metal-organic papers

catena-Poly[benzyltrimethylammonium [cadmium(II)-tri-μ_2-thiocyanato]]

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The title compound, $\{(C_{10}H_{16}N)[Cd(SCN)_3]\}_n$, contains $[(C_6H_5CH_2)N(CH_3)_3]^+$ cations lying between one-dimensional chains of stoichiometry $\{[Cd(SCN)_3]^-\}_n$. Each Cd^{II} ion is 3N,3S-hexacoordinated by thiocyanate ligands, in an octahedral *fac* arrangement. The asymmetric unit contains two cations and two anions.

Comment

In recent years, studies of the synthesis and properties of semiconductor materials such as CdS and CdSe have become an area of interest owing to the great scope for fundamental understanding of materials as well as potential technological applications (Zhang *et al.*, 1999), such as light-emitting devices, non-linear optical devices, solar cells and biological labels. As a result, the search for new precursors, such as salts containing $[Cd(SCN)_3]^-$, is receiving much attention. As the d^{10} configuration and softness of Cd^{II} permit a wide variety of geometries and coordination numbers, especially with the ambidentate ligand thiocyanate (SCN$^-$), 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. Thus, the structures of a number of one-dimensional single chains (Zhang *et al.*, 2001), two-dimensional networks (Zhang *et al.*, 1997) and three-dimensional structures (Thiele & Messer, 1980) have been reported and reviewed (Sun *et al.*, 2001). Of special interest are the low-dimensional structural motifs, since these relate to highly anisotropic physical properties. In 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), was undertaken.

(I)
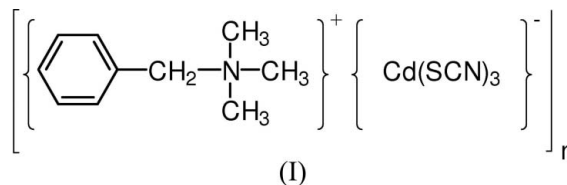
For (I), structure determination revealed the presence of four crystallographically independent components in the solid state: two $[(C_6H_5CH_2)N(CH_3)_3]^+$ cations and two $[Cd(SCN)_3]^-$ anions (Fig. 1). Each Cd^{II} ion is 3N,3S-hexacoordinated, and adopts a slightly deformed *fac* octahedral geometry. Thus, each S atom is *trans* to an N atom. One of the thiocyanate ions (S6/C6/N6) appears to be rotationally disordered about its central C atom, which modifies the Cd^{II}
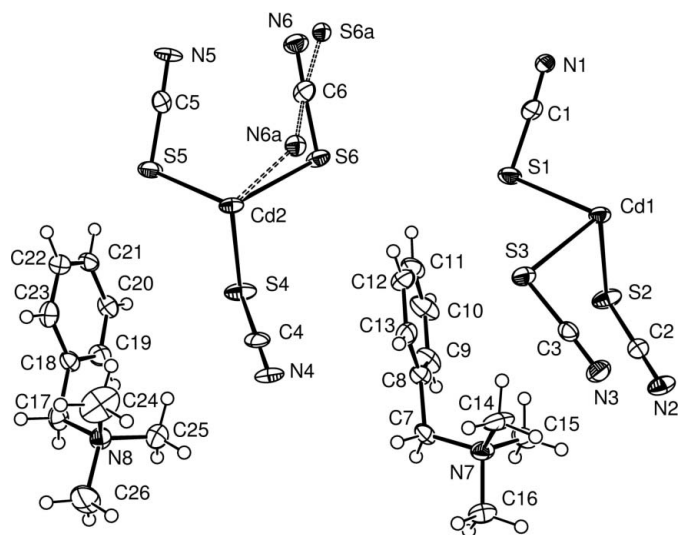
Figure 1
The contents of the asymmetric unit of (I), with displacement ellipsoids drawn at the 50% probability level for non-H atoms. The minor disorder component is indicated by dashed bonds.
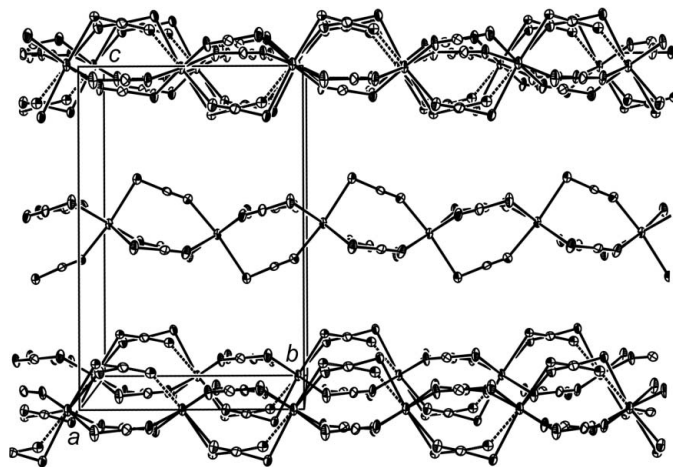

Figure 2
The polymeric $\{[Cd(SCN)_3]^-\}_n$ chains extending along the b-axis direction.

