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Poly[[di-μ_2-aqua-di-μ_5-croconato(2−)-nickel(II)dipotassium(I)] tetrahydrate]

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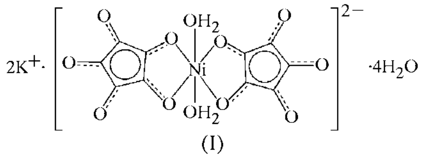
In the title compound, $\{[K_2Ni(C_5O_5)_2(H_2O)_2]\cdot 4H_2O\}_n$, the Ni atom lies on an inversion centre. Two inversion-related croconate [4,5-dihydroxy-4-cyclopentene-1,2,3-trionate(2−)] ligands and an Ni^{II} ion form a near-planar symmetrical $[Ni(C_5O_5)_2]^{2-}$ moiety. The near-square coordination centre of the moiety is then extended to an octahedral core by vertically bonding two water molecules in the $[Ni(C_5O_5)_2(H_2O)_2]^{2-}$ coordination anion. The crystal structure is characterized by a three-dimensional network, involving strong K···O···K binding, K···O—Ni binding and hydrogen bonding.

Comment

The dianion of 4,5-dihydroxy-4-cyclopentene-1,2,3-trione, $C_5O_5^{2-}$, commonly refered to as the croconate anion, belongs to the family of cyclic oxocarbons of the formula $C_nO_n^{2-}$ [n = 3–6 for deltate, squarate, croconate and rhodizonate anions, respectively] (Seitz & Imming, 1992). Previous reports (Brouca-Cabarrecq & Trombe, 1992*a*,*b*) reveal that croconate is a polydentate ligand. The strong and versatile coordination properties of the croconate ligand enable it to bond to metal ions *via* various modes. The reported structures of croconate transition metal complexes with no other co-ligands apart from water and ammonia show that their coordination modes can be classified into three types, namely a terminal mono-ligand coordination mode (type *A* in Fig. 1; Brouca-Cabarrecq & Trombe, 1992*a*,*b*), a symmetric bi-ligand coordination mode (type *B* in Fig. 1; Wang *et al.*, 2002) and various bridging coordination modes (types *C*, *D*, *E* and *F* in Fig. 1; Cornia *et al.*, 1993; Glick & Dahl, 1966; Brouca-Cabarrecq & Trombe, 1992*a*,*b*; Maji *et al.*, 2003). In this study, the title compound, (I), shows a symmetric coordination mode. To the best of our knowledge, this is the third example of this kind, in addition to $[Na_2Ni(C_5O_5)_2(H_2O)_2]\cdot 4H_2O$ and $[Cu_2Ni(C_5O_5)_2(H_2O)_2]\cdot 4H_2O$ (Wang *et al.*, 2002), in the family of croconate complexes.



(I)

The $[Ni(C_5O_5)_2(H_2O)_2]^{2-}$ anion of (I) (Fig. 2) consists of a planar $[Ni(C_5O_5)_2]^{2-}$ moiety with two croconate ligands having a symmetrical bidentate coordination mode, with two water molecules occupying the axial sites of the centrosymmetric octahedral array (Table 1).

There are two K^+ ions in (I), one on either side of the planar $[Ni(C_5O_5)_2]^{2-}$ moiety, tightly bound to atoms O4 and O5. The formal molecule in the crystal can then be identified as $[K_2Ni(C_5O_5)_2(H_2O)_2]$. With four further water molecules of crystallization, the title structure is thus formulated as $[K_2Ni(C_5O_5)_2(H_2O)_2]\cdot 4H_2O$.

The inner five-membered chelate ring is perfectly planar. The two five-membered chelate rings sharing a common central Ni atom are also perfectly coplanar. The least-squares plane derived from these nine coplanar atoms is defined as the molecular plane. On the other hand, the croconate ligand is not planar, with the terminal O1 atom being 0.519 (2) Å and atom C1 being 0.282 (3) Å above the molecular plane. As a result, the $[Ni(C_5O_5)_2]^{2-}$ moiety has a raised-head near-planar conformation. Other nearly coplanar atoms are K and O8

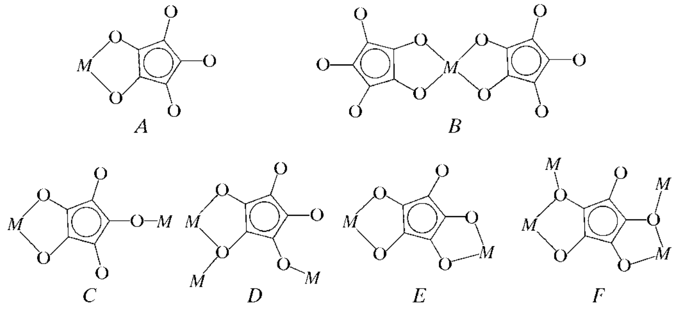


Figure 1
The various coordination modes for metal–croconate complexes.

