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Preparation and Characterization of Copper(II) Complexes with 1,4,8,11-Tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane

EIJI ASATO*, HANS TOFTLUND**, SIGEO KIDA†

Okazaki National Institutes, Institute for Molecular Science, Myodaiji, Okazaki 444 (Japan)

MASAHIRO MIKURIYA

Department of Chemistry, School of Science, Kwansei Gakuin University 01, Uegahara, Nishinomiya 662 (Japan)

and KEITH S. MURRAY

Department of Chemistry, Monash University, Clayton, Vic. 3168 (Australia)

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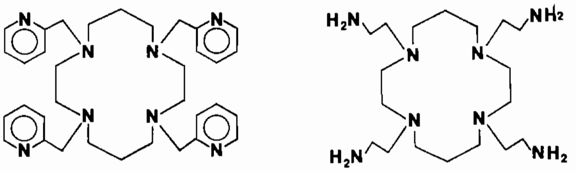
Abstract

Eight copper(II) complexes of the title ligand (tpmc) were synthesized, and characterized by elemental analyses, IR and Vis spectra, and magnetic measurements. The results are discussed in comparison with the previously reported results for taec complexes, where taec represents 1,4,8,11-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane. One of these is a 1:1 complex, though the others are dinuclear as in the case of taec complexes. Of these the crystal structures of $[Cu_2OH(tpmc)](ClO_4)_3 \cdot 2H_2O$ (2) and $[Cu_2NO_3(tpmc)](PF_6)_3$ (5) were determined by X-ray diffraction analyses. The hydroxo complex 2 crystallizes in the monoclinic space group *Cm* with unit cell parameters $a = 11.048(1)$, $b = 22.318(3)$, $c = 9.459(1)$ Å, $\beta = 111.95(1)°$, $V = 2163.2(5)$ Å^3 and $Z = 2$ and was refined to $R = 0.041$ and $R_w = 0.052$. The nitrato complex 5 crystallizes in the monoclinic space group $P2_1/n$ with unit cell parameters $a = 18.685(4)$, $b = 25.563(5)$, $c = 9.393(1)$ Å, $\beta = 92.59(2)°$, $V = 4482(2)$ Å^3 and $Z = 4$ and was refined to $R = 0.083$ and $R_w = 0.110$. In either compound the anion, OH^- or NO_3^-, is bound to both copper ions, but their coordination modes are substantially different from each other. No appreciable spin exchange coupling was observed for these complexes except the hydroxo complex in which an antiferromagnetic interaction is operating ($-2J = 86$ cm^{-1}). The result was reasonably explained in terms of the molecular structure.

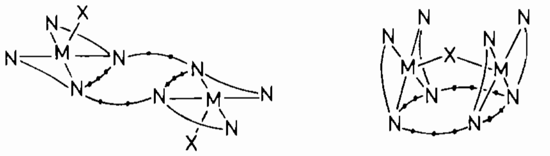
Introduction

A number of metal complexes of polyazamacrocycles with pendant donor groups on the nitrogen atoms have been synthesized in recent years [1–4]. These complexes have often shown interesting coordination behaviors and structures. Kida and his coworkers have synthesized a number of first row transition metal complexes with taec (1,4,8,11-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane, Fig. 1), all of which were proved to be dinuclear, though there are two types for the coordination mode as illustrated in Fig. 2 [3]. The taec complexes are unique in that (i) the complexes incorporate an anion in between the two coordinated metal ions with extremely high stability in aqueous solution and (ii) the divalent oxidation state of metal ions is more stable compared to the trivalent state in these complexes. Toftlund and his co-workers have synthesized various types of branched and cyclic



tpmc taec

Fig. 1. The octaamine ligands and their abbreviations.



(A) (B)

Fig. 2. Coordination modes of taec.

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*Present address: Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Fukuoka 812, Japan.

**Present address: Department of Chemistry, University of Odense, Campusvej 55, Odense M, DK 5230, Denmark.

†Author to whom correspondence should be addressed.

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2-pyridylmethylamine derivatives forming both mononuclear and polynuclear complexes which are of interest for their potential multiredox and catalytic features [4]. Thus, in this study, as an extension of the above studies, we have prepared 1,4,8,11-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (abbreviated as tpmc hereafter, Fig. 1) and its copper(II) complexes. In the course of this study the preparation and X-ray structural characterization of $[Cu_2Br_2(tpmc)](ClO_4)_2$ were reported by Alcock *et al.* [5]. The structure is of type (A) (Fig. 2) but with five-membered chelate rings around each copper rather than six-membered rings as shown. We report here the preparation and characterization of eight copper(II) complexes of tpmc all of which differ from Alcock's compound.

Experimental

Preparation of Compound

1,4,8,11-Tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (tpmc)

This compound was prepared using the method of Alcock *et al.* [5]. The crude product was recrystallized from a 1:5 mixture of ethanol and acetonitrile. *Anal.* Calc. for $C_{34}H_{44}N_8$: C, 72.30; H, 7.85; N, 19.85. Found: C, 72.11; H, 7.89; N, 19.48%.

