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Studies on Mixed Chelates. XXII. Five-Coordinate Copper(II) Chelates with *N*,*N*,*N'*,*N''*,*N''*-Pentamethyldiethylenetriamine and *β*-Diketonates[1)]

Noriko Shintani, Etsuko Nukui, Hiroshi Miyamae,† Yutaka Fukuda,*,†† and Kozo Sone*
Department of Chemistry, Faculty of Science, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112
† Department of Chemistry, Faculty of Science, Josai University, Sakado, Saitama 350-02
†† Coordination Chemistry Laboratories, Institute for Molecular Science, Myodaiji, Okazaki, Aichi 444

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Mixed Cu(II) chelates with *N*,*N*,*N'*,*N''*,*N''*-pentamethyldiethylenetriamine (pmdt) and five *β*-diketonate (dike) ligands, i.e., dipivaloylmethanate (dipm), acetylacetonate (acac), pivaloyltrifluoroacetonate (pfac), trifluoro- and hexafluoroacetylacetonate (tfac and hfac, respectively), were prepared and studied. Their general formula, $[Cu(dike)(pmdt)]ClO_4$, suggests that they are five-coordinated; X-ray crystal analyses confirmed that the chelates with acac and tfac are distorted square pyramidal, with the axial site occupied by one of the O atoms of dike. Similar structures are presumed for the remaining chelates on the basis of spectral similarities. In solutions, these five-coordinated chelates are solvated to various extents, showing a characteristic solvatochromism.

In connection with the foregoing studies concerning the five-coordinated mixed chelates, $[Ni(dike)(pmdt)]ClO_4$ (dike = a *β*-diketonate, pmdt = *N*,*N*,*N'*,*N''*,*N''*-pentamethyldiethylenetriamine),[2)] we prepared the corresponding Cu(II) chelates, and studied in some detail their structure as well as solvatochromic changes.

Compared with the Ni(II) chelates, which tend to change easily into six-coordinated species in polar solvents, the Cu(II) chelates seem to keep their five-coordinated square pyramidal framework in solution, since their spectra are influenced by the solvent to a smaller extent. Closer observations, however, have revealed the existence of a characteristic solvatochromism, which can be understood in terms of the solvation of the dissolved species. Structural and spectral data concerning these chelates, and a relevant discussion, are given in this paper.

Experimental

Preparation of Mixed chelates, $[Cu(dike)(pmdt)](ClO_4)$ (dike=dipm, acac, pfac, tfac, or hfac).[3)] The method used was practically the same as that used in the case of the Ni(II) chelates,[2)] except that (i) $Cu(ClO_4)_2 \cdot 6H_2O$ was used instead of $Ni(ClO_4)_2 \cdot 6H_2O$, and (ii) in the case of the acac chelate, MeOH was used for recrystallization, since 1,2-dichloroethane (DCE) leads to the disproportionation and separation of $Cu(acac)_2$.

Physical Measurements. The methods used in the spectral, magnetic and conductivity measurements were given in previous papers.[2,4)] The color, analytical data and magnetic moments of the new chelates are given in Table 1.

Crystal Structure Analyses. (A) $[Cu(acac)(pmdt)]ClO_4$: The crystals were grown from a MeOH solution. A bluish-green crystal having approximate dimensions of 0.4×0.3×0.25 mm was used. The unit-cell dimensions were refined by a least-squares fit for 30 reflections in the $29° < 2\theta < 32°$ range, measured on a Rigaku AFC-5 diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71069 Å). The crystallographic data are given in Table 2.

The reflections were collected in a 2θ–ω scan mode, up to $2\theta=60°$, with scan widths of $\Delta\omega=(1.0+0.5 \tan\theta)°$. The backgrounds were counted for 6 s at both ends of the scan. These standard reflections were recorded after every 150 measurements, and fluctuated within ±3%. A total of 3339 reflections were measured at a rate of 4° min^{-1} in ω, of which 2644 independent reflections were treated as being significant ($|F_o| > 3\sigma(|F_o|)$). The structure was solved by a heavy-atom method, and was refined by block-diagonal least-squares using the program system UNICS-III.[5)]

The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = (\sigma(F_o)^2 + 0.004|F_o|^2)^{-1}$. Atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[6)] All of the non-H atoms were refined anisotropically. The H atoms were located at the calculated positions. The final R (R_w) was 0.049 (0.045), which converged at 0.052 (0.049) for the enantiomer. The computations were carried out on a FACOM M-360 computer at the Computer Center of Josai University. The tables for the anisotropic thermal parameters of non-H atoms (Table A), the atomic parameters of the H atoms (Table B), the $F_o - F_c$ list (Table C) and the remaining bond distances and angles (Table D) are deposited as Document No. 67035 at the Office of the Editor of Bull. Chem. Soc. Jpn.

