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Studies on Mixed Chelates. I. Mixed Copper(II) Chelates with *N,N,N′,N′*-Tetramethylethylenediamine and a Bidentate Ligand

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Six new mixed copper(II) chelates with *N,N,N′,N′*-tetramethylethylenediamine and a bidentate ligand, *i.e.*, [Cu tmen en] $(ClO_4)_2$, [Cu tmen en] $(NO_3)_2 \cdot H_2O$, [Cu tmen en]$(SO_4) \cdot 4H_2O$, [Cu tmen gly](ClO_4), [Cu-tmen ox]$\cdot 4H_2O$ and [Cu tmen aca](ClO_4) were prepared, and their visible absorption spectra were compared with those of the bis-chelate ions and molecules, $[Cu\ en_2]^{2+}$, $[Cu\ gly_2]$, $[Cu\ ox_2]^{2-}$, and $[Cu\ aca_2]$. The results obtained indicate that steric factors play an important role in the formation and structure of these mixed chelates. The effects of various organic solvents on the electronic spectra of these chelates were also studied. (tmen=*N,N,N′,N′*-tetramethylethylenediamine, en=ethylenediamine, gly=glycinate ion, ox=oxalate ion, aca=acetylacetonate ion.)

Copper(II) chelates with *N,N,N′,N′*-tetramethylethylenediamine (tmen) were investigated by several workers. Meek and Ehrhardt[1] showed that copper(II) ion readily combines with tmen to form a dimeric chelate cation, $[tmen\ Cu(OH)_2\ Cu\ tmen]^{2+}$, while the monomeric bis-chelate cation, $[Cu\ tmen_2]^{2+}$ could not be prepared in spite of all their efforts. These results indicate that, when two molecules of tmen approach the central copper(II) ion, the bulky methyl groups on their donor *N* atoms collide strongly with each other, and the interligand steric hindrance is so large that the formation of bis-chelate becomes practically impossible.[2] On the other hand, Bertini and Mani[3] studied the metal complexes of tmen and related ligands, and showed that various monomeric copper(II) chelates containing one molecule of tmen and simple anionic ligands (Cu tmen X_2) can be prepared.

Recently we studied the formation of mixed copper(II) chelates with tmen and another chelating ligand. The ligands used are common ones (en, gly, ox, and aca) with no bulky groups around the donor atoms, and little steric hindrance is expected when one of them combines with copper(II) together with a tmen molecule. In agreement with this expectation, it was found that all these ligands form quite stable mixed chelates with tmen, the preparation and properties of which will be reported in this paper.

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[1] D. W. Meek and S. A. Ehrhardt, *Inorg. Chem.*, **4**, 584 (1965).

[2] D. W. Meek (*Inorg. Chem.*, **4**, 250 (1965)) pointed out, however, that the larger palladium(II) ion can form the bis-type chelate $[Pd\ tmen_2](NO_3)_2$.

[3] I. Bertini and F. Mani, *Inorg. Chem.*, **6**, 2032 (1967).

[4] Elementary analyses were performed at the Organic Microanalytical Section of the Institute of Physical and Chemical Research.

Experimental

Materials. The ligands used were obtained from Wako Pure Chemical Industries Ltd., and Tokyo Kasei Kogyo Co., Ltd. They were reagent grade samples and were used without further purification. Solvents used for spectral measurements were of "extra pure" or "spectro" grade.

Preparation of Mixed Chelates. a) [Cu tmen en]-$(ClO_4)_2$: 10 mmol of copper(II) perchlorate hexahydrate was dissolved in a small amount of water, and equimolar amounts of tmen and en were added with stirring. The resulting solution was concentrated on a water bath. The crude product which separated out was recrystallized from water. Reddish violet crystals (μ=1.84 B.M.).

