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Structure of [2,6-Bis(3,6-diazahex-2-yl)pyridine]iodocobalt(III) Iodide Dihydrate

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Abstract. $[\text{CoI}(\text{C}_{13}\text{H}_{25}\text{N}_5)]\text{I}_2 \cdot 2\text{H}_2\text{O}$, $M_r = 726.6$, monoclinic, $P2_1/c$, $a = 12.201$ (4), $b = 16.300$ (4), $c = 11.245$ (2) Å, $\beta = 92.18$ (2)°, $V = 2235$ (2) Å³, $Z = 4$, $D_x = 2.161$ g cm⁻³, $\lambda(\text{MoK}\alpha) = 0.71073$ Å, $\mu = 50.02$ cm⁻¹, $F(000) = 1376$, $T = 296$ K, $R = 0.044$ for 1994 unique observed data. The Co atom is octahedrally coordinated by the five N atoms of the organic ligand. The sixth position, *trans* to the pyridyl nitrogen, is coordinated by an iodine. The remaining iodines and water molecules form an intermolecular hydrogen-bonding network throughout the structure.

Introduction. The pentamine ligand epyden [2,6-bis(3,6-diazahex-2-yl)pyridine] forms a cobalt(II) complex which has a high affinity for dioxygen (Harris, Murase, Timmons & Martell, 1978), readily forming the complex $[\text{Co}_2(\text{epyden})_2\text{O}_2]^{4+}$ in aqueous solution at and above pH 4. An attempt to crystallize this dioxygen complex from a concentrated aqueous solution in the presence of iodide (to supply a large anion) resulted in displacement of the peroxide and crystallization of $[\text{Co}(\text{epyden})\text{I}]^{2+} \cdot 2\text{I}^- \cdot 2\text{H}_2\text{O}$ (Raleigh, 1984). This iodo-pentamine cobalt(III) complex is a new compound and the determination of its crystal structure is now described.

Experimental. 5.0 ml of a solution of 1.2 mmol of epyden.4HCl and 1.2 mmol of CoI_2 was adjusted to pH 5.6 and exposed to atmospheric oxygen. The dioxygen complex formed immediately, as indicated by its intense brown color. After the solution had been allowed to stand for 60 h at 288 K, the dark-red

crystals that formed were filtered off and examined for suitability for X-ray single-crystal structure analysis. Density not measured.

Dark-red equidimensional crystal cut to size ca 0.2 mm side, CAD-4 automated diffractometer, cell parameters from 25 centered medium- and high-angle reflections. Scans by θ - 2θ method, scan speed 2–20° min⁻¹, step width $A + 0.347(\tan\theta_{\lambda_{a2}})$ where $\theta_{\lambda_{a2}}$ is determined from $\theta_{\lambda_{a2}} = \theta_{\lambda_{a1}} + (\lambda_{a2} - \lambda_{a1})/\lambda_{a1} \cdot (360/2\pi)^\circ \tan\theta_{\lambda_{a1}}$ and A depends on the crystal mosaic spread and on the divergence of the primary beam, $A = 0.7^\circ$. Standard reflections every 110 measured, no drop-off in intensity. No absorption correction as crystal shape regular. Intensities calculated as $I = S(C - RB)$, where S = scan rate, C = total integrated peak count, B = total background count, and R = ratio of the scan time for the peak to the scan time for the background; estimated error calculated as $\sigma(I) = [S^2(C + R^2B) + (pI)^2]^{1/2}$ where the value of p was 0.05. Lorentz and polarization corrections applied. Weights as $1/\sigma(F_o)^2$ applied. Neutral-atom scattering factors used (Cromer & Waber, 1974), and metal atom corrected for both real and imaginary anomalous dispersion (Cromer, 1974). A total of 2878 unique data collected with $0 < 2\theta < 46^\circ$ ($h = 0-12$; $k = 0-17$; $l = -13-13$), 884 unobserved [$I < 3\sigma(I)$]. Absences: $0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$. Direct methods for two iodine positions, remaining structure by full-matrix least-squares refinement of F magnitudes with positional and anisotropic thermal parameters and difference Fourier techniques. H atoms not located. $R = 0.044$, $wR = 0.055$, $S = 1.47$. Final $\Delta/\sigma < 1.0$. Final difference Fourier map, random ripples $< 0.3 \text{ e } \text{Å}^{-3}$. PDP11/60 computer with programs from Enraf-Nonius SDP (Enraf-Nonius, 1975).

