arise from the π-cation-radical species. Analysis by band deconvolution of the spectra of both the neutral and oxidized ZnPc species[51] shows that there are many more transitions in these spectra than are apparent from such a qualitative analysis. However, the essence of the analysis presented here remains correct: the transitions at 825, 720, and 325 nm are degenerate, while the 500-nm transition is nondegenerate. Because the partially filled HOMO, in the $a_{2u}(2)a_{1u}(1)$ configuration, allows transitions from low-lying π MO's, we assign the 825-nm band to such a $\pi-\pi$ transition. The Q band is associated with the 720-nm band, being identified from the MCD spectrum by its degeneracy and complement of vibronic overtone bands lying to higher energy. The 500-nm band must be a transition from nondegenerate, low-lying π MO's or possibly from low-lying σ, n-type orbitals on the ring nitrogens to the a_{1u} π MO.

Conclusions

Photolysis of ZnPc in solutions containing alkyl halide acceptors results in the quantitative formation of the π-cation-radical species. The lack of side reactions makes this an attractive method of preparing the π-cation-radical species of main-group phthalocyanines. With transition-metal phthalocyanines, metal-centered reactions may quench the π-ring excited state in competition with ring oxidation.

Qualitative analysis of the magnetic circular dichroism spectrum of the $[ZnPc(-1)]^{\cdot+}$ species suggests that the Q band is at 720 nm and that the bands at 825 and 500 nm arise from $\pi-\pi$ transitions into the partially filled a_{1u} MO.

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Registry No. ZnPc, 14320-04-8; ZnPc(py), 20008-28-0; ZnPc(im), 106231-96-3; $ZnPc(CN^-)$, 106231-97-4; $[ZnPc(-1)]^{\cdot+}$, 53029-44-0; CBr_4, 558-13-4.

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Macrocyclic Dicarbinolamine Complexes of Nickel(II) with Planar $N_4(N_2)$ Ligands: Synthesis and Spectral and Electrochemical Properties

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Macrocyclic complexes of nickel(II) with highly unsaturated planar tetraaza $[N_4(N_2)]$ type ligands have been synthesized and characterized. These complexes are derived by the template condensation of the ligands 1,2,9,10-tetraphenyl-3,4,7,8-tetraazadeca-2,4,6,8-tetraene-1,10-dione (BG) and 5-methyl-1,2,9,10-tetraphenyl-3,4,7,8-tetraazadeca-2,4,6,8-tetraene-1,10-dione (BMG) with *o*-phenylenediamine (opdn), 3,4-dimethyl-*o*-phenylenediamine (dmopdn), and 3-methyl-*o*-phenylenediamine (dat) in the presence of nickel(II) acetate. Each of these complexes displays spectral, magnetic, and conductance behavior characteristic of square-planar nickel(II) complexes. The electrochemical properties as studied by cyclic voltammetry and polarography indicate the quasi-reversible nature of these systems. In all the complexes the dicarbinolamine moiety is found to be present, which is confirmed by IR, ^1H NMR, and mass spectral data. Molecular model (CPK models) studies clearly show that the phenyl groups must be perpendicular to the plane of the molecule and the hydroxyl groups are trans to each other. The factors governing the stabilization of the dicarbinolamine moiety are discussed.

Introduction

The synthesis and study of macrocyclic complexes, in which a large ligand structure maintains donor atoms in a planar fashion around the metal ion, represent an important current objective in the study of transition-metal systems. This is particularly true in the case of ligands containing N_4 donors as they serve as simple models for biologically occurring molecules such as heme proteins, cyanocobalamin, chlorophyll, and other related systems. The isolation and characterization[1] of nickel(II) porphyrins from oil and oil shale lend further support to the choice of transition-metal complexes of tetraaza macrocyclic ligands as biomodels.

Some metal-directed template condensations lead directly to conjugated metal complexes. Examples are metal-directed (a) condensation of propargylaldehyde with *o*-phenylenediamine,[2] (b) tetramerization of *o*-aminobenzaldehyde,[3] and (c) condensation of *o*-phenylenediamine with 2,4-pentanedione.[4] The completely conjugated macrocyclic complexes studied comprise neutral,[3] monoanionic,[5] and dianionic ligands primarily of 14-membered rings. The increasing unsaturation in the macrocyclic ligand results in the reduction of core size, which is found to exhibit more pronounced effects in 14-membered rings.

Earlier investigations on 14-membered highly conjugated systems have essentially dealt with imine type complexes with only a few reports[6-8] on the imine–carbinolamine and dicarbinolamine varieties. The monocarbinolamine metal complexes obtained from the aliphatic dicarbonyl and diamine compounds are rather unstable when compared to their aromatic analogues. It has been reported[9] that the free carbinolamines obtained from the aliphatic compounds are very difficult to isolate and are very sensitive to acids. The earlier reports on the isolation of dicarbinolamine complexes did not describe in detail the conditions under which the stabilization of such moieties are possible. Tasker et al.[10] have recently reported the isolation and X-ray crystal study of a macrocyclic dicarbinolamine complex obtained by the template condensation of 2,6-diformylpyridine and dihydrazinobipyridine in the presence of Zn(II) ion. However, they have not made an in-depth analysis of the reasons for the stabilization of such moieties. Nor there was any attempt to synthesize a series of

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complexes of this class by varying the substituents. The present report deals with the synthesis and systematic study on a series of dicarbinolamine macrocyclic Ni(II) complexes.

Experimental Section

Materials. Benzil was purchased from Loba and used without further purification. Glyoxal (45% in water) and methylglyoxal (50% in water) were obtained from E. Merck and Fluka, respectively. The diamines, viz. *o*-phenylenediamine, 3,4-dimethyl-*o*-phenylenediamine, and 3-methyl-*o*-phenylenediamine (purissimum, Fluka), were recrystallized from methanol before use. Ethanol and methanol were refluxed and distilled over lime. Dimethylformamide (DMF) was distilled twice over P_4O_{10} in vacuo and was stored under nitrogen in the dark. Tetraethylammonium perchlorate (TEAP) was recrystallized from water and dried at 80 °C in vacuo.[11] Benzene was refluxed, distilled, and stored over sodium.

