4- and 5-Coordinate Dinuclear Copper(II) Complexes with the Tetraacetyleanediide and an N-Alkylated Diamine or a Triamine

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Dedicated to Prof. Hitoshi Ohtaki on the occasion of his 60th birthday

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Dinuclear Cu(II) Complexes, 5-Coordinate Complexes, Chromotropism, Mixed Ligand Complexes, Anion Coordination

Six dinuclear copper(II) complexes have been prepared, $\text{Cu}_2(\text{taet})(\text{plam})_2\text{X}_2$ where taet = 1,1,2,2-tetraacetyleanediide, plam = N-alkylated polyamine such as tmen = N,N,N',N'-tetramethylethylenediamine or pmtdt = N,N,N',N'',N''-pentamethyldiethylenetriamine, X = a monovalent anion such as ClO_4^- , NO_3^- or Cl^- . These complexes are classified into two categories from the results of electronic spectra, IR spectra, and X-ray single crystal structure analysis as follows: (1) 4-coordinate–4-coordinate dinuclear, $[\text{Cu}_2(\text{taet})(\text{tmen})_2]\text{X}_2$ (where X = ClO_4^- or NO_3^-), (2) 5-coordinate–5-coordinate dinuclear, $[\text{Cu}_2(\text{taet})(\text{tmen})_2\text{Cl}_2]$, and $[\text{Cu}_2(\text{taet})(\text{pmtdt})_2]\text{X}_2$ (where X = ClO_4^- , NO_3^- , or Cl^-). The crystal structure of $\text{Cu}_2(\text{taet})(\text{tmen})_2(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1**) has been determined by the single crystal X-ray diffraction technique; monoclinic space group $\text{P}2_1/a$ with $a = 26.478(3)$, $b = 8.744(1)$, $c = 15.601(3)$ Å, $\beta = 106.195(9)^\circ$, and $V = 3468.9(8)$ Å³ for $Z = 4$. The final agreement factors are $R = 0.097$ ($R_w = 0.099$). The geometry of each Cu(II) moiety in the dinuclear cation (**1**) is 4-coordinate square planar with a N_2O_2 donor set. This tmen-dinuclear complex exhibits a very weak Cu(II)–Cu(II) interaction ($J = -0.5 \text{ cm}^{-1}$), and shows characteristic ESR spectra with seven hyperfine peaks in 1,2-dichloroethane solution at room temperature. This is not found for the corresponding pmtdt-dinuclear complex. All complexes obtained in this study are very soluble in many organic solvents. The tmen-dinuclear complexes show pronounced solvatochromic behavior-dependent on the solvent donor properties. This is not found for the corresponding pmtdt-dinuclears, which are stable as 5-coordinated species.

Introduction

So far, we have studied chromotropism of the transition metal complexes, especially the solvatochromism, of mixed ligand Ni(II) and Cu(II) complexes containing one N-alkylated polyamine (diamine or triamine) and one β -diketonate ligand [1–3]. These complexes are mononuclear and are found to be very stable and highly soluble in various organic solvents based on the mixed ligand system which provides a suitable combination of the bulky N-alkylated polyamine and slim β -diketonate. Their characteristic properties are reflected by the chromotropic phenomena in solu-

tion [4]. In continuing these studies, we have synthesized the branched tetraketonate ligand (abbreviated as taet = 1,1,2,2-tetraacetyleanediide) [5–7] to be combined with an N-alkylated polyamine (plam) such as N,N,N',N'-tetramethylethylenediamine (tmen) or N,N,N',N'',N''-pentamethyldiethylenetriamine (pmtdt) to form the dinuclear mixed ligand complexes; $(\text{plam})\text{M}(\text{taet})\text{M}(\text{plam})\text{X}_2$ [8–10], where M = Ni(II) and Cu(II), X[–] = an anion such as perchlorate (ClO_4^-), nitrate (NO_3^-), or chloride (Cl^-). Recently, we could obtain six dinuclear Cu(II) complexes, could determine one of the crystal structures (the perchlorate with tmen), and study some properties of these six complexes (solid and solution), especially their d–d spectra (chromo-

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tropic behavior), IR spectra, ESR and magnetic properties, which will be reported in this paper.

