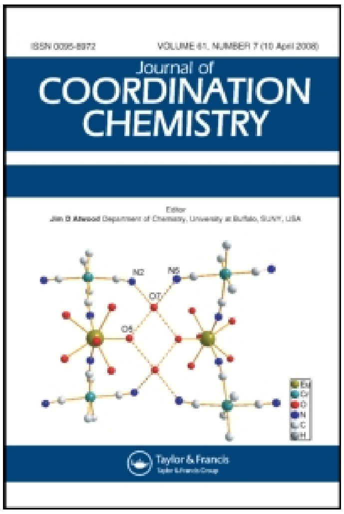

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SYNTHESES, STRUCTURAL VARIETIES AND CHROMOTROPIC PROPERTIES OF DINUCLEAR NICKEL(II) COMPLEXES WITH A TETRAKETONATE AND AN N-ALKYLATED ETHYLENEDIAMINE

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SYNTHESES, STRUCTURAL VARIETIES AND CHROMOTROPIC PROPERTIES OF DINUCLEAR NICKEL(II) COMPLEXES WITH A TETRAKETONATE AND AN N-ALKYLATED ETHYLENEDIAMINE

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Six dinuclear nickel(II) complexes of the form $Ni_2(teke)(tmen)_2X_2$ have been prepared, with teke being a tetraketonate such as 1,1,2,2-tetraacetylethanediide (taet) or 1,2-diacetyl-1,2-dibenzoylethanediide (dabe), tmen a *N,N,N′,N′*-tetramethylethylenediamine, and X^- is an anion, namely BPh_4^-, ClO_4^- or NO_3^-. The crystal structure of $Ni_2(taet)(tmen)_2(ClO_4)_2 \cdot 3H_2O$ was determined by X-ray methods, in which the geometries of the two Ni(II) ions in the dinulcear cation are different. One has an octahedral structure and the other is square planar. The structures of the two nickel moieties in the tetraphenylborate and the nitrate complexes are square planar – square planar and octahedral-octahedral, respectively. These complexes, which are very soluble in organic solvents, show characteristic chromotropic behaviour in solution due to solvent donor and acceptor properties.

KEYWORDS: solvatochromism, anion coordination, dinuclear complexes, mixed ligand complexes, X-ray structure

INTRODUCTION

In previous papers we reported the chromotropic behaviour of mononuclear Ni(II) mixed ligand complexes containing an *N*-alkylated ethylenediamine and a *β*-diketonate ligand (dike).[1–3] They are very stable as mixed ligand systems in the

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solid state and in solution. They also are soluble in various organic solvents so that chromotropic properties can easily be studied in solution.[4] To continue these investigations we used branched tetraketonate ligands obtained from the original β-diketonate as potential tetradentates[5–8] which should enable us to obtain binuclear complexes. The fact that many reports[5] concerning linear tetraketonate (mononuclear) complexes but few investigations of the branched species[6–8] exist further encouraged us in the present investigations.[9,10]

EXPERIMENTAL

Materials

Starting materials for synthesising the metal complexes were obtained from the Wako Pure Chemical Industrial Co. Ltd. and were used without further purification. Solvents for spectroscopic and conductivity measurements were 'spectro-grade' or dehydrated according to conventional methods.[11]

Synthesis of the ligands H_2taet and H_2dabe

To obtain these ligands the procedure of Charles[12] was applied with slight modifications. Well dried sodium acetylacetonate powder (Na acac) was suspended into 300 cm^3 of dry ether. To this a solution of iodine (25.4 g in 300 cm^3 of ether) was added drop by drop during 2.5 hours with vigorous stirring. The solution thus obtained was evaporated to dryness. The resulting solid was suspended in 500 cm^3 of H_2O with stirring and then left to stand for several hours. The undissolved residue was filtered off, washed with H_2O, and recrystallized from hot methanol. The yield was about 3.5%. To obtain H_2dabe, the same method was applied using sodium benzoyl-acetonate (Na bzac) as starting material. The ligands thus obtained were characterized by their melting points, and comparison of ^{1}H-NMR spectra of dinuclear $[Ni_2(teke)(tmen)_2]^{2+}$ with that of mononuclear $[Ni(dike)(tmen)]^+$ in $CDCl_3$, where the signal for the γ-methine of the β-diketonate disappeared in the case of the corresponding dinuclear system.

Syntheses of Dinuclear Complexes $[Ni_2(teke)(tmen)_2](X)_2 \cdot nH_2O$

The syntheses of the nitrate and perchlorate are similar to that of mononuclear Ni(dike)(tmen)X (where $X^- = NO_3^-$ or ClO_4^-) reported before.[3] The tetraphenylborates ($X^- = BPh_4^-$) were obtained from the nitrate complexes *via* anion exchange in 1,2-dichloroethane (DCE). Analytical data for the complexes are given in Table 1.

Structural determination

For X-ray analysis, we obtained a trihydrate by slowly growing a single crystal in DCE. Reddish brown crystals, $Ni_2(taet)(tmen)_2(ClO_4)_2 \cdot 3H_2O$, with approximate dimensions 0.3 × 0.3 × 0.3 mm were used. Accurate cell parameters were determined by a least-squares fit including 42 reflections within the range $24° < 2\theta < 26°$

Table 1 Analytical Data for the Dinuclear Complexes

Complex	Colour	C%	H%	N%
$Ni_2(taet)(tmen)_2(BPh_4)_2$	Red	70.82 (70.98)	7.70 (7.15)	4.91 (4.73)
$Ni_2(taet)(tmen)_2(ClO_4)_2 \cdot 3H_2O$	Reddish-brown	33.38 (33.07)	6.24 (6.31)	6.69 (7.01)
$Ni_2(taet)(tmen)_2(NO_3)_2$	Bluish-green	39.33 (39.44)	6.79 (6.62)	12.58 (12.54)
$Ni_2(dabe)(tmen)_2(BPh_4)_2$	Orange	73.22 (73.43)	6.73 (6.78)	4.30 (4.28)
$Ni_2(dabe)(tmen)_2(ClO_4)_2 \cdot 2H_2O$	Brown	41.47 (42.46)	5.84 (5.79)	7.19 (6.19)
$Ni_2(dabe)(tmen)_2(NO_3)_2$	Yellowish-green	47.62 (48.40)	6.00 (6.09)	10.78 (10.58)

[a] Calculated values are shown in parentheses.

measured by a Rigaku AFC-5 four-circle diffractometer with MoKα radiation (λ = 0.71069 Å) monochromated by graphite. Crystal data are given in Table 2.

