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Key indicators

Single-crystal X-ray study
T = 120 K
Mean $\sigma(C-C)$ = 0.008 Å
Some non-H atoms missing
R factor = 0.065
wR factor = 0.175
Data-to-parameter ratio = 16.0

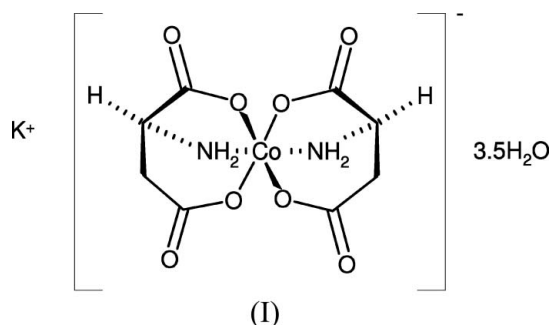
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Potassium *cis*-[(*R*)-aspartato(2-)][(*S*)-aspartato(2-)]-cobaltate(III) 3.5-hydrate at 120 K

The title compound, $K[Co(C_4H_4NO_4)_2] \cdot 3.5H_2O$, is a by-product resulting from adventitious oxidation, in the presence of racemic aspartic acid, of cobalt(II) in a cobaltous starting material. The presence of both enantiomeric forms of the tridentate aspartate ligand in the cobaltate anion is significant in eliminating the possibility of the existence of isomeric forms of the *cis*(N) isomer.

Comment

As part of our continuing study of transition metal complexes with amino acids (Felcman & de Miranda, 1997; de Miranda & Felcman, 2001; de Miranda *et al.*, 2002; Felcman *et al.*, 2003), we have isolated and characterized the title compound, (I), from an aqueous reaction mixture containing DL-aspartic acid (asp), guanidinoacetic acid (gaa) and Co^{II} (1:1:1). Crystals of (I) were obtained after several months. No crystalline complex containing gaa, either alone or in a mixed complex with asp, appeared in a similar time.



The asymmetric unit in the structure of (I) is shown in Fig. 1, and selected bond lengths and angles are given in Table 1. In the anion, an enantiomeric pair of asp dianions, with identical numbering of the atoms and distinguished by the suffixes *A* and *B*, act as tridentate ligands, creating octahedral coordination of atom Co1. The enantiomeric relationship of the asp dianions in the complex anion is evident in the torsion angles given in Table 1 and significant in later discussion of the isomerism of such complexes.

The K^+ cation caps one face of the coordination octahedron of the anion to give a $Co1 \cdots K1$ distance of 3.6502 (14) Å. Its sevenfold coordination (Fig. 2) is completed by two non-coordinating O atoms associated with two further cobaltate anions and by two water molecules. A complex arrangement of $K-O$ bonds connects the ions in layers parallel to (100), as shown schematically in Fig. 3. The connectivity creates, as the sub-unit, rings of four anions with four bridging K^+ ions, two of which are seen in the case of the eight octahedra nearest the

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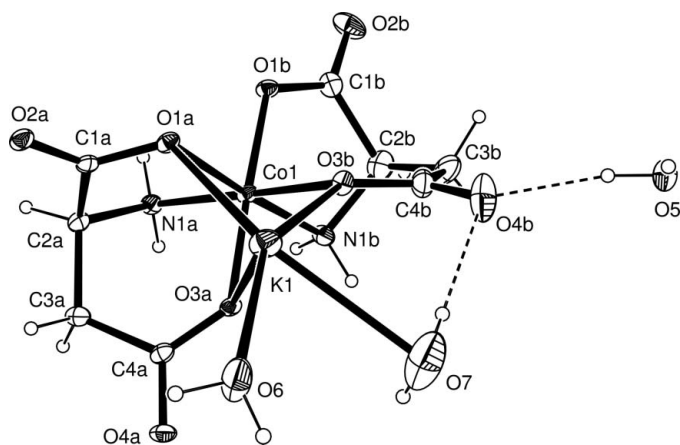


Figure 1
The asymmetric unit of (I). Displacement ellipsoids are drawn at the 20% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds.

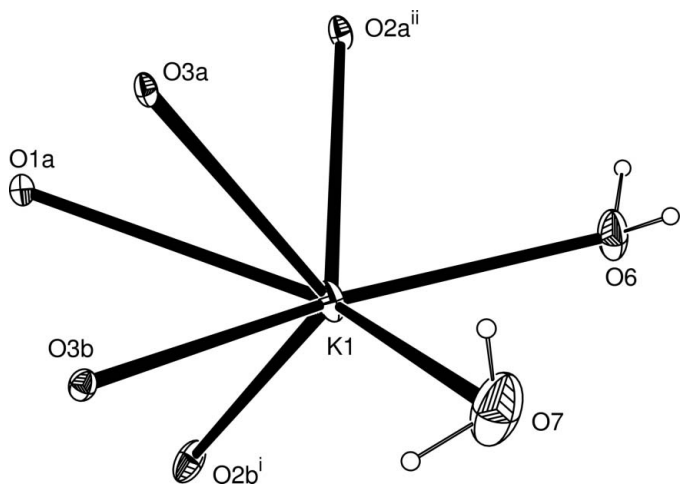


Figure 2
The coordination of the K^+ cation in (I). Displacement ellipsoids are drawn at the 10% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $-x + 2, -y + 1, -z + 1$.]

