Inorganica Chimica Acta, 171 (1990) 45–52

Synthesis and Characterization of Novel Binuclear Copper(II) and Nickel(II) Complexes with *N,N′,N″,N‴*-Tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (tpmc) Containing Various Anions. X-ray Analyses of $[Cu_2F(tpmc)](ClO_4)_3{\cdot}2CH_3CN$ and $[Cu_2Cl(tpmc)](ClO_4)_3{\cdot}H_2O$

GORDANA VUČKOVIĆ*, EIJI ASATO, NAOHIDE MATSUMOTO and SIGEO KIDA**

Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashi-ku, Fukuoka 812 (Japan)

(Received September 4, 1989)

Abstract

Seven copper(II) and three nickel(II) complexes with *N,N′,N″,N‴*-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane(tpmc), $[Cu_2X(tpmc)](ClO_4)_3$ (X = Cl, Br, I, N_3, NO_2), $[Cu_2Y_2(tpmc)](ClO_4)_2$ (Y = NCS, N_3), $[Ni_2(tpmc)](ClO_4)_4$ (orange and blue forms) and $[Ni_2Br_2(tpmc)](ClO_4)_2$ have been synthesized. The formation constants for the reaction

$$[Cu_2(tpmc)]^{4+} + X^- \rightleftharpoons [Cu_2X(tpmc)]^{3+}$$

$$X = F, Cl, Br, I, NO_2$$

were determined spectrophotometrically, and were revealed to be very high for the Cu–X binding in aqueous solution. X-ray analyses of $[Cu_2F(tpmc)](ClO_4)_3{\cdot}2CH_3CN$ and $[Cu_2Cl(tpmc)](ClO_4)_3{\cdot}H_2O$ showed halogeno bridged dinuclear structure. On the basis of the electronic spectra, IR spectra, stability constants and magnetic moments it is assumed that bromo, iodo, azido and nitrito complexes have similar structures to those of the fluoro and chloro complexes.

The orange form of $[Ni_2(tpmc)](ClO_4)_4$ was diamagnetic and its visible spectra was consistent with square-planar coordination. The blue form was paramagnetic (μ = 2.96 BM/Ni), hence the nickel ions are five coordinated.

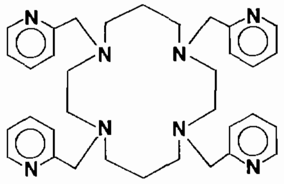
Introduction

Metal complexes with macrocyclic ligands are of great interest, because they have specific stabilization and redox properties [1].

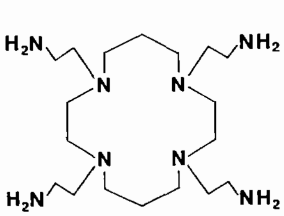
Many papers have been reported on the preparation and characterization of metal complexes with tetraazamacrocycles containing pendant arms on the ring nitrogen atoms [2]. These ligands formed generally 1:1 metal–ligand complexes [3], except for taec (*N,N′,N″,N‴*-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane) [4] and tpmc complexes [5, 6].

Kida *et al.* have reported the synthesis of numerous copper(II), nickel(II), cobalt(II) and chromium(II) complexes with an octaamine ligand, taec, which possesses four aminoethyl groups on the cyclam nitrogen atoms [2, 4] (Fig. 1). They showed interesting structural and chemical properties, i.e. invariable formation of dinuclear complex, strong affinity towards various anions to form anion-bridged complexes and unusual stabilization of divalent state of cobalt and chromium against oxidation to trivalent state.

An analogous octadentate ligand with 2-pyridylmethyl groups as pendant arms, tpmc (Fig. 1) also formed a similar type of complex. Alcock *et al.* [6] reported the synthesis of the ligand and the structure of $[Cu_2Br_2(tpmc)](ClO_4)_2$, in which each copper ion



tpmc



taec

Fig. 1. The octaamine ligands and their abbreviations.

---

*Present address: Institute of Chemistry, Faculty of Science, University of Beograd, P.O. Box 550, 11001 Beograd, Yugoslavia.

**Author to whom correspondence should be addressed.

0020-1693/90/$3.50

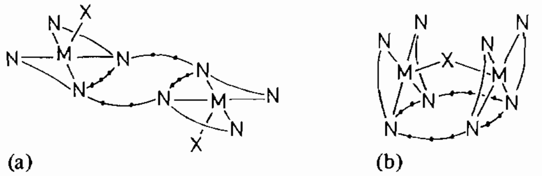


Fig. 2. Coordination modes of taec.

has a configuration inbetween square pyramid and trigonal bipyramid, with a bromide ion at the apex. A mononuclear ruthenium(II) complex with protonated tpmc was reported by Che *et al.* [7]. Kida *et al.* prepared and characterized a number of copper(II) and copper(I) complexes with tpmc [5]. With only one exception all were dinuclear. A series of complexes of general formula $[Cu_2Z(tpmc)]^{3+}$, where Z = F, OH, CH_3COO and NO_3, were shown to be of anion-bridged structure. For $[Cu_2(tpmc)]^{4+}$ the chair coordination mode of the ligand (Fig. 2(a) was assumed and for all other complexes the boat coordination mode (Fig. 2(b) similar to taec analogues.

Continuing these investigations, the preparation and properties of new seven copper(II) and three nickel(II) complexes with tpmc are reported here and compared with some previously reported tpmc and taec analogues.

