octahedral values (see Table IV): C(2)–Re(1)–As(1) (97.6°), C(13)–Re(2)–As(2) (98.2°), C(3)–Re(1)–As(1) (168.0°), C(14)–Re(2)–As(2) (167.0°), C(5)–Re(1)–As(1) (78.8°), and C(16)–Re(2)–As(2) (79.1°).

The two molecules in the asymmetric unit are chemically identical. The Re(1)–C(5)–O(5) and Re(2)–C(16)–O(10) angles are 125.5 (9) and 124.2 (6)°, respectively. Also the torsional angles [C(3)–Re(1)–C(5)–O(5)] and [C(14)–Re(2)–C(16)–O(10)] are −24.9 (1.0) and −27.5 (9)°, respectively. The only apparent source of these distortions is electrostatic repulsions between the atoms O(5) and O(10) on the bridging carbonyl groups and the atoms O(3) and O(8) on the carbonyl groups trans to the As atoms. The decrease in the angles As(1)–Re(1)–C(5) and As(2)–Re(2)–C(16) from 90° also contributes to an increase in the O(3)–O(5) and O(8)–O(10) separations, but the origin of this distortion is not clear. Idealized geometry at each of the atoms in the rings would lead to nonclosure of the rings. The sp^2 character of the carbon atoms maintains their endocyclic ring angles near 120°. Therefore, the strain is manifested at both the As and Re atoms in each ring. The orientations of the CF_3 groups are then fixed by their repulsive interactions with O(5) and O(10) and between themselves, as shown in Figure 2.

The nature of the deviations of the geometry of the rings from planarity was analyzed with the procedure of Cremer and Pople.[13] The puckering of five-membered rings is defined by a phase angle ϕ, whose value is a measure of the relative contribution of the twist and envelope conformations to the deviations from planarity of the ring atoms and q, the amplitude of puckering for the ring. For reference purposes, the value of q for the furanoid ring of sucrose is 0.353.[14] The procedure utilizes the torsional angles about the ring bonds and may be applied to rings with unequal bond lengths such as in the present case.

The values of q for the rings in molecule 1 and molecule 2 are 0.280 and 0.240, which indicates a substantial degree of puckering. The values of ϕ for the ring in molecule 1 and molecule 2 are 15.9 and 15.0°. A result of 0° would correspond to the envelope conformation, and a result of 18° would correspond to the twist conformation. On the basis of this criterion, the ring conformation is clearly twist.

The structure of the complex is consistent with the spectroscopic results discussed above.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada in the form of operating grants to L.M.M., B.E.R., and R.J.B., by the special program for scholars of Canada and the People's Republic of China, and by the University of Regina in the form of funds for computing.

Registry No. $C_{11}H_6AsF_6O_5Re$, 82113-00-6; $Re_2(CO)_{10}$, 14285-68-8.

Supplementary Material Available: Tables of the observed and calculated structure amplitudes, final thermal parameters, and nonessential bond lengths and bond angles (41 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Structures of (Carbonato)bis(2,2′-bipyridine)cobalt(III) and (Carbonato)bis(1,10-phenanthroline)cobalt(III) Complexes

ERIC C. NIEDERHOFFER,[1] ARTHUR E. MARTELL,* PHIL RUDOLF, and ABRAHAM CLEARFIELD

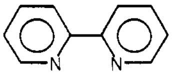
Received January 27, 1982

The crystal and molecular structures of *cis*-(carbonato)bis(2,2′-bipyridine)cobalt(III) nitrate pentahydrate, *cis*-$[Co(C_{10}H_8N_2)_2CO_3]NO_3\cdot5H_2O$ and *cis*-(carbonato)bis(1,10-phenanthroline)cobalt(III) bromide tetrahydrate, *cis*-$[Co(C_{12}H_8N_2)_2CO_3]Br\cdot4H_2O$, have been determined by single-crystal X-ray diffraction methods. The former compound conforms to the monoclinic space group $C2/c$ ($Z = 4$) with cell parameters $a = 10.931$ (4) Å, $b = 16.039$ (2) Å, $c = 14.435$ (2) Å, $\beta = 101.94$ (2)°, and $V = 2476$ (2) Å^3. Full-matrix least-squares refinement on 1306 unique reflections with $I > 3\sigma(I)$ gave $R_F = 0.046$ and $R_{wF} = 0.059$. The other compound also conforms to the space group $C2/c$ ($Z = 8$) with cell parameters $a = 28.251$ (8) Å, $b = 12.500$ (2) Å, $c = 14.299$ (3) Å, $\beta = 91.42$ (2)°, and $V = 5048$ (3) Å^3. Refinement of 1640 unique reflections with $I > 3\sigma(I)$ gave $R_F = 0.049$ and $R_{wF} = 0.058$. Both compounds contain cations that are slightly distorted from ideal octahedral geometry. The structural parameters are considered with respect to similar *cis*-(carbonato)polyaminecobalt(III) complexes. Ligand field and vibrational assignments are presented for these complexes. Analysis of the electronic absorption transitions $^1T_{1g}(O_h) \leftarrow {}^1A_{1g}(O_h)$ and $^1T_{2g}(O_h) \leftarrow {}^1A_{1g}(O_h)$ yields values of $10Dq$ and B.

Introduction

Considerable attention has been directed toward understanding the mechanisms of irreversible autoxidation reactions of cobalt dioxygen complexes. Much of the previous work has been concerned with the role of the ligand, with some structural verification of the resulting products.[2-5]

The presence of 2,2′-bipyridine (bpy, **1**), 1,10-phenanthroline (phen, **2**), or 2,2′,-2″-terpyridine (terpy, **3**) in the coordination sphere simplifies the reaction pathway. Autoxidation of the dibridged $[(\mu\text{-OH})(\mu\text{-}O_2)Co_2(bpy)_4]^{3+}$ and $[(\mu\text{-OH})(\mu\text{-}O_2)Co_2(phen)_4]^{3+}$ or the monobridged $[(\mu\text{-}O_2)Co_2(terpy)_2(L)_2]^{4+}$ (L = bpy or phen) in aqueous solution has been shown to result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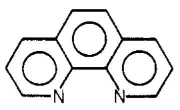
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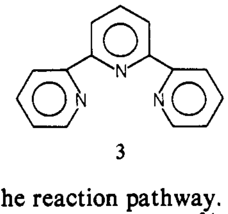
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[1] Abstracted in part from a dissertation to be submitted by Eric C. Niederhoffer to the Faculty of Texas A&M University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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in simple cobalt(III) complexes of the type *cis*-$[Co(L_2)(OH)(H_2O)]^{2+}$.[6-9] These complexes are thought to undergo a subsequent cis–trans isomerization.[6,10] The yellow and red complexes are formed simultaneously in the autoxidation reaction. The proposed reaction scheme,[6,10] Scheme I, raises several questions. Do the electronic absorption parameters reflect such an isomerization? If not, then what are the two products of the autoxidation reaction? We have isolated one of the major products by reaction of the red crystalline material with carbon dioxide. The resulting compounds *cis*-(carbonato)bis(2,2′-bipyridine)cobalt(III) nitrate pentahydrate (**4**) and *cis*-(carbonato)bis(1,10-phenanthroline)cobalt(III) bromide tetrahydrate (**5**) are compared with similar compounds on the basis of structural parameters and electronic and vibrational structure.