Reflection data were collected in a $2\theta - \omega$ scan mode, up to $2\theta = 50°$ (h = 32 to −32, k = 0 to −12, l = 0 to −15) with scan widths of $\Delta\omega = (1.1 + 0.5\tan\theta)°$. Three standard reflections were recorded after every 150 reflections and no significant change in intensity was observed, *i.e.*, the maximum variation of intensity data was less than 1.4%. A total of 5627 reflections was collected, of which 4850 were treated as significant ($F > 4\sigma(F)$). The structure was solved by direct methods using the program SHELX76 [13] and was refined by block-diagonal least-squares methods using the program UNICS III.[14] Atomic scattering factors were taken from 'International Tables for X-ray Crystallography'.[15] All non-hydrogen atoms were refined anisotropically. Four hydrogen atoms were located from Fourier synthesis. The position of all other hydrogen atoms except water hydrogen atoms were calculated. Max. Δ/ρ and max. $\Delta\rho$ in the final difference map were 0.108 and 1.77 eÅ^{-3}. If Cl(2′) and O(14′) and O(15′) as the small portion of a disordered perchlorate were excluded, the largest peak ($\Delta\rho$) in the final distance Fourier map remained as 2.7 eÅ^{-3} and several peaks between 1 and 2 eÅ^{-3} existed (in this case, R = 9.5% and R_w = 11.2%). Then, the largest peak was assigned to a disordered chloride Cl(2′). Other peaks were located *ca* 1.5 Å from Cl(2), and

Table 2 Crystal data for the complex $Ni_2(taet)(tmen)_2(ClO_4)_2 \cdot 3H_2O$.

Formula $Ni_2C_{22}H_{50}N_4O_{15}Cl_2$	
Crystal system	Monoclinic
Space group	$P2_1/a$
a(Å)	27.1425(17)
b(Å)	10.3055(6)
c(Å)	13.3744(10)
β(°)	95.439(6)
V(Å^3)	3724.21(42)
Z	4
Dc(g cm^{-3})	1.425
Independent reflections ($F > 4\sigma(F)$)	4850
R (R_w)[a]	0.0860 (0.098)

[a] $R_w = [\Sigma w(|Fo| - |Fc|)^2/\Sigma w|Fo|^2]^{0.5}$, where w = 1.

were therefore assigned to disordered oxygen atoms O(14′) and O(15′). Efforts to model disorder were not successful. Final R and R_w values were 0.086 and 0.098, respectively. Table 3 lists final coordinates of non-hydrogen atoms. Computations were carried out with a FACOM M-770/8 computer at the Computer Centre of

Table 3 Atomic Coordinates (x10^4 but x10^5 for Ni) of Non-Hydrogen Atoms and Equivalent Temperature Factors (Å^2). Estimated Standard Deviations are given in Parentheses.

Atom	*x/a*	*y/b*	*z/c*	*Beq*
Ni(1)	12302(4)	17848(11)	21002(8)	3.41
Ni(2)	15034(4)	57181(10)	-29582(8)	3.18
Cl(1)	2524(1)	6636(2)	-6320(2)	4.59
Cl(2)	274(1)	1535(3)	-3372(2)	4.54
Cl(2')	122(6)	377(29)	-156(16)	8.10
O(1)	1133(2)	3509(6)	1879(4)	4.73
O(2)	1314(2)	1426(5)	798(4)	4.27
O(3)	1958(2)	5108(6)	-1795(4)	4.32
O(4)	951(2)	5579(5)	-2102(4)	3.75
O(W1)	2126(2)	5430(6)	-3830(4)	4.91
O(W2)	1345(2)	3754(6)	-3419(5)	4.57
O(W3)	-164(2)	1806(5)	652(4)	3.97
O(8)	2906(4)	6762(11)	-6892(9)	13.84
O(9)	2626(5)	5646(8)	-5644(7)	12.17
O(10)	2110(4)	6296(10)	-6947(9)	13.18
O(11)	2444(4)	7783(9)	-5814(8)	11.47
O(12)	-122(5)	1403(14)	-4009(10)	16.12
O(13)	238(15)	508(15)	-2781(10)	15.02
O(14)	671(6)	1339(15)	-3846(12)	16.25
O(15)	312(10)	2251(21)	-2637(15)	18.83
O(14')	377(9)	2802(22)	-3622(22)	14.34
O(15')	-128(12)	2422(32)	-3099(29)	15.28
N(1)	1375(3)	-4(7)	2439(5)	4.00
N(2)	1111(3)	2071(7)	3473(5)	4.25
N(3)	1685(3)	7684(7)	-2608(6)	5.49
N(4)	1021(3)	6526(7)	-4129(5)	4.26
C(1)	1192(3)	4119(9)	1071(7)	4.29
C(2)	1283(3)	3581(8)	155(6)	3.55
C(3)	1322(3)	2235(9)	67(6)	3.94
C(4)	1149(5)	5616(9)	1188(7)	6.24
C(5)	1390(4)	1600(10)	-927(7)	6.00
C(6)	1836(3)	4617(10)	-1009(6)	4.43
C(7)	1354(3)	4398(8)	-751(6)	3.59
C(8)	929(3)	4891(8)	-1331(6)	3.39
C(9)	2269(4)	4227(14)	-279(8)	8.72
C(10)	424(3)	4594(10)	-1031(7)	4.69
C(11)	1461(4)	-78(11)	3555(7)	6.49
C(12)	1117(4)	761(11)	3988(7)	6.22
C(13)	1823(4)	-490(11)	2020(8)	6.26
C(14)	951(4)	-845(10)	2070(8)	6.47
C(15)	1515(4)	2885(11)	3972(7)	6.44
C(16)	631(4)	2697(13)	3559(7)	7.42
C(17)	1412(5)	8479(10)	-3466(13)	10.37
C(18)	936(6)	7825(12)	-3795(11)	10.57
C(19)	2208(4)	7976(10)	-2592(9)	7.03
C(20)	1543(6)	8013(11)	-1641(11)	9.55
C(21)	531(4)	5922(13)	-4198(9)	8.34
C(22)	1203(4)	6465(11)	-5139(8)	6.66

Josai University. Tables of anisotropic temperature factors for non-hydrogen atoms hydrogen positions and observed and calculated structure factors are available from Y.F.

