

The Crystal Structure of Lead(II) Diethyldithiocarbamate

BY HITOSHI IWASAKI AND HITOSI HAGIHARA

The Institute of Physical and Chemical Research, Rikagaku Kenkyusho, Wako-shi, Saitama, 351 Japan

(Received 6 March 1971)

The crystal structure of lead(II) diethyldithiocarbamate has been determined by X-ray methods. The crystal is monoclinic, with the space group Cc ; $a = 16.614 \pm 5$, $b = 11.781 \pm 4$, $c = 9.351 \pm 4$ Å, $\beta = 117^\circ 32' \pm 5'$ and $Z = 4$. Two carbamate ions are coordinated to the central metal atom through sulphur atoms, forming a monomeric complex molecule of bis(diethyldithiocarbamato)lead(II), $[\text{Pb}(\text{S}_2\text{CNET}_2)_2]$. Four Pb–S distances are 2.744, 2.786, 2.885 and 2.940 Å (errors: ~ 0.010 Å), and one ligand is closer to the lead atom than another by about 0.05 Å. The complex molecule assumes a strongly distorted pyramidal configuration. The angle S–Pb–S involving two shorter bonds is 96.2° , while the longer bonds make an angle of 133.2° . This structure is closely related to that of the yellow form of PbO .

Introduction

Dithio-alkyl compounds, such as alkylxanthates (MS_2COR) and dialkyldithiophosphates ($\text{MS}_2\text{P(OR)}_2$), where M is commonly Na or K, are widely used as collecting reagents in the flotation of the sulphide minerals (ZnS , PbS , FeS etc.). In order to shed light on the understanding of the flotation mechanism on an atomic scale, the crystal structures of alkylxanthates and diethyldithiophosphates of lead, zinc and iron have been extensively studied by Hagihara and his colleagues (Ikeda & Hagihara, 1966; Hagihara & Yamashita, 1966; Hagihara, Watanabe & Yamashita, 1968; Hagihara, Yoshida & Watanabe, 1969; Ito, Igarashi & Hagihara, 1969; Watanabe & Yamahata, 1970; Ito, 1972). The natures of the metal–sulphur bonds peculiar to these systems have thus been elucidated. Following these lines, the structure analysis of diethyldithiocarbamates $[\text{M}(\text{S}_2\text{CN}\dot{\text{E}}\text{t}_2)_2]$ was undertaken in order to obtain more exact information on the type of coordination between the sulphur atoms and a metal atom in related dithio-alkyl compounds of the heavy metals ($\text{M} = \text{Pb}$ and Hg). The present paper describes the crystal and molecular structure of lead(II) diethyldithiocarbamate.

Hagihara, Uchikoshi & Yamashita (1957) have performed the analysis of the electron diffraction patterns from galena surfaces when they are reacted with diethyldithiocarbamate ions in aqueous solutions. They have also measured the lattice constants of lead diethyldithiocarbamate by means of X-rays for the purpose of interpreting the surface diffraction patterns, but the crystal structure was left undetermined at that time.

The structure of the lead diethyldithiocarbamate is also reported by Zvonkova, Khvatkina & Ivanova (1968). However, their studies were only limited to two-dimensional projections, and it was difficult to find any correlations between the structure proposed by them and those of the related compounds hitherto published.

Experimental

Sodium diethyldithiocarbamate was added to an aqueous solution of lead acetate, and a fine powder of the desired compound was precipitated. By recrystallization from an acetone solution, needle-like yellowish single crystals were obtained. They belong to the monoclinic system, the c axis being coincident with the needle axis. The lattice constants were determined from the Straumanis-type oscillation photographs using $\text{Cu } K\alpha_1$ radiation ($\lambda = 1.54051$ Å). Powder patterns of a copper wire were superposed for calibration purpose.

Crystal data

Lead(II) diethyldithiocarbamate, $\text{Pb}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2$, M.W. 503.7.

Monoclinic, space group Cc (see next section), $a = 16.614 \pm 0.005$, $b = 11.781 \pm 0.004$, $c = 9.351 \pm 0.004$ Å, $\beta = 117^\circ 32' \pm 5'$, $V = 1623.1$ Å³; $Z = 4$, $D_x = 2.061$ g.cm⁻³, $F(000) = 960$ (without correction for anomalous dispersion), $\mu = 255.8$ cm⁻¹ for $\text{Cu } K\alpha$.

Hagihara *et al.* (1957) and Zvonkova *et al.* (1968) have also measured the cell constants of this compound. They are: $a = 16.7$, $b = 11.8$, $c = 9.33$ Å, $\beta = 118^\circ$ (by Hagihara *et al.*), and $a = 16.58$, $b = 11.75$, $c = 9.55$ Å, $\beta = 118^\circ$ (by Zvonkova *et al.*). These values are well in accordance with the present result.

The intensities of the reflexions were recorded on multi-film equi-inclination Weissenberg photographs with $\text{Cu } K\alpha$ radiation. They were visually estimated with a standard intensity scale. Nine layers $hk0$ to $hk8$ and ten layers $h0l$ to $h9l$ were collected using the crystals with cross sections of 0.08×0.09 mm and 0.11×0.14 mm respectively, and a total of 1491 independent non-zero reflexions were obtained. The observed intensities were corrected for Lorentz and polarization factors and also for absorption factors using a cylindrical approximation. The structure amplitudes were put on a common scale by least-squares, and the ab-

solute scale of $|F_o|$ was determined during the refinement procedures.