Physical Measurements. Microanalyses were carried out by using a Perkin-Elmer Model 540 C, H, and N analyzer at the Department of Organic Chemistry, University of Madras. The metal content was estimated by the atomic absorption method. Room-temperature magnetic measurements were made by the Gouy method using mercuric tetrakis(thiocyanato)cobaltate(II) as standard. UV–visible and near-infrared data were obtained with Beckman Model 25 and Kontron Uvicon recording spectrophotometers. Infrared spectra were obtained by using the potassium bromide disk method with Shimadzu-IR 408 and Perkin-Elmer 598 spectrophotometers, and calibrations of the instruments were made with polystyrene film.

^1H NMR spectra were obtained on a Varian EM-390 spectrometer using a $CDCl_3/Me_4Si$ solvent system. The ^{13}C NMR spectra were recorded on a JEOL-FX 90 spectrometer. The mass spectral data were obtained with a Varian MAT-112 mass spectrometer. Thermograms of the metal complexes were obtained on a Du Pont Model 990 (981-TG module) thermal analyzer heating at the rate of 10 °C/min under a nitrogen atmosphere.

Electrochemistry. Redox potentials were determined in DMF solvent with use of a PAR (Models 170, 173, and 175) system. The current output was monitored by a PAR Model 175 current follower, and the cyclic voltammograms were recorded on a Perkin-Elmer Hitachi Model 057 X-Y recorder. The electrode system consists of a saturated calomel electrode as reference electrode, a stationary platinum working electrode, and platinum foil functioning as the third electrode. The PAR Model 178 electrometer was used to connect the reference electrode to the potentiostat. The platinum electrode was cleaned by heating with hot acids and finally treated electrochemically.[12] Measurements were made at room temperature (27 ± 1 °C) in a specially designed glass cell[13] that contained a Luggin capillary and TEAP salt bridge. Polarograms were obtained on a Radelkis Model OH 105 universal polarograph. The cell assembly used in $E_{1/2}$ measurements was the same as the one used for CV experiments. Conductivity measurements in DMF solutions were made on a Elico Model 88 conductivity bridge.

Synthesis. Benzil Monohydrazone (BMH). Addition of hydrazine hydrate (99% solution) to a solution of benzil in hot ethanol results in the formation of benzil monohydrazone.[14]

1,2,9,10-Tetraphenyl-3,4,7,8-tetraazadeca-2,4,6,8-tetraene-1,10-dione (BG). BMH (30 g, 0.134 mol), glyoxal (45% solution, 12 mL) and 100 mL of dry benzene were refluxed in a round-bottom (RB) flask fitted with a Dean–Stark apparatus for 16–18 h. The heating was continued until no more water was collected in the graduated arm of the Dean–Stark apparatus, indicating the completion of the reaction. The reaction mixture was cooled to 0 °C and filtered. The crude product was repeatedly washed with ether until the washings were colorless. This product was finally recrystallized from a petroleum ether–benzene mixture. The golden yellow microcrystalline product was dried in a vacuum desiccator. This ligand is freely soluble in acetone, DMF, and ethyl acetate at room temperature: yield 80%; mp 182 °C.

5-Methyl-1,2,9,10-tetraphenyl-3,4,7,8-tetraazadeca-2,4,6,8-tetraene-1,10-dione (BMG). BMH (30 g, 0.134 mol) and methylglyoxal (50% solution, 12 mL) in 100 mL of dry benzene were refluxed in a RB flask connected to a Dean–Stark apparatus to remove the water formed during the course of the reaction. After 14–16 h of heating under reflux, the ligand separated out from the reaction mixture. This was cooled to 0 °C, filtered, and washed several times with ether until the washings did not show any color. Recrystallization of the product was carried out in a petroleum ether–benzene mixture, and the species was dried in vacuo at room temperature. The product is orange-yellow, and its solubility in organic solvents did not vary much from that of its unsubstituted analogue: yield 85%; mp 198 °C.

(4,9-Dihydroxy-3,4,9,10-tetraphenyl-6,7-benzo-1,2,5,8,11,12-hexaazacyclotetradeca-2,6,10,12,14-pentaenato)nickel(II). An alcoholic solution of the ligand BG (1.2 g, 2.5 mmol) and nickel(II) acetate (0.9 g, 3.75 mmol) was degassed for 30 min by passing purified nitrogen and was refluxed for $^1/_2$ h under a nitrogen atmosphere in a two-necked flask fitted with a double-surface reflux condenser and a dropping funnel with pressure equalizer. This assembly was connected to a vacuum line and the entire operation was carried out under a nitrogen atmosphere. To the hot mixture containing the metal and the ligand was added a degassed solution of *o*-phenylenediamine (1.25 g, 11 mmol) in 75 mL of ethanol, very slowly from the dropping funnel with constant stirring. The reaction mixture was refluxed for a period of 28 h, during which time the product started separating out as a deep red solid. The contents were cooled overnight to 0 °C and filtered, and the solids were washed several times with alcohol and petroleum ether. The resulting product was recrystallized from chloroform and dried in vacuo at 100 °C; yield 60%.

(4,9-Dihydroxy-3,4,9,10-tetraphenyl-6,7-(3,4-dimethylbenzo)-1,2,5,8,11,12-hexaazacyclotetradeca-2,6,10,12,14-pentaenato)nickel(II). A degassed alcoholic solution of the ligand BG (1.2 g, 2.5 mmol) and nickel(II) acetate (0.88 g, 3.6 mmol) was refluxed for 45 min under a nitrogen atmosphere, and to this hot mixture was added 3,4-dimethyl-*o*-phenylenediamine (1.2 g, 8 mmol) in 100 mL of alcohol, very slowly with constant stirring. After the addition of the diamine was over, the reaction mixture was refluxed for 30 h at a constant bath temperature. Then the solution was cooled to 0 °C and filtered, and the product was washed with alcohol and petroleum ether. Recrystallization of the crude sample from chloroform resulted in a dark red microcrystalline solid, yield 70%.

