

Coordination behaviour and two-dimensional-network formation in poly[[μ -aqua-diaqua(μ_5 -propane-1,3-diyl-dinitrilotetraacetato)dilithium(I)-cobalt(II)] dihydrate]: the first example of an $M^{\text{II}}-1,3\text{-pdta}$ complex with a monovalent metal counter-ion

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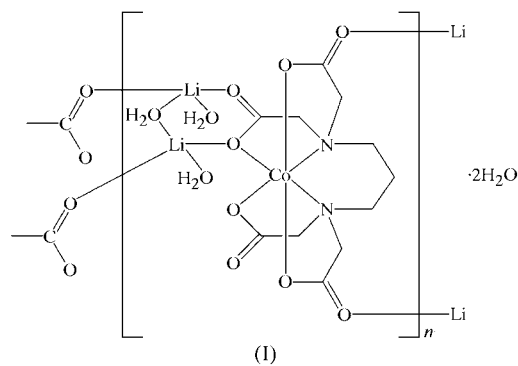
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The title compound, $\{[\text{CoLi}_2(\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_8)(\text{H}_2\text{O})_3]\cdot 2\text{H}_2\text{O}\}_n$, constitutes the first example of a salt of the $[\text{M}^{\text{II}}(1,3\text{-pdta})]^{2-}$ complex (1,3-pdta is propane-1,3-diyl-dinitrilotetraacetate) with a monovalent cation as counter-ion. Insertion of the Li^+ cation could only be achieved through application of the ion-exchange column technique which, however, appeared unsuccessful with other alkali metals and the ammonium cation. The structure contains two tetrahedrally coordinated Li^+ cations, an octahedral $[\text{Co}(1,3\text{-pdta})]^{2-}$ anion and five water molecules, two of which are uncoordinated, and is built of two-dimensional layers extending parallel to the (010) lattice plane, the constituents of which are connected by the coordinate bonds. $\text{O}-\text{H}_{\text{water}}\cdots\text{O}$ hydrogen bonds operate both within and between these layers. The crystal investigated belongs to the enantiomeric space group $P2_1$ with only one (Δ) of two possible optical isomers of the $[\text{Co}(1,3\text{-pdta})]^{2-}$ complex. A possible cause of enantiomer separation during crystallization might be the rigidification and polarization of the $[\text{M}(1,3\text{-pdta})]^{2-}$ core, resulting from direct coordination of Li^+ cations to three out of four carboxylate groups constituting the 1,3-pdta ligand. The structure of (I) differs considerably from those of the other $[\text{M}^{\text{II}}(1,3\text{-pdta})]^{2-}$ complexes, in which the charge compensation is realized by means of divalent hexaaqua complex cations. This finding demonstrates a significant structure-determining role of the counter-ions.

Comment

This work is a continuation of our study concerning the structural characteristics of 1,3-pdta complexes containing different metal(II) ions. The title compound, (I), constitutes the first example of a metal(II) complex of propane-1,3-diyl-dinitrilotetraacetate (1,3-pdta) with a monovalent metal as the charge-compensating ion. Our previous attempts to obtain $\text{M}_2[\text{Co}^{\text{II}}(1,3\text{-pdta})]$ complexes (where M is an alkali metal ion) using the same synthetic method as that used for the preparation of the series $[\text{M}(\text{H}_2\text{O})_6][\text{M}'(1,3\text{-pdta})]\cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Co}^{\text{II}}, \text{Mg}^{\text{II}}$ or Zn^{II} ; $\text{M}' = \text{Co}^{\text{II}}, \text{Zn}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Ni}^{\text{II}}$ or Mg^{II} ; Rychlewska *et al.*, 2000, 2005; Radanović *et al.*, 2001, 2003, 2004) were unsuccessful. More specifically, from a reaction mixture containing equivalent amounts of $\text{Ba}[\text{Co}^{\text{II}}(1,3\text{-pdta})]\cdot 8\text{H}_2\text{O}$ and Li_2SO_4 or Na_2SO_4 , only the homometallic complex salt $[\text{Co}^{\text{II}}(\text{H}_2\text{O})_6][\text{Co}^{\text{II}}(1,3\text{-pdta})]\cdot 2\text{H}_2\text{O}$ crystallized. Therefore, in order to obtain the title compound, (I), the ion-exchange column technique was applied. However, attempts to use the same technique for the preparation of the analogous salts with $\text{M} = \text{Na}^+, \text{K}^+, \text{NH}_4^+$ or Cs^+ always yielded the corresponding $[\text{Co}^{\text{III}}(1,3\text{-pdta})]^-$ complex.