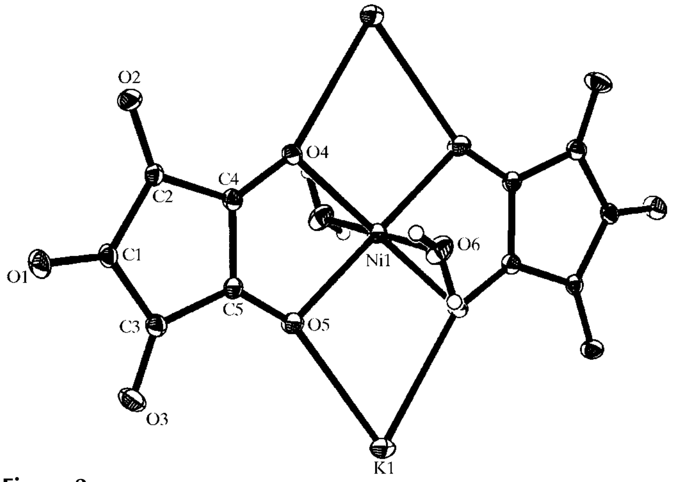


Figure 2
The formal $[K_2Ni(C_5O_5)_2(H_2O)_2]$ moiety in the crystal structure of (I), with displacement ellipsoids at the 30% probability level. Unlabelled atoms are related to labelled atoms by the symmetry code $(1 - x, 2 - y, 1 - z)$.

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(water), with deviations from the molecular plane of 0.346 (1) and 0.353 (2) Å, respectively.

As a good π-conjugation system, the croconate dianion ('free' ligand) in its simple salt has a planar D_{5h} conformation with five almost identical C$\overset{\cdots}{-}$O bonds and five almost identical C$\overset{\cdots}{-}$C bonds, such as in $Rb_2C_5O_5$ and $Cs_2C_5O_5$ crystals (Braga *et al.*, 2002). However, the coordinated ligand in its metal complexes commonly deviates from D_{5h} symmetry. The C$\overset{\cdots}{-}$O bond involving coordinated O atoms is longer than that involving the uncoordinated O atoms. In the title complex, the C$\overset{\cdots}{-}$O bond lengths are in the range 1.262 (3)–1.266 (3) Å for the coordinated O atoms and 1.235 (3)–1.244 (3) Å for the uncoordinated O atoms.

Perhaps the major determinant of the packing of the coordination anion is the K$\cdots$O interactions, and the second is the hydrogen bonding. The $[Ni(C_5O_5)_2(H_2O)_2]^{2-}$ anions are stacked face-to-face along the *b* axis. As shown in Figs. 3 and 4, every K^+ ion is connected to eight O atoms, with K$\cdots$O distances varying in the range 2.6737 (19)–3.042 (2) Å; five are croconate O atoms and three are water O atoms. The two shortest K$\cdots$O contacts are 2.6737 (19) Å (for K$\cdots$O5) and 2.7410 (19) Å (for K$\cdots$O4), which are between a K^+ ion and the two O atoms from the two ligands of the same coordination anion, indicating very strong binding between the K^+ ion and the coordination anion. These two K$\cdots$O distances can therefore be singled out as being of the intramolecular type. Based on various short contacts between $[Ni(C_5O_5)_2(H_2O)_2]^{2-}$ units, one coordination anion (at the centre of Fig. 3) has mainly ten neighbouring anions, interconnected by potassium bridging and hydrogen bonding. Because of centrosymmetry, only five pairs of such inter-anionic interactions need to be considered. The strongest interactions are between the central anion and its neighbour at $(-x, 2-y, 1-z)$ along the *a* axis, with two strong hydrogen bonds [O6—H$\cdots$O2$(-x, 2-y, 1-z)$ and O2$\cdots$H—O6$(-x, 2-y, 1-z)$ of 2.714 (3) Å] and an interaction between three O atoms and one K atom [O4/O5$(1-x, 2-y, 1-z)\cdots$K1$(1-x, 2-y, 1-z)\cdots$O1$(-x, 2-y, 1-z)$]. The interactions in this direction are further strengthened by a strong O6—H$\cdots$O7 hydrogen bond of 2.791 (3) Å. Thus, a one-dimensional chain can be recognized along the [100] direction. There are two other neighbouring anions, each of which is connected to the central anion *via* an interaction between four O atoms and one K atom. The remaining two interanionic interactions are relatively weak, with one interaction between three O atoms and one K atom.

