Å but completely consistent with bridging C–C bonds found in other species, viz., 1.561 (18) Å in $[(C_{10}H_8)Mo(CO)_3CH_3]_2$[4], 1.585 (15) Å in $(C_{10}H_8)_2Fe$[7], 1.567 (12) Å in $(C_{10}H_8)_2Fe_4(CO)_{10}$[6], 1.568 (7) Å in $(pentalenyl)_2Fe$,[22] and 1.584 (14) Å in 1,1′-tetramethylethyleneferrocene.[23]

Finally, we note that all hydrogen atoms have been located with reasonable precision. Individual C–H distances thus obtained range from 0.870 (29) to 0.978 (26) Å, averaging 0.939 Å. This is in good agreement with the value of 0.95 Å suggested by Churchill[24] as the optimum C–H distance for an x-ray crystallographic study.

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Registry No. $[(C_{10}H_8)Mn(CO)_3]_2$, 60965-83-5.

Supplementary Material Available: Listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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Cobalt(II)-Mediated Oxygenation of a Macrocyclic Ligand. X-Ray Structures of the Cobalt(II) and Cobalt(III) Products[1]

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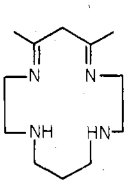
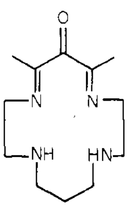
Diaquo(5,7-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,7-diene)cobalt(II) hexafluorophosphate, $[Co([14]4,7\text{-diene}N_4)(OH_2)_2](PF_6)_2$, reacts with O_2 to form a new macrocyclic ligand ($[14]4,7\text{-diene}N_4\text{-one}$) with a ketone oxygen on the central carbon of the 2,4-pentanediiminato moiety. The cobalt(II) center appears to be necessary for this reaction yet is not oxidized in the process. The crystal and molecular structures of $[Co([14]4,7\text{-diene}N_4\text{-one})(OH_2)_2](ClO_4)_2$ and $[Co([14]4,7\text{-diene}N_4\text{-one})Cl_2]ClO_4$ have been determined from three-dimensional x-ray data collected on an automatic diffractometer using Mo Kα radiation. The crystals of $[Co([14]4,7\text{-diene}N_4\text{-one})(OH_2)_2](ClO_4)_2$ belong to the space group $P2_1/c$ with $a = 10.371$ (2) Å, $b = 15.055$ (3) Å, $c = 14.467$ (3) Å, $\beta = 106.39$ (2)°, and $Z = 4$. The crystals of $[Co([14]4,7\text{-diene}N_4\text{-one})Cl_2]ClO_4$ belong to the space group *Pbca* with $a = 12.030$ (2) Å, $b = 12.995$ (2) Å, $c = 23.523$ (4) Å, and $Z = 8$. Full-matrix least-squares refinement yielded conventional discrepancy factors of 0.062 for 1835 observed counter data and 0.038 for 1894 observed counter data, respectively. The ketone oxygen in both complexes is bent up from the plane of the two imine bonds.

Introduction

Reactions of dioxygen with transition metal complexes are numerous and varied. Among the better characterized are dioxygen reactions which result in (1) oxidation only of the metal center,[2] (2) dehydrogenation of coordinated ligands,[3,4] or (3) formation of metal–dioxygen adducts.[5,6] While the present study was in progress, Weiss and Goedken[7] reported their discovery of a dioxygen–cobalt reaction in which a 2,4-pentanediiminato moiety of the coordination complex was converted into a β-diimine moiety with an α,β-unsaturated carbonyl; evidence for this reaction was based on infrared and proton magnetic resonance spectroscopy. We now find analogous behavior in the $Co^{II}([14]4,7\text{-diene}N_4)$[8] complexes recently reported by Cummings and co-workers.[9] Moreover we have isolated and structurally characterized the coordination complex product containing the α,β-unsaturated carbonyl in the macrocyclic $[14]4,7\text{-diene}N_4\text{-one}$ ligand.



$[14]4,7\text{-diene}N_4$



$[14]4,7\text{-diene}N_4\text{-one}$

Experimental Section

A. Preparation of Complexes. 1. $[Co([14]4,7\text{-diene}N_4\text{-one})Cl_2]ClO_4$.[8] A solution of $Co(O_2CCH_3)_2{\cdot}4H_2O$ (14 g) in 500 ml of H_2O was prepared. A condenser was attached and the solution deaerated by bubbling deoxygenated N_2; then *N*,*N*′-bis(2-aminoethyl)-1,3-propanediamine (9.2 g) was deaerated and added by syringe to the preparative solution. After warming of this solution 11.6 g of deaerated 2,4-pentanedione was added. The mixture was refluxed for 1 day under N_2. The resulting solution was poured into a large open beaker and 250 ml of concentrated HCl was added. The solution slowly turned green. A solution of $NaClO_4$ (30 g in 100 ml of water) was then added. After the mixture stood for 2 h, the green crystals were separated from the supernatant solution by filtration. The green solid was washed with ethanol and then ether; yield 6 g. Anal. Calcd for $CoCl_3C_{12}H_{22}N_4O_5$: C, 30.82; H, 4.74; N, 11.98. Found: C, 31.18; H, 4.70; N, 12.07.

2. [Co([14]4,7-dieneN$_4$-one)(OH$_2$)$_2$](ClO$_4$)$_3$. A suspension was formed of [Co([14]4,7-dieneN$_4$-one)Cl$_2$]ClO$_4$ (2.0 g) in 100 ml of 0.1 M $HClO_4$. A concentrated solution of $AgClO_4{\cdot}H_2O$ (2.3 g in 10 ml of H_2O) was added and the solution was stirred for several days at room temperature. The AgCl was removed by filtration and the filtrate was concentrated by evaporation under vacuum. After the mixture stood for 2 weeks in a covered but not sealed beaker, large crystals formed. The supernatant liquid was removed by filtration, and the crystals were air-dried; yield 1.5 g.

3. [Co([14]4,7-dieneN$_4$-one)(OH$_2$)$_2$](ClO$_4$)$_2$. One gram of [Co([14]4,7-dieneN$_4$-one)(OH$_2$)$_2$](ClO$_4$)$_3$ was dissolved in 5 ml of 1.0 M $HClO_4$ and the solution was deaerated with N_2. By use of a syringe, 5 ml of 0.5 M Cr^{2+} solution was added. The solution turned dark blue immediately and the product precipitated in small needles. The solid was quickly filtered in air and washed with a small portion of 2-propanol; yield 0.5 g. Anal. Calcd for $CoCl_2C_{12}H_{26}N_4O_{11}$: C, 27.08; H, 4.92; N, 10.53. Found: C, 27.17; H, 4.96; N, 10.57.

4. [Co(6-Me[14]4,7-dieneN$_4$)Cl$_2$]ClO$_4$. This compound was prepared using the procedure for [Co([14]4,7-dieneN$_4$-one)Cl$_2$]ClO$_4$. 3-Methyl-2,4-pentanedione was substituted for 2,4-pentanedione. The yields were comparable to those in section 1. The 3-methyl-2,4-pentanedione was prepared according to Johnson et al.;[10] two Cl^- ions may also be replaced by water using aqueous $AgClO_4$. Anal. Calcd for $CoCl_3C_{13}H_{26}O_4N_4$: C, 33.39; H, 5.60; N, 11.98. Found: C, 33.55; H, 5.46; N, 11.90.

5. [Co([14]4,7-dieneN$_4$)(OH$_2$)PF$_6$]PF$_6$ was prepared as described by Cummings and co-workers.[9]

B. Crystal Preparation. The crystals of [Co([14]4,7-dieneN$_4$-one)Cl$_2$]ClO$_4$ were easily grown by slow evaporation of a 1 M HCl solution of the complex. The [Co([14]4,7-dieneN$_4$-one)(OH$_2$)$_2$](ClO$_4$)$_2$ crystals were grown by slowly cooling a saturated solution of the complex in 1 M $HClO_4$ under an atmosphere of nitrogen.

