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Studies on Mixed Chelates. XVI. Mixed Copper(II) Chelates with 1,2-Dipiperidinoethane and β-Diketonates[1)]

Yutaka Fukuda,* Masako Cho, and Kozo Sone*
Department of Chemistry, Faculty of Science, Ochanomizu University,
Otsuka, Bunkyo-ku, Tokyo 112
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1,2-Dipiperidinoethane (dipe) forms mixed chelates of the type [Cu(dike)(dipe)]ClO_4 with $Cu(ClO_4)_2$ and various β-diketonate ions (dike); however, hexafluoroacetylacetonate (hfac) forms [Cu(hfac)$_2$(dipe)] instead. The strong solvatochromism of the former, and the high solubility and volatility of the latter, were compared with those of similar chelates studied so far.

1,2-Dipiperidinoethane (dipe; Fig. 1a) is a potential chelating agent which has been only little studied. Its chelate ring structure is similar to that of *N,N,N′,N′*-tetramethylethylenediamine (tmen), but the substituent groups on its N atoms ($-(CH_2)_5-$) are much larger, and form bulky piperidine rings with the N atoms. It is, therefore, expected to be a weaker ligand than tmen, since (i) the bulkiness and rigidity of the piperidine rings will hinder the formation of chelate ring, and (ii) even when the chelate ring is formed, the bulky ligand will disturb the proper arrangement of other ligands, and destabilize the whole complex.

In spite of these expectations, however, we could recently prepare a number of fairly stable metallic complexes containing dipe. One of them is a dimeric copper(II) complex, $[Cu_2(OH)_2(dipe)_2](ClO_4)_2$, which is very similar to the dimeric complexes formed by tmen and related diamines.[2)] In this paper, the preparations and various interesting properties of mixed copper(II) complexes with β-diketonate ions (dike) are reported.

Experimental

Preparation of the Complexes. (1) [Cu(dike)(dipe)]ClO_4 (dike=Dipivaloylmethanate (dipm), Acetylacetonate (acac), Benzoylacetonate (bzac), Dibenzoylmethanate (dibm), or Trifluoroacetylacetonate (tfac)): To an ethanolic solution of $Cu(ClO_4)_2\cdot 6H_2O$ (10 mmol in 30 ml), a mixture of a β-diketone and KOH (10 mmol each) dissolved in 10 ml of ethanol (EtOH) is added, and dipe (Tokyo Kasei Co.; 10 mmol in 10 ml of EtOH) is dropped in it upon warming. The mixture is stirred for 10 minutes, filtered, and kept in a freezer overnight. The obtained precipitate is recrystallized from acetone. A similar complex with hexafluoroacetylacetonate (hfac) could not be obtained in this way, and a mixture of [Cu(hfac)$_2$(dipe)] and unknown precipitate (maybe copper hydroxide) was obtained instead.

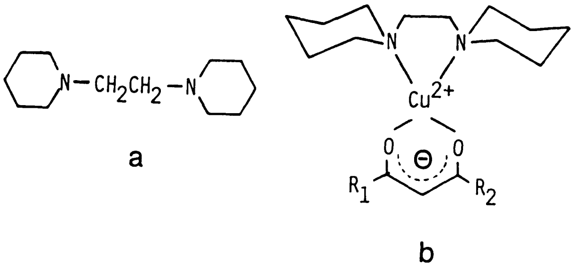

Fig. 1. Structures of dipe (a) and [Cu(dike)(dipe)]$^+$(b). The shape of the dipe moiety in (b) is assumed to be the same as that in [Ni(NO_3)(acac)(dipe)], the structure of which was determined by an X-ray study (Y. Fukuda, C. Fujita, H. Miyamae, H. Nakagawa, and K. Sone, *Bull. Chem. Soc. Jpn.*, in press (1989)).