It is noteworthy (Figs. 3 and 4) that the non-coordinated O atoms (O1 and O3) have been effectively involved in O$\cdots$K binding. This is simply the manifestation of the multichelate nature of the croconate ligand. The deviation of the terminal O1 atom from the molecular plane is the effect of a very short K1$\cdots$O1$(\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z)$ distance of 2.771 (2) Å. By comparison, the five-membered croconate ring in $[Na_2Ni(C_5O_5)_2(H_2O)_2]\cdot 4H_2O$ (Wang *et al.*, 2002), which also belongs to coordination mode *D*, is truly coplanar. This may be

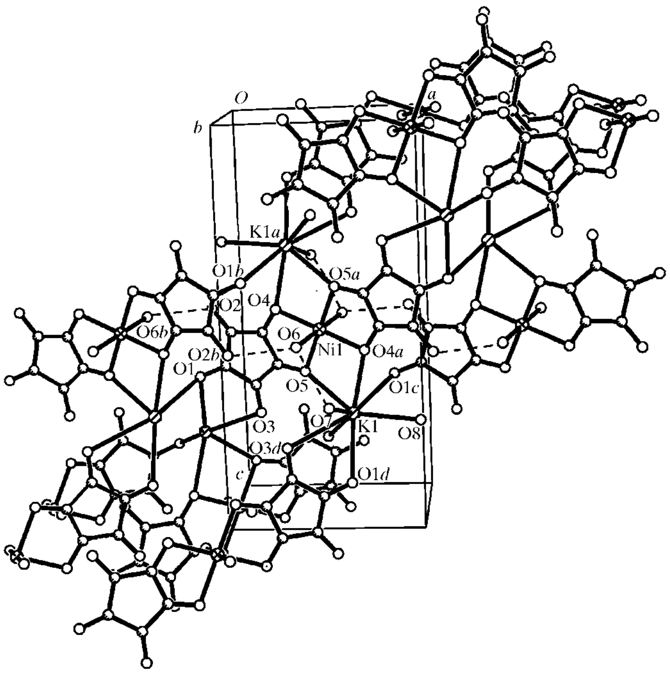

Figure 3
A view, along the *b* axis, of the packing diagram of (I). Atoms O1–O5 are the O atoms of the croconate ligand (of which atoms O4 and O5 are coordinated), atom O6 is the coordinated water O atom, and atoms O7 and O8 are the solvent water O atoms. [Symmetry codes: (*a*) $1-x, 2-y, 1-z$; (*b*) $-x, 2-y, 1-z$; (*c*) $1+x, y, z$; (*d*) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$.]

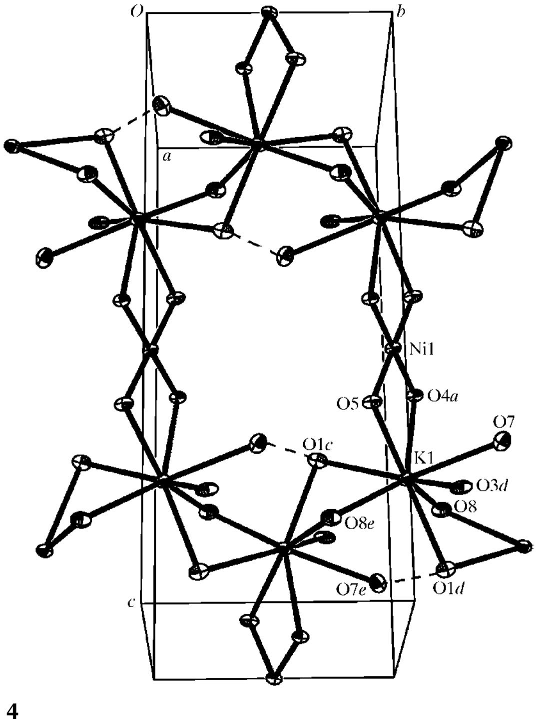

Figure 4
The grid formed by the two-dimensional network in the (101) plane. Isometric series of K^+ ions in the [010] direction and heterometallic series of K^+ and Ni^{II} ions in the [101] direction are connected by two kinds of multi-oxygen-bridging. Note that some atoms have been omitted for clarity. The eight satellite O atoms of a K^+ ion are also shown, of which O1, O3, O4 and O5 are from the croconate ligands, while O7 and O8 are from water molecules. [Symmetry codes: (*a*) $1-x, 2-y, 1-z$; (*c*) $1+x, y, z$; (*d*) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (*e*) $\frac{3}{2}-x, -\frac{1}{2}+y, \frac{3}{2}-z$.]

because the O$\cdots$Na interactions in that compound are not as strong as the O$\cdots$K interactions in (I).

