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Diammonium diaquabis(malonato-κ^2O,O')cobaltate(II) dihydrate

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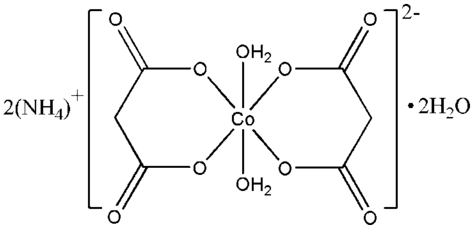
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.042; wR factor = 0.108; data-to-parameter ratio = 13.2.

The title complex, $(NH_4)_2[Co(C_3H_3O_4)_2(H_2O)_2]\cdot 2H_2O$, features a six-coordinate Co atom located on a center of symmetry. The octahedral O_6 coordination geometry is defined by two bidentate malonate ligands and two water molecules, with the latter in a *trans* configuration. The molecules are linked through O—H···O and N—H···O hydrogen-bonding interactions, forming a three-dimensional supramolecular network.

Related literature

For related literature, see: Delgado *et al.* (2006); Saadeh *et al.* (1993); Wang *et al.* (2005); Wuest (2005); Yolanda *et al.* (2002).



Experimental

Crystal data

$(NH_4)_2[Co(C_3H_3O_4)_2(H_2O)_2]\cdot 2H_2O$
M_r = 371.17
Triclinic, $P\overline{1}$
a = 6.950 (2) Å
b = 7.075 (2) Å
c = 7.433 (2) Å
α = 89.032 (5)°
β = 73.076 (5)°
γ = 88.062 (5)°
V = 349.45 (17) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.29 mm^{-1}
T = 298 (2) K
0.24 × 0.21 × 0.18 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.747, T_{max} = 0.801
1817 measured reflections
1285 independent reflections
1246 reflections with $I > 2\sigma(I)$
R_{int} = 0.057

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.107
S = 1.09
1285 reflections
97 parameters
4 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.76 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5A···O6^{i}	0.85	1.90	2.723 (3)	164
O5—H5B···O4^{i}	0.85	1.82	2.663 (3)	172
O6—H6A···O1^{ii}	0.84	2.57	3.336 (3)	153
O6—H6A···O2^{ii}	0.84	1.95	2.704 (3)	149
O6—H6B···O3^{iii}	0.85	2.57	3.063 (3)	118
O6—H6B···O5^{iii}	0.85	2.17	2.879 (3)	141
N1—H1A···O6^{iv}	0.85	2.16	2.950 (3)	155
N1—H1B···O3^{v}	0.85	1.97	2.805 (3)	165
N1—H1C···O4^{vi}	0.85	2.33	2.988 (3)	135
N1—H1D···O2	0.85	2.06	2.857 (4)	155

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+1, -y+1, -z$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1, -y, -z$; (v) $-x, -y+1, -z+1$; (vi) $x, y, z-1$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2245).

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supplementary materials

Acta Cryst. (2008). E**64**, m493 [**doi:10.1107/S1600536808004625**]

Diammonium diaquabis(malonato-$\kappa^2 O,O'$)cobaltate(II) dihydrate

H. Xu and **F. Wang**

Comment

In the design of supramolecular complexes, a well known and effective strategy is the matching of suitable hydrogen bond donors and acceptors (Wuest, 2005). Metal aqua-ions may act as excellent, readily available hydrogen bond donors with limited acceptor properties. Several novel complexes with metal aqua-ions have been reported (Delgado *et al.*, 2006; Saadeh *et al.*, 1993; Wang *et al.*, 2005; Yolanda *et al.*, 2002.) We report here the crystal structure of the title complex, (I), $[NH_4]_2[Co(C_3H_3O_4)_2(OH_2)_2]\cdot 2H_2O$, Fig. 1, in which the asymmetric comprises half a complex dianion, $[Co(C_3H_3O_4)_2(OH_2)_2]$, situated on a center of inversion, an ammonium cation and a water molecule of crystallization.