(2) [Cu(hfac)$_2$(dipe)]: To obtain this complex more easily, a mixture of hfacH and KOH (each 20 mmol, in 20 ml of EtOH) is added to an EtOH solution of $Cu(ClO_4)_2\cdot 6H_2O$ (10 mmol in 20 ml), and then dipe (10 mmol in 10 ml of EtOH) is dropped in it upon warming. The mixture is stirred for 10 minutes, filtered, and evaporated until green crystals begin to appear. The crystals obtained are recrystallized from 1,2-dichloroethane (DCE).

Physical Measurements. Regarding measurements of UV-visible and IR spectra, magnetic susceptibilities, electric conductivities, and TG-DTA curves of the complexes obtained, one should review Ref. 3.

Results and Discussion

(A) The Complexes [Cu(dike)(dipe)]ClO_4 (dike=dipm, acac, bzac, dibm, and tfac). The colors, analytical data and magnetic moments of these complexes are given in Table 1. The strong resemblance of these data and the spectral data (vide infra) to those of the mixed chelates of the type [Cu(dike)(diam)]ClO_4 (diam=*N,N′*-polyalkylethylenediamine, e.g., tmen) studied before[4—7)] indicates that these complexes should be formulated as the perchlorates of the chelate cations shown in Fig. 1b.

Spectral Data. As in the case of [Cu(dike)(diam)]ClO_4, all these complexes are strongly solvatochromic. Table 2 and Fig. 2 show the shifts of their d–d absorption band observed in various solvents, which are remarkably similar to the corresponding data for [Cu(dike)(tmen)]ClO_4[4)] and [Cu(dike)(teen)]ClO_4[5)] (teen= *N,N,N′,N′*-tetraethylethylenediamine). As with the latter two series of complexes, the $\tilde{\nu}_{max}$ for a certain complex decreases with an increase in the solvent donor number (DN),[8)] i.e., in the order 1,2-dichloroethane (DCE)→nitromethane (NM)→acetone (Me_2CO)→ methanol (MeOH)→*N,N*-dimethylformamide (DMF)→

Table 1. Colors, Analytical Data, and Magnetic Moments of the Complexes

Complex	C/%[a)]	H/%[a)]	N/%[a)]	μ_{eff}/B.M.
[Cu(dipm)(dipe)]ClO_4(**I**)(V)[b)]	50.89(50.92)	7.97(7.99)	5.19(5.16)	1.85
[Cu(acac)(dipe)]ClO_4(**II**)(V)	43.31(44.54)	6.68(6.82)	5.83(6.11)	1.81
[Cu(bzac)(dipe)]ClO_4(**III**)(B)	50.52(50.77)	6.36(6.39)	5.35(5.38)	1.83
[Cu(dibm)(dipe)]ClO_4(**IV**)(D)	54.20(55.66)	5.98(6.06)	4.79(4.81)	1.80
[Cu(tfac)(dipe)]ClO_4(**V**)(B)	38.87(39.85)	5.48(5.31)	5.45(5.47)	1.80
[Cu(hfac)$_2$(dipe)](**VI**)(G)	38.33(39.21)	3.90(3.89)	4.11(4.16)	2.01

a) Calculated values are in parentheses. b) Colors: V=violet, B=blue, D=dark (nearly black), G=green.

Table 2. Electronic Spectra of the Complexes: $\tilde{\nu}_{max}$ and ε_{max} Values in Solid State and in Various Solvents

