

Poly[*diaquatetra-μ-selenocyanato-cadmium(II)dipotassium(I)*]

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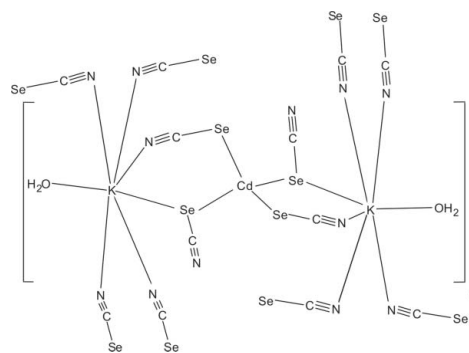
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Key indicators: single-crystal X-ray study; $T = 170$ K; mean $\sigma(\text{N}-\text{C}) = 0.012$ Å; R factor = 0.037; wR factor = 0.090; data-to-parameter ratio = 22.8.

In the title compound, $[\text{CdK}_2(\text{NCSe})_4(\text{H}_2\text{O})_2]_n$, the cadmium(II) cation is situated on a twofold rotation axis and is coordinated in a slightly distorted tetrahedral geometry by two symmetry-related μ -1,1,1,3 and two-symmetry related μ -1,1,3,3 bridging selenocyanate anions, all of which are Se bonded. These bridging selenocyanate anions are further coordinated to two symmetry-related potassium ions. Each of the potassium ions is coordinated by one terminally bonded water molecule and six selenocyanate anions, two of which are crystallographically independent. The asymmetric unit consists of one cadmium and one potassium cation, two bridging selenocyanate anions and one water molecule. The polymeric subunits are further connected *via* the selenocyanate anions into a three-dimensional coordination network. In this coordination network, intramolecular hydrogen bonds between neighbouring water molecules can be found.

Related literature

For general background to transition metal thio- and selenocyanates and *N*-donor ligands, see: Näther *et al.* (2007); Bhosekar *et al.* (2006); Wriedt & Näther (2010); Wriedt *et al.* (2010*a,b*). For related structures, see: Shi *et al.* (2007); Couhorn & Dronskowski (2004). For similar coordination modes in azido anions, see: El Fallah *et al.* (2008); Guo & Mak (1998).



Experimental

Crystal data

$[\text{CdK}_2(\text{NCSe})_4(\text{H}_2\text{O})_2]$

$M_r = 646.55$

Monoclinic, $C2/c$

$a = 21.574$ (3) Å

$b = 4.4055$ (4) Å

$c = 17.9316$ (19) Å

$\beta = 112.454$ (13)°

$V = 1575.1$ (3) Å³

$Z = 4$

Mo $K\alpha$ radiation

$\mu = 11.15$ mm⁻¹

$T = 170$ K

$0.05 \times 0.04 \times 0.03$ mm

Data collection

Stoe IPDS-1 diffractometer

Absorption correction: numerical

(*X-SHAPE* and *X-RED32*;

Stoe & Cie, 2008)

$T_{\text{min}} = 0.588$, $T_{\text{max}} = 0.713$

4687 measured reflections

1800 independent reflections

1355 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.057$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.090$

$S = 1.00$

1800 reflections

79 parameters

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.90$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.94$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1}-\text{H2}\cdots\text{O1}^i$	0.85	1.92	2.760 (6)	167

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

Data collection: *X-AREA* (Stoe & Cie, 2008); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2330).

References

- Bhosekar, G., Jess, I. & Näther, C. (2006). *Acta Cryst.* **E62**, m1859–m1860.
- Couhorn, U. & Dronskowski, R. (2004). *Z. Anorg. Allg. Chem.* **630**, 427–433.
- El Fallah, M. S., Vicente, R., Tercero, J., Elpelt, C., Rentschler, E., Solans, X. & Font-Bardia, M. (2008). *Inorg. Chem.* **47**, 6322–6328.
- Guo, G.-C. & Mak, T. C. W. (1998). *Angew. Chem. Int. Ed.* **37**, 3268–3270.
- Näther, C., Bhosekar, G. & Jess, I. (2007). *Eur. J. Inorg. Chem.* pp. 5353–5359.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Shi, W., Shafaei-Fallah, M., Zhang, L., Anson, C., Matern, E. & Rothenberger, A. (2007). *Chem. Eur. J.* **13**, 598–603.
- Stoe & Cie (2008). *X-AREA*, *X-RED32* and *X-SHAPE*. Stoe & Cie, Darmstadt, Germany.
- Wriedt, M., Jess, I. & Näther, C. (2010a). *Acta Cryst.* **E66**, m742.
- Wriedt, M., Jess, I. & Näther, C. (2010b). *Acta Cryst.* **E66**, m1014–m1015.
- Wriedt, M. & Näther, C. (2010). *Chem. Commun.* **46**, 4707–4709.