Physical measurements

Electronic spectra of the complexes in solution were observed with a Hitachi 340 spectrophotometer using 10 mm quartz cells and concentrations between 2.0×10^{-3} and 6.0×10^{-3} mol dm^{-3} except as mentioned differently in the text. Solid reflectance spectra of the complexes were obtained with the same spectrometer with an integrated sphere attachment using $BaSO_4$ as reference. IR spectra in the range 330–5040 cm^{-1} were measured using a JASCO A-3 IR spectrometer by the nujolmull method. Thermal analyses were performed with a ULVAC TG-DTA thermal analyser with heating rates of 1°C/min or 3°C/min. Magnetic data were collected with a Shimadzu MB-100 torsion magnetometer by the Faraday method at room temperature. Electric conductivity measurements were performed with a DKK AOC-10 conductivity outfit with a constant temperature water bath at 25±0.3°C. ^1H-NMR spectra were obtained with a JEOL JNM-GX270 FT-NMR spectrometer, with TMS maker, using $CDCl_3$ as solvent.

RESULTS AND DISCUSSION

Structural Variations of the Dinuclear Complexes in the Solid State

We have obtained six dinuclear, mixed ligand complexes of the general formula $Ni_2(L)(tmen)_2X_2 \cdot nH_2O$, where X^- is an anion such as tetraphenylborate, perchlorate, or nitrate.[9,10] L refers to 1,1,2,2,-tetraacetylethanediide (taet) or to 1,2-diacetyl-1,2-dibenzoylethanediide (dabe). Analytical data shown in Table 1 indicate that the perchlorates contain water molecules which are rather easily lost by heating to 60–100°C as observed by TG-DTA measurement. This explains the discrepancy between obtained and calculated analytical data. IR absorption data for the perchlorate in complexes with taet and dabe indicate that the anion does not coordinate to the metal ion.[16] In contrast to this, nitrate coordinates, as can be seen by weak, but split bands between 1800–1700 cm^{-1} (1770 and 1720 cm^{-1} for the taet complex, 1768 and 1720 cm^{-1} in the dabe case), indicating that the nitrate ion acts as a bidentate ligand in both cases.[17–19]

Table 4 lists magnetic moments, solid reflectance spectroscopic data and structure patterns of the complexes, among which the tetraphenylborates are diamagnetic and the nitrates have 3.1–3.2 B.M. per Ni(II) ion. The perchlorates, however, show rather small values of magnetic moments per single metal ion. This led us to the conclusion that one of the Ni(II) ions in the dinuclear system occurs in an octahedral and the other in a square planar environment. Figure 1 depicts solid reflectance spectra of taet complexes with three different anions (BPh_4^-, ClO_4^-, and NO_3^-). In this figure, two peaks around 10×10^3 cm^{-1} and 16×10^3 cm^{-1} indicate the octahedral moieties in the system, and the band at 20×10^3 cm^{-1} is due to the square planar species.[20] From these results, it is easily understandable that both nickel(II) ions in the dinuclear nitrate complexes are octahedral (Oh-Oh structure). For the tetraphenylborates, both Ni(II) ions are square planar (Sp-Sp). In the case

Table 4 Magnetic Moments and Solid State Reflectance Spectroscopic Data.

Complex	Magnetic Moment (B.M.) $\mu_{eff}/(2Ni)^a$	μ_{eff}/Ni^a	d-d Transition $\nu_{max}(10^3\ cm^{-1})$			Structure[e]
$Ni_2(taet)(tmen)_2(BPh_4)_2$	Diamagnetic		[d]	[d]	20.8	Sp-Sp
$Ni_2(taet)(tmen)_2(ClO_4)_2 \cdot 3H_2O$	3.14	2.22	9.8	16[b)]	20.8	Sp-Oh
$Ni_2(taet)(tmen)_2(NO_3)_2$	4.56	3.22	9.5	16.4	[d]	Oh-Oh
$Ni_2(dabe)(tmen)_2(BPh_4)_2$	0.21	0.15	[d]	[d]	21.2	Sp-Sp
$Ni_2(dabe)(tmen)_2(ClO_4)_2 \cdot 2H_2O$	3.56	2.51	9.4	15[b]	[c]	Sp-Oh
$Ni_2(dabe)(tmen)_2(NO_3)_2$	4.44	3.14	9.5	16.2	[d]	Oh-Oh

[a] Magnetic moment per complex cation (2Ni) and single nickel(II) ion. [b] Shoulder.
[c] Obscured by the strong ligand band. [d] Not observed. [e] Oh = octahedral, Sp = square planar; see text.

of the perchlorate complexes, however, we have two geometries in the dinuclear unit.[9] There are two possibilities for these structures; either one nickel centre is octahedral and the other one is square planar in the dinuclear unit (Oh-Sp), or a 1:1 mixture of Oh-Oh and Sp-Sp structures is present.

