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# Studies on Mixed Chelates. XIV. Influences of Solvent Polarity, and of Substituent Groups in β-Diketonate Ligands, on the Electronic Spectra of 5-Coordinated Mixed Copper(II) Chelates in Organic Solutions[1)]

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Several chelates of copper(II), Cu(tmen)(dike)X, were newly obtained where tmen=*N,N,N′,N′*-tetramethylethylenediamine, dike= a β-diketonate ion, and $X^-$= a halide or pseudohalide anion. These complexes exist as 5-coordinated species, with axially coordinated $X^-$, in nonpolar solvents. In more polar solvents, they are ionized according to the solvent polarity, and form the following equilibrium mixtures:

$$\underset{\text{5-coordinated}}{[\mathrm{Cu(tmen)(dike)X}]} \rightleftharpoons \underset{\text{4-coordinated (solvated, tetragonal)}}{[\mathrm{Cu(tmen)(dike)}]^+ + \mathrm{X}^-}$$

This equilibrium is controlled by (a) the strengths of acceptor and donor properties of the solvent, which can be expressed by its polarity factor (Pf), *i.e.*, a linear combination of the donor number and acceptor number of the solvent, and (b) the changes of the ligand field strength of dike caused by the electron-withdrawing and -releasing properties of its α-substituent groups.

In the previous papers,[1—3)] we reported the properties of mixed Cu(II) chelates of the general formula Cu(diam)(dike)X in solid state and in various solvents.[*1)]

All these chelates are easily soluble in various organic solvents, and characteristic solvatochromism (color change caused by the nature of the solvent) is observed in their solutions. Moreover, in the same solvent, the spectral and conductivity behaviors of the chelates with different anions show drastic changes according to the coordination power of the anion (anion effect).

When $X^-=ClO_4^-$, or $NO_3^-$, *e.g.* with [Cu(tmen)(acac)]$ClO_4$, the solvatochromism observed is mainly due to the solute-solvent interaction between the chelate cation and the solvent molecules. On the other hand, when $X^-$= a halide or pseudohalide anion, *e.g.* with [Cu(tmen)(acac)Cl], the chelate exists as 5-coordinated green species in solid crystals and in nonpolar solvents. Here the solvatochromism observed in polar solvents is due to the competition of $X^-$ and solvent molecules for the axial site(s) of the chelate cation, which leads to complicated solute-solute-solvent interactions.

In these former studies, a large number of chelates with various diamines and β-diketonates were prepared and studied, with $ClO_4^-$ or $NO_3^-$ as $X^-$, but only the chelates with tmen and acac were reported so far with a halide or pseudohalide anion as $X^-$.[4)] In continuation of these studies, therefore, we have prepared the latter type of chelates with tmen and various β-diketonates such as tfac, hfac and dipm. The effects of α-substituents in them, the anion ($X^-$), and solvent polarity on the formation of the 5-coordinated complexes in their solutions will be discussed in this paper.

## Experimental

*Materials.* The ligands used (tmen and dike) and metal salts were "Guaranteed Grade" or "Extra Pure," and the solvents used for physical measurements were "Dotite Spectrosol" of Dojindo Laboratories, or "Guaranteed Grade" of Wako Pure Chemical Industry Co. Ltd. They were used without further purification.

*Preparation of New Chelates.* 1) Cu(tmen)(dike)X(dike =dipm, tfac, or hfac, $X^-=Cl^-$ or $Br^-$): These complexes could be obtained by concentrating methanol solutions of the mixtures of $CuX_2$($CuCl_2\cdot 2H_2O$ or $CuBr_2$), tmen, and dike of which molar ratio was 1:1:1. The hfac-Cl-chelate was rather difficult to prepare, because the deep green crystals of the mixed chelate [Cu(tmen)(hfac)Cl] contained small amounts of its disproportionation products, *i.e.*, blue plates of [Cu(tmen)$Cl_2$] and light green crystals of [Cu(tmen)$(hfac)_2$]. The compositions of these by-products were ascertained by elemental analyses. To remove them, the crude deep green products were recrystallized from $CHCl_3$ or DCE, and washed with cold DCE and ether. Among these complexes, the tfac- and hfac-chelates are all green and stable in atmospheric moisture but the dipm-chelates absorb water to form the monohydrates, showing the color change from green to bluish-violet( Cu(tmen)(dipm)X·$H_2O$, see Table 1).

