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Studies on Mixed Chelates. XX. Mono- and Binuclear Nickel(II) and Copper(II) Complexes with *N*,*N*,*N′*,*N″*,*N‴*,*N‴*-Hexamethyltriethylenetetramine and β-Diketonates[1)]

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Nine mixed chelates of Ni(II) and Cu(II) with *N*,*N*,*N′*,*N″*,*N‴*,*N‴*-hexamethyltriethylenetetramine (hmtt) and β-diketonate (dike) ligands were prepared and characterized. Except for [Ni(dipm)(hmtt)]ClO_4 (dipm=dipivaloylmethanate), all of them were found to be binuclear chelates: (i) [M_2(dike)$_4$(hmtt)](M=Ni, dike=dipm, acac(acetylacetonate), tfac, or hfac(tri- or hexafluoroacetylacetonate); M=Cu, dike=hfac), (ii) [$Ni_2(NO_3)_2$(dike)$_2$(hmtt)](dike=dipm, acac), and (iii) [Cu_2(acac)$_2$(hmtt)]$(ClO_4)_2$. Although they are similar to their mononuclear analogues containing *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (tmen), a number of characteristic differences exist. Though the Ni(II) chelates are only slightly solvatochromic, the Cu(II) chelates are strongly so.

Extending our studies concerning the mixed chelates of Ni(II) and Cu(II) with *N*,*N*,*N′*,*N″*,*N″*-pentamethyldiethylenetriamine (pmdt) and β-diketonate (dike) ligands,[1,2)] we have also prepared and characterized a number of Ni(II) and Cu(II) complexes with *N*,*N*,*N′*,*N″*,*N‴*,*N‴*-hexamethyltriethylenetetramine (hmtt) and dike ligands (dipivaloylmethanate (dipm), acetylacetonate (acac), as well as tri- or hexafluoroacetylacetonate (tfac or hfac)).

Hmtt is a very bulky tetradentate ligand, still bulkier than pmdt; the steric hindrance among its six methyl groups and three -$(CH_2)_2$- chains disturbs its coordination around a single metallic cation. Its Ni(II) and Cu(II) chelates, [Ni(hmtt)]X_2 and [Cu(hmtt)]X_2, were formerly studied by Cristini et al.[3)] They were found to be square planar (and low spin in the case of Ni(II)) when X^- is a non-coordinating anion; their electronic spectra, however, revealed that the ligand field strengths (l.f.s) in them are notably weaker than those in $[Ni(en)_2]^{2+}$ and $[Cu(en)_2]^{2+}$, most probably due to the intramolecular steric strain in the hmtt ligand. Correspondingly, it was also found that they are easily converted into the 5- or 6-coordinated species by interactions with solvents and anions, thus becoming high-spin in the case of Ni(II).

When hmtt forms a mixed chelate with a dike, [M(dike) (hmtt)]$^+$ (M=Ni(II) or Cu(II)), hmtt is forced to occupy nonplanar coordination sites (of the cis-α or cis-β form) around M^{2+} under the influence of the strong ligand dike. The hmtt molecule is thereby folded and compressed, causing a much greater intramolecular strain than in the case of planar coordination. Moreover, there is some repulsion between the alkyl (or fluoroalkyl) groups of dike and those of hmtt, which also destabilizes the mixed complex. It is therefore expected that [M(dike) (hmtt)]$^+$ will be a notably weak complex, and will disproportionate easily into M(dike)$_2$ and [M(hmtt)]$^{2+}$ (or its solvated or solvolyzed product(s)) in solution.

It is now conceivable that, to avoid the formation of such highly strained species, hmtt and dike tend to form binuclear mixed complexes, [M_2(dike)$_2$(hmtt)]$^{2+}$ or [M_2(dike)$_4$(hmtt)](or possibly, [M_2A_2(dike)$_2$(hmtt)]$^{n\pm}$ when another chelating ligand (A) coexists), instead of the mononuclear complexes. Such binuclear complexes will be sterically more stable, and each of the two halves of such a complex will behave like the complex [M(dike) (tmen)]$^+$, [M(dike)$_2$(tmen)] or [M A (dike) (tmen)]$^{n'\pm}$ (tmen=*N*,*N*,*N′*,*N′*-tetramethylethylenediamine), which were systematically studied in the present series.[4)]

All of these expectations were found to be the case; among the nine chelates prepared, eight were binuclear with the expected structures; and only one, [Ni(dipm) (hmtt)]ClO_4, was mononuclear. The properties of these chelates are described in this paper.

