Studies on Mixed Chelates. XVII. Crystal Structure and Spectral Properties of Mixed Nickel(II) Nitrate Complexes Containing 1,2-Dipiperidinoethane and β-Diketonate Ligands

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Several new mixed nickel(II) nitrate complexes with 1,2-dipiperidinoethane (dipe) and β-diketonate ions (dike), [Ni(NO_3)(dike)(dipe)], have been obtained and characterized. The crystal structure of one of them, [Ni(NO_3)(acac)(dipe)], was determined by X-ray crystallography. The crystal is monoclinic with the space group *Cc*, $Z=4$, $a=9.0517(4)$, $b=21.932(1)$, $c=9.8814(6)$ Å, $\beta=88.151°$. Block-diagonal least-squares refinements have led to a final *R* value of 0.036 for 2471 reflections. It was confirmed that the nitrate ion in the octahedral complex acts as a bidentate ligand and that the conformation of the piperidine ring in dipe is a chair form. The spectral behaviors of these complexes in various organic solvents are discussed in comparison with those of similar complexes with other *N,N′*-alkylated ethylenediamine ligands (diam). It was concluded that, in a solvent with low polarity, the complexes are dissolved unchanged; in a more polar solvent, however, dissociation of NO_3^- takes place, producing solvated or unsolvated cationic species ([Ni(dike)(diam)(Solvent)$_2$]$^+$ (Oh) or [Ni(dike)(diam)]$^+$ (Square Planar)) according to the donor and acceptor properties of the solvent.

1,2-Dipiperidinoethane (($CH_2)_5N(CH_2)_2N(CH_2)_5$;dipe) is a potential bidentate ligand which has not been thoroughly studied so far.[1] The chelate ring structure of dipe is similar to that of *N,N,N′,N′*-tetramethylethylenediamine (tmen), but the bulky groups -($CH_2)_5$- on the N-donor atoms hinder the coordination of this ligand to the central metal ion, and also that of other ligands in the coordination sphere. Therefore, dipe is expected to be a weaker ligand than tmen.

We have reported the mixed nickel(II) complexes with various kinds of *N,N′*-alkylated ethylenediamines (diam) and β-diketonate ions (dike), many of which show remarkable chromotropic behaviors in the solid state or solutions.[2] While continuing this series of studies, we recently obtained several kinds of Ni(II) nitrates containing both dipe and dike, in which the nitrate ion acts as a bidentate ligand. In addition to the results regarding their IR and electronic spectra, as well as their electric conductivities in organic solvents, we have determined the crystal structure of [Ni(NO_3)(acac)(dipe)] in order to understand the mode of the nitrate coordination and the conformation of the dipe ligand. The structural results and a spectral comparison of the dipe complexes with similar mixed ligand complexes containing tmen and related ligands are discussed in this paper.[3–9]

Experimental

Materials. Nickel(II) nitrate hexahydrate, tmen, *N,N,N′*-triethylethylenediamine (Et_3en), and *N,N,N′,N′*-tetraethylethylenediamine (teen) (Wako Pure Chemical Co.), dipe (Aldrich), and all of dikeH (Dojindo Laboratory) were purchased and used without further purification. All solvents used for physical measurements were Guaranteed Reagent or Spectro grade; hygroscopic solvents were dried by conventional methods.[10]

General Preparation of Solid Complexes: [Ni(NO_3)(dike)(diam)] (dike:acetylacetonate (acac), benzoylacetonate (bzac), dibenzoylmethanate (dibm), dipivaloylmethanate (dipm), trifluoroacetylacetonate (tfac), and hexafluoroacetylacetonate (hfac) ions; diam:teen, Et_3en, tmen, and dipe). To an ethanolic solution of $Ni(NO_3)_2\cdot6H_2O$ (10 mmol in 30 ml of ethanol (EtOH)) a mixture of an appropriate β-diketone and KOH (10 mmol each) dissolved in 20 ml of EtOH is added; then, diam (10 mmol in 10 ml of EtOH) is dropped into it with vigorous stirring. After completing the reaction, the deep-green solution is filtered (to separate the precipitate of KNO_3) and dried up in a rotary evaporator. The crude crystals obtained are dissolved in hot 1,2-dichloroethane (DCE) and filtered; the solution is kept in a freezer for several days. The obtained complex is recrystallized again from hot DCE. [Ni(NO_3)(hfac)(dipe)] could not be obtained in this way, but a non-charged chelate [Ni(hfac)$_2$(dipe)] was formed instead. The dipm mixed complex was obtained as a hydrate, [Ni(NO_3)(dipm)(dipe)(H_2O)], in a small quantity, though it was rather unstable in solution and decomposed gradually to a mixture of the noncharged chelate [Ni(dipm)$_2$(dipe)] and an unknown green paste.[9]

Physical Measurements. The methods used in the measurements of IR and electronic spectra (solid and solution), magnetic susceptibilities, TG-DTA curves, and electric conductivities in solution are the same as those reported before.[11]

