

Les auteurs remercient Messieurs les Professeurs H. Brasseur et J. Toussaint pour l'intérêt qu'ils ont porté à ce travail, ainsi que Monsieur M. Vermeire pour la sélection et la préparation de l'échantillon.

#### Références

- AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1966). NRC Crystallographic programs for the IBM 360 system. National Research Council, Ottawa, Canada.
- BONAMARTINI, A., NARDELLI, M., PALMIERI, C. & PELIZZI, C. (1971). *Acta Cryst.* B27, 1775–1779.
- BONAMICO, M., DESSY, G. & VACIAGO, A. (1967). *Théor. Chim. Acta*, 7, 367–374.
- CRUICKSHANK, D. W. J. (1961). In *Computing Methods and the Phase Problem*. Edited by R. PEPINSKY, J. M. ROBERTSON & J. C. SPEAKMAN. Oxford: Pergamon Press.
- GENET, F. (1965). *Bull. Soc. Fr. Minér. Crist.* 88, 463–482.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.
- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* 17, 1040–1044.
- HELMHOLTZ, L. & KRUEH, R. F. (1952). *J. Amer. Chem. Soc.* 74, 1176–1181.
- LAMOTTE-BRASSEUR, J. (1972). *Bull. Soc. Roy. Sci. Liège*, 41, 337–340.
- MOROSIN, B. & LINGAFELTER, E. C. (1961). *J. Phys. Chem.* 65, 50–51.
- REMY, H. & LAVES, G. (1933). *Ber. dtsh. chem. Ges.* 66, 401–407.
- RUSSELL, J. H. & WALLWORK, S. C. (1969). *Acta Cryst.* B25, 1691–1695.
- STEADMAN, J. P. & WILLETT, R. D. (1970). *Inorg. Chem. Acta*, 4, 367–371.
- WILLETT, R. D. (1964). *J. Chem. Phys.* 41, 2243–2244.

*Acta Cryst.* (1973). B29, 246

## Thiourea Coordination Complexes of Pb(II) Salts. IV.\* Irregular Coordination in Bis(thiourea)lead(II) Formate Monohydrate $Pb(HCOO)_2 \cdot [SC(NH_2)_2]_2 \cdot H_2O$

BY ILAN GOLDBERG† AND F. H. HERBSTEIN

*Department of Chemistry, Technion, Israel Institute of Technology, Haifa, Israel*

(Received 2 September 1972; accepted 4 September 1972)

$Pb(HCOO)_2 \cdot 2tu \cdot H_2O$  (tu = thiourea) is triclinic with  $a = 12.58$  (2),  $b = 8.91$  (2),  $c = 5.94$  (3) Å,  $\alpha = 90^\circ 40'$  (30'),  $\beta = 106^\circ 10'$  (30'),  $\gamma = 98^\circ 25'$  (20'), space group  $P\bar{1}$ ,  $Z = 2$ . The structure was solved by Patterson and Fourier methods (using intensities visually estimated from Weissenberg photographs) and refined to  $R = 15.2\%$  by least-squares calculations. The first coordination sphere of  $Pb^{2+}$  has three sulphur atoms and five oxygen atoms in a distorted dodecahedral arrangement. The structure can be described in terms of two parallel  $\cdots S \cdots Pb \cdots S \cdots$  chains extended along [001], with each pair of centrosymmetrically related lead ions bridged by two similarly related formate ions. The sulphur atoms of the thiourea molecules in the chains are bicoordinate, while the bridging formate ions each have one monocoordinate and one bicoordinate oxygen atom. The remaining water molecule, thiourea molecule and formate ion of the formula unit are monocoordinately bonded to the same lead ion. The bonding within the chains is by ion–dipole forces, while the bonding between chains is by a fairly isotropic distribution of hydrogen bonds and by electrostatic interactions.