Found: C, 21.70; H, 5.22; N, 12.69%. Calcd for Cu tmen en $(ClO_4)_2$: C, 21.90; H, 5.51; N, 12.79%.[4]

b) [Cu tmen en]$(NO_3)_2 \cdot H_2O$: The method for preparation was the same as in the case of (a) except that copper(II) nitrate trihydrate was used instead of perchlorate. Violet crystals (μ=1.86 B.M).

Found: C, 25.97; H, 6.90; N, 21.37%. Calcd for Cu tmen en $(NO_3)_2 \cdot H_2O$: C, 25.16; H, 6.86; N, 22.20%.

c) [Cu tmen en]$(SO_4) \cdot 4H_2O$: 10 mmol of copper(II) sulfate pentahydrate was mixed with equimolar amounts of tmen and en in a small amount of water. A violet paste deposited from the solution. This crude gummy product was purified by suspending it in acetone, and the violet crystalline powder obtained was washed with acetone and ether (μ=2.11 B.M.).

Found: C, 23.24; H, 7.23; N, 13.97%. Calcd for Cu tmen en $SO_4 \cdot 4H_2O$: C, 23.55; H, 7.90; N, 13.73%.

d) [Cu tmen gly](ClO_4): 5 mmol of the dimeric chelate, [tmen Cu $(OH)_2$ Cu tmen] $(ClO_4)_2$, prepared according to literature[1] with some modifications and identified by elementary analyses, and 10 mmol of glyH were mixed in a mortar, and about 50 m*l* of methanol was added with stirring. The mixture was filtered and concentrated on a water bath. The crude product which separated out was recrystallized from methanol. Blue-violet crystals (μ= 1.94 B.M.).

Found: C, 27.25; H, 5.79; N, 11.70%. Calcd for Cu tmen gly (ClO_4): C, 27.20; H, 5.70; N, 11.89%.

e) [Cu tmen ox]$\cdot 4H_2O$: The method of preparation was the same as in the case of (a), except that aqueous solutions of copper(II) sulfate pentahydrate, tmen, and potassium oxalate were used as starting materials. Pale blue crystals (μ=2.19 B.M.).

Found: C, 28.54; H, 7.12; N, 8.32%. Calcd for Cu tmen ox$\cdot 4H_2O$: C, 28.26; H, 7.12; N, 8.25%.

f) [Cu tmen aca](ClO_4): 10 mmol of copper(II) perchlorate hexahydrate dissolved in aqueous ethanol (1 : 1) and solutions of tmen and acaH (10 mmol each) in the same solvent were mixed together, and 5 mmol of anhydrous sodium carbonate was added to neutralize acaH. The mixed solution was concentrated on a water bath, and the crude product separated out was recrystallized from ethanol. Reddish violet crystals (μ=1.92 B.M.).

Found: C, 34.81; H, 6.00; N, 7.12%. Calcd for Cu tmenaca(ClO_4): C, 34.92; H, 6.13; N, 7.40%.

Physical Measurements. The electronic absorption spectra of the solutions between 1000 nm (10.0 kK) and 340 nm (29.4 kK) were recorded with a Shimadzu multiconvertible D-40R spectrophotometer and 10 mm silica cells. The reflection spectra of solid samples were obtained with the same spectrophotometer with the reflection attachment and a MgO disks for reference. The magnetic susceptibility measurements were performed by the Gouy method with conventional technique. The IR spectra between 4000 cm^{-1} and 400 cm^{-1} were recorded with a JASCO IR-G spectrophotometer by means of Nujol-mull method.

Results and Discussion

All the mixed chelates obtained are fine crystals or apparently crystalline powders, with compositions shown in the experimental section. All of them have normal magnetic moments (1.84—2.19 B.M.), showing that there is no Cu–Cu interaction in them.

The reflection spectra of these crystals and the absorption spectra of their solutions in various solvents were studied in some detail. Figure 1 illustrates the reflection spectra of four mixed chelates which contain tmen and en, gly, ox, and aca. Figure 2 shows those of three [Cu tmen en]$^{2+}$ chelates, *i.e.*, perchlorate, nitrate, and sulfate.