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Table 1. Positional and equivalent isotropic thermal parameters with their e.s.d.'s in parentheses

	x	y	z	B _{eq} * (Å ²)
I(1)	0.54488 (7)	0.14608 (6)	0.48938 (9)	3.59 (2)
I(2)	0.75875 (8)	0.36132 (6)	0.42960 (9)	4.13 (2)
I(3)	0.17327 (8)	0.20347 (6)	0.53753 (9)	4.21 (2)
Co	0.6906 (1)	0.0815 (10)	0.3531 (1)	2.35 (3)
O(1)	0.3452 (7)	0.0017 (6)	0.2784 (8)	4.4 (2)
O(2)	0.2265 (12)	0.1420 (8)	0.2472 (13)	9.0 (4)
N(1)	0.6508 (8)	0.1650 (6)	0.2310 (9)	3.1 (2)
N(2)	0.5850 (7)	0.0072 (6)	0.2656 (8)	2.4 (2)
N(3)	0.7902 (8)	0.0267 (6)	0.2592 (9)	2.6 (2)
N(4)	0.8206 (8)	0.1463 (6)	0.4071 (9)	2.9 (2)
N(5)	0.7305 (7)	0.0047 (6)	0.4843 (9)	2.6 (2)
C(1)	0.5420 (11)	0.1409 (8)	0.173 (1)	3.7 (3)
C(2)	0.5509 (10)	0.0491 (8)	0.149 (1)	3.2 (3)
C(3)	0.6481 (9)	-0.0711 (7)	0.240 (1)	2.7 (3)
C(4)	0.7607 (10)	-0.0441 (7)	0.208 (1)	2.7 (3)
C(5)	0.8321 (11)	-0.0882 (8)	0.140 (1)	3.6 (3)
C(6)	0.9434 (12)	0.0554 (9)	0.131 (1)	4.2 (3)
C(7)	0.9728 (10)	0.0177 (8)	0.189 (1)	3.2 (3)
C(8)	0.8957 (10)	0.0579 (8)	0.255 (1)	2.9 (3)
C(9)	0.9133 (10)	0.1351 (8)	0.326 (1)	3.3 (3)
C(10)	0.8470 (11)	0.1210 (8)	0.537 (1)	3.4 (3)
C(11)	0.8423 (10)	0.0268 (8)	0.536 (1)	3.5 (3)
C(31)	0.5879 (11)	-0.1258 (8)	0.145 (1)	4.5 (3)
C(91)	0.9319 (11)	0.2100 (8)	0.248 (1)	4.2 (3)

* B_{eq} is calculated from the anisotropic β's (program TEMPER, Enraf-Nonius, 1975).

Discussion. Positional and equivalent isotropic thermal parameters for the compound are given in Table 1.* Bond distances, angles and interesting torsional angles are presented in Table 2. An ORTEPII diagram (Johnson, 1976) of the complex, together with the numbering scheme employed, is given in Fig. 1. Atoms I(2), I(3), O(1) and O(2) are located in the lattice as 2I⁻ and 2H₂O. A single good least-squares plane is found through the pyridine ring with $\chi^2 = 7.0$.

There is a single molecule in the asymmetric unit and each molecule is linked to the next by a hydrogen-bonding network. The network comprises the coordinated N atoms, the iodine and the water molecules. I(2) is hydrogen-bonded by N(1) from one molecule below and by N(4) from one molecule above it in the unit cell. The I(2)-N distances are ca 3.65 Å and the link is mainly in the c direction. Similarly, N(2) from one molecule and N(5) from another are hydrogen-bond-linked via water molecule O(1). O-N distances are ca 2.9 Å and the bonds occur in the ac direction across the unit cell. Water molecule O(2) has three tetrahedral hydrogen-bonding contacts, I(3) (3.5 Å); I(3) symmetry related (3.5 Å); and O(1) (2.7 Å), this last one forming a symmetric hydrogen bond. This has the effect of forming a hydrogen-bonding network starting with

N(5)-I(3)-O(2)-I(3)-N(5), the O(2) linking by hydrogen bonding to O(1) which forms part of the other network. This I(3)···O(2) network is oriented basically in the ac direction.

Table 2. Important bond distances (Å), bond angles (°) and torsional angles (°)

Numbers in parentheses are e.s.d.'s in the least-significant digits. E.s.d.'s for torsional angles are of the order of 5 for the least-significant digit.