$Cu_2(tpmc)(ClO_4)_4$ *(1)*

The ligand (tpmc) (0.59 g, 1 mmol) was suspended in acetonitrile (10 ml) at 60 °C. To this solution was added an aqueous solution (10 ml) of copper(II) perchlorate hexahydrate (0.74 g, 2 mmol). The temperature was kept at 60 °C for 20 min. Within two days at room temperature most of the acetonitrile was evaporated, and from the blue solution blue–violet crystals of the product were crystallized. Yield 0.60 g (55%). *Anal.* Calc. for $Cu_2C_{34}H_{44}N_8Cl_4O_{16}$: C, 37.48; H, 4.07; N, 10.28; Cu, 11.66. Found: C, 38.00; H, 4.27; N, 10.25; Cu, 11.40%.

$[Cu_2OH(tpmc)](ClO_4)_3 \cdot 2H_2O$ *(2)*

To a 1:1 mixture of acetonitrile and water (10 ml) containing 0.40 g (0.37 mmol) of **1** an aqueous sodium hydroxide solution (0.4 ml, 1 M) was added. Acetonitrile was evaporated in a rotary evaporator. The blue solution thus formed yielded green crystals. Yield 0.30 g (78.4%). *Anal.* Calc. for $Cu_2C_{34}H_{49}N_8Cl_3O_{15}$: C, 39.14; H, 4.74; N, 10.74; Cu, 12.18. Found: C, 39.14; H, 4.71; N, 10.94; Cu, 12.45%.

$[Cu_2F(tpmc)](BF_4)_3 \cdot H_2O$ *(3)*

Procedure 1. To a warm methanol solution (30 ml) of copper(II) tetrafluoroborate hexahydrate (0.35 g, 1 mmol) tpmc (0.28 g, 0.5 mmol) was added with stirring. The mixture was kept at about 50 °C with stirring until a blue product precipitated. After cooling to room temperature the product was filtered, washed with methanol, dissolved in a small amount of warm water, and reprecipitated by addition of methanol. The blue prismatic crystals were desiccated *in vacuo* over P_2O_5. Yield 0.098 g (20%). *Anal.* Calc. for $Cu_2C_{34}H_{46}N_8B_3F_{13}O$: C, 41.28; H, 4.69; N, 11.33; Cu, 12.54. Found: C, 41.57; H, 4.56; N, 11.57; Cu, 12.85%.

Procedure 2. The synthetic procedure was the same as that for **4** except for using $Cu(BF_4)_2 \cdot 6H_2O$ instead of copper(II) perchlorate. Yield 70%.

$[Cu_2F(tpmc)](ClO_4)_3$ *(4)*

To a suspension of the ligand (0.14 g, 0.25 mmol) in acetonitrile (5 ml) was added an aqueous solution (5 ml) containing copper(II) perchlorate hexahydrate (0.18 g, 0.5 mmol). To this mixture was added an aqueous sodium fluoride (0.011 g, 0.25 mmol) solution (2.5 ml). The solution was heated at 70 °C for 2 h, and then allowed to stand at room temperature for one day. The blue needles separated were collected by filtration, and desiccated over P_2O_5. Yield 0.17 g (67%). *Anal.* Calc. for $C_{34}H_{44}N_8O_{12}Cl_3FCu_2$: C, 40.40; H, 4.40; N, 11.10; Cu, 12.59. Found: C, 40.16; H, 4.42; N, 10.98; Cu, 12.19%.

$[Cu_2NO_3(tpmc)](PF_6)_3$ *(5)*

To a methanol solution (30 ml) of copper(II) nitrate trihydrate (0.25 g, 1 mmol), tpmc (0.28 g, 0.5 mmol) was added with stirring. A blue precipitate was immediately formed; when the mixture was stirred with heating, the precipitate was gradually dissolved to form a blue solution. To this solution was added a large excess of ammonium hexafluorophosphate. The mixture was refluxed for 30 min and allowed to stand at room temperature. The blue precipitate was filtered, washed with ethanol, and dried over P_2O_5 under vacuum. Yield 0.53 g (88%). *Anal.* Calc. for $Cu_2C_{34}H_{44}N_9P_3F_{18}O_3$: C, 34.35; H, 3.73; N, 10.60; Cu, 10.69. Found: C, 34.65; H, 3.83; N, 10.97; Cu, 10.96%.

$[Cu_2CH_3COO(tpmc)](ClO_4)_3$ *(6)*

An aqueous solution (10 ml) containing copper(II) perchlorate hexahydrate (0.18 g, 0.5 mmol) and copper(II) acetate monohydrate (0.10 g, 0.5 mmol) was added with stirring to tpmc (0.28 g, 0.5 mmol) suspended in a 1:1 mixture of water and acetonitrile. Acetonitrile was removed by N_2 bubbling at 60 °C, and an aqueous sodium perchlorate solution (0.5 ml, 6 M) was added. A blue crystalline product precipitated on cooling to room temperature. Yield 0.50 g (95%). *Anal.* Calc. for $Cu_2C_{36}H_{47}N_8Cl_3O_{14}$: C, 41.21; H, 4.52; N, 10.68; Cu, 12.11. Found: C, 41.15; H, 4.67; N, 11.13; Cu, 11.80%.

$Cu_3(tpmc)Br_6$ (7)

To a warm methanol solution (30 ml) of anhydrous copper(II) bromide (0.34 g, 1.5 mmol), tpmc (0.28 g, 0.5 mmol) was added with stirring. When the mixture was refluxed for 1 h with stirring, a dark blue precipitate appeared. The mixture was cooled to room temperature, and the precipitate was filtered, washed with methanol, and dried over P_2O_5 *in vacuo*. Yield 0.48 g (78%). *Anal.* Calc. for $Cu_3C_{34}H_{44}N_8Br_6$: C, 33.07; H, 3.59; N, 9.07; Cu, 15.44. Found: C, 32.82; H, 3.50; N, 9.07; Cu, 15.38%.

