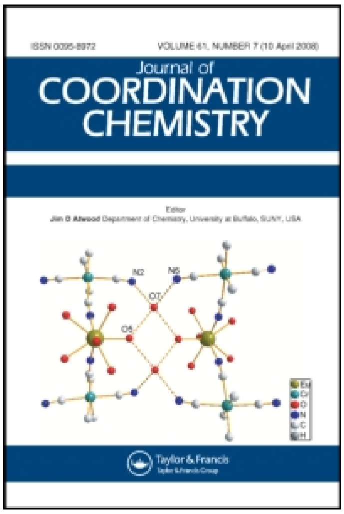

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TEMPLATE SYNTHESIS AND CHARACTERIZATION OF 14-π NICKEL(II) COMPLEXES WITH DISUBSTITUTED BENZON$_4$ MACROCYCLES

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The template reaction of a 1:1 mixture of the appropriate 4,5-disubstituted-1,2-phenylenediamine (*e.g.*, 4,5-dimethyl-1,2-phenylenediamine and 4,5-dichloro-1,2-phenylenediamine) and alkylenediamine (*e.g.*, ethylenediamine and propylenediamine) with 2,4-pentanedione in the presence of a nickel(II) salt gives a series of 14-π nickel(II) complexes with disubstituted benzoN$_4$ macrocycles, [Ni(Me$_4$-R$_2$Bzo[X]tetraeneN$_4$)] (where R = CH_3 or Cl; X = 14 or 15). These complexes are characterized by elemental analysis, mass, infrared, ^1H and ^{13}C NMR spectra. The electronic, ^1H and ^{13}C NMR spectra of these complexes are significantly affected by electronic effects of the disubstituent groups on the phenyl rings.

Keywords: template synthesis; 14-π nickel(II); macrocycle

INTRODUCTION

A large number of macrocyclic complexes based on the tetraaza[14]annulene nickel(II) complex (A) framework first described by Jäger[1–2] have been synthesized and characterized.[3–6] A and its other metal complexes have a number of structural features in common with the porphyrins[7–8] and these complexes have received much attention as catalysts and precursors for electrically conductive

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polymers.[9] The complexes contain the completely conjugated 16-π electron system like the porphyrins.[10]

In previous papers,[11–12] we reported a series of nickel(II) complexes with monosubstituted benzoN_4 macrocycles (**B**), [Ni(Me$_4$-RBzo[X]tetraeneN$_4$], where R = CH_3, H, Cl or NO_2 and X = 14 or 15, made by the template condensation of a 1:1 mixture of the appropriate 4-substituted 1,2-phenylenediamine and alkylenediamine with 2,4-pentanedione in the presence of a nickel(II) salt. These complexes contain the 14-π electron system with one saturated chelate ring and unsaturated six-membered chelate rings which contain nucleophilic centres. We have found that the spectroscopic properties of these 14-π complexes are almost the same as those of 16-π **A**.

Here we report the synthesis of new 14-π nickel(II) complexes with disubstituted benzoN_4 macrocycles, [Ni(Me$_4$-Me$_2$Bzo[14]tetraeneN$_4$)] (**14-2CH$_3$**), [Ni(Me$_4$-Cl$_2$Bzo[14]tetraeneN$_4$)] (**14-2Cl**), [Ni(Me$_4$-Me$_2$Bzo[15]tetraeneN$_4$)] (**15-2CH$_3$**), [Ni(Me$_4$-Cl$_2$Bzo[15]tetraeneN$_4$)] (**15-2Cl**) prepared by similar procedures to those described for the **B** series. We also studied the properties of the complexes, **14-2CH$_3$, 14-2Cl, 15-2CH$_3$** and **15-2Cl** by means of mass, infrared, electronic and NMR (^{1}H and ^{13}C) spectroscopy.