Complex[a)]	$\tilde{\nu}_{max}/10^3$ cm^{-1} (ε_{max})							
	Solid	DMSO(a)	DMF(b)	MeOH(c)	Me_2CO(d)	MeCN(e)	NM(f)	DCE(g)[b)]
I	17.3	16.1	16.4	16.8	17.2	17.2	18.8	19.2
		(129)	(137)	(133)	(130)	(152)	(157)	(159)
II	17.3	15.7	16.1	16.7	17.2	17.1	18.5	18.8
		(135)	(132)	(132)	(134)	(144)	(145)	(155)
III	17.2	15.8	16.1	16.7	17.2	17.1	18.3	18.5
		(152)	(143)	(154)	(154)	(163)	(176)	(173)
IV	17.5	15.7	16.1	16.7	17.1	16.9	18.3	18.3
		(147)	(144)	(171)	(166)	(166)	(212)	(180)
V	16.4	15.3	15.5	16.1	16.5	17.1	17.8	17.2
		(121)	(107)	(129)	(142)	(158)	(158)	(156)
VI	14.2	14.4	14.4	14.5	14.3	14.5	14.4	14.2
		(81)	(85)	(81)	(66)	(73)	(66)	(64)

a) Cf. Table 1. b) The DN values of the solvents a—g are, respectively, 29.8, 26.6, 19.1, 17.0, 14.1, 2.7, and 0.0.

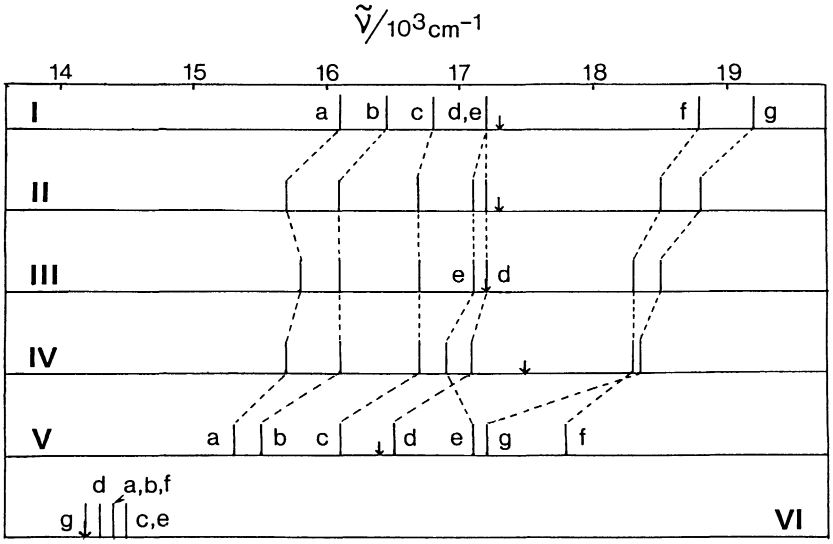

Fig. 2. Solvatochromism of the complexes: $\tilde{\nu}_{max}$ values of the complexes in various solvents. The $\tilde{\nu}_{max}$ in solid state are indicated by short arrows. As to the notations of the complexes (**I**—**VI**) and solvents (a—g), cf. Tables 1 and 2.

dimethyl sulfoxide (DMSO), while the $\tilde{\nu}_{max}$ in a certain solvent decreases with a decrease in the ligand field strength (l.f.s.) of dike, i.e., in the order dipm→acac→bzac→dibm→tfac. These resemblances prove, also in the present case, that the solvatochromism is caused by an axial coordination of solvent molecules onto the planar [Cu(dike)(dipe)]$^+$, which is strengthened by a decrease in the in-plane l.f.s. of the complex cation, as in the case of the tmen- and teen-containing complexes.[4,5)]

An apparent exception from these general trends has now been found in the $\tilde{\nu}_{max}$ values in acetonitrile

(MeCN). The DN of this solvent (14.1) is sensibly lower than that of acetone (17.0), so that the $\tilde{\nu}_{\max}$ in it should be higher than that in acetone. In fact, however, this is the case only with [Cu(tfac)(dipe)]-ClO_4, and with all other complexes (and also with the tmen- and teen-containing complexes, cf. Fig. 3), these two $\tilde{\nu}_{\max}$ values are nearly equal, or slightly in the opposite order.