$[Cu(tpmc)](ClO_4)_2 \cdot 2H_2O$ (8)

To a suspension of tpmc (0.59 g, 1 mmol) in acetonitrile (10 ml), and aqueous solution (10 ml) of copper(II) perchlorate hexahydrate (0.37 g, 1 mmol) was added. From the blue–green solution green crystals were separated upon cooling. Yield 0.50 g (59%). *Anal.* Calc. for $CuC_{34}H_{50}N_8Cl_2O_{11}$: C, 47.31; H, 5.60; N, 12.98; Cu, 7.42. Found: C, 47.66; H, 5.76; N, 12.80; Cu, 7.42%.

The elemental analyses for C, H, and N were carried out in the Chemical Materials Center of Institute for Molecular Science. The contents of copper were determined by EDTA titrations after decomposing the samples in hot concentrated perchloric acid.

Measurements

Infrared spectra were measured by a Hitachi 270-30 infrared spectrophotometer. UV and Vis spectra were measured by a Shimazu Multipurpose Spectrophotometer MPS-2000. Magnetic susceptibilities were determined by the Faraday method, calibration being made by use of $[Ni(en)_3]S_2O_3$, and Pascal's constants being used for diamagnetic correction. In the case where measurements were made down to liquid helium temperatures an automated Faraday balance using a superconducting magnet was employed (Monash University).

X-ray Structure Determination

The unit cell parameters and intensities for compounds 2 and 5 were measured on a Rigaku AFC-5R automated four-circle diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Crystal data are summarized in Table 1. The intensity data were collected by the θ–2θ and ω scan techniques for 2 and 5, respectively, with a scan rate of 4 min^{-1}. Three standard reflections were monitored every 100 reflections, and their intensities showed a good stability.

A total of N (cf. Table 1) reflections with $2\theta < 60$ (in the case of 2) and <50 (in the case of 5) were collected. The intensity data were collected for Lorentz–polarization effects and for absorption.

TABLE 1. Crystal data and data collection details[a]

	$[Cu_2OH(tpmc)](ClO_4)_3 \cdot 2H_2O$	$[Cu_2NO_3(tpmc)](PF_6)_3$
Formula	$Cu_2Cl_3O_{15}N_8C_{34}H_{49}$	$Cu_2P_3F_{18}O_3N_9C_{34}H_{44}$
Formula weight	1043.26	1188.77
Crystal system	monoclinic	monoclinic
Space group	*Cm*	$P2_1/n$
a (Å)	11.048(1)	18.685(4)
b (Å)	22.318(3)	25.563(5)
c (Å)	9.459(1)	9.393(1)
β (°)	111.95(1)	92.59(2)
V (Å^3)	2163.2(5)	4482(2)
Z	2	4
D_c (g cm^{-3})	1.60	1.76
Crystal size (nm)	0.34 × 0.41 × 0.52	0.35 × 0.25 × 0.08
μ(Mo Kα) (cm^{-1})	12.5	11.8
Scan mode	θ–2θ	ω
2θ range (°)	1.0–60	1.5–50.0
Total no. observed reflections	6609	6757
No. unique data with $\lvert F_o \rvert > 3\sigma(\lvert F_o \rvert)$	3104	3191
No. variables	326	611
R (%)	4.1	8.3
R_w (%)	5.2	11.0
Largest peak on D-Fourier (e A^{-3})	0.59	0.97

[a] Common data: graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ A), scan speed 4° min^{-1}, weighting scheme $w = [\sigma^2_{count} + (0.015\lvert F_o \rvert)^2]^{-1}$, scan width $(1.2 + 0.5 \tan\theta)°$.

Independent N_o (cf. Table 1) reflections with $|F_o| > 3\sigma(|F_o|)$ were considered as 'observed' and were used for the structure analysis. The structures were solved by the heavy-atom method for 2 and by the direct method for 5. Refinements were carried out by the block-diagonal least-squares method. The weighting scheme $w = [\sigma_{count}^2 + (0.015|F_o|)^2]^{-1}$ was employed. Hydrogen atoms were not included in the calculation. The final discrepancy factors $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ are listed in Table 1. All the calculations were carried out on the Hitachi M-680H computer at the Computer Center of the Institute for Molecular Science by the use of the UNICS-III [6], MULTAN 78 [7] and ORTEP [8] programs.

Atomic coordinates of 2 and 5 are summarized in Table 2.

Description of Structures

Complex 2

The crystal consists of dinuclear cations $[Cu_2OH(tpmc)]^{3+}$, ClO_4^- and H_2O. A perspective view of the complex cation is shown in Fig. 3. It has a mirror plane containing O1, C1 and C6 as required from the crystallographic symmetry. The two copper atoms are bridged by the hydroxide ion. The coordination mode of tpmc is similar to those of taec in $[Cu_2X(taec)](ClO_4)_3$ (X = F, Cl, Br, I, NO_2, NCO, N_3) [3], i.e. the two coordination units are linked by two $(CH_2)_3$ chains, but the Cu–Cu′ distance (3.712(1) Å) is significantly shorter than those of 5 and the taec complexes. The coordination geometry about the copper atoms may be regarded as a distorted trigonal bipyramid with N1, N4, and O1 atoms in the equatorial plane and N3 and N2 atoms in the apical positions. The pyridine nitrogen (N3) in the axial position is 0.132 Å closer to the copper than the corresponding equatorial atom. The copper atoms deviate from the equatorial plane toward the N2 atom by 0.02 Å. The water molecules are hydrogen bonded to the perchlorate ions, e.g. O9- - -O4 = 2.971(6), O10- - -O7($x, y, 1+z$) = 2.918(21) Å. Interatomic distances and angles are listed in Table 3.