EXPERIMENTAL

Materials and Instruments

$Ni(OAc)_2 \cdot 4H_2O$ was purchased from Aldrich. [Ni(Me$_4$-Bzo[14]tetraeneN$_4$)] (**14-2H**) and [Ni(Me$_4$-Bzo[15]tetraeneN$_4$)] (**15-2H**) were prepared by published methods.[11] All reagents and solvents used were of analytical grade.

EI mass spectra were determined with a JEOL MS-DX 300 gas chromatograph mass spectrometer at 70 eV using a direct inlet system. Infrared spectra 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 internal reference. Elemental analyses were performed by Kolon R & D Center. Electronic absorption spectra were obtained on a Shimadzu UV-265 spectrophotometer.

Synthesis of the new macrocyclic complexes

[Ni(Me$_4$-Me$_2$Bzo[14]tetraeneN$_4$)] (14-2CH$_3$)

Under a N_2 atmosphere, 0.04 mol (4.0 g) of 2,4-pentanedione was added to a methanol (50 cm^3) solution of nickel(II) acetate tetrahydrate (5.0 g, 0.02 mol).

To the hot (60°C) mixture as added 4,5-dimethyl-1,2-phenylenediamine (2.7 g, 0.02 mol) and ethylenediamine (1.2 g, 0.02 mol). 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 dichloromethane - methanol (1:1). Yield: 35%. *Anal.* Calcd for $C_{20}H_{26}N_4Ni$(%): C, 63.03; H, 6.88; N, 14.70. Found: C, 62.30; H, 7.23; N, 14.72. IR (KBr disc, cm^{-1}): ν(C=C) and ν(C=N) 1534, 1473, 1410; ν(aromatic) 737. Electronic spectra ($CHCl_3$ nm, ε): 377 (24030), 551 (2630). EIMS: *m/z* 380 $[M]^+$.

[Ni(Me$_4$-Cl$_2$Bzo[14]tetraeneN$_4$)] (14-2Cl.)

This was prepared from 2,4-pentanedione (4.0 g, 0.04 mol), nickel(II) acetate tetrahydrate (5.0 g, 0.02 mol), 4,5-dichloro-1,2-phenylenediamine (3.5 g, 0.02 mol), ethylenediamine (1.2 g, 0.02 mol) and methanol (50 cm^3) as described above. Yield: 54%. *Anal.* Calcd. for $C_{18}H_{20}N_4Cl_2Ni$(%): C, 51.23; H, 4.78; N, 13.88. Found: C, 51.26; H, 4.92; N, 14.11. IR (KBr disc, cm^{-1}): ν(C=C) and ν(C=N) 1533, 1483, 1411; ν(aromatic) 733. Electronic spectra ($CHCl_3$ nm, ε): 381 (22440), 542 (2720). EIMS: *m/z* 420 $[M]^+$.

[Ni(Me$_4$-Me$_2$Bzo[15]tetraeneN$_4$)] (15-2CH$_3$)

This was prepared from 2,4-pentanedione (4.0 g, 0.04 mol), nickel(II) acetate tetrahydrate (5.0 g, 0.02 mol), 4,5-dimethyl-1,2-phenylenediamine (2.7 g, 0.02 mol), propylenediamine (1.5 g, 0.02 mol) and methanol (50 cm^3), following the above procedure. Yield: 33%. *Anal.* Calcd for $C_{21}H_{28}N_4Ni$(%): C, 63.83; H, 7.14; N, 14.18. Found: C, 64.02; H, 7.13; N, 14.06. IR (KBr disc, cm^{-1}): ν(C=C) and ν(C=N) 1525, 1470, 1410; ν(aromatic) 748. Electronic spectra ($CHCl_3$ nm, ε): 397 (13380), 583 (1810). EIMS: *m/z* 394 $[M]^+$, 379 $[M-CH_3]^+$.