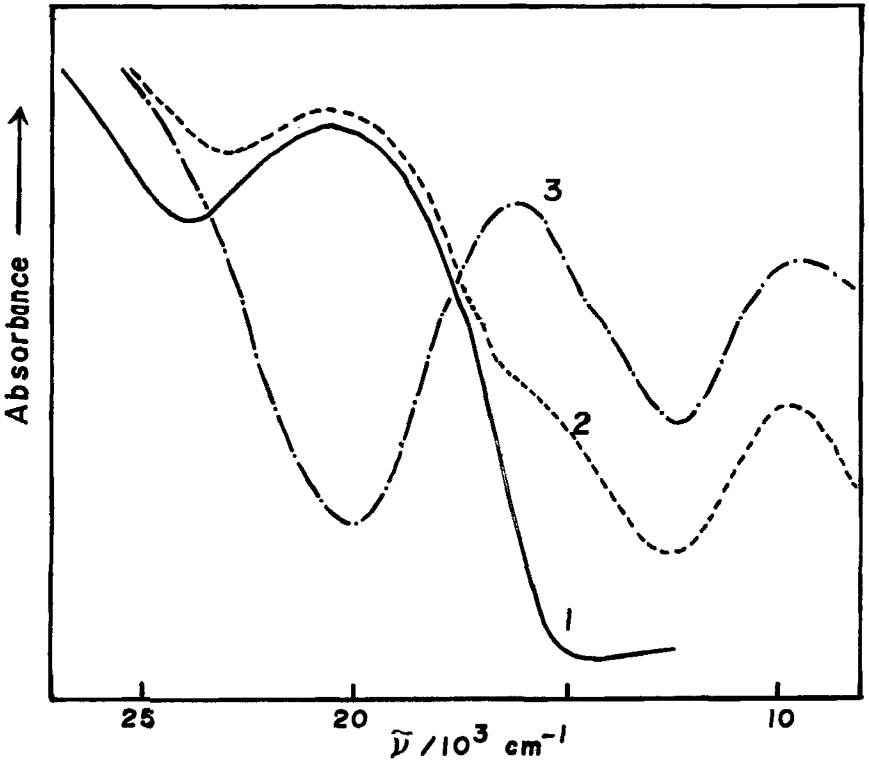


Figure 1 Solid state reflentance spectra of $Ni_2(taet)(tmen)_2X_2 \cdot nH_2O$; 1: X = BPh_4^- (n = 0), 2: X = ClO_4^- (n = 3), 3: X = NO_3^- (n = 0).

We have determined the crystal structure of the complex, $Ni_2(taet)(tmen)_2(ClO_4)_2 \cdot 3H_2O$ to clarify this structural problem. Figure 2 shows the crystal structure of this complex and Table 5 gives selected bond lengths and angles. These data show that this dinuclear complex has the Oh-Sp structure. So far there is no report of crystal data for the square planar structure of the Ni acac complex, and in this study we could obtain examples of square planar and octahedral structures

Table 5 Selected Bond Distances (Å) and Angles (°) in the Complex $Ni_2(taet)(tmen)_2(ClO_4)_2 \cdot 3H_2O$.

Ni(1)	- 0(1)	1.816(6)	Ni(1)	- O(2)	1.816(6)	Ni(1)	- N(1)	1.930(7)
Ni(1)	- N(2)	1.917(7)	Ni(2)	- O(3)	1.994(5)	Ni(2)	- O(4)	1.976(6)
Ni(2)	- 0(W1)	2.163(6)	Ni(2)	- O(W2)	2.147(6)	Ni(2)	- N(3)	2.127(8)
Ni(2)	- N(4)	2.115(7)	O(1)	- C(1)	1.274(10)	O(2)	- C(3)	1.286(10)
O(3)	- C(6)	1.240(11)	O(4)	- C(8)	1.257(10)	N(1)	- C(13)	1.474(13)
N(1)	- C(14)	1.487(13)	N(2)	- C(12)	1.516(13)	N(2)	- C(15)	1.488(13)
N(2)	- C(16)	1.469(14)	N(3)	- C(17)	1.541(16)	N(3)	- C(19)	1.452(14)
N(3)	- C(20)	1.424(17)	N(4)	- C(18)	1.436(15)	N(4)	- C(21)	1.464(14)
N(4)	- C(22)	1.483(13)	C(1)	- C(2)	1.388(12)	C(1)	- C(4)	1.556(13)
C(2)	- C(3)	1.398(12)	C(2)	- C(7)	1.502(11)	C(3)	- C(5)	1.508(13)
C(6)	- C(7)	1.403(13)	C(6)	- C(9)	1.508(14)	C(8)	- C(10)	1.495(12)
C(11)	- C(12)	1.434(16)	C(17)	- C(18)	1.485(19)	Ni(1)	- Ni(2)	7.981(2)
O(1)	- N(1)	- O(2)	94.2(3)	O(1)	- Ni(1)	- N(1)	174.7(3)	
O(1)	- N(1)	- N(2)	88.3(3)	O(2)	- Ni(1)	- N(1)	89.4(3)	
O(2)	- N(1)	- N(2)	176.2(3)	N(1)	- Ni(1)	- N(2)	88.4(3)	
O(3)	- N(2)	- O(4)	88.4(2)	O(3)	- Ni(2)	- O(W1)	85.4(2)	
O(3)	- Ni(2)	- O(W2)	91.1(2)	O(3)	- Ni(2)	- N(3)	90.9(3)	
O(3)	- Ni(2)	- N(4)	175.0(3)	O(4)	- Ni(2)	- O(W1)	167.7(2)	
O(4)	- Ni(2)	- O(W2)	87.4(2)	O(4)	- Ni(2)	- N(3)	96.6(3)	
O(4)	- Ni(2)	- N(4)	90.4(3)	O(W1)	- Ni(2)	- O(W2)	82.1(2)	
O(W1)	- Ni(2)	- N(3)	94.2(3)	O(W1)	- Ni(2)	- N(4)	96.7(3)	
O(W2)	- Ni(2)	- N(3)	175.6(3)	O(W2)	- Ni(2)	- N(4)	93.7(3)	
N(3)	- Ni(2)	- N(4)	84.4(3)	Ni(1)	- O(1)	- C(1)	126.4(6)	
Ni(1)	- O(2)	- C(3)	127.6(5)	Ni(2)	- O(3)	- C(6)	126.5(5)	
Ni(2)	- O(4)	- C(8)	127.9(5)	Ni(1)	- Ni(1)	- C(11)	107.0(6)	
Ni(1)	- N(1)	- C(13)	113.1(6)	Ni(1)	- Ni(1)	- C(14)	110.2(6)	
C(11)	- N(1)	- C(13)	107.9(7)	C(11)	- N(1)	- C(14)	110.2(8)	
C(13)	- N(1)	- C(14)	108.4(8)	Ni(1)	- N(2)	- C(12)	107.6(6)	
Ni(1)	- N(2)	- C(15)	109.5(6)	Ni(1)	- N(2)	- C(16)	112.0(5)	
C(12)	- N(2)	- C(15)	108.8(7)	C(12)	- N(2)	- C(16)	109.1(8)	
C(15)	- N(2)	- C(16)	109.8(8)	Ni(2)	- N(3)	- C(17)	104.9(6)	
Ni(2)	- N(3)	- C(19)	114.0(6)	Ni(2)	- N(3)	- C(20)	110.5(7)	
C(17)	- N(3)	- C(19)	107.6(9)	C(17)	- N(3)	- C(20)	113.4(9)	
C(19)	- N(3)	- C(20)	106.6(9)	Ni(2)	- N(4)	- C(18)	104.1(7)	
Ni(2)	- N(4)	- C(21)	112.0(6)	Ni(2)	- N(4)	- C(22)	114.9(6)	
C(18)	- N(4)	- C(21)	104.2(9)	C(18)	- N(4)	- C(22)	113.6(9)	
C(21)	- N(4)	- C(22)	107.7(8)	O(1)	- C(1)	- C(2)	126.8(8)	
O(1)	- C(1)	- C(4)	112.8(8)	C(2)	- C(1)	- C(4)	124.4(8)	
C(1)	- C(2)	- C(3)	119.5(8)	C(1)	- C(2)	- C(7)	122.3(7)	
C(3)	- C(2)	- C(7)	118.2(7)	O(2)	- C(3)	- C(2)	124.9(7)	
O(2)	- C(3)	- C(5)	113.6(8)	C(2)	- C(3)	- C(5)	121.5(8)	
O(3)	- C(6)	- C(7)	127.2(8)	O(3)	- C(6)	- C(9)	113.8(8)	
C(7)	- C(6)	- C(9)	119.0(8)	C(2)	- C(7)	- C(6)	118.8(7)	
C(2)	- C(7)	- C(8)	118.8(8)	C(6)	- C(7)	- C(8)	122.4(8)	
O(4)	- C(8)	- C(7)	123.4(8)	O(4)	- C(8)	- C(10)	116.8(7)	
C(7)	- C(8)	- C(10)	119.8(7)	N(1)	- C(11)	- C(12)	109.1(8)	
N(2)	- C(12)	- C(11)	109.4(9)					