Scheme I

$$2CoL_2^{2+} + O_2 \rightleftharpoons \underset{\text{brown}}{[(Co(L)_2)_2O_2(OH)]^{3+}} + H^+$$

$$\underset{\text{brown}}{[(Co(L)_2)_2O_2(OH)]^{3+}} \rightarrow 2\,\underset{\text{yellow}}{cis\text{-}[Co(L)_2(OH)(H_2O)]^{2+}} + H^+ \text{ (+peroxo reaction product)}$$

$$\underset{\text{yellow}}{cis\text{-}[Co(L)_2(OH)(H_2O)]^{2+}} \rightleftharpoons \underset{\text{red}}{trans\text{-}[Co(L)_2(OH)(H_2O)]^{2+}}$$

Experimental Section

Materials. All chemicals were of the highest purity available. Cobaltous bromide and cobaltous nitrate were obtained from Fisher Scientific Co. Cobaltous iodide was obtained from Alfa Products. The 1,10-phenanthroline and 2,2′-bipyridine was supplied by Aldrich Chemical Co. Nitrogen gas was purified by passing the gas through acidic vanadyl solutions and Ascarite. Oxygen gas was scrubbed with Ascarite. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Preparation of the Complexes. Two methods were used to prepare each of the compounds.[11] In the first preparation 1 mmol of the appropriate cobalt(II) salt was dissolved in 50 mL of doubly distilled H_2O under N_2. To this solution was added 2 mmol of either 2,2′-bipyridine or 1,10-phenanthroline, and the solution was stirred until the ligand completely dissolved. The atmosphere in the reaction vessel was changed to O_2, and the reaction mixture was stirred until a dark brown solution formed, characteristic of the dibridged cobalt dioxygen complex ($\lambda_{max} \approx 390$ nm, $\epsilon \approx 1300$ M^{-1} cm^{-1}).[6] When the solution stood in contact with laboratory air, red crystals began to form. The crystalline product was collected, filtered, and rinsed with cold H_2O. The crystals slowly lost solvent. The second method was a modification of the procedure of Springborg and Schaffer[12] for the preparation of the ethylenediamine analogues under a CO_2 atmosphere. A pink solid was obtained, which yielded red crystals upon recrystallization from H_2O. Suitable crystals for diffraction studies were obtained from the first method by slow recrystallization from H_2O. The final workup of crystals for analysis was carried out after a crystal had been mounted for X-ray analysis. In this process the nitrate lost 1 mol of water. Anal. Calcd for $[Co(C_{10}H_8N_2)_2CO_3]NO_3\cdot 5H_2O$: C, 43.24; H, 4.49; N, 12.00. Found:[13] C, 44.58; H, 4.40; N, 12.30. Calcd for $[Co(C_{12}H_8N_2)_2CO_3]Br\cdot 4H_2O$: C, 47.56; H, 3.83; N, 8.87. Found: C, 47.73; H, 3.84; N, 8.90.

Table I. Summary of Crystal Data[a]

	4	5
mol wt	583.40	631.33
color	red-orange	burgundy
cryst syst	monoclinic	monoclinic
space group	*C*2/*c*	*C*2/*c*
a, Å	10.931 (4)	28.251 (8)
b, Å	16.039 (2)	12.500 (2)
c, Å	14.435 (2)	14.299 (3)
β, deg	101.94 (2)	91.42 (2)
V, Å^3	2476 (2)	5048 (3)
ρ_{calcd}, g cm^{-3}	1.565	1.661
ρ_{obsd}, g cm^{-3} [b]	1.551	1.673
Z, molecules/unit cell	4	8
μ, cm^{-1}	7.96	24.43
radiation, Å	0.71069	0.71069
2θ(max), deg	48	50
data collected	2191	4442
data with $I > 3\sigma(I)$	1306	1640
no. of variables	175	343
R_F	0.046	0.049
R_{wF}	0.059	0.058
esd	1.434	1.374

[a] Ambient temperature of 23 °C. [b] Flotation in 1,2-dibromopropane–bromobenzene solutions.

Spectroscopic Determinations. Visible and ultraviolet spectra were recorded with a Cary 14 spectrophotometer equipped with a thermostating unit. Matched 1-cm quartz cells were used to record the spectra of the complexes in aqueous solution. Hydrolysis of the carbonato complexes is slow at 25 °C and pH 7, so that no absorbance correction is necessary. Spectra for the diaquo complexes were recorded for solutions of the carbonato complexes after treatment with an excess of HCl at 100 °C for 2 h. Infrared spectra were determined with a Sargent-Welch Pye Unicam SP3-200 infrared spectrophotometer. Samples were analyzed as KBr pellets. UV/vis (λ_{max}, nm (ϵ, M^{-1} cm^{-1})): **4**, 503 (118), 380 (~250) sh; **5**, 509 (136), 365 (~200) sh. IR (cm^{-1}): **4**, 1628, 1388; **5**, 1634.

Data Collection. The crystal of compound **4** had an irregular geometry based upon a domed cone. The base diameter was 0.042 mm with a side of 0.147 mm and top diameter of 0.126 mm. A crystal with a truncated-prism geometry was obtained for compound **5**. The base was square (0.147 mm) as was the apex (0.105) with a perpendicular distance between the apex and base of 0.084 mm. Data were collected on a CAD-4 automated diffractometer. Unit cell parameters were determined from a least-squares refinement of 25 reflections obtained at medium and high angles. Data collection parameters are listed in Table I. For both structures the space group was determined as *C*2/*c* or *Cc* from systematic absences *hkl* with $h + k = 2n + 1$ and $h0l$ with $l = 2n + 1$. As shown by the subsequent solution,[14] *C*2/*c* was the correct space group.

Graphite-monochromated Mo Kα radiation was used to collect intensity data. The θ–2θ scan technique was used at scan speeds ranging from 20°/min for the most intense reflections to 2°/min for the weakest. The angular scan width was $A = 0.347(\tan \theta_{\lambda_{\alpha1}}), \theta_{\lambda_{\alpha1}}),$ where $\theta_{\lambda_{\alpha2}}$ is determined from

$$\theta_{\lambda_{\alpha2}} = \theta_{\lambda_{\alpha1}} + \frac{\lambda_{\alpha2} - \lambda_{\alpha1}}{\lambda_{\alpha}} \frac{360}{2\pi} \tan \theta_{\lambda_{\alpha1}}$$

and A depends on the crystal mosaic spread and on the divergence of the primary beam. A for **4** was 0.7 and for **5** was 0.6. The scan was extended on each of the peaks by 25% for background determination. Three standard reflections measured every 150 reflections for **4** and every 180 reflections for **5** were used to place the intensity data on a common scale. Reflection intensities were calculated as $I = S(C - RB)$, where S = scan rate, C = total integrated peak count, B = total background count, the R = ratio of the scan time for the peak to the scan time for the background. Standard deviations were assigned as

$$\sigma(I) = [S^2(C + R^2B) + (pI)^2]^{1/2}$$

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(11) Crystals of $[Co(bpy)_2CO_3]I\cdot 5H_2O$ and $[Co(phen)_2CO_3]I\cdot 4H_2O$ were isolated and found to be isomorphous with **4** and **5**, respectively.

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(13) Analysis of **4** was performed after the structure determination was undertaken. The crystals were ground to a powder and kept in a dry environment, which gave the reported values. These values fit nicely to $[Co(C_{10}H_8N_2)_2CO_3]NO_3\cdot 4H_2O$. Anal. Calcd: C, 44.61; H, 4.29; N, 12.39.

(14) A structure solution in *Cc* was obtained, but bond lengths and angles were inconsistent with the required planarity of the ligands.

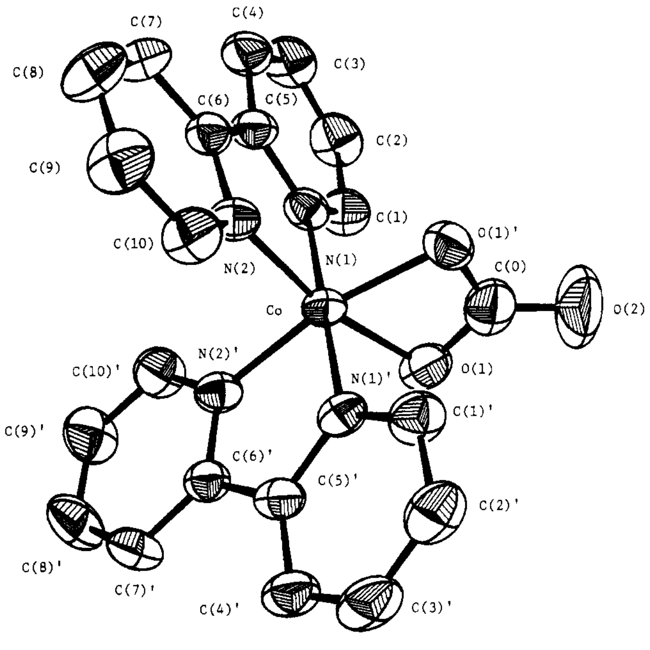

Figure 1. ORTEP[44] drawing of the complex cation $[Co(bpy)_2CO_3]^+$ at the 50% probability level.

The value of p was 0.05. Lorentz and polarization corrections were applied. Neutral-atom scattering factors[15] were used, and the metal atom was corrected for anomalous dispersion (both real and imaginary). No absorption corrections were made because the variation in μR was sufficiently small as to not introduce significant errors.