2) Cu(tmen)(dike)X(dike=dipm or tfac, $X^-=NCS^-$; dike=tfac, $X^-=I^-$). These compounds could be obtained by the anion exchange of [Cu(tmen)(dike)]$NO_3$ with NaX in acetone, which is very similar to the method described before.[3)] As the iodide complexes were very difficult to crystallize, we could obtain only one of them, Cu(tmen)(tfac)I. The green crystals obtained were recrystallized from DCE.

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[*1)] Abbreviations used in this article are as follows: diam= *N*-alkylated ethylenediamine, tmen=*N,N,N′,N′*-tetramethylethylenediamine, dike= a β-diketonate ligand ($R_1COCHCOR_2^-$), acac=acetylacetonate ($R_1=R_2=CH_3$), hfac=hexafluoroacetylacetonate ($R_1=R_2=CF_3$), tfac=trifluoroacetylacetonate ($R_1=CH_3$, $R_2=CF_3$), dipm=dipivaloylmethanate ($R_1=R_2=C(CH_3)_3$); DCE=1,2-dichloroethane, NM=nitromethane, DMF=*N,N*-Dimethylformamide, DMSO=dimethyl sulfoxide.

TABLE 1. ANALYTIAL DATA, COLOR, AND MAGNETIC MOMENTS OF THE COMPLEXES OBTAINED[a)]

| Complex | C(%) | H(%) | N(%) | Color | $\mu_{eff}$/BM |
|---|---|---|---|---|---|
| Cu(tmen)(tfac)Cl | 35.76(35.87) | 5.60(5.47) | 7.61( 7.61) | light green | 1.87 |
| Cu(tmen)(tfac)Br | 31.90(32.01) | 5.00(4.88) | 6.77( 6.79) | deep green | 1.85 |
| Cu(tmen)(tfac)I | 28.39(28.74) | 4.33(4.39) | 6.09( 6.09) | deep green | 1.81 |
| Cu(tmen)(tfac)NCS | 36.57(36.87) | 5.24(5.16) | 10.79(10.75) | green | 1.86 |
| Cu(tmen)(dipm)Cl·$H_2O$ | 48.86(49.02) | 8.81(8.95) | 6.86( 6.73) | bluish violet | 1.84 |
| Cu(tmen)(dipm)Br·$H_2O$ | 43.73(44.30) | 6.01(6.08) | 8.05( 8.09) | bluish violet | 1.80 |
| Cu(tmen)(dipm)NCS | 51.26(51.34) | 8.38(8.38) | 9.99( 9.98) | bluish green | 1.90 |
| Cu(tmen)(hfac)Cl | 31.25(31.29) | 4.13(4.06) | 6.79( 6.63) | green | 1.88 |
| Cu(tmen)(hfac)Br | 28.36(28.31) | 3.69(3.67) | 6.00( 6.00) | green | 1.87 |

a) Calculated values are shown in parentheses.

Elemental analyses of the prepared chelates were performed at the Laboratory of Organic Microanalysis of the Institute of Physical and Chemical Research.

*Physical Measurements.* The electronic spectra of the complex solutions ($5\times10^{-3}$ mol dm$^{-3}$) in visible region were measured with a Hitachi 340 Recording Spectrophotometer at room temperature (20—25 °C) in 10 mm quartz cells. 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 Torsion Magnetometer MB-100 at room temperature. Electric conductivities of the solutions ($1\times10^{-3}$ mol dm$^{-3}$) were measured with a Conductivity Outfit Model AOC-10 (Denki-Kagaku-Keiki Co. Ltd.) at 25±0.2 °C. TG-DTA measurements were performed with a Differential Thermal Analyser TGD-3000M (Sinku-Riko) under static air with the heating rate of 3 °C/min.