Complex 5

The crystal consists of dinuclear complex cation $[Cu_2NO_3(tpmc)]^{3+}$ and PF_6^-. A perspective drawing of the complex cation is illustrated in Fig. 4. The two copper atoms are bridged by the nitrate ion. The coordination geometry of Cu1 is distorted square pyramid, where the basal plane is formed by two nitrogens of the cyclam ring, a pendant arm nitrogen and a nitrate oxygen; and the apical position is occupied by another nitrogen of pendant arm. The coordination geometry of Cu2 can also be described as a square pyramid, but the basal plane is formed by two cyclam ring nitrogens and two pendant

TABLE 2. Fractional positional parameters (×10⁴) and thermal parameters of non-hydrogen atoms with their e.s.d.s in parentheses

	x	y	z	B_{eq} (Å^2)
$[Cu_2OH(tpmc)](ClO_4)_3\cdot 2H_2O$				
Cu	0(1)	832(1)	0(1)	2.7
Cl1	4060(1)	1795(1)	−3237(1)	3.9
Cl2	−2413(2)	0	−6941(2)	5.1
O1	−42(4)	0	802(4)	2.8
O2	4567(5)	2114(2)	−1835(5)	6.4
O3	2823(5)	2019(3)	−4148(6)	9.0
O4	3998(6)	1191(2)	−2802(7)	7.3
O5	4935(5)	1831(2)	−3999(6)	6.8
O6	−2918(10)	0	−5876(10)	19.6
O7	−3313(11)	0	−8442(8)	10.5
O8[a]	−2273(20)	578(7)	−6428(22)	13.6
O8′[a]	−1330(15)	313(7)	−6864(16)	11.8
O9	3321(12)	0	−4293(10)	9.5
O10	4056(22)	0	−773(22)	21.2
N1	479(3)	1074(2)	−1872(4)	3.1
N2	−1915(3)	1025(1)	−1430(4)	2.8
N3	1917(3)	959(2)	1088(4)	3.3
N4	−481(3)	1467(2)	1388(4)	3.4
C1	225(6)	0	−2688(7)	3.3
C2	1042(5)	570(2)	−2489(5)	3.6
C3	−719(5)	1343(2)	−3065(5)	3.8
C4	−1655(4)	1536(2)	−2318(5)	3.4
C5	−2748(4)	568(2)	−2507(4)	3.0
C6	−2920(6)	0	−1715(7)	3.0
C7	1506(5)	1539(2)	−1203(6)	3.8
C8	2459(4)	1301(2)	293(5)	3.5
C9	3776(5)	1418(3)	866(7)	5.1
C10	4557(5)	1192(3)	2237(8)	5.8
C11	4001(5)	838(2)	3069(7)	4.9
C12	2666(5)	741(2)	2455(6)	4.0
C13	−2625(4)	1250(2)	−480(5)	3.5
C14	−1758(4)	1595(2)	878(5)	3.1
C15	−2281(5)	2005(2)	1598(6)	4.1
C16	−1450(6)	2277(3)	2936(7)	4.9
C17	−134(5)	2137(3)	3472(6)	4.6
C18	310(5)	1741(2)	2677(6)	4.2
$[Cu_2NO_3(tpmc)](PF_6)_3$				
Cu1	1789(1)	1519(1)	6310(2)	3.2
Cu2	2932(1)	217(1)	3805(2)	3.0
O1	2176(6)	982(5)	7814(12)	4.9
O2	2708(7)	720(5)	5966(11)	4.7
O3	2766(9)	257(6)	7932(15)	8.5
N1	1465(8)	1932(6)	4468(15)	4.4
N2	792(6)	1181(5)	6230(14)	3.3
N3	2033(7)	−241(5)	3664(14)	3.5
N4	2618(7)	465(6)	1804(13)	3.6
N5	2649(7)	1970(6)	6197(16)	4.4
N6	1327(7)	1991(6)	8042(15)	4.3
N7	3287(7)	−351(5)	5207(14)	3.9
N8	3735(6)	715(5)	3599(14)	3.2
N9	2568(7)	648(6)	7258(14)	4.0
C1	657(8)	1994(8)	4737(20)	4.4
C2	336(9)	1451(7)	5060(18)	3.8

(continued)