Experimental

Preparations

The ligand, $[Cu_2(tpmc)](ClO_4)_4$, and $[Cu_2F(tpmc)](ClO_4)_3$ were obtained according to procedures described in the literature [6, 5].

$[Cu_2Cl(tpmc)](ClO_4)_3 \cdot H_2O$

To a solution of $[Cu_2(tpmc)](ClO_4)_4$ (545 mg, 0.5 mmol) in water (10 cm^3), sodium chloride (36 mg, 0.5 mmol) was added with stirring. When the mixture was refluxed it gradually turned into a transparent blue solution. The hot solution was filtered and left at room temperature for a few days. Blue needles which separated were collected, washed with methanol and dried in air. Yield 427 mg (82%).

$[Cu_2Br(tpmc)](ClO_4)_3$

Copper(II) perchlorate hexahydrate (92 mg, 0.25 mmol) was dissolved in the minimum amount of water and mixed with an acetonitrile solution (5 cm^3) of tpmc (71 mg, 0.125 mmol) and an aqueous solution (1.3 cm^3, 0.1 mol dm^{-3}) of sodium bromide. The mixture was stirred and heated at 70 °C on a water bath for 1 h to obtain a blue solution, from which blue microcrystals were separated on cooling at room temperature. The product was recrystallized from hot acetonitrile, washed with ether and dried over P_2O_5. Yield 98 mg (74%).

$[Cu_2N_3(tpmc)](ClO_4)_3$ and $[Cu_2(NO_2)(tpmc)](ClO_4)_3$

These complexes were obtained by a similar procedure to that for the bromo analogue. The azido complex crystallized in the form of light blue–green needles. Yield 81 mg (63%). The nitrito complex was obtained as indigo blue prismatic crystals. Yield 90 mg (69%).

$[Cu_2I(tpmc)](ClO_4)_3 \cdot H_2O$

An aqueous solution of sodium iodide (1.3 cm^3, 0.1 mol dm^{-3}) was mixed with $[Cu_2(tpmc)](ClO_4)_4$ (136 mg, 0.125 mmol) dissolved in a water–acetonitrile (1:1) mixture. When the mixture was stirred at 60 °C it became green. Further procedure was similar to that for the bromo analogue. Green crystals were obtained. Yield 114 mg (84%).

$[Cu_2(NCS)_2(tpmc)](ClO_4)_2$

This compound was obtained in the same way as that of the iodo complex, except a solution of sodium thiocyanate (2.6 cm^3, 0.1 mol dm^{-3}) was used instead of sodium iodide. It should be noted that even with a 2:1:1 molar ratio of copper:tpmc: thiocyanate the same product was obtained. Green crystals were recrystallized from a water–acetonitrile (3:1) mixture. Yield 112 mg (89%).

$[Cu_2(N_3)_2(tpmc)](ClO_4)_2$

The preparative method for this complex was the same as that of the thiocyanato complex, except for adding a large excess of sodium azide instead of sodium thiocyanate. Emerald green crystals were obtained. Yield was almost quantitative.

$[Ni_2(tpmc)](ClO_4)_4 \cdot xH_2O$ (x = 3,1)

The trihydrate was obtained according to the procedure described above for the bromo copper(II) complex, but without adding sodium bromide. Starting materials were tpmc (340 mg, 0.6 mmol) in acetonitrile (5 cm^3) and nickel perchlorate hexahydrate (440 mg, 1.2 mmol) in a small amount of water. Blue crystals which separated were recrystallized from a water–methanol mixture and air dried. TG analysis showed the loss of three molecules of crystal water. When the trihydrate was kept in a desiccator over P_2O_5 for one week, it lost two molecules of water. Orange crystals were obtained corresponding to $[Ni_2(tpmc)](ClO_4)_4 \cdot H_2O$. Yield of the orange product 420 mg (84%).

$[Ni_2Br_2(tpmc)](ClO_4)_2$

$[Ni_2(tpmc)](ClO_4)_4 \cdot H_2O$ (439 mg, 0.4 mmol) in a small amount of water was mixed with an aqueous solution of sodium bromide (10 cm^3, 0.1 mol dm^{-3}),

TABLE 1. Chemical analysis of compounds

Complex[a]	Analysis: found (calc.) (%)			
	C	H	N	Metal
$[Cu_2Cl(tpmc)](ClO_4)_3 \cdot H_2O$	39.47	4.37	10.74	12.14
$C_{34}H_{46}N_8O_{13}Cl_4Cu_2$	(39.13)	(4.44)	(10.74)	(12.18)
$[Cu_2Br(tpmc)](ClO_4)_3$	38.05	4.16	10.57	11.82
$C_{34}H_{44}N_8O_{12}BrCl_3Cu_2$	(38.16)	(4.14)	(10.47)	(11.88)
$[Cu_2I(tpmc)](ClO_4)_3 \cdot H_2O$	36.08	4.04	10.12	11.21
$C_{34}H_{46}N_8O_{13}ICl_3Cu_2$	(35.97)	(4.08)	(9.87)	(11.20)
$[Cu_2N_3(tpmc)](ClO_4)_3$	39.25	4.29	14.76	11.93
$C_{34}H_{44}N_{11}O_{12}Cl_3Cu_2$	(39.56)	(4.30)	(14.93)	(12.31)
$[Cu_2(NO_2)(tpmc)](ClO_4)_3$	39.32	4.29	12.23	12.08
$C_{34}H_{44}N_9O_{14}Cl_3Cu_2$	(39.41)	(4.28)	(12.16)	(12.26)
$[Cu_2(NCS)_2(tpmc)](ClO_4)_2$	42.48	4.39	13.98	12.36
$C_{36}H_{44}N_{10}O_8S_2Cl_2Cu_2$	(42.94)	(4.40)	(13.91)	(12.62)
$[Cu_2(N_3)_2(tpmc)](ClO_4)_2$	41.91	4.52	19.96	13.07
$C_{34}H_{44}N_{14}O_8Cl_2Cu_2$	(41.89)	(4.55)	(20.12)	(13.04)
$[Ni_2(tpmc)](ClO_4)_4 \cdot H_2O$	37.05	4.30	10.66	10.45
$C_{34}H_{46}N_8O_{17}Cl_4Ni_2$	(37.19)	(4.22)	(10.20)	(10.69)
$[Ni_2(Br)_2(tpmc)](ClO_4)_2$	39.25	4.20	10.77	11.00
$C_{34}H_{44}N_8O_8Br_2Cl_2Ni_2$	(39.23)	(4.26)	(10.76)	(11.28)