We see from Fig. 1 that among the mixed chelates the value of ν_{max} increases in the order en>aca>gly>ox. While the order en>gly>ox is that of the ordinary spectrochemical series, it is noteworthy that the value of the mixed acetylacetonate is remarkably larger than that of the mixed glycinate[5] (in aqueous solution, however, these values are nearly the same; *cf.* Fig. 6).

From Fig. 2, it can be seen that the band maximum

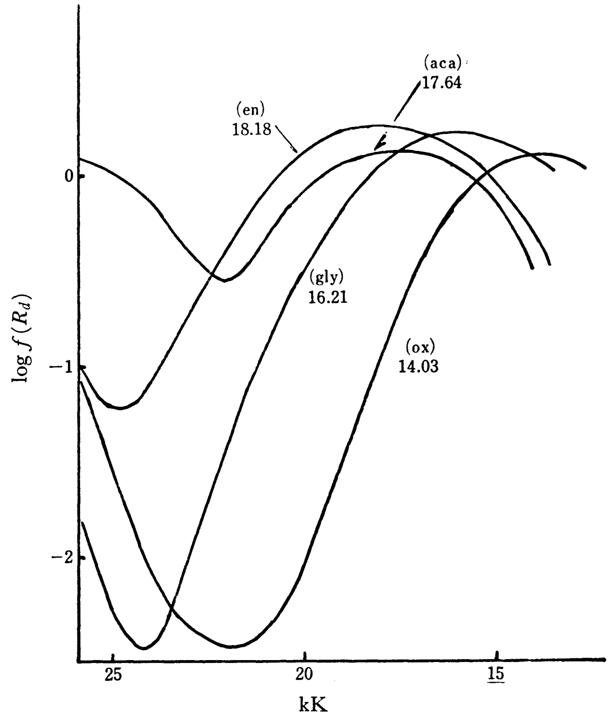

Fig. 1. Reflection spectra of the mixed chelates. Curves denoted by (en), (gly), (aca), and (ox) are those for [Cu tmen en]$(ClO_4)_2$, [Cu tmen gly](ClO_4), [Cu tmen aca](ClO_4) and [Cu tmen ox]$\cdot 4H_2O$, respectively. ν_{max} values are also given.

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[5] A somewhat similar situation was already pointed out in the spectra of [Cu aca_2] and [Cu gly_2]. Y. Fukuda and K. Sone, This Bulletin, **43**, 556 (1970).

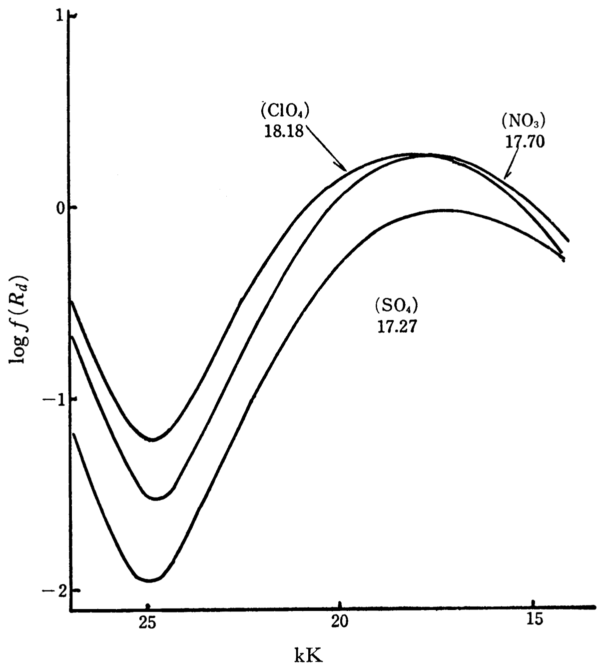

Fig. 2. Reflection spectra of the mixed chelates. Curves denoted by (ClO_4), (NO_3), and (SO_4) are those for [Cu tmen en]$(ClO_4)_2$, [Cu tmen en]$(NO_3)_2 \cdot H_2O$ and [Cu tmen en]$(SO_4) \cdot 4H_2O$, respectively. ν_{max} values are also given.