## Results and Discussion

*Properties of the Solid Complexes.* In Table 1, the analytical data, magnetic moments at room temperature and colors of the mixed chelates obtained in this study are summarized. All of the analytical data agree fairly well with the proposed formulas. The dipm-halide complexes are monohydrates. When they were dried under reduced pressure, their colors turned from bluish violet to green. The loss of one $H_2O$ in this process was confirmed by TG-DTA method. The magnetic moments of all these chelates were normal, showing that they are mononuclear Cu(II) chelates. Solid reflectance spectra of these chelates were very similar to those in nonpolar solvents (see Table 2). The bands of $\tilde{\nu}_{C\equiv N}$ of NCS$^-$ in the IR spectra of the thiocyanate chelates with dipm, acac, and tfac appeared at 2070—2075 cm$^{-1}$, and those of $\tilde{\nu}_{C\text{-}S}$ of these three chelates at 770—780 cm$^{-1}$, indicating that the NCS$^-$ ions in them are N-bonded monodentate.[5)] All these results, and comparison with the previous data,[3,4)] support that the green solid chelates with the general formula [Cu(tmen)(dike)X] (X$^-$: halide or pseudohalide ion; dike: dipm, acac, tfac, or hfac) are all 5-coordinated. Their structure, therefore, is quite different from the planar one expected for the nitrates or perchlorates, [Cu(tmen)(dike)]X (X$^-$=$NO_3^-$ or $ClO_4^-$).

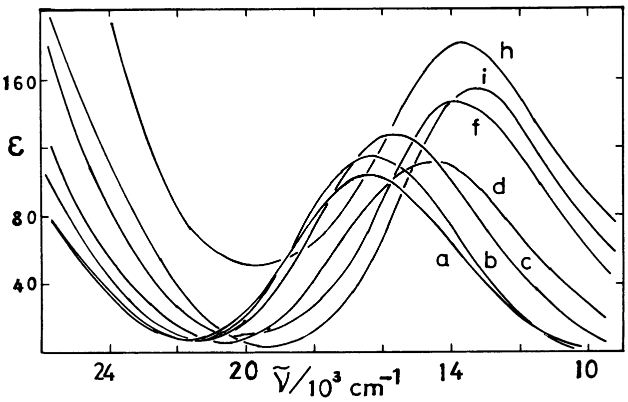

Fig. 1. Absorption spectra of [Cu(tmen)(tfac)Cl] in various solvents. The alphabetic notations **a** to **i**, on each curve are those for the solvents, and are the same as those in Table 2.

*Electronic Spectra of the Chelates in Various Solvents.* The characteristic properties of the chelates obtained are (1) their high solubility in various solvents, and (2) the drastic change in the color of the solution observed in going from one solvent to another, that is, strong solvatochromism of their solutions. In Fig. 1, the spectral changes of [Cu(tmen)(tfac)Cl] in various solvents are shown as an example of this solvatochromism. There are, in addition, (3) notable anion effect and (4) substituent effect of dike on the colors (or absorption spectra) of such solutions. All the spectral data ($\tilde{\nu}_{max}$ and $\varepsilon_{max}$ values of the d-d band) obtained are summarized in Table 2, including the previous data on Cu(tmen)(acac)X. A plot of $\tilde{\nu}_{max}$ values of the tfac-chelates is given in Fig. 2, which indicates the effects (2) and (3) more clearly.

At first, comparing the spectral and conductivity data (Table 3) of the chelates reported before, it can be seen that $ClO_4^-$ acts only as a counter ion of the chelate cation, and does not interact in any solvent with the latter. Consequently, the structure of [Cu(tmen)(tfac)]$ClO_4$ in solution depends only on the donor properties of the solvent used (Gutmann's donor number=DN), as was reported previously in similar systems.[4)] In other words, there exist only solute-solvent interactions in these systems: the spectral changes observed in such a

