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Disodium hexaaquacobalt(II) bis[di-hydrogen 1,2,4,5-benzenetetracarboxylate(2–)] tetrahydrate

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Abstract

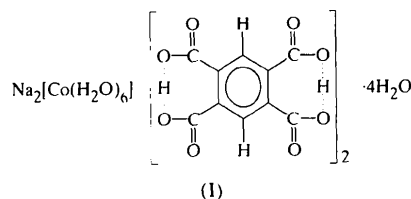
The title structure, $\text{Na}_2[\text{Co}(\text{H}_2\text{O})_6](\text{C}_{10}\text{H}_4\text{O}_8)_2 \cdot 4\text{H}_2\text{O}$, consists of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and Na^+ cations, dihydrogen 1,2,4,5-benzenetetracarboxylate(2–) (H_2btc) anions and water of crystallization. The $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and H_2btc ions, as well as the water molecules, are linked together by a three-dimensional network of hydrogen bonds. A short symmetrical intramolecular hydrogen bond between the COO^- and COOH groups is found to exist in the H_2btc ions.

Comment

Anions of 1,2,4,5-benzenetetracarboxylic or pyromellitic acid (H_4btc) have eight (btc) or four (H_2btc) potential donor O atoms and its complexes could be of practical interest (Ward & Luehrs, 1983). However, only a few first-row transition metal (Usubaliev *et al.*, 1982; Ward & Luehrs, 1983; Robl, 1987; Poleti *et al.*, 1988; Poleti & Karanović, 1989; Chen *et al.*, 1996; Zou *et al.*, 1998) and actinoid (Nectoux *et al.*, 1984; Cousson, 1985; Cousson *et al.*, 1986) complexes have been structurally characterized so far.

As part of our interest in benzenepolycarboxylate complexes, we tried to prepare a mixed-ligand Co^{II} complex containing 2,2'-bipyridine and btc ions. Instead, single crystals of the title compound, (I), were obtained. IR spectra indicated the absence of 2,2'-bipyridine and the presence of COOH groups, but comparison with powder-diffraction data showed that the complex is not isostructural with the previously described $[\text{Co}(\text{H}_2\text{O})_6](\text{H}_2\text{btc})$ (Ward & Luehrs, 1983).

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The structure consists of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, Na^+ and H_2btc ions, and water of crystallization (Fig. 1). The $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and H_2btc ions, as well as the water molecules, are linked together by a three-dimensional network of hydrogen bonds. A short intramolecular hydrogen bond also exists in the H_2btc ion.

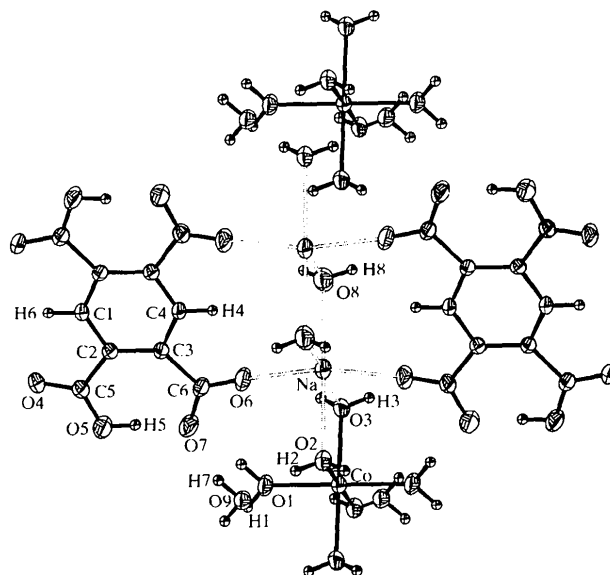


Fig. 1. Part of the structure of (I) viewed approximately along the *a* axis (40% probability displacement ellipsoids). H atoms are shown as circles of arbitrary radii.

The Co^{II} ions are situated at the inversion center (000); one pair of water O atoms, related to each other by an inversion center, is on the twofold axis and two other pairs are in the mirror plane. The octahedron around Co^{II} is not very distorted [with Co—O distances in the range 2.055 (2)–2.117 (2) Å and O—Co—O angles between 85.13 (11) and 94.87 (11)°]. The Co—O distances are comparable with those found in $[\text{Co}(\text{H}_2\text{O})_6](\text{H}_2\text{btc})$ (Ward & Luehrs, 1983).

