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# Facile Template Synthesis of Nickel(II) Complexes of Dibenzotetraaza[14]annulenes

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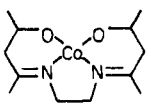
Syntheses of nickel(II) complexes of substituted dibenzotetraaza[14]annulenes are reported. In situ condensations of diamines with β-diketones or 1,5-benzodiazepinium salts in the presence of nickel(II) afforded symmetrically substituted macrocycles. Reaction of the [*N*′,*N*″-(1,3-propanediylidine)bis(1,2-benzenediaminato)]nickel(II) cation with β-diketones or keto acetals gave complexes that could be unsymmetrically substituted on the diimine chelate rings. Complexes with substituents on the benzenoid rings were generally more soluble in organic solvents than complexes substituted on the diimine rings. Hypsochromic shifts in the UV spectra of the complexes correlated with the degree of substitution in diimine-substituted complexes, but not in comparable phenylene-substituted complexes, for which only minor shifts in the UV spectra occurred.

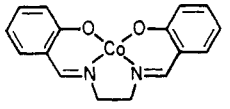
## Introduction

Many features of the characteristic cobalt–carbon bond chemistry of coenzyme $B_{12}$ are manifested by a variety of other cobalt complexes. Bis(dimethylglyoximato)cobalt, cobaloxime, is widely accepted and employed as a $B_{12}$ model.[1] Nevertheless, it suffers many limitations as a model for the cobalamins, particularly with respect to peripheral reactions.[2]

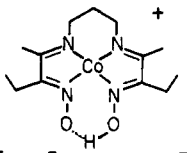
The search for $B_{12}$ analogues that more closely mimic the chemistry of $B_{12}$ or the mechanistic aspects of its enzymatic reactions have given rise to a variety of models including the organocobalt complexes of bis(acetylacetone) ethylenediimine (BAE), bis(salicylaldehyde) ethylenediimine (SALEN), and *N*′,*N*″-propanediylbis(2,3-pentanedione 2-imine 3-oxime) ($C_2$-(DO)(DOH)pn).[3,4]



[R-Co(BAE)B]



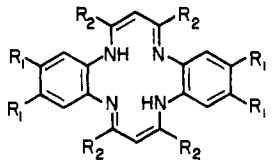
[R-Co(SALEN)B]



[R-Co[$C_2$(DO)(DOH)$_{pn}$]B]$^+$

While these model systems have been useful in elucidating the chemistry and possible mechanisms of action of the cobalamin coenzymes, there are still aspects of their chemistry that are irrelevant for cobalamins and features of the latter that are not reflected in the model systems.[3,4]

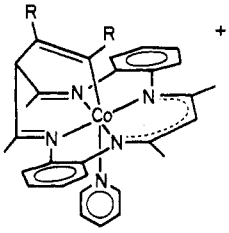
We were attracted to dibenzotetraaza[14]annulenes (DBTAA, **1**)[5] as a model system for coenzyme $B_{12}$ because of its potential capacity for accommodating a variety of substituents on the phenylene and diimine carbon atoms, through direct synthesis[6-9] or via addition/substitution reactions at the reactive β-methine carbon center of the macrocycle.[7,10-12]



**1**

Furthermore, the macrocycle can adopt conformations ranging from planar ($R_1$, $R_2$ = H)[13] to saddle shaped ($R_1$ = H, $R_2$ = $CH_3$)[14] and thus provide a variety of peripheral steric interactions. Additionally, the macrocycle is of interest because of its ability to stabilize unusual spin states, as well as incorporate metal ions with oxidation states 1+, 2+, and 3+ and form π anion and π cation radicals.[14]

Thus, Goedken[10] was able to prepare unusual high-spin five-coordinate cobalt(III) complexes of the type [Co($Me_4$-DBTAA)X], X = Cl, Br, I, or diamagnetic six-coordinate species, [Co($Me_4$-DBTAA)$(py)_2$]$^+$. In the latter complex, one of the axial pyridine ligands is much more labile than the other, allowing facile substitution of one of the bases with another ligand such as $NH_3$. These complexes are highly reactive at the methine carbons; e.g., acetylenes undergo cycloaddition reactions across the six-membered chelate ring to give complexes such as **2**.



**2**

This reactivity of the macrocycle and the central metal ion is relevant to $B_{12}$ studies since we and others have observed that even subtle differences in the electronic and/or ligand array of other cobalt complexes had a dramatic effect on the chemistry of cobalt–carbon bonds.[3,16,17]

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In this paper we report the synthesis of nickel(II) complexes of substituted dibenzotetraaza[14]annulenes by three procedures. In situ template reactions starting from either 1,2-diamines with β-diketones or 1,5-benzodiazepinium salts in the presence of nickel(II) afford symmetrical macrocycles. We also found the condensation of the [*N*,*N*″-(1,3-propanediylidine)bis(*o*-phenylenediamine)]nickel(II) cation with β-diketones to be a useful route to macrocyclic complexes unsymmetric with respect to substitution in the diiminato chelate rings.

The dibenzotetraaza[14]annulene macrocycle was first synthesized as its nickel complex by Jäger[18] under fairly severe conditions by reacting a β-keto iminato- or β-diketonato-nickel(II) complex with *molten* *o*-phenylenediamine, cyclization to the macrocycle being favored by acyl substituents at the β-methine carbon atoms of the six-membered chelate rings. Subsequent syntheses of this class of macrocycle often relied on template reactions in the presence of nickel(II) salts where the *o*-phenylenediamine component was added as the free base[7,9,10,19-22] or the preformed nickel(II) complex[9,23] and the source of the diiminato chelate ring was propynal,[19] 3-chloroacrolein,[24] β-dialdehydes,[9,23] β-diketones,[7,9,21,24,25] acetals,[20,27] or a preformed β-diketone–nickel(II) complex.[18] Removal of nickel from the macrocyclic complexes with acid followed by remetalation has then provided other metal complexes of **1**.[7,25]

A less favored synthetic approach to complexes of type **1** is through nontemplate reaction of *o*-phenylenediamine with propynal,[19,28] β-diketones,[29] β-dialdehydes,[30] 3-alkoxyacroleins,[22,31] 1,2-dithiolium salts,[8] or the bis(anil) condensation product of propynal with *o*-phenylenediamine,[32] followed by metalation of the free-base macrocycle.

