

crystals of Pt–salen crystallize from the solution together with TiCl and can be separated mechanically because of the colour. The product can be recrystallized from chloroform. Elemental analysis (%): C 41.21 (41.65), H 3.06 (3.06), N 6.07 (6.07), Pt 42.04 (42.28) (theoretical values in brackets).

Crystal data

[Pt(C₁₆H₁₄N₂O₂)]

$M_r = 461.39$

Monoclinic

$P2_1/c$

$a = 13.788 (2) \text{ \AA}$

$b = 7.3827 (12) \text{ \AA}$

$c = 14.0672 (17) \text{ \AA}$

$\beta = 105.66 (2)^\circ$

$V = 1378.8 (4) \text{ \AA}^3$

$Z = 4$

$D_x = 2.223 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 16 reflections

$\theta = 15.1\text{--}18.4^\circ$

$\mu = 10.182 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Fragment cut from a larger crystal

$0.38 \times 0.24 \times 0.15 \text{ mm}$

Red

Data collection

Stoe-modified Philips PW1100 diffractometer

ω - 2θ scans

Absorption correction:

ψ scan (X-RED; Stoe & Cie, 1994a)

$T_{\min} = 0.048$, $T_{\max} = 0.217$

4850 measured reflections

2425 independent reflections

2195 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 24.99^\circ$

$h = -16 \rightarrow 16$

$k = 0 \rightarrow 8$

$l = -16 \rightarrow 16$

3 standard reflections

frequency: 60 min
intensity decay: 3%

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.068$

$S = 1.051$

2425 reflections

191 parameters

H atoms constrained

$w = 1/[\sigma^2(F_o^2) + (0.0415P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 1.570 \text{ e \AA}^{-3}$

(0.89 \AA from Pt)

$\Delta\rho_{\min} = -2.026 \text{ e \AA}^{-3}$

(0.93 \AA from Pt)

Extinction correction:

SHELXL97 (Sheldrick, 1997a)

Extinction coefficient:

0.0071 (3)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Pt—N1	1.938 (5)	C8—N2	1.276 (8)
Pt—N2	1.950 (5)	C9—O2	1.310 (7)
Pt—O2	2.002 (4)	C15—C16	1.468 (9)
Pt—O1	2.006 (4)	C15—N1	1.497 (7)
C1—N1	1.288 (9)	C16—N2	1.483 (7)
C2—O1	1.305 (7)		
N1—Pt—N2	84.2 (2)	N1—Pt—O1	94.5 (2)
N2—Pt—O2	94.27 (19)	O2—Pt—O1	87.02 (15)

Data collection: STADIA (Stoe & Cie, 1994b). Cell refinement: STADIA. Data reduction: X-RED (Stoe & Cie, 1994a). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1997b). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a). Molecular graphics: PLATON (Spek, 1998) and ORTEPIII (Johnson & Burnett, 1996). Software used to prepare material for publication: SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1038). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 2061–2063

Bis[μ -(hydrogen benzene-1,2-dicarboxylato)-*O*:*O'*]bis[bis(1,10-phenanthroline-*N,N'*)cobalt(II)] bis(hydrogen benzene-1,2-dicarboxylate) dihydrate

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(Received 24 June 1999; accepted 6 August 1999)

Abstract

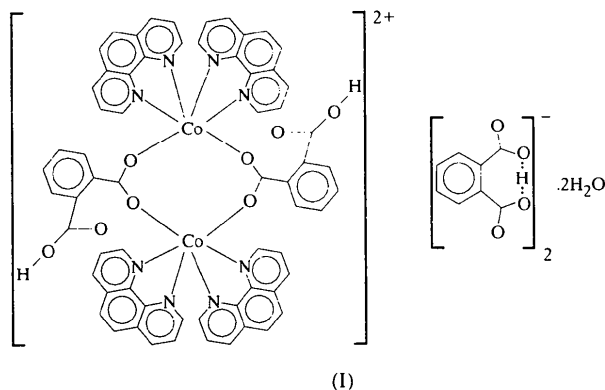
The structure of the title compound, [Co₂(C₈H₅O₄)₂-(C₁₂H₈N₂)₄](C₈H₅O₄)₂·2H₂O, consists of centrosym-

