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## Syntheses, crystal structures and chromotropic properties of Nickel(II) mixed ligand complexes containing *N*-methyl-1,4-diazacycloheptane and various β-diketonates

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#### Abstract

Six complexes, Ni(medach)(dike)X, have been newly obtained, where medach = *N*-methyl-1,4-diazacycloheptane, dike = a  $\beta$ -diketonate such as benzoylacetonate (bzac), dibenzoylmethanate (dibm), X = BPh<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> or dike: Ni(medach)(bzac)(NO<sub>3</sub>) (1a), Ni-(medach)(dibm)(NO<sub>3</sub>) (2a), Ni(medach)(bzac)(BPh<sub>4</sub>) (1b), Ni(medach)(dibm)(BPh<sub>4</sub>) (2b), Ni(medach)(bzac)<sub>2</sub> (1c), Ni(medach)(dibm)<sub>2</sub> (2c). X-ray single crystal structures of the complexes 1a, 2a, 1b and 2c have been determined and the structures of the complexes Ni-(medach)(acac)(NO<sub>3</sub>) (3a) and Ni(medach)(acac)BPh<sub>4</sub> (3b) (acac = acetylacetonate), reported previously, have also been clarified. In the cases of the tetraphenylborate and the nitrate complexes, two types of solvatochromism due to the donor and the acceptor interactions were observed in organic solvents. These spectral behaviors will be discussed in relation to the complex geometry and the donor and acceptor properties of the solvents, and also compared to those of the corresponding complexes containing a linear diamine such as *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (tmen), Ni(tmen)(dike)X.

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#### 1. Introduction

The synthesis of mixed ligand complexes is not a trivial procedure because the formation of homoleptic ligand complexes must be suppressed [1]. In the case of a diamine (diam), nitrogen-donor atoms of the ligand with bulky substituents prevent the stabilization of homoleptic bis- or trisdiamine complexes,  $[M(diam)_2]^{n+}$  or  $[M(diam)_3]^{n+}$ , but the ligand forms a bridging dinuclear  $\mu$ -hydroxo-complex,  $[(diam)M(OH)_2M(diam)]^{n+}$  [2]. On the other hand, a ternary complex has been formed with a suitable combination of ligands, i.e., a sterically demanding ligand (L, the diamine in this case) and a slim one (L', a  $\beta$ -diketonate in this case), the corresponding heteroleptic ligand complex,  $[MLL']^{n+}$ 

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will appear with characteristic properties such as chromotropic and catalytic ones [3]. In accordance with this rule, a number of mononuclear mixed ligand complexes can be prepared using N,N,N',N'-tetramethylethylenediamine (tmen) as the diam and  $\beta$ -diketonates (dike), M(tmen)-(dike)X (X = BPh<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> or dike) [4]. Mixed ligand Ni(II) complexes with  $\beta$ -diketonate and N-alkylated ethylenediamines show a number of interesting properties including solvatochromism or thermochromism [5].

Although macrocyclic polyamines are best characterized as chelating agents for transition metal ions [6], cyclic diamines have not been fully studied. The six-memberedring diamine, piperazine, does not form chelated complexes with the smaller transition metal (3d) ions such as copper(II) and nickel(II) [7]. The seven-membered-ring diamine, 1,4-diazacycloheptane (dach), and the eightmembered-ring diamine, 1,5-diazacyclooctane (daco), were examined as chelating agents for nickel(II) and copper(II),

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which are normally stable planar chelates,  $[M(L)_2]X_2$  [8]. Recently, dach and daco have been alkylated with ethylene sulfide to give a derivative with pendant arms, and then coordinated to the metal [9]. However, the related cyclic diamines have not been studied extensively for mixed chelate complex systems.

In this work, we have obtained new mixed complexes with the medach ligand and some kinds of  $\beta$ -diketonates (dike), Ni(medach)(dike)X, and have determined their crystal structures and the equilibrium constants between a square-planar structure and an octahedral one with coordinated strong donor solvent molecules [10].

