

having predominantly the  $s_A$  character. Such a mechanism is rather similar to that which results in the *negative* values of the FC term in  ${}^1K(A-F)$  due to the presence of a fluorine lone  $2s^2$  pair.<sup>4,7,8</sup> All these aspects will be discussed in detail elsewhere.<sup>22</sup>

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## Crystal and Molecular Structure of $\mu$ -Peroxo-bis[[1,11-bis(2-pyridyl)-2,6,10-triazaundecane]cobalt(III)} Tetraiodide Trihydrate. A Cobalt Dioxygen Complex of a Pentadentate Ligand

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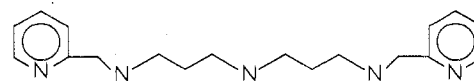
Single-crystal X-ray diffraction methods were employed to determine the structure of the reversible oxygen carrier  $\mu$ -peroxo-bis[[1,11-bis(2-pyridyl)-2,6,10-triazaundecane]cobalt(III)} tetraiodide trihydrate,  $[\text{Co}(\text{PYDPT})]_2\text{O}_2\text{I}_4\cdot 3\text{H}_2\text{O}$ ,  $(\text{CoN}_5\text{C}_{18}\text{H}_{27})_2\text{O}_2\text{I}_4\cdot 3\text{H}_2\text{O}$ . The opaque crystals conform to the monoclinic space group  $P2_1/c$  with unit cell dimensions  $a = 20.104$  (9) Å,  $b = 11.896$  (5) Å,  $c = 21.899$  (5) Å, and  $\beta = 116.33$  (10)°;  $Z = 4$ . The observed density is  $1.89$  g  $\text{cm}^{-3}$  and the calculated density is  $1.91$  (1) g  $\text{cm}^{-3}$ . Least-squares refinement with omission of hydrogen atoms gave an  $R$  index of 7.0% for 4191 reflections with intensities greater than  $4\sigma$ . The pyridyl nitrogens are cis to one another and to the dioxygen bridge in the distorted octahedral geometry around the cobalt atoms, so that an imine nitrogen is trans to the dioxygen bridge. The O-O distance of  $1.456$  (9) Å is consistent with the formulation of the dioxygen group as a peroxide ( $\text{O}_2^{2-}$ ) ion and assignment of the tripositive oxidation state to the cobalt ions. The structure is compared with that of the analogous cobalt dioxygen complex containing disalicylaldehyde 3,3'-iminobis(propanimine) as a ligand for which the structure has been determined. The fact that the cobaltous complex of the analogous *N*-ethyl substituted ligand 1,11-bis(2-pyridyl)-6-ethyl-2,6,10-triazaundecane (PYEDPT) does not react with molecular oxygen is attributed to steric hindrance at the oxygenation site.

### Introduction

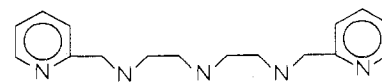
In the course of recent studies of the chemistry of dioxygen complexes of transition metals,<sup>1,2</sup> X-ray analysis has provided information on the bonding of both mononuclear and dinuclear dioxygen complexes.<sup>2</sup> These dioxygen complexes are now formally represented by one or more oxidized metal ions bound to a superoxo or peroxo dioxygen group. Some of the dinuclear compounds for which structures are available are monobridged, with the metal centers bound only by the peroxo moiety,<sup>3</sup> while others have  $\mu$ -amido<sup>4</sup> or  $\mu$ -hydroxo<sup>5</sup> bridges in addition to the peroxo bridge. In aqueous solution, the formation of a  $\mu$ -hydroxo bridge in addition to the  $\mu$ -peroxo bridge has generally been observed when there is a free coordination site on each of the metal ions after oxygenation; this bridge apparently stabilizes the dioxygen complex.<sup>6</sup> The most elegant method for preventing formation of the second bridge is to employ pentadentate ligands, so that donor groups may occupy all of the coordination sites of the metal except for the site at which oxygenation occurs. The aqueous solution behavior and oxygenation of several cobalt(II) complexes with suitable

pentacoordinate ligands have been reported.<sup>7,8</sup>

The complex chosen for study is of interest for several reasons: PYDPT (1) contains three amino and two pyridyl



1 PYDPT



2 PYDIEN

donor groups. These latter donors have the potential for  $\pi$  back-bonding, a process which should affect the  $\pi$  back-bonding, if any, to oxygen. It has been shown that  $\pi$  back-bonding from pyridyl groups to cobalt(II) enhances the stability of the ligand-cobalt bond.<sup>7</sup> The cobaltous complex of the ligand has the unusual ability to bind oxygen at low pH, but this is apparently due to formation of the metal-ligand complex in significant amounts at low pH rather than to

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exceptional stability of the dioxygen adduct.<sup>7</sup> Of greater interest is the observation that the cobalt dioxygen complex of PYDPT is approximately 4 orders of magnitude less stable than the complex of the analogous ligand 1,9-bis(2-pyridyl)-2,5,8-triazanonane (PYDIEN) (2), based upon the equilibrium constant ( $K_{O_2}$ ) for formation of the oxygen complex from the pre-formed metal-ligand complex.

$$K_{O_2} = [M_2L_2O_2] / [ML]^2[O_2]$$

PYDIEN has two-carbon bridges rather than three-carbon bridges between the central nitrogen and the two amine nitrogens. If this difference in stability has a steric basis resulting from the different conformations of the chelate rings, the crystal structure may provide data that would suggest reasons for the decrease in stability of the six-membered ring systems. It was also hoped that the structure would help explain why substitution of an ethyl group onto the central nitrogen atom of the ligand prevents formation of the oxygen adduct.

The crystal structure of the PYDPT cobalt dioxygen complex would also be of interest for comparison with the corresponding cobalt dioxygen complex containing disalicylaldehyde 3,3'-iminobis(propanimine) (SALDPT) as a ligand.<sup>9</sup> The latter is the only other pentadentate ligand for which a structure of the cobalt dioxygen complex is available. SALDPT is somewhat different from PYDPT in that it has two imine nitrogens, one amino nitrogen, and two phenolic oxygens, whereas the latter has three aliphatic and two aromatic amino groups.