(4,9-Dihydroxy-3,4,9,10-tetraphenyl-6,7-(3-methylbenzo)-1,2,5,8,11,12-hexaazacyclotetradeca-2,6,10,12,14-pentaenato)nickel(II). To the alcoholic solution of BG (1.2 g, 2.5 mmol) and nickel(II) acetate (0.9 g, 3.5 mmol) under reflux was added diaminotoluene (1.2 g, 9.8 mmol) in 50 mL of alcohol, slowly over a period of 45 min under a N_2 atmosphere. The heating was continued for 30 h, and the reaction mixture was cooled to 0 °C and filtered. The complex was repeatedly washed with alcohol and petroleum ether, recrystallized from chloroform, and dried in vacuo at 100 °C; yield 65%.

The procedure adopted in the synthesis of complexes derived from BMG is essentially the same as that of the complexes obtained from the ligand BG.

(4,9-Dihydroxy-5-methyl-3,4,9,10-tetraphenyl-6,7-benzo-1,2,5,8,11,12-hexaazacyclotetradeca-2,6,10,12,14-pentaenato)nickel(II). To the ligand BMG (1.25 g, 2.6 mmol) and nickel(II) acetate (0.9 g, 3.75 mmol) in alcohol under reflux was added for 1 h *o*-phenylenediamine (1.2 g, 8 mmol) in 50 mL of ethanol, and the heating was continued for 24 h. The deep red complex that separated out after the reaction mixture was cooled was filtered and washed several times with alcohol and petroleum ether. The complex was then recrystallized from chloroform and dried in vacuo at 100 °C; yield 70%.

(4,9-Dihydroxy-5-methyl-3,4,9,10-tetraphenyl-6,7-(3,4-dimethylbenzo)-1,2,5,8,11,12-hexaazacyclotetradeca-2,6,10,12,14-pentaenato)nickel(II). The ligand BMG (1.25 g, 2.6 mmol), nickel(II) acetate (0.9 g, 3.75 mmol), and 3,4-dimethyl-*o*-phenylenediamine (1.3 g, 9.5 mmol), which was added over a period of 30 min, were refluxed for a period of 36 h, and the product was purified as above; yield 55%.

(4,9-Dihydroxy-5-methyl-3,4,9,10-tetraphenyl-6,7-(3-methylbenzo)-1,2,5,8,11,12-hexaazacyclotetradeca-2,6,10,12,14-pentaenato)nickel(II). The reaction conditions maintained in the case of Ni(BMG-dat) were essentially the same as in the case of other nickel(II) complexes except that the total reaction time was 32 h; yield 60%.

Results and Discussion

Synthesis of Ligand Precursors. The syntheses of the ligands BG and BMG, open-chain β-amino diketo compounds, were achieved by the Schiff base condensation of 2 equiv of benzil monohydrazone and 1 equiv of a dicarbonyl compound, viz. glyoxal and methylglyoxal. The ready availability of the parent compound BMH and the formation of the N_2O_2 ligand in a single step has synthetic advantages over the multistep preparation of some of the N_2O_2 type ligands reported.[15] This type of conjugated

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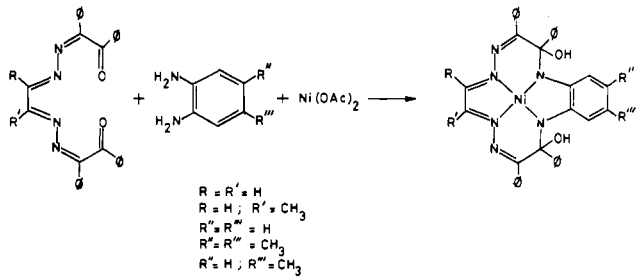
Table I. Analytical Data for the Nickel(II) Macrocyclic Complexes[a]

complex	molecular formula	anal. calcd, % C	H	N	M	anal. found, % C	H	N	M
[Ni(BG-opdn)]	$C_{36}H_{28}N_6O_2Ni$	68.06	4.4	13.23	9.24	68.21	4.2	14.10	9.45
[Ni(BG-dmopdn)]	$C_{38}H_{32}N_6O_2Ni$	69.01	4.8	12.71	8.88	68.75	4.7	12.20	8.80
[Ni(BG-dat)]	$C_{37}H_{30}N_6O_2Ni$	68.44	4.6	12.94	9.05	67.49	4.24	11.12	8.86
[Ni(BMG-opdn)]	$C_{37}H_{30}N_6O_2Ni$	68.44	4.6	12.94	9.05	67.83	4.60	11.89	8.65
[Ni(BMG-dmopdn)]	$C_{39}H_{34}N_6O_2Ni$	69.56	5.03	12.48	8.72	68.02	5.03	12.18	8.15
[Ni(BMG-dat)]	$C_{38}H_{32}N_6O_2Ni$	69.01	4.8	12.71	8.88	68.25	4.75	12.00	7.90

[a] All of the complexes are dull red.

Scheme I



azomethine is considered to be significant because of its relevance to a biologically important process, since rhodopsin,[16,17] a compound containing a conjugated azomethine function, is an intermediate involved in the chemistry of vision.

The free ligands are soluble in common organic solvents like benzene, chloroform, acetone, etc. They display two bands in the UV–visible region. The first band around 40 000 cm^{-1} is assigned to a $\pi \rightarrow \pi^*$ transition, and the second band centered around 30 000 cm^{-1} is assigned to an $n \rightarrow \pi^*$ transition. The bands for conjugation of the azomethine chromophore with olefinic or aryl groups differ considerably from those of unconjugated systems, since $\pi \rightarrow \pi^*$ transitions display a stronger absorption when compared to $n \rightarrow \pi^*$ transitions. Conjugation occurring through –N=C—C=N– diimine systems is common.

