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halides (iodide and bromide) with lithium metal is believed to occur *via* a radical intermediate at least some extent, and this observation provides the first spectroscopic evidence of a radical nature of an intermediate produced by single electron transfer (SET) pathway[7] in the reaction of an ethyl halides with lithium metal.

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## Template Synthesis of Nickel(II) Complexes with Dianionic BenzoN4 Macrocycles

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During a series of studies of tetraaza[14]annulene[1] nickel

(II) complex A, the macrocyclic complex obtained by template condensation of 1,2-phenylenediamine with 2,4-pentanedione in the presence of nickel(II) ion first described by Jäger,[2] a large number of macrocyclic complexes based on the macrocyclic complex A framework were synthesized and characterized.[3~5]

A
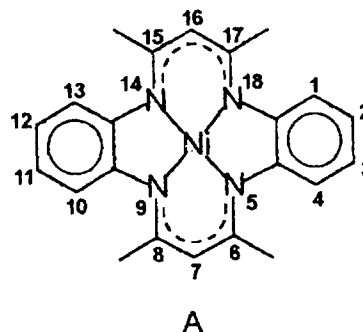
Tetraaza[14]annulene metal complexes have a number of structural features in common with the porphyrins[6,7] and the complexes have also received much attention as catalysts, and as precursors for electrically conductive polymers.[8] However, most macrocyclic complexes[9~12] obtained by Jäger method were symmetrical macrocyclic complexes which were formed from two molecules of diamine and two molecules of β-diketone.

In this paper, we report the synthesis of the new nickel(II) complexes with dianionic benzoN4 macrocycles, 2,4,9,11-tetramethyl-1,5,8,12-(benzo)tetraazacyclotetradecinato(2-)nickel (II) (**1a**), 2,4,10,12-tetramethyl-1,5,9,13-(benzo)tetraazacyclopentadecinato(2-)nickel(II) (**1b**), 2,4,9,11-tetramethyl-1,5,8,12-(14-nitrobenzo)tetraazacyclotetradecinato(2-)nickel(II) (**2a**) and 2,4,10,12-tetramethyl-1,5,9,13-(14-nitrobenzo)tetraazacyclopentadecinato(2-)nickel(II) (**2b**), by the template condensation of a 1:1 mixture of the appropriate phenylenediamine(*e.g.*, 1,2-phenylenediamine and 4-nitro-1,2-phenylenediamine) and alkyldiamine (*e.g.*, ethylenediamine and propylenediamine) with 2,4-pentanedione in the presence of nickel(II) salt. The spectroscopic properties of the nickel(II) macrocyclic complexes **1a**, **1b**, **2a** and **2b** shown in Figure 1 are also discussed.

Experimental

Measurement

Infrared spectra of the complexes were recorded as disks in KBr on a Perkin-Elmer 1430 IR spectrophotometer. [1]H (300 MHz) and [13]C (75.5 MHz) spectra were recorded with a Bruker instrument in $CDCl_3$ with TMS as an internal reference. Elemental analyses were performed by Kolon R & D center. Electronic absorption spectra were obtained on a Shimadzu UV-265 spectrophotometer.

Synthesis

All reagents and solvents used were of analytical grade. **2,4,9,11-tetramethyl-1,5,8,12-(benzo)tetraazacyclotetradecinato(2-)nickel(II)** (**1a**). The complex was prepared by a modification of the procedure described by Jäger[2] and Cameron.[13]