TABLE 2. THE $\tilde{\nu}_{max}$ (IN $10^3$ $cm^{-1}$) AND $\varepsilon_{max}$ (IN PARENTHESES) VALUES OF THE COMPLEXES IN VARIOUS SOLVENTS[a)]

| Cu(tmen)(tfac)X | $H_2O$ (=**a**) | MeOH (=**b**) | EtOH (=**c**) | DMSO (=**d**) | DMF (=**e**) | NM (=**f**) | $CH_3CN$ (=**g**) | DCE (=**h**) | Aectone (=**i**) |
|---|---|---|---|---|---|---|---|---|---|
| X=Cl | 16.46(103) | 16.33(114) | 15.69(128) | 14.60(111) | 13.94(137) | 13.89(147) | 13.79(148) | 13.75(181) | 13.33(158) |
| X=Br | 16.50( 84) | 16.39( 92) | 15.94(103) | 15.57( 87) | 14.93( 82) | 14.39(113) | 14.50(107) | 13.89(147) | 13.70(182) |
| X=I | 16.46(111) | 16.46(115) | 16.20(128) | 15.69(105) | 15.94( 97) | 16.20( 93) | 16.46(109) | 13.99(183) | 14.34(146) |
| X=NCS | 16.39(103) | 16.00(116) | 15.15(129) | 15.57(111) | 15.21(110) | 14.71(131) | 14.87(128) | 14.39(156) | 14.24(116) |
| Cu(tmen)(dipm)X | | | | | | | | | |
| X=Cl·$H_2O$ | — | 17.02(117) | 16.81(124) | 16.30(126) | 15.38(102) | 15.33(104) | 15.15(114) | 14.29(167) | 13.99(171) |
| X=Br·$H_2O$ | — | 17.02(126) | 16.88(134) | 16.39(126) | 16.46(110) | 17.39( 96) | 16.81(115) | 14.66(177) | 14.55(168) |
| X=NCS | — | 16.95(131) | 16.53(135) | 16.39(132) | 16.46(117) | 16.00(106) | 16.20(121) | 14.93(156) | 15.04(151) |
| Cu(tmen)(hfac)X | | | | | | | | | |
| X=Cl | — | 15.21(105) | 14.29(132) | 14.18(129) | 14.18(121) | 13.89(132) | 13.89(132) | 13.61(142) | 13.79(133) |
| X=Br | — | 15.27(106) | 14.34(147) | 14.08(141) | 13.99(153) | 13.99(173) | 13.94(179) | 13.75(200) | 13.89(195) |
| Cu(tmen)(acac)X | | | | | | | | | |
| X=Cl | 16.89(101) | 16.89(123) | 16.67(133) | 16.00(121) | 14.71(114) | 14.53(128) | 14.53(132) | 14.03(169) | 13.83(153) |
| X=Br | 16.89(101) | 16.84(108) | 16.72(130) | 16.21(129) | 16.21(112) | 15.82(103) | 16.08(112) | 14.45(173) | 14.39(154) |
| X=I | 16.89( 97) | 16.92(106) | 16.75(111) | 16.26(113) | 16.50(100) | 18.48( 96) | 17.27(100) | 15.15(135) | 16.47( 94) |
| X=NCS | 16.86( 99) | 16.84(121) | 16.29(123) | 16.21(125) | 16.21(111) | 15.48(118) | 15.67(115) | 14.71(153) | 14.79(138) |

a) The notation of the respective solvent in parentheses is used in this article (see Figs. 1, 2 and 5).

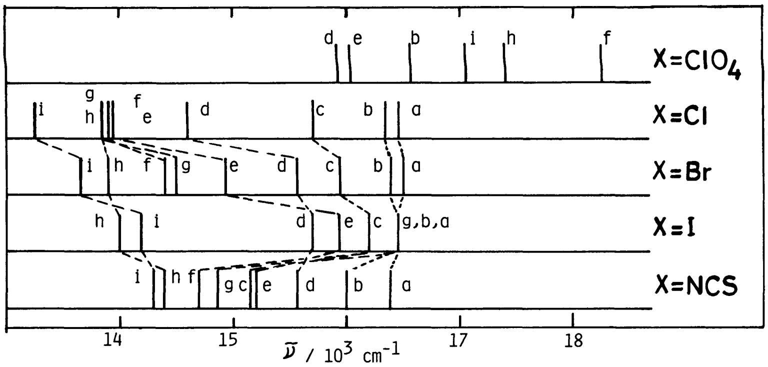

Fig. 2. The $\tilde{\nu}_{max}$ values of the complexes Cu(tmen)(tfac)X in various organic solvents. As to the notations **a** to **i**, *cf.* Fig. 1. The data for X=$ClO_4$ were taken from Ref. 2.

system will be called "Type A Solvatochromism." The characteristics of this solvatochromism are summarized schematically below, taking [Cu(tmen)(tfac)]$ClO_4$ as an example.