The infrared spectra of the ligands recorded on KBr disks indicated the presence of the C=N group and the free C=O group at 1665 and 1590 cm^{-1}, respectively. The relatively low frequency of absorption exhibited by the azomethine moiety is due to the presence of extensive conjugation in the inner ring of the molecule. The characteristic strong absorption for the α-diimine function at 1220 cm^{-1} as reported by Busch et al.[18,19] for macrocyclic complexes containing the α-diimine function has also been observed. The NMR spectra of the ligands display a complex multiplet in the region δ 7.2–7.9 for aromatic protons, and vinylic azomethine protons are displaced downfield to δ 8 due to larger deshielding. The methyl protons of the ligand BMG show a singlet at δ 2. This agrees with the values reported for the aliphatic *C*-methyl groups.[20] The mass spectra of both ligands (BG, BMG) show the molecular ion peak at m/z 470 and 484, respectively. In both cases the intensity of the M^+ ion peak is very weak.

Synthesis of Complexes. To the alcoholic solution of nickel(II) acetate and ligand under reflux was added the aromatic diamine in ethanol over a period of 30–50 min. Experiments designed to test the dependence of formation as well as the yield on variables strongly indicate that the presence of excess diamine determines whether or not the macrocyclic complexes form and that in the presence of excess diamine the rate of addition of the diamine and the total reaction time influence the yield of macrocyclic complexes. The optimized conditions have been described in detail in the Experimental Section.

Table II. Infrared Spectral Data for the Nickel(II) Macrocyclic Complexes

complexes	freq, cm^{-1} OH	C=N	C=N—N=C	others
[Ni(BG-opdn)]	3430	1605	1230	1290, 705
[Ni(BG-dmopdn)]	3480	1615	1230	1295, 710
[Ni(BG-dat)]	3430	1600	1235	1295, 710
[Ni(BMG-opdn)]	3470	1605	1215	1280, 690
[Ni(BMG-dmopdn)]	3420	1595	1210	1270, 695
[Ni(BMG-dat)]	3430	1605	1215	1270, 700

The analytical data of the complexes along with other physical properties are given in Table I. The room-temperature magnetic susceptibility measurements indicate that the nickel(II) complexes are diamagnetic, and the conductance studies in DMF solution show the nonionic nature of these complexes.

The infrared spectra of the complexes show a broad band in the 3450–3550-cm^{-1} region, which can be assigned to the stretching frequency of the free hydroxyl group. The observations made by earlier investigators[8] for analogous dicarbinolamine complexes confirm the view that the hydroxyl groups in the ring are not involved in any type of bonding and therefore are free. The absence of any bands due to free carbonyl or amine functional groups indicates that the cyclization has indeed taken place. The strong absorption in the region 1600–1610 cm^{-1} is attributed to the C=N group, which has experienced a positive shift of 10–25 cm^{-1} when compared to the signal for the free ligand, thus confirming the bonding of the azomethine nitrogen to the central metal ion. Medium-intensity bands around 1580 cm^{-1} due to aromatic C=C and two strong bands around 700–750 cm^{-1} due to the aromatic C—H out-of-plane mode have also been observed (Table II).

The electronic spectra of the complexes recorded in DMF solution and solid state offer the most convincing evidence concerning the geometry of the complexes.[21] Even though three spin-allowed transitions and three spin-forbidden transitions are possible[22] in this type of complexes, only a small number of bands are observed in their electronic spectra. Three bands have been observed in the visible region for these complexes. The higher energy band in the region 370–380 nm is assigned to a charge-transfer band, and the second band appearing in the 510–520-nm region is due to a $^1B_{1g} \leftarrow {}^1A_{1g}$ transition. The spectra recorded in chloroform solution also show no appreciable change in the peak position, implying that there is no solvent coordination to these complexes even in potentially coordinating solvents like DMF. The reflectance spectra of these complexes essentially contain features similar to those of the solution spectra, indicating that there is no change in geometry of complexes when going from solid state to solution. The assignments made by earlier workers[23,24] for the nickel(II) complexes of dianionic macrocyclic ligands lend support to this view.

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Table III. ^{1}H NMR Spectral Data for the Nickel(II) Macrocyclic Complexes[a]

complex	-CH (aromatic)	H—C=N-	-OH	$-CH_3$
[Ni(BG-opdn)]	7.13–7.40 (20 H, m) 6.7–6.80 (4 H, d)	7.43 (s)	5.03 (2 H, s)	
[Ni(BG-dmopdn)]	6.9–7.33 (20 H, m) 6.23–6.30 (2 H, d)	7.46 (s)	4.83 (2 H, s)	2.03 (3 H, s) 2.13 (3 H, s)
[Ni(BG-dat)]	7.0–7.36 (20 H, m) 6.36–6.46 (3 H, d)	7.40 (s)	4.90 (2 H, s)	2.2 (3 H, s)
[Ni(BMG-opdn)]	6.96–7.36 (21 H, m)[b] 6.60–6.76 (4 H, d)	NR[c]	4.73 (2 H, s)	1.76 (3 H, s)
[Ni(BMG-dmopdn)]	6.86–7.4 (21 H, m)[b] 6.23–6.33 (2 H, d)	NR	4.53 (2 H, s)	1.70 (3 H, s) 2.10 (6 H, s)
[Ni(BMG-dat)]	6.86–7.33 (21 H, m)[b] 6.30–6.40 (3 H, d)	NR	4.56 (2 H, s)	1.73 (3 H, s) 2.16 (3 H, s)

[a] All values are in δ. [b] Azomethine signal merges with that of phenyl protons. [c] NR = Not resolved.