## Experimental Section

Physical measurements were carried out as previously described.[6] The starting materials were obtained commercially and generally used without further purification, except for *o*-phenylenediamine, which was recrystallized from toluene, stored in the dark, and used within 2–4 weeks of purification. The [*N*,*N*″-(1,3-propanediylidene)bis(1,2-benzenediaminato)-*N*,*N*′,*N*″,*N*‴]nickel complexes and 1,5-benzodiazepinium salts used in the syntheses of the macrocyclic complexes were prepared as described previously.[6]

**Preparation of [7,16-Dihydrodibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecinato-*N*$^5$,*N*$^9$,*N*$^{14}$,*N*$^{18}$]nickel(II) Hemihydrate (3a). (a) In situ.**[33] The parent macrocyclic complex was prepared from an aqueous mixture of *o*-phenylenediamine, 1,1,3,3-tetramethoxypropane, and nickel(II) acetate tetrahydrate (2:2:1), as communicated previously.[27] The air-dried product was obtained as the hemihydrate. Anal. Calcd for $C_{18}H_{14}N_4Ni \cdot {}^1/_2H_2O$: C, 61.06; H, 4.27; N, 15.82. Calcd for $C_{18}H_{14}N_4Ni \cdot H_2O$: C, 59.55; H, 4.44; N, 15.43. Found: C, 60.46; H, 4.40; N, 15.40. NMR ($CDCl_3$, ppm): 7.66 (d, $J$ = 6 Hz, 4 H, ArNC*H*), 7.5–6.7 (m, 8 H, Ar *H*), 5.39 (t, $J$ = 6 Hz, 2 H, ArNCHC*H*). MS (*m*/*e* (% relative intensity)): $P^+$, 344 (100); $P^{2+}$, 172 (23). ES ($CHCl_3$, nm (ε): 426 (45 390).

**(b) Via Benzodiazepinium Salt.**[27] An aqueous DMF solution (20:50 mL) of 1,5-benzodiazepinium hexafluorophosphate (1.5 g, 0.005 mol) and nickel(II) acetate tetrahydrate (0.62 g, 0.0025 mol) was refluxed for 2 h. After the reaction mixture was cooled to room temperature and filtered, the filtrate was diluted with water to precipitate a flocculent brownish purple solid. The crude product was washed with water and methanol to give a purple solid. Soxhlet extraction of this material with chloroform gave 0.29 g (33% yield) of pure crystalline product.

The reaction was also carried out in aqueous methanol (25:100 mL) under the same conditions to give 0.20 g (23%) of the pure purple crystalline complex after purification.

**Preparation of [7,16-Dihydro-6-methyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecinato-*N*$^5$,*N*$^9$,*N*$^{14}$,*N*$^{18}$]nickel(II) (3b).** (a) An aqueous DMF solution (75:50 mL) of [*N*,*N*″-(1,3-propanediylidine)bis(1,2-benzenediaminato)-*N*,*N*′,*N*″,*N*‴]nickel(II) hexafluorophosphate (2.3 g, 0.005 mol) and excess 4,4-dimethoxy-2-butanone (2.0 mL) was refluxed for 3 h. The resulting reddish brown suspension was cooled and filtered and the solid washed with water. The reddish brown solid (1.2 g) was chromatographed on alumina (Camag, neutral, activity 1,100 g) with methylene chloride. A dark red band containing the desired macrocyclic complex was cleanly eluted. Pure product (0.23 g, 13%) was obtained after solvent removal and drying in vacuo at 80 °C for 48 h. Anal. Calcd for $C_{19}H_{16}N_4Ni$: C, 63.55; H, 4.49; N, 15.60. Found: C, 63.53; H, 4.61; N, 15.54. NMR ($CDCl_3$, ppm): 7.49, 7.45 (dd, $J$ = 7 Hz, 2 H, ArNC*H*), 7.3–6.6 (m, 9 H, Ar*H* + ArNC*H*), 5.29 (t, $J$ = 7 Hz, 1 H, ArNC($CH_3$)C*H*), 5.16 (d, $J$ = 7 Hz, 1 H, ArNCHC*H*), 2.46 (s, 3 H, $CH_3$). MS (*m*/*e* (% relative intensity)): $P^+$, 358 (100); $P^{2+}$, 179 (21). ES ($CHCl_3$, nm (ε): 421 (42 300).

(b) An aqueous DMF (3:2) solution (115 mL) containing [*N*,*N*″-(1-methyl-1,3-propanediylidine)bis(1,2-benzenediaminato)-*N*,*N*′,*N*″,*N*‴,′,′]-nickel(II) hexafluorophosphate (1.4 g, 0.003 mol) and excess 1,1,3,3-tetramethoxypropane (1.5 mL) was refluxed for 3 h. Filtration of the resulting suspension and aqueous washing left the macrocyclic complex as a purple solid (0.56 g, 52%). The crude product was purified by chromatography on alumina as described above.