Experimental

Materials

Starting materials (tmen, pmdt and Hacac = acetylacetone) for synthesizing metal complexes were obtained from Wako Pure Chemical Industrial Co. Ltd. or Nacalai Tesque Co. Ltd. as guaranteed grade and were used without further purification. Solvents used for spectral and electric conductivity measurements were "Spectro-grade" and dehydrated by conventional methods, if necessary [11]. The method used to obtain the bridging ligand (H_2taet) as reported already in a previous communication is similar to that reported by Charles [9, 12]. The ligand was characterized by its melting point and the comparison of the 1H NMR spectra of the ligand and that of the starting material (Hacac). The preparation of these complexes is similar to that of the perchlorate complexes reported before [8]. 20 mmol of the corresponding copper(II) salt (perchlorate, nitrate, or chloride) dissolved in ethanol (EtOH), 10 mmol of H_2taet with 10 mmol of Na_2CO_3 in aqueous EtOH, and 25 mmol of tmen (or pmdt) were mixed together under vigorous stirring. After half an hour, the resulting solution was filtered and stored in a silica-gel desiccator for several days. The obtained complexes were recrystallized from 1,2-dichloroethane (DCE). Colors and analytical data are shown in Table I.

Structural determination

Reddish violet crystals were grown from a DCE solution. Crystals of approximate dimensions of $0.3 \times 0.3 \times 0.3$ mm³ were used. Accurate cell parameters were determined by a least-squares fit of 38 reflections within the range $25^\circ < 2\theta < 30^\circ$ measured on a Rigaku AFC-5 diffractometer using Mo($K\alpha$) radiation ($\lambda = 0.71069$ Å) monochromated by graphite.

Crystal data: $Cu_2(taet)(tmen)_2(ClO_4)_2 \cdot H_2O = Cu_2C_{22}H_{46}N_4O_{13}Cl_2$, monoclinic, $P2_1/a$, $Z = 4$, $a = 26.478(3)$, $b = 8.744(1)$, $c = 15.601(3)$ Å, $\beta = 106.195(9)^\circ$, $V = 3468.9(8)$ Å³, $D_x = 1.48$ g cm⁻³, $\mu = 1.44$ mm⁻¹, $F(000) = 1608$, $T = 298$ K.

Reflection data were collected on a θ - 2θ scan mode, up to $2\theta = 55^\circ$ with scan range of $\omega = (1.0 + 0.5 \tan\theta)$. Backgrounds were counted for 6 s at both ends of scan. Three standard reflections were recorded after every 150 reflections. This crystal did not show any decomposition during data collection: the maximal variation of three intensity data decreased by only 3.0%. A total of 5260 reflections at the rate of 4 min⁻¹, of which 4242 reflections were treated as significant ($|F_o| > 4\sigma(|F_o|)$). Data were corrected for Lorentz-polarization effects, but not for those of absorption. The structure was solved by the heavy atom method by using the program SHELXS-86 [13] and was refined by block-diagonal least-squares with UNICS III [14]. The quantity minimized was $w(|F_o| - |F_c|)^2$, where $w = 1.0$. Atomic scattering factors were taken from the International Tables for X-Ray Crystallography [15a]. All the non-hy-

Table I. Colors, analytical and magnetic data of the complexes obtained.

Complex	Color ^a	C [%] ^c	H [%] ^c	N [%] ^c	Magnetic Moment ^d	
					μ_{eff}	μ_{eff}/Cu
$Cu_2(taet)(tmen)_2(ClO_4)_2 \cdot H_2O$	dark-violet (17.7)	33.73 (33.81)	6.06 (6.06)	7.10 (7.17)	2.69	1.90
$Cu_2(taet)(tmen)_2(NO_3)_2$	dark-green (17.8–15.6) ^b	38.59 (38.88)	6.57 (6.52)	12.66 (12.36)	2.73	1.93
$Cu_2(taet)(tmen)_2Cl_2 \cdot H_2O$	green (15.3)	40.22 (40.99)	7.02 (7.19)	8.01 (8.69)	2.50	1.77
$Cu_2(taet)(pmdt)_2(ClO_4)_2$	green (11.1, 12.8, 16.0)	38.02 (38.71)	6.55 (6.73)	9.77 (9.67)	2.50	1.77
$Cu_2(taet)(pmdt)_2(NO_3)_2 \cdot 1.5H_2O$	dark-green (10.6, 12.9, 15.3)	40.42 (40.97)	7.34 (7.49)	13.66 (13.65)	2.44	1.73
$Cu_2(taet)(pmdt)_2Cl_2 \cdot H_2O$	green (10.6, 13.3, 16.4)	43.10 (43.80)	7.41 (8.01)	10.83 (10.95)	2.38	1.69