TABLE 2. *(continued)*

	x	y	z	B_{eq} (A^2)
C3	795(9)	577(6)	5997(18)	3.5
C4	1197(9)	435(7)	4664(17)	3.5
C5	1476(8)	−134(6)	4800(18)	3.4
C6	1708(9)	−206(7)	2156(17)	3.9
C7	2281(10)	−15(7)	1164(18)	4.3
C8	2116(9)	949(7)	1726(18)	4.0
C9	2267(9)	1370(7)	2883(17)	3.4
C10	1543(10)	1688(7)	3030(18)	4.5
C11	1861(10)	2455(7)	4619(22)	5.1
C12	2553(10)	2424(7)	5447(19)	4.8
C13	3019(11)	2844(9)	5486(24)	7.2
C14	3640(14)	2776(8)	6408(26)	8.3
C15	3780(10)	2335(10)	7129(23)	7.6
C16	3262(10)	1915(8)	7072(19)	5.0
C17	465(9)	1250(7)	7690(18)	3.8
C18	687(9)	1772(7)	8338(17)	3.5
C19	244(10)	2018(7)	9326(18)	4.2
C20	524(10)	2464(7)	10065(18)	4.2
C21	1196(9)	2671(7)	9742(19)	4.1
C22	1576(9)	2431(7)	8725(20)	4.4
C23	2325(9)	−780(6)	3945(20)	4.0
C24	2829(10)	−759(7)	5191(21)	5.0
C25	2862(11)	−1130(7)	6269(23)	5.9
C26	3386(13)	−1082(9)	7400(27)	7.8
C27	3871(12)	−684(9)	7327(20)	7.1
C28	3844(9)	−302(8)	6214(20)	5.2
C29	3313(9)	577(8)	1162(17)	4.1
C30	3811(9)	866(7)	2199(17)	4.0
C31	4298(9)	1266(7)	1834(20)	4.4
C32	4753(10)	1487(8)	2903(20)	5.4
C33	4689(9)	1328(7)	4298(22)	5.0
C34	4181(9)	948(7)	4643(20)	4.3
P1	3483(3)	2719(2)	1264(6)	4.1
P2	594(3)	−729(2)	8524(5)	4.1
P3	4337(4)	−1104(3)	1660(7)	7.9
F1	3557(7)	2411(5)	2722(11)	7.0
F2	3170(7)	2216(5)	512(13)	7.5
F3	3790(6)	3224(4)	2030(13)	7.2
F4	4251(6)	2549(5)	891(14)	7.5
F5	2699(6)	2900(5)	1672(14)	7.6
F6	3386(8)	3029(5)	−164(12)	8.4
F7[b]	457(8)	−540(6)	6888(17)	4.8
F7′[c]	139(14)	−388(11)	7433(28)	5.6
F8[b]	819(9)	−178(7)	9052(18)	5.1
F8′[c]	1252(15)	−319(12)	8566(31)	7.1
F9[b]	805(9)	−1005(7)	9982(19)	5.8
F9′[c]	1038(18)	−966(14)	7179(37)	8.9
F10[b]	388(10)	−1305(8)	7898(21)	7.0
F10′[c]	77(13)	−1216(10)	8325(27)	5.3
F11[b]	−191(11)	−621(8)	8905(22)	7.7
F11′[c]	412(17)	−622(14)	10080(35)	8.6
F12[b]	1379(11)	−842(9)	8052(23)	8.3
F12′[c]	1259(17)	−1070(13)	9324(35)	8.5
F13[b]	4523(14)	−654(11)	2947(29)	12.0
F13′[c]	4264(19)	−639(15)	683(39)	10.3
F14[b]	4071(18)	−1082(14)	3152(38)	16.2
F14′[c]	3853(23)	−632(18)	2035(45)	12.4
F15[b]	4076(15)	−1466(11)	2792(30)	12.0
F15′[c]	4346(19)	−1744(15)	2195(39)	10.0
F16[b]	4372(9)	−1447(7)	312(19)	5.9
F16′[c]	4655(17)	−705(13)	565(34)	7.9
F17[b]	3473(13)	−1251(10)	1196(26)	10.0
F17′[c]	3634(21)	−807(16)	1211(42)	11.1
F18[b]	5161(11)	−1120(9)	2015(22)	7.8
F18′[c]	4894(31)	−1330(25)	2043(65)	19.7

[a], [b] and [c] denote atoms with occupancy factors with 0.5, 0.6, and 0.4, respectively.

(continued)

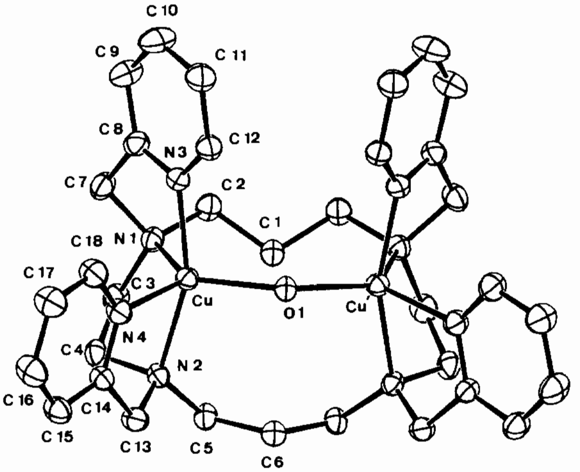

Fig. 3. Structure and numbering system for [Cu$_2$OH(tpmc)]$^{3+}$.

pyridyl nitrogens, and the apical position is occupied by another oxygen of the nitrate ion, the O–Cu bond being much tilted toward the two pendant groups coordinated to Cu2 (O2–Cu2–N4 = 123.0(5)°). The deviations of the basal atoms from the mean planes are within ±0.24 Å for the N1 N2 O1 N5 and N3 N4 N7 N8 planes. The Cu1 and Cu2 atoms are displaced by 0.08 and 0.24 Å, respectively, from the mean planes toward the apices. The coordination mode of tpmc in this complex is similar to that of taec in [Cu$_2$CH$_3$COO(taec)](ClO$_4$)$_3$·2H$_2$O [3d], where the Cu–Cu distance (4.758 Å) is comparable to that of the present tpmc complex (4.651 Å).

