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Studies on Mixed Chelates. XIX. 5-Coordinate Nickel(II) Complexes with *N,N,N′N″,N″*-Pentamethyldiethylenetriamine and *β*-Diketonates[1)]

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Mixed Ni(II) chelates with *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (pmdt) and a *β*-diketonate (dike) such as acetylacetonate(acac), dipivaloylmethanate(dipm), pivaloyltrifluoroacetonate(pfac), trifluoroacetylacetonate(tfac) or hexafluoroacetylacetonate(hfac) were prepared, and their structure and properites were studied. X-Ray crystal analysis confirmed that [Ni(acac)(pmdt)]ClO_4 is a distorted square pyramidal complex, and the solid reflection spectra of the remaining chelates indicated that most of them are also essentially square pyramidal. This structure is retained in a nonpolar solvent like 1,2-dichloroethane, but in strong donor solvents like DMSO or DMF it is converted into a 6-coordinated structure, $[Ni(dike)(pmdt)(Solvent)]^+$, containing a solvent molecule. The formation of this species is favored by increasing donor number(DN) of the solvent, and in the following order of dike:dipm<acac≪tfac, pfac≪hfac, which is almost opposite to the order of their pK_a values.

In the foregoing papers of this series[2—4)], it was reported that the 4-coordinate Ni(II) chelates with *N,N,N′,N′*-tetramethylethylenediamine(tmen; $Me_2N(CH_2)_2NMe_2$) and a *β*-diketonate (dike), [Ni(dike)(tmen)]X ($X=ClO_4^-$ or BPh_4^-) are soluble in various organic solvents, and are strongly solvatochromic, changing from red(square planar form) in 1,2-dichloroethane(DCE) to green (octahedral disolvated form) in dimethyl sulfoxide(DMSO) or *N,N*-dimethylformamide(DMF). The equilibrium between these two forms depends upon the donor properties of the solvent:

$$\underset{\text{4-coordinate(red)}}{[\mathrm{Ni(acac)(tmen)}]^+} + 2\mathrm{Solvent} \rightleftharpoons \underset{\text{6-coordinate(green)}}{[\mathrm{Ni(acac)(tmen)(Solvent)_2}]^+}$$

It shifts extremely to the left hand side in a weak donor solvent like DCE, and vice versa in a strong donor solvent like DMSO.

In order to compare with them, we have now prepared the corresponding mixed Ni(II) chelates with *N,N,N′,N″,N″*-pentamethyldiethylenetriamine(pmdt; $Me_2N(CH_2)_2NMe(CH_2)_2NMe_2$) and a dike, and studied their structure and solvatochromic changes. Pmdt is a bulky tridentate ligand which, like tmen, cannot form bis-type chelates with the metal ions of the first transition series, and has a marked tendency of forming 5-coordinate complex species with them. After the pioneering work of Ciampolini and Speroni,[5)] a large amount of works has been published on its complexes (cf., e.g., the series of Hendrickson et al.[6)] on its characteristic dimeric complexes with Cu(II)). As to its Ni(II) complexes, the species such as $[NiX_2(pmdt)]$,[5)] $[NiX(NH_3)(pmdt)]X\cdot nH_2O(X^-=Cl^-, Br^-$ or $I^-)$,[7)] and $[Ni(NH_3)_2(pmdt)](ClO_4)_2$[7)] have been studied; all of them are typically 5-coordinate, evidently owning to the bulkiness of pmdt which hinders the coordination of the 6th ligand.

As can be expected, most of the newly obtained mixed chelate were also found to be 5-coordinate, and they show a new kind of solvatochromism which will be discussed in this paper.

Experimental

Materials. The ligands used are pmdt, acetylacetone(Hacac), dipivaloylmethane(Hdipm), pivaloyltrifluoroacetone(Hpfac), trifluoroacetylacetone(Htfac) and hexafluoroacetylacetone(Hhfac). These and other reagents used are of the best commercial grade, and were used without further purification. Solvents used for spectral measurements are "Spectrograde"; if necessary, they were purified by distillation.

Syntheses of the Chelates, [Ni(dike)(pmdt)]ClO_4. 10 mmol of $Ni(ClO_4)_2\cdot 6H_2O$ were dissolved in 30 ml of methanol (MeOH), and 10 mmol of pmdt were added to it with stirring. Then a solution containing a diketone (Hdike) and KOH (10 mmol each) in 30 ml of MeOH was added to the mixture with heating and stirring. The resultant solution was filtered, and let stand for a few days. Crude green crystals which precipitated were recrystallized from DCE.