$[Cu(tmen)(tfac)]^+ \longrightarrow [Cu(tmen)(tfac)(Solv)_2]^+$

Structure: More planar ⟶ Tetragonal

⟶ More octahedral

$\tilde{\nu}_{max}$ of the solution: Higher ⟶ Lower

Solvent Polarity (DN): Small ⟶ Large

Color of the Complex: Violet ⟶ Blue

(Type A Solvatochromism)

The behaviors of halide- and NCS-chelates in various solvents are now very different. Here the anion in the complex can be coordinated to the chelate cation as well as the solvent molecules, so that the competition of these two types of ligands for the axial site(s) of the chelate cation takes place. These situations are so-called "solute-solute-solvent interaction," and are schematically shown in Fig. 3.

In a polar solvent, the negative center of the 5-coordinated complex, *i.e.*, the $X^-$ anion, attracts the positive ends of the solvent molecules (hydrogen bond will be formed when the solvent is amphiprotic). The Cu–X bond is weakened by this interaction, and finally dissociates off the $X^-$ anion. In the previous paper,[4)] we emphasized this effect, and stated that the main driving force to dissociate the anion $X^-$ from such a complex is the anion solvation power of the solvent used, which is expressed as the acceptor number (AN),[6,7)] the $E_T$ value,[8)] or the *Z* value.[9)]

TABLE 3. ELECTRIC CONDUCTIVITY DATA OF Cu(tmen)(dike)X IN VARIOUS SOLVENTS[a,b)]

| Complex | $CH_3CN$ | NM | DCE |
|---|---|---|---|
| Cu(tmen)(dipm)Cl·$H_2O$ | 67.2(45) | 38.5(45) | 0.7( 4) |
| Cu(tmen)(acac)Cl | 46.2(33) | 43.7(51) | 0.6( 3) |
| Cu(tmen)(tfac)Cl | 15.5(11) | 7.8( 9) | 0.3( 2) |
| Cu(tmen)(hfac)Cl | 6.2( 4) | 2.0( 2) | 0.3( 2) |
| Cu(tmen)(dipm)Br·$H_2O$ | 106.3(76) | 60.1(71) | 1.5( 8) |
| Cu(tmen)(acac)Br | — | 70.5(83) | 1.2( 6) |
| Cu(tmen)(tfac)Br | 49.2(35) | 17.5(21) | 0.3( 2) |
| Cu(tmen)(hfac)Br | 17.2(12) | 6.6( 8) | 0.6( 3) |
| Cu(tmen)(tfac)I | 120.9(86) | 54.8(65) | 4.3(22) |
| Cu(tmen)(dipm)NCS | 99.0(71) | 44.9(53) | 1.3( 7) |
| Cu(tmen)(acac)NCS | — | 56.6(65) | 1.1( 6) |
| Cu(tmen)(tfac)NCS | 43.7(31) | 13.8(16) | 0.3( 2) |

a) Standard values for a 1:1 electrolyte are 140, 85, and 20 in $CH_3CN$, NM, and DCE, respectively.[10)] b) The values in parentheses are the degree of the dissociation (%) of the anion based on the standard values given in a).

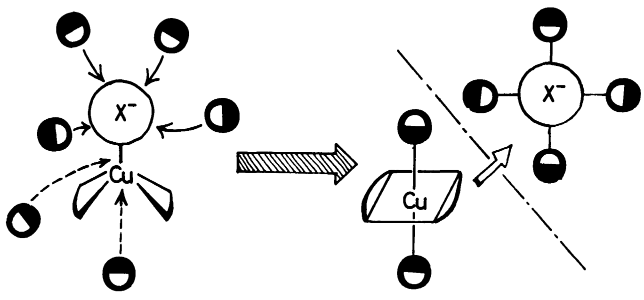

Fig. 3. Schematic representation of the dissociation process of the 5-coordinated complex in a polar organic solvent. The solvent molecules are shown here by half-shadowed balls; their white and dark halves, respectively, correspond to the positive and negative ends of the molecules.