Results and Discussion

All the copper(II) tpmc complexes obtained here are dinuclear except for 8. However, the formation of a 1:1 tpmc copper complex is notable, because in the case of taec all complexes so far obtained were dinuclear and all attempts to prepare mononuclear taec metal complexes were unsuccessful. The UV–Vis

TABLE 3. Selected interatomic distances and angles with their e.s.d.s in parentheses

$[Cu_2OH(tpmc)](ClO_4)_3 \cdot 2H_2O$

Distances (Å)

Cu–Cu′	3.712(1)	Cu–O1	2.012(4)
Cu–N1	2.100(4)	Cu–N2	2.086(3)
Cu–N3	1.999(4)	Cu–N4	2.131(4)
C1–C2	1.530(6)	N1–C2	1.506(7)
N1–C3	1.506(5)	C3–C4	1.518(8)
N2–C4	1.506(6)	N2–C5	1.491(5)
C5–C6	1.521(6)	N1–C7	1.492(6)
C7–C8	1.511(6)	C8–C9	1.374(7)
C9–C10	1.358(8)	C10–C11	1.407(11)
C11–C12	1.386(7)	N3–C12	1.340(6)
N2–C13	1.484(7)	C13–C14	1.497(6)
C14–C15	1.389(8)	C15–C16	1.394(7)
C16–C17	1.384(8)	C17–C18	1.365(9)
N4–C18	1.352(6)		

Angles (°)

Cu–O1–Cu′	134.5(2)	O1–Cu–N1	127.2(2)
O1–Cu–N2	106.0(1)	O1–Cu–N3	96.1(2)
O1–Cu–N4	109.6(2)	N1–Cu–N2	85.1(1)
N1–Cu–N3	81.1(2)	N1–Cu–N4	123.2(2)
N2–Cu–N3	157.9(1)	N2–Cu–N4	80.5(1)
N3–Cu–N4	92.8(2)	N1–C2–C1	111.1(5)
C2–C1–C2′	112.5(5)	N1–C3–C4	109.0(4)
N2–C4–C3	110.5(4)	N2–C5–C6	113.1(3)
C5–C6–C5′	113.1(5)	N1–C7–C8	107.8(4)
C8–C9–C10	120.5(6)	C9–C10–C11	119.2(5)
C10–C11–C12	118.2(5)	N3–C12–C11	121.6(6)
C8–N3–C12	119.9(4)	N3–C8–C9	120.6(4)
N2–C13–C14	112.3(4)	C14–C15–C16	118.6(5)
C15–C16–C17	118.7(6)	C16–C17–C18	119.2(5)
N4–C18–C17	123.1(5)	C14–N4–C18	117.8(4)
N4–C14–C15	122.6(4)		

$[Cu_2NO_3(tpmc)](PF_6)_3$

Distances (Å)

Cu1–O1	2.007(12)	Cu1–N1	2.093(14)
Cu1–N2	2.052(13)	Cu1–N5	1.985(14)
Cu1–N6	2.231(15)	Cu2–O2	2.456(11)
Cu2–N3	2.046(13)	Cu2–N4	2.045(13)
Cu2–N7	2.049(14)	Cu2–N8	1.983(13)
C1–C2	1.548(26)	C2–N2	1.525(21)
N2–C3	1.559(21)	C3–C4	1.532(24)
C4–C5	1.548(24)	N3–C5	1.549(21)
N3–C6	1.518(20)	C6–C7	1.531(25)
N4–C7	1.494(23)	N4–C8	1.551(23)
C8–C9	1.546(24)	C9–C10	1.589(25)
N1–C10	1.501(22)	N1–C11	1.530(23)
C11–C12	1.481(26)	C12–C13	1.381(29)
C13–C14	1.426(32)	C14–C15	1.337(32)
C15–C16	1.444(30)	N5–C16	1.386(22)
N5–C12	1.367(24)	N2–C17	1.536(21)
C17–C18	1.517(24)	C18–C19	1.418(25)
C19–C20	1.423(25)	C20–C21	1.408(25)
C21–C22	1.363(26)	N6–C22	1.367(23)
N6–C18	1.360(21)	N3–C23	1.501(21)
C23–C24	1.469(26)	C24–C25	1.387(28)
C25–C26	1.418(32)	C26–C27	1.365(33)
C27–C28	1.428(29)	N7–C28	1.381(22)
N7–C24	1.350(23)	N4–C29	1.485(22)
C29–C30	1.509(24)	C30–C31	1.422(25)
C31–C32	1.404(26)	C32–C33	1.383(28)
C33–C34	1.405(26)	N8–C34	1.393(22)
N8–C30	1.383(21)	O1–N9	1.253(19)
O2–N9	1.267(18)	O3–N9	1.232(20)

Angles (°)