Experimental

Synthesis of hmtt. Hmtt was synthesized by the methylation of triethylenetetramine (trien).[5)] Since commercial trien often contains *N*,*N*,*N*-tris(2-aminoethyl)amine (tren), it was first stirred in EtOH, to which concd HCl was added dropwise under cooling below 10°C. White tren·3HCl separated out at first, which was filtered away. Dropping more HCl, a yellowish creamy precipitate of trien·4HCl gradually separated out. This final precipitate was dissolved in a small amount of water with heating, and cold EtOH was slowly added to the solution to recrystallize the salt. After repeating the recrystallization several times, the trien in the salt was converted into hmtt with H_2CO and HCO_2H according to a procedure described in the literature.[5)] The final product was identified by means of the elementary analysis of hydrochloride (Found: C, 39.62; H, 8.97; N, 15.37%. Calcd for $C_{12}H_{34}N_4Cl_4$; C, 38.31; H, 9.11; N 14.89 %) as well as by a ^{1}H NMR measurement in D_2O, which revealed chemical shifts of five kinds of protons with the expected multiplicity.

Synthesis of the Mixed Chelates. The chelates were obtained by mixing $MX_2·6H_2O$ (M=Ni, X=ClO_4 or NO_3; M=Cu, X=ClO_4), dike (dikeH+KOH), and hmtt in EtOH, removing $KClO_4$ or KNO_3 and crystallizing from DCE or

Et_2O. A slight excess of hmtt was often used to suppress any disproportionation of the product, which often takes place.

(i) [Ni(dipm)(hmtt)]ClO_4. This could be obtained from a 1 : 1 : 2 mixture of $Ni(ClO_4)_2 \cdot 6H_2O$, dipm, and hmtt; disproportionation took place with all other dike's, and only $Ni(dike)_2$ separated out from the reaction mixture.

(ii) [Ni_2(dike)$_4$(hmtt)] (dike=dipm, acac, tfac, or hfac) and [Cu_2(hfac)$_4$(hmtt)]. These could be obtained from a 1 : 2 : 1 mixture of $Ni(ClO_4)_2 \cdot 6H_2O$ or $Cu(ClO_4)_2 \cdot 6H_2O$, the corresponding dike, and hmtt. The Cu chelate could be obtained only with hfac; disproportionation took place with all other dike's, and only $Cu(dike)_2$ separated out from the reaction mixture.

(iii) [$Ni_2(NO_3)_2$(dike)$_2$(hmtt)] (dike=dipm or acac). These could be obtained from a 1 : 1 : 1 mixture of $Ni(NO_3)_2 \cdot 6H_2O$, dike, and hmtt; when the dike used was tfac, [Ni_2(tfac)$_4$(hmtt)] was obtained instead. The use of $Cu(NO_3)_2 \cdot 6H_2O$ lead to disproportionation.

(iv) [Cu_2(acac)$_2$(hmtt)] (ClO_4)$_2$. This could be obtained from a 1 : 1 : 1 mixture of $Cu(ClO_4)_2 \cdot 6H_2O$, acac, and hmtt; beautiful violet crystals separated out rapidly from the reaction mixture when it was left standing in a refrigerator after filtration. In the course of time, however, $Cu(acac)_2$ gradually separated out from the same solution. When dipm or tfac was used as dike, the precipitation of $Cu(dike)_2$ took place from the outset, hindering the preparation of the mixed chelate. Disproportionation also took place when $Ni(ClO_4)_2 \cdot 6H_2O$ was used instead of $Cu(ClO_4)_2 \cdot 6H_2O$.

Physical Measurements. As for measurements of the electronic and IR spectra, the magnetic susceptibilities and electric conductivities of the chelates, cf. Refs. 1 and 6.

Results and Discussion

The formulas, composition, color, melting points, and effective magnetic moments (μ_{eff}; B.M.) of the obtained chelates are given in Table 1.