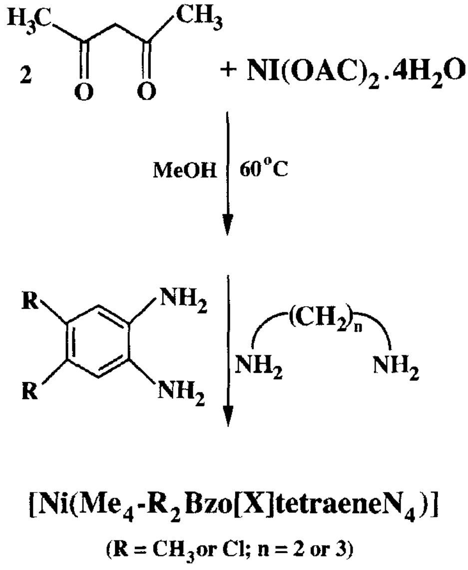
[Ni(Me$_4$-Cl$_2$Bzo[15]tetraeneN$_4$)] (15-2Cl$_1$)

This was prepared from 2,4-pentanedione (4.0 g, 0.04 mol), nickel(II) acetate tetrahydrate (5.0 g, 0.02 mol), 4,5-dichloro-1,2-phenylenediamine (3.5 g, 0.02 mol), propylenediamine (1.5 g, 0.02 mol) and methanol (50 cm^3), following the above procedure. Yield: 51%. *Anal.* Calcd for $C_{19}H_{22}N_4Cl_2Ni$(%): C, 52.34; H, 5.09; N, 12.85. Found: C, 52.06; H, 5.15; N, 13.05. IR (KBr disc, cm^{-1}): ν(C=C) and ν(C=N) 1527, 1474, 1420; ν(aromatic) 748. Electronic spectra ($CHCl_3$ nm, ε): 388 (19310), 565 (1480). EIMS: *m/z* 434 $[M]^+$, 419 $[M-CH_3]^+$.

RESULTS AND DISCUSSION

Synthesis of the new complexes

The macrocyclic complexes of **14-2R** and **15-2R** series were prepared following the synthetic route shown in Scheme I. Template condensation of a 1:1 mixture of 4,5-dimethyl-1,2-phenylenediamine and ethylenediamine with 2,4-pentanedione in the presence of nickel(II) ion gave **14-2CH$_3$**. By similar procedures, **14-2Cl**, **15-2CH$_3$** and **15-2Cl** were synthesized from 4,5-dichloro-1,2-phenylenediamine and ethylenediamine, 4,5-dimethyl-1,2-phenylenediamine and propylenediamine, and 4,5-dichloro-1,2-phenylenediamine and propylenediamine, respectively. The complexes **14-2Cl** and **15-2Cl** with two chloro substituents were prepared in 54 and 51% yields by the reactions mentioned above, respectively. However, the complexes **14-2CH$_3$** and **15-2CH$_3$** with two methyl substituents were obtained in 35 and 33% yields, respectively. These results indicate that the reaction is susceptible to electronic effects of substituent groups on the phenyl rings. Also, the results are comparable to those of the electrophilic substitution between the complex A and a series of *para*-substituted benzoyl chlorides.[6] Elemental analyses of all the complexes given in the Experimental Section are consistent with these formulations.



SCHEME I

Mass, IR and Electronic Spectra

MS data for **14-2CH$_3$**, **14-2Cl**, **15-2CH$_3$** and **15-2Cl** are given in the Experimental Section. EI mass spectra for **14-2CH$_3$**, **14-2Cl** and **15-2CH$_3$** show the presence of a molecular ion M$^+$ at *m/z* 380 (^{58}Ni), 420 (^{35}Cl, ^{58}Ni) and 394 (^{58}Ni), respectively. These peaks are the base peaks in each mass spectrum. **15-2Cl** exhibits a molecular ion M$^+$ at *m/z* 434 (^{35}Cl, ^{58}Ni) and which is not a base peak.

IR spectra of the new complexes show bands around 1530, 1480 and 1410 cm^{-1} assignable to ν(C═N) and ν(C═C) but no ν(N–H) absorption around 3200 cm^{-1}. This observation indicates the formation of C═N and C═C bonds and the disappearance of N-H groups, and the conjugated six membered chelate ring in the reaction.[13] The aromatic bands occur around 740 cm^{-1}.

