



Syntheses and crystal structures of bis(4-methylpyridine- κN)bis(selenocyanato- κN)zinc(II) and *catena*-poly[[bis(4-methylpyridine- κN)-cadmium(II)]-di- μ -selenocyanato- $\kappa^2 N:Se;\kappa^2 Se:N$]

Christian Näther* and Inke Jess

Received 30 January 2023

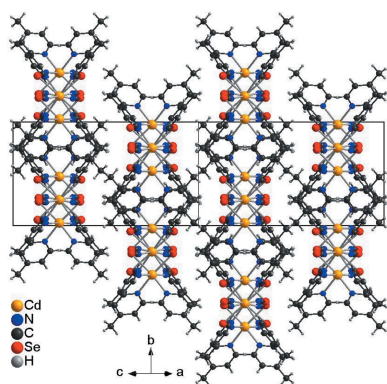
Accepted 1 February 2023

Institut für Anorganische Chemie, Universität Kiel, Max-Eyth Str. 2, 24118 Kiel, Germany. *Correspondence e-mail: cnaether@ac.uni-kiel.de

Edited by W. T. A. Harrison, University of Aberdeen, United Kingdom

Keywords: synthesis; crystal structure; Zn(NCSe)₂; Cd(NCSe)₂; coordination compounds; 4-methylpyridine.**CCDC references:** 2239352; 2239351**Supporting information:** this article has supporting information at journals.iucr.org/e

The reactions of Zn(NO₃)₂·6H₂O and Cd(NO₃)₂·4H₂O with KSeCN and 4-methylpyridine (C₆H₇N; 4-picoline) lead to the formation of crystals of bis(4-methylpyridine- κN)bis(selenocyanato- κN)zinc(II), [Cd(NCSe)₂(C₆H₇N)₂] (**1**), and *catena*-poly[[bis(4-methylpyridine- κN)cadmium(II)]-di- μ -selenocyanato- $\kappa^2 N:Se;\kappa^2 Se:N$], [Cd(NCSe)₂(C₆H₇N)₂]_n (**2**), suitable for single-crystal X-ray diffraction. The asymmetric unit of compound **1** consists of one Zn cation that is located on a twofold rotation axis as well as one selenocyanate anion and one 4-methylpyridine ligand in general positions. The Zn cations are tetrahedrally coordinated by two terminal N-bonding thiocyanate anions and two 4-methylpyridine ligands, forming discrete complexes. The asymmetric unit of compound **2** consists of two crystallographically independent Cd cations, of which one is located on a twofold rotation axis and the second on a center of inversion, as well as two crystallographically independent selenocyanate anions and two crystallographically independent 4-methylpyridine ligands in general positions. The Cd cations are octahedrally coordinated by two N- and two S-bonding selenocyanate anions and two 4-methylpyridine ligands and are linked into chains by pairs of selenocyanate anions. Within the chains, the Cd cations show an alternating *cis-cis-trans* and *all-trans* coordination and therefore, the chains are corrugated. PXRD investigations prove that the Zn compound was obtained as a pure phase and that the Cd compound contains a very small amount of an additional and unknown phase. In the IR spectrum of **1**, the CN stretching vibration of the selenocyanate anion is observed at 2072 cm⁻¹, whereas in the **2** it is shifted to 2094 cm⁻¹, in agreement with the crystal structures.



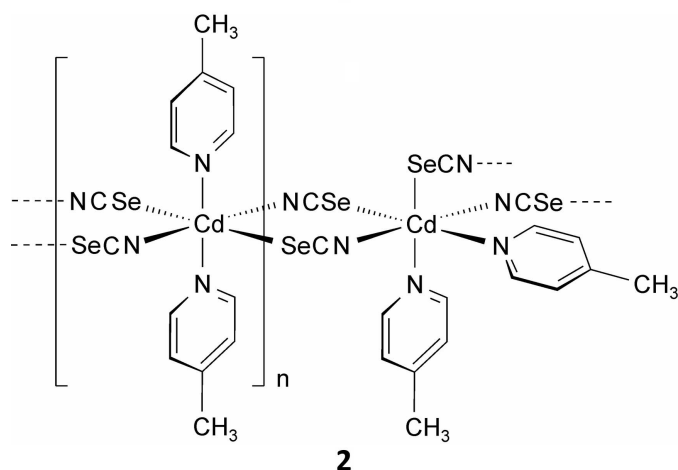
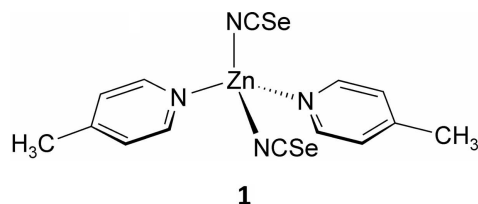
1. Chemical context

Thio- and selenocyanate anions are versatile ligands because of their variable coordination modes (Buckingham, 1994; Barnett *et al.*, 2002; Werner *et al.*, 2015a). The most common mode is the terminal coordination and μ -1,3-bridging mode, where the latter is more pronounced for chalcophilic metal cations, whereas the former dominates for less chalcophilic metal cations. For a given metal thio- or selenocyanate and a given mono-coordinating coligand, usually several compounds with a different ratio between the metal cation and the coligand are observed, for example $M(\text{NCX})_2(L)_4$ and $M(\text{NCX})_2(L)_2$, or in very few cases also $M(\text{NCX})_2(L)$ ($M = +2$ charge transition-metal cation, $X = \text{S, Se}$ and $L =$ neutral mono-coordinating coligand). For compounds with the composition $M(\text{NCX})_2(L)_4$ and octahedrally coordinated metal cations



Published under a CC BY 4.0 licence

most discrete complexes are observed and hundreds of them are reported in the literature. For ligand-deficient compounds with the composition $M(\text{NCS})_2(\text{L})_2$, the octahedral coordination still dominates, but some metal ions such as Co^{2+} can show both octahedral and tetrahedral coordination (Mautner *et al.*, 2018), whereas for Zn^{II} , the tetrahedral coordination is found exclusively.



For simple geometrical considerations, compounds with the composition $M(\text{NCX})_2(\text{L})_2$ and cations that shows an octahedral coordination must contain μ -1,3-bridging thio or selenocyanate anions, and in this case the structural variability is much larger. In practically all cases they consist of $M(\text{NCX})_2$ chains or layers, but compared to chain compounds, layered structures are rare. In most of the layered compounds, the transition-metal cations are linked by single μ -1,3-bridging anionic ligands into layers (Werner *et al.*, 2015b) or two metal cations are connected *via* pairs of anionic ligands into dinuclear units that condense into layers *via* single μ -1,3-bridging anions (Suckert *et al.*, 2016). Moreover, for an octahedral coordination, in principle five different isomers exist, including the all-*trans*, the all-*cis* and three *cis-cis-trans* coordinations. The majority of chain compounds show an all-*trans* coordination in which the metal cations are linked by pairs of anionic ligands, leading to the formation of linear chains (Banerjee *et al.*, 2005; Mautner *et al.*, 2018; Werner *et al.*, 2014; Rams *et al.*, 2020). Linear chains are also observed in compounds where the coligands are still in the *trans*-position, whereas the thiocyanate N and S atoms are in the *cis*-position (Rams *et al.*, 2017; Jochim *et al.*, 2018), but there are very few examples where the coligands are in the *cis*-position, leading to the formation of corrugated chains (Banerjee *et al.*, 2005; Shi, Chen & Liu, 2006; Makhoulouf *et al.*, 2022; Böhme *et al.*, 2020). Corrugated chains are also observed for an all-*cis* coordination, but only very few examples have been reported (Shi, Sun *et al.*, 2006; Zhang *et al.*, 2006; Marsh, 2009).

