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Studies on Mixed Chelates. V. Mixed Nickel(II) Chelates with *N,N,N′,N′*-Tetraethylethylenediamine and β-Diketones[1)]

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Fourteen mixed nickel(II) chelates with the general formula, Ni teen(β-dik)X, were newly obtained. Here teen is *N,N,N′,N′*-tetraethylethylenediamine, *i.e.*, a sterically hindered ligand with four bulky ethyl groups on the donor *N* atoms, β-dik is a β-diketonate ion, and X is an anion such as $B(C_6H_5)_4^-$, ClO_4^-, NO_3^- or β-dik. According to the coordination ability of the anion X, the structure of the mixed chelate changes from square planar to octahedral, remarkable solvent effects being observed on the absorption spectra of these chelates. The steric influence of the ligand "teen" was compared with that of the ligand "tmen", *i.e.*, its tetramethyl analog.

Many complexes of nickel(II) with ethylenediamine or its derivatives have been studied.[2–7)] The structures of these complexes are sometimes square planar and sometimes octahedral. Although the principal factors which determine the structures are steric and electronic, the former seems to be predominant in a number of cases. Thus *N,N,N′,N′*-tetramethylethylenediamine (tmen*) forms a dimeric chelate, [Ni tmen(OH)]$_2^{2+}$, instead of the bis-chelate [Ni tmen$_2$]$^{2+}$ in which a strong interligand repulsion occurs.[3)] On the other hand, the combination of tmen and the ligand which has no bulky group around the donor atom can form stable mixed complexes, *i.e.*, [Ni tmen(AA)][1,8)] or [Ni tmen X$_2$].[9)]

In the present study, a ligand with more bulky groups on the donor *N* atoms, *N,N,N′,N′*-tetraethylethylenediamine, which has been studied only little as a chelating agent, was chosen in order to obtain a series of new mixed chelates, Ni teen(β-dik)X, and the properties of the chelates were compared with those of the corresponding chelates of tmen.[1,8)]

Experimental

Materials. Commercial "Extra Pure" products were used except for $Ni(ClO_4)_2 \cdot 6H_2O$ prepared from freshly prepared nickel carbonate and perchloric acid and purified by recrystallization.[10)] Solvents for spectral measurements were of "Extra Pure" or "Spectro" grade. 1,2-Dichloroethane for electric conductivity measurements was redistilled and dehydrated.

Preparation of the Chelates. *[Ni teen dpm]B(C*$_6$*H*$_5$*)*$_4$*, [Ni teen aca]B(C*$_6$*H*$_5$*)*$_4$ *and [Ni teen dbm]B(C*$_6$*H*$_5$*)*$_4$: Equimolar amounts of nickel nitrate and an appropriate β-diketone (10 mmol each) were dissolved in 30 ml of acetone. To this solution, 5 mmol of Na_2CO_3 and an excess of teen (slightly above 15 mmol) were added with stirring. After filtration, the resulting mixture was dried up with a rotary evaporator, and the solid obtained was dissolved in 1,2-dichloroethane and filtered in order to separate a white precipitate. When solid $NaB(C_6H_5)_4$ (15 mmol) was added to this solution, the color of the solution turned from green to red, a white powder being precipitated. This was found to be a mixture of $NaNO_3$ and $NaB(C_6H_5)_4$ from the IR spectra. After filtration, the solution was concentrated in a silica-gel desiccator. Brilliant red crystals were obtained from the solution (except in the case of [Ni teen aca]B(C$_6$H$_5$)$_4$) and recrystallized from the same solvent. It was difficult to crystallize the aca mixed chelate, but it could be obtained as a crystalline powder from the red solution by addition of ether in excess and cooling with stirring. The same procedure was repeated for purification.