### 2. Experimental

#### 2.1. Materials and instrumentation

Nickel(II) nitrate hexahydrate, nickel(II) sulfate hexahydrate, N-methyl-1,4-diazacycloheptane (medach), acetylacetone (Hacac), benzoylacetone (Hbzac), dibenzoylmethane (Hdibm), anhydrous sodium carbonate, sodium tetraphenylborate and N,N,N',N'-tetramethylethylenediamine were purchased from Wako Chemical Co. Ltd. and used without further purification. As the solvents used for spectral measurements 1,2-dichloroethane (DCE), dimethylsulfoxide (DMSO), acetone (ACO) and nitromethane (NM) were used without further purification, all of the solvents were of guaranteed grade for spectral measurements.

Elemental analyses were performed on a Perkin–Elmer 2400 II CHN analyzer. Infrared spectra (400–4000 cm<sup>-1</sup>) were measured with a Perkin–Elmer FT-IR SPECTRUM 2000 using KBr disks. Electronic spectra of the complexes in solution were observed with Shimadzu UV-3100PC UV–VIS Scanning Spectrophotometer using 10 mm quartz cells and concentrations between  $1.0 \times 10^{-3}$  and  $5.0 \times 10^{-3}$  mol dm<sup>-3</sup>, except where mentioned differently in the text. Magnetic susceptibility measurements were performed by the Faraday method with a Shimadzu Torsion Magnetometer MB-100 at room temperature. Electric conductances of the solutions were measured with a Conductivity Outfit Model AOC-10 (Denki-Kagaku-Keiki Co. Ltd.) at  $25 \pm 0.2$  °C.

#### 2.2. Syntheses of chelates

#### 2.2.1. Chelates of the nitrate, $[Ni(medach)(dike)NO_3]$

To an ethanol solution of Ni(NO<sub>3</sub>)<sub>2</sub>  $\cdot$  6H<sub>2</sub>O (5 mmol in 30 cm<sup>3</sup> of ethanol), a mixture of the appropriate β-diketone (5 mmol) and anhydrous sodium carbonate (2.5 mmol) was added. The ligand, medach (5 mmol in 10 cm<sup>3</sup> of ethanol) was added dropwise to the metal-solution with vigorous stirring. After the reaction was complete, the green solution was filtered and concentrated using a rotary evaporator. The crude crystals obtained were recrystallized from DCE to yield bluish-green crystals. Yield: 70–85%.

Ni(medach)(bzac)NO<sub>3</sub> (**1a**). *Anal.* Calc. for  $C_{16}H_{23}N_{3}$ -O<sub>5</sub>Ni: C, 48.52; H, 5.85; N, 10.61. Found: C, 48.54; H, 5.88; N, 10.62%.  $\mu_{eff}$ : 3.12 B.M.

Ni(medach)(dibm)NO<sub>3</sub> (**2a**). *Anal.* Calc. for  $C_{21}H_{25}N_3$ -O<sub>5</sub>Ni: C, 54.92; H, 5.46; N, 9.14. Found: C, 55.06; H, 5.50; N, 9.17%.  $\mu_{eff}$ : 3.02 B.M.

## 2.2.2. Chelates of the tetraphenylborate, $[Ni(medach)(dike)]BPh_4$

The crude nitrate compounds (1 mmol) were dissolved in DCE, and sodium tetraphenylborate (1.5 mmol) was added with stirring and then filtered. During the procedure, the color of the solution changed from green to reddishorange. The crude crystals obtained were recrystallized from DCE to yield orange crystals. They were all diamagnetic. Yield: 70–85%.

Ni(medach)(bzac)BPh<sub>4</sub> (**1b**). *Anal.* Calc. for  $C_{40}H_{43}N_2$ -O<sub>2</sub>BNi: C, 72.14; H, 6.63; N, 4.33. Found: C, 73.54; H, 6.63; N, 4.29%.

Ni(medach)(dibm)BPh<sub>4</sub> (**2b**). *Anal.* Calc. for  $C_{45}H_{45}N_2$ -O<sub>2</sub>Ni: C, 75.51; H, 6.55; N, 3.96. Found: C, 75.55; H, 6.34; N, 3.92%.

## 2.2.3. Chelates of the ternary bis-diketonate, [Ni(medach)(dike)<sub>2</sub>]

 $NiSO_4 \cdot 6H_2O$  was dissolved in a small amount of water and a chloroform solution containing an equimolar amount of medach and two molar amounts of Hdike was added to it in a separatory funnel. Then sodium carbonate was added to the mixture with shaking. After standing for a minute, the chloroform layer was separated from the aqueous solution and evaporated. The crude crystals obtained were recrystallized from DCE to yield bluishgreen crystals. Yield: 70–85%.