^a Values in parentheses are the spectral peaks of the solid samples; ^b the nitrate complex has a very broad band in the range between 18 and 15 (10^3 cm⁻¹) which contains two components shown in the table; ^c calculated values are shown in parentheses; ^d measured at room temperature (18–25 °C). The value, μ_{eff} , means per molecule and the μ_{eff}/Cu for each Cu(II) ion.

drogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated. Max. D/σ and max. D/σ in the final difference map were 0.06 and 0.91 $e\text{\AA}^{-3}$. Final R (and R_w) value was 0.097 (0.099) ($w = 1/(\sigma^2 + 0.02 F^2)$). The final coordinates of non-hydrogen atoms are given in Table II. Fig. 1 shows the molecular structure of the dinuclear complex with numbering of the atoms. Selected bond distances and angles are given in Table III. Computations were carried out on a FACOM M-770/8 computer at the Computer

Fig. 1. Molecular structure of $[\text{Cu}_2(\text{taet})(\text{tmen})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$.

Table II. Atomic coordinates ($\times 10^4$) and thermal parameters ($\times 10^2$).

Atom	x	y	z	B_{eq}
Cu(1)	2185(1)	1927(2)	2486(1)	3.26(4)
Cu(2)	151(1)	2496(2)	-2373(1)	3.16(4)
Cl(1)	1268(1)	1759(4)	4260(2)	3.94(10)
Cl(2)	918(1)	6848(4)	-1978(2)	5.16(12)
O(1)	1890(3)	3571(8)	1738(4)	4.58(28)
O(2)	1747(3)	476(8)	1757(4)	3.82(26)
O(3)	51(3)	2731(9)	-1218(4)	3.60(24)
O(4)	863(3)	1891(9)	-1907(4)	3.93(25)
O(5)	1441(4)	1765(11)	3468(6)	6.82(39)
O(6)	1515(5)	2880(16)	4815(8)	12.87(62)
O(7)	735(4)	1911(14)	4043(7)	8.38(44)
O(8)	1394(5)	356(14)	4693(8)	16.05(57)
O(9)	814(5)	7165(12)	-2889(6)	8.48(46)
O(10)	753(6)	5451(14)	-1830(7)	13.47(71)
O(11)	735(6)	7953(15)	-1530(7)	12.04(61)
O(12)	1498(5)	6814(21)	-1604(9)	14.74(74)
O(13)	-169(4)	-188(10)	-2294(6)	6.09(36)
N(1)	2656(3)	3404(10)	3348(5)	2.90(28)
N(2)	2642(3)	209(10)	3164(6)	3.36(30)
N(3)	-558(4)	3527(11)	-2954(5)	3.79(32)
N(4)	238(3)	2324(12)	-3633(5)	3.78(30)
C(1)	1455(6)	4981(14)	496(8)	5.35(46)
C(2)	1554(5)	3471(12)	956(7)	3.60(38)
C(3)	1315(4)	2155(12)	577(6)	3.11(34)
C(4)	1412(5)	733(12)	998(6)	3.63(38)
C(5)	1107(6)	-661(14)	595(7)	5.71(50)
C(6)	2355(5)	4553(14)	3683(8)	4.42(44)
C(7)	2997(5)	4194(16)	2912(9)	5.22(49)
C(8)	2944(5)	2422(16)	4113(8)	6.12(47)
C(9)	3088(6)	972(16)	3783(10)	6.68(55)
C(10)	2837(6)	-754(17)	2541(10)	6.60(60)
C(11)	2346(5)	-750(14)	3617(8)	4.68(46)
C(12)	204(5)	2833(15)	337(7)	4.64(44)
C(13)	414(4)	2560(13)	-456(6)	3.53(35)
C(14)	939(4)	2205(13)	-349(6)	2.96(34)
C(15)	1150(5)	1894(13)	-1064(7)	3.70(37)
C(16)	1718(5)	1528(18)	-922(8)	5.51(50)
C(17)	-1007(5)	2471(19)	-2915(10)	6.93(57)
C(18)	-643(6)	4947(16)	-2515(8)	5.51(50)
C(19)	-572(6)	3836(17)	-3886(8)	6.52(54)
C(20)	-288(5)	2643(19)	-4247(7)	6.60(54)
C(21)	411(6)	767(16)	-3814(8)	5.55(53)
C(22)	640(6)	3438(16)	-3721(9)	5.89(54)

Center of Josai University. For further information on the structure determination, see reference [15b].

