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Crystal and Molecular Structure of μ-Peroxo-bis[(1,9-bis(2-pyridyl)-2,5,8-triazanonane)cobalt(III)] Tetraiodide. Effect of Chelate Ring Size on the Structures and Stabilities of Dioxygen Complexes[1]

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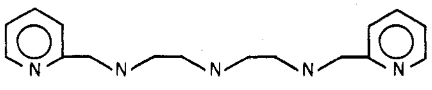
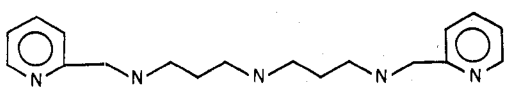
The structure of μ-peroxo-bis[(1,9-bis(2-pyridyl)-2,5,8-triazanonane)cobalt(III)] tetraiodide, $[Co(PYDIEN)]_2O_2I_4$, $Co_2C_{32}H_{46}N_{10}O_2I_4$, has been determined by single-crystal X-ray diffraction. The opaque crystals are orthorhombic, conforming to the space group *Fdd*2, with unit cell dimensions $a = 26.73$ (2) Å, $b = 32.19$ (1) Å, and $c = 10.049$ (6) Å; $Z = 8$. The observed density of 1.90 (1) $g{\cdot}cm^{-3}$ agrees well with the calculated value of 1.89 $g{\cdot}cm^{-3}$. Least-squares refinement gave an *R* index of 0.045 for 2167 observed reflections with intensities greater than 3σ. The O–O distance of 1.489 (8) Å and the Co–O–O angle of 112.5 (4)° are characteristic of peroxide bound to tripositive cobalt. The two pyridyl groups and the dioxygen moiety are cis to one another, the central (aliphatic) nitrogen donor of the ligand is trans to a pyridyl ring, and one of the secondary amino groups is trans to dioxygen in the distorted octahedral complex. The results of the structure determination provide an explanation for the difference in the oxygen affinities of $[Co(PYDIEN)]^{2+}$ and the cobaltous complex of 1,11-bis(2-pyridyl)-2,6,10-triazaundecane (PYDPT). Some of the Co–N bonds in $[Co(PYDIEN)]_2O_2I_4$ are shorter and thus stronger than those in $[Co(PYDPT)]_2O_2I_4{\cdot}3H_2O$, the structure of which has been reported previously. Donation of electron density from the ligand to cobalt increases the tendency of cobalt to transfer electron density to dioxygen and is probably the major factor affecting the stability of the oxygen complex. That the extent of donation from cobalt to dioxygen is different in the two structures can be seen by comparison of the Co–O and O–O bond distances.

Introduction

In a recent paper,[2a] the cobalt(II) complex of PYDIEN (**1**) was shown to have an affinity for molecular oxygen which is about 4 orders of magnitude larger than the oxygen affinity exhibited by the cobalt(II) complex of PYDPT (**2**). Differences in intrinsic basicity can account for differences in oxygen affinity;[2b] however, the intrinsic basicities of the ligands are approximately equal. Indeed, the ligands differ only in the number of methylene groups between the three central amine nitrogen atoms. A study[3] of ligands analogous to PYDIEN and PYDPT, in which the pyridyl groups have been replaced by imidazolyl groups, has confirmed that additional methylene groups between the aliphatic nitrogen atoms drastically decrease the oxygen affinity of the cobaltous complex. It would appear that the stability of the oxygen complex is affected by properties of the ligand other than basicity.



1, PYDIEN



2, PYDPT

The molecular structure of $[Co(PYDPT)]_2O_2I_4{\cdot}3H_2O$ was recently determined[4] by single-crystal X-ray diffraction. This work was performed in order to determine whether the structure of this complex could account for its lowered stability in solution. The structure did not exhibit any features which would prevent the close approach of dioxygen to the cobalt ion. Thus, it is unlikely that the stability of the complex is lowered by direct steric interaction between the ligand and dioxygen. Comparison with structural data for related complexes[5,6] gives no clue to the reason for the reduced stability of the oxygen complex of cobaltous PYDPT.

The crystal structure of $[Co(PYDIEN)]_2O_2I_4$ is reported in this paper. This structure was undertaken to determine whether any structural differences between the oxygen complexes containing PYDIEN and PYDPT exist. The difference in their stabilities might be explained by differences in geometry about the cobalt ion. A full comparison of the two structures is made; relevant data on the structure of $[Co(PYDPT)]_2O_2I_4{\cdot}3H_2O$[4] are included to facilitate this comparison.

Experimental Section

Materials. Reagent grade cobaltous chloride ($CoCl_2{\cdot}6H_2O$) and sodium iodide (NaI) were obtained from Fisher Scientific Co. and were used without further purification. 2-Pyridinecarboxaldehyde and bis(2-aminoethyl)amine were purchased from Aldrich Chemical Co. and the former was distilled prior to use. High-purity oxygen, nitrogen, and hydrogen gases were obtained from Airco Gas Products, Inc., and used as obtained. All other compounds employed in this research were reagent grade chemicals and solvents.

Preparation of 1,9-Bis(2-pyridyl)-2,5,8-triazanonane (PYDIEN). In a typical reaction, 0.10 mol of 2-pyridinecarboxaldehyde and 0.050 mol of bis(2-aminoethyl)amine 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 was shaken under 60 psi of hydrogen gas for 8 h. The catalyst was filtered from the clear solution and washed

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with 50 mL of absolute ethanol. The solution was transferred to a 250-mL volumetric flask and diluted to give a 0.20 M solution.

