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

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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.

Contribution from the Department of Chemistry,
University of British Columbia, Vancouver, B.C., Canada V6T 1Y6

[*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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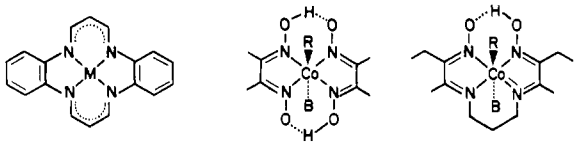
The synthesis and characterization of a series of nickel(II) complexes of linear tetradentate ligands derived from *N,N''*-(1,3-propanediylidene)bis(1,2-benzenediamine) are reported. The complexes were prepared in situ by condensation of a β-diketone or acetal with an appropriate *o*-phenylenediamine 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}.

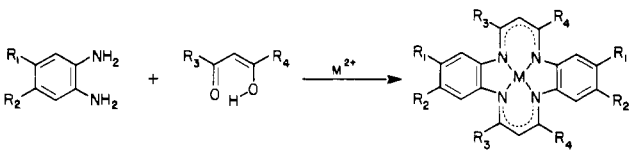


1a **1b** **1c**

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]

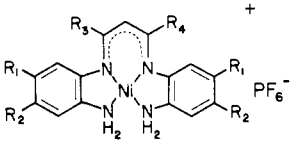
The macrocyclic Schiff base ligand is most commonly synthesized as its metal complex, **2**, by condensing *o*-phenylenediamines with β-dicarbonyls or β-acetals in the presence of metal ions (usually nickel(2+)). The synthesis is invariably carried out



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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We wish to report here the synthesis, isolation, and characterization of nickel(II) complexes of the linear tetradentate ligand **3** and studies related to the mechanism of the metal template synthesis of **3**.

We have shown earlier that the uncyclized chelate **3** is a precursor to the macrocyclic complex **2**.[11] Reaction of **3** with a variety of diketones clearly presents a synthetic route to unsymmetric dibenzotetraazaannulenes containing two different pentanediiminato chelate rings.

An additional degree of asymmetry is also possible in the synthesis of **2** or **3**. Honeybourne[10] has reported that a 1:1 mixture of diamines (e.g. *o*-phenylenediamine and 1,3-diaminopropane), when reacted with a β-diketone, leads to macrocyclic complexes, unsymmetric in the chelate rings derived from the diamine components.

Experimental Section

Physical Measurements. The electronic spectra (ES) were all obtained in solution with a Cary Model 17 recording spectrophotometer. Proton magnetic resonance spectra were obtained at 80 MHz with a Bruker WP-80 or at 60 MHz with a Varian T-60 spectrometer using tetramethylsilane (Me_4Si) as internal standard. Proton assignments were confirmed by spin decoupling or by addition of D_2O. Mass spectra were recorded with a Varian/Mat CH4B or Kratos/AEI MS-50 mass spectrometer. Microanalysis were all obtained by P. Borda of this department.

Preparations. The starting materials were obtained commercially and generally used without further purification. *o*-Phenylenediamine was recrystallized from toluene solution and stored in the absence of light; it was used within 2–4 weeks of purification. All solvents were reagent grade.

Preparation of [*N*,*N*″-(1,3-Propanediylidene)bis(1,2-benzenediaminato)-*N*,*N*′,*N*″,*N*‴]nickel(II) Hexafluorophosphate (3a). (a) In Situ. An aqueous suspension (150 mL) of *o*-phenylenediamine (4.3 g, 0.04 mol) 1,1,3,3-tetramethoxypropane (3.4 mL, 0.02 mol), nickel(II) chloride hexahydrate (4.8 g, 0.02 mol), and ammonium hexafluorophosphate (10 g, 0.06 mol) was heated in a 250-mL round-bottom flask.[12] The blue-gray suspension became a dark green solution after 15 min of heating, before turning reddish brown and producing a purplish brown suspension and foam after refluxing an additional 20 min. Cooling and then filtering the thick suspension gave a reddish brown solid and lemon yellow filtrate. The solid was washed with cold water (3 × 30 mL), air-dried for 18 h, and redissolved in acetone (40 mL). Dropwise addition of the filtered solution into excess ether (450 mL) precipitated a granular reddish brown solid, to give, after vacuum drying, 6.0 g (65%) of product. Anal. Calcd for $C_{15}H_{15}N_4NiPF_6$: C, 39.60; H, 3.32; N, 12.31. Found: C 40.10; H, 3.30; N, 12.54. NMR (acetone-d_6, ppm): 7.90 (d, J = 6 Hz, 2 H, ArNCH), 7.9–6.9 (m, 8 H, ArH), 5.62 (t + br s, J = 6 Hz, 1 H, C–CH–C), 5.68 (br s, 2 H, NH_2). ES (CH_3OH; λ_{max}, nm (ϵ)): 461 (23 000), 434 (19 380). MS (m/e): calcd for $C_{15}H_{14}N_4Ni$ ($P^+ - 1$), 308.0571; found, 308.0574.

(b) Via Benzodiazepinium Salt. 1,5-Benzodiazepinium hexafluorophosphate (0.15 g, 0.5 mmol) and *o*-phenylenediamine (0.06 g, 0.5 mmol) were dissolved in methanol (50 mL) to give a reddish orange solution. Addition of an aqueous solution (10 mL) of nickel(II) acetate tetrahydrate (0.13 g, 0.5 mmol) produced a dark orange suspension that did not change further after refluxing (2 h). The product was isolated by evaporating the reaction mixture to dryness under vacuum and purified by precipitation from acetone solution with excess ether.

