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Dipotassium hexakis({2,2′-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato}nickel(II)) tetracyanonickelate(II) methanol hexasolvate dihydrate

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In the crystal structure of the title compound, $K_2[Ni(C_{16}H_{14}N_2O_2)]_6[Ni(CN)_4]\cdot6CH_3OH\cdot2H_2O$, at 180 K, the nickel(II)–Schiff base units form dimeric associations across inversion centres. The K^+ cations occupy distorted octahedral sites surrounded by O atoms of the nickel(II)–Schiff base units, and the centrosymmetric $[Ni(CN)_4]^{2-}$ anions participate in a two-dimensional hydrogen-bond network that includes the uncoordinated methanol and water molecules.

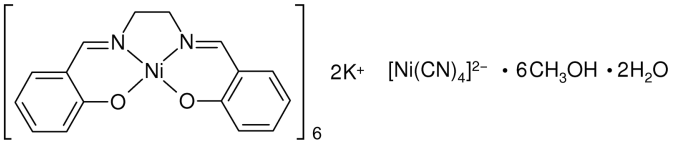
Key indicators

Single-crystal X-ray study
T = 180 K
Mean σ(C–C) = 0.010 Å
R factor = 0.055
wR factor = 0.145
Data-to-parameter ratio = 13.9

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

Comment

Crystals of the title compound, (I) (Table 1), were obtained from an attempt to add cyanide ligands to the complex $C_{16}H_{14}N_2NiO_2$ or [Ni(salen)] [H_2salen is *N*,*N*′-ethylenebis(salicylideneamine)].



(I)

In the crystal structure of (I) at 180 K (Fig. 1), the [Ni(salen)] units form centrosymmetric dimeric associations, in which the least-squares planes through the two complexes are parallel and the Ni···Ni separation is *ca* 3.3 Å [Ni1···Ni1^{i} 3.340 (2) and Ni2···Ni3^{ii} 3.323 (1) Å; symmetry codes: (i) $-x, -y, -z$; (ii) $\frac{1}{2}+x, y, \frac{1}{2}-z$].

These dimers lie in two distinct environments. Infinite stacks (containing atoms Ni2 and Ni3) are formed along [100] [lying at $(x, 0, \frac{1}{4})$, $(x, 0, \frac{3}{4})$, $(x, \frac{1}{2}, \frac{1}{4})$ and $(x, \frac{1}{2}, \frac{3}{4})$], in which the

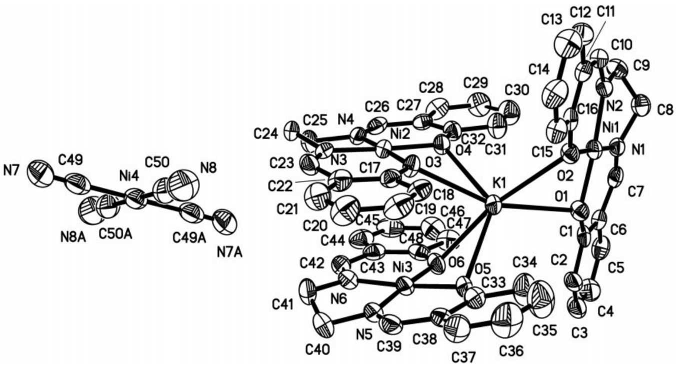


Figure 1
The cationic and anionic complexes in (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms and the uncoordinated methanol and water molecules have been omitted. The suffix A denotes symmetry code $(-x, -y, 1-z)$.

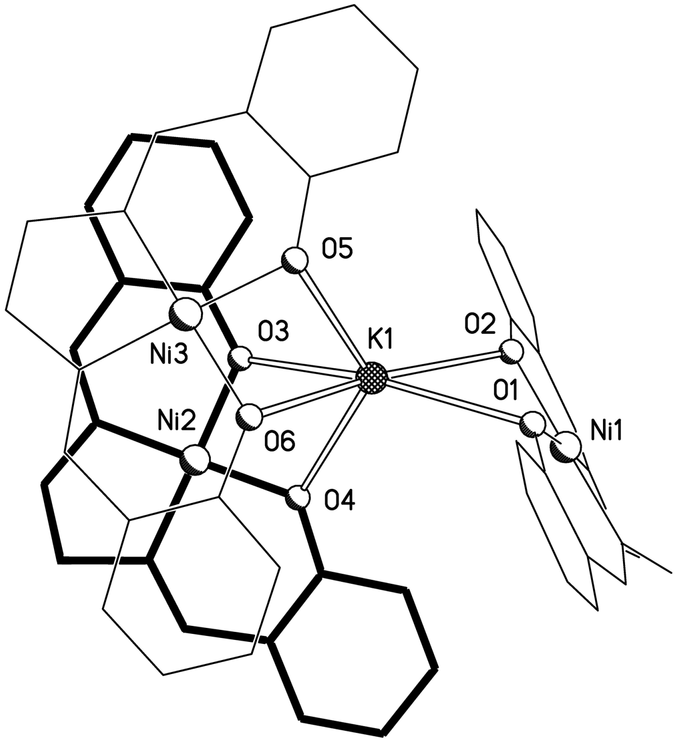


Figure 2
The distorted octahedral environment of K^+ in (I). The projection is approximately along [100], the direction of propagation of the extended stacks of the Ni2/Ni3 [Ni(salen)] dimers. The relative rotation of *ca* 40° described in the text refers to the angle between the O3···O4 vector in the Ni2 unit (heavy lines) and the O5···O6 vector in the Ni3 unit (thin lines). H atoms have been omitted.

