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Potassium *trans*-Tetraaquadicarbonatonickelate(II), $K_2[Ni(CO_3)_2(H_2O)_4]$

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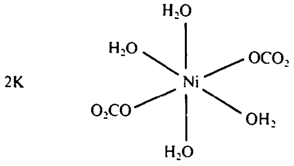
Abstract

The structure of potassium tetraaquadicarbonatonickelate(II), $K_2[Ni(CO_3)_2(H_2O)_4]$, can be described as a close-packed arrangement of $[Ni(CO_3)_2(H_2O)_4]^{2-}$ anions at the corners and the body centre of the monoclinic unit cell with K^+ cations located in the interstices. Each Ni atom is coordinated by four water O atoms and two monodentate carbonate O atoms arranged in a *trans* configuration at the corners of a slightly distorted octahedron, with Ni—O bond distances in the range 2.046 (2)–2.094 (3) Å. Hydrogen bonding takes place between water molecules and carbonate groups within and between the anions. The anions are linked into a three-dimensional network by the hydrogen bonding. Each K^+ ion has seven neighbouring O atoms at normal distances ranging from 2.699 (3) to 3.094 (3) Å. The carbonate group exhibits a deviation from D_{3h} symmetry [O—C 1.275 (4)–1.292 (5) Å; O—C—O 119.5 (3)–120.5 (3)°].

Comment

The title compound, (I), was first identified by Deville (1851) and was at first reported to be orthorhombic (Deville, 1852). On the basis of powder X-ray diffraction patterns, it was suggested that the compound was isostructural with $K_2[Co(CO_3)_2(H_2O)_4]$ (Harlow & Simonsen, 1976). However, no comment was made on the fact that the latter is isostructural with baylissite, $K_2Mg(CO_3)_2.4H_2O$ (Walenta, 1976; Bucat, Patrick, White & Willis, 1977). In order to investigate carbonates of the baylissite type systematically, the crystal structure of $K_2[Ni(CO_3)_2(H_2O)_4]$ has been determined by single crystal X-ray diffraction and confirmed to be isostructural with the analogous Co and Mg compounds.



(I)

The $[Ni(CO_3)_2(H_2O)_4]^{2-}$ anions in the title compound, in which each centrosymmetric Ni atom is bound to four water O atoms and two monodentate carbonate O atoms to form a slightly distorted octahedron in a *trans* configuration, occupy the centre and corners of the unit cell. In comparison with the water molecules, the better donor ability of the CO_3^{2-} anions is reflected by the shorter Ni—O bond length of 2.046 (2) Å to the carbonate group. The Ni—O bond length to the water O atom O5 is found to be longer than that to the water O atom O4, which is in contrast to the bond lengths observed in $K_2[Co(CO_3)_2(H_2O)_4]$ (Harlow & Simonsen, 1976). The longer Ni—O5 bond distance may result from the stronger repulsion between the carbonate group and water O atom O5, since the electron clouds of the $p\pi$ orbitals of the carbonate group are oriented roughly towards the O5 water O atoms. The water O atoms are strongly hydrogen bonded to the carbonate O atoms O2 and O3, which are not coordinated to the central Ni atom, with O···O distances in the range 2.565 (4)–2.727 (4) Å and nearly linear O—H···O angles varying from 164 to 168°. One hydrogen bond per asymmetric unit is formed within the anion, while the others are formed between adjacent anions, linking them into a three-dimensional network. The K^+ cations are located within cavities in the structure, each of which is formed by five complex anions, resulting in seven K···O contact distances in the range 2.699 (3)–3.094 (3) Å, the four shorter ones involving carbonate O atoms and the others water O atoms. The carbonate groups in the title compound deviate more significantly from the D_{3h} symmetry of the CO_3^{2-} ions in calcite (Sass, Vidale & Donohue, 1957) than those in the isostructural Co and Mg analogues; for these, the C—O bond distances are in the range 1.282 (4)–1.298 (3) Å and 1.284 (1)–1.291 (1) Å, respectively. The O—C—O angles, on the other hand, are in all cases close to 120°.

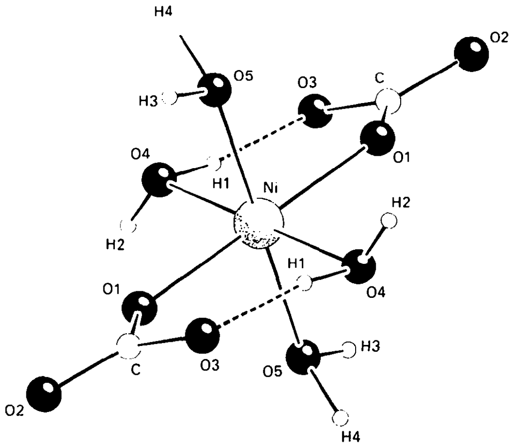


Fig. 1. A view of the $[Ni(CO_3)_2(H_2O)_4]^{2-}$ anion, showing the atomic numbering scheme.