Preparation of [*N*,*N*″-(1-Methyl-1,3-propanediylidene)bis(1,2-benzenediaminato)-*N*,*N*′,*N*″,*N*‴]nickel(II) Hexafluorophosphate (3b). (a) In Situ. Treatment of a warm aqueous solution (100 mL) containing 4,4-dimethoxy-2-butanone (2.6 mL, 0.02 mol), *o*-phenylenediamine (4.3 g, 0.04 mol), and nickel(II) chloride hexahydrate (4.8 g, 0.02 mol) with excess ammonium hexafluorophosphate (10 g) dissolved in 75 mL of water produced a dark greenish brown precipitate. This suspension thickened considerably upon heating until boiling just commenced (15 min). Cooling of the reaction mixture in an ice bath, followed by filtration of the thick green suspension and washing with ice water (100 mL), left an olive green solid (yield 3.8 g). The product was purified by dropwise addition of a filtered acetone solution (30 mL) into ether (300 mL) and vacuum drying of the precipitate to give 3.1 g (33%). Anal. Calcd for $C_{16}H_{17}N_4NiPF_6$: C, 40.98; H, 3.65; N, 11.95. Found: C, 40.72; H, 3.59; N, 12.07. NMR (acetone-d_6, ppm): 7.36 (d, J = 6 Hz, 1 H, ArNCH), 7.7–6.8 (m, 8 H, ArH), 5.43 (d, J = 6 Hz, 1 H, C–CH–C), 5.42 (br s, 2.5 H, NH_2), 2.50 (s, 3 H, CH_3). ES (CH_3OH); λ_{max}, nm (ϵ)): 416 (21 870). MS (m/e): calcd for $C_{16}H_{17}N_4Ni$ ($P^+ - 1$), 322.0728; found, 322.0728.

(b) Via Benzodiazepinium Salt. 2-Methyl-1,5-benzodiazepinium hexafluorophosphate (0.15 g, 0.5 mmol) and *o*-phenylenediamine (0.06 g, 0.5 mmol) were dissolved in methanol (40 mL) to give a yellow-orange solution. Addition of an aqueous solution (10 mL) of nickel(II) acetate tetrahydrate (0.13 g, 0.5 mmol) darkened the solution to yellow-brown. Refluxing the solution (2 h) afforded a dark green solution that had an electronic absorption spectrum consistent with quantitative conversion to the desired nickel(II) complex.

Preparation of [*N*,*N*″-(1,3-Dimethyl-1,3-propanediylidene)bis(1,2-benzenediamino)-*N*,*N*′,*N*″,*N*‴]nickel(II) Hexafluorophosphate (3c). (a) In Situ. Nickel(II) acetate tetrahydrate (5.0 g, 0.02 mol) was added to a methanolic solution (75 mL) of *o*-phenylenediamine (4.3 g, 0.04 mol) in a 250-mL round-bottom flask. Addition of 2,4-pentanedione (2.1 mL, 0.02 mol) gave a purple solution,[13] which slowly deposited a light blue precipitate. After the solution was refluxed for 15 min, the color of the reaction mixture changed to dark green. Continued refluxing (2 h) of the emerald green solution, followed by cooling to 5 °C, left only a trace amount of insoluble residue. The solution was filtered and the filtrate added dropwise to a NH_4PF_6 solution (30 g in 100 mL, neutralized to pH 7 with NaOH), producing a dark green precipitate in the presence of a dark reddish brown supernatant. Filtering and washing the precipitate with ice-cold water (100 mL) gave reddish brown filtrates of undiminished intensity. The green solid (5.0 g) was collected and dried in vacuo for 24 h.

A completely satisfactory procedure for purifying the crude product could not be found, but small quantities of the pure product could be obtained by first washing the crude material with CH_2Cl_2 (40 mL), dissolving and filtering the resulting solid through filter paper with a minimum amount of acetone (~25 mL), and then adding the filtrate dropwise to excess ether (250 mL). The dark green solid (1.0 g) thus obtained, after washing with ether and *n*-hexane and drying in vacuo at 80 °C (48 h), was analytically pure. Anal. Calcd for $C_{17}H_{19}N_4NiPF_6 \cdot {}^1/_2C_3H_6O$: C, 43.33; H, 4.31; N, 10.98. Found: C, 43.48; H, 4.34; N, 11.43. NMR (acetone-d_6, ppm): 7.5–6.7 (m, 8 H, ArH), 5.27 (s, 1 H, C–CH–C), 5.08 (br s, 2 H, NH_2), 2.33 (s, 6 H, CH_3). ES (CH_3OH; λ_{max}, nm (ϵ)): 416 (9850), 296 (10 060).

(b) Via Benzodiazepinium Salt. A methanolic solution (50 mL) of 2,4-dimethyl-1,5-benzodiazepinium hexafluorophosphate (0.32 g, 1.0 mmol) and *o*-phenylenediamine (0.11 g, 1.0 mmol) was treated with nickel(II) acetate tetrahydrate (0.25 g, 1.0 mmol). The resulting dark green solution was refluxed for 2 h. The electronic spectra of the reaction mixture were consistent with formation of the desired nickel chelate (418 nm) and showed the absence of any detectable nickel macrocyclic complex (393 nm).

Preparation of [*N*,*N*″-(1-Methyl-3-phenyl-1,3-propanediylidene)bis-(1,2-benzenediaminato)-*N*,*N*′,*N*″,*N*‴]nickel(II) Hexafluorophosphate (3d) via Benzodiazepinium Salt. A purple methanolic solution (50 mL) of 2-methyl-4-phenyl-1,5-benzodiazepinium hexafluorophosphate (0.38 g, 1.0 mmol) and *o*-phenylenediamine (0.11 g, 1.0 mmol) was treated with a methanolic solution (20 mL) of nickel(II) acetate tetrahydrate (0.25 g, 1.0 mmol). The resulting purple-brown solution turned dark green after refluxing (10 min) with no further changes after 2 h. After the solution was cooled, the product could be isolated by filtering the suspension and washing the solid with cold water.

