© 1998 The Chemical Society of Japan

Solvatochromism and Structure of Acetylacetonatocopper(II) Complexes with *N*,*N*′-Dipropyl-, *N*,*N*,*N*′,*N*′-Tetrapropyl-, and *N*,*N*- and *N*,*N*′-Diisopropylethylenediamines

Hiroshi Miyamae,* Hideyuki Kudo, Goro Hihara, and Kozo Sone

Department of Chemistry, Faculty of Science, Josai University, Sakado, Saitama 350-0295

(Received June 1, 1998)

Seven copper(II) complexes of the general formula [Cu(acac)(diam)]X were prepared, where acac and diam stand for acetylacetonate and one of the diamines in the title, and X^- for a bulky univalent anion, respectively. Their solvatochromism was compared with that of the corresponding complexes with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine and related diamines, to see the effect of their bulky *N*-alkyl groups. X-ray crystal analyses showed that the perchlorates of *N*,*N*′- and *N*,*N*-diisopropyl complexes are apparently 6- and 5-coordinated, respectively, in their crystals, although their ClO_4^- ions are held extremely weakly and are easily driven out by solvent molecules in solution, leading to their solvatochromism. The Cu–N and Cu–O(acac) bond distances in the former, 199.5(4)/202.4(5) and 190.6(4)/190.1(4) pm, respectively, are similar to each other, while the Cu–N(isopropyl)$_2$ distance, 206.4(9) pm, in the latter is notably longer than the Cu–NH_2 distance, 196(1) pm.

Copper(II) complexes of ethylenediamine derivatives with *N*-methyl and *N*-ethyl groups are rather well known, but little has been reported on those with higher *N*-alkyl.[1)] Recently we prepared seven acetylacetonato complexes with such diamines, i.e., *N*,*N*′-dipropyl-, *N*,*N*,*N*′,*N*′-tetrapropyl-, and *N*,*N*′- and *N*,*N*-diisopropylethylenediamines (abbreviated, respectively, as *s*-dpen, tpen, and *s*- and *u*-dipen), containing a bulky univalent counter ion (ClO_4^- or BPh_4^-). As expected from the behaviors of the analogous complexes with *N*,*N*,*N*′,*N*′-tetramethyl- and -tetraethylethylenediamines (tmen and teen),[2—5)] these complexes were found to be soluble in a large number of organic solvents, and strongly solvatochromic. As in the preceding studies on the tmen- and teen-containing systems, the new complexes were studied by means of spectra, and two of them, the perchlorate salts of *s*- and *u*-dipen complexes, were studied further by X-ray crystal analyses, in particular with respect to the axial coordination onto their quasi-planar complex cations. The results obtained are reported in this paper.

Experimental

Materials. All the reagents and solvents used were G. R. grade chemicals of highest purity. The diamines were the products of Lancaster Synthesis Ltd.

Preparation of the Complexes. (i) Complex Perchlorates. Among the complexes **I** to **VII** in Table 1, **I** and **IV** were prepared by mixing $Cu(ClO_4)_2\cdot 6H_2O$, acacH, the diamine (diam), and Na_2CO_3 in the molar ratio of 1 : 1 : 1 : 0.5 in an ethanol–water mixture (1 : 1 by vol), and filtering and concentrating the resulting mixture. The obtained crystals were washed with hexane and dried in a desiccator. **VI** was prepared by the reaction of 1 mol of $[Cu_2(OMe)_2(u\text{-dipen})_2](ClO_4)_2$[6)] with 2 mols of acacH in methanol[7)] from which single crystals separated out on cooling.

(ii) Complex Tetraphenylborates. The complexes **II**, **III**, and **V** were prepared as in the case of **I** and **IV**, adding an excess of $NaBPh_4$ (4 mols per 1 mol of $Cu(ClO_4)_2$) to the filtered reaction mixture. Crystals of **V** separated out easily, and were washed with ethanol and water. **II** was obtained as a viscous mass, which was dried in a desiccator, powdered, and washed with hexane. In the case of **III**, ethanol was added ahead of $NaBPh_4$ to the filtered reaction mixture, making it about 0.02 mol dm^{-3} in Cu^{2+}, and water was added slowly to the final mixture. Crystals that separated out were recrystallized from acetone. Crystals of **VII** were prepared by adding 1 mol of $NaBPh_4$ to 1 mol of Cu^{2+} in the filtered reaction mixture of **VI**, and then adding water; they were washed with ethanol.

In general, the complexes obtained are stable in organic solutions, but **VI** decomposes in 1,2-dichloroethane (DCE) in a short time. The reason for this is not clear.