Structure Solution and Refinement. The positions of the cobalt atom, one oxygen atom, and one nitrogen atom in **4** were determined by Patterson methods. In **5**, Patterson methods yielded the positions of the cobalt and bromine atoms. The remaining non-hydrogen positions were determined after one difference Fourier synthesis. Hydrogen positions were calculated from geometrical considerations after anisotropic refinement of the other positions. A C–H distance of 0.950 Å was used. The hydrogens were then included as fixed contributions in the final stages of refinement. Recalculation of the hydrogen positions followed by refinement was continued until no further improvement in the residual was achieved and the shift to error ratios were less than 0.001. R values were calculated as $R_F = [\sum||F_o| - |F_c||/\sum|F_o|$ and $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o^2|]^{1/2}$. Reflections were weighted as $w = 1/\sigma^2(F_o) = 4F_o^2/[\sigma(F_o^2)]^2$, where $\sigma(F_o^2) = [\sigma^2(I) + (pI^2)^2]^{1/2}/Lp$. The function minimized was $\sum w(|F_o| - |F_c|)^2$. Full-matrix least-squares refinement of **4** resulted in $R_F = 0.046$ and $R_{wF} = 0.059$. The estimated standard deviation of an observation of unit weight was 1.434. Compound **5** refined to $R_F = 0.049$ and $R_{wF} = 0.058$. The esd of an observation of unit weight was 1.374. Final difference maps were featureless.

Results and Discussion

Descriptions of Structures. Positional and thermal parameters for each of the compounds are presented in Tables II and III. Selected bond distances and angles are provided in Tables IV and V. Compound **4** has the cobalt atom, C(0), O(2), O(4), O(5) (H_2O), and N(3) (NO_3) lying on a crystallographic twofold axis. This corresponds to half a molecule per asymmetric unit. Compound **5** possesses a noncrystallographic

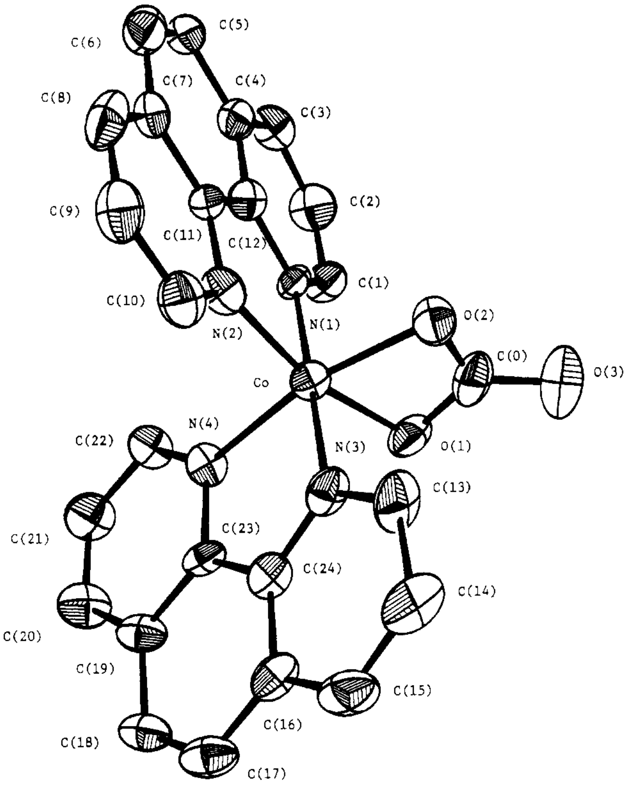

Figure 2. View of the complex cation $[Co(phen)_2CO_3]^+$.

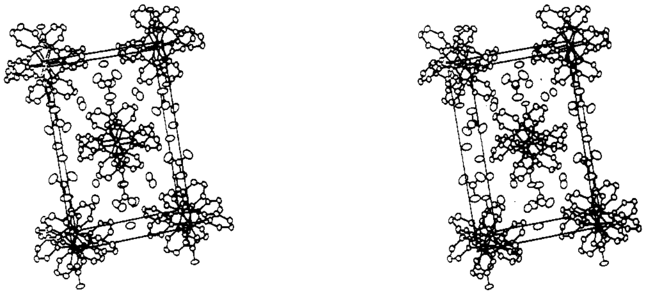

Figure 3. Stereo diagram of one unit cell showing the packing of the complex cations, nitrate anions, and water molecules for compound **4**. The view is down the c axis with the b axis vertical.

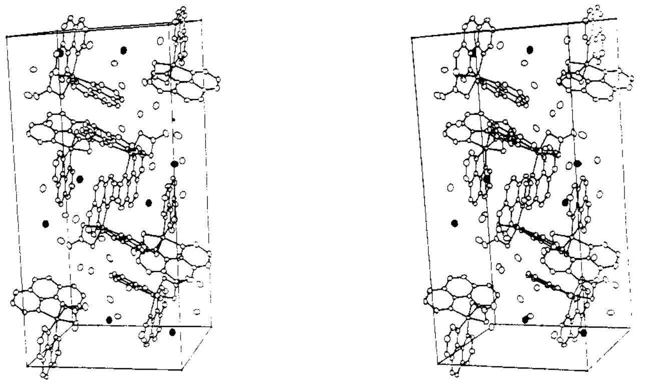

Figure 4. Stereo diagram of one unit cell showing the packing of the complex cations, bromide anions, and water molecules for compound **5**. The view is down the b axis with the a axis vertical. The bromide ions are black while the oxygen atoms (white) are, from upper right corner to center, O(4), O(6), O(7), and O(5).

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(15) All calculations were performed on a PDP11 computer using programs from: "Enraf-Nonius structure determination package" (SDP); Enraf-Nonius: Delft, Holland, 1975 (revised 1981).

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Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for 4[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	0.0000 (0)	−0.00591 (6)	0.2500 (0)	2.79 (3)	2.92 (4)	1.89 (3)	0	0.06 (3)	0
O(1)	−0.0567 (3)	−0.1023 (2)	0.3031 (2)	4.2 (2)	3.7 (2)	3.0 (1)	−0.6 (1)	0.1 (1)	0.6 (1)
O(2)	0.0000 (0)	−0.2257 (3)	0.2500 (0)	10.0 (5)	2.7 (3)	9.7 (4)	0	0.2 (4)	0
O(3)	0.4175 (6)	0.1283 (4)	0.6982 (5)	12.7 (5)	12.5 (4)	11.0 (4)	−4.4 (3)	−2.7 (4)	−1.3 (3)
O(4)	0.5000 (0)	0.2394 (5)	0.7500 (0)	18.9 (8)	6.2 (4)	18.1 (8)	0	6.0 (6)	0
O(5)	0.5000 (0)	0.0446 (5)	0.2500 (0)	14.1 (6)	5.8 (4)	7.2 (4)	0	−1.0 (4)	0
O(6)	0.4523 (5)	0.1620 (3)	0.3764 (4)	9.3 (3)	8.2 (3)	7.6 (3)	1.0 (3)	0.7 (2)	0.4 (3)
O(7)	0.2564 (5)	0.2649 (4)	0.5921 (4)	7.5 (3)	9.8 (3)	10.4 (4)	−0.8 (3)	−0.1 (3)	0.9 (3)
N(1)	−0.1427 (3)	−0.0055 (2)	0.1467 (2)	2.6 (1)	3.2 (2)	2.5 (1)	−0.2 (2)	0.0 (1)	−0.5 (2)
N(2)	0.0622 (3)	0.0766 (2)	0.1741 (2)	2.5 (2)	3.5 (2)	2.3 (1)	−0.2 (2)	0.3 (1)	−0.0 (1)
N(3)	0.5000 (0)	0.1654 (5)	0.7500 (0)	6.8 (4)	5.3 (4)	6.3 (4)	0	1.2 (3)	0
C(0)	0.0000 (0)	−0.1482 (5)	0.2500 (0)	4.4 (4)	3.8 (4)	4.2 (4)	0	−1.0 (3)	0
C(1)	−0.2447 (5)	−0.0518 (3)	0.1405 (3)	3.0 (2)	4.2 (2)	3.4 (2)	−0.3 (2)	0.1 (2)	−0.2 (2)
C(2)	−0.3367 (5)	−0.0541 (4)	0.0588 (4)	3.0 (2)	4.7 (3)	4.4 (2)	−0.6 (2)	−0.4 (2)	−0.8 (2)
C(3)	−0.3214 (5)	−0.0074 (4)	−0.0175 (4)	3.8 (2)	5.2 (3)	3.6 (2)	0.3 (3)	−1.3 (2)	−0.8 (2)
C(4)	−0.2174 (5)	0.0418 (3)	−0.0112 (3)	4.0 (2)	4.2 (2)	2.6 (2)	0.6 (2)	−0.4 (2)	−0.2 (2)
C(5)	−0.1281 (4)	0.0428 (3)	0.0722 (3)	3.1 (2)	3.3 (2)	2.1 (2)	0.5 (2)	0.3 (2)	−0.1 (2)
C(6)	−0.0143 (4)	0.0919 (3)	0.0897 (3)	3.0 (2)	3.0 (2)	2.3 (2)	0.2 (2)	0.3 (2)	−0.1 (2)
C(7)	0.0156 (5)	0.1501 (3)	0.0274 (3)	4.2 (2)	4.6 (3)	2.4 (2)	−0.1 (2)	0.7 (2)	0.9 (2)
C(8)	0.1238 (6)	0.1946 (4)	0.0530 (4)	5.5 (3)	5.2 (3)	4.5 (2)	−0.7 (2)	1.7 (2)	1.9 (2)
C(9)	0.2029 (5)	0.1781 (4)	0.1377 (4)	3.9 (2)	5.0 (3)	5.0 (3)	−1.6 (2)	1.0 (2)	0.6 (2)
C(10)	0.1690 (5)	0.1196 (3)	0.1974 (4)	3.4 (2)	4.4 (2)	3.7 (2)	−0.7 (2)	0.2 (2)	0.2 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-0.25(h^2a^2B_{11} + k^2b^2B_{22} + l^2c^2B_{33} + 2hkabB_{12} + 2hlacB_{13} + 2klbcB_{23})]$, where a, b, and c are reciprocal lattice constants. Estimated standard deviations in the least significant digits are shown in parentheses.