Preparation of $[Co(PYDIEN)]_2O_2I_4$. To 100 mL of absolute ethanol containing 0.050 mol of NaI was added 50 mL of the 0.20 M ligand solution. Dissolved oxygen was removed by refluxing the solution 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. No precipitate was observed after 12 h of stirring under nitrogen. When the solution containing the Co(II) complex was exposed to oxygen, it darkened immediately, and a crystalline precipitate formed after 30 min. The product was isolated and recrystallized from an ethanol/water mixture by slow evaporation. This method yielded crystals of suitable size and quality for X-ray analysis.

X-ray Data. A crystal approximately 0.2 × 0.2 × 0.1 mm^3 was mounted on a CAD-4 automated diffractometer and unit cell dimensions were determined from a least-squares treatment of 25 reflections obtained at medium and high Bragg angles. The values obtained are a = 26.73 (2) Å, b = 32.19 (1) Å, c = 10.049 (6) Å, and V = 8649 (16) $Å^3$; all angles were 90°. The following reflections were systematically absent in the intensity data collected subsequently: hkl with $h + k = 2n + 1$ and $k + l = 2n + 1$, $0kl$ with $k + l \neq 4n$, and $h0l$ with $l + h \neq 4n$. The space group was thus uniquely determined to be $Fdd2$. All intensity data were collected by using graphite-monochromated Mo Kα radiation (λ 0.709 30 Å). With Z = 8 the density was calculated to be 1.89 g·cm^{-3} as compared to the observed density of 1.90 (1) g·cm^{-3} obtained by flotation in an ethylene bromide–ethylene chloride mixture.

Intensity data were collected by the θ–2θ scan method at speeds which varied from ~20°/min for the most intense reflection to ~2°/min for the weakest reflections. The angular scan width was 0.5° before 2θ (Mo Kα) and 0.5° after 2θ (Mo Kα) and the angular range was $3° < 2\theta < 45°$. 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. Right and left backgrounds were each scanned 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, and R is the ratio of the scan time for the peak to the scan time for the background. The variance was calculated as $\sigma(I) = [S^2C + R^2B + (pI)^2]^{1/2}$, where p was chosen as 0.03.[7] Of the 2822 unique reflections originally scanned, 2167 with $I > 3\sigma$ were judged to be observed. The intensities as well as $\sigma(I)$ were corrected for Lorentz and double polarization[7] and for absorption; μ = 37.25 cm^{-1}.

Structure Solution and Refinement. Two iodide ions and the cobalt atom of the asymmetric unit (half of the molecule) were located from a map of electron density (E map) for the best phase set (absolute figure of merit 1.13) obtained by MULTAN.[7] Least-squares refinement of these atoms (two cycles) gave an R of 0.35. A difference Fourier synthesis revealed the nitrogen atoms and oxygen atom which occupy the coordination sphere around cobalt. Two subsequent repetitions of the least-squares refinement followed by difference Fourier synthesis revealed the positions of all of the remaining nonhydrogen atoms except for one carbon atom in each of the pyridyl rings. Positions for these atoms were calculated by assuming normal bond distances, angles, and ring planarity. Thereafter, the nonhydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated and included in the least-squares refinement, resulting in a significant improvement in the R index. Refinement of the hydrogen atom positions resulted in C–H bond distances of 0.9–1.0 Å and N–H distances of 0.8–0.9 Å; therefore, the hydrogen atom positions were fixed at C–H distances of 1.1 Å and N–H distances of 1.0 Å. All hydrogen atoms were arbitrarily assigned isotropic temperature factors (β_{iso}) of 3.5 $Å^2$. Three final cycles of least-squares refinement converged the structure at R_F = 0.045 and R_{wF} = 0.056 for 226 variables. The R values were calculated as $R_F = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$ with the reflections weighted as $w = 1/\sigma^2(F_o) = 4F_o^2/[\sigma(F_o^2)]^2$, where $\sigma(F_o^2) = [\sigma^2(I) + (0.03I)^2]^{1/2}/Lp$. The function minimized was $\sum w(|F_o| - |F_c|)^2$. The final difference map was featureless.

Results

Structure of the Dioxygen Complex. The structure consists of binuclear cations $[LCo{-}O{-}O{-}CoL]^{4+}$ and iodide counterions. No solvent molecules are present in the crystal. Positional and thermal parameters for all atoms are included in Table I.

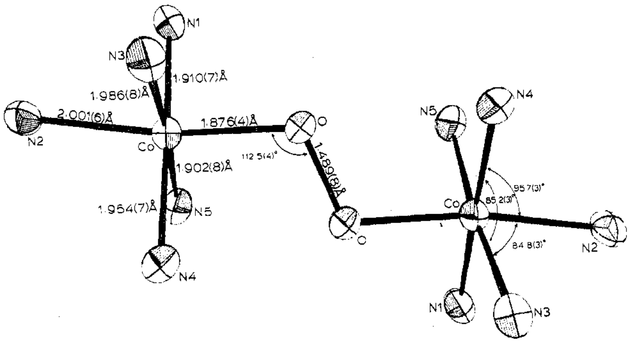

Figure 1. ORTEP[15] drawing of the coordination spheres around the cobalt atoms showing bond distances and selected angles. Thermal ellipsoids are shown at the 50% probability level.

