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Cadmium Selenite–Water (4/3) and Two Polymorphic Forms of Cadmium Selenite

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Abstract

Cadmium selenite has two polymorphic forms: $CdSeO_3(oP20)$ and $CdSeO_3(mP40)$. In the orthorhombic form the coordination polyhedron around cadmium is an octahedron and in the monoclinic form it is a trigonal prism. In $4CdSeO_3.3H_2O$ the coordination polyhedra are distorted between octahedra and trigonal prisms.

Comment

Like other transition metals, cadmium forms several selenites. The earliest reports as compiled in *Gmelin's Handbuch der Anorganische Chemie* (1925) describe the compounds $CdSeO_3$, $2CdSeO_3.3H_2O$, $3CdSeO_3.H_2SeO_3$, $2CdSeO_3.H_2SeO_3.H_2O$, $CdSe_2O_5$ and $Cd(NH_3)SeO_3$. Markovskii & Sapozhnikov (1961), Gospodinov & Bogdanov (1983) and Micka, Uchytilova & Ebert (1984) have reported two different modifications for anhydrous cadmium selenite. Thermal, IR and analytical data are also available in these publications.

The crystal structures of cadmium selenites are almost unknown. The only published structure is that of cadmium hydrogen selenite nitrate (Leskelä, Valkonen & Leskelä, 1984). We have now synthesized and solved the structures of seven different cadmium selenites: $CdSeO_3(oP20)$, $CdSeO_3(mP40)$, $4CdSeO_3.3H_2O$, $CdSe_2O_5$, $Cd_3(HSeO_3)_2(SeO_3)_2$, $(NH_4)Cd(SeO_3)_2$ and $Cd(NH_3)SeO_3$. The structures of the first three compounds are discussed in this paper and the other four structures will be reported shortly. Pearson notation is used for phase nomenclature (Leigh, 1990).

$CdSeO_3(oP20)$ is isomorphous with the selenites and tellurites of Mg, Mn, Co, Ni, Cu and Zn (Kohn, Inoue, Horie & Akimoto, 1976). All three compounds contain a three-dimensional network of cadmium-oxygen polyhedra. In $CdSeO_3(oP20)$ the CdO_6 octahedra share only corners, but in the other compounds edge-sharing occurs as well. In $CdSeO_3(mP40)$, CdO_6 trigonal prisms and SeO_3 tetrahedra share common edges and in $4CdSeO_3.3H_2O$ the $Cd(1)O_6$ octahedra and SeO_3 tetrahedra share common edges. The three structures are shown in Figs. 1–3.

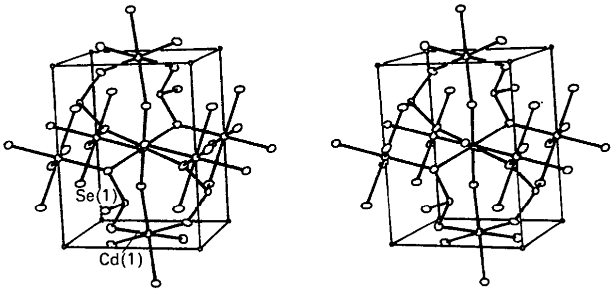

Fig. 1. Stereoscopic *ORTEP*II drawing of the unit cell of $CdSeO_3(oP20)$ showing 75% probability displacement ellipsoids. The *a* axis is horizontal and the *b* axis is vertical.

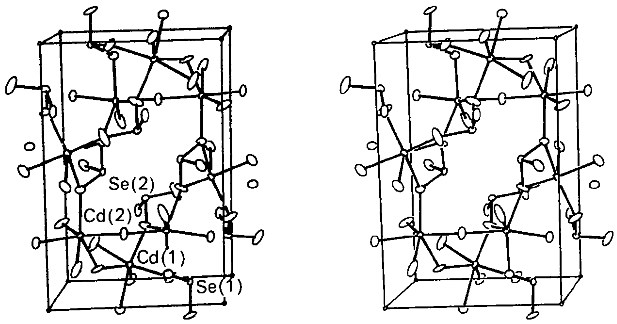

Fig. 2. A stereoscopic *ORTEP*II drawing of the unit cell of $CdSeO_3(mP40)$ showing 75% probability displacement ellipsoids. The *c* axis is horizontal and the *b* axis is vertical.

