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Studies on Mixed Chelates. XIII. Formation and Electronic Spectra of 5-Coordinated Mixed Copper(II) Chelates Containing *N*-Alkylated Ethylenediamine, Acetylacetonate, and Halide Anions[1]

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The visible absorption spectra of three new mixed chelates of copper(II), Cu(acac)(tmen)X (acac=acetylacetonate ion, tmen=*N,N,N′,N′*-tetramethylethylenediamine, and $X^-=Cl^-$, Br^-, or I^-) were studied in various organic solvents. The $\tilde{\nu}_{max}$ values of their d-d bands depend strongly on the nature of the solvent, similarly to the pseudohalide complexes reported in the preceding paper.[1] These data show the existence of the equilibrium:

$$\underset{\text{(5-coordinated)}}{[\mathrm{Cu(acac)(tmen)X}]} \rightleftharpoons \underset{\text{(4-coordinated, with axial solvation)}}{[\mathrm{Cu(acac)(tmen)}]^+ + \mathrm{X}^-}$$

in such solutions, which is shifted to the right hand side with increase of the solvent polarity and with decrease of the coordination ability of the X^- anion, *i.e.*, in the order $Cl^- \rightarrow Br^- \rightarrow I^-$.

We have prepared several mixed copper(II) chelates containing N-alkylated ethylenediamine(diam) and the β-diketonate ion (β-dik), Cu(β-dik)(diam)X, where X^- is an anion such as ClO_4^-, NO_3^-, or pseudohalide ions.[1,2] They are all soluble in various organic solvents, and the visible absorption spectra of such solutions reveal the existence of different kinds of solvent effects on their structures in solution. Such effects originate in the donor property and polarity of the solvent used, and the coordinating power of the anion X^-. In continuation of these studies, we have prepared the corresponding halide complexes, Cu(acac)(tmen)X, in which $X^-=Cl^-$, Br^- or I^-, and studied their visible absorption spectra in organic solvents. The results obtained and their probable explanations will be presented in this paper.

Experimental

Preparation of the New Complexes. An excess of an aqueous solution of potassium halide (KCl, KBr, or KI, *ca.* 20 mmol in 30 cm^3 of H_2O) was added to a solution of [Cu(acac)(tmen)]ClO_4[2] in water–ethanol (10 mmol in 20 cm^3), and the mixture was stirred for several hours. It was then filtered and concentrated under reduced pressure below room temperature until the complex formed as a crystalline powder. The crude bluish green crystals were recrystallized from 1,2-dichloroethane($ClCH_2CH_2Cl$=DCE). The Cl- and Br-complexes{Cu(acac)(tmen)X; X=Cl or Br} are stable at room temperature, but the crystals of the I-complex gradually decompose on standing, changing from bluish green to brown by the redox reaction between Cu(II) and I^-. Therefore, in the physical measurements a freshly prepared sample must be used and must be kept in a refrigerator when not in use.

Physical Measurements. The electronic spectra of the solutions (visible region) were measured with a Hitachi 340 Recording Spectrophotometer at room temperature (20—25 °C), in 10 cm quartz cells. The reflectance spectra of the solid samples were measured with the same instrument with a reflectance attachment, using $BaSO_4$ as the reference. Infrared spectra (400—5000 cm^{-1}) were measured as Nujol mulls with a JASCO IR-A3 Grating Spectrophotometer. Magnetic susceptibility measurements were performed with a Shimadzu Tortion Magnetometer MB-100. Electric conductivities of the solutions were measured with a conductivity outfit AOC-10 (Denki-kagaku Keiki Co. Ltd.) at 25±0.2 °C.

Results and Discussion

Properties of the Solid Complexes. Table 1 summarizes the analytical data and magnetic moments of the three new complexes. All show normal magnetic moments for monomeric Cu(II) complexes, but their colors (bluish green with different shades) are notably different from that of the perchlorate, [Cu(acac)(tmen)]ClO_4 (reddish violet), as are their visible reflectance spectra (see later).

