428 © 1981 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 54, 428—432 (1981) [Vol. 54, No. 2

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

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(Received June 5, 1980)

The visible absorption spectra of three new mixed chelates of copper(II), Cu(tmen)(acac)X (tmen=N,N,N',N'-tetramethylethylenediamine, acac=acetylacetonate ion, X=NCS, N_3, or NCO) were studied in various organic solvents. It was found that the $\tilde{\nu}_{max}$ values of their d-d bands depend strongly on the nature of the solvent, and shift in the opposite direction as compared with the case of [Cu(tmen)(acac)]ClO_4 studied before, where $\tilde{\nu}_{max}$ shifted to red with the increase of the donor number (DN) of the solvent. Here the magnitude of the red shift is affected not only by the DN, but also by other parameters of the solvent polarity, such as Kosower's Z or Reichardt's E_T. The obtained data can reasonably be explained, if an equilibrium

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

is assumed to exist in such solutions.

It was pointed out by Fukuda *et al.*[2)] that the visible absorption spectra of the mixed copper(II) chelates [Cu(tmen)(acac)]X (X=ClO_4, or NO_3) in organic solvents are strongly influenced by the nature of the solvent used. In general, it was observed that the d-d band is shifted to the red with the increase of the donor number (Gutmann's DN) of the solvent. The effect was explained as the result of the strengthening of the axial solvation, which decreases the apparent ligand field strength observed as $\tilde{\nu}_{max}$.

Recently we prepared three new complexes with the general formula Cu(tmen)(acac)X (X=NCS, N_3, or NCO), and studied their spectra in organic solvents. A number of fundamentally different behaviors were found out, as compared with the case of perchlorate or nitrate chelate. These results and their probable explanations will be presented in this paper.

Experimental

Preparation of the New Complexes. *i) Cu(tmen)(acac)(NCS)*: A large excess of KNCS(*ca.* 50 mmol) was added to a solution of [Cu(tmen)(acac)]ClO_4[2)] in 1,2-dichloroethane (=DCE, 10 mmol in *ca.* 50 cm^3). A few drops of methanol were added to the mixture, and it was heated at *ca.* 40 °C for several hours under constant stirring. The color of the solution changed from reddish violet to indigo, and then finally to deep green. Stirring was continued for a while after completion of this color change, and then the solution was cooled thoroughly by keeping it in a freezer for several hours. After filtering off the white precipitate formed (KNCS+$KClO_4$), the filtrate was evaporated to dryness, and further dried in vacuum. Since the green product obtained was seemingly quite raw, it was dissolved in DCE, and the solution was filtered and concentrated until it became noticeably viscous, and kept in the freezer again. The crystalline product obtained was further recrystallized from DCE. Deep green prismatic crystals were thus obtained.

ii) Cu(tmen)(acac)NCO: This complex could be obtained in the same way as i), using KNCO instead of KNCS. Deep green prismatic crystals were obtained.

iii) Cu(tmen)(acac)N_3: This complex could not be obtained in the same way as *i*). For its preparation, an excess of NaN_3 (15 mmol) was added to a solution of [Cu(tmen)(acac)]NO_3 in methanol(MeOH) (10 mmol in *ca.* 50 cm^3), and the mixture was stirred for some time. The color of the solution changed gradually from indigo to olive green; this solution was filtered to remove the white precipitate formed (NaN_3+$NaNO_3$), and transferred into a flask (A), which was connected with an inverted U-tube with another flask (B). The content of A was frozen with liquid nitrogen, and the whole system was evacuated and closed. The liquid N_2 around A was then removed, and B was cooled with it instead. Nearly all of the solvent in A was thus distilled into B, leaving the raw complex which crystallized out. The complex was separated from the mother liquor by filtration, dissolved in dichloromethane and filtered again. Similar procedures (*i.e.* dissolution in dichloromethane, filtration, and distillation of the solvent at low temperature) were repeated until a product of sufficient analytical purity was obtained. It was a bluish green powder, which had to be kept in a vacuum in a refrigerator, since spontaneous decomposition seemed to take place.

iv) Cu(tmen)(acac)NCSe: Deep green crystals which were very similar in appearance to Cu(tmen)(acac)NCS were obtained by the method i), using KNCSe instead of KNCS, but they were very unstable and decomposed in the course of recrystallization. Their identification with Cu(tmen)(acac)(NCSe) was, however, also supported by the close resemblance of its IR spectrum to that of the NCS-complex.

