a common feature of crystal structure of nitrito complexes.[13]

$[Cu_2(taec)(CH_3COO)](ClO_4)_3 \cdot 2H_2O$. A perspective drawing of the complex cation, $[Cu_2(taec)(CH_3COO)]^{3+}$, is illustrated in Fig. 5. The two copper ions are bridged by the acetate ion. There is, however, a significant difference between the coordination geometries about the two copper ions. As found in other $[Cu_2(taec)X](ClO_4)_3$ complexes, the coordination geometry of Cu(1) is a distorted square pyramid with two nitrogens of the cyclam ring and two nitrogens of the pendant amino groups in the basal plane and an oxygen atom of the acetate ion, O(1), in the apical position. The geometry of Cu(2) is also described as a square-pyramid, but in this case the apical position is occupied by the pendant amino nitrogen, N(8), and the basal plane is formed by one of the bridging-acetate oxygens, O(2), the pendant-amino nitrogen, N(7), and two nitrogens of the cyclam ring, N(3) and N(4). Thus, the coordination mode of taec is different from those of other $[Cu_2(taec)X](ClO_4)_3$ complexes (X=F, Br, I, N_3, NCO, NO_2). The Cu(1)–Cu(2) distance is 4.758(2) Å shorter than that of $[Cu_2(taec)I](ClO_4)_3$. One of two water molecules is hydrogen-bonded to the bridging acetate oxygen atom, O(2), and a pendant amino nitrogen, i.e., O(2)···OW(2) 2.831 (12), N(7)···OW(2) $(1-x, -y, 2-z)$ 2.983(12) Å. Another water molecule is hydrogen-bonded to the perchlorate oxygen, O(10), and the pendant-amino nitrogen, N(5), i.e., O(10)···OW(1) $(1/2+x, 1/2-y, 1/2+z)$ 2.780(15), N(5)···OW(1) $(1/2-x, 1/2+y, 3/2-z)$ 2.959 (12) Å.

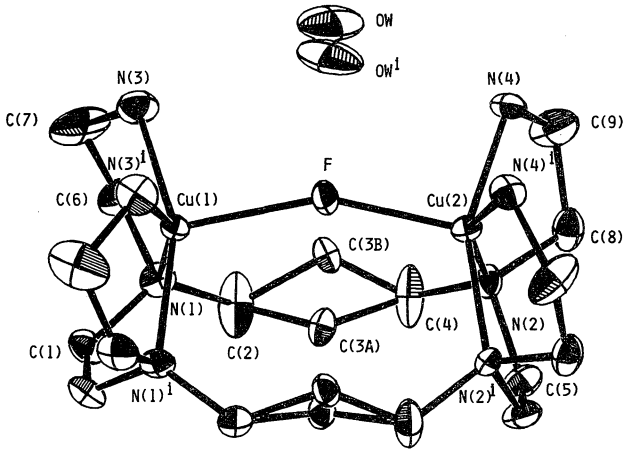

Fig. 3. ORTEP diagram of $[Cu_2(taec)F](ClO_4)_3 \cdot H_2O$.

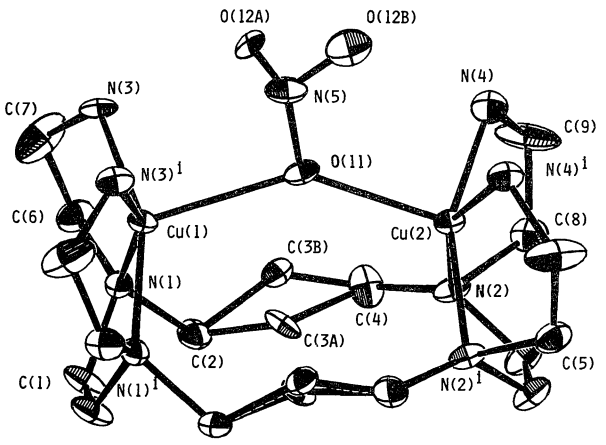

Fig. 4. ORTEP diagram of $[Cu_2(taec)(NO_2)](ClO_4)_3$.

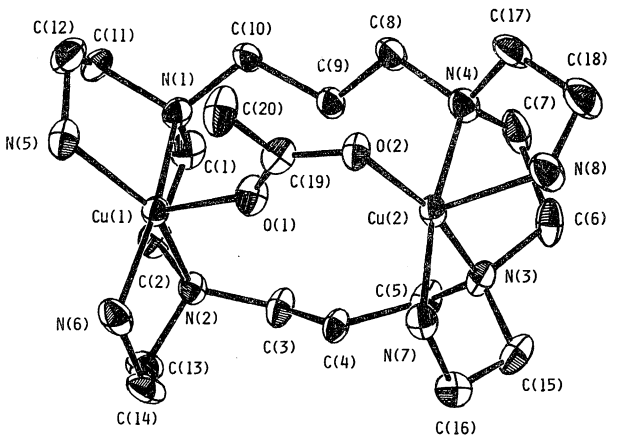

Fig. 5. ORTEP diagram of $[Cu_2(taec)(CH_3COO)](ClO_4)_3 \cdot 2H_2O$.

