Synthesis and Chromotropic Behavior of Nickel(II) Complexes with 1,4-Diazacycloheptane-*N*,*N'*-dicarboxylates in Solution

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A new series of nickel(II) complexes containing 1,4-diazacycloheptane-*N*,*N'*-dicarboxylates (dachdx, where x=a means the acetate derivative, x=m, e, and p are the α-methyl, α-ethyl, and α-propyl substituents of the carboxyl side chain, respectively) were prepared as solids, $Ni(dachdx)L_n$ ($L=H_2O$ or pyridine, $n=0$, 1, or 2). These complexes can be classified according to their geometry into three types: (1) Octahedral $[Ni(dachda)(H_2O)_2]$, (2) square planar [Ni(dachdx)](x=m, p, or e) and (3) penta-coordinate [Ni(dachdm)(py)]. In the solid state the strength of the bonds between the metal ion and the carboxylate groups increases in the order: Octahedral<penta-coordinate<square planar. In solution, some of these compounds show chromotropic behavior, e.g. solvatochromism, thermochromism, and inert salt or active salt effects. The stability constants of the Ni^{2+} complexes were determined by pH-titrations and spectrophotometry. The following equilibria were found:

$$[Ni(aq)]^{2+} + dachdx^{2-} \rightleftharpoons [Ni(dachdx)];$$

$$[Ni(dachdx)] + X^- \rightleftharpoons [Ni(dachdx)X]^-;$$

where $X^-=NCS^-$, Cl^-, or Br^-. It is shown that the substituent of the carboxylate side chain plays an important steric role, thus determining the value of the stability constant of [Ni(dachdx)].

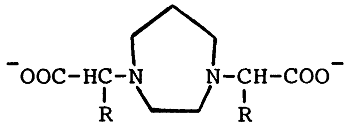
The chemistry of Ni^{2+} complexes with diaminodicarboxylates is interesting and manifold, since different structures and properties were found. For example the nickel(II) complex of ethylenediamine-*N*,*N'*-diacetate(edda), $[Ni(edda)(H_2O)_2]$, has an octahedral hexa-coordinate geometry in aqueous solution,[1] whereas the nickel(II) complex of 1,5-diazacyclooctane-*N*,*N'*-diacetate(dacoda), $[Ni(dacoda)(H_2O)]$, is penta-coordinate.[2] However, there are not many studies on the solution behavior of cyclic diamine-*N*,*N'*-dicarboxylate complexes (Scheme 1), because of difficulties encountered in the synthesis of such ligands and in the crystallization of their complexes. In particular there is no report about nickel(II) complexes of 1,4-diazacycloheptane-*N*,*N'*-dicarboxylates except our preliminary communication.[3] In continuation of such studies we describe now several nickel(II) complexes with the ligands dachdx. They show some interesting phenomena in solution, such as solvatochromism, thermochromism and inert salt ($NaClO_4$) or active salt (NCS^-) effects on the electronic spectra. In addition the stability constants of the following two equilibria were determined by means of potentiometric (Eq. 1, in aqueous media) and spectrophotometric methods (Eq. 2, in DMSO solutions):

$$[Ni(aq)^{2+}] + dachdx \rightleftharpoons [Ni(dachdx)(H_2O)_n];\ K_{NiL} \tag{1}$$

$$[Ni(dachdx)] + X^- \rightleftharpoons [Ni(dachdx)X]^-;\ K_{NiLX} \tag{2}$$

Experimental

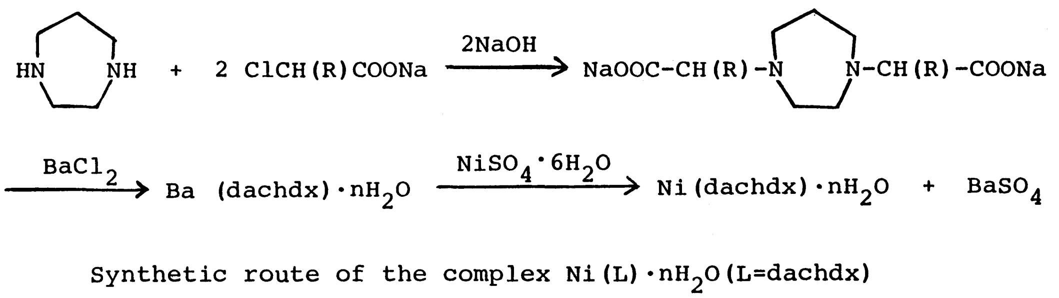
Syntheses. The synthetic route of the ligands and their Ni^{2+} complexes are shown in Scheme 2.



dachdx (L)

R	x	dachdx
H	a	dachda
CH_3	m	dachdm
CH_3CH_2	e	dachde
$CH_3CH_2CH_2$	p	dachdp

Scheme 1.