(B) $[Cu(tfac)(pmdt)]ClO_4$. The crystals were grown from a MeOH solution. A green crystal having approximate dimensions of 0.3×0.3×0.1 mm was used. The lattice constants were determined by least-squares calculations from 16 reflections over the $25° < 2\theta < 32°$ range. The crystal data are compared with the acac compound in Table 2.

The method used for data collection was essentially the same as that used in the case of $[Ni(acac)(pmdt)]ClO_4$.[2)] The reflections were measured up to $2\theta=60°$. Three standard reflections measured at each 150 measurements fluctuated within ±3%. From among the 3437 independent reflections measured, 2437 were used for the analysis, for which $|F_o| > 3\sigma(|F_o|)$.

The structure was solved by a direct method using MULTAN 78.[7)] Since it was found that there is a disorder of

Table 1. Analytical Data, Color, and Magnetic Moments of the New Chelates

	H/%	C/%	N/%	Color	μ_{eff}/B.M.
[Cu(dipm)(pmdt)]ClO_4	7.97	46.09	8.14	Bluish green	1.98
	(7.97)[a]	(46.32)	(8.10)		
[Cu(acac)(pmdt)]ClO_4	6.77	38.89	9.61	Bluish green	1.96
	(6.94)	(38.62)	(9.65)		
[Cu(tfac)(pmdt)]ClO_4	5.40	34.12	8.53	Blue	1.87
	(5.56)	(34.36)	(8.59)		
[Cu(pfac)(pmdt)]ClO_4	6.07	37.79	7.76	Blue	1.83
	(6.26)	(38.42)	(7.91)		
[Cu(hfac)(pmdt)]ClO_4	4.35	30.85	7.43	Blue	1.91
	(4.45)	(30.95)	(7.73)		

a) Calculated values are in parentheses.

Table 2. Crystal Data of the acac and tfac Chelates

Chelate	[Cu(acac)(pmdt)]ClO_4 ($CuC_{14}ClH_{30}N_3O_6$)	[Cu(tfac)(pmdt)]ClO_4 ($CuC_{14}ClF_3H_{27}N_3O_6$)
Formula weight	435.4	489.4
Space group	$P2_1$	$P2_1$
a/Å	8.780(2)	9.708(2)
b/Å	13.567(2)	13.020(2)
c/Å	8.566(1)	8.461(2)
β/°	91.77(1)	90.22(2)
V/Å^3	1019.9(2)	1069.4(4)
Z	2	2
d_x/g cm^{-3}	1.417	1.519
μ/cm^{-1}	12.35	12.05
$F(000)$	458	506

ClO_4^- ions, their O atoms could not be located with certainty. Thus, the O atoms for ClO_4^- were located as 3 sets with equivalent weight (1/3). For the present, therefore, only the positions of the non-ClO_4^- and non-H atoms could be refined anisotropically using block-diagonal least-squares, as in the case of [Ni(acac)(pmdt)]ClO_4, with R=0.068 (R_w=0.056). The quantity minimized was the same as that in (A). The tables for the anisotropic thermal parameters for non-H atoms (Table E), the atomic parameters of the H atoms (Table F), the F_o-F_c list (Table G) and the remaining bond distances and angles (Table H) are also deposited as Document No. 67035 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Both the acac and tfac complexes are isostructural. The results of these crystal analyses, and the structures of the chelate cations deduced from them, are shown in Tables 3 and 4 and Figs. 1, 2, and 3.