2,4-Pentanedione (0.04 mol, 4 g) was added to the methanol (50 mL) solution of nickel(II) acetate tetrahydrate (0.02
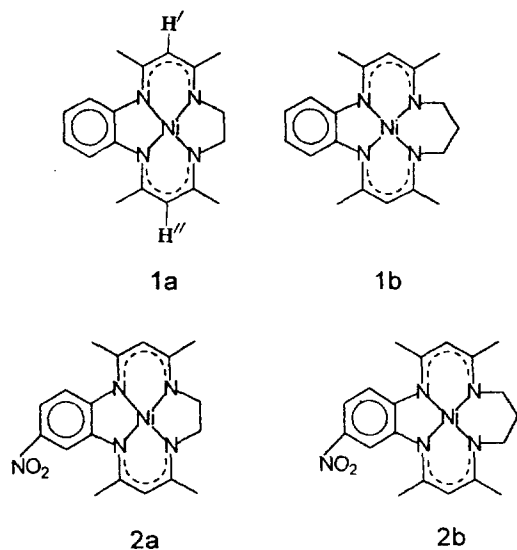
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Figure 1. Chemical structures of nickel(II) complexes with dianionic benzoN₄ macrocycles.

Table 1. ¹H NMR Data for the **1a, 1b, 2a** and **2b**.[a]

Compound	Methyl	Ethylene N-CH₂-	Propylene -CH₂-	Propylene N-CH₂-	Methine	Aromatic
1a	2.05(s)	3.35(s)			5.03(s)	6.68-7.28(m)
	2.38(s)					
1b	2.07(s)		2.32(m)	2.81(t)	4.88(s)	6.61-6.85(m)
	2.10(s)					
2a	2.11(s)	3.41(s)			5.16(s)	7.10-8.10(m)
	2.39(s)	3.42(s)			5.24(s)	
	2.46(s)					
2b	1.95(s)		2.33(m)	2.95(m)	4.93(s)	6.78-7.68(m)
	1.96(s)				5.05(s)	
	2.11(s)					
	2.14(s)					

[a]Chemical shifts in ppm from internal TMS. Measured in chloroform-d. Multiplicity of a proton signal is given in parentheses after δ-value: s=singlet, t=triplet, m=multiplet.

mol, 5 g). To the hot (60 °C) mixture was added 1,2-phenylenediamine (0.02 mol, 2.2 g) and ethylenediamine (0.02 mol, 1.2 g). The solution was refluxed until precipitation of the product was complete. The hot solution was filtered, washed with hot methanol, and air-dried. The product was recrystallized from methanol-dichloromethane (1 : 1) mixture. Yield: 42% Calcd for $C_{18}H_{22}N_4Ni$: C, 61.24; H, 6.24: N, 15.88. Found: C, 60.86; H, 6.31; N, 15.65%. IR (KBr, cm⁻¹): 1564, 1525 (diiminate), 746 (aromatic). UV-vis. (ε) in CHCl₃, nm: 347 (24700), 547 (3020).

2,4,10,12-tetramethyl-1,5,9,13-(benzo)tetraazacyclopentadecinato(2-)nickel(II) (1b). This complex was prepared by the procedure described above for the complex **1a**, except propylenediamine was used instead of the ethylenediamine. Yield: 40%. Calcd for $C_{19}H_{24}N_4Ni$: C, 62.18; H, 6.54: N, 15.27. Found: C, 61.85; H, 6.72; N, 15.03%. IR (KBr, cm⁻¹): 1551, 1532 (diiminate), 737 (aromatic). UV-vis. (ε) in CHCl₃, nm: 379 (22800), 569 (2190).

2,4,9,11-tetramethyl-1,5,8,12-(14-nitrobenzo)tetraazacyclotetradecinato(2-)nickel(II) (2a). This complex was also prepared by the procedure described above for the complex **1a**, except 4-nitro-1,2-phenylenediamine was used instead of the 1,2-phenylenediamine. Yield: 35%. Calcd for $C_{18}H_{21}N_5O_2Ni$: C, 54.31; H, 5.31: N, 17.59. Found: C, 54.18; H, 5.45; N, 17.26%.

IR (KBr, cm⁻¹): 1566, 1525 (diiminate), 765 (aromatic). UV-vis. (ε) in CHCl₃, nm: 399 (19600), 452 (12600), 526 (11200).