Physical Measurements. The UV-vis absorption spectra of the solutions (5×10^{-3} mol dm^{-3}), and the reflection spectra of powdery crystals, were recorded with a Shimadzu MPS-2000 spectrophotometer, the former with cells of 10 mm thickness. The magnetic moments μ were calculated from χ_{mol} values obtained with a Sherwood magnetic balance MSB-MKI after diamagnetic corrections.[8)]

X-Ray Crystal Analysis. The crystals of [Cu(acac)(*s*-dipen)]-ClO_4 (**IV**) and [Cu(acac)(*u*-dipen)]ClO_4 (**VI**) were obtained by recrystallization from an ethanol/water (1 : 1 by vol) mixture at ambient temperature. Intensities were measured on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71069 Å). The intensities of three standard reflections recorded every 150 measurements fluctuated within +1.1 to −1% for **IV** and 0 to −4% for **VI**, and no corrections for the deterioration were done. The data were corrected for Lp factors but not for absorption and extinction. Reflections with $I > 3\sigma(I)$ were regarded as observed.

Table 1. Color, Yields, Analytical Data, Magnetic Moments (μ_{corr}), and $\tilde{\nu}_{max}$ Values of the Solid Complexes Obtained

No.	Formula (Color/Yield)	Analysis[a)] H/%	C/%	N/%	μ_{corr}/B.M.	$\tilde{\nu}_{max}/10^3$ cm^{-1}
I	[Cu(acac)(*s*-dpen)]ClO$_4$	6.51	38.17	6.95	1.77	17.7
	(Bluish Violet/63%)	(6.70)	(38.42)	(6.89)		
II	[Cu(acac)(*s*-dpen)]BPh$_4$	7.49	69.36	4.42	1.77	18.1
	(Pale Bluish Violet/69%)	(7.57)	(70.97)	(4.47)		
III	[Cu(acac)(tpen)]BPh$_4$	8.41	73.34	3.90	1.73	20.2
	(Pale Reddish Violet/69%)	(8.37)	(72.71)	(3.94)		
IV	[Cu(acac)(*s*-dipen)]ClO$_4$	6.44	37.98	6.84	1.83	18.4
	(Violet/47%)	(6.70)	(38.42)	(6.89)		
V	[Cu(acac)(*s*-dipen)]BPh$_4$	7.53	70.72	4.48	1.80	18.1
	(Pale Violet/51%)	(7.57)	(70.97)	(4.47)		
VI	[Cu(acac)(*u*-dipen)]ClO$_4$	6.53	38.31	6.95	1.83	17.6
	(Bluish Violet/32%)	(6.70)	(38.42)	(6.89)		
VII	[Cu(acac)(*u*-dipen)]BPh$_4$	7.50	70.20	4.44	1.77	17.9
	(Pale Bluish Violet/62%)	(7.57)	(70.97)	(4.47)		

a) Calculated values are in parentheses.

The unit cell dimensions were calculated from the least-squares fit of 25 2θ values of $15 < 2\theta < 20°$ or $16 < 2\theta < 20°$ measured on the diffractometer for **IV** and **VI**, respectively. They are listed in Table 2.

The structures were solved by the heavy atom method. The Cu atom was located from the Patterson map, and successive *D*-maps showed the positions of non-H atoms. The structures were refined by full-matrix least-squares, assuming anisotropic thermal parameters. H-atoms were located from calculation with fixed isotropic thermal parameters equal to 3/2 U_{eq} for the atom to which they are attached, except for the H031 of 5/4 U_{eq} of the mother C atom. Atomic coordinates for non-H atoms are given in Table 3. Anisotropic thermal parameters, coordinates of H atoms, observed and calculated scattering factors, bond distances and angles, short contacts between the ions, and dihedral angles with calculated best planes are deposited as Document No. 71055 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Table 2. Crystal Data

Compound	IV	VI
Chemical formula	$CuC_{13}ClH_{27}N_2O_6$	
Formula weight	406.4	
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	*Pbca*
a/Å	8.490(3)	16.504(6)
b/Å	15.383(6)	29.216(6)
c/Å	8.232(4)	7.581(5)
α/°	98.00(4)	90
β/°	117.68(3)	90
γ/°	84.44(3)	90
V/Å^3	942.2(7)	3655.4(28)
Z	2	8
D_X/g cm^{-3}	1.432	1.476
D_m/g cm^{-3}	Not measured	
μ(Mo $K\alpha$)/mm^{-1}	1.33	1.37
F(000)	426	1704
Scan mode	θ–2θ	θ–2θ
Crystal size/mm^3	$0.55 \times 0.25 \times 0.25$	$0.5 \times 0.3 \times 0.1$
No. of rfls (obs. $I > 3\sigma(I)$)	2674	1664
No. of rfls (meas.)	4846	4965
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.060	0.069
$wR = [\Sigma w(F_o - F_c)^2/\Sigma w F_o^2]^{1/2}$	0.037	0.057
$S = [\Sigma w(F_o - F_c)^2/n - m)]^{1/2}$	3.518	2.961
Max. $\Delta(\rho)$/e Å^{-3}	.6	.8
Min. $\Delta(\rho)$/e Å^{-3}	−0.6	−0.6
Max. Δ/σ	0.10	0.07

All of the calculations were done using the Xtal 3.2 program system[9)] on a SUN-470 workstation at the Computer Center of Josai University.