Synthetic route of the complex $Ni(L)\cdot nH_2O$ (L=dachdx)

Scheme 2.

Table 1. Analytical Data, Color and Magnetic Moments of the Ni^{2+} Complexes

Complex	C%	H%	N%	Color	μ_{eff}[b]
Ni(dachda)·$2H_2O$	34.99(34.86)[a]	5.87(5.88)[a]	9.07(9.03)[a]	Green	3.23
Ni(dachdm)	43.90(43.58)	6.03(6.02)	9.31(9.22)	Orange	dia.
Ni(dachde)	47.46(47.01)	6.74(6.83)	8.51(8.43)	Orange	dia.
Ni(dachdp)	50.46(49.76)	7.33(7.40)	7.85(7.73)	Orange	dia.
Ni(dachdm)py	50.56(50.53)	6.10(5.88)	11.06(11.07)	Green	3.22

a) Calculated values are shown in parentheses. b) In B.M., dia.=diamagnetic.

Potentiometric Titrations. To prepare standard solutions of the ligands the recrystallized barium salts of dachdx were treated with a slight excess of 0.1 M H_2SO_4 (1M=1 mol dm^{-3}) to precipitate $BaSO_4$. After centrifugation the clear solutions were diluted to the desired volume and the exact concentration of the ligands was determined acidimetrically with 0.4 M NaOH. Typical concentrations: 2.4×10^{-3} M ligand with no metal addition or with 2.0×10^{-3} M $Ni(NO_3)_2$. The ionic strength was kept constant with KNO_3 to I=0.5 M and the temperature was controlled to 25 °C. The titrations with 0.4 M NaOH were run using the previously described titration unit.[4] The electrode was calibrated with two buffers and checked by titrating a standard mixture of HNO_3 and CH_3COOH in 0.5 M KNO_3. The calculation of the protonation and stability constants was done on a Hewlett-Packard HP 9835 computer using the program TITFIT.[5]

Spectral Measurements. Electronic spectra of solutions were obtained with a Hitachi 340 recording spectrophotometer using 10 mm quartz cells. The procedure for determining the stability constants of the complexes [Ni(dachdx)] with NCS^- ion in DMSO was that reported in the literature.[6] Powder reflectance spectra were recorded with the same instrument, attached with an integrating sphere, using $BaSO_4$ as a reference. Infrared spectra were recorded for Nujol mulls using a JASCO IR-A3 Grating spectrophotometer (5000—400 cm^{-1}).

Results and Discussion

Analytical data, magnetic moments and colors of the Ni^{2+} complexes are shown in Table 1. Since [Ni(dachda)$(H_2O)_2$] is very difficult to crystallize and only a small amount of crystals was obtained, they were used for the determination of the elemental analysis, the magnetic moment and the IR spectrum. For visible spectral measurements we prepared solutions of equimolar amounts of dachda and $[Ni(aq)]^{2+}$, starting from Ba(dachda) and $NiSO_4\cdot6H_2O$ as described previously.[3]

From the analytical data of Table 1 and other data such as magnetic moments, IR and electronic spectra (see later), one can classify the solid nickel(II) complexes according to the coordination geometries into three types. The type 1 complex, [Ni(dachda)$(H_2O)_2$], is a green paramagnetic octahedral complex. The type 2 complex, [Ni(dachdx)] where x=m, e, or p, are orange, diamagnetic and have square planar structure. The type 3 complex, [Ni(dachdm)py] which contains one pyridine, is pentacoordinate, green and paramagnetic.

Table 2. Carbonyl Stretching Modes (cm^{-1}) for the Ni(II) Complexes

Complex	I($\nu_{C=O}$)	II(ν_{C-O})	$\Delta\nu_{I,II}$
Ni(dachda)·$2H_2O$	1590	1400	190
Ni(dachdm)(py)	1630	1384	246
Ni(dachdm)	1758	1385	373
Ni(dachde)	1656	1360	296
Ni(dachdp)	1660	1348	312
Ni(edda)·$2H_2O$	1588	1398	190
Ni(edda)$(py)_2$·H_2O	1580	1402	178
	1570		168
Ni$(gly)_2$·$2H_2O$[a]	1589	1411	178
Pd$(gly)_2$[a]	1642	1374	268

a) Ref. 7.