Determination of the crystal structure

Since the space group cannot be uniquely assigned from the systematic absences ($hkl:h+k=\text{odd}; h0l:l=\text{odd}$) alone, both symmetry possibilities, $C2/c$ and Cc , were taken into account in solving the structure. The arrangement of the lead and sulphur atoms was easily deduced from a Patterson map. With $Z=4$, if one accepts the space group $C2/c$, the complex molecule must assume either a centrosymmetric or a twofold rotation configuration. However, both possibilities were excluded from packing considerations if the sulphur positions located on the basis of the Patterson map were kept. Another possibility with the space group $C2/c$ is that the molecule itself is asymmetric and that the structure is disordered. Again, this was proved not to be the case by successive refinements (R value did not reduce below 14%). Therefore, the space group is Cc , and one formula unit of $\text{Pb}(\text{S}_2\text{CNET}_2)_2$ per asymmetric unit remained to be determined.

The positions of the carbon and nitrogen atoms were found on a heavy-atom Fourier map. All the parameters were refined by block-diagonal least-squares using anisotropic temperature factors. The quantity $\sum w(kF_o - F_c)^2$ was minimized, where k is a scale factor, and w , the weight, was chosen as 0.3 if $F_o < 20$, $(80/F_o)$ if $F_o > 80$, and 1 for all others. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962), and those of Pb and S were corrected for anomalous dispersion after the relation:

$$f^2 = (f + \Delta f')^2 + (\Delta f'')^2,$$

where $\Delta f' = -4.0$, $\Delta f'' = 9.0$ (for Pb) and $\Delta f' = 0.3$, $\Delta f'' = 0.6$ (for S). These factors were assumed to be constant for all ranges of $\sin \theta/\lambda$. The final discrepancy

index $R = \sum(F_o - F_c)/\sum F_o$ was 0.079. The x and z parameters of the lead atom were also refined and later adjusted to be 0.0 for convenience. No extra peaks in

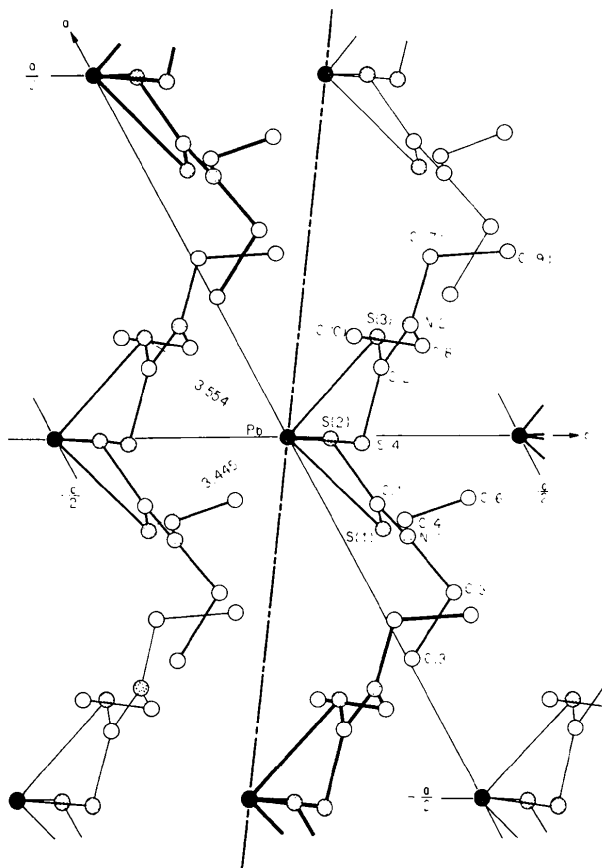


Fig. 1. Structure of lead(II) diethyldithiocarbamate projected along the b axis. Chain line indicates the $(10\bar{1})$ plane passing the origin.

Table 1. Fractional atomic coordinates ($\times 10^4$) and anisotropic thermal parameters ($\times 10^4$) in lead diethyldithiocarbamate

The estimated standard deviations are given in parentheses. The temperature factors refer to the expression:

$$\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)].$$

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Pb	0 (3)	34 (1)	0 (7)	46 (0)	83 (1)	187 (1)	-10 (1)	33 (1)	-2 (1)
S(1)	-1287 (5)	-545 (7)	935 (11)	43 (3)	55 (5)	253 (16)	0 (4)	40 (6)	-14 (8)
S(2)	-12 (6)	-2312 (9)	875 (13)	60 (5)	107 (8)	287 (19)	11 (5)	75 (8)	-25 (10)
S(3)	1376 (5)	508 (7)	3085 (11)	39 (3)	49 (5)	226 (14)	-1 (3)	15 (5)	5 (7)
S(4)	-82 (5)	2193 (7)	1503 (13)	36 (3)	64 (6)	301 (18)	8 (3)	36 (6)	28 (8)
N(1)	-1413 (22)	-2785 (25)	1411 (43)	74 (18)	71 (24)	354 (78)	16 (16)	99 (32)	-5 (33)
N(2)	1519 (14)	2650 (20)	3946 (26)	27 (9)	77 (20)	126 (34)	6 (11)	5 (14)	8 (21)
C(1)	-935 (18)	-1938 (19)	1119 (38)	39 (12)	22 (16)	207 (52)	-3 (11)	27 (21)	-11 (23)
C(2)	959 (19)	1892 (21)	2830 (46)	40 (13)	30 (17)	343 (78)	-14 (12)	75 (28)	-20 (29)
C(3)	-2164 (31)	-2404 (38)	1766 (62)	102 (31)	107 (39)	397 (117)	-48 (29)	125 (52)	12 (54)
C(4)	-1179 (35)	-4012 (30)	1516 (62)	101 (32)	46 (27)	403 (123)	6 (23)	40 (50)	-18 (43)
C(5)	-3080 (27)	-2549 (44)	86 (65)	53 (20)	157 (50)	416 (118)	18 (26)	81 (41)	25 (63)
C(6)	-874 (43)	-4451 (50)	3180 (74)	130 (43)	164 (53)	358 (118)	62 (44)	102 (58)	78 (71)
C(7)	2469 (23)	2388 (31)	5122 (50)	31 (10)	76 (26)	187 (46)	-11 (14)	-4 (17)	0 (28)
C(8)	1227 (28)	3850 (28)	3943 (47)	82 (24)	68 (26)	250 (71)	39 (20)	67 (35)	44 (35)
C(9)	2485 (26)	2288 (38)	6823 (49)	55 (19)	126 (39)	245 (74)	-12 (22)	38 (32)	4 (44)
C(10)	1351 (27)	4538 (34)	2665 (54)	66 (20)	74 (26)	294 (89)	2 (21)	35 (35)	5 (43)

the electron densities were found on the Fourier maps other than those arising from the diffraction ripples of the lead atoms.