### Experimental Section

**Materials.** Reagent grade cobaltous chloride ( $CoCl_2 \cdot 6H_2O$ ) and sodium iodide (NaI) were obtained from Fisher Scientific Co. and used without further purification. 2-Pyridinecarboxaldehyde and bis(3-aminopropyl)amine were purchased from Aldrich Chemical Co. and the former was distilled prior to use. Bis(3-aminopropyl)ethylamine was prepared according to published procedures<sup>10</sup> by reacting acrylonitrile with ethylamine and then reducing the purified product. High-purity oxygen, nitrogen, and hydrogen gases were obtained from Airco Gas Products, Inc., and used as obtained. All other chemicals and solvents were reagent grade.

**Preparation of the Ligands.** Preparation of PYDPT has been described previously.<sup>7</sup> The *N*-ethyl derivative was prepared in an analogous manner. In a typical reaction, 0.10 mol of 2-pyridinecarboxaldehyde and 0.050 mol of bis(3-aminopropyl)amine or bis(3-aminopropyl)ethylamine were mixed together in 150 mL of absolute ethanol. The yellow solution was then heated to boiling and allowed to cool to room temperature. Raney nickel catalyst was then added and the mixture shaken under 60 psi of hydrogen for 8 h. The catalyst was filtered from the clear solution and washed with 50 mL of absolute ethanol. The solution was transferred to a 250-mL volumetric flask and diluted to give a 0.2 M solution.

**Preparation of the Cobaltous Complexes.** [1,11-Bis(2-pyridyl)-2,6,10-triazaundecane]cobalt(II) Iodide,  $Co(PYDPT)_2$ . A 250-mL round-bottom flask was fitted with a nitrogen intake tube and a stirring bar. To 100 mL of absolute ethanol containing 0.050 mol of NaI was added 50 mL of the 0.2 M ligand solution. In order to remove dissolved oxygen, the solution was refluxed for 5 min under nitrogen. After the solution was cooled to room temperature, 0.010 mol of  $CoCl_2 \cdot 6H_2O$  in deoxygenated ethanol was added dropwise with stirring. A pink precipitate formed immediately and the mixture was stirred for 1 h after addition of the metal was completed. The product was filtered, washed with 50 mL of deoxygenated ethanol, and dried under vacuum for 3 h. Anal. Calcd for  $C_{18}H_{27}N_3CoI_2$ : C, 34.73; H, 3.70; N, 11.25. Found: C, 34.64; H, 4.27; N, 10.70.

[1,11-Bis(2-pyridyl)-2,6,10-triazaundecane]cobalt(II) Bromide,  $Co(PYDPT)Br_2$ . 2-Propanol, 100 mL, was added to a 250-mL flask fitted with a nitrogen intake tube and a stirring bar. To this was added 50 mL of the 0.2 M ligand solution. The solution was heated to reflux under nitrogen and then allowed to cool to room temperature.  $CoBr_2 \cdot 4H_2O$  in 50 mL of deoxygenated 2-propanol was added slowly to the stirred solution. The pink precipitate was filtered after 2 h and washed with 50 mL of deoxygenated 2-propanol. The product was then dried under vacuum at room temperature for 6 h. Anal.

Calcd for  $C_{18}H_{27}N_3CoBr_2$ : C, 40.59; H, 5.06; N, 13.16. Found: C, 40.09; H, 4.94; N, 12.86.

[1,11-Bis(2-pyridyl)-6-ethyl-2,6,10-triazaundecane]cobalt(II) bromide,  $Co(PYEtDPT)Br_2$ . The compound was prepared by the method described above for  $Co(PYDPT)Br_2$ . Anal. Calcd for  $C_{20}H_{31}N_3CoBr_2$ : C, 42.86; H, 5.54; N, 12.50. Found: C, 43.16; H, 5.76; N, 12.11.

### Preparation and Characterization of the Dioxygen Complexes.

$\mu$ -Peroxo-bis[1,11-bis(2-pyridyl)-2,6,10-triazaundecane]cobalt(III) Tetraiodide Trihydrate,  $[Co(PYDPT)_2O_2I_4 \cdot 3H_2O]$ . An aqueous solution of  $Co(PYDPT)_2$  was filtered into an evaporating dish and allowed to react with oxygen from the air. The solution slowly darkened, and small crystals were removed by filtration and washed with an ethanol-water mixture. The crystals were of the proper quality and size for X-ray analysis. Anal. Calcd for  $C_{36}H_{54}N_{10}O_2Co_2I_4 \cdot 3H_2O$ : C, 32.30; H, 4.53; N, 10.46. Found: C, 32.34; H, 4.49; N, 10.50.

To check the dioxygen content, a small sample of crystalline  $[Co(PYDPT)_2O_2I_4 \cdot 3H_2O]$  was heated at 100 °C under vacuum (10<sup>-2</sup> torr) for 8 h. Magnetic susceptibility measurements before and after heating indicated a change from diamagnetism to paramagnetism. Elemental analysis of the heated sample is as follows. Anal. Calcd for  $Co(PYDPT)_2$ : C, 34.73; H, 3.70; N, 11.25. Found: C, 32.97; H, 3.78; N, 10.44. In a similar experiment, a sample of the dioxygen complex was first ground to a fine powder and then heated as above. Anal. Found: C, 33.57; H, 3.92; N, 10.65.

$\mu$ -Peroxo-bis[1,11-bis(2-pyridyl)-2,6,10-triazaundecane]cobalt(III) Tetrabromide Hexahydrate,  $[Co(PYDPT)_2O_2Br_4 \cdot 6H_2O]$ . Aqueous solutions of  $Co(PYDPT)Br_2$  darken when exposed to air but no precipitate is formed. However, when a 50/50 mixture of 2-propanol and water is used as a solvent, exposure to air results in formation of a precipitate as the solution darkens. Attempts to grow crystals suitable for X-ray analysis were unsuccessful. Anal. Calcd for  $C_{36}H_{54}N_{10}O_2Co_2Br_4 \cdot 6H_2O$ : C, 36.12; H, 4.85; N, 11.70. Found: C, 35.89; H, 4.92; N, 11.58.