C. Spectroscopic Determinations. Visible, ultraviolet, and near-infrared spectra were determined using a Cary 14 spectrophotometer. Infrared spectra were determined with a Perkin-Elmer 621. Proton nuclear magnetic resonance spectra were determined with a Varian T60A.

D. X-Ray Structure Determinations. 1. Data Collection. A suitable dark blue crystal of [Co([14]4,7-dieneN$_4$-one)(OH$_2$)$_2$](ClO$_4$)$_2$ and a spherically ground crystal of [Co([14]4,7-dieneN$_4$-one)Cl$_2$]ClO$_4$ were mounted on glass fibers with epoxy cement and then mounted on a Syntex $P2_1$ four-circle diffractometer. Rotation and axial photographs, together with a small set of counter data, were used to determine the crystal systems and space groups, which were confirmed by examination of the intensity data. Fifteen reflections with 2θ between 15 and 28° for the Co(II) crystal and between 15 and 30° for the Co(III) were centered by the computer. Cell constants and errors were obtained by least-squares refinement of these setting angles. A summary of data collection parameters is listed in Table I.

Intensity data were collected using monochromatic Mo Kα radiation (a graphite monochromator in parallel geometry). The θ–2θ scan technique was used at a scan rate of 2.02°/min. Backgrounds were measured at each end of the scan for a total time equal to half the scan time. Intensities of three standard reflections were measured every 97 reflections, with no indication of crystal decomposition or crystal movement. The data were reduced to F^2 and $\sigma(F^2)$ by procedures previously described.[11]

Standard deviations were assigned as

$$\sigma(I) = [\sigma^2_{\text{counter}}(I) + (0.05I)^2]^{1/2}$$

where $\sigma_{\text{counter}} = (I + 4B)^{1/2}$, I is the net intensity, and B is the total background count. Lorentz and polarization corrections were applied. Extinction and absorption corrections were not applied. Data for which $F^2 \geq 2.5\ \sigma(F^2)$ were used in the solution and refinement of each structure.

Table I. Crystal Information

Compd	[CoL(OH$_2$)$_2$]-(ClO$_4$)$_2$	[CoLCl$_2$]ClO$_4$
Mol wt	532.20	467.62
Color	Dark blue	Green
Size, mm	0.33 × 0.18 × 0.16	Sphere; $r = 0.15$
Crystal systems	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pbca$
a, Å	10.371 (2)	12.030 (2)
b, Å	15.055 (3)	12.995 (2)
c, Å	14.467 (3)	23.523 (4)
β, deg	106.39 (2)	
V, Å^3	2166.9 (9)	3677.3 (5)
ρ_{calcd}, g cm^{-3}	1.631	1.689
ρ_{X}, g cm^{-3} (flotation)	1.629 (5)	1.68 (1)
Z, molecules/unit cell	4	8
μ, cm^{-1}	10.96	14.00
$F(000)$, e	1100	1920
Radiation, Å	0.710 688	0.710 688
2θ scan range, deg	Kα_1 − 1.0 to Kα_2 + 1.0	Kα_1 − 1.0 to Kα_2 + 1.0
Max deviation of standards during data collection, %	2.0	2.0
2θ(max), deg	45	45
Data collected	3121	2761
Data with $F^2 > 2.5\ \sigma(F^2)$	1835	1894
No. of variables	271	226
R_1	0.062	0.038
R_2	0.081	0.049
EOF	1.37	1.76

2. Solution and Refinement of the Structures. (a) [Co([14]4,7-dieneN$_4$-one)(OH$_2$)$_2$](ClO$_4$)$_2$. The cobalt position was obtained by solution of a Patterson map. A Fourier map based on the cobalt position yielded positions for all but the perchlorate oxygen atoms. After locating the oxygen atoms of the perchlorate anions, the positional and isotropic thermal parameters were refined by full-matrix least-squares procedures.[12] A difference synthesis suggested the unexpected existence of an atom of ~8 e located adjacent to the γ-carbon position of the α,β-unsaturated moiety. This contribution was assumed to be from a ketone oxygen atom because the bond distance was ~1.22 Å. Hydrogen atom positions were then calculated and thermal parameters assigned at 10% greater than the atom to which they are bound at a distance of 0.97 Å.

Refinement of all nonhydrogen parameters including anisotropic thermal parameters converged to final values of $R_1 = 0.062$ and $R_2 = 0.081$ for 271 variables. In the last stages of refinement the estimated error on F, $\sigma(F)$, was calculated by a least-squares polynomial fit of the function $||F_o| - |F_c|| = a + b|F_o|$.

A final difference map showed residual peaks in the range 0.9–0.6 e/Å^3 which were near the perchlorate oxygen atoms. The relatively high thermal motion of these atoms suggests a degree of disorder. This is not unusual for this type of anion. No attempt was made to develop a disorder model for these anions. The largest residual peak not associated with the anions was 0.32 e/Å^3. The largest parameter shift relative to its estimated standard deviation for the perchlorate anions was 0.85; for all remaining parameters the largest shift per error was 0.32. Table II lists the final nonhydrogen atomic positions and thermal parameters, along with their estimated standard deviations. Final observed and calculated structure factors (×10) are available.[13]

(b) [Co([14]4,7-dieneN$_4$-one)Cl$_2$]ClO$_4$. The Patterson map yielded the positions of the cobalt and the *trans*-dichloro ligands. The resulting Fourier map yielded all of the nonhydrogen positions of the ligand and the perchlorate group. Again there was a suggestion of a ketone oxygen atom bonded to the γ carbon and this was included in the refinement. The contributions from hydrogen atoms were calculated with distances of 0.97 Å and isotropic thermal parameters 10% greater than the atom to which they were bonded.

Full-matrix least-squares refinement of all nonhydrogen atomic coordinates and anisotropic thermal parameters converged to $R_1 = 0.038$, $R_2 = 0.049$, and an error of fit 1.76. The perchlorate anion was found to be somewhat disordered; the top five peaks in the final difference map (0.78–0.40 e/Å^3) were near the ClO_4^- oxygen atoms. The largest peak not associated with the ClO_4^- group was 0.23 e/Å^3. The maximum shift for any nonperchlorate parameter was 0.18 of its estimated standard deviation.

Final atomic parameters are listed in Table III with their estimated standard deviations. Final observed and calculated structure factors (×10) are available.[13]

Table II. Final Positional and Thermal Parameters for $[Co([14]4,7\text{-dieneN}_4\text{-one})(OH_2)_2](ClO_4)_2$[a,b]

