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# Diaquacobalt Tetracyanonickelate Tetrahydrate

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## Abstract

The synthesis and crystal structure of diaquacobalt tetracyanonickelate tetrahydrate are reported. The structure of $Co(H_2O)_2Ni(CN)_4.4H_2O$ is composed of alternating metal cyanide sheets and layers of hydrogen-bonded water molecules. The title compound is isostructural with $Cd(H_2O)_2Ni(CN)_4.4H_2O$.

## Comment

Many examples of two-dimensional structures composed of square-planar $M(CN)_4$ ($M$ = Ni, Pd, Pt) units linked to octahedral metal centers by coordination through the cyanide N atom have been reported (Iwamoto *et al.*, 1968) since the discovery of Hofmann's clathrate, $Ni(NH_3)_2Ni(CN)_4.C_6H_6$ (Hofmann & Kuspert, 1897). Most of these compounds contain ammonia or amines coordinated to the octahedral metal center to complete its coordination. A few examples are known which contain coordinated water molecules, *e.g.* $Ni(CN)_2.3H_2O$ (Mathey & Mazieres, 1974), $Cd(H_2O)_2Ni(CN)_4.4H_2O$ (Ham *et al.*, 1993) and $Fe(H_2O)_2Ni(CN)_4.2C_4H_8O_2$ (Kitazawa *et al.*, 1994), or clathrated water molecules, *e.g.* $Cd(NH_3)_2Ni(CN)_4.0.5H_2O$ (Kappenstein & Cernak, 1987) and $Ni(NH_3)_2Ni(CN)_4.0.5H_2O$ (Rayner & Powell, 1958). The new compound $Co(H_2O)_2Ni(CN)_4.4H_2O$ reported here is isostructural with $Cd(H_2O)_2Ni(CN)_4.4H_2O$.

The structure of $Co(H_2O)_2Ni(CN)_4.4H_2O$ is shown in Fig. 1. The structure is composed of alternating metal cyanide sheets and layers of hydrogen-bonded water molecules that alternate along the $a$ axis. The metal cyanide layers are displaced relative to each other so that the axial water molecules bound to the octahedral cobalt ions point towards the center of the square in the square-planar Ni—CN—Co array. Adjacent layers are related by a $2_1$ screw axis along **b** as noted by Ham *et al.* (1993). The inter-sheet distance is $a/2$ (6.09 Å). The cyanide layers are not planar but undulate because the $Ni(CN)_4^{2-}$ units alternate along **b** above and below a plane defined by the cobalt ions. The Ni—C bond lengths of 1.851 (3) and 1.864 (3) Å are nearly identical to the values observed in the Cd compound (1.857, 1.866 Å). The Co—N [2.095 (3), 2.101 (3) Å] and Co—O [2.128 (2) Å] bond lengths are typical of those found in other $Co^{2+}$ coordination compounds (Lu *et al.*, 1997). The shorter Co—$L$ distances compared with the corresponding Cd—$L$ distances largely account for the smaller unit cell observed for the cobalt phase.

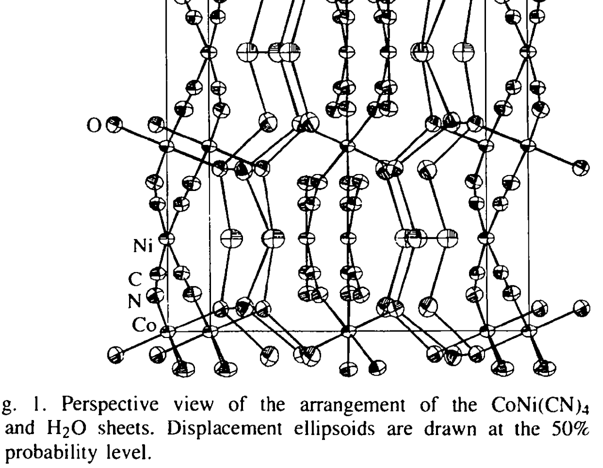

Fig. 1. Perspective view of the arrangement of the $CoNi(CN)_4$ and $H_2O$ sheets. Displacement ellipsoids are drawn at the 50% probability level.

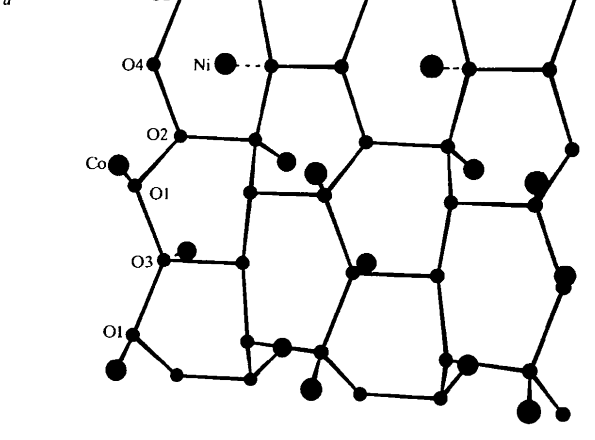

Fig. 2. The arrangement of the network water molecules.

