Acta Cryst. (1959). **12**, 727

The Crystal Structure of *bis*-Thiourea-Lead(II) Chloride

By Mario Nardelli and Giovanna Fava

Structural Chemistry Laboratory, Institute of Chemistry, University of Parma, Italy

(*Received* 2 *March* 1959 *and in revised form* 20 *April* 1959)

The X-ray analysis of the crystal structure of *bis*-thiourea-lead(II) chloride, $Pb[SC(NH_2)_2]_2Cl_2$, has shown that the rather uncommon coordination number of seven for lead occurs in this compound. The lead atom is bonded to four sulphur and two chlorine atoms at the corners of a distorted trigonal prism, and to a chlorine atom near the centre of a lateral face. The coordination polyhedra, sharing their bases, form polymeric chains running along the shortest axis, [010]. The study of the two-dimensional Fourier projection on (010) and of the three-dimensional Fourier lines parallel to [010] gave the following mean values of bond lengths:

$$Pb–S = 3{\cdot}02 \pm 0{\cdot}05 \text{ Å}, \quad Pb–Cl_I = 2{\cdot}75 \pm 0{\cdot}04 \text{ Å}, \quad Pb–Cl_{II} = 3{\cdot}22 \pm 0{\cdot}06 \text{ Å}.$$

1. Introduction

In a previous paper (Nardelli & Fava, 1958) an attempt was made to interpret the Patterson projections $P(U, W)$ and $P(U, V)$ for crystals of *bis*-thiourea–lead(II) chloride. This compound has an orthorhombic cell (space group C_{2v}^9–$Pna2_1$) with

$$a = 21{\cdot}20 \pm 0{\cdot}04, \quad b = 4{\cdot}06 \pm 0{\cdot}01, \quad c = 12{\cdot}02 \pm 0{\cdot}02 \text{ Å}.$$

The unit cell contains four molecules of

$$Pb[SC(NH_2)_2]_2Cl_2.$$

In addition to the coordinates of the lead atom, the coordinates of the sulphur and chlorine atoms were obtained, indicating an octahedral coordination around the heavy atom. The coordination polyhedra formed polymeric chains running parallel to [010].

The present investigation is concerned with the study of the electron-density distribution, and this made us modify our previous views on the distribution of ligands around the metal atom.

2. Intensity data

Multiple-film integrated Weissenberg photographs (Kodak-Crystallex, Cu $K\alpha$ radiation) were used to record the *h*0*l*, *h*1*l*, *h*2*l* and *hk*0 reflexions, and their intensities were determined photometrically. The independent reflexions observed were 151 *h*0*l* (possible 171), 171 *h*1*l* (possible 329), 172 *h*2*l* (possible 293), 59 *hk*0 (possible 106). The crystal-habit was acicular along [010]; for the photographs taken using this direction as a rotation axis a very slender needle was employed, and the specimen was treated as a cylinder ($\mu r = 2{\cdot}0$) in applying the absorption correction. The *hk*0 reflexions were recorded using a small fragment of mean diameter of 0·015 cm.; for this case the absorption correction for a spherical sample ($\mu r = 3{\cdot}0$) was used. Corrections for Lorentz and polarization factors were determined with the aid of a Cochran chart.

The structure factors of the *h*0*l* reflexions were scaled by Wilson's (1942) method; those of the other reflexions were correlated with the previous ones on the basis of those spots which were observed in more than one photograph. The absolute scale was improved successively by comparison with the calculated values. Isotropic temperature and scaling factors were determined by plotting $\log(F_c/F_o)$ against $\sin^2\theta$ for the reflexions of each photograph; the final mean value of B was 2·7 Å^2.

3. Determination of the *x*, *z* parameters

The Patterson $P(U, W)$ projection may be interpreted on the basis of the C_{2v}^9–$Pna2_1$ space group (the D_{2h}^{16} space group is also compatible with the systematic extinctions). The largest peak at $U = 0{\cdot}208$ and $W = 0{\cdot}500$ is due to the $(2x_{Pb}, 2z_{Pb})$ interaction. The small difference in the atomic number between S and Cl atoms did not allow us to distinguish Pb–S and Pb–Cl peaks, and therefore at this first stage we will label these atoms M_I, M_{II}, M_{III}, M_{IV}. Their coordinates, deduced from peaks of lower weight, are:

	x/*a*	*z*/*c*
M_I	0·15	0·08
M_{II}	0·10	0·44
M_{III}	0·24	0·27
M_{IV}	−0·01	0·25

A first Fourier projection $\varrho(X, Z)$ was calculated using the $\alpha(h0l)$ values given by these coordinates.

The refinement of this projection was rather cumbersome because of the absence of the symmetry centre. At the first stage the *x* and *z* coordinates of the heavy atoms were improved and the peaks from the light atoms were then recognized. From their relative positions it was possible to distinguish M_I and M_{II} as sulphur atoms, M_{III} and M_{IV} as chlorine atoms.