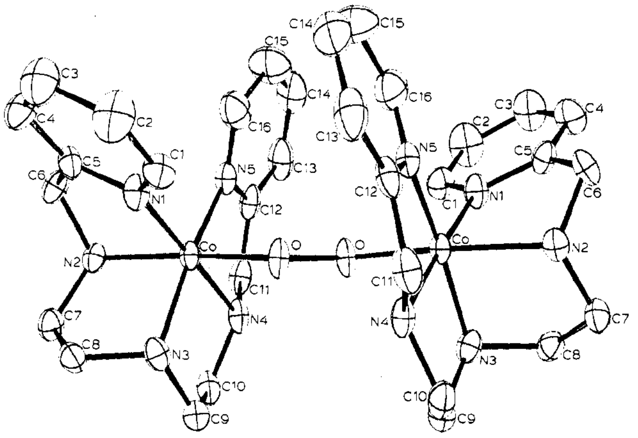

Figure 2. View of the complex cation $[Co(PYDIEN)]_2O_2^{4+}$. Thermal ellipsoids are shown at the 50% probability level.

The binuclear cation consists of cobalt(III) chelates linked together by a peroxide bridge. The peroxo nature of the dioxygen bridge is confirmed by the O–O distance (1.489 (8) Å). This value is very close to the bond distance previously reported for μ-peroxo-bis[(ethylenediamine)(diethylenetriamine)cobalt(III)] perchlorate (O–O = 1.488 (6) Å[5]), decaammine-μ-peroxo-dicobalt disulfate tetrahydrate (O–O = 1.47 Å[8]), and hydrogen peroxide (O–O = 1.48 (1) Å[9]). The halves of the molecule are crystallographically identical. Figure 1 illustrates the coordination shells of the complex cation.

The ligand forms exclusively five-membered chelate rings on binding to cobalt. There are very considerable distortions from octahedral geometry, although these distortions are not much larger than those observed in previously reported structures.[4–6,8,10] The pyridyl rings are cis to one another and to the dioxygen bridge. Trans to the dioxygen bridge is one of the aliphatic amino nitrogens (not the central amino nitrogen). The geometric arrangement of the ligands can be seen clearly in Figure 2. The present structure provides further confirmation of our previous observation[4] that the Co to trans N bond in μ-peroxo dicobalt complexes is lengthened (in comparison with Co to equatorial N bond distances) as the result of a trans effect exerted by dioxygen. Bond distances and angles of interest are given in Tables II and IV.

Figure 3 is an illustration of the complete unit cell. All four pyridyl rings are on the same side of the binuclear cation. Also visible in this illustration are close contacts between I2 and the hydrogen atoms bound to N2 and N3, probably the result of ion-dipole interactions. Close contacts between iodide anions and ligand nitrogen atoms are summarized in Table III.

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I1	0.44577 (2)	0.28972 (2)	0.0169 (1)	0.00131 (1)	0.00077 (1)	0.00931 (6)	0.00021 (1)	−0.00143 (5)	−0.00045 (4)
I2	0.05046 (3)	0.61074 (2)	0.0574 (1)	0.00116 (1)	0.00065 (1)	0.01776 (12)	−0.00044 (1)	0.00014 (6)	−0.00146 (5)
Co	0.33330 (4)	0.76301 (3)	0.0196 (1)	0.00052 (1)	0.00041 (1)	0.0071 (1)	−0.00007 (2)	−0.00003 (8)	−0.00014 (7)
O	0.2716 (2)	0.7354 (2)	0.0294 (8)	0.00049 (7)	0.00044 (5)	0.0125 (8)	0.0001 (1)	0.0005 (5)	−0.0001 (4)
N1	0.3608 (3)	0.7191 (2)	−0.0854 (10)	0.00074 (10)	0.00044 (6)	0.0103 (10)	−0.0002 (1)	0.0001 (6)	−0.0003 (5)
N2	0.4039 (3)	0.7837 (2)	0.0187 (10)	0.00071 (8)	0.00046 (6)	0.0081 (8)	0.0000 (1)	0.0006 (6)	−0.0011 (4)
N3	0.3522 (3)	0.7361 (2)	0.1902 (9)	0.00080 (10)	0.00054 (7)	0.0091 (9)	−0.0002 (1)	−0.0010 (6)	0.0002 (5)
N4	0.3068 (3)	0.8075 (2)	0.1315 (10)	0.00059 (9)	0.00050 (7)	0.0113 (10)	0.0001 (1)	−0.0002 (6)	−0.0003 (5)
N5	0.3124 (3)	0.7973 (2)	−0.1241 (10)	0.00060 (9)	0.00063 (7)	0.0094 (10)	−0.0001 (1)	0.0004 (5)	0.0003 (5)
C1	0.3391 (4)	0.6816 (3)	−0.110 (1)	0.0010 (1)	0.00067 (9)	0.009 (1)	−0.0003 (2)	−0.0005 (7)	−0.0017 (6)
C2	0.3602 (5)	0.6526 (3)	−0.190 (2)	0.0017 (2)	0.00060 (9)	0.019 (2)	−0.0001 (2)	0.0010 (11)	−0.0024 (8)
C3	0.4059 (5)	0.6613 (3)	−0.251 (2)	0.0014 (2)	0.00088 (11)	0.016 (2)	0.0000 (2)	0.0008 (10)	−0.0022 (9)
C4	0.4288 (4)	0.6995 (3)	−0.222 (1)	0.0013 (1)	0.00083 (10)	0.011 (1)	0.0003 (2)	0.0017 (9)	−0.0016 (7)
C5	0.4058 (3)	0.7274 (3)	−0.141 (1)	0.0007 (1)	0.00063 (8)	0.009 (1)	0.0003 (2)	−0.0009 (6)	−0.0009 (5)
C6	0.4264 (4)	0.7689 (3)	−0.110 (1)	0.0009 (1)	0.00063 (8)	0.010 (1)	−0.0003 (2)	0.0023 (7)	0.0002 (6)
C7	0.4312 (4)	0.7691 (3)	0.139 (1)	0.0007 (1)	0.00072 (9)	0.009 (1)	−0.0003 (2)	0.0003 (6)	0.0005 (6)
C8	0.4067 (4)	0.7294 (3)	0.193 (1)	0.0009 (1)	0.00077 (9)	0.007 (1)	0.0002 (2)	−0.0010 (6)	0.0001 (5)
C9	0.3313 (3)	0.7606 (4)	0.303 (1)	0.0008 (1)	0.00112 (11)	0.008 (1)	0.0002 (2)	−0.0000 (7)	0.0004 (6)
C10	0.3290 (3)	0.8061 (3)	0.265 (1)	0.0007 (1)	0.00084 (9)	0.011 (1)	0.0002 (2)	0.0006 (7)	−0.0016 (7)
C11	0.3091 (3)	0.8468 (3)	0.058 (1)	0.0008 (1)	0.00049 (7)	0.013 (1)	0.0000 (2)	0.0010 (7)	−0.0002 (6)
C12	0.2997 (3)	0.8371 (3)	−0.087 (1)	0.0007 (1)	0.00057 (8)	0.012 (1)	−0.0001 (2)	0.0015 (7)	0.0016 (6)
C13	0.2785 (4)	0.8647 (3)	−0.176 (2)	0.0010 (1)	0.00090 (10)	0.018 (2)	0.0003 (2)	0.0004 (10)	0.0034 (7)
C14	0.2685 (5)	0.8517 (4)	−0.305 (2)	0.0014 (2)	0.00145 (13)	0.016 (2)	0.0006 (3)	0.0004 (9)	0.0061 (7)
C15	0.2809 (6)	0.8128 (5)	−0.341 (2)	0.0024 (3)	0.00159 (16)	0.011 (2)	0.0001 (4)	−0.0009 (12)	0.0033 (9)
C16	0.3032 (4)	0.7846 (4)	−0.246 (2)	0.0012 (2)	0.00125 (13)	0.013 (2)	−0.0005 (2)	−0.0004 (9)	0.0013 (9)