Electronic Spectra of the Complexes in Various Solvents. These complexes are all readily soluble in various organic solvents, but here again the visible absorption spectra observed in such solvents are remarkably different from those of the perchlorate in the same solvents. For example, the spectra of the Cl-complex, [Cu(acac)(tmen)Cl], in four solvents are given in Fig. 1. The observed values of $\tilde{\nu}_{max}$ and ε_{max} for all these complexes are summarized in Table 2, and the shifts of $\tilde{\nu}_{max}$ of each one in various organic solvents are shown in Fig. 2, in comparison with the data of the perchlorate and the NCO-complex reported previously as the

Table 1. Elementary analyses and magnetic moments of the complexes obtained

Formula	C(%)[a]	H(%)[a]	N(%)[a]	μ_{eff}/BM
Cu(acac)(tmen)Cl	41.99(42.03)	7.44(7.38)	8.91(8.91)	1.85
Cu(acac)(tmen)Br	37.00(36.83)	6.54(6.46)	7.84(7.81)	1.84
Cu(acac)(tmen)I[b]	31.58(32.56)	5.51(5.71)	6.22(6.90)	1.74

a) Calculated values are in parentheses. b) The somewhat poorer agreements may be due to partial decomposition which occurred during handling prior to analysis. *Cf.* Experimental.

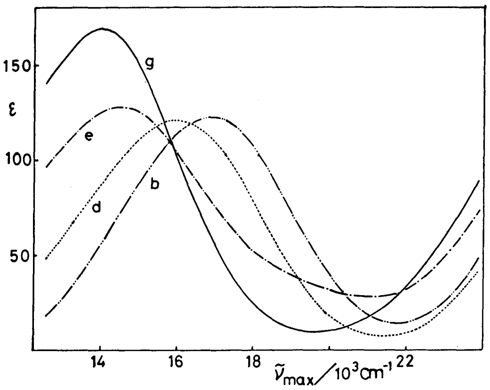

Fig. 1. Absorption spectra of [Cu(acac)(tmen)Cl] in various organic solvents. As to the symbols on the curves, *cf.* Fig. 2.

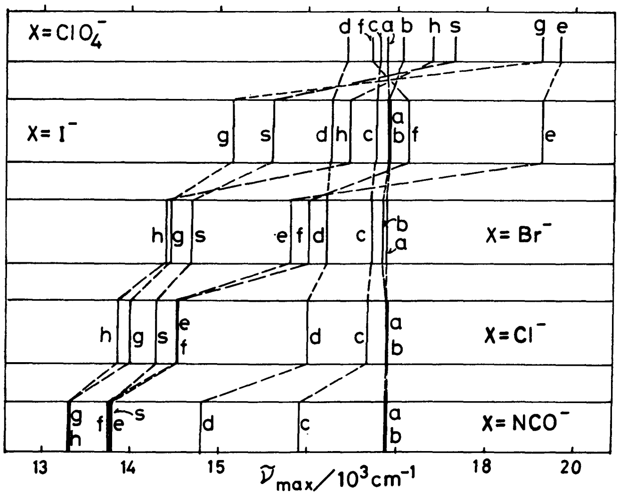

Fig. 2. Diagrammatic representation of the $\tilde{\nu}_{max}$ of the complexes shown in Table 2, and those of [Cu(acac)(tmen)]ClO$_4$ and [Cu(acac)(tmen)NCO]† reported previously.[1)] The symbols (a) to (h) correspond to the following solvents: a=H$_2$O, b=MeOH, c=EtOH, d=DMSO, e=NM, f=CH$_3$CN, g=DCE, and h=acetone. The value of the solid reflectance spectrum is shown by s.

reference.[1),†]

It was shown that the $\tilde{\nu}_{max}$ value of the perchlorate shifts to the red with the increase of the donor number of the solvent.[2,3)] However, the data in Fig. 2 clearly show that the values of the halide complexes shift to the red with the decrease of solvent polarity, *i.e.*, in apparently opposite direction as compared with the perchlorate. When X$^-$ is Cl$^-$ or Br$^-$, the order of $\tilde{\nu}_{max}$ in various solvents is expressed as:

$$\mathrm{H_2O} \geqq \mathrm{MeOH} > \mathrm{EtOH} > \mathrm{DMSO} > \mathrm{CH_3CN} \geqq \mathrm{NM} > \mathrm{DCE} \geqq \text{acetone}. \qquad \text{(i)}^{\dagger\dagger}$$

TABLE 2. $\tilde{\nu}_{max}$ AND ε_{max} VALUES OF [Cu(acac)(tmen)X] IN SOLID STATE AND IN VARIOUS SOLVENTS AT *ca.* 20 °C[a–c)]