Table 2 (cont.)

Table 2. Observed and calculated structure factors

h	k	l	F _o	F _c	Phase (deg)	Phase (deg)
0	0	0	100	100	0	0
1	0	0	100	100	0	0
2	0	0	100	100	0	0
3	0	0	100	100	0	0
4	0	0	100	100	0	0
5	0	0	100	100	0	0
6	0	0	100	100	0	0
7	0	0	100	100	0	0
8	0	0	100	100	0	0
9	0	0	100	100	0	0
10	0	0	100	100	0	0
11	0	0	100	100	0	0
12	0	0	100	100	0	0
13	0	0	100	100	0	0
14	0	0	100	100	0	0
15	0	0	100	100	0	0
16	0	0	100	100	0	0
17	0	0	100	100	0	0
18	0	0	100	100	0	0
19	0	0	100	100	0	0
20	0	0	100	100	0	0
21	0	0	100	100	0	0
22	0	0	100	100	0	0
23	0	0	100	100	0	0
24	0	0	100	100	0	0
25	0	0	100	100	0	0
26	0	0	100	100	0	0
27	0	0	100	100	0	0
28	0	0	100	100	0	0
29	0	0	100	100	0	0
30	0	0	100	100	0	0
31	0	0	100	100	0	0
32	0	0	100	100	0	0
33	0	0	100	100	0	0
34	0	0	100	100	0	0
35	0	0	100	100	0	0
36	0	0	100	100	0	0
37	0	0	100	100	0	0
38	0	0	100	100	0	0
39	0	0	100	100	0	0
40	0	0	100	100	0	0
41	0	0	100	100	0	0
42	0	0	100	100	0	0
43	0	0	100	100	0	0
44	0	0	100	100	0	0
45	0	0	100	100	0	0
46	0	0	100	100	0	0
47	0	0	100	100	0	0
48	0	0	100	100	0	0
49	0	0	100	100	0	0
50	0	0	100	100	0	0
51	0	0	100	100	0	0
52	0	0	100	100	0	0
53	0	0	100	100	0	0
54	0	0	100	100	0	0
55	0	0	100	100	0	0
56	0	0	100	100	0	0
57	0	0	100	100	0	0
58	0	0	100	100	0	0
59	0	0	100	100	0	0
60	0	0	100	100	0	0
61	0	0	100	100	0	0
62	0	0	100	100	0	0
63	0	0	100	100	0	0
64	0	0	100	100	0	0
65	0	0	100	100	0	0
66	0	0	100	100	0	0
67	0	0	100	100	0	0
68	0	0	100	100	0	0
69	0	0	100	100	0	0
70	0	0	100	100	0	0
71	0	0	100	100	0	0
72	0	0	100	100	0	0
73	0	0	100	100	0	0
74	0	0	100	100	0	0
75	0	0	100	100	0	0
76	0	0	100	100	0	0
77	0	0	100	100	0	0
78	0	0	100	100	0	0
79	0	0	100	100	0	0
80	0	0	100	100	0	0
81	0	0	100	100	0	0
82	0	0	100	100	0	0
83	0	0	100	100	0	0
84	0	0	100	100	0	0
85	0	0	100	100	0	0
86	0	0	100	100	0	0
87	0	0	100	100	0	0
88	0	0	100	100	0	0
89	0	0	100	100	0	0
90	0	0	100	100	0	0
91	0	0	100	100	0	0
92	0	0	100	100	0	0
93	0	0	100	100	0	0
94	0	0	100	100	0	0
95	0	0	100	100	0	0
96	0	0	100	100	0	0
97	0	0	100	100	0	0
98	0	0	100	100	0	0
99	0	0	100	100	0	0
100	0	0	100	100	0	0