**Preparation of [7,16-Dihydro-6,8-dimethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecinato-*N*$^5$,*N*$^9$,*N*$^{14}$,*N*$^{18}$]nickel(II) (3c).** Treatment of an ethanolic solution (60 mL) of [*N*,*N*″-(1,3-propanediylidene)bis(1,2-benzenediaminato)-*N*,*N*′,*N*″,*N*‴]nickel(II) hexafluorophosphate (0.23 g, 0.50 mmol) with 1 equiv of sodium hydroxide produced an orange-brown suspension. Addition of excess 2,4-pentanedione (1.0 mL) and refluxing for 18 h gave a purplish black residue. Chromatography on alumina (Camag, neutral, activity 3, 80 g) eluted with methylene dichloride gave the product as a pure compound which separated as a well-defined burgundy fraction. Further elution of the column removed trace amounts of the unsubstituted parent macrocyclic complex. The pure product (0.05 g, 27%) was obtained by recrystallizing with $CH_2Cl_2$–$C_2H_5OH$ and drying in vacuo at 80 °C. Anal. Calcd. for $C_{20}H_{18}N_4Ni$: C, 64.39; H, 4.86; N, 15.02. Found: C, 64.31; H, 5.00; N, 15.20. NMR ($CDCl_3$, ppm): 7.27 (d, $J$ = 6 Hz, 2 H, ArNC*H*), 7.2–6.6 (m, 8 H, Ar*H*), 5.16 (t, $J$ = 6 Hz, 1 H, ArNCHC*H*), 4.96 (s, 1 H, ArNC($CH_3$C*H*)), 2.27 (s, 6 H, $CH_3$). MS (*m*/*e* (% relative intensity)): $P^+$, 372 (100); $P^{2+}$, 186 (22). ES ($CHCl_3$, nm): 404 (34 540).

**Preparation of [7,16-Dihydro-6,15(17)-dimetbyldibenzo[*b*,*i*]-[1,4,8,11]tetraazacyclotetradecinato-*N*$^5$,*N*$^9$,*N*$^{14}$,*N*$^{18}$]nickel(II) (3d). (a) Via Chelate Intermediate.** Refluxing a dark green aqueous DMF solution (45:25 mL) containing [*N*,*N*″-(1-methyl-1,3-propanediylidene)bis(1,2-benzenediaminato)-*N*,*N*′,*N*″,*N*‴]nickel(II) hexafluorophosphate (1.1 g, 0.0024 mol) and excess 4,4-dimethoxy-2-butanone (1.5 mL) of 12 h produced a purplish green suspension. Filtration and aqueous washing left the product as a purple solid (0.21 g, 23%).

**(b) In Situ.** An aqueous DMF solution (75:50 mL) containing *o*-phenylenediamine (2.2 g, 0.02 mol), 4,4-dimethoxy-2-butanone (2.3 mL, 0.02 mol), and nickel(II) acetate tetrahydrate (2.5 g, 0.01 mol) was refluxed as a dark greenish brown suspension for 12 h. After it was cooled to room temperature, the reaction mixture was filtered and the purple product (0.84 g, 22%) collected and washed with water. The crude product was purified by recrystallization from methylene chloride–methanol or by column chromatography (Camag, neutral alumina, activity 3) of small portions eluted with methylene chloride. Anal. Calcd


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(33) Previous attempts by Honeybourne[20] to prepare the parent macrocyclic complex by simultaneous reaction of *o*-phenylenediamine, 1,1,3,3-tetramethoxypropane, metal dichloride, and hydrochloric acid were unsuccessful. Formation of the metal(II) *o*-phenylenediamine complex prior to addition of the acetal and acid was reported to be more satisfactory.

for $C_{20}H_{18}N_4Ni \cdot {}^1/_2H_2O$: C, 62.87; H, 5.01; N, 14.66. Found: C, 63.22; H, 5.10; N, 14.78. NMR ($CDCl_3$, ppm): 6.94 (d, $J$ = 7 Hz, 2 H, ArNC*H*), 7.2–6.5 (m, 8 H, Ar*H*), 5.06 (d, $J$ = 7 Hz, ArNCHC*H*), 2.36 (s, 6 H, $CH_3$). MS ($m/e$ (% relative intensity)): $P^+$, 372 (100); $P^{2+}$, 186 (22). ES ($CHCl_3$, nm ($\epsilon$)): 407 (38 730).

**(c) Via Benzodiazepinium Salt: Attempted Preparation.** A methanolic solution (40 mL) of 2-methyl-1,5-benzodiazepinium hexafluorophosphate (0.15 g, 0.005 mol) remained purple after addition of aqueous (10 mL) nickel(II) acetate tetrahydrate (0.06 g, 0.0025 mol). After it was refluxed for 10 min, the solution turned clear brown, with no further change after 2 h of refluxing. UV spectra of the reaction mixture showed no indication of the macrocyclic complex being present.

Carrying out the reaction after neutralizing the benzodiazepinium salt with 1 equiv of sodium hydroxide likewise did not result in formation of any macrocyclic complex.

**Preparation of [7,16-Dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecinato-$N^5$,$N^9$,$N^{14}$,$N^{18}$]nickel(II) (3e). (a) In Situ.** The macrocyclic complex was prepared from an aqueous ethanolic solution of nickel(II) acetate, *o*-phenylenediamine, and 2,4-pentanedione (1:2:2) by a modification of the procedure described by Goedken and Weiss.[25] Refluxing of the reaction mixture was carried out open to the atmosphere and proceeded for 4 h before the solvent was stripped off under vacuum. Extraction of the residue with water (250 mL) and removal of the magenta-brown to colorless filtrate left a dark green solid. This crude residue was washed into a flask with methylene dichloride (70 mL) and ethanol (10 mL). Solvent was then removed under reduced pressure and the resulting green solid dried.

Methylene chloride extracts (80 mL) of the crude product were chromatographed (9 × ${}^1/_2$ in. column) on neutral alumina (150 g, Camag, activity 1). Elution with methylene chloride cleanly removed a well-defined dark green band in about 125 mL of solvent. The pure product was obtained in 15–18% yield after removal of solvent. Further elution of the column afforded a trace amount of magenta solid ($\lambda_{CH_3OH}$ 355 nm) that was not further identified. Substantial amounts of dark green impurities remained at the top of the column.