Results and Discussion

The color, analytical data, magnetic moments (μ), and $\tilde{\nu}_{max}$ values of the d–d band in solid reflection spectra of the complexes obtained (**I**—**VII**) are shown in Table 1. They confirm their formulation given in the Table, and indicate that they are typical CuN_2O_2 complexes without any obvious magnetic or spectral anomalies.

Solvatochromism in Organic Solvents. Figure 1 shows the visible spectra of the complex **III** in a number of organic solvents. As was the case with the well-known complexes [Cu(acac)(tmen)]X and [Cu(acac)(teen)]X, the d–d band observed at 500—600 nm moves to the red with the increase of the *DN* (Gutmann's Donor Number) of the solvent. Similar spectral changes are shown by all other complexes obtained; the changes of their d–d band are summarized in Table 4 and are compared with those of the tmen, teen, and dipe (dipe = 1,2-dipiperidinoethane; see below) complexes in Fig. 2.

In general, the perchlorate and tetraphenylborate of the same complex cation, i.e. **I** and **II**, **IV** and **V**, or **VI** and **VII**, show nearly the same $\tilde{\nu}_{max}$ in most solvents. An exception is DCE in which the value of the complex perchlorate is notably

Table 3. Fractional Coordinates of Non-H Atoms with U_{eq}

Atom	x	y	z	U_{eq}
(a) [Cu(acac)(*s*-dipen)]ClO$_4$ (**IV**)				
Cu	0.03045(10)	0.21945(5)	0.21274(11)	0.05077
O01	0.1205(5)	0.1092(2)	0.3049(5)	0.05648
O02	−0.1949(5)	0.1753(2)	0.0378(5)	0.05467
C01	0.1282(9)	−0.0365(4)	0.3643(10)	0.09041
C02	0.0289(9)	0.0407(4)	0.2588(9)	0.06007
C03	−0.1462(9)	0.0348(4)	0.1253(9)	0.05720
C04	−0.2491(8)	0.0997(4)	0.0182(8)	0.05065
C05	−0.4343(8)	0.0841(4)	−0.1230(8)	0.06919
N1	0.2654(6)	0.2731(3)	0.3770(6)	0.04976
N2	−0.0496(6)	0.3405(3)	0.1285(7)	0.05459
C1	0.2654(8)	0.3594(4)	0.3165(9)	0.06595
C2	0.0821(8)	0.4019(4)	0.2651(9)	0.06624
C11	0.4335(7)	0.2180(4)	0.4201(8)	0.05201
C12	0.5942(8)	0.2637(4)	0.5689(9)	0.07332
C13	0.4492(8)	0.1850(4)	0.2467(9)	0.07442
C21	−0.2410(7)	0.3693(4)	0.0656(8)	0.05346
C22	−0.2830(8)	0.3907(5)	0.2263(9)	0.09413
C23	−0.2927(8)	0.4475(4)	−0.0407(9)	0.07365
Cl	0.1084(3)	0.2936(1)	−0.2625(3)	0.06683
O1a	0.0171(6)	0.2523(3)	−0.4426(6)	0.09917
O1b	0.2779(6)	0.3123(4)	−0.2220(7)	0.14230
O1c	0.0148(7)	0.3679(3)	−0.2342(8)	0.14235
O1d	0.1103(8)	0.2359(4)	−0.1423(7)	0.15910
(b) [Cu(acac)(*u*-dipen)]ClO$_4$ (**VI**)				
Cu	0.55870(10)	0.36554(6)	0.83693(23)	0.03778
O01	0.4822(5)	0.3164(3)	0.8365(13)	0.04316
O02	0.6373(6)	0.3318(3)	0.9592(12)	0.04308
N1	0.6420(6)	0.4145(3)	0.7579(17)	0.03503
N2	0.4736(7)	0.4078(4)	0.7578(15)	0.04132
C2	0.5073(9)	0.4551(5)	0.7573(22)	0.05373
C1	0.5905(9)	0.4543(4)	0.6900(18)	0.03994
C11	0.6970(8)	0.4301(5)	0.9037(20)	0.04018
C111	0.6477(10)	0.4465(5)	1.0608(20)	0.06255
C112	0.7601(9)	0.4662(5)	0.8602(20)	0.05429
C12	0.6919(8)	0.3951(5)	0.6127(19)	0.04380
C121	0.6368(9)	0.3691(6)	0.4805(20)	0.06890
C122	0.7575(8)	0.3606(5)	0.6600(22)	0.06477
C01	0.4173(9)	0.2483(6)	0.9161(23)	0.08053
C02	0.4886(10)	0.2801(5)	0.9229(21)	0.05246
C03	0.5576(11)	0.2684(4)	1.0231(20)	0.05128
C04	0.6253(9)	0.2933(5)	1.0360(19)	0.04082
C05	0.7002(9)	0.2750(5)	1.1339(20)	0.06454
Cl	0.4055(3)	0.4038(1)	1.2431(7)	0.05638
O1	0.4616(8)	0.3753(4)	1.1645(17)	0.11816
O2	0.3682(9)	0.4328(5)	1.1193(19)	0.14984
O3	o.4459(9)	0.4339(4)	1.3619(16)	0.11673
O4	0.3489(10)	0.3766(6)	1.3186(23)	0.19441

lower. This can be ascribed to the formation of ion pairs, as was pointed out in the case of the tmen complex.[10)]