### Introduction

During the study of  $\frac{3}{2}Pb(HCOO)_2 \cdot 4tu$  (tu = thiourea) (Goldberg & Herbstein, 1972b), large colourless triclinic rhombs were obtained from mother liquors that had been left to stand. A chemical analysis indicated that the composition of the rhombs was  $Pb(HCOO)_2 \cdot 2tu \cdot H_2O$ : measured and calculated weight percentages were C = 10.64, 10.28; H 2.50, 2.56; N 12.40, 11.98; O 17.47, 17.11; Pb 44.30, 44.35; S 9.71, 13.72; total 97.12, 100.00. As compounds of this type had not been investigated previously, it was decided to determine the crystal structure of the title compound. The proposed composition was confirmed and a rather complicated crystal structure found.

\* Part III: Goldberg & Herbstein (1972b).

† In part fulfilment of the requirements for M.Sc. degree in Chemistry.

### Experimental

Unit-cell dimensions were measured from Weissenberg [ $\lambda(Cu K\alpha) = 1.5418$  Å] and precession [ $\lambda(Mo K\alpha) = 0.7107$  Å] photographs.

#### Crystallographic results

$Pb(HCOO)_2 \cdot [SC(NH_2)_2]_2 \cdot H_2O$ ,  $M = 467.4$ ;  
 $\mu = 287$  cm<sup>-1</sup> (Cu K $\alpha$ ); triclinic;  
 $a = 12.58$  (2),  $b = 8.91$  (2),  $c = 5.94$  (3) Å,  
 $\alpha = 90^\circ 40'$  (30'),  $\beta = 106^\circ 10'$  (30'),  $\gamma = 98^\circ 25'$  (20');  
 $a^* = 0.08383$  (10),  $b^* = 0.1137$  (1),  $c^* = 0.1756$  (1) Å<sup>-1</sup>;  
 $\alpha^* = 86.8$  (5)°,  $\beta^* = 75.5$  (5)°,  $\gamma^* = 81.0$  (5)°.  
 $U = 631.4$  Å<sup>3</sup>;  
 $D_m = 2.47$  (1) g. cm<sup>-3</sup>,  $D_x = 2.46$  (1) g. cm<sup>-3</sup> for  $Z = 2$ .

No systematic absences, hence space group  $P1$  (No. 1) or  $P\bar{1}$  (No. 2).

The intensities of 1686  $hkl$  ( $l=0, 1, 2, 3$ ) reflexions were measured by the visual method from multiple-film equi-inclination Weissenberg photographs ( $\text{Cu } K\alpha$ ). Corrections were made for geometrical factors (Lp, spot-shape) and absorption (cylindrical crystal approximation;  $\mu R=3.8$  for the crystal used). Different layers were put on approximately the same scale by use of precession photographs ( $\text{Mo } K\alpha$ ).

### Determination and refinement of the structure

A three-dimensional Patterson synthesis showed a strong peak at (0.288, 0.402, 0.120). This was identified as being due to the vector between two Pb atoms related by a centre of symmetry, assuming the space group to be  $P\bar{1}$ . Encouraging agreement was obtained between the observed structure factors and those calculated for the Pb atoms alone. The positions of the other atoms were found from a series of electron-density and difference syntheses. Confirmation of the chemical composition was obtained from a difference synthesis based on structure factors calculated from the positions of the Pb and S atoms only ( $R=20\%$ ).

All C, N, O, atoms required by the postulated formula appeared as peaks of height  $5-7 \text{ e.}\text{\AA}^{-3}$  while the larger remaining peaks did not exceed  $2 \text{ e.}\text{\AA}^{-3}$  (no attempt was made to identify hydrogen atoms which were not included at any stage of this analysis). Introduction of all atoms into the structure-factor calculations gave  $R=15.3\%$ ,  $R_2=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}=4.34\%$ . After three cycles of full-matrix least-squares refinement convergence was reached at  $R=15.2\%$ ,  $R_2=3.95\%$ . The goodness of fit was 1.65. Shifts from the positions derived from the difference synthesis were negligible for Pb and S atoms but as large as  $0.18 \text{ \AA}$  for the  $z$  coordinates of some light atoms. Inspection of the structure-factor table (Table 2\*) showed that there were no serious individual discrepancies and it seems that the rather large value of  $R$  is due partly to measurement errors in the strong reflexions and partly to inadequate absorption corrections. Atomic parameters are listed in Table 1. The approximate e.s.d.'s of