Physical Measurements. The electronic spectra of the solutions (350—850 nm) were measured with a Hitachi 340 Recording Spectrophotometer at room temperature (20—25 °C), using 10 mm quartz cells. The reflection spectra of the solid samples (300—800 nm) were measured with the same instrument, using $BaSO_4$ as the reference. IR spectra (600—5000 cm^{-1}) were measured in nujol mulls with a JASCO IR-A3 Grating IR Spectrophotometer. Magnetic susceptibility measurements were performed with a Shimadzu Tortion Magnetometer MB-100 (NCS- and NCO-complexes at 31 °C, N_3-complex at 17 °C). Electric conductivities of the solutions were measured with a Yanagimoto Conductivity Outfit Model MY-7 at 25 °C.

Results and Discussion

Properties of the Solid Chelates. Table 1 summarizes the analytical data, colors and magnetic moments of the

TABLE 1. ELEMENTARY ANALYSES, COLORS, AND MAGNETIC MOMENTS OF THE CHELATES OBTAINED

Formula	C(%)[a)]	H(%)[a)]	N(%)[a)]	Color	μ_{eff}/BM
Cu(tmen)(acac)NCS	42.62(42.78)	7.71(6.88)	12.52(12.47)	bluish green	1.89
Cu(tmen)(acac)N_3	40.62(41.17)	7.13(7.23)	20.89(21.83)	bluish green	1.85
Cu(tmen)(acac)NCO	44.98(44.92)	8.01(7.23)	13.05(13.10)	green	1.92

a) Calculated values are in parentheses.

TABLE 2. ASSIGNMENT OF IR BANDS OF THE PSEUDOHALIDE IONS(X) IN THE COMPLEXES, Cu(tmen)(acac)X (cm^{-1})

X=NCS^-		X=N_3^-			X=NCO^-		
ν_{CN}	ν_{CS}	$\nu_{a(NNN)}$	$\nu_{s(NNN)}$	$\delta_{(NNN)}$	$\nu_{a(NCO)}$	$\nu_{s(NCO)}$	$\delta_{(NCO)}$
2070	770	2060	1330	640	2200	1305	620
		2030	1305				

three new chelates. All of them show normal magnetic moments expected for monomeric copper(II) chelates, but their colors are notably different from that of [Cu(tmen)(acac)]ClO_4 (reddish violet). The IR spectra of these chelates show sharp bands of the pseudohalide ions, and their positions shown in Table 2 indicate that all of these ions are coordinated to Cu(II) with their N atoms.[4)]

Electronic Spectra of the Chelates. As expected from the colors, the visible reflection spectra of these solid chelates are all quite different from that of [Cu(tmen)(acac)]ClO_4. These chelates are all readily soluble in various organic solvents, but the visible absorption spectra observed in them are also remarkably different from those of [Cu(tmen)(acac)]ClO_4 in the same solvents. As an example, the spectra of Cu(tmen)(acac)NCS in four solvents are given in Fig. 1. The observed values of $\tilde{\nu}_{max}$ and ε_{max} for all three chelates are summarized in Table 3 and the shifts of $\tilde{\nu}_{max}$ of each chelate are shown in Fig. 2, in comparison with the data of [Cu(tmen)(acac)]ClO_4.[2)]

As stated in the introduction, the $\tilde{\nu}_{max}$ value of the perchlorate shifts to the red approximately in the order of the donor number of the solvent. However, the data shown above clearly show that the $\tilde{\nu}_{max}$ of the pseudohalide complexes shift to the red with the decrease of solvent polarity, *i.e.* in apparently opposite direction as compared with the case of the perchlorate. The order of $\tilde{\nu}_{max}$ in various solvents is, nearly in all three cases, expressed as:

