

Luca Russo,^a Raj Pal Sharma,^b
Subhranshu Sharma,^b Rajni
Sharma^b and Kari Rissanen^{a*}^aNanoscience Center, Department of Chemistry,
University of Jyväskylä, PO Box 35, 40014
Jyväskylä, Finland, and ^bDepartment of
Chemistry, Panjab University, Chandigarh 160
014, India

Correspondence e-mail: krissane@cc.jyu.fi

Key indicators

Single-crystal X-ray study
 $T = 173$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.029
 wR factor = 0.052
Data-to-parameter ratio = 21.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**catena-Poly[benzyltriethylammonium
[tri- μ -thiocyanato- $\kappa^4\text{N}:\text{S};\kappa^2\text{S}:\text{N}$ -cadmate(II)]]**

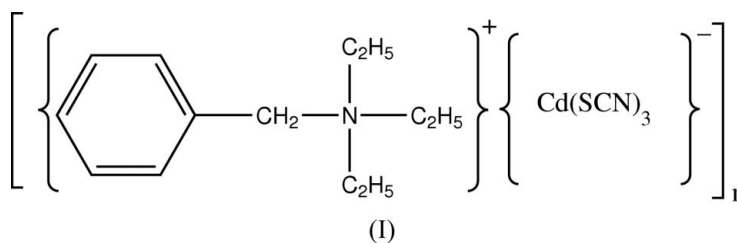
The title compound, $\{[(\text{C}_6\text{H}_5\text{CH}_2)\text{N}(\text{C}_2\text{H}_5)_3][\text{Cd}(\text{SCN})_3]\}_n$, contains benzyltriethylammonium cations lying between one-dimensional chains of stoichiometry $\{[\text{Cd}(\text{SCN})_3]^{-}\}_n$. Each Cd^{2+} ion is $3N,3S$ -hexacoordinated by thiocyanate ligands in an octahedral arrangement. The asymmetric unit contains one cation and one anion.

Received 16 May 2006

Accepted 25 July 2006

Comment

Coordination polymers of one, two and three-dimensional infinite frameworks involving cadmium(II) have been of great interest in recent years owing to their potential applications in various fields such as non-linear optical (NLO) materials (Zhang *et al.*, 1999; Chen *et al.*, 2002; Liu *et al.*, 2004). As the d^{10} configuration and softness of cadmium(II) permit a wide variety of geometries and coordination numbers, especially with the ambidentate thiocyanate (SCN^-) ligand, various structural types have been observed. Which structural type occurs depends on the size, shape and symmetry of the counter-cations and also on the ratio of Cd^{2+} to SCN^- ions.



In a continuation of our interest in the supramolecular chemistry of salts of simple metal complexes (Sharma *et al.*, 2005, 2006), the synthesis and characterization of the title compound, (I), were undertaken. The asymmetric unit contains one benzyltriethylammonium cation, three thiocyanate anions and a cadmium cation. Each Cd^{2+} ion is $3N,3S$ -hexacoordinated by thiocyanate ligands in an octahedral arrangement. Thus, each S atom is *trans* to an N atom (Fig. 1 and Table 1). Three examples of Cd^{2+} -thiocyanate chains with the same stoichiometry and morphology (Kuniyasu *et al.*, 1987; Chen *et al.*, 1994, 2002) were found in the Cambridge Structural Database (CSD, Version 5.27; Allen, 2002). Both Cd–S and Cd–N bonds lengths are in agreement with those found in analogous structures: the average observed Cd–S bond length [2.752 (9) Å] is significantly shorter than the sum of the Shannon ionic radius (Shannon, 1976) of Cd^{2+} and the Pauling ionic radius (Pauling, 1960) of S^- (3.28 Å), indicating a significant covalent contribution. The Cd–N bond lengths [2.340 (2) Å] are also shorter than the sum of Shannon's ionic