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metric dimeric [Co₂(μ-C₈H₅O₄)₂(C₁₂H₈N₂)₄]²⁺ complex units, hydrogen benzene-1,2-dicarboxylate (C₈H₅O₄⁻) counter-ions and water solvate molecules. The Co^{II} ions display a distorted octahedral environment, with Co—N distances in the range 2.134 (2)–2.170 (3) Å, and Co—O distances of 2.066 (2) and 2.082 (2) Å. A short intramolecular hydrogen bond is found in the uncoordinated C₈H₅O₄⁻ ions, with an O···O distance of 2.381 (7) Å. The cations, anions and water molecules are connected by three O—H···O hydrogen bonds of 2.530 (4), 2.698 (6) and 2.805 (4) Å.

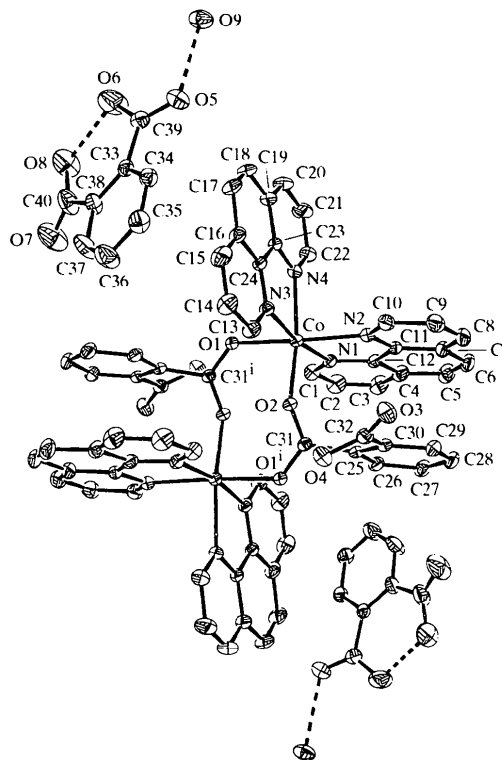
Comment

Numerous transition metal benzene-1,2-dicarboxylato(2-) (phthalato) complexes have been described in the literature (*e.g.* Bakalbassis & Terzis, 1994; Poleti *et al.*, 1990, and references therein). Of the few hydrogen benzene-1,2-dicarboxylate(1-) (Hbdc) compounds which have been structurally characterized, the Hbdc ion in [Ni(Hbdc)₂(H₂O)₄].2H₂O acts as a monodentate ligand (Adiwidjaja & Küppers, 1976), while in the case of [Cu(Hbdc)₂(H₂O)₂], Hbdc is a chelating ligand (Biagini Cingi *et al.*, 1969; Bartl & Küppers, 1980). In [Cu{SC(NH₂)₂]₃(Hbdc) (Biagini Cingi *et al.*, 1977), Hbdc ions are also not coordinated, but are only hydrogen bonded to the complex cation. In [Cu(N₃)Hbdc]_n·nH₂O (Escuer *et al.*, 1997), there is an infinite polymeric structure with the Hbdc ion in a bridging role. Continuing the study of this ligand, the title complex, (I), has been characterized and its crystal structure is presented here.



In the structure of (I), two Hbdc ions are also in a bridging role and each Co^{II} ion is surrounded by four N atoms from two 1,10-phenanthroline (phen) ligands and two O atoms from two Hbdc ions (Fig. 1). Ionized COO⁻ groups bridge the Co^{II} ions, thus connecting two Co(phen)₂ moieties to form centrosymmetric dimeric [Co₂(μ-C₈H₅O₄)₂(C₁₂H₈N₂)₄]²⁺ units. The geometry about Co^{II} is distorted octahedral (Table 1).

Bond distances and angles in the phen ligands and the coordinated Hbdc ions are as expected for this type of ligand (Nishigaki *et al.*, 1978; Poleti *et al.*, 1990). All



and anisotropy, we allowed for this as 0.5 occupancy riding H atoms, one on each of O6 and O8.

