Stable Highly Oxidizing Cobalt Complexes of Macrocyclic Ligands

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Abstract: The first crystallographically characterized neutral square-planar complex of cobalt in an oxidation state higher than 2+, $Co(\eta^4\text{-}1)$, is reported. Structural data for this new class of compounds indicate that the macrocycle in $Co(\eta^4\text{-}1)$ is
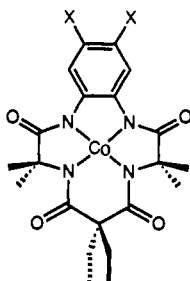
X = Cl, $Co(\eta^4\text{-}1)$
X = H, $Co(\eta^4\text{-}2)$
X = MeO, $Co(\eta^4\text{-}3)$

noninnocent; however, EPR data in toluene at 5.9 K ($S = 1/2$; $g_1 = 2.558$, $g_2 = 2.170$, $g_3 = 2.017$; $A_2 \approx 15$ G) show that the metal center is the primary resridence site of the unpaired electron. $Co(\eta^4\text{-}1)$ is a stable, yet potent, oxidant which is soluble in benzene and slightly soluble in pentane. The $Co(\eta^4\text{-}1)/[Co^{III}(\eta^4\text{-}1)]^-$ couple is reversible and found at 0.550 V vs Fc^+/Fc in CH_2Cl_2 (ca. 1.26 V vs NHE). $Co(\eta^4\text{-}1)$ slowly oxidized water, yielding $H[Co^{III}(\eta^4\text{-}1)]$, which may also be prepared by the reaction of $[Co^{III}(\eta^4\text{-}1)]^-$ with HBF_4. Both the redox and the acid/base chemistries of $[Co^{III}(\eta^4\text{-}1)]^-$ are reversible. Electrochemical and EPR data are also presented for $Co(\eta^4\text{-}2)$ and $Co(\eta^4\text{-}3)$.

Introduction

For the middle and later first row transition metals, chromium to copper, the number and variety of high-valent and/or strongly oxidizing complexes are limited by the small range of compatible ligands. Two properties of ligand complements are especially important in determining the compatibility: (i) the donor capacity, since strong donor ligands reduce the oxidizing properties of high-valent complexes and (ii) the ability of the ligand complement to resist oxidative destruction, since strongly oxidizing metal centers tend to rapidly degrade oxidatively sensitive ligands. Significant advantages can ensue from the development of ligand complements which have a high donor capacity combined with superior resistance to oxidative destruction. Such ligands have allowed for the isolation and study of analogues of more reactive and elusive putative intermediates in catalytic homogeneous oxidations.[2] Long-lived homogeneous catalysts[3] have been developed with ligand complements that are resistant to oxidation but not strongly donating.

In this report, we present the synthesis of a series of tetraamide macrocycles ($H_4[1]$–$H_4[3]$) which have been designed to afford strongly donating tetraamido-N ligands upon tetradeprotonation and to be resistant to oxidative destruction. It is demonstrated by the isolation and characterization of an unprecedented class

of square-planar cobalt compounds with high positive formal reduction potentials that the macrocycles possess the rare property of being compatible with strongly oxidizing coordination environments.
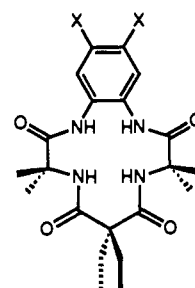
X = Cl, $H_4[1]$
X = H, $H_4[2]$
X = MeO, $H_4[3]$

It is also shown that an unusual and potentially useful combination of properties characterize the new class of cobalt compounds presented in this report: high positive formal potential, coordinative unsaturation of the oxidized species, intense coloration of the oxidized species with a clearly visible color change upon reduction, and high solubility of the oxidized form in nonpolar solvents with low solubility of the reduced form.

Experimental Section

Materials. All solvents and reagents were reagent grade (Aldrich) except for THF (Aldrich, Sureseal anhydrous) and CH_2Cl_2 (Fisher, reagent grade) and were used as received. Fuming nitric acid (Fisher) was used as received. Anhydrous $CoCl_2$ (Aldrich) was stored and manipulated in an inert atmosphere chamber under argon. Preparative TLC plates and fluorescent silica gel for nylon column chromatography were obtained from Analtech.

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Physical Measurements. ¹H NMR were measured at 300 MHz on an IBM NR/300 FT-NMR spectrometer. ¹H NMR data are reported in δ ppm vs (CH₃)₄Si with the deuterated solvent proton residuals used as internal standards. EPR spectra were recorded on a Bruker ER300 spectrometer. Infrared data were obtained on a Nicolet 5DXB FT-IR spectrophotometer, and UV–vis data were obtained on a Perkin-Elmer Lambda Array 3840 spectrophotometer. Crystal structures were solved by Crystalytics Co. of Lincoln, NE. Combustion analyses were performed by Midwest Microlab. Mass spectrometry was performed by the MS facility of the University of Pittsburgh.

Electrochemical Data. Cyclic voltammetry was performed on a Princeton Applied Research Model 173/179 potentiostat/digital coulometer equipped with positive feedback IR compensation and a Model 175 universal programmer. Current voltage curves were recorded on a Houston Instruments Model 2000 X-Y recorder. CH₂Cl₂ (Aldrich, Sureseal anhydrous) and [Et₄N][PF₆] (Fluka) were used as received. [Bu₄N][ClO₄] (Fluka) was vacuum dried at 80 °C. In all cases experiments were performed under N₂ with a supporting electrolyte concentration of 0.1 M. Cyclic voltammetry was performed in CH₂Cl₂ solutions of [Bu₄N][ClO₄] at a 3-mm Pt disk working electrode with a silver wire quasi-reference electrode and a Pt foil counter electrode. At the conclusion of each experiment, ferrocene (Fc) was added as an internal potential standard. All formal potentials were taken as the average of anodic and cathodic peak potentials and are reported vs the Fc⁺/Fc couple. Peak-to-peak separation of the Fc⁺/Fc couple was similar to that of the cobalt couples in all cases. Plots of peak current vs the square root of scan rate over the range 10–500 mV s⁻¹ were made and found to be linear for each cobalt system. Bulk electrolysis was performed in CH₂Cl₂ solutions of [Et₄N][PF₆] or [Bu₄N][ClO₄] in a standard three-component cell at Pt gauze working and counter electrodes with a silver wire quasi-reference electrode. The anodic current passed in oxidation equaled the cathodic current passed in reduction within 10%.

Safety Note. The organic azides produced in the following syntheses are never isolated in concentrated form in quantities greater than 20 mg.

Syntheses. **1,2-Bis(2-bromo-2-methylpropanamido)-4,5-dichlorobenzene.** 4,5-Dichloro-1,2-phenylenediamine (38.45 g) was dissolved in CH₂Cl₂ (550 mL), Et₃N (80 mL) was added, and then bromoisobutyryl bromide (100.0 g) was added via a constant pressure addition funnel (45 min), and the reaction was stirred (6 h) under N₂. Water and CH₂Cl₂ were added until all the solids dissolved. The layers were then separated, and the CH₂Cl₂ layer was extracted four times with dilute aqueous HBr and three times with dilute aqueous Na₂CO₃. Evaporating the CH₂Cl₂ solution to dryness yielded a black solid which was washed on a sintered glass crucible with pentane until the eluents were nearly colorless and the solid turned pale brown. Drying in vacuo yielded the product (76.21 g, 73.9%): ¹H NMR (CDCl₃) 8.68 (s, 2 H, amide NH), 7.70 (s, 2 H), 2.05 (s, 12 H); IR (Nujol) ῡ [cm⁻¹] = 3290 (amide NH), 1676 (amide). Anal. Calcd: C, 35.40; H, 3.40; N, 5.90. Found: C, 35.37; H, 3.38; N, 5.88.