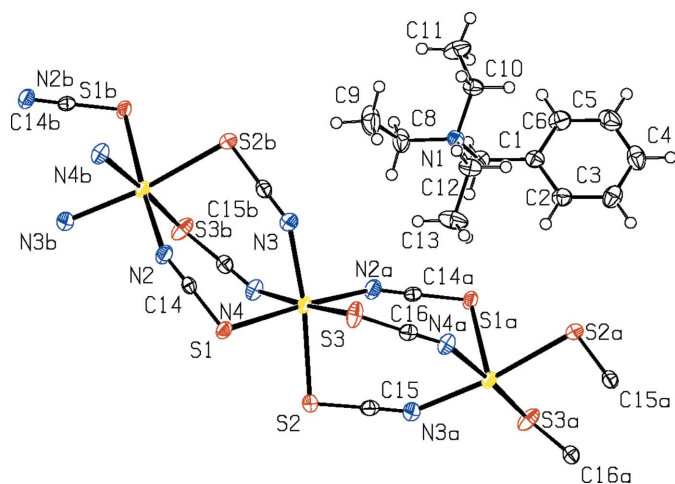


Figure 1
Fragment of (I), showing 50% probability displacement ellipsoids (arbitrary spheres for the H atoms). [Symmetry codes: (a) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z$; (b) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$.]

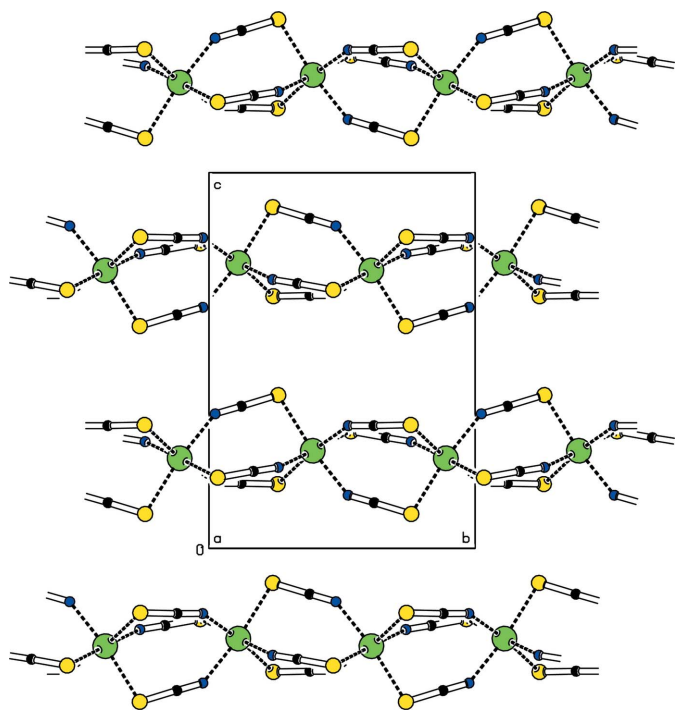


Figure 2
The polymeric $[\text{Cd}(\text{SCN})_3]_n$ chains extending along the b axis. Colour key: Cd green, C black, N blue and S yellow.

radii (2.41 Å; Shannon, 1976). The structure contains one-dimensional linear anionic chains. The chains are packed in a parallel fashion, running along the crystallographic b axis and surrounded by counter-cations (Fig. 2).

Experimental

Analytical grade reagents were used without any further purification. Benzyltriethylammonium chloride (1.0 g, 0.005 mol) was dissolved in 10 ml water. CdCl_2 (0.80 g, 0.004 mol) and ammonium thiocyanate

(1.00 g, 0.013 mol) were dissolved in 20 ml water by mechanical stirring. The solutions were mixed and a curd-like white solid precipitated immediately. This was filtered off and dried in air. Crystals of (I) were obtained after redissolving the white solid in an acetone-water mixture (4:1) at room temperature (m.p. 363 K). Elemental analysis calculated for $\text{C}_{16}\text{H}_{22}\text{CdN}_4\text{S}_3$: C 35.70, H 3.66, N 12.81, Cd 25.63%; found: C 35.66, H 3.56, N 12.72, Cd 25.34%.