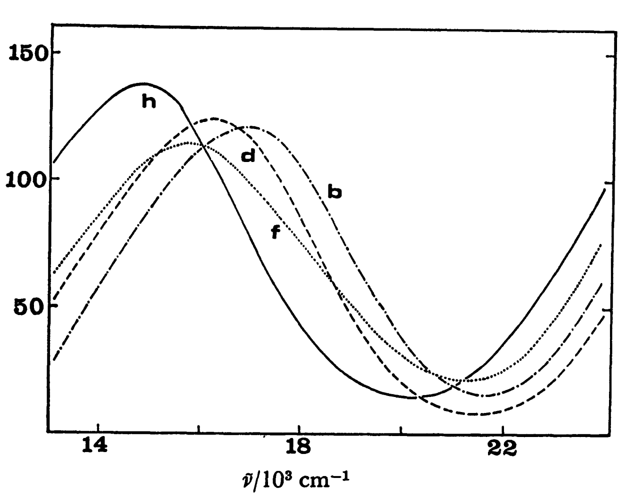

Fig. 1. Absorption spectra of [Cu(tmen)(acac)NCS] in various organic solvents. As to the symbols on the curves, *cf.* Fig. 2. Concentration: 5.5×10^{-3} M.

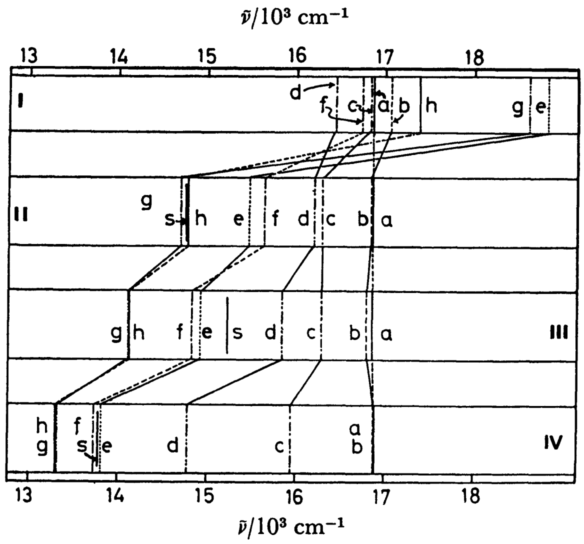

Fig. 2. Diagrammatic representation of the $\tilde{\nu}_{max}$ values of [Cu(tmen)(acac)]ClO_4 (I), [Cu(tmen)(acac)NCS](II), [Cu(tmen)(acac)NCO](III) and [Cu(tmen)(acac)N_3](IV) in various organic solvents. The symbols a to h correspond to the following solvents: a=H_2O b=MeOH, c=EtOH, d=DMSO, e=NM, f=AN, g=DCE, h=acetone. The $\tilde{\nu}_{max}$ of the solid reflection spectra are shown by S.

TABLE 3. $\tilde{\nu}_{max}$ AND ε_{max} VALUES OF Cu(tmen)(acac)X IN SOLID STATE AND IN VARIOUS SOLVENTS[a),b)]

	X=NCS	X=N_3	X=NCO
Solid	14.79	15.24	13.77
H_2O	16.86(99)	16.86(111)	16.89(105)
CH_3OH(MeOH)	16.84(121)	16.78(113)	16.89(118)
C_2H_5OH(EtOH)	16.29(123)	16.29(126)	15.92(108)
$(CH_3)_2SO$(DMSO)	16.21(125)	15.85(136)	14.79(101)
$(CH_3)_2NCHO$(DMF)	16.21(111)	15.34(137)	13.97(98)
CH_3NO_2(NM)	15.48(118)	14.93(136)	13.81(111)
CH_3CN(AN)	15.67(115)	14.84(138)	13.74(109)
$C_2H_4Cl_2$(DCE)	14.71(153)	14.12(159)	13.32(118)
$(CH_3)_2CO$	14.79(138)	14.12(157)	13.30(107)

a) $\tilde{\nu}_{max}$ in 10^3 cm^{-1}, ε_{max} in parentheses. b) Concentrations: 5.18—5.28×10^{-3} M in organic solutions of the NCS^- complex, and 5.92×10^{-3} M in its aqueous solution; 5.06—5.51×10^{-3} M in solutions of the N_3^- complex, and 7.23—7.50×10^{-3} M in those of the NCO^- complex, respectively (1 M=1 mol dm^{-3}).