**Attempted Preparation of  $[Co(PYEtDPT)_2O_2Br_4]$ .** An aqueous solution of  $Co(PYEtDPT)Br_2$  was allowed to react with air but no color change was apparent. Evaporation of the solution afforded only unreacted compound. Even when oxygen gas was bubbled directly through the solution no reaction was observed.

**X-ray Data.** Preliminary precession and Weissenberg photographs gave the following systematic absences:  $0k0$  with  $k = 2n + 1$  and  $k0l$  with  $l = 2n + 1$ . These fixed the space group as  $P2_1/c$ . A crystal 0.5 mm  $\times$  0.25 mm  $\times$  0.25 mm was mounted on a CAD-4 automated diffractometer with the long axis approximately parallel to the  $\Phi$  axis of the goniometer. Unit-cell dimensions were determined from a least-squares treatment of 25 reflections obtained at medium and high Bragg angles using graphite-monochromated  $Mo K\alpha_1$  ( $\lambda$  0.709 30 Å) radiation. The results were  $a = 20.104$  (9) Å,  $b = 11.896$  (5) Å,  $c = 21.898$  (5) Å,  $\beta = 116.33$  (10)°, and  $V = 4694$  (7) Å<sup>3</sup>. With  $Z = 4$  the density is calculated to be 1.91 (1) g cm<sup>-3</sup> as compared to the observed density of 1.89 g cm<sup>-3</sup> obtained by flotation in an ethylene bromide-ethylene chloride mixture.

Intensity data were collected on the same crystal by the  $\theta$ - $2\theta$  scan method with variable speeds ranging from  $\sim 20^\circ$ /min for the strongest reflections to  $\sim 2^\circ$ /min for the weakest. The angular scan width was 0.6° before  $2\theta(MoK\alpha_1)$  and 0.6° after  $2\theta(MoK\alpha_2)$ . Reflections were collected in the angular range  $3^\circ < 2\theta < 50^\circ$ . Three standard reflections were scanned every 200 reflections and used to place the data on a common scale. No systematic variation in the standards was observed. Backgrounds were scanned at both ends of the peak for 25% of the total scan time. Reflection intensities were calculated from peak and background measurements as  $I = S(C - RB)$ , where  $S$  is the scan rate,  $C$  is the total integrated peak count,  $B$  is the total background count, and  $R$  is the ratio of the scan time for the peak to the scan time for the background. The estimated error was calculated as  $\sigma(I) = [S^2(C + R^2B) + (pI)^2]^{1/2}$ , where  $p$  was chosen to be 0.03. Of the 6709 unique reflections originally scanned, 4194 were found with  $I > 4\sigma(I)$  and used in the structure solution and refinement. The intensities as well as  $\sigma(I)$  were corrected for Lorentz and double polarization<sup>11</sup> but not for absorption. Although  $\mu = 34.5$  cm<sup>-1</sup>, the near cylindrical shape of the crystal indicated a maximum variation of about 15% in the absorption.

**Structure Solution and Refinement.** The four iodide ions were located from a map of electron density ( $E$  map) for the best phase set obtained using MULTAN.<sup>11</sup> Least-squares refinement of these atoms (two cycles) gave an  $R$  of 0.41. A difference Fourier synthesis revealed