[Ni teen dpm]ClO$_4$ *and [Ni teen bza]ClO*$_4$: Equimolar amounts of nickel perchlorate and an appropriate β-diketone (10 mmol each) were dissolved in 30 ml of acetone, and 5 mmol of Na_2CO_3 and 15 mmol of teen were added with stirring. After filtration, the solution was dried up with a rotary evaporator and the red solid product was dissolved in 1,2-dichloroethane and concentrated by blowing air stream. A red crystalline powder was finally obtained by addition of ether to the concentrated dichloroethane solution. In the case of dpm, [Ni teen dpm$_2$] was obtained from the filtrate as a by-product.

[Ni teen aca NO$_3$*], [Ni teen bza NO*$_3$*] and [Ni teen dbm NO*$_3$*]*: Equimolar amounts of nickel nitrate and an appropriate β-diketone(10 mmol each) were dissolved in 30 ml of acetone, and 5 mmol of Na_2CO_3 and an excess of teen (15 mmol) were added with stirring. The solution was concentrated by blowing air stream. The blue or green crystals obtained were recrystallized from 1,2-dichloroethane.

[Ni teen dpm$_2$*], [Ni teen aca*$_2$*], [Ni teen bza*$_2$*], [Ni teen dbm*$_2$*], [Ni teen tfa*$_2$*] and [Ni teen hfa*$_2$*]*: Some of these chelates were obtained as by-products in the preparation of the mixed perchlorate chelates. In the case of tfa and hfa, however, only this type of chelate, [Ni teen β-dik$_2$], could be obtained as crystalline products. The general procedure of preparation of this type of chelate is as follows: 10 mmol of nickel sulfate or nitrate and 20 mmol of an appropriate β-diketone were dissolved in 50 ml of acetone, and 20 mmol of KOH suspended in 20 ml of methanol was added in order to neutralize the β-diketone. To the pale greenish blue solution in which [Ni (β-dik)$_2$(S)$_2$](where S=solvent molecule) was formed, an excess of teen(slightly more than 10 mmol) was added and then filtered. The solution was dried up with a rotary evaporator. After the crude blue or green solid obtained was dissolved in 1,2-dichloroethane, the filtrate was concentrated by blowing air stream until the crystals appeared. The crude product was recrystallized from 1,2-dichloroethane.

Physical Measurements. The electronic spectra of the chelate solutions in the range 340—1500 nm were recorded with a Hitachi EPS-3T spectrophotometer using 10 mm silica cells. The reflection spectra of solid samples in the range 400—750 nm were recorded with a Shimadzu Multiconvertible D-40R spectrophotometer with a reflection

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* Other abbreviations used in this article are: teen=*N,N,N′,N′*-tetraethylethylenediamine, dpm=dipivaloylmethanate, aca=acetylacetonate, bza=benzoylacetonate, dbm=dibenzoylmethanate, tfa=trifluoroacetylacetonate, hfa=hexafluoroacetylacetonate, diam=diamine, β-dik= a β-diketonate ion, and AA=a bidentate ligand such as β-dik.

Table 1. Analytical data and other properties of the chelates obtained

Chelate	Color	C%[a)]	H%[a)]	N%[a)]	μ_{eff}(BM)	$\Lambda_M(\Omega^{-1}\,cm^2\,M^{-1})$[b)]
[Ni teen dpm]$B(C_6H_5)_4$	Red	69.46(73.68)	8.10(8.67)	3.68(3.82)	Dia.	27.2
[Ni teen aca]$B(C_6H_5)_4$	Red	69.21(72.13)	7.47(7.93)	4.00(4.31)	(1.08)	27.2
[Ni teen dbm]$B(C_6H_5)_4$	Red	75.48(76.08)	6.95(7.18)	3.59(3.62)	Dia.	27.1
[Ni teen dpm]ClO_4	Red	51.36(49.09)	8.44(8.49)	5.54(5.45)	(0.28)	31.2
[Ni teen bza]ClO_4	Red	48.24(48.86)	7.03(6.77)	5.51(5.70)	Dia.	30.3
[Ni teen aca NO_3]	Blue	45.19(45.94)	8.09(7.97)	11.03(10.70)	3.10	0.7
[Ni teen bza NO_3]	Green	51.47(52.87)	7.08(7.32)	9.26(9.25)	3.11	0.5
[Ni teen dbm NO_3]	Green	57.95(58.16)	6.44(6.83)	8.11(8.14)	3.08	0.0
[Ni teen dpm_2]	Blue	63.85(64.10)	10.96(10.76)	4.66(4.67)	3.07	0.0
[Ni teen aca_2]	Blue	56.66(55.96)	9.23(8.92)	6.60(6.52)	3.07	0.0
[Ni teen bza_2]	Green	65.47(65.11)	7.80(7.65)	5.04(5.06)	3.07	0.0
[Ni teen dbm_2]	Green	70.73(70.91)	6.84(6.84)	4.11(4.14)	3.05	0.0
[Ni teen tfa_2]	Blue	44.50(44.71)	6.02(6.00)	5.21(5.21)	3.10	0.0
[Ni teen hfa_2]	Green	36.90(37.24)	3.88(4.06)	4.30(4.34)	3.18	0.0