\* Deposited with National Lending Library for Science and Technology, Boston Spa, England as Supplementary Publication No. SUP 30016. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

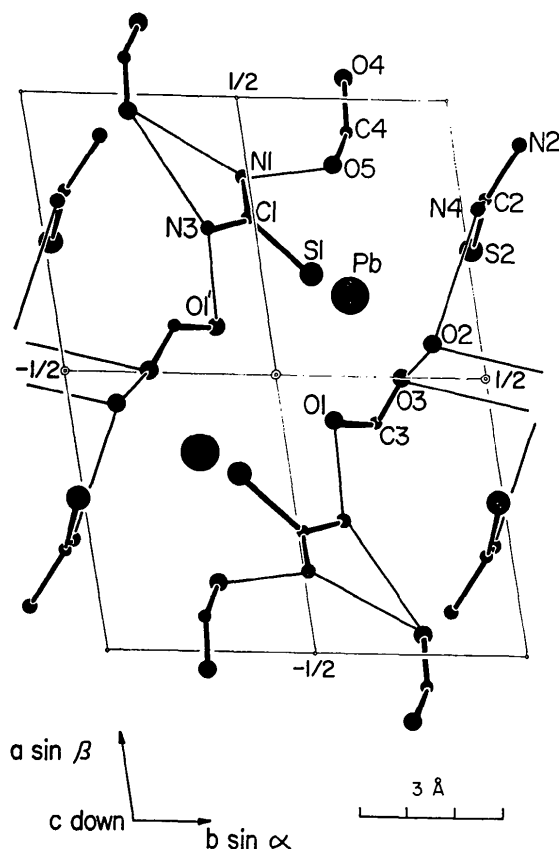


Fig. 1. Projection on (001). The origin of the coordinate system is at the centre of the diagram; the view is down the axis of the double chain referred to in the text. Some, but not all, of the close approaches to neighbouring chains are shown. The atoms numbered are those listed in Table 1.

Table 1. Fractional atomic coordinates, Debye-Waller factors, and their e.s.d.'s (in parentheses)

Isotropic Debye-Waller factor  $T=\exp(-8\pi^2 U' \sin^2 \theta / \lambda^2)$ .

	$x/a$	$y/b$	$z/c$	$U'(\text{\AA})^2$
Pb	0.1436 (1)	0.2059 (1)	0.0599 (3)	*
Formate ion				
O(1)	-0.084 (2)	0.124 (3)	-0.018 (7)	0.034 (7)
C(3)	-0.085 (2)	0.223 (3)	0.149 (9)	0.016 (7)
O(3)	-0.004 (3)	0.300 (4)	0.234 (6)	0.024 (6)
Formate ion				
O(4)	0.533 (2)	0.262 (3)	0.366 (7)	0.027 (6)
C(4)	0.438 (3)	0.251 (5)	0.317 (11)	0.039 (10)
O(5)	0.376 (2)	0.207 (3)	0.119 (7)	0.032 (7)
Water molecule				
O(2)	0.058 (3)	0.387 (4)	-0.288 (8)	0.033 (7)
Thiourea molecule				
S(1)	0.181 (1)	0.120 (1)	0.548 (3)	*
C(1)	0.281 (2)	-0.011 (3)	0.570 (8)	0.011 (6)
N(1)	0.353 (3)	-0.012 (4)	0.759 (9)	0.037 (9)
N(3)	0.260 (3)	-0.112 (4)	0.420 (9)	0.034 (8)
Thiourea molecule				
S(2)	0.229 (1)	0.511 (1)	0.225 (3)	*
C(2)	0.321 (3)	0.559 (4)	0.031 (12)	0.027 (9)
N(2)	0.423 (4)	0.663 (5)	0.108 (11)	0.051 (11)
N(4)	0.302 (3)	0.539 (4)	-0.161 (11)	0.040 (9)

\* The anisotropic Debye-Waller factors and their e.s.d.'s are in units of  $\text{\AA}^2$  and have the form

$$T = \exp \left( -2\pi^2 \sum_{i=1}^3 \sum_{j=1}^3 U'_{ij} h_i h_j a_i^* a_j^* \right)$$

where  $U'_{ij}$  are the coefficients of the (symmetric) atomic Debye-Waller tensor and  $a_i^*$  are the reciprocal lattice parameters.