A. Nickel(II) Chelates. Nickel(II) chelates are all green or blue, and their μ_{eff} values and electronic spectra (cf. Table 2) show that they are all high-spin octahedral species. In general, they are only poorly soluble in polar organic solvents, and somewhat better soluble in non-polar solvents. They are also rather poorly solvatochromic, unlike the Cu(II) chelates, which are remarkably solvatochromic.

a) [Ni(dipm)(hmtt)]ClO_4. This was the only mononuclear species obtained, with a M : dike : hmtt ratio of 1 : 1 : 1. Molecular models indicate that the hmtt in it is coordinated in the cis-β form, in which the N, N', and N'' atoms occupy the "*mer*" sites, in order to minimize intramolecular steric hindrance. Even then, the chelate is still in a highly strained state, so that the good overlap of ligand and metal orbitals is disturbed, making the ligand field in it remarkably weaker than that in common (i.e., less strained) NiN_4O_2-type chelates. This can be seen from the value of its $\tilde{\nu}_1$ (ca. 10 Dq; 8.7×10^3 cm^{-1}) which is ca. 15—20% lower than those of $[Ni(en)_2(H_2O)_2]^{2+}$ (10.8×10^3 cm^{-1}),[7] [Ni(acac)(2,3,2-tet)]$^+$ (11.0×10^3 cm^{-1}),[8] and [Ni(acac) (Me$_4$-2,3,2-tet)]$^+$ (10.1×10^3 cm^{-1}).[8] It is conceivable that the destabilizing effect of such a large strain in hmtt is partially compensated by the powerful coordination of dipm, which is the strongest ligand among the dike's used, in this particular complex.

Another peculiarity of this chelate is its solubility. As stated above, the prepared Ni(II) chelates were poorly soluble in polar solvents, and relatively soluble in non-polar solvents. This tendency is most apparent in this chelate, which is only very slightly soluble in most organic solvents, and notably soluble only in highly non-polar ones, such as 1, 2-dichloroethane (DCE), benzene, or hexane, and in ether. The $\tilde{\nu}_1$ values in such solutions (ca. 8.4×10^3 cm^{-1}) are still lower than that in the solid state, possibly due to the effect of ion-pair formation in such media.

b) [Ni_2(dike)$_4$(hmtt)] (dike=dipm, acac, tfac, or hfac). A chelate of this type is easily formed by any of the dike's used. Apparently, they are the binuclear analogues of [Ni(dike)$_2$(tmen)],[9,11] which are known to be soluble in a variety of organic solvents. The solubilities of the binuclear chelates are much less, however, due to their stronger intermolecular force (cf. the values of the melting points given in Table 1, and Ref. 9). Since a large part of it is seemingly the van der Waals' force, the chelates are still soluble in DCE, benzene, hexane or ether; the tfac and hfac chelates with polar CF_3 groups are soluble in acetone. More polar solvents, e.g. DMSO, cannot dissolve these chelates to a noticeable degree.

As in the case of [Ni(dike)$_2$(tmen)], the binuclear chelates are only slightly solvatochromic; a comparison of their spectra with each other reveals that their $\tilde{\nu}_1$(ca. 10 Dq) values do not increase in the order of the l.f.s. of dike, i. e., in the order hfac<tfac<acac<dipm, but increase in the order acac<dipm≈tfac<hfac (cf. Table 2). This may be due to the effect of ligand-to-metal π-bonding, by which the magnitudes of 10 Dq for stronger ligands are reduced,[10] or, possibly, some kind of molecular distorsion; approximately the same trend can be observed in the spectra of [Ni(dike)$_2$(tmen)].[11]

c) [$Ni(NO_3)_2$(dike)$_2$(hmtt)] (dike=dipm, acac). When $Ni(NO_3)_2 \cdot 6H_2O$ is used in the preparation, nitrate complexes of this type are obtained if the l.f.s. of dike is sufficiently strong (cf. Experimental). They are evidently analogues of [Ni(NO_3)(dike)(tmen)] studied before;[12] the electronic and IR spectra show that they contain, as in the case of tmen chelates, a chelated NO_3^- in its coordination sphere (cf. Tables 2 and 3). Using $Ni(ClO_4)_2 \cdot 6H_2O$ instead of $Ni(NO_3)_2 \cdot 6H_2O$, however, it was impossible to prepare [Ni_2(dike)$_2$(hmtt)](ClO_4)$_2$, the analogues of red, square planar [Ni(dike)(tmen)]ClO_4 which could be obtained so easily. Trials to obtain the corresponding tetraphenylborates from the nitrate complexes were also unsuccessful.[4]

As in the cases of a) and b), these chelates are only poorly soluble in polar organic solvents, and are soluble only in non-polar or slightly polar solvents, such

