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Structure of Hexaaquacobalt(II) *catena*-Tetraaqua-μ-[1,2,4,5-benzenetetracarboxylato(4 −)]-cobaltate(II) 7·36-Hydrate

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Abstract. $[Co(H_2O)_6][Co(C_{10}H_2O_8)(H_2O)_4].7{\cdot}36H_2O$, $M_r = 680{\cdot}74$, triclinic, $P\bar{1}$, $a = 9{\cdot}972\,(4)$, $b = 10{\cdot}921\,(4)$, $c = 6{\cdot}852\,(2)$ Å, $\alpha = 104{\cdot}89\,(2)$, $\beta = 103{\cdot}63\,(2)$, $\gamma = 93{\cdot}00\,(2)°$, $V = 695{\cdot}7\,(5)$ Å^3, $Z = 1$, $D_x = 1{\cdot}624$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}283$ mm^{-1}, $F(000) = 353{\cdot}6$, $T = 298$ K, $R = 0{\cdot}051$ for 1672 independent reflexions having $I \geq 3\sigma(I)$. The structure consists of hexaaquacations, polymeric anions and water of crystallization. Both Co atoms are in a distorted octahedral environment. The 1,2,4,5-benzenetetracarboxylate ion is coordinated in a bis monodentate manner and acts as a bridging ligand. Cations and anions are linked together by a three-dimensional network of hydrogen bonding.

Introduction. Salts of 1,2,4,5-benzenetetracarboxylic acid (H_4pyr = pyromellitic acid) are of potential practical interest (Ward & Luehrs, 1983). Due to the presence of four carboxylate groups, the tetraanion of this acid can coordinate in numerous ways. However, the crystal structures of only two transition metal–pyr complexes are known (Usubaliev, Shnulin & Mamedov, 1982; Poleti, Stojaković, Prelesnik & Herak, 1988). In addition, the structures of one thallium(I) (Day & Luehrs, 1988), one uranium(VI) (Cousson, Stout, Nectoux, Pages & Gasperin, 1986) and two neptunium(V) complexes (Nectoux, Abazli, Jove, Cousson, Pages, Gasperin & Choppin, 1984; Cousson, 1985) are also described. In order to study the factors that determine the coordination mode of the pyr ion the title compound was prepared and its crystal structure is described here. The structure of the analogous $[Co(H_2O)_6][H_2pyr]$ complex was recently published by other authors (Ward & Luehrs, 1983).

Table 1. *Non*-H-*atom fractional coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^3) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Co(1)	0	0	0	32·3 (2)
Co(2)	5000	5000	10000	19·3 (2)
O(1)	4790 (3)	3073 (3)	8409 (5)	26 (1)
O(2)	6868 (4)	2532 (3)	9686 (6)	41 (1)
O(3)	3827 (4)	2570 (3)	2752 (6)	40 (1)
O(4)	5973 (3)	3215 (3)	4776 (5)	28 (1)
O(*W*1)	1490 (5)	5 (5)	− 1723 (7)	62 (1)
O(*W*2)	1362 (5)	1345 (5)	2489 (7)	70 (1)
O(*W*3)	846 (5)	− 1533 (5)	1036 (8)	65 (1)
O(*W*4)	6407 (3)	5292 (3)	8252 (5)	28 (1)
O(*W*5)	3313 (3)	5273 (3)	7634 (5)	31 (1)
O(*W*6)	1985 (5)	2106 (4)	6928 (8)	64 (1)
O(*W*7)	8487 (5)	2089 (5)	4992 (7)	65 (1)
O(*W*8)*	696 (7)	4023 (7)	375 (19)	164 (4)
O(*W*9)†	455 (11)	3954 (10)	4766 (21)	151 (4)
C(1)	5480 (5)	− 43 (4)	7071 (7)	25 (1)
C(2)	5386 (5)	1125 (4)	6612 (7)	22 (1)
C(3)	4917 (5)	1169 (4)	4545 (8)	25 (1)
C(4)	5726 (5)	2336 (4)	8385 (7)	24 (1)
C(5)	4901 (5)	2425 (4)	4000 (7)	25 (1)

* Occupancy factor 0·93 (1).
† Occupancy factor 0·75 (1).