Table 1 (cont.)

	$U_{11}$	$U_{22}$	$U_{33}^\dagger$	$U_{12}$	$U_{13}$	$U_{23}$
Pb	0.0103 (7)	0.0148 (7)	-0.0166 (129)	-0.0021 (5)	0.0043 (7)	0.0017 (7)
S(1)	0.033 (4)	0.034 (4)	0.019 (19)	0.017 (3)	0.011 (5)	0.023 (5)
S(2)	0.023 (4)	0.021 (4)	0.005 (18)	-0.008 (3)	0.008 (4)	0.003 (4)

† The absolute values of  $U_{33}$  are in doubt because the inter-layer scale factors were not measured sufficiently accurately (Lingafelter & Donohue, 1966). No physical significance is to be ascribed to the negative value of  $U_{33}$  of Pb.

the atoms are,  $Pb = \sigma(x) \sim \sigma(y) \sim 0.001 \text{ \AA}$ ,  $\sigma(z) \sim 0.002 \text{ \AA}$ ;  $S = \sigma(x) \sim \sigma(y) \sim 0.01 \text{ \AA}$ ,  $\sigma(z) \sim 0.02 \text{ \AA}$ ; C, N,  $O = \sigma(x) \sim \sigma(y) \sim 0.03\text{--}0.07 \text{ \AA}$ ,  $\sigma(z) \sim 0.04\text{--}0.08 \text{ \AA}$ . The Debye-Waller factors cannot have much physical significance.

Computing procedures have been described in part I (Goldberg & Herbstein, 1972a); the weighting scheme used here was, however,  $w(hkl) = 1/|F_o|$  for  $|F_o| \geq 12$ ,  $w(hkl) = 12$  for  $|F_o| < 12$ .

### Description of the structure

The arrangement of the structural units ( $Pb^{2+}$  ions,  $HCOO^-$  ions, thiourea and water molecules) in the unit cell is shown in Fig. 1 [projection on (001)] and in Fig. 2 [projection on (010)] while important interatomic distances and angles are collected in Table 3 (the first coordination sphere about  $Pb^{2+}$ ) and Table 4 (distances between different structural units).

The first coordination sphere around  $Pb^{2+}$  contains eight atoms: three sulphur atoms from thiourea molecules [S(1), S(2), S(1'), shifted by  $-c$  from S(1)], four oxygen atoms from formate ions, [two of these from one formate ion, O(1) and O(3), and the other two from different formate ions, O(1') and O(5)], and one oxygen from a water molecule, O(2). These atoms are at the vertices of a distorted dodecahedron (Fig. 3), a coordination polyhedron often found among eight-coordinate species (Lippard, 1967). An elongated bisphenoid and a compressed bisphenoid are indeed found here as in a regular dodecahedron but edges that would be equal in a regular dodecahedron are far from equality here. These distortions must arise, at least in part, from the different radii of sulphur and oxygen atoms and from the geometrical constraints imposed by the bidentate nature of one formate ion.

Further description of the structure should be based on the stronger inter-unit interactions, with weaker interactions receiving secondary consideration. However, to the extent that interatomic distances give a measure of strength of interaction, the interactions between the different units appear to be roughly equally strong in different directions. This is what would be expected of ion-dipole interactions without covalent bonding. We have based our present description on primacy for  $Pb^{2+} \cdots S$  interactions, then  $Pb^{2+} \cdots O$  interactions and finally hydrogen bonding, but emphasize that other rankings are possible. The description of the structure would require appropriate modification if one of these was shown to be preferable.