As expected, the solution that was eluted from the lithium-exchange column did not show any evidence of optical activity, which indicates that the sample obtained is a racemate containing both right-handed (Δ) and left-handed (Λ) enantiomers. Upon crystallization, however, the compound underwent spontaneous resolution. This phenomenon has recently been reviewed by Perez-Garcia & Amabilino (2007). The solution obtained by dissolving a randomly selected group of crystals was optically active and did not undergo racemization for a period of several days. This points to the significant stability of the $\text{Li}_2[\text{Co}(1,3\text{-pdta})]$ complex and indicates that, at the macroscopic level, groups of crystals are formed which have predominantly one enantiomer, hence leading to chiral colonies. The chiral crystal of which the structure is reported in this paper contains molecules that display the Δ helicity.

The structure is built of two tetrahedrally coordinated Li^+ cations, an octahedral $[\text{Co}(1,3\text{-pdta})]^{2-}$ anion and five water molecules, two of which are uncoordinated. The coordination around the Co^{II} cation is octahedral and 1,3-pdta acts as a hexadentate ligand (Fig. 1). The in-plane *cis* bond angles are in a wide range $[79.60(9)–103.88(8)^\circ]$ and the in-plane *trans* bonds are bent by *ca* 11 and 16° (Table 1). The conformations

of the glycinate rings are envelope for the more puckered *G* rings and half-chair for the less-puckered *R* rings (see Fig. 1 for ring definitions). The six-membered diamine ring (*T*) approaches a half-chair form; the Cremer & Pople (1975) parameters (*PARST*; Nardelli, 1983) are $Q_T = 0.596$ (3) Å, $\varphi = -24.0$ (2)° and $\theta = 124.2$ (2)°.

The octahedral coordination of the Co^{II} ion by 1,3-pdta has previously been observed in two isostructural crystals with either hexaaquamagnesium(II) [Cambridge Structural Database (CSD, Version 5.29; Allen, 2002) refcode IMAFOR] or hexaaquacobalt(II) (CSD refcode IMAFIL) complexes as counter-ions (Radanović *et al.*, 2003). Comparison of these two crystal structures (determined at 120 K) with that of (I) (determined at room temperature) reveals significant differences at both the molecular and supramolecular levels. While the former $[\text{Co}(1,3\text{-pdta})]^{2-}$ complexes display C_2 molecular symmetry, the complex in (I) is asymmetric. The asymmetry is introduced to the system by Li^+ cations which are coordinated to three out of four carboxylate groups [one equatorial (eq) and two axial]. This asymmetry is particularly well reflected in the variation in the values of the $\text{Co}-\text{O}_{\text{eq}}$ bond lengths which represent, respectively, the longest [2.128 (2) Å] and shortest [2.063 (2) Å] $\text{Co}-\text{O}$ bonds in this complex. The longest $\text{Co}-$