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations<sup>a</sup>

atom	x	y	z	B <sub>11</sub>	B <sub>22</sub>	B <sub>33</sub>	B <sub>12</sub>	B <sub>13</sub>	B <sub>23</sub>
I1	0.52459 (7)	0.7517 (1)	0.42689 (7)	0.00344 (4)	0.00423 (9)	0.00323 (4)	-0.0009 (1)	0.00174 (6)	-0.0015 (1)
I2	0.68619 (7)	0.0471 (1)	0.30684 (6)	0.00401 (4)	0.00552 (9)	0.00243 (3)	0.0014 (1)	0.00248 (5)	-0.0006 (1)
I3	0.94120 (8)	0.5845 (1)	0.59064 (7)	0.00369 (4)	0.00607 (10)	0.00282 (4)	-0.0012 (1)	0.00106 (6)	-0.0003 (1)
I4	0.76666 (7)	-0.1675 (1)	0.72536 (6)	0.00351 (4)	0.00659 (10)	0.00252 (3)	-0.0006 (1)	0.00204 (5)	-0.0020 (1)
Co1	0.6632 (1)	0.3965 (2)	0.4195 (1)	0.00223 (6)	0.0023 (1)	0.00122 (5)	0.0002 (2)	0.00071 (8)	-0.0003 (2)
Co2	0.8492 (1)	0.1980 (2)	0.5858 (1)	0.00192 (6)	0.0031 (2)	0.00118 (5)	0.0001 (2)	0.00065 (8)	0.0000 (2)
O1	0.7342 (6)	0.2837 (9)	0.4648 (5)	0.0027 (4)	0.0024 (8)	0.0013 (3)	-0.0010 (9)	-0.0007 (5)	0.0002 (8)
O2	0.7964 (6)	0.3184 (9)	0.5281 (5)	0.0024 (3)	0.0032 (8)	0.0016 (3)	-0.0010 (9)	-0.0001 (5)	-0.0001 (8)
O3	0.1202 (7)	0.159 (1)	0.3593 (7)	5.7 (3) <sup>b</sup>					
O4	0.1579 (10)	0.363 (2)	0.1389 (9)	8.8 (5) <sup>b</sup>					
O5	0.3602 (13)	0.269 (2)	0.1546 (12)	11.9 (7) <sup>b</sup>					
N1	0.5834 (7)	0.291 (1)	0.4039 (6)	0.0022 (4)	0.0041 (10)	0.0016 (3)	0.002 (1)	0.0008 (5)	-0.0020 (10)
N2	0.5793 (8)	0.502 (1)	0.3667 (7)	0.0025 (5)	0.0047 (11)	0.0016 (4)	0.000 (1)	-0.0006 (7)	0.0000 (11)
N3	0.6667 (7)	0.342 (1)	0.3345 (5)	0.0041 (5)	0.0018 (9)	0.0006 (3)	-0.001 (1)	0.0014 (5)	-0.0010 (9)
N4	0.7461 (7)	0.503 (1)	0.4452 (6)	0.0031 (4)	0.0040 (10)	0.0022 (3)	-0.003 (1)	0.0028 (5)	-0.0028 (10)
N5	0.6635 (6)	0.452 (1)	0.5032 (6)	0.0018 (3)	0.0043 (10)	0.0014 (3)	0.001 (1)	0.0012 (5)	0.0007 (10)
N6	0.8538 (6)	0.275 (1)	0.6652 (5)	0.0020 (4)	0.0036 (10)	0.0005 (3)	-0.000 (1)	0.0002 (5)	0.0003 (9)
N7	0.9072 (7)	0.080 (1)	0.6546 (6)	0.0029 (4)	0.0032 (10)	0.0014 (3)	0.001 (1)	0.0012 (5)	0.0009 (10)
N8	0.9396 (7)	0.280 (1)	0.5965 (6)	0.0024 (4)	0.0036 (10)	0.0016 (3)	-0.000 (1)	0.0004 (6)	-0.0025 (10)
N9	0.8353 (7)	0.112 (1)	0.5048 (6)	0.0024 (4)	0.0045 (10)	0.0012 (3)	-0.000 (1)	0.0011 (5)	-0.0027 (10)
N10	0.7590 (7)	0.116 (1)	0.5753 (7)	0.0021 (4)	0.0019 (9)	0.0019 (4)	-0.001 (1)	-0.0011 (7)	-0.0012 (10)
C1	0.5930 (9)	0.181 (1)	0.4132 (9)	0.0025 (6)	0.004 (1)	0.0022 (5)	0.001 (1)	-0.0001 (8)	-0.001 (1)
C2	0.5304 (9)	0.108 (2)	0.3950 (8)	0.0037 (6)	0.005 (1)	0.0021 (4)	-0.003 (2)	0.0025 (7)	-0.000 (1)
C3	0.4598 (10)	0.152 (2)	0.3633 (9)	0.0033 (6)	0.005 (1)	0.0024 (5)	0.001 (2)	0.0017 (8)	-0.001 (1)
C4	0.4508 (10)	0.269 (2)	0.3537 (10)	0.0024 (6)	0.008 (2)	0.0028 (6)	-0.000 (2)	-0.0006 (10)	-0.003 (2)
C5	0.5135 (9)	0.331 (2)	0.3751 (9)	0.0023 (5)	0.007 (1)	0.0025 (5)	-0.003 (1)	0.0021 (7)	-0.001 (1)
C6	0.5119 (9)	0.456 (1)	0.3693 (9)	0.0028 (5)	0.002 (1)	0.0023 (5)	0.002 (1)	0.0004 (8)	-0.001 (1)
C7	0.5655 (11)	0.526 (2)	0.2938 (9)	0.0053 (7)	0.006 (2)	0.0023 (5)	-0.001 (2)	0.0030 (9)	-0.001 (2)
C8	0.5453 (12)	0.422 (2)	0.2475 (10)	0.0045 (8)	0.011 (2)	0.0023 (6)	-0.000 (2)	0.0008 (11)	-0.000 (2)
C9	0.5934 (11)	0.325 (1)	0.2732 (8)	0.0057 (8)	0.004 (1)	0.0015 (4)	0.004 (2)	0.0012 (9)	-0.002 (1)
C10	0.7128 (11)	0.395 (2)	0.3059 (9)	0.0054 (6)	0.009 (2)	0.0037 (5)	0.002 (2)	0.0063 (7)	-0.002 (2)
C11	0.7885 (11)	0.444 (2)	0.3625 (8)	0.0052 (7)	0.006 (2)	0.0021 (4)	-0.000 (2)	0.0038 (7)	-0.003 (1)
C12	0.7740 (10)	0.539 (1)	0.3952 (9)	0.0044 (6)	0.003 (1)	0.0030 (5)	0.000 (2)	0.0039 (8)	0.003 (1)
C13	0.7289 (9)	0.603 (1)	0.4805 (9)	0.0026 (5)	0.004 (1)	0.0031 (5)	-0.003 (1)	0.0025 (7)	0.001 (1)
C14	0.6987 (8)	0.553 (1)	0.5238 (8)	0.0017 (4)	0.004 (1)	0.0022 (4)	-0.001 (1)	0.0011 (7)	0.000 (1)
C15	0.7051 (9)	0.602 (1)	0.5852 (8)	0.0037 (5)	0.003 (1)	0.0029 (4)	-0.002 (1)	0.0032 (7)	-0.004 (1)
C16	0.6761 (9)	0.549 (2)	0.6229 (10)	0.0022 (5)	0.005 (1)	0.0031 (5)	0.003 (1)	0.0010 (8)	-0.002 (2)
C17	0.6411 (10)	0.443 (2)	0.6007 (8)	0.0029 (5)	0.012 (2)	0.0020 (4)	0.003 (2)	0.0016 (7)	-0.005 (1)
C18	0.6345 (8)	0.404 (1)	0.5393 (8)	0.0023 (5)	0.003 (1)	0.0021 (4)	0.000 (1)	0.0013 (7)	-0.001 (1)
C19	0.8349 (9)	0.387 (1)	0.6655 (8)	0.0026 (5)	0.002 (1)	0.0022 (4)	-0.001 (1)	0.0012 (7)	-0.002 (1)
C20	0.8397 (9)	0.437 (2)	0.7270 (9)	0.0022 (5)	0.007 (2)	0.0030 (5)	-0.001 (1)	0.0024 (7)	-0.003 (2)
C21	0.8644 (9)	0.373 (2)	0.7844 (8)	0.0031 (5)	0.008 (2)	0.0018 (4)	-0.001 (2)	0.0021 (7)	-0.003 (1)
C22	0.8842 (9)	0.259 (2)	0.7837 (8)	0.0029 (5)	0.005 (1)	0.0019 (4)	-0.003 (1)	0.0017 (7)	-0.000 (1)
C23	0.8756 (7)	0.213 (1)	0.7215 (7)	0.0015 (4)	0.004 (1)	0.0020 (4)	-0.002 (1)	0.0017 (6)	-0.001 (1)
C24	0.8923 (9)	0.091 (1)	0.7164 (9)	0.0026 (5)	0.001 (1)	0.0038 (5)	-0.000 (1)	0.0032 (7)	0.001 (1)
C25	0.9883 (9)	0.079 (2)	0.6734 (9)	0.0027 (5)	0.005 (1)	0.0031 (5)	0.001 (1)	0.0022 (8)	0.003 (1)
C26	1.0300 (10)	0.185 (2)	0.7089 (9)	0.0026 (6)	0.010 (2)	0.0018 (5)	0.000 (2)	0.0003 (8)	-0.002 (2)
C27	1.0021 (10)	0.292 (2)	0.6702 (10)	0.0025 (6)	0.006 (2)	0.0023 (5)	0.001 (2)	-0.0007 (9)	0.000 (2)
C28	0.9810 (9)	0.252 (2)	0.5535 (9)	0.0034 (5)	0.011 (2)	0.0037 (5)	-0.002 (2)	0.0051 (7)	-0.001 (2)
C29	0.9299 (11)	0.211 (2)	0.4824 (9)	0.0060 (7)	0.007 (2)	0.0019 (4)	-0.008 (2)	0.0029 (8)	-0.001 (1)
C30	0.8966 (9)	0.098 (2)	0.4837 (8)	0.0029 (5)	0.013 (2)	0.0020 (4)	-0.002 (2)	0.0028 (7)	-0.003 (2)
C31	0.7999 (9)	-0.000 (1)	0.5043 (8)	0.0032 (5)	0.004 (1)	0.0030 (4)	-0.002 (1)	0.0039 (6)	-0.002 (1)
C32	0.7478 (9)	0.026 (2)	0.5341 (8)	0.0021 (5)	0.006 (1)	0.0017 (4)	-0.000 (1)	0.0006 (7)	0.003 (1)
C33	0.6865 (9)	-0.047 (2)	0.5239 (9)	0.0024 (5)	0.005 (1)	0.0026 (5)	-0.000 (1)	0.0009 (9)	0.005 (1)
C34	0.6400 (11)	-0.018 (2)	0.5505 (9)	0.0045 (7)	0.008 (2)	0.0023 (5)	-0.000 (2)	0.0020 (8)	0.005 (1)
C35	0.6504 (10)	0.079 (2)	0.5885 (9)	0.0027 (6)	0.007 (2)	0.0023 (5)	0.001 (2)	0.0007 (8)	0.003 (2)
C36	0.7110 (8)	0.144 (1)	0.5973 (7)	0.0022 (5)	0.006 (1)	0.0010 (4)	0.002 (1)	0.0005 (6)	0.002 (1)