Because of the different coordination geometries of these complexes, it is interesting to look at the stretching frequencies of the carboxyl groups in the region 1700—1300 cm^{-1}. Table 2 gives the $\nu_{C=O}$ (I) and ν_{C-O} (II) bands of our complexes together with other data reported earlier,[7] as well as the difference between these two bands ($\Delta\nu_{I,II}$). From these data one can see that octahedral nickel(II) complexes with diaminedicarboxylate have $\Delta\nu_{I,II}$ values in the range 168—190 cm^{-1}, the pentacoordinate complex [Ni(dachdm)py] has $\Delta\nu_{I,II}$=246 cm^{-1} and those with square planar geometry have $\Delta\nu_{I,II}$ in the range of 296—373 cm^{-1}. [Ni(dachda)$(H_2O)_2$] and [Ni(dachdm)py] both show a similar IR change, when the complexes are heated. Before heating, the separation $\Delta\nu_{I,II}$ between the two peaks is relatively small, whereas after heating rather large one is observed (Eqs. 3 and 4) as follows (observed values shown in cm^{-1}).

$$[\mathrm{Ni(dachda)(H_2O)_2}] \xrightarrow[\text{heating}]{-2\mathrm{H_2O}} [\mathrm{Ni(dachda)}] \qquad (3)$$

	Oh	square planar
$\nu_{C=O}$	1590	1670, 1648
	190($\Delta\nu_{I,II}$)	302 or 280 ($\Delta\nu_{I,II}$)
ν_{C-O}	1400	1368

$$[\mathrm{Ni(dachdm)py}] \xrightarrow[\text{heating}]{-\mathrm{py}} [\mathrm{Ni(dachdm)}] \qquad (4)$$

	penta-coordinate	square planar
$\nu_{C=O}$ (I)	1630	1658
	246 ($\Delta\nu_{I,II}$)	
ν_{C-O} (II)	1384	(missing)

Table 3. Protonation and Stability Constants($mol^{-1}dm^3$) for the Ligand dachdx at $I=0.5$ M and $T=25\,°C$. Values in Parentheses are Standard Deviations

	Ligand(L)	dachda	dachdm	dachde	dachdp	edda[a)]
H^+	$\log K_{H,1}$	9.87(1)	10.20(1)	9.82(1)	9.88(1)	9.46
	$\log K_{H,2}$	5.98(1)	6.11(1)	5.74(1)	5.67(1)	6.42
Ni^{2+}	$\log K_{NiL}$	6.42(2)	6.22(1)	4.92(1)	5.09(1)	13.5

a) Values taken from Ref. 8.