O1–Cu1–N1	89.8(5)	N1–Cu1–N6	102.9(6)
N2–Cu1–N6	82.8(5)	N5–Cu1–N6	93.8(6)
N1–Cu1–N2	87.4(5)	N1–Cu1–N5	82.3(6)
O1–Cu1–N2	92.0(5)	O1–Cu1–N5	99.3(5)
O2–Cu2–N3	100.6(5)	O2–Cu2–N4	123.0(5)
O2–Cu2–N7	84.4(5)	O2–Cu2–N8	84.4(5)
N3–Cu2–N4	85.3(5)	N3–Cu2–N7	83.0(5)
N7–Cu2–N8	107.1(5)	N4–Cu2–N8	84.1(5)
N1–C1–C2	109.3(14)	N2–C2–C1	109.8(13)
C2–C3–C4	110.8(13)	C3–C4–C5	109.4(14)
N3–C5–C4	110.0(13)	N3–C6–C7	108.9(13)
N4–C7–C6	108.1(13)	N4–C8–C9	115.6(13)
C8–C9–C10	106.8(13)	N1–C10–C9	114.0(13)
N1–C11–C12	114.2(15)	C12–C13–C14	114.7(19)
C13–C14–C15	123.1(21)	C14–C15–C16	119.5(19)
N5–C16–C15	118.9(17)	C12–N5–C16	118.5(15)
N5–C12–C13	125.4(17)	N2–C17–C18	110.3(13)
C18–C19–C20	117.6(16)	C19–C20–C21	120.6(16)
C20–C21–C22	118.7(16)	N6–C22–C21	121.4(16)
C18–N6–C22	121.9(15)	N6–C18–C19	119.7(16)
N3–C23–C24	108.8(14)	C24–C25–C26	119.6(19)
C25–C26–C27	117.7(21)	C26–C27–C28	123.0(19)
N7–C28–C27	116.1(17)	C24–N7–C28	122.3(15)
N7–C24–C25	121.0(17)	N4–C29–C30	110.9(13)
C30–C31–C32	119.4(17)	C31–C32–C33	118.9(18)
C32–C33–C34	120.7(18)	N8–C34–C33	121.5(17)
C30–N8–C34	117.8(14)	N8–C30–C31	121.6(15)
O1–N9–O2	116.7(13)	O1–N9–O3	120.4(14)
O2–N9–O3	122.8(14)		

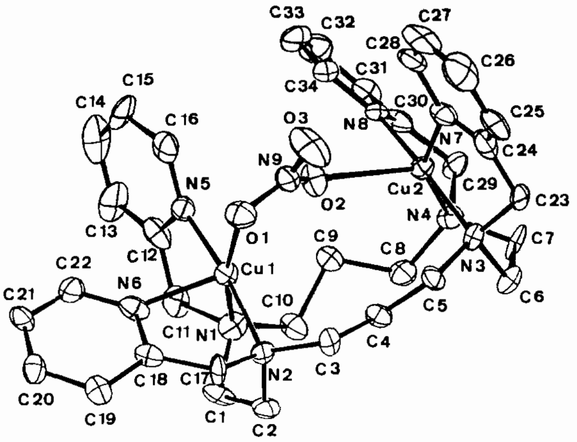

Fig. 4. Structure and numbering system for $[Cu_2NO_3(tpmc)]^{3+}$.

TABLE 4. Electronic spectral data and effective magnetic moments

Complex	λ_{max} (nm) (ϵ (dm^3 mol^{-1} cm^{-1}))	μ_B/copper (T (K))
$Cu_2(tpmc)(ClO_4)_4$	594^a, 670(316)^b, 680(340)^c	1.90(299.1), 1.86(87.2)
$[Cu_2OH(tpmc)](ClO_4)_3 \cdot 2H_2O$	868^a, 693(228)^b, 830(294)^c	1.73(297.8), 1.35(87.5)
$[Cu_2F(tpmc)](BF_4)_3 \cdot H_2O$	690^a, 677(295)^b, 690(404)^c	1.85(297.8), 1.82(87.2)
$[Cu_2F(tpmc)](ClO_4)_3$	680^a, 678(283)^b	1.84(289.7), 1.82(93.0)
$[Cu_2NO_3(tpmc)](PF_6)_3$	612^a, 627(320)^c	1.83(295.0), 1.85(87.2)
$[Cu_2CH_3COO(tpmc)](ClO_4)_3$	653^a, 651(293)^b, 655(301)^c	1.81(296.2), 1.80(87.2)
$Cu_3(tpmc)Br_6$	410^a, 520-620^a, 707(387)^b	1.80(296.6), 1.76(90.2)
$Cu(tpmc)(ClO_4)_2 \cdot 2H_2O$	614^a, 660(334)^c	1.87(297.8), 1.76(87.2)

[a]Reflectance spectra. [b]H_2O solution. [c]CH_3CN solution.

spectral features summarized in Table 4 suggest that the copper atom of **8** is coordinated in an unsymmetrical fashion, where the metal is outside the macrocyclic ring. In the case of 1,4,8,11-tetrakis-(carboxymethyl)-1,4,8,11-tetraazacyclotetradecane, the 1:1 complex was isolated, and it was shown that the copper ion resides in the center of the macrocyclic ring [9]. Very recently a 1:1 ruthenium(II) complex with tpmc has been reported [10]. In this case the ligand functions as a sexidentate ligand with three aliphatic and three pyridine nitrogen donors in an octahedral geometry. We suggest that complex **8** has a similar structure.

Since the IR spectra of the tetraperchlorate complex **1** and the triperchlorate complexes **2**–**7** are substantially different in the absorptions due to tpmc, the coordination mode and conformation of the ligand of **1** should be different from those of **2**–**7** as already demonstrated in tetraperchlorate and triperchlorate complexes of taec [3].