Ni(medach)(bzac)<sub>2</sub> (**1c**). *Anal.* Calc. for  $C_{26}H_{32}N_2O_4Ni$ : C, 63.03; H, 6.51; N, 5.66. Found: C, 62.68; H, 6.66; N, 5.63%.  $\mu_{eff}$  for **1c** · DCE: 2.66 B.M.

Ni(medach)(dibm)<sub>2</sub> (**2c**). *Anal.* Calc. for  $C_{36}H_{36}N_2O_4Ni$ : C, 69.81; H, 5.86; N, 4.52. Found: C, 69.72; H, 5.89; N, 4.39%.  $\mu_{eff}$ : 3.20 B.M.

#### 2.3. Equilibrium constants

The equilibrium constants  $(\log \beta)$  defined by Eq. (1) have been determined by a spectrophotometric method (calculation by a least-square method using the data sets from the electronic spectra at constant temperature,  $25 \pm 0.2$  °C). All spectral data, as a function of the total concentrations of the reactants, were computer-fitted to the appropriate equation, depending on the model to be tested. As a result, the equilibrium constants for each species ( $\log \beta$ ) and the molar extinction coefficients ( $\varepsilon_{calc}$ ) for each species in the solution were calculated. The number of points used for the calculation of equilibrium constants was 12 from each data set, which were picked up at every 10 nm wavelength in the range of 530–420 nm.

$$\begin{split} & [\text{Ni}(\text{diam})(\text{dike})]^{+} + 2S \xrightarrow{\beta} [\text{Ni}(\text{diam})(\text{dike})S_{2}]^{+} \\ & \beta = [\text{Ni}(\text{diam})(\text{dike})S_{2}]^{+} / [\text{Ni}(\text{diam})(\text{dike})]^{+}[S]^{2} \end{split} \tag{1}$$

The solvent ligand (S = DMSO) was added to a DCE solution of the respective complex, [Ni(diam)(dike)]BPh<sub>4</sub>.

### 2.4. X-ray crystallography

The measurements for complex 3a were made on a DIP2030K automated diffractometer with graphitemonochromatic Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 298 K. The measurements for complexes 1a, 2a, 1b, 3b, and 2c were made on a MXC03K automated diffractometer with graphite-monochromatic Mo K $\alpha$  radiation ( $\lambda = 0.71073$ Å) at 298 K. The unit cell parameters were determined by the least square method using 22 well-centered reflections for all the complexes. The reflections were corrected for Lorentz and Polarization effects but not for absorption. Every structure was solved by the direct method siR92 [11], and was refined by full matrix least-square techniques SHELXS-97 [12]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters. Crystallographic data and refinement parameters are detailed in Table 1.

## 3. Results and discussion

## 3.1. Synthesis and structure of the complexes, Ni(medach)(dike)X

We obtained eight mixed ligand complexes of the general formula Ni(medach)(dike)X (X = NO<sub>3</sub><sup>-</sup>, BPh<sub>4</sub><sup>-</sup> or

Table 1	
Crystallographi	e data

dike), which are classified into three types: i.e., type  $\mathbf{a} = \text{nitrate complexes, type } \mathbf{b} = \text{tetraphenylborate com-}$ plexes and type  $\mathbf{c} =$  ternary bis-diketonate complexes, and the numbers of the complexes, 1, 2 and 3, mean benzoylacetonate, dibenzovlmethanate and acetvlacetonate, respectively. Magnetic data of these complexes at room temperature are listed in the experimental section, which show the tetraphenylborate complexes are diamagnetic, and the nitrate and bis-dike complexes have values of nearly 3.0 B.M. These data mean that: (a) the Ni(II) coordination geometry in the tetraphenylborate complexes is square-planar with a N2O2 donor set (type b), and (b) those of the nitrate complexes (type  $\mathbf{a}$ ) and the ternary bis-dike complexes (type c) are octahedral with a N2O4 donor set.

Among these complexes we obtained six good single crystals for X-ray diffraction analysis, complexes 1a, 2a, 3a, 1b, 3b and 2c, whose crystal structures have been determined. For two acac-complexes, 3a and 3c, which were previously reported [10], the structures are clarified in this work. The ORTEP plots of complexes 1a, 1b and 2c as examples are depicted in Figs. 1-3, with the atom numbering scheme. Selected bond distances and angles are given in Table 2.