Determination of the Crystal Structure of [Ni(NO_3)(acac)(dipe)]. The crystal used for X-ray work was grown from a DCE solution. Crystal data are as follows: $NiC_{17}H_{31}N_3O_5$; M. W. 416.2; monoclinic; $a=9.0517(4)$, $b=21.932(1)$, $c=9.8814(6)$ Å, $\beta=88.151(4)°$; $U=1960.6(2)$ Å^3; $D_x=1.41$ g cm^{-3}; $Z=4$; space group *Cc*; μ (Mo *Kα*) $=1.02$ mm^{-1}. The intensity data were collected on a Rigaku automated four-circle diffractometer AFC-5 with the θ–2θ scan technique, scan range $(1.1+(1/2)\tan\theta)°$ and scan speed 3° min^{-1} in θ. Dimensions of the crystal used for the data collection were 0.38×0.34×0.21 mm. A total of 3036 independent reflections

Table 1. Analytical Data, Color, and Magnetic Moments of the Complexes Obtained

Complex	Color	C%[a]	H%[a]	N%[a]	μ_{eff}/BM
[Ni(NO_3)(dipe)(acac)]	Deep blue	49.02 (49.07)	7.70 (7.51)	10.06 (10.10)	3.23
[Ni(NO_3)(dipe)(tfac)]	Blue	43.47 (43.43)	6.18 (6.00)	9.11 (8.94)	3.10
[Ni(NO_3)(dipe)(bzac)]	Green	55.21 (55.26)	7.18 (6.96)	8.73 (8.29)	3.25
[Ni(NO_3)(dipe)(dipm)(H_2O)]	Green	54.86 (54.86)	9.01 (8.75)	8.30 (8.11)	—
[Ni(dipe)(dipm)$_2$]	Blue	64.62 (65.70)	10.31 (11.10)	4.46 (4.98)	—
[Ni(dipe)(hfac)$_2$]	Yellow green	39.33 (39.49)	3.95 (3.92)	3.81 (4.19)	—
[Ni(NO_3)(Et_3en)(acac)]	Deep blue	42.55 (42.89)	7.69 (7.48)	11.41 (11.54)	3.29

a) Calculated values in parentheses.

were measured ($2° < 2\theta < 60°$), using graphite monochromated Mo $K\alpha$ radiation, of which 2471 reflections were $|F_o| > 3\sigma(|F_o|)$. Corrections for Lorentz and polarization factors were made, but not for absorption. The structure was solved by the heavy-atom method using the UNICS-III program system.[12] A refinement was carried out by block-diagonal least-squares. Atomic scattering factors were taken from "International Tables for X-ray Crystallography".[13] The R and R_w values converged to 0.036 and 0.036, respectively. Computations were performed on FACOM M-360R and M-360 computers at the Computer Center of Josai University.

Results and Discussion

Solid Complexes. In Table 1, analytical data and some properties of the solid complexes obtained in this study, [Ni(NO_3)(dike)(dipe)], are listed. The complexes containing hfac or dipm seem to have a tendency to be converted into the non-charged octahedral complexes, [Ni(dike)$_2$(dipe)]. We could thus obtain only a small amount of a monohydrate, [Ni(NO_3)(dipm)(dipe)(H_2O)], and two noncharged complexes, [Ni(dipm)$_2$(dipe)] and [Ni(hfac)$_2$(dipe)], for these ligands. In the same table, the data on another nitrate complex with Et_3en are also given, which is similar in appearance and properties to those of the complexes of tmen and teen reported earlier.[3–5] From the colors and magnetic moments of the complexes, it can be seen that all these complexes have an octahedral geometry. There is a simple and very useful criterion for the coordination mode of NO_3 from the IR spectra, devised by Lever et al.[14] The key region is 1700—1800 cm^{-1}, where a weak combination band of the NO_3^- ion in a complex compound appears. This band is often split in two; when the splitting is small ($\Delta\tilde{\nu}_{NO_3}$=20—25 cm^{-1}), the NO_3^- ion is a monodentate ligand, but when it is larger, the ion is a bidentate ligand.[15,16] The IR data of the anhydrous complexes in this region are given in Table 2. All of the anhydrous nitrate complexes obtained here have a rather large splitting of this band ($\Delta\tilde{\nu}_{NO_3}$=45—50 cm^{-1}), showing that the NO_3^- ions in these anhydrous complexes act as bidentate ligands.[17] There is only one exception; the monohydrate [Ni(NO_3)(dipm)(dipe)(H_2O)] shows a small splitting ($\Delta\tilde{\nu}_{NO_3}$=18 cm^{-1}), which indicates that NO_3^- in it is a monodentate ligand.[18]

The difference between the C=O and C=C stretching frequencies of dike ($\Delta\tilde{\nu}_{dike}=\tilde{\nu}_{C=O}-\tilde{\nu}_{C=C}$) is also a characteristic value. As reported earlier,[3,4] this difference notably decreases in going from as octahedral (high-spin) Ni(II) complex to a square planar (low-spin) 4-coordinate one, indicating that, as the Ni–O(dike) bonds become stronger, the C=O bonds become weaker, and the C=C bonds become stronger.[20] This view is also supported by the bond distances of C=O and C=C of acac in its complexes with different coordination numbers.[21,22] The IR data are consistent with this view; the values of $\Delta\tilde{\nu}_{dike}$ observed in the range of 1600—1500 cm^{-1} ($\Delta\tilde{\nu}_{dike}$=78—115 cm^{-1}; cf. Table 2) are similer to those of the octahedral complexes studied before, confirming the octahedral structure of the new complexes.

