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Studies on Mixed Chelates. VI. Mixed Copper(II) Chelates with *N,N,N′,N′*-Tetraethylethylenediamine and Various *β*-Diketones

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Ten new mixed copper(II) chelates containing *N,N,N′,N′*-tetraethylethylenediamine and various *β*-diketones were prepared and the cause of the large variations of $\nu_{\max}$ values observed in the visible absorption spectra of their organic solutions was discussed in comparison with similar variations of the corresponding tetramethyl chelates.

In previous papers,[1,2] the authors reported on the mixed copper(II) chelates containing *N,N,N′,N′*-tetramethylethylenediamine(tmen) and various *β*-diketonate ions. It was found that the position of the d-d band of such chelates depends remarkably upon the coordination ability of the solvent and counter anion, and upon the nature of the substituent groups in the diketonate ions. The present study on the preparation and spectra of the corresponding chelates containing *N,N,N′,N′*-tetraethylethylenediamine(teen) was undertaken to see how the bulkiness of the *N*-alkyl groups affects the structure and spectra of these types of chelates.

Experimental

Preparation of the Chelates. *(I) [Cu(teen)aca]ClO₄*: Acetone solutions of $Cu(ClO_4)_2 \cdot 6H_2O$ and aca* (10 mmol each) were mixed together with teen** (15 mmol) with vigorous stirring. After the mixture had been filtered and concentrated, an excess of diethyl ether was added. Crystals of the chelate began to separate out when the vessel wall was scratched with a glass rod. They were washed with an acetone–diethyl ether mixture and dried in a vacuum.

(II) Other Chelates: Acetone solutions of $Cu(ClO_4)_2 \cdot 6H_2O$ (or $Cu(NO_3)_2 \cdot 3H_2O$) and a *β*-diketone (10 mmol each) were mixed together with teen (15 mmol) as in (I), and the filtered mixture was evaporated to dryness. The raw chelate thus obtained was purified by repeated crystallization from 1,2-dichloroethane, and dried in a vacuum.

The colors, magnetic moments, and analytical data of the new chelates are listed in Table 1. All the chelate perchlorates and nitrates are apparently similar to the tmen chelates reported before; however it was impossible to prepare [Cu(teen)hfa]NO_3, and a green chelate [Cu(teen)hfa$_2$] was obtained instead. For the physical measurements *cf.* previous papers.[1,2]

Discussion

Electronic Spectra. As in the case of the corresponding tmen chelates, all the teen chelates obtained are fairly soluble in a variety of organic solvents. Measurements of the visible absorption spectra in solution, and the reflection spectra in the solid state, revealed a close resemblance between these spectra and those of the corresponding tmen chelates. Here again it seems that the position of the d-d band depends on two factors, (1) the nature of the substituent groups in the *β*-diketonate ions, which controls the magnitude of the in-plane ligand field strength, and (2) the strength of the axial bonds formed between the central copper(II) and the counter anions or solvent molecules.

The data in organic solutions are of special interest. Fig. 1 shows some examples of the obtained spectra, *i.e.*, the spectra of [Cu(teen)aca]ClO_4 in five solvents. The variations of the $\nu_{\max}$ value of the d-d band of each chelate in organic solutions are summarized in Fig. 2.

The spectral variations among the chelate perchlorates are especially similar to those of the corresponding tmen chelates. Thus the $\nu_{\max}$ value for each chelate decreases in the following order of solvent,

$$1,2\text{-}C_2H_4Cl_2 > \text{acetone} > \text{MeOH} > \text{DMF} > \text{DMSO}$$

and the $\nu_{\max}$ value in one particular solvent decreases in the following order of the *β*-diketonate ion,

$$\text{dpm} > \text{aca} > \text{bza} > \text{dbm} \gg \text{hfa}$$

just as in the case of the tmen chelates.