least-squares planes through the [Ni(salen)] units of adjacent dimers are approximately parallel and the dimers are rotated by *ca* 40° with respect to each other (Fig. 2), resulting in an Ni2···Ni3 separation of 4.154 (1) Å. A second discrete [Ni(salen)] dimer (containing atom Ni1) is sited at (0, 0, 0), ($\frac{1}{2}$, $\frac{1}{2}$, 0), *etc*. The K^+ cations occupy sites between the [Ni(salen)] stacks and the discrete dimers, in which the O atoms form a heavily distorted octahedral environment, with the 'axial' sites (atoms O4 and O5) forming an angle of *ca* 60° with the approximate square plane formed by atoms O1, O2, O3 and O6 (Fig. 2).

The arrangement formed by the [Ni(salen)] dimers and the K^+ cations is two-dimensional, lying in (020). Projection on to the plane of one of these layers (Fig. 3) shows the square-planar $[Ni(CN)_4]^{2-}$ anions lying in voids. Thus, the structure of (I) may be considered to comprise layers of stoichiometry $(C_{16}H_{14}N_2NiO_2)_6K_2[Ni(CN)_4]$ in (020). The methanol and water molecules occupy pockets between these layers, forming hydrogen bonds to each other and to the $[Ni(CN)_4]^{2-}$ anions.

The hydrogen-bond network (Table 2) is itself two-dimensional, lying in (002). Projection on to a single one of these layers (Fig. 4) highlights an alternative view of the structure: the discrete [Ni(salen)] dimers lie within voids in the hydrogen-bond network, forming layers of stoichiometry $(C_{16}H_{14}N_2NiO_2)_2[Ni(CN)_4]\cdot 6CH_3OH\cdot 2H_2O$ in (002). These layers alternate with layers of stacked [Ni(salen)] dimers along the *c* direction, and the K^+ cations are sandwiched between them.

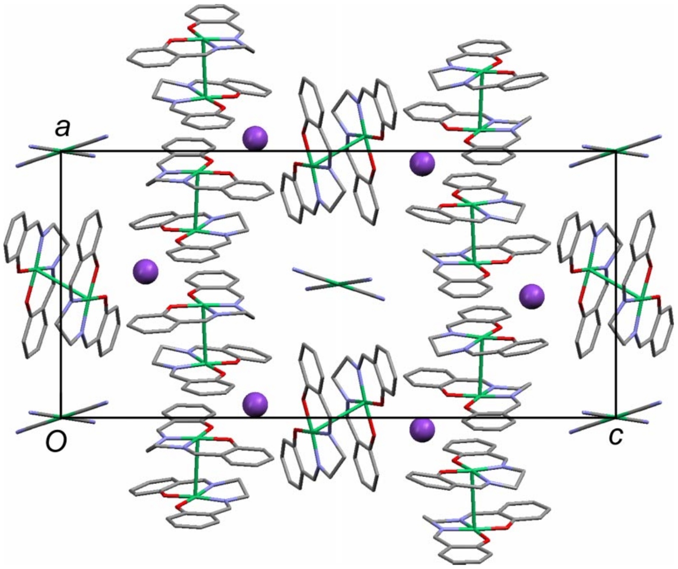


Figure 3
Projection on to the plane of a single layer in (020), showing stacks of [Ni(salen)] dimers running along [100] and discrete [Ni(salen)] dimers at ($\frac{1}{2}$, *b*, 0), (0, *b*, $\frac{1}{2}$), *etc*., with K^+ cations (purple spheres) and $[Ni(CN)_4]^{2-}$ anions lying between them. H atoms have been omitted.

Experimental

KCN (0.56 g, 8.6 mmol) dissolved in methanol (20 ml) was added to a mixture of nickel acetate tetrahydrate (0.74 g, 2.9 mmol) and $C_{16}H_{16}N_2O_2$ (H_2salen, 1.15 g, 4.3 mmol) dissolved in methanol (80 ml). The resulting red solution was heated for 1 h and crystals of (I) were deposited as orange needles over 4 d (yield 0.25 g). Spectroscopic analysis, IR: ν(CN) 2113 cm^{-1}.