Structure of [Ni(NO_3)(acac)(dipe)]. As stated above, evidences for the bidentate coordination of NO_3^- in the complexes studied can be obtained form IR spectra, and electronic spectral data and conductivity data in solution (vide infra) are also consistent with this view. We have now determined the crystal structure of [Ni(NO_3)(acac)(dipe)] to understand how such coordination takes place. The final atomic

Table 2. IR Data of the Nitrate Complexes[a)]

Complex	$\tilde{\nu}_{NO_3}$		$\Delta\tilde{\nu}_{NO_3}$	$\tilde{\nu}_{dike}$		$\Delta\tilde{\nu}_{dike}$
				$\tilde{\nu}_{C=O}$	$\tilde{\nu}_{C=C}$	
[I] [Ni(NO$_3$)(acac)(dipe)]	1772	1723	49	1600	1517	83
[II] [Ni(NO$_3$)(acac)(teen)][b)]	1772	1727	45	1603	1518	85
[III] [Ni(NO$_3$)(acac)(tmen)][c)]	1771	1725	46	1608	1519	89
[IV] [Ni(NO$_3$)(acac)(Et$_3$en)]	1768	1718	50	1592	1514	78
[V] [Ni(NO$_3$)(tfac)(dipe)]	1773	1726	47	1635	1520	115
[VI] [Ni(NO$_3$)(bzac)(dipe)]	1773	1728	45	1598	1510	88
[VII] [Ni(NO$_3$)(dipm)(dipe)(H$_2$O)]	1763	1745	18	—[d)]	—[d)]	—[d)]

a) The bands observed in the ranges of 1500—1650 cm^{-1} and 1700—1800 cm^{-1} are given. b) Ref. 5. c) Refs. 3 and 4. d) Assignment could not be done exclusively.

Table 3. Final Atomic Coordinates (×10^4 except ×10^5 for Ni) of the Non-Hydrogen Atoms and Their Thermal Parameters Given by the Equivalent Temperature Factors (Å^2) (Estimated Standard Deviations in Parentheses)

Atom	X	Y	Z	B_{eqv}
Ni	1496(9)	16562(2)	327(8)	2.20(1)
N(0)	2798(4)	1887(2)	622(4)	3.48(9)
O(N1)	1878(3)	1691(1)	1500(3)	3.59(8)
O(N2)	2280(3)	2047(1)	−505(3)	3.55(8)
O(N3)	4108(3)	1931(2)	836(4)	5.78(12)
O(1)	1074(3)	830(1)	−374(3)	3.25(7)
O(2)	−691(3)	1661(1)	−1815(2)	3.07(7)
C(1)	2204(6)	33(2)	−1603(5)	4.14(12)
C(2)	1232(4)	595(2)	−1536(4)	2.70(9)
C(3)	614(4)	805(2)	−2699(4)	2.95(9)
C(4)	−300(4)	1317(2)	−2795(3)	2.46(8)
C(5)	−888(5)	1480(2)	−4141(4)	3.91(12)
N(1)	−1628(3)	1287(1)	1121(3)	2.20(7)
N(2)	−779(3)	2519(1)	518(3)	2.37(7)
C(B1)	−2402(4)	1812(2)	1788(4)	2.87(9)
C(B2)	−2335(4)	2364(2)	889(4)	2.98(10)
C(A1)	−2617(4)	946(2)	213(4)	3.09(10)
C(A2)	−3826(5)	580(2)	962(5)	4.17(13)
C(A3)	−3188(6)	167(2)	2024(5)	4.54(13)
C(A4)	−2223(5)	518(2)	2945(4)	3.96(12)
C(A5)	−1039(4)	861(2)	2142(4)	3.05(10)
C(C1)	−34(4)	2830(2)	1649(4)	2.78(9)
C(C2)	−581(5)	3473(2)	1950(4)	3.31(10)
C(C3)	−524(5)	3871(2)	694(5)	3.72(11)
C(C4)	−1279(5)	3558(2)	−448(4)	3.71(11)
C(C5)	−694(5)	2921(2)	−686(4)	3.25(11)

parameters and their estimated standard deviations are listed in Table 3, and the bond distances and angles are shown in Table 4 (numbering scheme indicated in Fig. 1). Figure 2 shows the crystal structure projected on (10$\bar{1}$) plane.