1,2-Bis(2-amino-2-methylpropanamido)-4,5-dichlorobenzene. The above product (76.2 g) was suspended in EtOH (1.5 L), NaN₃ (CAUTION!) (60 g) dissolved in H₂O (900 mL) was added, and the solid dissolved as the reaction was heated to reflux. The mixture was heated under reflux (12 h), allowed to cool, and then extracted with CH₂Cl₂ (5.0 L). The CH₂Cl₂ solution was concentrated to 1.5 L, EtOH was added (1.5 L), the solution was concentrated to 2.0 L, and more EtOH was added (2.0 L). CAUTION! NMR analysis was performed on 3 mg of isolated material. The bulk diazide product was not isolated [¹H NMR (CDCl₃) 8.61 (s, 2 H, amide NH), 7.67 (s, 2 H), 1.65 (s, 12 H)]. (NH₄)₂S (125 mL, 23% aqueous solution) was added to the EtOH solution under N₂, and the reaction was stirred overnight. After a fraction of the solvent had been removed under reduced pressure, sulfur and insoluble polysulfides were filtered away. The filtrate was taken to dryness under reduced pressure, and the solid was dissolved in CH₂Cl₂ and extracted with ice cold aqueous NaOH (21 g in 700 mL of H₂O). The CH₂Cl₂ layer was separated and dried over Na₂SO₄. The CH₂Cl₂ was removed under reduced pressure, and the resultant dark brown solid was treated with CH₂Cl₂ (150 mL) and transferred to a sintered glass crucible. The dark brown solid was washed twice with small quantities of CH₂Cl₂ and then washed with Et₂O until a pale, sulfur-contaminated (10–20%), tan solid remained (10.73 g). The dark brown filtrates were combined and taken to dryness under reduced pressure, and the resultant brown solid was washed with Et₂O until most of the color had been removed, giving a sulfur-contaminated (10–20%), tan solid (16.15 g). The combined solids (total yield 26.88 g, 48% from diamide dibromide) were used in the macrocyclization without further purification. The compound may be purified on a preparative TLC plate (0.360 g compound, 20 × 20 cm 2000 micron silica gel plate, THF developing solvent, 0.225 g purified compound isolated): ¹H NMR (CDCl₃) 9.85 (br, s 2 H, amide NH), 7.88 (s, 2 H), 1.69 (br, 4 H, amine NH), 1.45 (s, 12 H); IR (Nujol) ῡ [cm⁻¹] = 3401, 3349, 3302, 3288, 3215 (amide and amine

NH), 1646 (amide). Anal. Calcd: C, 48.43; H, 5.81; N, 16.13. Found: C, 48.38; H, 5.76; N, 16.00.

5,6-(4,5-Dichlorobenzo)-3,8,11,13-tetraoxo-2,2,9,9-tetramethyl-12,12-diethyl-1,4,7,10-tetraazacyclotridecane, H₄[1]. The diamine (9.00 g), Et₃N (7.5 mL), and diethylmalonyl dichloride (2.4 mL) were added to CH₂Cl₂ (5.0 L) under N₂. Additions of identical quantities of the three reactants were repeated twice at seven hour intervals [totals: diamine, 27.00 g; Et₃N, 22.5 mL; diethylmalonyl dichloride, 7.2 mL]. The reaction mixture was stirred (7 h) and then extracted three times with dilute aqueous HBr and three times with dilute aqueous NaHCO₃. The CH₂Cl₂ layer was taken to dryness under reduced pressure. CH₂Cl₂ was added, and the solid (mostly macrocycle) (10.6 g) was filtered away. The solid was boiled as a suspension in a mixture of dichloroethane (75 mL) and CH₂Cl₂ (75 mL), and, after cooling, pure H₄[1] (8.023 g, 21.99%) was filtered away from the pale yellow solution: ¹H NMR (CDCl₃) 7.65 (s, 2 H), 7.46 (s, 2 H, amide NH), 6.40 (s, 2 H, amide NH), 2.06 (br, 4 H), 1.57 (s, 12 H), 0.88 (t, 6 H, 7.0 Hz); ¹H NMR (DMSO-d₆, 295 K) 8.33 (s, 2 H, amide NH), 7.75 (s, 2 H, amide NH), 7.65 (s, 2 H, aromatic), 1.98 (q/br, 4 H), 1.45 (s, 12 H), 0.76 (t, 6 H, 7.5 Hz); ¹H NMR (DMSO-d₆, 337 K) 8.24 (s, 2 H, amide NH), 7.67 (s, 2 H, aromatic), 7.55 (s, 2 H, amide NH), 2.02 (q, 4 H, 7.5 Hz), 1.48 (s, 12 H), 0.78 (t, 6 H, 7.5 Hz); IR (Nujol) ῡ [cm⁻¹] = 3454, 3346 (amide NH), 1706, 1688, 1645 (amide). Anal. Calcd for H₄[1]·0.5H₂O: C, 52.51; H, 6.08; N, 11.66. Found: C, 52.65; H, 5.86; N, 11.66 (H₂O found in NMR in addition to solvent background H₂O).

1,2-Bis(2-bromo-2-methylpropanamido)benzene. 1,2-Phenylenediamine (23.52 g) was dissolved in CH₂Cl₂ (550 mL), Et₃N (80 mL) was added, and then bromoisobutyryl bromide (100.0 g) was added via a constant pressure addition funnel (2 h), and the reaction mixture was stirred (6 h) under N₂. The CH₂Cl₂ reaction solution was extracted twice with dilute aqueous HBr and twice with dilute aqueous Na₂CO₃. Upon removal of the solvent under reduced pressure, a tan powder was obtained which was washed with pentane and collected (77.18 g, 87.4%); ¹H NMR 8.75 (s, 2 H, amide NH), 7.51 (m, 2 H), 7.27 (m, 2 H), 2.06 (s, 12 H); IR (Nujol) ῡ [cm⁻¹] = 3342, 3252 (amide NH), 1665 (amide). Anal. Calcd: C, 41.41; H, 4.47; N, 6.90. Found: C, 41.37; H, 4.37; N, 6.81.

1,2-Bis(2-amino-2-methylpropanamido)benzene. The above product (77.18 g) was dissolved in EtOH (1.8 L), an aqueous solution of NaN₃ (CAUTION!) (30.56 g in 1.0 L) was added, and the mixture was heated under reflux (12 h). Solvent was removed under reduced pressure until precipitation was initiated. CH₂Cl₂ was immediately added to redissolve the trace precipitate. The CH₂Cl₂ layer was separated, the aqueous layer was washed with more CH₂Cl₂, and the combined CH₂Cl₂ extracts were dried over Na₂SO₄. The CH₂Cl₂ was again removed under reduced pressure until precipitation was initiated, and EtOH was immediately added to redissolve the trace quantity of precipitate. The solution was again concentrated until precipitation initiated, and more EtOH was again immediately added to redissolve the trace quantity of precipitate. CAUTION! NMR analysis was performed on 3 mg of isolated material. The bulk diazide product was not isolated [¹H NMR (CDCl₃) 8.65 (s, 2 H, amide NH), 7.45 (m, 2 H), 7.20 (m, 2 H), 1.61 (s, 12 H)]. This solution was reduced in portions with H₂ in a bomb (50 psi) with 10% Pd/C. Because the reaction evolves one N₂ molecule for every H₂ molecule absorbed, frequent evacuation of the bomb and refilling with H₂ is advantageous (i.e., H₂ from the high pressure reservoir is not efficiently consumed). The mixture was filtered to remove the catalyst, the filtrate was taken to dryness, the resultant white solid was washed with pentane, and then dried (30.145 g, 57.0% yield from dibromide); ¹H NMR (CDCl₃) 9.78 (br, 2 H, amide NH), 7.61 (m, 2 H), 7.19 (m, 2 H), 1.88 (br, 4 H, amine NH), 1.45 (s, 12 H); IR (Nujol) ῡ [cm⁻¹] = 3389, 3360, 3309, 3245, 3190 (amide and amine NH), 1665 (amide). Anal. Calcd: C, 60.41; H, 7.97; N, 20.13. Found: C, 60.40; H, 8.01; N, 19.86.

5,6-Benzo-3,8,11,13-tetraoxo-2,2,9,9-tetramethyl-12,12-diethyl-1,4,7,10-tetraazacyclotridecane, H₄[2]. Diamine (4.135 g) was split into four equal portions. The first portion was added to CH₂Cl₂ (700 mL), followed by Et₃N (2.0 mL) and diethylmalonyl dichloride (0.63 mL), and the reaction mixture was stirred (3 h). The remaining three portions were added sequentially with the equivalent portions of Et₃N and diethylmalonyl dichloride waiting (3 h) between each addition. The reaction mixture was stirred (12 h) and then extracted twice with dilute aqueous HBr and twice with dilute aqueous Na₂CO₃. The CH₂Cl₂ solution was taken to dryness under reduced pressure, and the solid was redissolved in a minimum of CH₂Cl₂ and applied to the top of a UV-transparent dry nylon column (3-cm diameter) packed to a 45-cm height with fluorescent silica gel (60 Å pore size, 75–150 micron mesh, 4% UV 254 indicator). TLC (developed with Et₂O) of the solution before it was applied to the column showed four spots with Rf's of 0.42 (macrocycle), 0.54, 0.64, and 0.71 (diimide). The column was eluted with a 9:1 mixture of CH₂Cl₂/Et₂O until 400 mL had run through the bottom of the column.