The H_2btc anions are in special positions too, with two non-substituted ring C atoms (C1 and C4) on the twofold axis, and the C2—C3 bond bisected by the glide plane. As a consequence, the benzene ring is perfectly planar. Two carboxylate C atoms, C5 and C6, are out of the plane of the benzene ring by 0.009 (2) and 0.024 (2) Å, respectively. The whole anion does not deviate appreciably from planarity. The angles between

the benzene ring and the carboxylate groups are 1.5 (2)^o for C5/O4/O5 and 2.8 (2)^o for C6/O6/O7, while the O5/C5/C2/C3/C6/O7 six-membered ring (the ring closed by the intramolecular hydrogen bond) is tilted only 0.29 (7)^o with respect to the plane of the benzene ring. The geometry of the intramolecular hydrogen bond found in H₂btc is given in Table 2. Since both O—H distances are equal, the H atom is disorderly distributed into two positions symmetric with respect to the midpoint of the O5···O7 contact, and the COO⁻ and COOH groups are indistinguishable.

To the best of our knowledge, only three H₂btc compounds, [Co(H₂O)₆](H₂btc) (Ward & Luehrs, 1983), Li₂(H₂btc)·4H₂O (Jessen & Küppers, 1990) and UO₂·(H₂btc)·2H₂O (Cousson *et al.*, 1986), are described so far in the literature. Only in [Co(H₂O)₆](H₂btc) is the short intramolecular hydrogen bond found [O···O distance 2.381 (2) Å] and the H atom is also equidistant from the two O atoms. On the other hand, similar intramolecular hydrogen bonds are usual for hydrogen 1,2-benzenedicarboxylate(1-) ions (Hbdc) (Biagini Cingi *et al.*, 1969; Gonschorek & Küppers, 1975; Adiwidjaja & Küppers, 1978; Küppers, 1978; Bartl & Küppers, 1980). The O···O distances in these compounds are in the range 2.351 (9)–2.400 (2) Å. This means that in the present case, the reported bond is slightly longer than the mean value.

The Na⁺ cations lie on the mirror plane. They are surrounded by six O atoms, *i.e.* two O atoms of H₂btc anions with shorter, and four O atoms of H₂O molecules with longer Na···O contacts. The Na···O distances are between 2.269 (2) and 2.575 (3) Å, and angles are between 68.55 (9) and 109.87 (12)^o. The polyhedron around Na can be described as a flattened (along the O6···Na···O6 direction) and strongly distorted octahedron.

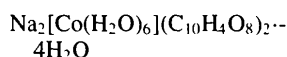
Except for the O6 atom, all O atoms of the H₂btc ion and all H₂O molecules are included in the three-dimensional network of hydrogen bonds (Table 2). Three H₂O molecules (O1, O2 and O3) around Co and the H₂O molecule (O8) from the Na polyhedron act as hydrogen-bond donors. The lattice H₂O molecule (O9) is both hydrogen-bond donor and acceptor connecting the Co coordination polyhedron with neighboring H₂btc ions.

Finally, it could be worth noting that an Ni^{II} and Hbdc complex with similar formula, K₂[Ni(H₂O)₆](Hbdc)₄·4H₂O, and packing has been reported (Biagini Cingi *et al.*, 1984). However, there is no intramolecular hydrogen bonding in this complex.

Experimental

The single crystals used for analysis were obtained by slow evaporation of a dilute aqueous solution containing Co²⁺, btc⁴⁻ and 2,2'-bipyridine.

Crystal data



M_r = 789.33

Monoclinic

*C*2/*m*

a = 7.320 (4) Å

b = 20.150 (5) Å

c = 10.448 (3) Å

β = 103.33 (4)^o

V = 1499.5 (10) Å³

Z = 2

D_x = 1.748 Mg m⁻³

D_m not measured

Mo Kα radiation

λ = 0.71069 Å

Cell parameters from 25 reflections

θ = 13.18–16.62^o

μ = 0.711 mm⁻¹

T = 299 (3) K

Needle

0.25 × 0.20 × 0.18 mm

Pink

Data collection

Enraf-Nonius CAD-4

diffractometer

ω/2θ scans

Absorption correction:

by integration (DeTitta, 1985)

T_{min} = 0.817, *T_{max}* = 0.838

1901 measured reflections

1807 independent reflections

1549 reflections with

I > 2σ(*I*)

R_{int} = 0.038

θ_{max} = 27.96^o

h = -9 → 9

k = 0 → 26

l = 0 → 12

2 standard reflections

frequency: 120 min

intensity decay: none

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.045

wR(*F*²) = 0.116

S = 0.987

1807 reflections

145 parameters

H atoms treated by a

mixture of independent

and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0744*P*)² + 1.4558*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.898 e Å⁻³

Δρ_{min} = -0.237 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3) \sum_i \sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$$

