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Bis(guanidinium) *trans*-diaquabis(malonato-κ^2O,O')cobaltate(II)

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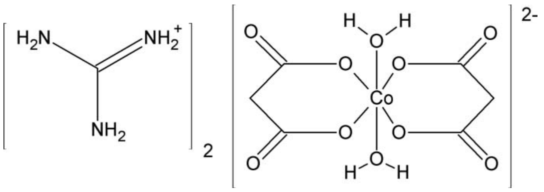
Key indicators: single-crystal X-ray study; *T* = 100 K; mean σ(C–C) = 0.002 Å; *R* factor = 0.031; *wR* factor = 0.091; data-to-parameter ratio = 30.0.

In the title compound, $(CH_6N_3)_2[Co(C_3H_2O_4)_2(H_2O)_2]$, the anions lie on crystallographic centres of inversion. The crystal structure adopts a layered structure, stabilized by an extensive network of N—H···O and O—H···O hydrogen bonds. One H atom of the guanidinium cation does not participate in any strong hydrogen bonds.

Related literature

For related literature, see: Cygler *et al.* (1976); Etter *et al.* (1990); Hemamalini *et al.* (2006); Videnova-Adrabińska *et al.* (2007); Zhao *et al.* (2007).



Experimental

Crystal data

$(CH_6N_3)_2[Co(C_3H_2O_4)_2(H_2O)_2]$
M_r = 419.23
Monoclinic, $P2_1/c$
a = 8.969 (3) Å
b = 11.524 (4) Å
c = 8.272 (3) Å
β = 111.61 (4)°
V = 794.9 (5) Å^3
Z = 2
Mo *K*α radiation
μ = 1.15 mm^{-1}
T = 100 (2) K
0.31 × 0.25 × 0.18 mm

Data collection

Oxford Diffraction Xcalibur PX CCD diffractometer
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2006)
T_{min} = 0.720, T_{max} = 0.848
11133 measured reflections
3445 independent reflections
2768 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.091
S = 1.03
3445 reflections
115 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.58 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N20—H201···O11	0.86	2.26	3.043 (2)	151
N20—H201···O1*W*^{i}	0.86	2.46	3.117 (2)	133
N10—H102···O21^{ii}	0.86	2.14	2.984 (2)	168
N10—H101···O12^{iii}	0.86	2.07	2.930 (2)	177
N30—H301···O22^{iii}	0.86	1.99	2.841 (2)	168
N30—H302···O21	0.86	2.08	2.934 (2)	173
O1*W*—H1*W*···O22^{iv}	0.82	1.85	2.633 (2)	160
O1*W*—H2*W*···O21^{v}	0.82	2.04	2.835 (2)	162

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+2, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x+1, y, z+1$; (iv) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (v) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BI2267).

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S1. Comment

Supramolecular motifs with malonate ions have been widely explored in crystal engineering (Hemamalini *et al.*, 2006, Zhao *et al.*, 2007). These ligands as part of $[M(\text{malonate})_2(H_2O)_2]^{2-}$ anions have been used as "robust anionic building blocks for crystal engineering of inorganic-organic hybrid materials" (Zhao *et al.*, 2007).

The title compound consists of *trans*-diaquabis(malonato-*O*,*O*′)-cobaltate(II) anions and guanidinium cations (Fig. 1). In each centrosymmetric anion, the central Co^{II} atom is octahedrally surrounded by two water ligands and two chelating malonate ligands. The guanidinium cation geometrical parameters agree with those previously reported (Cygler *et al.*, 1976).

The crystal adopts a layered structure, common for guanidinium salts (Fig. 2; Videnova-Adrabińska *et al.*, 2007). Alternate layers consist of the *trans*-diaquabis(malonato-*O*,*O*′)-cobaltate(II) anions and the guanidinium cations. Within each anion layer, both water ligands are involved in O—H···O hydrogen bonds. In two of these hydrogen bonds, the carboxyl O22 and O21 atoms from the malonate ligands act as acceptors (Fig. 3). Each guanidinium cation is hydrogen bonded to the anions from both neighbouring anion layers (Fig. 3). Atom H201 participates in a bifurcated N—H···O hydrogen bond to the malonate carboxyl O11 and water O1W atoms, constituting a $R^1_2(4)$ motif (Etter *et al.*, 1990). Atom H302 is involved in the N30—H302···O21 hydrogen bond with the malonate carboxyl O21 atom. This hydrogen bond along with the N20—H201···O11 hydrogen bonds forms a $R^2_2(8)$ motif (Etter *et al.*, 1990). The hydrogen bonds formed between the guanidinium cation and another anion layer are the following: N10—H102···O21, N10—H101···O12 and N30—H301···O22. The latter two form a $R^3_1(8)$ structural motif (Etter *et al.*, 1990). It is interesting to note that one guanidinium H atom (H202) is not involved in any strong hydrogen bonds.