atom	x	y	z	β_{iso}, Å^2	atom	x	y	z	β_{iso}, Å^2
H1	0.3020 (0)	0.6754 (0)	−0.0684 (0)	3.5000 (0)	H12	0.3557 (0)	0.7566 (0)	0.3891 (0)	3.5000 (0)
H2	0.3420 (0)	0.6222 (0)	−0.2060 (0)	3.5000 (0)	H13	0.3054 (0)	0.8239 (0)	0.3342 (0)	3.5000 (0)
H3	0.4233 (0)	0.6386 (0)	−0.3230 (0)	3.5000 (0)	H14	0.3665 (0)	0.8202 (0)	0.2610 (0)	3.5000 (0)
H4	0.4663 (0)	0.7066 (0)	−0.2641 (0)	3.5000 (0)	H15	0.2802 (0)	0.8683 (0)	0.0918 (0)	3.5000 (0)
H5	0.4675 (0)	0.7671 (0)	−0.1049 (0)	3.5000 (0)	H16	0.3461 (0)	0.8607 (0)	0.0667 (0)	3.5000 (0)
H6	0.4169 (0)	0.7906 (0)	−0.1951 (0)	3.5000 (0)	H17	0.2695 (0)	0.8971 (0)	−0.1466 (0)	3.5000 (0)
H7	0.4707 (0)	0.7638 (0)	0.1109 (0)	3.5000 (0)	H18	0.2484 (0)	0.8725 (0)	−0.3781 (0)	3.5000 (0)
H8	0.4294 (0)	0.7944 (0)	0.2125 (0)	3.5000 (0)	H19	0.2792 (0)	0.8021 (0)	−0.4531 (0)	3.5000 (0)
H9	0.4177 (0)	0.7025 (0)	0.1304 (0)	3.5000 (0)	H20	0.2909 (0)	0.7986 (0)	−0.3443 (0)	3.5000 (0)
H10	0.4195 (0)	0.7239 (0)	0.2953 (0)	3.5000 (0)	H21	0.4045 (0)	0.8152 (0)	0.0137 (0)	3.5000 (0)
H11	0.2935 (0)	0.7491 (0)	0.3257 (0)	3.5000 (0)	H22	0.3352 (0)	0.7083 (0)	0.1863 (0)	3.5000 (0)
					H23	0.2701 (0)	0.8002 (0)	0.1394 (0)	3.5000 (0)