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The first 200 mL contained nothing, the second 200 mL contained the diimide byproduct resulting from the addition of two molecules of diethylmalonyl dichloride to the diamine [^{1}H NMR (CDCl$_3$) 8.55 (s, 2 H, amide NH), 7.33 (m, 2 H), 7.23 (m, 2 H), 1.78 (s, 12 H), 1.77 (q, 8 H, 7.4 Hz), 1.05 (t, 12 H, 7.4 Hz)]. At this point, examination of the column with UV irradiation indicated that the macrocycle had separated from the other two byproducts. Elution was stopped, the column was turned on its side, and the macrocycle was separated by slicing the column 85 and 225 mm from the top. The silica gel in this 140 mm length of column was washed four times with boiling EtOH. The combined filtrates were taken to dryness under reduced pressure, yielding pure macrocycle as a white crystalline solid (1.451 g, 24.3%): ^{1}H NMR (CDCl$_3$) 7.55 (m, 2 H), 7.48 (br, 2 H, amide NH), 7.17 (m, 2 H), 6.46 (br, 2 H, amide NH), 2.07 (br, 4 H), 1.60 (s, 12 H), 0.89 (t, 6 H, 7.1 Hz); ^{1}H NMR (CD$_3$OD) 7.42 (m, 2 H), 7.22 (m, 2 H), 2.12 (q, 4 H, 7.3 Hz, 1.55 (s, 12 H), 0.87 (t, 6 H, 7.3 Hz); IR (Nujol) $\bar{\nu}$ [cm^{-1}] = 3395, 3363 (amide NH), 1702, 1680, 1652, 1635 (amide). Anal. Calcd for H$_4$[2]·H$_2$O: C, 59.98; H, 7.67; N, 13.36. Found: C, 60.36; H, 7.24; N, 13.01 (H$_2$O found in NMR in addition to solvent background H$_2$O.).

1,2-Dimethoxy-4,5-dinitrobenzene.[4] 1,2-Dimethoxybenzene (24.2 g) and glacial acetic acid (73 mL) were placed in a 500-mL flask and cooled with an ice/water bath to 0 °C. Using a dropping funnel, concentrated (70%) nitric acid (5.0 mL) was added dropwise; a dark yellow precipitate developed (1,2-dimethoxy-4-nitrobenzene). Fuming nitric acid (sp gr 1.50: 107 mL) was added dropwise (1–2 h). The precipitate slowly dissolved to give a yellow-orange solution, which was stirred (2 h). This solution was poured over 1.5 L of ice/water in a large beaker, mixed thoroughly, and allowed to stand until the ice had melted. The yellow solid was filtered off, washed with distilled water (until the pH of the washings was 4 or greater), and then dissolved in the minimum quantity of hot EtOH (about 750 mL) and left to crystallize overnight. The large yellow needles were filtered off and washed with small amounts of cold EtOH (32.4 g, 81%): mp 129.5–130.5 °C.

1,2-Bis(2-bromo-2-methylpropanamido)-4,5-dimethoxybenzene. 1,2-Dimethoxy-4,5-dinitrobenzene (10 g), MeOH (100 mL), and Pd/C catalyst (10% Pd, 0.3 g, slurried in MeOH) were placed in a bomb, and concentrated HCl (18 mL) was added. The mixture was hydrogenated (50 psi) until the pressure in the bomb stopped decreasing. The Pd/C was then filtered away, and the 1,2-diamino-4,5-dimethoxybenzene dihydrochloride solution was evaporated to dryness, dissolved in Et$_3$N (100 mL) and CH$_2$Cl$_2$ (400 mL), and poured quickly into a 1-L flask equipped with a pressure-equalizing addition funnel, a reflux condenser, and a CaCl$_2$ drying tube. N$_2$ was blown through the flask to minimize air oxidation of the free diamine. The solution was dark greenish-brown. The flask was cooled using ice/water, and then 2-bromoisobutyryl bromide (35 mL) was added dropwise with stirring (2 h). The mixture was stirred overnight. The resulting solution was extracted three times with dilute HBr and then three times with aqueous Na$_2$CO$_3$. The organic layer was dried with Na$_2$SO$_4$, then filtered and evaporated to dryness. This gave a sticky, dark brown solid, which was stirred (8 h) with a 1:2 Et$_2$O/pentane mixture (600 mL), filtered, and air-dried to give a pale brown powder (11.3 g, 54% from 1,2-Dimethoxy-4,5-dinitrobenzene): ^{1}H NMR (CDCl$_3$) 8.57 (s, 2 H, amide NH), 7.00 (s, 2 H), 3.84 (s, 6 H), 2.03 (s, 12 H); IR (Nujol): $\bar{\nu}$ [cm^{-1}] = 3301 (amide NH), 1668 (amide). Anal. Calcd: C, 41.22; H, 4.76; N, 6.01. Found: C, 41.35; H, 4.75; N, 5.99.

1,2-Bis(2-amino-2-methylpropanamido)-4,5-dimethoxybenzene. Bis-1,2-(2-bromo-2-methylpropanamido)-4,5-dimethoxybenzene (6.0 g) was stirred with EtOH (135 mL) in a 500-mL flask. A solution of sodium azide, NaN$_3$ (CAUTION!) (2.4 g, 0.037 mol), in distilled water (80 mL) was added, and the solution was heated under reflux overnight. The solution was evaporated under reduced pressure until precipitation was initiated and then extracted with CH$_2$Cl$_2$. The organic layer was dried over Na$_2$SO$_4$ and filtered. EtOH (50 mL) was added, and the CH$_2$Cl$_2$ was removed under reduced pressure. More EtOH (80 mL) was added, and evaporation continued to ensure all the CH$_2$Cl$_2$ had been removed. CAUTION! NMR analysis was performed on 3 mg of isolated material. The bulk diazide product was not isolated [^{1}H NMR (CDCl$_3$) 8.62 (s, 2 H, amide NH), 7.05 (s, 2 H), 3.87 (s, 6 H), 1.67 (s, 12 H)]. The solution was diluted to 350 mL with EtOH, and then aqueous 23% (NH$_4$)$_2$S solution was added (11.2 mL) under N$_2$. The mixture was stirred (36 h). The reaction solution was evaporated to dryness, and CH$_2$Cl$_2$ (160 mL) was added. This solution was cooled to 0–5 °C (ice/water bath) and then extracted twice with ice-cold 1 M aqueous NaOH. The organic phase was separated, dried with Na$_2$SO$_4$, filtered,

(4) This is a modified procedure of that published: Drake, N. L.; Anspon, H. D.; Draper, J. D.; Haywood, S. T.; Van Hook, J.; Melamed, S.; Peck, R. M.; Sterling, J. Jr.; Walton, E. W.; Whiton, A. *J. Am. Chem. Soc.* 1946, 68, 1536–1543.

and evaporated to dryness. The product was stirred for several hours in a mixture of CH$_2$Cl$_2$ (20 mL) and Et$_2$O (100 mL), and then the pale brown solid was filtered off and washed with a small amount of CH$_2$Cl$_2$ (1.9 g, 44% from diamide dibromide) [^{1}H NMR (CDCl$_3$) 9.62 (s, 2 H, amide NH), 7.15 (s, 2 H), 3.82 (s, 6 H), 1.94 (s, 4 H, amine NH), 1.40 (s, 12 H)]. A sample uncontaminated with sulfur suitable for analysis was prepared by hydrogenating the diazide with Pd/C (10%) at 50 psi in EtOH; IR (Nujol) $\bar{\nu}$ [cm^{-1}] = 3396, 3362, 3265 (amide and amine NH), 1651 (amide). Anal. Calcd: C, 56.79; H, 7.74; N, 16.56. Found: C, 57.04; H, 7.80; N, 15.92.