Crystal data

$(\text{C}_{13}\text{H}_{22}\text{N})[\text{Cd}(\text{NCS})_3]$
 $M_r = 478.96$
 Monoclinic, $P2_1/n$
 $a = 12.164$ (2) Å
 $b = 10.927$ (2) Å
 $c = 15.952$ (3) Å
 $\beta = 104.61$ (3)°
 $V = 2051.8$ (7) Å³

$Z = 4$
 $D_x = 1.551$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 1.38$ mm⁻¹
 $T = 173$ (2) K
 Block, colourless
 $0.60 \times 0.40 \times 0.20$ mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick 2003)
 $T_{\min} = 0.493$, $T_{\max} = 0.771$

18486 measured reflections
 4579 independent reflections
 3895 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$
 $\theta_{\max} = 27.4^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.052$
 $S = 1.25$
 4579 reflections
 217 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + 1.5462P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.51$ e Å⁻³
 $\Delta\rho_{\min} = -0.39$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cd1—S1	2.7543 (8)	Cd1—N2	2.359 (2)
Cd1—N1	2.291 (2)	Cd1—S3	2.7278 (8)
Cd1—S2	2.7738 (10)	Cd1—N3	2.371 (2)
S1—Cd1—N1	176.11 (5)	N1—Cd1—N3	91.50 (8)
S1—Cd1—S2	84.32 (2)	S2—Cd1—N2	172.82 (5)
S1—Cd1—N2	91.28 (6)	S2—Cd1—S3	91.83 (3)
S1—Cd1—S3	85.91 (3)	S2—Cd1—N3	93.37 (6)
S1—Cd1—N3	90.36 (6)	N2—Cd1—S3	93.51 (6)
N1—Cd1—S2	92.17 (6)	N2—Cd1—N3	80.96 (8)
N1—Cd1—N2	92.39 (8)	S3—Cd1—N3	173.27 (5)
N1—Cd1—S3	92.56 (6)		

H atoms were positioned geometrically and refined using a riding model, with C—H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic, C—H = 0.99 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for CH_2 , and C—H = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for CH_3 H atoms.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *EVALCCD* (Duisenberg *et al.*, 2003); data reduction: *EVALCCD*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP III* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2001), *MERCURY* (Version 1.4.1; Bruno *et al.*, 2002) and *CIFTAB* (Sheldrick, 1993).

We thank the Academy of Finland for a research grant (KR and LR).

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* **B58**, 389–397.
- Burnett, M. H. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
- Chen, D.-R., Hu, Q.-P., Meng, Y.-D. & Fan, Y.-P. (1994). *Jiegou Huaxue (Chin. J. Struct. Chem.)*, **13**, 235–238. (In Chinese).
- Chen, W., Liu, F. & You, X. (2002). *J. Solid State Chem.* **167**, 119–125.
- Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Shreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.
- Hooft, R. W. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Kuniyasu, Y., Suzuki, Y., Taniguchi, M. & Ouchi, A. (1987). *Bull. Chem. Soc. Jpn*, **60**, 179–183.
- Liu, F., Chen, W. & You, X. (2004). *J. Solid State Chem.* **169**, 199–207.
- Pauling, L. (1960). In *The Nature of the Chemical Bond*, 3rd ed. Ithaca, New York: Cornell University Press.
- Shannon, R. D. (1976). *Acta Cryst.* **A32**, 751–767.
- Sharma, R. P., Bala, R., Sharma, R., Vermani, B. K., Gill, D. S. & Venugopalan, P. (2005). *J. Coord. Chem.* **58**, 309–316.
- Sharma, R. P., Sharma, R., Bala, R., Vermani, B. K., Gill, D. S., Salas, J. M. & Quiros, M. (2006). *J. Mol. Struct.* **784**, 222–227.
- Sheldrick, G. M. (1993). *CIFTAB*. University of Göttingen, Germany. (Modified by W. Clegg, Newcastle University, England.)
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Sheldrick, G. M. (2001). *SHELXTL*. Version 6. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
- Zhang, H., Wang, X., Zhang, K. & Teo, B. K. (1999). *Coord. Chem. Rev.* **183**, 157–195.