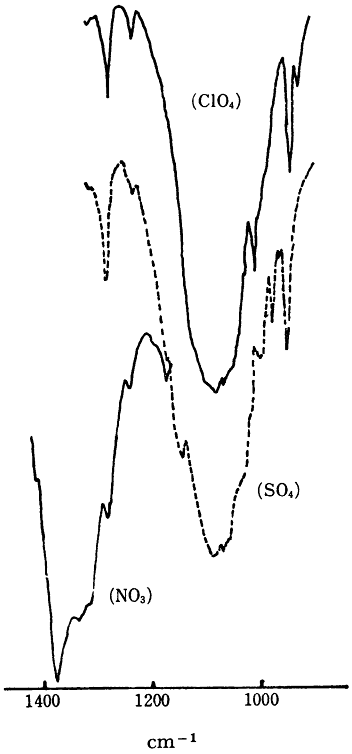

Fig. 3. Anion absorption bands in the infrared spectra of the three chelates shown in Fig. 2. The sharp band at 1375 cm^{-1}, which appears near the top of the NO_3^- band, is due to Nujol.

of [Cu tmen en]X_2 gradually moves to the red in the following order of X: $ClO_4^- \rightarrow NO_3^- \rightarrow SO_4^{2-}$. At first sight this seems to indicate that these anions interact to some extent with the complex cation in the crystals, and that the stronger the interaction (or, in other words, the anion's coordination ability), the lower the ν_{max} value of the mixed chelate. However, the IR spectra of these chelates illustrated in Fig. 3 clearly indicate that the bands of the anions are not remarkably split, *i.e.*, the interaction between the anion and the metal ion in these chelates is quite weak; this result seems reasonable because the mixed chelates contain a very bulky ligand (tmen), which will make the attachment of the oxo-acid anions above and below the planar chelate cation difficult. Therefore, it is more probable that the lowering of the ν_{max} value described above is due to the effect of the water of crystallization in the nitrate and sulfate, the molecules of which probably can coordinate more readily to the chelate cation than the oxo-acid anions.

Figure 4 illustrates the absorption spectra of [Cu tmen aca](ClO_4) in various solvents. This mixed chelate is especially soluble in many organic solvents, and the color of the solution obtained strongly depends on the solvent, varying from reddish violet (in 1,2-dichloroethane) to blue (in dimethylformamide). Figure 5 shows the relation between the ν_{max} value of this chelate in a solution and the donor number (DN) of the solvent; the latter, which was originally proposed by Gutmann,[6] is a measure of the donor strength (coordination or solvation ability) of the sol-