However, all of the structure types mentioned above are well known for thiocyanate coordination compounds, whereas the structures of selenocyanate compounds are not as well explored and it has not been thoroughly investigated whether compounds with thio- or selenocyanate anions and the same metal:coligand ratio always show the same structures and are, for example, isotopic. This might partly be traced back to the fact that some of the selenocyanate compounds are not very stable and that compounds with bridging anionic ligands are more difficult to prepare if less chalcophilic metal cations are used (Wriedt & Näther, 2010).

To investigate this in more detail, we prepared compounds based on $\text{Zn}(\text{NCSe})_2$ and $\text{Cd}(\text{NCSe})_2$, where the former metal ion prefers a tetrahedral and the latter an octahedral coordination. Cd^{II} is also very chalcophilic, which means that compounds with bridging anionic ligands can easily be prepared. 4-Methylpyridine ($\text{C}_6\text{H}_7\text{N}$) was selected as coligand, for which the corresponding thiocyanate compounds have been reported, whereas compounds with selenocyanate are unknown.

With $\text{Zn}(\text{NCS})_2$, compounds include three discrete complexes with the composition $\text{Zn}(\text{NCS})_2(4\text{-methylpyridine})_4$, in which the Zn cations are octahedrally coordinated by two terminal N-bonded thiocyanate anions and four 4-methylpyridine ligands [Cambridge Structural Database (Groom *et al.*, 2016) refcodes EFESOX and YORHAO (Lipkowski *et al.*, 1994) as well as QQQBUD (Ratho & Patel, 1969)]. Two of them (EFESOX and YORHAO) represent clathrates with additional 4-methylpyridine molecules or 4-methylpyridine and water molecules. There is also one 4-methylpyridine-deficient compound with the composition $\text{Zn}(\text{NCS})_2(4\text{-methylpyridine})_2$, in which the Zn cations are tetrahedrally coordinated by two terminal N-bonded thiocyanate anions and two 4-methylpyridine ligands (refcode VONTEX; Lipkowski, 1990).

With $\text{Cd}(\text{NCS})_2$, a solvate with the composition $\text{Cd}(\text{NCS})_2(4\text{-methylpyridine})_4 \cdot 4\text{-methylpyridine} \cdot \text{water}$ has been reported, in which the Cd cations are octahedrally coordinated by two terminal N-bonded selenocyanate anions and four 4-methylpyridine ligands [refcodes DEXYIO (Dyadin *et al.*, 1984), DEXYIO10, (Pervukhina *et al.*, 1986) and DEXYIO11 (Marsh, 1995)]. More importantly, two compounds with the composition $\text{Cd}(\text{NCS})_2(4\text{-methylpyridine})_2$ are found that represent isomers. In one of these, the Cd cations are octahedrally coordinated by two terminal N- and S-bonded selenocyanate anions and two 4-methylpyridine ligands in an all-*trans* coordination. The Cd cations are linked by pairs of selenocyanate anions into chains, which because of the all-*trans* coordination are linear (FAPCOO02; Neumann *et al.*, 2020). The second isomer was first reported in the triclinic space group $P\bar{1}$ (FAPCOO; Taniguchi *et al.*, 1986) but it was later pointed out that it is better described as monoclinic, in space group $C2/c$ (FAPCOO01; Marsh, 1995). In this compound, the Cd cations are also octahedrally coordinated, linked into chains, but they are corrugated because an alternating all-*trans* and *cis-cis-trans* coordination is observed. The thermodynamic relations were determined

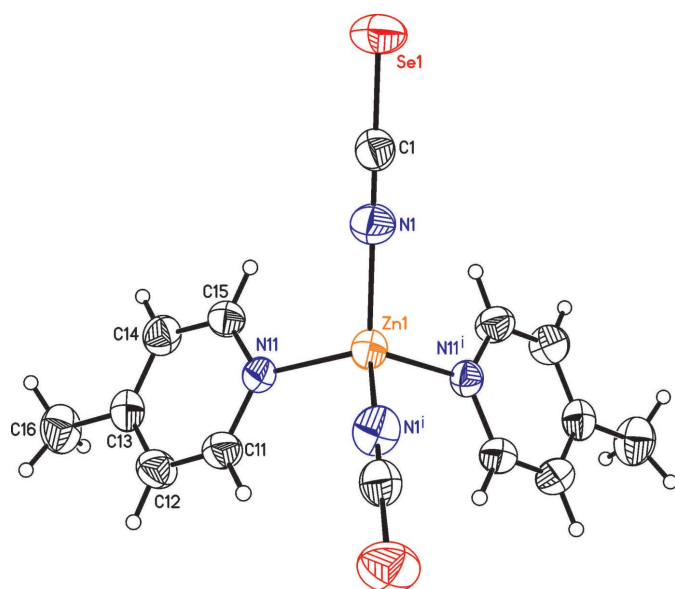
Table 1
 Selected geometric parameters (Å, °) for **1**.

Zn1–N1	1.945 (4)	Zn1–N11	2.021 (3)
N1–Zn1–N1 ⁱ	120.0 (3)	N1–Zn1–N11	106.45 (15)
N1–Zn1–N11 ⁱ	106.61 (15)	N11 ⁱ –Zn1–N11	110.59 (18)

 Symmetry code: (i) $-x, -y + 1, z$.

for both isomers, indicating that they are related by monotropism with the isomer with corrugated chains as the thermodynamically stable phase (Neumann *et al.*, 2020). Finally there is one 4-methylpyridine-deficient compound with the composition $\text{Cd}(\text{NCS})_2(4\text{-methylpyridine})$, in which the Cd cations are linked by pairs of anionic ligands into chains and each two of these chains are condensed into double chains *via* μ -1,1,3-(*S,N,N*)-bridging thiocyanate anions (refcode VUCBUT; Neumann *et al.*, 2020).

To search for new compounds related to those noted above, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were reacted with KSeCN and 4-methylpyridine (4-picoline)₂, which led to the formation of two compounds with the composition $\text{Zn}(\text{NCSe})_2(4\text{-methylpyridine})_2$ (**1**) and $\text{Cd}(\text{NCeS})_2(4\text{-methylpyridine})_2$ (**2**). IR spectroscopic investigations revealed that the CN stretching vibration is located at 2072 cm^{-1} for **1** and at 2094 cm^{-1} for **2**, indicating that compound **1** contains terminally coordinated anionic ligands, whereas in **2** this value is at the borderline between that expected for a terminal and a bridging coordination (Figs. S1 and S2 in the supporting information). For both compounds, single crystals were obtained and characterized by single-crystal X-ray diffraction. Based on the crystallographic data, PXRD patterns were calculated and compared with the experimental pattern, showing that compound **1** was obtained as a pure phase, whereas compound **2** is contaminated with a very small amount of an unknown phase (Figs. S3 and S4). It is noted that


Figure 1
 The molecular structure of **1** with displacement ellipsoids drawn at the 50% probability level. Symmetry code: (i) $-x, -y + 1, z$.

even if $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and KSeCN are used in excess in the synthesis, there are no hints of the formation of a 4-methylpyridine-deficient compound with the composition $\text{Cd}(\text{NCS})_2(4\text{-methylpyridine})$, as observed with $\text{Cd}(\text{NCS})_2$ (Neumann *et al.*, 2020).