The data in Fig. 2 clearly show that the dipropyl and diisopropyl complexes (**I**–**II**, **IV**–**VII**) are much less solvatochromic than the tetrapropyl compex **III**, i.e. the decrease of $\tilde{\nu}_{max}$ values of the former complexes in going from **a** to **f** (2.2—2.7×10^3 cm^{-1}) is much less than that of the latter (4.0×10^3 cm^{-1}), which lies between those of the tmen and teen complexes (3.4 and 5.1×10^3 cm^{-1}, respectively). The $\tilde{\nu}_{max}$ values of the former complexes in any solvent shift gradually to the red in the order of **I**–**II**<**IV**–**V**<**VI**–**VII**, or

$$s\text{-dpen} < s\text{-dipen} < u\text{-dipen}, \qquad (1)$$

and the complexes become somewhat more solvatochromic in the same order. It is interesting to note that similar trends

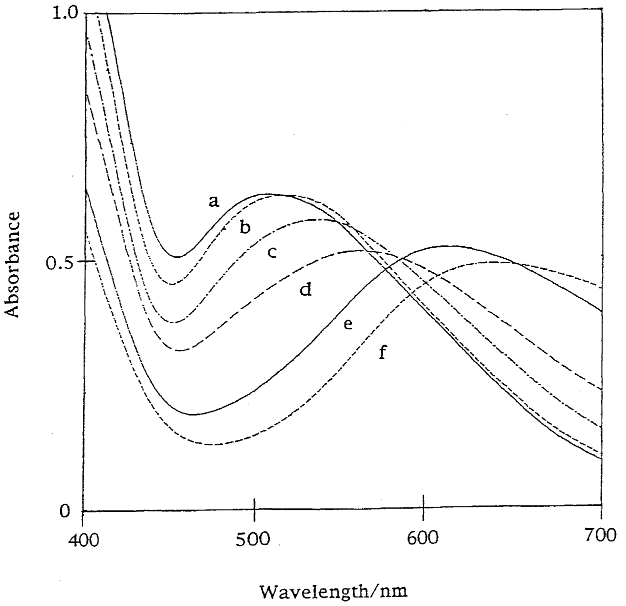

Fig. 1. The visible spectra of **III** in various organic solvents. The curves **a** to **f** (from left to right) represent, respectively, those in 1,2-dichloroethane, nitromethane, acetone, methanol, DMF, and DMSO. Concn 5×10^{-3} mol dm^{-3}.

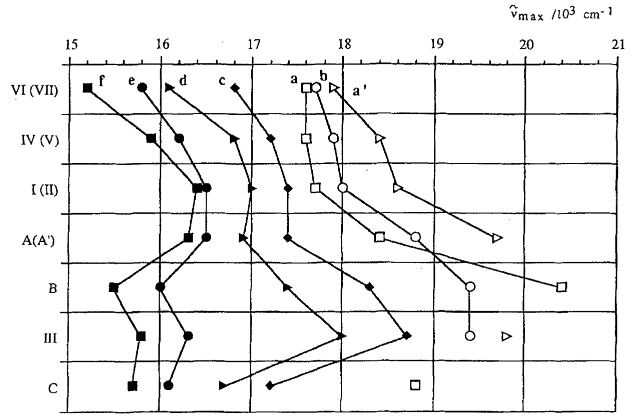

Fig. 2. $\tilde{\nu}_{max}$ values of complexes **I**, **III**, **IV**, and **VI** in various organic solvents are shown together with those of [Cu(acac)(tmen)]ClO$_4$ (**A**),[10] [Cu(acac)(teen)]ClO$_4$ (**B**),[14] and [Cu(acac)(dipe)]ClO$_4$ (**C**).[13] The meaning of the symbols **a** to **f** are the same as in Fig. 1. The $\tilde{\nu}_{max}$ values for **II**, **V**, **VII**, and [Cu(acac)(tmen]BPh$_4$ (**A′**),[10] are nearly the same as those of **I**, **IV**, **VI**, and A respectively, except in 1,2-dichloroethane where their values (and that of **III**) are given with **a′** (see text).

have been observed in the case of similar complexes with *s*- and *u*-deen (*N,N′*- and *N,N*-diethylethylenediamine).[2,3,11]

It is now known that these spectral changes are due, in the main, to the changes in the degree of axial solvation of the complexes. This solvation, which tends to shift the d–d band to the red, is increased by the donor power (*DN*) of the solvent, but hampered by the steric hindrance of the *N*-alkyl groups. In the complexes of tmen, teen, and deen, it is known that the increase of this steric hindrance tends to make the complex more solvatochromic, bringing about a larger structural change with progressive solvation of the complex caused by the increase of *DN*.[2,3]

The order (1) can now be taken as that of the increase of this steric hindrance, which is expected to change in this way,[12] or as that of the decrease of N_2O_2 ligand field strength in the complexes, since ligands with larger steric hindrance are usually bound more weakly, shifting the d–d band to the red. So the spectral features of the dipropyl or diisopropyl complexes may be explained, at least qualitatively, on the basis of these concepts.

