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Studies on Mixed Chelates. VIII. Mixed Copper(II) Chelates with *N,N'*- and *N,N*-Dialkylethylenediamines and Acetylacetone

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Synopsis. Mixed chelates [Cu(diamine)(acac)]X (diamine: *N,N'*- and *N,N*-dialkylethylenediamines) were studied. Two such chelates with diethyl ligands were obtained in crystalline state, while the formation of chelate cations $[Cu(diamine)(acac)]^+$ in 80% dioxane was studied with dimethyl ligands, and their formation constants estimated. The importance of steric effect in the bis-diamine chelates on the ease of formation of this type of chelate was pointed out.

The authors have studied the mixed chelates of the type [Cu(diamine)(acac)]X, with diamines such as 2,2'-bipyridine, 1,10-phenanthroline, and *N,N,N',N'*-tetramethyl- and tetraethylethylenediamines (bpy, phen, tmen and teen; acac=acetylacetonate ion)[1-4] and observed that (i) they are formed quite easily in appropriate organic solutions, *i.e.*, their formation constants are quite high; (ii) the ν_{max} values of their d-d band often do not obey the rule of Kida[5], which says that the ν_{max} of a mixed chelate CuAB is the mean of the values of its parent chelates CuA_2 and CuB_2; and (iii) the ν_{max} of the tmen and teen chelates are influenced strongly by the nature of the solvents used.

Extending these studies, the authors studied similar mixed chelates with *N,N'*-dimethyl, *N,N*-dimethyl-, *N,N'*-diethyl- and *N,N*-diethylethylenediamines (abbreviated as sym-dmen, unsym-dmen, sym-deen and unsym-deen, respectively).

Experimental

Preparation of the Chelates. $[Cu(sym\text{-}deen)(acac)]ClO_4$ and $[Cu(unsym\text{-}deen)(acac)]ClO_4$ are prepared as follows. $Cu(ClO_4)_2 \cdot 6H_2O$ (5 mmol) is dissolved in ethanol, and acetylacetone (5 mmol), Na_2CO_3 (2.5 mmol) and deen (5 mmol) are added successively. The crystals which separate out from the mixture are recrystallized from ethanol.

Physical Measurements. The methods and instruments used in this work were the same as those in the previous papers of this series.[1-4]

Results and Discussions

Crystalline Chelates. Although it was tried to prepare the chelates with all the four diamines, using several anions of low coordination power, it was found that many of such chelates are very hard to crystallize, and only the two in Table 1 could be obtained with sufficient purity, which are apparently very similar to the chelate $[Cu(tmen)(acac)]ClO_4$ studied before.

The values of ν_{max} in their electronic spectra (Table 2) show a strong solvent effect, which is comparable to that observed with $[Cu(tmen)(acac)]ClO_4$,[1,2] and that the unsym-deen chelate is a little more sensitive than the sym-deen chelate toward solvent change.

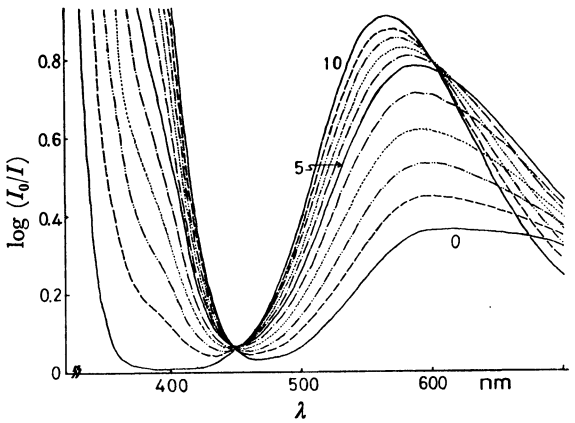

Fig. 1. Electronic spectra of the mixtures of $[Cu(sym\text{-}dmen)_2](ClO_4)_2(CuA_2)$ and $[Cu(acac)_2](CuB_2)$ in 80% dioxane at 18 °C. Total chelate concentration 0.91×10^{-2} M, cell thickness 1 cm. The ratio $[CuA_2]$: $[CuB_2]$ in each sample is 10: 0 (Curve 10), 9: 1, 8: 2, 7: 3, 6: 4, 5: 5 (Curve 5), 4: 6, 3: 7, 2: 8, 1: 9, and 0: 10 (Curve 0).

TABLE 1. COLORS, COMPOSITIONS[a] AND MAGNETIC MOMENTS OF THE CHELATES

No.	Chelate	Color	C %	H %	N %	μ_{eff} (B.M.)
I	$[Cu(sym\text{-}deen)(acac)]ClO_4$	Reddish violet	35.46 (34.92)	6.58 (6.13)	7.52 (7.40)	1.83
II	$[Cu(unsym\text{-}deen)(acac)]ClO_4$	Reddish violet	34.79 (34.92)	6.18 (6.13)	7.39 (7.40)	1.81

a) Calculated values in parentheses.