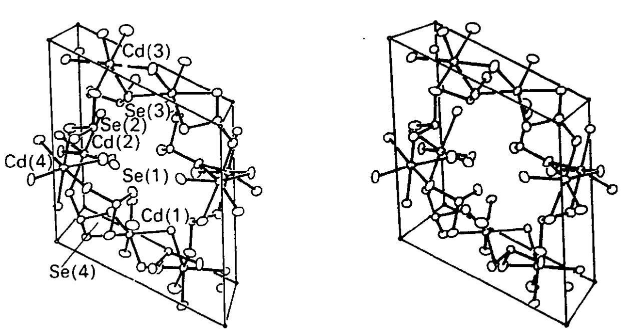

Fig. 3. A stereoscopic *ORTEP*II drawing of the unit cell of $4CdSeO_3.3H_2O$ showing 75% probability displacement ellipsoids. The *a* axis is tilted slightly from the horizonal and the *c* axis is vertical.

Experimental

$CdSeO_3$(*oP*20), $CdSeO_3$(*mP*40) and $4CdSeO_3.3H_2O$ were crystallized from an aqueous solution of cadmium acetate and selenious acid. The anhydrous compounds were crystallized by slow evaporation at 313 K and $4CdSeO_3.3H_2O$ was crystallized by slow evaporation at 295 K. In both methods selenious acid was present in excess.

$CdSeO_3$(*oP*20)

Crystal data

$CdSeO_3$
$M_r = 239.36$
Orthorhombic
Pnma
$a = 6.2773$ (6) Å
$b = 8.0850$ (26) Å
$c = 5.2939$ (4) Å
$V = 268.68$ (9) Å^3
$Z = 4$
$D_x = 5.92$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6.97\text{-}15.40°$
$\mu = 21.27$ mm^{-1}
$T = 298$ K
Prismatic
0.30 × 0.20 × 0.20 mm
White

Data collection

Enraf-Nonius CAD-4 diffractometer
$2\theta/\omega$ scans
Absorption correction: *DIFABS* (Walker & Stuart, 1983)
$T_{min} = 0.88$, $T_{max} = 1.17$
1006 measured reflections
1006 independent reflections

738 observed reflections $[I > 3\sigma(I)]$
$\theta_{max} = 39.99°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 9$
3 standard reflections frequency: 30 min intensity variation: <2%

Refinement

Refinement on F
$R = 0.022$
$wR = 0.029$
$S = 1.52$
738 reflections
29 parameters
Unit weights applied
$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 1.65$ e Å^{-3}
$\Delta\rho_{min} = -3.21$ e Å^{-3}

Extinction correction: $|F_c| = |F_o|(1 + gI_c)$ (Stout & Jensen, 1968)
Extinction coefficient: $g = 6.06 \times 10^{-7}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* $CdSeO_3$(*oP*20)

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

	x	y	z	U_{eq}
Cd(1)	0	0	0	0.0069 (1)
Se(1)	0.02906 (7)	1/4	0.51643 (9)	0.0049 (1)
O(1)	0.0904 (7)	1/4	0.2024 (7)	0.0079 (6)
O(2)	0.1743 (4)	0.0871 (4)	0.6308 (5)	0.0091 (5)

Table 2. *Selected geometric parameters* (Å) *for* $CdSeO_3$(*oP*20)

Cd(1)—O(1)	2.357 (2)	Cd(1)—O(2)	2.271 (3)
Cd(1)—O(1)	2.357 (2)	Se(1)—O(1)	1.706 (4)
Cd(1)—O(2)	2.348 (3)	Se(1)—O(2)	1.713 (3)
Cd(1)—O(2)	2.348 (3)	Se(1)—O(2)	1.713 (3)
Cd(1)—O(2)	2.271 (3)		

$CdSeO_3$(*mP*40)

Crystal data

$CdSeO_3$
$M_r = 239.36$
Monoclinic
$P2_1/c$
$a = 5.7084$ (5) Å
$b = 12.8283$ (11) Å
$c = 8.5860$ (8) Å
$\beta = 101.210$ (8)°
$V = 616.7$ (1) Å^3
$Z = 8$
$D_x = 5.16$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.99\text{-}12.15°$
$\mu = 18.54$ mm^{-1}
$T = 298$ K
Prismatic
0.20 × 0.10 × 0.10 mm
White

Data collection

Enraf-Nonius CAD-4 diffractometer
$2\theta/\omega$ scans
Absorption correction: *DIFABS* (Walker & Stuart, 1983)
$T_{min} = 0.90$, $T_{max} = 1.09$
3946 measured reflections
3946 independent reflections

2862 observed reflections $[I > 3\sigma(I)]$
$\theta_{max} = 39.98°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 23$
$l = -15 \rightarrow 15$
3 standard reflections frequency: 60 min intensity variation: <2%