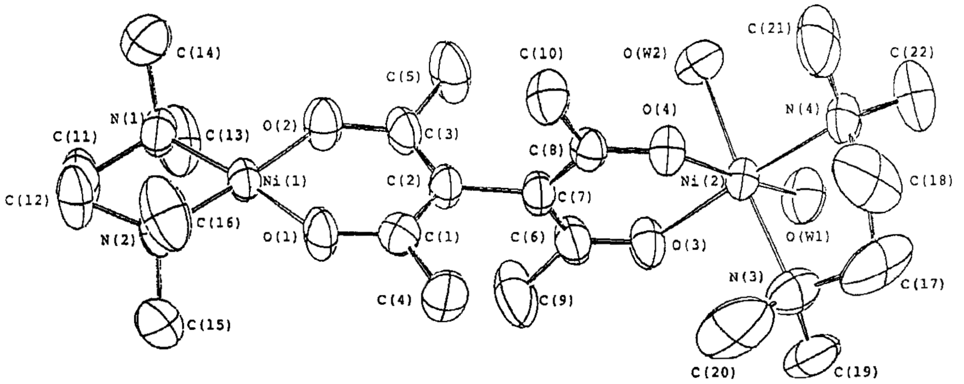
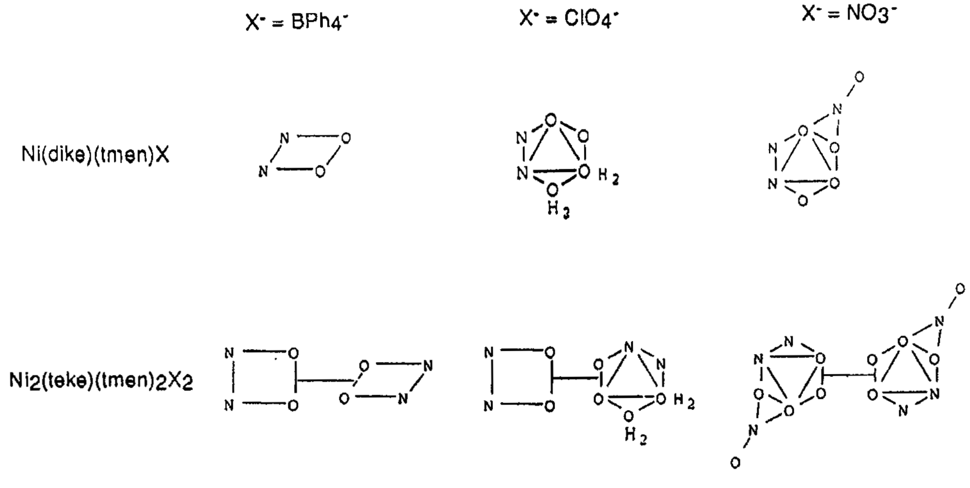


Figure 2 Atomic numbering and the structure of the complex in $Ni_2(taet)(tmen)_2(ClO_4)_2 \cdot 3H_2O$. Thermal ellipsoids are drawn at the 50% probability level. Two counter ions (ClO_4^-) and one water molecule of crystallization are omitted for clarity.

with acac in the tetraketonate ligand. One should also point out that Gutmann's bond length variation rules are clearly revealed, *i.e.*, the Ni-O(taet) bond length of the square planar part (4 coordinate, low spin) is shorter than that of the octahedral part (6 coordinate, high-spin).[21]

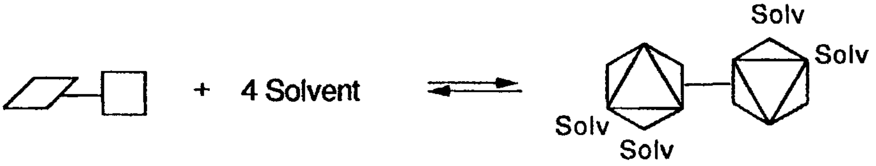
It is also of interest to compare mononuclear mixed ligand complexes such as Ni(acac)(tment)X and Ni(bzac)(tmen)X, where acac=acetylacetonate, bzac = benzoylacetonate, X^- = BPh_4^-, ClO_4^- or NO_3^-, and the corresponding dinuclear ones, as shown in Scheme 1.



Scheme 1 Comparison of the structures of dinuclear complexes obtained with those of the corresponding mononuclear ones in the solid state.