S2. Experimental

The title complex was prepared by dissolving guanidinium carbonate (4 mmol, 720 mg) and malonic acid (2 mmol, 208 mg) in water (20 ml). The mixture was stirred for about 1 h at room temperature. Subsequently, $Co(ClO_4)_2$ (1 mmol, 366 mg) was added to the resulting solution and stirred for about 3 h at room temperature. The solution yielded crystals after 10 d.

S3. Refinement

The malonate H atoms were generated in their calculated positions. All remaining H atoms were found in difference Fourier maps and their positions were refined initially with the water O—H bond lengths and guanidinium N—H bond lengths restrained to be 0.820 (1) and 0.860 (1) Å, respectively. In the final stages of refinement, these H atoms were constrained to ride on their parent atoms (AFIX 3 instruction) with $U_{iso}(H) = 1.2U_{eq}(\text{parent atom})$.

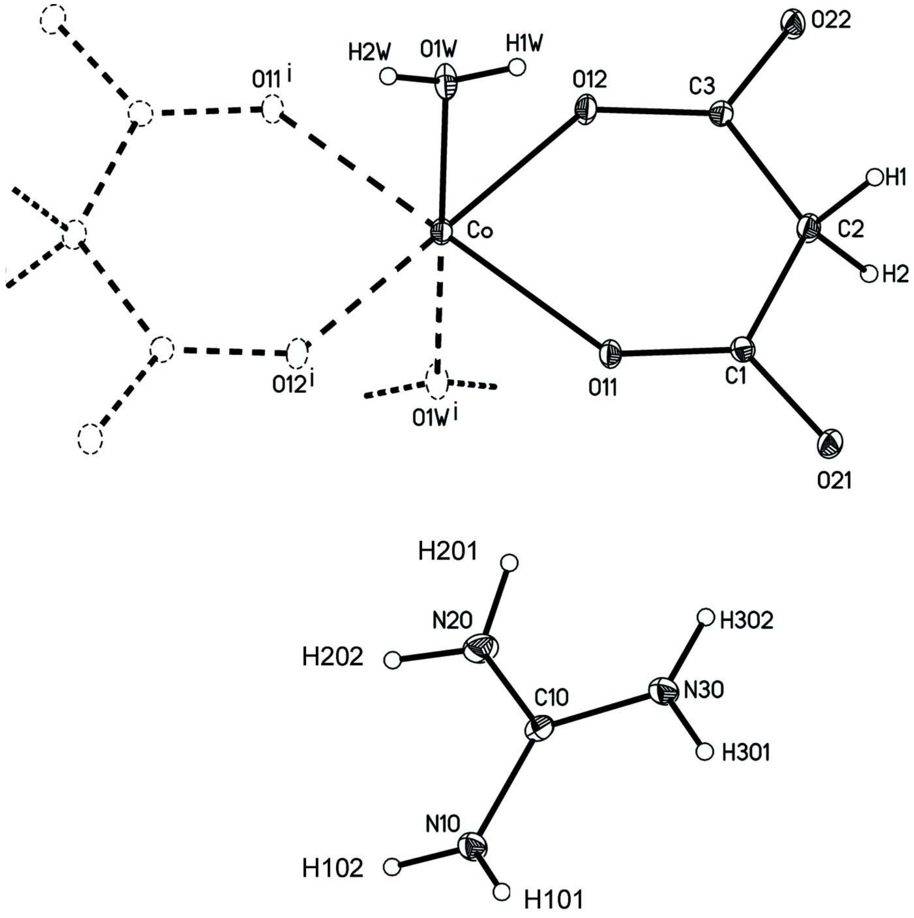

Figure 1

The molecular structure of the title compound with displacement ellipsoids at 30% probability for non-H atoms. The part indicated with dashed lines is generated by the symmetry operation -*x* + 1, -*y* + 1, -*z* + 1.