Electronic absorption data for the new complexes are given in the Experimental Section. The absorption bands around 380 nm can be attributed to charge transfer (CT) transitions from metal to ligand because the molar extinction coefficients are much larger than those normally assigned to ligand-field transitions.[14–15] The absorption bands in the 550–580 nm range can be attributed to ligand-field transitions. This behaviour is compatible with that observed for square-planar nickel(II) complexes with four nitrogen donors. [6, 14–15] The ligand-field transitions for **14-2R** and **15-2R** series are compiled in Table I. A feature of the data is the variation of the position of the band maximum for the ligand-field transitions. The ligand-field transitions of **14-2CH$_3$** and **15-2CH$_3$** show 5 and 13 nm shifts of λ_{max} to longer wavelengths compared with **14-2H** and **15-2H**, respectively. However, the λ_{max} of **14-2Cl** and **15-2Cl** have 4 and 5 nm hypsochromic shifts relative to **14-2H** and **15-2H**, respectively. The results are attributed to the electronic properties of the substituent group[16] and are supported by similar observations with nickel(II) tetraazaN$_4$ macrocycles.[17]

TABLE I Ligand-field transitions of macrocyclic nickel(II) complexes with substituent corresponding to those with no substituent on phenyl ring[a]

Compound	λ_{max} $(\varepsilon)^b$	Δ^c
14-2CH$_3$	551 (2630)	5
14-2H	546 (2200)	nil
14-2Cl	542 (2720)	–4
15-2CH$_3$	583 (1810)	13
15-2H	570 (1720)	nil
15-2Cl	565 (1480)	–5

[a] In chloroform at room temperature. [b]nm (M^{-1}cm^{-1}) [c]Δ = λ_{max} of macrocylic nickel(II) complexes with subtituent- λ_{max} corresponding to those with no substituent on the phenyl ring.

^{1}H and ^{13}C NMR Spectra

14-2CH$_3$, **14-2Cl**, **15-2CH$_3$** and **15-2Cl** were most readily characterized by a combination of ^{1}H and ^{13}C NMR spectra. ^{1}H NMR chemical shifts and their assignments are listed in Table II. ^{1}H NMR spectra of these complexes in CDCl$_3$ solution show two singlets at δ1.92-2.38 for the methyl protons at diimine positions and one singlet at δ6.84-7.18 for aromatic protons. In the spectra of **14-2CH$_3$** and **15-2CH$_3$**, methyl protons on the phenyl rings are observed as a singlet at δ2.05 and 1.90, respectively. The γ-carbon sites of the diimine framework of **A** have been found to be reactive nucleophilic centre.[9,18] Thus, the chemical shift values in NMR spectra of the sites for **14-2R** and **15-2R** series are worthy of separate note. The methine proton peaks (H′and H″ for **14-2CH$_3$** and **15-2CH$_3$** with two methyl substituents and those for **14-2Cl** and **15-2Cl** with two chloro substituents on the phenyl ring are equivalent and show one singlet, respectively (Table II). These peaks of **14-2CH$_3$** and **15-2CH$_3$** are shifted about 0.05 and 0.02 ppm upfield relative to **14-2H** and **15-2H** with no substitient on the phenyl ring, respectively. On the other hand, the peaks of **14-2Cl** and **15-Cl** show slight downfield shifts by 0.04 and 0.03 ppm relative to **14-2H** and **15-2H**, respectively. The results are attributed to the shielding and deshielding effects of the substituents on the phenyl rings.