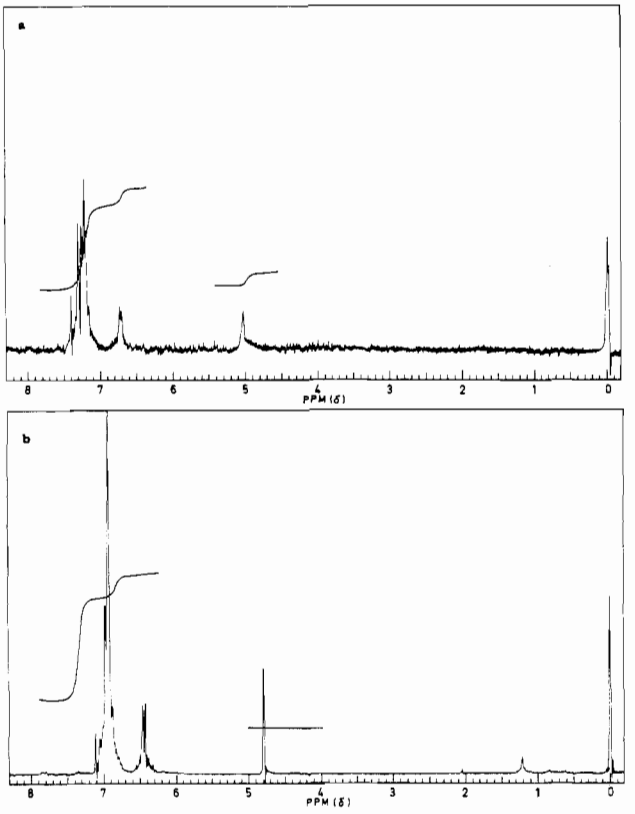

Figure 1. ^{1}H NMR (90 MHz) spectra of [Ni(BG-opdn)] (solvent $CDCl_3/Me_4Si$): (a) before the addition of D_2O; (b) after the addition of D_2O.

The ^{1}H NMR spectral data of the complexes are presented in Table III. The resonances of the methyl groups attached to the benzo ring occur in the vicinity of δ 2.2 and appear as a singlet. The methyl group attached to the carbon atom of the α-diimine group is highly shielded and hence appears near δ 1.7 as a sharp singlet. The hydroxyl proton signal appears in the region δ 4.5–5, and its presence has been unequivocally confirmed by D_2O exchange studies. A few drops of D_2O was added to the chloroform solution of the complex, the mixture was cooled to 0 °C, and the spectra were recorded. The signal due to the hydroxyl group disappears, and an HOD peak appears in the same region; integration of this signal confirms the above assignment (Figure 1). The aromatic resonances occur in the usual δ 7–8 region as a complex multiplet. However, the resonances of the benzo ring protons appear in an upfield position (δ 6.8) as a doublet when compared to the position of phenyl protons which is indicative of the greater shielding experienced by these protons. The ^{13}C NMR spectra of the complexes were recorded in $CHCl_3$–$CDCl_3$–Me_4Si solvent. The aromatic carbon resonances are observed in the 120–130 ppm region as in the case of other aromatic compounds.

Table IV. Important m/z Peaks in the Mass Spectra of the Macrocyclic Complexes of Nickel(II)

complex	m/z
[Ni(BG-opdn)]	634, 528, 390, 320, 238, 165
[Ni(BG-dmopdn)]	662, 528, 394, 320, 216, 160
[Ni(BG-dat)]	648, 528, 390, 296, 238, 165
[Ni(BMG-opdn)]	648, 542, 390, 320, 238, 146
[Ni(BMG-dmopdn)]	676, 542, 394, 334, 238, 160
[Ni(BMG-dat)]	662, 542, 394, 334, 238, 160

It has been reported[25] that the meta carbons are insensitive to substitution in the phenyl ring and the para position in monosubstituted benzene is said to be more sensitive to changes in π density in the ring. However, in the present series, no appreciable change in the position of the benzo ring signal has been observed on the introduction of methyl groups in the ring. The methyl carbon resonance is observed in the region 15–20 ppm, which is within the reported range[26,27] for this group. Also, the carbinolamine carbons are expected to appear in slightly upfield when compared to the other aromatic carbon signal, as large upfield shifts were observed[28] when hydroxyl groups were substituted for methyl groups in alkyl carbonium ions. In general, the results obtained from ^{13}C NMR spectra are consistent with those of ^{1}H NMR spectra, confirming the validity of the proposed structure.

Further confirmation of the structure of the complexes is provided from a study of the mass spectra of the complexes.[29] All the nickel(II) macrocyclic complexes exhibited a molecular ion peak (M^+) in their mass spectra. In the ionization process two possibilities can be visualized, viz.: (a) the electron is removed from a molecular orbital localized mainly on the metal; (b) the electron is removed from a molecular orbital localized mainly on the π system of the ligand. Even though the present results do not give conclusive evidence to distinguish between these two possibilities, the second possibility has been suggested in the present complexes in accordance with the results reported for β-diketonate complexes,[30] where the π-electron delocalization is quite appreciable.

In the case of metalloporphyrins, the fragmentation of the complex occurs without the loss of the central metal ion. The complexes under study, with a highly conjugated inner ring, appear to closely follow the same behavior. The intensity of the molecular ion peak is weak as in the case of dialkoxide derivatives of Ni-

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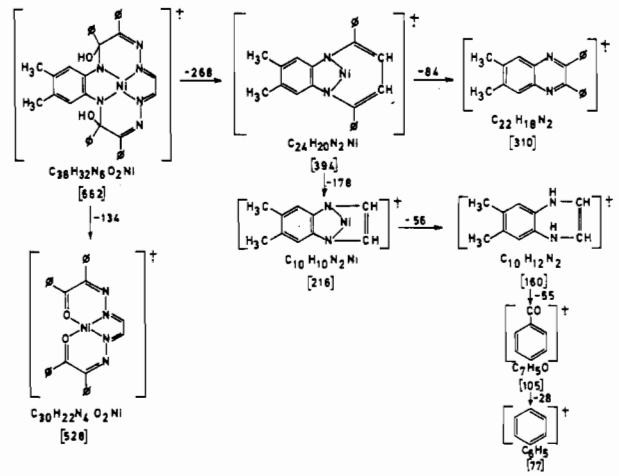

Figure 2. Mass spectral fragmentation pattern of the macrocyclic complex [Ni(BG-dmopdn)].