Physical measurements

Electronic spectra of the complexes in solution were performed with a Shimadzu 3100 spectrophotometer with 10 mm quartz cells. The concentrations of the solutions were usually in the range between $2.5\text{--}5.0 (\times 10^{-3}) \text{ mol}^{-1} \text{ dm}^{-3}$ except if mentioned differently in the text. The solid reflectance spectra of these complexes were obtained with the same spectrometer with an integrated sphere attachment and BaSO_4 as a reference. IR spectra in the range $400\text{--}5040 \text{ cm}^{-1}$ were measured with a Shimadzu FT-IR Spectrometer 8100 by Nujol-Mull method. Thermal analyses were performed with a ULVAC TG-DTA Thermal Analyzer with heating rates of $1^\circ\text{C}/\text{min}$ or $3^\circ\text{C}/\text{min}$. Magnetic data were collected with a Shimadzu Torsion Magnetometer MB-100 by the Faraday method at room temperature. Variable temperature ($4\text{--}270 \text{ K}$) magnetic susceptibilities were measured by a high-sensitivity Faraday balance with super-conducting magnet (Oxford Instruments, Inc.). Temperature was measured by a Pt thermometer and by a carbon-resistance thermometer, which were calibrated against a magnetic thermometer with the use of a paramagnetic complex $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ [16a]. ESR spectra were taken with a JEOL JES-FE2XG spectrometer (X-band) attached a standard MnO maker. Electric conductivity measurements were performed with a DKK AOC-10 Conductivity Outfit with a constant temperature water bath at $25 \pm 0.3^\circ\text{C}$.

Table III. Bond lengths (Å) and angles (°).