101	0	0	100	100	0	0
102	0	0	100	100	0	0
103	0	0	100	100	0	0
104	0	0	100	100	0	0
105	0	0	100	100	0	0
106	0	0	100	100	0	0
107	0	0	100	100	0	0
108	0	0	100	100	0	0
109	0	0	100	100	0	0
110	0	0	100	100	0	0
111	0	0	100	100	0	0
112	0	0	100	100	0	0
113	0	0	100	100	0	0
114	0	0	100	100	0	0
115	0	0	100	100	0	0
116	0	0	100	100	0	0
117	0	0	100	100	0	0
118	0	0	100	100	0	0
119	0	0	100	100	0	0
120	0	0	100	100	0	0
121	0	0	100	100	0	0
122	0	0	100	100	0	0
123	0	0	100	100	0	0
124	0	0	100	100	0	0
125	0	0	100	100	0	0
126	0	0	100	100	0	0
127	0	0	100	100	0	0
128	0	0	100	100	0	0
129	0	0	100	100	0	0
130	0	0	100	100	0	0
131	0	0	100	100	0	0
132	0	0	100	100	0	0
133	0	0	100	100	0	0
134	0	0	100	100	0	0
135	0	0	100	100	0	0
136	0	0	100	100	0	0
137	0	0	100	100	0	0
138	0	0	100	100	0	0
139	0	0	100	100	0	0
140	0	0	100	100	0	0
141	0	0	100	100	0	0
142	0	0	100	100	0	0
143	0	0	100	100	0	0
144	0	0	100	100	0	0
145	0	0	100	100	0	0
146	0	0	100	100	0	0
147	0	0	100	100	0	0
148	0	0	100	100	0	0
149	0	0	100	100	0	0
150	0	0	100	100	0	0
151	0	0	100	100	0	0
152	0	0	100	100	0	0
153	0	0	100	100	0	0
154	0	0	100	100	0	0
155	0	0	100	100	0	0
156	0	0	100	100	0	0
157	0	0	100	100	0	0
158	0	0	100	100	0	0
159	0	0	100	100	0	0
160	0	0	100	100	0	0
161	0	0	100	100	0	0
162	0	0	100	100	0	0
163	0	0	100	100	0	0
164	0	0	100	100	0	0
165	0	0	100	100	0	0
166	0	0	100	100	0	0
167	0	0	100	100	0	0
168	0	0	100	100	0	0
169	0	0	100	100	0	0
170	0	0	100	100	0	0
171	0	0	100	100	0	0
172	0	0	100	100	0	0
173	0	0	100	100	0	0
174	0	0	100	100	0	0
175	0	0	100	100	0	0
176	0	0	100	100	0	0
177	0	0	100	100	0	0
178	0	0	100	100	0	0
179	0	0	100	100	0	0
180	0	0	100	100	0	0
181	0	0	100	100	0	0
182	0	0	100	100	0	0
183	0	0	100	100	0	0
184	0	0	100	100	0	0
185	0	0	100	100	0	0
186	0	0	100	100	0	0
187	0	0	100	100	0	0
188	0	0	100	100	0	0
189	0	0	100	100	0	0
190	0	0	100	100	0	0
191	0	0	100	100	0	0
192	0	0	100	100	0	0
193	0	0	100	100	0	0
194	0	0	100	100	0	0
195	0	0	100	100	0	0
196	0	0	100	100	0	0
197	0	0	100	100	0	0
198	0	0	100	100	0	0
199	0	0	100	100	0	0
200	0	0	100	100	0	0

Description of the structure and discussion

Final atomic parameters are given in Table 1, and the structures projected along the *b* and *c* axes are illustrated in Figs. 1 and 2 respectively. The observed and calculated structure amplitudes are shown in Table 2.

As is seen in Figs. 1 and 2, the crystal consists of a complex molecule of bis(diethyldithiocarbamato)lead(II), [Pb(S₂CNET₂)₂]. This molecule is monomeric like those of the related lead compounds such as the ethylxanthate (Hagihara *et al.*, 1966), isopropylxanthate-pyridine (Hagihara *et al.*, 1969), *n*-butylxanthate (Hagihara *et al.*, 1968) and diethyldithiophosphate (Ito, 1972). The diethyldithiocarbamate of nickel (Bonamico, Dessy, Mariani, Vaciego & Zambonelli, 1965) is also monomeric, whereas those of copper (Bonamico, Dessy, Mugnoli, Vaciego & Zambonelli, 1965; O'Connor & Maslen, 1966) and zinc (Bonamico, Mazzone, Vaciego & Zambonelli, 1965) are dimeric in crystals. The network structure as proposed by Zvonkova *et al.* (1968) does not exist at least in this acentric crystal used in the present study.

Interatomic distances and bond angles are given in Table 3, and molecular dimensions are shown in Figs.

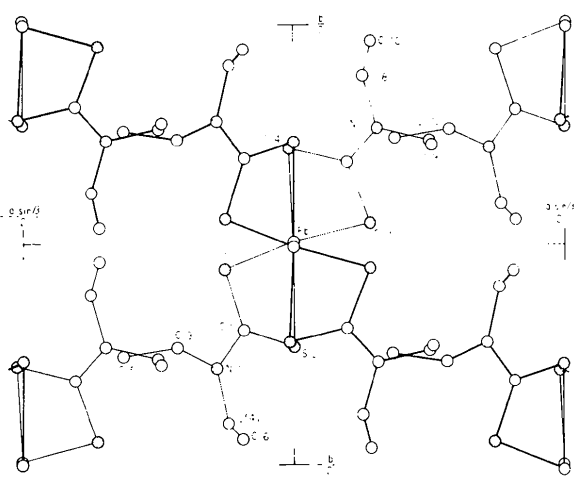


Fig. 2. Structure projected along the *c* axis.

3 and 4. Four sulphur atoms are coordinated to the central lead atom in a distorted pyramidal fashion, although the basal four atoms are far from coplanar. Pb-S distances are 2.744, 2.786, 2.885 and 2.940 Å, and within the experimental error, they are distinctly different from each other. In each bidentate ligand one sulphur atom [S(1) or S(3)] is closely attached to the lead atom to form a relatively strong coordination bond, the average of the Pb-S distances being 2.765 Å.