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

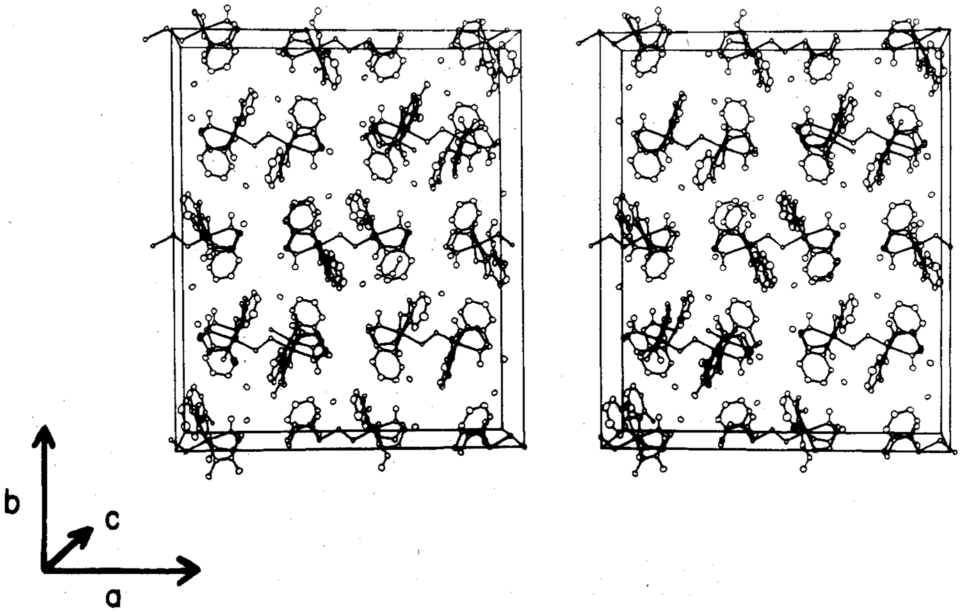

Figure 3. Stereodiagram of one unit cell showing the packing of the complex cations and the iodide anions. The view is down the c axis with the b axis vertical.

Comparison with the Structure of $[Co(PYDPT)]_2O_2I_4 \cdot 3H_2O$.[4] The geometry about the cobalt ion is distorted octahedral in the complexes of both PYDIEN and PYDPT. Both PYDIEN and PYDPT wrap around the cobalt ion in the same manner. In addition, all four pyridyl rings are on the same side of the binuclear complex cation in both the PYDIEN and PYDPT complexes, perhaps due to hydrophobic interactions between the pyridyl rings. These facts indicate that

Table II. Selected Bond Distances and Bond Angles and Their Standard Deviations

(a) Bond Distances (Å)

N1–C1	1.365 (10)	N5–C16	1.311 (15)
C1–C2	1.351 (14)	C16–C15	1.446 (17)
C2–C3	1.398 (16)	C15–C14	1.342 (19)
C3–C4	1.404 (13)	C14–C13	1.383 (21)
C4–C5	1.360 (12)	C13–C12	1.386 (14)
C5–N1	1.353 (10)	C12–N5	1.377 (11)
C5–C6	1.477 (12)	C12–C11	1.506 (16)
C6–N2	1.507 (11)	C11–N4	1.468 (11)
N2–C7	1.486 (12)	N4–C10	1.471 (14)
C7–C8	1.537 (13)	C10–C9	1.515 (13)
C8–N3	1.472 (10)	C9–N3	1.491 (12)

(b) Bond Angles (deg)

O1–Co1–N1	91.0 (2)	N1–Co1–N5	97.1 (3)
O1–Co1–N2	170.8 (2)	N2–Co1–N3	84.8 (3)
O1–Co1–N3	88.4 (3)	N2–Co1–N4	95.7 (3)
O1–Co1–N4	89.9 (3)	N2–Co1–N5	94.6 (3)
O1–Co1–N5	93.2 (3)	N3–Co1–N4	85.1 (3)
N1–Co1–N2	83.2 (3)	N3–Co1–N5	169.6 (3)
N1–Co1–N3	93.2 (3)	N4–Co1–N5	84.6 (3)
N1–Co1–N4	178.1 (3)	Co–O–O	122.5 (4)
C5–N1–C1	118.5 (7)	C12–N5–C16	119.8 (9)
N1–C1–C2	122.8 (8)	N5–C16–C16	119.8 (11)
C1–C2–C3	119.1 (9)	C16–C15–C14	120.6 (12)
C2–C3–C4	117.8 (10)	C1–C14–C13	119.1 (11)
C3–C4–C5	120.3 (9)	C14–C13–C12	119.3 (11)
C4–C5–N1	121.4 (8)	C13–C12–N5	121.4 (11)
C4–C5–C6	123.7 (8)	C13–C12–C11	124.0 (9)
N1–C5–C6	114.9 (7)	N5–C12–C11	114.5 (8)
C5–C6–N2	108.6 (7)	C12–C11–N4	107.6 (7)
C6–N2–C7	113.6 (6)	C11–N4–C10	118.2 (7)
C8–N3–C9	115.7 (7)		

Table III. Nitrogen–Iodide Close Contacts and N-H-I Distances and Angles

(a) Distances (Å)

I1–N2[a]	4.664 (6)	I2–H21[f]	2.707
I1–N3[b]	4.475 (7)	I2–H22[g]	2.699
I2–N2[c]	3.631 (5)		
I2–N3[d]	3.608 (6)		
I2–N4[e]	3.780 (7)		

(b) Angles (deg)

I2–H21[f]–N2	151.5	I2–H22[g]–N3	150.7

[a] N2 at $1 - x$, $1 - y$, z. [b] N3 at x, $y - {}^1/_2$, $z - {}^1/_2$. [c] N2 at ${}^1/_2 - x$, ${}^3/_2 - y$, z. [d] N3 at $x - {}^1/_4$, ${}^5/_4 - y$, $z - {}^1/_4$. [e] N4 at ${}^1/_4 - x$, $y - {}^1/_4$, $z - {}^1/_4$. [f] H21 at ${}^1/_2 - x$, ${}^3/_2 - y$, z. [g] H22 at $x - {}^1/_4$, ${}^5/_4 - y$, $z - {}^1/_4$.

the interactions between the ligand donor atoms and the cobalt ion and the interactions between the halves of the complex cation are qualitatively the same for the oxygen complexes of the two ligands. Differences in the extent of the interaction between ligand donor atoms and the cobalt ion can be observed, however, in the bond distances and angles.