coordination geometry at 9% of the Cd2 metal sites. Both the Cd—S and Cd—N bond lengths show considerable variation (Table 1). Similar distances (Cd—S = 2.688–2.743 Å and Cd—N = 2.279–2.379 Å) are observed in $[(CH_3)_4N][Cd(SCN)_3]$, which is also $3N,3S$-coordinated (Kuniyasu *et al.*, 1987). The average Cd—N—C and Cd—S—C angles in (I) (142.11 and 98.93°, respectively) are also comparable with those in $[(CH_3)_4N][Cd(SCN)_3]$. The $\{[Cd(SCN)_3]^-\}_n$ chains (Fig. 2) propagate along the b-axis direction, with $[Cd(SCN)_6]$ octahedra linked in a face-sharing manner *via* the shared SCN⁻ ligands. The $[(C_6H_5CH_2)N(CH_3)_3]^+$ cations occupy positions between the chains. It is generally believed that the relative arrangement of the anionic $\{[Cd(SCN)_3]^-\}_n$ chains is strongly influenced by the size and shape of the cation. With larger cations, parallel alignment of the $\{[Cd(SCN)_3]^-\}_n$ chains is expected; this is observed in (I).

Experimental

Analytical grade reagents were used without any further purification. Benzyltrimethylammonium chloride (1.0 g, 0.005 mol) was dissolved in 10 ml water, while $CdCl_2$ (0.98 g, 0.004 mol) and ammonium thiocyanate (1.22 g, 0.016 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 (1:1) at room temperature. The salt decomposes at 393 K and is insoluble in organic solvents (C_2H_5OH, CCl_4 and CH_3Cl), but soluble in DMSO and hot water. IR (KBr, ν, cm⁻¹): 2116 (*s*), 2087 (*s*, SCN), 1660 (*m*), 1553 (*m*), 1081 (*s*), 1028 (*s*), 1002 (*s*). ¹H NMR (d_6-DMSO, 298 K): δ 7.2 (*s*, 5H, HAr), 4.2 (*s*, 2H, ArCH₂), 2.6 (*s*, 9H, CH₃). ¹³C NMR (d_6-DMSO, 298 K): δ 128–133 (Ar), 126 (SCN), 68 (ArC), 25 (CH₃).

Crystal data

$(C_{10}H_{16}N)[Cd(SCN)_3]$	$Z = 4$
$M_r = 436.88$	$D_x = 1.666$ Mg m⁻³
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 9.9668\ (3)$ Å	$\mu = 1.61$ mm⁻¹
$b = 10.8210\ (3)$ Å	$T = 123\ (2)$ K
$c = 16.5299\ (5)$ Å	Needle, colourless
$\beta = 102.351\ (2)°$	$0.35 \times 0.08 \times 0.06$ mm
$V = 1741.50\ (9)$ Å³	

Data collection

Nonius KappaCCD diffractometer	31141 measured reflections
φ and ω scans	7120 independent reflections
Absorption correction: multi-scan	5777 reflections with $I > 2\sigma(I)$
(*SORTAV*; Blessing, 1997)	$R_{int} = 0.060$
$T_{min} = 0.880$, $T_{max} = 0.908$	$\theta_{max} = 27.1°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0138P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.041$	$+ 2.3495P]$
$wR(F^2) = 0.067$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
7120 reflections	$\Delta\rho_{max} = 0.92$ e Å⁻³
394 parameters	$\Delta\rho_{min} = -0.57$ e Å⁻³
H-atom parameters constrained	Absolute structure: Flack (1983), 3074 Friedel pairs
	Flack parameter: $-0.04\ (2)$

Table 1
Selected geometric parameters (Å, °).

Cd1—N1[i]	2.293 (5)	Cd2—N4[iii]	2.294 (5)
Cd1—N3[ii]	2.320 (5)	Cd2—N5[iv]	2.341 (5)
Cd1—N2[ii]	2.369 (5)	Cd2—N6[iv]	2.361 (6)
Cd1—S3	2.6749 (15)	Cd2—S5	2.6925 (15)
Cd1—S1	2.7231 (15)	Cd2—S4	2.7097 (15)
Cd1—S2	2.7350 (15)	Cd2—S6	2.762 (2)
C1—S1—Cd1	94.81 (18)	C2—N2—Cd1[i]	144.8 (4)
C2—S2—Cd1	99.67 (17)	C3—N3—Cd1[i]	146.7 (4)
C3—S3—Cd1	99.07 (18)	C4—N4—Cd2[iv]	155.3 (4)
C4—S4—Cd2	95.24 (18)	C5—N5—Cd2[iii]	149.3 (4)
C5—S5—Cd2	98.12 (18)	C6—S6—Cd2	102.2 (2)
C1—N1—Cd1[ii]	155.1 (4)	C6—N6—Cd2[iii]	140.2 (6)

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

One SCN⁻ ligand (S6/C6/N6) was modelled as disordered by a rotation about the C atom, giving two S and two N sites. The site occupancies of the two components were refined to 0.911 (7):0.089 (7). All H atoms were placed in geometrically idea-

lized positions and refined using a riding model: C—H = 0.95 Å for CH, 0.99 Å for CH_2 and 0.98 Å for CH_3; $U_{iso}(H) = 1.2U_{eq}(C)$ for CH and CH_2, and $U_{iso}(H) = 1.5U_{eq}(C)$ for CH_3. We have noted that many crystals from the sample were twinned so that they appeared C-centred monoclinic.

Data collection: *COLLECT* (Hooft, 1988) and *DENZO* (Otwinowski & Minor, 1997); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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