

Potassium tris(acetylacetonato)nickelate(II)
0.3-hydrateReinaldo Atencio,^{a*} Julián Reyes,^a Karina Ramírez,^a Teresa González^a and Ysaías Alvarado^b^aLaboratorio de Síntesis y Caracterización de Nuevos Materiales, Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 21827, Caracas 1020-A, Venezuela, and ^bLaboratorio de Electrónica Molecular, Departamento de Química, Facultad Experimental de Ciencias, La Universidad del Zulia, Apartado 526, Maracaibo, Venezuela

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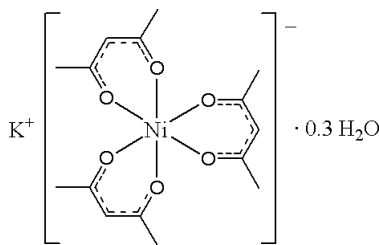
Key indicators

Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$
H-atom completeness 98%
Disorder in solvent or counterion
 R factor = 0.027
 wR factor = 0.079
Data-to-parameter ratio = 8.3For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The crystal structure of the title compound, $\text{K}[\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_3] \cdot 0.3\text{H}_2\text{O}$, comprises a columnar array with $\text{K} \cdots \text{O}$ interactions between the K^+ ions and the O atoms on opposite faces of the NiO_6 octahedron of the complex anion. The columns are maintained, almost exclusively, by hydrophobic methyl–methyl interactions.

Comment

Homoleptic anionic coordination compounds with the acetylacetonate ligand (acac) have been scarcely studied. So far, only a very few crystal structures have been deposited in the Cambridge Structural Database (CSD; Version 5.25; Allen, 2002). The first was reported by Watson & Lin (1966) and was formulated as $\text{Ag}[\text{Ni}(\text{acac})_3] \cdot 2\text{AgNO}_3 \cdot \text{H}_2\text{O}$; this may be described as a mixed anionic compound with an intricate three-dimensional polymeric structure. Nine years later, Greaney *et al.* (1975) reported the crystal structure of the monohydrate $\text{K}[\text{Cd}(\text{acac})_3] \cdot \text{H}_2\text{O}$, which shows a columnar arrangement of anion– K^+ –anion and water molecules that help to sustain the columns. More recently, Li *et al.* (2003) described the crystal structure of anhydrous $\text{Na}[\text{Co}(\text{acac})_3]$. It contains columnar arrays as before, but both the sodium ion and the anion lie on a threefold axis. Another two structures containing $[\text{M}(\text{acac})_3]^-$ ions ($M = \text{Co}^{\text{II}}$ and Ni^{II}) have been reported by Santarsiero *et al.* (1981). In these crystal structures, the counter-ion is a bulky tetrabutylammonium cation and a columnar array is not observed. We describe here the synthesis and crystal structure of the title compound, $\text{K}[\text{Ni}(\text{acac})_3] \cdot 0.3\text{H}_2\text{O}$, (I).



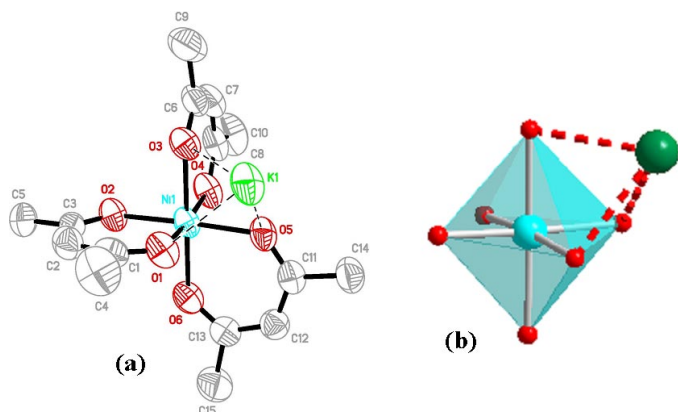
(I)

The asymmetric unit of (I) is composed of a potassium cation, one complex anion $[\text{Ni}(\text{acac})_3]^-$ and a water molecule of crystallization with site occupancy 30%. The metal complex contains three acetylacetonate (acac) ligands coordinated through their O atoms and forming a distorted octahedral environment around the Ni^{II} center. The oxygen disposition around the metal (Fig. 1*a*) results in Ni–O bond distances [2.049 (3)–2.137 (3) Å] and O–Ni–O bond angles