a) Calculated values in parentheses. b) 1.0×10^{-3} M solution in 1,2-dichloroethane at 25 °C.

attachment and MgO disks for reference. Measurements were performed at room temperature, *ca.* 20 °C. The magnetic susceptibility was measured by the Faraday method with a Shimadzu Tortion Magnetometer MB-100 using $HgCo(NCS)_4$ and Mohr's salt as standard samples for calibration. The IR spectra of the solid chelates in the range 400—4000 cm^{-1} were recorded with a JASCO IR-G spectrophotometer by the Nujol-mull method. The electric conductivity measurements were carried out with a Yanagimoto Conductivity Outfit MY-7 using 1,2-dichloroethane as the solvent.

Results and Discussion

General Properties of the Chelates. The compositions of the chelates obtained as crystals or fine crystalline powders can be expressed with the general formula, Ni teen (β-dik) X, where X is an anion such as $B(C_6H_5)_4^-$, ClO_4^-, NO_3^- or β-dik. The results of chemical analyses and other properties are given in Table 1. As in the case of the tmen chelates,[1,8)] these chelates can be classified into two types. Type 1 chelates with $B(C_6H_5)_4^-$ or ClO_4^- are diamagnetic and red,** while type 2 chelates with NO_3^- or one more β-diketone are paramagnetic (*ca.* 3 BM) and green or blue. These facts, together with the spectral features give the formula for each chelate (Table 1).

Table 1 also gives the electric conductivity data of the chelates in 1,2-dichloroethane solution. According to the criterion by Geary[11)] who has pointed out that a 1 : 1 electrolyte in 1,2-dichloroethane shows a molar conductivity of *ca.* 23 $ohm^{-1}\,M^{-1}\,cm^2$, all type 1 chelates should be 1 : 1 electrolytes, while all the type 2 chelates are clearly non-charged complexes. This also supports the formulation of these chelates given in Table 1.

Electronic Spectra. Figures 1, 2, and 3 show the absorption spectra of the mixed chelates, Ni teen bza X, in various solvents and in solid state. The other mixed chelates also show similar spectra. Their spectral data are given in Table 2.

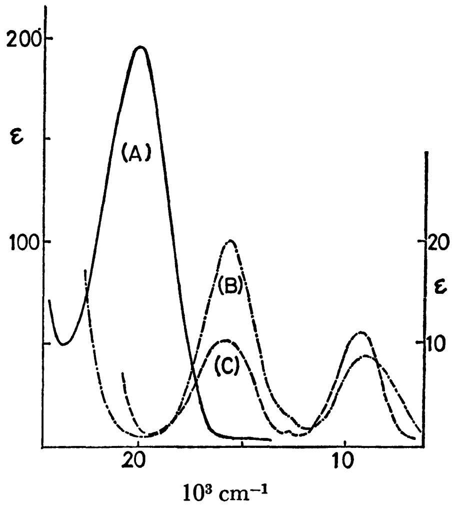

Fig. 1. Absorption spectra of the chelates of the bza series in 1,2-dichloroethane. (A), [Ni teen bza]ClO_4; (B), [Ni teen bza NO_3]; (C), [Ni teen bza_2]. The scale on the left refers to (A), and that on the right to (B) and (C).