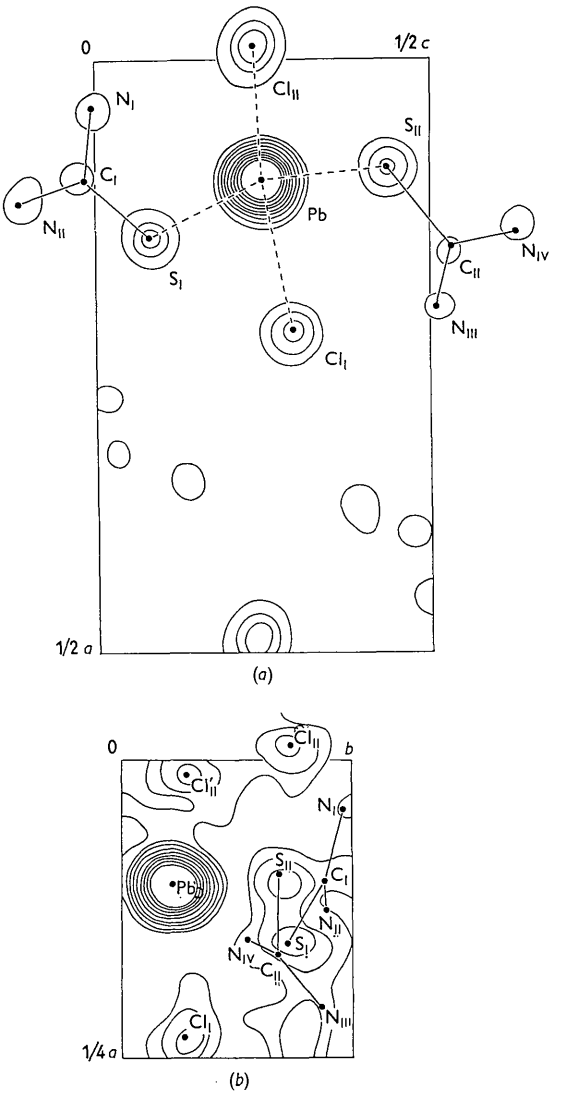

Fig. 1. Final projections of (*a*) $\varrho(X, Z)$ and (*b*) $\varrho(X, Y)$; contour interval 5 e.Å^{-2}; zero contour omitted.

Further refinements were obtained by projections without the heavy-atoms (Pb, S, Cl) contributions, and finally with $(F_o - F_c)$ syntheses. The final projection of $\varrho(X, Z)$ is represented in Fig. 1(*a*)); this corresponds to the x/a and z/c coordinates reported in Table 1.

The reliability index at the final stage of refinement was $R(h0l) = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0{\cdot}114$ (considering only the observed F_o).

4. Determination of the *y* parameters

For the determination of the y parameters we used at first the rough coordinates of the heavy atoms obtained from the $P(U, V)$ projection:

$$y_{Pb}/b = y_{Cl_I}/b = y_{Cl_{II}}/b = \quad 0{\cdot}228$$
$$y_{S_I}/b = 0{\cdot}278, \quad y_{S_{II}}/b = -0{\cdot}272\,.$$

Considering only one formula unit, these coordinates correspond to a planar distribution of the heavy atoms, as previously suggested by Cox *et al.* (1937).

A first $\varrho(X, Y)$ projection was calculated for the coordinates given, but it was of no use for further refinements, except for the lead atom, because of the numerous superpositions. It was therefore necessary to consider the three-dimensional distribution of the electron density. Because of the enormous amount of work required due to the lack of a symmetry centre, we considered only the three-dimensional distribution of $\varrho(X_s, Y, Z_s)$ along the line running through the centre of the s atom and parallel to [010]. These electron densities were calculated from the $F_o(h0l)$, $F_o(h1l)$ and $F_o(h2l)$ structure amplitudes and the phase angles obtained from the previous coordinates. Most surprisingly the resulting coordinate y/b of Cl_{II} was increased by nearly $\frac{1}{2}$, while we had used about the same coordinate y/b for Pb, Cl_I and Cl_{II}. This result was confirmed by successive calculations of $\varrho(X_s, Y, Z_s)$ functions, taking into account also the contributions of the light atoms. The final $\varrho(X, Y)$ projection is represented in Fig. 1(*b*), in which the points indicating the position of the light atoms correspond to the coordinates obtained from examination of the three-dimensional Fourier lines.

The final coordinates are reported in Table 1; their standard deviations were estimated using the expression (Cruickshank, 1949)

$$\tfrac{1}{2}\sigma(x_s) = \frac{2\pi}{aS}\left\{\sum_2 h^2(F_o - F_c)^2\right\}^{\frac{1}{2}} \Big/ \frac{\partial^2 \varrho}{\partial x^2}\,,$$

Table 1. *Final atomic coordinates with their standard deviations*

	x/a	y/b	z/c
Pb	0·105 ± 0·0002	0·229 ± 0·001	0.250 ± 0·0002
Cl_I	0·232 ± 0·002	0·268 ± 0·004	0·294 ± 0·002
Cl_{II}	−0·013 ± 0·002	0·708 ± 0·006	0·238 ± 0·002
S_I	0·154 ± 0·002	0·725 ± 0·009	0·084 ± 0·002
S_{II}	0·095 ± 0·002	0·697 ± 0·007	0·434 ± 0·002
C_I	0·106 ± 0·004	0·883 ± 0·010	−0·013 ± 0·007
C_{II}	0·160 ± 0·009	0·661 ± 0·025	0·527 ± 0·008
N_I	0·042 ± 0·004	0·963 ± 0·019	−0·007 ± 0·008
N_{II}	0·124 ± 0·007	0·894 ± 0·026	−0·121 ± 0·009
N_{III}	0·207 ± 0·009	0·872 ± 0·017	0·519 ± 0·006
N_{IV}	0·150 ± 0·005	0·542 ± 0·030	0·629 ± 0·012

