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Structure of a Ternary Cobalt(II) Complex: Triaqua(2,2′-bipyridyl)(monophenyl phosphato)cobalt(II) Monohydrate

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Abstract. $[Co(C_{10}H_8N_2)(C_6H_5OPO_3H)(H_2O)_3].H_2O$, monoclinic, $P2_1/c$, $a = 7{\cdot}145\,(3)$, $b = 24{\cdot}141\,(6)$, $c = 11{\cdot}495\,(4)$ Å, $\beta = 94{\cdot}90\,(4)°$, $V = 1975{\cdot}5\,(8)$ Å^3, $Z = 4$, $D_m = 1{\cdot}54\,(1)$ (flotation in chloroform and carbon tetrachloride), $D_x = 1{\cdot}544\,(1)$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo }K\alpha) = 1{\cdot}03$ mm^{-1}, $F(000) = 948$, $T = 293$ K. Final $R = 0{\cdot}058$ for 2238 observed reflections. The Co$^{\text{II}}$ coordination is a distorted octahedron, best described as a shortened tetragonal bipyramid, formed by the chelating bipyridyl ligand, three water molecules (two axial), and one oxygen atom of the phosphate group. Co—O(ax) are 2·060 (4), Co—O(eq) are 2·123 (4) for O—P and 2·139 (4) for O(water), Co—N(eq) average to 2·129 (5) Å.

Introduction. The structure of the title compound has been determined as a further step in the synthesis and structural study of metal(II) complexes with aryl phosphates and other coordinating *N*, *N*-, *N*—O, and O—O donor ligands. This study complements the recently published structures of the mixed-ligand complexes $[Cu(bpy)_2(MPhP)].MPhP.H_2O$ (MPhP = monophenyl phosphate) (Głowiak, Szemik & Wnęk, 1986) and $[Cu(DPhP)_2(H_2O)_2]$ (DPhP = diphenyl phosphate) (Głowiak & Szemik, 1987).

Experimental. The compound was obtained by reaction of cobalt(II) monophenyl phosphate and 2,2′-bipyridyl in aqueous solution. Orange crystals, 0·35 × 0·40 × 0·48 mm, unit-cell dimensions from a least-squares fit for 15 reflections ($22 < 2\theta < 30°$), Syntex $P2_1$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, variable θ–2θ scans, $2\theta_{\text{max}} = 55°$, scan rate 2·0–29·3° min^{-1}. Two standard reflections every 50 measurements (intensity variation ±5%), 2878 independent reflections ($0 \le h \le 9$, $0 \le k \le 30$, $-16 \le l \le 15$), 2238 with $I > 3\sigma(I)$, Lp corrections, absorption ignored. Patterson and Fourier method for structure determination, full-matrix least-squares anisotropic refinement, H atoms of water molecules could not be located from difference Fourier syntheses and were not included, other H atoms were included in calculated positions and fixed isotropic thermal parameter $B = 5{\cdot}5$ Å^2, 253 parameters refined, final $R = 0{\cdot}058$, $wR = 0{\cdot}065$ for 2238 reflections, $S = 3{\cdot}58$, minimizing $\sum w(|F_o| - |F_c|)^2$, $w = 1/\sigma^2(F)$, $(\Delta/\sigma)_{\text{max}} = 0{\cdot}25$, $(\Delta\rho)_{\text{max}} = +0{\cdot}53$ and $(\Delta\rho)_{\text{min}} = -0{\cdot}45$ e Å^{-3}, scattering factors from *International Tables for X-ray Crystallography* (1974). Computer programs: Syntex (1976) *XTL* system.

Discussion. The final parameters for non-hydrogen atoms are listed in Table 1.* Bond lengths and valence angles are given in Table 2. Fig. 1 shows a perspective view of $[Co(bpy)(MPhP)(H_2O)_3].H_2O$ including the atomic nomenclature used here.