Refinement

Refinement on F
$R = 0.043$
$wR = 0.062$
$S = 4.36$
2862 reflections
92 parameters
Unit weights applied
$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 3.12$ e Å^{-3}
$\Delta\rho_{min} = -4.39$ e Å^{-3}

Extinction correction: $|F_c| = |F_o|(1 + gI_c)$ (Stout & Jensen, 1968)
Extinction coefficient: $g = 5.60 \times 10^{-7}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* $CdSeO_3$(*mP*40)

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

	x	y	z	U_{eq}
Cd(1)	0.1830 (1)	0.07755 (4)	0.38823 (7)	0.0070 (1)
Cd(2)	0.37795 (9)	0.74434 (4)	0.35202 (6)	0.0060 (1)
Se(1)	0.4147 (1)	0.02604 (6)	0.76717 (9)	0.0065 (1)
Se(2)	0.0287 (1)	0.16879 (6)	0.9798 (1)	0.0072 (1)
O(1)	0.5954 (11)	0.0790 (5)	0.6529 (8)	0.0108 (10)
O(2)	0.5347 (12)	−0.0952 (5)	0.7734 (9)	0.0139 (12)
O(3)	0.1568 (11)	0.0193 (6)	0.6331 (8)	0.0152 (12)
O(4)	−0.2229 (12)	0.2386 (6)	0.9136 (7)	0.0139 (12)
O(5)	0.2427 (12)	0.2619 (6)	1.0016 (10)	0.0190 (12)
O(6)	−0.0321 (13)	0.1494 (8)	1.1600 (9)	0.0241 (12)

Table 4. *Selected geometric parameters* (Å) *for* $CdSeO_3$(*mP*40)

Cd(1)—O(1)	2.436 (7)	Cd(2)—O(4)	2.351 (7)
Cd(1)—O(2)	2.333 (8)	Cd(2)—O(5)	2.293 (7)
Cd(1)—O(3)	2.264 (7)	Cd(2)—O(6)	2.305 (8)
Cd(1)—O(3)	2.280 (7)	Se(1)—O(1)	1.697 (7)
Cd(1)—O(5)	2.275 (7)	Se(1)—O(2)	1.696 (7)
Cd(1)—O(6)	2.293 (7)	Se(1)—O(3)	1.685 (6)
Cd(2)—O(1)	2.272 (6)	Se(2)—O(4)	1.694 (7)
Cd(2)—O(2)	2.270 (7)	Se(2)—O(5)	1.693 (7)
Cd(2)—O(4)	2.291 (6)	Se(2)—O(6)	1.669 (8)

$4CdSeO_3.3H_2O$

Crystal data

$4CdSeO_3.3H_2O$
M_r = 1011.48
Monoclinic
$P2_1$
a = 9.4746 (9) Å
b = 8.7696 (3) Å
c = 10.1455 (5) Å
β = 117.371 (5)°
V = 748.61 (9) Å^3
Z = 2
D_x = 4.49 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 8.04–13.41°
μ = 15.32 mm^{-1}
T = 298 K
Prismatic
0.30 × 0.30 × 0.20 mm
White

Data collection

Enraf-Nonius CAD-4 diffractometer
$2\theta/\omega$ scans
Absorption correction: *DIFABS* (Walker & Stuart, 1983)
$T_{\min}$ = 0.89, $T_{\max}$ = 1.27
4845 measured reflections
4845 independent reflections

3672 observed reflections $[I > 3\sigma(I)]$
$\theta_{\max}$ = 40.00°
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 15$
$l = -18 \rightarrow 16$
3 standard reflections
frequency: 60 min
intensity variation: <2%

Refinement

Refinement on F
R = 0.024
wR = 0.028
S = 1.82
3672 reflections
208 parameters
Unit weights applied
$(\Delta/\sigma)_{\max}$ = 0.005
$\Delta\rho_{\max}$ = 1.30 e Å^{-3}
$\Delta\rho_{\min}$ = −1.01 e Å^{-3}

Extinction correction: $|F_c| = |F_o|(1 + gI_c)$ (Stout & Jensen, 1968)
Extinction coefficient: $g = 3.40 \times 10^{-7}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 5. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* $4CdSeO_3.3H_2O$