2,4,10,12-tetramethyl-1,5,9,13-(14-nitrobenzo)tetraazacyclopentadecinato(2-)nickel(II) (2b). This complex was prepared by the same procedure used for the complex **2a**, except propylenediamine was used instead of the ethylenediamine. Yield: 36%. Calcd for $C_{19}H_{23}N_5O_2Ni$: C, 55.38; H, 5.62: N, 16.99. Found: C, 55.62; H, 5.32; N, 16.56%. IR (KBr, cm⁻¹): 1560, 1529 (diiminate). 761 (aromatic). UV-vis. (ε) in CHCl₃, nm: 401 (20200), 473 (14600), 573 (7730).
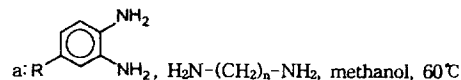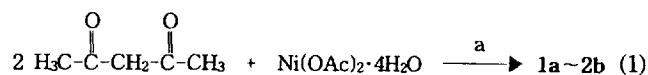
Results and Discussion

The new nickel(II) macrocyclic complexes **1a, 1b, 2a** and **2b** were synthesized according to eq. 1.

$$2\ H_3C-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3\ +\ Ni(OAc)_2\cdot 4H_2O\ \xrightarrow{\ a\ }\ \textbf{1a}\sim\textbf{2b}\ (1)$$

a: R—(benzene ring)—NH₂ / NH₂, H_2N-$(CH_2)_n$-NH_2, methanol, 60 °C

1a: R=H, n=2   **1b**: R=H, n=3   **2a**: R=NO₂, n=2   **2b**: R=NO₂, n=3

Template condensation of a 1 : 1 mixture of 1,2-phenylenediamine and ethylenediamine with 2,4-pentanedione in the presence of nickel(II) ion gave **1a**. By similar procedure, **1b**, **2a** and **2b** were synthesized from 1,2-phenylenediamine and propylenediamine, 4-nitro-1,2-phenylenediamine and ethylenediamine, and 4-nitro-1,2-phenylenediamine and propylenediamine, respectively. We have also synthesized other nickel(II) complexes with dianionic benzoN₄ macrocycles with chloro and methyl substituent on the phenyl ring using the method described in eq. 1 and the study of the substituent effect on the properties of the macrocyclic complexes is in progress.

We characterized the spectral properties of the new complexes **1a, 1b, 2a** and **2b** by means of UV-visible, infrared, ¹H and ¹³C NMR spectroscopy. The electronic absorption spectral data for **1a, 1b, 2a** and **2b** are given in the experimental section. The absorption bands ranging from 347 to 573 nm are reasonably attributed to π→π* transitions within a ligand molecule and charge transfer (CT) transitions from metal to ligand since the molar extinction coefficients of the bands (2190-24700 M⁻¹cm⁻¹) are much larger than those commonly assigned to ligand-field transitions.[14] The ligand-field bands were not assigned for the present complexes, because all the ligand-field bands were obscured by intense π→π* and CT transition bands.

Significant absorptions in the infrared spectra of **1a, 1b, 2a** and **2b** correspond to the C=C and C=N stretching vibra-

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Table 2. ^{13}C NMR Data for the **1a, 1b, 2a** and **2b.**^{a}

Comp.	Methyl	Ethylene N-$\underline{C}$-	Propylene -C-$\underline{C}$-C-	Propylene N-$\underline{C}$-	Methine	Aromatic		Diiminate
1a	20.29	52.65			103.86	119.50	119.99	154.74
	23.12					145.26		157.89
1b	21.04		31.89	50.94	103.97	120.05	120.45	155.01
	21.26					146.10		160.46
2a	20.60	52.64			105.21	114.37	115.56	153.72
	20.62	53.22			107.42	117.79	138.88	154.57
	23.06					144.62	150.78	159.21
	23.11							159.90
2b	20.60		31.47	50.88	105.23	114.89	116.46	153.74
	21.13			51.25	107.07	118.53	139.57	154.62
	21.48					146.09	152.07	161.70
	21.61							162.52