The non-coordinated and coordinated water molecules form a hydrogen-bonded network. Six water molecules are arranged in a folded distorted hexagonal ring as shown in Fig. 2. The O—H···O distances range from 2.749 (4) to 2.855 (4) Å with an average value of 2.808 Å. Three distinct types of water molecule can be identified in the network: three water molecules are only held by hydrogen bonding, one weakly interacts with $Ni(CN)_4^{2-}$ centers [2.788 (4) Å], and two are coordinated to cobalt ions. As anticipated from this bonding arrangement, thermogravimetric analysis data show the loss of the interlayer water molecules in three well defined steps.

## Experimental

A sample of $K_2Ni(CN)_4$ (0.138 g, 0.573 mmol) dissolved in 10 ml water was placed in a screw-capped tube. A water–ethanol layer (5 ml) followed by a layer of $Co(SCN)_2$ (0.2 g, 1.143 mmol) in 10 ml ethanol was added carefully. Orange prismatic crystals formed in the middle layer after 7 d. The product loses water on standing in ambient air but is stable when protected by a thin film of epoxy. Thermogravimetric analysis (2 K $min^{-1}$ in $N_2$) showed three distinct weight losses (293–325, 325–343, 345–387 K) corresponding to stepwise removal of three, one and two water molecules, respectively, from the structure.

### *Crystal data*

$Co(H_2O)_2Ni(CN)_4.4H_2O$
$M_r = 329.82$
Orthorhombic
*Pnma*
$a = 12.178\ (3)$ Å
$b = 13.885\ (3)$ Å
$c = 7.143\ (3)$ Å
$V = 1207.8\ (6)$ Å$^3$
$Z = 4$
$D_x = 1.814$ Mg m$^{-3$}
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5.94$–$11.52°$
$\mu = 2.950$ mm$^{-1}$
$T = 293\ (2)$ K
Prism
0.55 × 0.25 × 0.20 mm
Orange

### *Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega$ scan
Absorption correction: empirical *via* $\psi$ scans (Enraf–Nonius, 1989)
$T_{min} = 0.524$, $T_{max} = 0.554$
1706 measured reflections
1706 independent reflections

1139 reflections with $I > 2\sigma(I)$
$\theta_{max} = 27.95°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 9$
3 standard reflections
frequency: 60 min
intensity decay: none

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.107$
$S = 1.061$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.500$ e Å$^{-3}$
$\Delta\rho_{min} = -0.501$ e Å$^{-3}$
Extinction correction: none

1366 reflections
79 parameters
All H-atom parameters fixed
$w = 1/[\sigma^2(F_o^2) + (0.0620P)^2 + 1.1555P]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Ni1—C2 | 1.851 (3) | Co2—O1 | 2.128 (2) |
| Ni1—C1 | 1.864 (3) | C1—N1 | 1.136 (4) |
| Co2—N2 | 2.095 (3) | N2—C2$^{i}$ | 1.140 (4) |
| Co2—N1 | 2.101 (3) | Ni1—O3 | 2.788 (4) |
| C2$^{ii}$—Ni1—C2 | 88.9 (2) | O1—Co2—O1$^{iii}$ | 180 |
| C2—Ni1—C1 | 90.2 (1) | N1—C1—Ni1 | 174.6 (3) |
| C1—Ni1—C1$^{ii}$ | 90.0 (2) | C1—N1—Co2 | 161.4 (3) |
| N2$^{iii}$—Co2—N2 | 180 | N2$^{i}$—C2—Ni1 | 177.4 (3) |
| N2—Co2—N1 | 89.6 (1) | C2$^{i}$—N2—Co2 | 177.1 (3) |
| N1$^{iii}$—Co2—N1 | 180 | Co2—O1—O2 | 110.7 (1) |
| N2—Co2—O1 | 88.6 (1) | Co2—O1—O3$^{iv}$ | 120.1 (1) |
| N1—Co2—O1 | 87.3 (1) | Co2—O1—O2$^{v}$ | 107.0 (1) |

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

Table 2. *Hydrogen-bonding geometry (Å, °)*

| *D*—H···*A* | *D*···*A* | H···*A* | *D*—H···*A* |
|---|---|---|---|
| O1—H1A···O2 | 2.749 (3) | 1.788 | 168.0 |
| O2—H2A···O4 | 2.803 (3) | 1.951 | 173.4 |
| O4—H4A···O2 | 2.803 (3) | 1.912 | 143.1 |
| O3—H3A···O4$^{i}$ | 2.849 (3) | 1.887 | 173.6 |
| O3—H3A···O4$^{ii}$ | 2.849 (3) | 1.887 | 173.6 |
| O1—H1B···O2$^{iii}$ | 2.855 (3) | 1.964 | 169.0 |
| O2—H2B···O1$^{iv}$ | 2.855 (3) | 1.938 | 162.5 |

| *A*···*A*···*A* | *A*···*A*···*A* |
|---|---|
| O1···O2···O4 | 106.4 (1) |
| O2···O1···O2$^{iii}$ | 102.2 (1) |
| O2···O1···O3$^{v}$ | 110.2 (1) |
| O3$^{v}$···O1···O2$^{iii}$ | 105.0 (1) |

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

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *RC*85 (Baird, 1985). Program(s) used to solve structure: *SHELXS*96 (Sheldrick, 1996*a*). Program(s) used to refine structure: *SHELXL*96 (Sheldrick, 1996*b*). Molecular graphics: *DIAMOND* (Brandenburg, 1996). Software used to prepare material for publication: *SHELXL*96.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS1042). Services for accessing these data are described at the back of the journal.