supporting information

Acta Cryst. (2010). E66, i70–i71 [doi:10.1107/S1600536810034938]

Poly[diquatetra- μ -selenocyanato-cadmium(II)dipotassium(I)]**Thorben Reinert, Jan Boeckmann, Inke Jess and Christian Näther****S1. Comment**

In our ongoing investigations on the synthesis, structures and properties of transition metal thio- and selenocyanates and N-donor ligands (Näther, Bhosekar & Jess (2007); Bhosekar *et al.* (2006); Wriedt & Näther (2010); Wriedt, Jess & Näther (2010*a,b*)) we have reacted cadmium(II) dinitrate with potassium selenocyanate and pyrimidine in water in order to prepare cadmium selenocyanato coordination polymers with pyrimidine as co-ligand. In this reaction single crystals were obtained, which were identified as the title compound by single-crystal X-ray diffraction.

In the title compound of composition $[\text{CdK}_2(\text{NCSe})_4(\text{H}_2\text{O})_2]_n$ (Fig. 1) the cadmium cation is located on a twofold rotation axis and is coordinated to ten potassium cations *via* two μ -1,1,1,3 bridging and two μ -1,1,3,3 bridging selenocyanato anions. The cadmium cation is coordinated by Se atoms of four selenocyanato anions in a slightly distorted tetrahedral geometry. The Cd—Se distances range between 2.655 (7) Å and 2.672 (8) Å and the Se—Cd—Se angles range between 106.68 (21)° and 116.96 (17)° (Tab. 1). The potassium cations are each heptacoordinated by three N-atoms of three μ -1,1,1,3 bridging selenocyanato anions, two N-atoms of two μ -1,1,3,3 bridging selenocyanato anions, one Se-atom of one μ -1,1,3,3 bridging selenocyanato anion and one terminally bonded water molecule within an irregular geometry. The K—N distances range between 2.805 (69) Å and 3.083 (71) Å, the K—O distance amounts to 2.763 (45) Å and the K—Se distance is 3.694 (16) Å. The angles around the K atoms range between 63.10 (2)° and 155.51 (19)° (Tab. 1). The large K—Se and K—K distances are not unusual and similar values can be found in related structures (Shi *et al.*, 2007; Couhorn & Dronskowski, 2004). The Cd and K atoms are connected by the bridging selenocyanato anions into a three-dimensional coordination network (Fig. 2). It must be noted that the present bridging modes of the selenocyanato anions are observed for the first time in a coordination polymer and similar coordination modes can be found for azido anions (El Fallah *et al.*, 2008; Guo & Mak, 1998).

S2. Experimental

$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was obtained from Merck, KNCSe and pyrimidine were obtained from Alfa Aesar. 1 mmol (174 mg) $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 2 mmol (288 mg) KNCSe , 4 mmol (320 mg) pyrimidine and 3 ml acetonitrile were reacted in a closed snap-cap vial without stirring. After the mixture had been standing for several days in the dark at room temperature colourless block shaped single crystals of the title compound were obtained.

S3. Refinement

The O—H hydrogen atoms were located in difference map, set to idealized distances and refined isotropic using a riding model with $U_{\text{eq}}(\text{H}) = 1.5 * U_{\text{eq}}(\text{O})$.

Poly[diquatetra- μ -selenocyanato-cadmium(II)dipotassium(I)]

Crystal data

[CdK₂(NCSe)₄(H₂O)₂]
 $M_r = 646.55$
 Monoclinic, $C2/c$
 Hall symbol: $-C\ 2yc$
 $a = 21.574\ (3)\ \text{\AA}$
 $b = 4.4055\ (4)\ \text{\AA}$
 $c = 17.9316\ (19)\ \text{\AA}$
 $\beta = 112.454\ (13)^\circ$
 $V = 1575.1\ (3)\ \text{\AA}^3$
 $Z = 4$