Co-N(1)	1.981 (8)	N(1)-I(1)	3.239 (9)
Co-N(2)	1.999 (8)	N(1)-I(2)	3.708 (9)
Co-N(3)	1.868 (8)	N(2)-I(1)	3.434 (8)
Co-N(4)	1.982 (8)	N(2)-O(1)	2.936 (11)
Co-N(5)	1.981 (8)	N(4)-I(1)	3.523 (8)
Co-I(1)	2.613 (2)	N(4)-I(2)	3.596 (8)
N(1)-C(1)	1.508 (13)	N(5)-I(1)	3.233 (8)
N(2)-C(2)	1.512 (13)	N(5)-I(3)	3.602 (8)
N(2)-C(3)	1.524 (12)	N(5)-O(1)	2.859 (11)
N(3)-C(4)	1.334 (12)	I(1)-N(1)	3.239 (9)
N(3)-C(8)	1.386 (13)	I(1)-N(2)	3.434 (8)
N(4)-C(9)	1.488 (13)	I(1)-N(4)	3.523 (8)
N(4)-C(10)	1.536 (14)	I(1)-N(5)	3.233 (8)
N(5)-C(11)	1.507 (13)	I(2)-N(1)	3.708 (9)
C(1)-C(2)	1.541 (15)	I(2)-N(4)	3.596 (8)
C(3)-C(4)	1.501 (14)	I(3)-N(2)	3.602 (8)
C(8)-C(9)	1.504 (15)	O(1)-N(2)	2.936 (11)
C(10)-C(11)	1.535 (15)	O(1)-N(5)	2.859 (11)

N(1)-Co-N(2)	86.5 (3)	C(4)-C(3)-C(31)	114.4 (9)
N(1)-Co-N(3)	94.8 (4)	N(3)-C(4)-C(3)	112.5 (9)
N(1)-Co-N(4)	91.0 (4)	N(3)-C(8)-C(9)	113.8 (9)
N(1)-Co-N(5)	175.7 (4)	N(4)-C(9)-C(8)	109.4 (8)
N(1)-Co-I(1)	88.6 (3)	N(4)-C(9)-C(91)	112.8 (9)
N(2)-Co-N(3)	81.6 (4)	C(8)-C(9)-C(91)	112.0 (1)
N(2)-Co-N(4)	165.2 (3)	N(4)-C(10)-C(11)	105.0 (9)
N(2)-Co-N(5)	96.9 (3)	N(5)-C(11)-C(10)	105.9 (9)
N(2)-Co-I(1)	95.3 (2)	I(1)-N(1)-I(2)	167.6 (3)
N(3)-Co-N(4)	84.1 (4)	I(1)-N(2)-O(1)	79.3 (2)
N(3)-Co-N(5)	88.4 (4)	I(1)-N(4)-I(2)	77.1 (2)
N(3)-Co-I(1)	175.2 (3)	I(1)-N(5)-I(3)	154.6 (3)
N(4)-Co-N(5)	86.4 (4)	I(1)-N(5)-O(1)	76.0 (3)
N(4)-Co-I(1)	99.2 (2)	I(3)-N(5)-O(1)	98.5 (3)
N(5)-Co-I(1)	88.4 (2)	N(1)-I(1)-N(2)	48.1 (2)
C(2)-N(2)-C(3)	109.4 (8)	N(1)-I(1)-N(4)	49.2 (2)
C(4)-N(3)-C(8)	122.6 (9)	N(1)-I(1)-N(5)	75.4 (2)
C(9)-N(4)-C(10)	114.1 (8)	N(2)-I(1)-N(4)	69.1 (2)
N(1)-C(1)-C(2)	105.3 (8)	N(2)-I(1)-N(5)	53.0 (2)
N(2)-C(2)-C(1)	107.5 (9)	N(4)-I(1)-N(5)	47.1 (2)
N(2)-C(3)-C(4)	105.9 (8)	N(1)-I(2)-N(4)	92.0 (2)
N(2)-C(3)-C(31)	112.3 (8)	N(2)-O(1)-N(5)	113.9 (3)

N(2)-Co-N(1)-C(1)	20.1	N(4)-Co-N(3)-C(8)	-7.8
N(3)-Co-N(1)-C(1)	101.3	N(5)-Co-N(3)-C(4)	79.8
N(4)-Co-N(1)-C(1)	-174.5	N(5)-Co-N(3)-C(8)	-94.4
N(5)-Co-N(1)-C(1)	-120.4	I(1)-Co-N(3)-C(4)	32.3
I(1)-Co-N(1)-C(1)	-75.3	I(1)-Co-N(3)-C(8)	-141.9
N(1)-Co-N(2)-C(2)	9.7	N(1)-Co-N(4)-C(9)	-79.2
N(1)-Co-N(2)-C(3)	126.9	N(1)-Co-N(4)-C(10)	155.7
N(3)-Co-N(2)-C(2)	-85.8	N(2)-Co-N(4)-C(9)	0.8
N(3)-Co-N(2)-C(3)	31.5	N(2)-Co-N(4)-C(10)	-124.2
N(4)-Co-N(2)-C(2)	-71.0	N(3)-Co-N(4)-C(9)	15.5
N(4)-Co-N(2)-C(3)	46.2	N(3)-Co-N(4)-C(10)	-109.5
N(5)-Co-N(2)-C(2)	-173.1	N(5)-Co-N(4)-C(9)	104.3
N(5)-Co-N(2)-C(3)	-55.9	N(5)-Co-N(4)-C(10)	-20.8
I(1)-Co-N(2)-C(2)	97.9	I(1)-Co-N(4)-C(9)	-168.0
I(1)-Co-N(2)-C(3)	-144.9	I(1)-Co-N(4)-C(10)	67.0
N(1)-Co-N(3)-C(4)	-103.1	N(1)-Co-N(5)-C(11)	-64.1
N(1)-Co-N(3)-C(8)	82.7	N(2)-Co-N(5)-C(11)	155.6
N(2)-Co-N(3)-C(4)	-17.4	N(3)-Co-N(5)-C(11)	74.3
N(2)-Co-N(3)-C(8)	168.4	N(4)-Co-N(5)-C(11)	-10.0
N(4)-Co-N(3)-C(4)	166.4	I(1)-Co-N(5)-C(11)	-109.3