$$H_2O > MeOH > EtOH > DMSO > DMF > \\ NM > AN > DCE \approx Acetone. \qquad (i)$$

Now it can be noted that this order (i) is not the order of DN of the solvents, but can better be correlated with the order of Kosower's Z values,⁵⁾ or Reichardt's E_T values,⁶⁾ which are other parameters of solvent polarity. Table 4 shows these correlations.

TABLE 4. DN, Z, AND E_T VALUES OF THE SOLVENTS$^{a)}$

Solvent	DN	Z	E_T
H_2O	18.0	94.6	63.1
MeOH	23.5	83.6	55.5
EtOH	30.0	79.6	51.9
DMSO	29.8	71.1	45.0
DMF	26.6	68.5	43.8
NM	2.7	—	46.3
AN	14.1	71.3	46.0
DCE	0.0	—	41.9
$(CH_3)_2CO$	17.0	65.7	42.2

a) See Refs. 5—7. The DN values of MeOH and EtOH are those of DeWitte and Popov,¹³⁾ and may not be strictly comparable with those of the other solvents proposed by Gutmann.

Thus we can understand that the order (i) is the order of the increase of Z or E_T, except a few small discrepancies. Since Z and E_T are linear functions of each other,⁵⁾ and more E_T values are available for the present study, we shall use E_T in our following discussions.

Before going further, it may be of interest to compare the meanings of these polarity parameters. The DN is a measure of the donor ability of the solvent or its Lewis basicity, *i.e.* its tendency to donate an electron pair to a positive solute particle. On the other hand, E_T is a measure of the polar influence of the solvent on the interactions between charged particles (or between charged parts inside of a large molecule) dissolved in it.

Now the pseudohalide ions (NCS^-, N_3^-, and NCO^-) are all good ligands, and their coordination ability is generally expected to be much higher than that of common organic solvents. Therefore, it will be possible to explain our spectral results of the NCS-complex in the following way:

(i) In a highly polar solvent like H_2O or MeOH, where the E_T values are highest among the solvents tried, the Cu–NCS bond is remarkably weakened, and remarkable dissociation of the complex into $[Cu(tmen)(acac)]^+$ and NCS^- takes place. The $[Cu(tmen)(acac)]^+$ planar cation formed has vacant coordination sites above and below it, and they are immediately occupied (*i.e.* solvated) by the solvent molecules. This is the reason why the $\tilde{\nu}_{max}$ of the complex in these solvents are nearly the same as those of the perchlorate in the same solvents, where similar nearly complete dissociation of the anion is expected to occur.

It is interesting to note that the very important step involved in these changes is the dissociation of the strongly coordinated NCS^- ion from the complex, since the surrounding solvent molecules will spontaneously occupy the coordination sites which are open to them. In other words, the effect of E_T (polar influence of the solvent to weaken the polar bond (Cu–NCS) in the solute) is seemingly more important than that of DN (the ease of coordination of the solvent molecules to the vacant coordination sites produced around Cu^{2+}) in these changes. Further supports of this view will be found in the following examples.

(ii) In a highly non-polar solvent like DCE, where both the E_T and DN values are the lowest, the solvent can neither drive out the NCS^- ion from the complex, nor occupy its coordination site. Thus the complex is dissolved in the form of the 5-coordinated molecule, [Cu(tmen)(acac)(NCS)], which shows a d-d band of much lower $\tilde{\nu}_{max}$ and somewhat higher ε_{max} than those of the solvated tetragonal ions formed in highly polar solvents.