The geometry about the six-coordinate cobalt atom involves a slightly distorted octahedron with a characteristic foreshortening (0·07 Å) along the O(6)—Co—

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51039 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional parameters and equivalent isotropic thermal parameters for nonhydrogen atoms with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{1}{3}\textstyle\sum_i B_{ii}.$$

	x	y	z	B_{eq}(Å^2)
Co	0·29001 (12)	0·00869 (4)	0·30063 (7)	2·6 (1)
P	0·1829 (2)	0·0963 (1)	0·5051 (1)	2·7 (1)
O(1)	0·3179 (6)	0·0752 (2)	0·4218 (4)	3·4 (4)
O(2)	0·2116 (6)	0·0725 (2)	0·6269 (4)	3·4 (4)
O(3)	−0·0194 (6)	0·0928 (2)	0·4563 (4)	3·6 (4)
O(4)	0·2411 (7)	0·1616 (2)	0·5167 (4)	4·1 (4)
O(5)	0·3206 (7)	−0·0540 (2)	0·4324 (4)	3·7 (4)
O(6)	0·0027 (5)	0·0085 (2)	0·3067 (3)	2·7 (3)
O(7)	0·5778 (6)	0·0102 (2)	0·2980 (3)	2·9 (3)
O(8)	0·6623 (9)	0·3709 (3)	−0·1774 (5)	7·1 (6)
N(1)	0·2748 (7)	−0·0522 (2)	0·1654 (4)	2·9 (4)
N(2)	0·2603 (7)	0·0579 (2)	0·1469 (4)	2·8 (4)
C(1)	0·2832 (11)	−0·1070 (3)	0·1788 (6)	4·1 (6)
C(2)	0·2819 (13)	−0·1433 (3)	0·0869 (7)	5·0 (7)
C(3)	0·2652 (13)	−0·1224 (3)	−0·0251 (7)	4·7 (7)
C(4)	0·2532 (11)	−0·0660 (3)	−0·0412 (6)	4·2 (7)
C(5)	0·2595 (9)	−0·0317 (3)	0·0559 (5)	3·0 (5)
C(6)	0·2484 (9)	0·0299 (3)	0·0453 (5)	2·9 (5)
C(7)	0·2274 (11)	0·0566 (3)	−0·0605 (6)	3·9 (6)
C(8)	0·2166 (12)	0·1138 (3)	−0·0641 (6)	4·5 (7)
C(9)	0·2271 (12)	0·1419 (3)	0·0407 (7)	4·5 (7)
C(10)	0·2497 (10)	0·1134 (3)	0·1427 (6)	3·9 (6)
C(11)	0·1804 (14)	0·1944 (3)	0·6048 (6)	4·3 (7)
C(12)	0·3103 (15)	0·2153 (3)	0·6876 (8)	6·1 (9)
C(13)	0·2558 (23)	0·2497 (4)	0·7759 (8)	7·4 (12)
C(14)	0·0677 (25)	0·2629 (4)	0·7781 (9)	7·8 (13)
C(15)	−0·0598 (17)	0·2422 (4)	0·6976 (9)	7·5 (11)
C(16)	−0·0079 (15)	0·2076 (3)	0·6086 (7)	5·8 (8)

Table 2. *Bond lengths* (Å) *and selected valence angles* (°) *with e.s.d.'s in parentheses*

Co—O(1)	2·123 (4)	C(15)—C(16)	1·395 (14)
Co—O(5)	2·139 (5)	C(16)—C(11)	1·387 (14)
Co—O(6)	2·060 (4)	N(1)—C(1)	1·332 (9)
Co—O(7)	2·060 (4)	C(1)—C(2)	1·372 (11)
Co—N(1)	2·135 (5)	C(2)—C(3)	1·378 (11)
Co—N(2)	2·124 (5)	C(3)—C(4)	1·376 (11)
P—O(1)	1·505 (3)	C(4)—C(5)	1·387 (9)
P—O(2)	1·510 (4)	C(5)—N(1)	1·349 (8)
P—O(3)	1·507 (5)	C(5)—C(6)	1·495 (9)
P—O(4)	1·633 (5)	C(6)—N(2)	1·346 (8)
O(4)—C(11)	1·385 (9)	C(6)—C(7)	1·373 (9)
C(11)—C(12)	1·367 (13)	C(7)—C(8)	1·383 (11)
C(12)—C(13)	1·393 (14)	C(8)—C(9)	1·379 (11)
C(13)—C(14)	1·383 (24)	C(9)—C(10)	1·358 (10)
C(14)—C(15)	1·340 (18)	C(10)—N(2)	1·343 (9)

