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## The Crystal Structure of Lead(II) Thiocyanate

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The title compound has four  $\text{Pb}(\text{NCS})_2$  units in a cell with  $a=9.661$ ,  $b=6.544$ ,  $c=8.253$  Å and  $\beta=92.37^\circ$ , belonging to the space group  $C2/c$ . The structure has been refined to  $R=4.7\%$  for 974 Mo data. The lead atom lies on a twofold axis and is environed by four nitrogen and four sulphur atoms. The NCS unit has  $\text{N}-\text{C}=1.172$  (10),  $\text{C}-\text{S}=1.639$  (8) Å, and  $\text{N}-\text{C}-\text{S}=178.6$  (8)°; it makes contacts with four Pb atoms via two  $\text{Pb}-\text{N}$  [2.687 (7), 2.781 (7) Å] and two  $\text{Pb}-\text{S}$  [2.996 (2), 3.135 (2) Å] bonds.

### Introduction

Some years ago we reported (Mokuolu & Speakman, 1966) the crystal structure of lead thiocyanate. The results were of low accuracy, as they were based on limited data with copper radiation, and only crudely corrected for absorption which was high. We now report a more precise determination.

### Experimental

Lead thiocyanate was prepared by a standard method. Good crystals are easily grown by slowly cooling a saturated solution in hot water. They develop a yellowish cast and are said to be sensitive to light, but they seem to be very stable to X-rays. The counts from standard reflexions did not change significantly over long periods. The following crystal data were established from diffractometer measurements with Mo  $K\alpha$  radiation ( $\lambda=0.71069$  Å):  $\text{Pb}(\text{NCS})_2$ ,  $M=323.4$ , monoclinic,  $a=9.661 \pm 0.004$ ,  $b=6.544 \pm 0.003$ ,  $c=8.253 \pm 0.003$  Å,  $\beta=92.37 \pm 0.02^\circ$ ,  $U=521.3$  Å<sup>3</sup>,  $Z=4$ ,  $D_m=4.082$  g cm<sup>-3</sup> [Huttner & Knappe, 1930; the value of 3.82 cited in Groth (1908) originated from Schabus (1850)],  $D_c=4.12$  g cm<sup>-3</sup>, absorption coefficient (Mo  $K\alpha$ )  $\mu=316$  cm<sup>-1</sup>. Space group  $C2/c$  or  $Cc$ : absences,  $hkl$  when  $h+k$  odd;  $h0l$  when either  $h$  or  $l$  odd;  $0k0$  when  $k$  odd. The former (No. 15) was

adopted because the goniometric evidence indicates the point group  $2/m$ , and the choice was vindicated by the analysis. The lead atom must lie in a special position, and the two thiocyanate groups are equivalent.

Operation of the transformation matrix  $0, 0, -\frac{1}{2}/0, 1, 0/-1, 0, \frac{1}{2}$  converts the cell defined above to one with  $a'=4.1265$ ,  $b'=6.544$ ,  $c'=10.661$  Å,  $\beta'=115.12^\circ$ . The agreement between the ratios corresponding to this pseudo-cell and those given by Groth is impressive evidence of the accuracy of the goniometric method when applied to good crystals:

Goniometric	0.6310:	1:	1.6288;	$115^\circ 6\frac{1}{2}'$
Diffractometer	0.6306:	1:	1.6291;	$115^\circ 7'$

Intensities were measured on a Hilger-Watts four-circle diffractometer, with a graphite monochromator and Mo  $K\alpha$  radiation, the  $\omega-2\theta$  scan being used. The crystal had dimensions  $0.21 \times 0.11 \times 0.25$  mm and was mounted about  $[1\bar{1}0]$ . To apply absorption corrections (by *ABSORB* from the University of Maryland's X-RAY 72 System), the shape of this crystal was defined by 13 faces, each with its normal distance from a point near the centre. Transmission factors for intensities ranged from 0.025 to 0.100. Two sets of data were collected: (I) with  $\theta$  out to  $25^\circ$ , and (II) from  $25$  to  $34^\circ$ . The other usual corrections were applied and standard deviations assessed by the formula,  $\sigma^2(I)=C+(T_p/T_B)^2(B_1+B_2)+0.04 I^2$ , where  $I$  is the derived intensity,  $C$  the integrated peak count over time  $T_p$ , and  $B_1, B_2$  are the two background counts over time  $T_B$ .