Table 1. Analytical Data, Color, Melting Points, and Magnetic Moments of the Chelates Obtained

No.	Chelate	C/%$^{a)}$	H/%$^{a)}$	N/%$^{a)}$	Color(mp/°C)	μ_{eff}/B. M. $^{b)}$
I	[Ni(dipm)(hmtt)]ClO$_4$	48.55	8.41	9.34	Pale green	3.24
		(48.31)	(8.64)	(9.80)		
II	[Ni$_2$(dipm)$_4$(hmtt)]	61.49	9.55	5.34	Pale blue	4.46
		(62.23)	(9.88)	(5.18)	(225)	(3.15)
III	[Ni$_2$(acac)$_4$(hmtt)]	50.18	7.52	7.70	Pale blue	4.45
		(51.36)	(7.86)	(7.49)	(180)	(3.15)
IV	[Ni$_2$(tfac)$_4$(hmtt)]	39.73	4.58	5.86	Pale blue	4.52
		(40.03)	(4.83)	(5.84)	(152)	(3.20)
V	[Ni$_2$(hfac)$_4$(hmtt)]	31.51	2.90	4.71	Light green	4.52
		(32.68)	(2.92)	(4.77)	(213$^{c)}$)	(3.20)
VI	[Ni$_2$(NO$_3$)$_2$(dipm)$_2$(hmtt)]	48.54	8.03	10.22	Light blue	4.40
		(48.71)	(8.18)	(10.02)	(172)	(3.11)
VII	[Ni$_2$(NO$_3$)$_2$(acac)$_2$(hmtt)]	38.84	6.27	11.88	Light blue	4.41
		(39.42)	(6.62)	(12.54)		(3.12)
VIII	[Cu$_2$(hfac)$_4$(hmtt)]	32.67	2.86	4.56	Light green	2.89
		(32.41)	(2.90)	(4.73)		(2.04)
IX	[Cu$_2$(acac)$_2$(hmtt)](ClO$_4$)$_2$	34.78	5.62	7.12	Dark violet	2.55
		(35.02)	(5.88)	(7.42)		(1.80)

a) Found (Calcd). b) In the case of the binuclear species, the values for one mole of metallic ion are given in parentheses.
c) A small endothermic peak on the DTA curve, presumably of some kind of phase transition, was observed at 175°C.

Table 2. Values of $\tilde{\nu}_{\mathrm{max}}/10^3$ cm^{-1} ($\varepsilon_{\mathrm{max}}$/mol^{-1} dm^3 cm^{-1} in Parentheses) in the Electronic Spectra of the Ni(II) Chelates

Chelate	Solid	Solution$^{a)}$	
I	8.70, 16.31	DCE:	8.40(8.34), 16.39(11.6)
		C$_6$H$_6$:	8.47(7.16), 16.39(10.0)
II	9.43, 16.33	DCE:	9.62(23.8), 16.39(22.2)
		C$_6$H$_6$:	9.57(22.0), 16.46(19.9)
III	9.22, 16.07	DCE:	9.33(20.6), 16.20(15.4)
		C$_6$H$_6$:	9.43(21.6), 16.20(18.8)
IV	9.43, 16.00	DCE:	9.57(18.6), 16.20(16.8)
		Me$_2$CO:	9.63(17.8), 16.26(16.5)
V	9.62, 16.13	DCE:	10.00(13.1), 16.39(21.0)
		Me$_2$CO:	10.00(14.9), 16.26(22.9)
VI	9.43, 16.20	DCE:	9.57(19.0), 16.26(36.2)
		NM:	9.45(17.7), 16.16(35.3)
VII	9.01, 16.20	DCE:	9.30(18.7), 16.10(34.6)
		NM:	9.43(16.4), 16.13(32.4)

a) Concn : ca. 5×10^{-3} mol dm^{-3}.