The two thiourea molecules per formula unit fill different structural roles. One is bonded [through S(2)] to a single  $Pb^{2+}$  ion, with  $Pb \cdots S(2) = 2.83 (2) \text{ \AA}$  and  $\angle Pb-S(2)-C(2) = 99 (3)^\circ$ . The second thiourea molecule bridges [through S(1)] the two  $Pb^{2+}$  ions separated by translation along [001] [ $Pb \cdots S(1) = 2.93 (2) \text{ \AA}$  and  $S(1) \cdots Pb' = 3.30 (2) \text{ \AA}$ ]. The bond angles are  $Pb-S(1)-C(1) = 102 (2)$  and  $Pb'-S(1)-C(1) = 113 (3)^\circ$  and thus both  $Pb \cdots S$  distances and  $Pb-S-C$  angles differ significantly. The  $Pb^{2+}$  ion and one of the

thiourea molecules  $\left[ S(1)-C(1) \begin{matrix} \leftarrow N(1) \\ \leftarrow N(3) \end{matrix} \right]$  of the asymmetric unit constitute the repeat unit of an infinite chain along [001]. A second, parallel chain is related to the first chain by the centres of symmetry at the origins of the unit cells. The lead ions of these two chains (here Pb and Pb'' related by the centre of symmetry at the origin) are each bridged by two formate ions, each of which has one of its oxygen atoms bonded monocoordinately to one lead ion [ $Pb-O(3) = Pb''-O(3') = 2.59 (4) \text{ \AA}$ ] and its second oxygen atom bonded bicoordinately to Pb and Pb'' [ $Pb-O(1) = Pb''-O(1') =$

Table 3. Distances  $X \cdots Y$  and  $X-Pb-Y$  angles for atoms in the first coordination sphere about  $Pb^{2+}$ 

		Distances $X \cdots Y$ (Å)							
		Y→							
		First bridging formate		Second bridging formate		Mono-coordinate formate		Water	
X	Pb	S(1)	S(1')	S(2)	O(3)	O(1)	O(1')	O(5)	O(2)
		2.93	3.30	2.83	2.59	2.75	2.91	2.84	2.72
Angles	S(1)		5.94	4.04	3.19	4.02	3.61	4.01	5.45
$X-Pb-Y$ (°)	S(1')	144		5.14	5.55	4.75	3.91	3.59	3.30
	S(2)	89	114		3.26	4.71	5.69	3.64	3.27
	O(3)	70	140	74		2.09	4.36	5.19	3.47
	O(1)	90	103	115	46		3.24	5.55	3.42
	O(1')	76	78	165	105	70		4.25	4.94
	O(5)	88	71	80	146	165	95		4.58
	O(2)	150	66	72	82	77	123	111	

2.75 (4) Å;  $\text{Pb}-\text{O}(1')=\text{Pb}''-\text{O}(1)=2.94$  (4) Å]. Thus these two formate ions are both bidentate, one with respect to Pb and the other with respect to  $\text{Pb}''$ , and

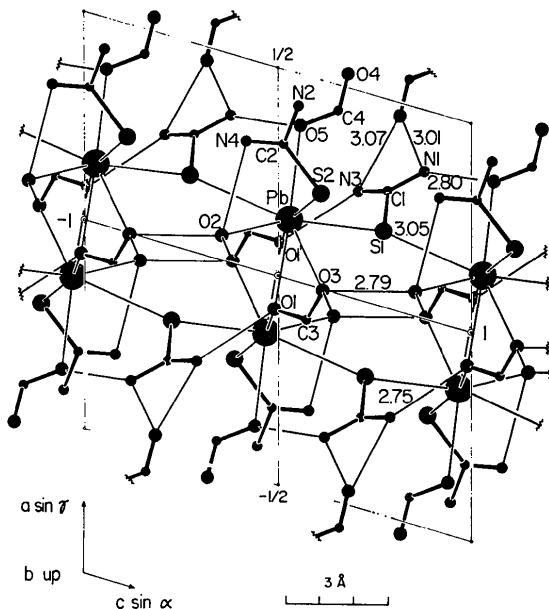


Fig. 2. Projection on (010). The double chain referred to in the text runs parallel to  $c \sin \alpha$ . Some, but not all, of the close approaches to neighbouring chains are shown.

they form a pair of bridges between Pb and  $\text{Pb}''$ . The second formate group of the asymmetric unit has one bond to Pb [ $\text{Pb}\cdots\text{O}(5)=2.84$  (4) Å] while O(5) is definitely and O(4) possibly hydrogen-bonded to  $\text{NH}_2$  groups of thiourea molecules (Table 4). The oxygen of the water molecule has a bond to Pb [ $\text{Pb}\cdots\text{O}(2)=2.75$  (4) Å], and forms hydrogen bonds to bidentate formate groups and, perhaps, to thiourea molecules. Thus the double chains on which the present description of the structure is based are hydrogen-bonded to surrounding double chains and a rather densely packed structure results.