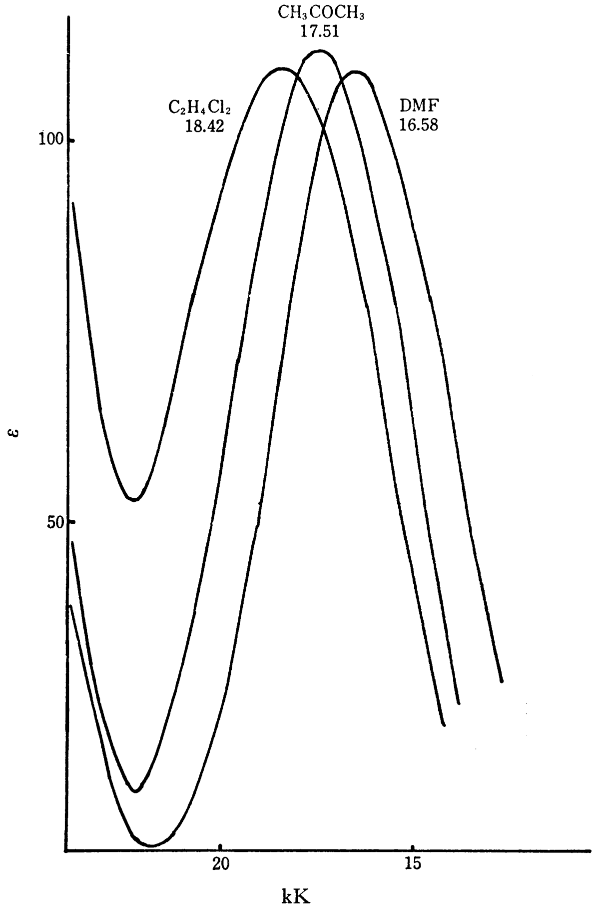

Fig. 4. Absorption spectra of [Cu tmen aca](ClO_4) in 1,2-dichloroethane, acetone, and *N*,*N*-dimethylformamide (DMF). ν_{max} values are also given.

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[6] V. Gutmann, "Coordination Chemistry in Non-Aqueous Solutions," Springer-Verlag, Wien & New York (1967).

vent. It can be seen that there is an approximately linear relation between ν_{max} and DN, and, the larger the coordinating ability of the solvent, the smaller the corresponding ν_{max} value, the order of change being $CH_3NO_2 > C_2H_4Cl_2 > CH_3COCH_3 \gtrsim C_6H_5CN > CH_3CN > THF > MeOH \gtrsim H_2O > DMF > DMSO$. This solvent effect can be explained in the same manner as in the case of the data in Fig. 2, *i.e.*, by assuming the coordination of the solvent molecules above and below the chelate cation which is in solution. The strength of this coordination will increase with the increase of DN, making the ligand field more and more octahedral, and shifting the absorption band to the lower frequencies.[7]

The spectra of other mixed chelates obtained also show a similar solvent effect; but they are not soluble in many organic solvents, and in certain cases, apparent decomposition takes place. In Table 1 are shown the band maxima of these chelates in some solvents. The reason why the ν_{max} values in DMF of the en, gly, and ox chelates are generally higher than those in H_2O is not clear as yet.

TABLE 1. ν_{max}(kK) AND ε_{max} VALUE (THE LATTER IN PARENTHESES) OF THE MIXED CHELATES IN VARIOUS SOLVENTS

Mixed chelate	CH_3OH	H_2O	DMF
[Cu tmen en]$(ClO_4)_2$	18.25(95)	17.64(85)	17.70(97)
[Cu tmen gly](ClO_4)	17.33(97)	16.95(98)	17.12(102)
[Cn tmen ox]$\cdot 4H_2O$	16.53(127)	16.21(126)	16.72(119)