## 3.1.1. Structure of [Ni(medach)(bzac)NO<sub>3</sub>] (1a, type a)

Complex 1a crystallizes in the monoclinic space group  $P2_1/c$ . The nickel atom is coordinated to give an octahedral geometry with two N atoms of the bidentate medach ligand, two O atoms of the bidentate bzac ligand and

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	1a	$2a \cdot DCE$	3a	1b	3b · ACO	2c
Empirical formula	C <sub>16</sub> H <sub>23</sub> N <sub>3</sub> O <sub>5</sub> Ni	C23H29N3O5NiCl2	C <sub>11</sub> H <sub>21</sub> N <sub>3</sub> O <sub>5</sub> Ni	C40H43BN2O2Ni	C38H47BN2O3Ni	C <sub>36</sub> H <sub>36</sub> N <sub>2</sub> O <sub>4</sub> Ni
Formula weight	396.09	557.12	334.02	653.32	649.30	619.40
Crystal dimensions	$0.50 \times 0.30 \times 0.25$	$0.40 \times 0.35 \times 0.30$	$0.35 \times 0.25 \times 025$	$0.35 \times 0.30 \times 0.20$	$0.35 \times 0.30 \times 0.20$	$0.40 \times 0.25 \times 0.20$
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\overline{1}$	C2/c
$T(\mathbf{K})$	298	298	298	298	298	298
a (Å)	11.026(4)	8.230(4)	13.1740(10)	17.953(7)	9.712(3)	22.920(10)
b (Å)	13.818(5)	11.940(10)	15.3210(10)	10.790(3)	13.411(4)	8.876(5)
c (Å)	14.865(9)	13.54(2)	7.7830(10)	18.666(4)	13.50(2)	18.160(10)
α (°)	90	92.00(10)	90	90	94.23(5)	90
β (°)	127.66(6)	105.71(5)	106.894(3)	109.61(2)	91.37(5)	119.37(5)
γ (°)	90	95.97(5)	90	90	95.31(2)	90
$V(\text{\AA}^3)$	1793.0(15)	1271.(2)	1503.1(2)	3406.(2)	1745.(2)	3219.(3)
Ζ	4	2	4	4	2	4
$D_{\rm c} ({\rm Mg}{\rm m}^{-3})$	1.467	1.456	1.476	1.274	1.125	1.278
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
$\mu (\mathrm{mm}^{-3})$	1.11	1.01	1.31	0.61	0.59	0.64
Reflections collected	4475	6090	3344	8501	7699	3932
Independent reflections	3858	5839	3166	8241	7402	2816
Reflections used	3741 ( $I > 2\sigma$ )	4919 ( <i>I</i> > 3 <i>σ</i> )	3043 ( $I > 2\sigma$ )	5366 ( $I > 3\sigma$ )	4657 ( $I > 3\sigma$ )	2256 ( $I > 2\sigma$ )
$R^{\mathrm{a}}$	0.0529	0.070	0.0468	0.064	0.055	0.0901
$R_w^{b}$	0.1559	0.135	0.1349	0.085	0.074	0.2437
S (fit on F)	1.028	1.349	1.038	1.644	1.337	1.097

<sup>a</sup> 
$$R = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|.$$

<sup>b</sup> 
$$R = [(\sum_{w} (||F_{o}| - |F_{c}||)^{2} / \sum |F_{o}|^{2})^{1/2}]$$



Fig. 1. ORTEP diagram of the complex  $[Ni(medach)(bzac)NO_3]$  (1a). Thermal ellipsoids are at 50% probability.

two O atoms of the bidentate NO<sub>3</sub> ligand as shown in Fig. 1. The angles O(1)–Ni(1)–N(3), O(2)–Ni(1)–O(3), O(4)–Ni(1)–N(2), O(1)–Ni(1)–O(2), O(3)–Ni(1)–O(4), and N(3)–Ni(1)–N(2) are 173.97°, 158.68°, 160.11°, 91.00°, 59.92° and 76.60°, respectively. The bite angle of the NO<sub>3</sub> ligand to the metal center is too narrow and the bond lengths of Ni(1)–O(3) 2.167 Å and Ni(1)–O(4) 2.173 Å are rather longer than those of the Ni–O(bzac) (Ni(1)–O(1) = 2.009, Ni(1)–O(2) = 2.003 Å). The structural strain



Fig. 2. ORTEP diagram of the complex  $[Ni(medach)(bzac)]^+$  (1b). Thermal ellipsoids are at 50% probability.