Crystal data

$K_2[Ni(C_{16}H_{14}N_2O_2)]_6[Ni(CN)_4]\cdot 6CH_4O\cdot 2H_2O$
$M_r = 2419.29$
Orthorhombic, *Pbca*
$a = 14.3214\ (14)$ Å
$b = 24.855\ (2)$ Å
$c = 29.709\ (3)$ Å
$V = 10575.3\ (16)$ Å^3
$Z = 4$

$D_x = 1.520$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3789 reflections
$\theta = 2.7–19.7°$
$\mu = 1.38\ mm^{-1}$
$T = 180\ (2)$ K
Lath, orange
0.25 × 0.06 × 0.02 mm

Data collection

Bruker-Nonius X8 APEXII CCD diffractometer
Thin-slice ω and φ scans
Absorption correction: multi-scan, (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.718$, $T_{max} = 0.973$
67 154 measured reflections

8982 independent reflections
4508 reflections with $I > 2\sigma(I)$
$R_{int} = 0.149$
$\theta_{max} = 24.7°$
$h = -16 \rightarrow 16$
$k = -29 \rightarrow 27$
$l = -34 \rightarrow 34$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.145$
$S = 1.00$
8982 reflections
647 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0539P)^2 + 17.6992P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.03$ e Å^{-3}
$\Delta\rho_{min} = -0.63$ e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

K1—O6	2.672 (4)	Ni1—O2	1.852 (4)
K1—O4	2.708 (4)	Ni2—N4	1.840 (5)
K1—O5	2.713 (4)	Ni2—N3	1.843 (5)
K1—O2	2.719 (4)	Ni2—O4	1.850 (4)
K1—O3	2.741 (4)	Ni2—O3	1.851 (4)
K1—O1	2.743 (4)	Ni3—N5	1.833 (5)
Ni1—N2	1.842 (5)	Ni3—N6	1.846 (5)
Ni1—N1	1.842 (5)	Ni3—O6	1.850 (4)
Ni1—O1	1.851 (4)	Ni3—O5	1.859 (4)
N2—Ni1—N1	86.3 (2)	N3—Ni2—O3	94.3 (2)
N2—Ni1—O1	175.9 (2)	O4—Ni2—O3	85.14 (18)
N1—Ni1—O1	94.2 (2)	N5—Ni3—N6	86.6 (2)
N2—Ni1—O2	94.7 (2)	N5—Ni3—O6	176.8 (2)
N1—Ni1—O2	178.7 (2)	N6—Ni3—O6	94.6 (2)
O1—Ni1—O2	84.76 (17)	N5—Ni3—O5	94.4 (2)
N4—Ni2—N3	86.0 (2)	N6—Ni3—O5	175.1 (2)
N4—Ni2—O4	94.7 (2)	O6—Ni3—O5	84.60 (19)
N3—Ni2—O4	177.1 (2)	C50—Ni4—C49^{i}	89.6 (3)
N4—Ni2—O3	177.2 (2)	C50—Ni4—C49	90.4 (3)

Symmetry code: (i) $-x, -y, -z+1$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W···O2S	0.84	1.93	2.770 (11)	180
O1W—H2W···O3S	0.84	1.73	2.571 (12)	179
O1S—H1S···N7^{ii}	0.84	2.00	2.838 (10)	179
O2S—H2S···N8^{iii}	0.84	2.02	2.861 (11)	180
O3S—H3S···O1S	0.84	2.05	2.895 (12)	179

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

The combination of a relatively small crystal and a relatively large unit cell gave weak diffraction [*ca* 50% observed at the $I > 2\sigma(I)$ level to a resolution of 0.85 Å, with $R_{\rm int}$ *ca* 15%]. H atoms bound to C atoms were positioned geometrically and allowed to ride during subsequent refinement, with C—H = 0.95 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ for Csp^2, and C—H = 0.99 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ for the methylene groups. The H atoms of the hydroxyl groups in the methanol molecules and in the water molecule were included so as to form a reasonable hydrogen-bond network: the H atoms were placed along the vector from the parent O atom to the closest acceptor atom, with O—H = 0.84 Å, and subsequently allowed to ride on their parent atoms with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm O})$. The methyl H atoms of the methanol molecules were then placed so as to form approximately staggered arrangements with the OH groups. The largest peak in the residual electron density lies in the vicinity of one of the methanol molecules.

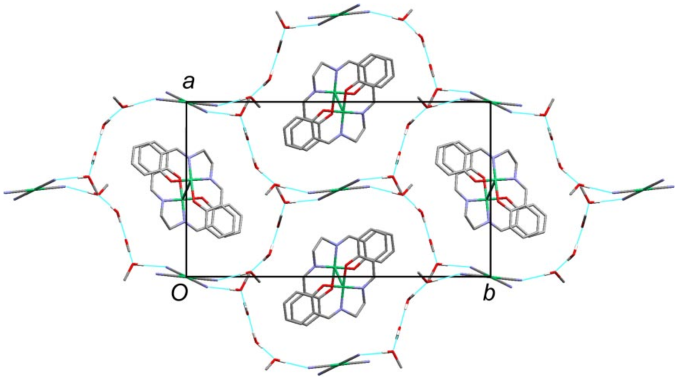

Figure 4
Projection on to the plane of a single layer in (002), showing the hydrogen-bond network between the $[{\rm Ni(CN)_4}]^{2-}$ anions and the methanol and water molecules. Discrete [Ni(salen)] dimers lie in voids in this network. H atoms bound to C atoms have been omitted.

Data collection: *APEX2* (Bruker-Nonius, 2004); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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