[a] tpmc = *N,N′,N″,N‴*-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane.

and the mixture was heated with stirring on a water bath for 1 h. The colour gradually changed from blue to green. An excess of sodium perchlorate and $\frac{1}{10}$ of volume ethanol were added. After a few hours green crystals separated, were filtered and washed with ethanol. The product was recrystallized from hot water and desiccated over P_2O_5. Yield 360 mg (76%).

Carbon, hydrogen and nitrogen analyses were carried out at the Service Center of Elemental Analysis, Kyushu University. The metal analyses were made with a Shimadzu AA-680 atomic adsorption spectrophotometer. Analytical data are given in Table 1.

Measurements

Electronic spectra were recorded with a Shimadzu multipurpose spectrophotometer model MPS-2000 at room temperature. IR spectra were measured with a JASCO IR-810 spectrophotometer in Nujol mull and KBr disk. Magnetic susceptibilities were measured by the Faraday method, and calibrated by using $[Ni(en)_3]S_2O_3$. Diamagnetic corrections were made with Pascal's constants. TG analysis was done by Rigaku Differential Thermogravimetric Analyser.

X-ray Crystal Structure Analyses

A single crystal of $[Cu_2F(tpmc)](ClO_4)_3 \cdot 2CH_3CN$ suitable for X-ray structure determination was obtained by the diffusion method in an H-tube, with saturated acetonitrile solution of the complex in one tube, and ether in another. Single crystals of $[Cu_2Cl(tpmc)](ClO_4)_3 \cdot H_2O$ were grown by slow evaporation of its saturated aqueous solution at room temperature. Diffraction data were obtained on a Rigaku Denki AFC-5 automated four-circle diffractometer with graphite-monochromated Mo Kα radiation at ambient temperature. Pertinent crystallographic parameters are given in Table 2. Three standard reflections were monitored every 100 reflections measured, and their intensities showed a good stability for the chloro complex, but decreased for the fluoro complex during the course of the measurement due to the decomposition of the crystal. Reflection data were corrected for Lorentz–polarization effects, but not for absorption. The structures were solved by the standard heavy atom method. Refinements were carried out by the block diagonal least-squares method, where the function minimized is $\Sigma w(|F_o| - |F_c|)^2$. The equal weight is taken for all reflections. The calculations were carried out on FACOM-M 780 computer at the Computer Center of Kyushu University using the UNICS III [8] program system. Positional parameters of non-hydrogen atoms are given in Tables 3 and 4, respectively. Selected interatomic bond distances and angles are given in Table 5.

Determination of Stability Constants

The equilibrium constants for the reaction

$$[Cu_2tpmc]^{4+} + X^- \rightleftharpoons [Cu_2X(tpmc)]^{3+}$$

X = F, Cl, Br, I, NO_2

$$K = \frac{(Cu_2X(tpmc)^{3+})}{(Cu_2(tpmc)^{4+})(X^-)}$$

were determined spectrophotometrically [9]. Aqueous solutions of $[Cu_2(tpmc)](ClO_4)_4$ (2.5 mM, 10 cm^3) and $NaClO_4$ (50 mM, 5 cm^3) were mixed in a 25 cm^3 measuring flask, where mM denotes mmol dm^{-3}. To this solution was added an aqueous solution of NaX (10 mM; 0.75, 1.00, 1.25, 1.75, 2.50, 5.00 or 10.00 cm^3: or 20 mM; 7.5 or 10 cm^3), and the volume of the solution was adjusted to 25 cm^3 by adding water. The solutions were thermostated at 21 °C prior to the absorbance measurements. The measurements were carried out with a thermostated 1 cm cell. The stability constants were estimated by a similar way to that described in ref. 10 by using the least-squares method. The log K values are given in Table 6, together with the values for taec analogues for comparison.