The analytical data, colors, and magnetic moments of the obtained chelates are shown in Table 1. The pfac and hfac chelates were found to be monohydrates; TG-DTA data show that they lose their water at about 70 °C in static air.

Measurements of Electronic Spectra. Electronic spectra of solutions were obtained with a Hitachi 340 recording spectrophotometer using 10 mm quartz cells at room temperature (ca. 20 °C). The electronic spectral data ($\tilde{\nu}_{max}$ and ε_{max}) in various organic solvents are deposited as Document No. 9099 (Table A) at the Office of the Editor of Bull. Chem. Soc. Jpn. Powder reflection spectra were recorded with the same instrument equipped with an

Table 1. Analytical Data, Color, Magnetic Moments, and K Values of the New Chelates

	C%[a]	H%[a]	N%[a]	Color	μ_{eff}/B.M.	K[b]
[Ni(dipm)(pmdt)]ClO_4	45.87 (46.76)	8.03 (8.04)	8.08 (8.18)	Green	3.25	1.5
[Ni(acac)(pmdt)]ClO_4	39.04 (39.05)	6.78 (7.02)	9.84 (9.76)	Green	3.22	3.2
[Ni(pfac)(pmdt)(H_2O)]ClO_4	37.35 (37.63)	6.07 (6.13)	7.76 (7.74)	Green	3.23	25[c]
[Ni(tfac)(pmdt)]ClO_4	34.62 (34.62)	5.43 (5.62)	8.67 (8.67)	Green	3.24	19.4
[Ni(hfac)(pmdt)(H_2O)]ClO_4	30.38 (30.22)	4.14 (4.50)	7.78 (7.55)	Light green	2.78[d]	88[c]

a) Calculated values are in parentheses. b) See text. c) Measured with dehydrated chelates. d) The reason for this smaller value is an open question.

integrating sphere, using $BaSO_4$ as the reference. The determination of the equilibrium constants(K) of the equilibrium(1) (see text) was made with a JASCO Ubest-30 spectrophotometer. A series of DCE solutions containing 10 mM (M=mol·dm^{-3}) of the 5-coordinate species and various amounts (between 0.2 M and 1.5 M) of DMSO was prepared with each chelate, and their spectra between 500 and 850 nm were measured at 25±0.5 °C, using the DCE solution (10 mM) of the same chelate with no DMSO as the reference. The values of K were then calculated from the obtained absorbances by means of the Benesi–Hildebrand plots.[8]

Other Physical Measurements. Infrared spectra (400—5000 cm^{-1}) were measured in Nujol mulls with a JASCO IR-A3 Grating Spectrophotometer. Magnetic susceptibility measurements were performed with a Shimadzu Torsion Magnetometer MB-100 at room temperature. Thermogravimetry-differential thermal analysis (TG-DTA) measurements were performed with a Differential Thermal Analyser TGD-3000M (Shinku-Riko) under static air with the heating rate of 3 °C min^{-1} or 1 °C min^{-1}.

Crystal Structure Analysis of [Ni(acac)(pmdt)]ClO_4. Green plate crystals were grown from a DCE solution. Crystals of approximate dimensions 0.3×0.3×0.4 mm^3 were used. The unit cell dimensions and space group were determined from oscillation and Weissenberg photographs. Accurate cell parameters were determined by a least-squares fit for 18 reflections within the range $18° < 2\theta < 28°$ measured on a Rigaku AFC-4 diffractometer with Mo $K\alpha$ radiation (λ= 0.71069 Å) monochromated by graphite.

Crystal Data: Mr=430.57, $NiC_{14}ClH_{30}N_3O_6$, monoclinic, $P2_1$, a=8.8285(8), b=13.467(1), c=8.590(1) Å, β=92.25(2), V=1020.5(2) Å^3, Z=2, d=1.401 g cm^{-3}, μ=10.49 cm^{-1}, F(000)= 456.