horizontal mid-line of Fig. 3. When the layer is seen edge-on, as in Fig. 4, it is clear that the distribution of the anions creates grooves running in the direction of c in which the K^+ cations lie.

Also shown in Fig. 4 are the water molecules which, for the choice of origin used in the refinement of the structure, occur in layers centred on $x = \frac{1}{2}$ and alternate with layers of anions centred on $x = 0$, the whole arrangement being replicated by cell translation in the direction of a . As shown in Table 2, a large number of $N-H \cdots O$ and $O-H \cdots O$ hydrogen bonds are present in the structure of (I). Only those hydrogen bonds involving the O5 water molecule, which is the only water molecule not contributing to the immediate coordination of the K^+ ion, provide connectivity between adjacent layers of ions. The $O5-H5A \cdots O4B$ hydrogen bond is directed to one

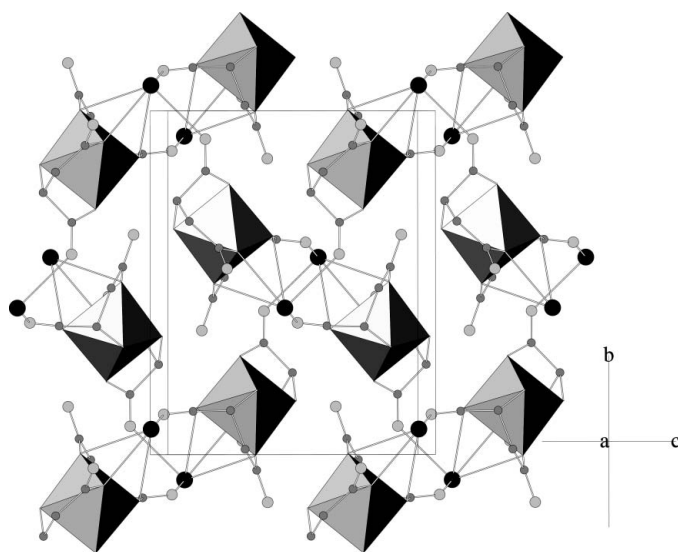


Figure 3
A schematic view of a layer of ions in (I). The cobaltate anions are represented by coordination octahedra. Circles of arbitrary radii represent other atoms, large and black for K and lighter and decreasing in size for O and C in that order. H atoms and water molecules have been omitted for clarity.

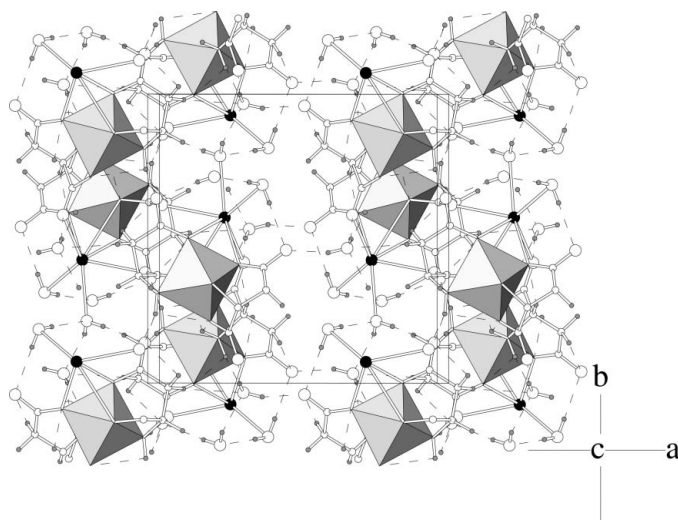


Figure 4
A schematic representation of the unit cell contents of (I), viewed along [001]. The cobaltate anions are represented by coordination octahedra. Circles of arbitrary radii represent other atoms, large and black for K and lighter and decreasing in size for O, C and H in that order. Dashed lines represent hydrogen bonds.

of the neighbouring layers and the other three, of the form $N1B-H11B \cdots O5^{iv}$, $O6-H6A \cdots O5^v$ and $O5-H5B \cdots O2B^v$ [symmetry codes: (iv) $-x + 1, -y + 1, -z$; (v) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$], to the other. Also given in Table 2 are details of two weak $C-H \cdots O$ hydrogen bonds.