<sup>a</sup> The form of the anisotropic thermal parameter is  $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$ . <sup>b</sup> Isotropic thermal parameter in Å<sup>2</sup>.

the cobalt atoms, the bridge oxygens, and nine of the nitrogens. The remaining nonhydrogen atoms were found by difference Fourier methods. All atoms except the oxygen atoms of water were refined anisotropically in the final solution.

Comparison of calculated and observed structure factors indicated that three reflections with asymmetric backgrounds should be omitted because of a large error which may have occurred in their measurement. After location of all nonhydrogen atoms, three cycles of full-matrix least-squares refinement converged the structure at  $R(F) = 0.070$  and  $R(wF) = 0.100$  for 499 variables. The residuals were calculated as  $R(F) = [\sum |F_o| - |F_c|] / \sum |F_o|$  and  $R(wF) = [\sum w(|F_o| - |F_c|)^2] / \sum w|F_o|^2$  with the reflections weighted as  $w = 1/\sigma^2(F_o) = 4F_o^2 / [\sigma(F_o^2)]^2$  and  $\sigma(F_o^2) = [\sigma^2(I) + (0.05F_o^2)]^{1/2} / Lp$ . The function minimized was  $\sum w(|F_o| - |F_c|)^2$ . A final difference Fourier map

showed peaks ranging from slightly less than 1 to  $\sim 0.3 \text{ e}/\text{Å}^3$  in the vicinity of hydrogen atom positions and some slight positive density ( $0.1\text{--}0.2 \text{ e}/\text{Å}^3$ ) around the iodine positions indicating that the thermal ellipsoids for these atoms did not quite duplicate their anisotropic motion completely.

### Description of the Structure

The structure consists of binuclear cations [LCo-O-O-CoL]<sup>4+</sup> (L = PYDPT), iodide anions, and neutral water molecules. Positional and thermal parameters obtained for all atoms in the structure are given in Table I.

The binuclear cation is a cobalt dimer with the cobalt atoms linked by a dioxygen bridge. Bond lengths and angles for the

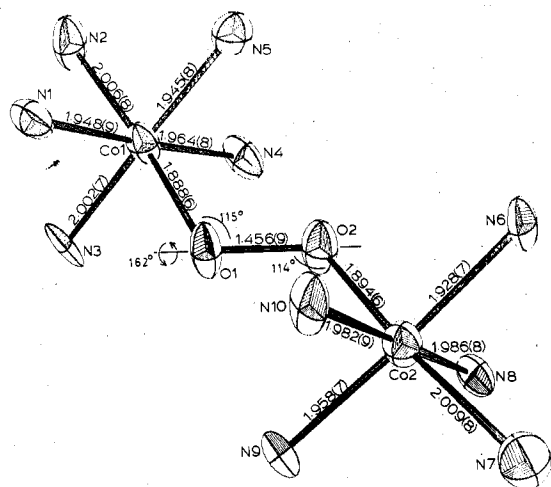


Figure 1. ORTEP<sup>17</sup> drawing of the coordination sphere around the cobalt atoms showing bond distances and selected angles.