Table 3. *Interatomic distances and angles with standard deviations*

(a) Distances and angles within a molecule

Pb—S(1)	2.744 (9) Å	Pb—S(3)	2.786 (9) Å
Pb—S(2)	2.885 (11)	Pb—S(4)	2.940 (10)
S(1)—C(1)	1.724 (24)	S(3)—C(2)	1.745 (27)
S(2)—C(1)	1.709 (37)	S(4)—C(2)	1.635 (27)
C(1)—N(1)	1.378 (48)	C(2)—N(2)	1.362 (34)
N(1)—C(3)	1.501 (71)	N(2)—C(7)	1.481 (36)
N(1)—C(4)	1.488 (48)	N(2)—C(8)	1.495 (43)
C(3)—C(5)	1.614 (57)	C(7)—C(9)	1.584 (66)
C(4)—C(6)	1.489 (85)	C(8)—C(10)	1.535 (69)
S(1)—S(2)	2.988 (14)	S(3)—S(4)	2.947 (12)
S(1)—S(4)	3.702 (12)	S(3)—S(2)	4.027 (13)
S(1)—S(3)	4.114 (15)		
S(2)—S(4)	5.346 (18)		
Pb—S(1)—C(1)	89.5 (1.2)°	Pb—S(3)—C(2)	87.8 (1.1)°
Pb—S(2)—C(1)	85.2 (0.9)	Pb—S(4)—C(2)	84.8 (1.2)
S(1)—C(1)—S(2)	121.0 (1.9)	S(3)—C(2)—S(4)	121.4 (1.6)
S(1)—C(1)—N(1)	120.6 (2.7)	S(3)—C(2)—N(2)	114.9 (1.9)
S(2)—C(1)—N(1)	118.3 (2.2)	S(4)—C(2)—N(2)	123.2 (2.1)
C(1)—N(1)—C(3)	116.2 (3.0)	C(2)—N(2)—C(7)	123.3 (2.5)
C(1)—N(1)—C(4)	124.0 (3.9)	C(2)—N(2)—C(8)	120.8 (2.1)
C(3)—N(1)—C(4)	119.6 (4.1)	C(7)—N(2)—C(8)	115.7 (2.4)
N(1)—C(3)—C(5)	105.0 (4.3)	N(2)—C(7)—C(9)	106.1 (3.4)
N(1)—C(4)—C(6)	111.0 (4.6)	N(2)—C(8)—C(10)	109.9 (3.6)
S(1)—Pb—S(2)	64.1 (0.3)	S(3)—Pb—S(4)	61.9 (0.2)
S(1)—Pb—S(4)	81.2 (0.3)	S(2)—Pb—S(3)	90.5 (0.3)
S(1)—Pb—S(3)	96.2 (0.4)		
S(2)—Pb—S(4)	133.2 (0.4)		

(b) Intermolecular contacts less than 3.8 Å

Symmetry code:

<i>a</i>	<i>x</i>	<i>y</i>	<i>z</i>
<i>b</i>	<i>x</i>	− <i>y</i>	−0.5 + <i>z</i>
<i>c</i>	0.5 + <i>x</i>	−0.5 − <i>y</i>	0.5 + <i>z</i>
<i>d</i>	−0.5 + <i>x</i>	0.5 − <i>y</i>	−0.5 + <i>z</i>
<i>e</i>	0.5 + <i>x</i>	0.5 + <i>y</i>	<i>z</i>
<i>f</i>	−0.5 + <i>x</i>	−0.5 + <i>y</i>	−1 + <i>z</i>
<i>g</i>	−0.5 + <i>x</i>	−0.5 + <i>y</i>	<i>z</i>
<i>h</i>	<i>x</i>	−1 + <i>y</i>	<i>z</i>

Atom in <i>a</i>	to	Atom in	Distance
Pb		S(1) <i>b</i>	3.445 (11) Å
Pb		S(3) <i>b</i>	3.554 (11)
S(2)		N(2) <i>b</i>	3.759 (32)
S(2)		C(8) <i>b</i>	3.772 (53)
S(2)		C(5) <i>c</i>	3.761 (47)
S(4)		C(7) <i>d</i>	3.688 (38)
N(2)		C(3) <i>e</i>	3.615 (72)
C(1)		C(9) <i>f</i>	3.756 (48)
C(2)		C(3) <i>e</i>	3.778 (75)
C(2)		C(5) <i>e</i>	3.655 (80)
C(3)		C(7) <i>g</i>	3.470 (83)
C(3)		C(10) <i>g</i>	3.734 (76)
C(5)		C(9) <i>f</i>	3.587 (84)
C(6)		C(8) <i>h</i>	3.794 (82)

On the contrary the other sulphur atom [S(2) or S(4)] makes a weak bond, and the average Pb-S separation (2.913 Å) is slightly shorter than the sum of the ionic radii of Pb²⁺ and S²⁻ (3.04 Å). This kind of structure is widely found among the alkylxanthates and in the diethyldithiophosphate of lead.

The angle S-Pb-S involving two shorter bonds is 96.2°, while the longer bonds make an angle of 133.2°. Similar values are obtained in other PbS₄ systems (Table 4). Essentially the same feature is also found in the structure of the yellow form of plumbous oxide, in which a lead atom is surrounded by four oxygen atoms, forming a flat four-sided pyramid (Kay, 1961). Two of the Pb-O distances are around 2.22 Å and the other two 2.49 Å, and the short bonds make an angle of 90.4° while the other 147.5°. Thus, the central part of the diethyldithiocarbamate and related complexes of lead can be regarded as having strongly distorted yellow-PbO structures. In the case of the diethyldithiocarbamate, one non-bonding S-S distance [S(1)-S(4), 3.702 Å] is of normal van der Waals type, while the other [S(2)-S(3), 4.027 Å] is much longer. The stable asymmetric configuration characteristic of PbS₄ systems so far found seems to be obtained by a distortion from the ideal yellow PbO structure until one of the non-bonding S-S separations attains the van der Waals contact.

Both the difference between Pb-S(1) and Pb-S(3) distances and that between Pb-S(2) and Pb-S(4) are about 0.05 Å. In other words one ligand is closer to the metal atom than another by about 0.05 Å. Such a difference has also been found in other PbS₄ systems (Table 4). The present result is the first example in

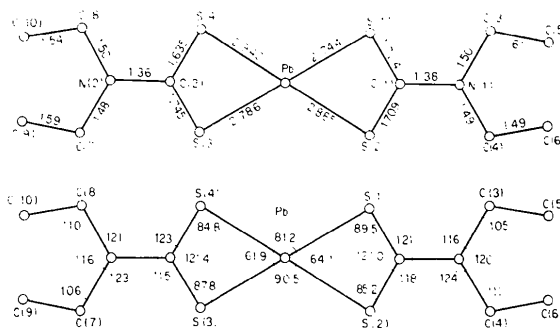


Fig. 3. Bond distances and angles.