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for 5[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	0.43340 (5)	0.1415 (1)	0.3700 (1)	5.75 (7)	5.94 (7)	4.69 (6)	−0.75 (7)	−0.10 (6)	−0.07 (6)
Co	0.37083 (5)	−0.3179 (1)	0.15630 (9)	2.30 (6)	1.93 (5)	2.26 (5)	−0.04 (6)	−0.01 (5)	−0.09 (6)
O(1)	0.3812 (2)	−0.3306 (5)	0.2865 (4)	3.2 (3)	3.1 (3)	2.5 (3)	0.1 (3)	−0.7 (3)	0.7 (3)
O(2)	0.3155 (2)	−0.3687 (6)	0.2142 (4)	2.7 (3)	3.7 (3)	2.3 (3)	−0.5 (3)	−0.2 (3)	−0.0 (3)
O(3)	0.3210 (3)	−0.3916 (6)	0.3715 (5)	6.8 (5)	4.4 (4)	3.6 (4)	−1.7 (4)	1.2 (4)	0.3 (3)
O(4)	0.4523 (3)	−0.0744 (6)	0.6491 (6)	7.1 (5)	3.5 (4)	5.8 (4)	−0.3 (4)	−1.4 (4)	0.9 (4)
O(5)	0.2715 (3)	−0.3072 (7)	−0.3625 (5)	5.4 (4)	5.7 (5)	4.2 (4)	0.6 (4)	−0.5 (4)	−0.6 (4)
O(6)	0.3930 (3)	−0.0684 (7)	0.4896 (6)	3.3 (4)	6.0 (5)	6.3 (5)	0.1 (4)	0.3 (4)	−0.8 (4)
O(7)	0.3196 (3)	−0.2151 (7)	0.4844 (6)	5.8 (5)	5.7 (5)	6.9 (5)	−0.5 (4)	2.3 (4)	−2.0 (4)
N(1)	0.3496 (3)	−0.1737 (6)	0.1721 (5)	2.2 (3)	1.9 (4)	1.5 (3)	0.3 (3)	−0.1 (3)	0.3 (3)
N(2)	0.3441 (3)	−0.3035 (6)	0.0304 (5)	2.6 (4)	2.4 (4)	2.7 (4)	−0.1 (4)	0.4 (3)	−0.6 (4)
N(3)	0.3942 (3)	−0.4628 (6)	0.1418 (5)	3.8 (4)	1.4 (4)	2.5 (4)	0.1 (4)	0.3 (4)	0.0 (3)
N(4)	0.4355 (3)	−0.2776 (6)	0.1255 (5)	2.0 (4)	1.8 (4)	2.5 (4)	−0.9 (3)	−0.2 (3)	−0.5 (3)
C(0)	0.3380 (4)	−0.3630 (8)	0.2944 (7)	4.6 (6)	2.2 (5)	3.5 (5)	−0.5 (5)	0.5 (5)	0.8 (6)
C(1)	0.3542 (4)	−0.1094 (8)	0.2450 (7)	3.6 (5)	2.1 (5)	2.3 (5)	0.7 (4)	0.0 (4)	−0.3 (4)
C(2)	0.3328 (4)	−0.0092 (9)	0.2456 (7)	4.0 (6)	3.5 (6)	2.9 (5)	0.3 (5)	−0.1 (5)	−0.8 (5)
C(3)	0.3041 (4)	0.0242 (8)	0.1743 (7)	3.0 (5)	2.1 (5)	3.7 (5)	−0.0 (4)	0.6 (5)	−0.4 (4)
C(4)	0.2987 (4)	−0.0415 (8)	0.0954 (7)	2.6 (5)	2.4 (5)	2.9 (5)	0.1 (4)	0.4 (4)	0.6 (4)
C(5)	0.2705 (4)	−0.0149 (9)	0.0132 (7)	2.1 (5)	4.0 (6)	3.5 (5)	0.0 (5)	0.2 (4)	1.6 (5)
C(6)	0.2685 (4)	−0.0831 (9)	−0.0605 (7)	3.0 (5)	4.5 (6)	2.9 (5)	−0.7 (5)	−0.2 (4)	0.7 (5)
C(7)	0.2931 (3)	−0.1823 (8)	−0.0605 (6)	2.3 (4)	2.8 (5)	2.5 (4)	−0.3 (4)	0.6 (4)	0.5 (4)
C(8)	0.2929 (4)	−0.2562 (9)	−0.1337 (7)	4.0 (6)	3.4 (5)	2.5 (5)	−1.3 (5)	−0.3 (5)	0.9 (4)
C(9)	0.3167 (4)	−0.3480 (9)	−0.1258 (7)	4.1 (6)	3.5 (6)	2.4 (5)	−0.6 (5)	0.5 (4)	−0.8 (4)
C(10)	0.3427 (4)	−0.3705 (9)	−0.0411 (7)	3.3 (5)	3.1 (5)	2.9 (5)	−0.2 (5)	0.5 (4)	−0.3 (5)
C(11)	0.3202 (3)	−0.2092 (7)	0.0208 (6)	1.6 (4)	2.1 (5)	1.7 (4)	0.0 (4)	−0.0 (4)	0.2 (4)
C(12)	0.3224 (3)	−0.1394 (8)	0.0974 (7)	2.1 (5)	1.4 (4)	3.0 (5)	−0.6 (4)	−0.0 (4)	0.2 (4)
C(13)	0.3712 (4)	−0.5545 (8)	0.1516 (8)	4.4 (6)	1.8 (4)	4.3 (5)	−1.0 (5)	0.7 (5)	0.4 (5)
C(14)	0.3950 (4)	−0.6534 (8)	0.1526 (8)	5.7 (6)	0.4 (4)	5.6 (6)	−0.5 (5)	−0.3 (6)	0.2 (4)
C(15)	0.4439 (4)	−0.6540 (9)	0.1422 (8)	4.5 (6)	2.6 (5)	4.1 (5)	1.6 (5)	−0.1 (5)	−0.3 (5)
C(16)	0.4687 (4)	−0.5589 (8)	0.1305 (7)	3.3 (5)	1.6 (4)	2.5 (5)	−0.4 (4)	−0.6 (4)	0.1 (4)
C(17)	0.5182 (4)	−0.5508 (8)	0.1187 (7)	3.5 (5)	2.5 (5)	3.4 (5)	1.1 (5)	−0.6 (5)	−0.7 (5)
C(18)	0.5392 (4)	−0.4547 (8)	0.1070 (7)	2.5 (5)	3.0 (5)	3.0 (5)	1.0 (5)	−0.4 (4)	−0.7 (5)
C(19)	0.5130 (3)	−0.3570 (8)	0.1083 (7)	2.3 (5)	2.9 (5)	2.4 (4)	0.5 (4)	−0.8 (4)	−0.9 (4)
C(20)	0.5313 (4)	−0.2534 (8)	0.0965 (8)	2.2 (5)	3.0 (5)	4.5 (6)	−0.8 (4)	−0.8 (4)	−0.5 (5)
C(21)	0.5025 (4)	−0.1680 (8)	0.1005 (8)	3.8 (6)	1.8 (5)	5.3 (6)	−0.2 (5)	0.4 (5)	0.2 (5)
C(22)	0.4539 (3)	−0.1816 (8)	0.1153 (7)	2.5 (5)	1.6 (4)	3.6 (5)	−0.4 (4)	0.2 (4)	−0.5 (5)
C(23)	0.4642 (3)	−0.3661 (7)	0.1220 (6)	3.3 (5)	1.6 (4)	1.3 (4)	1.1 (4)	−0.2 (4)	−0.5 (4)
C(24)	0.4420 (4)	−0.4652 (8)	0.1317 (7)	2.9 (5)	1.7 (5)	2.5 (5)	−0.3 (4)	−0.2 (4)	−0.2 (4)