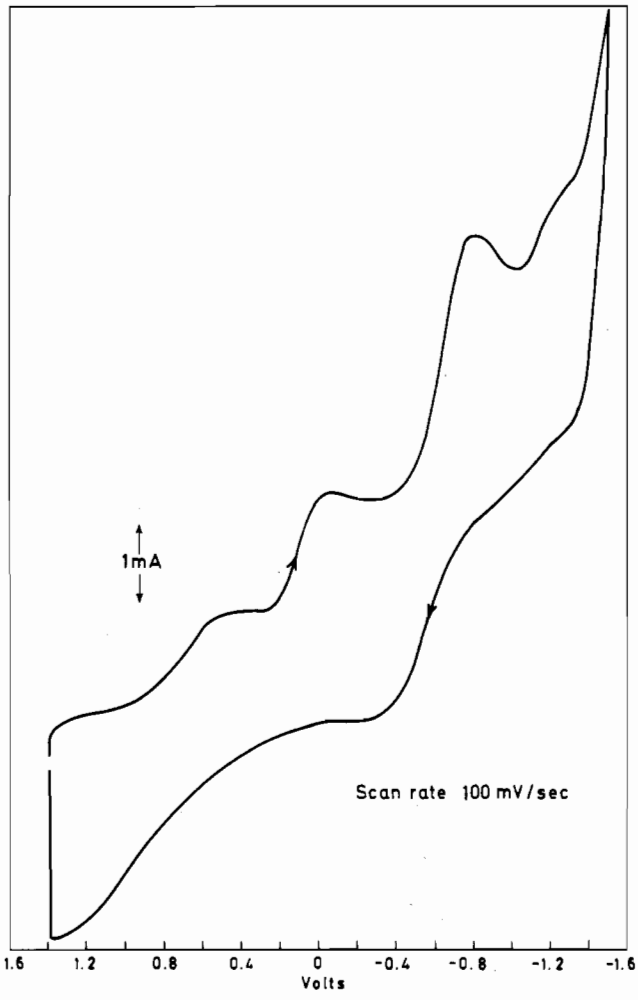

Figure 3. Cyclic voltammogram of [Ni(BMG-dmopdn)] (1.2×10^{-3} DMF solution, with 0.1 M TEAP, scan rate 100 mV/s).

(TAAB) complexes.[31] The important m/z peaks in the mass spectra of the macrocyclic complexes have been presented in Table IV. A tentative mechanism for the fragmentation of the complexes is given in Figure 2. The initial fragmentation involves the cleavage of the aromatic benzo ring with two nitrogen atoms, which leads to the formation of the nickel complex of the precursor N_2O_2 ligand. This peak is observed in the case of all six macrocyclic complexes. In another pathway, the hydroxyl groups of

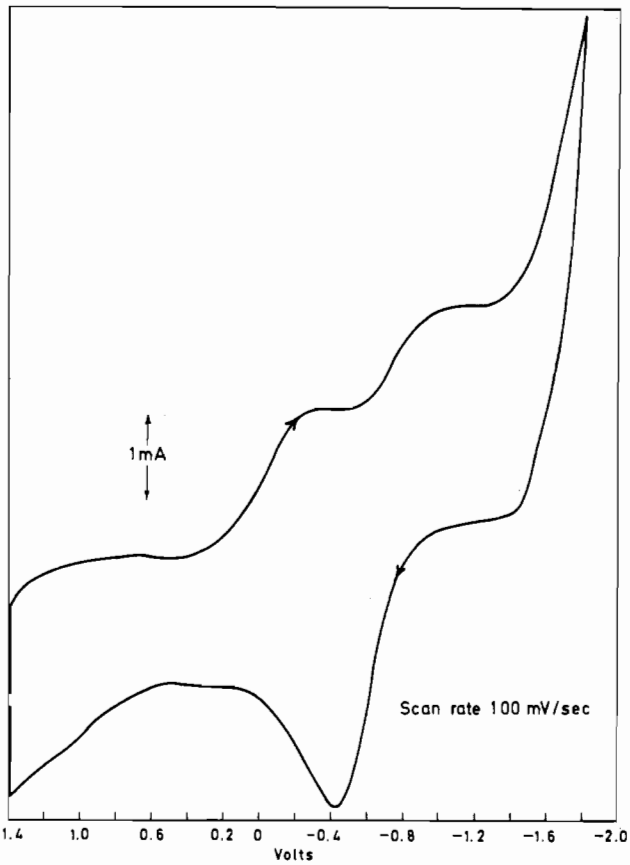

Figure 4. Cyclic voltammogram of [Ni(BMG-dat)] (1.2×10^{-3} DMF solution, with 0.1 M TEAP), scan rate 100 mV/s).

the carbinolamines form an intermediate oxirane ring with the neighboring carbon atom, which is followed by the migration of the H atom to the neighboring nitrogen atom. The subsequent cleavage of the oxirane ring leads to formation of the bond between the phenyl carbon atom and the olefinic carbon atom. The H atom attached to the β-nitrogen migrates to the α-nitrogen atom and a new C=C bond is established with the subsequent elimination of O—C—N—H group and the formation of a new C—N bond. In the case of [Ni(BG-dmopdn)], the loss of two O—C(=O)– groups results in the formation of a m/z 216 fragment. The loss of the central metal ion and the subsequent abstraction of two H atoms gives rise to the m/z 160 fragment.