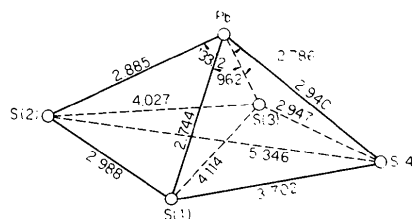


Fig. 4. Structure of PbS₄ pyramid in lead(II) diethyldithiocarbamate.

which this difference has been observed to be greater than the experimental errors. It is interesting that an ionic structure of the type $(\text{Et}_2\text{NCS}_2)^-(\text{PbS}_2\text{CNET}_2)^+$ seems to remain after the formation of the neutral molecule.

Table 4. *A comparison of dimensions in lead ethylxanthate (I), lead diethyldithiocarbamate (II) and lead diethyldithiophosphate (III)*

	Estimated standard deviations in parentheses.		
	I	II	III
Pb-S(1) [$\equiv d(1)$]	2.742 (28) Å	2.744 (9) Å	2.754 (6) Å
Pb-S(2) [$\equiv d(2)$]	2.839 (30)	2.885 (11)	2.996 (5)
Pb-S(3) [$\equiv d(3)$]	2.786 (29)	2.786 (9)	2.790 (6)
Pb-S(4) [$\equiv d(4)$]	2.950 (33)	2.940 (10)	3.022 (6)
Av. [$d(1), d(3)$]	2.764	2.765	2.772
Av. [$d(2), d(4)$]	2.895	2.913	3.009
$\Delta[d(1), d(3)]$	0.044	0.042	0.044
$\Delta[d(2), d(4)]$	0.111	0.055	0.026
S(1)-S(2)	2.985 (37)	2.988 (14)	3.350 (8)
S(3)-S(4)	2.939 (40)	2.947 (12)	3.361 (7)
S(1)-S(4)	4.164 (40)	3.702 (12)	3.744 (8)
S(2)-S(3)	3.772 (42)	4.027 (13)	3.767 (9)
S(1)-Pb-S(2)	64.6 (0.8)°	64.1 (0.3)°	71.1 (0.2)°
S(3)-Pb-S(4)	61.6 (0.8)	61.9 (0.2)	70.6 (0.2)
S(1)-Pb-S(3)	98.1 (0.9)	96.2 (0.4)	94.1 (0.2)
S(2)-Pb-S(4)	137.2 (1.0)	133.2 (0.4)	138.2 (0.2)
S(1)-Pb-S(4)	94.0 (0.9)	81.2 (0.3)	80.7 (0.2)
S(2)-Pb-S(3)	84.2 (0.9)	90.5 (0.3)	81.1 (0.2)

I Hagihara *et al.* (1966)

II Present work

III Ito (1972)

The differences in the four Pb-S lengths are also observed in the *n*-butylxanthate (Hagihara *et al.*, 1968) and in the isopropylxanthate-pyridine (Hagihara *et al.*, 1969). From the results so far mentioned it is concluded that these asymmetric natures are common and characteristic in the lead-dithioalkyl compound systems, and do not merely arise from systematic errors. This is in marked contrast to the compounds of the lower transition metals such as iron, cobalt and nickel, which tend to have structures with relatively high symmetry (Watanabe & Yamahata, 1970; Merlino, 1968, 1969; Franzini, 1963; McConnell & Kastalsky, 1967; Kastalsky & McConnell, 1969; Jones, Ansell & Katz, 1969; Shetty & Fernando, 1969; Gasparri, Nardelli & Villa, 1967; Bonamico, Dessy, Mariani, Vaciago & Zambonelli, 1965; Bonamico, Dessy, Mugnoli, Vaciago & Zambonelli, 1965; Bonamico, Mazzone, Vaciago & Zambonelli, 1965; Peyronel & Pignedoli, 1967).

Although the accuracy in the positions of carbon and nitrogen atoms is not very high, the diethyldithiocarbamate ligands are planar except for the methyl groups. The lead atom lies in neither plane of the two ligands. The best-fit planes formed by the intra-molecular bonds and the angles between them are listed in Table 5.

The crystal structure essentially consists of molecular columns which run parallel to the *c* axis. In each column, molecules of $[\text{Pb}(\text{S}_2\text{CNET}_2)_2]$ are successively stacked upon one another so that the adjacent molecules

are related by the operation of a glide-plane. Although the molecular contacts are normal, two relatively short Pb-S distances are found within the column (3.445 and 3.554 Å). Since the dipole moment possessed by the molecule is approximately directed toward the *c* axis, the moment is not cancelled within a column. Furthermore, this polarity is not cancelled between adjacent columns, and the crystal is polar in the *c* direction. It is interesting that the needle axis of the crystal coincides with the direction of the molecular stacking.

In the case of lead ethylxanthate (Hagihara *et al.*, 1966), a similar column exists parallel to the *b* axis, and in this column two relatively close Pb-S contacts are found. The direction in which crystals develop most easily is parallel to the *b* axis, but the polarity is cancelled between the neighbouring columns (space group $P2_1/c$). In lead diethyldithiophosphate (Ito, 1972) a similar relation holds between the direction of easy growth and that of the molecular columns containing two close Pb-S contacts, but in that case the column itself is non-polar and the character of the contacts is somewhat different.