Experimental. Pink, air-unstable crystals obtained from a diluted water solution (pH approx. 6) containing $Co(NO_3)_2$ and Na_4pyr in 2:1 molar ratio. Because of efflorescence a thin rectangular plate crystal (*ca* 0·16 × 0·16 × 0·09 mm) was coated with cyanoacrilate glue. Philips PW1100 automatic diffractometer, Mo $K\alpha$ (graphite-monochromated) radiation. Cell parameters (32 reflexions, $6 < \theta < 23°$) using a locally improved version (Cannillo, Germani & Mazzi, 1983) of the Philips *LAT* routine. Data collection: $\theta_{max} < 25°$ ($|h| \leq 11$, $|k| \leq 12$, $l \leq 8$), ω scan, three standard reflexions (600, 080, 004) every 4 h, max. variation 5·5% (no correction), 2452 unique reflexions, 1672 observed with $I \geq 3\sigma(I)$. Lp and semi-empirical correction for absorption (min. 0·999, max. 1·085; North, Phillips & Mathews, 1968). Co atoms located by Patterson method, remaining atoms during standard full-matrix least squares and Fourier synthesis performed with a locally rewritten

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version of *ORFLS* (Busing, Martin & Levy, 1962). All atoms refined anisotropically. Partial occupation of O(*W*8) and O(*W*9) sites proposed on the basis of peak heights in the ΔF map and thermal parameters. These occupation factors were also included in refinement (see Table 1). H atoms not located. Reflexion 100 omitted because of its too large $F_o - F_c$ value. Scattering factors for neutral atoms and anomalous dispersion from *International Tables for X-ray Crystallography* (1974). Geometry calculations by *CSU* program (Vicković, 1986). Final agreement parameters: $R = 0.0508$, $wR = 0.0565$, $w = 1/\sigma^2(F_o)$, $S = 1.046$ for 178 independent parameters, $(\Delta/\sigma)_{\max} < 1.0$ for occupation and temperature factors of O(*W*8) and O(*W*9), $(\Delta/\sigma) < 0.3$ for the other parameters, maximum height in final ΔF synthesis 0·72 e Å^{-3}, secondary-extinction coefficient = 1·5 (4) × 10^{-4} (Coppens & Hamilton, 1970).

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

Co(1)—O(*W*1)	2·105 (6)	O(3)—C(5)	1·249 (6)
Co(1)—O(*W*2)	2·079 (4)	O(4)—C(5)	1·253 (5)
Co(1)—O(*W*3)	2·120 (6)	C(1)—C(2)	1·393 (7)
Co(2)—O(1)	2·081 (3)	C(1)—C(3^i)	1·392 (6)
Co(2)—O(*W*4)	2·109 (4)	C(2)—C(3)	1·397 (7)
Co(2)—O(*W*5)	2·136 (3)	C(2)—C(4)	1·508 (5)
O(1)—C(4)	1·264 (6)	C(3)—C(5)	1·511 (7)
O(2)—C(4)	1·239 (6)		

O(*W*1)—Co(1)—O(*W*2)	88·4 (2)	C(1)—C(2)—C(4)	119·0 (4)
O(*W*1)—Co(1)—O(*W*3)	89·8 (2)	C(3)—C(2)—C(4)	120·6 (4)
O(*W*2)—Co(1)—O(*W*3)	91·9 (2)	C(2)—C(3)—C(5)	121·2 (4)
O(1)—Co(2)—O(*W*4)	86·8 (1)	O(1)—C(4)—O(2)	125·4 (4)
O(1)—Co(2)—O(*W*5)	89·9 (1)	O(1)—C(4)—C(2)	115·7 (4)
O(*W*4)—Co(2)—O(*W*5)	90·4 (1)	O(2)—C(4)—C(2)	118·9 (4)
Co(2)—O(1)—C(4)	127·9 (3)	O(3)—C(5)—O(4)	125·4 (4)
C(2)—C(1)—C(3^i)	119·5 (4)	O(3)—C(5)—C(3)	116·8 (4)
C(1)—C(2)—C(3)	120·4 (4)	O(4)—C(5)—C(3)	117·8 (4)

Symmetry operation: (i) $1-x, -y, 1-z$.