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>U_{eq}</i> |
|----|-------------|--------------|---------------|-----------------------|
| Co | 0 | 0 | 0 | 0.0276 (2) |
| Na | -0.3168 (2) | 0 | -0.32640 (13) | 0.0410 (3) |
| O1 | 0 | 0.10198 (11) | 0 | 0.0410 (6) |
| O2 | -0.2917 (3) | 0 | -0.0833 (2) | 0.0343 (5) |
| O3 | -0.0282 (4) | 0 | 0.1972 (2) | 0.0367 (5) |
| O4 | 0.3107 (2) | 0.39593 (8) | 0.3010 (2) | 0.0407 (4) |
| O5 | 0.2016 (3) | 0.31233 (9) | 0.1738 (2) | 0.0553 (5) |
| O6 | 0.3064 (3) | 0.11200 (8) | 0.3033 (2) | 0.0528 (5) |
| O7 | 0.1999 (3) | 0.19404 (9) | 0.1733 (2) | 0.0556 (6) |
| O8 | 0.6680 (5) | 0 | 0.4359 (3) | 0.0549 (7) |
| O9 | 1/2 | 0.09615 (11) | 0 | 0.0369 (5) |
| C1 | 1/2 | 0.32083 (13) | 1/2 | 0.0278 (6) |
| C2 | 0.3974 (3) | 0.28895 (9) | 0.3886 (2) | 0.0271 (4) |
| C3 | 0.3975 (3) | 0.21888 (9) | 0.3887 (2) | 0.0277 (4) |
| C4 | 1/2 | 0.18714 (14) | 1/2 | 0.0279 (6) |
| C5 | 0.2968 (3) | 0.33584 (11) | 0.2808 (2) | 0.0323 (4) |
| C6 | 0.2962 (3) | 0.17102 (10) | 0.2827 (2) | 0.0342 (5) |

Table 2. *Hydrogen-bonding geometry* (Å, °)

| D—H...A | D—H | H...A | D...A | D—H...A |
|---------------------------|----------|----------|-----------|---------|
| O5—H5...O7 | 1.20 (4) | 1.19 (4) | 2.384 (3) | 171 (4) |
| O1—H1...O7 | 0.80 (3) | 1.96 (3) | 2.764 (2) | 178 (4) |
| O2—H2...O9 ⁱⁱ | 0.75 (3) | 1.99 (3) | 2.729 (3) | 170 (2) |
| O3—H3...O4 ⁱⁱⁱ | 0.77 (3) | 2.00 (3) | 2.748 (3) | 166 (3) |
| O8—H8...O4 ⁱⁱⁱ | 0.82 (4) | 2.08 (5) | 2.856 (3) | 158 (4) |
| O9—H7...O5 ^{iv} | 0.87 (3) | 1.90 (3) | 2.764 (2) | 178 (2) |

Symmetry codes: (i) $-x, -y, -z$; (ii) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (iii) $\frac{1}{2} + x, y - \frac{1}{2}, z$; (iv) $\frac{1}{2} - x, \frac{1}{2} - y, -z$.

The structure was solved by heavy-atom and difference-Fourier methods, and refined by the full-matrix least-squares method. All H atoms were found in ΔF maps, but those connected to C atoms were placed at calculated positions using a riding model [$C-H = 0.93$ Å and $U_{iso}(H) = 1.2U_{eq}(C)$]. H atoms from the H₂O molecules and COOH groups were refined isotropically. The intensities were corrected for absorption with the program *ABSORB* (DeTitta, 1985).

Data collection and cell refinement: *CAD-4 Software* (Enraf-Nonius, 1989). Data reduction: a local modification of *MolEN* (Fair, 1990). Program used to solve structure: *SHELXS86* (Sheldrick, 1990). Program used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP5f* (McArdle, 1994). Software used to prepare material for publication: *SHELXL93*. Weighted least-squares planes: *PARST* (Nardelli, 1983, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1397). Services for accessing these data are described at the back of the journal.

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The red form of [Re(phen)(CO)₃(H₂O)]-CF₃SO₃·H₂O

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Abstract

The coordination geometry of the cations in the red form of aquatricarbonyl(1,10-phenanthroline-*N,N'*)rhenium(I) trifluoromethanesulfonate hydrate, [Re(C₁₂H₈N₂)(CO)₃(H₂O)]CF₃SO₃·H₂O, is approximately octahedral, with a facial arrangement of the linearly coordinated carbonyl ligands. The phenanthroline (phen) ligands interleave to form a columnar π -stacked structure.

Comment

The water-soluble [Re(phen)(CO)₃(H₂O)]⁺ trifluoromethanesulfonate salt is a useful reagent for coupling [Re(phen)(CO)₃]⁺ to an imidazole group of a protein histidine (Connick *et al.*, 1995). We have found that the aqua complex forms both yellow and red crystalline solids, and that both materials dissolve to give spectroscopically indistinguishable yellow solutions. However, the room-temperature emission spectrum of the red crystals exhibits maxima near 550 and 670 nm. The high-energy yellow–green emission is characteristic of rhenium diimine tricarbonyl complexes and evidently arises from a film of yellow material formed on the surface of the red crystals. However, the red color and low-energy emission are less common for these complexes (Schanze *et al.*, 1993; Wrighton & Morse, 1974). In order to elucidate the origins of these spectroscopic properties, we have undertaken a structural study of the red form of this salt, (I).