(iii) In a solvent of intermediate polarity such as EtOH, DMSO, DMF, NM, or AN, the situations are more complicated. In the first three solvents, the DN values are even much higher than those of H_2O and MeOH, but the E_T values are noticeably lower. So it is more difficult to drive off the NCS^- ion in these solvents. In NM and AN, on the other hand, the DN values are much lower, but the E_T values are comparable to those of DMSO or DMF. These solvents will be able to drive out NCS^- ions from the complex to some extent, *i.e.* more or less like DMSO and DMF, but will not be able to occupy the vacant sites produced so readily. At any rate, in these solvents, there will be incomplete dissociation of NCS^- from the complex, leading to an equilibrium

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

which shifts to the right hand side with the increase of DN and E_T. As the d-d bands of the complexes on both sides of (1) are broad and of comparable intensity, they will mutually overlap, and lead to the formation of an apparent spectral maximum, which will shift to the red with the increase of [Cu(tmen)(acac)(NCS)] in the equilibrium mixture, *i.e.* with the decrease of DN and E_T. The fact that the observed shift is more closely related to E_T than to DN indicates that the main driving force of the forward reaction of (1) is the weakening of Cu–NCS bond, and not the strength of solvation. The most striking evidence for this view is the case of acetone, which has a DN much higher than those of NM or AN, but a E_T which is very low and comparable with that of DCE. The observed $\tilde{\nu}_{max}$ in acetone is in the vicinity of that in DCE, showing that no coordination of the solvent can occur unless it can drive out the NCS^- by its polar influence.

The results of the N_3- and NCO-complexes can be explained in the same way, but the comparison of the three pseudohalide complexes shows that the ease of 5-coordinate complex formation increases in the order:

$$NCS^- < N_3^- < NCO^-. \qquad (ii)$$

This can most clearly be seen by comparing the data of the NCS-complex with those of the NCO-complex. In the latter case, all the $\tilde{\nu}_{max}$ values shift to the red, and flock together at the left end of Fig. 2, leaving only the values in very polar solvents (H_2O and MeOH) which remain nearly unchanged from those of the perchlorate. This means that NCO^- is bound strongly to Cu(II), so that even solvents like DMSO or EtOH can ionize it only partially. It is also clear that N_3^- comes just between NCS^- and NCO^- in its coordination power.

This order of the coordination ability of pseudohalide ions may be related to the values of their "optical electronegativities," proposed by Jørgensen.[8] The values for the σ- and π-optical electronegativities of halide and pseudohalide ions are:

Ligand	σ	π	Ligand	σ	π
Cl^-	3.4	3.0	NCO^-	—	3.0
Br^-	3.3	2.8	NNN^-	—	2.8
I^-	3.0	2.5	NCS^-	—	2.6

Although the σ-values for the pseudohalide ions are lacking, we can see that the π-values of Cl^-, Br^-, and I^- are comparable to those of NCO^-, N_3^-, and NCS^-, respectively. It is well known that the coordination tendencies of the halide ions toward 3d transition metal cations are, in general, in the order $Cl^- > Br^- > I^-$, so we can suppose that the order of the pseudohalide ions should be $NCO^- > N_3^- > NCS^-$, as is observed in Fig. 2. One can also imagine that the "hardness" of these ions increases just in the order (ii), *i.e.* from NCS^- with the soft S to N_3^- with highly delocalized π-system and then to NCO^- with much more rigid electronic structure, and that the coordination of an anion onto $[Cu(tmen)(acac)]^+$ is favored when it is hard, since the interaction may be weak and chiefly electrostatic in nature.

TABLE 5. MOLAR CONDUCTIVITIES OF THE CHELATES (Ω^{-1} cm^2 mol^{-1}, 25 °C) AND APPROXIMATE DEGREES OF DISSOCIATION (%, IN PARENTHESES)[b]

X-	DCE	NM	DMSO
NCS-	1.1(6)	56.6(65)	39.8(100)
N_3^-	1.0(5)	27.0(32)	32.0(92)
NCO-	0.5(3)	21.7(26)	14.8(42)

a) Concentration of the solutions: $\approx 10^{-3}$ 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. 9).