Solvatochromism of dinuclear complexes in solution

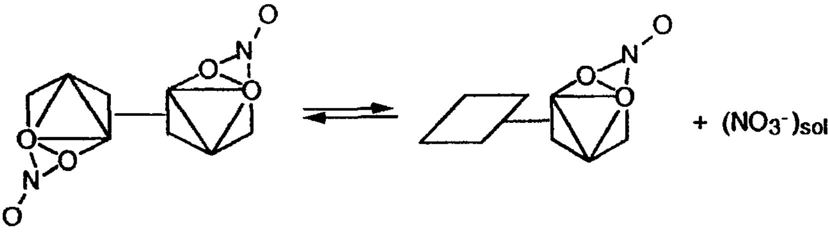
Dinuclear complexes obtained in this study are easily soluble in many organic solvents such as 1,2-dichloroethane (DCE), nitromethane (NM), acetone (Ac), acetonitrile (An), alcohols (ROH), *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), which have different donor and acceptor strengths.[21,22] Figure 3 shows the electronic spectra of $[Ni_2(taet)(tmen)_2](BPh_4)_2$ in DCE, NM, Ac, and DMSO. In an inert solvent like DCE or NM (with very weak donor strength), the spectra (curves 1 and 2, respectively) show only one strong peak in the 20-21 × 10^3 cm^{-1} region, which means that there is only one type of square planar species present in solution. On the other hand, the spectra in a strong donor solvent like DMSO (curve 4) show two bands with rather weak intensities at 10 × 10^3 cm^{-1} and 16 × 10^3 cm^{-1}, which reveals octahedral nickel centres in the system. The equilibrium shown in (*1*) is shifted extremely to the right hand side in this solvent.



$$[Ni_2(tmen)_2(teke)]^{2+} + 4Solvent \rightleftharpoons [Ni_2(tmen)_2(teke)(Solvent)_4]^{2+} \qquad (1)$$

A thermochromic change between octahedral and square planar species can not be observed in such inert and strong donor solvents because of the positions of the equilibrium. The equilibrium (*1*) shifts remarkedly to the left or the right hand side depending upon the donor abilities of the solvent used. For intermediate donor-strength solvents like Ac (curve 3), however, we could obtain an 'in between – equilibrium' between octahedral and square planar species which shows thermochromism: The colour of the solution changes to red on heating and to green on cooling.[23] These thermochromic and solvatochromic properties in solutions are also clearly observable in the corresponding perchlorate complexes.

The absorption spectra of the nitrate complex, $[Ni_2(taet)(tmen)_2(NO_3)_2]$, dissolved in the same solvents, are shown in Fig. 4. In a weak donor solvent like DCE (curve 2), the complex shows the spectra of octahedral species exhibiting two bands at 9.7 × 10^3 and 16.3 × 10^3 cm^{-1} with the latter band being stronger than the former (the ratio of the peak intensities is 2:1). This pattern is very similar to that of the corresponding mononuclear nitrate chelate $[Ni(acac)(tmen)(NO_3)]$.[19] Acetone solutions show also similar behaviour. Although in DMSO (curve 4) the pattern refers also to octahedral species, the positions and intensities are different from those of the nitrate chelates. Obviously the NO_3^- anion dissociates from the central metal ion due to the coordination of the stronger donor DMSO. This is supported by electric conductivity measurements discussed later (Table 6). Curve 1 in Figure 4 corresponds to NM solutions and is similar to the pattern found for the perchlorate in an intermediate donor solvent. In this case, as NM is non-coordinating, this behaviour is explained by the partial dissociation of the NO_3^- ligand due to the acceptor properties of this solvent, solvating the anion (*2*).



$$[Ni_2(tmen)_2(teke)(NO_3)_2] \rightleftharpoons [Ni_2(tmen)_2(teke)(NO_3)]^+ + (NO_3^-)_{solv} \qquad (2)$$

Table 6 gives electric conductivity data for the complexes in four solvents. The standard values of 2:1 electrolytes in respective solvents are shown in the same table, from which it can be seen that the nitrate complexes in NM are dissociated into NO_3^- and the square planar complex to about 10–15%.[24] In DCE or Ac, the nitrate complexes show non-electrolytic behaviour. On the other hand, in very strong donor solvent or solvents with considerable acceptor properties like DMSO the nitrates show anion dissociation. Consequently, solutions of the nitrate complexes were strongly influenced by the donor and acceptor properties of the solvents used. Scheme 2 shows the influence of the respective properties of the solvents (Oh refers to octahedral NO_3^- bidentate coordination and Oh′ means octahedral with two solvent molecules coordinated for differentiating the two

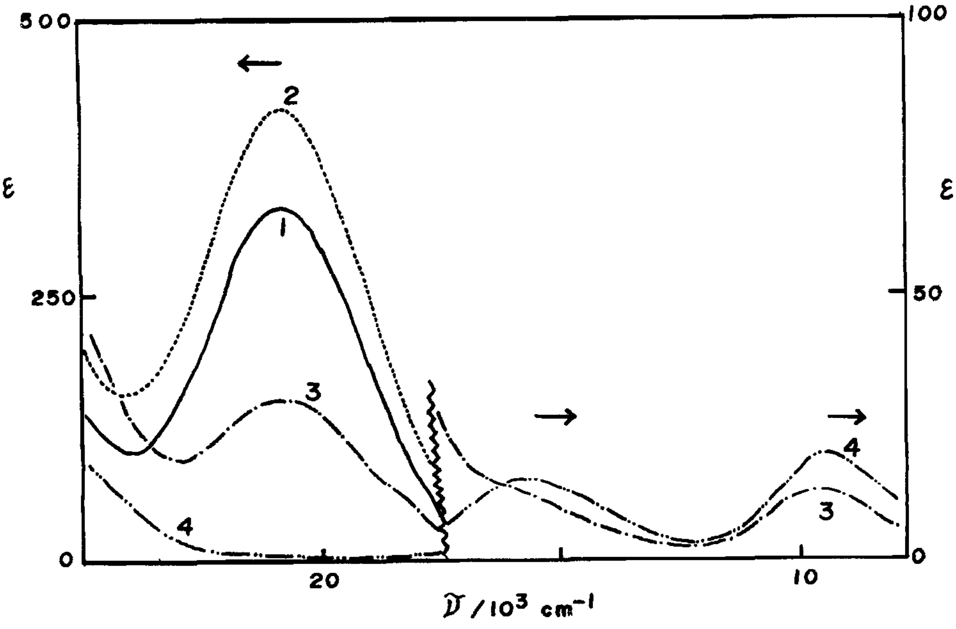


Figure 3 Absorption spectra of $[Ni_2(taet)(tmen)_2](BPh_4)_2$ in various organic solvents at room temperature (25°C); 1 = Nitromethane(NM), 2 = 1, 2-dichloroethane(DCE), 3 = acetone (Ac), 4 = dimethylformamide (DMSO).

