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

Mo—O(1)	1.970 (2)	O(1)—Mo—O(2)	89.8 (1)
Mo—O(2)	1.959 (2)	O(1)—Mo—O(3)	88.9 (1)
Mo—O(3)	1.965 (2)	O(2)—Mo—O(3)	89.8 (1)
Li—O(1)	2.142 (2)	O(1)—Li—O(2)	88.7 (1)
Li—O(2)	2.099 (2)	O(1)—Li—O(3)	89.92 (9)
Li—O(3)	2.155 (2)	O(2)—Li—O(3)	89.2 (1)
		Mo—O(1)—Li	151.9 (1)
		Mo—O(2)—Li	152.2 (1)
		Mo—O(3)—Li	151.1 (1)
La—O(1)	2.430 (2)	La—O(1)	2.687 (2)
La—O(2)	2.409 (3)	La—O(1)	2.724 (2)
La—O(2)	2.496 (3)	La—O(3)	2.660 (2)
La—O(3)	2.446 (2)	La—O(3)	2.776 (2)

For ease of comparison with the perovskite structure, the non-conventional $P2_1/n$ setting was retained. Data were corrected for Lorentz and polarization effects. The structure was solved with the aid of *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and subsequent difference Fourier syntheses. Refinements of the occupancy factors for the Li and Mo sites confirmed that they are fully occupied. All calculations were performed on a Digital MicroVAX 3100.

Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: DU1142). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Cadmium Hexacyanoiridate(III) Dodecahydrate

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Abstract

Single crystals of tricadmium bis[hexacyanoiridate(III)] dodecahydrate, $Cd_3[Ir(CN)_6]_2.12H_2O$, were synthesized by the 'slow-diffusion U-tube' method. The disordered structure crystallizes in the cubic space group $Fm\bar{3}m$ (No. 225) with a lattice constant of 10.848 (1) Å and one-and-a-third molecules in the unit cell. Divalent Cd atoms are linked to the Ir atoms by linear cyanide bridges. When disorder occurs cavities are formed, a water molecule, O2, replaces an Ir atom and a cyanide bridge is replaced with a coordinated water molecule, O1. A hydrogen-bonding network is set up between O1, O2, and O3 within the cavities of the crystal lattice. Dehydration and IR studies were conducted on single crystals of the title compound. The compound is isostructural with the dodecahydrates of $Cd_3[Co(CN)_6]_2$ and $Mn_3[Co(CN)_6]_2$.

Comment

IR, dehydration, electron diffraction and powder and single-crystal X-ray diffraction methods have been employed to investigate the structural and morphological relationships of the transition metal ferro-, ferri- and cobalticyanides (Milligan *et al.*, 1970; Beall, Milligan, Korp & Bernal, 1977; Mullica, Oliver, Milligan & Hills, 1979). However, in spite of the structural investigations of the hydrated Prussian blue analogs, there are still questions concerning the zeolitic water structure in these materials. A clear understanding of the water network is essential in order to model the H_2O transport in the semi-permeable membranes. Several structural investigations of the transition metal hexacyanides have led to proposals of various models for the face-centered cubic lattice (Keggin & Miles, 1936; Ludi & Güdel, 1968; Ludi, Güdel & Ruegg, 1970; Ron, Ludi & Engel, 1973; Beall *et al.*, 1977). The present investigation of $Cd_3[Ir(CN)_6]_2.12H_2O$ was initiated in order to determine whether other transition metal hexacyanide compounds fit the model proposed by Beall *et al.* (1977) and to further our interest in compounds analogous to Prussian blue.

The metal-atom positions (Cd and Ir) and the C1 and N1 atoms of the cyanide ligands were located by employing the Patterson heavy-atom method. The model proposed by Beall *et al.* (1977) was used as a result of the solution obtained from the Patterson mapping. Due to the extremely high correlation between the O1 and N1 atoms and Ir and O2 atoms, related by competitiveness for the same positional sites, successive alternate refinements of these atoms were invoked. Fig. 1 is a representation of the $Cd_3[Ir(CN)_6]_2.12H_2O$ disordered structure based on the Beall model. The figure depicts two distinct types of units. The first type, represented in the lower portion of the drawing, shows an ordered arrangement of the metal atoms and the cyanide bridges with a water molecule (O4) located at its center. The second type of unit, represented by the upper and larger part of the figure, displays the disorder when one Ir atom is missing from the unit cell and is replaced by O2. O1 completes the coordination around the Cd atom in an octahedral arrangement. O3 is located in a tetrahedral manner about O2. The O2 and O3 water molecules are located in cavities and are positioned by a hydrogen-bonding network.

Experimental bond distances for Cd—N [2.273 (7) Å], Ir—C [2.010 (7) Å] and C—N [1.141 (9) Å] are in good agreement with those found in the Cambridge Structural Database (Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1989). The oxygen–oxygen contact distances [O1···O2 3.08 (2), O1···O3 2.72 (2), O2···O3, 2.81 (3) Å] vary somewhat, signifying strong to weak hydrogen bonds. A strong broad peak at 3515 cm^{-1} with a shoulder at 3413 cm^{-1} attest to the presence of hydrogen bonding and the shoulder can be related to a different type of hydrogen bond. The uncoordinated O4 water molecule is zeolitic and is greater than 3.89 Å from its nearest neighbor.