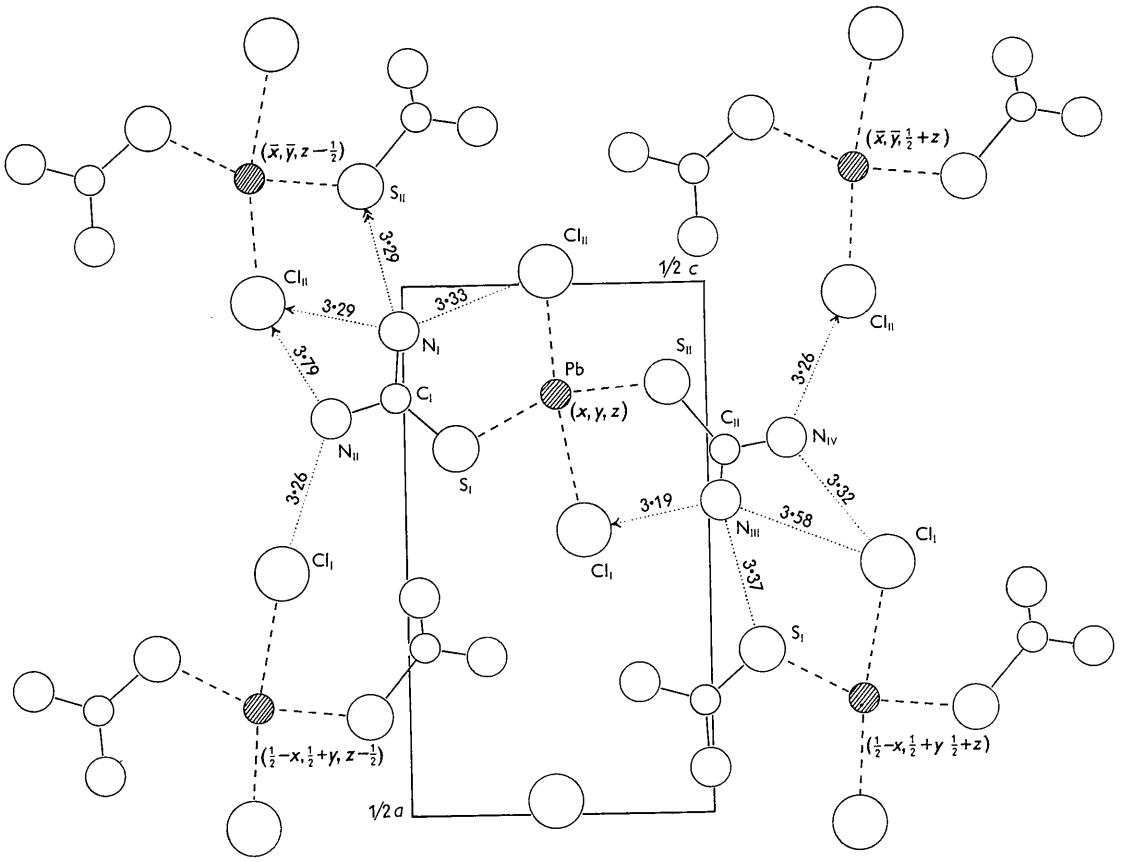

Fig. 2. Projection on (010). Interatomic distances indicated by dotted lines; one arrow-head indicates that the distance is to the atom immediately above of that of which coordinates are reported.

an analogous one for $\sigma(z_s)$ and

$$\tfrac{1}{2}\sigma(y_s) = \frac{2\pi}{bV}\left\{\sum_3 k^2(F_o-F_c)^2\right\}^{\frac{1}{2}} \Big/ \frac{\partial^2\varrho}{\partial y^2} .$$

The two-dimensional and three-dimensional electron-density standard deviations were $[\sigma(\varrho)]_S = 1{\cdot}31$ e.Å^{-2} and $[\sigma(\varrho)]_V = 0{\cdot}59$ e.Å^{-3} respectively.

The factor $\frac{1}{2}$ introduced in these formulae arises from the lack of symmetry-centre (Cruickshank, 1950). The curvature $\partial^2\varrho/\partial r^2$ was calculated assuming that the electron density near the centre of an atom can be expressed as

$$\varrho(r) = \varrho(0)\exp[-pr^2] ,$$

and the constant p was evaluated from graphical plots of $\log\varrho(r)$ versus r^2 for each atom.

The reliability indices (including only the observed F_o) corresponding to the final coordinates are:

$$R(hk0) = 0{\cdot}180, \quad R(h1l) = 0{\cdot}149, \quad R(h2l) = 0{\cdot}160 .$$

In Table 2 are listed the F_o, F_c and α values for the reflexions considered.

5. Discussion

The most interesting feature of the structure is that each lead atom coordinates four sulphur and three chlorine atoms and the resulting coordination polyhedron is a distorted trigonal prism in which a seventh coordination position exists beyond one lateral face.

This distribution arises from the fact that the S_I, S_{II} and Cl_{II} are nearly equidistant from two Pb atoms belonging to a row parallel to [010]; the coordination polyhedra are linked through their bases to form polymeric chains. The lack of crystallographic equivalence of S_I and S_{II} is insufficient to give a corresponding chemical difference; on the other hand, the Cl_I and Cl_{II} atoms are both crystallographically and chemically distinct. The Cl_I atom is located approximately over the centre of a lateral face of the trigonal prism and therefore is bonded only to one lead atom. The observed coordination is rather infrequent; it is likely that the coordination bonds can be described by hybrid wave-functions involving the 5*f* orbitals of lead. Fig. 2 shows, diagrammatically, the projection on the (010) plane. In Fig. 3 is represented a clinographic projection of the polymeric chain described. Bond distances