2. Structural commentary

The asymmetric unit of compound **1** consists of one selenocyanate anion and one 4-methylpyridine ligand in general positions, as well as one Zn^{II} cation that is located on a twofold rotation axis (Fig. 1). The Zn cations are tetrahedrally coordinated by two symmetry-related terminal N-bonded selenocyanate anions and two symmetry-related 4-methylpyridine ligands (Fig. 1). The tetrahedra are slightly distorted with the $\text{N}_s\text{--Zn--N}_s$ (s = selenocyanate) angle as the largest (Table 1). It is noted that compound **1** is isotopic to $\text{Zn}(\text{NCS})_2(4\text{-methylpyridine})_2$ reported by Lipkowski (1990).

The asymmetric unit of compound **2** consists of two crystallographically independent Cd cations, of which Cd1 is located on a twofold rotation axis whereas Cd2 is located on a center of inversion, as well as two crystallographically independent selenocyanate anions and two crystallographically independent 4-methylpyridine ligands (Fig. 2). Both Cd cations are octahedrally coordinated by two N- and two S-bonding selenocyanate anions and two 4-methylpyridine ligands but Cd1 is in a *cis-cis-trans* coordination with the pyridine N atoms of the 4-methylpyridine ligand in the *cis* position, whereas Cd2 is in an *all-trans* coordination (Fig. 2). Both octahedra are slightly distorted but Cd1 is more distorted than Cd2 (Table 2). The Cd cations are linked by pairs of selenocyanate anions into chains that show an alternating *cis-cis-trans* and *all-trans* coordination. Because of the former, these chains are corrugated (Fig. 3).

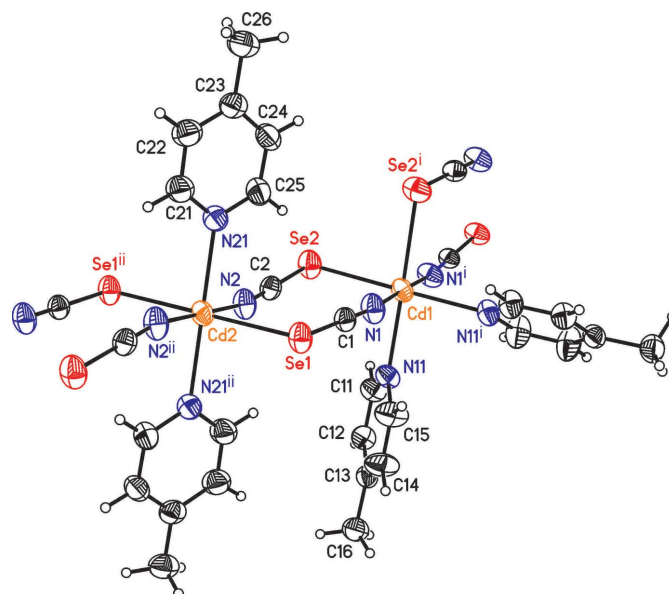

Figure 2
 The coordination spheres of the two Cd cations in **2** with displacement ellipsoids drawn at the 50% probability level. Symmetry codes: (i) $-x + 1, y, -z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + 1$.

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

Cd1—N1	2.338 (3)	Cd2—N2	2.328 (4)
Cd1—N11	2.362 (4)	Cd2—N21	2.370 (4)
Cd1—Se2	2.8085 (6)	Cd2—Se1	2.8073 (5)
N1 ⁱ —Cd1—N1	178.5 (2)	N2 ⁱⁱ —Cd2—N2	180.0
N1—Cd1—N11 ⁱ	92.29 (13)	N2—Cd2—N21 ⁱⁱ	90.70 (14)
N1—Cd1—N11	86.63 (14)	N2—Cd2—N21	89.30 (14)
N11 ⁱ —Cd1—N11	87.53 (18)	N21 ⁱⁱ —Cd2—N21	180.0
N1 ⁱ —Cd1—Se2	82.62 (11)	N2—Cd2—Se1 ⁱⁱ	84.99 (10)
N1—Cd1—Se2	98.42 (10)	N21—Cd2—Se1 ⁱⁱ	89.86 (9)
N11 ⁱ —Cd1—Se2	169.06 (8)	N2—Cd2—Se1	95.01 (10)
N11—Cd1—Se2	90.90 (9)	N21—Cd2—Se1	90.14 (9)
Se2—Cd1—Se2 ⁱ	92.64 (3)	Se1 ⁱⁱ —Cd2—Se1	180.000 (16)

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

Compound **2** is isotypic to the second isomer of $\text{Cd}(\text{NCS})_2(4\text{-methylpyridine})_2$ that crystallizes in the monoclinic space group $C2/c$ (Marsh, 1995). In this context, it is noted that two modifications are also known for the corresponding Fe compound $\text{Fe}(\text{NCS})_2(4\text{-methylpyridine})_2$ (Neumann *et al.*, 2020), of which form **I** is isotypic to compound **2** and the corrugated chain isomer of $\text{Cd}(\text{NCS})_2(4\text{-methylpyridine})_2$, whereas form **II** of the Fe compound is isotypic to the linear chain isomer. For the Fe isomers, the same thermodynamic relations were found as for the isomers with $\text{Cd}(\text{NCS})_2$ with the corrugated chain isomer as the thermodynamically stable form (Neumann *et al.*, 2020). Moreover, compound **2** is also isotypic to $\text{Cd}(\text{NCS})_2(4\text{-chloropyridine})_2$ reported by Goher *et al.* (2003; refcode EMASIU). This can be traced back to the fact that the van der Waals radii of a methyl

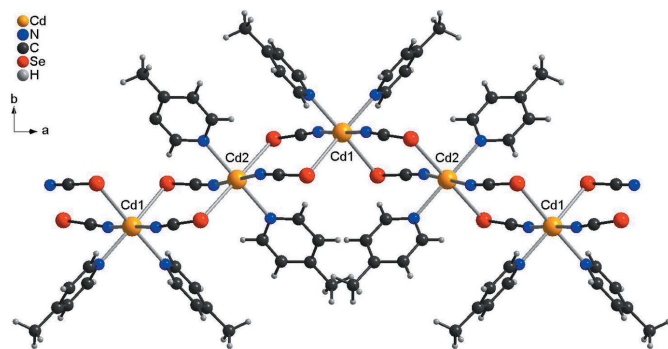


Figure 3
View of part of a chain in the crystal structure of compound **2** showing the alternating *cis-cis-trans* and *all-trans* coordination.