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

	x	y	z	U_{eq}
Cd(1)	0.31914 (4)	0.341†	1.01338 (4)	0.0111 (1)
Cd(2)	0.04193 (5)	0.32973 (6)	0.34225 (4)	0.0111 (1)
Cd(3)	0.32007 (5)	0.73798 (6)	0.99353 (4)	0.0119 (1)
Cd(4)	0.98243 (5)	0.23509 (6)	0.65491 (4)	0.0117 (1)
Se(1)	0.36334 (6)	0.5363 (1)	1.33902 (6)	0.0113 (1)
Se(2)	0.23874 (6)	0.5371 (1)	0.67117 (5)	0.0092 (1)
Se(3)	0.66810 (6)	0.5366 (1)	1.22914 (5)	0.0088 (1)
Se(4)	0.03258 (7)	0.16177 (9)	1.00634 (6)	0.0116 (1)
O(1)	0.3129 (5)	0.5494 (7)	1.1558 (4)	0.0151 (9)
O(2)	0.1872 (5)	0.5420 (9)	1.3431 (5)	0.0162 (9)
O(3)	0.4369 (6)	0.7116 (7)	1.4007 (5)	0.0181 (11)
O(4)	0.2560 (6)	0.5277 (8)	0.8440 (5)	0.0172 (10)
O(5)	0.1555 (5)	0.3659 (6)	0.6022 (5)	0.0142 (9)
O(6)	0.0815 (6)	0.6556 (7)	0.5859 (5)	0.0191 (10)
O(7)	0.8553 (5)	0.5213 (6)	1.2493 (5)	0.0146 (10)
O(8)	0.5919 (5)	0.3663 (6)	1.1463 (5)	0.0127 (9)
O(9)	0.5874 (5)	0.6615 (7)	1.0883 (5)	0.0163 (10)
O(10)	0.0409 (5)	0.2967 (6)	0.8893 (5)	0.0141 (9)
O(11)	0.2330 (5)	0.1664 (7)	1.1312 (5)	0.0160 (10)
O(12)	−0.0497 (5)	0.2626 (7)	1.0979 (5)	0.0170 (10)
O(13)‡	0.2616 (6)	0.1795 (7)	1.3983 (5)	0.0179 (11)
O(14)‡	−0.2358 (6)	0.3820 (7)	0.5394 (6)	0.0215 (13)
O(15)‡	0.4023 (7)	−0.0930 (7)	1.1810 (6)	0.0228 (13)

† Coordinate fixed to define origin.
‡ Water O atom.

Table 6. *Selected geometric parameters* (Å) *for* $4CdSeO_3.3H_2O$

Cd(1)—O(1)	2.348 (6)	Cd(4)—O(2)	2.339 (6)
Cd(1)—O(4)	2.247 (6)	Cd(4)—O(5)	2.256 (6)
Cd(1)—O(8)	2.310 (4)	Cd(4)—O(6)	2.336 (5)
Cd(1)—O(9)	2.270 (6)	Cd(4)—O(7)	2.333 (5)
Cd(1)—O(10)	2.372 (4)	Cd(4)—O(10)	2.244 (5)
Cd(1)—O(11)	2.307 (6)	Cd(4)—O(14)	2.252 (5)
Cd(2)—O(2)	2.311 (7)	Se(1)—O(1)	1.696 (5)
Cd(2)—O(5)	2.366 (5)	Se(1)—O(2)	1.688 (5)
Cd(2)—O(6)	2.238 (6)	Se(1)—O(3)	1.684 (6)
Cd(2)—O(7)	2.302 (5)	Se(2)—O(4)	1.686 (5)
Cd(2)—O(12)	2.294 (5)	Se(2)—O(5)	1.689 (5)
Cd(2)—O(13)	2.301 (6)	Se(2)—O(6)	1.691 (5)
Cd(3)—O(1)	2.355 (6)	Se(3)—O(7)	1.694 (5)
Cd(3)—O(4)	2.284 (6)	Se(3)—O(8)	1.702 (5)
Cd(3)—O(8)	2.249 (6)	Se(3)—O(9)	1.678 (5)
Cd(3)—O(9)	2.354 (5)	Se(4)—O(10)	1.703 (6)
Cd(3)—O(12)	2.297 (5)	Se(4)—O(11)	1.731 (4)
Cd(3)—O(15)	2.248 (6)	Se(4)—O(12)	1.707 (6)

The quality of the crystal of $CdSeO_3$(*mP*40) was very poor, which explains the large R value. The absolute structure of $4CdSeO_3.3H_2O$ was checked. The set of coordinates generated from Table 5 using the operation $1 - x$, $1 - y$, $1 - z$ led to an R value of 0.032, whereas the correct set resulted in an R value of 0.024. Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989). Data reduction and other calculations were performed using *MolEN* (Fair, 1990). Lorentz and polarization corrections were applied to the data. The Cd and Se atoms were located by direct methods using the program *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: AB1066). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1994). C**50**, 994–996