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# Lithium Hexafluoroarsenate Monohydrate, $LiAsF_6.H_2O$

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## Abstract

$LiAsF_6.H_2O$ crystallizes with the $NaPF_6.H_2O$ structure type. $[AsF_6]^-$ anions with nearly ideal octahedral geometry (As—F 1.71–1.72 Å) and water molecules form chains *via* weak F···H—O hydrogen bonds. The complex anions and water molecules exhibit a CsCl-like arrangement, with the octahedral holes partially occupied by $Li^+$ cations.

## Comment

$LiAsF_6.H_2O$ crystallizes with the $NaPF_6.H_2O$ structure type (space group *Imma*, $Z = 4$). The structure type was first described by Bode (Bode, 1954; Bode & Teufer, 1956) with atomic coordinates determined by Weissenberg film methods. The P/As atoms situated at the origin of the unit cell form the centres of nearly regular octahedra of $F^-$ ions (Fig. 1). Even though the site symmetry of the complex anions is only $2/m$, the F—As—F angles deviate by only 0.03° from ideal octahedral values. The As—F distances are 1.707 (2) (2×) and 1.722 (1) Å (4×). These values correspond to the distances found in the anhydrous alkali metal hexafluoroarsenates $RbAsF_6$ (1.713 Å) and $CsAsF_6$ (1.714 Å), which crystallize with the $LiSbF_6$ structure type (Loss & Röhr, 1998). While the As—F distances in $(H_3O)AsF_6$ (Mootz & Wiebcke, 1986) are also in the same range (1.701–1.742 Å, somewhat influenced by strong hydrogen bonding), the data for $NaAsF_6$ [1.78 (4) Å; Loss & Röhr, 1998] and $LiAsF_6$ [1.74 (4) Å; Röhr & Kniep, 1994] are uncertain because they are derived from powder data by Rietveld refinement.

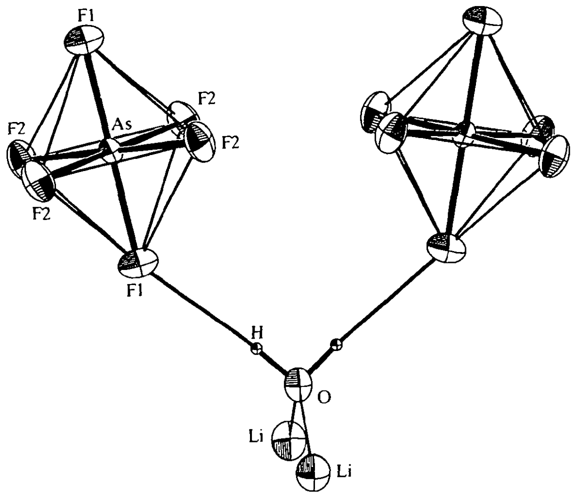

Fig. 1. A view of the $[AsF_6]^-$ octahedra and a connecting water molecule (50% probability ellipsoids).

In the crystal structure of the title compound, the O atoms of the water molecules are tetrahedrally coordinated by two H atoms and two $Li^+$ cations. The $[AsF_6]^-$ anions are connected to the water molecules *via* weak linear two-centre hydrogen bonds (Falk & Knop, 1973), with F1···O distances of 2.99 (1) Å and F1···H—O angles of 175 (3)°, to form chains running along the [010] direction (Fig. 2). The octahedra in the chains are alternately tilted with respect to the *c* axis

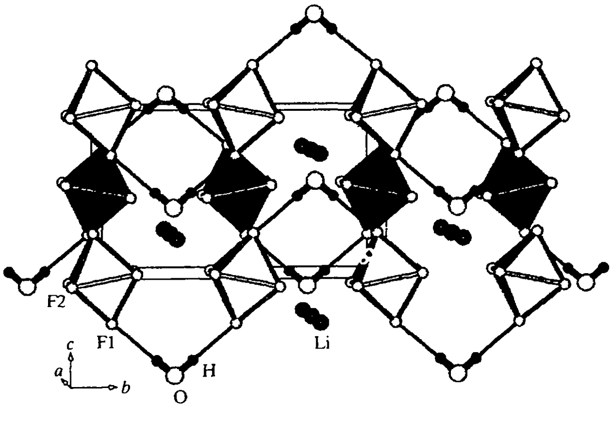

Fig. 2. The crystal structure of $LiAsF_6.H_2O$ viewed down [100], with chains of water-connected $[AsF_6]^-$ octahedra running along [010] at a height of $x = 0$ (light grey) and $x = \frac{1}{2}$ (dark grey).

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