	X=Cl	X=Br	X=I
Solid[d)]	14.3	14.8	15.6
H$_2$O	16.89(101)	16.89(101)	16.89(97)
CH$_3$OH(MeOH)	16.89(123)	16.84(108)	16.92(106)
C$_2$H$_5$OH(EtOH)	16.67(133)	16.72(130)	16.75(111)
(CH$_3$)$_2$SO(DMSO)	16.00(121)	16.21(129)	16.26(113)
(CH$_3$)$_2$NCHO(DMF)	14.71(114)	16.21(112)	16.50(100)
CH$_3$NO$_2$(NM)	14.53(128)	15.82(103)	18.48(96)
CH$_3$CN	14.53(132)	16.08(112)	17.27(100)
C$_2$H$_4$Cl$_2$(DCE)	14.03(169)	14.45(173)	15.15(135)
(CH$_3$)$_2$CO	13.83(153)	14.39(154)	16.47(94)

a) $\tilde{\nu}_{max}$ in 10^3 cm^{-1}, ε_{max} in parentheses. b) Concentrations: *ca.* 5×10^{-3} M (1 M=1 mol/dm^3). c) It can be noted that there is a remarkable increase in ε_{max} when most of the complex is in the 5-coordinated state (*cf.* the values for the Cl- and Br-complexes in DCE and acetone, and for the I-complex in DCE). Such an increase in band intensity is often observed when a 5-coordinated Cu(II) complex is formed in solution. d) Solid reflectance spectral peaks are broad.

These results are similar to those observed for pseudohalide complexes[1)] (compare the data of Cl- and NCO-complexes in Fig. 2, for example), and indicate that the same type of equilibrium as that observed in the solutions of the pseudohalide complexes is established. The equilibrium of the dissociation and formation of the 5-coordinated complex species as shown in Eq. 1:

$$\underset{\text{(5-coordinated)}}{[\mathrm{Cu(acac)(tmen)X}]} \rightleftharpoons \underset{\text{(4-coordinated, with axial solvation)}}{[\mathrm{Cu(acac)(tmen)}]^+} + \mathrm{X}^- \qquad (1)$$

is shifted to the right hand side with increase of solvent polarity; this is generally expressed in terms of their E_T or Z values.[3)]

Like the pseudohalide complexes, the spectra in DCE and acetone, which are the most non-polar solvents used ($E_\mathrm{T}\simeq 42$), can be ascribed to the 5-coordinated complexes, [Cu(acac)(tmen)X]; the fact that these complexes are practically non-electrolytes in DCE supports this view (see below). On the other hand, the spectra in H$_2$O and MeOH, which are the most polar solvents used (E_T=55—63), are nearly the same as those of the perchlorate in these solvents, and are ascribed to the 4-coordinated ionic complexes [Cu(acac)(tmen)]$^+$ with axial solvation.

The spectra in other solvents with intermediate polarity correspond to equilibrium mixtures containing these two complex species. In EtOH and DMSO, the spectra are similar to those of the perchlorate, but their $\tilde{\nu}_{max}$ are shifted toward the red, indicating the coexistence of small amounts of [Cu(acac)(tmen)X]. The shift is larger in CH$_3$CN, and still larger in NM. These results show that the extent of formation of [Cu(acac)(tmen)X] increases in the order of EtOH<DMSO<CH$_3$CN<NM. It is thus concluded that the solvent series (i) is essencially the order of the shift of the equilibrium (1) to the right hand side, just as in the case of the pseudohalide complexes.

[†] In Fig. 2 of the preceding paper (Ref. 1), the symbols III and IV mean the N$_3$- and NCO-complex, respectively (the reverse given there was a mistake; *cf.* the data in Table 3 of the same paper).

[††] The abbreviations of the solvent names used are as follows: NM: CH$_3$NO$_2$, DCE: ClCH$_2$CH$_2$Cl, DMSO: (CH$_3$)$_2$SO (see also in Table 2).