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Refinement

Refinement started from our earlier parameters (1966), and was by the full-matrix least-squares program *CRYLSQ* of X-RAY 72, with weights based on  $\sigma(I)$ . Scattering functions were from *International Tables for X-ray Crystallography* (1962), allowance being made for dispersion at the lead atom. Initially work was restricted to the 456 of the 490 independent reflexions covered in set I for which  $I > 2\sigma(I)$ . Anisotropic vibration was allowed only for the lead and sulphur atoms, and convergence was at  $R=6.3\%$ .

Table 1 (cont.)

Table 1. Structure factors,  $F_o$  and  $10 \times F_c$

Table 1 (cont.) showing structure factors and differences. Includes columns for h, k, l, F\_o, and F\_c. The table is split into multiple sections for different reflections.

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Set II consisted of 636 independent reflexions, of which 32 were rejected because  $I < 2\sigma(I)$  or for other reasons. Refinement with set II yielded not only a lower R value (4.4%), but also standard deviations roughly half those from set I. This difference was attributed to errors, notably extinction, associated with low-order terms. Accordingly all terms (about 50) with  $\sin \theta < 0.22$  ( $\theta < 12.7^\circ$ ) were excluded from set I, as well as a few from set II which had both  $|F_o|$  and  $|F_c|$  nearly zero, and the remaining terms were combined. The resulting compacted set I/II, of 974 terms, was used in the final stages of refinement. At a late stage two least-squares cycles were performed with anisotropic vibrational parameters for carbon and nitrogen, as well as sulphur, but with all 9 parameters for lead held invariant. Subsequently the resulting anisotropic parameters for carbon and nitrogen were used in structure-factor calculations, but not refined further. At convergence  $R=4.7\%$ ,  $R_w = \sqrt{(\sum w\Delta^2 / \sum w|F_o|^2)} = 5.4\%$ , and the standard deviation of an observation of unit weight was 2.54. Structure factors for a rather fuller set of 1035 data are given in Table 1. For this set  $R=5.9\%$  and  $R_w=6.1\%$ . Table 2 carries a weighting analysis, whilst Table 3 lists coordinates and vibrational parameters. An electron-density 'difference' synthesis after convergence showed only three features of significance: these were 'peaks' with maximum densities of  $-5.5$ ,  $-5.7$  and  $+5.2 \text{ e } \text{\AA}^{-3}$ , all within 1 Å of the position of the lead atom. We attribute them to imperfections in our absorption correction, not to imperfections in our absorption correction, but to imperfections compounded by errors in scaling. We do not consider them to be of chemical significance.

Table 2. *Weighting-scheme analysis* ( $N$ =numbers of terms in group)

$ F_o $	$N$	$\langle w\Delta^2 \rangle$	$R$ (%)
0-20	77	11.8	30.0
20-40	139	5.6	6.3
40-60	188	3.7	3.6
60-80	201	5.5	3.6
80-100	129	6.4	3.7
100-125	117	5.7	4.0
125-180	106	8.0	4.9
180-320	17	13.5	7.1
sin $\theta$			
0.00-0.22	0	-	-
0.22-0.27	52	14.2	6.6
0.27-0.31	61	9.7	5.7
0.31-0.34	59	6.7	4.6
0.34-0.37	68	6.1	4.5
0.37-0.39	50	5.1	4.2
0.39-0.41	56	4.8	4.4
0.41-0.43	54	6.3	4.2
0.43-0.45	81	6.9	4.0
0.45-0.47	76	6.1	4.3
0.47-0.49	82	4.9	4.1
0.49-0.51	98	4.8	4.1
0.51-0.53	94	5.4	4.5
0.53-0.59	143	5.0	4.8

A second crystal of more nearly spherical shape was also used to collect a third set of intensity data, which were roughly corrected for absorption on the assumption that the crystal was strictly spherical. After refinement to  $R=8.2\%$ , none of the chemical results – though they were of lower precision – differed significantly from those in Tables 3 and 4.