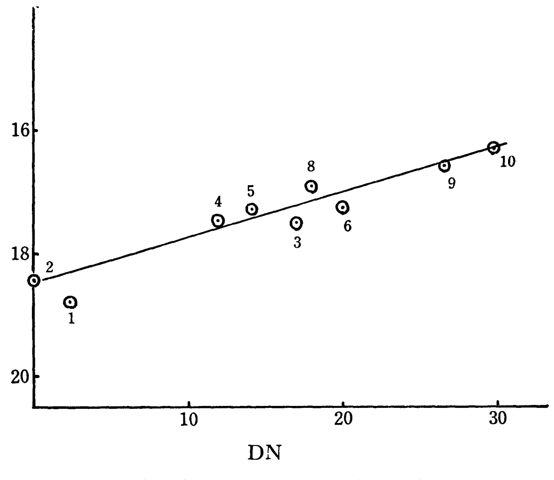

Fig. 5. The relation between ν_{max} and DN in the solutions of [Cu tmen aca](ClO_4) in various solvents. The circles 1 to 10 refer to: 1, CH_3NO_2 (18.80, 2.7); 2, CH_2ClCH_2Cl (18.42, —); 3, CH_3COCH_3(17.51, 17.0); 4, C_6H_5CN(17.48, 11.9); 5, CH_3CN(17.30, 14.1); 6, THF (17.27, 20.0); 7, (not shown) CH_3OH(16.98, —); 8, H_2O(16.92, 18.0); 9, DMF(16.58, 26.6); 10, DMSO(16.31, 29.8). (The numbers in parentheses are those of ν_{max} and DN in each solvent).

Spectral Comparison of the Mixed and Parent Chelates. Recently the nature of the mixed chelates has attracted the interest of many workers[8] and a large number of studies have been published. Among them, Sone and co-workers[9] studied mixed copper(II) chelates containing 2,2′-bipyridine (or 1,10-phenanthroline) and another bidentate ligand(A-A)(=en, gly, ox, or aca), and concluded that the strong interligand steric hindrance in $[Cu\,bip_2]^{2+}$ plays an important role in the following equilibrium:

$$[Cu\,bip_2]^{2+} + [Cu(A\text{-}A)_2]^{m+} \rightleftarrows 2[Cu\,bip(A\text{-}A)]^{n+} \qquad (1)$$

In other words, an equilibrium of this type is forced strongly to the right hand side by the fact that the repulsion between two bulky ligands in $[Cu\,bip_2]^{2+}$ disappears in the course of mixed chelate formation.

From the results of the present study, it is easy to see that, in an equimolar mixture of Cu^{2+}, tmen and (A-A), an extreme case of type (1) equilibrium takes place, where one of the components on the left hand side of the equation (*i.e.* $[Cu\,tmen_2]^{2+}$) is so unstable sterically that it cannot exist at all.[1] On the other hand, in the mixed chelate formed, model studies show that the ligand(A-A) does not exhibit any remarkable steric hindrance with tmen; therefore, its formation by way of type (1) equilibrium will be very strongly favored. The facts that the mixed tmen chelates can be obtained easily from such solutions, and they seem to be quite stable in aqueous solutions,[10] are in conformity with this view.

The importance of steric factors in the formation and structure of these mixed chelates is also reflected in Fig. 6, where the positions of the maxima of the mixed and parent chelates in aqueous solutions are illustrated. It is known that, in many types of mixed copper chelates, Kida's rule[11] holds well, which states that the following relation

$$\nu_{AB} = 1/2(\nu_{A_2} + \nu_{B_2}) \qquad (2)$$

exists between ν_{AB} (the ν_{max} value expected for a mixed chelate [Cu AB]) and ν_{A_2} and ν_{B_2} (the ν_{max} values of its parent chelates, $[Cu\,A_2]$ and $[Cu\,B_2]$). To test the applicability of this rule to the present data, however, it is necessary to know the value of ν_{tmen_2}. Although this can not be obtained experimentally, an estimate of its magnitude can be made in the following way.

Table 2 shows the data of Meek, Ehrhardt, Yokoi, and Isobe on the ν_{max} values of the bis-chelates $[Cu\text{-}A_2]^{2+}$ of some *N*-alkylated ethylenediamines.[1,12] It can be seen, in general, that the value decreases with

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[7] a) Other examples of similar spectral effects caused by solvent molecules are found in C. K. Jørgensen, "Inorganic Complexes," Academic Press, London & New York (1963), p. 106, and also in K. Sone and S. Utsuno, This Bulletin, **39**, 1813 (1966). b) Increase of ion-pairs in relatively nonpolar solvents might also influence the spectra to some extent. However, the effect of solvation would be of primary importance since in most cases solvent molecules will be more easily bound by the metal ion than ClO_4^-, which is a very poor donor and also very bulky (*cf.* the preceding text).