$F(000) = 1176$
 $D_x = 2.726\ \text{Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$
 Cell parameters from 4533 reflections
 $\theta = 2.5\text{--}27.5^\circ$
 $\mu = 11.15\ \text{mm}^{-1}$
 $T = 170\ \text{K}$
 Block, colourless
 $0.05 \times 0.04 \times 0.03\ \text{mm}$

Data collection

Stoe IPDS-1
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ Scans scans
 Absorption correction: numerical
 ($X\text{-SHAPE}$ and $X\text{-RED32}$; Stoe & Cie, 2008)
 $T_{\min} = 0.588$, $T_{\max} = 0.713$

4687 measured reflections
 1800 independent reflections
 1355 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.057$
 $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.5^\circ$
 $h = -28 \rightarrow 26$
 $k = -5 \rightarrow 4$
 $l = -23 \rightarrow 23$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.090$
 $S = 1.00$
 1800 reflections
 79 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map

Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.052P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.90\ \text{e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.94\ \text{e \AA}^{-3}$
 Extinction correction: $SHELXL97$ (Sheldrick,
 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.00083 (16)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cd1	0.5000	0.53865 (16)	0.7500	0.02159 (19)
Se1	0.39046 (3)	0.19271 (15)	0.71167 (3)	0.02260 (18)
C1	0.3440 (3)	0.3582 (16)	0.6125 (4)	0.0257 (13)

N1	0.3131 (3)	0.4620 (16)	0.5497 (3)	0.0320 (13)
Se2	0.49070 (3)	0.85366 (16)	0.61994 (3)	0.02357 (19)
C2	0.5606 (4)	0.6741 (17)	0.6015 (4)	0.0293 (15)
N2	0.6047 (4)	0.5706 (16)	0.5900 (4)	0.0381 (15)
K1	0.32739 (8)	0.9210 (4)	0.44900 (8)	0.0291 (3)
O1	0.2416 (3)	0.8171 (13)	0.2915 (3)	0.0375 (12)
H1	0.1999	0.8495	0.2786	0.056*
H2	0.2463	0.6824	0.2602	0.056*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.0190 (3)	0.0260 (4)	0.0195 (3)	0.000	0.0071 (2)	0.000
Se1	0.0206 (3)	0.0229 (3)	0.0237 (3)	-0.0014 (2)	0.0078 (2)	0.0018 (2)
C1	0.022 (3)	0.026 (4)	0.033 (3)	-0.006 (3)	0.015 (3)	-0.004 (3)
N1	0.028 (3)	0.037 (4)	0.028 (3)	-0.003 (3)	0.007 (2)	0.002 (3)
Se2	0.0244 (3)	0.0258 (4)	0.0208 (3)	0.0022 (3)	0.0089 (2)	0.0020 (2)
C2	0.038 (4)	0.029 (4)	0.022 (3)	-0.004 (3)	0.013 (3)	-0.002 (3)
N2	0.047 (4)	0.033 (4)	0.048 (3)	0.008 (3)	0.033 (3)	0.002 (3)
K1	0.0348 (8)	0.0263 (8)	0.0292 (7)	0.0001 (6)	0.0155 (6)	-0.0005 (6)
O1	0.032 (3)	0.042 (3)	0.039 (3)	-0.007 (3)	0.015 (2)	-0.008 (2)

Geometric parameters (Å, °)