Discussion. Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.* The atomic numbering scheme and packing of the molecules are shown in Fig. 1.

The structure consists of $[Co(H_2O)_6]^{2+}$ cations, polymeric $[—Co(H_2O)_4—(pyr)—]_n$ anions parallel to the [011] direction, and water of crystallization. All carboxylate and water O atoms take part in a three-dimensional network of hydrogen bonds. Two water molecules, O(*W*8) and O(*W*9), situated in the tunnels running parallel to the z axis and delimited by Co octahedra (Fig. 1) are weakly bonded [O(*W*)···O(*W*) distances greater than 2·81 Å]. This fact explains their disorder, high thermal parameters, and the instability of the compound. It should be noticed that between these water molecules and their centrosymmetric pairs exist very short contacts [O(*W*8)···O(*W*8^i): 2·70 (1) Å; O(*W*9)···O(*W*9^{ii}): 2·48 (2) Å; symmetry code: (i) $-x$, $1-y$, $-z$; (ii) $-x$, $1-y$, $1-z$]. The Co atoms are in a distorted octahedral environment; the Co(1) octahedron is slightly more regular with bond distances a little shorter (Table 2).

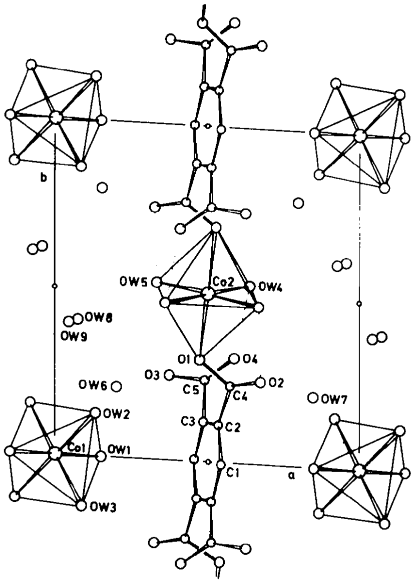

Fig. 1. Projection of the structure onto the *ab* plane. Only intramolecular hydrogen bonds (dotted lines) are shown for clarity.

Bond lengths and bond angles in the pyr anion (Table 2) are in accordance with previously found values (Usubaliev, Shnulin & Mamedov, 1982; Poleti, Stojaković, Prelesnik & Herak, 1988). The carboxylate groups are inclined with respect to the benzene ring at 53·4 (1) (coordinated) and 48·4 (1)° (uncoordinated). The C—O bond distances have close values [av. 1·251 (6) Å; Table 2]. Such geometry was also previously reported (Usubaliev, Shnulin & Mamedov, 1982; Poleti, Stojaković, Prelesnik & Herak, 1988).

The pyr ion is coordinated in a bis monodentate manner. This resembles the situation found in the $[Ni_2(en)_2(H_2O)_6(pyr)].4H_2O$ complex (en = ethylenediamine; Poleti, Stojaković, Prelesnik & Herak, 1988), although this complex is only a binuclear one. In both structures intramolecular hydrogen bonds between uncoordinated carboxylate O atoms and coordinated water molecules are found. Thus, it seems that this kind of intramolecular hydrogen bonding is characteristic for such a pyr anion coordination.