### Results

As the crystal-chemical unit (CCU) consists of only one atom of each type, no arabic numbers are needed. To distinguish between different symmetry-related units, the following roman numerals are used:

CCU	$x$	$y$	$z$	V	$x$	$-y$	$\frac{1}{2}+z$
I	$x$	$1+y$	$z$	VI	$1-x$	$-1+y$	$\frac{1}{2}-z$
II	$1-x$	$-y$	$-z$	VII	$1-x$	$y$	$\frac{1}{2}-z$
III	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	VIII	$\frac{1}{2}+x$	$-\frac{1}{2}+y$	$z$
IV	$x$	$-1+y$	$z$	IX	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$

The lead atom lies on a twofold axis. It is environed – as is shown in the stereo picture of Fig. 1 – by four nitrogen and four sulphur atoms belonging to eight different thiocyanate groups. The thiocyanate unit is coordinated to two lead atoms through its nitrogen atom, and to two others through its sulphur atoms.

Table 3. *Fractional coordinates* ( $\times 10^5$ ) and *mean-square vibrational amplitudes* ( $\text{\AA}^2, \times 10^4$ ) with standard deviations in parentheses

	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Pb	50000	-38813 (5)	25000	194 (3)	136 (3)	173 (3)	0	4 (1)	0
N	44260 (71)	27512 (107)	5293 (83)	191 (29)	201 (30)	201 (28)	-46 (24)	7 (22)	46 (24)
C	38176 (80)	13498 (101)	10249 (93)	201 (29)	121 (24)	207 (29)	5 (21)	-23 (22)	8 (21)
S	29328 (21)	-5766 (35)	17180 (32)	181 (8)	181 (8)	464 (12)	39 (6)	74 (7)	132 (8)

Table 4. *Interatomic distances* ( $\text{\AA}$ ) and *angles* ( $^\circ$ ), with standard deviations in parentheses

Pb-S	2.996 (2)	Pb-N <sup>II</sup>	2.687 (7)
Pb-S	3.135 (2)	Pb-N <sup>IV</sup>	2.781 (7)
Angles round Pb			
N <sup>II</sup> ...N <sup>V</sup>	148.0 (2)	N <sup>IV</sup> ...N <sup>V</sup>	135.9 (2)
N <sup>II</sup> ...N <sup>IV</sup>	73.6 (2)	N <sup>IV</sup> ...N <sup>VI</sup>	75.2 (3)
S...S <sup>VII</sup>	87.58 (10)	S...S <sup>IX</sup>	72.52 (7)
S...S <sup>VIII</sup>	144.22 (6)	S <sup>VIII</sup> ...S <sup>IX</sup>	138.55 (10)
N <sup>IV</sup> ...S	109.3 (2)	N <sup>IV</sup> ...S <sup>VIII</sup>	76.1 (2)
N <sup>IV</sup> ...S <sup>VII</sup>	144.4 (1)	N <sup>IV</sup> ...S <sup>IX</sup>	71.3 (2)
N <sup>V</sup> ...S	80.8 (2)	N <sup>V</sup> ...S <sup>VII</sup>	76.2 (2)
N <sup>V</sup> ...S <sup>VIII</sup>	120.8 (2)	N <sup>V</sup> ...S <sup>IX</sup>	71.5 (2)
N-C	1.172 (10)	N-C-S	178.6 (8)
C-S	1.639 (8)	C-S-Pb <sup>I</sup>	106.1 (3)
C-N-Pb <sup>I</sup>	120.4 (6)	C-S-Pb <sup>III</sup>	106.8 (3)
C-N-Pb <sup>II</sup>	131.8 (6)	Pb-S-Pb <sup>III</sup>	144.2 (1)
Pb <sup>I</sup> -N-Pb <sup>II</sup>	106.4 (2)	(Sum	357.1)
(Sum	358.6)		

Details are shown in Fig. 2. Relevant geometrical results are listed in Table 4.

### Discussion

The Pb-S and Pb-N distances all exceed the sums of the Pauling covalent radii,\* 2.62 and 2.28 Å respectively. Therefore these contacts may not have much covalent character; they are rather ionic than covalent, even possibly van der Waals contacts in the case of Pb...S. A corresponding difference in the 'hardness'

\* We take the radius of Pb(II) as 1.58 Å (Pauling, 1966).