The dimensions of the thiourea molecules and the formate ions are compatible with standard values but are not accurate enough to warrant discussion. The  $\text{Pb}\cdots\text{S}$  distances are similar to those found in similar structures; the  $\text{Pb}\cdots\text{O}(3)$  distance of 2.59 Å is rather longer than that [2.45 (2) Å] found in hexakis(anti-pyridine)lead(II) perchlorate (Vijayan & Viswamitra, 1966). It seems clear that hydrogen bonds are formed between  $\text{N}(1)\cdots\text{O}(5)$ ,  $\text{N}(3)\cdots\text{O}(1)$  and  $\text{O}(2)\cdots\text{O}(3)$  (see Table 4 for detailed designations of which atoms are actually involved here), but the nature of the other interactions cannot be clarified without knowledge of hydrogen atom positions. In some instances electrostatic interactions may be important; this is also possible for  $\text{N}(3)\cdots\text{S}(2)$  and  $\text{N}(4)\cdots\text{S}(2)$  where hydrogen bonds seem unlikely.

Some  $\text{O}\cdots\text{S}$  distances of 3.2 Å are also found, but

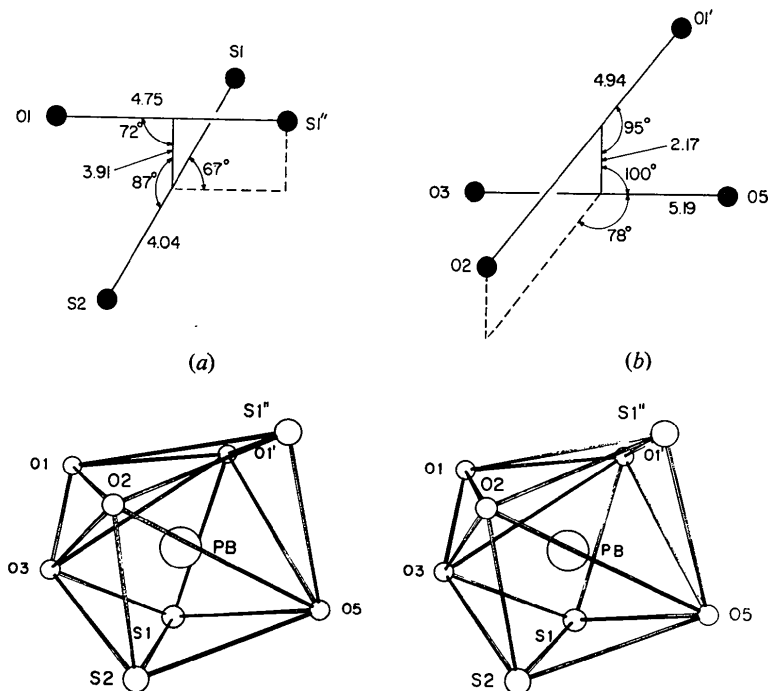


Fig. 3. The first coordination sphere about  $\text{Pb}^{2+}$  shown as a distorted dodecahedron oriented with its approximate fourfold inversion axis vertical [stereodiagrams by *ORTEP* (Johnson, 1965)]. This figure should be compared with the regular dodecahedron shown by Lippard (1967, see Fig. 4 on p. 128). Dimensions of the distorted dodecahedron are in Table 3. A measure of the distortion is given by the unequal edges of the two bisphenoids (elongated, insert (a), A vertices; compressed, insert (b), B vertices) and by the deviations of the angles from the values of  $90^\circ$  found in the undistorted dodecahedron.