TABLE 2. Crystal data and data collection details

	$[Cu_2F(tpmc)](ClO_4)_3 \cdot 2CH_3CN$	$[Cu_2Cl(tpmc)](ClO_4)_3 \cdot H_2O$
Formula	$Cu_2Cl_3O_{12}FN_{10}C_{38}H_{50}$	$Cu_2Cl_4O_{13}N_8C_{34}H_{46}$
Formula weight	1091.32	1043.69
Crystal system	monoclinic	monoclinic
Space group	$P2_1/a$	$P2_1/n$
a (Å)	21.543(4)	15.054(2)
b (Å)	18.020(4)	22.452(2)
c (Å)	11.987(2)	12.895(1)
β (°)	91.13(2)	92.48(1)
V (Å^3)	4652.5	4354.7
Z	4	4
D_c (g cm^{-3})	1.56	1.59
Crystal size (mm)	0.20 × 0.40 × 0.40	0.50 × 0.30 × 0.30
μ(Mo Kα) (cm^{-1})	11.6	12.9
Scan mode	$\theta - 2\theta$	$\theta - 2\theta$
2θ range (°)	2.5–42	2.5–45
No. unique data with $\lvert F_o \rvert > 3\sigma(\lvert F_o \rvert)$	3654	4398
No. variables	578	772
R (%)	8.8	6.1
R_w (%)	9.4	6.5
Largest peak on D-Fourier (e A^{-3})	1.10	0.88

Results and Discussion

Copper(II) Complexes

A dinuclear structure of all the complexes is assumed on the basis of their elemental analyses. For $[Cu_2F(tpmc)](ClO_4)_3 \cdot 2CH_3CN$ and $[Cu_2Cl(tpmc)](ClO_4)_3 \cdot H_2O$ such a structure was confirmed by X-ray analysis.

Description of Structures

$[Cu_2F(tpmc)](ClO_4)_3 \cdot 2CH_3CN$

The crystal consists of $[Cu_2F(tpmc)]^{3+}$, ClO_4^- and acetonitrile molecules (Fig. 3). The Cu...Cu distance of 3.993(2) Å is significantly shorter than in the taec analogue [11] (Table 7). The copper atoms are bridged by the fluoride ion. The bond distances Cu–F are 2.068(8) and 2.079(8) Å respectively, which are also shorter than those in the taec analogue (Table 7). The coordination mode of tpmc is similar to those of taec in $[Cu_2Z(taec)]^{3+}$ (Z = F, Cl, Br, I, NO_2, NCO, N_3), i.e. the two coordination units are linked by the two $-(CH_2)_3-$ chains of the cyclam ring. The coordination geometry of each copper is a distorted square pyramid, but interestingly, the apical bond (Cu–F) is not so elongated as expected for copper compounds. The basal plane is formed by two cyclam nitrogens and two pendant arm nitrogens, and the apical position is occupied by the fluoride ion. The deviation of the basal atoms from the mean planes is within ±0.21 and ±0.05 Å for the N1, N2, N5 and N6 and N3, N4, N7 and N8 planes, respectively. The copper atoms are pushed from the basal planes towards the fluoride ion by 0.37 and 0.38 Å. The differences between the taec and tpmc fluoro complexes may be explained in terms of hydrogen bond formation between the fluoride ion and the amino hydrogens of the pendant arms. Such hydrogen bonds may enlarge the Cu–F bond distances in the taec complex. In the case of the tpmc complex there is no possibility for such bonds. It is also known that aromatic substituents on the cyclam ring form a more rigid structure than aliphatic ones, so that the flexibility of taec is larger than tpmc. This can produce a longer Cu...Cu distance in the taec complex.

$[Cu_2Cl(tpmc)](ClO_4)_3 \cdot H_2O$

The crystal consists of $[Cu_2Cl(tpmc)]^{3+}$, ClO_4^- and a crystal water molecule. A perspective view of $[Cu_2Cl(tpmc)]^{3+}$ is shown in Fig. 4. The two copper atoms with the distance of 4.470(2) Å are bridged by the chloride ion. The distances of Cu1–Cl1 and Cu2–Cl1 are 2.553(2) and 2.502(2) Å, respectively, and the angle Cu1–Cl1–Cu2 is 124.3(1)°. The coordination mode of tpmc is similar to that in the fluoro complex. The coordination geometry of each copper can be described as a distorted square pyramid. The deviation of the basal atoms from the mean planes are within ±0.21 Å, respectively. The Cu1 and Cu2 atoms are displaced by 0.33 and 0.35 Å from the mean planes toward the apices.

Electronic spectral data for the complexes are given in Table 8. Band positions of reflectance spectra

TABLE 3. Fractional positional parameters (×10^4) and thermal parameters of non-hydrogen atoms for [Cu_2F(tpmc)]$(ClO_4)_3 \cdot 2CH_3CN$ [a]

