Three-co-ordinate Thiocyanate in Cadmium Dithiocyanate

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The crystal structure of the title compound has been determined from three-dimensional *X*-ray data. Crystals are monoclinic, space group $P2_1/n$, with $Z = 4$ in a unit cell of dimensions: $a = 7.39(1)$, $b = 13.10(2)$, $c = 5.86(1)$ Å, $\beta = 112.1(3)°$. The structure was solved by Patterson and Fourier methods and refined by least-squares techniques to *R* 0.033 for 1 059 observed reflections measured by diffractometer. Cadmium is octahedrally surrounded by four sulphur and by two *trans*-nitrogen atoms with a slightly distorted geometry. Cd–N (2.24 Å) and Cd–S (2.76 Å) bond distances are all close to normal covalent bond values.

EXAMPLES of co-ordination of the thiocyanate group through sulphur (M–SCN), nitrogen (M–NCS), or both (M–NCS–M) are well known.[1] Less-common types of bonding have also been reported: three-co-ordinate thiocyanate, with three bonds through sulphur atom in $[NH_4][Ag(SCN)_2]$;[2] two-co-ordinate thiocyanate with bridging nitrogen in $[Cu(NH_2CH_2CH_2NH_2)_2(NCS)][ClO_4]$,[3] and $[Cu\{NH_2CH_2CH_2N{:}C(NH_2)NHC(NH)NH_2\}(NCS)][SCN]$,[4] and with bridging sulphur in $K_2[Pd(SCN)_4]$;[5] three-co-ordinate thiocyanate with bonded nitrogen and bridging sulphur in $[Ag(SCN)(PPr^n{}_3)]$,[6] in $[CoHg_2(SCN)_6(C_6H_6)]$,[7] in $[Cu(NH_3)_2(NCS)_2]$,[8,9] in $[Cu(NH_2CH_2CH_2NH_2)(NCS)_2]$,[10] and in $[Cu_2(NCS)_3(NH_3)_3)]$.[11] The bridging bonds in the crystal structures of some of the above mentioned compounds [2,3,6–10] are symmetrical and rather long (2.7—3.1 Å), while they are unsymmetrical, one being much shorter than the other, in the remaining cases.

TABLE 1

Positional and anisotropic thermal parameters * (× 10^4), with estimated standard deviations in parentheses

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cd	1 167(1)	1 309(1)	4 421(1)	143(2)	35(1)	143(4)	−3(0)	76(2)	−11(1)
S(1)	2 456(4)	−363(2)	−2 495(5)	96(4)	30(1)	130(8)	−1(2)	46(4)	−11(3)
S(2)	7(3)	2 966(2)	11 444(5)	100(4)	30(1)	111(8)	12(2)	35(4)	−5(2)
N(1)	2 144(12)	464(7)	1 748(18)	97(15)	37(5)	162(33)	0(7)	39(17)	−9(9)
N(2)	292(13)	2 143(7)	7 172(16)	148(18)	37(5)	143(31)	11(7)	77(19)	−9(10)
C(1)	2 267(12)	133(8)	−8(18)	66(14)	28(5)	131(30)	6(7)	25(16)	5(10)
C(2)	187(13)	2 476(8)	8 946(19)	96(18)	26(5)	132(33)	7(7)	37(19)	15(11)

* The temperature factor is of the form: $\exp-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$.

Peculiar bonding situations of the thiocyanate group are also present in some metal thiocyanates, where the two co-ordination sites of the bridging anion are not sufficient to fill the co-ordination sphere of the cation: *e.g.* in Ag(SCN),[12] $Hg(SCN)_2$,[13] and $Pb(SCN)_2$.[14] We wished to determine the crystal structures of other metal thiocyanates in order to investigate the influence of the metal atom on the co-ordination of the anion, and we report here the crystal structure determination of $Cd(SCN)_2$.

EXPERIMENTAL

The compound was prepared by mixing equimolar solutions of $CdSO_4$ and $Ba(SCN)_2$; colourless prismatic crystals were formed by evaporation of an aqueous solution.