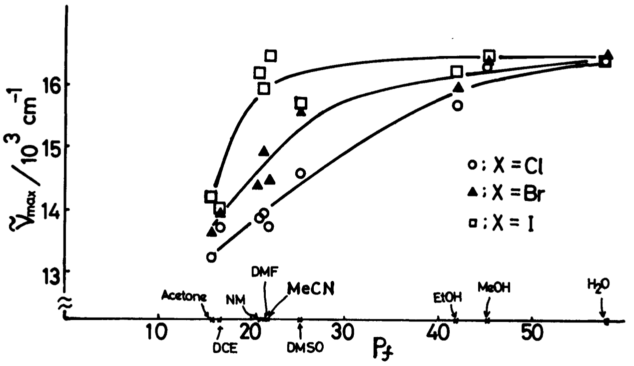

Fig. 4. The correlation between the $\tilde{\nu}_{max}$ values of the complexes Cu(tmen)(tfac)X in various solvents and the solvent parameter $P_f$.

A look at Fig. 3 suggests, however, that there is another cooperative factor, *i.e.*, the coordination power of the solvent to the metal ion which corresponds to the donor number (DN) of the solvent. In fact, although there is a general correlation between the $\tilde{\nu}_{max}$ of the solutions of these types of chelates and AN of their solvents,[*2] there are certain deviations which indicate that, when two solvents have similar AN values, the one with the larger DN favors the change shown in Fig. 3.

Taking this into account, we have newly introduced a new polarity parameter of the solvent, polarity factor ($P_f$), which is a linear combination of AN and DN. Figure 4 shows the relation between the $\tilde{\nu}_{max}$ of the tfac-halide-chelates and $P_f$ values of the solvents which, in this paticular case, were taken to be equal to

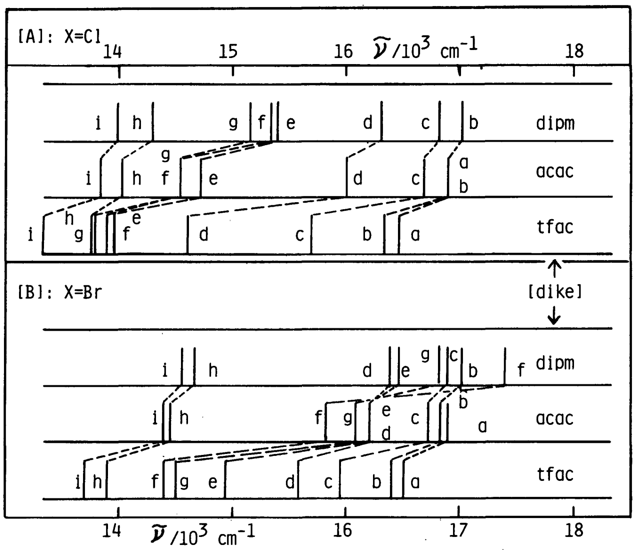

Fig. 5. The $\tilde{\nu}_{max}$ values of the complexes Cu(tmen)(dike)X in various solvents, [A]=[Cu(tmen)(dike)Cl] and [B]=[Cu(tmen)(dike)Br]. As to the notations a to i, *cf.* Fig. 1.

(AN+0.2DN). The fact that the change in Fig. 3 is favored with the increase of this $P_f$, and in the order of $I^->Br^->Cl^-$, is clearly seen from these curves. Similar curves can also be obtained for the Cl- or Br-acac-chelates, although the points for the I-acac-complex tend to scatter.[1)]