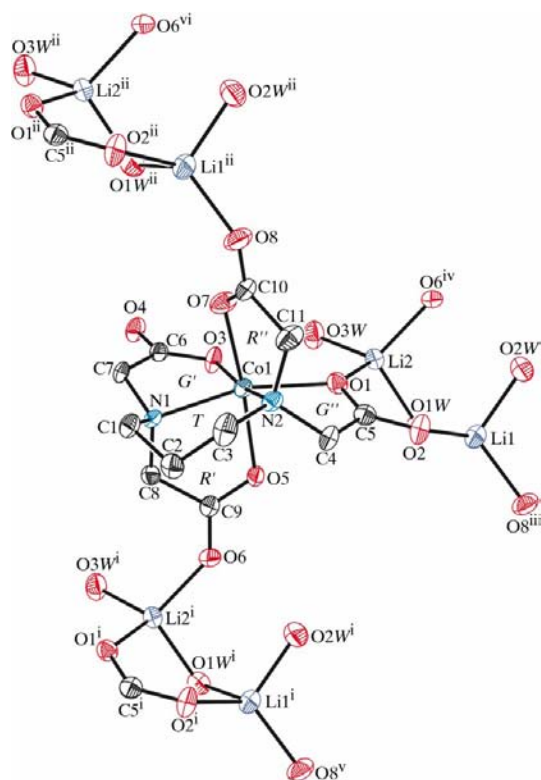


Figure 1

A portion of the structure of (I), showing one $[\text{Co}(1,3\text{-pdta})]^{2-}$ complex and several attached Li^+ counter-ions. Displacement ellipsoids are drawn at the 40% probability level. The configuration around the Co^{II} cation is Δ . *G*, *R* and *T* indicate rings discussed in the *Comment*. Primes and double primes distinguish between two symmetry-independent equatorial (*G*) and out-of-plane (*R*) glycinate rings. [Symmetry codes: (i) $x + 1, y, z$; (ii) $x, y, z - 1$; (iii) $x, y, z + 1$; (iv) $x - 1, y, z$; (v) $x + 1, y, z + 1$; (vi) $x - 1, y, z - 1$.]

O bond is formed to the O atom that is simultaneously coordinated to the Li^+ cation, while the shortest involves an O atom from the only carboxylate that is exclusively coordinated to the Co^{II} cation. The analogous $\text{Co}-\text{O}_{\text{eq}}$ bond length observed in the C_2 symmetrical $[\text{Co}(1,3\text{-pdta})]^{2-}$ complexes, in which the carboxylate groups are only coordinated to the central Co^{II} atom, is 2.055 (2) Å (average of two independent measurements).

The Li^+ cations each display a tetrahedral environment but the form of coordination differs (Fig. 1). Atom $\text{Li}1$ is surrounded by two water molecules ($\text{O}1\text{W}$ and $\text{O}2\text{W}$) and two carboxylate O atoms [$\text{O}2$ and $\text{O}8^{\text{iii}}$; symmetry code: (iii) $x, y, z + 1$] that are not directly coordinated to the Co atom, while atom $\text{Li}2$ is bonded to two water molecules ($\text{O}1\text{W}$ and $\text{O}3\text{W}$) and to two carboxylate O atoms [$\text{O}6^{\text{iv}}$ and $\text{O}1$; symmetry code: (iv) $x - 1, y, z$], of which the former is not coordinated to Co while the latter is. The $\text{Li}-\text{O}$ bond lengths and angles in the two LiO_4 tetrahedra display rather wide ranges of 1.857 (6)–2.014 (6) Å and 99.1 (3)–120.2 (3)°, respectively. The two Li^+ cations are joined *via* the mediating water molecule $\text{O}1\text{W}$; the distance between the water-bridged Li^+ cations is only 3.085 (8) Å and the angle at the O atom is 102.2 (2)°. The two Li^+ cations are additionally bridged by one of the two equatorial carboxylate groups ($\text{O}1-\text{C}5-\text{O}2$). This leads to the formation of the puckered six-membered ring shown in Fig. 1. Simultaneous bridging of Li^+ ions by a carboxylate group and a water molecule has also been observed in crystalline phases of other lithium complexes, including the simplest one, *i.e.* lithium fumarate (Kansikas & Hermansson, 1989). A search of the CSD yielded 20 such structures, displaying a significant variation of the ring puckering.

The ions connected by coordinate bonds form uncharged two-dimensional layers parallel to (010) (Fig. 2). The layer construction is further supported by a system of $\text{O}-\text{H}\cdots\text{O}$

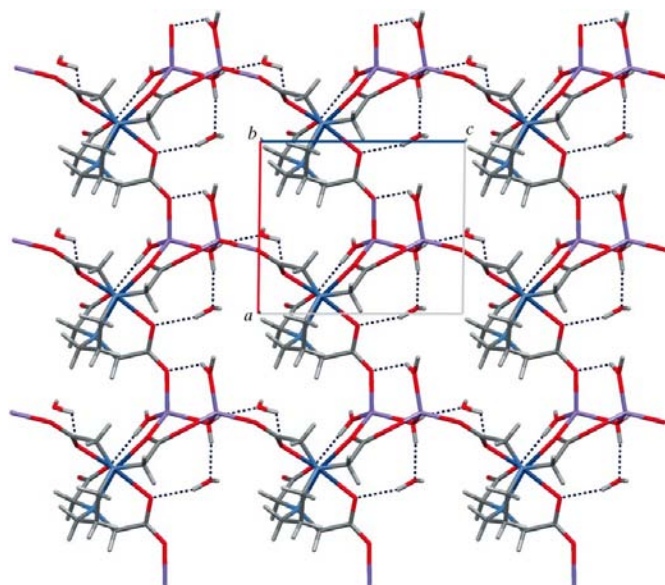


Figure 2

A view down the monoclinic [010] direction, illustrating the structure of the two-dimensional layer. Dashed lines represent hydrogen bonds.