This spectral anomaly, which has been overlooked hitherto in this series of studies, may possibly be due to the slim, linear shape of MeCN molecule, and its "head-on" mode of coordination (i.e., the fact that ∠Cu-N-C=180°); these properties will facilitate the coordination of MeCN, especially when there is a steric hindrance, and so may make it an apparently stronger ligand than Me_2CO in certain cases. However, it may be due to another effect, i.e., the fact that the reacting particles in the present system (Cu^{2+} in the complex cation and MeCN) are rather "soft", and can form a "π-back bond" in the following way.

$$Cu^{2+} \longleftarrow N{\equiv}C{-}CH_3 \longleftrightarrow Cu^{2+} \underset{\sigma}{\overset{\pi}{\rightleftharpoons}} N{=}C{-}CH_3$$

Even a small contribution from this type of bonding will make the σ-bond synergetically stronger, and the apparent l.f.s. of MeCN notably higher. The sensitive dependence of the magnitude of the observed spectral anomaly on the electronic nature of dike, and similar spectral anomalies observed in MeCN solutions of [Ni(dike)(diam)]ClO_4,[9] seem to indicate the importance of the π-back bonding in the present case.

One more point of interest in Fig. 2 is a disappearance of the anomaly in DCE observed with [Cu(acac)(tmen)]ClO_4. It was formerly noted that the $\tilde{\nu}_{\max}$ of this complex in DCE is apparently lower than that in NM, although the DN of DCE (=0) is lower than that of NM (=2.7). This anomaly was ascribed to the formation of ion pairs by means of an axial coordination of ClO_4^- in DCE; it was shown that the use of BPh_4^- instead of ClO_4^- eliminates this anomaly.[4,10]

Now this anomaly does not appear with [Cu(dipm)(dipe)]ClO_4 and [Cu(acac)(dipe)]ClO_4, and with [Cu(acac)(teen)]ClO_4, as shown in Fig. 3, i.e., $(\tilde{\nu}_{\max})_{DCE} > (\tilde{\nu}_{\max})_{NM}$ in every case. It is plausible that the bulky substituents on dipe and teen hinder the approach of ClO_4^- ions, and suppress ion-pair formation.

The values of $(\tilde{\nu}_{\max})_{DCE}$ and $(\tilde{\nu}_{\max})_{NM}$, however, get closer in going to [Cu(bzac)(dipe)]ClO_4 and [Cu(dibm)(dipe)]ClO_4, and in the case of [Cu(tfac)(dipe)]-ClO_4 the anomaly described above appears again more drastically. These facts, and the conductivity data shown below, lead to the following conclusion: the degree of ion-pair formation, which is low with the dipm and acac complexes, gradually increases in going to the bzac and dibm complexes, and then drastically in going to the tfac complex. In this last complex, in which the l.f.s. of tfac is the lowest among the dike's used (or the positive charge on Cu(II) is highest), the bulkiness of dipe is seemingly insufficient to effectively hinder the coordination of ClO_4^-.

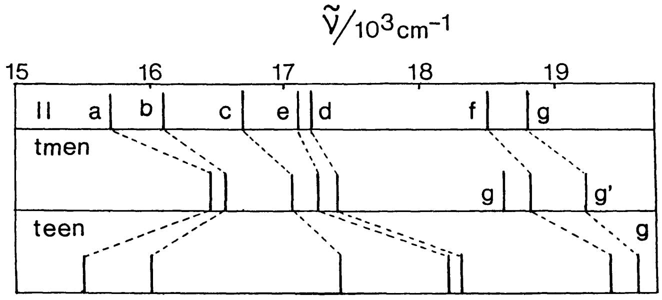

Fig. 3. Comparison of the solvatochromic changes of [Cu(acac)(dipe)]ClO_4, [Cu(acac)(tmen)]ClO_4, and [Cu(acac)(teen)]ClO_4. The notations of solvents are the same as those in Fig. 2. The $\tilde{\nu}_{\max}$ of the tmen complex in DCE(g) is too low owing to the ion-pair formation (see text); the value for [Cu(acac)(tmen)]-BPh_4 (g′) is therefore given for a better comparison.