Table 2. *Observed and calculated structure factors with their phase angles*

h k l	$\|F_o\|$	$\|F_c\|$	α	h k l	$\|F_o\|$	$\|F_c\|$	α	h k l	$\|F_o\|$	$\|F_c\|$	α	h k l	$\|F_o\|$	$\|F_c\|$	α	h k l	$\|F_o\|$	$\|F_c\|$	α	h k l	$\|F_o\|$	$\|F_c\|$	α
0 0 2	282	257	182	12 0 0	49	25	0	26 0 4	29	29	132	5 1 14	–	12	0	11 1 10	–	8	197	18 1 2	74	67	182
4	307	326	5	1	133	145	193	Q 1 1	199	258	182	6 1 0	85	86	0	11	–	19	8	3	79	83	3
6	277	266	187	2	–	15	106	3	264	306	13	1	203	236	352	12	–	2	292	4	50	45	348
8	175	174	359	3	139	137	346	5	155	157	189	2	132	147	174	13	–	8	146	5	81	78	183
10	103	113	175	4	–	2	200	7	130	132	164	3	211	207	183	12 1 0	137	175	180	6	37	32	152
12	86	102	0	5	151	144	167	9	136	157	197	4	154	154	357	1	–	17	18	7	62	57	9
14	45	59	149	6	59	40	204	11	–	43	340	5	174	161	20	2	144	185	342	8	64	58	3
2 0 0	106	68	0	7	120	111	10	13	60	66	188	6	81	97	169	3	–	34	16	9	54	50	184
1	211	307	181	8	–	27	198	1 1 0	51	28	0	7	153	145	165	4	142	152	184	10	42	41	190
2	104	82	188	9	111	128	173	1	49	35	114	8	109	114	2	5	37	19	336	11	32	35	359
3	222	230	0	10	–	12	112	2	39	23	278	9	84	76	11	6	150	164	347	19 1 0	–	12	0
4	152	137	316	11	85	81	358	3	55	34	343	10	70	84	177	7	–	12	129	1	–	5	256
5	268	272	185	12	–	4	50	4	55	39	6	11	61	58	182	8	133	139	167	2	–	12	191
6	98	88	160	13	59	54	203	5	–	21	108	12	54	59	4	9	–	15	235	3	–	4	277
7	187	186	5	14 0 0	133	152	180	6	–	13	46	13	59	62	336	10	86	97	0	4	–	22	1
8	80	83	333	1	68	60	206	7	–	20	17	14	46	51	193	11	–	10	199	5	–	12	174
9	82	82	166	2	133	145	13	8	32	28	358	7 1 0	37	33	180	12	84	85	174	6	–	4	199
10	68	68	162	3	–	25	130	9	–	18	162	1	35	13	316	13	–	6	268	7	–	4	223
11	108	139	10	4	156	154	171	10	–	16	272	2	39	37	259	13 1 0	47	55	180	8	–	12	0
12	41	47	346	5	67	46	319	11	–	12	330	3	69	38	172	1	–	24	151	9	–	1	75
13	57	70	176	6	117	110	5	12	–	11	337	4	–	18	213	2	–	5	288	10	–	5	195
14	26	25	192	7	–	22	67	13	–	5	210	5	35	23	31	3	40	28	27	20 1 0	47	54	180
15	40	48	353	8	90	94	183	14	–	7	214	6	–	3	179	4	–	18	190	1	57	57	175
4 0 0	213	285	180	9	34	27	334	15	–	9	31	7	–	20	150	5	–	16	152	2	55	63	4
1	123	110	170	10	84	85	1	2 1 0	135	150	180	8	–	14	172	6	–	7	25	3	100	89	357
2	120	114	351	11	35	22	71	1	38	28	24	9	–	14	21	7	–	17	334	4	62	63	154
3	104	93	13	12	50	59	182	2	259	354	1	10	–	10	283	8	–	22	179	5	58	55	169
4	107	126	166	13	–	3	22	3	55	37	268	11	–	12	183	9	–	17	188	6	57	59	353
5	137	132	147	16 0 0	112	128	180	4	220	248	181	12	–	4	159	10	–	2	10	7	58	55	354
6	175	194	359	1	142	172	357	5	–	10	237	13	–	13	4	11	–	4	27	8	49	46	168
7	89	87	36	2	25	31	3	6	161	157	359	14	–	2	358	12	–	6	7	9	70	64	181
8	104	125	173	3	157	157	187	7	50	56	319	8 1 0	156	198	0	13	–	11	157	21 1 0	–	3	180
9	81	92	164	4	69	62	185	8	147	168	184	1	93	119	192	14 1 0	35	37	180	1	–	23	185
10	91	110	5	5	136	124	0	9	–	27	201	2	172	199	168	1	125	159	357	2	–	5	132
11	46	55	3	6	80	76	17	10	94	116	0	3	108	102	10	2	92	93	11	3	–	14	354
12	71	90	192	7	120	106	201	11	–	33	23	4	176	163	31	3	129	152	178	4	–	10	15
13	30	36	204	8	–	12	166	12	55	71	168	5	83	75	199	4	74	61	193	5	–	8	176
14	54	52	7	9	81	76	353	13	–	27	199	6	150	133	185	5	131	133	6	6	–	3	54
15	36	34	3	10	28	25	0	14	71	71	8	7	71	67	15	6	–	9	357	7	–	12	5
6 0 0	169	162	180	11	56	56	173	15	56	21	54	8	114	101	1	7	126	120	171	8	–	4	323