In the case of the complex **III**, the steric hindrance to axial solvation caused by its four propyl groups gets very strong, causing a drastic solvatochromism as in the case of the tmen and teen complexes.[2,3,12] The solvatochromic changes among these complexes, in the main, vary in the order tmen<teen>tpen; it can be noted that, in going from teen to tpen, the steric hindrance gets so strong that the d–d band in most solvents is shifted to the blue (except in those of very low *DN* where an opposite shift takes place, possibly

Table 4. Electronic Spectra of the Complexes in Various Solvents: $\tilde{\nu}_{max}$ Values with ε_{max} in Paretheses

Complex[a)]	$\tilde{\nu}_{max}$/10^3 cm^{-1} (ε_{max})					
	DMSO (**f**)	DMF (**e**)	MeOH (**d**)	Acetone (**c**)	MeNO$_2$ (**b**)	DCE (**a**)
I	16.4	16.5	17.0	17.4	18.0	17.7
	(101)	(96)	(92)	(88)	(88)	(92)
II	16.2	16.4	16.8	17.2	18.2	18.6
	(96)	(92)	(90)	(88)	(87)	(87)
III	15.8	16.3	18.0	18.7	19.4	19.8
	(98)	(104)	(103)	(114)	(126)	(126)
IV	15.9	16.2	16.8	17.2	17.9	17.6
	(97)	(92)	(88)	(92)	(96)	(89)
V	15.9	16.2	16.8	17.2	18.1	18.4
	(96)	(90)	(87)	(89)	(91)	(104)
VI	15.2	15.8	16.1	16.8	17.7	17.6
	(131)	(120)	(107)	(107)	(81)	(99)
VII	15.2	15.8	16.1	16.8	17.6	17.9
	(117)	(115)	(101)	(110)	(89)	(86)

a) Cf. Table 1.

due to the decrease of ligand field), leading to a decrease of solvatochromism with increasing steric effect.

The spectra of $[Cu(acac)(dipe)]ClO_4$[13] is interesting in this connection. This complex is much less solvatochromic than **III**, and its d–d band is shifted to the red, somewhat like the dipropyl and diisopropyl complexes. This is certainly related to the rigidity of its piperidyl groups which limits the steric hindrance to axial solvation.

Now another kind of solvatochromism is observed at the blue end of the spectra in Fig. 1; here the absorption curve, which ascends monotonously toward UV where the strong bands of acac appear, is strongly shifted toward UV in going from nonpolar to polar solvents, approximately in the order of increasing *DN*, even after corrections for the overlapping d–d band. The same kind of spectral shift, which is opposite to that of the d–d band, is observed in the other complexes studied, and also in similar complexes with tmen and teen.[10,14] This may be due to the presence of a ligand-to-metal (probably acac-to-Cu(II)) CT band in the near UV underlying the absorption in question, whereas the energy for such a CT will increase with increasing solvation of the chelate.[15,16]

Structures of Diisopropyl Complexes. Structures of the *s*- and *u*-dipen complexes **IV** and **VI**, and their crystals, are shown in Figs. 3, 4, and 5, and important numerical data in them in Tables 3 and 5.

The complex cation in **IV** is nearly planar and almost has 2-fold symmetry; the two Cu–N bonds in it are practically of the same distance (199.5(4)/202.4(5) pm), as well as the two Cu–O bonds (190.6(4)/190.1(4) pm). The former distances are similar to those observed in some $[Cu(en)_2]^{2+}$ complexes.[17] The dihedral angle between CuO_2 and CuN_2 coordination planes is 3.4(2)°. The isopropyl groups protrude in equatorial directions on each side of the chelate plane, minimizing the steric hindrance to axial coordination. The five membered chelate ring is puckered; the torsion angle of N1–Cl–C2–N2 of −52.7(8)° is quite normal, but the mean value of 39.4(7)° for C–C–N–Cu in the chelate shows a slight deformation.

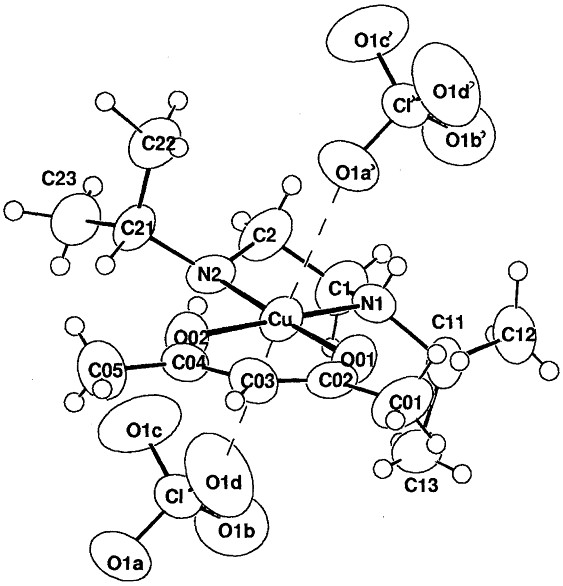

Fig. 3. Structure of **IV** with the numbering of C, N, and O atoms.