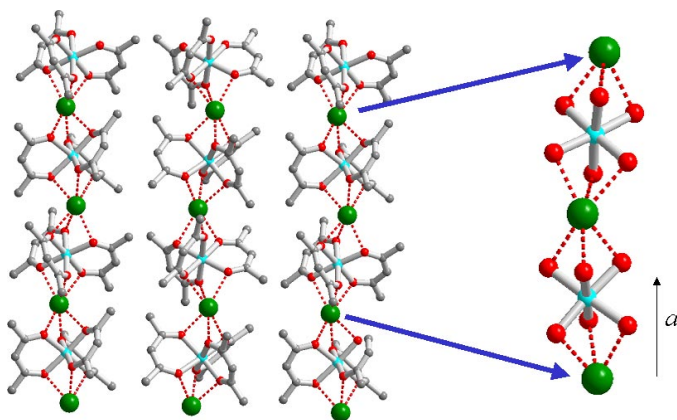
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Figure 1

(a) A representation of the building block of (I), showing displacement ellipsoids at the 50% probability level. The water molecule is not included. (b) The octahedral environment around the Ni^{II} center, showing how the K⁺ cation is attached *via* a K⁺···O interaction to one of the faces of the octahedron.

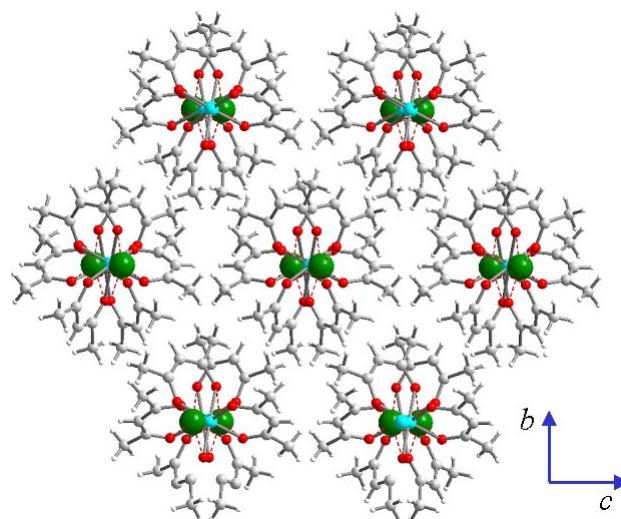

Figure 2

A view of the columns observed in the crystal structure of (I).

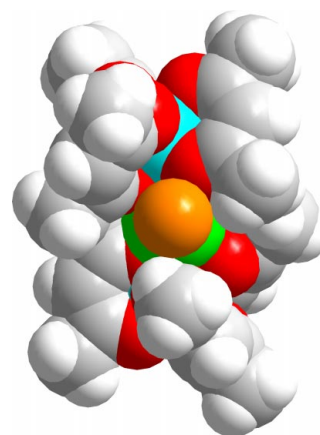
[86.69 (12)–93.75 (13)°] that are similar to those observed [2.04 (6) Å and 90 (3)°, respectively] for Ag[Ni(acac)₃]-2AgNO₃·H₂O (Watson & Lin, 1966).

The potassium cation is asymmetrically attached to the NiO₆ octahedron (Fig. 1*b*) on the face formed by atoms O1, O3 and O5 *via* K⁺···O interactions [K1···O1 = 2.788 (3) Å, K1···O3 = 2.804 (3) Å and K1···O5 = 2.689 (3) Å]. This building block is self-assembled through K⁺···O interactions, building a columnar arrangement along the *a* axis (Fig. 2), in which the O atoms are those of the opposite face to that previously mentioned [K1···O2ⁱⁱ = 2.763 (3) Å, K1···O4ⁱⁱ = 2.748 (3) Å and K1···O6ⁱⁱ = 2.819 (4) Å; symmetry code: (ii) $\frac{1}{2} + x, \frac{1}{2} - y, z$]. The columns are parallel to one another and perpendicular to the *bc* plane (Fig. 3), and they are maintained, almost exclusively, by hydrophobic methyl–methyl interactions.

The synthesis reported here resulted in a direct precipitation of (I) with a very high yield (> 90%). A striking feature of this synthetic route is that, even when freshly distilled THF was used to avoid water molecules of crystallization, the crystal structure appears partially hydrated. The observed columns show accessible spaces where water molecules can be


Figure 3

The crystal structure of (I), viewed along the *a* axis. Water molecules of crystallization have been omitted for clarity.