Crystal Data.—$C_2N_2CdS_2$, *M* 228.72, Monoclinic, $a = 7.39(1)$, $b = 13.10(2)$, $c = 5.86(1)$ Å, $\beta = 112.1(3)°$, $U = 525.2$ Å^3, D_m (flotation) 2.83 g cm^{-3}, $Z = 4$, $D_c = 2.89$ g cm^{-3}, $F(000) = 424$. Space group $P2_1/n$ from systematic absences. Mo-K_α radiation, $\lambda = 0.710\,7$ Å; $\mu(\text{Mo-}K_\alpha) = 47.25$ cm^{-1}. Unit cell parameters and their estimated standard deviations were determined by a least-squares fit to 17 values of θ, χ, ϕ accurately measured by use of a very narrow counter aperture.

Intensity Measurements.—A crystal of dimensions 0.010 × 0.016 × 0.066 cm was mounted on a Siemens automatic single-crystal AED diffractometer, with the *c* axis nearly coincident with the polar ϕ axis of the goniostat. A total of 1 114 independent intensities up to $2\theta \leqslant 56°$ were recorded, by use of the θ—2θ scan method; the procedure was similar to that previously described.[15] The values of I and $\sigma(I)$, extrapolated to a unit scan-time, were corrected for Lorentz-polarization effects. No absorption or extinction corrections were applied. Of 1 114 reflections, 55 having $I/\sigma(I) < 2$ were considered unobserved and were not used in the analysis.

Solution and Refinement of the Structure.—The positions of cadmium and one sulphur atom were determined from a three-dimensional Patterson synthesis; a subsequent three-dimensional Fourier map gave the positions of the remaining atoms. The *R* factor, obtained by use of the overall tem-

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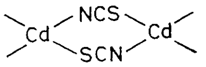
perature and scale factors derived from a Wilson plot, was 0.23 for 1 059 observed reflections. Both positional and isotropic thermal parameters were then refined by four cycles of full-matrix least-squares to R 0.08; the quantity minimized was $\Sigma w(\Delta F)^2$ where $w = 4F_o^2/[\sigma^2(F_o^2) + (0.12\,F_o^2)]^2$.[16] Four more cycles, by use of block-diagonal least-squares and anisotropic thermal parameters, reduced R to 0.033 and R' to 0.075 $[R' = \Sigma w(\Delta F)^2/\Sigma(wF_o^2)]$, for 1 059 observed reflections. The value of the goodness of fit, S, was 1.2 $\{S = [\Sigma w(\Delta F)^2/(m - n)]^{\frac{1}{2}}$, where m is the number of Δ values and n the number of variables$\}$. The final R for all 1 114 measured reflections is 0.035. Atomic scattering factors were interpolated from values given in ref. 17. Final atomic parameters, with estimated standard deviations, are given in Table 1. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21552 (7 pp., 1 microfiche).*

DISCUSSION

The crystal structure (Figure 1) consists of eight-membered rings,



packed so that sulphur atoms face cadmium atoms of the nearest adjacent rings; the resulting co-ordination around cadmium and sulphur is as shown in Figure 2: cadmium is octahedrally surrounded by four sulphur and by two *trans*-nitrogen atoms, with a slightly distorted geometry, as shown by the range of the bond angles involving the metal (86—94°); sulphur bonds to three atoms along the direction of a very distorted tetrahedron. Bond distances are shown in Figure 2 and bond angles in Table 2. The mean Cd–S (2.76 Å) and Cd–N (2.24 Å) bond distances are in the range reported for other octahdral cadmium thiocyanate complexes.[18,19] Their values, compared to those obtained as the sum of tetrahedral covalent radii[20] (2.52 and 2.18 Å), show that Cd–S are more elongated than are Cd–N distances, although the difference between the bonds is opposite and much more evident in Hg(SCN)$_2$,[13] where there are two strong Hg–S bonds (2.38 Å) and four ionic interactions Hg–N (2.81 Å); no comparison is possible with Pb(SCN)$_2$, which has an ionic structure, with Pb$^{\mathrm{II}}$ surrounded by four sulphur and four nitrogen atoms at distances equal to the sum of the ionic radius of Pb$^{\mathrm{II}}$ and of the van der Waals radii of the ligands.