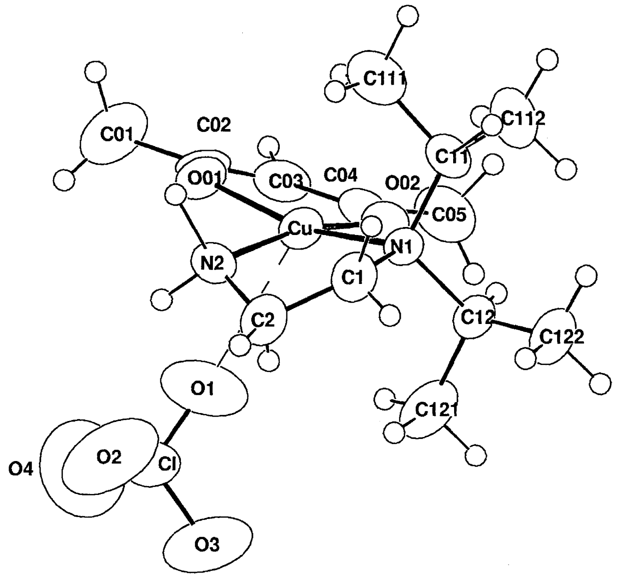

Fig. 4. Structure of **VI** with the numbering of C, N, and O atoms.

Two ClO_4^- ions lie above and below the chelate; the distances of their Cu–O contact, 286.6(6) and 334.4(8) pm, are much longer than the sum of the radii of Cu^{2+}(CN 6) and O^{2-} (213 pm), and comparable with, or even longer than, the sum of the van der Waals radii of Cu and O (290 pm).[18] The Cu–O(ClO_4) distances found in Cu(II) complexes lie, in general, between these extremes; when two ClO_4^- ions are coordinated axially to a planar complex of Cu(II) with neutral ligands, the Cu–O(ClO_4) bond distances are ca. 255 pm (259.4(3) pm for $[Cu(eten)_2](ClO_4)_2$;[19] 253.9(2) pm for $[Cu(Me_4\text{-}232\text{-}tet)(ClO_4)_2]$;[20] 253.0(3) & 257.3(3) pm for $[Cu(\alpha,\omega,\text{-}N\text{-}Me_2\text{-}232\text{-}tet)(ClO_4)_2]$;[21] 246.6(8) & 264.0(8) pm for $[Cu(dmso)_4](ClO_4)_2$;[22] eten = *N*-ethylethylenediamine; Me_4-232-tet = 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane, α,ω-*N*-Me_2-232-tet = 2,5,9,12-tetraazatridecane, and dmso = dimethyl sulfoxide), while that for a complex with only one ClO_4^- ion, $[Cu(ClO_4)(Me_2\text{-}232\text{-}tet)]ClO_4$ (Me_2-232-tet = 1,9-diamino-3,7-dimethyl-3,7-diazanonane),[23] is slightly longer (262.0(3) pm).

Thus the Cu–O(ClO_4) distances observed in the *s*-dipen complex are by far the longest. The distance shows that the forces holding ClO_4^- ions in this complex are marginally weak. Such ions will be easily driven out from the coordination sphere by solvent molecules in solution, which will be more sensibly bonded with the increase in their donor power, leading to the observed solvatochromism.

The cation in **VI**, on the other hand, is very different. Here one of the two Cu–N bonds (Cu–N(isopropyl)$_2$: 206.4(9) pm) is notably longer than the other (Cu–NH_2: 196.2(10) pm), as in the case of $[Cu(u\text{-}deen)_2](ClO_4)_2$.[19] This difference induces a smaller change in the distances of the Cu–O bonds that are *trans* to them (191.9(8)/188.2(8) pm), and a twist of the two coordination planes (20.3(4)°) with respect