Tetraammineplatinum(II) Aquapentachloroiridate(III) Dihydrate, $[Pt(NH_3)_4][IrCl_5(H_2O)].2H_2O$

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Abstract

The crystal is built up from planar $Pt(NH_3)_4^{2+}$ cations, octahedral $IrCl_5(H_2O)^{2-}$ anions and two H_2O molecules. The coordination of these ions is 6/6, thus leading to a NaCl crystal structure. Electrostatic interactions and N···Cl, N···O and N···N short contacts (possible hydrogen bonds) take part in the packing of the structure and form a three-dimensional network.

Comment

The title compound is one of a series of inorganic platinum–iridium complexes (Garnier, 1993) which are reforming-catalyst precursors. The diffusion of K_3IrCl_6 and $Pt(NH_3)_4Cl_2$ in a tetramethoxysilane gel led to $[Pt(NH_3)_4][IrCl_6]_2$ (Michelot, 1986) as well as the title compound.

The complex crystallizes with nearly octahedral $Ir(H_2O)Cl_5^{2-}$ anions, planar $Pt(NH_3)_4^{2+}$ cations and two H_2O molecules. The coordination of these ions is 6/6 with distances of 5.41–6.16 Å between Pt and Ir. The structure may also be regarded as comprising layers parallel to (001) with the two hydration H_2O molecules (O2, O3) located between and inside these layers.

The Pt—N bond lengths in related structures containing the $Pt(NH_3)_4^{2+}$ ion are in the range 2.01 (2)–2.08 (1) Å (Endres, Keller, Moroni, Nöthe & Dong, 1978; Khodadad & Rodier, 1987, 1989; Rochon & Melanson, 1980; Tanaka, Tsujikawa, Toriumi & Ito, 1986; Toffoli, Khodadad, Rodier & Viossat, 1987), which compare favourably with our average value of 2.04 (1) Å. The Ir atom has a more distorted octahedral environment with an Ir—Cl mean distance of 2.36 (2) Å. The Ir—Cl distances in related structures containing the octahedral $IrCl_6^{3-}$ anion are in the range 2.335 (8)–2.359 (4) Å (Gray, Gulliver, Levason & Webster, 1982; Williams, Flack & Vincent, 1980). Of interest are the N···N, N···O and N···Cl short contacts (possible hydrogen bonds) which form a three-dimensional network.

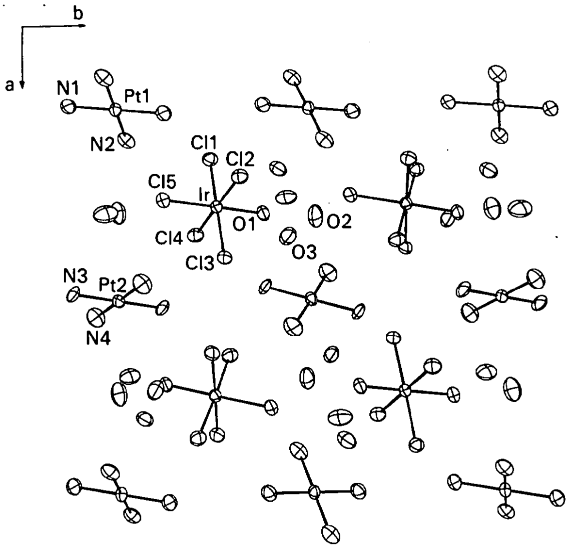

Fig. 1. A *MACORTEP* (Michalowicz & Andre, 1991) view of the packing of the ions in the *ab* plane of the title compound.

Experimental

Crystals were grown by diffusion of K_3IrCl_6 and $Pt(NH_3)_4Cl_2$ in tetramethoxysilane gel. Chemical analysis: Ir/Pt = 1 (quantitative electron microprobe).

Crystal data

$[Pt(NH_3)_4][IrCl_5(H_2O)].$-$2H_2O$
$M_r = 686.74$
Tetragonal
$I4_1/a$
$a = 15.655$ (2) Å
$c = 23.554$ (3) Å
$V = 5773$ (1) Å^3
$Z = 16$
$D_x = 3.161$ Mg m^{-3}
$D_m = 3.14$ Mg m^{-3}
D_m measured by flotation

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 11.62$–$21.53°$
$\mu = 19.89$ mm^{-1}
$T = 294$ K
Parallelepiped
0.164 × 0.114 × 0.100 mm
Orange