Atom	x	y	z	Atom	x	y	z
Co(1)	0.2572 (1)	0.0771 (1)	0.2225 (1)	N(13)	0.1093 (8)	0.0483 (5)	0.2779 (5)
N(2)	0.1460 (8)	0.1725 (5)	0.1565 (6)	C(14)	0.0187 (11)	0.1265 (7)	0.2637 (9)
C(3)	0.1767 (10)	0.2358 (6)	0.1101 (7)	C(15)	0.0070 (11)	0.1642 (7)	0.1659 (9)
C(3m)	0.0837 (13)	0.3095 (8)	0.0614 (9)	O(16)	0.3631 (7)	0.1681 (5)	0.3472 (5)
C(4)	0.3198 (10)	0.2444 (7)	0.1014 (7)	O(17)	0.1469 (8)	−0.0158 (5)	0.0898 (5)
O(4k)	0.3534 (8)	0.3162 (5)	0.0773 (6)	Cl(18)	0.7110 (3)	0.2498 (2)	0.3567 (2)
C(5)	0.4143 (10)	0.1685 (7)	0.1143 (7)	O(19)	0.5820 (10)	0.2813 (9)	0.3133 (10)
C(5m)	0.5271 (12)	0.1787 (9)	0.0697 (9)	O(20)	0.7838 (14)	0.2840 (10)	0.2972 (12)
N(6)	0.3964 (7)	0.0996 (5)	0.1625 (6)	O(21)	0.7707 (14)	0.2894 (10)	0.4435 (9)
C(7)	0.4919 (12)	0.0241 (8)	0.1782 (10)	O(22)	0.7201 (18)	0.1640 (8)	0.3613 (12)
C(8)	0.5032 (12)	−0.0118 (8)	0.2759 (9)	Cl(23)	0.1851 (3)	0.3908 (2)	0.3568 (2)
N(9)	0.3655 (8)	−0.0259 (5)	0.2845 (6)	O(24)	0.0665 (14)	0.3899 (10)	0.2884 (10)
C(10)	0.3673 (12)	−0.0472 (7)	0.3858 (8)	O(25)	0.1883 (20)	0.3207 (11)	0.4159 (10)
C(11)	0.2283 (12)	−0.0661 (8)	0.3943 (8)	O(26)	0.2183 (15)	0.4688 (8)	0.4049 (11)
C(12)	0.1396 (12)	0.0155 (8)	0.3789 (8)	O(27)	0.2825 (15)	0.3701 (10)	0.3138 (14)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B_{iso}, Å^2
Co(1)	3.05 (6)	2.56 (5)	2.91 (6)	−0.11 (5)	0.91 (4)	−0.06 (5)	2.81 (2)
N(2)	3.62 (38)	3.12 (38)	3.51 (38)	0.35 (30)	1.24 (31)	0.28 (33)	3.34 (17)
C(3)	4.88 (53)	2.87 (47)	2.56 (41)	−0.11 (39)	0.20 (39)	−0.08 (37)	3.38 (21)
C(3m)	6.67 (70)	4.46 (60)	5.83 (66)	1.19 (51)	1.87 (55)	1.50 (51)	5.36 (31)
C(4)	4.32 (49)	4.01 (51)	2.37 (40)	−1.08 (43)	0.87 (36)	−0.08 (37)	3.37 (20)
O(4k)	6.79 (46)	3.91 (39)	6.52 (47)	−2.10 (34)	1.94 (38)	0.59 (34)	5.11 (21)
C(5)	3.27 (46)	3.97 (53)	4.20 (50)	−0.69 (40)	1.79 (39)	−0.76 (42)	3.51 (24)
C(5m)	5.24 (63)	6.69 (72)	6.13 (68)	−0.31 (55)	3.32 (54)	−0.11 (56)	5.35 (31)
N(6)	3.10 (36)	3.31 (41)	4.07 (40)	−0.07 (30)	1.16 (31)	−0.37 (33)	3.42 (19)
C(7)	5.38 (65)	5.48 (69)	7.52 (76)	1.82 (53)	3.51 (59)	0.83 (58)	5.29 (33)
C(8)	4.48 (55)	4.41 (59)	6.98 (76)	1.22 (45)	1.97 (53)	0.99 (53)	4.94 (30)
N(9)	4.46 (43)	3.07 (38)	3.67 (39)	0.34 (32)	1.30 (32)	−0.36 (31)	3.62 (20)
C(10)	6.09 (65)	4.57 (57)	3.81 (54)	1.69 (48)	0.94 (47)	1.16 (43)	4.55 (29)
C(11)	5.84 (65)	5.35 (67)	4.29 (55)	−0.50 (53)	1.35 (49)	1.13 (48)	4.99 (30)
C(12)	5.95 (63)	5.19 (62)	3.81 (54)	−0.43 (51)	2.19 (47)	0.67 (46)	4.58 (28)
N(13)	4.58 (40)	3.20 (36)	2.87 (35)	−0.72 (32)	1.44 (31)	0.22 (29)	3.31 (17)
C(14)	3.86 (52)	4.06 (52)	6.49 (67)	0.18 (42)	2.42 (48)	0.93 (47)	4.34 (26)
C(15)	3.65 (51)	4.11 (55)	6.55 (68)	0.41 (41)	1.44 (47)	1.17 (48)	4.52 (28)
O(16)	4.89 (37)	3.95 (35)	4.82 (38)	−0.88 (29)	0.93 (30)	−1.28 (30)	4.43 (17)
O(17)	6.96 (46)	4.75 (40)	4.18 (37)	−0.59 (34)	0.80 (32)	−0.69 (31)	5.22 (20)
Cl(18)	4.40 (14)	4.14 (13)	5.53 (15)	−0.48 (11)	1.21 (12)	0.36 (12)	4.65 (6)
O(19)	5.9 (5)	13.2 (10)	13.1 (9)	2.6 (6)	1.1 (6)	1.8 (8)	10.0 (4)
O(20)	12.7 (9)	15.8 (13)	18.8 (13)	2.8 (9)	10.1 (10)	6.6 (11)	12.6 (5)
O(21)	13.2 (10)	13.3 (11)	9.1 (8)	0.3 (8)	−1.6 (7)	−4.3 (7)	11.3 (4)
O(22)	24.1 (16)	5.2 (6)	17.1 (13)	−3.3 (8)	−0.4 (12)	2.8 (7)	12.4 (5)
Cl(23)	4.33 (14)	4.49 (14)	4.62 (13)	0.68 (10)	1.30 (11)	0.75 (11)	4.41 (6)
O(24)	13.2 (10)	15.5 (12)	11.4 (9)	8.4 (9)	−4.0 (8)	−2.8 (8)	11.4 (5)
O(25)	25.3 (17)	17.0 (13)	7.9 (8)	−9.3 (12)	−0.8 (9)	5.8 (9)	12.8 (5)
O(26)	16.6 (11)	7.9 (7)	14.9 (11)	−2.5 (7)	7.5 (9)	−5.7 (7)	10.6 (4)
O(27)	14.5 (11)	13.7 (11)	25.5 (18)	−4.8 (9)	13.9 (12)	−9.3 (12)	12.6 (5)

[a] Estimated standard deviations in the last significant figure are given in parentheses. [b] Anisotropic thermal parameters are of the form $T = \exp[-{}^1/_4(\Sigma B_{ii}H_i^2a^*{}_i^2 + \ldots + \Sigma B_{ij}H_iH_j\, a^*{}_ia^*{}_j + \ldots)]$ and isotropic thermal parameters are of the form $T = \exp[-B_{iso}(\sin^2\theta)/\lambda^2]$.

Results

A. Reactions of $Co([14]4,7\text{-dieneN}_4)$ Complexes with O_2. In the synthesis of $[Co([14]4,7\text{-dieneN}_4\text{-one})Cl_2]ClO_4$ we have capitalized on the observation that nearly all the macrocyclic ligand–cobalt(II) complexes are rapidly air oxidized in acidic halide solutions.[14] As shown in Figure 1, $Co^{II}([14]4,7\text{-dieneN}_4)$ reacts with oxygen in the absence of halides to form $Co^{II}([14]4,7\text{-dieneN}_4\text{-one})$ as the first identifiable product. That other complexes are formed as intermediates is indicated by the lack of isosbestic points, the enhanced ultraviolet absorptivities of reacting solutions, and the initial formation of an intermediate species with absorption maximum at about 540 nm. After about 4 h the spectroscopic changes indicated that at least 65% of the starting material was converted to $Co^{II}([14]4,7\text{-dieneN}_4\text{-one})$. Precise analysis of the reaction stoichiometry is complicated by the slow oxidation of $Co^{II}([14]4,7\text{-dieneN}_4\text{-one})$ to cobalt(III). In contrast to the reactivity in neutral solution, $Co^{II}([14]\text{dieneN}_4)$ showed no signs of oxidation in 1.5 h in aerated 1 M $HClO_4$.