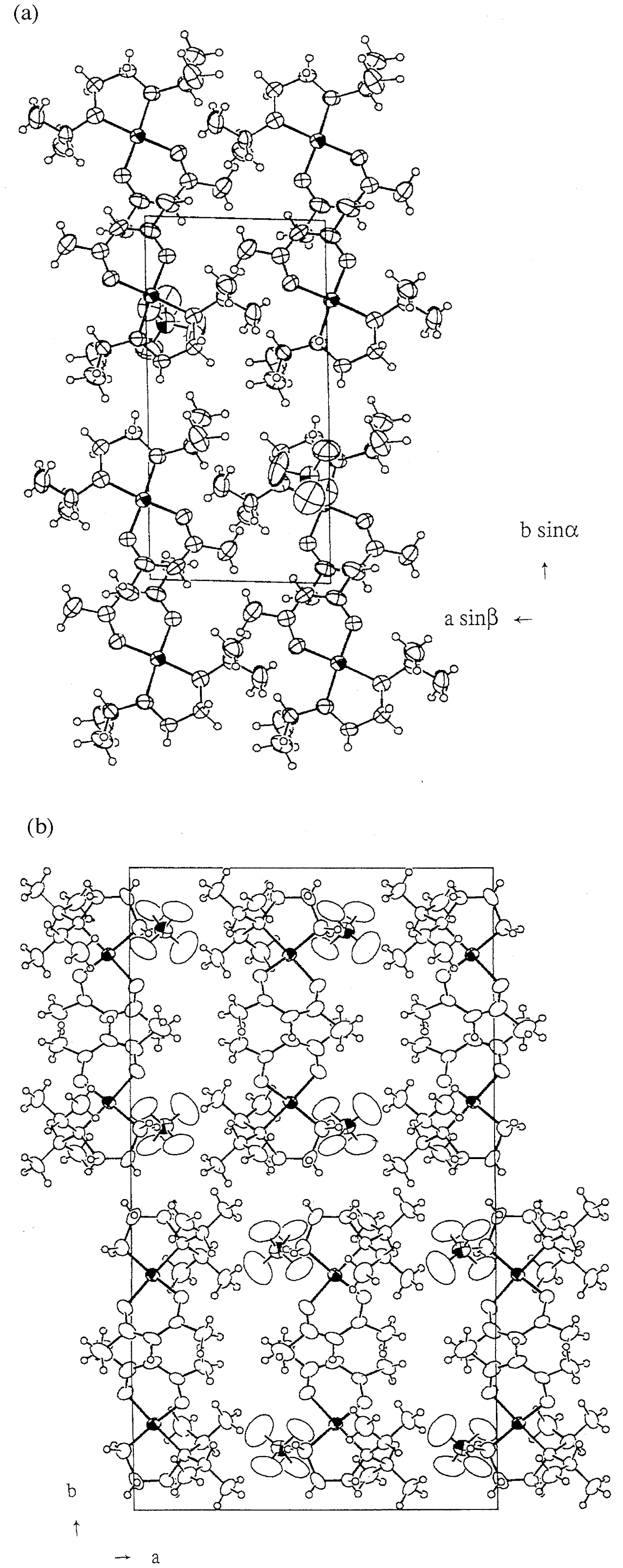

Fig. 5. Crystal packing of **IV** (a) and **VI** (b).

Table 5. Selected Bond Distances/pm and Angles/° around Cu Atom, and Dihedral Angles/° among CuN_2, CuO_2, and acac Planes

Compound	IV	VI
Cu–N(1)	202.1(5)	207.1(10)
Cu–N(2)	199.8(4)	196.8(11)
Cu–O(1)	190.1(3)	191.4(9)
Cu–O(2)	189.9(4)	188.4(9)
Cu···O–ClO_3	286.5(6)/333.8(8)	297(1)
N(1)–Cu–N(2)	85.1(2)	87.3(4)
O(1)–Cu–O(2)	93.5(2)	93.8(4)
CuN_2 and CuO_2	3.7(2)	20.3(4)
CuN_2 and acac	4.3(2)	21.1(4)
CuO_2 and acac	5.1(2)	9.2(5)

to each other. One of the two isopropyl groups now protrudes strongly above the Cu atom, blocking one of the axial positions, so that only a ClO_4^- ion can contact it, again marginally weakly, from below (Cu–O: 297.4(9) pm), approaching from the side of the NH_2 group. Steric hindrance of two bulky substituents on the same N atom lowers the torsion angle of N1–C1–C2–N2 to −43(1)°, and compresses that of Cu–N1–C1–C2 much more strongly to 24(1)°.

So the strong steric effect of the very bulky N(isopropyl)$_2$ group makes the complex **VI** strongly unsymmetric and deformed, leading to a 5-coordinated structure. The decrease of its apparent ligand field accompanying such structural changes are reflected in its $\tilde{\nu}_{\max}$ values in crystals (Table 1), which is notably lower than that in **IV**. In solution, however, most of these structural anomalies (in particular, the strong interligand twist which imposes the 5-coordination) seem to be removed under the interaction with solvent molecules, so that solvatochromic changes that are essentially similar to those of **IV** take place.

Crystal Packing. The packing modes of **IV** and **VI** are slightly different. In **IV**, two complex cations form a dimeric unit with overlapping acac ligands. The units form a belt along the *a*-axis, in which one of the two isopropyl groups of a complex lies between the methyl and isopropyl groups of the neighboring unit, while the other is directed outside the belt. The latter isopropyl group is in contact with another belt to stay in an aliphatic circumstance, forming a sheet along the *ab*-plane. The sheets are connected through weak contacts of Cu···O–(ClO_2)–O···Cu along the *c*-axis. In addition, there are two kinds of bifurcated O···H–N hydrogen bonds, which support the stacking, i.e., (a) O1c and O1d with N2 of 337(1) and 329(1) pm, and (b) O1a and O1b with $N1^i$ of 314.3(9) and 321.8(9) pm, where the symmetry operation i: $x, y, z-1$.