5,6-(4,5-Dimethoxybenzo)-3,8,11,13-tetraoxo-2,2,9,9-tetramethyl-12,12-diethyl-1,4,7,10-tetraazacyclotridecane, H$_4$[3]. CH$_2$Cl$_2$ (400 mL) was placed in the reaction vessel. The reagents were added in four portions, separated by 4-h intervals. At each addition, 1,2-bis(2-amino-2-methylpropanamido)-4,5-dimethoxybenzene (0.48 g), Et$_3$N (0.78 mL), and diethylmalonyl dichloride (0.26 mL) were added. After the last addition, stirring was continued overnight. The solution was extracted three times with dilute HBr and three times with aqueous Na$_2$CO$_3$, and then the organic layer was dried with Na$_2$SO$_4$, filtered, and evaporated to dryness. The pure compound was isolated by repeated recrystallization from CH$_2$Cl$_2$/pentane. The product was an off-white microcrystalline solid (0.605 g, 23.1%): ^{1}H NMR (CD$_2$Cl$_2$) 7.26 (s, 2 H, amide NH), 7.01 (s, 2 H), 6.41 (s, 2 H, amide NH), 3.80 (s, 6 H), 2.07 (br, 4 H), 1.54 (s, 12 H), 0.90 (t, 6 H); IR (Nujol) $\bar{\nu}$ [cm^{-1}] = 3451, 3391, 3347 (amide NH), 1695, 1670, 1655 (amide). Anal. Calcd for H$_4$[3]·^{1}/$_3$H$_2$O: C, 58.96; H, 7.46; N, 11.96. Found: C, 58.90; H, 7.26; N, 11.76 (^{1}/$_3$H$_2$O found in NMR in addition to solvent background H$_2$O).

Li[Co^{III}(η^4-1)]. A dry, deoxygenated THF (60 mL) solution of H$_4$[1] (0.504 g) was frozen with liquid N$_2$, and *tert*-butyllithium (2.52 mL, 1.7 M in pentane) was added under N$_2$. After warming, anhydrous CoCl$_2$ (0.175 g, 1.3 equiv) was added just before the THF finished thawing (−108 °C). Upon further warming, a green precipitate (presumably a Co(II) complex) gradually developed. After stirring (20 °C, 30 min), air was admitted, rapidly converting the green-yellow suspension to a dark purple solution. The mixture was filtered through silica gel, and the purple compound was eluted with acetone. The solution was evaporated to dryness under reduced pressure, and the resultant solid was washed copiously with CH$_2$Cl$_2$ yielding the product as a purple powder (0.536 g, 93.5%): ^{1}H NMR (CD$_3$CN) 3.88 (br, 12 H), −0.85 (br, 4 H), −2.81 (br, 6 H), −6.55 (br, 2 H); ^{1}H NMR (THF-d_8) 3.98 (br, 12 H), −0.70 (br, 4 H), −2.65 (br, 6 H), −6.82 (br, 2 H); ^{1}H NMR (D$_2$O) −1.60 (br, 4 H), −2.50 (br, 12 H), −7.37 (br, 6 H), −21.12 (br, 2 H).

[Ph$_4$P][Co^{III}(η^4-1)] and [Bu$_4$N][Co^{III}(η^4-1)]. Aqueous [Ph$_4$P]Cl (excess) was added to aqueous Li[Co^{III}(η^4-1)], and the precipitate was collected. X-ray quality crystals were grown by vapor diffusion of pentane into a 1,2-dichloroethane solution: UV−vis (CH$_2$Cl$_2$) λ_{max} [nm] (ϵ) = 430 (3350), 516 (9150), 612 (2970); ^{1}H NMR of [Ph$_4$P][Co^{III}(η^4-1)] (CDCl$_3$) 7.32 (br, 8 H, [Ph$_4$P]$^+$), 6.95 (br, 8 H, [Ph$_4$P]$^+$), 6.76 (br, 4 H, [Ph$_4$P]$^+$), 4.15 (br, 12 H), −0.95 (br, 4 H), −2.90 (br, 6 H), −5.72 (br, 2 H). Crystalline [Bu$_4$N][Co^{III}(η^4-1)] was prepared analogously using [Bu$_4$N]Cl: IR [Bu$_4$N][Co^{III}(η^4-1)] (Nujol) $\bar{\nu}$ [cm^{-1}] = 1648, 1593, 1571. Anal. Calcd for [Ph$_4$P][Co^{III}(η^4-1)]: C, 62.44; H, 5.12; N, 6.47. Found: C, 62.38; H, 4.99; N, 6.40.

H[Co^{III}(η^4-1)]. Aqueous HBF$_4$ was added to aqueous Li[Co^{III}(η^4-1)] (0.075 g), and the precipitate (0.049 g) was collected and crystallized by vapor diffusion of pentane into an acetone solution: IR (Nujol) $\bar{\nu}$ [cm^{-1}] = 1671, 1618, 1611; UV−vis (acetone) λ_{max} [nm] (ϵ) = 342 (3400), 430 (3500), 516 (8400); MS (70 eV), m/z 526 (M$^+$, 8%): mp = 312 °C; ^{1}H NMR (acetone-d_6) only one broad peak located (−9.5 ppm). The complex is also produced by reduction of Co(η^4-1) with H$_2$O.

Co(η^4-1). In an inert atmosphere chamber, Li[Co^{III}(η^4-1)] (0.137 g) and excess (NH$_4$)$_2$Ce(NO$_3$)$_6$ were ground together on a sintered glass crucible in dry benzene. The benzene developed an intense blue color as Co(η^4-1) formed. The blue solution was filtered away from the solids, fresh benzene was added to the crucible, and grinding was repeated. This grinding and collection procedure was repeated until the blue color in the benzene extracts had diminished significantly. Removal of the benzene under reduced pressure yielded the metallic red-purple powdery product (0.069 g, 51%). X-ray quality crystals were grown by vapor diffusion of pentane into a benzene solution: UV−vis (benzene) λ_{max} [nm] (ϵ) = 344 (4900), 386 (4500), 524 (7400), 626 (26000), 670 (shoulder 9800); IR (Nujol) $\bar{\nu}$ [cm^{-1}] = 1716, 1616, 1599; FAB MS of Co(η^4-1) (sulfolane matrix, *anions* detected) m/z 525 (M$^-$, 100%).

Li[Co^{III}(η^4-2)]. A dry, deoxygenated THF (38 mL) solution of H$_4$[2] (0.210 g) was frozen with liquid N$_2$, and *tert*-butyllithium (1.1 mL, 1.7 M in pentane) was added under N$_2$. After warming, anhydrous CoCl$_2$ (0.085 g) was added just before the THF finished thawing (−108 °C). Upon further warming, a green precipitate (presumably a Co(II) complex) gradually developed. After stirring (20 °C, 30 min), air was ad-

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mitted, rapidly converting the green-yellow suspension to a dark purple solution. The mixture was filtered through silica gel, and the purple compound was eluted with acetone. The solution was evaporated to dryness under reduced pressure, and the resultant solid was washed copiously with CH_2Cl_2 yielding the product as a purple powder (0.206 g, 85.0%).

[**Bu₄N**][**Co**^{III}(η⁴-2)]. Excess aqueous [Bu₄N]Cl was added to aqueous Li[Co^{III}(η⁴-1)] (0.114 g), the precipitate was collected and dissolved in 50:50 EtOH/H₂O, and crystals of [Bu₄N][Co^{III}(η⁴-2)] (0.115 g) grew upon evaporation of the EtOH: UV–vis (CH_2Cl_2) λ_{max} [nm] (ϵ) = 426 (2700), 516 (9000), 630 (2400); ¹H NMR (CDCl₃) 3.69 (br, [Bu₄N]⁺, 8 H), 2.69 (br, [Bu₄N]⁺, 8 H), 1.68 (br, [Bu₄N]⁺, 8 H), 0.77 (br, [Bu₄N]⁺, 12 H), −0.69 (br, 12 H), −0.94 (br, 6 H), −2.72 (br, 4 H), −4.35 (br, 2 H), −21.64 (br, 2 H); IR (Nujol) $\bar{\nu}$ [cm⁻¹] = 1648, 1635, 1590, 1572. Anal. Calcd for [Bu₄N][Co^{III}(η⁴-2)]: C, 63.50; H, 8.93; N, 10.01. Found: C, 63.39; H, 8.72; N, 9.97.

