

## Zinc cadmium selenocyanate

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## Key indicators

Single-crystal X-ray study

$T = 291$  K

Mean  $\sigma(\text{N}-\text{C}) = 0.009$  Å

$R$  factor = 0.033

$wR$  factor = 0.075

Data-to-parameter ratio = 26.3

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

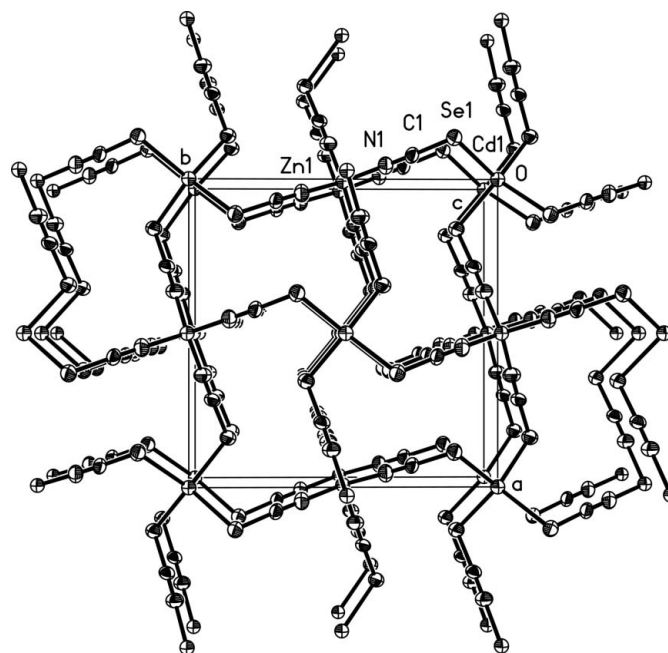
The crystal structure of a new bimetallic selenocyanate, zinc cadmium selenocyanate or poly[tetra- $\mu_2$ -selenocyanato-cadmium(II)zinc(II)],  $[\text{ZnCd}(\text{SeCN})_4]_n$ , is an infinite three-dimensional network in which the slightly distorted  $\text{CdSe}_4$  and  $\text{ZnN}_4$  tetrahedra are connected by  $-\text{SeCN}-$  bridges. The whole structure can be viewed as a diamondoid network with Cd and Zn nodes and  $-\text{SeCN}-$  spacers.

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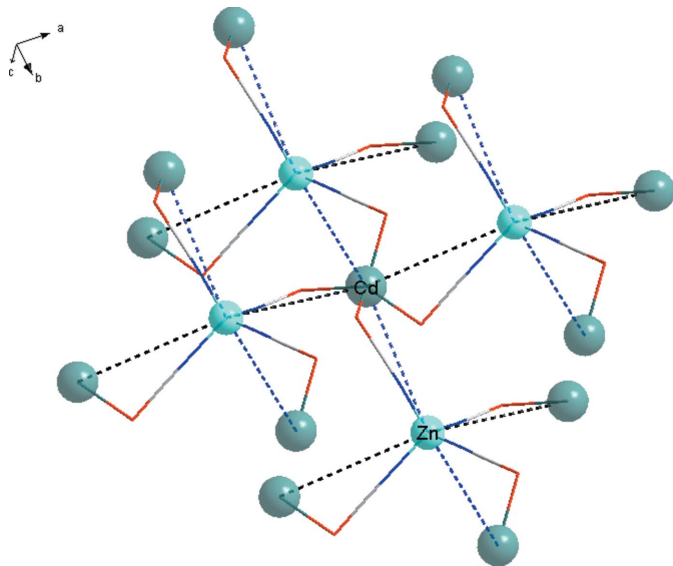
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## Comment

Non-centrosymmetric materials are of special interest in materials chemistry owing to their technologically important properties, such as ferroelectricity and second-order non-linear optical (SONLO) behavior (Halasyamani & Poeppelmeier, 1998). The diamondoid network has been recognized as a potential structural motif for the construction of non-centrosymmetric solids. A non-centrosymmetric diamondoid net will arise if asymmetrical bridging ligands are used to link tetrahedrally coordinated metal centers (Evans *et al.*, 1999). Numerous coordination compounds with diamondoid networks have been synthesized over the past few years that exhibit SONLO effects (Wang, Xu, Lu, Yuan, Zhang, Meng *et al.*, 2001; Evans & Lin, 2002; Li *et al.*, 2006). Among these, zinc cadmium thiocyanate  $[\text{ZnCd}(\text{SCN})_4]$ , abbreviated as ZCTC) is prominent for its relatively strong second harmonic



**Figure 1**  
Packing diagram of ZCSC (viewed down the  $c$  axis). Displacement ellipsoids are drawn at the 50% probability level.



**Figure 2**  
The diamondoid structure of ZCSC.

generation (SHG) effect and short UV cutoff wavelength (Wang, Xu, Lu, Yuan, Zhang, Xu *et al.*, 2001).