TABLE II ^{1}H NMR data for **14-2R** and **15-2R** series[a]

Compound	*Methyl*	Aromatic *Methyl*	Ethylene N-C$\underline{H}_2$-	Propylene -C$\underline{H}_2$-,N-C$\underline{H}_2$-	*Methine*	*Aromatic*
14-2CH$_3$	2.17 (s) 2.38 (s)	2.05 (s)	3.34 (s)		4.98 (s)	6.95 (s)
14-2H[b]	2.05 (s) 2.38 (s)		3.35 (s)		5.03 (s)	6.68(m) 7.28(m)
14-2Cl	2.07 (s) 2.35 (s)		3.37 (s)		5.07 (s)	7.18 (s)
15-2CH$_3$	2.09 (s) 2.13 (s)	1.90 (s)		2.30(m) 2.79(t)	4.86 (s)	6.63 (s)
15-2H[b]	2.07 (s) 2.10 (s)			2.32(m) 2.81(t)	4.88 (s)	6.61(m) 6.85(m)
15-2Cl	1.92 (s) 2.07 (s)			2.34(m) 2.82(t)	4.91 (s)	6.84 (s)

[a] Chemical shifts in ppm from internal TMS. Measured in CDCl$_3$ at 300 Mhz. Multiplicity of a proton signal is given in parentheses after δ-value: s = singlet, t = triplet, m = multiplet. [b] Ref. 11.

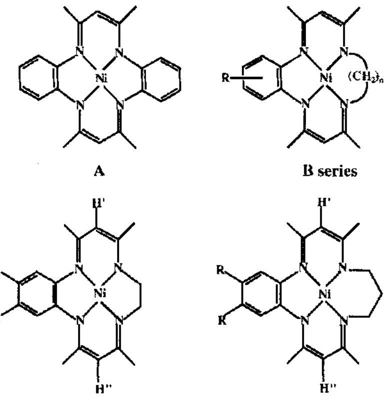
^{13}C NMR data for **14-2R** and **15-2R** series are presented in Table III. ^{13}C NMR spectra of **14-2CH$_3$** and **14-2Cl** give 10 and 9 resonance peaks rather than 20 and 18 peaks, respectively, indicating that there is at least two fold symmetry in these complexes. This result is comparable to resonances observed for **14-2H**,

15-2CH$_3$, **15-2H** and **15-2Cl** (Table III). The methine resonances of **14-2CH$_3$** and **15-2CH$_3$** are shifted upfield by about 0.58 and 0.49 ppm relative to **14-2H** and **15-2H**, respectively. These resonances of **14-2Cl** and **15-2Cl** also show downfield shifts by 0.98 and 0.88 ppms relative to **14-2H** and **15-2H** respectively. This result is in agreement with the corresponding ^{1}H NMR behaviour.

TABLE III ^{13}C NMR data for 14-2R and 15-2R series[a]

Compound	*Methyl*	*Aromatic Methyl*	*Ethylene* *N–C–*	*Propylene* *C–C–C*	*N–C–*	*Methine*	*Aromatic*	*Diiminate*
14-2CH$_3$	20.28 23.18	19.75	52.60			103.28	121.18 127.37 120.70	154.61 157.49
14-2H[b]	20.29 23.12		52.65			103.86	119.50 119.99 145.26	154.74 157.89
14-2Cl	20.51 22.90		52.75			104.84	119.93 121.27 144.65	154.24 158.77
15-2CH$_3$	21.01 21.22	19.60		31.90	50.86	103.48 127.83	121.66 160.06 144.06	154.83
15-2H[b]	21.04 21.26			31.89	50.94	103.97 120.45	120.05 160.46 146.10	155.01
15-2Cl	20.78 21.45			31.66	50.96	104.85	120.73 121.84 145.68	154.40 161.38

[a] Chemical shifts in ppm from internal TMS. Measured in CDCl$_3$ at 75.5 Mhz. [b] Ref. 11.



A **B series**

14-2R series **15-2R** series

14-2CH$_3$: R = CH$_3$
14-2H: R = H
14-2Cl: R = Cl

15-2CH$_3$: R = CH$_3$
15-2H: R = H
15-2Cl: R = Cl

FIGURE 1 Chemical structures of various nickel(II) complexes with 16-π (A) and 14-π (B) macrocycles.

Acknowledgments

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