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Poly[bis(sulfolane-κO)di-μ_2-thiocyanato-cadmium(II)]

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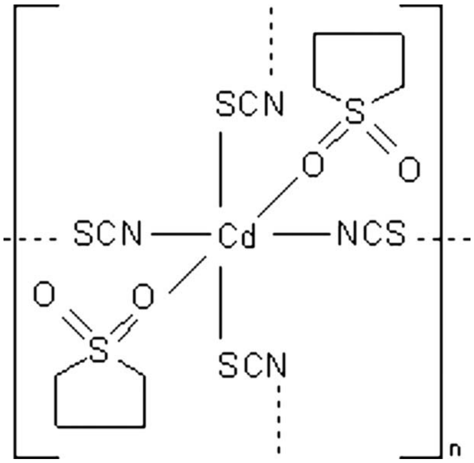
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.004 Å; R factor = 0.020; wR factor = 0.056; data-to-parameter ratio = 20.0.

In the title complex, $[Cd(SCN)_2(C_4H_8O_2S)_2]_n$, the Cd^{II} atom, on an inversion centre, is within a distorted $N_2S_2O_2$ octahedron and the five-membered ring has a distorted envelope conformation. In the crystal structure, neighbouring Cd atoms are connected by –SCN– bridges, leading to the formation of an infinite three-dimensional –Cd–NCS–Cd– network.

Related literature

For related literature, see: Chenskaya *et al.* (2000); Lipkowski (1990); Ouchi & Taniguchi (1988); Ozutsmi *et al.* (1989); Pearson (1966); Shannon (1976); Taniguchi *et al.* (1986, 1987); Taniguchi & Ouchi (1987*a*,*b*); Wang *et al.* (2000); Yamaguchi *et al.* (1985); Zhu *et al.* (2006).



Experimental

Crystal data

$[Cd(SCN)_2(C_4H_8O_2S)_2]$
M_r = 468.89
Triclinic, $P\bar{1}$
a = 5.9138 (1) Å
b = 8.5561 (2) Å
c = 9.4413 (2) Å
α = 115.246 (1)°
β = 96.147 (1)°
γ = 94.512 (1)°
V = 425.48 (5) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.79 mm^{-1}
T = 294 (2) K
0.31 × 0.23 × 0.19 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*APEX2*; Bruker, 2005)
T_{min} = 0.585, T_{max} = 0.710
3857 measured reflections
1937 independent reflections
1881 reflections with $I > 2\sigma(I)$
R_{int} = 0.014

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.056
S = 1.08
1937 reflections
97 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.62 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd1—N1	2.251 (2)	C5—N1	1.147 (3)
Cd1—O2	2.4192 (17)	C5—S2	1.644 (2)
Cd1—S2^i	2.6875 (11)		
N1—C5—S2	178.52 (17)	O2—Cd1—S2^i	89.81 (6)
N1^{ii}—Cd1—N1	180	N1—Cd1—S2^{iii}	88.25 (6)
N1^{ii}—Cd1—O2	90.81 (7)	O2—Cd1—S2^{iii}	90.19 (6)
N1—Cd1—O2	89.19 (7)	S2^i—Cd1—S2^{iii}	180
O2—Cd1—O2^{ii}	180	C5—N1—Cd1	165.48 (15)
N1—Cd1—S2^i	91.75 (6)	C5—S2—Cd1^{iv}	101.40 (7)
S1—C1—C2—C3	37.9 (2)	C2—C3—C4—S1	35.0 (3)
C2—C1—S1—C4	−15.3 (2)	C3—C4—S1—C1	−11.2 (2)
C1—C2—C3—C4	−48.4 (3)		

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2227).

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supplementary materials

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Poly[bis(sulfolane-κ*O*)di-μ_2-thiocyanato-cadmium(II)]

X.-Q. Wang, J.-D. Fan, W.-T. Yu, D. Xu and **W.-L. Liu**

Comment

A variety of polymeric structures of the monometallic thiocyanates of the IIB metals and of their Lewis base adducts are interesting themes of structural chemistry and nonlinear optics (Lipkowski, 1990; Wang, *et al.*, 2000; Chenskaya *et al.*, 2000; Zhu *et al.*, 2006). According to the hard and soft acids and bases (HSAB) theory (Pearson, 1966), cadmium is a rather soft metal, although its softness is less than that of mercury or lead. Therefore, it is expected that the N and S atoms of the thiocyanate ion are able to bond easily with Cd, and that SCN-bridged polymeric complexes are stable (Yamaguchi *et al.*, 1985; Taniguchi *et al.*, 1986, 1987; Taniguchi & Ouchi, 1987a,b; Ouchi & Taniguchi, 1988; Ozutsmi *et al.*, 1989). In the present work, the title sulfolane adduct of $Cd(SCN)_2$, (I), has been characterized.