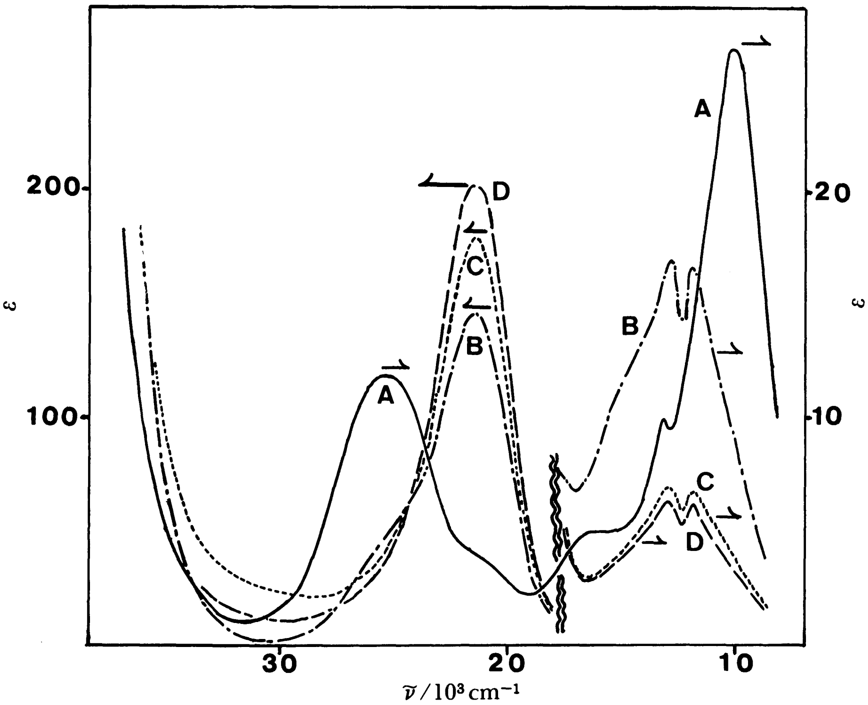


Fig. 1. Electronic absorption spectra of Ni(dachdx) in H_2O at room temperature. A: [Ni(dachda)(H_2O)$_2$] (5.0×10^{-2} M) (——), B: [Ni(dachdm)] (5.2×10^{-3} M) (–·–·–), C: [Ni(dachde)] (5.0×10^{-3} M) (······), D: [Ni(dachdp)] (4.9×10^{-3} M) (----).

The $\Delta\nu_{I,II}$ values might reflect the strength of the coordinative bond between the metal ion and the carboxylate group. In square planar chelates the metal-ligand bonds are stronger than those in the other two geometries, whereas the bonds in the octahedral structure are the weakest. Since the carboxylate groups in the square planar complex are coordinated more covalently to the metal ion, they become more asymmetrical, whereas the ones in complexes with octahedral geometry being more ionic are less asymmetrical. Consequently the $\Delta\nu_{I,II}$ values reflecting this asymmetry are large for square planar complexes and small for octahedral ones.

The protonation and formation constants of the ligands are given in Table 3. The protonation constants are typical for diamine-*N*,*N'*-dicarboxylates as a comparison with EDDA shows.[8)] With Ni^{2+} complexes of the stoichiometry NiL are formed, the stability of which is described by K_{NiL} (Eq. 1). The ligands with small substituent groups, dachda and dachdm, give more stable complexes than dachde and dachdp indicating that steric effects are important (Table 3). However, as we shall discuss later, the complexes NiL formed by these ligands differ from each other, being a mixture of species with different geometies, and this steric effect could play also an important role for determining the predominant species in solution.

The electronic spectra of the Ni^{2+} complexes in aqueous solution are shown in Fig. 1 and the values are given in Table 4. The shapes of the spectra of the complexes with dachdm, dachde, and dachdp (the type 2 complexes) are very similar to each other. Since the peak intensities at 21×10^3 cm^{-1} decrease in the order: [Ni(dachdp)]>[Ni(dachde)]>[Ni(dachdm)], the amount of the square planar species also decreases in the same order. On the other hand, the weak shoulder at 25×10^3 cm^{-1}, which is observed only in the case of dachdm, and the band at ca. 13×10^3 cm^{-1} are due to a pentacoordinate species. This latter species, with an absorption at 13×10^3 cm^{-1} which was also observed more or less distinctly for the complexes of dachde or dachdp, has a spectrum quite similar to that of [Ni-

Table 4. Electronic Absorption Spectra of the Ni(II) Complexes in H_2O

Complex	ν_{max} (10^3 cm^{-1}) and ε_{max} in parentheses (M^{-1}cm^{-1})				
Ni(dachda)·$2H_2O$	10.3	13.2	16.1	21.3	25.6
	(26.4)	(10.6)	(5.1)	(3.9)	(11.9)
Ni(dachdm)	11.9	13.0	21.5	25.3	
	(16.8)	(17.0)	(146.7)	(47.5)	
Ni(dachde)	11.9	13.0	21.5		
	(6.8)	(6.8)	(179.5)		
Ni(dachdp)	11.9	13.0	21.5		
	(6.2)	(6.3)	(202.3)		
Ni(edda)$(H_2O)_2$[a]	9.9	13.2	16.4	27.2	
	(12.6)	(1.9)	(4.2)	(7.2)	
Ni(dacoda)(H_2O)[a]	12.3	13.1	15.8	26.4	
	(21.4)	(25.3)	(28.0)	(86.5)	

a) Values taken from Ref. 2.