Cu(1)–O(1)	1.89(1)	Cu(1)–O(2)	1.88(1)
Cu(1)–N(1)	2.02(1)	Cu(1)–N(2)	2.03(1)
Cu(2)–O(3)	1.90(1)	Cu(2)–O(4)	1.90(1)
Cu(2)–N(3)	2.05(1)	Cu(2)–N(4)	2.05(1)
Cl(1)–O(5)	1.43(1)	Cl(1)–O(6)	1.35(2)
Cl(1)–O(7)	1.36(1)	Cl(1)–O(8)	1.40(1)
Cl(2)–O(9)	1.40(1)	Cl(2)–O(10)	1.34(2)
Cl(2)–O(11)	1.36(2)	Cl(2)–O(12)	1.49(2)
O(1)–C(2)	1.30(2)	O(2)–C(4)	1.29(2)
O(3)–C(13)	1.31(1)	O(4)–C(15)	1.32(2)
N(1)–C(6)	1.47(2)	N(1)–C(7)	1.45(2)
N(1)–C(8)	1.50(2)	N(2)–C(9)	1.46(2)
N(2)–C(10)	1.48(2)	N(2)–C(11)	1.46(2)
N(3)–C(17)	1.52(2)	N(3)–C(18)	1.47(2)
N(3)–C(19)	1.47(2)	N(4)–C(20)	1.48(2)
N(4)–C(21)	1.49(2)	N(4)–C(22)	1.48(2)
C(1)–C(2)	1.49(2)	C(2)–C(3)	1.37(2)
C(3)–C(4)	1.39(2)	C(3)–C(14)	1.51(2)
C(4)–C(5)	1.50(2)	C(8)–C(9)	1.46(2)
C(12)–C(13)	1.51(2)	C(13)–C(14)	1.39(2)
C(14)–C(15)	1.41(2)	C(15)–C(16)	1.49(2)
C(19)–C(20)	1.49(2)	O(13)–Cu(2)	2.51(2)
O(1)–Cu(1)–O(2)	93.6(4)	O(1)–Cu(1)–N(1)	89.8(4)
O(1)–Cu(1)–N(2)	166.8(4)	O(2)–Cu(1)–N(1)	175.9(4)
O(2)–Cu(1)–N(2)	89.6(4)	N(1)–Cu(1)–N(2)	87.6(4)
O(3)–Cu(2)–O(4)	93.1(4)	O(3)–Cu(2)–N(3)	91.1(4)
O(3)–Cu(2)–N(4)	177.5(4)	O(4)–Cu(2)–N(3)	168.9(4)
O(4)–Cu(2)–N(4)	89.0(4)	N(3)–Cu(2)–N(4)	86.7(4)
O(5)–Cl(1)–O(6)	109.7(8)	O(5)–Cl(1)–O(7)	110.1(7)
O(5)–Cl(1)–O(8)	109.3(8)	O(6)–Cl(1)–O(7)	111.7(8)
O(6)–Cl(1)–O(8)	108.7(9)	O(7)–Cl(1)–O(8)	107.3(8)
O(9)–Cl(2)–O(10)	112.1(9)	O(9)–Cl(2)–O(11)	112.7(9)
O(9)–Cl(2)–O(12)	107.2(9)	O(10)–Cl(2)–O(11)	112.2(10)
O(10)–Cl(2)–O(12)	105.4(10)	O(11)–Cl(2)–O(12)	106.7(10)
Cu(1)–O(1)–C(2)	126.2(8)	Cu(1)–O(2)–C(4)	126.2(8)
Cu(2)–O(3)–C(13)	125.8(7)	Cu(2)–O(4)–C(15)	127.8(8)
Cu(1)–N(1)–C(6)	112.3(7)	Cu(1)–N(1)–C(7)	110.0(8)
Cu(1)–N(1)–C(8)	104.3(7)	C(6)–N(1)–C(7)	108.2(10)
C(6)–N(1)–C(8)	108.5(10)	C(7)–N(1)–C(8)	113.7(10)
Cu(1)–N(2)–C(9)	105.1(8)	Cu(1)–N(2)–C(10)	110.1(9)
Cu(1)–N(2)–C(11)	110.8(7)	C(9)–N(2)–C(10)	109.2(10)
C(9)–N(2)–C(11)	112.7(10)	C(10)–N(2)–C(11)	108.9(10)
Cu(2)–N(3)–C(17)	110.3(8)	Cu(2)–N(3)–C(18)	113.9(8)
Cu(2)–N(3)–C(19)	106.6(8)	C(17)–N(3)–C(18)	105.8(10)
C(17)–N(3)–C(19)	110.3(10)	C(18)–N(3)–C(19)	110.0(10)
Cu(2)–N(4)–C(20)	105.7(9)	Cu(2)–N(4)–C(21)	111.8(8)
Cu(2)–N(4)–C(22)	108.4(8)	C(20)–N(4)–C(21)	109.5(11)
C(20)–N(4)–C(22)	113.0(11)	C(21)–N(4)–C(22)	108.4(10)
O(1)–C(2)–C(1)	112.0(11)	O(1)–C(2)–C(3)	125.1(11)
C(1)–C(2)–C(3)	122.8(11)	C(2)–C(3)–C(4)	123.1(11)
C(2)–C(3)–C(14)	119.3(10)	C(4)–C(3)–C(14)	117.6(10)
O(2)–C(4)–C(3)	125.4(11)	O(2)–C(4)–C(5)	113.3(11)
C(3)–C(4)–C(5)	121.3(11)	N(1)–C(8)–C(9)	110.1(11)
N(2)–C(9)–C(8)	112.9(11)	O(3)–C(13)–C(12)	112.3(10)
O(3)–C(13)–C(14)	126.2(10)	C(12)–C(13)–C(14)	121.5(10)
C(3)–C(14)–C(13)	119.6(10)	C(3)–C(14)–C(15)	116.7(10)
C(13)–C(14)–C(15)	123.7(10)	O(4)–C(15)–C(14)	123.0(10)
O(4)–C(15)–C(16)	114.9(10)	C(14)–C(15)–C(16)	122.1(11)
N(3)–C(19)–C(20)	111.7(13)	N(4)–C(20)–C(19)	111.8(13)
O(13)–Cu(2)–O(3)	85.2(3)	O(13)–Cu(2)–O(4)	91.9(3)
O(13)–Cu(2)–N(3)	98.7(4)	O(13)–Cu(2)–N(4)	96.2(4)

Results and Discussion

Structures and properties of the dinuclear complexes in the solid state

Six dinuclear mixed ligand Cu(II) complexes with two kinds of polyamines (tmen and pmtdt), tetraketonate bridging ligand (taet) and different anions have been obtained. Analytical data are collected in Table I which also contains their color and magnetic moments at room temperature. The complexes [(tmen)Cu(taet)Cu(tmen)]X₂ (hereafter called the tmen-dinuclear complexes) with ClO₄[−] and Cl[−] anions contain water of crystallization which is rather easily lost by heating near 100 °C in a TG-DTA apparatus. The former (perchlorate) lost its H₂O at less than 100 °C and the latter (chloride) near 65 °C. On the other hand, for the pmtdt-dinuclear complexes [(pmtdt)Cu(taet)Cu(pmtdt)]X₂ with NO₃[−] and Cl[−] anions, it is difficult to remove the water of crystallization by heating, especially as the chloride is very hygroscopic, so that there are some difficulties in handling the samples. These properties are reflected in the discrepancy in the analytical data between obtained values and calculated ones, especially for the chlorides. This means that the counter anion in the pmtdt-dinuclear complexes (especially the chloride) interacts much more strongly with the water molecules in crystallization than that of the tmen ones.