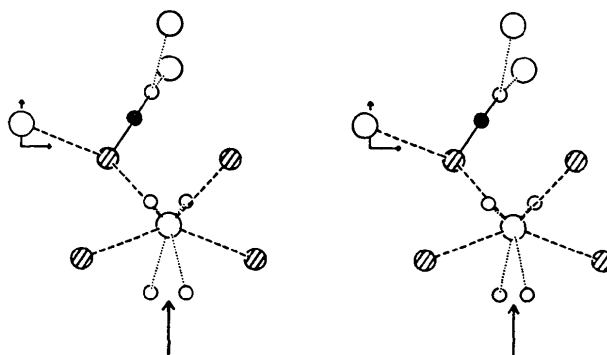


Fig. 1. Stereoscopic view of the crystal structure of  $\text{Pb}(\text{NCS})_2$ . The largest circles represent Pb atoms, the hatched circles S, and the filled circles C. The directions of  $a$  and  $b$  axes are indicated.

of the sulphur and nitrogen atoms is suggested by the vibrational parameters. The centre of mass of the linear NCS ion lies between the sulphur and carbon

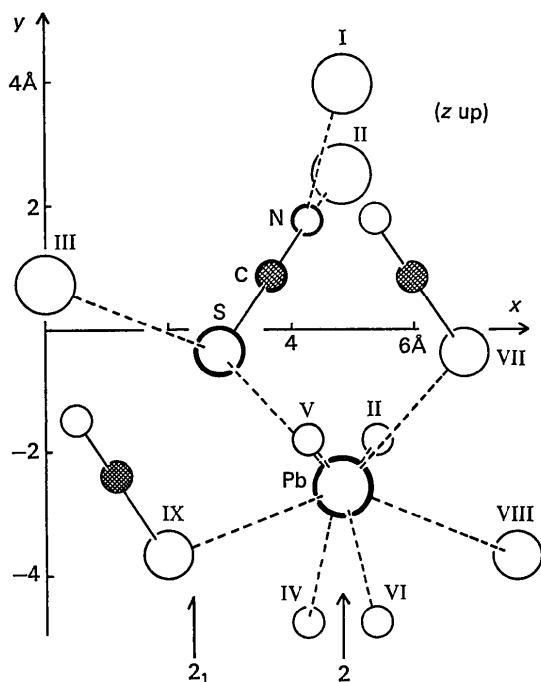


Fig. 2. The main features of the structure of  $\text{Pb}(\text{NCS})_2$ . The four atoms of the crystal-chemical unit (CCU) are represented by thicker circles; other symmetry-related units are denoted by roman numerals according to a code explained in the text.

atoms, about 1.0 Å from the former. If the ion were unconstrained, or nearly equally constrained at each end, it would be expected to rotate, or librate, about this point. Any motion would be about twice as great as the nitrogen as at sulphur. The parameters of Table 3 tell a different story. The r.m.s. amplitude at the nitrogen atom is about 0.14 Å and not far from isotropic. At sulphur, the vibration is highly anisotropic, and has a maximum amplitude of 0.23 Å, in a direction which makes angles of about 80, 68 and 25° respectively with the positive directions of  $a$ ,  $b$  and  $c$ . It is not far from perpendicular to the plane of the  $\text{Pb} \cdots \text{S} \cdots \text{Pb}^{\text{III}}$  triangle marked in Fig. 2.

The bonding of the metal atom in mercury(II) thiocyanate (Beauchamp *et al.*, 1972) is in sharp contrast to that just described:  $\text{Hg}-\text{S}=2.381(6)$  and  $\text{Hg} \cdots \text{N}=2.81(1)$  Å. The sums of the covalent radii are  $\sim 2.48$  and 1.78 Å, respectively. The former bond is thus strong, with high covalent character, whilst the latter is extremely weak.