**(b) Via 2,4-Dimethyl-1,5(3*H*)-Benzodiazepine.** The procedure was the same as described previously.[34]

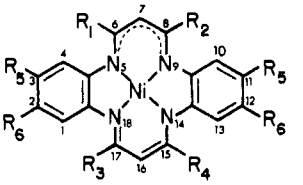
**(c) Via 2,4-Dimethyl-1,5(3*H*)-benzodiazepinium Hexafluorophosphate: Attempted Preparation.** A solution of the benzodiazepinium salt (0.32 g, 0.001 mol) in ethanol (50 mL) was treated with an aqueous nickel(II) acetate (0.13 g, 0.0005 mol) solution (25 mL). After the mixture was refluxed for 2 h, the color changed from purple to pale yellow-green, with no precipitate evident. The UV spectrum of this solution was consistent with the presence of 2-methylbenzimidazole and 2-methylbenzimidazolium salt only. Substituting aqueous DMF (1:2) as the reaction solvent did not change the outcome of the reaction.

**(d) Via Cationic Intermediate.** Addition of excess 2,4-pentanedione to a methanolic solution of [*N*,*N*″-(1,3-dimethyl-1,3-propanediylidine)-bis(benzenediaminato)-*N*,*N*′,*N*″,*N*‴]nickel(II) acetate, prepared in situ,[6] instantly afforded a magenta solution at room temperature. UV spectra of the reaction mixture were dominated by absorption bands ($\lambda_{max}$ 343 nm) attributable to the macrocyclic complex. Residual traces of the bis(imino aminato) reagent were evident as a weak shoulder at 418 nm on one side of the complex absorption band.

**Preparation of [7,16-Dihydro-2,11(12)-dimethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecinato-$N^5$,$N^9$,$N^{14}$,$N^{18}$]nickel(II) (3f).** An aqueous solution (150 mL) containing 3,4-diaminotoluene (2.4 g, 0.02 mol), 1,1,3,3-tetramethoxypropane (3.5 mL, 0.02 mol), and nickel(II) acetate tetrahydrate (2.5 g, 0.01 mol) was refluxed for 18 h. After the mixture was cooled, the purple product (3.4 g) was collected by filtration and washed with water (50 mL) and methanol (75 mL). Reprecipitation of a methylene chloride solution of the crude product with ethanol afforded purple crystals, which were dried in vacuo at ambient temperature. Anal. Calcd for $C_{20}H_{18}N_4Ni$: C, 64.39; H, 4.86; N, 15.02. Found: C, 64.56; H, 4.84; N, 14.78. NMR ($CDCl_3$, ppm): 7.7–7.5 (m, 4 H, ArNC*H*), 7.4–6.5 (m, 6 H, Ar*H*), 5.27 (t, $J$ = 7 Hz, 2 H, ArNCHC*H*), 2.27 (s, 6 H, $CH_3$). MS ($m/e$ (% relative intensity)): $P^+$, 372 (100); $P^{2+}$, 186 (24). ES ($CHCl_3$, nm ($\epsilon$)): 431 (64 060).

**Preparation of [7,16-Dihydro-2,11(12)-di-*tert*-butyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecinato-$N^5$,$N^9$,$N^{14}$,$N^{18}$]nickel(II) (3g).** Refluxing an aqueous DMF (40:25 mL) solution containing 3,4-diamino-1-*tert*-butylbenzene (0.82 g, 0.005 mol), 1,1,3,3-tetramethoxypropane (0.9 mL, 0.005 mol), and nickel(II) acetate tetrahydrate (0.66 g, 0.0025 mol) for 12 h produced a thick purple suspension. Filtration of the cooled reaction mixture and washing with water left 1.0 g (95%) of purple solid. The product was purified by column chromatography on alumina (Camag, neutral, activity 3) with methylene chloride and dried in vacuo at 80 °C. Extensive decomposition occurred on the column, and only two- thirds of the product applied to the column was recovered as a purple crystalline product. Anal. Calcd for $C_{26}H_{30}N_4Ni$: C, 68.95; H, 6.61; N, 12.25. Found: C, 67.42; H, 6.48; N, 12.00. NMR ($CDCl_3$, ppm): 7.67–7.57 (dd, $J$ = 6.5 Hz, 4 H, ArNC*H*), 7.4–6.8 (m, $J$ = 6 Hz, Ar*H*), 5.32, 5.26 (tt, $J$ = 6.5 Hz, 2 H, ArNCHC*H*), 1.32 (s, 18 H, $CH_3$). MS ($m/e$ (% relative intensity)): $P^+$, 456 (100); $P^{2+}$, 228 (11). ES ($CHCl_3$, nm ($\epsilon$)): 431 (82 880).

**Table I.** [Dibenzotetraaza[14]annulene]nickel(II) Complexes Prepared in This Study



**3**

| complex | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ | $R_6$ |
|---|---|---|---|---|---|---|
| **3a** | H | H | H | H | H | H |
| **3b** | $CH_3$ | H | H | H | H | H |
| **3c** | $CH_3$ | $CH_3$ | H | H | H | H |
| **3d** | $CH_3$ | H | $CH_3$ | H | H | H |
| **3e** | $CH_3$ | $CH_3$ | $CH_3$ | $CH_3$ | H | H |
| **3f** | H | H | H | H | $CH_3$ | H |
| **3g** | H | H | H | H | $C(CH_3)_3$ | H |
| **3h** | H | H | H | H | $CH_3$ | $CH_3$ |