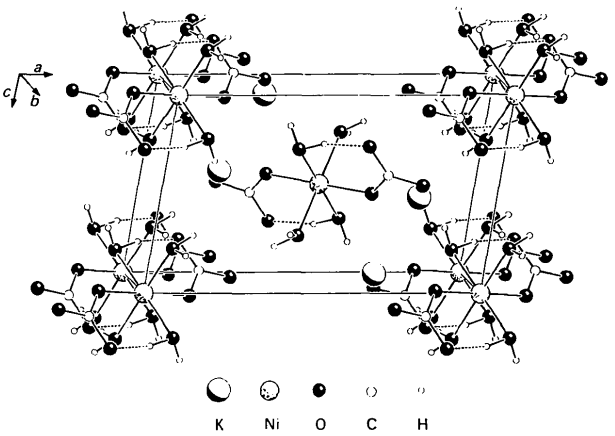


Fig. 2. The atomic arrangement in the unit cell. Hydrogen bonds between the complex anions are omitted for clarity.

Experimental

The title compound was prepared by dropwise addition of 2 ml of an aqueous solution of $Ni(CH_3COO)_2$ (1 *M*) to a stirred solution of carbonates made by dissolving 10 g of K_2CO_3 and 5 g of $KHCO_3$ in 50 ml of H_2O. When the first-formed pale green precipitate was completely dissolved, the resulting solution was allowed to stand at room temperature. Multiply twinned green crystals were grown overnight. Unfortunately, this method produced no crystals suitable for X-ray analysis. The crystalline product was filtered off, washed rapidly with ice-cold water and alcohol, and was finally dried under vacuum.

The following steps were taken to grow single crystals suitable for X-ray analysis. 50 g of K_2CO_3 was dissolved in 50 ml of water and was heated to 368 K, at which temperature 2 g of finely powdered $Ni(CH_3COO)_2.4H_2O$ was added little by little, with vigorous stirring. While adding the acetate, a pale green precipitate formed, which was deposited when stirring stopped. After the mixture was cooled to room temperature, a few multiply twinned crystals were placed on the precipitate. Green crystals in the form of truncated octahedra were finally formed after several weeks. One crystal was selected from the mother liquor and examined using a polarizing microscope and by the oscillation technique using a Weissenberg camera. The density was measured pycnometrically by using dodecane as a medium.

Crystal data

$K_2[Ni(CO_3)_2(H_2O)_4]$
$M_r = 328.97$
Monoclinic
$P2_1/n$
$a = 11.408$ (4) Å
$b = 6.156$ (1) Å
$c = 6.755$ (2) Å
$\beta = 99.69$ (2)°
$V = 467.6$ (2) Å^3
$Z = 2$
$D_x = 2.337$ Mg m^{-3}
$D_m = 2.314$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 3$–$12°$
$\mu = 3.011$ mm^{-1}
$T = 293$ K
Truncated octahedron
0.125 × 0.075 × 0.05 mm
Green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{min} = 0.957$, $T_{max} = 1.0$
2964 measured reflections
1286 independent reflections
970 observed reflections $[|F_o| \geq 4\sigma(F_o)]$

$R_{int} = 0.023$
$\theta_{max} = 30°$
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 8$
$l = -9 \rightarrow 9$
3 standard reflections monitored every 100 reflections
intensity variation: insignificant

Refinement

Refinement on F
$R = 0.053$
$wR = 0.030$
$S = 3.767$
970 reflections
86 parameters
Only H-atom U's refined
$w = 3.8878/\sigma^2(F)$

$(\Delta/\sigma)_{max} = 0.05$
$\Delta\rho_{max} = 0.88$ e Å^{-3}
$\Delta\rho_{min} = -1.23$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
K	0.3153 (1)	0.1456 (1)	0.0825 (1)	0.0226 (2)
Ni	1/2	1/2	1/2	0.0148 (2)
C	0.3231 (3)	0.1526 (6)	0.5783 (5)	0.0166 (10)
O1	0.3505 (2)	0.3109 (4)	0.4690 (4)	0.0187 (8)
O2	0.2214 (2)	0.0627 (4)	0.5345 (4)	0.0216 (8)
O3	0.3977 (2)	0.0857 (4)	0.7308 (4)	0.0212 (8)
O4	0.5930 (2)	0.2777 (4)	0.6975 (4)	0.0200 (8)
O5	0.5502 (2)	0.3355 (4)	0.2562 (4)	0.0228 (8)

Table 2. *Selected geometric parameters* (Å, °)