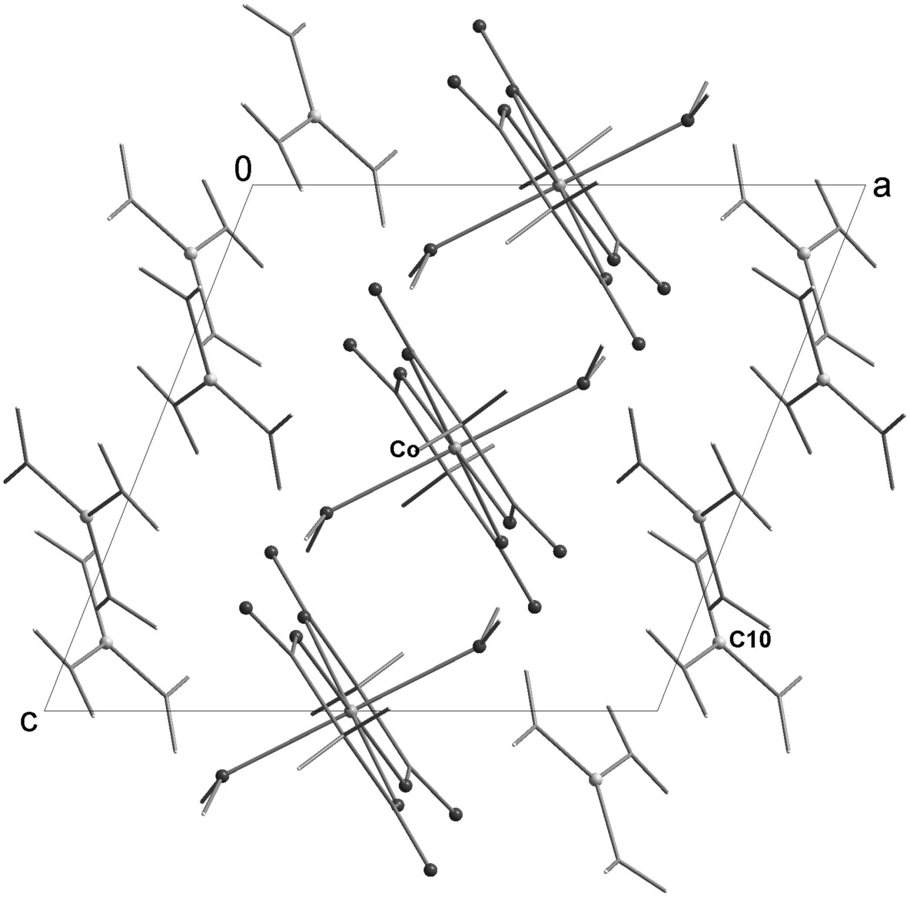

Figure 2

View of the crystal structure along [010] showing cation and anion layers parallel to the *bc* plane.