hydrogen bonds, in which water molecules act as the proton donors, and the acceptors are either carboxylate O atoms or uncoordinated water molecules (Table 2). The layers are both chiral and polar. There are two such layers per unit cell, related by the twofold screw axis along the *b* direction (Fig. 3). Neighbouring layers are antiparallel, as required by the twofold symmetry, and are joined by hydrogen bonds. This supramolecular arrangement differs dramatically from the packing observed in the analogous $[M(\text{H}_2\text{O})_6][\text{Co}^{\text{II}}(1,3\text{-pdta})]\cdot 2\text{H}_2\text{O}$ complexes mentioned above [$M = \text{Mg}^{\text{II}}$ (CSD refcode IMAFOR) or Co^{II} (CSD refcode IMAFIL); Radanović *et al.*, 2003], which form centrosymmetric crystal structures containing distinct octahedral cationic and anionic species. A somewhat similar layered arrangement of complex anions to that present in (I) has been observed in those $[M^{\text{III}}(1,3\text{-pdta})]^-$ complexes which also underwent enantiomer separation during the crystallization process, *i.e.* those with $M = \text{Cr}^{\text{III}}$ (CSD refcode BACRUS; Herak *et al.*, 1984), Fe^{III} (CSD refcode JEPKEU; Okamoto *et al.*, 1990) and V^{III} (CSD refcode PATZIT; Robles *et al.*, 1993), all containing Na^+ as the counter-ion. As in (I), the Na^+ ions in these crystals are coordinated to three out of four carboxylate groups of the 1,3-pdta ligand but are situated in between rather than within the anionic layers. A somewhat similar, though more symmetrical, mode of cation/anion bonding is observed in the $\text{K}[\text{Co}(1,3\text{-pdta})]$ complex (CSD refcode TMACOK; Nagao *et al.*, 1972), which also forms chiral crystals. This analogy in packing prompts us to propose that a possible cause of enantiomer separation during the crystallization process might be the rigidification and polarization of the $M(1,3\text{-pdta})$ core,

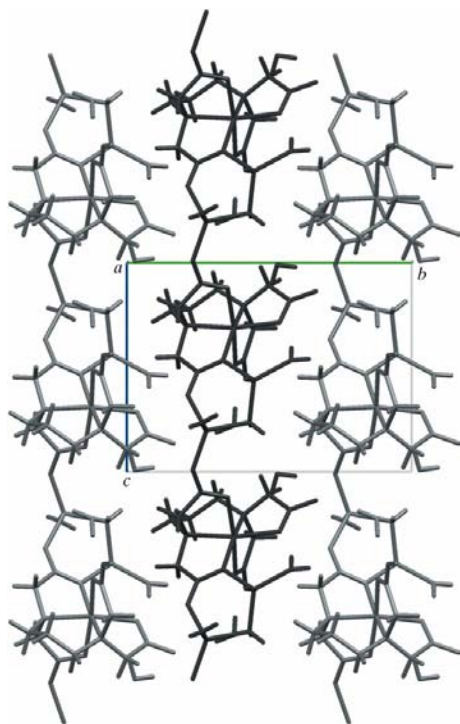


Figure 3

A side view of the (010) layers. Successive layers along *b* are related by the 2_1 axis.

resulting from the direct coordination of the alkali metal counter-ions to the carboxylate groups constituting the 1,3-pdta ligand. This rigidification may account for the occurrence of one particular orientation and chirality of the constituent complex anions in a layer and cause the noncentrosymmetric packing of neighbouring layers to be energetically preferable.