	x	*y*	*z*	B_{eq} (A^2)
Cu1	545(1)	2374(1)	2435(1)	3.3
Cu2	2191(1)	1355(1)	2448(1)	3.3
F	1468(3)	2096(4)	2702(6)	2.1
N1	109(5)	1767(7)	3643(10)	4.1
N2	11(5)	1769(6)	1302(10)	3.9
N3	1998(6)	534(6)	1282(10)	4.1
N4	2055(5)	534(6)	3606(10)	3.7
N5	546(6)	3168(7)	3645(10)	4.4
N6	771(6)	2931(6)	1054(9)	3.9
N7	2536(5)	1883(7)	1126(9)	3.8
N8	2667(5)	1809(7)	3757(10)	3.9
C1	−337(7)	1240(9)	3076(14)	5.2
C2	−556(7)	1551(9)	1943(14)	5.0
C3	308(8)	1083(9)	804(15)	5.3
C4	1007(7)	1167(9)	618(13)	4.5
C5	1331(7)	426(8)	899(13)	4.4
C6	2226(7)	−155(8)	1863(14)	4.7
C7	1928(8)	−195(8)	3045(13)	4.9
C8	1585(7)	725(10)	4463(13)	4.6
C9	923(6)	811(8)	3829(12)	3.8
C10	554(7)	1406(9)	4447(12)	4.7
C11	−246(7)	2353(9)	4286(13)	4.9
C12	164(8)	3017(9)	4460(13)	4.8
C13	95(9)	3457(10)	5389(14)	6.4
C14	457(9)	4093(12)	5482(15)	6.9
C15	878(10)	4255(11)	4658(17)	7.1
C16	931(9)	3778(10)	3719(15)	6.1
C17	−168(7)	2316(9)	401(13)	5.0
C18	394(7)	2817(8)	196(11)	3.9
C19	478(8)	3127(9)	−847(13)	5.2
C20	986(9)	3598(10)	−967(15)	6.1
C21	1401(9)	3703(10)	−96(15)	6.5
C22	1265(8)	3359(9)	936(13)	4.8
C23	2388(8)	665(9)	268(13)	5.0
C24	2589(7)	1465(8)	182(12)	4.1
C25	2844(8)	1721(10)	−786(13)	5.5
C26	3052(8)	2445(11)	−807(13)	6.2
C27	3019(8)	2876(9)	162(13)	4.9
C28	2747(7)	2574(8)	1099(12)	4.3
C29	2695(7)	516(9)	4219(13)	4.6
C30	2853(7)	1304(9)	4508(12)	4.2
C31	3187(7)	1487(10)	5480(13)	4.8
C32	3317(7)	2234(10)	5685(14)	5.4
C33	1600(8)	−2373(5)	−230(9)	6.1
C34	1900(7)	−2118(4)	712(7)	4.7
C12	4579(2)	−2999(1)	1576(2)	5.2
O2A	4342(6)	−3596(3)	1555(6)	7.2
O2B	3903(5)	−2643(3)	1967(5)	5.7
O2C	5294(9)	−2968(8)	2328(16)	13.8
O2D	5101(11)	−2741(6)	941(13)	12.2
O2E	4387(17)	−2917(9)	420(14)	13.9
C13	6023(2)	751(2)	2967(2)	7.5
O3A	5424(6)	641(4)	2135(6)	8.3
O3B	6146(9)	193(5)	3504(9)	11.2
O3C	6786(8)	997(7)	2771(13)	15.3
O3D	5572(13)	1160(7)	3599(12)	14.3
O3E	5638(25)	707(20)	3885(19)	12.7
O3F	5475(44)	1233(29)	2546(49)	15.2
C14	2206(4)	1259(3)	7967(4)	14.1
O4A	1207(11)	1469(6)	7607(10)	13.3
O4B	2317(15)	1348(7)	6952(8)	19.2
O4C	1629(14)	1865(9)	8257(16)	14.6
O4D	3004(15)	1491(10)	8688(15)	13.5
O4E	1481(16)	900(9)	8240(19)	16.8
O4F	2754(27)	577(11)	8194(20)	18.1
OW	4834(8)	2281(8)	3160(11)	16.8

[a] Values in parentheses are e.s.d.s.

TABLE 4. Fractional positional parameters (×10^4) and thermal parameters of non-hydrogen atoms for [Cu_2Cl(tpmc)]$(ClO_4)_3 \cdot H_2O$ [a]

	x	*y*	*z*	B_{eq} (A^2)
Cu1	1829(1)	342(0)	2721(1)	3.0
Cu2	3220(1)	−1357(0)	2001(1)	3.1
Cl1	1897(1)	−682(1)	1869(2)	3.3
N1	2469(5)	856(3)	1663(5)	3.6
N2	2771(5)	658(3)	3791(5)	3.3
N3	4299(5)	−1215(3)	3008(5)	3.5
N4	3992(5)	−997(3)	881(5)	3.7
N5	753(5)	506(3)	1776(5)	3.6
N6	1344(5)	−33(3)	3991(5)	3.2
N7	2737(5)	−1761(3)	3250(5)	3.3
N8	2669(5)	−1828(3)	762(5)	3.7
C1	3192(7)	1202(4)	2230(7)	4.3
C2	2979(6)	1262(4)	3364(7)	3.9
C3	3609(6)	307(4)	3903(7)	3.7
C4	3502(6)	−365(4)	3896(6)	3.3
C5	4376(6)	−625(4)	3552(7)	4.0
C6	5053(6)	−1276(4)	2310(7)	4.4
C7	4902(7)	−887(4)	1358(8)	4.7
C8	3602(7)	−457(4)	359(6)	4.1
C9	3542(6)	73(4)	1099(7)	3.9
C10	2816(7)	503(4)	768(6)	4.1
C11	1753(7)	1268(4)	1257(6)	4.4
C12	886(7)	957(4)	1119(6)	4.1
C13	227(8)	1144(5)	401(7)	5.6
C14	−556(8)	852(6)	389(9)	6.9
C15	−709(8)	394(5)	1058(9)	6.5
C16	−28(6)	222(4)	1723(7)	4.5
C17	1572(7)	−98(5)	5822(6)	4.5
C18	1717(6)	169(4)	4886(6)	3.3
C19	2287(6)	707(4)	4777(6)	3.9
C20	1015(8)	−584(5)	5856(8)	5.5
C21	615(7)	−788(4)	4938(7)	4.7
C22	805(6)	−505(4)	4026(7)	4.0
C23	4284(6)	−1716(4)	3761(7)	4.1
C24	3361(7)	−1870(4)	3997(7)	3.9
C25	3119(8)	−2121(4)	4942(7)	5.2
C26	2255(8)	−2268(5)	5077(8)	5.8