To confirm all these points of view, further spectral and conductometric measurements were carried out. Some data of them are shown in Table 5; it can clearly be seen that all the three chelates are nearly non-electrolytes in DCE, and the NCS- and N_3-chelates are nearly 1 : 1 electrolytes in DMSO, while in all other cases there is an ionization equilibrium, and the degree of ionization increases, in every case, in the order of DCE<NM<DMSO and $NCS^- < N_3^- < NCO^-$ just as expected from the above discussions.

As to the spectral measurements, a number of observations were made with the NCS-chelate which is the easiest to prepare. It was found first that the spectrum of this chelate in NM is remarkably dependent on concentration (*cf.* Fig. 3); its $\tilde{\nu}_{max}$ shifts to the red with increasing concentration and its ε_{max} increases, just as observed with the decrease of solvent polarity. Furthermore, the addition of KNCS to such a solution causes similar spectral changes, while the substitution of a part of NCS^- with ClO_4^- (this can conveniently be done by mixing the nitromethane solutions of $[Cu(tmen)(acac)]ClO_4$ and [Cu(tmen)(acac)(NCS)]) shifts the band in the opposite way. In all cases, a clear-cut isosbestic point appears on the curves, showing the existence of an equilibrium between two distinct species (*cf.* Fig. 4).** All these evidences indicate the existence of the equilibrium of the type (1) in these solutions. Very similar spectral changes were also observed in AN. The spectra of the same complex in H_2O or DCE are, on the other hand, not remarkably dependent on concentration, showing that they are either perfectly ionized or unionized, and that in acetone (which is very much like that in DCE) is affected only slightly by the addition of KNCS. All these facts are in line with the viewpoints proposed above. It may be added that the curve 6 of Fig. 4, *i.e.*, that of a NM solution of $[Cu(tmen)(acac)]^+$ with a large excess of NCS ($\tilde{\nu}_{max}$: 15.15×10^3 cm^{-1}, ε_{max}: 126), is very similar to those of the complex [Cu(tmen)(acac)-NCS] in DCE or acetone, indicating again the formation of the 5-coordinated species in NM, and also the fact that its spectrum is influenced only little by the solvent, *i.e.*, the 5-coordinated complex is only weakly solvated

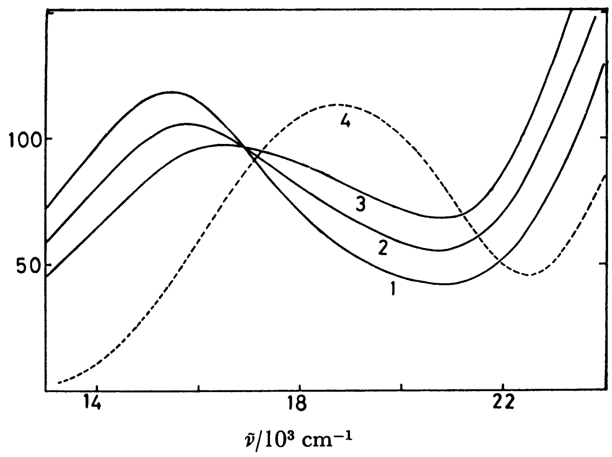

Fig. 3. Concentration dependence of the absorption spectra of [Cu(tmen)(acac)NCS] in NM, curves 1, 2, and 3 are those for 5.24×10^{-3}, 2.52×10^{-3} and 1.27×10^{-3} M solutions, respectively. Curve 4 is that of $[Cu(tmen)(acac)]ClO_4$ in the same solvent.

** Strangely, the curve of $[Cu(tmen)(acac)]ClO_4$ itself slightly deviates from the isosbestic point, and its UV absorption is remarkably weaker than that of all other systems in Figs. 3 and 4. The reason for such deviations is not clear as yet, but may be due to the effect of ion-pair formation,[10] or the coexistence of a small amount of another species with strong ultraviolet absorption in the NCS^--containing solutions. These and other problems (e.g. solubility relationship) are hindering the estimation of K values of (1) from these data at present.