Discussion

The structures of all the present complexes except for $[Cu_2(taec)(CH_3COO)](ClO_4)_3 \cdot 2H_2O$ are essentially the same as those of previously reported $[Cu_2(taec)X](ClO_4)_3$ (X=Br, N_3, NCO),[2,5] where the coordination

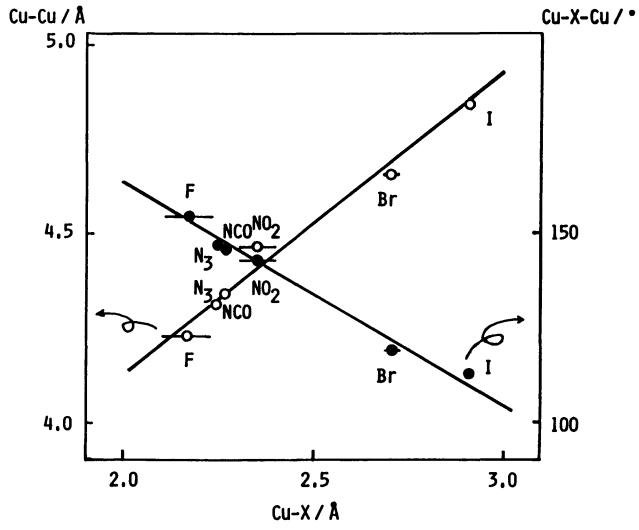

Fig. 6. Correlations of Cu-Cu distance (O) and Cu-X-Cu angle (●) with Cu-X distance.

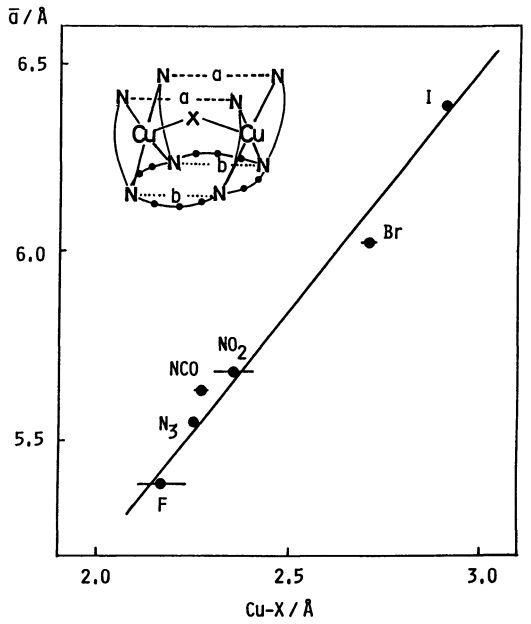

Fig. 7. Correlation between Cu-X and average value of a in $[Cu_2(taec)X](ClO_4)_3$. Parameters a and b represent the N-N distances indicated by ------ and ·····, respectively.

mode of taec is the boat form as shown in Fig. 1(B), and an anion, X, is incorporated into the "cavity" of $[Cu_2(taec)]^{4+}$. Coordination geometry of each copper ion can be described as an elongated square-pyramid. The in-plane Cu-N distances are in the range of 1.988—2.111 Å. The displacement of the copper ion from the basal plane is in the range of 0.38—0.48 Å. The Cu-X and Cu-Cu distances increase and the Cu-X-Cu angle decreases in the increasing order of bridging atom size, $F<N_3<NCO<NO_2<Br<I$ (Fig. 6). The decrease of the Cu-X-Cu angle implies that the anion is pushed out in some degree from the center of the complex cation. It is interesting to see the "cavity" size as a function of the size of X^-. The size may be expressed by two parameters a and b defined in Fig. 7. The a value increases from 5.382 Å to 6.393 Å with increasing the size of bridging atom of X or Cu-X distance, whereas b varies little (4.800—4.912 Å). In other words, the $[Cu_2(taec)]^{4+}$ slightly varies its configuration to accommodate the anion though the expansion of the "cavity" size is limited so that the larger anion tends to be somewhat pushed out from the center of the complex cation as already stated. However, in the case of $X=CH_3COO$, the acetate ion can not take a bridging mode similar to that of NO_2^- in $[Cu_2(taec)(NO_2)](ClO_4)_3$ because of steric hindrance between its methyl group and the pendant amino groups. Thus, one of the pendant amino group (N(8)) is pushed out from the equatorial coordination position of the copper ion and located at the axial position. Instead, the equatorial coordination position is occupied by another oxygen of the acetate ion.

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