The coordination polyhedron of the Co atom is that of an elongated octahedron defined by an O_6 donor set. Four carboxylate O atoms, derived from two bidentate malonate ligands, build the equatorial plane, whereas two water molecules occupy the axial sites. As expected the Co—O_{axial} distance [2.1020 (19) Å] is longer than the Co—$O_{equatorial}$ distances [2.0502 (18) and 2.0592 (17) Å]. The bond angles around the cobalt atom are close to that expected for an ideal octahedron. The molecules are linked through O—H···O and N—H···O hydrogen-bonding interactions and form a 3-D supramolecular network, Fig. 2 and Table 2.

Experimental

Crystals of (I) were obtained by a diffusion method. In one arm of an U-tube was placed $[NH_4]_2[C_3H_2O_4]$ (30 mg, 0.2 mmol) in water/ethanol (1:1; 10 ml) and in the other $[Co(ClO_4)_2]\cdot 6H_2O$ (37 mg, 0.1 mmol) in water/ethanol (1:1; 10 ml). The purple crystals were collected by filtration, washed with distilled water, followed by ethanol and dried under reduced pressure for 2 h. Analysis found: C 19.24, H 5.27, N 7.32; $C_6H_{20}CoN_2O_{12}$ requires: C 19.42, H 5.43, N 7.55.

Refinement

All H atoms were placed geometrically with C—H, N—H and O—H distances of 0.97, 0.85 and 0.85 Å, respectively, and with $U_{iso}(H) = 1.2U_{eq}(C, N, O)$. Hydroxyl-H atoms were allowed to rotate to best fit the experimental electron density.

Figures

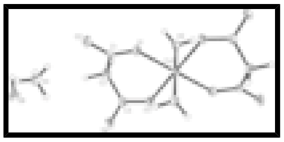

Fig. 1. The structure of (I) expanded to show the coordination geometry of the Co atom which sits on a center of inversion; the unlabelled atoms are related by the symmetry operation −*x*, 2 − *y*, 1 − *z*. The figure shows 30% probability displacement ellipsoids and the atom-numbering scheme.

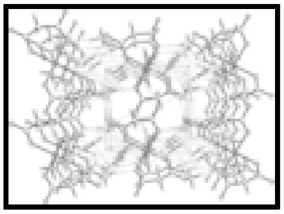

Fig. 2. The 3-D superamolecular structure of (I). Hydrogen bond interactions are shown as dashed lines.

Diammonium diaquabis(malonato-κ^2*O,O'*)cobalt(II) dihydrate

Crystal data

$(NH_4)_2[Co(C_3H_3O_4)_2(H_2O)_2]\cdot 2H_2O$
$M_r = 371.17$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 6.950$ (2) Å
$b = 7.075$ (2) Å
$c = 7.433$ (2) Å
$\alpha = 89.032$ (5)°
$\beta = 73.076$ (5)°
$\gamma = 88.062$ (5)°
$V = 349.45$ (17) Å^3

$Z = 1$
$F_{000} = 193$
$D_x = 1.764$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 1285 reflections
$\theta = 2.9$–25.5°
$\mu = 1.29$ mm^{-1}
$T = 298$ (2) K
Block, purple
0.24 × 0.21 × 0.18 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Monochromator: graphite
$T = 298(2)$ K
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
$T_{min} = 0.747$, $T_{max} = 0.801$
1817 measured reflections

1285 independent reflections
1246 reflections with $I > 2\sigma(I)$
$R_{int} = 0.057$
$\theta_{max} = 25.5$°
$\theta_{min} = 2.9$°
$h = -8\rightarrow 8$
$k = -7\rightarrow 8$
$l = -6\rightarrow 8$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.107$
$S = 1.09$
1285 reflections

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0668P)^2 + 0.0816P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.39$ e Å^{-3}