In order to explore further the reactivity of complexes containing the 2,4-pentanediiminato moiety, we have synthesized cobalt complexes with a methyl group replacing one of the hydrogens on the central carbon atom of this moiety. Applying the previous synthetic procedure to the methylated compound, we see that no oxygen added to the ligand although the oxidation to cobalt(III) went as expected. In $Me_2SO\text{-}d_6$ the NMR spectrum of $Co(6\text{-Me}[14]4,7\text{-dieneN}_4)Cl_2^+$ exhibited a new methyl doublet ($J \approx 16$ Hz) at 1.8 ppm and a poorly resolved quartet at 4.9 ppm. In D_2O the methyl doublet collapsed to a singlet, and the quartet was not observed. We infer that ligand oxidation was inhibited in the new complex.

Finally, some preliminary experiments indicated that $Co^{II}([14]4,7\text{-dieneN}_4\text{-one})$ coordinates oxygen at the cobalt reversibly. In acetonitrile at −23 °C the original blue solution turns yellow within 1 min of O_2 bubbling. If N_2 is subsequently bubbled through the yellow solution, the blue color returns.

B. Spectroscopic Characterization of the New Complexes. Electronic absorption and infrared spectra are summarized in Table IV and shown in Figure 2, respectively. The lower energy of the metal to ligand absorption band in $Co^{II}([14]4,7\text{-dieneN}_4\text{-one})$ than in $Co^{II}([14]4,7\text{-dieneN}_4)$ strongly suggests a lowering of the energy of the ligand π^* system through a conjugation effect. However, the infrared spectra

Table III. Final Positional and Thermal Parameters for $[Co([14]4,7\text{-diene}N_4\text{-one})Cl_2]ClO_4$[a,b]

Atom	x	y	z	Atom	x	y	z
Co(1)	0.042 04 (5)	0.049 13 (5)	0.135 38 (3)	C(11)	0.1434 (5)	−0.1735 (4)	0.1854 (2)
N(2)	0.086 4 (3)	0.138 2 (3)	0.074 0 (2)	C(12)	0.1816 (4)	−0.1423 (4)	0.1263 (2)
C(3)	0.030 5 (4)	0.207 2 (4)	0.049 4 (2)	N(13)	0.1804 (3)	−0.0276 (3)	0.1189 (2)
C(3m)	0.068 8 (5)	0.279 2 (4)	0.003 9 (2)	C(14)	0.2176 (4)	0.0009 (4)	0.0611 (2)
C(4)	−0.091 2 (4)	0.216 7 (4)	0.065 0 (2)	C(15)	0.2015 (4)	0.1146 (4)	0.0553 (2)
O(4k)	−0.155 6 (3)	0.241 6 (3)	0.027 5 (2)	Cl(16)	−0.0579 (1)	−0.0454 (1)	0.0750 (1)
C(5)	−0.136 1 (4)	0.194 5 (4)	0.123 1 (2)	Cl(17)	0.1392 (1)	0.1489 (1)	0.1957 (1)
C(5m)	−0.240 3 (4)	0.251 3 (5)	0.138 6 (3)	Cl(18)	0.0262 (1)	−0.0069 (1)	0.3645 (1)
N(6)	−0.088 4 (3)	0.127 6 (3)	0.153 6 (2)	O(19)	−0.0633 (7)	0.0563 (7)	0.3522 (4)
C(7)	−0.134 7 (4)	0.096 5 (4)	0.209 1 (2)	O(20)	0.0996 (4)	−0.0109 (6)	0.3195 (2)
C(8)	−0.116 9 (4)	−0.018 4 (4)	0.213 6 (2)	O(21)	0.0789 (8)	0.0148 (9)	0.4132 (3)
N(9)	0.000 3 (3)	−0.038 7 (3)	0.200 0 (2)	O(22)	−0.0172 (7)	−0.1040 (5)	0.3725 (4)
C(10)	0.021 7 (4)	−0.151 7 (4)	0.197 3 (2)				

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B_{iso}, Å^2
Co(1)	1.61 (3)	1.72 (3)	1.88 (3)	−0.03 (2)	−0.02 (2)	−0.04 (2)	1.73 (2)
N(2)	1.91 (16)	2.09 (17)	2.16 (18)	0.03 (15)	−0.19 (15)	−0.06 (14)	2.05 (6)
C(3)	2.63 (23)	2.52 (23)	2.08 (21)	−0.42 (19)	−0.21 (18)	−0.21 (18)	2.36 (10)
C(3m)	4.49 (28)	2.49 (25)	3.12 (25)	−0.45 (21)	0.06 (22)	0.67 (20)	3.19 (12)
C(4)	2.89 (23)	2.36 (23)	3.51 (26)	0.66 (19)	−0.73 (22)	0.48 (20)	2.72 (9)
O(4k)	3.86 (19)	7.04 (26)	5.16 (22)	1.34 (20)	−0.91 (18)	1.68 (21)	4.79 (7)
C(5)	1.64 (20)	2.63 (23)	3.83 (27)	0.20 (18)	0.05 (19)	−0.64 (21)	2.50 (10)
C(5m)	2.87 (24)	4.64 (31)	5.86 (35)	1.78 (24)	0.42 (24)	−0.46 (27)	3.86 (12)
N(6)	1.95 (17)	2.28 (18)	2.46 (19)	0.10 (15)	0.17 (15)	−0.33 (15)	2.20 (7)
C(7)	2.73 (24)	3.80 (26)	3.05 (26)	0.34 (20)	1.07 (20)	−0.41 (21)	2.97 (11)
C(8)	2.81 (25)	3.29 (26)	3.45 (28)	−0.37 (20)	0.71 (20)	0.09 (20)	3.10 (14)
N(9)	2.29 (18)	2.26 (18)	2.62 (19)	−0.33 (15)	0.29 (15)	0.23 (15)	2.34 (8)
C(10)	3.82 (27)	2.22 (23)	4.24 (28)	0.15 (21)	0.27 (23)	0.90 (22)	3.20 (11)
C(11)	3.96 (28)	2.52 (25)	4.84 (31)	0.97 (21)	0.15 (24)	1.30 (22)	3.34 (13)
C(12)	3.03 (24)	2.41 (23)	4.77 (29)	0.91 (20)	0.11 (22)	0.19 (22)	3.13 (11)
N(13)	1.87 (16)	1.89 (18)	2.75 (19)	0.17 (14)	−0.07 (14)	−0.06 (14)	2.13 (9)
C(14)	2.46 (24)	2.85 (25)	3.30 (25)	0.37 (19)	0.74 (20)	−0.10 (21)	2.76 (11)
C(15)	1.97 (21)	3.29 (26)	3.04 (24)	−0.31 (19)	0.55 (19)	0.15 (20)	2.64 (11)
Cl(16)	2.82 (6)	2.79 (6)	2.84 (6)	−0.51 (5)	−0.46 (4)	−0.56 (5)	2.71 (3)
Cl(17)	2.83 (6)	3.02 (6)	2.77 (6)	−0.79 (5)	−0.50 (5)	−0.35 (5)	2.74 (2)
Cl(18)	4.59 (8)	4.76 (8)	3.44 (7)	−0.25 (7)	0.22 (6)	0.32 (6)	4.20 (3)
O(19)	12.0 (5)	16.5 (7)	14.7 (6)	9.0 (5)	5.0 (4)	6.9 (5)	11.1 (3)
O(20)	5.4 (3)	16.4 (5)	5.5 (3)	0.3 (3)	1.8 (2)	2.3 (3)	7.4 (1)
O(21)	16.1 (6)	25.3 (10)	7.7 (4)	−0.1 (7)	−3.0 (5)	−6.6 (5)	13.0 (3)
O(22)	14.7 (6)	7.5 (4)	19.2 (7)	−3.9 (4)	5.6 (6)	2.0 (4)	11.3 (2)

[a] Estimated standard deviations in the last significant figure are given in parentheses. [b] Anisotropic thermal parameters are of the form $T = \exp[-{}^1/_4(\Sigma B_{ii}H_i{}^2a^*{}_i{}^2 + \ldots + \Sigma B_{ij}H_iH_ja^*{}_ia^*{}_j + \ldots)]$ and isotropic thermal parameters are of the form $T = \exp[-B_{iso}(\sin^2\theta)/\lambda^2]$.