When tpmc was reacted with $Cu(BF_4)_2 \cdot 6H_2O$ in a 1:2 ratio in warm methanol, blue crystals were obtained. The elemental analyses of C, H, N and Cu are compatible with the values either for $[Cu_2OH(tpmc)](BF_4)_3 \cdot H_2O$ or $[Cu_2F(tpmc)](BF_4)_3 \cdot H_2O$. However, the compound is more likely to be the fluoro complex rather than the hydroxo one, since the visible and IR spectra of this compound coincide with those of $[Cu_2F(tpmc)](ClO_4)_3$ (**4**) except for absorptions due to counterions in the IR region. Furthermore, as described in 'Experimental' of synthetic procedure 2 for **3**, the same product was obtained by the reaction of copper(II) tetrafluoroborate, tpmc and sodium fluoride with a much better yield. In fact, Reedijk and Hoedt have shown that BF_4^- can release F^- in the presence of azole ligands [11].

In view of the close resemblance in coordination structure between the nitrato complex **5** and the taec analogue $[Cu_2CH_3COO(taec)](ClO_4)_3 \cdot 2H_2O$ [3d], the structure of the acetato complex **6** is very likely to be similar to those of **5** and the taec analogue. This view is supported by the fact that the IR spectrum of **6** shows bands at 1408 and 1563 cm^{-1} which are assignable to ν_s and ν_a of COO^-, and correspond to the 1405 and 1560 cm^{-1} bands observed for the taec analogue.

Considered from the structure of the ligand, **7** is not likely to be a trinuclear complex in spite of the metal/ligand ratio of 3:1. The most probable structure of **7** is described as $[Cu_2Br_2(tpmc)][CuBr_4]$ in analogy with the X-ray characterized complex $[Cu_2Br_2(tpmc)](ClO_4)_2$ reported by Alcock *et al.* [5]. This view is supported by the fact that the powder reflectance spectrum of **7** in the visible region shows strong broad absorptions at about 550 and 620 nm which are similar to those of $[N(C_2H_5)_4]_2[CuBr_4]$.

Table 4 summarizes the absorption peaks in the visible region and the magnetic moments at room temperature and near liquid nitrogen temperature. A considerably large red shift is observed for **1** and **8** when the solid sample is dissolved in water. This suggests that weakly coordinated perchlorate ions are displaced by water molecules in these complexes. In contrast to those, the fluoro, nitrato and acetato complexes undergo a small red shift, suggesting that little aquation takes place with the Cu–anion linkage.

All magnetic moments, except for **2**, are normal at both room and low temperatures, indicating little or no spin coupling between copper ions. This result could be expected for the nitrato complex **5**, since the bridging nitrate ion coordinates to one of the coppers at the apical site of the square pyramid while to the other at the basal site. Considered from the above result the fluoro complexes **3** and **4** are very likely to assume a structure similar to halogeno taec complexes [3b, d] in which a halide ion links the two copper ions at the apical sites of square pyramids.

The temperature dependence of magnetic susceptibility was determined for **2**. As shown in Fig. 5, the experimental data display a maximum at 80 K indicative of medium sized antiferromagnetic coupling between the two coppers. These data can be fitted to the Bleaney–Bowers equation [12] for a spin Hamiltonian $\mathcal{H} = -2JS_1S_2$ ($S_1 = S_2 = 1/2$)

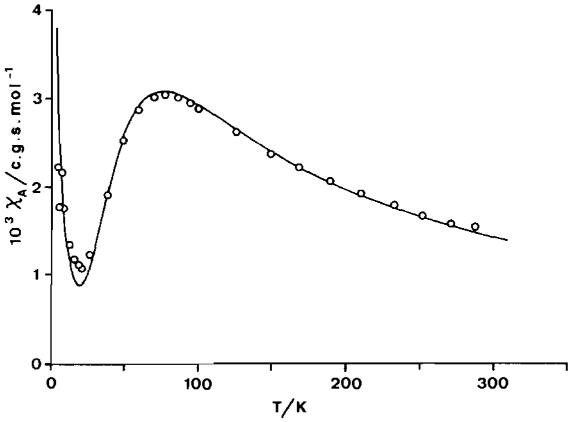

Fig. 5. Magnetic susceptibilities vs. temperature for [Cu_2OH-(tpmc)]$(ClO_4)_3 \cdot 2H_2O$. The solid line was calculated from the Bleaney–Bowers equation with $2J = -86$ cm^{-1}, $g = 2.23$ and $N\alpha = 60 \times 10^{-6}$ cgs emu.

using the parameters, $J = -43$ cm^{-1}, $g = 2.23$, and $N\alpha = 60 \times 10^{-6}$ cgs emu. The sharp rise in χ_{Cu} at low temperatures is due to the presence of 3.5% of the ubiquitous monomer impurity. The size of J is generally compatible with the molecular structure (Fig. 3), where the bridging hydroxo oxygen atom occupies an equatorial position around each copper. Strictly, in a perfect trigonal bipyramidal structure, each copper(II) would have a d_{z^2} ground configuration and hence negligible magnetic coupling. However, distortion from a trigonal bipyramid will lead to mixing of the xy component into the magnetic orbital and therefore lead to a weak antiferromagnetic coupling operative via the bridging OH group. There are a few other singly bridged μ-hydroxo copper(II) macrocycles known to compare with 2 [13]. These examples have different Cu–Cu separations, Cu–O–Cu angles and coordination geometries compared with those of 2, and generally, except for one example [14], display stronger antiferromagnetic coupling.

Supplementary Material

Tables of structure factors and anisotropic parameters are available from author S.K.

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