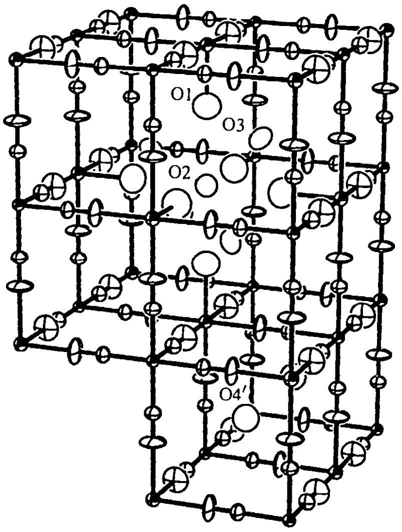

Fig. 1. A representation of the ordered and disordered structural units in $Cd_3[Ir(CN)_6]_2.12H_2O$. O1 is shown bonded to Cd. O2 is at the center of the cell surrounded by four tetrahedrally arranged O3 atoms. The lower part of the figure shows two O4 atoms. Displacement ellipsoids are shown at 50% probability.

Experimental

Clear cubic crystals of the title compound were prepared by the 'slow diffusion U-tube' method using dilute aqueous solutions of $CdCl_2$ and $K_3Ir(CN)_6$. Starting materials were of reagent grade and were used without further purification. After six months of storing the U-tubes in the dark, clear colorless crystals suitable for crystallographic and spectroscopic analysis were obtained. The density D_m was measured by flotation in bromoform and bromobenzene.

Crystal data

$Cd_3[Ir(CN_6)]_2.12H_2O$
$M_r = 1250.06$
Cubic
$Fm\bar{3}m$
$a = 10.848$ (1) Å
$V = 1276.6$ (2) Å^3
$Z = 1.333$
$D_x = 2.17$ Mg m^{-3}
$D_m = 2.15$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.08$–28.00°
$\mu = 8.567$ mm^{-1}
$T = 292$ K
Cube
0.15 × 0.13 × 0.12 mm
Colorless

Data collection

Enraf–Nonius CAD-4-*F* diffractometer
ω–2θ scans
Absorption correction: combination of ψ scan and spherical (Enraf–Nonius, 1985)
$T_{min} = 0.187$, $T_{max} = 0.235$
1093 measured reflections
316 independent reflections

252 observed reflections $[F > 4\sigma(F)]$
$R_{int} = 0.0234$
$\theta_{max} = 45.00°$
$h = -3 \rightarrow 21$
$k = -3 \rightarrow 21$
$l = -3 \rightarrow 21$
3 standard reflections
frequency: 120 min
intensity decay: 1.0%

Refinement

Refinement on F
$R = 0.026$
$wR = 0.032$
$S = 1.099$
252 reflections
16 parameters
No H atoms located
$w = 1/[\sigma^2(F) + 0.0003F^2]$
$(\Delta/\sigma)_{max} = 0.159$
$\Delta\rho_{max} = 1.246$ e Å^{-3}
$\Delta\rho_{min} = -0.779$ e Å^{-3}

Extinction correction: *SHELXTL-Plus* (Sheldrick, 1989)
Extinction coefficient: 0.00016 (4)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

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

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

	Occupancy	x	y	z	U_{eq}
Cd	1.00	0	0	1/2	0.0295 (3)
Ir	0.667	0	0	0	0.0224 (2)
C1	0.667	0	0.1853 (6)	0	0.036 (2)
N1	0.667	0	0.2905 (6)	0	0.074 (4)
O1	0.333	0	0.284 (2)	0	0.12 (1)
O2	0.333	0	0	0	0.07 (3)
O3	0.125	0.150 (2)	x	x	0.071 (8)
O4	0.333	1/4	1/4	1/4	0.11 (3)

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

Cd—N1	2.273 (7)	Ir—C1	2.010 (7)
Cd—O1	2.35 (2)	C1—N1	1.141 (9)
Cd—O1—O3	122.3 (6)	O3—O2—O3^{iii}	109.5 (7)
O3—O1—O3^{i}	115. (1)	O1—O3—O1^{iv}	106.4 (7)
O1—O2—O3^{ii}	125.3 (7)	O1—O3—O2	67.6 (6)

Symmetry codes: (i) $-x, y, -z$; (ii) $-x, -y, -z$; (iii) $-x, -y, z$; (iv) z, x, y.

The crystals were conoscopically examined using a Zeiss Photomicroscope II equipped with two crossed polarizers in order to determine the optical quality and to verify the isotropic nature of the crystals. A Perkin Elmer TGS-1 thermobalance was used to determine the thermal dehydration and yielded 12.1 (1) water molecules per formula unit. Pertinent IR spectral data were obtained using the pressed pellet method on a Mattson FTIR spectrometer. Lack of additional symmetry in the crystal structure was verified by employing the *MISSYM* program (Gabe, Le Page, Charland, Lee & White, 1989). The structure was solved by the heavy-atom Patterson method. As stated, results from the Patterson synthesis dictated using the model proposed by Beall *et al.* (1977) for the structure refinement. The excess electron density in the difference Fourier map is in the area of the transition metals and is quite normal for heavy-metal atoms.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *Software*. Data reduction: *Structure Determination Package* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1989). Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus XP*. Software used to prepare material for publication: *CIFGEN* (local program).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1126). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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