In (I), the Cd^{II} atom is within a distorted $N_2S_2O_2$ octahedron (Fig. 1). The Cd—N, Cd—O and Cd—S bonds are shorter, longer and shorter, respectively, than the sums of the ionic radii, *i.e.* 2.41, 2.30 and 2.79 Å, respectively (Shannon, 1976). The bond angles (Table 1) deviate significantly from ideal octahedral geometry. The C—N—Cd and C—S—Cd bond angles (close to 180° and 90°, respectively) show that the these groups are quasi-linear and significantly bent, respectively.

The five-membered S1/C1–C4 ring is not planar, having a distorted envelope conformation, with C2 as the flap atom displaced by 0.589 (3) Å from the mean plane of the other four atoms. It has also a pseudo twofold axis passing through atom S1 and the mid-point of the C2—C3 bond, as evidenced by the torsion angles (Table 1).

In the crystal structure, neighbouring Cd atoms are connected by –SCN– bridges, which leads to the formation of an infinite three-dimensional –Cd—NCS—Cd–network.

Experimental

$Cd(SCN)_2$ was prepared by the reaction of $Cd(NO_3)_2.4H_2O$ (6.170 g, 20 mmol) and NH_4SCN (3.045 g, 40 mmol) in water (6 ml). The crystalline powder of $Cd(SCN)_2$ (3.438 g, 15 mmol) was dissolved in water (50 ml) at about 313 K, and then sulfolane (2.5 ml) was added. The mixture was left standing at room temperature, yielding colourless crystals of (I) suitable for X-ray vrystal structure analysis. IR (Nicolet 20 SX FTIR spectrometer; cm^{-1}): 2945.88 and 2878.38 [ν(CH)], 2107.92 and 2078.99 [ν(CN)], 1447.39, 1409.78, 1384.71, 1290.21 and 1254.53 [δ(HCH)], 1204.39, 1145.57, 1108.92, 1086.75, 1031.78, 991.28, 672.10, 570.85 and 516.85 [ν(SO)], 967.17 and 907.39 [2δ(SCN)], 735.75[ν(CS)], 465.75, 418.50 and 407.89 [δ(SCN)]. Raman (NXR FT-Raman spectrometer using InGaAs laser at 1064 nm, cm^{-1}): 3008.5, 2977.6 and 2947.9 [ν(CH)], 2107.0 [ν(CN)], 1450.5, 1253.0 [δ(HCH)], 1132.8, 1095.2, 1073.9, 1026.2, 666.5 and 561.5 [ν(SO)], 967.0 and 877.3 [2δ(SCN)], 777.9 and 734.0 [ν(CS)], 476.9 and 444.9 [δ(SCN)], 385.5 [ν(CdN)], 260.9 [ν(CdO)], 193.7, 161.7 and 129.0 [ν(CdS)].

Refinement

H atoms were positioned geometrically, with C—H = 0.97 Å, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

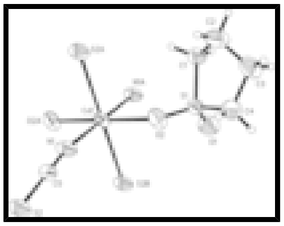
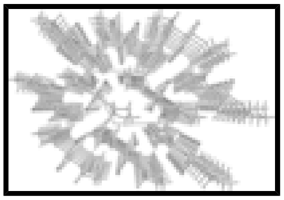


Fig. 1. A fragment of the polymeric structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Atoms N1A, O2A, S2A and S2B are at the symmetry positions (1 - *x*, -*y*, 1-*z*), (1 - *x*, -*y*, 1 - *z*), (*x* - 1, *y*, *z*) and (2 - *x*, -*y*, 1 - *z*), respectively.