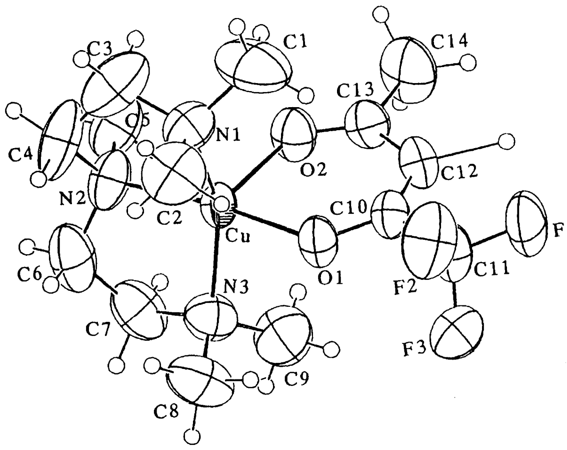


Fig. 1. The structure of the tfac chelate, with the numbering of the C, N, O, and F atoms. The structure of the acac chelate is nearly the same, except that the F atoms are lacking.

Results and Discussion

Structure and Properties of the Chelates Obtained in the Solid State. The data in Table 1 show that (i) the compositions of the five new chelates are all compatible with their formulation as [Cu(dike)(pmdt)]ClO_4; (ii) they are normal Cu(II) chelates, each with one unpaired electron; and (iii) they are green to blue in color; the $\tilde{\nu}_{max}$ of their powder reflection spectra in Table 5 are quite low, lying at the red part of the visible spectrum, and increasing in the order

$$\text{dipm} < \text{acac} < \text{pfac} \approx \text{tfac} < \text{hfac},$$

i.e., in the order of decreasing basicity (or ligand field strength (l.f.s.)) of dike.[2] All of these data strongly suggest that these chelates are five-coordinated, and, in particular, that they assume a structure which is essentially similar to that found in [Ni(dike)(pmdt)]ClO_4, i.e., an approximately square pyramidal structure, in which one of the O atoms of dike occupies the axial

Table 3. Atomic Parameters for [Cu(acac)(pmdt)]ClO_4 (a) and [Cu(tfac)(pmdt)]ClO_4 (b) [a)]

Atom	x	y	z	B_{eqv} [b)]	Atom	x	y	z	B_{eqv} [b)]
(a) [Cu(acac)(pmdt)]ClO_4					(b) [Cu(tfac)(pmdt)]ClO_4				
Cu	2293(0)	2488(1)	4967(0)	2.88(1)	Cu	7228(1)	3248(1)	9847(1)	2.98(2)
Cl	−1544(1)	861(1)	804(1)	4.34(4)	N1	5472(6)	2849(4)	11110(7)	3.88(17)
O01	−363(6)	536(5)	−140(6)	10.27(23)	N2	6774(7)	2048(5)	8407(7)	4.27(19)
O02	−2933(5)	368(5)	404(6)	9.07(19)	N3	8212(7)	3874(5)	7903(7)	4.53(19)
O03	−1183(7)	653(5)	2376(5)	10.11(22)	O1	7449(4)	4522(4)	11048(5)	3.61(13)
O04	−1733(8)	1892(4)	698(7)	11.09(24)	O2	8899(5)	2589(4)	11115(6)	4.32(15)
N1	274(4)	2816(3)	6073(4)	3.53(10)	C1	4423(8)	3676(7)	10824(13)	6.71(32)
N2	1706(5)	3606(3)	3478(4)	4.30(12)	C2	5769(10)	2715(8)	12777(10)	6.50(31)
N3	3519(5)	1938(3)	3128(4)	4.21(11)	C3	4999(9)	1852(6)	10439(11)	5.48(28)
C3	−334(6)	3731(4)	5337(7)	5.13(17)	C5	7622(9)	1135(7)	8776(11)	5.69(28)
C1	−792(6)	1973(5)	5829(7)	5.77(18)	C6	6933(11)	2407(8)	6740(10)	6.91(33)
C2	532(6)	2971(5)	7774(6)	5.13(16)	C4	5251(9)	1830(7)	8680(11)	6.35(31)
C4	33(7)	3752(5)	3639(7)	6.02(19)	C8	7343(9)	4732(7)	7332(10)	6.08(30)
C5	2554(7)	4515(4)	3828(6)	5.45(18)	C9	9643(9)	4240(9)	8253(12)	7.73(37)
C6	2016(8)	3233(5)	1879(6)	6.25(20)	C7	8200(13)	3017(7)	6740(10)	8.02(38)
C7	3491(8)	2709(5)	1932(6)	6.60(21)	C10	8411(7)	4684(6)	12064(8)	3.28(18)
C8	2813(9)	1044(5)	2541(7)	7.16(23)	C11	8315(8)	5786(6)	12714(9)	4.17(22)
C9	5115(7)	1708(8)	3590(8)	8.64(28)	C12	9436(7)	4085(6)	12627(8)	3.56(20)
O1	2567(3)	1282(2)	6142(3)	3.54(8)	C13	9609(6)	3019(5)	12133(8)	3.41(22)
O2	3995(4)	3212(2)	6306(4)	4.08(9)	C14	10741(10)	2391(8)	12924(12)	6.71(32)
C11	3482(7)	136(4)	8026(6)	5.07(16)	F1	9329(5)	6026(4)	13680(6)	6.07(16)
C10	3537(5)	1149(4)	7284(5)	3.45(12)	F2	8334(6)	6460(4)	11564(6)	6.59(17)
C12	4579(5)	1827(4)	7903(5)	3.69(13)	F3	7167(5)	5922(4)	13476(6)	5.92(16)
C13	4706(5)	2826(3)	7419(5)	3.42(12)	Cl	3214(2)	4619(2)	5904(2)	5.04(6)
C14	5804(6)	3468(4)	8349(6)	4.81(15)	O3	4114(24)	4697(21)	4497(29)	10.1(7)
					O4	2745(19)	5192(16)	7272(24)	7.2(5)
					O5	3849(32)	4053(28)	7173(42)	15.1(10)
					O6	2000(16)	4751(13)	5107(18)	4.7(3)
					O7	1989(19)	5316(17)	5687(24)	7.1(5)
					O8	2335(35)	3808(33)	5441(47)	17.9(13)
					O9	2867(25)	3509(25)	6422(32)	12.7(9)
					O10	3375(18)	4820(14)	7483(20)	5.7(4)
					O11	4340(15)	5174(12)	5003(18)	4.4(3)
					O12	3701(20)	3560(17)	5939(25)	8.5(6)
					O13	4430(29)	5003(22)	5537(36)	12.1(8)
					O14	2501(23)	4384(22)	4544(29)	9.8(7)