Experimental

All commercially obtained reagent-grade chemicals were used without further purification. An aqueous solution (10 ml) of $[\text{Mg}(\text{H}_2\text{O})_6][\text{Co}^{\text{II}}(1,3\text{-pdta})]\cdot 2\text{H}_2\text{O}$ (1.50 g, 2.83 mmol), prepared as described by Radanović *et al.* (2003), was passed through a column packed with Merck I cation exchanger in the Li^+ form. The eluate was evaporated at room temperature to a volume of 2 ml and the $\text{Li}_2[\text{Co}^{\text{II}}(1,3\text{-pdta})]\cdot 5\text{H}_2\text{O}$ complex was crystallized after addition of ethanol and cooling in a refrigerator for 2 d. The red-violet crystals were removed by filtration and air-dried (yield 0.92 g). The complex was checked by UV-Vis spectroscopy and its spectrum compared with that obtained for the $[\text{Mg}(\text{H}_2\text{O})_6][\text{Co}^{\text{II}}(1,3\text{-pdta})]\cdot 2\text{H}_2\text{O}$ complex (Radanović *et al.*, 2003). Analysis calculated for $\text{C}_{11}\text{H}_{24}\text{CoLi}_2\text{N}_2\text{O}_{13}$: C 28.40, H 5.20, N 6.02%; found: C 28.44, H 5.10, N 6.00%.

Crystal data

$[\text{CoLi}_2(\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_8)(\text{H}_2\text{O})_3]\cdot 2\text{H}_2\text{O}$	$V = 937.44$ (8) Å ³
$M_r = 465.13$	$Z = 2$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 7.8767$ (4) Å	$\mu = 0.98$ mm ⁻¹
$b = 12.7381$ (6) Å	$T = 293$ (2) K
$c = 9.3440$ (4) Å	$0.20 \times 0.15 \times 0.08$ mm
$\beta = 90.756$ (4)°	

Data collection

Kuma KM-4-CCD κ -geometry diffractometer	7554 measured reflections
Absorption correction: multi-scan (CrysAlisPro; Oxford Diffraction, 2007)	3069 independent reflections
$T_{\text{min}} = 0.846$, $T_{\text{max}} = 0.924$	2487 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$	H-atom parameters constrained
$wR(F^2) = 0.052$	$\Delta\rho_{\text{max}} = 0.28$ e Å ⁻³
$S = 0.94$	$\Delta\rho_{\text{min}} = -0.25$ e Å ⁻³
3069 reflections	Absolute structure: Flack (1983),
262 parameters	with 1334 Friedel pairs
1 restraint	Flack parameter: -0.017 (12)

Table 1

Selected geometric parameters (Å, °).

Co1—O3	2.063 (2)	Co1—O1	2.128 (2)
Co1—O7	2.088 (2)	Co1—N2	2.129 (3)
Co1—O5	2.0932 (17)	Co1—N1	2.133 (2)
O3—Co1—O1	103.88 (8)	O1—Co1—N2	78.23 (9)
O7—Co1—O1	101.31 (9)	O3—Co1—N1	79.60 (9)
O3—Co1—N2	169.01 (8)	O1—Co1—N1	163.80 (8)
O7—Co1—N2	79.38 (9)	N2—Co1—N1	101.43 (9)

H atoms attached to C atoms were placed in calculated positions and refined using a riding model, with $\text{C—H} = 0.97$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. H atoms attached to hydroxyl groups and water molecules were located in subsequent difference Fourier maps; their O—H distances were standardized to 0.85 Å and they were thereafter refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. The absolute

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>
O1W—H1WA...O4W	0.85	1.92	2.703 (3)	152
O1W—H1WB...O5W	0.85	1.97	2.720 (3)	147
O2W—H2WA...O4 ⁱ	0.85	1.95	2.784 (3)	165
O2W—H2WB...O6 ⁱⁱ	0.85	2.10	2.790 (3)	138
O3W—H3WA...O3	0.85	1.92	2.743 (3)	163
O3W—H3WB...O2 ⁱⁱⁱ	0.85	2.37	3.041 (3)	137
O4W—H4WA...O5	0.85	2.01	2.832 (2)	163
O4W—H4WB...O4 ^{iv}	0.85	2.09	2.910 (3)	162
O5W—H5WA...O7 ^v	0.85	2.51	2.992 (3)	117
O5W—H5WB...O8 ⁱⁱⁱ	0.85	2.11	2.931 (3)	164

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

configuration of the complex was established as Λ on the basis of the Flack absolute structure parameter (Flack, 1983), which refined to a value of -0.017 (12).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlisPro* (Oxford Diffraction, 2007); data reduction: *CrysAlisPro*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97* and *publCIF* (Westrip, 2008).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3137). Services for accessing these data are described at the back of the journal.

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