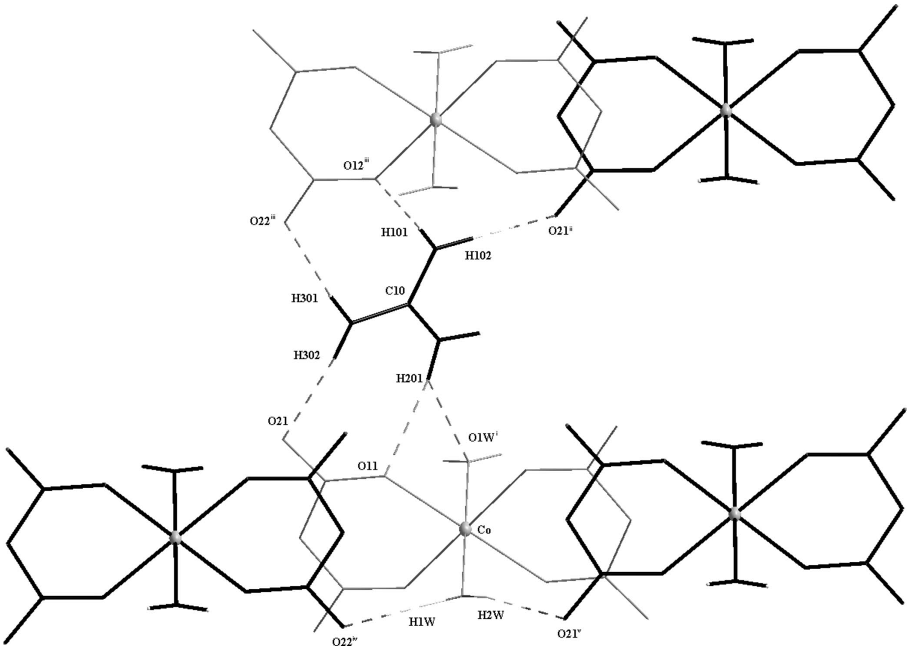

Figure 3

View of the hydrogen bonding scheme. The non-aqueous H atoms not participating in any hydrogen bonds have been omitted and the neighbouring ions have been denoted with different colour (gray and black). The hydrogen bonds are indicated with dashed lines. Symmetry operations: (i) -*x* + 1, -*y* + 1, -*z* + 1; (ii) -*x* + 2, *y* - 1/2, -*z* + 3/2; (iii) *x* + 1, *y*, *z* + 1; (iv) *x*, -*y* + 3/2, *z* + 1/2; (v) -*x* + 1, *y* - 1/2, -*z* + 3/2.

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Crystal data

$(CH_6N_3)_2[Co(C_3H_2O_4)_2(H_2O)_2]$
$M_r = 419.23$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 8.969$ (3) Å
$b = 11.524$ (4) Å
$c = 8.272$ (3) Å
$\beta = 111.61$ (4)°
$V = 794.9$ (5) Å^3
$Z = 2$
$F(000) = 434$
$D_x = 1.752$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9403 reflections
$\theta = 2$–35°
$\mu = 1.15$ mm^{-1}
$T = 100$ K
Block, pink
0.31 × 0.25 × 0.18 mm

Data collection

Oxford Diffraction XcaliburPX CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
ω & φ scans
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2006)
$T_{min} = 0.720$, $T_{max} = 0.848$
11133 measured reflections
3445 independent reflections
2768 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 36.5°$, $\theta_{min} = 3.0°$
$h = -14 \rightarrow 14$
$k = -15 \rightarrow 17$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.091$
$S = 1.03$
3445 reflections
115 parameters
0 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
$w = 1/[\sigma^2(F_o^2) + (0.060P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{iso}*/U_{eq}$
Co	0.5000	0.5000	0.5000	0.00962 (6)
O11	0.63731 (9)	0.63701 (7)	0.64141 (10)	0.01133 (14)
O21	0.73793 (9)	0.81502 (7)	0.69642 (10)	0.01402 (15)
O12	0.36319 (9)	0.61700 (7)	0.32127 (10)	0.01255 (15)
O22	0.26743 (9)	0.78487 (7)	0.19808 (10)	0.01408 (16)
N10	1.18921 (11)	0.52517 (9)	0.97198 (13)	0.01332 (17)
H101	1.2399	0.5498	1.0759	0.016*
H102	1.2123	0.4595	0.9380	0.016*
N20	0.96719 (12)	0.53173 (10)	0.71656 (13)	0.01675 (19)
H201	0.8722	0.5562	0.6569	0.020*
H202	0.9805	0.4605	0.6947	0.020*
N30	1.01516 (11)	0.68018 (9)	0.91834 (13)	0.01470 (17)
H301	1.0815	0.7133	1.0096	0.018*
H302	0.9314	0.7147	0.8478	0.018*
C2	0.49632 (12)	0.79769 (10)	0.45438 (14)	0.01213 (19)
H1	0.5473	0.8466	0.3909	0.015*
H2	0.4393	0.8512	0.5055	0.015*
O1W	0.33221 (11)	0.50357 (6)	0.62312 (12)	0.01377 (16)
H1W	0.3146	0.5620	0.6696	0.017*
H2W	0.3253	0.4567	0.6947	0.017*
C3	0.36771 (11)	0.72673 (9)	0.31750 (13)	0.00952 (17)
C10	1.05660 (12)	0.57952 (10)	0.86977 (13)	0.01182 (18)
C1	0.63218 (11)	0.74416 (9)	0.60624 (13)	0.00945 (17)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co	0.01041 (10)	0.00690 (11)	0.01022 (10)	−0.00018 (6)	0.00225 (7)	0.00026 (6)
O11	0.0121 (3)	0.0070 (4)	0.0123 (3)	0.0000 (2)	0.0014 (2)	−0.0010 (3)
O21	0.0127 (3)	0.0093 (4)	0.0154 (4)	−0.0015 (3)	−0.0004 (3)	−0.0020 (3)
O12	0.0138 (3)	0.0070 (4)	0.0124 (3)	−0.0008 (3)	−0.0003 (3)	0.0009 (3)
O22	0.0134 (3)	0.0086 (4)	0.0144 (4)	0.0002 (3)	−0.0017 (3)	0.0021 (3)
N10	0.0120 (4)	0.0128 (4)	0.0128 (4)	0.0013 (3)	0.0018 (3)	−0.0006 (3)
N20	0.0125 (4)	0.0190 (5)	0.0153 (4)	−0.0012 (3)	0.0011 (3)	−0.0049 (4)