a) Positional parameters are multiplied by 10^4. Thermal parameters are given by the equivalent temperature factors (Å^2). b) $B_{eqv}=\frac{4}{3}\mathrm{trace}(\beta\times G)$

position.[8)] The similarity between the IR spectra of the Cu(II) and Ni(II) chelates, a part of which is shown in Table 5, is also in harmony with this conclusion.[9)]

A more direct proof for the proposed structure can be obtained from the data of the X-ray crystal analyses. The structures of the acac and tfac complexes (cf. Figs. 1 and 2 and Tables 3 and 4) confirm that these chelates are distorted square pyramidal. The Cu(II) atom is surrounded by three N atoms of pmdt and one O atom of dike, which form approximately a square; the remaining O of dike occupies the axial site. The square pyramidal coordination suffers a distortion toward a trigonal bipyramid structure, the N1–Cu–N3 and O1–Cu–N2 bond angles being ca. 153 and 170°, respectively. The N2–C5 (methyl) and Cu–O2 bonds lie on the same plane, so that the chelates have almost a mirror symmetry with respect to the molecular plane of dike. There is no large difference between the dispositions of the ligand atoms in the 1st coordination spheres of these two chelates; also those in [Ni(acac)(pmdt)]ClO_4 are quite similar to them.[2)] In both of the copper(II) chelates, the Cu(II) atom lies ca. 35 pm above the average plane of (N1–N2–N3–O1), and the Cu–N and Cu–O distances are all comparable with those in other square pyramidal Cu(II) complexes reported in the literature.[10)]

In the chelate ring of dike, there are two kinds of C–O bonds (C10–O1 and C13–O2) as well as two kinds of C–C bonds (C10–C12 and C12–C13), which are not exactly equivalent. In the case of [Ni(acac)(pmdt)]ClO_4, the differences in their lengths, i.e., Δ_{CO}=(C10–O1)−(C13–O2) and Δ_{CC}=(C13–C12)−(C12–C10), are quite small (Δ_{CO}=4.4 pm, Δ_{CC}=1.1 pm); in the case of the Cu(II) chelates, on the other hand, these differences are larger in the acac chelate (Δ_{CO}=5.0 pm, Δ_{CC}=3.3 pm), and Δ_{CC} is still larger in the tfac chelate (Δ_{CO}=4.9 pm,