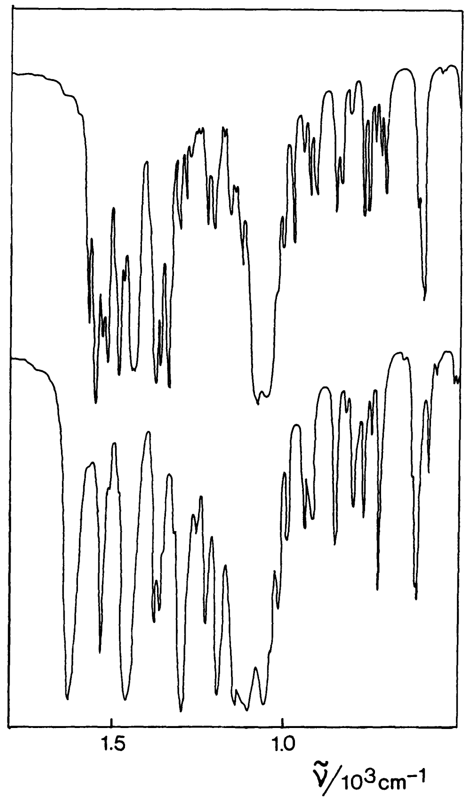

Fig. 4. Comparison of the IR spectra of [Cu(dipm)(dipe)]ClO_4 (above) and [Cu(tfac)(dipe)]ClO_4 (below).

The coordination of ClO_4^- also occurs in crystals of the tfac complex. This can be seen from its IR spectrum, in which the peak of ClO_4^- near 1100 cm^{-1} is notably split, showing the deformation from T_d symmetry.[11] No such splitting takes place in the IR spectra of the other complex perchlorates. Figure 4 shows a part of the obtained spectra.[12]

Apart from such few anomalies, Fig. 2 may be taken as a fairly regular array of solvents and dike ligands arranged in the order of their coordination abilities (DN of the solvents and l.f.s. of the dike's). In fact, these complexes of dipe (and those of teen, as reported before)5,6) are even more strongly solvatochromic than [Cu(acac)(tmen)]ClO_4, which was often referred to as an excellent indicator of solvent DN.7,13)

A comparison of the complexes of dipe, tmen, and teen given in Fig. 3 reveals some interesting trends. In going from tmen to teen, the d–d band moves to the blue in most solvents, except in solvents of very high DN (i.e., DMF and DMSO) where it moves to the red. This can be taken as an indication that (1) the thermal motion of the four ethyl groups of teen weakens the axial coordination of most solvents, making the complex more planar than in the case of tmen, while (2) strong solvent like DMF and DMSO can overcome this steric hindrance and get coordinated effectively, making the complex more regular octahedral, owing to the decreased in-plane l.f.s. produced by bulky teen, than in the case of tmen. On the other hand, in going from tmen to dipe, the d–d band of the complex $[Cu(acac)(diam)]^+$ moves to the red in all solvents, and the movement is larger in solvents of higher DN. In the dipe complex, the ends of the ethyl groups in teen are bound together in the form of piperidine rings, so that their free movements are strongly suppressed, and the movements toward axial directions become particularly difficult. The large steric hindrance to axial coordination in the teen complex is, thus, mostly lost in the dipe complex. Thus, it is probable that the spectral difference between the complex of dipe and that of tmen is mainly the result of the decreased l.f.s. of bulky and rigid dipe, which tends to make its complex more octahedral, in any solvent, than that of tmen.

Two factors which are expected to weaken the complexes of dipe were pointed out at the outset of this paper. The data in Fig. 3 indicate how the effects of both factors, i.e., the weakening of l.f.s. caused by large substituents, and steric hindrance to coordination of solvent molecules, can be recognized in solutions of the teen complex; however, only the first of them is apparent in those of the dipe complex, where the free motion of the substituent groups is restricted by ring formation.