Table 3. Values of $\tilde{\nu}_{\mathrm{max}}$/cm^{-1} of the Characteristic NO$_3^-$ Bands in the IR Spectra of [Ni$_2$(NO$_3$)$_2$(dike)$_2$(hmtt)]

Chelate	Solid	Solution$^{a)}$ (FT-IR in DCE)
VI	1770, 1715	1773, 1719
VII	1770, 1720	1772, 1717

a) In the solution spectra, two weaker bands were observed at ca. 1750 cm^{-1} and ca. 1735 cm^{-1}. They suggest that a part of NO$_3^-$ is acting as a monodentate ligand in solution, making the chelate partly 5-coordinate. Further studies in this direction is certainly of interest.

as DCE or nitromethane(NM). The spectra in such solvents are not very different from those in the solid state, except that the second band ($\tilde{\nu}_2$, at ca. 16×10^3 cm^{-1}) in the solution spectra is much stronger than the first ($\tilde{\nu}_1$, at ca. 9×10^3 cm^{-1}), as in the case of [Ni(NO$_3$)(dike)(tmen)].[12] The NM solution of the dipm chelate (**VI**) is slightly thermochromic, and a new band appears at ca. 20×10^3 cm^{-1} on heating to 60°C; its intensity, however, is ca. 50% of that of the corresponding band of [Ni(NO$_3$)(dipm)(tmen)] which appears under the same conditions (Fig. 1). These observations show that dissociation of a small part(presumably a few percent) of NO$_3^-$ from **VI**, leading to the square planar species [Ni$_2$(dipm)$_2$(hmtt)]$^{2+}$ or, more probably, [(dipm)Ni(hmtt)Ni(dipm)(NO$_3$)]$^+$ which contains both square planar and octahedral Ni(II), takes place in NM, but more weakly than the dissociation of [Ni(NO$_3$)(dipm)(tmen)] into [Ni(dipm)(tmen)]$^+$ and NO$_3^-$ (ca. 7% at 20°C).[4]

In the case of the corresponding acac chelates, **VII**

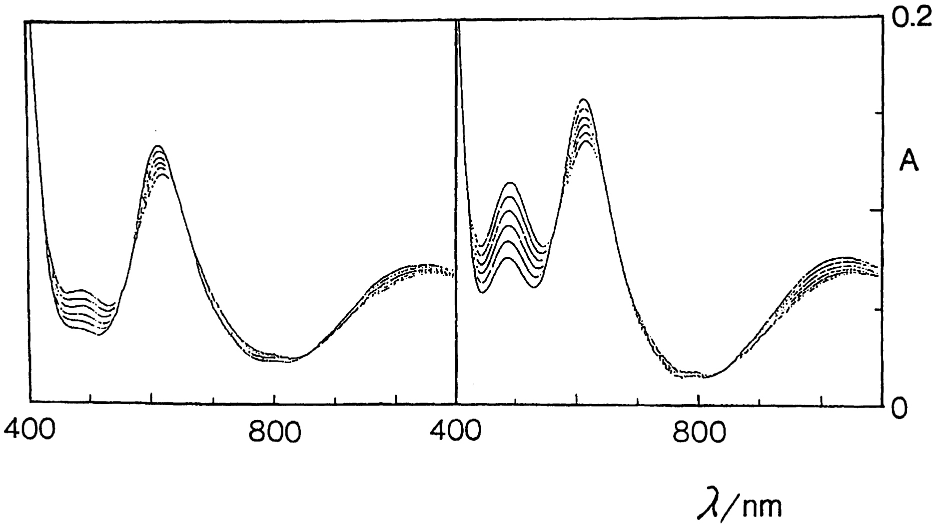
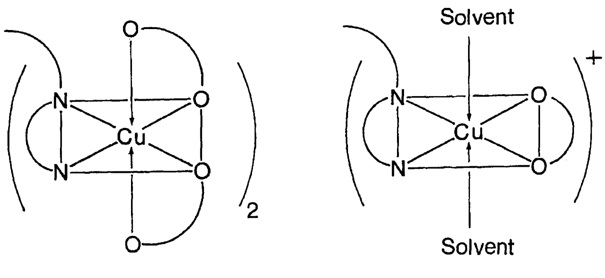


Fig. 1. Thermochromism of NM solutions of the chelate **VI** (left; ca. 4×10^{-3} mol dm^{-3}) and [Ni(NO$_3$)(dipm)(tmen)] (right; ca. 8×10^{-3} mol dm^{-3}). The bands at ca. 600 and 1000 nm decrease, and that at ca. 500 nm increases, with the temperature change from 10 to 60°C. Temp interval: 10°C; A=absorbance.