Poly[Bis(sulfolane-κ*O*)di-μ₂-thiocyanato-cadmium(II)]

Crystal data

$[Cd(SCN)_2(C_4H_8O_2S)_2]$	$Z = 1$
$M_r = 468.89$	$F_{000} = 234$
Triclinic, $P\overline{1}$	$D_x = 1.830$ Mg m^{-3}
Hall symbol: -P 1	Mo *K*α radiation λ = 0.71069 Å
$a = 5.9138$ (1) Å	Cell parameters from 3568 reflections
$b = 8.5561$ (2) Å	θ = 2.4–27.6°
$c = 9.4413$ (2) Å	μ = 1.79 mm^{-1}
α = 115.246 (1)°	$T = 294$ (2) K
β = 96.147 (1)°	Prism, colourless
γ = 94.512 (1)°	0.31 × 0.23 × 0.19 mm
$V = 425.48$ (2) Å^3	

Data collection

Bruker APEXII CCD area-detector diffractometer	1937 independent reflections
Radiation source: fine-focus sealed tube	1881 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.014$
$T = 294(2)$ K	$\theta_{max} = 27.6°$
φ and ω scans	$\theta_{min} = 2.4°$
Absorption correction: multi-scan	$h = -7\rightarrow6$

(APEX2; Bruker, 2005)	
$T_{\min} = 0.585$, $T_{\max} = 0.710$	$k = -10 \rightarrow 11$
3857 measured reflections	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 0.1407P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.020$	$(\Delta/\sigma)_{\max} = 0.017$
$wR(F^2) = 0.056$	$\Delta\rho_{\max} = 0.42$ e Å^{-3}
$S = 1.08$	$\Delta\rho_{\min} = -0.62$ e Å^{-3}
1937 reflections	Extinction correction: none
97 parameters	
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	
Hydrogen site location: inferred from neighbouring sites	

Special details

Experimental. IR (Nicolet 20 SX FTIR spectrometer; cm^{-1}): 2945.88 and 2878.38 [ν(CH)], 2107.92 and 2078.99 [ν(CN)], 1447.39, 1409.78, 1384.71, 1290.21 and 1254.53 [δ(HCH)], 1204.39, 1145.57, 1108.92, 1086.75, 1031.78, 991.28, 672.10, 570.85 and 516.85 [ν(SO)], 967.17 and 907.39 [2δ(SCN)], 735.75[ν(CS)], 465.75, 418.50 and 407.89 [δ(SCN)]. Raman (NXR FT-Raman spectrometer using InGaAs laser at 1064 nm, cm^{-1}): 3008.5, 2977.6 and 2947.9 [ν(CH)], 2107.0 [ν(CN)], 1450.5, 1253.0 [δ(HCH)], 1132.8, 1095.2, 1073.9, 1026.2, 666.5 and 561.5 [ν(SO)], 967.0 and 877.3 [2δ(SCN)], 777.9 and 734.0 [ν(CS)], 476.9 and 444.9 [δ(SCN)], 385.5 [ν(CdN)], 260.9 [ν(CdO)], 193.7, 161.7 and 129.0 [ν(CdS)].

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.

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 > 2sigma(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 (Å^2)

	x	y	z	$U_{\rm iso}*/U_{\rm eq}$
Cd1	0.5000	0.0000	0.5000	0.03334 (8)
S1	0.31205 (8)	0.13344 (6)	0.20978 (6)	0.03717 (11)
S2	1.32208 (8)	0.25374 (7)	0.72442 (6)	0.04356 (13)
O1	0.2601 (3)	−0.0393 (2)	0.0826 (2)	0.0583 (4)
O2	0.4885 (3)	0.1593 (2)	0.3410 (2)	0.0489 (4)
N1	0.8515 (3)	0.1461 (2)	0.6227 (2)	0.0418 (4)