The general features of these spectra are similar to those of the corresponding tmen chelates.[1,8)] These data indicate that type 1 chelates in 1,2-dichloroethane (a very weakly coordinating solvent) and in solid state are all square planar,[12,13)] while type 2 chelates in the same solvent have octahedral structures, in which not only a β-diketonate ion but also a nitrate ion seem to act as a bidentate ligand. They show that, in a strongly coordinating solvent like DMF, the square planar chelate cation [Ni teen β-dik]$^+$ in type 1 chelates are quantitatively converted into the octahedral solvated species [Ni teen β-dik S_2]$^+$ (S= solvent molecule); on the other hand, in a solvent with intermediate coordinating ability like acetone, the spectra indicate that these two species coexist in

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** Weak paramagnetism, shown by two of them, might be due to impurities. In fact, type 1 chelates (especially the aca chelate; *cf.* Experimental) were difficult to purify, and even after repeated trials some of them could not be made as pure as most of the type 2 chelates.

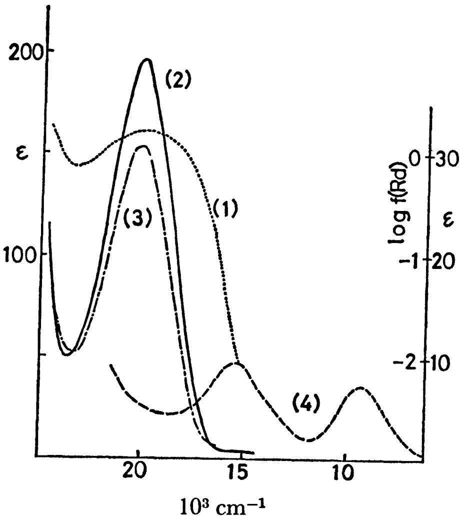

Fig. 2. Absorption spectra of the chelate, [Ni teen bza]ClO_4, in various organic solvents. (1), solid reflectance spectrum; (2), in 1,2-dichloroethane; (3), in acetone; (4), in DMF. The scale on the left refers to (2) and (3), and those on the right to (1) and (4).

equilibrium.***

$$[\text{Ni teen }\beta\text{-dik}]^+ + 2\text{S} \rightleftharpoons [\text{Ni teen }\beta\text{-dik S}_2]^+ \qquad (1)$$

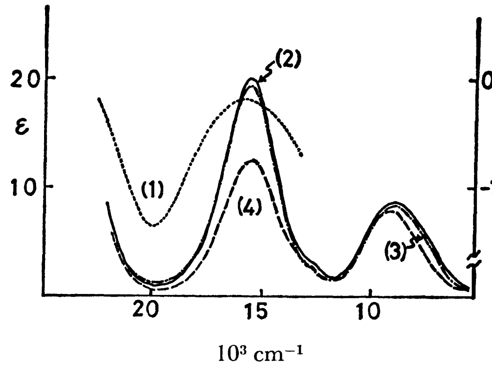

Fig. 3. Absorption spectra of the chelate, [Ni teen bza NO_3], in various organic solvents. Notations are the same as those in Fig. 2. The scale on the right refers to (1), and that on the left to the others.

As can be seen from Fig. 3 and Table 2, there is a small but noticeable difference between the spectrum of a nitrate chelate in 1,2-dichloroethane and that in DMF, and the outlook of the latter spectrum is similar to that of [Ni teen β-dik S_2]$^+$. These facts, together with the information from conductivity data and IR data, lead to the view that a nitrate chelate has the structure [Ni teen β-dik NO_3] both in solid state and in an inert solvent, while in a solvent with stronger

Table 2. Electronic spectra of the chelates in solid state and in various solvents (10^3 cm^{-1}, $\varepsilon_{\max}$ in parentheses)

