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

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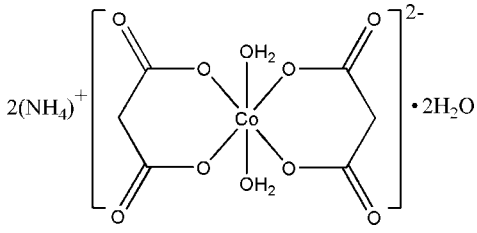
Key indicators: single-crystal X-ray study; $T$ = 298 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.042; $wR$ factor = 0.108; data-to-parameter ratio = 13.2.

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
$\alpha$ = 89.032 (5)°
$\beta$ = 73.076 (5)°
$\gamma$ = 88.062 (5)°
$V$ = 349.45 (17) Å$^3$
$Z$ = 1
Mo $K\alpha$ radiation
$\mu$ = 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—H5$A$···O6$^{i}$ | 0.85 | 1.90 | 2.723 (3) | 164 |
| O5—H5$B$···O4$^{i}$ | 0.85 | 1.82 | 2.663 (3) | 172 |
| O6—H6$A$···O1$^{ii}$ | 0.84 | 2.57 | 3.336 (3) | 153 |
| O6—H6$A$···O2$^{ii}$ | 0.84 | 1.95 | 2.704 (3) | 149 |
| O6—H6$B$···O3$^{iii}$ | 0.85 | 2.57 | 3.063 (3) | 118 |
| O6—H6$B$···O5$^{iii}$ | 0.85 | 2.17 | 2.879 (3) | 141 |
| N1—H1$A$···O6$^{iv}$ | 0.85 | 2.16 | 2.950 (3) | 155 |
| N1—H1$B$···O3$^{v}$ | 0.85 | 1.97 | 2.805 (3) | 165 |
| N1—H1$C$···O4$^{vi}$ | 0.85 | 2.33 | 2.988 (3) | 135 |
| N1—H1$D$···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).

## References

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# supporting information

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

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

**Haiyun Xu and Fengwu Wang**

### S1. 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), $[NH_4]_2[Co(C_3H_3O_4)_2(OH_2)_2].2H_2O$, 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.

### S2. 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 $[Co(ClO_4)_2].6H_2O$ (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.

### S3. 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) = 1.2$U_{eq}$(C, N, O). Hydroxyl-H atoms were allowed to rotate to best fit the experimental electron density.

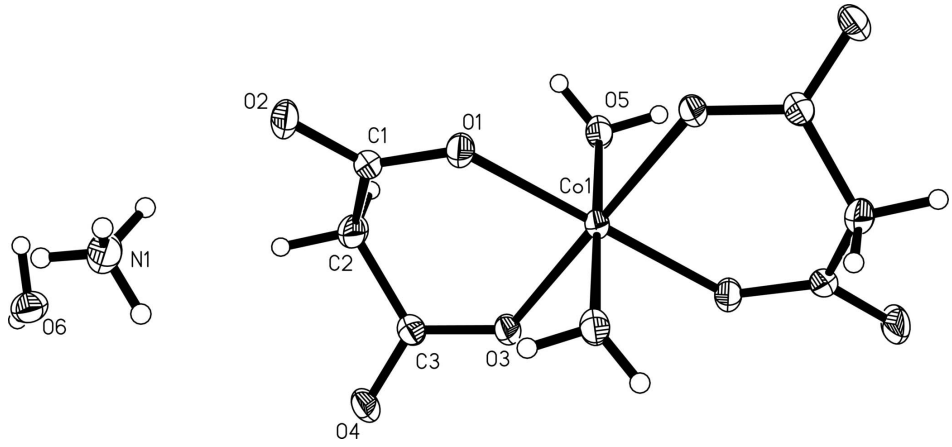


**Figure 1**

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.

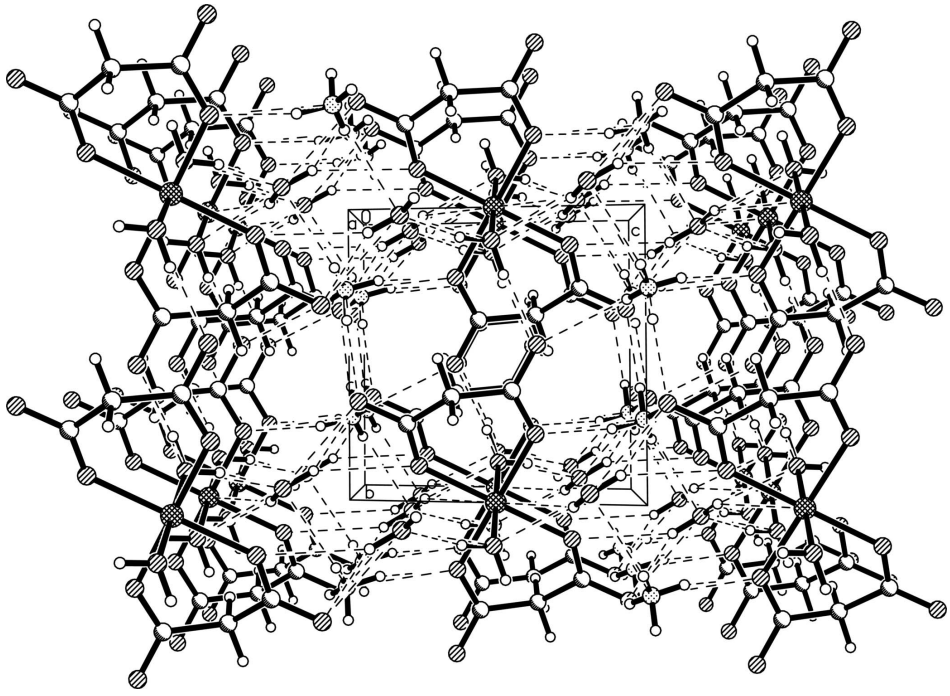

**Figure 2**

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

**Diammonium diaquabis(malonato-$\kappa^2O,O'$)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 K
Block, purple
0.24 × 0.21 × 0.18 mm

*Data collection*

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ 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→8
$k$ = −7→8
$l$ = −6→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
97 parameters
4 restraints
Primary atom site location: structure-invariant direct methods

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$^{-3}$
$\Delta\rho_{min}$ = −0.76 e Å$^{-3}$

*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 $F^2 > \sigma(F^2)$ 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 (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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, º)*

| | | | |
|---|---|---|---|
| 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 code: (i) −*x*, −*y*+2, −*z*+1.

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O5—H5*A*···O6$^{ii}$ | 0.85 | 1.90 | 2.723 (3) | 164 |
| O5—H5*B*···O4$^{ii}$ | 0.85 | 1.82 | 2.663 (3) | 172 |
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| N1—H1*B*···O3$^{vi}$ | 0.85 | 1.97 | 2.805 (3) | 165 |
| N1—H1*C*···O4$^{vii}$ | 0.85 | 2.33 | 2.988 (3) | 135 |
| N1—H1*D*···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.