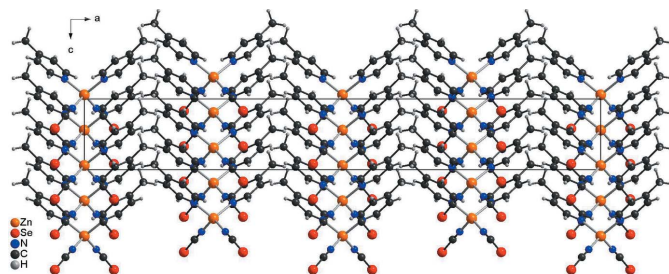


Figure 4
Crystal structure of compound **1** viewed along the *b*-axis direction.

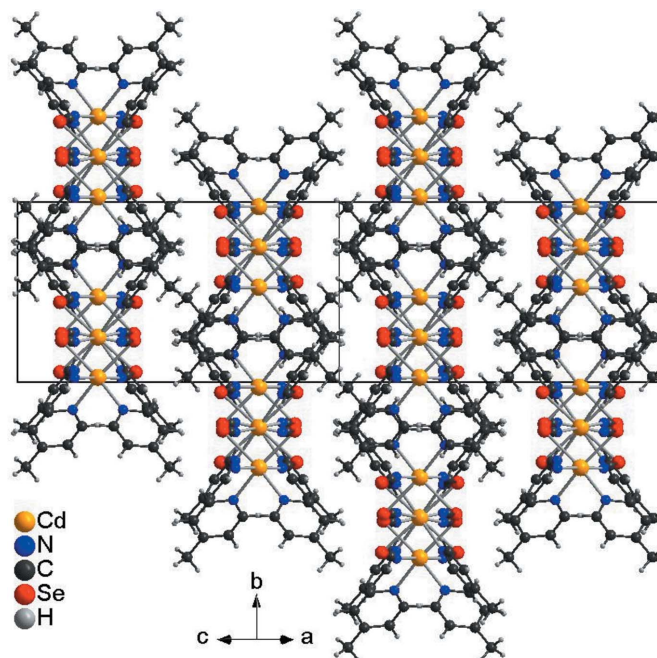


Figure 5
Crystal structure of compound **2** viewed along [101].

group and a chlorine atom are comparable, which is expressed by the so-called chloro–methyl exchange rule (Desiraju & Sarma, 1986 and references cited therein).

Finally, it is noted that some compounds with the general composition $\text{Cd}(\text{NCSe})_2(L)_2$ with L as a monocoordinating coligand are reported, in which the Cd cations are linked by pairs of anionic ligands into chains, but the majority of compounds show an *all-trans* coordination and the formation of linear chains. An overview is given in the database survey.

3. Supramolecular features

In the crystal structure of compound **1**, the discrete complexes are arranged into columns that propagate along the *c*-axis direction (Fig. 4). Within these columns, the selenocyanate anions and the 4-methylpyridine ligands always point in the same direction, from which the non-centrosymmetric arrangement is visible (Fig. 4). There are no directional intermolecular interactions between the complexes and nor is there any indication of π – π interactions.

In compound **2**, the chains are closely packed and propagate along the [101] direction (Fig. 5). As in compound **1**, no pronounced intermolecular interactions are observed.

4. Database survey

According to a search in the Cambridge Structural Database (CSD Version 5.43, March 2022; Groom *et al.*, 2016), no selenocyanate coordination compounds with 4-methylpyridine as anionic ligand have been reported but many compounds with the thiocyanate as anion can be found. Those with $\text{Zn}(\text{NCS})_2$ and $\text{Cd}(\text{NCS})_2$ were already mentioned in the *Chemical context* section (see above).

Table 3
Experimental details.

	1	2
Crystal data		
Chemical formula	[Zn(NCSe) ₂ (C ₆ H ₇ N) ₂]	[Cd(NCSe) ₂ (C ₆ H ₇ N) ₂]
<i>M_r</i>	461.58	508.61
Crystal system, space group	Orthorhombic, <i>Fdd2</i>	Monoclinic, <i>C2/c</i>
Temperature (K)	293	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	37.3964 (18), 18.4780 (7), 5.1164 (2)	20.7296 (11), 9.4896 (3), 19.7364 (10)
α , β , γ (°)	90, 90, 90	90, 113.794 (3), 90
<i>V</i> (Å ³)	3535.5 (3)	3552.5 (3)
<i>Z</i>	8	8
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	5.51	5.33
Crystal size (mm)	0.25 × 0.20 × 0.20	0.18 × 0.14 × 0.10
Data collection		
Diffractometer	Stoe IPDS2	Stoe IPDS2
Absorption correction	Numerical (<i>X-RED</i> and <i>X-SHAPE</i> ; Stoe, 2008)	Numerical (<i>X-RED</i> and <i>X-SHAPE</i> ; Stoe, 2008)
<i>T_{min}</i> , <i>T_{max}</i>	0.305, 0.547	0.321, 0.446
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	14188, 1953, 1823	17056, 3469, 2911
<i>R_{int}</i>	0.027	0.038
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.649	0.617
Refinement		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.029, 0.067, 1.13	0.039, 0.076, 1.13
No. of reflections	1953	3469
No. of parameters	97	194
No. of restraints	1	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.26, -0.22	0.74, -0.63
Absolute structure	Flack <i>x</i> determined using 675 quotients [[<i>I</i> ⁺)-(<i>I</i> ⁻)]/[<i>I</i> ⁺ +(<i>I</i> ⁻)] (Parsons et al., 2013)	-
Absolute structure parameter	0.012 (8)	-

Computer programs: *X-AREA* (Stoe, 2008), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2016/6* (Sheldrick, 2015b), *DIAMOND* (Brandenburg & Putz, 1999) and *pubCIF* (Westrip, 2010).

It is also noted that several Cd(NCSe)₂ chain compounds are reported in the CSD, but in all of them the Cd cations show an all-*trans* coordination and are linked into linear chains [BIWTOR (Fettouhi *et al.*, 2008), DAYWAE (Sadhu *et al.*, 2017), DOJBK (Choudhury *et al.*, 2008), FAPGAG (Jess *et al.*, 2012), FIMJIW (Werner *et al.*, 2013), NAQXIO (Boeckmann, Jess *et al.*, 2011), OLOZAO (Li & Liu, 2003), OWOHOY (Boeckmann, Reinert & Näther, 2011), QIPYAP (Secondo *et al.*, 2000) and ZANQAI (Werner *et al.*, 2012)].

However, in this context it is noted that some selenocyanate compounds with pyridine as coligand are found, of which those with the composition *M*(NCSe)₂(pyridine)₂ (*M* = Zn, Co, Ni, Cd) are of the most interest. The Zn compound crystallizes as discrete complexes with a tetrahedral coordination (OWOJEQ; Boeckmann, Reinert & Näther, 2011), whereas the compounds with Fe^{II}, Co^{II} and Cd^{II} crystallize as linear chains with an all-*trans* coordination [CAQVIB (Boeckmann *et al.*, 2012), ITISUA (Boeckmann & Näther, 2011)].

5. Synthesis and crystallization

Synthesis

Zn(NO₃)₂·6H₂O and Cd(NO₃)₂·4H₂O were purchased from Sigma Aldrich and KSeCN was purchased from Alfa Aesar. All chemicals were used without any further purification.

Synthesis of compound 1.