Chelate	Solid	$C_2H_4Cl_2$	Acetone	DMF
[Ni teen dpm]$B(C_6H_5)_4$	20.12	20.12(137)	20.16(142)	15.5(6.08) 9.40(5.90)
[Ni teen aca]$B(C_6H_5)_4$	20.16	20.20(146)	20.20(120)	15.5(7.59) 9.29(7.01)
[Ni teen dbm]$B(C_6H_5)_4$	20.16	20.12(232)[a)]	20.20(190)[a)]	15.5(7.32) 9.26(6.37)
[Ni teen dpm]ClO_4	20.12	20.16(148)	20.12(154)	15.5(6.68) 9.35(6.85)
[Ni teen bza]ClO_4	19.92	20.12(195)[a)]	20.12(154)	15.5(9.53) 9.30(7.32)
[Ni teen aca NO_3]	15.90	15.6(19.6) 9.01(8.84)	15.6(18.2) 9.03(9.51)	15.5(11.7) 9.22(7.55)
[Ni teen bza NO_3]	15.90	15.6(19.9) 9.01(8.84)	15.6(19.3) 9.03(8.33)	15.5(12.5) 9.17(7.95)
[Ni teen dbm NO_3]	15.65	15.6(20.9) 9.01(9.12)	15.6(20.9) 9.03(9.30)	15.5(14.1) 9.17(7.95)
[Ni teen dpm_2]	16.00	15.9(9.60) 9.30(10.0)	insoluble	insoluble
[Ni teen aca_2]	16.10	15.7(7.05) 9.17(9.90)	15.7(7.85) 9.23(10.1)	15.7(7.10) 9.20(9.60)
[Ni teen bza_2]	15.92	15.9(10.3) 9.30(11.1)	15.9(10.7) 9.30(11.3)	15.8(9.80) 9.30(10.4)
[Ni teen dbm_2]	16.31	16.0(14.2) 9.30(12.2)	insoluble	16.0(14.2) 9.30(9.86)
[Ni teen tfa_2]	15.90	15.7(9.65) 9.35(9.30)	15.8(9.50) 9.35(9.40)	15.7(10.6) 9.30(9.10)
[Ni teen hfa_2]	16.00	15.8(13.0) 9.51(8.60)	15.8(13.2) 9.50(8.05)	15.8(14.2) 9.43(9.02)

a) Apparent values which are probably somewhat higher than the true ones because of the partial overlap of this band with the strong ligand band (or CT band) in the UV.

*** The coexistence of these two species is more evident in the case of the tmen chelates (*cf.* Table 5), but a comparison of the data shows that the same situation takes place with the teen chelates.

coordinating power the following equilibrium is established:

$$[\text{Ni teen } \beta\text{-dik NO}_3] + 2\text{S} \rightleftharpoons [\text{Ni teen } \beta\text{-dik S}_2]^+ + \text{NO}_3^-. \qquad (2)$$

Finally, the spectra of the bis-β-diketonate chelates show that they retain their octahedral structures in the solid state and also in any solvent. All the structural information correspond very closely to that obtained in the studies of the tmen chelates.[1,8]

Infrared Spectra. The IR spectra of all these chelates are naturally highly complicated. The discussion will be restricted to those of the perchlorate and nitrate anions. As to the perchlorate ion, the spectra show that it merely acts as a counter ion of the square planar cation [Ni teen β-dik]$^+$.[15] In the IR spectra of the nitrate chelates, it was not easy to assign the bands to a coordinated nitrate or the simple counter ion with sufficient accuracy.

Lever *et al.* pointed out the usefulness of the weak band at *ca.* 1750 cm^{-1} (a combination band of ν_1 and ν_4) as a criterion to distinguish whether a nitrate ion in a complex is a coordinating ligand or merely a counter ion.[14] From a large number of data, they concluded that, (1) when this band is not split, the nitrate ion is not bound in the complex, and acts only as a counter ion; (2) when it is split slightly (about 5 to 20 cm^{-1}), the ion acts as a monodentate ligand; and (3) when the splitting is much larger (about 30 to 50 cm^{-1}), the ion acts as a bidentate ligand.