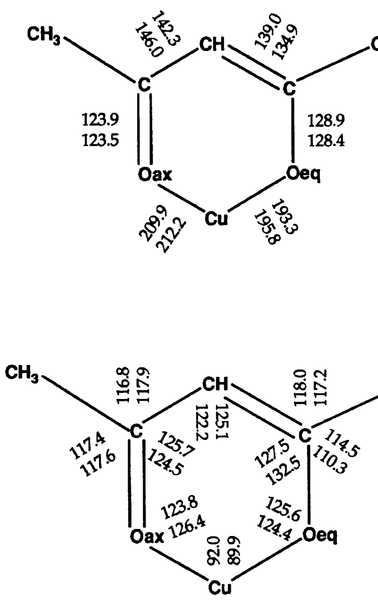


Fig. 2. Comparison of the bond distances and angles with the chelate rings of dike ligands. (a) Bond distances (pm); (b) bond angles (°). Upper values are for acac, while lower ones are for tfac. The mode of partial localization of the π-system is also indicated.

Table 4. Selected Bond Lengths (pm) and Angles (°)

(a) [Cu(acac)(pmdt)]ClO_4			
Cu–N1	208.3(3)	N1–Cu–N2	85.6(1)
Cu–N2	203.6(4)	N1–Cu–N3	152.9(1)
Cu–N3	207.4(4)	N1–Cu–O1	92.1(1)
Cu–O1	193.3(3)	N1–Cu–O2	104.6(1)
Cu–O2	209.9(3)	N2–Cu–N3	85.3(1)
C10–C11	151.6(7)	N2–Cu–O1	168.9(1)
C10–C12	139.0(6)	N2–Cu–O2	98.9(1)
C12–C13	142.3(6)	N3–Cu–O1	91.8(1)
C13–C14	150.7(6)	N3–Cu–O2	101.9(1)
O1–C10	128.9(5)	O1–Cu–O2	92.0(1)
O2–C13	123.9(5)		
(b) [Cu(tfac)(pmdt)]ClO_4			
Cu–N1	208.2(6)	N1–Cu–N2	86.6(2)
Cu–N2	202.8(6)	N1–Cu–N3	152.5(2)
Cu–N3	207.2(6)	N1–Cu–O1	91.9(2)
Cu–O1	195.8(5)	N1–Cu–O2	105.4(2)
Cu–O2	212.2(5)	N2–Cu–N3	85.8(2)
C10–C11	154.0(10)	N2–Cu–O1	171.1(2)
C10–C12	134.9(10)	N2–Cu–O2	99.0(2)
C12–C13	146.0(10)	N3–Cu–O1	91.6(2)
C13–C14	152.4(12)	N3–Cu–O2	101.9(2)
O1–C10	128.4(8)	O1–Cu–O2	89.9(2)
O2–C13	123.5(8)		

$\Delta_{CC}=11.1$ pm). This is apparently the result of the fact that, in the Cu(II) chelates, the Cu–O1 (equatorial) bond is noticeably shorter than the Cu–O2 (axial) bond; the difference is 16.6 pm in the acac chelate, and 16.4 pm in the tfac chelate, whereas it is only −1.4 pm in the Ni-acac chelate. These data show that there is a considerable Jahn–Teller effect in the case of Cu(II) systems. As expected from the bond-length variation rule of Gutmann,[11,12] a consecutive lengthening and shortening of bonds in dike is brought about by it, though the stronger and polar C–O bonds are less affected than the C–C bonds. In the case of tfac, the electron-withdrawing effect of its CF_3 group at C10 also favors such a structural change, or partial localization of the π-system on the C13–O2 and C10–C12 bonds, and affects the C–C bonds still more strongly. The angle O1–C10–C12 is thereby increased to 133°, a value which also speaks for a notable accumulation of electron density on the C10–C12 bond. A similar partial localization effect is also observed in the Schiff-base ligand formed from en and tfac.[13,14]

Packing diagrams of the crystals are compared in Fig. 3. The structure comprises layers of cations aligned in the **ab** plane and intercalated anions. To accommodate a large CF_3 group instead of a CH_3 group, the cell volume of the tfac chelate is slightly larger than that of the acac chelate (Table 2). However, the difference in the cell dimensions shows that the distance between the layers (which is almost parallel to the **c**) remains unchanged. The volume change is brought about by an expansion of **a** (by ca. 93 pm) of the tfac chelate with respect to that of the acac chelate, while **b** shrinks by ca. 55 pm. The elongation of **a** causes a loose packing around the ClO_4^- ions, reducing their mutual overlap along **b** (see Fig. 3). This fact is connected with the disordered orientation of the anion in the tfac chelate. The ClO_4^- ions are far away from the metal atom in both crystals (>420 pm), as in the case of the Ni chelate.