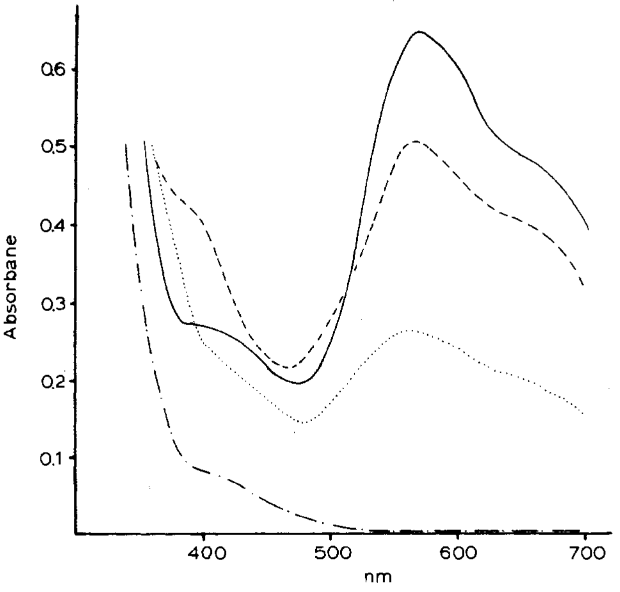


Figure 1. Visible absorption spectra of the species in the reaction of $Co([14]4,7\text{-diene}N_4)^{2+}$ with dioxygen in water, pH 7: – • –, with $[Co([14]4,7\text{-diene}N_4)(OH_2)_2](ClO_4)_2$ purged of O_2; ····, after 1 h in air; ---, after 4 h in air; —, with equivalent concentration of $Co([14]4,7\text{-diene}N_4\text{-one})^{2+}$.

Table IV. Absorption Spectra of Complexes

	λ, nm (ϵ)	
Complex	Ligand field transitions	Charge transfer
$Co([14]4,7\text{-diene}N_4\text{-one})Cl_2{}^{+}$[a]	616 (33), 410 sh (87)	310 sh (2215), 256 (18.7 × 10^3), 227 (17.2 × 10^3)
$Co([14]4,7\text{-diene}N_4\text{-one})(OH_2)_2{}^{3+}$[b]	550 (30), 410 sh (90)	320 sh (798), 260 sh (14 × 10^3)
$Co(6\text{-Me}[14]4,7\text{-diene}N_4)(OH_2)_2{}^{3+}$[b]	605 sh (23), 500 (89)	390 (582), 310 sh (3.13 × 10^3)
$Co([14]4,7\text{-diene}N_4\text{-one})(OH_2)_2{}^{2+}$		670 (529), 570 (760), 490 sh (404), 315 sh (1578), 258 sh (6818)

[a] In 1 M HCl. [b] In 1 M $HClO_4$.

have been singularly uninformative. Infrared spectra of $Co^{II}([14]4,7\text{-diene}N_4)$, $Ni^{II}([14]4,7\text{-diene}N_4)$, and $Cu^{II}([14]4,7\text{-diene}N_4)$ all have an intense absorption band at approximately 1680 cm^{-1} and no other bands which can be attributed to a C═N stretch. Similarly, $[Co([14]4,7\text{-diene}N_4\text{-one})(OH_2)_2](ClO_4)_2$ has a strong and sharp infrared absorption at 1678 cm^{-1} and a weaker, broad peak at 1640 cm^{-1}, the latter undoubtedly the HOH deformation frequency; $[Co([14]4,7\text{-diene}N_4\text{-one})Cl_2]ClO_4$ has a single strong peak in this region, at 1692 cm^{-1}. We infer that the carbonyl and imine stretching frequencies are very nearly degenerate in this family of compounds.

The ^1H NMR spectrum of $Co([14]4,7\text{-diene}N_4\text{-one})(OH_2)_2{}^{3+}$ in D_2O shows the degenerate methyl (C(3m) and

Table V. Bond Distances (Å) and Bond Angles (deg)[a,b]