From the X-ray results, it is noted that (1) the NO$_3^-$ is really a bidentate ligand, which is coordinated to the Ni(II) ion with the two bonds, Ni–O(N1) and Ni–O(N2) of nearly the same length. The bite angle, (∠O(N1)–Ni–O(N2)=60.13°), is rather narrow; such a value is not so rare among the data on the bidentate nitrates.[23)] The Ni–O(NO$_3$) bonds are remarkably longer than Ni–O(acac), explaining the easy cleavage of Ni–O(NO$_3$) bonds in some solvents (DMSO or CH$_3$NO$_2$; vide infra). The terminal N(O)–O(N3) bond length is shorter than the other two N–O bonds because both of the O atoms of the latter bonds are coordinated to the central metal ion. It is now quite obvious that this complex and also the nitrate complexes [Ni(NO$_3$)(dike)(diam)] of other diam and dike with similar properties are octahedral complexes with the bidentate NO$_3^-$ ligand, in agreement with the expectation from Lever's criterion. The crystallographic data of this compound are the first evidence for a bidentate coordination mode of NO$_3^-$ in Ni(II) complexes. (2) The bond distances between Ni(II) and the acac ligand, and those in this ligand itself, are nearly the same as those reported for another octahedral Ni(II) complex, [Ni(acac)$_2$(py)$_2$] (py=pyridine).[24)] Although there is no crystal data for the planar [Ni(acac)(dipe)]$^+$ (vide infra), the preliminary X-ray data for the dinuclear Ni(II) complex, [(tmen)Ni(1)(tetraketonate)Ni(2)(tmen)(H$_2$O)$_2$]$^{2+}$, in which the coordination sphere of Ni(1) is square planar and that of Ni(2) is octahedral, indicate that the coordinate bonds in the square planar arrangement are much shorter than those in the octahedral species.[25)] (3) Both piperidine rings in dipe are in the chair conformation, and the three bidentate ligands, i.e. dipe, acac, and NO$_3^-$, are placed so as to minimize the interligand

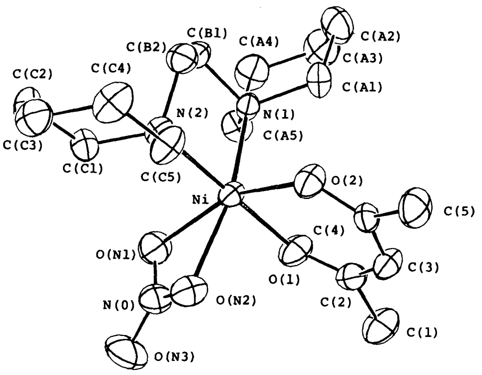

Fig. 1. Molecular structure of the complex [Ni(NO$_3$)(acac)(dipe)] with atom numbering projected on the O(N1)–O(1)–N(1) plane.

Table 4. Bond Distances (Å) and Angles in the Complex $[Ni(NO_3)(acac)(dipe)]$ (Estimated Standard Deviations in Parentheses)