The thermograms of the complexes do not show any weight loss until 200 °C, indicating that there is no water of hydration in the complexes. The decomposition of the complexes mainly occurs in two stages. This is evident from the two inflections in the thermograms, one occurring in the range 250–300 °C and the other at 350–400 °C. A stable greenish residue was obtained above 700 °C, which is due to the formation of nickel oxide. In all these cases thermograms are recorded under a nitrogen atmosphere and the degradation behavior in air has not been investigated.

The electrochemistry of the macrocyclic complexes was investigated in dry DMF with TEAP as supporting electrolyte in a three-electrode assembly specially designed for this purpose. Figures 3 and 4 show some typical I–E curves of nickel(II) macrocyclic complexes, and the relevant data are collated in Table V. The redox behavior of complexes of monoanionic and other dianionic ligands have been reported.[32,33] The monoanionic nickel(II) complexes synthesized by Cummings and Sievers[33] have been found to exhibit irreversible oxidation at 0.27 and 0.23 V and cathodic reductions at −2.30 and −2.34 V. The effect of conjugation of the imine linkages in the macrocyclic ring has also

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Table V. Electrochemical Data for the Nickel(II) Macrocyclic Complexes[a]

complexes	E_{p_c}, V	E_{p_a}, V	ΔE, mV	$E_{1/2}$(pol),[b] V
[Ni(BG-opdn)]	−0.060 −0.610	−0.350	260	−0.735
[Ni(BG-dmopdn)]	−0.070 −0.690	−0.390	300	−0.685
[Ni(BG-dat)]	−0.800	−0.400	400	−0.730
[Ni(BMG-opdn)]	−0.700	−0.100		−0.610
[Ni(BMG-dmopdn)]	−0.050 −0.790	−0.300		−0.670
[Ni(BMG-dat)]	−0.240 −0.980	−0.420		−0.635

[a] $E_{1/2}$ vs. SCE with a Pt electrode; solvent DMF/TEAP, scan rate 100 mV/s. [b] Polarographic reduction potential.

been highlighted,[32,34] wherein the $E_{1/2}$ value for oxidation of Ni^{2+} was found to be 100 mV more than that of the saturated analogues. However, this increase is twofold when the imines are conjugated. The diimino macrocyclic ligands are good π acceptors and are found to stabilize low-valent transition-metal species.[35-37] Several authors have correlated[38-40] the data obtained for the ferrocene couple by using the Hammett or Taft relations.

The presence of methyl substituents in the complexes under study shifts the $E_{1/2}$ values to more negative potentials. The cathodic reduction potentials (E_{p_c}) of the complexes range from −0.610 V for [Ni(BG-opdn)] to −0.980 V in the case of [Ni(BMG-dat)]. The introduction of a methyl group on the benzo ring does shift the reduction potentials to more negative range. There is an increase of 190 mV when a methyl group is introduced on the benzo ring. However, this increase is only 80 mV when two methyl groups are introduced on the ring. Similarly, a methyl group on the vinylic carbon of the α-diimine shifts E_{p_c} by 90 mV. In the case of the remaining two nickel complexes, where there is a methyl group on the α-diimine function, the shift is 280 and 90 mV for the introduction of one and two methyl groups, respectively. The paradoxical behavior exhibited by these complexes on the introduction of the second methyl group could not be satisfactorily explained. Interestingly, the same trend is observed in the E_{p_a} values also except in the case of [Ni(BMG-opdn)]. This value is −0.100 V in contrast to the −0.300 to −0.420 V potential range observed in the other macrocyclic complexes.

The effect of remote substituents on the electrode potential has clearly indicated that the position of the substituent is also important in tuning the properties of the parent molecule. The reduction potentials ($E_{1/2}$) in the case of [Fe(Me_2[15]tetraenatoN$_4$)] and [Fe(Me_6[15]tetraenatoN$_4$)] have been reported to be −2.47 and −2.57 V, respectively. The addition of four methyl groups has shifted the reduction potential only by 100 mV. However, in the case of [Ni(Me_2[14]aneN$_4$)]$^{2+}$ and [Ni(Me_6[14]aneN$_4$)]$^{2+}$, two axial methyl groups have contributed to the half-wave potential to the tune of 183 mV. These data clearly show[34] that the presence of additional methyl groups need not be always additive and the total contribution may not be equal to

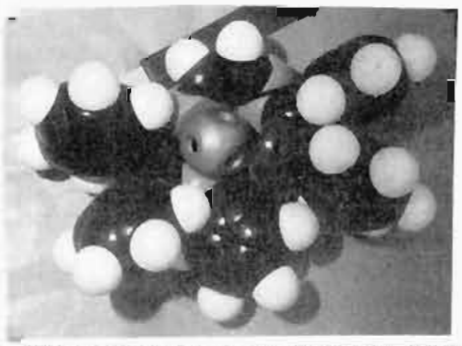
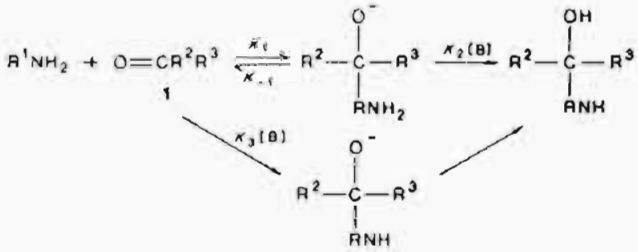


Figure 5. CPK model for the macrocyclic complex [Ni(BG-opdn)].

Scheme II



the simple arithmetic sum of the individual contribution to the reduction potential. The study of variation of reduction potentials (E_0) of 1,4-benzoquinones and substituted benzoquinone in both alcoholic and aqueous solutions has shown[41] that the introduction of a second methyl group on the ring decreases the E_0 value at least by 0.06 V and this effect is more pronounced when the methyl groups are on adjacent carbon atoms (e.g. 2,3-dimethyl-1,4-benzoquinone). It has already been reported[42] that the additive relationship for ortho positions is difficult to rationalize and the largest deviation in the shieldings seems to occur in the ^{13}C spectrum of 2,3-dimethylaniline, to occur, although smaller abnormalities are present in the other dimethyl-substituted anilines.