According to this criterion, the nitrate ions in the mixed chelates [Ni teen β-dik NO$_3$] are apparently bidentate ligands. As an example, the IR data of a nitrate chelate, [Ni teen aca NO$_3$], are shown in Fig. 4, in which important bands are marked with arrows. They are at 1723 and 1774 cm^{-1}, respectively, and the splitting is 51 cm^{-1}. The corresponding bands of the other nitrate chelates [Ni teen bza NO$_3$] (B) and [Ni teen dbm NO$_3$] (C) are also shown.

In previous papers,[1,8] a number of mixed nitrate chelates [Ni tmen β-dik NO$_3$] were characterized and concluded to be octahedral and to contain a bidentate nitrate ion, by means of the d-d spectra, electric conductivities and IR spectra. Application of the criterion of Lever *et al.* to these tmen chelates confirmed that they contain the bidentate nitrate ion as expected, with a *ca.* 50 cm^{-1} splitting. The values are given in Table 3 together with those of the teen chelates. It seems that the formulation of the nitrate chelates of teen and tmen as [Ni diam β-dik NO$_3$] with a bidentate nitrate ion is well established.

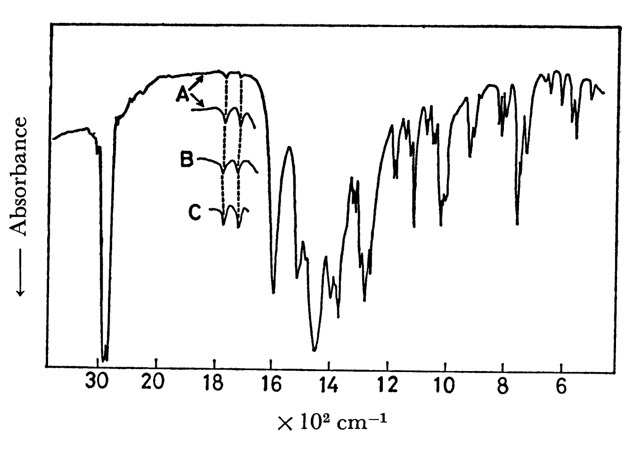

Fig. 4. IR spectra of the chelates; (A), [Ni teen aca NO$_3$]; (B), [Ni teen bza NO$_3$]; (c), [Ni teen dbm NO$_3$]. The data of the latter two are shown only in the range of 1700—1800 cm^{-1}.

Table 3. IR data of the nitrate chelates of tmen and teen

Only bands in the 1700—1800 cm^{-1} region useful as a criterion of the mode of coordination of the nitrate ion are given. Δ is the difference between the ν values of the two bands.

Chelate	ν(cm^{-1})		Δ(cm^{-1})
[Ni tmen aca NO$_3$]	1766	1718	48
[Ni tmen bza NO$_3$]	1767	1717	50
[Ni tmen dbm NO$_3$]	1767	1720	47
[Ni tmen tfa NO$_3$[	1769	1721	48
[Ni teen aca NO$_3$]	1774	1723	51
[Ni teen bza NO$_3$]	1773	1724	49
[Ni teen dbm NO$_3$]	1768	1720	48

Comparison of the Mixed Chelates of Teen with Those of Tmen. There are great similarities between the teen chelates obtained in this study and the tmen chelates studied before. The differences between the two groups of chelates will now be considered in some detail.

Ease of Formation and Isolation of the Chelate: Although various mixed chelates containing teen and β-diketonate ions have been obtained, they are not so numerous as those of tmen. The ease of preparation of the mixed chelates is shown in Table 4 for a comparison of teen and tmen. The circle shows that the corresponding chelate can be more or less easily obtained, the triangle that the chelate cannot be isolated as solid crystals, although there is definite spectral evidence that it actually exists in solution, and the cross that the chelate cannot be obtained and that there is no evidence of its formation even in solution. It can be seen that the formation of the teen chelates is, in general, more difficult than that of the tmen chelates.