Previous results showed that, in general, increasing strength of the $Cu^{2+}$–$X^-$ bond brings about the stabilization of 5-coordinate species which, in its turn, is reflected on the decrease of its $\tilde{\nu}_{max}$. Comparing the $\tilde{\nu}_{max}$ values in solvents of very low $P_f$ (DCE or acetone) where the 5-coordinate species predominate, it can be seen that they change in the order of $Cl^-<Br^-<I^-$, indicating that the stabilities of the 5-coordinated species are in the opposite order. The conductivity data (see below) also show that the Cl-complex is more stable than the Br-complex, and the I-complex is the most unstable, as the 5-coordinate species in the same solvent. Thus it is evident that the stability order of the 5-coordinate complexes, [Cu(tmen)(dike)X], in solution is $Cl^->Br^->I^-$. Comparison with the data of the NCS-complex shows that it comes between $Cl^-$ and $Br^-$, or sometimes near $Cl^-$ or $Br^-$ in this series, although its exact position seems to depend markedly on the solvent used.

Figure 5 shows the $\tilde{\nu}_{max}$ diagram of the Cl- and Br-complexes with different kinds of dike in various solvents, including the data of the corresponding acac-complexes reported previously. The $\tilde{\nu}_{max}$ of a chelate containing $Cl^-$ or $Br^-$ changes, in general, in the order of MeOH>EtOH>DMSO>DMF>NM>$CH_3CN$>DCE≃ acetone in various solvents (*i.e.*, nearly in the order of $P_f$), with some ambiguity at hfac-chelates. And, in the same solvent, for example in MeOH, EtOH, or DMSO, it changes as dipm>acac>tfac>hfac, with

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[*2] This correlation of $\tilde{\nu}_{max}$ with AN (and that with Pf) can be understood with the view that the $\tilde{\nu}_{max}$ of a solution is determined by the position of the equilibrium (1) in it (see later). In fact, the absorption band observed is a superposition of the band of [Cu(tmen)(dike)X] and that of [Cu(tmen)(dike)(Solv)$_2$]$^+$, and the latter is susceptible to type A solvatochromism, changing somewhat from one solvent to another. Nevertheless, examination of the data indicates, in most cases, that the above view can be taken as a reasonable approximation.

the change of the α-substituent groups in dike. This is the same as the order of the ligand field strengths of the dike ligands, although the degree of the shift of the $\tilde{\nu}_{max}$ from one another is different in each solvent; *e.g.*, in MeOH and EtOH the shifts of the $\tilde{\nu}_{max}$ of the hfac-chelate from that of the dipm-chelate are rather large, but that in DCE is very small.*3) The conductivity data (see below), on the other hand, reveal that the degree of dissociation of the dipm-chelate (for example, Cu(tmen)(dipm)Cl: 45 % in $CH_3CN$) is, in most cases, larger than those of the corresponding chelates of acac, tfac, or hfac, which decreases in this order (33, 11, and 3%, respectively, in $CH_3CN$). All these data mean that, as the equatorial ligand field of the chelate is weakened by the α-substituents, the coordination of the axial ligand $X^-$ is strengthened, and the equilibrium leading to the tetragonal, solvated [Cu(tmen)(dike)] cation (see below) is thus shifted to the left hand side.

The characteristics of the spectral changes in the present systems, which will be called "Type B Solvatochromism," can thus be summarized as follows:

$$[\mathrm{Cu(tmen)(dike)X}] + n(\mathrm{Solv}) \rightleftharpoons [\mathrm{Cu(tmen)(dike)(Solv)_2}]^+ + \mathrm{X^-(Solvated)} \qquad (1)$$

Structure: 5-Coordinated $\rightleftharpoons$ Tetragonal
$\tilde{\nu}_{max}$ of the solution : Lower ⟶ Higher
Solvent Polarity (Pf) : Small ⟶ Large
Anion Effect($X^-$): $Cl^-$ ⟶ ($NCS^-$) ⟶ $Br^-$ ⟶ $I^-$
Substituent Effect(dike): hfac ⟶ tfac ⟶ acac ⟶ dipm
Color of Solution: Green ⟶ Bluish violet
(Type B Solvatochromism)

The anion effect and substituent effect may be called, respectively, the "Axial Ligand Field Variation Effect" and "Equatorial Ligand Field Variation Effect" on the Type B solvatochromism. Owing to the latter effect, the tetragonal structure is stabilized especially in the case of the dipm chelates. This may be reflected in the easy formation of monohydrates of these chelates, Cu(tmen)(dipm)X·$H_2O$ (see experimental).