The IR data of the perchlorate and nitrate moieties in both of the complexes of tmen and pmtdt indicate that the anions do not interact with the metal ions [17, 18]. IR bands of the perchlorates of tmen- and pmtdt-dinuclear complexes show a strong broad band at around 1100 cm^{−1} and a sharp band at 620 cm^{−1}, which means that the anions is free from coordination. As there are some ambiguities in work of other research groups [19], it is of interest to note the IR criterion for the coordination mode of a nitrate ion. For mixed ligand complex systems, the criteria are as follows [20–22]: In the range between 1700–1800 cm^{−1}, *i.e.*, (1) ionic NO₃[−]; one weak band (ν_1 – ν_4 combination band) at near 1750 cm^{−1}, (2) monodentate NO₃[−]; weak splitting of the band in the same region (less than 20 cm^{−1}), (3) bidentate NO₃[−]; stronger splitting larger than 20 cm^{−1}. In this study for the nitrates of our dinuclear complexes, we

could obtain only one band at 1750 cm^{-1} (for the tmen-dinuclear complex) or 1748 cm^{-1} (for the pmtdt one). So, we concluded that the NO_3^- ions acts as the counter ion in both cases.

The chloride complexes, $\text{Cu}_2(\text{taet})(\text{plam})_2\text{Cl}_2$, of tmen and also pmtdt are green, and similar to the corresponding mononuclear complexes, $[\text{Cu}(\text{acac})(\text{tmen})\text{Cl}]$ and $[\text{Cu}(\text{acac})(\text{pmtdt})]\text{ClO}_4$, respectively, are showing both of the Cu(II) moieties to be 5-coordinate in the dinuclear unit. The spectral behavior and electric conductivities in solutions of these dinuclear complexes support this conclusion [23, 24]. Therefore, we have classified our dinuclear complexes into the following groups with the plausible structure as shown in Fig. 2.

It is obvious from the crystal structure of the tmen-perchlorate complex, $[\text{Cu}_2(\text{taet})(\text{tmen})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (Fig. 1 and Table III) that the taet ligand is bridging tetradentate

and that the dihedral angle of the acetylacetonate moieties of taet is nearly at 90° (83.7°). The coordination geometries in this dinuclear complex are close to a square planar structure around both Cu(II) ions with the N_2O_2 donor set from 2 N's of tmen and 2 O's of taet. The water molecule of crystallization is placed near one of the Cu(II) ions ($2.51\text{ \AA}$) which means that Cu is 5-coordinated. However, these water molecules are removed in a desiccator within a few days without noticeable color change. The four values of Cu(II)–O bond lengths between Cu(II) ions and the oxygen atoms of the taet ligand are very similar to each other and also to those of $\text{Cu}(\text{acac})_2$ [25].

All the complexes are found to be paramagnetic with magnetic moments of 1.8–1.7 B.M. at room temperature. This is not different from a normal paramagnetism of Cu(II) ion. Data of temperature-dependent magnetic susceptibilities of $[\text{Cu}_2(\text{taet})(\text{tmen})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ between 4–260 K are shown in Fig. 3. We obtained $J = -0.5\text{ cm}^{-1}$ as a weak intermetallic interaction (*i.e.*, weak anti-ferromagnetism, $g = 2.13$, $p = 0.01$, $N_A = 88 \times 10^{-6}\text{ cgs emu mol}^{-1}$) [16b].

Spectral behaviors of the dinuclear complexes in solution

The dinuclear complexes obtained in this study are readily soluble in many organic solvents like

Fig. 2. Structural varieties of the complexes, $\text{Cu}_2(\text{taet})(\text{Y})_2\text{X}_2$; Y = tmen or pmtdt, X = ClO_4 , NO_3 or Cl.

Fig. 3. Magnetic susceptibility of $[\text{Cu}_2(\text{taet})(\text{tmen})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ at various temperatures, (○): μ_{eff} (B.M.), (□) X_{corr} (molar susceptibility corrected). The solid line shows the theoretical values calculated by the modified Bleaney-Bowers equation [16b].

Fig. 4. Electronic absorption spectra of $[\text{Cu}_2(\text{taet})(\text{tmen})_2](\text{ClO}_4)_2$ in various solvents; A: in nitromethane, B: in methanol, C: in dimethyl sulfoxide.