Table 2. Final Atomic Coordinates with Their Estimated Standard Deviations, Multiplied by 10^4 for All the Atoms

Atom	x	y	z	B(eq)
Ni	7731(1)	3485	4983(1)	2.9
N(1)	9740(7)	3090(5)	3875(8)	3.9
N(2)	8312(9)	2327(5)	6504(7)	4.3
N(3)	6443(8)	4017(5)	6807(7)	4.2
O(1)	7507(6)	4739(4)	3819(6)	3.8
O(2)	6178(6)	2781(4)	3733(6)	3.8
O(3)	2892(11)	5562(10)	9545(14)	9.5
O(4)	382(11)	5347(10)	10119(12)	9.7
O(5)	1889(18)	3998(9)	9350(18)	12.0
O(6)	1161(13)	5160(11)	7597(8)	9.6
C(1)	9472(11)	2903(9)	2188(10)	5.4
C(2)	10827(10)	3913(8)	4104(13)	5.3
C(3)	10293(11)	2165(7)	4612(12)	5.3
C(4)	9966(13)	2148(8)	6337(13)	5.5
C(5)	7442(12)	1411(6)	6160(11)	4.8
C(6)	7988(15)	2717(8)	8077(9)	6.1
C(7)	6484(14)	3222(7)	8012(10)	5.7
C(8)	7197(17)	4909(8)	7462(13)	6.7
C(9)	4866(13)	4261(15)	6344(16)	8.3
C(10)	6536(9)	4864(6)	2683(8)	3.8
C(11)	6549(12)	5863(7)	1899(12)	5.2
C(12)	5527(9)	4143(6)	2088(9)	3.8
C(13)	5425(9)	3158(6)	2636(9)	3.8
C(14)	4334(11)	2481(7)	1765(11)	4.9
Cl	1579(2)	5019(2)	9185(2)	4.5

Reflection data were collected on a 2θ–ω scan mode, up to 2θ=55° with scan widths of $\Delta\omega$=(1.0+0.35 tan θ). Backgrounds were counted for 5 s at both ends of scan. Three standard reflections were recorded after every 50 reflections. This crystal was slowly decomposed probably due to deliquescence, of which intensity data decreased by 10%. The data were corrected using standard reflections. A total of 2447 reflections were collected at the rate of 8° (2θ) min^{-1}, of which 2203 were treated as significant ($|F_o| > 3\sigma(|F_o|)$). The structure was solved by the direct method by using the program MALTAN78[9] and was refined by full matrix least-squares with SHELX76.[10] The quantity minimized was $\sum\omega(|F_o|-|F_c|)^2$, where $\omega=(\sigma(F_o)^2+0.004|F_o|^2)^{-1}$. Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[11] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms found in the difference Fourier maps and derived geometrically were refined isotropically. Max. Δ/ρ and max. $\Delta\rho$ in the final difference map were 0.30 and 0.55 e Å^{-3} (within 1 Å from Nickel). Final R (and R_W) was 0.053 (0.059). The final coordinates of non-hydrogen atoms are given in Table 2. Computations were carried out on IBM 4381-R24 computer at the Computer Center of Ochanomizu University. The tables for the anisotropic temperature factors for non-hydrogen atoms (Table B), the F_o–F_c list (Table C), the atomic parameters for the H atoms (Table D) and remaining bond distances and angles (Table E) are deposited as Document No. 9099 at the Office of the Editor of Bull.

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Results and Discussion

Structure of Crystalline Chelates. As can be seen from Table 1, we obtained five new chelates of two types, one formulated as [Ni(dike)(pmdt)]ClO_4 and the other as [Ni(dike)(pmdt)(H_2O)]ClO_4. They are all green high-spin d^8 chelates, with magnetic moments corresponding to two unpaired electrons.

The structure of [Ni(acac)(pmdt)]ClO_4 with the atomic numbering is presented in Fig. 1, and its selected bond lengths and angles are shown in Table 3. The atoms in the first coordination sphere form a distorted square pyramid, a typical 5-coordinate structure; the three N atoms of pmdt (N1, N2, N3) and one O atom of acac (O1) form a distorted square around Ni(II), which is capped by another O of acac (O2). The four atoms forming the distorted square are not exactly coplanar; two (N1, N3) are below and two (N2, O1) are above, each ca. 0.1 Å away from the mean plane. The central Ni(II), on the other hand, lies at 0.31 Å above it. It is also noted that an O(O6) of ClO_4^- is located at the opposite side of the cap, seemingly occupying the 6th coordination site. But the Ni-O6 distance is so long (4.33 Å) that no significant bonding is expected along it. The bond lengths between the nickel(II) ion and five donor atoms are nearly the same as those reported for another distorted square pyramidal nickel(II) complex [Ni{5-Cl-SALen-N(C_2H_5)$_2$}$_2$],⑫ and

Table 3. Bond Lengths (Å) and Angles (°)