As shown in Fig. 4, there is a two-dimensional network in the (101) plane, which consists of rectangular grids. Along the [010] direction, the zigzag but isometric series of K^+ ions is connected by a kind of multi-oxygen-bridging, forming a uniform chain. In the [101] direction (vertical direction in Fig. 4), there is another kind of zigzag chain which is characterized by heteronuclear two-oxygen-bridging between K and Ni. Retrieving the third chain mentioned above along the [100] direction, the crystal structure of (I) definitely has a three-dimensional network.

Hydrogen bonding in the crystal structure of (I) is strong (Table 2), and mainly occurs between water and the O atoms of the croconate ligands. It plays an important role in the formation and stabilization of the three-dimensional structure. For example, the O6—H$\cdots$O2($-x$, $2-y$, $1-z$) and O6—H$\cdots$O7 hydrogen bonds help to set up intermolecular interactions along the *a* axis (Fig. 3), while O7($\frac{3}{2}-x$, $-\frac{1}{2}+y$, $\frac{3}{2}-z$)—H$\cdots$O1($\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$) makes a contribution to hold the chain along the *b* axis (Fig. 4).

Experimental

$NiCl_2 \cdot 6H_2O$ (0.09 g) dissolved in water (5 ml) was added to a stirred aqueous solution (10 ml) of $K_2(C_5O_5)_2 \cdot 3H_2O$ (0.1 g), and the resulting transparent green solution was filtered into a vial at room temperature. Slow evaporation of the filtrate at room temperature gave parallelepiped-shaped crystals of (I) after several weeks. IR (KBr, ν, cm^{-1}): 1510 (*vs*), 1589 (*s*), 1639 (*s*) (C$\overset{\cdots}{-}$C and C$\overset{\cdots}{-}$O hybrid vibration mode in the $C_5O_5^{2-}$ plane).

Crystal data

$[K_2Ni(C_5O_5)_2(H_2O)_2] \cdot 4H_2O$
$M_r = 525.11$
Monoclinic, $P2_1/n$
$a = 8.0145$ (14) Å
$b = 6.6600$ (10) Å
$c = 16.489$ (4) Å
$\beta = 90.200$ (18)°
$V = 880.1$ (3) Å^3
$Z = 2$
$D_x = 1.982$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 51 reflections
$\theta = 4.7$–$14.3°$
$\mu = 1.66$ mm^{-1}
$T = 293$ (2) K
Prism, green
0.40 × 0.38 × 0.20 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: ψ scan (*XSCANS*; Siemens, 1996)
$T_{min} = 0.549$, $T_{max} = 0.715$
2853 measured reflections
2022 independent reflections
1617 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 27.5°$
$h = -10 \rightarrow 1$
$k = -8 \rightarrow 1$
$l = -21 \rightarrow 21$
3 standard reflections every 97 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.083$
$S = 1.02$
2022 reflections
134 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2 + 0.2576P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.59$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0125 (15)

Table 1
Selected geometric parameters (Å).

C1—O1	1.240 (3)	Ni1—O6	2.043 (2)
C1—C2	1.479 (3)	Ni1—O4	2.0722 (17)
C1—C3	1.479 (3)	Ni1—O5	2.0819 (18)
K1—O5	2.6737 (19)	C2—O2	1.244 (3)
K1—O4^{i}	2.7410 (19)	C2—C4	1.445 (3)
K1—O1^{ii}	2.771 (2)	C3—O3	1.235 (3)
K1—O7	2.821 (2)	C3—C5	1.454 (3)
K1—O8^{iii}	2.880 (2)	C4—O4	1.266 (3)
K1—O8	2.989 (2)	C4—C5	1.432 (3)
K1—O1^{iv}	3.022 (2)	C5—O5	1.262 (3)
K1—O3^{ii}	3.042 (2)		

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O6—H1$\cdots$O2^{v}	0.85	1.89	2.714 (3)	164
O6—H2$\cdots$O7	0.85	1.95	2.791 (3)	169
O7—H3$\cdots$O8^{vi}	0.85	2.29	3.043 (3)	149
O7—H4$\cdots$O1^{vii}	0.85	2.15	2.847 (3)	140
O8—H5$\cdots$O2^{i}	0.85	2.04	2.877 (3)	167
O8—H6$\cdots$O3^{vi}	0.85	2.07	2.917 (3)	173

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

All H atoms were initially located in difference Fourier maps and then allowed to ride on their parent O atoms in the refinement, with O—H distances constrained to 0.85 Å and $U_{iso}(H) = 1.5U_{eq}(O)$.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1416). Services for accessing these data are described at the back of the journal.

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