1,2-dichloroethane (DCE), nitromethane (NM), chloroform, acetone, acetonitrile (ACN), alcohols (ROH), *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), *etc.* with different donor and acceptor properties [26, 27]. This means that many alkyl substituents around the polyamines and ketonate moieties with their hydrophobic properties cover the first coordination sphere having hydrophilic properties. Fig. 4 and 5 show electronic spectra of $[\text{Cu}_2(\text{taet})(\text{tmen})_2](\text{ClO}_4)_2$ and $[\text{Cu}_2(\text{taet})(\text{pmdt})_2](\text{ClO}_4)_2$ in NM, MeOH, and DMSO, respectively. In an inert solvent like NM (with very weak donor strength), the *d-d* absorption maxima of both of the perchlorates are nearly

the same as those of the solid reflectance spectra for the square planar (tmen) and 5-coordinate (pmdt) complexes without anion (ClO_4^-) coordination. The peak positions of the chelates in various solvents are shown in Fig. 6 with those of the corresponding mononuclear acac systems (see also Table IV, which is the list of peak positions of the complexes in various solvents). The absorption peak of the tmen-Cl-dinuclear complex in the solid state is at $15.3 \times 10^3 \text{ cm}^{-1}$ which is very different from that of the corresponding ClO_4 salt (the tmen- ClO_4 -dinuclear complex; $17.7 \times 10^3 \text{ cm}^{-1}$). In an inert solvent like DCE, the electric conductivity of the tmen-Cl-dinuclear complex shows that the complex exists as a non-electrolyte. For the perchlorate (tmen- ClO_4 -dinuclear complex), the electric conductivity is $17.8 \text{ S cm}^2 \text{ mol}^{-1}$ under the same conditions (in DCE at 25°C), which is small value for a 2:1 electrolyte. From these data, we conclude that (1) in the perchlorate system, $[(\text{plam})\text{Cu}(\text{taet})\text{Cu}(\text{plam})](\text{ClO}_4)_2$, absorption peaks of the tmen-dinuclear complex in various solvents are much more sensitive to the donor strength of the solvents used than those of the corresponding pmtdt one under the same condition. This means that the structure of the tmen-dinuclear complexes can be affected by the donor strength of the solvent and change more easily from the square planar to the solvated octahedral form. On the other hand, the pmtdt-dinuclear complexes still retain their coordination number

Fig. 5. Electronic absorption spectra of $[\text{Cu}_2(\text{taet})(\text{pmdt})_2](\text{ClO}_4)_2$ in various solvents; A: in nitromethane, B: in methanol, C: in dimethyl sulfoxide.

Table IV. Comparison of the d–d bands of the dinuclear complex with the corresponding mononuclear complex in various organic solvents at room temperature ($\tilde{\nu}_{\max}/10^3 \text{ cm}^{-1}$; $\epsilon_{\max}/\text{M}^{-1} \text{ cm}^{-1}$ in parentheses).

Solvent	$\text{Cu}_2(\text{taet})(\text{tmen})_2(\text{ClO}_4)_2 \cdot \text{H}_2\text{O} - \text{Cu}(\text{acac})(\text{tmen})\text{ClO}_4$	$\text{Cu}_2(\text{taet})(\text{pmdt})_2(\text{ClO}_4)_2$	$\text{Cu}(\text{acac})(\text{pmdt})\text{ClO}_4$	
1,2-Dichloroethane (DCE)	18.40 (279)	18.55 (114)	12.32 (521), 14.93 (sh)	12.45 (224)
Nitromethane (NM)	19.30 (387)	18.77 (115)	12.44 (476), 15.15 (sh)	12.59 (230)
Acetonitrile (ACN)	17.51 (301)	17.33 (118)	12.29 (500), 15.15 (sh)	12.53 (219)
Acetone (ACO)	17.80 (304)	17.42 (111)	–	12.62 (224)
Methanol (MeOH)	17.30 (303)	17.06 (119)	12.22 (505), 14.93 (sh)	12.59 (222)
DMF	16.84 (291)	16.53 (114)	12.44 (496), 15.02 (sh)	12.76 (222)
DMSO	16.48 (332)	16.26 (129)	12.48 (500), 14.93 (sh)	12.83 (227)

Fig. 6. Comparison of $\nu_{\max}$ of $[\text{Cu}_n(\text{L})(\text{Y})_n](\text{ClO}_4)_n$ ($\text{L} = \text{taet}$, $n = 2$; $\text{L} = \text{acac}$, $n = 1$; $\text{Y} = \text{tmen}$ or pmdt) in various solvents at room temperature.