[a] The form of the anisotropic thermal parameter is $\exp[-0.25(h^2a^2B_{11} + k^2b^2B_{22} + l^2c^2B_{33} + 2hkabB_{12} + 2hlacB_{13} + 2klbcB_{23})]$, where a, b, and c are reciprocal lattice constants. Estimated standard deviations in the least significant digits are shown in parentheses.

twofold axis along Co, C(0), and O(3). Each asymmetric unit contains one complete molecule. Each complex contains planar aromatic ring systems. Views of each complex are presented in Figures 1 and 2. The complete unit cell arrangements are given in Figures 3 and 4.

Structural Comparisons. The central cation coordination in **4** and **5** is distorted from true octahedral geometry. Angles in the coordination sphere differ as much as 21° from ideal 90°. These distortions can be rationalized after considering the restrictions imposed by the ligands. Each bipyridyl and

Table IV. Selected Bond Distances (Å) and Bond Angles (Deg) and Their Estimated Standard Deviations for $[Co(bpy)_2CO_3]NO_3\cdot 5H_2O$ (4)

A. Bond Distances

Co-O(1)	1.887 (3)	O(1)-C(0)	1.308 (5)
Co-N(1)	1.923 (3)	O(2)-C(0)	1.243 (8)
Co-N(2)	1.930 (3)		

B. Bond Angles

O(1)-Co-O(1)′	69.93 (21)	N(1)-Co-N(2)	83.19 (14)
O(1)-Co-N(1)	92.07 (14)	N(1)-Co-N(2)′	96.52 (14)
O(1)-Co-N(1)′	88.27 (13)	N(2)-Co-N(2)′	93.40 (21)
O(1)-Co-N(2)	167.67 (14)	Co-O(1)-C(0)	89.28 (33)
O(1)-Co-N(2)′	98.46 (15)	O(1)-C(0)-O(1)′	111.51 (59)
N(1)-Co-N(1)′	179.58 (22)	O(1)-C(0)-O(2)	124.24 (29)

Table V. Selected Bond Distances (Å) and Bond Angles (Deg) and Their Estimated Standard Deviations for $[Co(phen)_2CO_3]Br\cdot 4H_2O$ (5)

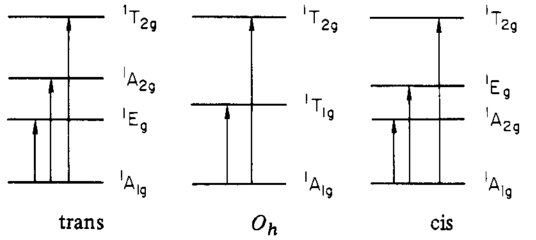
A. Bond Distances

Co-O(1)	1.884 (6)	Co-N(4)	1.956 (7)
Co-O(2)	1.896 (6)	O(1)-C(0)	1.293 (11)
Co-N(1)	1.915 (7)	O(2)-C(0)	1.298 (11)
Co-N(2)	1.943 (7)	O(3)-C(0)	1.266 (11)
Co-N(3)	1.941 (7)		

B. Bond Angles

O(1)-Co-O(2)	69.5 (3)	N(1)-Co-N(3)	178.3 (3)
O(1)-Co-N(1)	90.2 (3)	N(1)-Co-N(4)	94.7 (3)
O(1)-Co-N(2)	166.1 (3)	N(2)-Co-N(3)	96.5 (3)
O(1)-Co-N(3)	89.0 (3)	N(2)-Co-N(4)	96.4 (3)
O(1)-Co-N(4)	96.9 (3)	N(3)-Co-N(4)	83.9 (3)
O(2)-Co-N(1)	90.0 (3)	Co-O(1)-C(0)	89.3 (6)
O(2)-Co-N(2)	97.5 (3)	Co-O(2)-C(0)	88.7 (6)
O(2)-Co-N(3)	91.2 (3)	O(1)-C(0)-O(2)	112.5 (9)
O(2)-Co-N(4)	165.7 (3)	O(1)-C(0)-O(3)	123 (1)
N(1)-Co-N(2)	84.6 (3)	O(2)-C(0)-O(3)	124 (1)

Chart I



phenanthroline has an average N–N bite of 2.56 and 2.60 Å, respectively. This results in the smaller deviations from octahedral geometry. However, with an O–O bite of 2.15 Å the carbonato liqand is greatly strained in its coordination about the cobalt atom. One consequence of this is that within the five-membered chelate ring, the N–Co–N angle is smaller than the N–Co–N angle defined by two ligands. This same effect is seen in similar carbonato complexes as indicated in Table VI. Compounds **6**, **9**, and **10** have N–Co–N angles closer to 90°. This is due to the absence of a five-membered ring. Thus the complex can open up to lessen ligand–ligand interactions. Even the ethylenediamine complex **7** has some freedom, which is due in part to the formation of a staggered chelate ring.

Bond lengths in both cations are completely reasonable. An examination of the complexes in Table VI reveals two groups of Co–N bond distances (based on Co–N2 and Co–N3, which are trans to the carbonato ligand). Long bonds (2.01 Å) are found in compounds **6** and **10**. Shorter distances are reflected by the other components. These distances may be rationalized on the basis of the stability of the complexes.[26] Both ammonia and pyridine form weaker complexes with Co(III) than ethylenediamine. Even though 2,2′-bipyridine and 1,10-phenanthroline are weaker σ donors, the stabilities of their coordination complexes are greater. This is probably due to favorable interactions of the Co(III) t_{2g} orbitals with the ligand π^* orbitals. The Co–O bond distances (1.88–1.92 Å) are all much shorter than those found in $[Co(en)_2(H_2O)_2]^{3+}$ (1.94 Å). There may be some interaction of the cobalt center with the π system of the carbonato ligand as well as a simple electrostatic effect between a trivalent cation with a divalent anion.

Each bidentate ligand in **4** and **5** has an interesting geometry that is due to the distorted coordination. The bipyridine ligand has two rings, which are planar but slightly bent (5.9°) and rotated about C(5)–C(6) (4.8°). However, in **5** the phenanthroline must adhere to greater restriction toward rotation because of the presence of a fused third ring. The three rings are planar with a very small bowing (1–2°). There is no significant rotation about C(11)–C(12) or C(23)–C(24) within experimental error. A recent crystal structure determination of Hennig et al.[23] has shown significant distortion from planarity with the ligands in $[Co(phen)_2CO_3]^+$. Those results are inconsistent with the present investigation. The carbonato ligand has no unusual bonding parameters. The C(0)–C(1) and C(0)–O(2) bond lengths in **4** and C(0)–O(1), C(0)–O(2), and C(0)–O(3) bond lengths in **5** are consistent with bidentate coordination. The two coordinated oxygens have more single bond (sp^3) character than the unbound oxygen. Thus the equal and longer $C–O_{coord}$ bonds and the shorter $C–O_{uncoord}$ bond are not at all surprising.

Spectroscopic Parameters. Compound **4** has infrared bands centered at 1628 and 1388 cm^{-1} indicative of a bidentate carbonato group[31,32] and free nitrate anion.[32] Only one infrared band centered at 1634 cm^{-1} is present in **5**, indicating the bidentate carbonato ligand. Further interpretation of the vibrational spectra is hampered by the numerous ligand bands present. It is interesting to note that Zocchi et al.[21] reported a similar compound in 1971. This compound was reported to contain a bidentate nitrato group as well as a free nitrate anion. The only evidence for the nitrato ligand was the crystal structure determination. Compound **4** is isomorphous with the *cis*-$[Co(bpy)_2NO_3](NO_3)(OH)\cdot 4H_2O$ described in the paper by Zochhi et al.[21] The latter is the only report of a bidentate nitrato group with trivalent cobalt. Without additional information it is difficult to rationalize this discrepancy.[33] The fact that **4** and **11** are isomorphous and isostructural indicates that **4** is probably formulated incorrectly. A summary of spectroscopic data is given in Table VII.