The structure obtained here is consistent with the observed electron diffraction patterns from galena surfaces which are reacted with the collecting reagents (Hagihara *et al.*, 1957; Hagihara, Sakurai & Ikeda, 1967). According to Hagihara *et al.* (1957), when a galena surface is reacted with diethyldithiocarbamate ions, the crystals of the lead complex are easily deposited on the surface even when the concentration of the anions is low. On the other hand, when surfaces are reacted with alkylxanthates or diethyldithiophosphate, monomolecular layers of some lead compounds adsorbed on the atom sites of the surface lattice are formed. Hagihara *et al.* analysed the observed electron diffraction patterns in the case of diethyldithiocarbamate and concluded that the $(10\bar{1})$ plane of the deposits is parallel to the galena surface, but the crystals are otherwise randomly orientated. The normal of the $(10\bar{1})$ plane and the *c* axis of the lead diethyldithiocarbamate make an angle of 6° and the latter is coincident with the direction of the molecular stacking (Fig. 1). The observed electron diffraction patterns, therefore, come from a fibre structure, in which the fibre axis is approximately the *c* axis of the deposited crystal, *i.e.* the direction of easy growth. If the monolayer of the complex is produced on the galena surface, the *c* axis is most likely perpendicular to the surface. Once a monolayer is formed, the polarity of the complex molecule produces a heavy surface moment, which will be responsible for the subsequent stacking of the molecules upon the deposited layer. Thus the crystallization of the lead diethyldithiocarbamate on the galena surface proceeds rapidly along the *c* axis, which becomes nearly perpendicular to the surface. The polarity of the crystal will not be irrelevant to the fact that a monolayer is not observed in the electron diffraction patterns.

The block-diagonal least-squares refinement of the structure was carried out using the program *RBDLS-32*

Table 5. Equations of planes

Equations are expressed in the form $AX+BY+CZ=D$, where X , Y and Z are coordinates along the cell edges in Å. Those for planes 1, 2 and 3 are the least-squares planes, with all weights equal to 1.

Planes 1 and 2 are the ligand I and II respectively. Plane 3 corresponds to the mean 'basal plane' of the PbS_4 pyramid. The values of A , B , C , D are multiplied by 10^4 .

Plane	A	B	C	D	Atoms defining the plane
1	1750	1115	7865	2891	S(1), S(2), C(1), N(1), C(3), C(4)
2	-7208	-2340	9118	7930	S(3), S(4), C(2), N(2), C(7), C(8)
3	-4246	-1239	9916	14897	S(1), S(2), S(3), S(4)
4	2314	2157	7342	87	Pb, S(1), S(2)
5	-8042	-4430	7232	-179	Pb, S(3), S(4)
6	3540	-3210	6153	-129	Pb, S(1), S(4)
7	9299	-2130	-6958	-86	Pb, S(2), S(3)
8	-2865	9527	427	384	Pb, S(1), S(3)
9	8564	119	618	5	Pb, S(2), S(4)
10	-3227	-3530	9279	17274	S(1), S(2), S(3)
11	-772	-1029	9150	10309	S(1), S(2), S(4)
12	-4890	1403	9895	18202	S(1), S(3), S(4)
13	-6816	-1206	9551	11242	S(2), S(3), S(4)

Deviations of atoms from the planes (Å)

Plane	Pb	S(1)	S(2)	S(3)	S(4)	C(1)	C(2)
1	-0.285	-0.047	0.047	2.446	1.080	0.01	2.32
2	-0.802	1.695	0.605	0.049	-0.017	1.82	-0.05
3	-1.495	0.364	-0.332	0.326	-0.358	0.49	0.18
4				2.767	1.549	-0.09	2.78
5		2.653	1.833			3.04	-0.34
6			1.383	2.405		0.84	1.49
7		-2.451			-1.647	-1.68	0.83
8			-2.592		2.522	-1.72	1.74
9		-1.785		2.142		-1.29	1.55
10	-1.742				-1.291	0.55	-0.57
11	-1.035			1.370		0.28	1.04
12	-1.815		-1.382			-0.35	0.33
13	-1.129	1.245				1.21	0.45
	N(1)	C(3)	C(4)	C(5)	C(6)		
1	-0.03	0.07	-0.04	-1.46	1.21		
	N(2)	C(7)	C(8)	C(9)	C(10)		
2	0.02	-0.04	0.04	1.42	-1.39		

Angles between the planes (°)

	2	3	4	5	6	7	8	9	10	11	12	13
1	60.9	37.9	7.0	78.6	27.7	81.1	87.5	49.0	40.2	19.1	39.4	55.0
2		23.0	66.3	19.6	66.9	35.3	85.3	73.5	27.4	43.4	28.2	7.9
3			43.5	41.3	47.4	50.4	85.0	84.4	14.4	20.8	15.8	17.9
4				84.6	32.2	83.4	87.5	46.3	47.0	25.8	42.8	59.9
5					78.1	39.4	76.6	60.7	40.2	60.0	47.8	27.4
6						82.3	60.3	41.2	39.6	28.7	57.4	64.4
7							64.0	50.3	60.8	69.7	42.0	34.5
8								73.4	70.6	79.8	79.3	89.6
9									80.1	63.6	88.4	77.7
10										21.2	30.2	26.3
11											28.7	38.7
12												20.3

written by one of the authors (H.I.). Other calculations were performed using the program system UNICS (Sakurai, Ito, Iwasaki, Watanabe & Fukuhara, 1967). All the computations were carried out on the FACOM 270-30 computer installed in the Computer Centre of this Institute.

The authors are indebted to Dr T. Ito of our laboratory for showing us his results on lead diethyldithiophosphate prior to publication.

References

BONAMICO, M., DESSY, G., MARIANI, C., VACIAGO, A. & ZAMBONELLI, L. (1965). *Acta Cryst.* **19**, 619.
 BONAMICO, M., DESSY, G., MUGNOLI, A., VACIAGO, A. & ZAMBONELLI, L. (1965). *Acta Cryst.* **19**, 886.
 BONAMICO, M., MAZZONE, G., VACIAGO, A. & ZAMBONELLI, L. (1965). *Acta Cryst.* **19**, 898.
 FRANZINI, M. (1963). *Z. Kristallogr.* **118**, 393.
 GASPARRI, G. F., NARDELLI, M. & VILLA, A. (1967). *Acta Cryst.* **23**, 384.