The asp ligands can be considered to have three distinct atom types available for bonding to the central metal atom because, on the basis of the labelling scheme used in this report, atom O1 is part of the carboxylate group directly

attached to the asymmetric centre (C2) of the ligand and is distinguishable, therefore, from atom O3, which is part of a carboxylate group which is β to the asymmetric centre. When the octahedral complex is formed with one asp in each of its two enantiomeric forms, as is the case in (I), only one *cis*(N) isomer is possible in which *cis*(O1) and *cis*(O3) also occur. If, however, both asp ligands in the complex have the same enantiomeric form, say L, as in the cobaltate(III) compounds described by Oonish *et al.* (1973, 1975), the *cis*(N) arrangement is found in two isomeric forms, one with *trans*(O1) and the other with *trans*(O3), as is clearly demonstrated by Oonish *et al.* (1973).

The presence of Co^{III} in (I), determined by the application of charge-balance considerations to the structural model, is at variance with the nature of the Co^{II} salt starting material. However, the bond lengths and angles within the cobaltate anion in (I) are in good agreement with those found in other structures containing this type of anion such as, for example, those described by Oonish *et al.* (1973, 1975) and several other related structures. In contrast, recourse to the Cambridge Structural Database (Version 5.26; Allen, 2002) by means of the Chemical Database Service of the EPSRC (Fletcher *et al.*, 1996) has revealed only one example of a cobaltous aspartate species, namely cobaltous aspartate trihydrate, (II) (Doynes *et al.*, 1957), which is polymeric, has a Co:asp ratio of 1:1 [as distinct from 1:2 in (I)] and displays different (slightly longer) Co–N and C–O bond distances from those observed in the cobaltate anion in (I). It seems reasonable to suggest that, had not oxidation of the Co^{II} of the starting material to Co^{III} taken place resulting in the formation of (I), then (II) might well have been the product of the reaction.

Experimental

To a hot solution (333 K) of guanidinoacetic acid (0.3513 g, 3 mmol) and DL-aspartic acid (0.3993 g, 3 mmol) in deionized water (100 ml) was slowly added a solution of cobalt(II) nitrate hexahydrate (0.8732 g, 3 mmol) in deionized water (5 ml). The reaction mixture was stirred at 333 K for 8 h, slowly cooled to 277 K, and the pH adjusted to 6.0 with KOH (3 M). The initial white precipitate which formed was filtered off and the filtrate was stored in a covered, but not sealed, vessel. Dark-blue crystals began to form after the fifth month and were collected after six months, washed with absolute ethanol and dried at 323 K. Although electron paramagnetic resonance spectroscopy indicated the presence of at least some Co^{II} in the bulk product, it is clear that the sample crystal, containing Co^{III}, is a by-product of this reaction, arising from Co^{III} either present as an impurity or created by oxidation of the initial Co^{II} by oxygen in the air.

Crystal data

K[Co(C₄H₅NO₄)₂].3.5H₂O
M_r = 423.27
 Monoclinic, *P*2₁/*c*
a = 12.4853 (13) Å
b = 12.4689 (13) Å
c = 9.6914 (8) Å
 β = 92.952 (7)°
V = 1506.7 (3) Å³
Z = 4

D_x = 1.866 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 3129 reflections
 θ = 2.9–27.5°
 μ = 1.48 mm⁻¹
T = 120 (2) K
 Block, dark blue
 0.40 × 0.30 × 0.08 mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
T_{min} = 0.517, *T_{max}* = 0.891
 16788 measured reflections

3330 independent reflections
 2568 reflections with *I* > 2σ(*I*)
R_{int} = 0.045
 θ_{max} = 27.5°
h = -16 → 15
k = -16 → 16
l = -12 → 12