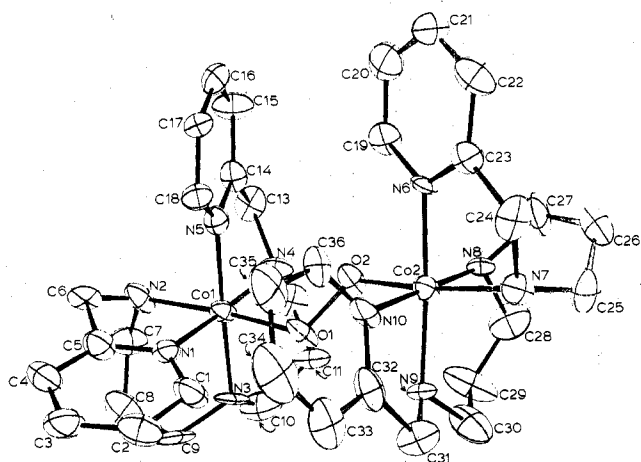


Figure 2. View of the complex cation  $[\text{Co}(\text{PYDPT})]_2\text{O}_2^{4+}$ .

atoms in the coordination sphere of cobalt are given in Figure 1. The O—O and Co—O bond distances and the Co—O—O angle are consistent with peroxide bound to Co(III) and are comparable to those obtained in other  $\mu$ -peroxo-bridged cobalt(III) dimers such as  $[(\text{NH}_3)_{10}\text{Co}_2\text{O}_2](\text{SO}_4)_2^3$  (O—O = 1.47 Å, Co—O = 1.88 Å, Co—O—O = 112°). Except for fairly small differences in distances and angles, the conformations about the two cobalt atoms are identical, as may be seen in the

illustration of the complete dimer (Figure 2).

The ligand forms both five- and six-membered chelate rings on binding to cobalt; the distortions from octahedral geometry about the cobalt atoms might be expected to result from strain introduced by six-membered ring formation. For example, the nitrogen trans to the dioxygen bridge is not collinear with the Co—O bond; the N—Co—O angle is 173–174°. However, similar distortion is observed for  $\mu$ -peroxo-bis[ethylenediamine](diethylenetriamine)cobalt(III) perchlorate,<sup>12</sup> which involves only five-membered rings. The significant variation of most of the angles around carbon in the three-carbon bridges from an ideal 109.5° angle may be an indication of strain. Of the six-membered chelate rings formed, one is in a chair conformation with C29 bent upward 0.75 Å and Co2 bent downward 0.25 Å from the mean plane formed by N8, C28, C30, and N9, while the remaining three are irregular in conformation, forming neither boat nor chair.

It should also be noted that the Co—N distances (excluding Co to pyridyl N distances) are significantly longer than those for peroxo complexes of ammonia such as decaammine- $\mu$ -peroxo-dicobalt.<sup>3</sup> The bond lengths are only slightly longer than those for the ethylenediamine diethylenetriamine complex previously mentioned,<sup>12</sup> however (Table II). Although the differences in bond lengths in this latter case are not statistically significant, the fact that all of the bonds are slightly longer in the PYDPT complex may have some significance. The only Co—N bonds which are certainly longer in the present complex are those of N3 and N8, which are part of both six-membered rings. It is interesting that the distance between Co and the nitrogen trans to dioxygen is normally much longer than the other cobalt-to-nitrogen bonds as exhibited in this structure. This indicates that the peroxide ion exerts a powerful trans effect on nitrogen.

The pyridyl rings are cis and approximately perpendicular to one another and cis to the dioxygen bridge. Trans to the dioxygen bridge is one of the amine nitrogens other than the central nitrogen of the ligand. The other noncentral amine nitrogen is thus trans to a pyridyl nitrogen; this nitrogen is not collinear with the Co—N(py) bond but makes an angle of about 174° with it. The central amine nitrogen is approximately collinear with the Co—N(py) bond trans to it, the angles being 178–179°. Bond distances and angles of interest are given in Table III. Torsional angles about bonds involved in two of the six-membered chelate rings are also included.

Figure 3 is an illustration of the complete unit cell. The ligands form rows along the direction of the *a*—*c* diagonal and the iodide ions run perpendicular to this, separating the dimers. Closer inspection reveals that four iodide ions and three water

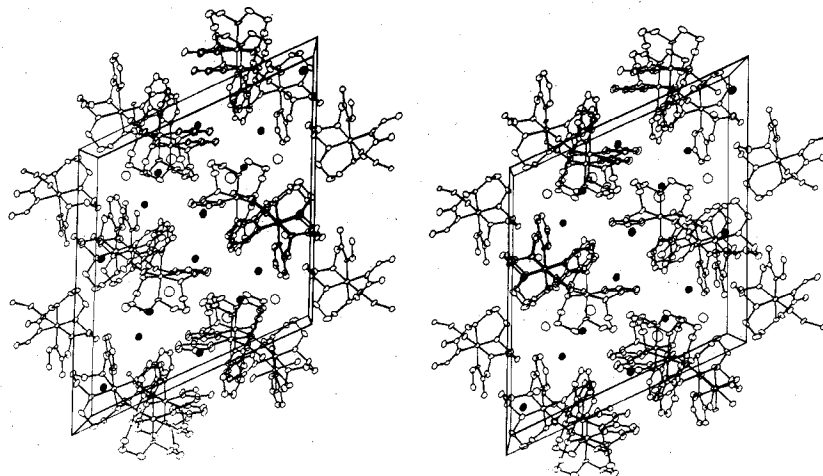


Figure 3. Stereo diagram of one unit cell showing the packing of the complex cations, iodide anions, and water molecules. The view is down the *b* axis with the *c* axis vertical. The iodide ions (black) are, from the center of the unit cell to the upper right corner, I1, I2, I4, and I3. The oxygen atoms (white, isotropic) are O5, O4, and O3.

Table II. Co-N Bond Distances (Å) for Selected  $\mu$ -Peroxo Complexes

compd	trans position	cis position			ref	
[Co(PYDPT)] <sub>2</sub> O <sub>2</sub> <sup>4+</sup>	2.006 (8)	1.964 (8)	2.002 (7)		this work	
	2.009 (8)	1.958 (7)	1.986 (8)			
[Co(en)(dien)] <sub>2</sub> O <sub>2</sub> <sup>4+</sup>	1.998	1.948	1.976	1.941	1.943	15
[Co(NH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> O <sub>2</sub> <sup>4+</sup> <sup>a</sup>	1.985 (9)	1.961 (9)	1.951 (9)	1.964 (9)	1.947 (9)	4
	1.981 (9)	1.966 (9)	1.953 (9)	1.960 (9)	1.952 (9)	

<sup>a</sup> Esd's were not given: in ref 15.