0.5 mmol (143 mg) of Zn(NO₃)₂·6H₂O and 1 mmol (144 mg) of KSeCN were reacted with 1 mmol (97.2 μ l) of 4-methylpyridine in 2 ml of ethanol. The reaction mixture was stirred for 2 d and the colorless precipitate was filtered off, washed with a very small amount of ethanol and dried at room temperature. Single crystals were obtained from the filtrate by slow evaporation of the solvent.

Synthesis of compound 2.

0.5 mmol (154 mg) of Cd(NO₃)₂·4H₂O and 1 mmol (144 mg) of KSeCN were reacted with 1 mmol (97.2 μ l) of 4-methylpyridine in 2 ml of ethanol. The reaction mixture was stirred for 2 d and the colorless precipitate was filtered off, washed with a very small amount of ethanol and dried at room temperature. Single crystals were obtained from the filtrate by slow evaporation of the solvent.

Experimental details

The XRPD measurements were performed with a Stoe Transmission Powder Diffraction System (STADI P) equipped with a MYTHEN 1K detector and a Johansson-type Ge(111) monochromator using Cu *K* α ₁ radiation (λ = 1.540598 Å).

The IR spectra were measured using an ATI Mattson Genesis Series FTIR Spectrometer, control software: WINFIRST, from ATI Mattson.

Thermogravimetry and differential thermoanalysis (TG-DTA) measurements were performed in a dynamic nitrogen

atmosphere in Al₂O₃ crucibles using a STA-PT 1000 thermobalance from Linseis. The instrument was calibrated using standard reference materials.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. C-bound H atoms were positioned with idealized geometry (C–H = 0.93–0.96 Å; methyl H atoms allowed to rotate but not to tip) and were refined isotropically with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ (1.5 for methyl H atoms) using a riding model.

Acknowledgements

This work was supported by the state of Schleswig-Holstein.

References

- Banerjee, S., Wu, B., Lassahn, P. G., Janiak, C. & Ghosh, A. (2005). *Inorg. Chim. Acta*, **358**, 535–544.
- Barnett, S. A., Blake, A. J., Champness, N. R. & Wilson, C. (2002). *Chem. Commun.* pp. 1640–1641.
- Boeckmann, J., Jess, I., Reinert, T. & Näther, C. (2011). *Eur. J. Inorg. Chem.* pp. 5502–5511.
- Boeckmann, J. & Näther, C. (2011). *Chem. Commun.* **47**, 7104–7106.
- Boeckmann, J., Reinert, T. & Näther, C. (2011). *Z. Anorg. Allg. Chem.* **637**, 940–946.
- Boeckmann, J., Wriedt, M. & Näther, C. (2012). *Chem. Eur. J.* **18**, 5284–5289.
- Böhme, M., Jochim, A., Rams, M., Lohmiller, T., Suckert, S., Schnegg, A., Plass, W. & Näther, C. (2020). *Inorg. Chem.* **59**, 5325–5338.
- Brandenburg, K. & Putz, H. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Buckingham, D. A. (1994). *Coord. Chem. Rev.* **135–136**, 587–621.
- Choudhury, R. R., Choudhury, C. R., Batten, S. R. & Mitra, S. (2008). *Struct. Chem.* **19**, 645–649.
- Desiraju, G. R. & Sarma, J. A. R. P. (1986). *Proc. Indian Acad. Sci. Chem. Sci.* **96**, 599–605.
- Dyadin, Yu. A., Kislykh, N. V., Chekhova, G. N., Podberezskaya, N. V., Pervukhina, N. V., Logvinenko, V. A. & Oglezneva, I. M. J. (1984). *J. Inclusion Phenom. Mol. Recognit. Chem.* **2**, 233–240.
- Fettouhi, M., Wazeer, M. I. M. & Isab, A. A. (2008). *Inorg. Chem. Commun.* **11**, 252–255.
- Goher, A. S., Mautner, F. A., Abu-Youssef, M. A. M., Hafez, A. K., Badr, A. M. A. & Gspan, C. (2003). *Polyhedron*, **22**, 3137–3143.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Jess, I., Boeckmann, J. & Näther, C. (2012). *Dalton Trans.* **41**, 228–236.
- Jochim, A., Rams, M., Neumann, T., Wellm, C., Reinsch, H., Wójtowicz, G. M. & Näther, C. (2018). *Eur. J. Inorg. Chem.* pp. 4779–4789.
- Li, D. & Liu, D. (2003). *Appl. Organomet. Chem.* **17**, 321–322.
- Lipkowski, J. (1990). *J. Coord. Chem.* **22**, 153–158.
- Lipkowski, J., Soldatov, D. V., Kislykh, N. V., Pervukhina, N. V. & Dyadin, Y. A. (1994). *J. Inclusion Phenom. Mol. Recognit. Chem.* **17**, 305–316.
- Makhlouf, J., Valkonen, A. & Smirani, W. (2022). *Polyhedron*, **213**, 115625.
- Marsh, R. E. (1995). *Acta Cryst.* **B51**, 897–907.
- Marsh, R. E. (2009). *Acta Cryst.* **B65**, 782–783.
- Mautner, F. A., Traber, M., Fischer, R. C., Torvisco, A., Reichmann, K., Speed, S., Vicente, R. & Massoud, S. S. (2018). *Polyhedron*, **154**, 436–442.
- Neumann, T., Gallo, G., Jess, I., Dinnebier, R. E. & Näther, C. (2020). *CrystEngComm*, **22**, 184–194.
- Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* **B69**, 249–259.
- Pervukhina, N. V., Podberezskaya, N. V., Bakakin, V. V., Kislikh, N. V., Chekhova, G. N. & Dyadin, Yu. A. (1986). *J. Struct. Chem.* **26**, 934–941.
- Rams, M., Jochim, A., Böhme, M., Lohmiller, T., Ceglarska, M., Rams, M. M., Schnegg, A., Plass, W. & Näther, C. (2020). *Chem. Eur. J.* **26**, 2837–2851.
- Rams, M., Tomkowicz, Z., Böhme, M., Plass, W., Suckert, S., Werner, J., Jess, I. & Näther, C. (2017). *Phys. Chem. Chem. Phys.* **19**, 3232–3243.
- Ratho, T. & Patel, T. (1969). *Indian J. Phys.* **43**, 166–169.
- Sadhu, M. H., Solanki, A., Kundu, T., Hingu, V., Ganguly, B. & Kumar, S. B. (2017). *Polyhedron*, **133**, 8–15.
- Secondo, P. M., Land, J. M., Baughman, R. G. & Collier, H. L. (2000). *Inorg. Chim. Acta*, **309**, 13–22.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **C71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **A71**, 3–8.
- Shi, J. M., Chen, J. N. & Liu, L. D. (2006). *Pol. J. Chem.* **80**, 1909–1912.
- Shi, J. M., Sun, Y. M., Liu, Z. & Liu, L. D. (2006). *Chem. Phys. Lett.* **418**, 84–89.
- Stoe (2008). *X-Area, X-RED32 and X-SHAPE*. Stoe & Cie, Darmstadt, Germany.
- Suckert, S., Rams, M., Böhme, M., Germann, L. S., Dinnebier, R. E., Plass, W., Werner, J. & Näther, C. (2016). *Dalton Trans.* **45**, 18190–18201.
- Taniguchi, M., Shimoi, M. & Ouchi, A. (1986). *Bull. Chem. Soc. Jpn*, **59**, 2299–2302.
- Werner, J., Boeckmann, J., Jess, I. & Näther, C. (2012). *Acta Cryst.* **E68**, m704.
- Werner, J., Jess, I. & Näther, C. (2013). *Z. Naturforsch. Teil B*, **68**, 643–652.
- Werner, J., Rams, M., Tomkowicz, Z. & Näther, C. (2014). *Dalton Trans.* **43**, 17333–17342.
- Werner, J., Runčevski, T., Dinnebier, R., Ebbinghaus, S. G., Suckert, S. & Näther, C. (2015a). *Eur. J. Inorg. Chem.* **2015**, 3236–3245.
- Werner, J., Tomkowicz, Z., Reinert, T. & Näther, C. (2015b). *Eur. J. Inorg. Chem.* **2015**, 3066–3075.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Wriedt, M. & Näther, C. (2010). *Chem. Commun.* **46**, 4707–4709.
- Zhang, S.-G., Li, W.-N. & Shi, J.-M. (2006). *Acta Cryst.* **E62**, m3506–m3608.