Ligand Field Strength in the Chelates: Although the coordination ability of the ligand "teen" has not been studied thoroughly, it is easy to see that the steric hindrance caused by the ethyl groups in teen, which increases the interligand repulsion in its chelate, will be much more effective than that of the methyl groups in tmen.

In this connection, it is of interest to compare the apparent ligand field strength(l.f.s.) in the teen chelate with that in the tmen chelate. Spectral data of the square planar species, [Ni teen β-dik]B(C$_6$H$_5$)$_4$ in 1,2-dichloroethane are given in Table 2, and those of the corresponding chelates of tmen in Table 5. From a comparison of [Ni teen aca]B(C$_6$H$_5$)$_4$ and [Ni tmen aca]B(C$_6$H$_5$)$_4$, we see that the l.f.s. in the former is slightly weaker than that in the latter. This probably reflects the increased steric hindrance of the ethyl

Table 4. Variations in the ease of formation and isolation of the mixed chelates, Ni diam β-dik X (A) is a mixed chelate containing teen as a diamine, (B) the corresponding tmen chelate. As to the remarks, ○ shows that the corresponding chelate could be obtained, △ the chelate could not be obtained but was found to exist in solution, × no chelate formation could be found in this study.

β-dik	X									
	$B(C_6H_5)_4$		ClO_4		$2H_2O\cdot ClO_4$		NO_3		β-dik	
	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)
dpm	○	○	○	○	×	×	△	△	○	○
aca	○	○	△	○	×	○	○	○	○	○
bza	△	○	○	○	×	○	○	○	○	○
dbm	○	○	△	○	×	○	○	○	○	○
tfa	×	○	×	×	×	×	×	○	○	○
hfa	×	×	×	×	×	×	×	×	○	○

Table 5. Spectral data of the square planar mixed chelates with tmen in solid state and in various solvents (10^3 cm^{-1}, ε_{max} in parentheses)[1,8]

Chelate	Solid	$C_2H_4Cl_2$	Acetone	DMF
[Ni tmen dpm]$B(C_6H_5)_4$	20.33	20.49(153)	20.37(75.1) 9.47(6.5)	16.08(8.4) 9.70(9.5)
[Ni tmen aca]$B(C_6H_5)_4$	20.33	20.53(151)	20.49(31.5) 16.26(8.9) 9.43(8.3)	15.87(7.8) 9.60(9.5)
[Ni tmen dbm]$B(C_6H_5)_4$	20.66	20.49(263)	20.00(sh[a]) 16.03(9.7) 9.49(9.3)	16.08(9.4) 10.13(9.5)
[Ni tmen dpm]ClO_4	20.62	20.53(150)	20.37(56.5) 15.90(sh[a]) 9.45(4.6)	15.97(6.3) 9.74(7.6)
[Ni tmen bza]ClO_4	20.83	20.45(176)	20.33(16.4) 16.00(8.7) 9.43(8.9)	15.97(8.6) 9.58(9.8)

a) sh=shoulder

groups in the diamine, to which the decreased ease of formation of the teen chelates also seems to be related.

Relative Stability of the Square Planar Chelates: Another point of interest is that, in the case of a teen chelate of type 1, the equilibrium (1) established in a solvent of intermediate coordination ability is shifted remarkably to the left hand side, in comparison with that of the corresponding tmen chelate. This can be seen in acetone solutions, but a better comparison can be made with the use of a mixed solvent containing a large amount of an inert solvent and a little of a strongly coordinating solvent. Figure 5 shows the absorption spectra of [Ni teen dpm]$B(C_6H_5)_4$ and [Ni tmen dpm]$B(C_6H_5)_4$ in various mixtures of 1,2-dichloroethane and DMF. In both these cases, the intensity of the band at *ca.* 20000 cm^{-1} decreases with the increase of the DMF content in the solvent, but the decrease in the case of the tmen chelate is far more drastic, showing that the equilibrium in 1,2-dichloroethane,

$$[\mathrm{Ni\ diam\ }\beta\text{-dik}]^+ + 2\mathrm{DMF} \rightleftharpoons [\mathrm{Ni\ diam\ }\beta\text{-dik\ }(\mathrm{DMF})_2]^+$$

is shifted more strongly to the right hand side. Approximate calculations with these data and also with the spectral data in acetone solution (Tables 2 and 5), lead to the values in Table 6.[†]