1	161	184	353	12	42	38	197	3 1 0	–	2	0	9	106	51	204	8	63	42	196	9	–	10	179
2	170	201	34	18 0 0	93	97	0	1	78	67	117	10	76	64	212	9	90	85	4	22 1 0	56	81	180
3	178	162	171	1	96	98	242	2	53	45	40	11	–	30	15	10	25	8	10	1	–	20	29
4	198	166	169	2	94	74	180	3	66	60	26	12	59	58	355	11	67	68	180	2	116	97	4
5	196	199	355	3	58	52	164	4	25	25	167	13	28	24	187	12	–	16	83	3	–	17	162
6	135	114	27	4	102	86	9	5	37	20	164	14	39	45	175	15 1 0	–	12	180	4	54	84	182
7	134	129	171	5	108	94	349	6	–	28	305	9 1 0	46	38	0	1	–	6	254	5	35	35	323
8	95	73	212	6	73	63	182	7	61	25	31	1	–	17	90	2	–	24	345	6	67	59	356
9	89	99	345	7	93	86	166	8	–	11	173	2	34	16	135	3	–	11	243	7	–	17	209
10	74	68	0	8	70	56	2	9	–	20	162	3	–	14	192	4	43	21	175	8	86	61	184
11	92	102	180	9	46	42	339	10	–	10	12	4	–	14	40	5	–	12	341	23 1 0	–	1	180
12	43	41	339	10	44	38	188	11	–	9	4	5	–	10	97	6	–	10	3	1	–	9	152
13	54	67	0	11	70	66	186	12	–	6	156	6	–	15	148	7	–	6	267	2	–	9	25
14	25	29	14	20 0 0	107	113	0	13	–	10	159	7	20	19	115	8	–	20	153	3	–	7	7
15	30	34	180	1	34	32	163	14	–	9	328	8	–	22	8	9	–	7	209	4	–	10	163
8 0 0	197	208	0	2	58	57	163	15	–	8	29	9	–	14	97	10	–	9	18	5	–	3	144
1	212	286	14	3	27	40	345	4 1 0	139	141	180	10	–	10	196	11	–	10	216	6	–	9	0
2	152	187	186	4	75	75	354	1	189	219	359	11	–	4	265	12	–	14	147	7	–	9	333
3	222	238	178	5	–	29	198	2	142	132	330	12	–	5	10	16 1 0	92	122	0	24 1 0	–	0	180
4	148	122	2	6	96	84	183	3	229	264	174	13	–	4	329	1	49	49	352	1	84	68	5
5	212	195	357	7	45	48	340	4	107	113	198	14	–	9	176	2	103	122	183	2	21	19	259
6	152	125	183	8	53	56	349	5	161	177	343	10 1 0	89	120	180	3	99	95	185	3	106	72	182
7	164	140	204	9	21	30	194	6	105	106	340	1	129	165	164	4	97	98	17	4	–	109	288
8	87	87	358	10	49	51	173	7	181	177	167	2	91	96	2	5	50	35	355	5	62	53	13
9	128	117	354	22 0 0	–	10	180	8	85	96	169	3	139	149	0	6	94	84	193	6	–	12	272
10	66	60	182	1	87	81	174	9	139	172	358	4	86	85	191	7	45	33	187	25 1 0	–	1	180
11	81	84	164	2	24	32	315	10	44	55	4	5	137	134	191	8	69	61	17	1	–	5	315
12	42	42	342	3	56	55	14	11	77	94	165	6	90	78	15	9	73	54	8	2	–	8	331
13	41	40	14	4	–	27	203	12	55	54	175	7	134	138	344	10	55	46	194	3	–	1	192
14	30	33	161	5	75	68	187	13	74	80	358	8	34	26	189	11	–	17	132	4	–	6	218
10 0 0	181	206	0	6	–	32	326	14	72	39	352	9	90	93	189	12	39	36	9	5	–	4	320
1	68	56	167	7	61	53	346	5 1 0	64	42	180	10	–	28	346	17 1 0	–	12	0	26 1 0	41	49	0
2	170	212	195	8	26	34	164	1	20	12	335	11	70	73	13	1	–	16	313	1	–	16	252
3	100	92	20	9	24	32	192	2	73	56	3	12	–	21	171	2	–	0	–	2	57	42	182
4	223	232	341	24 0 0	91	85	180	3	25	19	86	13	71	72	175	3	–	17	223	3	–	7	15
5	69	73	205	1	–	26	327	4	58	28	190	11 1 0	–	3	180	4	–	11	211	0 2 2	223	233	2
6	175	166	176	2	84	83	359	5	–	16	83	1	–	17	175	5	–	8	290	4	229	209	187
7	33	38	62	3	–	23	188	6	36	27	345	2	30	30	148	6	–	10	204	6	203	216	5
8	135	126	2	4	68	67	185	7	–	15	299	3	37	39	179	7	–	13	207	8	140	127	177
9	29	19	225	5	–	18	46	8	47	35	167	4	–	13	79	8	–	2	297	10	75	93	358
10	126	126	173	6	61	66	13	9	–	10	1	5	35	22	169	9	–	10	2	12	80	80	182
11	–	8	34	26 0 0	–	16	180	10	–	16	35	6	–	10	226	10	–	4	176	14	32	49	336
12	73	73	4	1	72	64	357	11	–	10	62	7	–	22	342	11	–	5	217	1 2 0	37	29	180
13	–	9	206	2	–	6	234	12	–	14	132	8	–	9	9	18 1 0	–	0	–	1	104	81	204
14	49	57	178	3	65	61	183	13	–	8	94	9	–	2	110	1	71	93	185	2	51	27	328