Co(η⁴-2). Li[Co^{III}(η⁴-2)] (33 mg) and excess (NH₄)₂Ce(NO₃)₆ (300 mg) were suspended in dry CH_2Cl_2 (5 mL) and stirred (1 h). The resulting dark blue solution was filtered from the suspension, and the CH_2Cl_2 was removed under vacuum. The solids were resuspended in CH_2Cl_2 (5 mL) and stirred again (1 h). The resulting dark blue solution was filtered from the suspension and combined with the previously obtained product. The CH_2Cl_2 was again removed under vacuum, benzene was added, and the benzene was removed under vacuum to give a metallic purple solid (16 mg, 49%): UV–vis (benzene) λ_{max} [nm] (ϵ) = 525 (6000), 614 (15000), 630 (3000); IR (CH_2Cl_2) $\bar{\nu}$ [cm⁻¹] = 1720, 1640, 1593. Anal. Calcd for Co^{III}(η⁴-2)·C₆H₆·3H₂O: C, 55.01; H, 6.50; N, 9.50. Found: C, 55.30; H, 6.64; N, 9.26.

Li[Co^{III}(η⁴-3)]. To a frozen solution of H₄[3] (0.108 g) in dry, deoxygenated THF (25 mL) under N₂ was added *tert*-butyllithium (0.58 mL, 1.7 M in pentane) followed immediately upon thawing by anhydrous CoCl₂ (0.047 g, 1.3 equiv). The mixture was allowed to warm to room temperature and was stirred (1 h) under N₂ to give a green suspension (presumably a Co(II) complex). Air was admitted, and a dark red-purple solution developed rapidly. The solution was filtered, evaporated to dryness, washed twice with CH_2Cl_2, then extracted with MeOH, and filtered through a pad of diatomaceous earth. Evaporation yielded the product as a dark purple-red solid: 0.061 g; ¹H NMR (CD₃OD) 12.85 (s, 6 H), 2.48 (br, 12 H), 1.32 (br, 2 H), 0.05 (br, 4 H), −2.11 (br, 6 H).

[**Et₄N**][**Co**^{III}(η⁴-3)]. To a solution of Li[Co^{III}(η⁴-3)] (0.040 g) in MeOH was added [Et₄N]F·H₂O (0.020 g), and the mixture was stirred (10 min). The solvent was removed under reduced pressure, and the resulting solid was extracted with CH_2Cl_2 and filtered through a diatomaceous earth pad. Diffusion of Et₂O into a CH_2Cl_2 solution yielded the pure compound as dark red-purple crystals (0.042 g, 85%): ¹H NMR (CD₃OD) 12.80 (br, 6 H); 3.12 (q, 8 H, CH₂ of [Et₄N]⁺), 2.41 (br, 12 H), 1.33 (br, 2 H), 1.05 (t, 12 H, Me of [Et₄N]⁺), −0.02 (br, 4 H), −2.16 (br, 6 H); IR (Nujol) $\bar{\nu}$ [cm⁻¹] = 1648, 1621, 1588, 1570. Anal. Calcd for [Et₄N][Co^{III}(η⁴-3)]·0.5H₂O: C, 56.70; H, 7.83; N, 10.66. Found: C, 56.95; H, 7.79; N, 10.65.

Co(η⁴-3). Li[Co^{III}(η⁴-3)] (0.058 g) was stirred with excess (NH₄)₂Ce(NO₃)₆ suspended in dry CH_2Cl_2. A deep blue color developed in the mixture containing the purple suspended Li[Co^{III}(η⁴-3)]. Stirring was continued until all the purple solid had reacted (2.5 h). The intense blue solution was filtered and evaporated to dryness. The residue was extracted with benzene and filtered. Large metallic purple-red single crystals of the product were obtained from benzene/pentane solution (0.048 g, 84%): IR (Nujol) $\bar{\nu}$ [cm⁻¹] = 1701, 1690, 1627, 1616, 1593; UV–vis (benzene) λ_{max} [nm] (ϵ) = 654 (40000). Anal. Calcd for Co(η⁴-3)·0.5C₆H₆: C, 56.12; H, 5.89; N, 10.07. Found: C, 56.10; H, 5.96; N, 10.09. The concentration of a saturated solution in benzene was 24 mM.

X-ray Data Collection and Structure Refinement of [Ph₄P][Co^{III}(η⁴-1)] and Co(η⁴-1). Crystal data: single crystals of [Ph₄P][Co^{III}(η⁴-1)] are triclinic (space group $P\bar{1}$-C_i^1 (no. 2) at 20 ± 1 °C), with a = 11.429 (3) Å, b = 13.245 (3) Å, c = 14.227 (3) Å, α = 97.11 (2)°, β = 92.74 (2)°, γ = 96.21 (2)°, V = 2120.5 (9) Å³, and Z = 2). A total of 7757 independent reflections having 2θ(Mo Kα) < 50.7° (the equivalent of 0.80 limiting Cu Kα spheres) were collected on a computer-controlled Nicolet autodiffractometer using full (0.90°-wide) ω scans and graphite-monochromated Mo Kα radiation. Single crystals of Co(η⁴-1) are tetragonal (space group $P4_12_12$-D_4^4 (no. 92) at 20 ± 1 °C), with a = 10.515 (2) Å, c = 21.681 (3) Å, V = 2397.3 (9) Å³, and Z = 4. A total of 1665 independent reflections having 2θ(Mo Kα) < 55° (the equivalent of 1.0 limiting Cu Kα spheres) were collected on a computer-controlled Nicolet autodiffractometer using full (1.5°-wide) ω scans and graphite-monochromated Mo Kα radiation. The structures were solved using direct methods techniques with the Nicolet SHELXTL software package as modified at Crystalytics Company. The resulting structural parameters have been refined to convergence R_1 (unweighted, based on F) =

Scheme I

X = Cl, H₄[1]; X = H, H₄[2]; X = MeO, H₄[3]
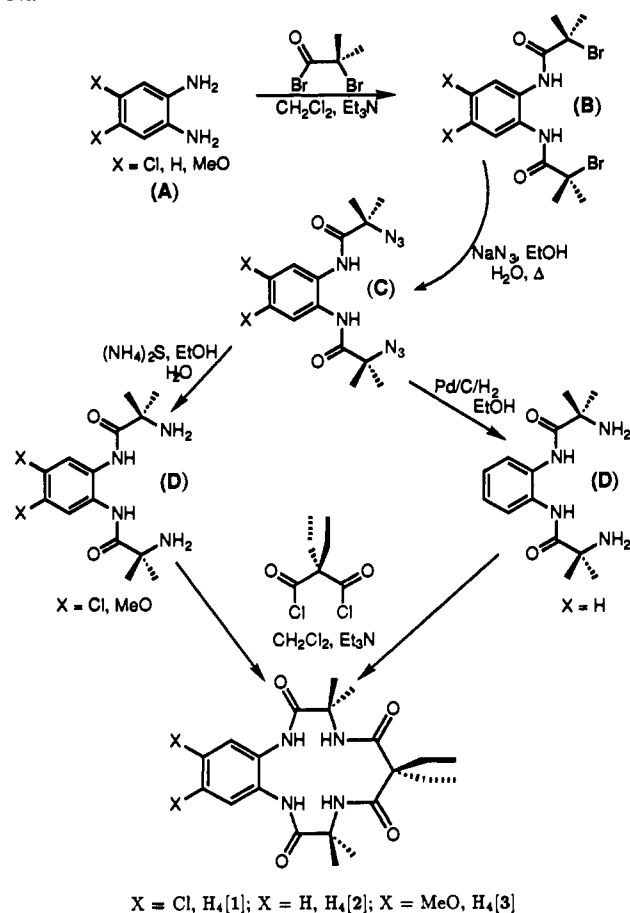
0.037 for 5243 independent reflections having $2\theta_{MoK\alpha}$ < 50.7° and $I > 3\sigma(I)$ for [Ph₄P][Co^{III}(η⁴-1)] and R_1 (unweighted, based on F) = 0.041 for 1163 independent reflections having $2\theta_{MoK\alpha}$ < 55.0° and $I > 3\sigma(I)$ for Co(η⁴-1) using counter-weighted cascade block-diagonal least-squares techniques and a structural model which incorporated anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. The methyl groups were included in the refinement as idealized sp³-rigid rotors and gave final values for the C–C–H angles which ranged from 105° to 112° for [Ph₄P][Co^{III}(η⁴-1)] and from 102° to 120° for Co(η⁴-1). The remaining hydrogen atoms were fixed at idealized sp²- or sp³-hybridized positions with a C–H bond length of 0.96 Å. The oxygen atom of a partial water molecule of crystallization was refined to an occupany factor of 0.30 (1) for [Ph₄P][Co^{III}(η⁴-1)]. For Co(η⁴-1), the correctness of the enantiomeric description was verified by a series of refinement cycles in which the multiplier of $\Delta f''$ was varied; this multiplier refined to a value of 1.0 (1).
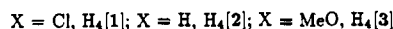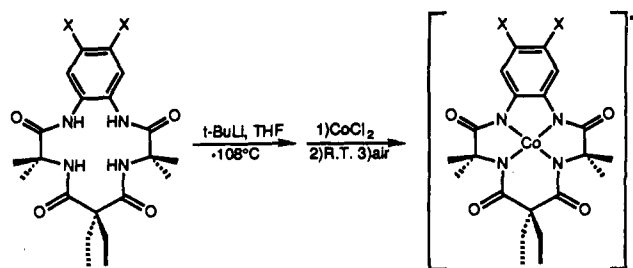
Results and Discussion