(5-coordinated) without any solvent effect, *i.e.*, they are stable as the 5-coordinate dinuclear complex:

(2) In the case of the tmen-dinuclear complex, we could obtain an interesting anion effect but not for the case of the pmtd one. Although the anion ClO_4^- acts as the counter ion without coordination to Cu(II) in both cases (tmen and pmtd), the chloride anions can coordinate to Cu(II) to form 5-coordinated structures in the tmen-dinuclear complexes. In the case of the pmtd-dinuclear complexes one of the anions (Cl^-) acts only as the counter ion.

$[\text{Cu}_2(\text{taet})(\text{tmen})_2\text{Cl}_2] \text{ --- 5-coordinate--5-coordinate}$

$[\text{Cu}_2(\text{taet})(\text{pmdt})_2\text{Cl}_2] \text{ --- 5-coordinate--5-coordinate}$

The electric conductivity of the latter complex (pmtd-Cl-dinuclear) in DCE, which is $17.3 \text{ S cm}^2 \text{ mol}^{-1}$ at 25°C , is similar to the tmen- ClO_4 -dinuclear complex in the same solvent ($17.8 \text{ S cm}^2 \text{ mol}^{-1}$ at 25°C) [24]. Here we can conclude that the ligand pmtd is rather bulky and has a large steric hindrance in the coordination sphere for the coordination of an additional ligand like a halide ion.

Finally, in addition to the steric reason mentioned above, it is also of interest to note the difference of the ligand field strength (l.f.s.) of the dinuclear complexes between the tmen system and the pmtd one. As for the tmen case, each Cu(II) chromophore has a N_2O_2 donor set and for the pmtd case it is a N_3O_2 donor set, the l.f.s. of the latter case is much stronger than that of the former. This means that the degree of coordination unsaturation in the case of the tmen-dinuclear system is larger than that of the pmtd-dinuclear one. In other words, solvatochromism and anion interaction with the central metal ion occur more effectively in the tmen-dinuclear system than in the pmtd analogues.

Fig. 7. ESR spectra in DCE at room temperature.

A) $[\text{Cu}(\text{acac})(\text{tmen})]\text{ClO}_4$.

B) $[\text{Cu}_2(\text{taet})(\text{tmen})_2](\text{ClO}_4)_2$.

C) $[\text{Cu}(\text{acac})(\text{pmdt})]\text{ClO}_4$.

D) $[\text{Cu}_2(\text{taet})(\text{pmdt})_2](\text{ClO}_4)_2$.

Small signals at higher magnetic field (especially in C and D) are the signals of the MnO marker.

ESR spectra of these complexes in DCE at room temperature are shown in Fig. 7 with those of the corresponding mononuclear complexes

$[\text{Cu}(\text{acac})(\text{tmen})]\text{ClO}_4$ and

$[\text{Cu}(\text{acac})(\text{pmdt})]\text{ClO}_4$. ESR spectra of both

mononuclear complexes (tmen and pm dt) show four peaks due to hyperfine coupling with $(^{63}+^{65})\text{Cu}$ nuclear spin ($3/2$), whereas a marked difference is shown in the ESR spectra between the

dinuclear tmen and pm dt complexes. For the pm dt-dinuclear complex only one broad signal, which seems to originate from the collapse of many splittings, is observed. On the other hand, marked seven hyperfine splitting is identified in the spectra for the tmen-dinuclear complex. This can be explained by the relatively strong electron spin coupling (exchange interaction) between two $\text{Cu}(\text{II})$ ions. The reason for the observation of a single broadened signal for the pm dt-dinuclear complex is explained in the following two ways. (i) The substantially large intrinsic line width, *i.e.*, the short electron spin-spin relaxation time T_{2e} , conceals the hyperfine splitting as observed in the tmen-dinuclear complex. (ii) The exchange interaction between two electron spins on the $\text{Cu}(\text{II})$ ions is weaker than that in the tmen-dinuclear complex (the weak limit of the interaction gives four hyperfine splittings in the ESR spectra as the corresponding mononuclear complexes). Such intermediate electron spin coupling gives quite complicated spectra [28–30] and each peak is often

superimposed. The reason (i) is less important if there is no large change in the coordination structure between mono- and dinuclear pm dt complex, because the line width of each peak in the mononuclear pm dt complex is similar to that in the corresponding tmen one. If reason (ii) is important to give the difference in the ESR spectral pattern for the tmen-dinuclear and pm dt-dinuclear complexes, the weaker exchange interaction in the latter complex may be attributed to the difference in the coordination structures between these two complexes, *i.e.*, square planar–square planar and 5-coordinate–5-coordinate. The localized electron spin on the $d_{x^2-y^2}$ orbital in the Sq–Sq complex (the tmen-dinuclear complex) might give larger interaction.

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