Preparation of [*N*,*N*″-(1,3-Propanediylidene)bis(4(5)-methyl-1,2-benzenediaminato)-*N*,*N*′,*N*″,*N*‴]nickel(II) Hexafluorophosphate (3e) in situ. In aqueous suspension (150 mL) of 4-methyl-*o*-phenylenediamine (4.9 g, 0.04 mol), 1,1,3,3-tetramethoxypropane (3.4 mL, 0.02 mol), nickel(II) chloride hexahydrate (4.8 g, 0.02 mol), and ammonium hexafluorophosphate (10 g, 0.06 mol) was refluxed for 30 min. After it was cooled in an ice bath, the reaction mixture was filtered and the solid washed with cold water (100 mL) and air-dried: yield 7.9 g. Anal. Calcd for $C_{17}H_{19}N_4NiPF_6$: C, 42.27; H, 3.97; N, 11.60. Found: C, 42.44; H, 4.10; N, 11.44. NMR (acetone-d_6, ppm): 7.83, 7.77 (dd, J = 7 Hz, 2 H, ArNCH), 7.64–6.73 (m, 6 H, ArH), 5.62 (m, 1 H, C–CH–C), 5.42 (br s, 4 H, NH_2), 2.34 (s, 6 H, CH_3).

Preparation of [*N*,*N*″-(1,3-Propanediylidene)bis(3,4-dimethyl-1,2-benzenediaminato)-*N*,*N*′,*N*″,*N*‴]nickel(II) Acetate (3f). Refluxing an aqueous solution (125 mL) of 4,5-dimethyl-*o*-phenylenediamine (2.7 g, 0.02 mol), 4,4-dimethoxy-2-butanone (3.5 mL, 0.02 mol), and nickel(II) acetate tetrahydrate (2.5 g, 0.01 mol) for 3 h gave a brown precipitate

(12) Changing the reaction stoichiometry to 2:2:1 (*o*-phen:acetal:Ni(II)) does not change the course of the reaction. No evidence of the fully cyclized macrocyclic complex was observed in the UV spectra. The yield diminishes if $Ni(OAc)_2 \cdot 4H_2O$ is used. Unless excess NH_4PF_6 is added, a mixture of Cl^- and PF_6^- salts precipitate.

(13) The species responsible for the purple color has been identified as the 2,4-dimethyl-(1*H*)-1,5-benzodiazepinium cation.[8]

that showed UV spectra characteristic of the linear chelate complex. The solid was collected by filtration, washed with water and methanol, and air-dried. ES (CH_3OH; λ_{max}, nm): 440, 467.

Preparation of 1-Phenyl-3-[(*o*-aminophenyl)imino]-1-butanone (8). A mixture of *o*-phenylenediamine (23.6 g, 0.2 mol), benzoylacetone (32.4 g, 0.2 mol), and *p*-toluenesulfonic acid (0.10 g) was refluxed for 2.5 h with removal of water in a Dean Stark wate separator. Removal of solvent and trituration of the residue with benzene–petroleum ether (1:4, 150 mL) and diethyl ether (75 mL) left a yellow crystalline solid (28.2 g) of moderately pure monoanil (yield 55%). Recrystallization from ether affords the pure product, mp 115–118 °C. Anal. Calcd for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.10. Found: C, 75.96; H, 6.24; N, 11.32. NMR ($CDCl_3$, ppm): 8.0–7.2 (m, 5 H, C_6H_5), 7.2–6.4 (m, 4 H, phenylene), 5.84 (s, 1 H, C–CH–C), 3.86 (br s, 2 H, $ArNH_2$), 1.93 (s, 3 H, CH_3). ES (CH_3OH; λ_{max}, nm): 348, 402.

Preparation of 1,5-Benzodiazepinium Hexafluorophosphate: Modification of the Procedure of Lloyd et al.[14] Addition of 1,1,3,3-tetramethoxypropane (8.4 mL, 0.05 mol) to a warm ethanolic solution (25 mL) of *o*-phenylenediamine (5.4 g, 0.05 mol) and 65% aqueous hexafluorophosphoric acid (10 mL) immediately resulted in a color change from dark yellow to dark green. The solution then turned yellowish orange and deposited a microcrystalline reddish orange precipitate over 1 h. Filtering the suspension and washing the solid with ethanol gave 8.7 (60%) of brick red product after drying in vacuo. The crude product was purified by precipitation from an acetone solution with ether. The benzodiazepinium salt thus obtained was pure by UV spectroscopy but contained some adsorbed acetone even after prolonged drying in vacuo. Anal. Calcd for $C_9H_9N_2PF_6$: C, 37.26; H, 3.13; N, 9.66. Found: C, 37.26; H, 3.70; N, 9.46. NMR (acetone-d_6, ppm): 8.70 (d, J = 11 Hz, 2 H, ArNC–H), 7.71 (br s, 4 H, ArH), 7.70–6.15 (br m, 1 H, C–H). ES (CH_3OH; λ_{max}, nm): 263, 272, 410.