Fig. 3. ORTEP diagram of the complex  $[Ni(medach)(dibm)_2]$  (2c). Thermal ellipsoids are at 50% probability.

of the ligand NO<sub>3</sub> affects the easy dissociation of the NO<sub>3</sub> ligand from the coordination sphere in acceptor or strong donor solvents. Another structural interest is that the axial bonds Ni(1)–O(2) and Ni(1)–O(3) are repelled by the cyclic medach ligand, which means that the angle O(2)–Ni(1)–O(3) 158.68° is smaller than the other equatorial *trans*-bonds. This interligand repulsion between medach and the axial donor atoms (NO<sub>3</sub>) may reflect the another reason for the weakened coordination ability of the NO<sub>3</sub> ligand. The structures of **2a** and **3a** show also similar structural properties as explained in this case of **1a**.

### 3.1.2. Structure of [Ni(medach)(bzac)]BPh<sub>4</sub> (1b, type b)

Complex **1b** crystallizes in the monoclinic space group  $P2_1/c$ . As shown in Fig. 2, the nickel atom is coordinated with medach and bzac to give a square-planar geometry and the uncoordinating anion BPh<sub>4</sub><sup>-</sup>. The N2O2 donor set from medach and bzac and the central Ni atom are located on the same plane. If we compare these metal-ligand bond distances and their bite angles with those of

Table 2									
Selected	bond	lengths (Å	) and	angles	(°) for	complexes	1a, 1	<b>b</b> and	2c

	1a	1b		2c
Ni(1)-O(1)	2.009(3)	1.819(3)	Ni(1)-O(3)	2.01(14)
Ni(1)–O(2)	2.003(3)	1.831(3)	Ni(1)-O(4)	2.05(14)
Ni(1)–N(2)	2.093(4)	1.936(4)	Ni(1) - N(2)	2.14(14)
Ni(1) - N(3)	2.093(3)	1.887(4)		
Ni(1)–O(3)	2.167(3)			
Ni(1)–O(4)	2.173(3)			
O(1)–Ni(1)–O(2)	91.00(11)	95.80(14)	O(3)-Ni(1)-O(4)	88.(6)
N(2)–Ni(1)–N(3)	76.60(14)	81.3(2)	N(2)-Ni(1)-N'(2)	76.(5)

the corresponding octahedral nitrate complex **1a**, this planar complex has shorter bond lengths Ni–O(bzac) 1.819 and 1.831 Å and Ni–N(medach) 1.936 and 1.887 Å and wider bite angles O(1)–Ni(1)–O(2) 95.80 and N(2)–Ni(1)– N(3) 81.3° than those of the octahedral complex. In this planar complex, the tertiary N-donor of medach coordinates more weakly to the metal center than the secondary N–M bond. The chelate angle of medach in this square-planar mixed complex is almost the same as the angle in the bis-dach square-planar homoleptic complex, [Ni(dach)<sub>2</sub>]-Cl<sub>2</sub> · 2H<sub>2</sub>O 82.2° [13]. It means that the chelate angle of the cyclic dach ligand was determined by the rigid conformation of the ligand and the same metal-ligand bond length. The crystal structure of **3b** show also same geometry as **1b**.

#### 3.1.3. Structure of $[Ni(medach)(dibm)_2]$ (2c, type c)

Complex 2c crystallizes in the monoclinic space group C2/c. As shown in Fig. 3, the nickel atom is coordinated to give an octahedral geometry with two N atoms of the bidentate medach ligand and four O-donor atoms from two bidentate dibm ligands, forming the non-charged complex. The medach ligand in the structure is disordered and the structural data is not so well refined. The characteristic properties of this type of complex in the solid state shows the plasticity of the non-charged weak intermolecular interaction in the case of ternary bis-hexafluoroacetylacetonate (hfac), [M(tmen)(hfac)<sub>2</sub>] [14]. Due to the very weak intermolecular interaction in this crystal, the diamine (medach) moiety of the complex can easily move position at the temperature for this X-ray crystal determination. Therefore, we could not determine the position of medach ligand with certain accuracy. For the complex 1c, a good single crystal for X-ray analysis could not be obtained.