Ligand Syntheses. The macrocyclic chelates have been developed in an iterative ligand refinement process, in which limiting structural features such as sites of sensitivity to oxidation,[5] poor coordination properties,[6] and nonplanar amide formation[7] have been identified and replaced or blocked. The new macrocycles are synthesized according to the procedures summarized in Scheme I. The aromatic *o*-phenylenediamines (A) react with bromo-isobutyrylbromide to give the diamidedibromides (B). After investigating a series of unsuccessful pathways to the diamidediamines (D), the route through the diazides (C) was found to lead reproducibly to the pure diamidediamines in high yields. The

(5) Anson, F. C.; Christie, J. A.; Collins, T. J.; Coots, R. J.; Furutani, J. J.; Gipson, S. L.; Keech, J. T.; Krafft, T. E.; Santarsiero, B. D.; Spies, G. H. *J. Am. Chem. Soc.* **1984**, *106*, 4460–4472.

(6) Collins, T. J.; Santarsiero, B. D.; Spies, G. H. *J. Chem. Soc., Chem. Commun.* **1983**, 681–682.

(7) (a) Collins, T. J.; Coots, R. J.; Furutani, T. T.; Keech, J. T.; Peake, G. T.; Santarsiero, B. D. *J. Am. Chem. Soc.* **1986**, *108*, 5333–5339 and references therein. (b) Collins, T. J.; Workman, J. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 912–914 and references therein.

Scheme II

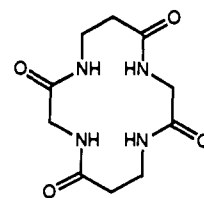X = Cl, H₄[1]; X = H, H₄[2]; X = MeO, H₄[3]

Figure 1. Margerum and Rybka's macrocyclic tetrapeptide. The tetra-deprotonated form was characterized in both Cu(II) and Cu(III) complexes. The Cu(III) complex ($E° = 0.48$ V vs NHE) slowly decomposed by processes involving H-atom abstraction β to the metal.[11]

diazides are not isolated or stored but are reduced in situ to the diamidediamines. The macrocyclization reactions reproducibly give yields of 20–30%. The major side products are not polymeric species, but four-membered ring mono- and diimides produced by alternative intramolecular cyclization processes. It is likely that the macrocycles exhibit intramolecular hydrogen bonding in aprotic solvents of lower polarity, since the quartet expected in the ¹H NMR spectra for the ethyl methylene is broad in these solvents. The quartet appears as such in polar protic solvents or in solvents such as DMSO-d_6 at elevated temperature.

Metal Insertions. Cobalt can be inserted into each of the macrocycles to give cobalt(III) complexes in very high yields according to the procedure outlined in Scheme II. The cobalt anions have been isolated as their Li⁺, [Ph₄P]⁺, [Et₄N]⁺, and/or [Bu₄N]⁺ salts. The cobalt(III) complexes are all dark purple in the solid state and in solution, and the UV–vis spectra remain effectively constant in aprotic potentially coordinating and non-coordinating solvents. In addition, the cobalt(III) complexes exhibit the well-resolved, paramagnetically shifted ¹H NMR spectra found for all the rare square-planar cobalt(III) ($S = 1$) systems.[8f,j,k] The dependencies of the proton chemical shifts on the solvent donor properties are small (see Experimental Section for Li[Co^{III}(η^4-1)] and [Ph₄P][Co^{III}(η^4-1)]), further indicating that the four-coordinate planar structures established in the solid state (see below) are also the most likely structures in aprotic solutions. In water, in which only the Li⁺ salt has appreciable solubility, the magnetic behavior is more complex (see Experimental Section for Li[Co^{III}(η^4-1)]).

A number of research groups have studied the chemistry of macrocyclic transition-metal complexes with one, two, or three amido-N ligands since Kimura and Kodama's first report of such a complex in 1979.[9] In all these cases, the amide unit is part of a macrocycle in which one or more neutral Lewis base ligands, such as amines, are also present. It is reasonable to assume that metal insertion proceeds first by coordination to these accessible or unmasked donor atoms. (The protonated amide does not contain a σ-donating lone pair to lead the coordination process.) Subsequent amide deprotonation/coordination gives the macrocyclic complexes. The technical challenge of effecting metal insertions into polyamide macrocycles free of unmasked donor groups has been one of the primary obstacles hindering the development of this area. Prior to our work,[2b,10] the chemistry of

macrocyclic ligands containing exclusively amido-N donors was limited to Margerum and Rybka's study of the copper chemistry of the macrocycle shown in Figure 1.[11] Among other things, this important contribution demonstrated that metal insertion to give a tetraamido-N complex is possible for a macrocyclic tetraamide. In this system, metal insertion was performed in the presence of aqueous sodium hydroxide and freshly precipitated Cu(OH)₂. However, this approach has not led to macrocyclic complexes for any first row metals from chromium to copper when applied to the tetraamides described here. The insertion procedure described in detail here is an efficient procedure for coordination of tetra-amido-N macrocycles of this report to the first row metals chromium,[10c] manganese,[2b] iron,[10b] cobalt,[10a] and nickel.[10d] Copper is coordinated by other means.[10e] The key features of this method include the use of an anhydrous solvent (THF), low temperatures when bases strong enough to decompose THF are employed, strong bases to deprotonate the ligand prior to metal addition, and the use of divalent transition-metal salts which have some solubility in THF. After the metals have been inserted into the ligands and metal oxidation has been accomplished, the complexes are hydrolytically stable. For instance, [Bu₄N][Co^{III}(η^4-1)] can be prepared by adding excess aqueous [Bu₄N]OH to aqueous Li-[Co^{III}(η^4-1)] and collecting the precipitate. Stable protonated species, such as H[Co^{III}(η^4-1)], can be prepared either by allowing solutions of Co(η^4-1) to oxidize water or by treating aqueous Li[Co^{III}(η^4-1)] with aqueous HBF₄. The hydrolytic stability is general, even the Cr(V)≡O and Mn(V)≡O complexes of these ligands are stable in aqueous solutions.[2b,10c]

Oxidation of the Cobalt(III) Anionic Complexes. This family of ligands[2b,10] is capable of supporting unprecedented crystalline highly oxidized species such as mononuclear five-coordinate iron(IV)–chloro[10b] and manganese(V)–oxo[2b] complexes. As tetradentate tetraamido-N ligands, the macrocycles are distinguished from more conventional ligand complements by the strong donor capacity of the amido-N ligand, which results in a significant stabilization of higher oxidation state metal centers, a phenomenon first elucidated by Margerum and co-workers.[12] As a result of the negative charge and strong donor capacity of the macrocyclic tetraamido-N ligands, the iron(IV) and manganese(V) tetra-amido-N complexes are not strongly oxidizing.[10b,2b] However, in CH₂Cl₂, each of the square-planar cobalt(III) anions can be oxidized by one electron to give stable neutral molecules which can be produced by bulk electrolysis or chemical oxidation: E_f(Co(η^4-1)/[Co^{III}(η^4-1)]⁻) = 0.550 V (vs Fc⁺/Fc, ca. 1.26 V vs NHE), E_f(Co(η^4-2)/[Co^{III}(η^4-2)]⁻) = 0.385 V (vs Fc⁺/Fc, ca. 1.09 V vs NHE), E_f(Co(η^4-3)/[Co^{III}(η^4-3)]⁻) = −0.010 V (vs Fc⁺/Fc, ca. 0.70 V vs NHE). As expected, the oxidation results