Preparation of 2-Methyl-1,5-benzodiazepinium Hexafluorophosphate: Modification of the Procedure of Lloyd et al.[14] Addition of aqueous hexafluorophosphoric acid (10 mL, 65%) to an ethanolic (25 mL) suspension of *o*-phenylenediamine (5.4 g, 0.05 mol) produced a light yellow-brown solution. A purple solution resulted when 4,4-dimethoxy-2-butanone (6.5 mL, 0.05 mol) was added. Cooling in an ice bath induced crystallization of a purple solid over a 1 h period. The solid was filtered and washed with cold ether–ethanol (2:1). Recrystallization by adding ether to a saturated acetone solution produced 3.2 g (yield 22%) of a purple crystalline solid, mp 174 °C. Anal. Calcd for $C_{10}H_{11}N_2PF_6$: C, 39.49; H, 3.65; N, 9.21. Found: C, 39.79; H, 3.70; N, 9.32. NMR (acetone-d_6, ppm): 8.72 (br s, 2 H, NH), 7.02–6.03 (m, 4 H, Ar–H), 4.10 (d, J = 9 Hz, 1 H, ArNC–CH), 1.86 (s, 3 H, CH_3). ES (CH_3OH; λ_{max}, nm): 262, 270.

Preparation of 2,4-Dimethyl-1,5-benzodiazepine: Modification of Barltrop's Procedure.[15] *p*-Toluenesulfonic acid (0.2 g) was added to a stirred slurry of *o*-phenylenediamine (108 g, 1 mol) and 2,4-pentanedione (101 mL, 1 mol) in benzene (400 mL). The mixture was then refluxed for 6 h while the water continuously removed in a Dean Stark separator. The solvent was removed under reduced pressure and the resulting yellow-brown solid washed with benzene–petroleum ether (1:3) to yield, after vacuum drying, 140 g (81%) of pure product.

Preparation of 2,4-Dimethyl-1,5-benzodiazepinium Hexafluorophosphate: Modification of Barltrop's Procedure.[15] The dark purple solution resulting from adding 2,4-pentanedione (18 mL) to *o*-phenylenediamine in ethanol (70 mL)–glacial acetic acid (30 mL) was warmed for 5 min. After it was cooled to room temperature, this solution was added slowly to a concentrated aqueous ammonium hexafluorophosphate solution (60 g, 100 mL). The resulting purple crystals were filtered off, washed with water, and air dried. The product was purified by adding an acetone solution dropwise to ether, followed by filtering and washing with ether to yield 31.8 g (56%) of the pure product. NMR (acetone-d_6, ppm): 8.53 (br s, 1 H, NH), 7.2–6.4 (m, 4 H, Ar–H), 4.40 (s, 1 H, C–CH–C), 1.90 (s, 6 H, CH_3).

Preparation of 2-Methyl-4-phenyl-1,5-benzodiazepinium Hexafluorophosphate.[15] Addition of aqueous hexafluorophosphoric acid (65%, 10 mL) to an ethanolic suspension (25 mL) of *o*-phenylenediamine (5.4 g, 0.05 mol) and benzoylacetone (8.1 g, 0.05 mol) immediately produced a purple solution that slowly deposited a copious amount of purple crystals as it cooled to room temperature (the reaction is exothermic). After further cooling to 5 °C, the reaction mixture was filtered, and the solid was washed with ethanol and ether. Three crops of product were recovered from the filtrate and added to the original crop of crystals. The crude product was recrystallized by adding an acetone solution dropwise to ether. The resulting purple crystalline solid was filtered off, washed with ether, and dried in vacuo to give 13.5 g (71%) of product. Anal. Calcd for $C_{16}H_{15}N_2PF_6$: C, 50.53; H, 3.98; N, 7.37. Found: C, 51.03;, H, 4.16; N, 7.28. NMR (acetone-d_6, ppm): 8.99 (br m, 1.5 H, NH), 7.59 (m, 5 H, C_6H_5), 6.81 (m, 4 H, Ar–H), 4.82 (s, 1 H, C–CH–C), 2.12 (s, 3 H, CH_3).

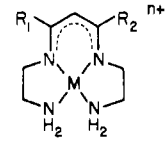
Table I. Nickel(II) Complexes Prepared in This Study

complex	R_1	R_2	R_3	R_4
3a	H	H	H	H
3b	H	H	H	CH_3
3c	H	H	CH_3	CH_3
3d	H	H	CH_3	C_6H_5
3e	CH_3(H)	H(CH_3)	H	H
3f	CH_3	CH_3	H	H

Results and Discussion

In an earlier communication we reported[11] that an uncyclized nickel chelate **3** (R_1–R_4 = H) could be isolated from the nickel(II)-mediated template reaction of *o*-phenylenediamines with 1,1,3,3-tetramethoxypropane. Subsequent to our report, the appearance[8] of this type of complex in, and isolation[16] from, a reaction mixture was reported by others, but such intermediate have never been adequately characterized. The uncyclized nickel chelates of type **3** prepared in this study are shown in Table I.

Occasionally, metal complexes of linear tetradentate ligands have been observed as intermediates during the synthesis of macrocyclic complexes.[17] Only rarely in metal ion assisted condensation reactions of diamines with diketones or, indeed, in the majority of *in situ* Schiff base syntheses, have intermediate species been isolated and characterized. For example, complexes of the type **4** have been prepared by the template reaction of 2,4-pentanedione with tris(ethylenediamine)metal complexes (**4**, M = Au, n = 2)[18] or from the reaction of pentanedione and free base ethylenediamine with the metal salt (**4**, M = Ni, n = 1).[19]



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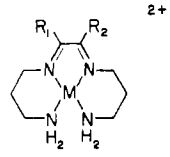
Metal template condensations of 1,2-diketones with 1,3-diaminopropane and the metal(II) chloride yield related complexes of the type **5**[20] while **6** and **7** are formed as intermediates in the



5

synthesis of Curtis-type macrocycles by reaction of acetone with an ethylenediamine metal complex[21–23] or with 1,4-hydrazinophthalazine and the metal salt, respectively.[24] Curtis[22] and