The stereochemistry of the complexes can be better understood by examination of molecular models (Figure 5). Models suggest that the four nitrogen atoms that are involved in the coordination lie in one plane and so too is the benzo ring. However, the four phenyl groups attached to the inner ring must lie almost perpendicular to the plane of the inner ring. This situation is analogous to that encountered in the tetraphenylporphyrin complexes, where the phenyl groups attached to the periphery of the ligands are orthogonal to the plane of the tetrapyrrole inner ring.[43-45] The proximity of the phenyl groups prevents their coplanarity in the present case. The free rotations of the phenyl groups are thus very much restricted by steric interference, and hence the overlap of the π systems in the phenyl rings and the inner ring could be expected to be very small unlike in the case of metalloporphyrin.

Another interesting feature suggested by examination of models is the orientation of the hydroxyl groups of the dicarbinolamine moiety in the molecule. Due to steric constraints the cis arrangement of the hydroxyl groups is not favored; instead they are most likely oriented in trans positions. This is in contrast to the observation made by Tasker et al.[10] from the X-ray crystal structure of a dicarbinolamine complex of Zn(II) obtained by the template condensation of 2,6-diacetylpyridine and dihydrazinobipyridyl. This is because of the fact that the crowding of phenyl groups in the present series of complexes does not permit the cis

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orientation of the hydroxyl groups.

Reaction with Acids. Dry HCl gas was passed into the methanolic solutions of the complexes for 15 min. The infrared spectra of the resulting products indicated that the complexes have undergone decomposition.

A few drops of perchloric acid was added to 0.1 M alcoholic solutions of the complexes and stirred overnight. The dark colored products that separated were filtered, thoroughly washed with water and ether, and finally dried in vacuo at 100 °C. Infrared spectra of the products showed a weak perchlorate absorption in the 1100-cm^{-1} region. However, the OH absorption in the 3400-cm^{-1} region did not disappear. Addition of a few more drops of the acid resulted in the decomposition of the complexes.

Several attempts to isolate the ligands by demetalation of the complexes were not successful.

Factors Affecting the Stabilization of Dicarbinolamines. The mechanism of the formation of Schiff bases via an intermediate carbinolamine has been well established. The reaction of a dicarbonyl compound with a diamine can give rise to three different products according to the reaction conditions and the nature of the reactants. They are (a) diimine, (b) imine–carbinolamine, and (c) dicarbinolamine. Earlier reports on the isolation of imine–carbinolamine complexes have shown that the quantities of the diamine, the dicarbonyl compound, and the metal salt are essentially equimolar. But, in the present case the large excess of diamine in the reaction mixture essentially provides basic conditions for the reaction. In the case of a general-base-catalyzed addition of an amine to a carbonyl compound, Scheme II has been proposed.

The base catalyst B^- and compound **1** react according to the Eigen diffusion mechanism,[46] and if $K_1 << K_{-1}$, carbinolamine formation will not be very fast. The excess diamine present in the reaction mixture of the present series of complexes acts as a base catalyst in the formation of the carbinolamine.

Leussing et al.[47] have reported that, unlike Pb^{2+}, Mn^{2+}, and Zn^{2+}, metal ions like Co^{2+}, Cu^{2+}, and Ni^{2+} were ineffective promoters in the Schiff base formation reaction when they act as a template. The inactivity of the latter group of metal ions, which has partially filled d orbitals, was ascribed to rigid M–L geometries imposed by the ligand field splitting of the 3d orbital. Also, the reacting ligands are found to be more rigidly held by the most strongly acidic ions and hence less free to react with each other.

Ring strain introduced by the 120° bond angle of the imine group is less in the six membered chelate ring than in the five-membered chelate ring of the macrocycle. The presence of bulky phenyl groups in the reactants also renders the relief of steric strain all the more difficult. The results of various kinetic studies and the formation of carbinolamine, viz. dehydration of carbinolamines formed from 4-chlorobenzaldehydes[48] and hydrazines and carbinolamine formation for a secondary amine,[49] have clearly established the role of pH in the stabilization of the carbinolamine. At neutral and slightly alkaline pH the dehydration of carbinolamine becomes the rate-determining step and hence the stabilization of carbinolamine is facilitated.[50]

This study also confirms the suggestion made by Tasker et al.[10] that formation of the planar conjugated macrocycle proceeds via dicarbinolamine before any elimination of water occurs. The rigidity of the macrocyclic ligand precursor, by virtue of its complete conjugation and the steric hindrance offered by bulky aromatic diamines, does not favor the dehydration of the carbinolamine. Surprisingly, the presence of electron-releasing methyl groups either in the benzo ring of the diamine or in the vinylic carbon of the diimine has not changed the nature of the resulting product. In light of the foregoing discussion it is not unreasonable to suggest that the combination of all the factors indicated above has resulted in the stabilization of dicarbinolamine complexes isolated in the present investigation.

Acknowledgment. I am grateful to Prof. V. T. Ramakrishnan for his helpful discussions in interpreting the mass spectra, to Dr. E. Ponnusamy for recording the mass spectra, and to Dr. R. Balasubramanian and Dr. Sur for their help in microanalysis.

Registry No. Ni(BG-opdn), 99119-31-0; Ni(BG-dmopdn), 104198-70-1; Ni(BG-dat), 104198-71-2; Ni(BMG-opdn), 104198-72-3; Ni(BMG-dmopdn), 104198-73-4; Ni(BMG-dat), 104213-75-4; BG, 99044-72-1; BMG, 104198-74-5; opdn, 95-54-5; dmopdn, 3171-45-7; dat, 496-72-0; BMH, 5344-88-7; glyoxal, 107-22-2; methylglyoxal, 78-98-8.

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