Table 2 (*cont.*)

h k l	$\|F_o\|$	$\|F_c\|$	α
1 2 3	73	33	336
4	37	16	152
5	89	62	175
6	54	45	10
7	51	40	347
8	-	6	132
9	34	26	168
10	-	24	342
11	-	28	14
12	-	18	215
13	-	15	193
14	-	7	4
2 2 0	40	38	180
1	166	223	1
2	68	61	0
3	146	132	173
4	78	69	134
5	186	181	9
6	58	66	337
7	148	140	182
8	43	53	161
9	69	83	356
10	44	60	336
11	76	89	186
12	-	30	175
13	55	54	0
14	23	23	1
3 2 0	96	65	180
1	26	12	30
2	70	44	21
3	-	16	323
4	65	43	178
5	-	4	354
6	78	51	14
7	-	12	192
8	-	12	245
9	-	5	109
10	-	27	331
11	-	13	240
12	-	19	220
13	-	5	351
14	-	8	323
4 2 0	136	158	0
1	83	78	31
2	91	101	168
3	83	78	170
4	98	121	354
5	90	84	342
6	133	138	177
7	48	48	192
8	58	83	350
9	52	60	357
10	68	82	185
11	40	44	173
12	64	79	12
4 2 13	-	31	26
14	31	41	184
5 2 0	51	39	0
1	87	67	39
2	21	24	101
3	59	20	153
4	31	27	39
5	81	40	5
6	-	9	212
7	41	29	201
8	-	7	358
9	-	15	21
10	-	4	255
11	-	19	191
12	-	5	184
13	-	9	50
14	-	4	253
6 2 0	123	127	0
1	143	146	173
2	134	131	200
3	107	103	353
4	136	104	351
5	140	125	172
6	138	84	208
7	112	113	355
8	77	64	31
9	68	80	166
10	54	55	171
11	60	74	2
12	-	28	26
13	47	47	175
7 2 0	79	48	0
1	-	13	209
2	77	48	186
3	-	15	18
4	84	56	338
5	-	11	247
6	72	50	185
7	-	23	309
8	-	16	355
9	-	10	321
10	33	37	158
11	-	3	155
12	-	23	12
13	-	11	109
8 2 0	116	132	180
1	148	175	184
2	113	116	2
3	186	172	6
4	128	113	185
5	168	146	171
6	98	84	5
7	108	96	24
8	60	59	179
8 2 9	82	83	175
10	-	43	2
11	61	63	353
12	29	37	170
13	31	36	183
9 2 0	28	28	0
1	66	57	187
2	31	37	222
3	59	31	359
4	34	25	310
5	76	54	156
6	32	26	186
7	42	29	8
8	-	8	309
9	41	40	169
10	-	7	155
11	-	17	352
12	-	5	347
13	-	15	174
10 2 0	132	162	180
1	39	51	12
2	122	149	7
3	48	56	200
4	157	155	162
5	37	34	41
6	120	114	1
7	-	24	135
8	97	107	181
9	-	25	47
10	88	97	345
11	-	3	243
12	54	57	180
13	-	8	15
11 2 0	-	8	0
1	45	39	198
2	46	34	13
3	32	25	341
4	-	17	151
5	48	35	179
6	-	15	11
7	-	19	47
8	-	4	232
9	-	13	133
10	-	14	352
11	-	16	347
12	-	10	212
12 2 0	40	38	180
1	77	99	15
2	-	16	166
3	94	110	174
4	-	3	188
5	105	112	343
6	-	12	13
7	65	83	185
12 2 8	-	11	39
9	76	86	4
10	-	6	353
11	64	70	181
12	-	4	182
13 2 0	30	33	180
1	-	26	16
2	-	5	279
3	-	19	195
4	-	15	198
5	-	14	4
6	-	18	359
7	-	10	215
8	-	12	242
9	-	15	31
10	-	13	339
11	-	3	62
12	-	13	303
14 2 0	85	109	0
1	49	49	2
2	91	116	185
3	-	12	299
4	98	99	353
5	-	36	50
6	78	88	185
7	-	23	252
8	65	73	8
9	-	17	168
10	57	68	175
11	22	15	242
15 2 0	-	8	0
1	29	28	36
2	29	28	176
3	29	23	127
4	-	31	0
5	-	25	13
6	-	11	158
7	-	17	177
8	-	16	357
9	-	11	42
10	-	12	157
11	-	20	180
16 2 0	70	71	0
1	95	124	186
2	-	28	185
3	103	118	3
4	37	33	11
5	96	97	185
6	57	55	186
7	75	71	4
8	-	11	193
9	54	57	182
10	21	21	191
17 2 0	41	44	0
1	-	10	114
2	40	29	180
3	-	10	24
4	-	21	350
5	-	7	78
6	44	36	171
7	-	13	322
8	-	15	358
9	-	12	201
10	-	21	161
11	-	14	6
18 2 0	71	79	180
1	70	63	177
2	69	76	358
3	42	42	327
4	67	67	188
5	73	70	177
6	57	56	4
7	61	60	346
8	46	48	183
9	32	41	159
1 0	-	1	0
2	40	26	185
3	-	8	222
4	30	19	351
5	-	7	264
6	37	27	165
7	-	14	191
8	-	13	0
9	-	2	258
10	-	9	177
11	86	68	180
20 2 0	1	-	29
2	48	46	355
3	22	28	177
4	54	49	175
5	-	26	1
6	69	65	355
7	29	35	166
8	39	36	167
9	-	19	180
21 2 0	32	19	180
1	-	7	239
2	-	13	356
3	-	5	255
4	-	9	225
5	-	11	174
6	-	15	351
7	-	3	77
22 2 0	-	22	0
1	65	64	358
2	-	25	141
3	44	45	185
4	-	20	10
5	65	53	13
6	-	25	156
23 2 0	-	9	180
1	28	14	346
2	-	6	100
3	24	15	169
4	-	5	99
5	-	14	15
24 2 0	94	70	0
1	24	23	149
2	76	60	185
3	-	14	6
4	56	44	6
25 2 0	-	13	0
0 2 0	360	300	180
1 3 0	-	7	180
2	98	117	0
3	-	30	0
4	56	61	0
5	73	56	0
6	69	60	180
7	-	12	0
8	85	101	180
9	-	36	180
10	-	53	180
11	-	11	180
12	68	71	0
13	39	44	0
14	-	0	-
15	-	11	0
16	49	71	180
17	-	12	180
18	-	29	180
19	-	22	180
20	-	20	0
21	-	3	0
0 4 0	81	104	0
1	-	36	0
2	-	14	0
3	59	62	0
4	-	56	180
5	-	20	180
6	-	42	180
7	-	48	180
8	46	46	0
9	-	26	180
10	41	44	0
11	-	22	0
12	-	12	0
13	-	26	0
14	-	47	180
15	-	16	180
1 5 0	-	5	0
2	-	33	180
3	-	7	180
4	-	22	180