^{a} Chemical shifts in ppm from internal TMS. Measured in chloroform-d.
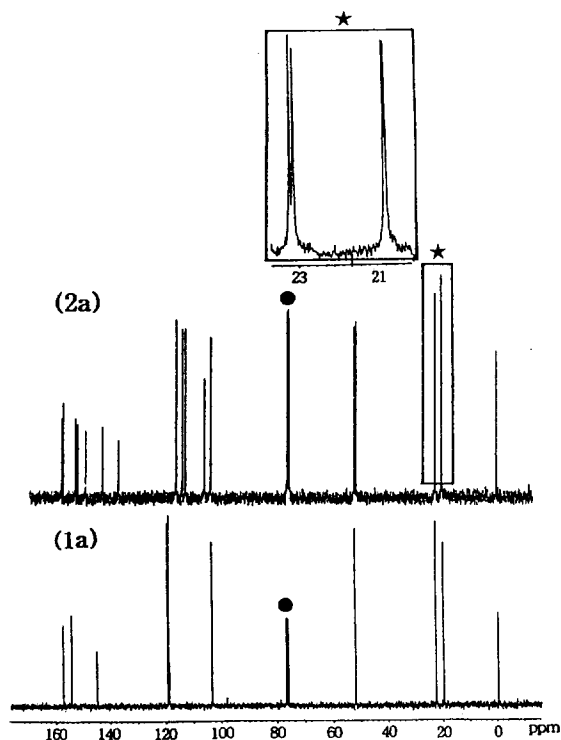

Figure 2. 75.5 MHz ^{13}C NMR spectra of **1a** and **2a** in chloroform-d: (●) solvent peaks; (★) methyl peaks of **2a**.

tions of the conjugated six-membered chelate ring which occur at ~1550 and 1530 cm^{-1}, respectively.[15]

The complexes **1a, 1b, 2a** and **2b** were most readily characterized by a combination of ^{1}H and ^{13}C NMR spectra. The assignments were made by the comparisons of the spectra with those of other nickel(II) macrocyclic complexes reported earlier.[10,16~18] ^{1}H NMR chemical shifts and their assignments for the complexes **1a, 1b, 2a** and **2b** are listed in Table 1.

The 7,16-positions of tetraaza[14]annulene nickel(II) complex A have been found to be a reactive nucleophilic center

which was named methine site.[9] Thus, the chemical shift values in NMR spectra for the methine site of these complexes are worth special mentioning. The methine proton peaks (H' and H'') for **1a** and **1b** with no substituent on phenyl ring are equivalent and show sharp singlets at δ=5.03 and δ=4.88 ppms, respectively. On the other hand, the methine proton peaks for **2a** and **2b** with a nitro substituent on the phenyl ring are nonequivalent and show two singlets, respectively (see Table 1). These peaks are shifted downfield about 0.05-0.21 ppm relative to **1a** and **1b**. These downfield shifts are attributed to the deshielding effect of the nitro substituent on phenyl ring.

^{13}C NMR data and their assignments for **1a, 1b, 2a** and **2b** are summarized in Table 2 and the spectra of **1a** and **2a** are shown in Figure 2. The ^{13}C NMR spectra of **1a** and **1b** show to be 9 and 10 resonance peaks rather than 18 and 19 peaks, respectively, indicating that there are at least a symmetry plane in these complexes. On the other hand, the ^{13}C NMR spectra of **2a** and **2b** show 18 and 19 resonance peaks, respectively, due to the lower symmetry. The resonances of methine carbon of **1a** and **1b** are observed at δ=103.86 and 103.97 ppms, respectively. The methine resonances of **2a** and **2b** are shifted downfield about 1.3-3.5 ppm relative to **1a** and **1b**. This result is in agreement with the corresponding ^{1}H NMR spectral behavior.