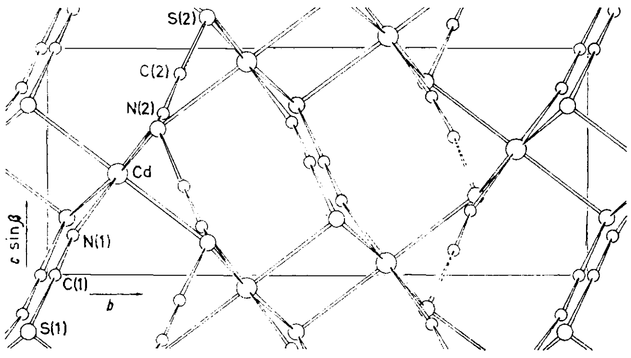


FIGURE 1 Projection of the crystal structure along the *a* axis. Dashed bonds are to atoms translated by *a* with respect to those shown

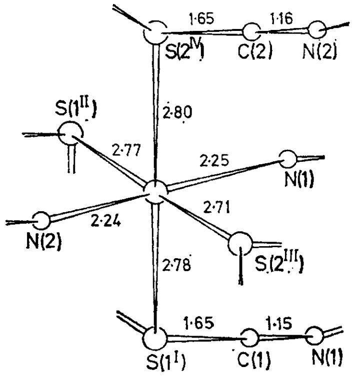


FIGURE 2 Bond distances in the co-ordination polyhedron around cadmium and sulphur. Symmetry operations are defined in Table 2. Calculated standard deviations are in the range 0.007—0.014 Å

TABLE 2

Bond angles (°), with standard deviations in parentheses

S(1$^{\mathrm{I}}$)–Cd–S(1$^{\mathrm{II}}$)	87.4(4)	S(2$^{\mathrm{III}}$)–Cd–S(1$^{\mathrm{II}}$)	178.4(1)
S(1$^{\mathrm{I}}$)–Cd–S(2$^{\mathrm{III}}$)	94.2(4)	S(1$^{\mathrm{I}}$)–Cd–N(2)	92.2(3)
S(1$^{\mathrm{I}}$)–Cd–S(2$^{\mathrm{IV}}$)	173.4(1)	S(1$^{\mathrm{II}}$)–Cd–N(1)	86.7(3)
S(1$^{\mathrm{I}}$)–Cd–N(1)	90.6(3)	N(1)–Cd–N(2)	178.2(3)
S(1$^{\mathrm{I}}$)–Cd–N(2)	90.9(4)	Cd–S(1$^{\mathrm{II}}$)–Cd($^{\mathrm{V}}$)	92.6(4)
		Cd–S(1$^{\mathrm{II}}$)–C(1$^{\mathrm{II}}$)	98.1(4)
S(2$^{\mathrm{IV}}$)–Cd–S(I$^{\mathrm{II}}$)	87.0(4)	Cd–S(2$^{\mathrm{IV}}$)–Cd($^{\mathrm{IV}}$)	124.7(6)
S(2$^{\mathrm{IV}}$)–Cd–S(2$^{\mathrm{III}}$)	91.5(4)	Cd–S(2$^{\mathrm{III}}$)–C(2$^{\mathrm{III}}$)	99.0(4)
S(2$^{\mathrm{IV}}$)–Cd–N(2)	85.6(4)	Cd–N(1)–C(1)	164.3(8)
S(2$^{\mathrm{IV}}$)–Cd–N(2)	92.9(4)	Cd–N(2)–C(2)	165.5(8)
		N(1)–C(1)–S(1)	178.8(11)
S(2$^{\mathrm{III}}$)–Cd–N(1)	93.1(3)	N(2)–C(2)–S(2)	179.0(12)
S(2$^{\mathrm{III}}$)–Cd–N(2)	88.0(3)		

Roman numeral superscripts denote the following equivalent positions relative to the reference molecule at x,y,z:

I	$-x, -y, -z$	IV	$\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$
II	$x, y, 1 + z$	V	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$
III	$x, y, -1 + z$		

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