VIII VIIIa

Fig. 2. Structure of **VIII**; the CuN$_2$O$_4$ groups in it are partially converted into **VIIIa** in polar solvents.

and [Ni(NO$_3$)(acac)(tmen)], the same type of dissociation occurs still more weakly; thus, in the case of **VII**, the appearance of the new band can scarcely be detected, and even with [Ni(NO$_3$)(acac)(tmen)] it is only observable with a great care.[12)]

It is now reasonable to assume, in going from acac to dipm, the increased l.f.s. of dike tends to favor the formation of square planar (i.e., low spin) species; in fact, it is the case. Going from mononuclear to binuclear species, on the other hand, the dissociation leading to such species is apparently hindered. Its reason, which may be connected with the inability to prepare [Ni$_2$(dike)$_2$(hmtt)](ClO$_4$)$_2$ or [Ni$_2$(dike)$_2$(hmtt)](BPh$_4$)$_2$, is still an open question.

B. Cu(II) Chelates. Although nearly as much preparative efforts have been made as in the case of the Ni(II) chelates, only two copper(II) mixed chelates could thus far be prepared. Unlike the Ni(II) chelates, however, they are soluble in a large variety of polar and nonpolar solvents, and are highly solvatochromic in them, like the Cu(II) chelates with tmen (and similar diamines) or pmdt and dike.[2,4)]

a) [Cu$_2$(hfac)$_4$(hmtt)]. The structure of this chelate had already been studied by Bailey et al.[13)] by means of X-ray crystal analysis. Their results are sketched as **VIII** in Fig. 2; each of the two Cu(II) ions is at the center of an elongated N$_2$O$_4$ octahedron, a common geometry among the copper(II) complexes, in which the lengths of the Cu–O$_{\mathrm{ax}}$, Cu–O$_{\mathrm{eq}}$, and Cu–N bonds are 232—236, 198—200, and 205—208 pm, respectively.

Now, the solid reflection spectrum of this chelate shows a very wide absorption, apparently composed of two bands, the main band at 14.2×10^3 cm^{-1} and a narrower and weaker band at 9.4×10^3 cm^{-1}, and a shoulder at ca. 23×10^3 cm^{-1} (cf. Fig. 3). The shape of this spectrum is retained in DCE, in which the chelate is dissolved as a non-electrolyte (cf. Table 4). However, in going to more polar solvents,[14,15)] the main band is shifted slightly to the blue with a strong increase in its intensity, while the weaker band and the shoulder tend to disappear. At the same time, the molar conductivity (Λ_{M}) values indicate that the chelate begins to dissociate, first as a 1:1 electrolyte, and then, finally (in DMSO), as a 2:1 electrolyte.[16)]

All of these facts show that the strong solvatochromism of this chelate is brought about by a progressive dissociation of hfac anions, and the solvation of the resulting chelate species, in polar solvents. The neutral, 6-coordinated CuN$_2$O$_4$ groups in the original chelate are thereby converted progressively, along with an increase in the solvent polarity, into the cationic, axially solvated structure **VIIIa** (cf. Fig. 2). The chelate **VIII** is thus in strong contrast to [Ni$_2$(dike)$_4$hmtt], which tend to retain their own structure under all circumstances.

b) [Cu$_2$(acac)$_2$(hmtt)] (ClO$_4$)$_2$. This type of chelate could be obtained only with acac; the use of other dike's

Table 4. Values of $\tilde{\nu}_{\mathrm{max}}/10^3$ cm^{-1} and $\varepsilon_{\mathrm{max}}/\mathrm{mol^{-1}dm^3cm^{-1}}$ of the Cu(II) Chelates, and of $\Lambda_{\mathrm{M}}/\mathrm{ohm^{-1}\,cm^2\,mol^{-1}}$ of **VIII**, in Various Solvents

State	**VIII**		**IX**
	$\tilde{\nu}_{\mathrm{max}}(\varepsilon_{\mathrm{max}})$	Λ_{M} a)	$\tilde{\nu}_{\mathrm{max}}(\varepsilon_{\mathrm{max}})$
Solid	9.43, 14.24		18.5
Solution b)			
DCE (0/—) c)	9.52(38), 14.00(74)	0	
Me_2CO (17/12.5)	9.7sh(59), 14.40(158)	32.1	17.39(241)
NM (2.7/20.5)	14.58(225)	41.9	17.88(260)
MeCN (14.1/19.3)	14.49(195)	74.8	16.70(240)
MeOH (20/41.3)	14.52(222)	65.3	15.82(200)
DMF (24/16)	14.71(214)	63.4	15.66(221)
DMSO (29.8/19.3)	15.02(260)	67.9	14.50(223)

a) The standard values for 1 : 1 electrolytes in the solvents used are : 75—95 (NM), 100—140 (Me_2CO), 120—160(MeCN), 80—115 (MeOH), 65—90 (DMF), and ca. 35 (DMSO). Cf. Ref. 20. b) Concn : ca. 2.5×10^{-3} mol dm^{-3}. c) (DN/AN); cf. Ref. 16.