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Prediction of Soil Sorption Coefficients for Organic Nonelectrolytes from Solvatochromic Parameters

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The fate of an organic chemical introduced into the environment depends on a variety of physical, chemical and biological processes. The soil (or sediment)-water sorption coefficient, which is often expressed on the basis of organic carbon (K_{oc}) or organic matter (K_{om}), is one of the key input parameters in models to estimate the mobility and fate of contaminants. This parameter provides an indication of the extent to which a chemical partitions between the solid and solution phases in soil or between water and sediment in aquatic ecosystems, and indicates whether a chemical is likely to leach through soil or be immobile. Since the experimental determination of K_{oc} is difficult and expensive, a number of estimation methods for K_{oc}, most of which are regression equations with water solubility, octanol-water partition coefficient or bioconcentration factor, have been developed.[1,2]

However, these models suffer from several shortcomings such as (1) low precision of water solubility, octanol-water partition coefficient and BCF data and (2) limited range of applicability of the models so developed.[3] Recently, molecular connectivity indices have been successfully used to predict K_{oc} for nonpolar compounds.[3~6] However, extension of the model to polar compounds has been problematic. Accuracy and range of applicability of molecular connectivity models are superior to the other correlational models based on above-memtioned empirical parameters. However, as we have pointed out elsewhere[7] these models are not able to give a quantitative information on the solute-target system interactions which determine the property of interest.

In this paper we report the use of the Kamlet-Taft solvatochromic parameters[8] in the linear solvation energy relationship (LSER)[9,10] to correlate and predict K_{oc}. It has been demonstrated that many disparate physicochemical, biochemical, toxicological, pharmacological properties of organic nonelectrolytes that depend on solute/solvent interactions and aqueous solubilities in a variety of media can be correlated, rationalized, and predicted by the application of this methodology. Examples include octanol-water[11~13] and triolein-water partition coefficients,[14] gas-blood partition coefficients,[15] aqueous solubilities,[16] inhibition of bioluminescence in *Photobacterium phosphoreum* (the Microtox test),[17] toxicities to the Golden Orfe Fish[18] and binding to bovine serum albumin,[14] binding into the β-cyclodextrin cavity,[19] bioconcentration factors in fish[20] and retention behavior of solutes in gas and liquid chromatography.[21~29]

The LSER for a property of solutes (SP) that depends on solute-solvent interactions is given by eq. 1, which specifically identifies and evaluates the individual solute-solvent interactions that contribute to the SP.

$$SP = SP_o + mV_I/100 + s\pi^* + d\delta + b\beta_m + a\alpha_m \qquad (1)$$

The coefficients m, s, d, b and a are obtained by multiple linear regression of SP vs. the solute parameters. The $mV_I/100$ term measures the endoergic process of separating the solvent molecules to provide a suitably sized cavity for the solute. V_I is computer-calculated intrinsic molecular volume of the solute.[30] V_I is scaled by 1/100 so that it should cover roughly the same range as the other independent variables. The $s\pi^*$ and $d\delta$ term together measure exoergic solute-solvent dipole-dipole and dipole-induced dipole interactions; π^* is the solvatochromic parameter which measures the ability of a molecule to stabilize a neighboring charge or dipole, and to induce a dipole in a neighboring nondipolar molecule. The δ term in eq. 1 is a polarizability correction parameter, equal to 0.0 for non-polyhalogenated aliphatic compounds, 0.5 for polyhalogenated aliphatics, and 1.0 for single-ring aromatic compounds. For some multiple-ring aromatic compounds δ has values of 2.0.[13] Exoergic effects of hydrogen bonding interactions are measured by $b\beta_m$ and $a\alpha_m$ terms; β and α are the solvatochromic parameters that measure hydrogen bond acceptor (HBA) basicity and hydrogen bond donor (HBD) acidity, respectively. The subscript m indicates that for compounds capable of self-association, the parameter applies to the non-self-associated "monomer" solute, rather than the self-associated "oligomer" solvent. For non-self-associating compounds, $\alpha_m = \alpha$, $\beta_m = \beta$. The solvatochromic parameters of over 500 compounds available at present were