supporting information

Acta Cryst. (2023). E79, 136-141 [https://doi.org/10.1107/S2056989023000920]

Syntheses and crystal structures of bis(4-methylpyridine- κN)bis(selenocyanato- κN)zinc(II) and *catena*-poly[[bis(4-methylpyridine- κN)cadmium(II)]-di- μ -selenocyanato- $\kappa^2 N:Se;\kappa^2 Se:N$]

Christian Näther and Inke Jess

Computing details

For both structures, data collection: *X-AREA* (Stoe, 2008); cell refinement: *X-AREA* (Stoe, 2008); data reduction: *X-AREA* (Stoe, 2008); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2016/6* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg & Putz, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Bis(4-methylpyridine- κN)bis(selenocyanato- κN)zinc(II) (I)

Crystal data

[Zn(NCSe)₂(C₆H₇N)₂]

$M_r = 461.58$

Orthorhombic, *Fdd2*

$a = 37.3964$ (18) Å

$b = 18.4780$ (7) Å

$c = 5.1164$ (2) Å

$V = 3535.5$ (3) Å³

$Z = 8$

$F(000) = 1792$

$D_x = 1.734$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 14188 reflections

$\theta = 2.2\text{--}27.5^\circ$

$\mu = 5.51$ mm⁻¹

$T = 293$ K

Block, colorless

0.25 × 0.20 × 0.20 mm

Data collection

STOE IPDS-2

diffractometer

ω scans

Absorption correction: numerical

(X-Red and X-Shape; Stoe, 2008)

$T_{\min} = 0.305$, $T_{\max} = 0.547$

14188 measured reflections

1953 independent reflections

1823 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.2^\circ$

$h = -48 \rightarrow 48$

$k = -23 \rightarrow 23$

$l = -6 \rightarrow 5$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.067$

$S = 1.13$

1953 reflections

97 parameters

1 restraint

Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0306P)^2 + 2.9003P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.26$ e Å⁻³

$\Delta\rho_{\min} = -0.22$ e Å⁻³

Absolute structure: Flack x determined using
675 quotients $[(F^+)-(F^-)]/[(F^+)+(F^-)]$ (Parsons et al.,
2013)
Absolute structure parameter: 0.012 (8)

Special details

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

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Zn1	0.000000	0.500000	0.44116 (13)	0.05955 (17)
Se1	0.05719 (2)	0.30585 (3)	0.91932 (12)	0.1023 (2)
N11	0.03820 (7)	0.54594 (16)	0.2162 (7)	0.0548 (7)
C11	0.03560 (12)	0.6142 (2)	0.1324 (10)	0.0702 (12)
H11	0.016846	0.642476	0.193939	0.084*
C1	0.03662 (12)	0.3754 (3)	0.7402 (9)	0.0681 (11)
N1	0.02308 (11)	0.4217 (2)	0.6310 (9)	0.0806 (11)
C15	0.06600 (11)	0.5073 (2)	0.1294 (9)	0.0651 (10)
H15	0.068456	0.459745	0.185725	0.078*
C12	0.05934 (12)	0.6443 (2)	-0.0402 (10)	0.0748 (12)
H12	0.056342	0.691924	-0.095090	0.090*
C16	0.11412 (15)	0.6356 (4)	-0.3232 (15)	0.0985 (16)
H16A	0.115697	0.686987	-0.298495	0.148*
H16B	0.106438	0.625496	-0.498454	0.148*
H16C	0.137157	0.614117	-0.294057	0.148*
C14	0.09088 (11)	0.5347 (2)	-0.0380 (11)	0.0734 (11)
H14	0.110202	0.506325	-0.089267	0.088*
C13	0.08745 (11)	0.6043 (3)	-0.1317 (9)	0.0670 (11)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0556 (3)	0.0672 (3)	0.0558 (3)	-0.0044 (3)	0.000	0.000
Se1	0.1184 (4)	0.0790 (3)	0.1095 (5)	0.0235 (3)	-0.0162 (4)	0.0132 (4)
N11	0.0497 (14)	0.0573 (16)	0.0573 (19)	-0.0027 (12)	-0.0047 (14)	0.0011 (15)
C11	0.065 (2)	0.064 (2)	0.081 (3)	0.0077 (18)	0.007 (2)	0.006 (2)
C1	0.069 (2)	0.073 (3)	0.063 (3)	-0.007 (2)	-0.002 (2)	0.002 (2)
N1	0.081 (2)	0.088 (3)	0.073 (3)	0.002 (2)	-0.007 (2)	0.017 (2)
C15	0.063 (2)	0.0566 (19)	0.076 (3)	0.0029 (16)	0.0013 (19)	-0.001 (2)
C12	0.080 (3)	0.069 (2)	0.075 (3)	-0.001 (2)	0.008 (3)	0.013 (2)
C16	0.090 (3)	0.120 (4)	0.085 (3)	-0.019 (3)	0.021 (3)	0.015 (4)
C14	0.063 (2)	0.076 (3)	0.081 (3)	0.0048 (18)	0.011 (2)	-0.007 (3)
C13	0.064 (2)	0.079 (3)	0.057 (3)	-0.014 (2)	0.0001 (18)	-0.0001 (19)

Geometric parameters (\AA , $^\circ$)