The electronic spectra are consistent with the geometry of the complex. For cobalt(III) the electronic transitions $^1T_{1g}(O_h) \leftarrow {}^1A_{1g}(O_h)$ and $^1T_{2g}(O_h) \leftarrow {}^1A_{1g}(O_h)$ are expected. Although

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(26) The Co–N average bond distance is based on Co–N2 and Co–N3, which are trans to the carbonato ligand.

(27) Josephsen, J.; Schaffer, C. E. *Acta Chem. Scand., Ser. A*, **1977**, *A31*, 813.

(28) Kanazawa, Y.; Matsumoto, T. *Acta Crystallogr., Sect. B* **1975**, *B32*, 282.

(29) The cell constants reported in ref 22 were used as input for a DeLaunay reduction. The fully reduced cell suggested a higher symmetry is possible.

(30) The structure determination of ref 21 has such high bond distance and angle esd's to warrant more accurate parameters.

(31) Nakamoto, K. "Infrared Spectra of Inorganic and Coordination Compounds"; Wiley-Interscience: New York, 1970.

(32) Palade, D. M.; Ll'ina, E. S.; Chudaeva, G. V. *Zh. Neorg. Khim.* **1972**, *17*, 2480.

(33) Ion-exchange column chromatography characterization of **4** and **5** vs. standard Co(III) cations supports the univalent complex cation. A nitrato ligand would necessitate a divalent complex cation. Zocchi et al. prepared the alleged nitrato complex by dissolving $Co(NO_3)_2\cdot 6H_2O$ and 2,2′-bipyridine in H_2O. This was left in contact with laboratory air. We envision oxygenation of the cobaltous complex followed by autoxidation in the presence of CO_2 leading to the carbonato complex, not the nitrato species.

Table VI. Comparison of Bond Distances and Bond Angles for a Series of $[CoN_4CO_3]^+$ Complexes[a]

Bond Lengths, A

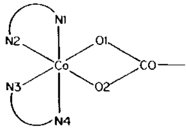
no.	compd	Co–N1	Co–N2	Co–N3	Co–N4	Co–O1	Co–O2	C0–O1	C0–O2	C0–O3
6	*cis*-$[Co(NH_3)_4CO_3]Br$[16]	1.953 (14)	2.031 (22)	2.031 (22)	1.931 (18)	1.905 (11)	1.905 (11)	1.336 (18)	1.336 (18)	1.237 (20)
7	*cis*-$[Co(en)_2CO_3]Cl$[17]	1.922 (8)	1.944 (8)	1.976 (7)	1.985 (8)	1.895 (7)	1.934 (7)	1.34 (1)	1.31 (1)	1.22 (1)
8	*cis*-$[Co(en)_2CO_3]I\cdot 2H_2O$[18]	1.940 (3)	1.943 (3)	1.943 (3)	1.940 (3)	1.907 (2)	1.907 (2)	1.306 (3)	1.306 (3)	1.234 (6)
9	*cis*-$[Co(tn)_2CO_3]ClO_4$[19]	1.97 (2)	1.97 (2)	1.94 (2)	1.95 (2)	1.94 (1)	1.89 (1)	1.32 (2)	1.32 (2)	1.22 (2)
10	*cis*-$[Co(pyr)_4CO_3]ClO_4$[20]	1.974 (6)	1.996 (5)	2.004 (4)	1.985 (7)	1.895 (3)	1.892 (3)	1.330 (6)	1.319 (5)	1.210 (3)
4	*cis*-$[Co(bpy)_2CO_3]NO_3\cdot 5H_2O$[b]	1.923 (3)	1.930 (3)	1.930 (3)	1.923 (3)	1.887 (3)	1.887 (3)	1.308 (5)	1.308 (5)	1.243 (8)
11	*cis*-$[Co(bpy)_2NO_3]NO_3\cdot OH\cdot 4H_2O$[21]	1.922 (2)	1.936 (2)	1.936 (2)	1.922 (2)	1.888 (2)	1.888 (2)	1.312 (4)	1.312 (4)	1.237 (6)
12	*cis*-$[Co(bpy)_2CO_3]I\cdot 5H_2O$[b]				isomorphous with our *cis*-$[Co(phen)_2CO_3]Br\cdot 4H_2O$					
13	*cis*-$[Co(phen)_2CO_3]Cl\cdot 3H_2O$[22]	1.945 (14)	1.932 (14)	1.934 (14)	1.928 (12)	1.883 (12)	1.882 (11)	1.331 (22)	1.284 (23)	1.198 (21)
5	*cis*-$[Co(phen)_2CO_3]Br\cdot 4H_2O$[b]	1.915 (7)	1.943 (7)	1.956 (7)	1.941 (7)	1.896 (6)	1.884 (6)	1.298 (11)	1.293 (11)	1.266 (11)
14	*cis*-$[Co(phen)_2CO_3]Br\cdot 4H_2O$[23]	1.940 (6)	1.949 (6)	1.963 (6)	1.940 (6)	1.889 (4)	1.895 (4)	1.332 (8)	1.315 (8)	1.213 (8)
15	*cis*-$[Co(phen)_2CO_3]I\cdot 4H_2O$[b]				isomorphous with our *cis*-$[Co(phen)_2CO_3]Br\cdot 4H_2O$					
16	*cis*-$[Co(3,8\text{-dmtrien})CO_3]ClO_4$[24]	1.957 (5)	1.946 (5)	1.935 (5)	1.958 (5)	1.929 (4)	1.901 (4)	1.314 (8)	1.296 (8)	1.236 (8)
17	*cis*-$[Co(tacd)CO_3]ClO_4\cdot H_2O$[25]	1.920 (22)	1.927 (12)	1.925 (11)	2.016 (22)	1.925 (11)	1.909 (9)	1.308 (16)	1.324 (15)	1.219 (16)

Bond Angles, Deg

compd no.	N1–Co–N2	N1–Co–N3	N1–Co–N4	N1–Co–O1	N1–Co–O2	N2–Co–N3	N2–Co–N4	N2–Co–O1	N2–Co–O2	N3–Co–N4
6	92.8 (8)	92.8 (8)	NA	88.9 (5)	88.9 (5)	94.3 (9)	89.3 (8)	97.7 (7)	NA	89.3 (8)
7	87.7 (4)	92.5 (4)	177.1 (4)	92.7 (4)	92.1 (4)	94.7 (4)	92.1 (4)	98.6 (4)	167.7 (4)	84.5 (4)
8	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
9	91.9 (7)	93.5 (7)	NA	85.9 (6)	86.4 (6)	94.8 (7)	91.4 (7)	97.7 (6)	NA	89.7 (7)
10	91.38 (14)	93.19 (12)	NA	87.16 (12)	86.84 (13)	100.91 (12)	90.45 (13)	94.85 (12)	NA	88.06 (13)
4	83.19 (14)	96.52 (14)	179.58 (22)	88.27 (13)	92.07 (14)	93.40 (21)	96.52 (14)	98.46 (15)	167.67 (14)	83.19 (14)
11	83.27 (9)	96.35 (9)	NA	88.31 (9)	92.13 (9)	93.53 (10)	96.35 (9)	NA	NA	83.27 (9)
12				isomorphous with our *cis*-$[Co(bpy)_2CO_3]NO_3\cdot 5H_2O$						
13	84.3 (6)	NA	175.5 (6)	NA	NA	NA	NA	NA	164.1 (6)	84.0 (6)
5	84.6 (3)	94.7 (3)	178.3 (3)	90.0 (3)	90.2 (3)	96.4 (3)	96.5 (3)	97.5 (3)	166.1 (3)	83.9 (3)
14	84.2 (2)	NA	177.7 (2)	NA	NA	96.1 (2)	NA	NA	164.8 (2)	83.8 (2)
15				isomorphous with our *cis*-$[Co(bpy)_2CO_3]NO_3\cdot 5H_2O$						
16	85.7 (2)	86.7 (2)	NA	NA	NA	98.0 (2)	NA	97.3 (2)	NA	85.9 (2)
17	86.6 (9)	86.8 (10)	NA	90.2 (9)	94.2 (8)	103.0 (5)	85.2 (8)	94.5 (5)	NA	86.01 (1)