(8) For other examples fo the rare Co(III) square-planar geometry see: (a) Eisenberg, R.; Dori, Z.; Gray, H. B.; Ibers, J. A. *Inorg. Chem.* **1968**, 7, 741. (b) Baker-Hawkes, M. J.; Billig, E.; Gray, H. B. *J. Am. Chem. Soc.* **1966**, 88, 4870. (c) Dorfman, J. R.; Rao, Ch. P.; Holm, R. H. *Inorg. Chem.* **1985**, 24, 453. (d) Fikar, R.; Koch, S. A.; Millar, M. M. *Inorg. Chem.* **1985**, 24, 3311. (e) Rao, Ch. P. Dorfman, J. R.; Holm, R. H. *Inorg. Chem.* **1986**, 25, 428. (f) van der Put, P. J.; Schilperoord, A. A. *Inorg. Chem.* **1974**, 13, 2476. (g) Bour, J. J.; Beurskins, P. T.; Steggerda, J. J. *J. Chem. Soc., Chem. Commun.* **1972**, 221. (h) Birker, P. J. M. W. L.; Bour, J. J.; Steggerda *Inorg. Chem.* **1973**, 12, 1254. (i) Birker, P. J. M. W. L.; Beurskins, P. T. *J. R. Neth. Chem. Soc.* **1974**, 93, 218. (j) Brewer, J. C.; Collins, T. J.; Smith, M. R.; Santarsiero, B. D. *J. Am. Chem. Soc.* **1988**, 110, 423–428. (k) Collins, T. J.; Richmond, T. G.; Santarsiero, B. D.; Treco, B. G. R. T. *J. Am. Chem. Soc.* **1986**, 108, 2088–2090. References a–f concern aliphatic and aromatic thiolate ligands. References g–i concern innocent biuret ligands.

(9) For a review of work performed with macrocyclic ligands containing one, two, or three amides, see: Kimura, E. *J. Coord. Chem.* **1986**, 15, 1–28.

(10) (a) Collins, T. J.; Uffelman, E. S. *Angew. Chem., Int. Ed. Engl.* **1989**, 28, 1509–1511. (b) Collins, T. J.; Kostka, K. L.; Münck, E.; Uffelman, E. S. *J. Am. Chem. Soc.* **1990**, 112, 5637–5639. (c) Collins, T. J.; Slebodnick, C.; Uffelman, E. S. *Inorg. Chem.* **1990**, 29, 3432–3436. (d) Collins, T. J.; Nichols, T. R.; Uffelman, E. S. *J. Am. Chem. Soc.* **1991**, 113, 4708–4709. (e) Collins, T. J.; Slebodnick, C.; Uffelman, E. S., to be submitted for publication. (f) Collins, T. J.; Kostka, K. L.; Uffelman, E. S. *Inorg. Chem.* **1991**, in press.

(11) (a) Margerum, D. W.; Rybka, J. S. *Inorg. Chem.* **1980**, 19, 2784–2790. (b) Rybka, J. S.; Margerum, D. W. *Inorg. Chem.* **1981**, 20, 1453–1458.

(12) See, for example: (a) Margerum, D. W. *Pure Appl. Chem.* **1983**, 55, 23–34. (b) Margerum, *Oxidases Relat. Redox Syst., Proc. Int. Symp., 3rd, 1979* **1982**, 193–206.

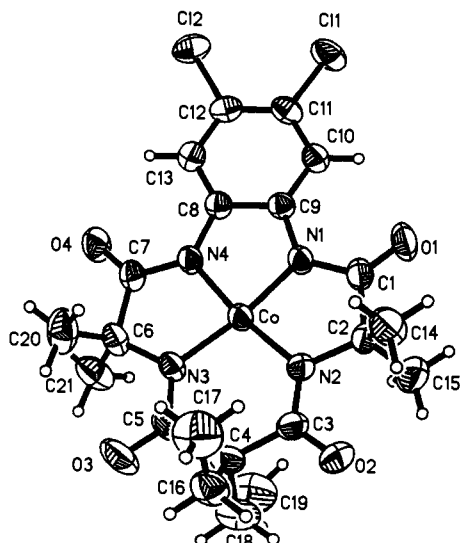**Figure 2.** Molecular structure of the anion of [Ph₄P][Co^{III}(η⁴-1)]. ORTEP drawing with all non-hydrogen atoms drawn to encompass 50% of electron density. Selected bond distances [Å]: Co–N1, 1.827 (2); Co–N2, 1.823 (2); Co–N3, 1.829 (2); Co–N4, 1.819 (2); N1–C9, 1.406 (3); N4–C8, 1.415 (3); C8–C9, 1.411 (4); C8–C13, 1.376 (4); C12–C13, 1.387 (4); C11–C12, 1.380 (4); C10–C11, 1.386 (4); C9–C10, 1.387 (4). N1, N2, N3, and N4 each deviate from their mean plane by no more than 0.02 Å. Co sits in this mean plane.
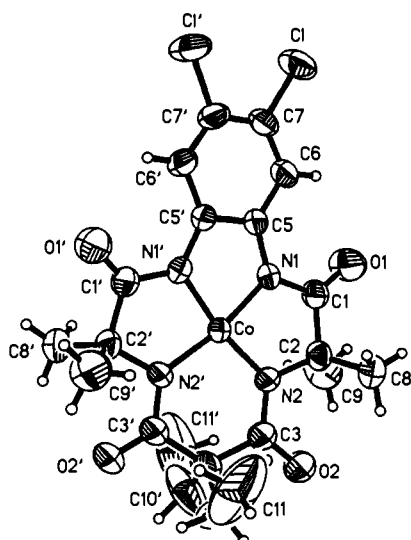

Figure 3. Molecular structure of Co(η⁴-1). ORTEP drawing with all non-hydrogen atoms drawn to encompass 50% of electron density. Selected bond distances [Å] (a 2-fold crystallographic rotation axis passes through Co and C4): Co–N1, 1.823 (4); Co–N2, 1.805 (4); N1–C5, 1.353 (6); C5–C5′, 1.432 (9); C5′–C6′, 1.398 (7); C6′–C7′, 1.350 (8); C7–C7′, 1.428 (10). N1, N1′, N2, and N2′ each deviate from their mean plane by no more than 0.05 Å. Co sits in this mean plane.

in a pronounced increase in the C–O IR stretching frequencies ([Bu₄N][Co^{III}(η⁴-1)] IR (Nujol) $\bar{\nu}$ [cm⁻¹] = 1648, 1593, 1571; Co(η⁴-1) IR (Nujol) $\bar{\nu}$ [cm⁻¹] = 1716, 1616, 1599). Fast atom bombardment mass spectrometry of the neutrals, with the equipment set to examine *anions*, gives spectra in which the base peak is that of the parent compound [FAB MS of Co(η⁴-1) (sulpholane matrix): m/z 525 (M⁻, 100%)]. Co(η⁴-1), Co(η⁴-2), and Co(η⁴-3) can all be isolated as crystalline compounds. The existence of the stable neutral species shows that the dichloro- and diproteo-substituted ligands are indeed stable in strongly oxidizing complexes. The methoxy groups lower the formal potential of Co(η⁴-3) such that the complex is only mildly oxidizing. The solubility of Co(η⁴-1) in benzene is 60 mM; it dissolves in Nujol and silicone grease and is even somewhat pentane soluble. Thus, Co(η⁴-1) is a noteworthy complex, a potent electron-transfer oxidant soluble in hydrocarbons.
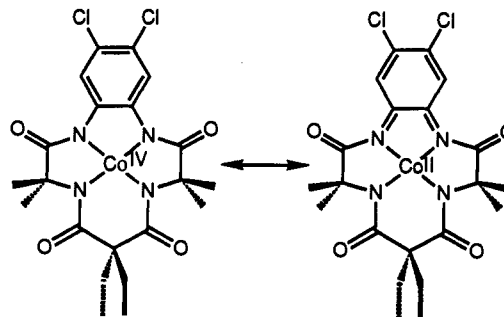

Figure 4. Two resonance contributors to the structure of Co(η⁴-1).