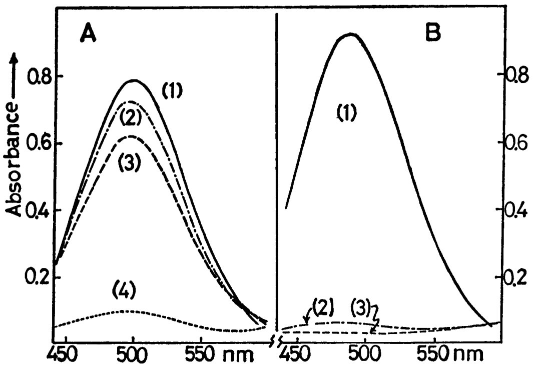

Fig. 5. Absorption spectra of the chelates, [Ni diam dpm]$B(C_6H_5)_4$, dissolved in various $C_2H_4Cl_2$-DMF mixtures. A and B show the case of the teen chelate (conc. 6.1×10^{-3} M) and that of the tmen chelate (conc. 5.9×10^{-3} M), respectively. The content of DMF in the solvent is: 0%; (2), 0.5%; (3), 1%; (4), 5%.

We see that the apparent value of the equilibrium constant, *K*, of Eq. 1 in acetone increases *ca.* 20—40 times with the change of [Ni teen β-dik]$^+$ to their

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[†] In these calculations it was assumed that the true molar extinction coefficient of the band at *ca.* 20000 cm^{-1} of a square planar chelate is, in any solvent, practically equal to that in 1,2-dichloroethane.

TABLE 6. PERCENTAGE OF [Ni teen β-dik]$^+$, REMAINING UNSOLVATED IN THE EQUILIBRIUM MIXTURES PRODUCED BY DISSOLVING TYPE 1 CHELATES OF teen IN ACETONE AND IN 1,2-DICHLOROETHANE CONTAINING 1% DMF

The value for [Ni tmen dpm]$B(C_6H_5)_4$ in the mixed solvent ($C_2H_4Cl_2$+1% DMF), obtained from Fig. 5, is very low (<4%).

Chelate	Acetone[a]	$C_2H_4Cl_2$+1%DMF
[Ni teen dpm]$B(C_6H_5)_4$	100 (49)	82
[Ni teen dpm]ClO_4	100 (38)	75
[Ni teen aca]$B(C_6H_5)_4$	82 (21)	65
[Ni teen bza]ClO_4	78 (9)	46
[Ni teen dbm]$B(C_6H_5)_4$	83 (8)	29

a) The values for the corresponding tmen chelates are given in parentheses.

tmen analogs. It can also be seen that the K values among the teen chelates increase in the order dpm→aca→bza→dbm, which is just the same as that observed among the tmen chelates.[1)]

As regards this remarkable difference between the chelates of teen and those of tmen, it is natural to expect that the more bulky ethyl groups on teen hinder the coordination of the solvent molecules at the 5th and 6th coordinating sites of the square planar chelate cation more strongly than the smaller methyl groups on tmen. The fact that the chelates [Ni diam β-dik $(H_2O)_2$]ClO_4, which could be easily obtained with tmen and a number of β-dik, could not be obtained at all with teen (*cf.* Table 4) may also be due to the same kind of steric effect.

All the perceptible differences between the chelates of teen and those of tmen are thus ascribed to the difference in magnitude of the steric effect caused by the N-alkyl groups of their ligands. The observed differences are, however, rather small, and the formation of octahedral complexes is by no means made impossible with the use of teen in spite of the great increase in the bulkiness of these groups.

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