compd no.	N3–Co–O1	N3–Co–O2	N4–Co–O1	N4–Co–O2	O1–Co–O2	O1–C0–O2	O1–C0–O3	O2–C0–O3	Co–O1–C0	Co–O2–C0
6	NA	97.7 (7)	89.5 (6)	89.5 (6)	70.5 (5)	110.4 (1.3)	124.8 (1.4)	124.8 (1.4)	89.5 (8)	89.5 (8)
7	165.9 (4)	97.6 (4)	90.2 (4)	88.7 (4)	69.1 (4)	110 (1)	124 (1)	125 (1)	91 (1)	90 (1)
8	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
9	NA	98.7 (6)	90.2 (6)	89.6 (6)	68.8 (5)	110.4 (1.7)	NA	NA	NA	NA
10	NA	94.97 (12)	91.07 (12)	90.96 (12)	69.28 (12)	108.7 (3)	125.5 (4)	125.8 (4)	90.7 (2)	91.2 (2)
4	167.67 (14)	98.46 (15)	92.07 (14)	88.27 (13)	69.93 (21)	111.51 (59)	124.24 (29)	124.24 (29)	89.28 (33)	89.28 (33)
11	NA	NA	92.13 (9)	88.31 (9)	69.92 (11)	111.2 (4)	124.4 (2)	124.4 (2)	NA	NA
12					isomorphous with our *cis*-$[Co(bpy)_2CO_3]NO_3\cdot 5H_2O$					
13	165.1 (6)	NA	NA	NA	68.4 (5)	108.1 (1.1)	122.2 (1.2)	129.7 (1.2)	NA	NA
5	165.7 (3)	96.9 (3)	91.2 (3)	89.0 (3)	69.5 (5)	112.5 (9)	124 (1)	123 (1)	88.7 (6)	89.3 (6)
14	NA	NA	NA	NA	69.8 (2)	108.7 (6)	125.0 (7)	126.3 (7)	NA	NA
15					isomorphous with our *cis*-$[Co(bpy)_2CO_3]NO_3\cdot 5H_2O$					
16	NA	96.1 (2)	NA	NA	68.6 (2)	111.6 (5)	123.1 (6)	125.3 (6)	89.0 (4)	90.8 (4)
17	NA	94.1 (4)	99.5 (9)	96.3 (8)	68.4 (4)	110.0 (1.1)	125.7 (1.2)	123.3 (1.2)	90.4 (8)	90.6 (7)

[a] Abbreviations: en = ethylenediamine; tn = trimethylenediamine; 3,8-dmtrien = 3,8-dimethyltriethylenetetramine; tacd = 1,4,7,10-tetraazacyclododecane; NA = not applicable. All element numbering is in reference to the following structure:



[b] This work.

Table VII. Spectroscopic Data

compd	λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$)
cis-$[Co(en)_2CO_3]Cl$[a]	511.5 (132.7), 359.5 (121.1)
cis-$[Co(en)_2Cl_2]Cl$[a]	534.5 (98.9), 388 (91.4) sh
cis-$[Co(en)_2(H_2O)Cl]SO_4\cdot 2H_2O$[a]	516 (87.9), 375 (72)
cis-$[Co(en)_2(H_2O)_2]Br_3\cdot H_2O$[a]	492 (76.3), 358 (60.8)
cis-$[Co(en)_2(OH)_2]\cdot {}^1/_2S_2O_6$[a]	517 (94.4), 371 (102.3)
trans-$[Co(en)_2Cl_2]Cl$[a]	618 (37.2), 455 (28.2) sh, 400 (378) sh
cis-$[Co(phen)_2CO_3]Br\cdot 4H_2O$[b]	509 (136), 365 (~200) sh
cis-$[Co(bpy)_2CO_3]NO_3\cdot 5H_2O$[b]	503 (118), 380 (~250) sh
cis-$[Co(phen)_2Cl_2]Cl$[c]	607 (49), 536 (55), 392 (510) sh
cis-$[Co(bpy)_2Cl_2]Cl$[d]	585 (54), 526 (63), 376 (630) sh
cis-$[Co(phen)_2(H_2O)_2]^{3+}$[b]	500 (~50), 370 (~300)
cis-$[Co(bpy)_2(H_2O)_2](NO_3)_3\cdot H_2O$[e]	489 (44), 356 (350)
cis-$[Co(bpy)_2(OH)(H_2O)](NO_3)_2$[e]	498 (58), 361 (320)
cis-$[Co(bpy)_2(OH)_2]NO_3$	502 (54), 361 (490)

[a] Reference 12. [b] This work. [c] Reference 42. [d] Reference 36. [e] Reference 37.

Table VIII. Values of 10*Dq* and *B* (cm^{-1})[a]

cation	10*Dq*	*B*
cis-$[Co(en)_2CO_3]^+$	20 470	562.6
cis-$[Co(en)_2Cl_2]^+$	19 620	471.6
cis-$[Co(en)_2(H_2O)Cl]^{2+}$	20 320	486.1
cis-$[Co(en)_2(H_2O)_2]^{3+}$	21 320	507.1
cis-$[Co(en)_2(OH)_2]^+$	20 280	511.4
cis-$[Co(phen)_2CO_3]^+$	20 600	521.0
cis-$[Co(bpy)_2CO_3]^+$	20 830	420.5
cis-$[Co(phen)_2(H_2O)_2]^{3+}$	20 970	464.2
cis-$[Co(bpy)_2(H_2O)_2]^{3+}$	21 450	509.2
cis-$[Co(bpy)_2(OH)(H_2O)]^{2+}$	21 060	509.1
cis-$[Co(bpy)_2(OH)_2]^+$	20 890	522.2
cis-$[Co(phen)_2Cl_2]^+$	18 270[b]	600.6
cis-$[Co(bpy)_2Cl_2]^+$	18 750[b]	554.5

[a] Calculated from Table VII. [b] ${}^1T_{1g}$ state is split by lower symmetry. The result is an average of two peaks.

the actual ligand field is of lower symmetry, this has only a small effect upon the model. A bidentate ligand lowers the effective local symmetry sufficiently to lift the threefold degeneracy of the ${}^1T_{1g}$ state. Thus the ${}^1T_{1g}$ state splits into a ${}^1E_g$ and ${}^1A_{2g}$ state (octahedral labels are retained for simplicity). The magnitude[34] of the splitting is twice as large for a trans configuration than a cis configuration, but the electronic states are inverted as indicated in Chart I. This splitting would be pronounced only for ligands with greatly different ligand field strengths. In the situation where the ligand field difference is small, the splitting results in a broadening of the low-energy electronic band.

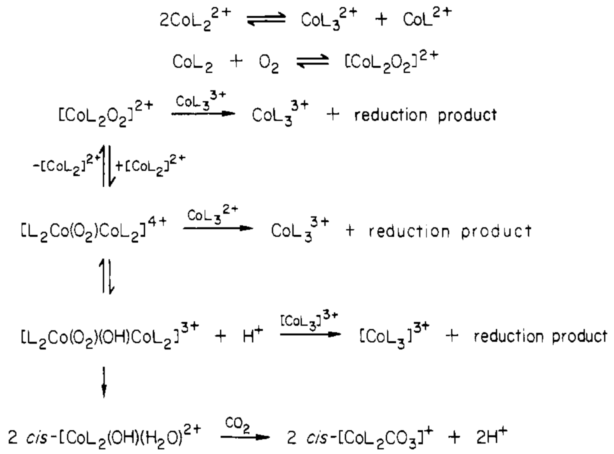
Each state energy[34,35] can be written in terms of the Racah parameters:

$$
\begin{aligned}
{}^1A_{1g}&: \quad -24Dq + 5B + 8C - 120B^2/10Dq \\
{}^1T_{1g}&: \quad -14Dq + 5B + 7C - 34B^2/10Dq \\
{}^1T_{2g}&: \quad -14Dq + 21B + 7C - 118B^2/10Dq
\end{aligned}
$$

With use of the spectral parameters from Table VII and $C = 4B$ for strong-field complexes, solutions of the equations for 10*Dq* and *B* were obtained and are listed in Table VIII.

The results reported for 10*Dq* are consistent with the spectrochemical series and a previous calculation on polypyridyl systems.[38] In general bpy > phen > en > H_2O > OH^- > CO_3^{2-} > Cl^- in ligand field strength. The variation of Racah parameter *B* is more than would be expected and is probably a result of the simplicity of the model.