**Preparation of [7,16-Dihydro-2,3,11,12-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecinato-$N^5$,$N^9$,$N^{14}$,$N^{18}$]nickel(II) (3h).** Refluxing an aqueous DMF solution (75:50 mL) of 4,5-dimethyl-*o*-phenylenediamine (2.7 g, 0.02 mol), 1,1,3,3-tetramethoxypropane (3.5 mL, 0.02 mol), and nickel(II) acetate tetrahydrate (2.5 g, 0.01 mol) for 10 h afforded a thick purple suspension. After the reaction mixture was cooled and filtered, a purple solid (4.0 g, 99%) was obtained, which was washed with water (200 mL) and methanol (350 mL). Due to its extremely low solubility, the product could be purified in only very small quantities by column chromatography on alumina eluted with methylene chloride. Conducting the reaction in an aqueous medium affords only the uncyclized cationic chelate complex **4** ($R_1$, $R_2$ = H; $R_5$, $R_6$ = $CH_3$). Anal. Calcd for $C_{22}H_{22}N_4Ni$: C, 65.87; H, 5.53; N, 13.97. Found: C, 66.44; H, 5.70; N, 13.50. NMR ($CDCl_3$, ppm): 7.75 (d, $J$ = 6 Hz, 4 H, ArNC*H*), 7.02 (s, 4 H, Ar*H*), 5.26 (t, $J$ = 6 Hz, 2 H, ArNCHC*H*), 2.18 (s, 12 H, $CH_3$). MS ($m/e$ (% relative intensity)): $P^+$, 400 (100), $P^{2+}$, 200 (17). ES ($CHCl_3$, nm ($\epsilon$)): 434 (54 510).

**Preparation of 4-Butyl-*o*-phenylenediamine.** The title compound was prepared in a six-step synthesis by following essentially the procedure of Clark and Pessolano.[35] Our starting material, however, was *tert*-butylbenzene rather than the *tert*-butylanilide. *tert*-Butylbenzene was treated with nitric acid at room temperature and the *p*-nitro derivative thus formed was isolated by fractional distillation. Hydrogenation of the product over palladium catalyst was followed by acetylation with acetic anhydride to yield the starting material of the literature procedure. The final product was isolated as the free base by reduction of 4-*tert*-butyl-2-nitroaniline with aqueous hydrazine over palladium. Clark and Pessolano isolated 4-*tert*-butyl-*o*-phenylenediamine as its dihydrochloride salt in their procedure.

**Preparation of 4-Methyl-*o*-phenylenediamine.** This compound was prepared as the free base by the procedure of Clark and Pessolano.[35] Our starting material was *p*-aminotoluene, which was acetylated with acetic anhydride to give the *p*-methylanilide. From this point on, our synthesis essentially followed the literature procedure.

## Results and Discussion

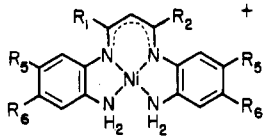
The new macrocyclic complexes **3b–d** (Table I) were synthesized by cyclizing the [*N*,*N*″-(1,3-propanediylidine)bis(*o*-phenylenediaminato)]nickel(II) complex **4** with β-diketones or β-keto acetals as described in the Experimental Section.

Complexes **3a** ($R_1$–$R_4$ = H) and **3e** ($R_1$–$R_4$ = $CH_3$) have been prepared earlier by more direct methods, starting from *o*-phenylenediamine and 1,1,3,3-tetramethoxypropane[27,36] and

(34) Cutler, A. R.; Dolphin, D. *Can. J. Chem.* **1977**, *55*, 3062.

(35) Clark, R. L.; Pessolano, A. A. U. S. Patent 2 933 503, April 19, 1960.

(36) Wuu, Y.-M.; Peng, S.-M.; Chang, H. *J. Inorg. Nucl. Chem.* **1980**, *42*, 839.

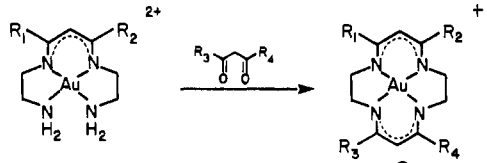


4

2,4-pentanedione,[25] respectively. We also prepared these complexes in this study using the appropriate tricyclic chelate complex **4** and a diimine precursor.

Complexes of the type **4** were shown previously[6] to be intermediates in the template in situ synthesis of macrocyclic complexes **3**. These intermediates, in which condensation of only one β-diketone or acetal has occurred, can be readily isolated as pure and stable compounds by suitable choice of reaction conditions. In this study, we have demonstrated the viability of this synthetic procedure with 1,3-propanedione derivatives to maintain the core dibenzotetraaza[14]annulene framework, while varying the substituents on the diiminato chelate rings. Clearly, a logical extension of this procedure is to alter the macrocycle size by using mono- or dicarbonyl compounds of different chain lengths, though that was not investigated in this work.

The reactions of carbonyl-containing compounds with diamino complexes to effect ring closure via Schiff base condensation is well established in the literature. Thus, Everett and co-workers[37] reacted β-diketones with the related bis(imino amino) complex **5** to prepare a variety of substituted 14-membered macrocyclic complexes (**6**).



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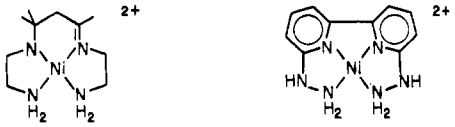
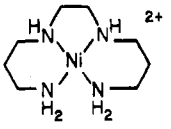
Similarly, Curtis-type Schiff base condensation of acetone with diamine complexes **7**[38] and **8**[39] have yielded macrocyclic complexes.



7 8

Glyoxal has also been found to condense with $[Ni(3,2,3\text{-tet})]^{2+}$ (**9**) to give a macrocyclic complex containing a diiminato five-membered chelate ring derived from the β-dialdehyde.[40]



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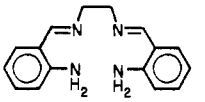
Black and Lane[41] investigated the template reaction between tetradentate diamines such as **10** and β-diketones in the presence of nickel salts as a general method for synthesizing macrocyclic structures. However, they encountered difficulties in obtaining pure products because of the structural complexity of their compounds.

MacDermott and Busch[42] observed that the ring closure reaction



10

is a general one for a variety of ketones and β-hydroxy ketones in reactions where the intermediate complex **7** may be isolated, or generated in situ during the course of the reaction.