*Electric Conductivities of the Chelates.* Electric conductivity data (molar conductance) of the chelates in three solvents($CH_3CN$, NM, and DCE) are summarized in Table 3. These and similar results obtained in other solvents in Table 2 can be explained as follows, supporting the conclusions of the spectral observations.

1) In alcohols and $H_2O$, almost all of the complexes dissociate strongly into $[Cu(tmen)(dike)(Solv)_2]^+$ and $X^-$, except the hfac-Cl-complex which decomposes into $[Cu(tmem)(hfac)_2]$ and $[Cu(tmen)Cl_2]$ in water (see next section). This is quite natural because the solvents have large DN and AN, so that their $P_f$ are high, and the equilibrium (1) is shifted strongly to the right hand side.

2) In a solvent with a lower $P_f$, such as $CH_3CN$ or NM, there is a smaller ionization of the complexes, *i.e.*, the equilibrium (1) is shifted to the right to a limited extent.

3) In the case of 2), there is a characteristic anion effect on the equilibrium. For example, the equilibrium of [Cu(tmen)(tfac)X] is shifted to the left hand side in the order of $Cl^- > NCS^- > Br^- > I^-$ in most solvents, as pointed out in last section.

4) In the case of 2), there is also a notable substituent effect on the equilibrium, as stated in the last section. The stability of the 5-coordinate species is found to increase as follows:

$$\mathrm{dipm} < \mathrm{acac} < \mathrm{tfac} < \mathrm{hfac},$$

although an apparent reversal of dipm and acac is observed at times (*cf.* the data in NM).

5) In a solvent with very low $P_f$ such as DCE or acetone, most of the chelates studied here exist as the stable 5-coordinate green species. In this case, notable anion effects and substituent effect cannot be observed.

*Ligand Rearrangement Reaction of Cu(tmen)(hfac)Cl.* As mentioned above, the tfac- or hfac-chelates containing electron-withdrawing $CF_3$ groups have a weak equatorial ligand field and favor axial coordination of the anion $X^-$. In the extreme case of the hfac-Cl-chelate, these effects make the 5-coordinate species unstable, so that a ligand rearrengment reaction (or disproportionation) occurs in water:

$$2[\mathrm{Cu(tmen)(hfac)Cl}] \rightleftharpoons [\mathrm{Cu(tmen)(hfac)_2}] + [\mathrm{Cu(tmen)Cl_2}].$$

The identity of each of the two disproportionation products was checked by their elementary analyses and spectral properties reported in the literature.[11] A very similar disproportionation was formerly observed with analogous Ni(II) chelates,[12] where the reaction could occur also in solid state and with other dike, *e.g.*, acac:

$$\underset{\text{greenish blue}}{2[\mathrm{Ni(tmen)(acac)X(OH_2)}]} \xrightarrow{\Delta} \underset{\text{green}}{[\mathrm{Ni(tmen)(acac)_2}]} + \underset{\text{violet}}{[\mathrm{Ni(tmen)X_2}]}$$

The non-charged stable chelate, $[Ni(tmen)(acac)_2]$, formed by this thermal reaction was very volatile, so it was easy to separate the two disproportionation products from each other.[12]

In the copper system, at present, we could not observe such a thermal reaction. Any drastic weight loss, or release or absorption of heat, could not be observed by TG-DTA technique, until a complicated decomposition begins to take place. This difference

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*3) In the case of the bromide-dipm complex, the $\tilde{\nu}_{max}$ of most complexes tend to flock together, showing type A solvatochromism to some extent, and only those in DCE and acetone are left apart from them. This is similar to the result observed with the iodide-tfac complex (*cf.* Fig. 2), and indicates that the stronger ligand field of dipm hinders the coordination of $Br^-$ quite remarkably, while the weaker tfac can do so only toward $I^-$.

between the Cu(II)- and the Ni(II)-chelates may be explained by the crystal field stabilization energies and the complex-forming powers of these metal ions (Irving-William's rule) and the Jahn-Teller effect in the copper(II) system. More precise work along this line is now in progress.

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