The Co to pyridyl nitrogen bond distances are shorter[11] in the present structure than in the PYDPT complex. All of the remaining Co–N bonds are also somewhat shorter in the present structure, but the differences are not statistically significant.[11] The O–O bond is definitely longer in the PYDIEN-containing complex and the Co–O bond appears shorter, although the difference in Co–O bond lengths is only marginally significant.[11] Table IV gives the Co–O and O–O bond distances for both the PYDIEN and the PYDPT cobalt–dioxygen complexes in a form which simplifies comparison.

The angles around aliphatic carbon atoms are closer to the tetrahedral angle of 109.5° in the oxygen complex of PYDIEN than in that of PYDPT (Table V). Comparison of the shapes of the thermal ellipsoids of the carbon and nitrogen atoms indicates that the atoms of the PYDPT ligand, especially those involved in the six-membered chelate rings, are more constrained in their motion than are the corresponding atoms of PYDIEN. The Co–O–O angle is smaller in the PYDIEN complex (112.5 (4)°) than in the PYDPT complex (114.3 (5)° and 115.4 (5)°). Other angles for which comparison is of interest are the N–Co–N angles involving only aliphatic nitrogen atoms and the O–Co–trans N angles. These angles are given for both complexes in Table VI.

Discussion

The complex $[Co^{II}(PYDPT)]^{2+}$ has a greater affinity for dioxygen than does the analogous PYDIEN complex, indicating that the oxygen complex $[Co(PYDPT)]_2O_2^{4+}$ is considerably less stable than the oxygen complex $[Co(PYDIEN)]_2O_2^{4+}$.[1] A large difference is to be expected if the *overall* stability constants (eq 1) are compared, since the larger

$$K_{O_2}' = [(CoL)_2O_2^{4+}]/([Co^{2+}]^2[L]^2[O_2]) \qquad (1)$$

chelate rings formed by PYDPT lower the stability of the $[Co(PYDPT)]^{2+}$ complex. The constants compared, however, describe the reaction of dioxygen with the *preformed* Co(II)–ligand complex (eq 2). These constants are a measure

$$K_{O_2} = [(CoL)_2O_2^{4+}]/([CoL^{2+}][O_2]) \qquad (2)$$

of oxygen affinity and should be affected only by the extent

Table IV. Comparison of Bond Distances for $[Co(PYDIEN)]_2O_2^{4+}$ and $[Co(PYDPT)]_2O_2^{4+}$ (Å)

compd	O–O	Co–O	N1–Co	N2–Co	N3–Co	N4–Co	N5–Co
$[Co(PYDIEN)]_2O_2^{4+}$	1.489 (8)	1.876 (4)	1.910 (7)	2.001 (6)	1.986 (8)	1.954 (7)	1.902 (8)
$[Co(PYDPT)]_2O_2^{4+}$ [a]	1.456 (9)	1.888 (6)	1.948 (9)	2.006 (8)	2.002 (7)	1.964 (8)	1.945 (8)
		1.894 (6)	1.928 (7)[b]	2.009 (8)[c]	1.986 (8)[d]	1.958 (7)[e]	1.982 (9)[f]

[a] Values from ref 7. [b] N6–Co. The numbering difference arises because the halves of $[Co(PYDPT)]_2O_2^{4+}$ are not crystallographically identical. Only bonds to atoms occupying identical positions in the coordination sphere are compared. [c] N7–Co. [d] N8–Co. [e] N9–Co. [f] N10–Co.

Table V. Comparison of Bond Angles around Aliphatic Carbons in $[Co(PYDIEN)]_2O_2^{4+}$ and $[Co(PYDPT)]_2O_2^{4+}$ (deg)

PYDIEN		PYDPT			
atoms	angle	atoms	angle	atoms	angle
N2–C7–C8	109.9 (7)	N2–C7–C8	114.1 (10)[a]	N7–C25–C26[b]	114.9 (9)[a]
		C7–C8–C9	116.8 (11)[a]	C25–C26–C27[b]	115.7 (10)[a]
C7–C8–N3	107.1 (7)	C8–C9–N3	117.6 (9)[a]	C26–C27–N8[b]	116.0 (9)[a]
N3–C9–C10	109.7 (8)	N3–C10–C11	113.2 (10)[a]	N8–C28–C29[b]	113.2 (10)[a]
		C10–C11–C12	110.2 (11)[a]	C28–C29–C30[b]	112.2 (10)[a]
C9–C10–N4	105.9 (8)	C11–C12–N4	111.4 (9)[a]	C29–C30–N8[b]	109.6 (11)[a]

[a] Values from ref 7. [b] These atom designations result from the fact that the halves of $[Co(PYDPT)]_2O_2^{4+}$ are not crystallographically identical. Only analogous angles are compared.

Table VI. Comparison of Bond Angles around the Cobalt Ion in $[Co(PYDIEN)]_2O_2^{4+}$ and $[Co(PYDPT)]_2O_2^{4+}$ (deg)

PYDIEN		PYDPT			
atoms	angle	atoms	angle	atoms	angle
N2-Co-N3	84.8 (3)	N2-Co-N3	92.07 (35)[a]	N7-Co-N8[b]	93.48 (34)[a]
N2-Co-N4	95.7 (3)	N2-Co-N4	98.80 (37)[a]	N7-Co-N9[b]	96.73 (34)[a]
N3-Co-N4	85.1 (3)	N3-Co-N4	95.87 (34)[a]	N8-Co-N9[b]	96.87 (33)[a]
N2-Co-O	170.8 (2)	N2-Co-O1	173.32 (31)[a]	N7-Co-O2[b]	174.56 (3)[a]

[a] Values from ref 7. [b] These atom designations result from the fact that the halves of $[Co(PYDPT)]_2O_2^{4+}$ are not crystallographically identical. Only analogous angles are compared.