The synthesis of the macrocyclic complexes **3b–d** are straightforward and involve refluxing a solution of the bis(imino amino)nickel(II) complex with excess β-diketone or acetal. When the reaction mixture is cooled, the desired macrocyclic complex separates out from the reaction mixture in yields ranging from 13% for 6-Me-DBTAA to 27% for 6,8-$Me_2$-DBTAA after purification.

The compounds prepared in this study did not present any difficulties in purification. Column chromatography of the crude products on alumina with methylene dichloride as eluent gave well-separated bands from which the pure complex could be obtained.

Clearly, the advantage of this synthetic procedure via **4** lies in its potential for creating unsymmetric macrocycles with dissimilar diiminato chelate rings by condensing **4** with a different diimine precursor. This procedure thus makes possible the synthesis of dibenzotetraaza[14]annulene complexes with substitution patterns that would be otherwise impossible with the procedures pioneered by Jäger[18] and Hiller.[19]

An additional benefit is the flexibility in selecting the starting material for the synthesis since the cationic complex **4** can be derived from the top or bottom part of the complex. For example, 6-Me-DBTAA was prepared by condensing **4** ($R_1$, $R_2$ = H) with 4,4-dimethoxy-2-butanone or **4** ($R_1$ = $CH_3$, $R_2$ = H) with 1,1,3,3-tetramethoxypropane. Both reactions appear to be equally facile.

Macrocyclic complexes symmetrically substituted on the diiminato moieties can be obtained by using the same diimine precursor as in the synthesis of **4**, e.g., **3d**. However, the synthesis of symmetric complexes via this procedure does not offer any significant advantage over the direct in situ synthesis, which does not require isolation of the intermediate.

Attempts to prepare the 6,8,15-$Me_3$-DBTAA complex by reacting the monomethyl cationic intermediate with acetylacetone were unsuccessful. Refluxing the mixture in aqueous DMF solution effects a color change from dark green to yellow. But UV spectra of the solution after 23 h of refluxing showed only a shoulder at ~400 nm, which could arise from the macrocyclic complex at a low concentration. No attempt was made to isolate the product from the reaction mixture. Carrying out the reaction in ethanolic solution resulted in mainly unreacted bis(imino amino) complex being recovered, even after 24 h of refluxing.

The failure of the monomethyl bis(imino amino) complex to produce the macrocyclic complex with 2,4-pentanedione is surprising, since it condenses readily with the diacetal and tetraacetal. In an analogous reaction, the dimethyl bis(imino amino) complex reacts instantly with 2,4-pentanedione under similar reaction conditions at room temperature to yield the tetramethyl macrocyclic complex **3e**.

An alternate route to dibenzotetraaza[14]annulenes involves refluxing a solution of an appropriately substituted 1,5-benzodiazepine or its salt in the presence of nickel(II) acetate.[34] We have applied that reaction in this study to give the parent nickel macrocyclic complex **3a** and the 6,8,15,17-$Me_4$-DBTAA complex **3e** in yields up to 33%.

The benzodiazepinium salt first converts to the free base by losing a proton and then undergoes hydrolytic ring opening to a monoanil intermediate.[6,43] This monoanil may degrade to a

(37) (a) Kim, J.-H.; Everett, G. W., Jr. *Inorg. Chem.* **1979**, *18*, 3145. (b) Brawner, S. A.; Lin, I. J. B.; Kim, J.-H.; Everett, G. W., Jr. *Inorg. Chem.* **1978**, *17*, 1304.
(38) Curtis, N. F. *J. Chem. Soc., Dalton Trans.* **1972**, 1357.
(39) Lewis, J.; Wainwright, K. P. *J. Chem. Soc., Chem. Commun.* **1974**, 169.
(40) Barefield, E. K.; Wagner, F.; Hodges, K. D. *Inorg. Chem.* **1976**, *15*, 1370.
(41) Black, D. St. C.; Lane, M. J. *Aust. J. Chem.* **1970**, *23*, 2027.
(42) MacDermott, T. E.; Busch, D. H. *J. Am. Chem. Soc.* **1967**, *89*, 5780.
(43) (a) Lloyd, D.; McDougall, R. H.; Marshall, D. R. *J. Chem. Soc.* **1965**, 3785. (b) Barltrop, J. A.; Richards, C. G.; Russell, D. M.; Ryback, G. *J. Chem. Soc.* **1959**, 1132. (c) Halford, J. O. Fitch, R. M. *J. Am. Chem. Soc.* **1963**, *85*, 3354.

2-substituted benzimidazole and ketone, as we observe with the 2,4-dimethyl-1,5-benzodiazepinium cation, or undergo a metal template cyclization to the macrocyclic complex, as in the synthesis of **3e** from 2,4-dimethyl-1,5-benzodiazepine.

We were unable to prepare the nickel complexes of 6,15-$Me_2$-DBTAA (**3d**) and 6,17-$Me_2$-8,15-$Ph_2$-DBTAA by the benzodiazepinium procedure but succeeded in producing benzimidazole together with other uncharacterized species.

It therefore appears that dibenzotetraaza[14]annulene formation via template condensation of benzodiazepine or its acid salt has limited usefulness as a general synthetic procedure. However, benzodiazepinium salts can be prepared in quantity with use of established procedures.[43] and conveniently stored as a stock reagent for macrocycle synthesis with metal salts as needed. But the benzodiazepinium synthetic procedure is less efficient than the one-step in situ synthesis from *o*-phenylenediamine and β-diketone or acetyl since they share the same precursors, and one more isolation and purification step is needed.

Cis and trans isomers are possible for **3d**, **3f**, and **3g**. NMR spectra of **3g** are consistent with the presence of only the cis isomer. The two β-methine protons on the propanediiminato moieties of the macrocycle show up as a multiplet (two overlapping triplets), which collapses to two singlets when spin decoupled from the α-methine protons. The four α-methine protons occur as a pair of doublets which reduce to a pair of singlets when decoupled from the β-methine protons. In comparison, a mixture of cis and trans isomer should show two pairs of doublets (with some overlapping likely) for the α-methine protons, which would collapse to two pairs of singlets. The presence of the trans isomer can be ruled out since we should see only a single triplet from the β-methine protons, which would collapse to a singlet upon irradiation of the N=CH proton resonances.