Three intermolecular hydrogen bonds also exist in the structure (Table 2). The water molecule (O9) acts as both a hydrogen-bond donor and a hydrogen-bond acceptor, bridging the coordinated Hbdc ions. Thus, centrosymmetric 12-membered rings are formed and neighbouring dimeric cations are further dimerized by hydrogen bonds. The second water H atom is directed toward the uncoordinated Hbdc ion.

Experimental

Crystals of (I) were prepared by the slow evaporation of a dilute EtOH–H₂O (1:5) solution (pH = 3.84) containing Co(NO₃)₂, 1,10-phenanthroline and KC₈H₅O₄ in a 1:1:2 molar ratio. Analysis calculated for C₄₀H₂₈CoN₄O₉: C 62.6, H 3.7, Co 7.7, N 7.3%; found: C 62.5, H 3.6, Co 8.1, N 7.6%.

Crystal data

[Co₂(C₈H₅O₄)₂(C₁₂H₈N₂)₄]
(C₈H₅O₄)₂·2H₂O

M_r = 1535.23

Triclinic

P $\bar{1}$

a = 11.611 (2) Å

b = 12.140 (7) Å

c = 13.584 (4) Å

α = 110.13 (4)°

β = 97.62 (2)°

γ = 94.56 (4)°

V = 1765.7 (12) Å³

Z = 1

D_x = 1.444 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.7107 Å

Cell parameters from 25

reflections

θ = 11.7–16.7°

μ = 0.550 mm⁻¹

T = 299 (3) K

Prismatic

0.23 × 0.18 × 0.14 mm

Orange

Data collection

Enraf–Nonius CAD-4
diffractometer

$\omega/2\theta$ scans

Absorption correction:

by integration (*ABSORB*;

DeTitta, 1985)

T_{min} = 0.907, *T_{max}* = 0.935

8024 measured reflections

7684 independent reflections

4810 reflections with

I > 2σ(*I*)

R_{int} = 0.024

θ_{\max} = 27.95°

h = -15 → 15

k = -15 → 15

l = 0 → 17

2 standard reflections

frequency: 120 min

intensity decay: none

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.050

wR(*F*²) = 0.126

S = 0.985

7684 reflections

499 parameters

H atoms: see below

w = 1/[σ²(*F_o*²) + (0.0588*P*)²]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.315 e Å⁻³

Δρ_{min} = -0.280 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for

Crystallography (Vol. C)

Table 1. Selected bond lengths (Å)

Co—O1	2.066 (2)	O2—C31	1.254 (3)
Co—O2	2.082 (2)	O3—C32	1.222 (4)
Co—N1	2.139 (2)	O4—C32	1.303 (4)
Co—N2	2.136 (2)	O5—C39	1.208 (4)
Co—N3	2.134 (2)	O6—C39	1.249 (4)
Co—N4	2.170 (3)	O7—C40	1.191 (6)
O1—C31 ⁱ	1.255 (3)	O8—C40	1.276 (6)

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

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

D—H...A	D—H	H...A	D...A	D—H...A
O4—H1O4...O9 ⁱⁱ	0.84 (4)	1.70 (3)	2.530 (4)	173 (4)
O9—H1O9...O5	0.83 (5)	1.87 (5)	2.698 (6)	179 (5)
O9—H2O9...O3 ⁱⁱⁱ	0.79 (4)	2.04 (3)	2.805 (4)	162 (5)

Symmetry codes: (ii) $x, y - 1, z$; (iii) $1 - x, 1 - y, -z$.

H atoms connected to carbon were placed at calculated positions using a riding model [C—H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C)]. In the uncoordinated Hbdc ion, two half-occupancy H atoms were placed one on each of O6 and O8 and treated as riding using the *SHELXL97 AFIX147* option (Sheldrick, 1997) [O—H = 0.82 Å and *U*_{iso}(H) = 1.2*U*_{eq}(O)]. The H atoms from the H₂O molecule and the COOH group in the coordinated Hbdc ion were refined isotropically.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: local modification of *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97*. Molecular graphics: *ORTEX7e* (McArdle, 1995, Burnett & Johnson, 1996). Software used to prepare material for publication: *SHELXL97*.

This work was supported financially by the Ministry for Science and Technology of the Republic of Serbia.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1046). Services for accessing these data are described at the back of the journal.

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