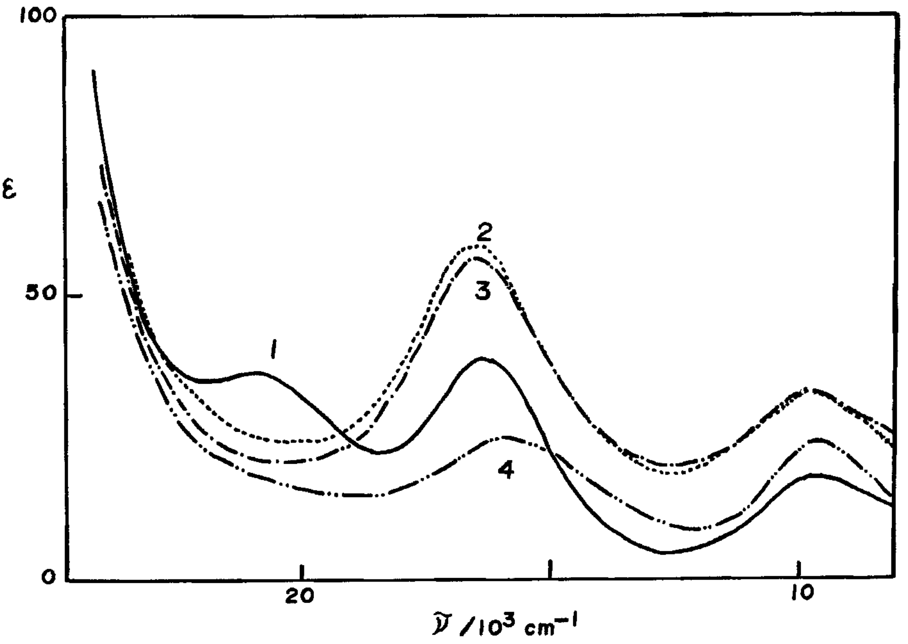
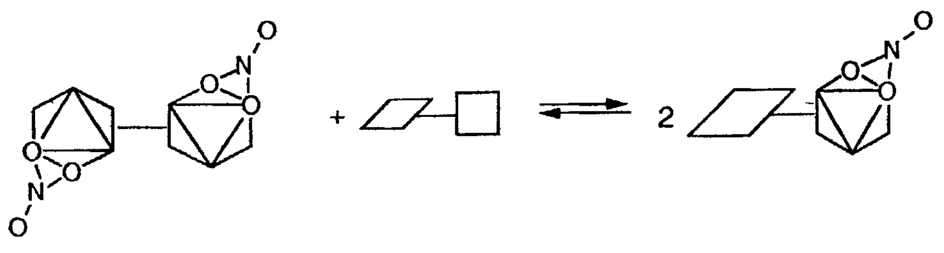


Figure 4 Absorption spectra of $[Ni_2(taet)(tmen)_2(NO_3)_2]$ in various organic solvents at room temperature (25°C); 1 = NM, 2 = DCE, 3 = Ac, 4 = DMSO.

species). Table 7 shows all electronic spectroscopic data for these complexes in four kinds of solvents.

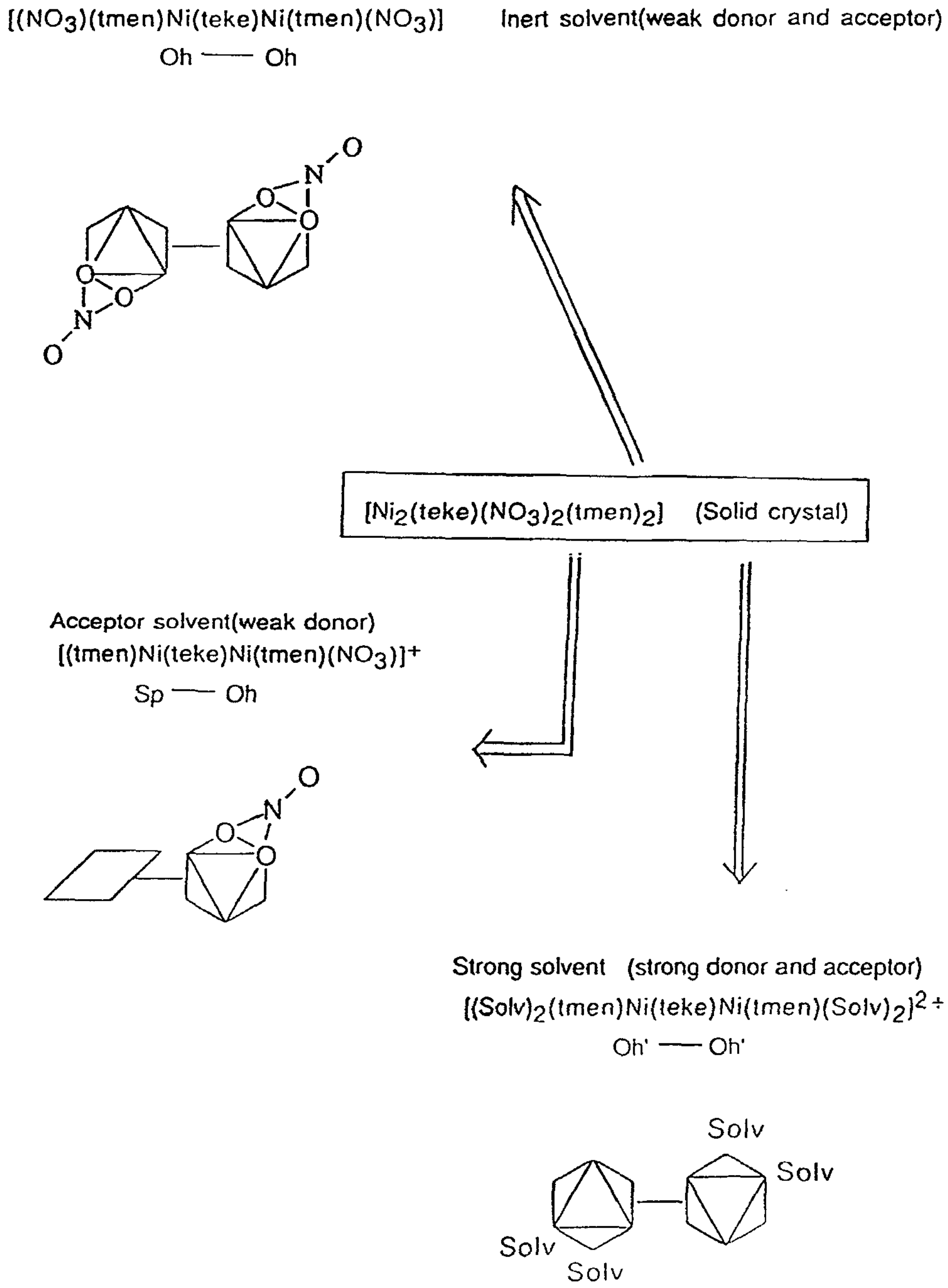
The equilibrium constants of the following equations (*3*)