Distance			
Ni-O(N1)	2.168(3)	N(1)-C(B1)	1.490(5)
Ni-O(N2)	2.161(3)	N(1)-C(A1)	1.489(5)
Ni-O(1)	2.030(3)	N(1)-C(A5)	1.485(5)
Ni-O(2)	2.001(3)	N(2)-C(B2)	1.483(5)
Ni-N(1)	2.070(3)	N(2)-C(C1)	1.489(5)
Ni-N(2)	2.118(3)	N(2)-C(C5)	1.482(5)
N(0)-O(N1)	1.259(5)	C(B1)-C(B2)	1.501(6)
N(0)-O(N2)	1.272(5)	C(A1)-C(A2)	1.529(6)
N(0)-O(N3)	1.214(6)	C(A2)-C(A3)	1.515(7)
O(1)-C(2)	1.262(5)	C(A3)-C(A4)	1.495(7)
O(2)-C(4)	1.269(5)	C(A4)-C(A5)	1.514(6)
C(1)-C(2)	1.515(6)	C(C1)-C(C2)	1.522(6)
C(2)-C(3)	1.374(5)	C(C2)-C(C3)	1.517(6)
C(3)-C(4)	1.399(5)	C(C3)-C(C4)	1.503(7)
C(4)-C(5)	1.492(6)	C(C4)-C(C5)	1.510(6)
Angle			
O(N1)-Ni-O(N2)	59.6(1)	O(N1)-N(0)-O(N2)	116.3(3)
O(N1)-Ni-O(1)	82.1(1)	O(N1)-N(0)-O(N3)	122.3(4)
O(N1)-Ni-O(2)	156.0(1)	O(N2)-N(0)-O(N3)	121.4(4)
O(N1)-Ni-N(1)	103.4(1)	O(1)-C(2)-C(1)	114.9(4)
O(N1)-Ni-N(2)	96.2(1)	O(1)-C(2)-C(3)	125.9(4)
O(N2)-Ni-O(1)	87.0(1)	C(1)-C(2)-C(3)	119.2(4)
O(N2)-Ni-O(2)	97.8(1)	O(2)-C(4)-C(3)	125.2(3)
O(N2)-Ni-N(1)	162.7(1)	O(2)-C(4)-C(5)	116.1(3)
O(N2)-Ni-N(2)	92.6(1)	C(3)-C(4)-C(3)	118.8(4)
O(1)-Ni-O(2)	89.5(1)	C(2)-C(3)-C(4)	125.7(4)
O(1)-Ni-N(1)	93.6(1)	N(1)-C(B1)-C(B2)	110.6(3)
O(1)-Ni-N(2)	178.1(1)	N(2)-C(B2)-C(B1)	110.6(3)
O(2)-Ni-N(1)	99.4(1)	C(B1)-N(1)-C(A1)	111.7(3)
O(2)-Ni-N(2)	92.4(1)	C(B1)-N(1)-C(A5)	111.1(3)
N(1)-Ni-N(2)	86.3(1)	C(A1)-N(1)-C(A5)	109.3(3)
Ni-O(N1)-N(0)	91.6(2)	N(1)-C(A1)-C(A2)	114.0(3)
Ni-O(N2)-N(0)	91.5(2)	C(A1)-C(A2)-C(A3)	111.5(4)
Ni-O(1)-C(2)	125.4(2)	C(A2)-C(A3)-C(A4)	111.0(4)
Ni-O(2)-C(4)	126.0(1)	C(A3)-C(A4)-C(A5)	110.8(4)
Ni-N(1)-C(B1)	105.9(2)	C(A4)-C(A5)-N(1)	113.9(3)
Ni-N(1)-C(A1)	110.8(2)	C(B2)-N(2)-C(C1)	111.7(3)
Ni-N(1)-C(A5)	108.0(2)	C(B2)-N(2)-C(C5)	111.1(3)
Ni-N(2)-C(B2)	102.6(2)	C(C1)-N(2)-C(C5)	108.4(3)
Ni-N(2)-C(C1)	113.1(2)	N(2)-C(C1)-C(C2)	114.8(3)
Ni-N(2)-C(C5)	109.9(2)	C(C1)-C(C2)-C(C3)	111.8(4)
		C(C2)-C(C3)-C(C4)	110.4(4)
		C(C3)-C(C4)-C(C5)	111.9(4)
		C(C4)-C(C5)-N(2)	114.7(3)

repulsions. The chelate bite angles, ∠O(1)–Ni–O(2) (for acac) and ∠N(1)–Ni–N(2) (for dipe), are 89.48° and 85.87°, respectively.

Three tables for atomic coordinates of the H atoms (Table A), mean square displacement tensors of atoms (Table B), and structure factors (Table C) are deposited at the Chemical Society of Japan, Document No. 8858.

Electronic Spectra in Solution. Figure 3 shows the electronic spectra of $[Ni(NO_3)(acac)(dipe)]$ in four kinds of organic solvents, i.e., DCE, CH_3NO_2, acetone, and DMSO. In Table 5, the spectral data for similar complexes are summarized. From these data, it can be seen that two kinds of spectral changes take place with changes in solvent polarity.

[I] The spectra in DCE, acetone and EtOH are nearly of the same pattern, showing two bands ($\tilde{\nu}_1$ and $\tilde{\nu}_2$; $\tilde{\nu}_1 < \tilde{\nu}_2$) which correspond to the octahedral structure of the complexes. The spectral shape is, however, somewhat anomalous, i.e., the values of the intensity ratio of the two bands ($R=\varepsilon(\tilde{\nu}_2)/\varepsilon(\tilde{\nu}_1)$) are nearly the same in these solvents and are about 2, whereas the same ratio for a typical octahedral complex (e.g., $[\mathrm{Ni\ en_3}]^{2+}$) is nearly 1.[26)] The same type of anomaly is also observed in the spectra of the solid nitrate complexes. This anomaly is probably related to the existence of a highly strained 4-membered chelate ring of NO_3^- in the coordination sphere (vide supra). On the other hand, in the case of DMSO solutions, the values of R are close to unity, so that the spectra look quite normal. The electric conductivity

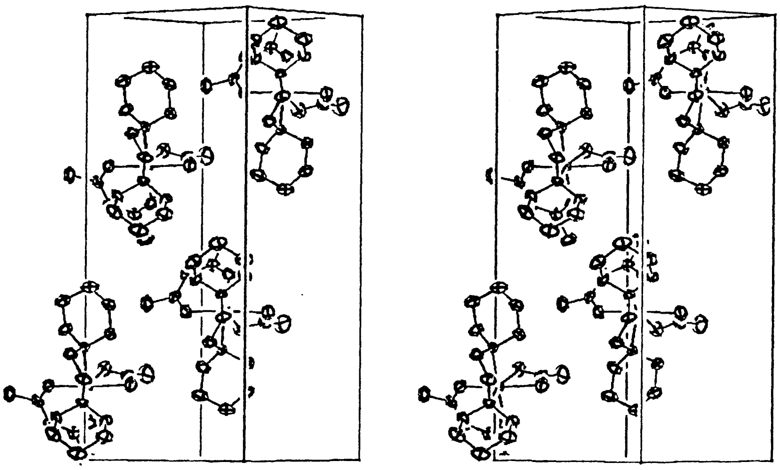

Fig. 2. Stereoscopic view of a unit cell projected on the (101) plane; horizontal [10$\bar{1}$], vertical b.