		N(1)-Ni-N(2)	84.5(3)
Ni-N(1)	2.114(7)	N(1)-Ni-N(3)	155.7(3)
Ni-N(2)	2.086(7)	N(1)-Ni-O(1)	93.2(2)
Ni-N(3)	2.098(6)	N(1)-Ni-O(2)	102.3(2)
Ni-O(1)	1.968(5)	N(2)-Ni-N(3)	85.1(3)
Ni-O(2)	1.954(6)	N(2)-Ni-O(1)	167.7(3)
N(1)-C(1)	1.481(14)	N(2)-Ni-O(2)	97.6(3)
N(1)-C(2)	1.474(13)	N(3)-Ni-O(1)	92.3(2)
N(1)-C(3)	1.472(12)	N(3)-Ni-O(2)	100.8(3)
N(2)-C(4)	1.492(14)	O(1)-Ni-O(2)	94.8(2)
N(2)-C(5)	1.477(14)	Ni-N(1)-C(1)	112.2(5)
N(2)-C(6)	1.488(15)	Ni-N(1)-C(2)	107.7(5)
N(3)-C(7)	1.488(14)	Ni-N(1)-C(3)	106.8(5)
N(3)-C(8)	1.474(16)	C(1)-N(1)-C(2)	109.7(8)
N(3)-C(9)	1.470(22)	C(1)-N(1)-C(3)	108.3(8)
O(1)-C(10)	1.284(10)	C(2)-N(1)-C(3)	112.1(7)
O(2)-C(13)	1.240(10)	Ni-N(2)-C(4)	106.1(5)
O(3)-Cl	1.396(13)	Ni-N(2)-C(5)	112.6(5)
O(4)-Cl	1.422(14)	Ni-N(2)-C(6)	104.7(5)
O(5)-Cl	1.408(16)	C(4)-N(2)-C(5)	110.4(8)
O(6)-Cl	1.411(14)	C(4)-N(2)-C(6)	111.6(8)
C(3)-C(4)	1.521(15)	C(5)-N(2)-C(6)	111.1(8)
C(6)-C(7)	1.491(18)	Ni-N(3)-C(7)	105.9(5)
C(10)-C(11)	1.505(14)	Ni-N(3)-C(8)	108.3(6)
C(10)-C(12)	1.401(12)	C(7)-N(3)-C(8)	108.8(9)
C(12)-C(13)	1.412(12)	C(7)-N(3)-C(9)	110.3(10)
C(13)-C(14)	1.503(13)	C(8)-N(3)-C(9)	109.2(11)
		Ni-O(1)-C(10)	123.3(5)
		Ni-O(2)-C(13)	124.2(5)
		N(1)-C(3)-C(4)	111.0(8)
		N(2)-C(4)-C(3)	108.4(9)
		N(2)-C(6)-C(7)	109.2(10)
		N(3)-C(7)-C(6)	110.6(10)
		O(1)-C(10)-C(11)	116.2(7)
		O(1)-C(10)-C(12)	125.6(7)
		C(11)-C(10)-C(12)	118.2(8)
		C(10)-C(12)-C(13)	125.3(8)
		O(2)-C(13)-C(12)	126.8(8)
		O(2)-C(13)-C(14)	116.4(8)
		C(12)-C(13)-C(14)	116.8(8)
		O(3)-Cl-O(4)	110.0(8)
		O(3)-Cl-O(5)	109.4(8)
		O(3)-Cl-O(6)	109.1(8)
		O(4)-Cl-O(5)	113.1(9)
		O(4)-Cl-O(6)	109.4(8)
		O(5)-Cl-O(6)	105.7(9)

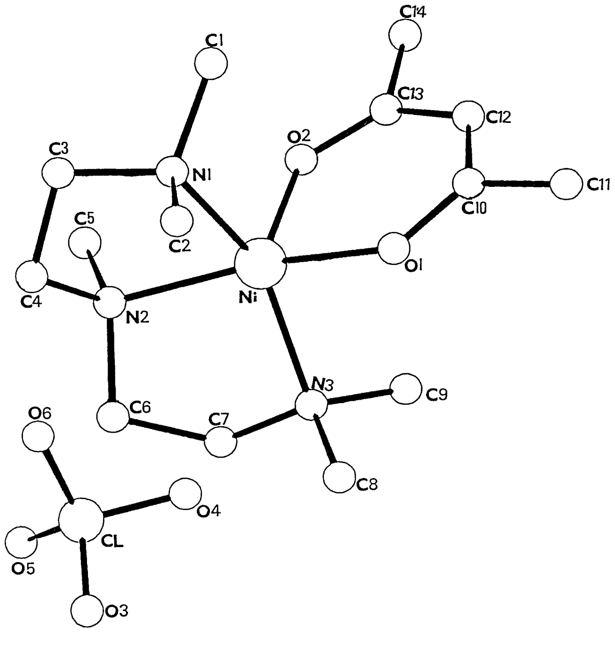

Fig. 1. Structure of [Ni(acac)(pmdt)]ClO_4.