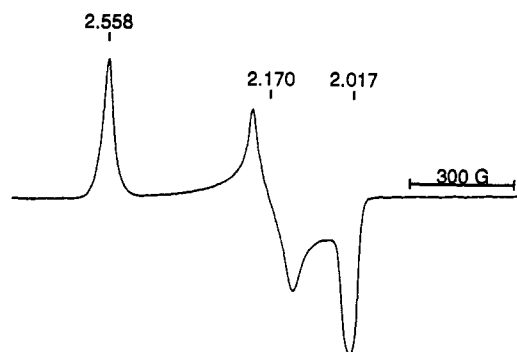**Figure 5.** EPR spectrum of Co(η⁴-1), at 5.9 K, 9.46 GHz, in toluene (six scan average, 1500 G scan range, 3100 G midrange), hyperfine coupling $(A_2) \approx 15$ G. Spin quantitation against a Cu(ClO₄)₂ standard was satisfactory for a $S = 1/2$ system (1.0 ± 0.1 unpaired electrons calculated per molecule).

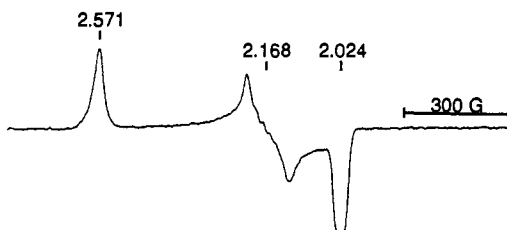**Figure 6.** EPR spectrum of Co(η⁴-2) at 6.3 K, 9.46 GHz, in toluene (1500 G scan range, 3100 G midrange), hyperfine coupling $(A_2) \approx 19$ G.

The aromatic groups in the macrocyclic framework introduce the possibility of ligand noninnocence, and we will now present evidence to indicate that the site of oxidation in the planar complexes is best viewed as being delocalized over both the metal center and the phenylenediamide.

Structural Studies. Co(η⁴-1) is the first crystallographically characterized neutral square-planar cobalt complex in an oxidation state higher than +II.[8,13] The molecular structures of [Co^{III}-(η⁴-1)]⁻ and Co(η⁴-1) are shown in Figures 2 and 3, respectively. The coordination environments around each cobalt center are best described as square-planar. For the [Co^{III}(η⁴-1)]⁻ anion, the four nitrogen atoms each deviate from their mean plane by no more than 0.02 Å, with the Co atom sitting in this mean plane. For Co(η⁴-1), the four nitrogen atoms each deviate from their mean plane by no more than 0.05 Å. The Co atom sits in this mean plane. At the 3σ confidence level, the average Co–N bond distances, 1.814 (4) Å for Co(η⁴-1) and 1.825 (2) Å for [Co^{III}(η⁴-1)]⁻, are indistinguishable. The most significant structural difference is found in the shortening of the two aromatic C to N bond distances and the distortions that occur in the aromatic ring upon

(13) The only other high-valent structure of neutral four-coordinate cobalt is the tetrahedral Co^{IV}(norbornyl)₄ complex. Byrne, E. K.; Richeson, D. S.; Theopold, K. H. *J. Chem. Soc., Chem. Commun.* **1986**, 1491–1492. For work done with this system, see: (a) Bower, B. K.; Tennent, H. G. *J. Am. Chem. Soc.* **1972**, *94*, 2512. (b) Byrne, E. K.; Theopold, K. H. *J. Am. Chem. Soc.* **1987**, *109*, 1282–1283.
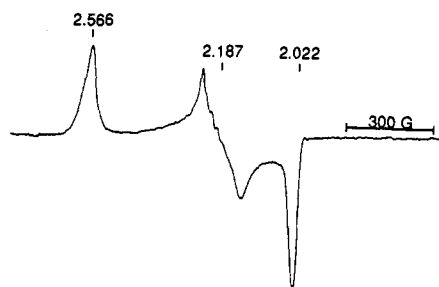
Figure 7. EPR spectrum of Co(η^4-3) at 4.6 K, 9.46 GHz, in toluene (four scan average, 1500 G scan range, 3100 G midrange), hyperfine coupling (A_2) ≈ 19 G.

oxidation. For Co(η^4-1), a 2-fold crystallographic rotation axis passes through Co and C4. The N1–C5/N1′–C5′ (1.353 (6) Å) and C6–C7/C6′–C7′ (1.350 (8) Å) distances of this neutral molecule show evidence of significantly higher bond orders than the comparable bonds of the anion: bond distances [Å] N1–C9, 1.406 (3); N4–C8, 1.415 (3); C10–C11, 1.386 (4); C12–C13, 1.387 (4). Although the differences are less pronounced, a trend to lower bond orders is suggested in the distances for the C5–C5′ (1.432 (9)), C5–C6/C5′–C6′ (1.398 (7) Å), and C7–C7′ (1.428 (10) Å) bonds of the neutral species when compared with the comparable bonds of the anion: bond distances [Å] C8–C9, 1.411 (4); C8–C13, 1.376 (4); C9–C10, 1.387 (4); C11–C12, 1.380 (4). These changes suggest that ligand-centered oxidation is important in the neutral species since the trends in the data can be rationalized by invoking increased contributions from resonance structures (e.g., Figure 4) which lower the formal oxidation state at the metal. While the X-ray data for [Co^{III}(η^4-1)]$^-$ and Co(η^4-1) suggest the involvement of the ligand extended π system in the site of oxidation, EPR evidence clearly shows that the metal is the primary location of the unpaired electron in the highly oxidizing $S = 1/2$ molecules.

EPR Studies. The EPR data for the oxidized square-planar cobalt complexes in glasses of anhydrous toluene at 4–7 K are presented in Figures 5–7. The spectra for the three different complexes are rhombic and clearly show that the unpaired electron is strongly interacting with the metal center in each case. At this point, we are avoiding calling the compounds Co(IV) species, since there are quantum mechanical mechanisms for the noninnocent ligand to share its delocalized *paired* π-electrons with the metal. The structural changes observed are strong evidence for mixing of resonance structures of the type shown in Figure 4, with limiting cases of a square-planar Co(IV) species or a square-planar Co(II) species. Spin quantitation against aqueous Cu(ClO$_4$)$_2$ for Co(η^4-1) shows that there is 1 ± 0.1 unpaired electron per cobalt center. All three complexes exhibit g_1 at 2.558–2.571, g_2 at 2.168–2.187 (A_2 15–19 G), and g_3 at 2.017–2.024. There is no change in the

deep blue color of toluene glasses of Co(η^4-1), Co(η^4-2), or Co-(η^4-3) saturated with water. The EPR spectrum of a toluene glass containing Co(η^4-3) and saturated with H$_2$^{17}O (45% ^{17}O) is indistinguishable from that of a dry glass. These data indicate that trace water in the toluene does not coordinate to the vacant axial sites of the neutral species. When apical ligands are coordinated to these complexes, the EPR spectra obtained have nearly isotropic *g* values, and they constitute the subject of a forthcoming paper.

Conclusion

Co(η^4-1), Co(η^4-2), and Co(η^4-3) are all stable. The long term stability of the strong electron-transfer oxidants, Co(η^4-1) and Co(η^4-2), demonstrate the resistance of the macrocyclic tetra-amido-*N* ligands to oxidative degradation. This is an important finding, since it shows that these ligand complements, known to be excellent for stabilizing high-valent metal centers, are also compatible with strongly oxidizing systems. This work also establishes that complexes with *cis*-amido-*N* donors can be resistant to reductive degradation processes, such as N–N bond formation or homolytic M–N bond cleavage. As shown by X-ray crystallographic evidence, the aromatic macrocycles are not innocent in the neutral oxidized complexes. Consequently, no claim is made concerning assignments of formal oxidation states of the cobalt centers beyond the obvious conclusion that integer assignments of +II, +III, or +IV are not appropriate. The ability to partially and reversibly oxidize the ligands without decomposition does permit the formal potential of the redox couples of the complexes to be varied over 500 mV by changing the aromatic substituents. We are continuing to study the reactivity and properties of these complexes and related complexes of other metals.

Supplementary Material Available: Listings of atomic coordinates, anisotropic thermal parameters for non-hydrogen atoms, bond lengths involving non-hydrogen atoms, bond angles involving non-hydrogen atoms, crystal structure data, hydrogen atom parameters, nonbonded distances, and torsional angles and complete details of the analysis for [Ph$_4$P][Co^{III}(η^4-1)] and Co(η^4-1) (42 pages); listing of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.