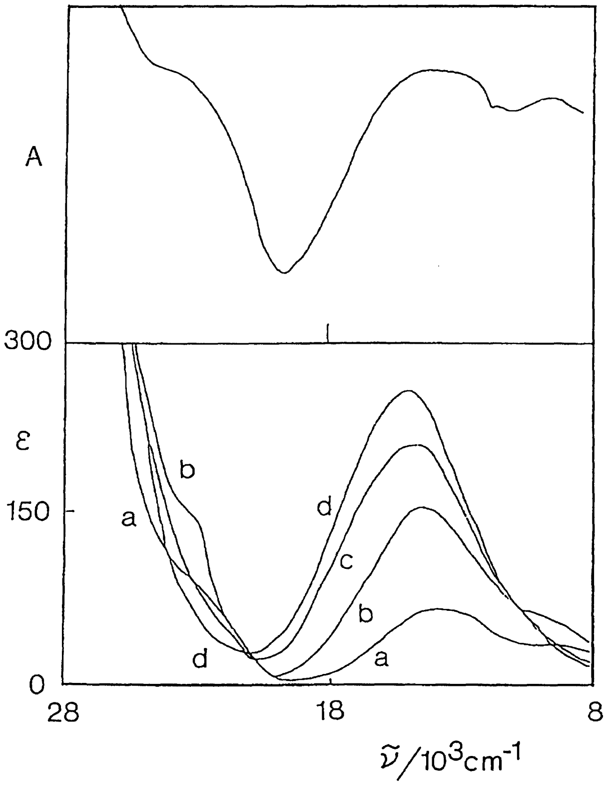


Fig. 3. Electronic spectra of the chelate **VIII**. Above: solid state; below: solutions in DCE (a), Me_2CO (b), DMF (c), and DMSO (d). A=absorbance.

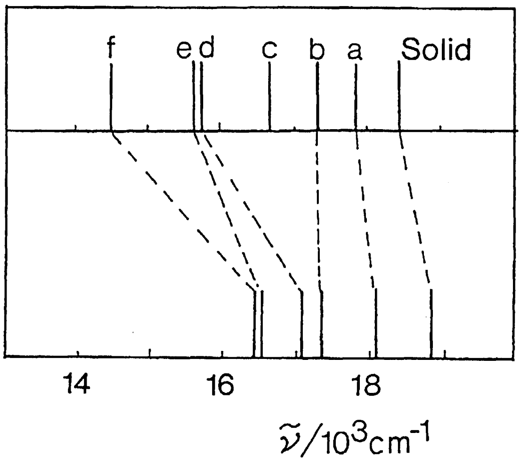


Fig. 4. Solvatochromism of the chelate **IX** (above) and [Cu(acac)(tmen)] ClO_4 (below); the lines a—f show, respectively, the $\tilde{\nu}_{\mathrm{max}}$ in NM, Me_2CO, MeCN, MeOH, DMF, and DMSO.

has led to disproportionation. This chelate is also soluble in a variety of solvents, and is very strongly solvatochromic, as is its monomuclear analogue [Cu(acac)(tmen)]ClO_4;[17] in fact, the solvatochromism of the binuclear species is more remarkable, as can be seen from Fig. 4 and Table 4. In most solvents, the $\tilde{\nu}_{\mathrm{max}}$ of the band of the binuclear chelate is lower than that of the mononuclear chelate, indicating that the former interacts with the solvent molecules more strongly than the latter. This strong solvation may be related primarily to the high positive charge of the binuclear species, although steric and electronic factors are certainly taking part in it.

Although the number of chelates studied has been limited by synthetic difficulties, it is probable that more species can be isolated by modification of preparative methods, e.g., by working in non-alcoholic media. It is hoped that such species (especially Cu(II) chelates) can supply more clues for the understanding of the differences between analogous mono- and binuclear species, as in the case of the studies on the mixed chelates with diamines and tetraketonates.[18—20]

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