(continued)

TABLE 4. *(continued)*

	x	*y*	*z*	B_{eq} (Å^2)
C27	1636(8)	−2152(5)	4303(8)	5.5
C28	1881(7)	−1893(4)	3395(7)	4.2
C29	4036(7)	−1478(4)	90(7)	4.6
C30	3158(7)	−1782(4)	−71(7)	4.3
C31	2870(9)	−2019(5)	−1031(8)	6.2
C32	2090(9)	−2313(5)	−1095(8)	6.9
C33	1600(8)	−2373(5)	−230(9)	6.1
C34	1900(7)	−2118(4)	712(7)	4.7
Cl2	4579(2)	−2999(1)	1576(2)	5.2
O2A	4342(6)	−3596(3)	1555(6)	7.2
O2B	3903(5)	−2643(3)	1967(5)	5.7
O2C	5294(9)	−2968(8)	2328(16)	13.8
O2D	5101(11)	−2741(6)	941(13)	12.2
O2E	4387(17)	−2917(9)	420(14)	13.9
Cl3	6023(2)	751(2)	2967(2)	7.5
O3A	5424(6)	641(4)	2135(6)	8.3
O3B	6146(9)	193(5)	3504(9)	11.2
O3C	6786(8)	997(7)	2771(13)	15.3
O3D	5572(13)	1160(7)	3599(12)	14.3
O3E	5638(25)	707(20)	3885(19)	12.7
O3F	5475(44)	1233(29)	2546(49)	15.2
Cl4	2206(4)	1259(3)	7967(4)	14.1
O4A	1207(11)	1469(6)	7607(10)	13.3
O4B	2317(15)	1348(7)	6952(8)	19.2
O4C	1629(14)	1865(9)	8257(16)	14.6
O4D	3004(15)	1491(10)	8688(15)	13.5
O4E	1481(16)	900(9)	8240(19)	16.8
O4F	2754(27)	577(11)	8194(20)	18.1
OW	4834(8)	2281(8)	3160(11)	16.8

[a]Values in parentheses are e.s.d.s.

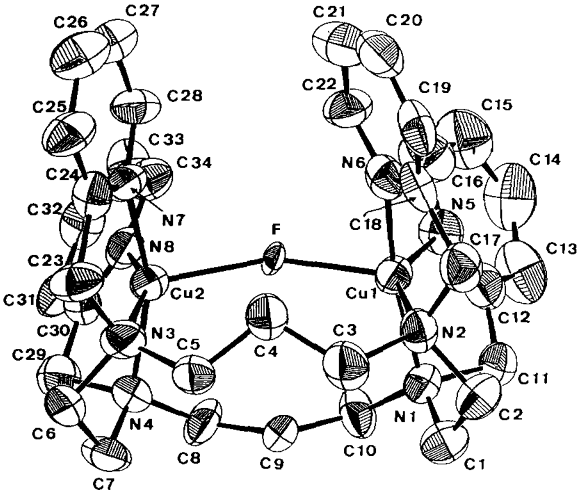


Fig. 3. ORTEP diagram for [Cu$_2$F(tpmc)](ClO$_4$)$_3$·2CH$_3$CN.

in the visible region for the bromo, mono azido and thiocyanato complexes were nearly the same as those of their water solution. However, the iodo and nitrito complexes showed a red shift, whereas the diazido complex showed a blue shift.

TABLE 5. Selected interatomic distances and angles[a]

[Cu$_2$F(tpmc)](ClO$_4$)$_3$·2CH$_3$CN

Distances (Å)

Cu1–Cu2	3.993(2)	Cu1–F	2.068(8)
Cu1–N1	2.055(12)	Cu1–N2	2.072(12)
Cu1–N5	2.037(13)	Cu1–N6	2.005(12)
Cu2–F	2.079(8)	Cu2–N3	2.071(12)
Cu2–N4	2.053(12)	Cu2–N7	2.004(12)
Cu2–N8	2.030(12)		

Angles (°)

Cu1–F–Cu2	148.6(4)	F–Cu1–N1	102.4(4)
F–Cu1–N2	119.5(4)	F–Cu1–N5	94.2(4)
F–Cu1–N6	90.0(4)	N1–Cu1–N2	85.8(5)
N1–Cu1–N5	82.4(5)	N1–Cu1–N6	165.8(5)
N2–Cu1–N5	145.9(5)	N2–Cu1–N6	82.1(5)
N5–Cu1–N6	103.8(5)	F–Cu2–N5	89.8(4)
N3–Cu2–N4	85.0(5)	N3–Cu2–N7	83.0(5)
N3–Cu2–N8	154.3(5)	N4–Cu2–N7	159.5(5)
N4–Cu2–N8	81.1(5)	N7–Cu2–N8	103.3(5)

[Cu$_2$Cl(tpmc)](ClO$_4$)$_3$·H$_2$O

Distances (Å)

Cu1–Cu2	4.470(2)	Cu1–Cl1	2.553(2)
Cu2–Cl1	2.502(2)	Cu1–N1	2.058(7)
Cu1–N2	2.061(7)	Cu1–N5	2.018(7)
Cu1–N6	2.007(7)	Cu2–N3	2.061(7)
Cu2–N4	2.059(7)	Cu2–N7	2.011(7)
Cu2–N8	2.059(8)		

Angles (°)

Cu1–Cl1–Cu2	124.3(1)	N1–Cu1–N2	85.6(3)
N2–Cu1–N6	82.1(3)	N5–Cu1–N6	104.9(3)
N1–Cu1–N5	83.3(3)	N3–Cu2–N4	85.9(3)
N4–Cu2–N8	83.0(3)	N7–Cu2–N8	104.0(3)
N3–Cu2–N7	82.4(3)		

[a]Values in parentheses are e.s.d.s.