A comparable, though very different, crystal structure is that of the lead thiocyanate complex studied by Metz & Weiss (1973). Here too the space group is  $C2/c$ , and the lead atom lies on a twofold axis, but six contacts from lead to the ligand are nearly coplanar and in a great circle parallel to the axis. Nearly perpendicular to this circle, on either side, are the two contacts to thiocyanate ions. These are to the sulphur atoms, the nitrogen atoms being free. However, the sulphur atoms again have a large (and maximum) vibrational amplitude roughly at right angles to  $\text{Pb} \cdots \text{S}$ , which has a length of 2.894(3) Å. Hagihara, Yoshida & Watanabe (1969) have reported  $\text{Pb} \cdots \text{S}$  distances of 2.722(19), 2.833(18), 2.896(13) and

Table 5. Comparison of bond lengths (Å) and angles (°) in NCS units

(The numbers shown in parentheses are estimated standard deviations, except in the first case, for which see the text.)

Compound (Average of 25)	1.20 (6)	1.64 (7)	-	Reference
Ni complex	1.19 (3)	1.62 (3)	180	{ Ferrari <i>et al.</i> (1965) Farago & James (1965) Rasmussen (1959)
Cu complex				
NCS bonded	1.142 (7)	1.612 (5)	177.4 (5)	Jain & Lingafelter (1967)
NCS not bonded	1.168 (7)	1.624 (5)	178.4 (5)	
Zn complex				Andreotti <i>et al.</i> (1969)
NCS bonded	1.135 (7)	1.644 (5)	178.5 (5)	
NCS not bonded	1.140 (12)	1.625 (8)	176.1 (8)	
KNCS	1.149 (14)	1.689 (13)	178.3 (12)	Akers <i>et al.</i> (1968)
$\text{NH}_4\text{NCS}$	1.15	1.63	180	Zavodnik <i>et al.</i> (1972)
$\text{CH}_2(\text{NCS})_2$	1.194 (12)	1.677 (9)	176.4 (10)	Konnert & Britton (1971)
Thiourea adduct	1.142 (17)	1.588 (13)	174.1 (10)	Eriksen & Hauge (1972)
$\text{Hg}(\text{NCS})_2$	1.18 (3)	1.62 (2)	177.5 (13)	Beauchamp & Goutier (1972)
Zn complex	1.151 (6)	1.623 (5)	178.9 (6)	Bigoli <i>et al.</i> (1973)
Pb complex	1.141 (10)	1.581 (10)	178.1 (5)	Metz & Weiss (1973)
$\text{Pb}(\text{NCS})_2$	1.172 (10)	1.639 (8)	178.9 (7)	Present work

Sums of covalent radii

N=C	1.29	S-C( $sp^3$ )	1.81	} Pauling (1966)
N≡C	1.15	S-C( $sp$ )	1.75	
		S=C	1.61	

3.057 (16) Å in an isopropylxanthate-pyridine complex.

The geometry of the thiocyanate, or isothiocyanate, residue has attracted attention. Ferrari, Braibanti, Bigliardi & Lanfredi (1965) have tabulated results from 21 studies covering a wide range of compounds containing NCS units, which were found to be linear or nearly so. Four other studies are amongst those listed by Farago & James (1965). Though many of these are based on early work of low precision, we include average bond lengths in Table 5, along with some more recent individual results, for comparison with our own findings. (For the averaged values the figures in parentheses are indications of scatter rather than true measures of precision.)

The most obvious conclusion to be drawn from this table is that the NCS unit is remarkably invariant, and therefore remarkably stable. Whether it be ionically or covalently coordinated, and bonded at nitrogen or sulphur, or at both, its N-C and C-S distances show little evidence of significant variation. The N-C-S angle deviates only a little from linearity. The simple bond diagram  $[:N\equiv C-\ddot{S}:]^-$  is the best conventional representation, though the unconventional  $N\equiv C=S$  would be better.

The infrared spectrum may be more sensitive to small changes in the bonds at, and within the NCS unit (Nelson & Shepherd, 1965; Raymond & Basolo, 1966). The spectrum of lead thiocyanate in a potassium bromide disc (with which, however, it appears to react slowly) showed a strong peak at about  $2055\text{ cm}^{-1}$  and a weaker one at about  $750\text{ cm}^{-1}$ . But according to the information collected by Ross (1972), the interpretation of the spectra of thiocyanates may not be simple.

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