[8] *Cf. e.g.*, a) R. DeWitt and J. I. Watters, *J. Amer. Chem. Soc.*, **76**, 3810 (1954); S. Kida, This Bulletin, **29**, 805 (1956) (earlier studies); b) "Proceeding of the 3rd Symposium on Coordination Chemistry," ed. by M. T. Beck, Akademiai Kiado, Budapest (1970) (recent results).

[9] K. Sone, S. Utsuno, and T. Ogura, *J. Inorg. Nucl. Chem.*, **31**, 117 (1969); *cf.* also Ref. 5.

[10] S. Utsuno, unpublished results; G. F. Condike and A. E. Martell, Ref. 13.

[11] S. Kida, (see Ref. 8).

[12] H. Yokoi and T. Isobe, This Bulletin, **42**, 2187 (1969).

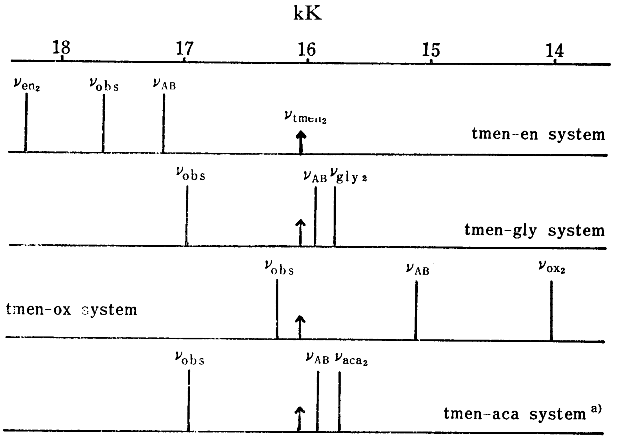

Fig. 6. ν_{max} values of the mixed chelates and the parent bis-chelates in aqueous solutions. The observed values for the mixed chelates and those calculated from Kida's rule are denoted by ν_{obs} and ν_{AB}, respectively, and the imaginary ν_{tmen_2} value (see text) is shown by a short arrow in each system.

(a) Since [Cu aca$_2$] is insoluble in H_2O, its ν_{max} given in this figure is that of DMF solution, so that only approximate comparison can be made. However, the shift of ν_{obs} from ν_{AB} described in the text is still very evident.

TABLE 2. ν_{max} VALUES (kK) OF THE COPPER(II) CHELATES OF EN AND ITS *N*-ALKYLATED DERIVATIVES (DIFFERENCES NEIGHBORING VALUES ARE SHOWN IN ITALIC; IMAGINARY BETWEEN VALUES ARE SHOWN IN PARENTHESES)

Complex	Solid[1]				Aqueous solution[12] [a]
I. [Cu en$_2$](ClO$_4$)$_2$	19.05	→	*0.77*	→	18.28
	↓				
	0.53				
	↓				
II. [Cu (*N*,*N'*-Me$_2$en)$_2$]-(ClO$_4$)$_2$	18.52	→	*0.85*	→	17.67
	↓				
	0.82				
	↓				
III. [Cu (*N*,*N*,*N'*-Me$_3$en)$_2$]-(ClO$_4$)$_2$	17.70				
	↓				
	(*0.82*)				
	↓				
IV. [Cu tmen$_2$](ClO$_4$)$_2$	(16.88)[b]	→	(*0.85*)	→	(16.03)[b]

a) The original data of Yokoi and Isobe refer to solutions in CH_3OH-H_2O (1:1), but it was found that the values in H_2O are nearly the same.

b) Extrapolations leading to these values are based on the assumption that (i) there is a decrease of *ca.* 0.82 kK in going from III to IV, just as in going from II to III, and (ii) there is a shift of *ca.* 0.85 kK in going from solid to solution spectrum of IV. Naturally these assumptions are not entirely reliable, and it is possible that the true values are considerably lower, since the introduction of a fourth CH_3 group in the ligand (*N*,*N*,*N'*-Me$_3$en) to form tmen will increase the interligand repulsion much more than that of the third in *N*,*N'*-Me$_2$en. However, even a considerable variation of these values (and those of ν_{AB} derived from them) will not alter the general picture described in the text.