Table 4. Band Maxima of the Powder Reflection Spectra

Chelate	$\tilde{\nu}_{max}/10^3$ cm^{-1}			
[Ni(dipm)(pmdt)]ClO_4	10.79	13.33	16.26	27.06
[Ni(acac)(pmdt)]ClO_4	10.98	12.90	16.36	26.78(sh)$^{b)}$
[Ni(pfac)(pmdt)(H_2O)]ClO_4	10.12	16.29		
[Ni(pfac)(pmdt)]$ClO_4$$^{a)}$	10.80	13.16	16.44	26.5(sh)$^{b)}$
[Ni(tfac)(pmdt)]ClO_4	11.05	13.07	16.45	26.5(sh)$^{b)}$
[Ni(hfac)(pmdt)(H_2O)]ClO_4	10.53	16.28		

a) Measured after dehydration of the hydrated chelate (see text). b) sh=shoulder.

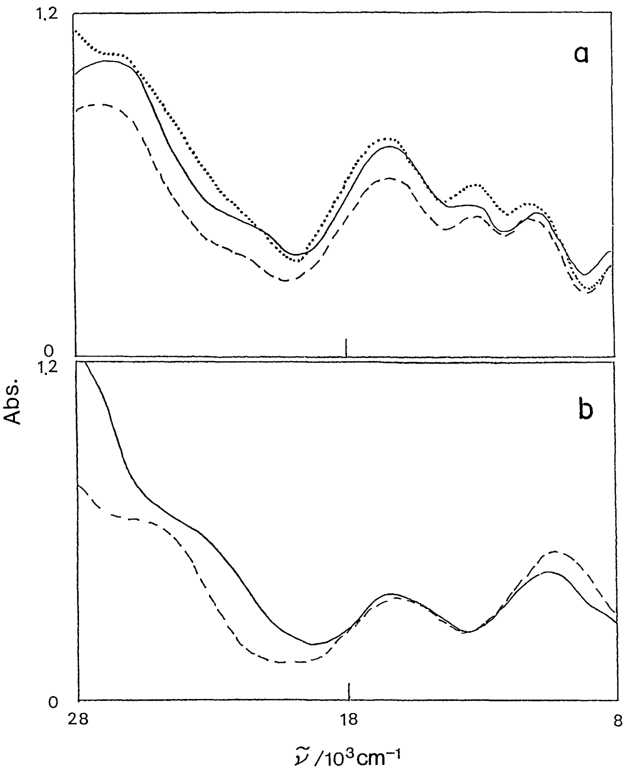

Fig. 2. Powder reflection spectra of the new 5-coordinate chelates $[Ni(dike)(pmdt)]ClO_4$ (a) and 6-coordinate hydrates $[Ni(dike)(pmdt)(H_2O)]ClO_4$ (b). The dike's in (a) are dipm (—), acac (----), and tfac (·····); those in (b) are hfac (—) and pfac (----).

for the related octahedral Ni(II) complexes.[13]

The solid reflection spectra of the dipm, acac, and tfac chelates are now very similar (cf. Fig. 2a), showing 4 bands at ca. 11×10^3 cm^{-1}, 13×10^3 cm^{-1}, 16×10^3 cm^{-1} and 27×10^3 cm^{-1}. This fact indicates that all these chelates are stereochemically similar, i.e., are 5-coordinated square pyramidal chelates; in fact the positions of these bands are not very different from those of the square pyramidal Ni(II) chelate mentioned above, the spectrum of which was explained with a crystal field model.[12,14] Although the angular overlap model shows that such a Ni(II) complex should be unstable in comparison with the 6-coordinate octahedral one,[15] the obtained complexes are apparently very stable, probably owing to the steric hindrance of the bulky groups on pmdt.

On the other hand, the hydrated pfac and hfac chelates show spectra of a different type, with only two bands at ca. 10×10^3 cm^{-1} and 16×10^3 cm^{-1}, which is characteristic to Ni(II) chelates of 6-coordinate structure (Fig. 2b). This indicates that these chelates should be formulated as $[Ni(dike)(pmdt)(H_2O)]ClO_4$ with an H_2O molecule at the 6th coordination site. When the hydrated pfac chelate is heated at 60 °C in vacuum, a remarkable spectral change takes place, until the spectrum becomes quite similar to those in Fig. 2a. The ν_{OH} band in its IR spectrum is lost at the same time. These changes show that the chelate become 5-coordinated by dehydration.