TABLE 3. ACCEPTOR NUMBERS(AN) OF THE SOLVENTS USED

Solvent	AN
H_2O	54.8
MeOH	41.3
EtOH	37.1
DMSO	19.3
DMF	16.0
CH_3CN	19.3
NM	20.5
DCE	—
Acetone	12.5

It is also interesting to note that the series (i) can also be taken as the order of the acceptor numbers (AN) of Gutmann (*cf.* Table 3) of the solvents,[3] which is the measure of their ability to combine with the negatively charged particles or negative ends of dipoles. This is natural, since a solvent with a high AN will be able to pull out the X^- ions from the coordination sphere of [Cu(acac)(tmen)X] more easily than that of a lower AN.[†††] A practical reason for our preference for the E_T scale is that the value of DCE, in which the contrast between the spectrum of the perchlorate and those of the halide and pseudohalide complexes is largest, is lacking in Gutmann's table.

Comparison of the data for Cl- and Br-complexes reveals further that, in every solvent (with the exception of H_2O and MeOH) the band of the Cl-complex is shifted more to the red than that of the Br-complex, and in solvents of lower polarity (DCE, acetone, CH_3CN, and NM), the $\tilde{\nu}_{max}$ of the Cl-complex tend to flock together around *ca.* 14×10^3 cm^{-1}. These facts indicate that Cl^- is more strongly bound with $[Cu(acac)(tmen)]^+$ than Br^- in any solvent, except in H_2O and MeOH where no such combination occurs.

The data for the I-complex, on the other hand, show more complexity. The $\tilde{\nu}_{max}$ values in DCE, DMSO, H_2O, and alcohols can be expected by comparison with the Cl- and Br-complexes, but those in acetone and NM (especially the latter) are nearer to the values of the perchlorate in the same solvents, and the value in CH_3CN is even higher than that of the perchlorate. Although the meaning of these $\tilde{\nu}_{max}$ is still not fully understood, it is thus clear that appreciable formation of the 5-coordinated complex occurs only in DCE (and to a much less extent in acetone). In most other solvents, the $\tilde{\nu}_{max}$ values are closer to those of the perchlorate, showing that most of the I^- ions merely dissociate in such solvents. Therefore, the I-complex may be taken as an intermediate between the Br-complex and the perchlorate complex in its behavior.

Electric Conductivities of the Complexes. Conductometric measurements were carried out on some of these solutions to gain information on the equilibrium (1). Some data are shown in Table 4. They show that, in DMSO, all the three complexes are 1 : 1 electrolytes.

TABLE 4. MOLAR CONDUCTIVITIES (Λ_M) OF THE COMPLEXES (Ω^{-1} cm^2 mol^{-1}, AT 25.0 °C)[a] AND APPROXIMATE DEGREES OF DISSOCIATION (%, IN PARENTHESES)[b]

Complex	DCE	NM	DMSO
Cu(acac)(tmen)Cl	0.6(3)	43.7(51)	32.6(93)
Cu(acac)(tmen)Br	1.2(6)	70.5(83)	36.1(100)
Cu(acac)(tmen)I	6.6(33)	83.6(98)	35.4(100)

a) Concentration: *ca.* 1×10^{-3} M. b) Calculated on the assumption that the Λ_M values of a typical 1:1 electrolyte in these three solvents are 20, 85, and 35 Ω^{-1} cm^2 mol^{-1}, respectively (see Ref. 4).

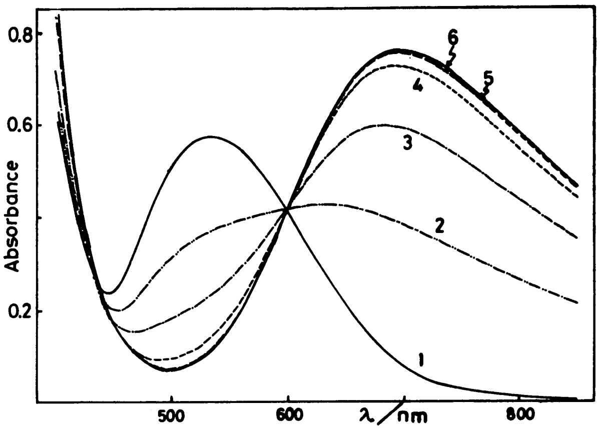

Fig. 3. The effect of Cl^- ions on the spectrum of $[Cu(acac)(tmen)]^+$ in NM (concentration: 5.01×10^{-3} M). The curve 1 is that of $[Cu(acac)(tmen)]ClO_4$, and 2 to 6 correspond to solutions in which the $[Cu(acac)(tmen)]^+$: Cl^- ratios are 1: 0.5, 1: 1, 1: 2, 1: 3, and 1: 4, respectively.