Atoms	[Co([14]4,7-dieneN$_4$-one)-(OH$_2$)$_2$](ClO$_4$)$_2$	[Co([14]4,7-dieneN$_4$-one)-Cl$_2$]ClO$_4$	Atoms	[Co([14]4,7-dieneN$_4$-one)-(OH$_2$)$_2$](ClO$_4$)$_2$	[Co([14]4,7-dieneN$_4$-one)-Cl$_2$]ClO$_4$
Cobalt Coordination Sphere					
Distances					
Co(1)-N(2)	1.918 (8)	1.925 (4)	Co(1)-N(13)	1.969 (8)	1.979 (4)
Co(1)-N(6)	1.913 (8)	1.920 (4)	Co(1)-X(16)	2.284 (7)	2.230 (1)
Co(1)-N(9)	1.976 (8)	1.967 (4)	Co(1)-X(17)	2.389 (7)	2.250 (1)
Angles					
N(2)-Co(1)-N(6)	93.9 (3)	94.3 (2)	N(13)-Co(1)-X(16)	93.8 (3)	92.9 (1)
N(6)-Co(1)-N(9)	86.5 (3)	85.8 (2)	N(2)-Co(1)-X(17)	87.4 (3)	89.0 (1)
N(9)-Co(1)-N(13)	92.9 (3)	94.2 (2)	N(6)-Co(1)-X(17)	89.5 (3)	88.7 (1)
N(13)-Co(1)-N(2)	86.5 (3)	85.6 (2)	N(9)-Co(1)-X(17)	89.3 (3)	88.8 (1)
N(2)-Co(1)-X(16)	91.9 (3)	90.2 (1)	N(13)-Co(1)-X(17)	86.9 (3)	88.7 (1)
N(6)-Co(1)-X(16)	89.8 (3)	89.7 (1)	X(16)-Co(1)-X(17)	178.9 (3)	178.1 (3)
N(9)-Co(1)-X(16)	91.5 (3)	92.0 (1)			
Macrocycle					
Distances					
N(2)-C(3)	1.26 (1)	1.263 (6)	N(9)-C(10)	1.50 (1)	1.492 (6)
C(3)-C(4)	1.53 (1)	1.515 (7)	C(10)-C(11)	1.51 (2)	1.517 (8)
C(4)-C(5)	1.48 (1)	1.498 (7)	C(11)-C(12)	1.51 (2)	1.508 (7)
C(5)-N(6)	1.29 (1)	1.264 (6)	C(12)-N(13)	1.49 (1)	1.502 (6)
N(6)-C(7)	1.48 (1)	1.475 (6)	N(13)-C(14)	1.48 (1)	1.480 (6)
C(7)-C(8)	1.49 (1)	1.512 (7)	C(14)-C(15)	1.50 (2)	1.497 (7)
C(8)-N(9)	1.48 (1)	1.470 (6)	C(15)-N(2)	1.49 (1)	1.485 (6)
C(3)-C(3m)	1.51 (1)	1.494 (7)	C(5)-C(5m)	1.49 (1)	1.500 (7)
C(4)-O(4k)	1.22 (1)	1.219 (6)			
Angles					
Co(1)-N(2)-C(3)	128.7 (7)	128.5 (3)	C(7)-C(8)-N(9)	108.2 (9)	107.4 (4)
N(2)-C(3)-C(4)	120.4 (9)	117.5 (4)	C(8)-N(9)-Co(1)	106.6 (6)	107.9 (3)
C(3)-C(4)-C(5)	123.1 (9)	123.6 (4)	C(8)-N(9)-C(10)	111.6 (8)	110.6 (4)
C(4)-C(5)-N(6)	119.8 (8)	119.2 (4)	Co(1)-N(9)-C(10)	117.5 (6)	119.5 (3)
C(5)-N(6)-Co(1)	128.9 (7)	127.5 (3)	Co(1)-N(9)-C(10)	117.5 (6)	119.5 (3)
C(5)-N(6)-C(7)	120.5 (8)	121.2 (4)	N(9)-C(10)-C(11)	118.9 (9)	111.0 (4)
Co(1)-N(6)-C(7)	110.6 (6)	111.2 (3)	C(10)-C(11)-C(12)	112.9 (9)	114.3 (4)
N(6)-C(7)-C(8)	107.2 (9)	106.1 (4)	C(11)-C(12)-N(13)	111.4 (9)	112.2 (4)
C(12)-N(13)-Co(1)	120.0 (6)	118.9 (3)	C(14)-C(15)-N(2)	107.2 (8)	107.3 (4)
C(12)-N(13)-C(14)	110.4 (8)	111.1 (4)	C(15)-N(2)-Co(1)	110.7 (6)	111.0 (3)
Co(1)-N(13)-C(14)	107.7 (6)	108.0 (3)	C(15)-N(2)-C(3)	120.6 (8)	120.5 (4)
N(13)-C(14)-C(15)	108.1 (9)	106.9 (4)			
N(2)-C(3)-C(3m)	126 (1)	127.5 (5)	O(4k)-C(4)-C(5)	119.3 (9)	118.9 (5)
C(3m)-C(3)-C(4)	114.0 (9)	114.9 (4)	C(4)-C(5)-C(5m)	115.8 (9)	115.3 (5)
C(3)-C(4)-O(4k)	117 (1)	117.4 (5)	C(5m)-C(5)-N(6)	124 (1)	125.4 (5)
Perchlorate Groups					
Distances					
Cl(18)-O(19)	1.39 (1)	1.385 (7)	Cl(18)-O(21)	1.37 (1)	1.340 (7)
Cl(18)-O(20)	1.39 (1)	1.381 (5)	Cl(18)-O(22)	1.30 (1)	1.378 (7)
Cl(23)-O(24)	1.34 (1)		Cl(23)-O(26)	1.36 (1)	
Cl(23)-O(25)	1.35 (1)		Cl(23)-O(27)	1.36 (1)	
Angles					
O(19)-Cl(18)-O(20)	102.5 (9)	111.1 (4)	O(20)-Cl(18)-O(21)	102.8 (9)	111.2 (5)
O(19)-Cl(18)-O(21)	113.1 (9)	114.9 (6)	O(20)-Cl(18)-O(22)	110.8 (9)	108.2 (5)
O(19)-Cl(18)-O(22)	114.2 (9)	106.2 (6)	O(21)-Cl(18)-O(22)	112.3 (9)	104.8 (6)
O(24)-Cl(23)-O(25)	108.1 (9)		O(25)-Cl(23)-O(26)	113.1 (9)	
O(24)-Cl(23)-O(26)	115.6 (9)		O(25)-Cl(23)-O(27)	102.8 (9)	
O(24)-Cl(23)-O(27)	107.7 (9)		O(26)-Cl(23)-O(27)	108.5 (9)	

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] X represents axial oxygen and chlorine atoms for the Co^{II} and Co^{III} complexes, respectively.

C(5m)) resonance at 3.2 ppm and no resonances detectable further downfield from TMS than 4.5 ppm. This would rule out any vinyl protons in the complex.

C. Description of Structures. Both complexes crystallize in the meso configuration, with the N–H groups pointing to the same side of the N$_4$ plane; the cobalt atoms are six-coordinated with four equatorial nitrogen donor atoms from the macrocycle. The cobalt(II) complex has aquo groups (Co–O = 2.284 (7) and 2.387 (7) Å) in the axial sites and the cobalt(III) complex has chloro groups (Co–Cl = 2.230 (1) and 2.250 (1) Å). The numbering scheme for the cations is shown in Figure 3. The bond distances and angles are listed in Table V. Stereoscopic views of the cations with their thermal ellipsoids are shown in Figures 4 and 5. Both complexes have very similar bond distances and angles. The C—C, C—N, and C=N distances are typical for N$_4$ macrocyclic complexes.[15-17] The degree of torsional strain, as measured by dihedral angles about the ligands, is small (see Figure 6).

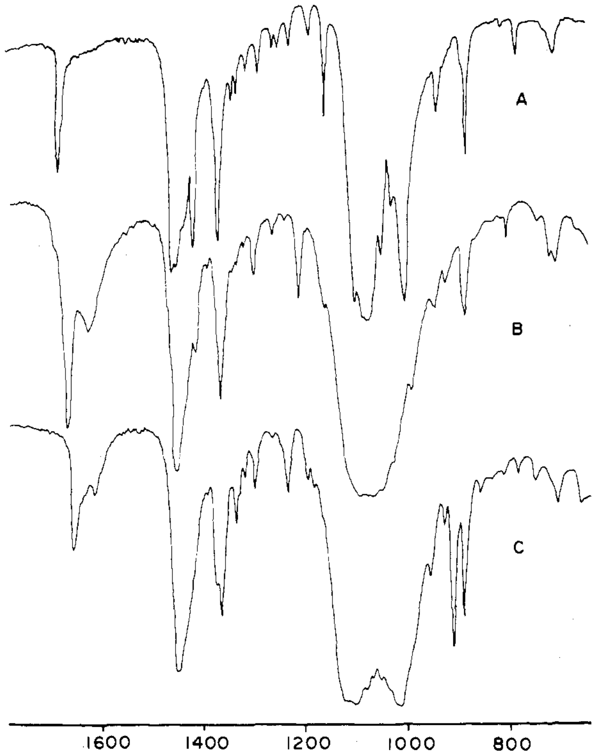


Figure 2. Infrared spectra in Nujol of (A) [Co([14]4,7-dieneN_4-one)Cl_2](ClO_4), (B) [Co([14]4,7-dieneN_4-one)$(OH_2)_2$]$(ClO_4)_2$, and (C) [Co(6-Me[14]4,7-dieneN_4)$(OH_2)_2$]$(ClO_4)_3$.

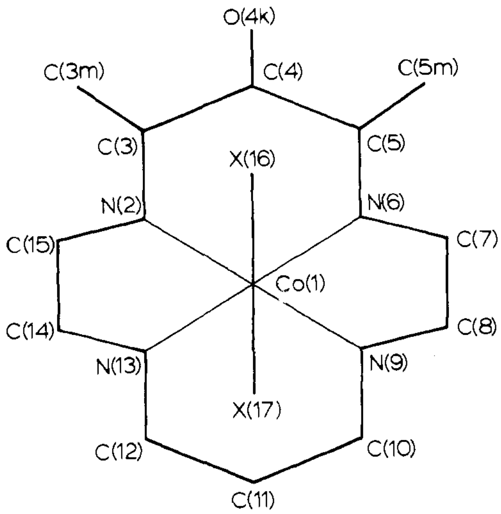


Figure 3. Numbering scheme used to describe both molecular structures.