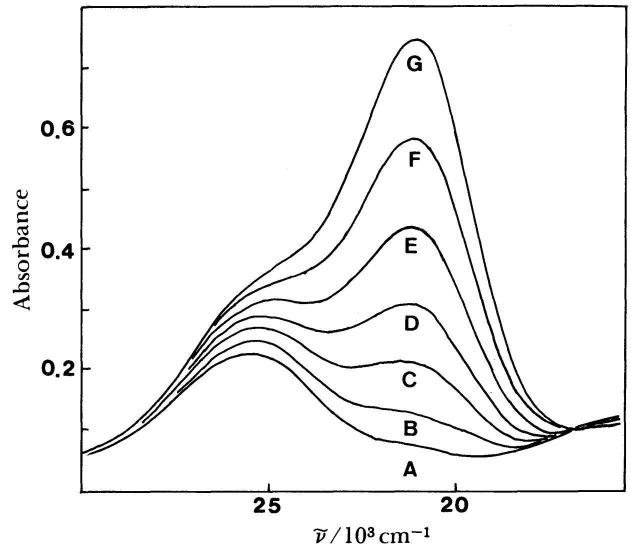


Fig. 2. Temperature effect on the electronic absorption spectra of [Ni(dachda)$(H_2O)_2$] (2.3×10^{-2} M) in H_2O. Curves A to G are the spectra measured at A (293 K), B (313), C (323), D (333), E (343), F (353), and G (363), respectively.

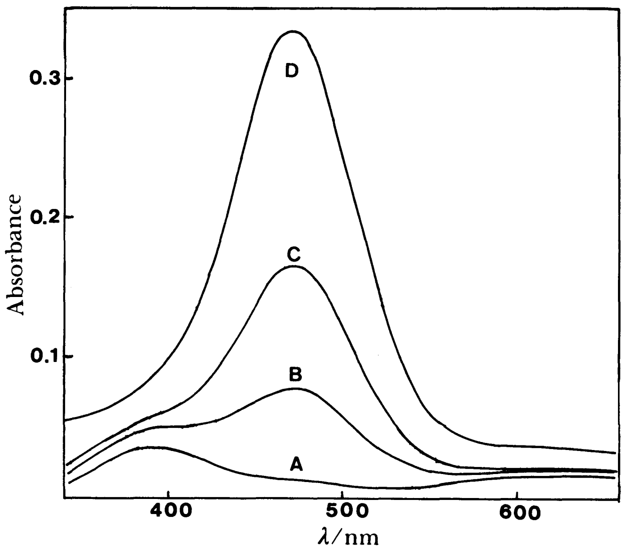


Fig. 3. Inert salt effect on the absorption spectra of [Ni(dachda)$(H_2O)_2$] (4.6×10^{-3} M) in H_2O at room temperature. Concentration of $NaClO_4$ added; A=0.0 M, B=2.0 M, C=3.0 M, and D=large excess amounts of $NaClO_4$.

(dacoda)(H_2O)] in aqueous solution.[2] The order of the amount of penta-coordinate species is the reverse of that for the square planar species given above. The type 2 complexes form equilibrium mixtures of the planar and the penta-coordinate species in aqueous solution, in which the square planar form is predominant. For example, in the case of [Ni(dachdm)] we have Eq. 5.

$$[\mathrm{Ni(dachdm)}] + H_2O \rightleftharpoons [\mathrm{Ni(dachdm)}(H_2O)] \qquad (5)$$

Finally, the spectrum of [Ni(dachda)$(H_2O)_2$] is rather different from the other ones. A comparison of this spectrum (Fig. 1) with those typical for planar, penta-coordinate and hexa-coordinate species (Table 4) indicates that in aqueous solution the dachda complex is predominantly a mixture of penta-coordinate and hexa-coordinate species, whereas the square planar form is only present in a minor amount ([Ni(dachda)$(H_2O)_2$] $\rightleftharpoons$ [Ni(dachda)(H_2O)]+H_2O). The peak at 17×10^3 cm^{-1} is the second transition expected in octahedral geometry $^3A_{1g} \rightarrow {}^3T_{1g}(F)$,[9] whereas the other two peaks $^3A_{1g} \rightarrow {}^3T_{2g}$, $^3A_{1g} \rightarrow {}^3T_{1g}(P)$ are obscured under the strong bands of the penta-coordinate species.