in these chains, with their standard deviations, are:

$$\begin{aligned}
\mathrm{Pb\text{–}Cl_I} &= 2{\cdot}75 \pm 0{\cdot}04\ \text{Å} \\
\mathrm{Pb\text{–}Cl_{II}} &= 3{\cdot}17 \pm 0{\cdot}03 \\
\mathrm{Pb\text{–}Cl'_{II}} &= 3{\cdot}28 \pm 0{\cdot}03 \\
\mathrm{Pb\text{–}S_I} &= 3{\cdot}02 \pm 0{\cdot}03 \\
\mathrm{Pb\text{–}S'_I} &= 3{\cdot}04 \pm 0{\cdot}03 \\
\mathrm{Pb\text{–}S_{II}} &= 2{\cdot}92 \pm 0{\cdot}03 \\
\mathrm{Pb\text{–}S'_{II}} &= 3{\cdot}10 \pm 0{\cdot}03
\end{aligned}$$

The atoms marked with a prime have coordinates $(x, y-1, z)$; the others have coordinates (x, y, z).

The standard deviations reported, $\sigma(d)$, were calculated by means of the formula:

$$\sigma^2(d) = [\sigma^2(x_1) + \sigma^2(x_2)] \cos^2 \alpha + [\sigma^2(y_1) + \sigma^2(y_2)] \cos^2 \beta + [\sigma^2(z_1) + \sigma^2(z_2)] \cos^2 \gamma$$

in which $\sigma(x_1)$, $\sigma(x_2)$ etc. are the standard deviations (in Å) of the coordinates of the atoms 1 and 2 and $\cos \alpha$, $\cos \beta$, $\cos \gamma$ are the direction cosines of the line joining the atoms.

The angles between the coordination bonds are:

$$\begin{aligned}
\mathrm{S_I\text{–}Pb\text{–}S_{II}} &= 95{\cdot}2° \\
\mathrm{S'_I\text{–}Pb\text{–}S'_{II}} &= 91{\cdot}3 \\
\mathrm{Cl_{II}\text{–}Pb\text{–}S_I} &= 80{\cdot}4 \\
\mathrm{Cl'_{II}\text{–}Pb\text{–}S'_I} &= 78{\cdot}3 \\
\mathrm{Cl_{II}\text{–}Pb\text{–}S_{II}} &= 65{\cdot}1 \\
\mathrm{Cl'_{II}\text{–}Pb\text{–}S'_{II}} &= 61{\cdot}9 \\
\mathrm{S_I\text{–}Pb\text{–}S'_I} &= 84{\cdot}1 \\
\mathrm{S_{II}\text{–}Pb\text{–}S'_{II}} &= 84{\cdot}7 \\
\mathrm{Cl_{II}\text{–}Pb\text{–}Cl'_{II}} &= 78{\cdot}0 \\
\mathrm{Cl_I\text{–}Pb\text{–}S_I} &= 75{\cdot}6 \\
\mathrm{Cl_I\text{–}Pb\text{–}S'_I} &= 80{\cdot}2 \\
\mathrm{Cl_I\text{–}Pb\text{–}S_{II}} &= 83{\cdot}6 \\
\mathrm{Cl_I\text{–}Pb\text{–}S'_{II}} &= 88{\cdot}3
\end{aligned}$$

The standard deviations of these angles, calculated by means of the formula given by Ahmed & Cruickshank (1953), are about 1°.

The $\mathrm{Pb\text{–}Cl_{II}}$ bond is remarkably longer than $\mathrm{Pb\text{–}Cl_I}$ and this is explained by considering that $\mathrm{Cl_{II}}$ forms two coordinative bonds and $\mathrm{Cl_I}$ only one.

Reliable information on bond distances, involving divalent lead and chlorine in crystalline chlorides, is not available in the chemical literature. The value