97 parameters	$\Delta\rho_{min}$ = −0.76 e Å^{-3}
4 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of F^2 > 2sigma(F^2) is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.0000	1.0000	0.5000	0.0246 (2)
C1	0.2349 (4)	0.7294 (4)	0.2083 (4)	0.0302 (6)
C2	0.3182 (4)	0.6385 (4)	0.3572 (4)	0.0371 (7)
H2A	0.3696	0.5128	0.3143	0.045*
H2B	0.4320	0.7108	0.3638	0.045*
C3	0.1802 (4)	0.6198 (3)	0.5553 (3)	0.0265 (5)
N1	0.1772 (4)	0.2806 (4)	0.0011 (3)	0.0438 (6)
H1B	0.0825	0.2715	0.1031	0.053*
H1A	0.2558	0.1845	−0.0309	0.053*
H1C	0.1082	0.3123	−0.0726	0.053*
H1D	0.2470	0.3754	0.0071	0.053*
O1	0.1213 (3)	0.8738 (3)	0.2439 (2)	0.0322 (4)
O2	0.2920 (4)	0.6563 (3)	0.0484 (3)	0.0501 (6)
O3	0.0789 (3)	0.7649 (2)	0.6328 (2)	0.0315 (4)
O4	0.1752 (3)	0.4670 (2)	0.6380 (3)	0.0371 (5)
O5	0.2733 (3)	1.1242 (3)	0.4906 (3)	0.0347 (5)
H5A	0.3694	1.1179	0.3893	0.042*
H5B	0.2513	1.2374	0.5296	0.042*
O6	0.6141 (3)	0.0563 (3)	0.2034 (3)	0.0391 (5)
H6B	0.7011	0.0079	0.2521	0.047*
H6A	0.6729	0.1133	0.1038	0.047*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0283 (3)	0.0183 (3)	0.0245 (3)	0.00435 (19)	−0.0037 (2)	−0.00096 (19)
C1	0.0355 (14)	0.0214 (13)	0.0272 (13)	−0.0012 (11)	0.0012 (11)	−0.0005 (10)
C2	0.0345 (15)	0.0327 (15)	0.0364 (15)	0.0115 (12)	0.0003 (12)	0.0024 (12)

C3	0.0301 (13)	0.0227 (13)	0.0276 (13)	0.0007 (10)	−0.0103 (11)	−0.0007 (10)
N1	0.0573 (17)	0.0370 (14)	0.0322 (13)	0.0090 (12)	−0.0063 (12)	−0.0035 (10)
O1	0.0394 (11)	0.0270 (10)	0.0266 (9)	0.0088 (8)	−0.0047 (8)	−0.0021 (7)
O2	0.0817 (18)	0.0295 (11)	0.0280 (11)	0.0148 (11)	−0.0001 (11)	−0.0061 (8)
O3	0.0435 (11)	0.0218 (9)	0.0250 (9)	0.0067 (8)	−0.0040 (8)	0.0008 (7)
O4	0.0534 (13)	0.0203 (10)	0.0353 (11)	0.0045 (9)	−0.0099 (9)	0.0013 (8)
O5	0.0310 (10)	0.0241 (10)	0.0430 (11)	0.0009 (8)	−0.0012 (8)	−0.0054 (8)
O6	0.0400 (11)	0.0414 (12)	0.0322 (11)	−0.0001 (9)	−0.0054 (9)	0.0059 (9)

Geometric parameters (Å, °)