(14) Lloyd, D.; McDougall, R. H.; Marshall, D. R. *J. Chem. Soc.* **1965**, 3785.
(15) Barltrop, J. A.; Richards, C. G.; Russell, D. M.; Ryback, G. *J. Chem. Soc.* **1959**, 1132.
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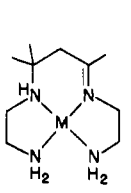
(18) Brawner, S. A.; Lin, I. J. B.; Kim, J.-H.; Everett, G. W., Jr. *Inorg. Chem.* **1978**, *17*, 1304.
(19) Elfring, W. H., Jr.; Rose, N. J. *Inorg. Chem.* **1975**, *14*, 2759.
(20) (a) Taylor, L. J.; Rose, N. J.; Busch, D. H. *Inorg. Chem.* **1968**, *7*, 785. (b) Pelizzi, C. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 249. (c) Lindoy, L. F.; Moody, W. E.; Lewis, J.; Matheson, T. W. *J. Chem. Soc., Dalton Trans.* **1976**, 1965.
(21) MacDermott, T. E.; Busch, D. H. *J. Am. Chem. Soc.* **1967**, *89*, 5780.
(22) (a) Blight, M. M.; Curtis, N. F. *J. Chem. Soc.* **1962**, 3016. (b) House, D. A.; Curtis, N. F. *J. Am. Chem. Soc.* **1964**, *86*, 1331.
(23) Curtis, N. F. *J. Chem. Soc., Dalton Trans.* **1972**, 1357.
(24) Rosen, W. *Inorg. Chem.* **1971**, *10*, 1832.



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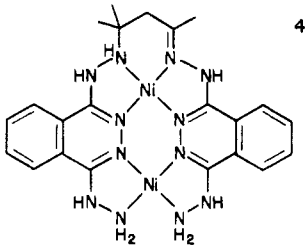


7

Busch[21] have also showed the broad generality of the reaction of ethylenediamine complexes with α,β-diketones and β-hydroxyketones to form compounds like **6** which could react further to yield macrocyclic complexes if the reaction conditions are altered.

The syntheses of the linear chelate complexes **3** are straightforward, but it is necessary to optimize the solvent and nickel(II) salt used, since yield and purity are somewhat dependent on these parameters. A deterimental effect on the yield also results from excess reaction times, but this can be avoided by monitoring the product concentration in the reaction by UV spectroscopy to determine the optimum reaction time.

The synthesis of the dimethyl complex, **3c**, is quite sensitive to reaction conditions. In an aqueous medium with $Ni(OAc)_2$, a tan solid, with an electronic spectrum of 2-methylbenzimidazole, is precipitated upon addition of NH_4PF_6 solution at pH 7 after the reaction mixture is refluxed for 4 h. If the reaction in aqueous solution is caried out with $NiCl_2$, the solid precipitated with NH_4PF_6 shows a UV spectrum consistent with a mixture of 2-methylbenzimidazole and its salt.

A pale blue solid precipitates from methanolic solution during initial stages of the in situ reaction of *o*-phenylenediamine and 2,4-pentanedione with nickel(II). Its identity has not been determined. The precipitate does not appear to be $Ni(acac)_2$ by virtue of its reactivity (authentic $Ni(acac)_2$ remains unchanged in refluxing methanol with an excess of *o*-phenylenediamine), or $[Ni(o\text{-phen})_2]^{2+}$ because of its low solubility ($Ni(o\text{-phen})_2(OAc)_2$ is very soluble in water and methanol). It may be a nickel complex of some combiation of *o*-phenylenediamine and acetylacetone that could react further with *o*-phenylenediamine or acetylacetone to give the complex **3c**.

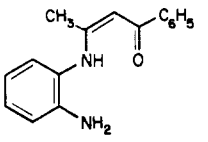
We were also successful in preparing the nickel(II) complexes **3a–d** by refluxing aqueous methanol or DMF solutions of 1,5-benzodiazepinium salts in the presence of nickel(II) acetate.

In aqueous solution benzodiazepinium salts are known to give reactions characteristic of *o*-phenylenediamine and the β-diketones from whch they are derived.[15] It has been reported for 2,4-disubstituted benzodiazepinium salts that hydrolytic decomposition occurs via a deprotonation step followed by ring opening to the corresponding monoanil.[14,15,25] This suggests that a monoanil is also an intermediate in the synthesis of **3**. The benzodiazepinium cation has been observed as an intermedate in the in situ synthesis of tetramethyldibenzotetraaza[14]annulene (**2**: R_1, R_2 = H; R_3, R_4 = CH_3) from *o*-phenylenediamine and 2,4-pentanedione with nickel(II) ion.[8] It is responsible for the deep purple color that develops before the reaction is heated.

In order to establish the intermediacy of monoanil in the synthesis of **3**, we attempted to synthesize various monoanils to determine whether they could form the linear tetradentate ligand **3** or the macrocycle **2**. Many of these attempts, however, were frustrated by instability of the monoanils.

Hydrolysis of an aqueous suspension of the unsubstituted 1,5-benzodiazepinium salt with aqueous base resulted in products from which pure materials could not be isolated. We did not see any trace of benzimidazole[26] or of the metal-free dibenzotetraaza[14]annulene macrocycle. The reaction of *o*-phenylenediamine with malonaldehyde (prepared in situ) was similarly unfruitful in synthesizing a product from which pure monoanil could be isolated or even unambiguously identified.

A stable monoanil, **8**, was obtained by reacting *o*-phenylenediamine with benzoylacetone. Prolonged reflux of a mixture of



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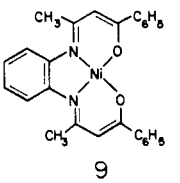
the monoanil and nickel(II) acetate in aqueous methanol or aqueous DMF solution produced a green solution that showed a UV spectrum identical with that of the uncyclized nickel complex **3** (R_1, R_2 = H; R_3 = CH_3; R_4 = C_6H_5) (λ_{max} = 428, 262 nm). An insoluble residue was also produced in trace amounts, tentatively identified as the macrocyclic complex **2** (R_3 = CH_3, R_4 = C_6H_5) (λ_{max} = 600, 402 nm).