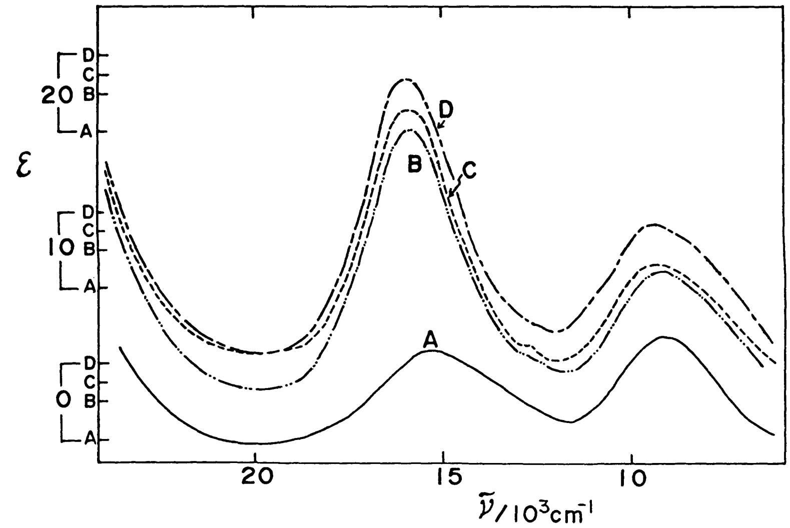

Fig. 3. Absorption spectra of [Ni(NO_3)(acac)(dipe)] in various solvents. Concn: 4×10^{-2} mol dm^{-3}, temp: ca. 20 °C. A=DMSO, B=acetone, C=CH_3NO_2, D=DCE.

data shown in Table 6 indicate now that the complex species in DCE or acetone are non-charged ones, while those in DMSO are 1 : 1 electrolytes.

These results lead to the conclusion that, in a solvent such as DCE (DN=0, AN=16.7)[28] or acetone (DN=17.0, AN=12.5) which have a relatively low polarity, the complex structure in the solid state remains unchanged, i.e., the species in the solution is the non-charged complex [Ni(NO_3)(acac)(diam)]:

$$\underset{\text{(Solid)}}{[\text{Ni(NO}_3\text{)(acac)(diam)]}} \longrightarrow \underset{\text{Blue/Green, Oh } (R\approx 2)}{[\text{Ni(NO}_3\text{)(acac)(diam)]}}$$

When the complex is dissolved in DMSO (DN=29.8, AN=19.3) which is a more polar solvent, however, it dissociates the NO_3^- ion to form the solvated cations [Ni(acac)(diam)(Solvent)$_2$]$^+$:

$$\underset{\text{Blue/Green, Oh } (R\approx 2)}{[\text{Ni(NO}_3\text{)(acac)(diam)]}} \rightleftarrows \underset{\text{Blue, Oh } (R\approx 1)}{[\text{Ni(acac)(diam)(Solvent)}_2]^+} + NO_3^- \quad (1)$$

This equilibrium is strongly shifted to the right hand side in DMSO; the strain in the coordination sphere is thereby lost, and the spectrum of the solution looks quite normal.

[II] Although the occurrence of the spectral change (I) was already indicated in our former studies,[2-5] there is another kind of spectral change (II) which we have overlooked hitherto. This change occurs in CH_3NO_2 solutions where, according to the conductivity data (Table 6), partial dissociation of the complexes occurs, which increases in the following order of diam:

Table 5. Absorption Spectra of the Complexes $[\mathrm{Ni(NO_3)(dike)(diam)}]$ in Solid State and in Various Solvents ($\tilde{\nu}_{\mathrm{max}}/10^3\ \mathrm{cm^{-1}}$, $\varepsilon_{\mathrm{max}}$ in Parentheses, Concn: $4\times10^{-2}\ \mathrm{mol\ dm^{-3}}$, Temp: ca. 20 °C)