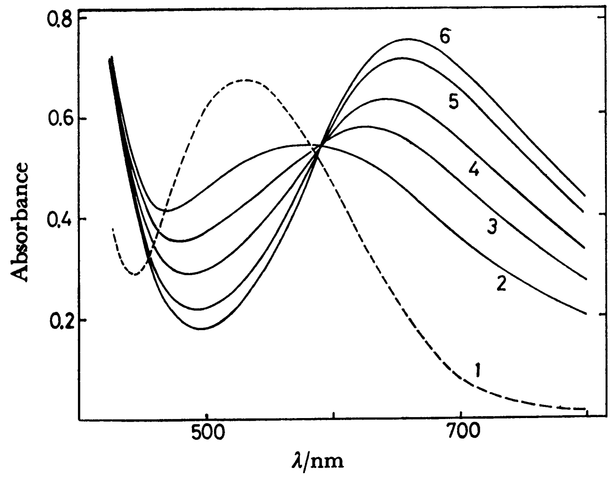

Fig. 4. The effect of NCS$^-$ ions on the spectrum of [Cu(tmen)(acac)]$^+$(concentration: 6×10^{-3} M) in NM. The curve 1 is that of [Cu(tmen)(acac)]ClO_4 and curves 2 to 6 correspond to solutions in which the ratios [Cu(tmen)(acac)]$^+$: NCS$^-$ are 1 : 0, 1 : 0.5, 1 : 0.75, 1 : 1, 1 : 1.5, and 1 : 2 respectively.

in solution.†

Finally, mention may be made of the structure of these three chelates in solid state. The comparison of the $\tilde{\nu}_{max}$ values of the solids (*cf.* Table 3) with those of the solutions indicates that the NCS-complex is typically 5-coordinate in its solid and to be formulated as [Cu(tmen)(acac)X]. The same can probably be said as to the NCO-complex. In the case of N_3-complex, the $\tilde{\nu}_{max}$ value is noticeably higher to be purely 5-coordinate: here the N_3-ions may be forming bridges between the [Cu(tmen)(acac)]$^+$ cations, making the Cu^{2+} in it to some extent 6-coordinate.[11] Some such bridge formation may also be present in the NCO-complex, in which the $\tilde{\nu}_{max}$ is slightly higher than that in DCE and comparable with those in NM or AN.[12]

Thus it is evident that these three new chelates are interesting examples of the stereochemistry of copper(II), with which one can easily observe the competition of pseudohalide ions and solvents for the coordination sites above or below the chelate plane with the aid of their visible spectra.

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 347033 from the Ministry of Education, Science and Culture.

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† The viewpoints stated here are supported further by the comparison of these data with those of the corresponding halide complexes,[14] which will be reported in another paper.

References

1) Part XI: N. Hoshino, Y. Fukuda, and K. Sone, *Bull. Chem. Soc. Jpn.*, **54**, 420 (1981).

2) Y. Fukuda and K. Sone, *Bull. Chem. Soc. Jpn.*, **45**, 465 (1972); Y. Fukuda, A. Shimura, M. Mukaida, E. Fujita and K. Sone, *J. Inorg. Nucl. Chem.*, **36**, 1265 (1974).

3) V. Gutmann, "Coordination Chemistry in Non-Aqueous Solutions," Springer, Wien (1968).

4) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 3d ed, John-Wiley, New York (1978).

5) E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley Internat. Ed., Toppan, Tokyo (1968).

6) K. Dimroth, C. Reichardt, T. Spiepmann, and F. Bohlmann, *Ann.*, **661**, 1 (1963).

7) J. Burgess, "Metal ions in Solutions," Ellis Horwood, Chichester (1978).

8) C. K. Jørgensen, "Oxidation Numbers and Oxidation States," Springer, Berlin (1969).

9) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).

10) H. Yoneda, *Bull. Chem. Soc. Jpn.*, **29**, 68 (1956).

11) U. Müller, "Structure and Bonding," ed by J. D. Dunitz *et al.*, Springer, Berlin (1973).

12) J. Kohout, M. Hvastijova, and J. Gazo, *Coord. Chem. Rev.*, **27**, 141 (1978).

13) W. J. DeWitte and A. I. Popov, *J. Solution Chem.*, **5**, 231 (1976).

14) H. Kimura, Y. Fukuda, and K. Sone, unpublished data (1979).