In addition, the above solutions are thermochromic: The color of the aqueous solution of [Ni(dachda)$(H_2O)_2$] changes from blue-green to orange when the temperature of the solution is raised (Fig. 2). The peak intensity at 21×10^3 cm^{-1} gradually increases as the temperature increases, indicating that Eq. 6 is shifted to the right hand side (where n=1 or 2).

$$\underset{\text{Blue-green (room temp)}}{[\mathrm{Ni(dachda)}(H_2O)_n]} \underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}} \underset{\text{Orange (high temp)}}{[\mathrm{Ni(dachda)}]} + nH_2O \qquad (6)$$

Addition of an inert salt such as $NaClO_4$ to an aqueous solution of [Ni(dachda)$(H_2O)_2$] gives rise to this phenomenon more easily. Finally, when a large excess of $NaClO_4$ is added to this solution, the color of the solution changes already at room temperature from blue-green to orange (Eq. 7, see Fig. 3). This color change (inert salt effect) is explained by decreasing of coordination ability of solvent molecules due to the solvation of large amounts of the inert salt in solution.

$$\underset{\text{Blue-green (room temp)}}{[\mathrm{Ni(dachda)(H_2O)}_n]} \xrightarrow{\text{excess NaClO}_4} \underset{\text{Orange(room temp)}}{[\mathrm{Ni(dachda)}]} + n\mathrm{H_2O} \quad (7)$$

On the other hand, aqueous solutions of the type 2 compounds show a color change from orange to green when the temperature decreases, e.g. Eq. 8.

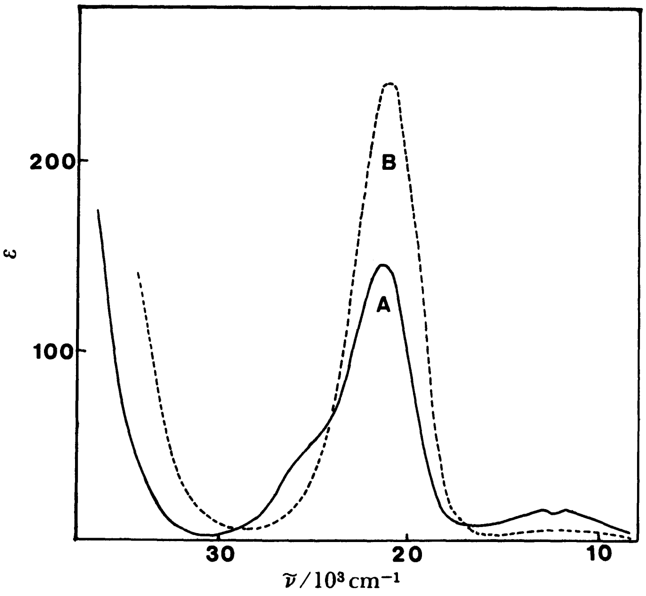
$$\underset{\text{Orange (room temp)}}{[\mathrm{Ni(dachdm)}] + \mathrm{H_2O}} \xrightarrow{\text{cooling}} \underset{\text{Green (low temp)}}{[\mathrm{Ni(dachdm)(H_2O)}]} \quad (8)$$

We have also noticed that the type 2 complexes, especially the complex [Ni(dachdm)], show solvatochromism. The spectra of this complex in DMSO and H_2O are shown in Fig. 4. The spectrum in DMSO is typical for a planar species, whereas in H_2O there is a mixture of square planar and penta-coordinate species. This is rather strange since from the donor strength of DMSO and H_2O one would expect the opposite.[10] That the species in DMSO solution is square planar and there is no solvent coordination, is probably due to (1) steric effects in solvent coordination, DMSO being larger than H_2O and also (2) the hydrogen bond between carboxylato groups in dachdm and solvent molecules. In other words, the C=O groups can interact with H_2O molecules but not with DMSO molecules, so that H_2O can approach to the central metal ion more easily than DMSO.