Co1—O1	2.0502 (18)	C2—H2B	0.9699
Co1—O1^{i}	2.0502 (18)	C3—O4	1.231 (3)
Co1—O3^{i}	2.0592 (17)	C3—O3	1.272 (3)
Co1—O3	2.0592 (17)	N1—H1B	0.8500
Co1—O5^{i}	2.1020 (19)	N1—H1A	0.8500
Co1—O5	2.1020 (19)	N1—H1C	0.8500
C1—O2	1.252 (3)	N1—H1D	0.8500
C1—O1	1.253 (3)	O5—H5A	0.8498
C1—C2	1.516 (4)	O5—H5B	0.8498
C2—C3	1.512 (4)	O6—H6B	0.8500
C2—H2A	0.9699	O6—H6A	0.8378
O1—Co1—O1^{i}	180	C1—C2—H2A	107.8
O1—Co1—O3^{i}	89.76 (7)	C3—C2—H2B	107.3
O1^{i}—Co1—O3^{i}	90.24 (7)	C1—C2—H2B	107.8
O1—Co1—O3	90.24 (7)	H2A—C2—H2B	107.1
O1^{i}—Co1—O3	89.76 (7)	O4—C3—O3	122.4 (2)
O3^{i}—Co1—O3	180	O4—C3—C2	119.0 (2)
O1—Co1—O5^{i}	87.61 (8)	O3—C3—C2	118.6 (2)
O1^{i}—Co1—O5^{i}	92.39 (8)	H1B—N1—H1A	116.6
O3^{i}—Co1—O5^{i}	90.37 (8)	H1B—N1—H1C	99.2
O3—Co1—O5^{i}	89.63 (8)	H1A—N1—H1C	116.0
O1—Co1—O5	92.39 (8)	H1B—N1—H1D	109.3
O1^{i}—Co1—O5	87.61 (8)	H1A—N1—H1D	108.6
O3^{i}—Co1—O5	89.63 (8)	H1C—N1—H1D	106.4
O3—Co1—O5	90.37 (8)	C1—O1—Co1	127.52 (17)
O5^{i}—Co1—O5	180	C3—O3—Co1	127.00 (16)
O2—C1—O1	122.7 (3)	Co1—O5—H5A	118.7
O2—C1—C2	116.3 (2)	Co1—O5—H5B	109.9
O1—C1—C2	121.0 (2)	H5A—O5—H5B	111.0
C3—C2—C1	118.6 (2)	H6B—O6—H6A	109.3
C3—C2—H2A	107.7		

Symmetry codes: (i) $-x$, $-y+2$, $-z+1$.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5A···O6^{ii}	0.85	1.90	2.723 (3)	164
O5—H5B···O4^{ii}	0.85	1.82	2.663 (3)	172
O6—H6A···O1^{iii}	0.84	2.57	3.336 (3)	153
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N1—H1B···O3^{vi}	0.85	1.97	2.805 (3)	165
N1—H1C···O4^{vii}	0.85	2.33	2.988 (3)	135
N1—H1D···O2	0.85	2.06	2.857 (4)	155

Symmetry codes: (ii) *x*, *y*+1, *z*; (iii) −*x*+1, −*y*+1, −*z*; (iv) −*x*+1, −*y*+1, −*z*+1; (v) −*x*+1, −*y*, −*z*; (vi) −*x*, −*y*+1, −*z*+1; (vii) *x*, *y*, *z*−1.

Fig. 1

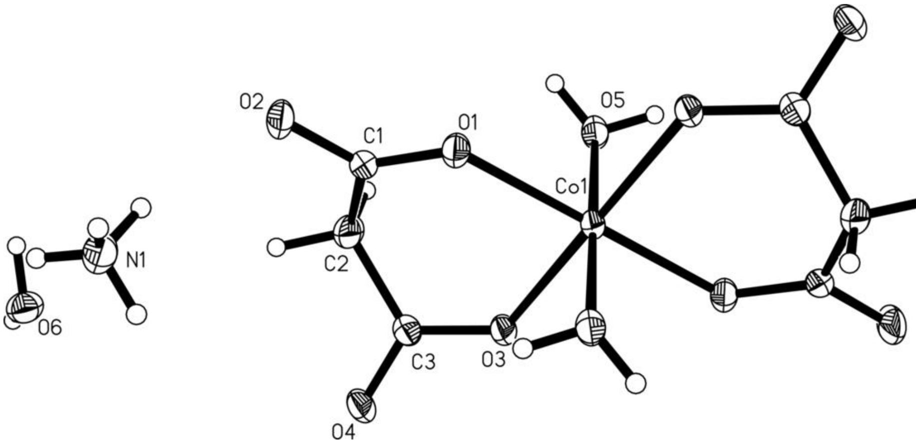

Fig. 2