The reflection and IR spectra of the hydrated hfac chelate, however, were found to change only little by such a treatment, although TG-DTA data show that it is dehydrated nearly as easily as the hydrated pfac chelate. Here it seems that the dehydrated chelate absorbs atmospheric water so readily, that most of it reverts to the hydrated state in the course of spectral measurements. Thus the spectrum of the dehydrated hfac chelate in solid state has not yet been obtained.

Solvatochromism in Organic Solvents. When these chelates are dissolved in DCE, they form green solutions. The spectra of the solutions of the acac, dipm, tfac chelates show strong bands at ca. 16×10^3 cm^{-1} and 26×10^3 cm^{-1}, and weaker bands (or shoulders) at ca. 11×10^3 cm^{-1} and 13×10^3 cm^{-1}. The spectra thus resemble those of their solids (in the case of the pfac chelate, that of the dehydrated one), indicating that the 5-coordinate structure in the solid state is retained in DCE solution.

In the case of the dipm and acac chelates, similar spectra are observed also in a number of other solvents, i.e., nitromethane(NM), methanol(MeOH), ethanol(EtOH), acetone, and acetonitrile(MeCN). However, the solutions in DMF and DMSO show different spectra with two peaks at ca. 9×10^3 cm^{-1} and 16×10^3 cm^{-1}, which are similar to the solid spectra of hydrated chelates of pfac and hfac. This spectral change indicates that, in these solvents of very high DN (Gutmann's donor number),[16] a solvent molecule combines with the 5-coordinated chelate, and converts it into a 6-coordinate species, $[Ni(dike)(pmdt)(Solvent)]^+$.

A closer look at these spectral data, some of which are shown in Figs. 3a—3c, reveals further that, in the case of the acac chelate, the ε values of the two strong bands of the 5-coordinated species gradually decrease in the order of

$$DCE>NM>Acetone>EtOH>MeOH$$

with the increase of the DN of the solvent, indicating that the equilibrium

$$[Ni(dike)(pmdt)]^+ + Solvent \rightleftharpoons [Ni(dike)(pmdt)(Solvent)]^+ \quad (1)$$

established in these solutions is shifted to the right hand side with the increase of solvent DN. In the case of the dipm chelate, on the other hand, the ε values in these solvents are mostly not very different from each other, showing that the 5-coordinated species predominates in them. (A notable exception from these general tendencies is the case of MeCN; while its DN lies between those of NM and acetone, the ε values of the bands of the 5-coordinate species in it are lower than