Zn1—N1	1.945 (4)	C15—C14	1.362 (7)
Zn1—N1 ⁱ	1.945 (4)	C15—H15	0.9300
Zn1—N11 ⁱ	2.021 (3)	C12—C13	1.368 (6)
Zn1—N11	2.021 (3)	C12—H12	0.9300
Se1—C1	1.756 (5)	C16—C13	1.513 (7)
N11—C11	1.335 (5)	C16—H16A	0.9600
N11—C15	1.337 (5)	C16—H16B	0.9600
C11—C12	1.371 (6)	C16—H16C	0.9600
C11—H11	0.9300	C14—C13	1.379 (6)
C1—N1	1.140 (5)	C14—H14	0.9300
N1—Zn1—N1 ⁱ	120.0 (3)	C14—C15—H15	118.6
N1—Zn1—N11 ⁱ	106.61 (15)	C13—C12—C11	119.9 (4)
N1 ⁱ —Zn1—N11 ⁱ	106.44 (15)	C13—C12—H12	120.1
N1—Zn1—N11	106.45 (15)	C11—C12—H12	120.1
N1 ⁱ —Zn1—N11	106.61 (15)	C13—C16—H16A	109.5
N11 ⁱ —Zn1—N11	110.59 (18)	C13—C16—H16B	109.5
C11—N11—C15	117.0 (4)	H16A—C16—H16B	109.5
C11—N11—Zn1	121.9 (3)	C13—C16—H16C	109.5
C15—N11—Zn1	121.0 (3)	H16A—C16—H16C	109.5
N11—C11—C12	122.9 (4)	H16B—C16—H16C	109.5
N11—C11—H11	118.5	C15—C14—C13	120.1 (4)
C12—C11—H11	118.5	C15—C14—H14	120.0
N1—C1—Se1	177.9 (4)	C13—C14—H14	120.0
C1—N1—Zn1	179.3 (4)	C12—C13—C14	117.2 (4)
N11—C15—C14	122.9 (4)	C12—C13—C16	121.4 (4)
N11—C15—H15	118.6	C14—C13—C16	121.3 (5)

Symmetry code: (i) $-x, -y+1, z$.**catena-Poly[[bis(4-methylpyridine- κ N)cadmium(II)]-di- μ -selenocyanato- κ^2 N:Se; κ^2 Se:N] (II)***Crystal data*[Cd(NCSe)₂(C₆H₇N)₂] $M_r = 508.61$ Monoclinic, $C2/c$ $a = 20.7296$ (11) \AA $b = 9.4896$ (3) \AA $c = 19.7364$ (10) \AA $\beta = 113.794$ (3) $^\circ$ $V = 3552.5$ (3) \AA^3 $Z = 8$ $F(000) = 1936$ $D_x = 1.902$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA

Cell parameters from 17056 reflections

 $\theta = 2.2\text{--}26.0^\circ$ $\mu = 5.33$ mm⁻¹ $T = 293$ K

Block, colorless

0.18 \times 0.14 \times 0.10 mm*Data collection*

STOE IPDS-2

diffractometer

 ω scans

Absorption correction: numerical

(X-Red and X-Shape; Stoe, 2008)

 $T_{\min} = 0.321, T_{\max} = 0.446$

17056 measured reflections

3469 independent reflections

2911 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.038$

$\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 2.2^\circ$
 $h = -25 \rightarrow 25$

$k = -8 \rightarrow 11$
 $l = -24 \rightarrow 24$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.076$
 $S = 1.13$
 3469 reflections
 194 parameters
 0 restraints
 Primary atom site location: dual

Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0229P)^2 + 7.6388P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.74 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.63 \text{ e } \text{\AA}^{-3}$

Special details

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cd1	0.500000	0.47303 (5)	0.250000	0.05827 (14)
Cd2	0.750000	0.250000	0.500000	0.05746 (13)
N1	0.5569 (2)	0.4762 (5)	0.37921 (19)	0.0724 (11)
C1	0.5986 (2)	0.4628 (4)	0.4381 (2)	0.0539 (10)
Se1	0.66318 (2)	0.44348 (6)	0.53116 (2)	0.06746 (15)
N2	0.6944 (2)	0.2763 (5)	0.3720 (2)	0.0715 (11)
C2	0.6512 (2)	0.2729 (5)	0.3135 (2)	0.0582 (10)
Se2	0.58388 (3)	0.26863 (6)	0.22157 (3)	0.07812 (18)
N11	0.57906 (18)	0.6528 (4)	0.2507 (2)	0.0640 (9)
C11	0.6021 (2)	0.6648 (5)	0.1971 (2)	0.0700 (12)
H11	0.585089	0.601802	0.157671	0.084*
C12	0.6496 (3)	0.7651 (5)	0.1968 (3)	0.0679 (12)
H12	0.663234	0.769834	0.157369	0.081*
C13	0.6773 (2)	0.8592 (5)	0.2548 (3)	0.0629 (11)
C14	0.6536 (3)	0.8466 (6)	0.3102 (3)	0.0938 (18)
H14	0.670037	0.907735	0.350437	0.113*
C15	0.6059 (3)	0.7438 (6)	0.3062 (3)	0.0909 (18)
H15	0.591248	0.737234	0.344883	0.109*
C16	0.7307 (3)	0.9687 (6)	0.2579 (3)	0.0824 (15)
H16A	0.776309	0.925625	0.273302	0.124*
H16B	0.732202	1.040818	0.292621	0.124*
H16C	0.717741	1.009812	0.209722	0.124*
N21	0.67039 (19)	0.0657 (4)	0.4930 (2)	0.0641 (9)
C21	0.6897 (3)	-0.0359 (6)	0.5440 (3)	0.0803 (15)
H21	0.736013	-0.036657	0.578951	0.096*
C22	0.6451 (3)	-0.1392 (6)	0.5477 (3)	0.0844 (15)
H22	0.661708	-0.207526	0.584525	0.101*

C23	0.5759 (3)	-0.1424 (5)	0.4974 (3)	0.0708 (13)
C24	0.5563 (3)	-0.0392 (6)	0.4441 (3)	0.0744 (13)
H24	0.510543	-0.037549	0.407877	0.089*
C25	0.6039 (3)	0.0619 (6)	0.4438 (3)	0.0736 (13)
H25	0.588663	0.130929	0.407229	0.088*
C26	0.5257 (3)	-0.2518 (6)	0.5017 (4)	0.0890 (17)
H26A	0.479146	-0.212412	0.484738	0.133*
H26B	0.540300	-0.282538	0.552103	0.133*
H26C	0.525360	-0.330752	0.471169	0.133*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.0473 (2)	0.0720 (3)	0.0452 (2)	0.000	0.00794 (18)	0.000
Cd2	0.0497 (2)	0.0680 (3)	0.0476 (2)	0.0026 (2)	0.01232 (19)	0.00515 (19)
N1	0.061 (2)	0.095 (3)	0.045 (2)	0.012 (2)	0.0049 (17)	-0.0056 (19)
C1	0.051 (2)	0.058 (3)	0.052 (2)	0.0048 (18)	0.021 (2)	-0.0023 (18)
Se1	0.0620 (3)	0.0856 (4)	0.0431 (2)	0.0160 (2)	0.0091 (2)	-0.0016 (2)
N2	0.068 (2)	0.097 (3)	0.044 (2)	0.018 (2)	0.0162 (18)	0.0062 (19)
C2	0.062 (3)	0.059 (3)	0.055 (2)	0.008 (2)	0.025 (2)	0.0001 (19)
Se2	0.0686 (3)	0.0937 (4)	0.0547 (3)	0.0124 (3)	0.0068 (2)	-0.0188 (2)
N11	0.056 (2)	0.078 (3)	0.059 (2)	-0.0090 (19)	0.0253 (17)	-0.0172 (19)
C11	0.070 (3)	0.083 (3)	0.056 (2)	-0.013 (3)	0.024 (2)	-0.019 (2)
C12	0.071 (3)	0.077 (3)	0.061 (3)	-0.003 (2)	0.033 (2)	-0.010 (2)
C13	0.054 (2)	0.065 (3)	0.070 (3)	-0.001 (2)	0.025 (2)	-0.012 (2)
C14	0.113 (4)	0.100 (4)	0.084 (4)	-0.043 (4)	0.057 (3)	-0.045 (3)
C15	0.110 (4)	0.102 (4)	0.084 (4)	-0.035 (4)	0.063 (3)	-0.039 (3)
C16	0.077 (3)	0.081 (4)	0.096 (4)	-0.012 (3)	0.042 (3)	-0.018 (3)
N21	0.061 (2)	0.069 (2)	0.062 (2)	0.0001 (19)	0.0245 (18)	0.0037 (19)
C21	0.073 (3)	0.079 (4)	0.073 (3)	-0.007 (3)	0.014 (3)	0.007 (3)
C22	0.088 (4)	0.074 (3)	0.082 (3)	-0.009 (3)	0.025 (3)	0.006 (3)
C23	0.076 (3)	0.064 (3)	0.082 (3)	-0.006 (3)	0.042 (3)	-0.019 (3)
C24	0.054 (3)	0.082 (4)	0.083 (3)	-0.005 (2)	0.023 (2)	-0.014 (3)
C25	0.060 (3)	0.082 (3)	0.074 (3)	0.004 (3)	0.022 (2)	0.003 (3)
C26	0.089 (4)	0.080 (4)	0.114 (5)	-0.018 (3)	0.058 (4)	-0.022 (3)