Complex	Solid	DCE	CH_3NO_2	Acetone	DMSO
$[\mathrm{Ni(NO_3)(acac)(dipe)}]$	9.80	9.25(9.1)	9.37(8.6)	9.26(8.7)	9.18(6.7)
	16.13	15.92(19.0)	15.95(18.7)	15.87(17.8)	15.34(5.8)
			20(sh)[a,b]		
$[\mathrm{Ni(NO_3)(acac)(teen)}]$	9.00	9.09(8.9)	9.09(7.0)	9.07(8.8)	8.94(4.9)
	15.75	15.75(20.6)	15.68(16.5)	15.69(19.6)	15.15(4.9)
			20.09(20.4)		
$[\mathrm{Ni(NO_3)(acac)(tmen)}]$	9.68	9.60(9.7)	9.55(9.3)	9.55(9.5)	9.49(6.8)
	16.54	16.29(19.6)	16.26(19.5)	16.26(18.8)	15.80(5.2)
			20.0(sh)[b]		
$[\mathrm{Ni(NO_3)(acac)(Et_3en)}]$	9.80	9.58(9.8)	9.54(9.3)	9.53(10.9)	9.34(4.7)
	16.67	16.39(21.9)	16.34(20.9)	16.31(21.8)	15.72(4.2)
			20.0(sh)[b]		
$[\mathrm{Ni(NO_3)(tfac)(dipe)}]$	9.52	9.31(17.1)	9.47(9.9)	9.29(8.8)	9.11(5.8)
	16.25	15.98(28.4)	15.83(20.9)	15.85(18.1)	15.13(6.9)
$[\mathrm{Ni(NO_3)(bzac)(dipe)}]$	8.94	9.31(9.1)	9.34(9.0)	9.29(9.5)	9.01(6.3)
	15.64	15.92(19.6)	15.85(20.2)	15.88(18.8)	15.20(5.5)
			20(sh)[b]		

a) sh=shoulder. b) This band is very weak at room temperature (see Ref. 29).

Table 6. Molar Conductivity Data of the Complexes $[\mathrm{Ni(NO_3)(dike)(diam)}]$ in Various Organic Solutions ($\Lambda_{\mathrm{M}}/\mathrm{S\ cm^2\ mol^{-1}}$, Concn: $2\times10^{-2}\ \mathrm{mol\ dm^{-3}}$, Temp: 25±0.1 °C)

[A] $[\mathrm{Ni(NO_3)(dike)(dipe)}]$				
dike	DCE	CH_3NO_2	Acetone	DMSO
tfac	0.02	6.80	1.65	32.97
bzac	0.03	3.77	0.91	41.06
acac	0.05	5.06	0.93	30.46
[B] $[\mathrm{Ni(NO_3)(acac)(diam)}]$				
diam	DCE	CH_3NO_2	Acetone	DMSO
dipe	0.05	5.06	0.93	30.46
teen	0.30	33.77	2.01	33.84
tmen	0.04	4.73	1.29	36.99
Et_3en	0.06	6.26	1.45	34.31
Ref.[a]	20.89	100.6	137.8	39.10
	(10—24)	(75—95)	(100—140)	(ca. 35)

a) The values for $[\mathrm{Ni(acac)(tmen)}]\mathrm{ClO_4}$, i.e., a typical 1:1 electrolyte, in the respective solvents, and standard values for an 1:1 electrolyte in parentheses.[27]

$$\text{teen} \gg \text{Et}_3\text{en} > \text{dipe} \sim \text{tmen}.$$

The values of *R* in these solutions do not change so much from 2; however, a new band appears at ca. $20\times10^3\ \mathrm{cm^{-1}}$, which can be assigned to the unsolvated square planar chelate cation $[\mathrm{Ni(dike)(diam)}]^+$.[2–5] This change can, thus, be ascribed to the change:

$$\underset{\text{Blue/Green, Oh } (R\approx2)}{[\mathrm{Ni(NO_3)(acac)(diam)}]} \rightleftarrows \underset{\text{Red, square planar}}{[\mathrm{Ni(acac)(diam)}]^+} + \mathrm{NO_3^-} \quad (2)$$

In this case, the solvent (CH_3NO_2) is a very weak donor, but a relatively strong acceptor (DN=2.7, AN=20.5). Since the coordination of NO_3^- in the complex is weak (vide supra), a part of the NO_3^- ions can be solvated and dissociated from the complex by interaction with this acceptor solvent. On the other hand, the solvent molecules will not coordinate effectively to Ni(II) to form an octahedral species, as those in Eq. 1, owing to their poor donor ability, so that the "naked"square planar cation newly appears in solution.

Figure 4 shows the absorption spectra of four kinds of $[\mathrm{Ni(NO_3)(acac)(diam)}]$ in CH_3NO_2. It can be seen that the relative intensity of the band at ca. $20\times10^3\ \mathrm{cm^{-1}}$, which is an approximate measure for the formation of the square planar species in this solvent, decreases in the order of diam

$$\text{teen} \gg \text{Et}_3\text{en} > \text{tmen} \gtrsim \text{dipe}^{29)} \quad (3)$$

for this series of complexes, which is nearly in parallel with the expectation from the conductivity data. It is easy to understand that the free movements of the ethyl groups on the N-donor atoms of teen will strongly destabilize the octahedral chelate by their steric hindrance, so that the equilibrium in Eq. 2 will be shifted strongly to the right-hand side. This destabilizing effect will decrease in the order teen>Et_3en> tmen, with the decrease in size and number of the alkyl groups. The piperidino groups of dipe are very bulky, but their free movements (and especially those toward the axial sites) are strongly restricted by their rigid ring structure.[1] Therefore, the complex $[\mathrm{Ni(NO_3)(acac)(dipe)}]$ will be much more stable than the corresponding complexes with teen or Et_3en, and comparable to that of tmen (or even more than that, if the decreased ligand field strength (l.f.s.) of dipe (vide infra) is taken into account), with respect to the equilibrium of Eq. 2. The above-mentioned ligand order will, thus, come about.