## 3.2. Solvatochromic behavior with the structure change of the complexes in solution

# 3.2.1. Electric conductivity data of the chelates in various solvents

Table 3 gives the electrical conductivity data at room temperature for the complexes in some organic solvents with different donor numbers (DN) and acceptor numbers (AN) [15]. The standard values of 1:1 electrolytes in the respective solvents are shown in the same table [16]. It

Table 3			
Molar conductivity (ohm <sup>-1</sup>	$\rm cm^2  mol^{-1}$	at $25 \pm 0.2$	2 °C)

	DCE	NM	DMSO	ACO
Ni(medach)(bzac)NO <sub>3</sub> (1a)	0.13	7.65	23.43	2.13
Ni(medach)(dibm)NO <sub>3</sub> (2a)	0.07	7.55	22.91	1.54
Ni(medach)(acac)NO <sub>3</sub> (3a)	0.13	9.26	24.41	1.49
Ni(medach)(azac)BPh <sub>4</sub> (1b)	11.91	42.10	11.49	6.31
Ni(medach)(dibm)BPh <sub>4</sub> ( <b>2b</b> )	11.04	44.08	12.96	7.18
Ni(medach)(acac)BPh <sub>4</sub> (3b)	12.95	36.45	10.69	3.89
$Ni(medach)(dibm)_2$ (2c)	0.072	2.66	0.96	0.003
1:1 Electrolytes [16]	10–24	75–95	35	100-140

can be seen from the table that the ionization of  $NO_3^$ from the complexes in NM is about 10%, which indicates partial dissociation into the  $NO_3^-$  anion and the cationic planar complex,  $[Ni(medach)(dike)]^+$ . In DCE or ACO, the nitrate complexes show almost non-electrolytic behavior, which means that the species in solution is the same as that of the solid state. On the other hand, in a very strong donor solvent like DMSO, the conductivity data show that the nitrate complexes are almost 1:1 electrolytes. Consequently the nitrate complexes are strongly influenced by the respective (donor and acceptor) properties of the solvents for coordination and dissociation of the  $NO_3^$ ion. These data support the following section on spectral chromotropic behaviors (Scheme 1).

### 3.2.2. The nitrate complexes [Ni(medach)(dike)NO<sub>3</sub>] (type **a**)

Fig. 4 shows the typical electronic absorption spectra of the nitrate complex **1a** in various organic solvents. These spectra were measured at room temperature in DCE, NM, ACO and DMSO. In Table 4, all of the spectral data for the complexes in these solvents are summarized.

The spectra in DCE and ACO have nearly the same pattern, showing two bands corresponding to the similar spectral pattern of octahedral complexes (Eq. (2)). The anomaly of the spectra is their intensity, which means that the intensity of the first band, at ca.  $10 \times 10^3$  cm<sup>-1</sup>, is nearly half of that of the second band,  $16.5 \times 10^3$  cm<sup>-1</sup>. It is probably due to the existence of the bidentate nitrate ion, i.e., the deformation from a regular octahedral structure and the smaller four membered chelate ring of the NO<sub>3</sub> ligand. On the other hand, in the case of DMSO although the spectra also show octahedral bands, the spectral profile is different from that in DCE, especially the intensity profile is drastically changed. The electric conductivity data mentioned above also support that the complexes in DCE or ACO are non-charged octahedral with the coordination of NO<sub>3</sub>, while those in DMSO are 1:1 electrolytes and octahedral with the coordination of the solvent molecules (Eq. (3)). In NM, with intermediate acceptor and poor donor properties, the nitrate ion is partially dissociated from the octahedral complex and gives square-planar spectra (Eq. (4)), which shows a new solvatochromism.

$$[Ni(medach)(dike)(NO_3)] \rightarrow [Ni(medach)(dike)(NO_3)] (2)$$
  
[Ni(medach)(dike)(NO\_3)] + 2DMSO

$$\rightarrow [Ni(medach)(dike)(DMSO)_2]^+ + NO_3^-$$
(3)  
[Ni(medach)(dike)(NO\_3)]  $\rightarrow [Ni(medach)(dike)]^+ + NO_3^-$ 

(4)