For **3f**, the NMR evidence for cis and trans isomers was not clear-cut. The α-methine proton resonances were observed as a complex multiplet instead of the simple doublet pair observed for **3g**. The β-methine protons showed a triplet with asymmetric band shapes, suggestive of two overlapping triplets shifted slightly apart. However, decoupling the α- and β-methine proton spins showed a single resonance for the β-methine and a single main absorption containing some fine structure for the α-methine proton. NMR spectra of the uncyclized diimino amino intermediate of **3f** indicated the presence of either an equimolar mixture of cis isomers or the trans isomer.[6]

In the analogous phenylene-substituted ligand 2,11-(12),6,8,15,17-$Me_6$-DBTAA, Dabrowiak[7] observed a complex $^{13}C$ NMR spectrum attributable to a mixture of cis and trans isomers. Similar complexes containing an ethoxy or benzoyl substituent (in place of methyl) on each benzenoid ring were also obtained as isomeric mixtures from their in situ template syntheses; their $^1H$ NMR spectra showed three β-methine singlets, indicating the presence of the cis and trans isomers.[7,26]

We did not observe any evidence of cis and trans isomers in the NMR spectra of **3d**. The α- and β-methine protons produced doublets, arising from coupling with the adjacent methine proton. The 6,17-dimethyl substitution pattern was observed in an X-ray crystal structure determination of **3d** prepared by condensing *N,N'-o*-phenylenebis(1-amino-1-buten-3-one)nickel(II) with *o*-phenylenediamine. The bis(keto amine)nickel(II) complex was itself synthesized in a template reaction of *o*-phenylenediamine with a β-ketone.[44]

**On Increasing Solubility of the Macrocycle in Organic Solvents.** One of the difficulties in working with dibenzotetraaza[14]-annulenes and, indeed, with many macrocyclic systems is often their limited solubility in organic solvents. Thus, the low solubilities of **3a** and **3b** precluded the recording of their CW $^1H$ NMR spectra. The unusually high solubility of the 6,8,15,17-$Me_4$DBTA complex **3e** arises from the saddle-shaped deformation of the macrocycle due to steric interactions of the diiminato methyl group with the benzenoid rings.[45] Nonplanarity of the ligand inhibits the aggregation that leads to reduced solubility, a characteristic of planar, fully conjugated macrocycles such as porphyrins and phthalocyanines.

**Table II.** Solubility of Macrocyclic Complexes in Chloroform at Room Temperature

| | **3a** | **3h** | **3g** | **3f** | **3d** | **3e** |
|---|---|---|---|---|---|---|
| sol, $10^3$M | 2.0 | 3.5 | 16.3 | 27.9 | 28 | 873 |

**Table III.** Hypsochromic Shift in the UV Spectra of DBTAA Complexes

| | **3a** | **3b** | **3d** | **3c** | **3e** |
|---|---|---|---|---|---|
| | parent | 6-Me | 6,17-$Me_2$ | 6,8-$Me_2$ | 6,8,15,17-$Me_4$ |
| $\lambda_{max}$, nm | 426 | 421 | 407 | 404 | 394 |

Addition of alkyl groups to the outer periphery of planar macrocycles in order to enhance solubility is well-known. For example, octaethylporphyrin is more soluble than octamethylporphyrin in organic solvents by at least 3 orders of magnitude, while the unsubstituted porphine is practically insoluble. Consequently, we prepared a series of dibenzotetraaza[14]annulene complexes, **3f–h**, containing alkyl substituents on the phenylene rings.

These complexes were prepared with the in situ method by refluxing a mixture of the appropriately substituted *o*-phenylenediamine, tetramethoxypropane, and nickel(II) acetate. The purple products were readily separated by filtration of the cooled reaction mixture and purified by column chromatography on alumina or recrystallized from methylene dichloride solution. The syntheses were somewhat dependent on the solvent medium. For example, the attempted synthesis of the 2,3,11,12-$Me_4$-DBTAA complex **3h** in aqueous solution resulted in formation of the bis(imino amino) intermediate **4**; in aqueous DMF solution, the macrocyclic complex forms readily.

As expected, the complexes substituted with alkyl groups on the benzenoid rings exhibited improved solubilities in organic solvents as shown in Table II.

The solubility of the 2,3,11,12-$Me_4$-DBTAA complex **3h** was only marginally improved over that of the parent complex. The 2,12-$Me_2$-DBAA complex **3f** showed a 14-fold increase in solubility in chloroform but was still considerably less soluble than **3e**. These results indicate that the short-chain methyl and *tert*-butyl substituents had relatively little impact on inhibiting aggregation of these complexes in organic solvents. It is likely therefore that the macrocyclic ligands, substituted on the benzenoid rings, retain an essentially planar conformation, unlike those complexes with diimine substituents, which are deformed by steric interactions between the methyl groups and the ortho aromatic hydrogens.

It is interesting to note that the hypsochromic shift and reduction in molar absorptivities in the UV spectra can be related to the incorporation of methylsubstituents on the diiminato chelate ring as shown in Table III.

It probably rises in part from reduced π-bond delocalization in the macrocyclic ligand as distortion increases with increased diimine substitution.[12] By comparison, complexes substituted on the benzenoid moieties, **3f–h**, show absorption bands with only small shifts (≤8 nm) relative to the unsubstituted complex, suggesting fairly small distortions from planarity in these macrocyclic complexes.

At first glance, a more fruitful avenue for increasing the solubility of dibenzotetraaza[14]annulene complexes appears to be through introduction of bulky $R_1$–$R_4$ substituents at the methine carbon atoms in **3**. One problem with this approach is that increasing steric bulk at these positions impedes Schiff base cyclization to the macrocyclic complex. Thus, Dabrowiak[7] found that 2,6-dimethyl-3,5-heptanedione and 2,2,6,6-tetramethyl-3,5-heptanedione did not form macrocyclic complexes in template reactions with *o*-phenylenediamine and nickel(II) salts. Fur-

(44) Hanic, F.; Handlovic, M.; Lindgren, O. *Collect. Czech. Chem. Commun.* **1972**, *37*, 2119.