The same 1-methyl-2-phenyl-substituted complex, **3**, was synthesized more directly by refluxing a methanolic solution of a 2-methyl-4-phenyl-1,5-benzodiazepinium salt, *o*-phenylenediamine, and nickel(II) acetate. During the reaction, a transient shoulder (~330 nm) develops on the intense 262-nm band in the UV spectrum, which probably arises from the monoanil intermediate.

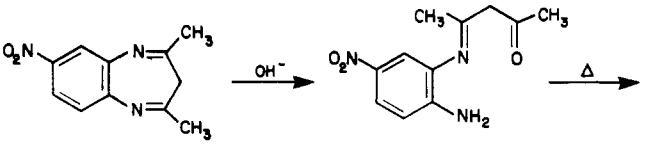
In contrast, Eilmes[27] reported that the ketoiminato complex **9** separated from ethanolic solution when $Ni(o\text{-phen})_2Cl_2$ was reacted with a large excess of benzoylacetone. A 2:2:1 mixture



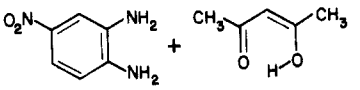
9

of *o*-phenylenediamine–benzoylacetone–nickel(II) acetate in anhydrous butanol gave the macrocyclic complex in 53% yield.

The involvement of a monoanil intermediate has been established[14] in the base hydrolysis of 2,4-dimethyl-7-nitro-(3*H*)-1,5-benzodiazepine (**10**). At room temperature, the monoanil, **11**,



10 11

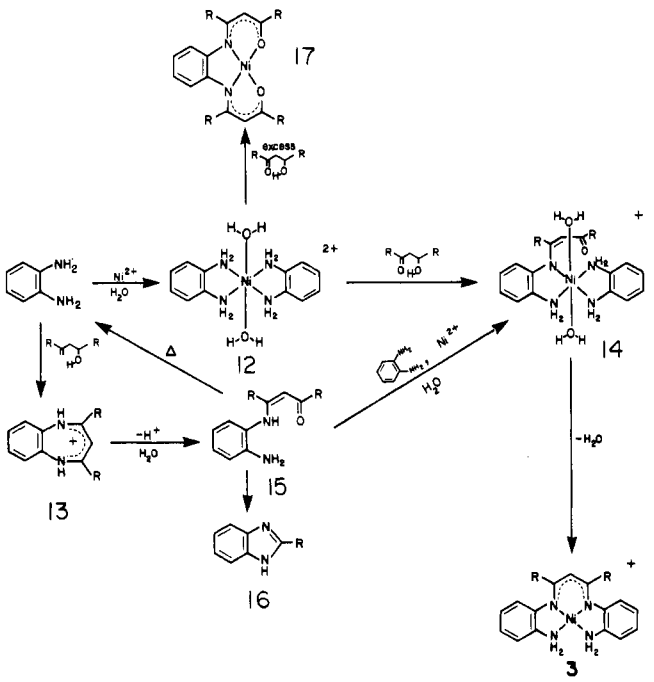


is formed, with the UV spectrum of the solution showing a clean isosbestic point. If the solution is heated, however, complete hydrolysis occurs and 4-nitro-1,2-diaminobenzene and acetylacetone are produced. Hydrolytic ring openings for benzodiazepinium salts possessing unsubstituted 2(4)-positions apparently occur even more readily.[28] Thus monoanil formation on hydrolysis of benzodiazepinium salts is well established, and it is likely that a similar mechanism applies in the formation of cationic tricyclic nickel(II) complexes, **3**, as shown in Scheme I.

o-Phenylenediamine forms a bis(*o*-phenylenediamine)nickel(II) complex, **12**, at room temperature. As the temperature is raised, the reaction may take two routes. Free base *o*-phenylenediamine

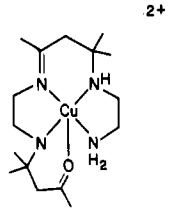
(25) Halford, J. O.; Fitch, R. M. *J. Am. Chem. Soc.* **1963**, *85*, 3354.
(26) Benzodiazepinium salts frequently decompose to benzimidazoles and ketones when heated with water.[14]
(27) Eilmes, J.; Pelan, D.; Sledziewska, E. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1980**, *28*, 371.
(28) (a) Ruske, W.; Hufner, E. *J. Prakt. Chem.* **1962**, *18*, 156. (b) Weissenfels, M.; Kache, R.; Krauter, W. *J. Prakt. Chem.* **1967**, *35*, 166.

Scheme I



can form a benzodiazepinium salt, **13**, with β-diketone, or [Ni(*o*-phen)$_2$]$^{2+}$ can react with 1 mol of β-diketonate to give a monoanil such as **14**. An intramolecular Schiff reaction with elimination of water from the monoanil complex results in formation of the chelate complex **3**. If the benzodiazepinium salt is present in the reaction mixture, it may undergo hydrolytic decomposition via the free base to the monoanil, **15**, which can form a nickel(II) complex intermediate, **14**. Alternately, the monoanil may decompose further to *o*-phenylenediamine and β-diketone, which can, of course, react to form the chelate complex **3** via the nickel(II) template condensation. The monoanil can also recyclize as the 2-substituted benzimidazole, **16**.