N30	0.0111 (4)	0.0136 (4)	0.0158 (4)	0.0014 (3)	0.0008 (3)	−0.0014 (3)
O1W	0.0200 (4)	0.0074 (4)	0.0180 (4)	0.0006 (3)	0.0118 (3)	0.0001 (3)
C1	0.0094 (4)	0.0088 (5)	0.0102 (4)	0.0004 (3)	0.0037 (3)	−0.0012 (3)
C2	0.0126 (4)	0.0082 (5)	0.0119 (4)	−0.0008 (3)	0.0002 (3)	−0.0002 (3)
C3	0.0096 (4)	0.0082 (5)	0.0101 (4)	−0.0003 (3)	0.0029 (3)	0.0003 (3)
C10	0.0101 (4)	0.0126 (5)	0.0123 (4)	−0.0023 (3)	0.0035 (3)	−0.0002 (3)

Geometric parameters (Å, º)

Co—O11	2.078 (1)	O11—C1	1.2655 (14)
Co—O12	2.043 (2)	O21—C1	1.2656 (14)
Co—O1W	2.105 (2)	O12—C3	1.2659 (14)
N10—C10	1.334 (2)	O22—C3	1.2567 (14)
N20—C10	1.343 (2)	C2—C1	1.5218 (16)
N30—C10	1.325 (2)	C2—C3	1.5229 (16)
Co—O12^{i}	2.0429 (11)	C2—H1	0.99
Co—O11^{i}	2.0777 (10)	C2—H2	0.99
Co—O1W^{i}	2.1053 (11)		

O12—Co—O11	88.8 (1)	O11^{i}—Co—O1W^{i}	95.39 (4)
O12—Co—O1W	89.5 (1)	O1W—Co—O1W^{i}	180.0
O11—Co—O1W	95.4 (1)	C1—O11—Co	130.40 (7)
N30—C10—N10	120.2 (1)	C3—O12—Co	131.37 (7)
N30—C10—N20	120.6 (1)	C1—C2—C3	123.57 (10)
N10—C10—N20	119.2 (2)	C1—C2—H1	106.4
O12^{i}—Co—O12	180.0	C3—C2—H1	106.4
O12^{i}—Co—O11	91.18 (5)	C1—C2—H2	106.4
O12^{i}—Co—O11^{i}	88.82 (5)	C3—C2—H2	106.4
O12—Co—O11^{i}	91.18 (5)	H1—C2—H2	106.5
O11—Co—O11^{i}	180.0	O22—C3—O12	122.12 (10)
O12^{i}—Co—O1W	90.50 (4)	O22—C3—C2	115.15 (10)
O11^{i}—Co—O1W	84.61 (4)	O12—C3—C2	122.72 (9)
O12^{i}—Co—O1W^{i}	89.50 (4)	O11—C1—O21	122.56 (10)
O12—Co—O1W^{i}	90.50 (4)	O11—C1—C2	122.38 (9)
O11—Co—O1W^{i}	84.61 (4)	O21—C1—C2	115.05 (10)

C3—C2—C1—O11	−8.6 (2)	O1W^{i}—Co—O12—C3	−87.46 (10)
C3—C2—C1—O21	172.6 (1)	Co—O12—C3—O22	−176.83 (7)
O12^{i}—Co—O11—C1	174.90 (9)	Co—O12—C3—C2	4.47 (15)
O12—Co—O11—C1	−5.10 (9)	C1—C2—C3—O22	−177.85 (10)
O1W—Co—O11—C1	−94.49 (9)	C1—C2—C3—O12	0.93 (16)
O1W^{i}—Co—O11—C1	85.51 (9)	Co—O11—C1—O21	−170.78 (7)
O11^{i}—Co—O12—C3	177.14 (9)	Co—O11—C1—C2	10.54 (14)
O1W—Co—O12—C3	92.54 (10)		

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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