In NM, however, only the I-complex is a 1 : 1 electrolyte, and partial ionization takes place with other complexes, the degree of which increases from the Cl-complex to the Br-complex. In DCE, the same tendency is observed much more apparently.

These data are compatible with the expectation from the spectral data. They can be summarized by stating that the degree of ionization of [Cu(acac)(tmen)X] increases, in every case, in the order of DCE<NM<DMSO and $Cl^-<Br^-<I^-$.

Solution Equilibria of the Complexes in NM. Comparison with the Pseudohalide Complexes: More spectral measurements on the systems of $[Cu(acac)(tmen)]ClO_4+Et_4NX$ (X=Cl or Br) in NM were made by varying the molar ratio $[Cu(acac)(tmen)]^+/X^-$ continuously. Figure 3 shows some of the curves obtained. Analysis of these data provides an estimation of the equilibrium constants K of these systems.[5] The same K's could also be estimated from the data in Table 4, by comparing the obtained Λ_M (molar conductivity) values with the mean values of common 1 : 1 electrolytes in the solvents used.[4] The K values obtained in both ways are shown in Table 5. The good agreement may be fortuitous, but it can be seen from these data (and the values of the NCS-complex estimated with the data in the preceding paper)[1] that the coordination abilities

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[†††] An apparent exception is that NM tends to come after CH_3CN and DMSO in the present series; here, however, the AN are nearly the same, and the large difference in their DN may be acting to upset the order.

Table 5. Values of the equilibrium constant, K, of Eq. 1 in NM, estimated from spectra (K^a) and conductometric data (K^b)

Complex	K^a	K^b
Cu(acac)(tmen)Cl	0.46×10^{-3}	0.35×10^{-3}
Cu(acac)(tmen)Br	1.52×10^{-3}	1.69×10^{-3}
Cu(acac)(tmen)NCS[a]	0.67×10^{-3}	0.74×10^{-3}

a) These values were estimated from the data in Ref. 1.

of the ions studied increase in the order of $Cl^- > NCS^- > Br^-$ in NM.

It is desirable to make similar measurements on all the other systems, *i.e.*, in every solvent and with every halide or pseudohalide ion, but it is not always practicable owing to experimental difficulties, *e.g.*, unfavorable solubility. Comparison of Fig. 2 with the corresponding figure in the preceding work,[1)] however, indicates that the coordination abilities of the halide and pseudohalide ions in organic solvents toward $[Cu(acac)(tmen)]^+$ can be arranged, approximately, in the following order:

$$I^- < Br^- \approx NCS^- < Cl^- \approx N_3^- < NCO^-.$$

This sequence may be of some interests, since it is often stated that pseudohalide ions are stronger ligands than halide ions,[6)] and the spectrochemical series also states that the ligand field caused by NCS^- is much stronger than those of the halide ions. The "spectrochemical series for axial ligands" found by Addison *et al.*[7)] also indicates the same trend. In the present case, however, the two series Cl^-–Br^-–I^- and NCS^-–N_3^-–NCO^- run nearly parallel (or intermixed together), although I^- is probably the weakest, and NCO^- the strongest ligand among all these ions. More studies on related complexes will be necessary for the proper understanding of this sequence.

Structures of the Complexes in Solid State. The fact that the $\tilde{\nu}_{max}$ values of the solid Cl- and Br-complexes (*cf.* Table 2 and Fig. 2) are similar to those of their DCE solutions indicates the 5-coordinated structure of these complexes in solid state. Even for the I-complex, the $\tilde{\nu}_{max}$ is near that in DCE, suggesting the same structure.

However, the bands of the solids are all rather broad, and the possibility of other structures (*e.g.*, a 6-coordinated one in which X^- ions are bound weakly above and below the chelate plane as the bridging ligand) cannot be ruled out with certainty. At any rate, there is a strong axial influence of X^-, and the structures of the complexes in these solids are far from square planar.

It is now clear that these three complexes and the three pseudohalide complexes reported previously provide an interesting group of mixed chelates of Cu(II), with which one can observe the competition of anions and solvent molecules for the axial coordination sites by means of their visible absorption spectra.

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