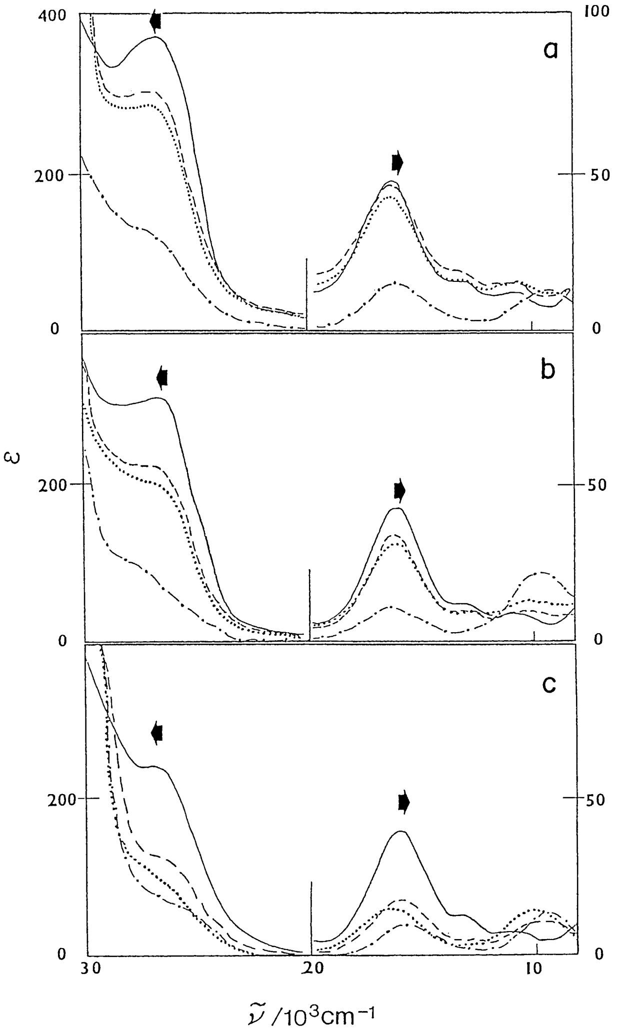

Fig. 3. Electronic spectra of $[Ni(dipm)(pmdt)]ClO_4$ (a), $[Ni(acac)(pmdt)]ClO_4$ (b), and $[Ni(tfac)(pmdt)]ClO_4$ (c) in DCE (—), MeOH (----), MeCN (·····), and DMSO (-·-·-). Concn: ca. 1.0×10^{-3} M (M= mol dm^{-3}).

those in methanol, suggesting that the rod-like (and π-electron rich) molecule of MeCN can get into the sterically hindered 6th coordination site of Ni(II) more easily than alcohols and acetone, as was observed also in other cases[17]).

In the case of the tfac chelate, the ε values of the bands of the 5-coordinate species in acetone (e.g., 31 at 16.13×10^3 cm^{-1}) are notably lower than those in DCE(40) and NM(37), and the spectra in alcohols and MeCN are nearly those of the 6-coordinate species. Similar trends are observed also with the pfac chelate; here the coordinated H_2O molecule in the solid hydrate readily dissociates from Ni in an organic solvent, so that the spectra of the hydrated and dehydrated chelates in it are nearly the same. In the case of the hydrated hfac chelate, the spectra show that the 6-coordinate species exist predominantly in all solvents, even in DCE; comparison of their $\tilde{\nu}_{\max}$ values

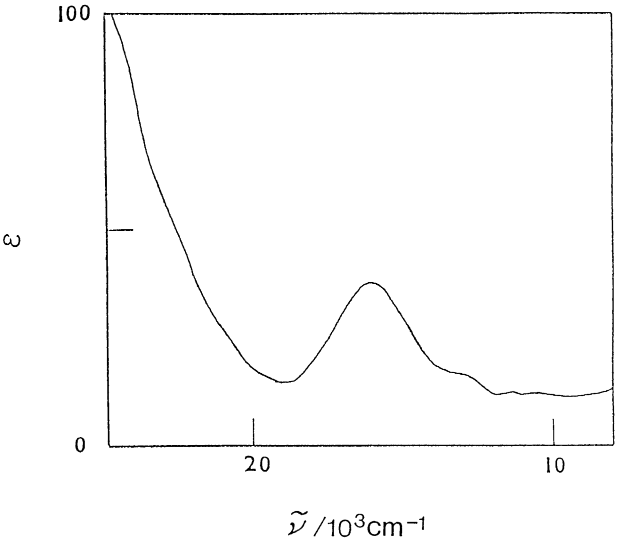

Fig. 4. Electronic spectrum of a DCE solution containing $[Ni(hfac)(pmdt)]ClO_4$ (see text). Concn: ca. 1.0×10^{-3} M.

(e.g., 10.4 and 16.1 in DCE, 9.8 and 16.0 in Me_2CO and 9.4 and 15.7 in DMSO, in 10^3 cm^{-1}) with those of the solid (10.5 and 16.3) shows that the 6th ligand is water in solvents of low DN, but it is substituted by a solvent molecule in more polar solvents.

Comparison of all these spectra thus leads to the conclusion that the equilibrium (1) is shifted to the right hand side with the increase of solvent DN (except MeCN; see above), and in the following order of the dike ligands:

$$\text{dipm} < \text{acac} \ll \text{tfac},\ \text{pfac} \ll \text{hfac} \qquad (2)$$

That is to say , the hfac chelate tends to be 6-coordinate in all solvents, combining with water when the coordination ability of the solvent is too low. The tfac and pfac chelates are 5-coordinate in DCE, but are converted to the 6-coordinate species even in solvents of relatively low DN. On the other hand, the dipm chelate is 5-coordinate (or mainly so) in most solvents tried, and gets 6-coordinate only in solvents of very high DN, and the acac chelate comes between these extremes.