The monoanil condensation product of 1 mol of β-diketone with [Ni(phen)$_2$]$^{2+}$ may exist transiently with a pendant oxygen[29] that would then participate in a second Schiff reaction to yield **3**. The free carbonyl group of the keto imine may also coordinate to the metal ion, subsequently undergoing an intramolecular imine formation to yield **3**. The second mechanism may be less likely since stabilization of the keto imine by carbonyl coordination does not favor further Schiff base condensation with a coordinated amino group. Thus, Curtis[23] found that the complex **18** was stable



18

and was readily isolated. The presence of a strong base such as ammonia or pyridine was necessary to displace the keto-donor group before cyclization occurred.

Pertinent to this discussion is the observation[6,7,30] that keto imine complexes such as **17** tend not to react with 1,2-diamines to yield the fully cyclized macrocyclic complex, even though the nucleophilicities of amines when they are free bases are greater than when coordinated. Such reactions proceed only when there are strongly forcing conditions or when electron-withdrawng β substituents such as –COR or –COOR are present in the β (meso) position of the keto iminato chelate ring of **17** and other related complexes. Keto imines are formed only when specific conditions prevail, i.e., when exces β-diketone is present in the reaction mixture.[7,27,31]

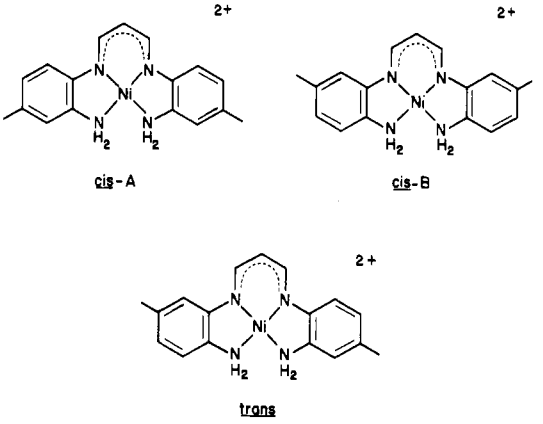
Our success in synthesizing chelate complexes of the type **3** from benzodiazepinium precursors and from the monoanil **7** therefore support the participation of monoanils as intermediates in the metal template condensation of *o*-phenylenediamine with β-diketones. Furthermore, reaction of the 2-methyl-4-phenylbenzodiazepinium salt with *o*-phenylenediamine and nickel(II) ion shows features in the UV spectra that can be attributed to a monoanil intermediate.

NMR Spectra of Chelate Complexes, 3. All the complexes prepared in this study can be considered as derivatives of **3a** with methyl substituents on the diiminato chelate ring (**3b,c**) or on the phenylene ring (**3d**). Their proton NMR spectra therefore all share common features.[7,32]

We previously reported[11] that the ^{1}H NMR spectrum of **3a** was consistent with magnetically nonequivalent protons on each coordinated amine group, giving rise to resonances at δ 5.68 and 3.36. We have reexamined the data and found that the amino protons are indeed equivalent and that the δ 3.36 signal arises from water impurity. The N–H methine proton resonances overlap those of the methine C–CH–C proton. On addition of D_2O, the δ 5.68 signal sharpens to the indicated triplet while the intense HOD signal absorbs at δ 3.3. Addition of CF_3CO_2H completely eliminates the δ 3.36 singlet without altering the δ 5.68 signal. Low integrations observed for the resonances centered at δ 5.68 most likely result from amino proton exchange with the water impurity.

The NMR spectrum of **3d** also shows the presence of water at δ 3.15, while **3b** and **3c** do not show any signals near δ 3.0.

Three geometric isomers of **3d** are possible in the template condensation of 4-methyl-*o*-phenylenediamine with tetramethoxypropane:



cis-A cis-B trans

The NMR spectrum of **3d** shows two doublets, of equal intensity, centered at δ 7.83 and 7.77, which together integrate for a total of two protons. This and the observed multiplet (instead of a triplet) at δ 5.62 (methine C–CH–C) suggest that an equimolar mixture of isomers (cis-A + cis-B) or exclusively the trans isomer is present.

The occurrence of cis and trans isomers is also indicated in NMR spectra of the macrocyclic complex **2** (R_1 = CH_3; R_2–R_4 = H) formed by in situ template synthesis, which proceeds via the bis(imino aminato) intermediate.[33] Similarly, cis and trans isomers were found by L'Eplattenier[7] and Dabrowiak[9] for related phenylene-substituted dibenzotetraaza[14]annulene complexes, **2** (R_1 = OC_2H_5, COC_6H_5; R_2 = H; R_3, R_4 = CH_3). The β-

(29) A related complex with a coordinated primary amino and free keto group has been suggested[22] as an intermediate in the formation of a Curtis macrocycle. The β-amino ketone complex undergoes intramolecular imine formation to yield the cyclized complex.
(30) (a) Truex, T. J.; Holm, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 4529. (b) Bamfield, P. *J. Chem. Soc. A* **1969**, 2021.
(31) Kaneoya, H.; Yamakawa, K. *Chem. Pharm. Bull.* **1976**, *24*, 1934.
(32) Honeybourne, C. L. *Tetrahedron Lett.* **1974**, 3075.
(33) Cutler, A. R.; Alleyne, C. S.; Dolphin, D. *Inorg. Chem.*, preceding paper in this issue.

methine proton resonances appeared as three singlets corresponding to two nonequivalent protons in the cis configuration plus one set of two equivalent protons in the trans configuration. The β-methine proton resonances of the uncyclized intermediates **3** leading to these complexes would be expected to have a similar appearance.