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* Lists of structure factors, anisotropic thermal parameters, dihedral angles, possible hydrogen bonds and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51974 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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[Bis-μ-iodo-bis(tricarbonylrhenio)-(*Re*—*Re*)][μ-iodo-bis(tetracarbonylrhenio)-(*Re*—*Re*)]indium(III) and Bis(pentacarbonylrhenio)(tetracarbonyl-bis-μ-iodo-rhenio)indium(III)

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Abstract. $[\{\mathrm{(CO)_3Re}(\mu\text{-}\mathrm{I})_2\mathrm{Re(CO)_3}\}\mathrm{In}\{\mathrm{(CO)_4Re}(\mu\text{-}\mathrm{I})\mathrm{Re(CO)_4}\}]$, $M_r = 1632{\cdot}5$, monoclinic, $C2/c$, $a = 16{\cdot}176\,(3)$, $b = 11{\cdot}798\,(3)$, $c = 16{\cdot}147\,(4)$ Å, $\beta = 115{\cdot}36\,(1)^\circ$, $U = 2785{\cdot}1$ Å^3, $Z = 4$, $D_x = 3{\cdot}892$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71073$ Å, $\mu(\mathrm{Mo}\ K\alpha) = 21{\cdot}72$ mm^{-1}, $F(000) = 2816$, $T = 298\,(1)$ K, $R = 0{\cdot}0416$ for 1829 unique reflections. The spiro μ_4-In atom is bound to the four Re atoms of two bidentate chelate ligands $[\mathrm{Re_2(CO)_8}(\mu\text{-}\mathrm{I})]^-$ and $[\mathrm{Re_2(CO)_6}(\mu\text{-}\mathrm{I})_2]^{2-}$ each with a Re—Re bond. The mean values of the metal—metal bond lengths are In—Re = 2·801 (1) and 3·073 (2) Å. $[\mathrm{(CO)_4Re}(\mu\text{-}\mathrm{I})_2\mathrm{In}\{\mathrm{Re(CO)_5}\}_2]$, $M_r = 1319{\cdot}4$, triclinic, $P\overline{1}$, $a = 7{\cdot}202\,(1)$, $b = 11{\cdot}821\,(3)$, $c = 15{\cdot}664\,(4)$ Å, $\alpha = 87{\cdot}92\,(2)$, $\beta = 83{\cdot}17\,(3)$, $\gamma = 78{\cdot}25\,(1)^\circ$, $U = 1296{\cdot}2$ Å^3, $Z = 2$, $D_x = 3{\cdot}379$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71073$ Å, $\mu(\mathrm{Mo}\ K\alpha) = 17{\cdot}42$ mm^{-1}, $F(000) = 1152$, $T = 298\,(1)$ K, $R = 0{\cdot}0419$ for 3416 unique reflections. The molecular structure shows as the central fragment a folded four-membered $\mathrm{Re}(\mu\text{-}\mathrm{I})_2\mathrm{In}$ ring with a dihedral angle of 23·7°. The mean values of the ring bond parameters are Re—I = 2·826 (1), In—I = 3·025 (1) Å, and bond angles subtended at (μ-I) 94·1 (1), In 79·8 (1) and Re 86·7 (1)°.

Introduction. In the course of our investigations on bonding capabilities between transition-metal carbonyl fragments (M') and main-group metals (M) in cluster compounds (Haupt & Flörke, 1988) both title compounds were synthesized and each crystal structure determined. Of special interest in this family of heterometallic compounds are the stereochemistry and other properties of those compounds with a so-called naked M atom (Herrmann, 1986). The first title compound shows a spirocyclic μ_4-In atom bound to four Re atoms of the different bidentate chelate ligands $[\mathrm{Re_2(CO)_8}(\mu\text{-}\mathrm{I})]^-$ and $[\mathrm{Re_2(CO)_6}(\mu\text{-}\mathrm{I})]^{2-}$. It is the first structurally determined sample with a spiro μ_4 third main-group metal attached to four transition-metal atoms. The structural analysis of the other title substance continues an earlier characterization of halogeno bridging bonds in similar compounds of the type $\{\mathrm{In}[M'\mathrm{(CO)_5}]_2\}_2(\mu\text{-}X)_2$ (M' = Mn, Re) (Haupt, Wolfes & Preut, 1976, 1979).

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