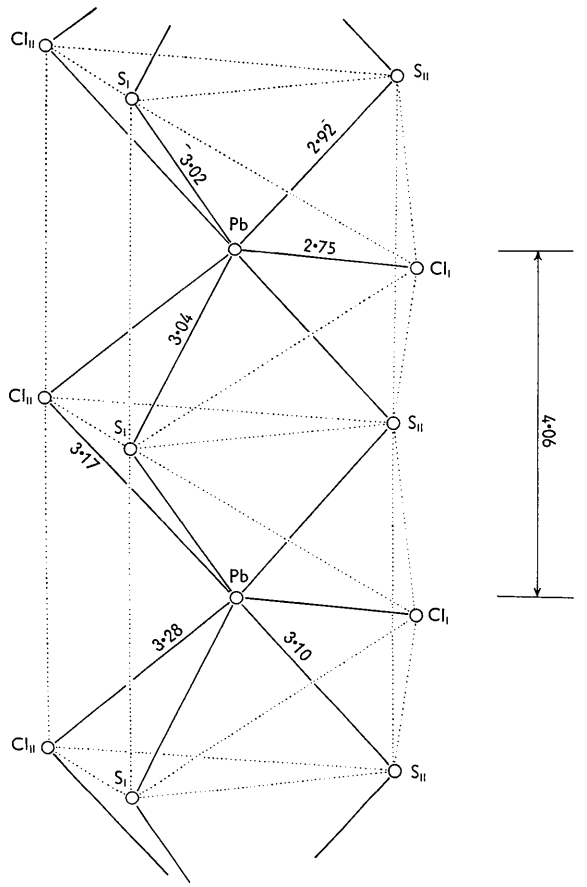

Fig. 3. Clinographic projection of a polymeric chain.

generally reported is about 3·1 Å (as a mean value); the distances Pb–Cl_{II}, found in this work are fairly close to this. The value found for Pb–Cl_I is intermediate between the value for Pb–Cl_{II} and that observed in $PbCl_2$ vapours (2·47 Å, Lister & Sutton, 1941). The mean value of the distance Pb–S is $3·02 \pm 0·05$ Å, which is not far from that found in galena (2·97 Å, Wasserstein, 1951).

The presence of the very heavy lead atom did not allow us to locate the light atoms with accuracy. The bond distances found in the molecules of thiourea roughly agree with those (given in brackets) reported by Kunchur & Truter (1958) for thiourea:

S_I–C_I	$= 1·68 \pm 0·09$ Å	(1·71 Å)
S_{II}–C_{II}	$= 1·78 \pm 0·17$	
C_I–N_I	$= 1·40 \pm 0·12$	(1·33)
C_I–N_{II}	$= 1·35 \pm 0·14$	
C_{II}–N_{III}	$= 1·32 \pm 0·20$	
C_{II}–N_{IV}	$= 1·34 \pm 0·17$	

The bond angles on the Cl_{II}, S_I and S_{II} atoms are:

Pb–Cl'_{II}–Pb′	= 78·0°
Pb–S'_I–Pb′	= 84·1
Pb–S'_I–C'_I	= 89·5
Pb–S_I–C_I	= 120·4
Pb–S'_{II}–Pb′	= 84·7
Pb–S'_{II}–C'_{II}	= 116·9
Pb–S_{II}–C_{II}	= 111·5

The standard deviations of bond angles involving heavy atoms are approximately the same as those already reported; the standard deviations of bond angles involving carbon atoms are quite large because of the large error in the estimated coordinates of the light atoms. Thus it is not possible to give a significant comparison of the angles on the sulphur atom with the analogous ones found in *bis*-thiourea–nickel(II) thiocyanate (Nardelli, Braibanti & Fava, 1957), in which there are also sulphur atoms of thiourea molecules bonded coordinatively by two adjacent metal atoms. The interatomic non-bonded distances shorter than 4 Å and in the same polymeric chain are:

$N_{III} \cdots Cl_I$	$= 3·69 \pm 0·08$ Å
$N_{III} \cdots Cl_I(x, 1+y, z)$	$= 3·19 \pm 0·08$
$N_I \cdots Cl_{II}$	$= 3·33 \pm 0·10$

Between atoms in different chains the distances are:

$N_I \cdots Cl_{II}(\bar{x}, 1-y, z-\frac{1}{2})$	$= 3·29 \pm 0·10$ Å
$N_{II} \cdots Cl_{II}(\bar{x}, 1-y, z-\frac{1}{2})$	$= 3·79 \pm 0·12$
$N_{IV} \cdots Cl_{II}(\bar{x}, 1-y, \frac{1}{2}+z)$	$= 3·26 \pm 0·12$
$N_{IV} \cdots Cl_I(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z)$	$= 3·32 \pm 0·13$
$N_{III} \cdots Cl_I(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z)$	$= 3·58 \pm 0·10$
$N_{II} \cdots Cl_I(\frac{1}{2}-x, \frac{1}{2}+y, z-\frac{1}{2})$	$= 3·26 \pm 0·14$
$N_I \cdots S_{II}(\bar{x}, 2-y, z-\frac{1}{2})$	$= 3·29 \pm 0·09$
$N_{III} \cdots S_I(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z)$	$= 3·37 \pm 0·17$

The packing of chains and the orientation of thiourea molecules are probably determined by the hydrogen bonds between NH_2 groups and Cl atoms.

The authors wish to thank Prof. Luigi Cavalca for his interest in this work.

References

Ahmed, F. R. & Cruickshank, D. W. J. (1953). *Acta Cryst.* **6**, 385.

Cox, E. G., Shorter, A. S. & Wardlaw, W. (1937). *Nature, Lond.* **139**, 71.

Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65.

Cruickshank, D. W. J. (1950). *Acta Cryst.* **3**, 72.

Kunchur, N. R. & Truter, M. R. (1958). *J. Chem. Soc.* p. 2551.

Lister, M. & Sutton, L. E. (1941). *Trans. Faraday Soc.* **37**, 406.

Nardelli, M., Braibanti, A. & Fava, G. (1957). *Gazz. Chim. Ital.* **87**, 1209.

Nardelli, M. & Fava, G. (1958). *Gazz. Chim. Ital.* **88**, 536.

Wasserstein, B. (1951). *Amer. Min.* **36**, 102.

Wilson, A. J. C. (1942). *Nature, Lond.* **150**, 152.