Table III. Selected Bond Distances, Bond Angles, and Torsional Angles and Their Standard Deviations

(a) Bond Distances			
N1-C1	1.316 (13)	N6-C19	1.389 (12)
C1-C2	1.433 (15)	C19-C20	1.436 (15)
C2-C3	1.374 (15)	C20-C21	1.364 (16)
C3-C4	1.403 (17)	C21-C22	1.414 (16)
C4-C5	1.357 (16)	C22-C23	1.406 (14)
C5-N1	1.350 (13)	C23-N6	1.333 (12)
C5-C6	1.490 (15)	C23-C24	1.501 (14)
C6-N2	1.484 (14)	C24-N7	1.517 (14)
N2-C7	1.523 (14)	N7-C25	1.495 (14)
C7-C8	1.539 (18)	C25-C26	1.524 (17)
C8-C9	1.449 (18)	C26-C27	1.494 (17)
C9-N3	1.502 (14)	C27-N8	1.550 (13)
N3-C10	1.474 (15)	N8-C28	1.543 (14)
C10-C11	1.588 (18)	C28-C29	1.519 (17)
C11-C12	1.433 (15)	C29-C30	1.505 (17)
C12-N4	1.498 (14)	C30-N9	1.505 (14)
N4-C13	1.542 (14)	N9-C31	1.510 (13)
C13-C14	1.460 (15)	C31-C32	1.491 (15)
C14-N5	1.367 (12)	C32-N10	1.353 (14)
C14-C15	1.418 (15)	C32-C33	1.444 (15)
C15-C16	1.361 (17)	C33-C34	1.350 (17)
C16-C17	1.421 (17)	C34-C35	1.392 (18)
C17-C18	1.372 (15)	C35-C36	1.378 (15)
C18-N5	1.304 (13)	C36-N10	1.298 (13)
(b) Bond Angles, Deg			
O1-Co1-N1	90.22 (31)	O2-Co2-N6	91.82 (30)
O1-Co1-N2	173.32 (31)	O2-Co2-N7	174.56 (31)
O1-Co1-N3	85.79 (31)	O2-Co2-N8	85.30 (31)
O1-Co1-N4	87.71 (33)	O2-Co2-N9	88.68 (31)
O1-Co1-N5	93.43 (31)	O2-Co2-N10	94.67 (30)
N1-Co1-N2	83.44 (35)	N6-Co2-N7	82.85 (32)
N1-Co1-N3	89.51 (33)	N6-Co2-N8	89.14 (32)
N1-Co1-N4	174.08 (35)	N6-Co2-N9	174.00 (33)
N1-Co1-N5	92.40 (34)	N6-Co2-N10	90.79 (35)
N2-Co1-N3	92.07 (35)	N7-Co2-N8	93.48 (34)
N2-Co1-N4	98.80 (37)	N7-Co2-N9	96.73 (34)
N2-Co1-N5	88.91 (34)	N7-Co2-N10	86.54 (33)
N3-Co1-N4	95.87 (34)	N8-Co2-N9	96.87 (33)
N3-Co1-N5	177.94 (35)	N8-Co2-N10	179.92 (30)
N4-Co1-N5	82.19 (34)	N9-Co2-N10	83.21 (36)
Co2-O2-O1	114.34 (45)	Co1-O1-O2	115.40 (46)
N1-C5-C6	112.1 (9)	N6-C23-C24	117.2 (9)
C4-C5-C6	122.5 (11)	C22-C23-C24	120.8 (10)
N2-C6-C5	112.4 (9)	N7-C24-C23	106.7 (8)
C6-N2-C7	111.4 (8)	C24-N7-C25	112.2 (8)
N2-C7-C8	114.1 (10)	N7-C25-C26	114.9 (9)
C7-C8-C9	116.8 (11)	C25-C26-C27	115.7 (9)
N3-C9-C8	117.6 (9)	N8-C27-C26	116.0 (9)
C9-N3-C10	103.2 (9)	C27-N8-C28	104.4 (9)
N3-C10-C11	113.2 (10)	N8-C28-C29	113.2 (10)
C10-C11-C12	110.2 (11)	C28-C29-C30	112.2 (10)
N4-C12-C11	111.4 (9)	N9-C30-C29	109.6 (11)
C12-N4-C13	112.6 (8)	C30-N9-C31	110.2 (9)
N4-C13-C14	105.1 (8)	N9-C31-C32	103.5 (11)
N5-C14-C13	116.6 (9)	C31-C32-C33	121.5 (11)
C13-C14-C15	124.0 (9)	N10-C32-C31	121.0 (9)
(c) Torsional Angles, Deg			
Co2-N7-C5-C26	63.8	Co2-N8-C28-C29	31.9
N7-C25-C26-C27	-58.0	N8-C28-C29-C30	67.1
C25-C26-C27-N9	-5.7	C28-C29-C30-N9	76.5
C26-C26-N8-Co2	55.6	C29-C30-N9-Co2	-50.1
C27-N8-Co2-N7	-41.0	C30-N9-Co2-N8	17.5
N8-Co2-N7-C25	-13.7	N9-Co2-N8-C25	-90.4

Table IV. Oxygen-to-Iodide Close-Contact Distances and Angles

Distances, Å			
I1-O5	3.501 (16)	I4-O4	3.539 (12)
I2-O5	3.638 (16)	I4-O3	3.516 (9)
I2-O4	3.570 (12)	I3-O3	3.642 (10)
Angles, Deg			
I1-O5-I2	118 (1)	I4-O3-I3	121 (1)
I2-O4-I4	98 (1)		

molecules alternate to form an irregular chain. The O-I distances of about 3.5 Å indicate some interaction between the hydrogens of water and the large iodide ions, with ionic radii of about 2.2 Å. Furthermore, the I-O-I angles are within allowable limits for interaction of each water molecule with two iodide ions simultaneously. These distances and angles are presented in Table IV. Unfortunately, the large thermal motion of the water molecules made accurate determination of the hydrogen atom positions impossible. Thus, these bonds are inferred from the interatomic distances and angles of the nonhydrogen atoms. One further hydrogen bond between the hydrogen atom on N7 and the oxygen from one of the water molecules (O3) is likely. The N-O distance is 2.88 (1) Å and the C-N-O angles are 99 and 94°. A hydrogen bond here would account for the low thermal motion of O3 compared with that for the other water oxygen atoms. It also helps account for minor differences in distances and angles about Co1 and Co2, since no hydrogen bond is formed by the corresponding nitrogen in the other half of the dimer.