Table 1. Colors, analytical data,[a)] magnetic moments and molar conductivities of the chelates

No.	Chelate	Color	C%	H%	N%	μ_{eff} (B.M.)	Λ_M[b)]
1	[Cu(teen)dpm]ClO_4	Wine	47.64(48.54)	8.37(8.54)	5.49(5.39)	1.71	32.3
2	[Cu(teen)aca]ClO_4	Wine	41.24(41.47)	7.01(7.19)	6.42(6.45)	1.76	34.4
3	[Cu(teen)bza]ClO_4	Wine	47.75(48.28)	6.81(6.69)	5.67(5.63)	1.77	31.6
4	[Cu(teen)dbm]ClO_4	Wine	52.90(53.65)	6.37(6.31)	4.98(5.01)	1.71	31.2
5	[Cu(teen)hfa]ClO_4	Blue	33.29(33.16)	4.94(4.82)	5.01(5.16)	1.73	9.3
6	[Cu(teen)dpm]NO_3	Blue	52.68(52.31)	9.37(9.20)	8.88(8.72)	1.79	25.1
7	[Cu(teen)bza]NO_3	Green	52.25(52.33)	7.07(7.25)	9.38(9.15)	1.76	20.2
8	[Cu(teen)dbm]NO_3	Wine	57.41(57.62)	6.78(6.78)	8.14(8.06)	1.77	21.9
9	[Cu(teen)tfa]NO_3	Blue	39.67(39.95)	6.10(6.26)	9.15(9.32)	1.81	6.6
10	[Cu(teen)hfa$_2$]	Green	37.12(36.95)	3.69(4.04)	4.14(4.31)	1.81	—

a) Calculated values in parentheses. b) 1×10^{-3}M solution in 1,2-dichloroethane at 25 °C.

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* Abbreviations for the names of the diketonate ions are the same as those given in Part V of this series.[3]

** Aldrich Chemical Co., Milwaukee, USA.

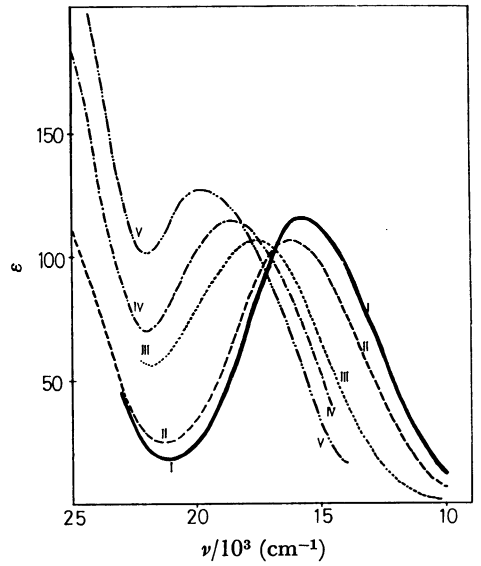

Fig. 1. Electronic absorption spectra of [Cu(teen)aca]-ClO_4 in various solvents. (*Cf.* also Fig. 2).

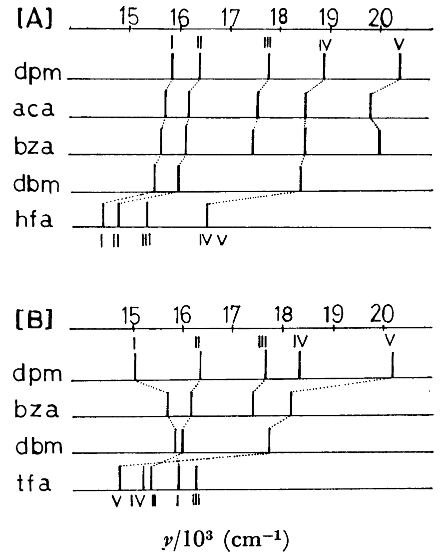

Fig. 2. Variations of the ν_{max} values of the chelates [Cu-(teen)β-dik]X in various solvents. [A]: $X=ClO_4$, [B]: $X=NO_3$. The solvents studied in Figs. 1 and 2 are: DMSO(I), DMF(II), MeOH(III), acetone (IV) and 1,2-dichloroethane (V); concn ≈5 mM.