Table VII. Comparison of Oxygen to Equatorial Nitrogen Distances (Nonbonded) in $[Co(PYDIEN)]_2O_2^{4+}$ and $[Co(PYDPT)]_2O_2^{4+}$ (Å)

PYDIEN		PYDPT			
atoms	dist	atoms	dist	atoms	dist
N1-O	2.701	N1-O1	2.719	N6-O2[a]	2.746
N3-O	2.693	N3-O1	2.652	N8-O2[a]	2.630
N4-O	2.713	N4-O1	2.672	N9-O2[a]	2.693
N5-O	2.745	N5-O1	2.792	N10-O2[a]	2.850
av	2.713	av	2.709	av	2.730

[a] These atom designations result from the fact that the halves of $[Co(PYDPT)]_2O_2^{4+}$ are not crystallographically identical. Only analogous distances are compared.

of electron donation from cobalt to dioxygen and by any steric factors that might hinder the close approach of dioxygen to the cobalt atom. It thus appears that the two additional methylene groups of PYDPT and the correspondingly larger size of the chelate rings formed by PYDPT must affect either the steric environment of dioxygen or the ability of the cobalt atom to donate electron density to dioxygen.

Steric factors which may hinder oxygenation should be observed in the oxygen to equatorial nitrogen distances. Table VII gives these values for both complexes. The values are essentially constant in the PYDIEN complex, the maximum variation being only 0.05 Å. Two distances in the PYDPT complex (N3-O1 and N8-O2) are shorter than the corresponding distance in the PYDIEN complex by 0.04 and 0.06 Å, respectively. Other distances in the PYDPT complex (N5-O1 and N10-O2) are longer than the corresponding distance in the PYDIEN complex by 0.05 and 0.09 Å, respectively. The average oxygen to equatorial nitrogen distance is approximately the same in each case. One could argue that these distances would be somewhat shorter in the PYDPT complex if the Co–O distance were reduced to the value of 1.876 (4) Å observed in the PYDIEN complex. With or without this argument, however, the structural data do not conclusively demonstrate that the Co–O distance is lengthened by steric factors.

Reduced donation from nitrogen to cobalt should result in a reduction in the stability of the oxygen complex, since donor ability has already been shown to be the major factor affecting oxygen complex stability, as measured by K_{O_2} (eq 2).[2b,12] Cobalt donates electron density to the π^* antibonding orbital of O_2, so that the O–O bond length should be reduced if the electron donation from cobalt to dioxygen is decreased in the compound containing the larger chelate rings. Reduced electron donation should also weaken, and thus lengthen, the Co–O bonds. Larger chelate rings could reduce nitrogen to cobalt coordination by preventing the donor atoms from moving inward toward the cobalt ion and attaining optimum Co–N bond distances.

The structural data obtained for the cobalt–dioxygen complexes of PYDIEN and PYDPT provide considerable support for the hypothesis outlined above. An increase in the Co to pyridyl N distances on moving from the PYDIEN complex to the PYDPT complex indicates that the presence of additional methylene groups does result in longer Co–N distances. The shorter O–O distance and longer Co–O distances in the PYDPT complex demonstrate a reduced donation of electron density from the cobalt ion to the dioxygen moiety in this complex. In addition, the Co–O–O angles in the PYDPT complex are much larger than the Co–O–O angle in the PYDIEN complex. This is consistent with a reduction in the peroxide character of the dioxygen ligand[13] in the PYDPT complex, a result which is expected if the electron donation from the cobalt ion to dioxygen is reduced. The data given here do not, however, conclusively establish this hypothesis.

The question of how the chelate ring size might exert its effect on the Co to pyridyl N distances remains. At first glance, one might expect the aliphatic N distances to increase, since these nitrogen atoms are involved in the six-membered chelate rings. This reasoning is fallacious. The aliphatic nitrogen atoms are much better σ donors than the pyridyl nitrogen atoms. Lengthening of the cobalt–aliphatic nitrogen bonds would, for this reason, have a much greater effect on oxygen complex stability than does lengthening of the Co to pyridyl nitrogen bonds. Thus, the ligand will adjust to allow optimum bonding between cobalt and aliphatic nitrogen atoms at the expense of bonding between cobalt and pyridyl nitrogen atoms. The cobalt to nitrogen bonds cannot all attain their optimum bond lengths since the bonds between atoms in the six-membered rings would then be prohibitively strained. Indeed, the nonideal bond angles around carbon atoms in the six-membered chelate rings of the PYDPT complex indicate that the bonds of the chelate ring were strained in this complex. The N–Co–N angles which involve only aliphatic nitrogens provide support for the suggestion that the ligand is adjusting to allow maximum cobalt–aliphatic nitrogen bonding. These angles are much larger in the PYDPT complex than in the PYDIEN complex. The aliphatic nitrogens are required to move farther apart and occupy more of the surface of the cobalt coordination "sphere" in order to bind maximally without causing an undue increase in bonding strain for the bonds of the six-membered chelate rings.