A quantitative support to this view was obtained by the determination of K of the equilibrium(1) for each chelate, using DMSO as the coordinating solvent and studying the equilibrium in DCE. In the case of the hfac chelate, special care was taken to remove water from the system; using freshly dehydrated materials, a DCE solution which shows a typical spectrum of a 5-coordinate species (i.e., which contains the 5-coordinate chelate $[Ni(hfac)(pmdt)]^+$; cf. Fig. 4) was obtained and used for study. The obtained K values (Table 1) increase in the order of (2), or with the decrease of the pK_a of the dike ligand (cf. Fig. 5);[18–20] since the latter values can be taken as the measures of the ligand field strengths of the dike ligands, these

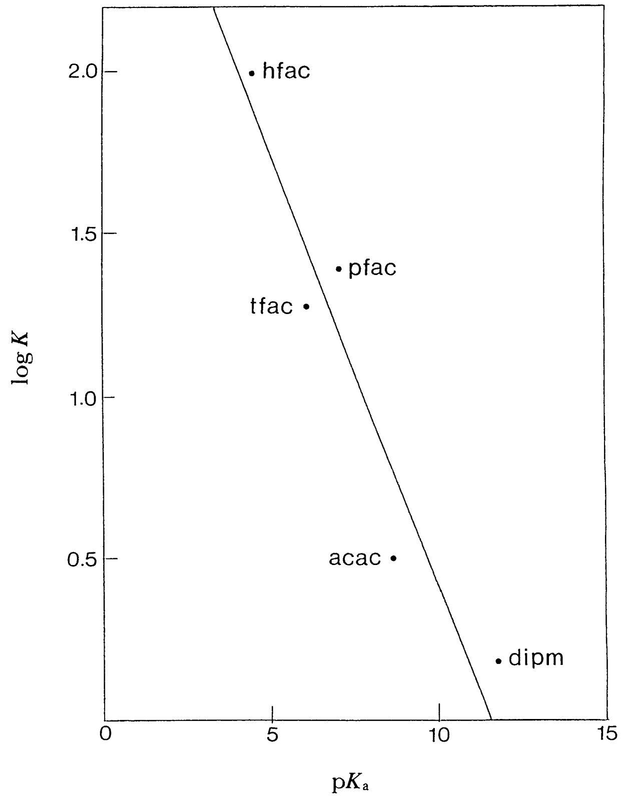

Fig. 5. Relation between pK_a of dike[19,20] and log *K* for the formation of [Ni(dike)(pmdt)(DMSO)]ClO$_4$ in DCE.

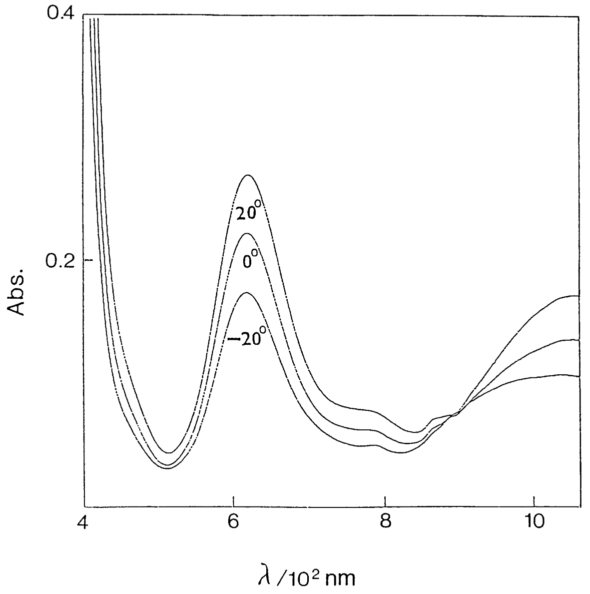

Fig. 6. Temperature dependence of the spectrum of [Ni(acac)(pmdt)]ClO$_4$ in a DCE–DMSO solution. Concn of the chelate: 9.88×10^{-3} M; concn of DMSO: 2.26×10^{-1} M.

results lead to the reasonable conclusion that the tendency of a [Ni(dike)(pmdt)]$^+$ type chelate to combine with solvent (i.e., its Lewis acidity) increases with the decrease of the ligand field strength (i.e., Lewis basicity) of dike.

It was also found that the DCE solutions of the dipm, acac, tfac, and pfac chelates containing DMSO are thermochromic; the data of the acac chelate are in Fig. 6. The band at 16×10^3 cm^{-1} becomes stronger and that at 10×10^3 cm^{-1} weaker, with the rise of temperature, forming an isosbestic point, and showing that the equilibrium(1) is shifted to the left hand side by heating. Similar but smaller spectral changes were also obtained with the dipm, tfac, and pfac chelates; in these cases, the equilibrium (1) is shifted more strongly to the left (dipm) or right (tfac, pfac) hand side than acac, so that the systems seem to be more insensitive to the temperature change.

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