Table VI

Selected Best Planes[a]

Plane	Atom	Displacement, Å Co([14]4,7-dieneN_4-one)-$(OH_2)_2^{2+}$	Co([14]4,7-dieneN_4-one)-Cl_2^+
1	Co(1)	−0.059	0.040
	N(2)*	−0.002	0.004
	N(6)*	0.002	−0.004
	N(9)*	−0.002	0.004
	N(13)*	0.002	−0.004
	X(16)	−2.342	2.269
	X(17)	2.330	−2.209
2	N(2)	−0.350	0.629
	C(3)*	0.007	0.003
	C(3m)	0.454	−0.693
	C(4)*	−0.023	−0.009
	O(4k)*	0.008	0.003
	C(5)*	0.007	0.003
	C(5m)	0.467	−0.626
	N(6)	−0.363	0.582
3	Co(1)	−0.246	0.270
	N(2)*	0.000	0.013
	C(3)*	0.000	−0.014
	C(3m)	0.178	−0.288
	C(4)	−0.233	0.330
	O(4k)	−0.551	0.923
	C(5)*	0.000	0.014
	C(5m)	0.214	−0.170
	N(6)*	0.000	−0.013

Equations of Planes:[b] $aX + bY + cZ - d = 0$

	Co([14]4,7-dieneN_4-one)-$(OH_2)_2^{2+}$	Co([14]4,7-dieneN_4-one)Cl_2^+
Plane 1	$a = -0.2263$ $b = -0.5927$ $c = -0.7730$ $d = -3.414$	$a = -0.5193$ $b = -0.5778$ $c = -0.6297$ $d = -2.677$
Plane 2	$a = -0.0760$ $b = -0.2395$ $c = -0.9679$ $d = -2.441$	$a = -0.1349$ $b = -0.9595$ $c = -0.2473$ $d = -2.923$
Plane 3	$a = -0.1796$ $b = -0.4845$ $c = -0.8562$ $d = -3.276$	$a = -0.4334$ $b = -0.7117$ $c = -0.5529$ $d = -2.704$

[a] Atoms marked by an asterisk were used to define the plane.
[b] The equations of the plane are in angstroms and are relative to orthogonal axes *a, b, c** for the cobalt(II) structure and *a, b, c* for the cobalt(III) structure.

There are no exceptionally short intermolecular contacts. Hydrogen bonding to the perchlorato anions is probably very weak as suggested by the large thermal ellipsoids in the ClO_4^- groups.

Selected best plane calculations are listed in Table VI. In the cobalt(II) complex the cobalt is 0.06 Å out of the N_4 plane, and in the cobalt(III) complex the cobalt is 0.04 Å out of the N_4 plane. In each complex the bond distances (C–C = 1.51 Å (average), C–O = 1.22 Å (average)), angles (C–C–C = 123.4° (average)), and coplanarity (±0.003 Å) of atoms C(3), C(4), O(4k), and C(5) correspond to sp^2 hybridization of C(4). This is interesting in view of the strain present in [Ni([14]-dienoN_4)]PF_6 reported by Richardson and Sievers[17] (C–C–C is 128 (2)°), where there is formally sp^2 hybridization also, and in [Co([14]4,7-dieneN_4)$(OH_2)PF_6$]PF_6, reported by Roberts et al.[9] (C–C–C is 121.9 (7)°), where there is formally sp^3 hybridization at this position.

While the Co^{II}–O distances differ by ~0.10 Å, the Co^{III}–Cl distances differ by only 0.02 Å. In the case of the Co(II) species the trans oxygen atoms are the same distance from the N_4 plane, ruling out N–H···O repulsion (the N–H···O distance is greater than 3.0 Å). It thus appears that minor perturbations such as packing or very weak nonbonded interactions can affect the distances in the weak Co(II) axial positions, whereas the strong bonding to the axial Co(III) ligands is not perturbed by these effects.

The bonding scheme in the α,β-diimine ring resembles that of a quinone. The uncomplexed duroquinone molecule, $C_{10}O_2H_{12}$, is essentially planar.[18] The α,β-diimine moiety is not planar, with the methyl group being 0.461 Å (average) and 0.660 Å (average), respectively for the Co(II) and Co(III) complexes, out of the plane formed by C(3), C(4), O(4k), and C(5), whereas the nitrogen atoms are out of the plane by 0.357 Å (average) and 0.606 Å (average), respectively, on the other side of this plane.

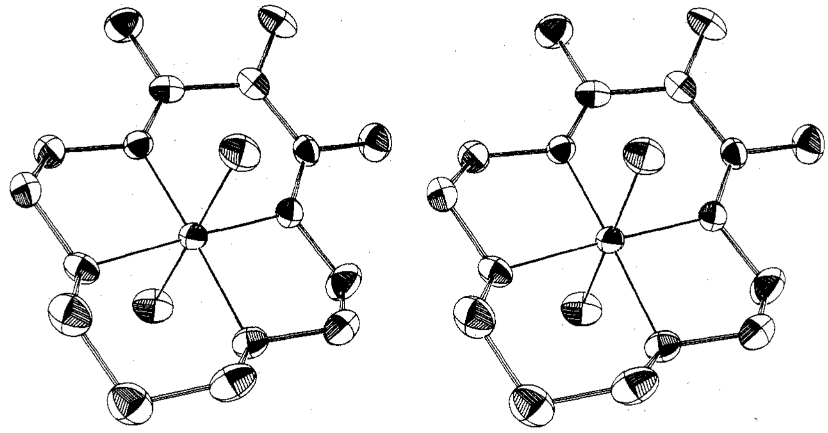


Figure 4. Stereoview of $[Co([14]4,7\text{-dieneN}_4\text{-one})(OH_2)_2](ClO_4)_2$ showing 25% probability envelopes.

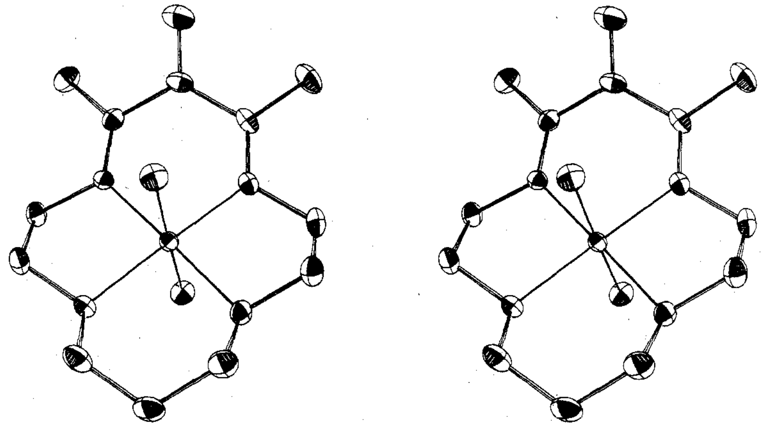


Figure 5. Stereoview of $[Co([14]4,7\text{-dieneN}_4\text{-one})Cl_2]ClO_4$ showing 25% probability envelopes.

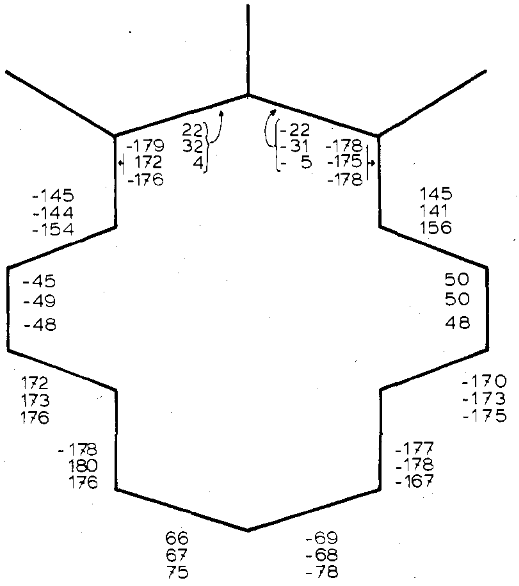
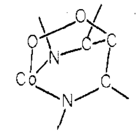


Figure 6. Dihedral angles (in deg). The top value shown for any bond corresponds to the value found in $[Co([14]4,7\text{-dieneN}_4\text{-one})(OH_2)_2](ClO_4)_2$, the middle value is for $[Co([14]4,7\text{-dieneN}_4\text{-one})Cl_2]ClO_4$, and the bottom value corresponds to the value for $[Co([14]4,7\text{-dieneN}_4)OH_2](PF_6)_2$. Estimated standard deviations are approximately 1°.