Conductometric Data. Table 3a shows the molar conductivity values of the acac and tfac complexes in various solvents. They show, in general, that these complexes are 1 : 1 electrolytes.14) One exception is the tfac complex in DCE; strong ion-pair formation is indicated here. Table 3b shows that the degree of ion-pair formation in DCE increases in the order dipm→acac→bzac→dibm→tfac, and also in the order teen→dipe→tmen. These results are in general agreement with the expectation from spectral data, if the ionic conductivities of the complex cations are reasonably assumed to be comparable to one another.

(B) The Complex [Cu(hfac)$_2$(dipe)]. When hfac is used as dike, no complex of the type (A) could be prepared, and a green, apparently 6-coordinated complex of this composition was obtained instead.15) This complex is highly soluble in various nonpolar solvents, and it sublimes at ca. 175 °C (or at ca. 100 °C in vacuum) so that it can be purified by sublimation. The intermolecular attraction in this complex is therefore very weak; in this respect it is very similar to the complexes [Ni(dike)$_2$(diam)], and the corresponding Co(II) and Zn(II) complexes, studied before.16,17)

The electronic spectra of this complex in organic solvents were also studied. Here, $\tilde{\nu}_{max}$ changes only slightly with solvent polarity, showing that there is no solvent molecule in the coordination sphere. A small shift to the blue, which occurs roughly in parallel with solvent acceptor number (AN),8) is recognized. This may be due to an interaction of the solvent molecules, which now act as acceptors, with the twelve C–F groups covering the surface of the complex:

C—F·····Solvent (Acceptor).

A somewhat similar solvatochromism was recently observed in solutions of $[Co(edta)]^-$ and related

Table 3a. Molar Conductivities (Λ_M) of [Cu(acac)(dipe)]ClO_4 (**II**) and [Cu(tfac)(dipe)]ClO_4 (**V**) in Various Solvents at 25 °C. Concn: 5×10^{-3} mol dm^{-3}

Complex	Λ_M/ohm^{-1} cm^2 mol^{-1}						
	DCE	NM	MeCN	Me$_2$CO	MeOH	DMF	DMSO
II	20.8	95.9	159.2	147.2	96.6	68.2	33.8
V	8.9	93.1	157.8	139.0	97.2	77.8	34.5
Standard 1 : 1 electrolytes14)	10—24	75—95	120—160	100—140	80—115	65—90	ca. 35

Table 3b. Molar Conductivities (Λ_M/ohm^{-1} cm^2 mol^{-1}) of Various Complexes in DCE at 25 °C. Concn: 5×10^{-3} mol dm^{-3}

Complex a)	**I**	**II**	**III**	**IV**	**V**	**VI**	[Cu(acac)(tmen)]ClO_4	[Cu(acac)(teen)]ClO_4
Λ_M	22.0	20.8	18.1	17.2	8.95	0.22	16.9	28.1

a) Cf. Table 1.

macrocyclic complexes.[18]

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9) These complexes exist in an equilibrium of the type

$$[\mathrm{Ni(dike)(diam)}]^+ + 2\mathrm{Solv} \rightleftharpoons [\mathrm{Ni(dike)(diam)(Solv)_2}]^+$$

(Solv=solvent molecule) in organic solvents; here the equilibrium in MeCN is shifted more strongly to the right hand side than that in Me_2CO, and the l.f.s. in $[Ni(dike)(diam)(MeCN)_2]^+$ is notably higher than that in $[Ni(dike)(diam)(Me_2CO)_2]^+$, probably owing to the same reason as in the case of the Cu(II) analogues. Cf. Ref. 7.

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12) Similar coordination of ClO_4^- in solid was observed formerly in the case of $[Cu(hfac)(tmen)]ClO_4$ and $[Cu(hfac)(teen)]ClO_4$. Cf. Refs. 4 and 5.

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