3.2.3. The tetraphenylborate complexes [Ni(medach)(dike)]BPh<sub>4</sub> (type **b**)

Fig. 5 shows the typical electronic absorption spectra of the tetraphenylborate complex **1b** in various organic solvents. These spectra were measured at room temperature in DCE, NM, ACO and DMSO. In Table 4, all of the



Scheme 1. Solid structure and solvatochromic behaviors of the complexes in solution.

spectral data for the complexes in these solvents are summarized. In non-coordinated solvents like DCE or NM, the spectra are similar to those of the square-planar species reported earlier [17]. Also in an intermediate coordinating solvent like ACO, they are dissolved as predominantly square-planar species. This is critically different from similar complexes with linear chain diamines, such as tmen, in which the complexes exist as an equilibrium mixture of the square-planar and octahedral species (Eq. (5)). This is a characteristic property of the cyclic diamine. In a strong donor solvent like DMSO, the spectra indicate that the only species in solution is octahedral (Eq. (6)).



Fig. 4. UV-Vis absorption spectra of [Ni(medach)(bzac)NO<sub>3</sub>] (1a).

$$2[Ni(medach)(dike)]BPh_4 + 2S \rightarrow [Ni(medach)(dike)(S)_2]^+$$

$$+ [Ni(medach)(dike)]^{+} + 2BPh_{4}^{-}$$
(5)

$$[Ni(medach)(dike)]BPh_4 + 2DMSO$$

$$\rightarrow [Ni(medach)(dike)(DMSO)_2]^+ + 2BPh_4^-$$
(6)

## 3.2.4. The ternary bis-diketonato complexes, [Ni(medach)(dike)<sub>2</sub>] (type c)

In any kind of solvent, these ternary bis-dike complexes do not show any solvatochromism, which means the spectra in all of the solvents used are similar and any solvent coordination could not be observed.

It is noteworthy that the chelates are very soluble in various organic solvents with high concentrations, which means that there are weak intermolecular interactions in the crystal. As already known for the structure of Ni-(acac)<sub>2</sub>, the chelate is rather insoluble in organic solvents and it is not mononuclear but the trinuclear  $[Ni_3(acac)_6]$ [18], in which each nickel(II) center is octahedral (other kinds of diketonate chelates also show similar structures). The homoleptic trinuclear,  $[Ni_3(dike)_6]$  is dissociated into the heteroleptic mononuclear,  $[Ni(medach)(dike)_2]$ , by the addition of the diamine (medach) (Eq. (7)).

$$[Ni_3(dike)_6] + 3medach \rightarrow 3[Ni(medach)(dike)_2]$$
(7)

The resultant mononuclear mixed chelates, with very bulky substituent groups on each diamine and diketonate, show very high solubility in various organic solvents, which

Table 4					
Wave numbers $(V_{\text{max}} \times 10^3 \text{ cm}^{-1})$	) and molar absorption coefficient (a	$\varepsilon_{\rm max}/\times 10^3  {\rm mol}^{-1}  {\rm d}$	$m^3 cm^{-1}) o$	f the d–d transition	band (at 25 °C)

	DCE	NM	DMSO	ACO
Ni(medach)(acac)NO <sub>3</sub>	9.98(12.64)	10.01(10.90)	9.57(12.89)	9.98(12.26)
	16.56(18.86)	16.57(16.10)	15.61(7.75)	16.50(17.72)
		21.28(21.03)		
Ni(medach)(bzac)NO <sub>3</sub>	10.00(12.74)	10.10(11.66)	9.60(13.23)	10.05(12.43)
	16.57(19.35)	16.58(18.52)	15.63(8.78)	16.52(18.95)
Ni(medach)(dibm)NO <sub>3</sub>	10.04(12.71)	10.09(11.54)	9.63(13.37)	10.02(12.21)
	16.57(19.83)	16.63(18.05)	15.75(9.59)	16.53(18.61)
Ni(medach)(bzac)BPh <sub>4</sub>	21.10(151.7)	21.14(127.9)	9.56(11.15)	21.14(123.9)
			15.58(6.33)	、 <i>、 、</i>
Ni(medach)(bzac)BPh <sub>4</sub>	21.21(211.0)	21.28(211.7)	9.60(13.18)	21.23(187.2)
			15.63(8.26)	、 <i>、 、</i>
Ni(medach)(dibm)BPh <sub>4</sub>	21.12(164.4)	21.19(169.6)	9.56(14.13)	21.14(162.1)
	· · · · ·	× ,	15.64(7.94)	,
Ni(medach)(dibm) <sub>2</sub>	9.72(15.17)	9.77(14.58)	9.72(14.30)	9.70(14.14)
	16.45(18.15)	16.37(16.87)	16.35(17.34)	16.42(17.89)