$$[Ni_2(taet)(NO_3)_2(tmen)_2] + [Ni_2(taet)(tmen)_2]^{2+} \rightleftharpoons 2\,[Ni_2(taet)(NO_3)(tmen)_2]^{+} \quad (3)$$

are found to be 96 ± 3 in DCE.[10] In this solvent no free NO_3^- ions are observed. It is obvious that NO_3^- ion has rather strong coordination properties and the solvent cannot solvate the anion due to the relatively small acceptor and the negligible donor properties of the solvent ($DN_{DCE} = 0$, $AN_{DCE} = 17.6$).

Dinuclear mixed Ni(II) complexes show in part properties similar to those of the monomeric systems. However, the close interrelations between solvent properties,



Scheme 2 Structural changes of $[Ni_2(teke)(tmen)_2(NO_3)_2]$ in various organic solvents.

Table 6 Molar Conductivities of the Complexes in Various Solvents (at 25°C, S cm^2 mol^{-1}).

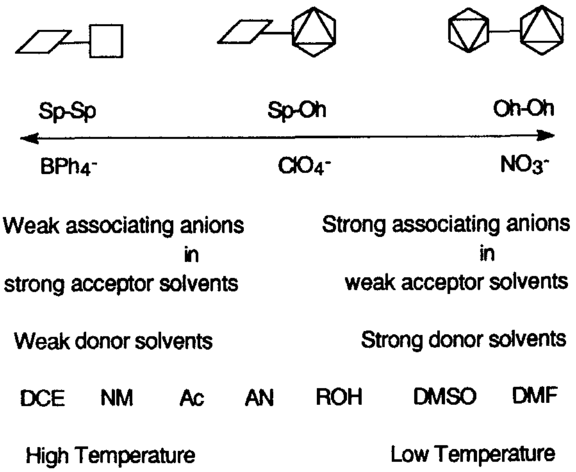
	Solvent			
Complex	NM	DCE	Ac	DMSO
$Ni_2(taet)(tmen)_2(BPh_4)_2$	140	27.0	189	42.2
$Ni_2(taet)(tmen)_2(ClO_4)_2 \cdot 3H_2O$	158	18.4	211	59.1
$Ni_2(taet)(tmen)_2(NO_3)_2$	19.6	0.3	7.0	67.5
$Ni_2(dabe)(tmen)_2(BPh_4)_2$	118	17.5	166	39.4
$Ni_2(dabe)(tmen)_2(ClO_4)_2 \cdot 2H_2O$	172	18.1	245	63.2
$Ni_2(dabe)(tmen)_2(NO_3)_2$	15.6	0.2	5.6	62.0
Standard electrolyte	150–180[a]	10–24[b]	160–200[a]	35[b]

[a]Standard 1:2 electrolytes shown in Ref. 24. [b]Standard 1:1 electrolytes shown in Ref. 24.

Table 7 Spectroscopic Data for the Complexes in various solvents, $\nu_{max}/10^3$ cm^{-1} (ε_{max}/M^{-1} cm^{-1}).

	Solvent			
Complex	NM	DCE	Ac	DMSO
$Ni_2(taet)(tmen)_2(BPh_4)_2$			9.62(12.4)	9.43(20.4)
			16(ca.13)a)	15.70(15.5)
	20.66(330)	20.70(395)	20.80(152)	
$Ni_2(taet)(tmen)_2(ClO_4)_2 \cdot 3H_2O$			9.62(13.7)	9.43(21.9)
			16(ca.15)a	15.73(16.7)
	20.66(349)	20.60(387)	20.80(152)	
$Ni_2(taet)(tmen)_2(NO_3)_2$	9.60(18.1)	9.60(33.9)	9.66(32.9)	9.48(24.2)
	16.30(39.2)	16.30(61.9)	16.30(56.5)	15.87(25.1)
	20.95(36.8)			
$Ni_2(dabe)(tmen)_2(BPh_4)_2$			9.50(14.4)	9.45(18.9)
			16(ca.16)a	15.70(14.7)
	20.80(472)	20.90(514)	ca.20.5(ca.270)a)	
$Ni_2(dabe)(tmen)_2(ClO_4)_2 \cdot 2H_2O$			9.90(24..3)	9.52(21.1)
			ca.16(ca.65)b)	15.80(25.1)
	b	b	b	
$Ni_2(dabe)(tmen)_2(NO_3)_2$	9.70(19.1)	9.60(19.9)	9.60(20.9)	9.40(20.7)
	16.40(42.2)	16.30(40.7)	16.30(43.1)	15.65(17.1)

[a]Shoulder. [b]Obscured by strong absorption of dabe ligand in the near UV region.



Scheme 3 Factors influencing the structure of $[Ni_2(teke)(tmen)_2]^{2+}$.

anion-coordination abilities and temperature dependence of the structures of the described complexes lead us to the conclusion that both donor and acceptor properties of solvents and anions[25] (Table 2) cannot be described by independent parameters. The results support others obtained from the recently defined DN scale for anions as well as the bond length and the bond angle variation rules.[26]

Acknowledgements

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