Behavior of the Chelates in Solution. The electronic spectral data of the new chelates in various organic solvents are collected in Table 6. As in the case of the solid reflection spectra, the spectra comprise a single, wide d-d band. The shift of the $\tilde{\nu}_{max}$ value for each chelate caused by the change in the solvent is shown in Fig. 4, together with that of the well-known chelates of the CuN_2O_2 type, [Cu(dike)(tmen)]ClO_4 (tmen=N,N,N',N'-tetramethylethylenediamine).[15]

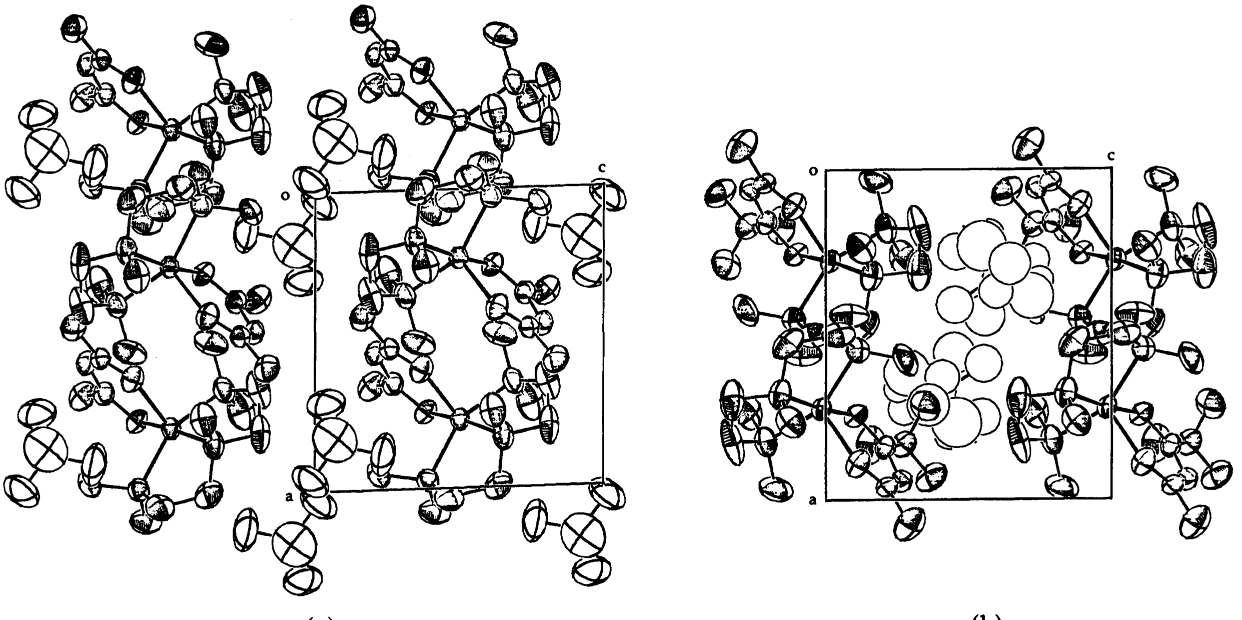
It can be seen that the solvatochromic changes of the two systems are very different. As a whole, the pmdt chelates are less solvatochromic than the tmen chelates; as in the case of the solid spectra, the $\tilde{\nu}_{max}$ values of the pmdt chelates in solution increase in the order

$$\text{dipm} < \text{acac} < \text{pfac} < \text{tfac} < \text{hfac}.$$

With the exception of the hfac chelate, the $\tilde{\nu}_{max}$ of each chelate generally increases in the order

$$\text{DCE} < MeNO_2 \approx \text{MeOH} < \text{EtOH}$$
$$\approx \text{MeCN} \approx Me_2CO < \text{DMF} < \text{DMSO},$$

i.e., approximately with the increase in the *DN* (Gutmann's donor number) of the solvent.[11,16] This characteristic solvatochromism, which is just opposite to that observed in the tmen chelates, is most notable



(a) **(b)**

Fig. 3. Packing diagrams of the crystals. (a) $[Cu(acac)(pmdt)]ClO_4$, (b) $[Cu(tfac)(pmdt)]ClO_4$.