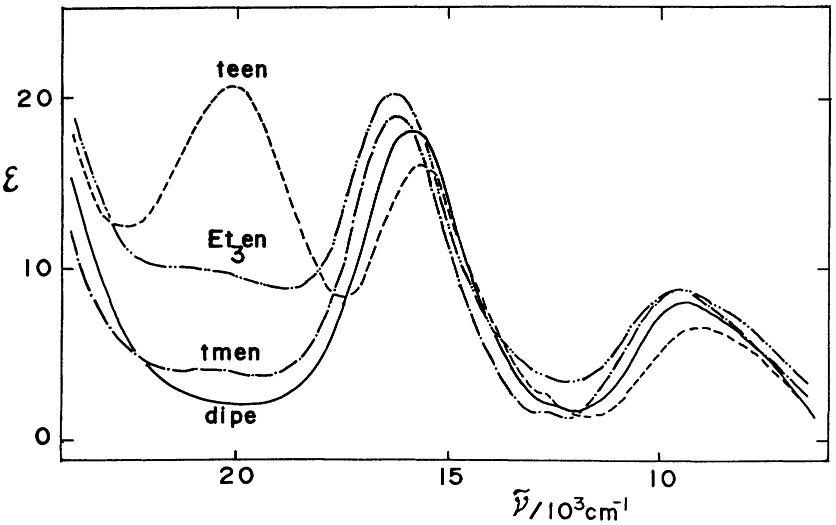

Fig. 4. Absorption spectra of [$Ni(NO_3)(acac)(diam)$] (diam=teen, Et_3en, dipe, and tmen) in CH_3NO_2. Concn: 4×10^{-2} mol dm^{-3}, temp: ca. 20 °C.

The spectra of these nitrate complexes in CH_3NO_2 show concentration and temperature dependence, especially in the vicinity of the band of the square planar species. In each case, a gradual increase of the square planar species takes place at lower concentrations and at higher temperatures, showing that the nitrate dissociation is favored by dilution and heating, and confirming the existence of the equilibrium shown in Eq. 2. Quantitative aspects of this equilibrium, and also those of the equilibria observed in EtOH solutions,[30] are now under study.

Finally, it may be pointed out that the differences among the l.f.s. of the diamines used in this study can be estimated from the values of $\tilde{\nu}_1$ of the octahedral nitrate complexes in DCE. Although such differences are not large, the data in Table 5 indicate that the order of decreasing l.f.s. of the diamines is:

$$\text{tmen} > \text{Et}_3\text{en} > \text{dipe} > \text{teen}. \qquad (4)$$

It is generally conceivable that a ligand with a strong donor property will tend to form a square planar complex with Ni(II), and to shift the solution equilibrium between a square planar complex and an octahedral one to the side of the former. The order of Eq. 4, however, dose not coincide with that of Eq. 3, indicating that the steric hindrance of the bulky substituent groups on the N-donor atoms is important in determining the equilibrium.

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17) The fact that the IR spectra of the complexes [$Ni(NO_3)$(dike)(tmen)] and [$Ni(NO_3)$(dike)(teen)] indicate

the existence of bidentate NO_3^- was already pointed out in our former studies.[3–6]

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28) DN and AN are donor number and acceptor number of the solvent, respectively; cf. Ref. 20.

29) In the case of the acac–dipe complex, this band is nearly imperceptible on the curve in Fig. 4. However, an analysis of the absorption curve indicates its existence. Upon heating the solution to ca. 40 °C, or upon diluting it to 4×10^{-3} mol dm^{-3}, it appears as a clear hump, with an intensity which is apparently comparable to that of the tmen complex under the same conditions. Therefore, the positions of tmen and dipe in this order are quite near, as indicated by the conductivity data (cf. Table 6).

30) In EtOH solutions of the complex, it seems that the equilibria of (Eq. 1) and (Eq. 2) take place at the same time, i.e., there is a partial ionization of NO_3^- (cf. Table 6), but the cations formed are an equilibrium mixture of [Ni(dike)(diam)(EtOH)$_2$]$^+$ and [Ni(dike)(diam)]$^+$. The proportion of the latter ion in this mixture decreases again in the order of teen $\gg$ Et$_3$en $>$ tmen $\approx$ dipe.