Table 4. Distances between atoms in different units of the structure

Parent atom Atom in asymmetric unit 55501	Neighbour atom			Distance (Å)	Angle (°)
	Designation of neighbour atom	Asymmetric unit			
N(1)	O(4)	65602		3.01	C(1)-N(1)···O(4) 99
	O(5)	55601		2.80	C(1)-N(1)···O(5) 120
N(3)	O(1)	55502		2.75	C(1)-N(3)···O(1) 122
	O(4)	65602		3.07	C(1)-N(3)···O(4) 96
	S(2)	54501		3.47	C(1)-N(3)···S(2) 154
N(2)	O(4)	66602		3.07	C(2)-N(2)···O(4) 108
	O(4)	66502		3.08	C(2)-N(2)···O(4) 101
N(4)	O(2)	55501		3.05	C(2)-N(4)···O(2) 101
	O(4)	66502		3.02	C(2)-N(4)···O(4) 112
	S(2)	55401		3.50	C(2)-N(4)···S(2) 174
O(2)	O(3)	55401		2.79	
	O(3)	56502		3.00	

## Notes:

- (1) Designation of the atoms is based on the system used by Johnson (1965). The 'parent' atom is in the asymmetric unit 55501 at  $x, y, z$  (coordinates listed in Table 1). The 'neighbour' atoms are designated as follows:  $xyz, 01; \bar{x}\bar{y}\bar{z}, 02$ ; origin of unit cell is 555 and shifts in  $a, b, c$  directions are denoted by increments in 1st, 2nd, 3rd digits respectively. Only one of the many symmetry-related distances is given in this Table; many of these are shown in Fig. 1.
- (2) The 'parent' atom has been chosen as the hydrogen bond donor [an ambiguity exists for N(4)···O(2)].
- (3) The angle shown is  $X-Y(H)\cdots Z$  where  $Z$  is the neighbour atom designated in columns 2 and 3 of the Table.
- (4) An upper limit of 3.1 Å has been set for N···O and O···O interactions, and of 3.6 Å for N···S interactions.

have not been listed because they are presumably repulsive.

### Discussion

To the best of our knowledge the only similar structure reported is that of mono(thiourea) lead(II) acetate (Nardelli, Fava & Branchi, 1960), where the essential structural unit can be described as consisting of two parallel chains of alternating  $Pb^{2+}$  ions and thiourea groups. There are also weaker  $Pb\cdots S$  bonds between the parallel chains and the sulphur atoms are thus tricoordinate. One carboxyl group has both its oxygen atoms bonded to the same lead ion, whereas the other bridges between two adjacent lead ions through its two oxygen atoms. There is distorted dodecahedral coordination of three sulphur atoms and five oxygens about each  $Pb^{2+}$  ion. Thus both structures have quite complicated arrangements of ionic, ion-dipole and hydrogen-bonding interactions extending in three dimensions.  $Pb\cdots O$  interactions are relatively more important in mono(thiourea) $Pb(II)$  acetate (distances of 2.37, 2.44, 2.62, 2.63 Å) than in the present compound, while  $Pb\cdots S$  interactions are relatively less important (distances of 3.09, 3.45, 3.60 Å). Although both structures have been described in terms

of pairs of parallel chains, the anisotropy of the structures does not appear to be particularly marked and the bonding between different chemical units occurs without marked preference for particular directions; it is not known if this also holds for other physical properties.

We are grateful to Dr Dov Rabinovich (Weizmann Institute) for assistance with computing.

### References

- GOLDBERG, I. & HERBSTEIN, F. H. (1972a). *Acta Cryst.* B28, 400-405.  
 GOLDBERG, I. & HERBSTEIN, F. H. (1972b). *Acta Cryst.* B28, 410-415.  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.  
 LINGAFELTER, E. C. & DONOHUE, J. (1966). *Acta Cryst.* 20, 321.  
 LIPPARD, S. J. (1967). *Progress in Inorganic Chemistry*, Vol. VIII, p. 109.  
 NARDELLI, M., FAVA, G. & BRANCHI, G. (1960). *Acta Cryst.* 13, 898-904.  
 VIJAYAN, M. & VISWAMITRA, M. A. (1966). *Acta Cryst.* 21, 522-532.