Table 5. d–d Band Maxima in the Powder Reflection Spectra ($\tilde{\nu}_{max}$), and $\tilde{\nu}_{C=O}$ and $\tilde{\nu}_{C=C}$ Bands in the IR Spectra of the Chelates

Chelate	$\tilde{\nu}_{max}/10^3 cm^{-1}$	$\tilde{\nu}_{C=O}, \tilde{\nu}_{C=C}/cm^{-1}$ a)			
$[Cu(dipm)(pmdt)]ClO_4$	12.86	1590^w	*1570*	1530^w	1500
$[Cu(acac)(pmdt)]ClO_4$	13.53	*1590*	1510		
$[Cu(tfac)(pmdt)]ClO_4$	14.03	*1640*	1520		
$[Cu(pfac)(pmdt)]ClO_4$	14.37	*1640*	1620^w	1595^w	1510
$[Cu(hfac)(pmdt)]ClO_4$	15.35	*1650*	1590^w	1550	1520

a) The band which can be ascribed mainly to the C=O stretching is shown in italic.[9]

Table 6. Band Maxima of the Absorption Spectra ($\tilde{\nu}_{max}/10^3$ cm^{-1} (ε_{max}/mol^{-1} dm^3 cm^{-1})) of the Chelates in Various Organic Solvents (Concn : ca. 5×10^{-3} mol dm^{-3})

dike Solvent	dipm	acac	tfac	pfac	hfac
DCE	12.46(230)	12.45(224)	13.57(238)	13.46(235)	14.84(231)
$MeNO_2$	12.52(228)	12.59(230)	13.76(259)	13.67(234)	15.20(242)
Me_2CO	12.56(232)	12.62(224)	13.91(211)	13.84(226)	15.19(230)
MeCN	12.54(228)	12.53(219)	13.88(227)	13.77(223)	15.05(242)
MeOH	12.50(227)	12.59(222)	13.79(226)	13.68(228)	14.98(238)
EtOH	12.53(230)	12.53(222)	13.81(232)	13.73(229)	15.06(240)
DMF	12.67(228)	12.76(222)	14.10(234)	14.02(232)	15.02(248)
DMSO	12.77(231)	12.83(227)	14.23(239)	14.10(238)	14.85(244)

in the case of the tfac and pfac chelates; in the case of the dipm and acac chelates it is only slightly perceptible. The $\tilde{\nu}_{max}$ of the hfac chelate does not change in the same manner, but, in most cases, changes in an apparently irregular way, which is difficult to correlate with the structure and polarity of the solvent.

Based on these data, one can deduce their plausible explanation as follows:

1) The dipm and acac chelates, the dike's of which are those of high l.f.s., tend to retain their five-coordinated structure in solution; they are thus solvated only weakly in any solvent, and are therefore only slightly solvatochromic, although the small spectral changes observed are of the same type as those observed with the tfac and pfac chelates.

2) The tfac and pfac chelates, with dike's of somewhat lower l.f.s., are solvated more strongly in solutions, and thereby become distinctly solvatochromic. In