The explanations presented in this paper appear reasonable, but the structural data presented do not strongly favor either explanation. The observed destabilization may be due to a combination of these factors. Structural details obtained on these complexes are also insensitive to a number of additional factors which might reduce the stability of the dioxygen complex of cobaltous PYDPT in solution. It is unlikely, however, that bond distances and angles will be significantly different in aqueous solution than they are in the crystalline state. The close similarity of the two complexes makes any difference in solvent effects equally unlikely. The explanations given are thus the only ones presently available which are consistent both with the observed solution chemistry and with the structural details of the crystalline dioxygen complexes.

The ideas expressed here may be applicable to at least one other reported structure, that of μ-peroxo-bis[(3,3′-diamino-di-*n*-propylamine)bis(salicylaldehyde)cobalt(III)] perchlorate.[6] This complex forms four six-membered metal–chelate rings. The O–O distance is relatively short (1.45 Å), and the Co–O distance relatively long (1.93 Å). In addition, the Co–O–O angle of 118.5° is quite large. It thus appears that the six-membered chelate rings may be destabilizing this complex in a manner analogous to that in which the cobalt–dioxygen complex of PYDPT is destabilized, but it is also possible that the use of O donors in place of N donors may be responsible for the structural features cited.

Calorimetric studies of the oxygenation of cobaltous PYDIEN and PYDPT and of the cobaltous complexes of other similar ligands are presently being undertaken to provide further information about the thermodynamics of oxygenation in solution and the factors influencing the metal–dioxygen affinities in complexes of this type. Studies of the oxygenation equilibria for cobaltous complexes of terdentate and tetradentate ligands which form six-membered chelate rings with cobalt are planned. Such studies will indicate whether the effect of chelate ring size on the stability of dioxygen complexes is a general phenomenon or one peculiar to complexes containing pentadentate ligands.

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Registry No. $[Co(PYDIEN)]_2O_2I_4$, 71230-49-4; **1**, 58214-73-6; 2-pyridinecarboxaldehyde, 1121-60-4; bis(2-aminoethyl)amine, 111-40-0.

Supplementary Material Available: A table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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(13) Compare, for example, the Co–O–O angle of 120.7 (10) and 121.8 (7)° in a typical superoxo complex, potassium decacyano-μ-superoxodicobalt(III) monohydrate,[14] with the Co–O–O angle of 110.0 (3)° in a typical peroxo complex, μ-peroxo-bis[(ethylenediamine)(diethylenetriamine)cobalt(III)] perchlorate.[5] An increase in the charge on dioxygen is seen to result in a decrease in the Co–O–O angle.

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New Multidentate Ligands. 18. Synthesis of 1,4-Bis(bis(2-aminoethyl)aminomethyl)benzene: Binuclear Chelating Tendencies and Mixed-Ligand Binuclear Chelate Formation

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The synthesis of 1,4-bis(bis(2-aminoethyl)aminomethyl)benzene hexahydrochloride (PXBDE) and the aqueous solution equilibria of this new hexadentate ligand with Cu(II), Ni(II), Co(II), and Zn(II) in both the presence and the absence of auxiliary bidentate ligands are described. At 25 °C and 0.10 M ionic strength, the protonation constants for PXBDE are 10.06, 9.71, 9.11, 8.57, 1.8, and 1.2 log units. The log K values of the 1:1 metal chelate stability constants ($K = [MH_2L]/[M][H_2L]$) are 13.21, 9.20, 6.84, and 7.19 with the above metals, respectively. For some metal ions at higher pH less protonated forms of the metal chelate, MHL^{3+} and ML^{2+}, are also found. ML^{2+} reacts with excess metal ion to form a binuclear complex (M_2L^{4+}), while in <0.001 M solutions excess PXBDE fails to form a 1:2 metal–ligand complex with any of the above metal ions. PXBDE was found to form mixed-ligand complexes in the presence of metal ions and such bidentate ligands as ethylenediamine and glycine. The logarithms of the equilibrium formation constants for the most fully coordinated glycine species, $\beta = [M_2L'_2L]/[M]^2[L']^2[L]$, where L′ = glycine, L = PXBDE, and M = Cu(II), Ni(II), Co(II), or Zn(II), are 37.96, 30.16, 23.38, and 25.56, respectively. Similarly when L′ = ethylenediamine, the corresponding constants are 40.18, 31.68, 23.32, and 27.08. The probable arrangements of the coordination sites in the complexes studied and possible applications of the mixed-ligand systems are discussed.

Introduction

Ligands with two multidentate moieties separated by a rigid bridge such as *p*- or *m*-xylene form binuclear complexes in which the metal ions are held apart at a sufficient distance such that the two groups of donor atoms could not coordinate to the same metal ion, and the binuclear complexes would thus be stable relative to other types of coordinate bond arrangement. However, by appropriate adjustment of the size of the ligand backbone, the metal–metal distance would be rendered suitable for binding a small molecule or ion simultaneously to both coordinated metal centers. Binuclear complexes of "wishbone" ligands of this type may provide interesting models for studying catalytic reactions of biological systems in which concerted effects of both metal ions are involved. The first ligand to be synthesized with this idea in mind, *P,P,P′,P′*-tetrakis(2-diphenylphosphinoethyl)-α,α'-diphospha-*p*-xylene, was reported by Taqui Khan and Martell[1] and was shown to preferentially form binuclear chelates of Ru(II), Rh(I), and Ir(I). A similar bis-tetradentate ligand,[2] containing amino oxygen ether and thioether donor groups,

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