Evidently, the manifested strain in the C(3)–C(4)–C(5) angles in $Ni([13]dienoN_4)^+$ and $Co([14]4,7\text{-dieneN}_4)(OH_2)_2{}^{2+}$ (both of which are ~10° greater than expected; vide supra) is alleviated in the present ligand by (1) the formation of a >C=O bond at the γ position and (2) torsional perturbation about the C(3)–C(4) and C(4)–C(5) bonds with a subsequent folding about C(3)–C(5) by the six-membered ring into a boat configuration for the cobalt(II) species and a twisted-boat conformation for the cobalt(III) complex. The reduced angle strain in the present compounds (at a slight cost in torsional strain, Figure 6) is likely a major factor in their ease of preparation by oxidation of the *diene* complexes.

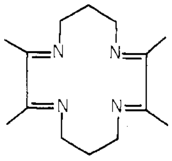
Discussion

While our synthesis of $Co([14]4,7\text{-dieneN}_4\text{-one})Cl_2{}^+$ involves only minor modifications of the Cummings procedure[9] for $Co^{II}([14]4,7\text{ dieneN}_4)$, the synthesis is smooth and efficient and does not involve isolation of any intermediates. In the absence of halide, the reaction of $Co^{II}([14]4,7\text{-dieneN}_4)$ involves initial formation of $Co^{II}([14]4,7\text{-dieneN}_4\text{-one})$. The apparent stability of $Ni^{II}([14]4,7\text{-dienoN}_4)$ and $Cu^{II}([14]\text{-}4,7\text{-dienoN}_4)$ complexes argues for dependence of the oxygenation on cobalt(II). Intermediate formation of a bridging oxo complex (I) such as proposed by Weiss and Goedken[6] would be consistent with our observations, and suggests that both efficient dioxygen adduct formation and the nucleophilicity of the bridging diiminato carbon are crucial to formation of the $[14]4,7\text{-dieneN}_4$-one complexes. That our synthesis of $Co([14]4,7\text{-dieneN}_4\text{-one})Cl_2{}^+$ was not significantly complicated by formation of $Co([14]4,7\text{-dieneN}_4)Cl_2{}^+$ suggests that the facile oxidation pathway in the presence of halide does not involve blocking of reaction pathways involving dioxygen adducts or intermediates such as I.

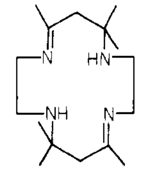


I

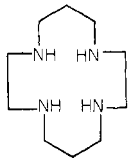
The necessity of a reactive ligand site in the formation of N_4-one complexes is strongly indicated by a variety of information now in hand. The difference in behavior between Co^{II}([14]4,7-dieneN_4) and other cobalt(II) complexes containing macrocyclic ligands is striking. For example, aerated solutions of the cobalt(II) complexes of [14]teteneN_4 and [14]4,11-dieneN_4 are stable for many hours; Co^{II}([14]aneN_4) reacts rapidly with O_2 to form μ-peroxo complexes;[15] and methylation at C(6) of the [14]4,7-dieneN_4 ligand inhibits formation of Co([14]4,7-dieneN_4-one)Cl_2^+ from Co^{II}(6-Me[14]4,7-dieneN_4). The pronounced increase with pH in the rate of formation of Co^{II}([14]4,7-dieneN_4-one) from Co^{II}([14]4,7-dieneN_4), together with the above observations, suggests that oxygenation of the ligand involves nucleophilic attack of C(6) on a coordinated dioxygen. The exploration of more intimate mechanistic questions will require other kinds of information.



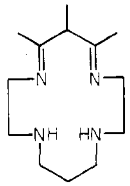
[14]teteneN_4



[14]4,11-dieneN_4



[14]aneN_4



6-Me[14]4,7-dieneN_4

Registry No. [Co([14]4,7-dieneN_4-one)Cl_2]ClO_4, 61025-60-3; [Co([14]4,7-dieneN_4-one)$(OH_2)_2$]$(ClO_4)_3$, 61025-62-5; [Co([14]-4,7-dieneN_4-one)$(OH_2)_2$]$(ClO_4)_2$, 61025-64-7; [Co(6-Me[14]4,7-dieneN_4)Cl_2]ClO_4, 61025-66-9; [Co([14]4,7-dieneN_4)(OH_2)]$(PF_6)_2$, 59982-25-1; Co(6-Me[14]4,7-dieneN_4)$(OH_2)_2^{3+}$, 61025-67-0; $Co(O_2CCH_3)_2$, 71-48-7; *N,N'*-bis(2-aminoethyl)-1,3-propanediamine, 4741-99-5; 2,4-pentanedione, 123-54-6; 3-methyl-2,4-pentanedione, 815-57-6.

Supplementary Material Available: Listings of structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Support of this research by the National Institutes of Health (Grant AM 14341) is gratefully acknowledged.

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(8) Abbreviations: [14]4,7-dieneN_4 = 5,7-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,7-diene; [14]4,7-dieneN_4-one = 5,7-dimethyl-1,4,8,-11-tetraazacyclotetradeca-4,7-diene-6-one; 6-Me[14]4,7-dieneN_4 = 5,6,7-trimethyl-1,4,8,11-tetraazacyclotetradeca-4,7-diene; [14]teteneN_4 = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; [14]4,11-dieneN_4 = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; [14]aneN_4 = 1,4,8,11-tetraazacyclotetradecane; [14]4,7-dienoN_4 is used to designate the anionic form of [14]4,7-dieneN_4 (deprotonated at C(6)).

(9) (a) S. C. Cummings, G. W. Roberts, and J. A. Cunningham, paper presented at the 168th National Meeting of the American Chemical Society, Atlantic City, N.J., Sept 1974; (b) G. W. Roberts, S. C. Cummings, and J. A. Cunningham, *Inorg. Chem.*, **15**, 2503 (1976).

(10) A. W. Johnson, E. Markham, and R. Price, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 785.

(11) (a) Local versions of the following programs were used: (i) SYNCOR, W. Schmonsees' program for data reduction; (ii) FORDAP, A. Zalkin's Fourier program; (iii) ORFLS and ORFFE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function and error program; (iv) ORTEP, C. K. Johnson's program for drawing crystal models; (v) HFINDR, A. Zalkin's hydrogen position calculation program, modified by T.J.A. (b) Scattering factors, including anomalous dispersion corrections for Co and Cl, were taken from "International Tables for X-Ray Crystallography", Vol. IV, J. A. Ibers and W. C. Hamilton, Ed., Kynoch Press, Birmingham, England, 1974.

(12) The function minimized was $\sum w(|F_o| - |F_c|)^2$. $R_1 = \sum|F_o| - |F_c||/\sum|F_o|$, $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|^2)]^{1/2}$, $w = 1/\sigma(F_o)^2$, EOF = $(\sum w||F_o| - |F_c||^2/(m - n))^{1/2}$, m = number of data, n = number of variables.

(13) Supplementary material.

(14) For a recent example see R. Dreos, G. Tauzher, G. Costa, and M. Green, *J. Chem. Soc.*, 2329 (1975).

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