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42523 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Inspection of the Co—N bond lengths shows a considerable shortening of the Co—N(3) distance of about 0.133 Å compared to an average Co—N distance of 1.986 (2) Å for those remaining. This shortening was not expected for the pyridine nitrogen which has relatively low basicity. Normal pyridine nitrogen donors have a Co—N distance between 2.04 and 1.94 Å (Clearfield, Gopal, Kline, Sipski & Urban, 1978; Bombieri, Forsellini, Del Pra & Tobe, 1980, 1981; Niederhoffer, Raleigh, Martell, Rudolf & Clearfield, 1982). A possible rationale for the shortened bond length may be attributed to another geometrical feature imposed by the pyridine ring. This effect is seen in the bond angles in the five-membered rings containing the pyridine nitrogen. Significant reductions in the trigonal bond angles are observed in the N(3)—C(4)—C(3) bond angle (112.5°) and in the N(3)—C(8)—C(9) bond angle (113.8°) as well as reduced octahedral bond angles in the N(2)—Co—N(3) bond angle (81.6°) and in the N(3)—Co—N(4) bond angle (84.1°). All other angles forming the five-membered chelate rings containing pyridine N(3) nitrogen are less than or close to the regular tetrahedral value. The Co—N(3) bond length is thus reduced relative to other Co—pyridine—nitrogen bond distances in order to reduce angular strain in the five-membered chelate rings containing the pyridine nitrogen.

In the autoxidation involving the intermediate peroxy-bridged cobalt complex the only reaction products are a cobalt(III) complex of the original pentamine and hydrogen peroxide. However, parallel studies of the autoxidation of cobalt(II) complexes of similar polyamines, 1,9-bis(2-pyridyl)-2,5,8-triazanonane (pydien) and 1,11-bis(2-pyridyl)-2,6,10-triazaundecane (pydpt) (Raleigh & Martell, 1984), show

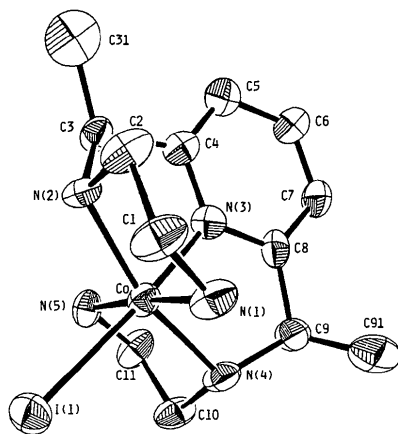


Fig. 1. An ORTEP projection of the title compound. Probability ellipsoids are at the 20% level.

them to undergo dehydrogenation in the autoxidation process to form diimines with double bonds conjugated to the pyridine rings. It is highly probable that there are three factors assisting dehydrogenation of the coordinated polyamines in these dioxygen complexes. Previously, conjugation and conformation of the polyamine in the coordination sphere of the cobalt have been cited as factors in reducing the activation energy in dehydrogenation (Raleigh & Martell, 1984). An additional third factor may be that one of the secondary nitrogen bond angles, which is normally tetrahedral, approaches a trigonal bond angle. For the cobalt dioxygen complex containing pydien the angle is 118.2 (7)° (Timmons, Niswander, Clearfield & Martell, 1979) and for that containing pydpt the angle is 112.6 (8)° (Timmons, Clearfield, Martell & Niswander, 1979). The pydien value is very close to the trigonal angle in 2,12-bis(2-pyridyl)-3,7,11-triazatrideca-2,11-diene(methyl)cobalt(III) diiodide dihydrate [118.1 (9)°] (Stotter & Trotter, 1977) and the pydpt angle is intermediate between tetrahedral and trigonal angles. Therefore less energy would be involved in the transformation of tetrahedral to trigonal bonds in the dehydrogenation reactions of the polyamine complexes.

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