O(1)—Co—O(5)	94·1 (2)	O(3)—P—O(4)	108·2 (3)
O(1)—Co—O(6)	91·0 (2)	Co—O(1)—P	130·1 (2)
O(1)—Co—O(7)	87·6 (2)	Co—N(1)—C(1)	127·0 (5)
O(1)—Co—N(1)	173·7 (2)	Co—N(1)—C(5)	115·0 (4)
O(1)—Co—N(2)	96·9 (2)	Co—N(2)—C(6)	115·9 (4)
O(5)—Co—O(6)	90·9 (2)	Co—N(2)—C(10)	126·1 (4)
O(5)—Co—O(7)	88·9 (2)	P—O(4)—C(11)	121·3 (5)
O(5)—Co—N(1)	91·4 (2)	O(4)—C(11)—C(12)	118·9 (7)
O(5)—Co—N(2)	168·9 (2)	O(4)—C(11)—C(16)	121·3 (7)
O(6)—Co—O(7)	178·6 (2)	C(1)—N(1)—C(5)	118·1 (6)
O(6)—Co—N(1)	91·9 (2)	N(1)—C(1)—C(2)	123·3 (7)
O(6)—Co—N(2)	90·0 (2)	N(1)—C(5)—C(4)	121·6 (6)
O(7)—Co—N(1)	89·5 (2)	N(1)—C(5)—C(6)	116·1 (6)
O(7)—Co—N(2)	90·4 (2)	C(6)—N(2)—C(10)	118·0 (6)
N(1)—Co—N(2)	77·6 (2)	N(2)—C(6)—C(5)	115·4 (5)
O(1)—P—O(2)	114·7 (3)	N(2)—C(6)—C(7)	121·9 (6)
O(1)—P—O(3)	113·0 (3)	N(2)—C(10)—C(9)	122·7 (7)
O(1)—P—O(4)	101·9 (3)	C(4)—C(5)—C(6)	122·0 (6)
O(2)—P—O(3)	112·0 (3)	C(5)—C(6)—C(7)	122·7 (6)
O(2)—P—O(4)	106·1 (3)		

O(7) axis, giving a shortened tetragonal bipyramid. The axial positions are occupied by the oxygen atoms from two water molecules. In the equatorial plane the cobalt atom is coordinated by two nitrogen atoms of the bipyridyl ligand, one oxygen atom of the phosphate group and the oxygen atom of the third water molecule. The two shorter axial distances Co—O(6) and Co—O(7) are equal at 2·060 (4) Å while the longer distances in the equatorial plane are: Co—O(1) (phosphate) 2·123 (4), Co—N(2) 2·124 (5), Co—N(1) 2·135 (5) and Co—O(5) (*W*) 2·139 (4) Å. Valence angles for *trans* ligands are O(6)—Co—O(7) 178·6 (2), O(1)—Co—N(1) 173·7 (2) and O(5)—Co—N(2) 168·9°.

Deviations from regular octahedral coordination are also visible in the valence angles for *cis* ligands: from 96·9 (2)° for O(1)—Co—N(2) to 77·6 (2)° for N(1)—Co—N(2). The mean Co—N 2·129 (5) Å and Co—O 2·095 (8) Å distances are comparable to those in $[Co(IMP)(H_2O)_5].3H_2O$ (IMP = inosine monophosphate) (Aoki, 1975).

The geometries of the bipyridyl and phosphate moieties are typical, and similar to those found in the ternary complex $[Cu^{II}(bpy)_2(MPhP)].(MPhPH)_2(H_2O)$ (Głowiak *et al.*, 1986), glycinium diphenyl phosphate (Głowiak & Wnęk, 1985), glycinium monophenyl phosphate (Głowiak & Szemik, 1986) and $[Cu(DPhP)_2(H_2O)_2]$ (Głowiak & Szemik, 1987).

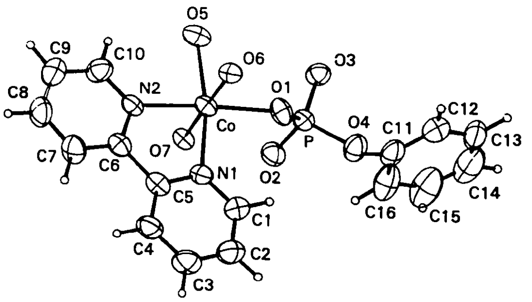

Fig. 1. An *ORTEP* (Johnson, 1976) drawing of the title compound with the atom-numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level.

The P—O(4) bond of 1·633 (5) Å is close to the literature value for a P—O single bond [1·64 Å (Cruickshank, 1961)]. The other three P—O bonds: P—O(1) 1·505 (5), P—O(2) 1·510 (4) and P—O(3) 1·507 (5) Å are intermediate between single and double bonds and are, together, characteristic of an ionic form of the phosphate group. The O—P—O angles range from 101·9 (3) to 114·7 (3)°, the latter value corresponding to the angle between the longest and the shortest P—O bonds.