Figure 4

A space-filling representation of the site where the water molecule (orange) is hosted.

accommodated (Fig. 4) by allowing direct K⁺···O(water) interaction [2.940 (5) Å]. However, only *ca* 30% of these spaces are filled by the water molecules. Thus, the asymmetric K⁺···O(acac) distances described above can be attributed to the presence of this water molecule, as reported for the crystal structure of the monohydrate K[Cd(acac)₃]·H₂O (Greaney *et al.*, 1975).

Experimental

Compound (I) was synthesized from potassium [hydridotris(3,5-dimethylpyrazol-1-yl)borate and Ni(acac)₂ in a molar ratio of 1:1. Each reagent was dissolved separately in THF that had been previously distilled. On mixing the two solutions, pale-green needle-shaped crystals of (I) were obtained.

Crystal data

K[Ni(C₅H₇O₂)₃]·0.3H₂O
M_r = 400.53
 Orthorhombic, *Pna*2₁
a = 13.272 (3) Å
b = 9.905 (2) Å
c = 15.533 (3) Å
V = 2042.0 (7) Å³
Z = 4

D_x = 1.303 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 10
 θ = 23.3–31.0°
 μ = 1.18 mm⁻¹
T = 298 (2) K
 Needle, pale green
 0.42 × 0.22 × 0.20 mm

Data collection

Rigaku AFC-7S diffractometer
 ω - 2θ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\min} = 0.638$, $T_{\max} = 0.799$
 1789 measured reflections
 1744 independent reflections
 1582 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.006$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = 0 \rightarrow 15$
 $k = -11 \rightarrow 3$
 $l = -1 \rightarrow 17$
 3 standard reflections
 every 150 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.079$
 $S = 1.06$
 1744 reflections
 209 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 0.3003P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.16 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.18 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack (1983), 1
 Friedel pair
 Flack parameter = 0.05 (3)

Table 1

Selected geometric parameters (\AA , $^\circ$).

Ni1—O5	2.049 (3)	K1—O5	2.689 (3)
Ni1—O1	2.053 (3)	K1—O4 ⁱⁱ	2.748 (3)
Ni1—O2	2.054 (3)	K1—O2 ⁱⁱ	2.763 (3)
Ni1—O4	2.079 (3)	K1—O1	2.788 (3)
Ni1—O6	2.123 (3)	K1—O3	2.804 (3)
Ni1—O3	2.137 (3)	K1—O6 ⁱⁱ	2.819 (4)
Ni1—K1	3.3936 (11)	K1—O1W	2.940 (5)
Ni1—K1 ⁱ	3.3963 (10)		
O5—Ni1—O1	88.16 (12)	O1—Ni1—O3	87.63 (12)
O5—Ni1—O2	176.74 (14)	O2—Ni1—O3	90.86 (13)
O1—Ni1—O2	92.83 (11)	O4—Ni1—O3	86.92 (13)
O5—Ni1—O4	92.61 (12)	O6—Ni1—O3	179.28 (13)
O1—Ni1—O4	174.52 (16)	Ni1—O3—K1	85.64 (11)
O2—Ni1—O4	86.69 (12)	Ni1—O6—K1 ⁱ	85.60 (13)
O5—Ni1—O6	87.41 (13)	Ni1—O1—K1	87.65 (11)
O1—Ni1—O6	91.71 (14)	Ni1—O2—K1 ⁱ	88.38 (11)
O2—Ni1—O6	89.46 (13)	Ni1—O4—K1 ⁱ	88.31 (11)
O4—Ni1—O6	93.75 (13)	Ni1—O5—K1	90.46 (11)
O5—Ni1—O3	92.28 (12)		

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

C-bound H atoms were treated using a riding model (C—H = 0.93 and 0.96 \AA), with $U_{\text{iso}}(\text{H})$ parameters set at $1.2U_{\text{eq}}(\text{C})$ [$1.5U_{\text{eq}}(\text{C})$ for methyl H atoms]. After the initial refinement, the highest peak ($0.58 \text{ e } \text{\AA}^{-3}$) of the residual electron density suggested a partial-occupancy water molecule of crystallization. A refinement of the occupancy factor of atom O1W converged to 26.3 (11)%. In subsequent cycles of refinement, the occupancy of O1W was fixed at 30% and its positional parameters were refined isotropically without introducing the water H atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXTL-NT* (Bruker, 1998); program(s) used to refine structure: *SHELXTL-NT*; molecular graphics: *SHELXTL-NT* and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXTL-NT*.

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