Fig. 5. UV–Vis absorption spectra of  $[Ni(medach)(bzac)]BPh_4$  (1b). The left axis is for DMSO solution and the right axis is for DCE, NM and ACO solutions.

means the mixed chelates have hydrophobic properties and weak intermolecular interactions.

#### 3.3. Equilibrium constants

Fig. 6 shows an example of the spectra obtained in the course of the titration procedure of [Ni(medach)(bzac)]-BPh<sub>4</sub> in DCE solution. The absorption maximum of the square-planar species decreases on addition of donor solvent, DMSO, and the absorption band of the octahedral species in the region between 570 and 600 nm increases. A titration procedure can be used to evaluate formation constants. Equilibrium constants (log  $\beta$ ) according to the reaction are given in Table 5.

The d-d band positions and the corresponding molar absorption coefficients are shifted by a change in the sub-

stituents at the diamine ligand. On the other hand, an increase in equilibrium constants of these complexes can be seen with increasing electron-withdrawing and decreasing electron-releasing effects of the substituent group on the  $\beta$ -diketonate ligand; dibm > bzac > acac.

The medach complexes prefer the square-planar geometry to the octahedral geometry. The steric hindrance to axial coordination at the N-donor atoms appears to be much smaller for tmen complexes than the corresponding medach complexes.

#### 4. Conclusion

We have obtained six new mixed chelate complexes with the ligand bzac or dibm as a  $\beta$ -diketonate, medach and three kinds of monoanion, nitrate, tetraphenylborate or



Fig. 6. Spectral changes of [Ni(medach)(bzac)]BPh<sub>4</sub> (**1b**) with the addition of DMSO ligand: (a) square-planar spectral decrease and (b) octahedral spectral increase. The initial concentration of the complex in DCE solution was  $8.0 \times 10^{-3}$  mol dm<sup>-3</sup> (initial amount of solution: 20 ml) and the light path was 1 cm. The solution was titrated with DMSO–DCE solution ( $8.0 \times 10^{-1}$  mol dm<sup>-3</sup>). Ratios of DMSO/complex are 0, 0.25, 0.50, 0.70, 1.00, 1.35 and 1.85 ((a) spectral curves from top to bottom; (b) those from bottom to top, respectively).

Table 5 Stability constants  $(\log \beta) \pmod{-1} dm^3$ 

[Ni(medach)(dike)]BPh <sub>4</sub>	[Ni(tmen)(dike)]BPh4
$2.32\pm0.01$	$4.50\pm0.01$
$3.04\pm0.01$	$5.20\pm0.02$
$3.13\pm0.02$	$5.31\pm0.01$
	[Ni(medach)(dike)]BPh <sub>4</sub> 2.32 $\pm$ 0.01 3.04 $\pm$ 0.01 3.13 $\pm$ 0.02

one more  $\beta$ -diketonate, and have determined their crystal structures. These complexes are classified as three categories, type a (octahedral with a bidentate nitrate coordination), type **b** (square-planar with tetraphenylborate as a counter anion) and type **c** (octahedral with two  $\beta$ -diketonate ligands). Type a complexes show solvatochromic behavior due to the change of acceptor property of the solvents. Type **b** complexes show another type of solvatochromism due to the change of donor properties of the solvents. Type c complexes are inert stable octahedral complexes without any chromotropic behavior in various solvents. The medach ligand in the mixed chelate [Ni(dike)- $(medach)^{\dagger}$  has a much stronger influence on the axial coordination of the donor solvents, which means that the series of the medach mixed ligand system exist as the more stable square-planar structure in comparison to the complexes of the linear N-alkylated diamines, such as the tmen analogue.

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#### Appendix A. Supplementary material

CCDC 208117, 212342, 207923, 212341, 208119, and 208118 contain the supplementary crystallographic data for **1a**, **2a**, **3a**, **1b**, **3b**, and **2c**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam. ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly. 2006.11.003.

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