Although there is no effective overlapping of acac ligands in **VI**, its complex cations form dimeric units as in the case of **IV**. The isopropyl groups in such a unit are gathered on the same side of it, and belts of two rows of cations are formed along the *a*-axis. A ClO_4^- anion is accommodated in a vacancy between bulky isopropyl and flat amino groups. In this situation, a ClO_4^- can form a Cu–O contact and two kinds of O···H–N hydrogen bonds, O2···H–N2 and O3···H–$N2^{ii}$ of 335(2) and 311(2) pm respectively, where ii: $x, y, z+1$. The belts are set in a way that the isopropyl groups approach each other.

Owing to the good packing of bulky isopropyl and ClO_4^- anions observed in **VI**, the density of its crystal (1.476 $g\,cm^{-3}$) is slightly higher than that of **IV** (1.432 $g\,cm^{-3}$).

References

1) Cf. D. A. House, "Comprehensive Coordination Chemistry," ed by G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Pergamon, Oxford (1987), Vol. 2, p. 23 ff.

2) K. Sone and Y. Fukuda, "Ions and Molecules in Solution," Elsevier, Amsterdam (1983), p. 251.

3) K. Sone and Y. Fukuda, "Inorganic Thermochromism," Springer, Heidelberg (1987).

4) R. W. Soukup and R. Schmid, *J. Chem. Educ.*, **62**, 459 (1985).

5) M. Sandström, I. Persson, and P. Persson, *Acta Chem. Scand.*, **44**, 653 (1990).

6) This complex is obtained by concentrating a 1 : 2 mixture of $Cu(ClO_4)_2 \cdot 6H_2O$ and *u*-dipen in methanol. Cf. T. Masutani, B. S. Thesis, Josai University, Japan, 1995.

7) Y. Fukuda, A. Shimura, M. Mukaida, E. Fujita, and K. Sone, *J. Inorg. Nucl. Chem.*, **36**, 1265 (1974).

8) R. L. Carlin, "Magnetochemistry," Springer, Heidelberg (1986), p. 3.

9) S. R. Hall, D. F. Howard, and J. M. Sewart, "Xtal 3.2 Reference Manual," University of Western, Australia (1992).

10) R. W. Soukup and K. Sone, *Bull. Chem. Soc. Jpn.*, **60**, 2286 (1987).

11) A. B. P. Lever and E. Mantovani, *Inorg. Chem.*, **10**, 817 (1971).

12) This is because (i) bulky *N*-isopropyl groups are expected to be more sterically active than *N*-propyl groups, and (ii) *N*-alkyl groups in *s*-complexes of *en* derivatives usually tend to occupy equatorial positions with respect to the chelate ring, in *u*-dipen, however, one such group is forced to occupy an axial position, increasing axial steric hindrance (cf. Ref. 1).

13) Y. Fukuda, M. Cho, and K. Sone, *Bull. Chem. Soc. Jpn.*, **62**, 51 (1989).

14) Y. Fukuda, Y. Miura, and K. Sone, *Bull. Chem. Soc. Jpn.*, **50**, 142 (1977).

15) Other kinds of Cu(II) complexes also show similar CT bands in near UV. Cf. e.g., S. Kida, Y. Nishida, and M. Sakamoto, *Bull. Chem. Soc. Jpn.*, **46**, 2428 (1973).

16) K. Sone and Y. Fukuda, *Rev. Inorg. Chem.*, **11**, 123 (1991).

17) Y. Komiyama and E. C. Lingerfelter, *Acta Crystallogr.*, **17**, 1145 (1964); B. W. Brown and E. C. Lingerfelter, *Acta Crystallogr.*, **17**, 254 (1964).

18) J. E. Huheey, "Inorganic Chemistry," 3rd ed, Harper International, p. 258 (1983).

19) I. Grenthe, P. Paoletti, M. Sanderström, and S. Glikberg, *Inorg. Chem.*, **18**, 2687 (1979).

20) A. Wang, T. -J. Lee, T. -Y. Chi, F. -L. Liao, G. -S. Liu, and C. -S. Chung, *Acta Crystallogr., Sect. C*, **C52**, 806 (1996).

21) T. -L. Liu, Y. -L. Liu, and C. -S. Chung, *Acta Crystallogr., Sect. C*, **C51**, 2275 (1995).

22) A. J. Blake, R. S. Grimditch, S. Parsons, and M. Schröder, *Acta Crystallogr., Sect. C*, **C52**, 514 (1996).

23) T. -H. Lu, J. -L. Lin, K. Shu, Y. -Z. Yuan, and C. -S. Chung, *Acta Crystallogr., Sect. C*, **C49**, 2112 (1993).