In this paper, we report the synthesis and structure of zinc cadmium selenocyanate  $[\text{ZnCd}(\text{SeCN})_4]$ , abbreviated as ZCSC], which is isostructural with ZCTC. Some preliminary investigations, such as thermal stability and SHG efficiency, show that to some extent ZCSC has properties better than those of ZCTC. The local coordination environment around the Cd and Zn atoms in ZCSC can be described as distorted tetrahedral,  $\text{CdSe}_4$  and  $\text{ZnN}_4$ , respectively. The  $-\text{SeCN}-$ bridges link these tetrahedra, thus forming infinite three-dimensional networks (Fig. 1). However, if each  $-\text{SeCN}-$ bridge is considered as a single bond, the whole structure might be defined as a diamondoid network with Cd and Zn nodes

(Fig. 2). Each tetrahedron has two types of  $\text{Zn}\cdots\text{Cd}\cdots\text{Zn}$  (or  $\text{Cd}\cdots\text{Zn}\cdots\text{Cd}$ ) angles,  $92.30$  and  $156.90^\circ$ , respectively. These angles have a significant distortion from the ideal tetrahedral angle of  $109.5^\circ$  in diamond. It is noticeable that the almost linear bridging ligand does not link the metal nodes in a straight line (the Cd atom is not colinear with the ligand, see the angles in Table 1). This kink plays an important role in the construction of non-centrosymmetric three-dimensional networks. In addition, the ligand incorporates electronic asymmetry (push-pull effects) which are essential for SONLO behavior. Preliminary experimental results show that ZCSC displays much stronger powder SHG efficiency than urea. Thermogravimetric analysis shows that weight loss takes place at  $563$  K. Compared with bimetallic thiocyanates (Wang *et al.*, 2001a), ZCSC has a higher thermal stability.

## Experimental

$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{ZnCl}_2$  and  $\text{KSeCN}$  were reacted in a 1:1:4 molar ratio in water. The resulting precipitate was dissolved in a dilute KCl

solution. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of this solution. The SHG effect of the crystal was studied by the Kurtz powder technique (Kurtz & Perry, 1968). Thermogravimetric analysis was carried out on an SDT Q600 thermal analyser at a scanning rate of  $20$  K  $\text{min}^{-1}$ .

## Crystal data

$[\text{ZnCd}(\text{SeCN})_4]$   
 $M_r = 597.69$   
Tetragonal,  $I\bar{4}$   
 $a = 11.3310$  (6) Å  
 $c = 4.6314$  (8) Å  
 $V = 594.63$  (11) Å<sup>3</sup>  
 $Z = 2$   
 $D_x = 3.338$  Mg  $\text{m}^{-3}$

Mo  $K\alpha$  radiation  
Cell parameters from 48 reflections  
 $\theta = 5.1\text{--}15.7^\circ$   
 $\mu = 16.01$   $\text{mm}^{-1}$   
 $T = 291$  (2) K  
Prism, colourless  
 $0.18 \times 0.12 \times 0.10$  mm

## Data collection

Bruker P4 diffractometer  
 $\omega$  scans  
Absorption correction: multi-scan (*XSCANS*; Bruker, 1996)  
 $T_{\text{min}} = 0.107$ ,  $T_{\text{max}} = 0.203$   
2112 measured reflections  
867 independent reflections  
801 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.014$   
 $\theta_{\text{max}} = 29.8^\circ$   
 $h = -15 \rightarrow 15$   
 $k = -15 \rightarrow 15$   
 $l = -6 \rightarrow 6$   
3 standard reflections every 97 reflections  
intensity decay: none

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.033$   
 $wR(F^2) = 0.075$   
 $S = 1.09$   
867 reflections  
33 parameters  
 $w = 1/[\sigma^2(F_o^2) + (0.0301P)^2 + 4.6035P]$   
where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.54$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.54$  e Å<sup>-3</sup>  
Extinction correction: *SHELXTL*  
Extinction coefficient: 0.0079 (7)  
Absolute structure: Flack (1983), 383 Friedel pairs  
Flack parameter: 0.00 (3)

**Table 1**

Selected geometric parameters (Å, °).

Cd1—Se1 <sup>i</sup>	2.6640 (7)	Se1—C1	1.824 (7)
Zn1—N1	1.959 (7)	N1—C1	1.143 (9)
Se1 <sup>i</sup> —Cd1—Se1 <sup>ii</sup>	107.709 (16)	C1—Se1—Cd1	94.4 (2)
Se1 <sup>ii</sup> —Cd1—Se1	113.06 (3)	C1—N1—Zn1	176.2 (6)
N1—Zn1—N1 <sup>iii</sup>	111.8 (4)	N1—C1—Se1	178.4 (6)
N1—Zn1—N1 <sup>iv</sup>	108.3 (2)		

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

Data collection: *XSCANS* (Bruker, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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