- HAGIHARA, H., SAKURAI, T. & IKEDA, T. (1967). *Proceedings of the Fourth International Congress on Surface Active Substances* (held 1964, Brussels). Vol. 2, p. 361. New York: Gordon & Breach.
- HAGIHARA, H., UCHIKOSHI, H. & YAMASHITA, S. (1957). *Proceedings of the Second International Congress on Surface Activity*. Vol. 3, p. 343. London: Butterworths.
- HAGIHARA, H., WATANABE, Y. & YAMASHITA, S. (1968). *Acta Cryst.* **B24**, 960.
- HAGIHARA, H. & YAMASHITA, S. (1966). *Acta Cryst.* **21**, 350.
- HAGIHARA, H., YOSHIDA, N. & WATANABE, Y. (1969). *Acta Cryst.* **B25**, 1775.
- IKEDA, T. & HAGIHARA, H. (1966). *Acta Cryst.* **21**, 919.
- International Tables for X-ray Crystallography* (1962). Vol. III, p. 201. Birmingham: Kynoch Press.
- ITO, T. (1972). To be published.
- ITO, T., IGARASHI, T. & HAGIHARA, H. (1969). *Acta Cryst.* **B25**, 2303.
- JONES, P. E., ANSELL, G. B. & KATZ, L. (1969). *Acta Cryst.* **B25**, 1939.
- KASTALSKY, V. & MCCONNELL, J. F. (1969). *Acta Cryst.* **B25**, 909.
- KAY, M. I. (1961). *Acta Cryst.* **14**, 80.
- MCCONNELL, J. F. & KASTALSKY, V. (1967). *Acta Cryst.* **22**, 853.
- MERLINO, S. (1968). *Acta Cryst.* **B24**, 1441.
- MERLINO, S. (1969). *Acta Cryst.* **B25**, 2270.
- O'CONNOR, B. H. & MASLEN, E. N. (1966). *Acta Cryst.* **21**, 828.
- PEYRONEL, G. & PIGNEDOLI, A. (1967). *Acta Cryst.* **23**, 398.
- SAKURAI, T., ITO, T., IWASAKI, H., WATANABE, Y. & FUKUHARA, M. (1967). *Rep. Inst. Phys. Chem. Res.* **43**, 62.
- SHETTY, P. S. & FERNANDO, Q. (1969). *Acta Cryst.* **B25**, 1294.
- WATANABE, Y. & YAMAHATA, K. (1970). *Sci. Papers Inst. Phys. Chem. Res.* **64**, 71.
- ZVONKOVA, Z. V., KHVATKINA, A. N. & IVANOVA, N. S. (1968). *Soviet Phys.-Cryst.* **12**, 926.

Acta Cryst. (1972). **B28**, 513

X-ray Crystallography of the $\text{Cl}_3[\text{N}(\text{CH}_3)_2]_3\text{P}_3\text{N}_3$ Compounds. I. Crystal Structure of the Geminal 2,2,4-Trichloro-4,6,6-trisdimethylaminocyclotriphosphazatriene

BY F. R. AHMED AND D. R. POLLARD*

Biochemistry Laboratory, National Research Council of Canada, Ottawa, Canada

(Received 1 April 1971)

The crystal structure of the geminal 2,2,4-trichloro-4,6,6-trisdimethylaminocyclotriphosphazatriene, $\text{Cl}_3[\text{N}(\text{CH}_3)_2]_3\text{P}_3\text{N}_3$, has been determined by the symbolic addition procedure, and has been refined by least-squares to $R = 0.05$ for the 2495 observed reflexions. The unit cell is monoclinic, $P2_1/n$, with $a = 15.867$, $b = 11.869$, $c = 8.861$ Å, $\beta = 93^\circ 44'$, $Z = 4$. The P_3N_3 ring has a distorted boat conformation. The two bonds of each P-N-P segment are of different lengths, 1.546 ± 0.001 and 1.607 ± 0.001 Å for two of the segments, and 1.563 and 1.592 Å for the third, but the average of the two bonds in each segment is 1.577 Å. The endocyclic N-P(NMe₂)₂-N angle is only 113.1° , while the N-PCl₂-N and N-PCl(NMe₂)-N angles are 120.7 and 119.0° . The P-N ligands are of nearly equal lengths 1.628, 1.639, and 1.642 ($\sigma = 0.004$) Å, but the P-Cl ligands are of significantly different lengths 1.992, 2.014 and 2.051 ($\sigma = 0.002$) Å.

Introduction

The X-ray crystal structure analysis of small phosphonitrilic systems is intended to enhance the understanding of the P-N bonding mechanism, since the theoretical concepts of valency in these compounds are usually complicated due to the wide variety of *d*-orbitals and the different symmetries of the *p*- and *d*-orbitals, Paddock (1964). Beside the academic interest in the valency problem, there has been an increasing industrial interest in the phosphonitriles because of their use as fire proofing reagents (Shaw, 1968).

In all the trimeric phosphonitriles examined so far by X-rays, the molecular formulae were of the types

$\text{R}_6\text{P}_3\text{N}_3$ and $\text{R}_4\text{R}'_2\text{P}_3\text{N}_3$, with two like substituents (R_2 or R'_2) at each P atom. A study of the crystal structure of $\text{Cl}_5\text{FP}_3\text{N}_3$ by Olthof (1969) did not quite achieve the objectives of the analysis since the F atom was found to be equally distributed over the six halogen positions. The present series on the $\text{Cl}_3[\text{N}(\text{CH}_3)_2]_3\text{P}_3\text{N}_3$ compounds has been undertaken in order to examine the stereochemistry of the P_3N_3 ring as the positions of the substituents on the ring are altered. These compounds were characterized by Keat & Shaw (1965) who also supplied suitable crystals for the X-ray analysis. The three compounds of this series are: (I) geminal 2,2,4-trichloro-4,6,6-trisdimethylamino-, (II) *cis* non-geminal 2,4,6-trichloro-2,4,6-trisdimethylamino- and (III) *trans* non-geminal 2,4,6-trichloro-2,4,6-trisdimethylamino-cyclotriphosphazatriene. The crystal

* National Research Council Postdoctoral Fellow.