(45) Weiss, M. C.; Bursten, B.; Peng, S.-M.; Goedken, V. L. *J. Am. Chem. Soc.* **1976**, *98*, 8021.

thermore, diamines having substituents that would sterically hinder other substituents on the diimine methine carbons also prefer not to cyclize.

**Acknowledgment.** This work was supported by the United States National Institutes of health (Grant No. GM 29198) and the Canadian Natural Sciences and Engineering Research Council.

**Registry No.** **3a**, 39251-81-5; **3b**, 96394-65-9; **3c**, 62081-95-2; **3d**, 95267-95-1; **3e**, 51223-51-9; **3f**, 96394-70-6; **3g**, 96411-84-6; **3h**, 57574-24-0; **4**($R_1 = R_2 = R_5 = R_6 = H$)·$PF_6$, 62081-93-0; **4**($R_1 = CH_3$, $R_2 = R_5 = R_6 = H$)·$PF_6$, 96213-12-6; **4**($R_1 = R_2 = CH_3$, $R_5 = R_6 = H$)·$CH_3CO_2$, 96394-66-0; 4,4-dimethoxy-2-butanone, 5436-21-5; 1,1,3,3-tetramethoxypropane, 102-52-3; 2,4-pentanedione, 123-54-6; *o*-phenylenediamine, 95-54-5; 2-methyl-1,5-benzodiazepinium hexafluorophosphate, 96213-21-7; 3,4-diaminotoluene, 496-72-0; 3,4-diamino-1-*tert*-butylbenzene, 68176-57-8; 4,5-dimethyl-*o*-phenylenediamine, 3171-45-7; 1,5-benzodiazepinium hexafluorophosphate, 62086-50-4; *N,N''*-(1,3-propanediylidene)bis(*o*-phenylenediamine), 96394-67-1; *N,N''*-(1-methyl-1,3-propanediylidene)bis(*o*-phenylenediamine), 96394-68-2; *N,N''*-(1,3-dimethyl-1,3-propanediylidene)bis(*o*-phenylenediamine), 96394-69-3.

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# [*N,N''*-(1,3-Propanediylidene)bis(1,2-benzenediaminato)]nickel(II) Complexes: Intermediates in the Template Synthesis of Dibenzotetraaza[14]annulenes

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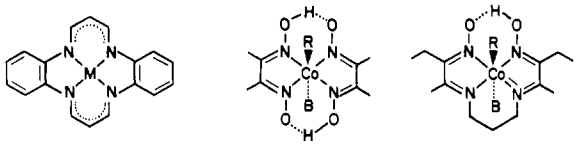
The synthesis and characterization of a series of nickel(II) complexes of linear tetradentate ligands derived from *N,N''*-(1,3-propanediylidene)bis(1,2-benzenediamine) are reported. The complexes were prepared in situ by condensation of a β-diketone or acetal with an appropriate *o*-phenylenediamine in the presence of a nickel(II) salt. 1,5-Benzenediazepinium salts were also used as ligand precursors in preparing the complexes. Evidence is presented which indicates that monoanils participate as intermediates in the metal template condensation of these diamines with β-diketones.

## Introduction

Few classes of coordination compounds have been subjected to as much attention as Schiff base complexes formed from the condensation of amines with carbonyl derivatives. We developed an interest in Schiff base complexes, and dibenzotetraaza[14]-annulenes **1a**,[1] in particular, as potential models of coenzyme $B_{12}$.

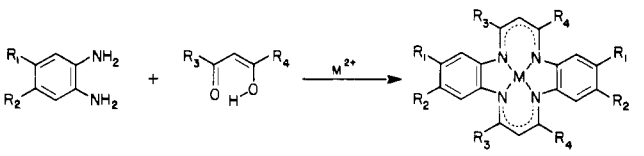


**1a** **1b** **1c**

Related tetraaza complexes, such as organocobaloximes **1b** and the organocobalt complexes of *N',N''*-propanediylbis(2,3-pentanedione 2-imine-3-oxime), R-Co[$C_2$(DO)(DOH)$_{pn}$]$B^+$ (**1c**), have been widely accepted and employed as $B_{12}$ models. However, unwanted reactions at the periphery of such macrocycles can limit their usefulness.[2]

Dibenzotetraaza[14]annulene complexes have also received much attention by other workers as models of tetrapyrrolic biological systems,[3] as catalysts,[4] and more recently, as precursors for electrically conductive polymers.[5]

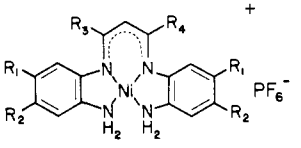
The macrocyclic Schiff base ligand is most commonly synthesized as its metal complex, **2**, by condensing *o*-phenylenediamines with β-dicarbonyls or β-acetals in the presence of metal ions (usually nickel(2+)). The synthesis is invariably carried out



**2**

in a one-step in situ procedure to give a symmetrical macrocyclic complex with the same diiminato or phenylene ring opposite to each other in the square-planar complex.[6-10]

In a previous communication[11] we reported that mixtures of either a benzodiazepinium salt and nickelous ion or *o*-phenylenediamine, tetramethoxypropane, and nickelous ion gave the dibenzotetraaza[14]annulene macrocyclic complex **2** ($R_1$–$R_4$ = H) via a noncyclized intermediate, **3** ($R_1$–$R_4$ = H).



**3**

(1) This class of dianionic ligands has the more systematic name 7,16-dihydrodibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine. It is also abbreviated 2,3:9,10-$Bzo_2$[14]hexaene-1,4,8,11-$N_4$.
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