TABLE 6. Stability constants for tpmc and taec [Cu$_2$XL]$^{3+}$

X$^-$	log *K*	
	tpmc	taec [a]
F$^-$	3.03 ± 0.17	3.93 ± 0.13
Cl$^-$	4.80 ± 0.17	5.14 ± 0.08
Br$^-$	3.77 ± 0.07	4.78 ± 0.12
I$^-$	2.76 ± 0.10	4.46 ± 0.17
NO$_2$$^-$	4.20 ± 0.12	

[a]Results are taken from ref. 10.

The formation constants obtained are listed in Table 6. These values are very high compared to the formation constants for nitrito and halogeno complexes from a simple aqueous copper(II) ion [9], suggesting that the anion is bound to both copper atoms. By comparing these data with those previously

TABLE 7. Some selected X-ray data for $[Cu_2F(tpmc)]^{3+}$ and $[Cu_2F(taec)]^{3+}$ [a]

	$[Cu_2F(tpmc)]^{3+}$	$[Cu_2F(taec)]^{3+}$ [b]
Cu–X–Cu	148.6(4)°	154.0(2)°
Cu...Cu	3.993(2) Å	4.229(2) Å
Cu–X	2.068(8) Å	2.234(10) Å
	2.079(8) Å	2.106(10) Å
Deviation of Cu atom	0.37 Å	0.41 Å
from the basal plane	0.38 Å	0.47 Å

[a]Values in parentheses are e.s.d.s. [b]Data taken from ref. 11.

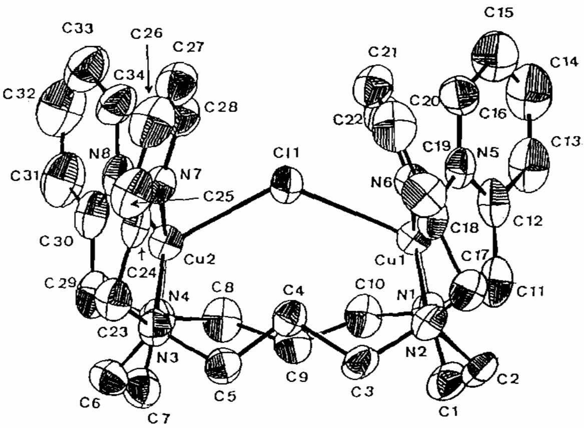


Fig. 4. ORTEP diagram for $[Cu_2Cl(tpmc)](ClO_4)_3 \cdot H_2O$.

reported for taec analogue (see Table 6) it can be seen that constants for tpmc copper(II) complexes are lower than those for corresponding taec complexes, but still much higher than those in ordinary copper–halogeno compounds.

It should be noted that the iodo complex of tpmc has the lowest stability among the halogeno complexes, but this was not the case for the taec analogue.

The hydrophobic environment around X^- may also be a factor which enhances the stability of all these complexes.

IR spectra of all complexes have a band around 1600 cm^{-1} due to skeletal vibration of the pyridine ring and a broad band of ClO_4^- around 1100 cm^{-1}. Both, mono- and diazido complexes show a sharp strong signal due to the $\nu(N_3^-)$ at 2049 cm^{-1}, and the thiocyanato complex a sharp strong band at 2070 cm^{-1} and a sharp signal at 480 cm^{-1}, due to $\nu(SCN^-)$ and $\delta(SCN^-)$, respectively. The IR spectra of all the halogeno complexes are similar, suggesting similar structures to those of the fluoro and chloro complexes. For thiocyanato bridged complexes the stretching frequency of SCN^- is expected in the region higher than 2100 cm^{-1} [12]. Since the band was observed at a lower wave number, it seems that each NCS^- group is singly coordinated to each copper atom, as in the case of $[Cu_2Br_2(tpmc)]^{2+}$, for which Alcock *et al.* determined the structure by X-ray analysis [6].

All magnetic moments (per copper atom) at room temperature were within the range 1.76–1.93 BM

TABLE 8. Electronic spectra and effective magnetic moments per metal atom at room temperature (BM)

Complex	λ_{max} (nm) (ϵ (dm^3 mol^{-1} cm^{-1}))		μ_B [a]
	Aqueous solution	Reflectance	
$[Cu_2Cl(tpmc)](ClO_4)_3 \cdot H_2O$	676(375)	663	1.80
$[Cu_2Br(tpmc)](ClO_4)_3$	678(283)	680	1.82
$[Cu_2I(tpmc)](ClO_4)_3 \cdot H_2O$	710(323)	694	1.80
	410(487)		
$[Cu_2(N_3)(tpmc)](ClO_4)_3$	656(397)	654	1.76
$[Cu_2(NO_2)(tpmc)](ClO_4)_3$	636(252)	616	1.82
$[Cu_2(NCS)_2(tpmc)](ClO_4)_2$	673(273)	670; 400	1.78
$[Cu_2(N_3)_2(tpmc)](ClO_4)_2$	664(195)	780; 390	1.93
$[Ni_2(tpmc)](ClO_4)_4 \cdot 3H_2O$	812(sh)(6)	788(sh)	2.96
	600(13)	579	
	372(28)	363	
$[Ni_2(tpmc)](ClO_4)_4 \cdot H_2O$	the same as the above complex	788(sh)	diamagnetic
		470	
		395	
$[Ni_2Br_2(tpmc)](ClO_4)_2$	815(sh)(25)	807	3.25
	590(37)	628	
	378(62)	463(sh)	
		397	

[a]For all the complexes Nα = 0 was assumed.