The type 2 compounds show an "active salt effect," which means that, when a coordinating anion such as NCS^- is added to the solution, Equilibrium 9 is shifted to the right, i.e. from a square planar species a penta-coordinate one is formed.

$$\underset{\text{Orange, planar}}{[\mathrm{Ni(dachdx)}] + \mathrm{NCS^-}} \rightleftharpoons \underset{\text{Green, 5-coordinate}}{[\mathrm{Ni(dachdx)(NCS)}]^-} \quad (9)$$

A typical penta-coordinate spectrum of $[\mathrm{Ni(dachdm)(NCS)}]^-$ is shown in Fig. 5, which was obtained from the DMSO solution with a large excess of NH_4NCS. The formation constants of the penta-coordinate complexes $[\mathrm{Ni(dachdx)X}]^-$ (Eq. 2) with three coordinating anions $X^-=NCS^-$, Br^-, and Cl^- were determined spectrophotometrically in DMSO solutions by the Hildebrand-Benesi method[6] at room temperature (Table 5). The anion coordination decreases in the



Fi 4. Electronic absorption spectra of [Ni(dachdm)] in H_2O (A; 5.2×10^{-3} M) and in DMSO (B; 2.5×10^{-3} M) at room temperature.

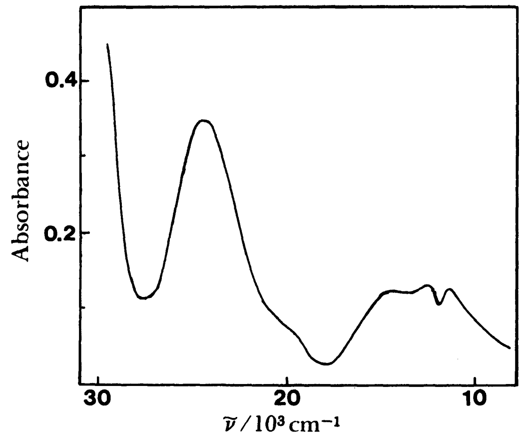


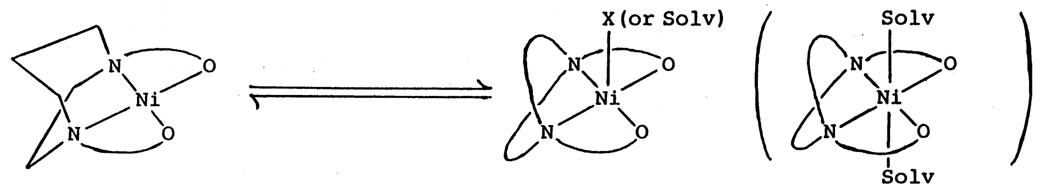
Fig. 5. Electronic absorption spectra of [Ni(dachdm)] (5.0×10^{-2} M) in DMSO with large excess of NH_4NCS at room temperature.

Table 5. Stability Constants ($mol^{-1}\,dm^3$) of the Complex $[\mathrm{Ni(dachdx)X}]^-$ in DMSO at Room Temperature (25 °C)[a]

		Ni(dachdm)	Ni(dachde)	Ni(dachdp)
Cl^-	NH_4Cl	59(2)	29(1)	26(1)
	$(Et)_4NCl$	55(2)	26(1)	24(1)
NCS^-	NH_4NCS	30(1)	13(1)	12(1)
Br^-	NH_4Br	5(1)	4(1)	—
	$(Et)_4NBr$	5(1)	3(1)	—

a) Values in parentheses are standard deviations.

Conclusion: Some Chromotropic Phenomena of the Chelates, [Ni(dachdx)$(H_2O)_n$]



Sq. Pl. ⟷ 5-Coord. (6-Coord.)

Structure: Square Planar (Sq. Pl.) ⟷ 5-Coord. (or 6-Coord.)
Substituent Effect (R): C_3H_7–, C_2H_5–, CH_3– ⟷ (H–)
Solvent Effect: DMSO ⟷ H_2O
Temperature Effect: High Temp ⟷ Low Temp
Inert Salt Effect ($NaClO_4$ in H_2O): Higher Concn ⟷ Lower Concn
Active Salt Effect (NR_4X in DMSO): Lower Concn ⟷ Higher Concn
Active Salt Effect (Anion Coordination): Br^- ⟷ NCS^- ⟷ Cl^-

Scheme 3.

order $Cl^- > NCS^- > Br^-$, whereas the order of increasing stability of the penta-coordinate species is the following:

$$[\mathrm{Ni(dachdm)}] > [\mathrm{Ni(dachde)}] > [\mathrm{Ni(dachdp)}].$$

It is concluded that the substituent at the carboxylate side chain of these ligands plays a very important role in the determination of the structure and the solution behavior of the Ni^{2+} complexes.

Finally, we can summarize the observed chromotropic phenomena due to the structural change between square planar and 5-coordinate structure (or 6-coordinate octahedral one) as shown in Scheme 3.

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