## Discussion

The only structure previously reported for a dioxygen complex with a pentadentate ligand was that of  $\mu$ -peroxo-[disalicylaldehyde 3,3'-iminobis(propaniminato)]cobalt(III)-toluene, [Co(SALDPT)]<sub>2</sub>O<sub>2</sub>·C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>.<sup>9</sup> The Co-O-O-Co torsional angle is lower in the SALDPT complex than in the present structure, but this apparently depends only on crystal packing forces. The SALDPT complex has an O-O bond distance of 1.45 Å, essentially the same as that of [Co(PYDPT)]<sub>2</sub>O<sub>2</sub><sup>4+</sup>. The Co-O bond distances as well as the Co-O-O angles are also very similar in the two compounds. In addition, both have distorted geometries about Co. In spite of these similarities, there are substantial differences between the two compounds. [Co(SALDPT)]<sub>2</sub>O<sub>2</sub> is a neutral complex. The Schiff-base ligand has an O<sub>2</sub>N<sub>3</sub> donor set and is dinegative. Moreover, SALDPT forms six-membered chelate rings exclusively on binding to cobalt and the arrangement of the donors is different, with one of the terminal phenolic oxygen donors trans to the dioxygen ligand and the two imine groups trans to each other. This difference in ligand arrangement is probably the result of the presence of a Schiff base rather than any other differences (such as coordinate bond strength) between the two ligands. Thus, when the Schiff-base form of a ligand similar to PYDPT binds cobalt, the arrangement of the donors is the same as that observed for SALDPT.<sup>13</sup> The change in going from a C-N double bond to a C-N single bond obviously produces less restrictive movement of the ligand and therefore possibly a less strained structure. Alternately, PYDPT may wrap around the metal so as to avoid placement of a pyridyl group trans to the dioxygen bridge. Since pyridine

can act as a  $\pi$  acceptor, it may possibly accept electron density from the metal ion by  $\pi$  back-bonding. Placed trans to the dioxygen ligand, it might compete with that ligand for back-bonding to the metal. For the same reason, two pyridyls trans to one another would tend to destabilize the complex. Indeed, the fact that the two pyridyl groups are roughly perpendicular indicates that, if they back-bond, they will accept electrons from different d orbitals, as would be expected. The  $\pi$ -acceptor properties may thus explain why the two pyridyl groups and the dioxygen bridge are all cis. Note, however, that pyridine is trans to dioxygen in certain cobalt(III) mononuclear complexes with bound superoxide ion, e.g., superoxo-*N,N'*-ethylenebis(acetylacetonone iminato)cobalt(III) pyridinate;<sup>14</sup> unfortunately, the superoxo and the  $\mu$ -peroxo complexes cannot be directly compared.

Indications of strain previously described are not sufficient to explain the difference in solution stabilities for PYDIEN and PYDPT dioxygen complexes. It has been postulated<sup>15</sup> that the additional strain imposed by the six-membered chelate rings and/or the manner in which the ligand is forced to wrap around the cobalt ion may prevent the amine nitrogens from approaching to their ideal bonding distances when cobalt(II) is oxidized to cobalt(III) by binding of dioxygen. This problem would be less pronounced or completely absent for PYDIEN, where only five-membered chelate rings are formed. Thus, the PYDIEN dioxygen complex might be expected to be considerably more stable than the PYDPT complex, as is actually observed. The present structure provides insufficient evidence to resolve this issue, although it does not by any means rule out the hypothesis. Determination of the structure of the analogous dioxygen complex cation with PYDIEN may yield further information about this problem as well as indicate whether the all-cis configuration of the pyridyl donors and the dioxygen ligand is peculiar to the present structure or general for this type of ligand.

It is interesting that the central nitrogen donor is cis to the dioxygen ligand in both the SALDPT and PYDPT  $\mu$ -peroxo-dicobalt complexes. It has been shown<sup>16</sup> that compounds of the type Co(SALRDPT), where R is a substituent on the central donor, do not form stable dioxygen complexes. The suggestion was made that steric hindrance produced by the R group is largely responsible for this observation. Steric hindrance may be possible for any ligand PYRDPT, as well, if R is on the central donor. In an effort to test this hypothesis, Co(PYEtDPT)I<sub>2</sub> was prepared. Oxygenation of the compound was attempted in aqueous solution but no color change was

apparent and evaporation of the solution provided only the unreacted complex. Considering that the central donor, and therefore the ethyl group, would be cis to the dioxygen ligand in such a compound, it appears that the ethyl group effectively reduced the stability of the dioxygen complex either by preventing dimerization or by blocking the position of attack. A crystal structure of the Co(II) complex would be required to determine which of these two considerations is the more important factor in the inhibition of oxygenation.

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**Registry No.** [Co(PYDPT)]<sub>2</sub>O<sub>2</sub>I<sub>4</sub>·3H<sub>2</sub>O, 69069-35-8; [Co(PYDPT)]<sub>2</sub>O<sub>2</sub>Br<sub>4</sub>, 69126-62-1; Co(PYDPT)I<sub>2</sub>, 69069-36-9; Co(PYDPT)Br<sub>2</sub>, 69069-37-0; Co(PYEtDPT)Br<sub>2</sub>, 69069-38-1.

**Supplementary Material Available:** A table of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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