C1	0.0585 (4)	0.2137 (3)	0.2838 (3)	0.0474 (5)
H1A	−0.0782	0.1404	0.2130	0.057*
H1B	0.0545	0.2189	0.3882	0.057*
C2	0.0768 (5)	0.3954 (3)	0.2911 (3)	0.0604 (6)
H2A	0.1752	0.4783	0.3875	0.072*
H2B	−0.0737	0.4329	0.2900	0.072*
C3	0.1777 (5)	0.3854 (3)	0.1473 (3)	0.0559 (6)
H3A	0.0662	0.3217	0.0518	0.067*
H3B	0.2221	0.5016	0.1571	0.067*
C4	0.3848 (4)	0.2918 (3)	0.1400 (3)	0.0507 (5)
H4A	0.5189	0.3727	0.2069	0.061*
H4B	0.4167	0.2357	0.0322	0.061*
C5	1.0453 (3)	0.1882 (2)	0.6641 (2)	0.0313 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.01888 (11)	0.03835 (12)	0.04516 (12)	0.00468 (7)	0.00290 (7)	0.02091 (9)
S1	0.0352 (2)	0.0394 (2)	0.0443 (2)	0.01258 (19)	0.00901 (19)	0.0234 (2)
S2	0.0227 (2)	0.0446 (3)	0.0495 (3)	0.00226 (19)	0.00154 (19)	0.0089 (2)
O1	0.0628 (11)	0.0463 (8)	0.0592 (9)	0.0139 (8)	0.0077 (8)	0.0165 (7)
O2	0.0399 (8)	0.0564 (9)	0.0595 (9)	0.0059 (7)	0.0001 (7)	0.0359 (8)
N1	0.0239 (8)	0.0412 (8)	0.0523 (9)	0.0050 (6)	0.0061 (7)	0.0129 (7)
C1	0.0368 (11)	0.0630 (13)	0.0554 (12)	0.0179 (10)	0.0174 (9)	0.0338 (11)
C2	0.0557 (15)	0.0549 (13)	0.0758 (16)	0.0272 (12)	0.0236 (13)	0.0273 (12)
C3	0.0543 (14)	0.0506 (12)	0.0758 (16)	0.0154 (11)	0.0105 (12)	0.0386 (12)
C4	0.0526 (13)	0.0558 (12)	0.0649 (13)	0.0190 (10)	0.0239 (11)	0.0410 (11)
C5	0.0281 (9)	0.0300 (8)	0.0364 (8)	0.0073 (6)	0.0075 (7)	0.0139 (6)

Geometric parameters (Å, °)

Cd1—N1^{i}	2.251 (2)	C1—H1B	0.9700
Cd1—N1	2.251 (2)	C2—C3	1.513 (4)
Cd1—O2	2.4192 (17)	C2—H2A	0.9700
Cd1—O2^{i}	2.4192 (17)	C2—H2B	0.9700
Cd1—S2^{ii}	2.6875 (11)	C3—C4	1.507 (3)
Cd1—S2^{iii}	2.6875 (11)	C3—H3A	0.9700
S2—Cd1^{iv}	2.6875 (11)	C3—H3B	0.9700
O1—S1	1.4341 (19)	C4—S1	1.785 (2)
O2—S1	1.4580 (17)	C4—H4A	0.9700
C1—C2	1.521 (3)	C4—H4B	0.9700
C1—S1	1.785 (2)	C5—N1	1.147 (3)
C1—H1A	0.9700	C5—S2	1.644 (2)
C2—C1—S1	103.85 (16)	N1^{i}—Cd1—N1	180.00 (10)
C2—C1—H1A	111.0	N1^{i}—Cd1—O2	90.81 (7)
S1—C1—H1A	111.0	N1—Cd1—O2	89.19 (7)
C2—C1—H1B	111.0	N1^{i}—Cd1—O2^{i}	89.19 (7)

S1—C1—H1B	111.0	N1—Cd1—O2^{i}	90.81 (7)
H1A—C1—H1B	109.0	O2—Cd1—O2^{i}	180.0
C1—C2—C3	107.17 (19)	N1^{i}—Cd1—S2^{ii}	88.25 (6)
C1—C2—H2A	110.3	N1—Cd1—S2^{ii}	91.75 (6)
C3—C2—H2A	110.3	O2—Cd1—S2^{ii}	89.81 (6)
C1—C2—H2B	110.3	O2^{i}—Cd1—S2^{ii}	90.19 (6)
C3—C2—H2B	110.3	N1^{i}—Cd1—S2^{iii}	91.75 (6)
H2A—C2—H2B	108.5	N1—Cd1—S2^{iii}	88.25 (6)
C4—C3—C2	106.69 (19)	O2—Cd1—S2^{iii}	90.19 (6)
C4—C3—H3A	110.4	O2^{i}—Cd1—S2^{iii}	89.81 (6)
C2—C3—H3A	110.4	S2^{ii}—Cd1—S2^{iii}	180.00 (2)
C4—C3—H3B	110.4	C5—N1—Cd1	165.48 (15)
C2—C3—H3B	110.4	S1—O2—Cd1	127.40 (10)
H3A—C3—H3B	108.6	O1—S1—O2	116.68 (11)
C3—C4—S1	105.34 (16)	O1—S1—C4	111.75 (13)
C3—C4—H4A	110.7	O2—S1—C4	108.46 (12)
S1—C4—H4A	110.7	O1—S1—C1	111.28 (13)
C3—C4—H4B	110.7	O2—S1—C1	109.89 (12)
S1—C4—H4B	110.7	C4—S1—C1	96.99 (11)
H4A—C4—H4B	108.8	C5—S2—Cd1^{iv}	101.40 (7)
N1—C5—S2	178.52 (17)		
O2—Cd1—N1—C5	−101.9 (7)	C2—C1—S1—C4	−15.3 (2)
O2^{i}—Cd1—N1—C5	78.1 (7)	C2—C1—S1—O1	−131.90 (18)
S2^{ii}—Cd1—N1—C5	−12.1 (7)	C1—C2—C3—C4	−48.4 (3)
S2^{iii}—Cd1—N1—C5	167.9 (7)	C2—C3—C4—S1	35.0 (3)
N1^{i}—Cd1—O2—S1	−5.53 (13)	C3—C4—S1—C1	−11.2 (2)
N1—Cd1—O2—S1	174.47 (13)	C3—C4—S1—O1	105.05 (19)
S2^{ii}—Cd1—O2—S1	82.72 (13)	C3—C4—S1—O2	−124.95 (19)
S2^{iii}—Cd1—O2—S1	−97.28 (13)	Cd1—O2—S1—O1	−54.85 (16)
S1—C1—C2—C3	37.9 (2)	Cd1—O2—S1—C4	177.92 (11)
C2—C1—S1—O2	97.29 (18)	Cd1—O2—S1—C1	73.02 (15)