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New Synthesis and Structure of Diferrocenylmercury Monohydrate

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Abstract. $[\{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)\}_2Hg].H_2O$, $M_r = 588{\cdot}67$, monoclinic, $P2_1/c$, $a = 7{\cdot}705\,(5)$, $b = 10{\cdot}200\,(2)$, $c = 10{\cdot}618\,(2)$ Å, $\beta = 103{\cdot}11\,(3)°$, $V = 812{\cdot}7\,(9)$ Å^3, $Z = 2$, $D_x = 2{\cdot}405$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 111{\cdot}9$ cm^{-1}, $F(000) = 560$, $T = 295\,(1)$ K, $R = 0{\cdot}0388$, $wR = 0{\cdot}0507$, 1050 unique reflections, 673 reflections with $I > 3\sigma(I)$. Diferrocenylmercury is made by reaction of chloromercuryferrocene, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4HgCl)$, with cysteine. The coplanar cyclopentadienyl rings of the two antiparallel ferrocenyl moieties are linked linearly through an Hg atom; the C—Hg distance is 2·06 (2) Å; the mean Fe—C and C—C distances are 2·04 (2) and 1·41 (3) Å, respectively; the cyclopentadienyl rings are eclipsed.

Introduction. Diferrocenyl compounds $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)]_2X$, abbreviated Fc_2X, containing various bridging atoms or groups X are known (*Dictionary of Organometallic Compounds,* 1984), but only the compound in which X is CH_2CH_2 has been analyzed crystallographically (Doyle, Baenziger & Davis, 1974). Diferrocenylmercury has been prepared before by reaction of chloromercuryferrocene, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4HgCl)$ or FcHgCl, with several agents (Nesmeyanov, Perevalova, Golovnya & Nesmeyanova, 1954; Rausch, Vogel & Rosenberg, 1957; Rausch, 1963; Roling, Roling & Rausch, 1971). This report of the reaction with cysteine contributes to the study of reactions between mercurials and biological thiols (Taylor & Carty, 1977; Rabenstein, 1978). This crystallographic analysis complements the previous synthetic and spectroscopic studies of diferrocenylmercury, and it may contribute to the study of other diferrocenyl and diferricenium compounds.

Experimental. Chemicals were obtained from Aldrich Chemical Co. Chloromercuryferrocene (36·4 mg, 86 μmol) was dissolved, with stirring, in a mixture of 100 mL of DMF and 900 mL of 85 m*M* phosphate buffer at pH 7·0 and the solution was filtered. L-Cysteine, CysSH (5·2 mg, 43 μmol), was dissolved, with stirring, in the clear filtrate. The yellow precipitate, formed overnight at 277 K, was filtered, dried in air, and dissolved in 2 mL of benzene. Slow evaporation of benzene over ten days gave needle-like yellow crystals.

A crystal, 0·04 × 0·03 × 0·25 mm, was mounted on a glass fiber on an Enraf–Nonius CAD-4 diffractometer. Lattice parameters were measured from 25 reflections ($14 \leq 2\theta \leq 30°$); because of macroscopic twinning, the orientation of the c axis was confirmed with photographs. An empirical correction for absorption was based on ψ scans; after the structure was solved, a numerical correction was applied (Walker & Stuart, 1983); transmission coefficients were 0·765 to 1·236. 2192 reflections in the $+h$ hemisphere were collected by the ω–2θ scan method; $0 \leq 2\theta \leq 45°$; $[(\sin\theta)/\lambda]_{\max} = 0{\cdot}5384$ Å^{-1}. The intensities of the standard reflections $\bar{1}0\bar{4}$, $\bar{1}3\bar{5}$, $2\bar{2}\bar{6}$ varied by 0·30%. $R_{\text{int}} = 0{\cdot}0440$ for the 673 unique observed reflections with $I > 3\sigma(I)$.

The Fe, C and Hg atoms were located directly by the program *SHELXS*86 (Sheldrick, 1986) and refined anisotropically on the basis of F^2 magnitudes. The O atom was located from a difference Fourier synthesis and refined isotropically. The H atoms in calculated positions [C—H = 0·95 Å, $B_H = 1{\cdot}3 \times B(\text{iso})_C$] were used only for the calculation of F. 110 parameters were refined. The final R and wR values were 0·0388 and 0·0507; $w = 1/\sigma^2(|F_o|)$. The largest shift in the final cycle was 0·01 e.s.d.; the largest peak was 1·63 e Å^{-3}; $S = 1{\cdot}22$. Scattering factors and anomalous-scattering

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