TABLE 2. $\nu_{max}/10^3$ cm^{-1} AND ε_{max} (IN PARENTHESES) OF THE CHELATES IN VARIOUS SOLVENTS

No.	CH_3NO_2	$ClCH_2CH_2Cl$	CH_3CN	H_2O	80%-Dioxane	DMF	DMSO
I	18.18(87)	17.79(83)	17.12 (92)	16.69 (85)	16.69 (93)	16.56 (92)	16.37 (98)
II	18.28(95)	17.64(98)	17.09(106)	16.50(103)	16.47(108)	16.39(108)	16.05(117)

Stability Studies in Solution. The formation of the mixed chelates were also studied in solution. [Cu(sym-(or unsym-)dmen)$_2$]$(ClO_4)_2$ and [Cu(acac)$_2$] were dissolved in 80% dioxane (v/v), and the method of continuous variation was applied to the visible spectra of their mixtures (Fig. 1). The plots clearly indicate the formation of 1 : 1 mixed chelates in solution, with formation constant $K([CuAB]^2/[CuA_2][CuB_2])$ estimated to be 500—600 at 18 °C. The same method applied to the system [Cu(sym-deen)$_2$]$(ClO_4)_2$–[Cu(acac)$_2$] yielded similar results with a still higher value of K(*ca.* 2500 at 18 °C).

Although the accuracy of this estimation is not high,[6] comparison of these values with the K of [Cu(en)(acac)]$^+$ in 75% dioxane reported formerly by Kida (2.6)[5] clearly shows that K increases strongly with the increase in the bulkiness of the *N*-alkyl groups in the diamine.* Now the expression for K can be written as follows:

$$K = (k_{AB} \cdot k_{BA})/(k_{2A} \cdot k_{2B})$$

Here $k_{AB}=[CuAB]/[CuA][B]$, $k_{BA}=[CuAB]/[CuB][A]$, $k_{2A}=[CuA_2]/[CuA][A]$, and $k_{2B}=[CuB_2]/[CuB][B]$.

If A and B are identified with a diamine (en, dmen or deen) and acac, respectively, the data in the literature (*cf.* Table 3) show that k_{2A} decreases remarkably in

Table 3. Values of k_2 for various diamines (25 °C, $I \rightarrow 0$)[7]

Diamine	k_{2A}	Diamine	k_{2A}
en	9.07	sym-deen	5.57
sym-dmen	6.94	unsym-deen	5.47
unsym-dmen	6.83		

going from en to dmen's and deen's (to *ca.* 1/150 and 1/3500 of the original value, respectively), owing to the increasing interligand repulsion in the bis-chelate. On the other hand, k_{2B} is naturally independent of A, and model study indicates that the interligand repulsion in CuAB will be nearly absent, so that the changes of k_{AB} and k_{BA} accompanying the change in A will be small. Thus it can be expected that the value of K is determined chiefly by $1/k_{2A}$, which increases about 150 and 3500 times in going from en to dmen's and deen's, respectively. The changes observed among the experimental values of K given above (*ca.* 200 and 1000 times) are not far from this expectation. These considerations thus give further support to the previously expressed view that the stability of the bpy-, phen- and tmen-containing mixed chelates is, to a large part, due to such an effect.[1]

It may be added that, if it is assumed that the spectra of the solutions containing the parent chelates in 1 : 1 ratio are very nearly those of the mixed chelates themselves (the fairly large K values support this view), their ν_{max} values satisfy Kida's rule approximately, indicating that the interligand repulsion in the bis-diamine chelates is not so strong to distort them remarkably from common tetragonal symmetry** (Table 4).

Table 4. $\nu_{max}/10^3$ cm^{-1} of the chelates [Cu(diamine)$_2$]$^{2+}$ and [Cu(diamine)-(acac)]$^+$ in 80% dioxane

Diamine	ν_{max} (bis-chelate)	ν_{max} (mixed chelate)
sym-dmen	17.61	16.98(16.87[a])
unsym-dmen	17.73	16.75(16.93)
sym-deen	17.24	16.69(16.69)
unsym-deen	17.04	16.50(16.59)

a) Values calculated with Kida's rule (ν_{max} for [Cu(acac)$_2$]: 16130 cm^{-1}) are in parentheses.

References

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7) Data of R. Näsänen taken from "Stability Constants of Metal-Ion Complexes" (Compiled by L. G. Sillén and A. E. Martell), Supplement No. 1, The Chemical Society, London (1971).

* K for [Cu(unsym-deen)(acac)]$^+$ could not be estimated with reasonable accuracy, possibly owing to the errors introduced by the smaller stability of [Cu(unsym-deen)$_2$]$^{2+}$ than those of the other bis-chelates. On the other hand, the values of K for the [Cu(diamine)(acac)]$^+$-type chelates with *N*-methyl- and *N*-ethylethylenediamines were found to be 9—10 (75% dioxane, 20 °C), lying between those of [Cu(en)(acac)]$^+$ and [Cu(dmen)(acac)]$^+$ (Y. Kuma, unpublished study).

** *Cf.*, *e.g.*, the data of [Cu(bpy)$_2$]$^{2+}$, [Cu(phen)$_2$]$^{2+}$ and their mixed chelates studied before.[4]