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

Fig. 1

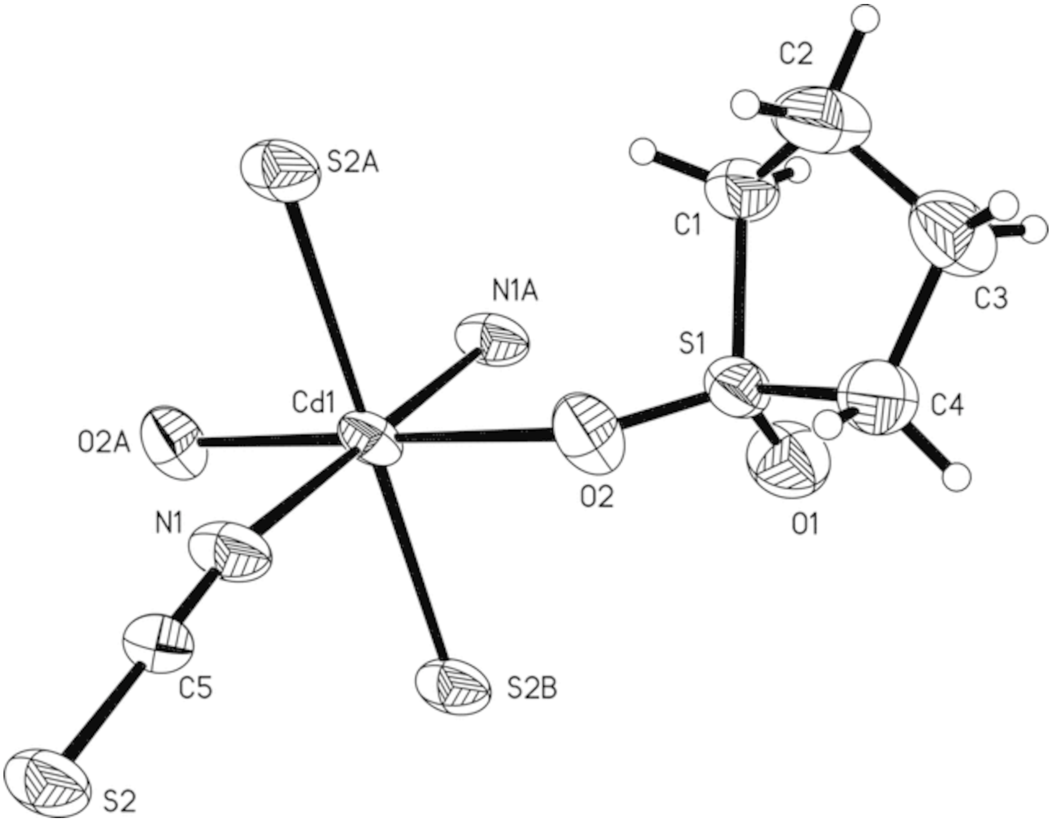


Fig. 2