Cd1—Se2	2.6548 (7)	Se2—C2	1.841 (7)
Cd1—Se1	2.6720 (8)	C2—N2	1.143 (10)
Se1—C1	1.827 (7)	N2—K1 ⁱⁱⁱ	2.847 (7)
C1—N1	1.161 (9)	N2—K1 ^{iv}	2.904 (7)
N1—K1	2.806 (6)	K1—O1	2.760 (5)
N1—K1 ⁱ	3.076 (7)	O1—H1	0.8501
N1—K1 ⁱⁱ	3.083 (7)	O1—H2	0.8500
Se2—Cd1—Se2 ^v	116.97 (4)	N1 ^{vi} —K1—N1 ⁱⁱ	63.1 (2)
Se2—Cd1—Se1	108.03 (2)	O1—K1—Se2	152.89 (13)
Se2 ^v —Cd1—Se1	106.66 (2)	N1—K1—Se2	73.29 (13)
Se2—Cd1—Se1 ^v	106.66 (2)	N2 ⁱⁱⁱ —K1—Se2	74.08 (15)
Se2 ^v —Cd1—Se1 ^v	108.03 (2)	N2 ^{iv} —K1—Se2	81.55 (15)
Se1—Cd1—Se1 ^v	110.45 (4)	N1 ^{vi} —K1—Se2	81.53 (12)
C1—Se1—Cd1	97.2 (2)	N1 ⁱⁱ —K1—Se2	129.50 (11)
N1—C1—Se1	178.5 (6)	O1—K1—K1 ^{vi}	99.55 (13)
C1—N1—K1	138.2 (5)	N1—K1—K1 ^{vi}	136.11 (14)
C1—N1—K1 ⁱ	96.6 (5)	N2 ⁱⁱⁱ —K1—K1 ^{vi}	139.52 (14)
K1—N1—K1 ⁱ	96.89 (17)	N2 ^{iv} —K1—K1 ^{vi}	39.54 (13)
C1—N1—K1 ⁱⁱ	105.1 (5)	N1 ^{vi} —K1—K1 ^{vi}	39.22 (12)
K1—N1—K1 ⁱⁱ	103.6 (2)	N1 ⁱⁱ —K1—K1 ^{vi}	80.38 (13)
K1 ⁱ —N1—K1 ⁱⁱ	116.9 (2)	Se2—K1—K1 ^{vi}	94.61 (3)
C2—Se2—Cd1	98.1 (2)	O1—K1—K1 ⁱ	80.45 (13)
C2—Se2—K1	118.2 (2)	N1—K1—K1 ⁱ	43.89 (14)

Cd1—Se2—K1	119.93 (3)	N2 ⁱⁱⁱ —K1—K1 ⁱ	40.48 (14)
N2—C2—Se2	178.1 (7)	N2 ^{iv} —K1—K1 ⁱ	140.46 (13)
C2—N2—K1 ⁱⁱⁱ	152.8 (6)	N1 ^{vi} —K1—K1 ⁱ	140.78 (12)
C2—N2—K1 ^{iv}	105.5 (6)	N1 ⁱⁱ —K1—K1 ⁱ	99.62 (13)
K1 ⁱⁱⁱ —N2—K1 ^{iv}	99.98 (19)	Se2—K1—K1 ⁱ	85.39 (3)
O1—K1—N1	110.08 (18)	K1 ^{vi} —K1—K1 ⁱ	180.00 (9)
O1—K1—N2 ⁱⁱⁱ	80.18 (19)	O1—K1—K1 ⁱⁱ	92.68 (12)
N1—K1—N2 ⁱⁱⁱ	78.66 (19)	N1—K1—K1 ⁱⁱ	40.35 (13)
O1—K1—N2 ^{iv}	94.85 (19)	N2 ⁱⁱⁱ —K1—K1 ⁱⁱ	111.46 (15)
N1—K1—N2 ^{iv}	154.22 (19)	N2 ^{iv} —K1—K1 ⁱⁱ	148.48 (14)
N2 ⁱⁱⁱ —K1—N2 ^{iv}	99.98 (19)	N1 ^{vi} —K1—K1 ⁱⁱ	76.76 (12)
O1—K1—N1 ^{vi}	123.42 (18)	N1 ⁱⁱ —K1—K1 ⁱⁱ	36.10 (12)
N1—K1—N1 ^{vi}	96.89 (17)	Se2—K1—K1 ⁱⁱ	104.44 (5)
N2 ⁱⁱⁱ —K1—N1 ^{vi}	155.49 (19)	K1 ^{vi} —K1—K1 ⁱⁱ	108.99 (4)
N2 ^{iv} —K1—N1 ^{vi}	73.55 (17)	K1 ⁱ —K1—K1 ⁱⁱ	71.01 (4)
O1—K1—N1 ⁱⁱ	75.99 (16)	K1—O1—H1	118.5
N1—K1—N1 ⁱⁱ	76.4 (2)	K1—O1—H2	126.1
N2 ⁱⁱⁱ —K1—N1 ⁱⁱ	136.7 (2)	H1—O1—H2	108.6
N2 ^{iv} —K1—N1 ⁱⁱ	117.42 (19)		

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+1/2, -y+3/2, -z+1$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1, -y+2, -z+1$; (v) $-x+1, y, -z+3/2$; (vi) $x, y+1, z$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H2 \cdots O1 ^{vii}	0.85	1.92	2.760 (6)	167

Symmetry code: (vii) $-x+1/2, y-1/2, -z+1/2$.