Geometric parameters (Å, °)

Cd1—N1 ⁱ	2.338 (3)	C13—C14	1.373 (6)
Cd1—N1	2.338 (3)	C13—C16	1.501 (7)
Cd1—N11 ⁱ	2.362 (4)	C14—C15	1.370 (7)
Cd1—N11	2.362 (4)	C14—H14	0.9300
Cd1—Se2	2.8085 (6)	C15—H15	0.9300
Cd1—Se2 ⁱ	2.8086 (6)	C16—H16A	0.9600
Cd2—N2 ⁱⁱ	2.328 (4)	C16—H16B	0.9600
Cd2—N2	2.328 (4)	C16—H16C	0.9600
Cd2—N21 ⁱⁱ	2.370 (4)	N21—C25	1.329 (6)
Cd2—N21	2.370 (4)	N21—C21	1.332 (6)

Cd2—Se1 ⁱⁱ	2.8073 (5)	C21—C22	1.369 (7)
Cd2—Se1	2.8073 (5)	C21—H21	0.9300
N1—C1	1.142 (5)	C22—C23	1.378 (7)
C1—Se1	1.793 (4)	C22—H22	0.9300
N2—C2	1.141 (5)	C23—C24	1.373 (7)
C2—Se2	1.788 (5)	C23—C26	1.497 (7)
N11—C15	1.329 (6)	C24—C25	1.377 (7)
N11—C11	1.329 (5)	C24—H24	0.9300
C11—C12	1.372 (6)	C25—H25	0.9300
C11—H11	0.9300	C26—H26A	0.9600
C12—C13	1.381 (6)	C26—H26B	0.9600
C12—H12	0.9300	C26—H26C	0.9600
N1 ⁱ —Cd1—N1	178.5 (2)	C11—C12—C13	120.3 (4)
N1 ⁱ —Cd1—N11 ⁱ	86.63 (14)	C11—C12—H12	119.8
N1—Cd1—N11 ⁱ	92.29 (13)	C13—C12—H12	119.8
N1 ⁱ —Cd1—N11	92.30 (13)	C14—C13—C12	116.2 (4)
N1—Cd1—N11	86.63 (14)	C14—C13—C16	121.5 (4)
N11 ⁱ —Cd1—N11	87.53 (18)	C12—C13—C16	122.3 (4)
N1 ⁱ —Cd1—Se2	82.62 (11)	C15—C14—C13	119.9 (5)
N1—Cd1—Se2	98.42 (10)	C15—C14—H14	120.0
N11 ⁱ —Cd1—Se2	169.06 (8)	C13—C14—H14	120.0
N11—Cd1—Se2	90.90 (9)	N11—C15—C14	124.2 (5)
N1 ⁱ —Cd1—Se2 ⁱ	98.42 (10)	N11—C15—H15	117.9
N1—Cd1—Se2 ⁱ	82.62 (11)	C14—C15—H15	117.9
N11 ⁱ —Cd1—Se2 ⁱ	90.90 (9)	C13—C16—H16A	109.5
N11—Cd1—Se2 ⁱ	169.06 (8)	C13—C16—H16B	109.5
Se2—Cd1—Se2 ⁱ	92.64 (3)	H16A—C16—H16B	109.5
N2 ⁱⁱ —Cd2—N2	180.0	C13—C16—H16C	109.5
N2 ⁱⁱ —Cd2—N21 ⁱⁱ	89.30 (14)	H16A—C16—H16C	109.5
N2—Cd2—N21 ⁱⁱ	90.70 (14)	H16B—C16—H16C	109.5
N2 ⁱⁱ —Cd2—N21	90.70 (14)	C25—N21—C21	116.0 (4)
N2—Cd2—N21	89.30 (14)	C25—N21—Cd2	123.7 (3)
N21 ⁱⁱ —Cd2—N21	180.0	C21—N21—Cd2	120.0 (3)
N2 ⁱⁱ —Cd2—Se1 ⁱⁱ	95.00 (10)	N21—C21—C22	123.7 (5)
N2—Cd2—Se1 ⁱⁱ	84.99 (10)	N21—C21—H21	118.1
N21 ⁱⁱ —Cd2—Se1 ⁱⁱ	90.14 (9)	C22—C21—H21	118.1
N21—Cd2—Se1 ⁱⁱ	89.86 (9)	C21—C22—C23	120.4 (5)
N2 ⁱⁱ —Cd2—Se1	85.00 (10)	C21—C22—H22	119.8
N2—Cd2—Se1	95.01 (10)	C23—C22—H22	119.8
N21 ⁱⁱ —Cd2—Se1	89.86 (9)	C24—C23—C22	115.8 (5)
N21—Cd2—Se1	90.14 (9)	C24—C23—C26	122.8 (5)
Se1 ⁱⁱ —Cd2—Se1	180.000 (16)	C22—C23—C26	121.4 (5)
C1—N1—Cd1	161.8 (4)	C23—C24—C25	120.7 (5)
N1—C1—Se1	179.0 (4)	C23—C24—H24	119.7
C1—Se1—Cd2	97.03 (13)	C25—C24—H24	119.7
C2—N2—Cd2	159.7 (4)	N21—C25—C24	123.3 (5)
N2—C2—Se2	179.5 (5)	N21—C25—H25	118.4

C2—Se2—Cd1	94.25 (14)	C24—C25—H25	118.4
C15—N11—C11	115.8 (4)	C23—C26—H26A	109.5
C15—N11—Cd1	122.2 (3)	C23—C26—H26B	109.5
C11—N11—Cd1	121.9 (3)	H26A—C26—H26B	109.5
N11—C11—C12	123.5 (4)	C23—C26—H26C	109.5
N11—C11—H11	118.3	H26A—C26—H26C	109.5
C12—C11—H11	118.3	H26B—C26—H26C	109.5

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