Scheme II



A previous study in this laboratory[6] interpreted some spectral features of bis(bipyridine)- and bis(phenanthroline)cobalt(III) complexes in aqueous solution as a cis–trans isomerization.[27]

$$
\underset{\text{yellow}}{cis\text{-}[Co(phen)_2(OH)(H_2O)]^{2+}} \rightleftharpoons \underset{\text{red}}{trans\text{-}[Co(phen)_2(OH)(H_2O)]^{2+}}
$$

McKenzie[39–41] and Palade[42] have pointed out steric arguments against the trans configuration The present results are consistent with the cis geometry. Comparison of spectral data does not rationalize the yellow product. This complex cannot be the simple bis(polypyridyl)cobalt(III) cation. The electronic absorption band at 470 nm suggests that a stronger ligand field is present.[43]

Since the electronic spectra do not drastically change upon substitution of a bidentate carbonato ligand for coordinated hydroxy or aquo ligands, we suggest that the autoxidation pathway proceeds with retention of the cis geometry. The initial formation of the cobalt bis(phenanthroline) or cobalt bis(bipyridyl) dioxygen complex is followed by olation to the μ-hydroxy–μ-peroxo species. This second bridge serves to "lock in" the dioxygen moiety. Decomposition of this species can lead to either the initial reactants or to the trivalent cobalt product which can be effectively trapped with carbon dioxide as the carbonato complex. A modified scheme is indicated (Scheme II). The isolation of a tris(pryidyl-type)cobalt(III) product may indicate either a complicated ligand-exchange process or a simple oxidation of the initial equilibrium-controlled cobalt(II) species. The latter could arise from direct oxidation by the intermediate monobridged or dibridged dioxygen complex. At this time it is uncertain which is occurring. Further work is in progress to determine the fate to the coordinated dioxygen and establish a comprehensive product distribution.

---

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(43) Preliminary results on this yellow intermediate suggests the presence of $[Co(phen)_3]^{3+}$ or $[Co(bpy)_3]^{3+}$. A crystal structure of the former is in the final stages of refinement (R_w = 7.2%). This is disturbing since it suggests a more complex autoxidation pathway.

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Inorg. Chem. **1982**, *21*, 3741-3749 **3741**

Acknowledgment. This work was supported by The Robert A. Welch Foundation Grant No. A-259 (A.E.M. and E.C.N.) and National Science Foundation Grant No. CHE79-16160 (A.C. and P.R.).

Registry No. *cis*-[Co($C_{10}H_8N$)$_2$$CO_3$]$NO_3$·$5H_2O$, 82583-18-4; *cis*-[Co($C_{12}H_8N_2$)$_2$$CO_3$]Br·$4H_2O$, 74325-78-3.

Supplementary Material Available: Calculated and observed structure factors for complex **4** (Table A) and complex **5** (Table B), hydrogen atom positional and thermal parameters (Table C), complete bond distances and bond angles for **4** (Table D) and **5** (Table E), least-squares planes for **4** (Table F) and **5** (Table G), and representative infrared spectra for **4** and **5** (Figure A) (21 pages). Ordering information is given on any current masthead page.

Contribution from the Istituto di Chimica Generale ed Inorganica, Università di Padova, 35100 Padova, Italy,
Istituto di Chimica Generale ed Inorganica, Università di Parma, 43100 Parma, Italy,
Institut de Chimie, Université Louis Pasteur, Strasbourg, France, and Institut für Anorganische Chemie,
Universität Regensburg, D-8400 Regensburg 1, West Germany

Molecular Structure and Experimental Electron Density of (μ-Methylene)bis[dicarbonyl(η^5-cyclopentadienyl)manganese] at 130 K[1]

DORE A. CLEMENTE,*[2,3] M. CINGI BIAGINI,[4] BERNARD REES,[2] and WOLFGANG A. HERRMANN[5]

Received November 30, 1981

The molecular structure and the experimental electron-density distribution of (μ-CH_2)[CpMn(CO)$_2$]$_2$ at 130 K have been determined from single-crystal X-ray diffraction data up to $(\sin\theta)/\lambda = 1.06$ Å^{-1} with use of the X–X technique. The electron deformation density maps revealed no significant charge density accumulation on the Mn–Mn bond, in contrast with the other bonds: 0.55 e Å^{-3} in the C–C bonds of the cyclopentadienyl group, 0.90 e Å^{-3} in C–O. Peaks are also observed in the carbon lone-pair region of the CO groups (0.70 e Å^{-3}) and in the metal region: the latter are essentially concentrated along the axis joining Mn to the centroid of the cyclopentadienyl ring and in a plane almost parallel to the cyclopentadienyl ring, at a distance of about 0.60 Å from the metal nucleus. A charge accumulation corresponding to a σ lone pair of methylene is visible. Atomic charges were determined both by least-squares refinement and by direct integration. Both methods indicate small charges. The carbonyl oxygen atoms are predicted to be negative and so are the carbon atoms of the cyclopentadienyl rings. Mn atoms seem also slightly negative; however, the diffuseness of the 4s shell makes this charge difficult to determine. While all theoretical calculations predict a large negative charge on the methylene carbon, the experimental charge is not significantly different from zero.

Introduction

A number of structural and chemical investigations have been carried out recently on μ-methylene complexes.[6] The theory of bonding in such complexes[7] shows that bridging methylene can act as a σ donor to the metal through a filled a_1 orbital and as a π-electron acceptor using a high-lying p_π empty orbital of symmetry b_1. In this respect bridging methylene thus shows some analogy with bridging carbonyl. On the other hand theoretical studies[8] have shown that the methylene carbon is negatively charged. No experimental determination of the charge density distribution in this class of compounds has been done as yet, and it seemed therefore interesting to submit the title compound to a so-called X–X analysis.

Also of interest is the metal–metal bond, formally of multiplicity 1. The title compound is analogous with $Mn_2(CO)_{10}$ but with a Mn–Mn separation about 0.1 Å shorter. In $Mn_2(CO)_{10}$, as in most metal–metal-bonded complexes studied so far, no significant charge density accumulation had been observed in the middle of the bond.[9]

The purpose of the present study is to determine accurately the molecular structure, the electron-density distribution, and the atomic charges in order to gain a better understanding of the bonding in this class of μ-methylene compounds. A preliminary account of part of this work has been given elsewhere.[10]

Table I. Crystal Data and Data Collection

Crystal Data

trans-(μ-CH_2)[(η^5-C_5H_5)Mn(CO)$_2$]$_2$
cryst: space group $Pccn$ (D_{2h}^{10}, No. 56); $Z = 4$
unit cell at room temperature:[a] $a = 7.275$ (6), $b = 15.367$ (8), $c = 12.835$ (8) Å; $V = 1434.9$ Å^3
unit cell at 130 K:[a] $a = 7.161$ (4), $b = 15.177$ (6), $c = 12.703$ (6) Å; $V = 1380.6$ Å^3
cryst I: spherical; diameter 0.28 ± 0.02 mm
cryst II: spherical; diameter 0.33 ± 0.02 mm
abs: linear abs coeff $\mu = 19.24$ cm^{-1} ($\mu R_1 = 0.27$, $\mu R_2 = 0.32$)
transmission factor: cryst I, 0.671–0.681; cryst II, 0.626–0.638
weighted path length $\bar{T}$: cryst I, 0.019–0.020 cm; cryst II, 0.022–0.024 cm

Diffraction Measurements

scanning mode: continuous $\omega/2\theta$
scanning interval in θ: cryst I, $1.6 + 0.2 \tan\theta$; cryst II, $1.7 + 0.2 \tan\theta$
scanning speed in ω: 2.4° min^{-1}
bkgd determn: during 20 s at each end of the interval
no. of measmts up to $(\sin\theta)/\lambda$: 1.06 Å^{-1} ($\theta = 49°$) not including std reflctns: cryst I, 7430 reflctns ($\bar{h}kl$, and some $\bar{h}kl$); cryst II, 14 026 reflctns (hkl, $\bar{h}\bar{k}\bar{l}$, and some $\bar{h}kl$)

[a] As the mean of two spherical samples.

Experimental Section

Air-stable crystals of (μ-CH_2)[CpMn(CO)$_2$]$_2$ (Cp = C_5H_5) were obtained by recrystallization from pentane at –78 °C and were ground

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(1) Research was carried out at the Università di Padova e Parma, at the Université Louis Pasteur, and at the Universität Regensburg under contract with the Italian CNR for international projects and supported by the Italian CNR by Grant Nos. 80.00317.03 and 81.00581.03.

(2) Université Louis Pasteur.

(3) Present address: Università di Padova.

(4) Università di Parma.

(5) Universität Regensburg.

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