(Table 8), which was slightly higher than the spin only value (1.73 BM). Judging from these data there is no significant magnetic interaction between two copper atoms, which is consistent with the assumed geometry. Of all the copper complexes with tpmc, only the OH^- bridged complex was reported to show antiferromagnetic interaction [5].

Nickel(II) Complexes

An aqueous solution containing tpmc and nickel(II) perchlorate hexahydrate gave blue crystals of $[Ni_2(tpmc)](ClO_4)_4 \cdot 3H_2O$, whose magnetic moment of 2.96 BM/Ni and reflectance electronic spectra were compatible with the five-coordinated nickel centers which were presumed from the elemental analyses and analogy with the copper analogues. TG analysis showed the loss of three molecules of water. The blue crystals change colour to orange when kept in a P_2O_5 desiccator for one week. The yellow compound was essentially diamagnetic, and was assumed to adopt a square-planar coordination. The reflectance spectrum in the visible region showed a distinct band at 470 nm, hence is compatible with the above assumption, but it immediately changes to blue when dissolved in water. The aqueous solutions of both forms showed the same spectral pattern, corresponding to five- or six-coordinated nickel centers.

Reflectance and solution spectra of the dibromo green complex correspond to five- or six-coordinated nickel and its magnetic moment (3.25 BM/Ni) also suggests a high-spin nickel state. Since its IR spectrum has a similar pattern to those of $[Cu_2Y_2(tpmc)](ClO_4)_2$ complexes, a similar structure is proposed.

In conclusion, although there are many differences between taec and tpmc complexes in various aspects in detail, there exists good similarities in the principal aspects, such as the facile formation of dinuclear entities and the strong incorporation of an anion inbetween two metal ions.

Supplementary Material

Tables of structure factors and anisotropic parameters are available from author Sigeo Kida.

Acknowledgements

We wish to thank Mr Keiji Inoue of Kyushu University for the magnetic susceptibility measurements. This work was partly supported by the fellowship to Gordana Vučković from the Japan Society for the Promotion of Science, to which the authors' thanks are due.

References

1 G. A. Melson, *Coordination Chemistry of Macrocyclic Compounds,* Plenum, New York, 1979.

2 I. Murase, M. Mikuriya, H. Sonoda, Y. Fukuoda and S. Kida, *J. Chem. Soc., Dalton Trans.,* (1986) 953, and refs. cited therein.

3 (a) H. Stetter and W. Frank, *Angew. Chem., Int. Ed. Engl., 15* (1976) 686; (b) C. M. Madeyski, J. P. Michael and R. D. Hancock, *Inorg. Chem., 23* (1984) 1487; (c) K. P. Wainwright, *J. Chem. Soc., Dalton Trans.,* (1980) 2117; (d) (1983) 1149.

4 (a) I. Murase, M. Mikuriya, H. Sonoda and S. Kida, *J. Chem. Soc., Chem. Commun.,* (1984) 692; (b) M. Mikuriya, S. Kida and I. Murase, *Bull. Chem. Soc. Jpn., 60* (1987) 1355; (c) *60* (1987) 1681; (d) M. Mikuriya, S. Kida, T. Kohzuma and I. Murase, *Bull. Chem. Soc. Jpn., 61* (1988) 2666; (e) E. Asato, S. Kida and I. Murase, *Inorg. Chem., 28* (1989) 801.

5 (a) E. Asato, H. Toftlund, S. Kida, M. Mikuriya and K. S. Murray, *Inorg. Chim. Acta, 165* (1989) 207; (b) E. Asato, S. Hashimoto, N. Matsumoto and S. Kida, *J. Chem. Soc., Dalton Trans.,* (1990), in press.

6 N. W. Alcock, K. P. Balakrishnan and P. Moore, *J. Chem. Soc., Dalton Trans.,* (1986) 1743.

7 Ch.-M. Che, W.-T. Tang and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.,* (1988) 2879.

8 (a) S. Kawano, *Rep. Comput. Cent. Kyushu Univ., 16* (1983) 113; (b) T. Sakurai and K. Kobayashi, *Rep. Inst. Phys., Chem. Res., Wako, 55* (1979) 69.

9 L. G. Sillen and A. E. Martel (eds.), *Stability Constants,* The Chemical Society, London, 1971.

10 S. Kida, I. Murase, C. Harada, L. Daizeng and M. Mikuriya, *Bull. Chem. Soc. Jpn., 59* (1986) 2595.

11 M. Mikuriya, S. Kida and I. Murase, *Bull. Chem. Soc. Jpn., 60* (1987) 1681.

12 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds,* Wiley, New York, 3rd edn., 1978.