TABLE 3. ν_{max} (kK) VALUES OF EN AND TMEN MIXED CHELATES IN AQUEOUS SOLUTIONS

[Cu en gly]$^+$ [8]	16.95	[Cu tmen gly]$^+$	16.95
[Cu en ox][10]	16.18	[Cu tmen ox]	16.21
[Cu en aca]$^+$ [10]	17.01[a]	[Cu tmen aca]$^+$	16.92

a) 75% dioxane solution.

increasing *N*-methyl groups, indicating the loosening of the coordinate bonds caused by interligand steric repulsion, and there is also a shift of *ca.* 0.8 kK in going from solid to aqueous solution. Extrapolation of these values to the case of aqueous solution of the imaginary bis-chelate [Cu tmen$_2$]$^{2+}$ gives an approximate value of 16.0 kK for its ν_{max}. Substituting this value and the values of ν_{en_2}, ν_{gly_2}, and ν_{ox_2} taken from literature into Eq. (2), the values of ν_{AB} shown in Fig. 6 can be obtained. It can be seen readily that, in all the cases studied, Kida's rule does not hold and ν_{obs} of a mixed chelate is remarkably larger than its ν_{AB}. It is only in the case of [Cu tmen en]$^{2+}$ that ν_{obs} lies between ν_{tmen_2} and ν_{en_2}; in all other cases, ν_{obs} is much larger than both ν_{tmen_2} and $\nu_{(\mathrm{AA})_2}$, and the difference between ν_{obs} and ν_{AB} increases in the order:

$$\mathrm{en} < \mathrm{gly} \simeq \mathrm{aca} < \mathrm{ox} \qquad (3)$$

The reason for these results can be explained in terms of the following two factors. (1) The steric effect is very plausible. Although there will be no remarkable interligand repulsion in any of the mixed chelates studied, it is quite possible that a slight repulsion exists in the case of [Cu tmen en]$^{2+}$, since the four protruding H atoms of the amino groups of en will contact the four methyl groups of tmen to some extent. This repulsion will weaken the coordinate bonds; therefore, the ν_{max} of this chelate will be shifted to the red in comparison with ν_{en_2}, and will be approximately the same as that of [Cu(*N*,*N'*-Me$_2$en)$_2$]$^{2+}$ in which a repulsion of similar magnitude is expected. On the other hand, this kind of repulsion is probably much smaller in [Cu tmen gly]$^+$, since gly has only one amino group, and is practically absent in [Cu tmen ox] and [Cu tmen aca]$^+$, so that their spectra will generally resemble those of the corresponding en chelates. All these expectations agree quite well with the observed results, as can be seen from the data in Table 2 and Table 3.

(2) The charge of the mixed chela temust also be taken into account. As already pointed out by other investigators,[13] the coordination of a doubly negative ox anion to [Cu tmen]$^{2+}$ will be energetically more favorable than that of a neutral en. Furthermore, the entropy change due to the reduced solvation will also favor the formation of neutral [Cu tmen ox] from the components, in preference to the singly charged gly or aca mixed species and still higher charged [Cu tmen en]$^{2+}$. It is therefore possible that these electrostatic effects also contribute to some extent to the spectral changes described above.

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[13] *Cf.*, *e.g.*, G. A. L'Heureux and A. E. Martell, *J. Inorg. Nucl. Chem.*, **28**, 481 (1966); G. F. Condike and A. E. Martell, *ibid.*, **31**, 2455 (1969); H. Sigel, Ref. 8b, p. 191. The paper of Condike and Martell also contains stability data on [Cu tmen ox].