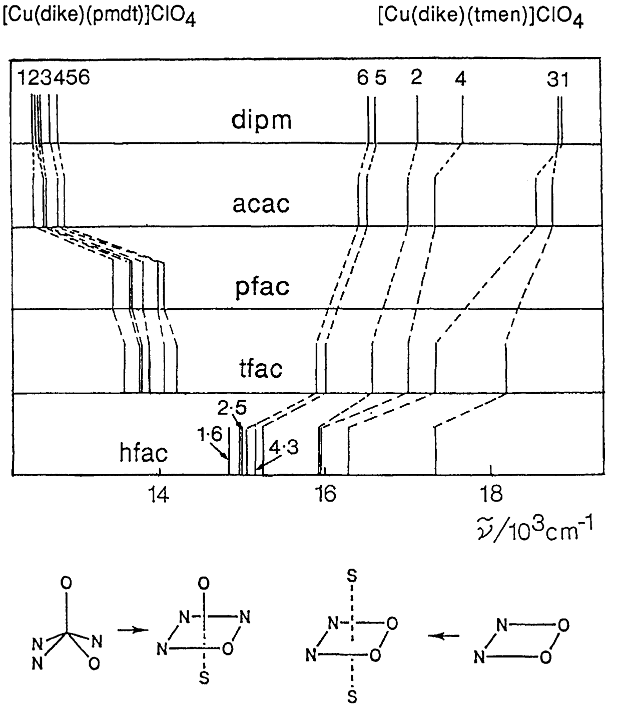


Fig. 4. Solvatochromism of $[Cu(dike)(pmdt)]ClO_4$ and $[Cu(dike)(tmen)]ClO_4$. The $\tilde{\nu}_{max}$ values of each chelate in various solvents (DCE(1), MeOH(2), NM-(3), acetone(4), DMF(5), and DMSO(6)) are shown by vertical lines. The models proposed for the two types of spectral changes are given below; cf. Refs. 8 and 15, and Fig. 5.

other words, the overall ligand field in these chelates is more susceptible to solvent influences than that in the cases of dipm and acac chelates, and the square pyramidal chelate is thereby transformed, progressively, along with an increase in the solvent polarity (which can be expressed approximately with *DN*) into an octahedral structure with an increase in $\tilde{\nu}_{max}$. The observed solvatochromism is brought out in this way (cf. Fig. 5).

3) In the case of the hfac chelate, the l.f.s. of the dike is still lower, so that its solvation occurs most heavily. Here, the structure and spectrum of the chelate would presumably be influenced more specifically by the donor–acceptor properties and steric requirements of the solvent molecules, and possibly also by ion-pair formation and dissociation in certain cases. In fact, the molar conductivity of this chelate in DCE (9.7 $ohm^{-1}\,cm^2\,mol^{-1}$) is smaller, and that in DMSO (48 $ohm^{-1}\,cm^2\,mol^{-1}$) is larger, than the values of the other chelates, which show their 1 : 1 dissociation in these solvents;[17] the former may be the result of ion-pair formation, while the latter may be due to a partial ionization of the chelate cation, i.e.,

$$[Cu(hfac)(pmdt)]^+ + n\mathrm{DMSO} \rightleftharpoons [Cu(DMSO)_n(pmdt)]^{2+} + \mathrm{hfac}^-,$$

since both of these changes are quite plausible when this chelate with the weakest dike is dissolved in a solvent of very low or very high *DN*, respectively.[15,17] The lack of a simple correlation between the solvatochromism of this chelate and solvent polarity may thus result from these complications.

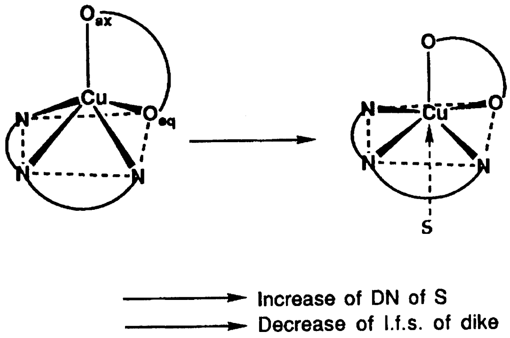


Fig. 5. A model for the solvation of the chelate in a donor solvent. The weakening of the ligand field of dike by solvation will take place mainly at O_{ax}, under the action of the donor solvent molecule (S) approaching from below the N_3O plane. The Cu–O_{ax} bond, which is longer than the Cu–O_{eq} bond from the outset (A), becomes thereby still longer, enhancing π-electron localization in the chelate ring (cf. Fig. 2) and stabilizing the Cu–O_{eq} bond. The chelate thus goes over into the structure (B), which is more or less similar to the elongated octahedral structure of most Cu(II) complexes.

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8) It is to be noted that the Cu(II) chelates are usually elongated octahedral, but if one of the axial ligands (L_{ax}) is bonded very strongly they are often converted into five-coordinated ones with a square-pyramidal structure. Such a chelate shows a d–d band near the red end of the visible spectrum, the $\tilde{\nu}_{max}$ of which tends to decrease with the strengthening of the Cu–L_{ax} bond (or the increase of the ligand field or donor power of L_{ax}). Cf., e.g.: K. Sone and Y. Fukuda, "Inorganic Thermochromism," Springer, Heidelberg (1987).

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interesting to note that the frequency of the italicized band in Table 5 (and that of the Ni(II) chelates, too) increases in the order of dipm < acac < pfac ≈ tfac < hfac, i.e, in the order of the decreasing l.f.s. of dike. Cf. also: K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 3rd ed, Wiley, New York (1978).

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