Ni—O1	2.046 (2)	O4^{v}—H1	0.93 (3)
Ni—O4	2.074 (2)	O5^{i}—H3^{i}	0.91 (5)
Ni—O5	2.094 (3)	O4^{v}—H2^{i}	0.84 (5)
C—O1	1.292 (5)	O5^{i}—H4^{i}	1.02 (3)
C—O2	1.275 (4)	O3^{ii}···H1^{vii}	1.65 (4)
C—O3	1.289 (4)	O2^{iii}···H2^{iii}	1.85 (5)
K^{i}···O1^{i}	2.768 (3)	O2^{i}···O4^{v}	2.678 (4)
K^{i}···O3^{ii}	2.723 (3)	O3^{v}···O4^{v}	2.565 (4)
K^{i}···O5^{i}	2.978 (3)	O3^{ii}···H4^{viii}	1.67 (3)
K^{i}···O1	2.779 (3)	O2^{iii}···H3^{vii}	1.84 (5)
K^{i}···O2^{iii}	2.699 (3)	O2^{ix}···O5^{i}	2.727 (3)
K^{i}···O4^{iv}	3.094 (3)	O3^{iv}···O5^{i}	2.658 (4)
K^{i}···O4^{v}	2.814 (3)		
O1—Ni—O4^{v}	89.0 (1)	O5^{i}···K^{i}···O2^{iii}	80.0 (1)
O1—Ni—O5	88.7 (1)	O5^{i}···K^{i}···O4^{v}	128.2 (1)
O4^{v}—Ni—O5	89.5 (1)	O1···K^{i}···O2^{iii}	126.9 (1)
O1—C—O2	119.5 (3)	O1···K^{i}···O4^{iv}	66.6 (1)
O1—C—O3	120.5 (3)	O5^{i}···K^{i}···O4^{iv}	86.1 (1)
O2—C—O3	120.0 (3)	O1^{i}···K^{i}···O4^{v}	70.9 (1)
O1^{i}···K^{i}···O3^{ii}	148.9 (1)	O1···K^{i}···O4^{v}	62.2 (1)
O1^{i}···K^{i}···O5^{i}	60.4 (1)	O2^{iii}···K^{i}···O4^{iv}	164.9 (1)
O1^{i}···K^{i}···O1	112.2 (1)	O2^{iii}···K^{i}···O4^{v}	79.6 (1)
O1^{i}···K^{i}···O2^{iii}	85.2 (1)	O4^{iv}···K^{i}···O4^{v}	104.9 (1)
O1^{i}···K^{i}···O4^{iv}	82.7 (1)	H1—O4^{v}—H2^{i}	100 (5)
O3^{ii}···K^{i}···O5^{i}	88.7 (1)	O4^{iv}—H1^{vi}···O3^{iv}	165 (4)
O3^{ii}···K^{i}···O1	96.8 (1)	O4^{iv}—H2···O2	168 (6)
O3^{ii}···K^{i}···O2^{iii}	86.1 (1)	H4^{i}—O5^{i}—H3^{i}	99 (4)
O3^{ii}···K^{i}···O4^{iv}	99.6 (1)	O5^{vii}—H3^{vii}···O2^{iii}	164 (4)
O3^{ii}···K^{i}···O4^{v}	136.3 (1)	O5^{i}—H4^{i}···O3^{iv}	165 (3)
O5^{i}···K^{i}···O1	152.7 (1)		

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

All non-H atoms were found in a Patterson map. The H atoms were located using difference Fourier syntheses. Refinement of all positional and displacement parameters (isotropic for H atoms and anisotropic for non-H atoms) was carried out using a full-matrix least-squares method. Data reduction including Lorentz–polarization correction: *DATNEU* (Fröhlich & Tebbe, 1979). Program used for empirical absorption correction: *SDP* (Enraf–Nonius, 1985). Program used to solve the structure: *SHELXS*86 (Sheldrick, 1985). Program used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *SCHAKAL* (Keller, 1988).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SH1076). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Rhodium(I) Complexes with 1,5-Diazabicyclo[4.3.0]non-5-ene (dbn) as a Ligand: [RhCl(nbd)(dbn)] (I) and $[Rh(dbn)_2(cod)][PF_6]$ (II) (nbd = Norbornadiene, cod = 1,5-Cyclooctadiene)

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Abstract

Both of the complexes studied, (η^4-bicyclo[2.2.1]hepta-2,5-diene)chloro(1,5-diazabicyclo[4.3.0]non-5-ene-N^5)-rhodium(I), $[RhCl(C_7H_8)(C_7H_{12}N_2)]$, (I), and ($\eta^4$-1,5-cyclooctadiene)bis(1,5-diazabicyclo[4.3.0]non-5-ene-N^5)rhodium hexafluorophosphate, $[Rh(C_7H_{12}N_2)(C_8H_{12})][PF_6]$, (II), show planar quadratically coordinated Rh atoms with dbn as and N-donor ligand. Two different conformations of the dbn ligand are present in each complex. The Rh–ligand bond distances and angles depend on the different N, Cl and diene coordination of the metal atoms.

Comment

In a recent paper we reported [RhCl(cod)(dbn)], the first Rh^{I} complex with dbn as a ligand to be characterized by means of an X-ray analysis (Flörke, Ortmann & Haupt, 1992). This and related complexes are used successfully as catalysts for the polymerization of phenylacetylene. Molecular weights up to 900 000 with 86% turnover have been achieved (Kowalzik, 1993). In the course of these investigations, the new compounds [RhCl(nbd)(dnb)], (I), and $[Rh(dbn)_2(cod)][PF_6]$, (II), were crystallized.

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