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.065
wR (*F*²) = 0.175
S = 1.09
 3330 reflections
 208 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0839P)^2 + 4.5102P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 1.24 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.64 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Co1–O1 <i>B</i>	1.886 (3)	K1–O6	2.766 (4)
Co1–O3 <i>A</i>	1.899 (3)	K1–O7	2.799 (6)
Co1–N1 <i>A</i>	1.902 (4)	K1–O2 <i>A</i> ⁱ	2.821 (4)
Co1–N1 <i>B</i>	1.909 (4)	K1–O2 <i>B</i> ⁱⁱ	2.862 (4)
Co1–O3 <i>B</i>	1.917 (3)	K1–O3 <i>A</i>	3.078 (4)
Co1–O1 <i>A</i>	1.921 (3)	K1–O1 <i>A</i>	3.092 (3)
K1–O3 <i>B</i>	2.759 (3)		
O1 <i>B</i> –Co1–O3 <i>A</i>	177.34 (14)	N1 <i>A</i> –Co1–O3 <i>B</i>	174.29 (15)
O1 <i>B</i> –Co1–N1 <i>A</i>	89.62 (16)	N1 <i>B</i> –Co1–O3 <i>B</i>	88.27 (16)
O3 <i>A</i> –Co1–N1 <i>A</i>	91.48 (16)	O1 <i>B</i> –Co1–O1 <i>A</i>	90.54 (13)
O1 <i>B</i> –Co1–N1 <i>B</i>	86.38 (15)	O3 <i>A</i> –Co1–O1 <i>A</i>	91.97 (13)
O3 <i>A</i> –Co1–N1 <i>B</i>	91.08 (15)	N1 <i>A</i> –Co1–O1 <i>A</i>	84.57 (15)
N1 <i>A</i> –Co1–N1 <i>B</i>	97.02 (18)	N1 <i>B</i> –Co1–O1 <i>A</i>	176.52 (15)
O1 <i>B</i> –Co1–O3 <i>B</i>	92.85 (15)	O3 <i>B</i> –Co1–O1 <i>A</i>	90.26 (14)
O3 <i>A</i> –Co1–O3 <i>B</i>	86.27 (14)		
N1 <i>A</i> –C2 <i>A</i> –C3 <i>A</i> –C4 <i>A</i>	50.6 (6)	N1 <i>B</i> –C2 <i>B</i> –C3 <i>B</i> –C4 <i>B</i>	–45.0 (7)
C1 <i>A</i> –C2 <i>A</i> –C3 <i>A</i> –C4 <i>A</i>	–67.7 (5)	C1 <i>B</i> –C2 <i>B</i> –C3 <i>B</i> –C4 <i>B</i>	72.8 (7)

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

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N1 <i>A</i> –H11 <i>A</i> ...O2 <i>A</i> ⁱⁱⁱ	0.92	2.29	2.930 (5)	126
N1 <i>A</i> –H11 <i>A</i> ...O4 <i>A</i> ^{iv}	0.92	2.32	3.011 (5)	131
N1 <i>A</i> –H12 <i>A</i> ...O4 <i>A</i> ^v	0.92	2.06	2.981 (5)	177
N1 <i>B</i> –H11 <i>B</i> ...O5 ^{vi}	0.92	2.04	2.942 (6)	168
N1 <i>B</i> –H12 <i>B</i> ...O1 <i>B</i> ⁱⁱⁱ	0.92	2.34	2.925 (5)	121
N1 <i>B</i> –H12 <i>B</i> ...O1 <i>A</i> ⁱⁱⁱ	0.92	2.49	3.166 (5)	130
O5–H5 <i>A</i> ...O4 <i>B</i>	0.84	1.87	2.685 (6)	163
O5–H5 <i>B</i> ...O2 <i>B</i> ^{vii}	0.84	1.94	2.777 (6)	169
O6–H6 <i>A</i> ...O5 ^{vii}	0.84	2.07	2.826 (6)	149
O6–H6 <i>B</i> ...O4 <i>A</i> ^{viii}	0.84	2.08	2.914 (6)	174
O7–H7 <i>A</i> ...O6 ^{ix}	0.84	2.23	3.074 (11)	17
O7–H7 <i>B</i> ...O4 <i>B</i>	0.84	2.20	3.038 (10)	179
C2 <i>B</i> –H21 <i>B</i> ...O3 <i>B</i> ⁱⁱⁱ	1.00	2.48	3.419 (7)	156
C3 <i>A</i> –H32 <i>A</i> ...O5 ^x	0.99	2.59	3.328 (7)	132

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

As indicated by PLATON (Spek, 2003), the structural model used here sustains two symmetry-related [at ($\frac{1}{2}, 0, 0$) and ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)] solvent-accessible regions, each of volume 19 Å³, per unit cell. Excluded from each of these regions of the structural model were two low electron density (approximately 2 e Å⁻³) features. This was accompanied by

the suppression, by means of the SQUEEZE option of *PLATON*, of their contribution to the intensity data. These features, less than 3 Å from the K⁺ ion, less than 1 Å apart and with site occupancy factors estimated to be of the order of 0.25, are perceived as representing additional highly disordered water molecules solvating the K⁺ ion and present in total to the extent of 0.5H₂O per formula unit. The additional half-molecule of water has been included in the molecular formula but is, of course, absent from the structural model. In the final stages of refinement, H atoms attached to C and N atoms were placed in calculated positions, with C–H distances for tertiary and secondary C atoms of 1.00 and 0.99 Å, respectively, and for N, treated as secondary C, with N–H distance 0.92 Å. These H atoms were then refined with a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$. Approximate positions for the H atoms of the water molecules were obtained from difference maps, the geometry of the water molecules idealized to give O–H distances of 0.84 Å and H–O–H angles in the range 101–105°, and the H atoms then refined with a riding model, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. In the final difference map, the largest peak is 1.01 Å from atom C2B.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *ATOMS for Windows* (Dowty, 1998); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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