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**, 62081-93-0; **3b**, 96213-12-6; **3c**, 96213-14-8; **3d**, 96213-16-0; **3e**, 96213-18-2; **3f**, 96213-19-3; **13** (R = H), 62086-50-4; **13** (R = Me, R = H), 96213-21-7; **13** (R = Me), 96213-22-8; **13** (R = Me, R = Ph), 96213-23-9; *o*-phenylenediamine, 95-54-5; 1,1,3,3-tetramethoxypropane, 102-52-3; 4,4-dimethoxy-2-butanone, 5436-21-5; 2,4-pentanedione, 123-54-6; 4-methyl-*o*-phenylenediamine, 496-72-0; 4,5-dimethyl-*o*-phenylenediamine, 3171-45-7; benzoylacetone, 93-91-4; 1-phenyl-3-[(*o*-aminophenyl)imino]-1-butanone, 96213-24-0.

Contribution from Rocketdyne, A Division of Rockwell International, Canoga Park, California 91304

Synthesis and Characterization of NF_4CrF_6 and Reaction Chemistry of CrF_5

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Received October 2, 1984

NF_4CrF_6, a new stable NF_4^+ salt containing an energetic counterion, was prepared by treatment of CrF_5 with an excess of NF_4HF_2 in HF solution. The composition and ionic nature of NF_4CrF_6 was established by elemental analysis, vibrational and ^{19}F NMR spectroscopy, and its X-ray powder pattern. Reactions of CrF_5 with H_2O in HF, ClF_3, FNO, Cl_2, $CFCl_3$, and KrF_2 were studied to determine its acidity and oxidizing power. With FNO, a stable 1:1 adduct is formed, which on the basis of its vibrational spectra has the ionic structure $NO^+CrF_6^-$. The reaction of $NOCrF_6$ with NO produced $(NO^+)_2CrF_6^{2-}$, which by controlled pyrolysis was converted to $NO^+CrF_5^-$. With stoichiometric amounts of H_2O in HF, CrF_5 did not form a stable $OH_3^+CrF_6^-$ salt but the reaction resulted in hydrolysis to CrF_3O. The influence of the strong Lewis acids AsF_5 and SbF_5 on the oxidizing power of CrF_5 was also investigated. On the basis of the fact that CrF_5–SbF_5 mixtures can oxidize O_2 (IP = 12.06 eV) but not NF_3 (IP = 13.00 eV), the following qualitative oxidizer strength scale is proposed: $KrF^+ > PtF_6 > SbF_5 + F_2$ + activation energy > CrF_5–SbF_5. The results of a normal-coordinate analysis of CrF_6^- and CrF_6^{2-} show the expected decrease in force constants with increasing negative charge.

Introduction

Chromium pentafluoride is a known, powerful oxidizer capable of fluorinating, for example, Xe to XeF_2 and XeF_4.[2,3] Furthermore, it is known that the oxidizing power of CrF_5 can be enhanced by the addition of a strong Lewis acid, such as SbF_5.[4] Thus, these CrF_5–Lewis acid mixtures can oxidize O_2 to O_2^+ and therefore are assigned an electron affinity comparable to that of PtF_6.[4] In view of this demonstrated high oxidizing power of CrF_5, the known existence of the CrF_6^- anion,[4] and the exceptional stability of NF_4^+ salts,[5,6] the synthesis of the new oxidizer $NF_4^+CrF_6^-$ appeared feasible.

Experimental Section

Apparatus. Volatile materials were manipulated in stainless-steel vacuum lines equipped with Teflon–FEP U-traps, 316 stainless-steel bellows-seal valves, and a Heise Bourdon tube-type pressure gauge.[7] Either quartz or sapphire tubes or Teflon–FEP ampules, equipped with stainless-steel valves, were used as reaction vessels. The lines and other hardware used were passivated with ClF_3 and, if HF was to be used, with HF. Nonvolatile or marginally volatile materials, such as SbF_5 and CrF_5, were handled in the dry N_2 atmosphere of a glovebox. Antimony pentafluoride was added to the reactors with a Teflon-needle syringe, and CrF_5, due to its tackiness at ambient temperature, was preferably handled after it had been cooled by liquid nitrogen. Metathetical reaction and solvolysis studies were carried out in HF solution by using an apparatus consisting of two Teflon–FEP U-traps interconnected through a coupling containing a porous Teflon filter.[8]

High-pressure, high-temperature reactions were carried out in 95- or 1000-cm^3 Monel cylinders equipped with Monel valves. The loaded cylinders were placed into an oven set at the desired reaction temperature. Decomposition studies were carried out in a sapphire reactor (Tyco Co.). The reactor was connected to a stainless-steel valve by a Swagelok compression fitting using Teflon ferrules. The reactor was heated by immersion into a stirred oil bath.

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. Spectra of solids were obtained by using dry powders pressed between AgCl or AgBr windows in an Econo press (Barnes Engineering Co.). Spectra of gases were obtained by using a Teflon cell of 5-cm path length equipped with AgCl windows. Raman spectra were recorded on either a Cary Model 83 or a Spex Model 1403 spectrophotometer using the 488-nm exciting line of an Ar ion laser or the 647.1-nm exciting line of a Kr ion laser, respectively. Sealed quartz, Teflon–FEP, or sapphire tubes were used as sample containers in the transverse-viewing–transverse-excitation mode. A previously described[9] device was used for recording the low-temperature spectra. The ^{19}F NMR spectra of the samples contained in sealed, 5-mm-o.d. Teflon–FEP tubes (Wilmad Glass Co.) were recorded at 84.6 MHz on a Varian Model EM390 spectrometer equipped with a variable-temperature probe. X-ray diffraction patterns of the powdered samples in sealed 0.5-mm quartz capillaries were obtained by using a General Electric Model XRD-6 diffractometer, Ni-filtered Cu Kα radiation, and a 114.6-mm-diameter Philips camera.

Elemental analyses were performed by Mikroanalytische Laboratorien, Elbach, West Germany.

Materials. Literature methods were used for the syntheses of NF_4SbF_6,[10] KrF_2,[11] $KrFSbF_6$,[12] and FNO[13] and for the drying of HF.[14]

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