The variations among the chelate nitrates seem to be more complicated, poor solubility and the appearance of shoulder-like curves sometimes hindering the correct locating of the bands. However, it can be recognized that the ν_{max} in 1,2-dichloroethane and acetone decrease drastically in going from dpm to tfa, probably for the same reason as that for a similar spectral anomaly observed among the spectra of the tmen chelates in 1,2-dichloroethane, *i.e.*, the coordination of NO_3^- to the chelate cation.

The general features shown in Fig. 2 are thus fairly similar to the corresponding figure of the tmen chelates,[2] but the spectra of the teen chelates seem to be more sensitive to the changes of solvent, anion and substituent groups. For example, in going from DMSO to 1,2-dichloroethane, the ν_{max} of [Cu(tmen)dpm]ClO_4 changes from 16600 to 18900 cm^{-1}, while that of [Cu(teen)dpm]ClO_4 changes from 15800 to 20400 cm^{-1}. One can also compare the complicated pattern of Fig. 2 [B] with the corresponding figure of the tmen chelates, which looks more regular except for the above-mentioned anomaly of 1,2-dichloroethane solutions.

This spectral sensitivity of the teen chelates seems strange, since the four bulky *N*-ethyl groups in teen can be expected to hinder the approach of the solvents and anions more strongly than the *N*-methyl groups of tmen, so that the electronic structure of the teen chelate should be more insensitive to the changes of environment. In fact, the mixed nickel(II) chelates of teen and β-diketonate ions were found to be much more reluctant to combine with solvent molecules and change from square planar to octahedral than the corresponding tmen chelates.[3]

The cause of this spectral sensitivity might be found in the fact that copper(II), unlike nickel(II), tends to form axial bonds even with ligands lying far away from it, and even when they lie considerably outside the z-axis. That is, the axial bonds are considerably elastic or flexible in nature.[4]

It is thus conceivable that the above-mentioned steric hindrance in the teen chelates works only when the coordination ability of the solvent or anion is very low and the in-plane l.f.s. is sufficiently large; in such a case a highly planar chelate structure will result, and its ν_{max} may be higher than that of its tmen analogue. On the other hand, when the coordination ability of the solvent or anion becomes higher and the in-plane l.f.s. lower, the steric hindrance will be readily overcome, and a more or less deformed tetragonal structure will result. The effective l.f.s. in such a structure may be somewhat weaker, and its ν_{max} lower, than that of its tmen analogue, because there will be larger interligand repulsions and structural deformations in the teen system. The observed larger spectral variations among the teen chelates may be a reflection of all these effects.

It should be added that the chelate [Cu(teen)hfa_2] shows only a small variation of ν_{max} in various solvents

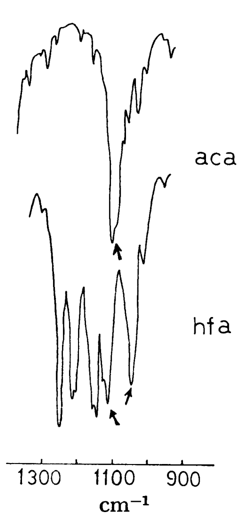

Fig. 3. IR spectra of [Cu(teen)β-dik]ClO_4 in Nujol mulls.

(14080 to 14580 cm^{-1} in DMSO, methanol and 1,2-dichloroethane) probably owing to its 6-coordinate structure which somewhat resembles the chelate [Cu bip hfa$_2$] reported by Veidis *et al.*$^{5)}$

Evidence of Perchlorate Coordination. The data in Fig. 2 suggest that, in 1,2-dichloroethane with very poor coordination ability, and with hfa with the weakest l.f.s. among the diketonate ions used, even ClO_4^- gets coordinated to some extent, since the ν_{max} of [Cu(teen)-hfa]ClO_4 in this solvent is remarkably low and nearly the same as that of the same chelate in acetone. This leads further to the supposition that the same kind of perchlorate coordination will also occur in the crystals of this chelate. The conductivity data in Table 1, and the fact that the IR main peak of ClO_4^- which appears single in other chelates is apparently split in the spectrum of this chelate (Fig. 3) support these suppositions. Similar observations have been made on the tmen system.$^{2)}$

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