Acta Cryst. (1960). **13**, 253

The Crystal Structure of the Binuclear Thiocyanate Complex α-$[Pt_2(SCN)_2Cl_2(P(C_3H_7)_3)_2]$

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(*Received* 30 *July* 1959)

α-$[Pt_2(SCN)_2Cl_2(P(C_3H_7)_3)_2]$ crystallises in the monoclinic system, space-group $P2_1/n$, with the unit-cell dimensions

$$a = 7{\cdot}54 \pm 0{\cdot}02,\ b = 13{\cdot}62 \pm 0{\cdot}03,\ c = 15{\cdot}09 \pm 0{\cdot}03\ \text{Å};\ \beta = 95{\cdot}0°.$$

The density is 1·937 g.cm.$^{-3}$, and there are two molecules in the unit cell (calculated density 1·930 g.cm.$^{-3}$); the molecule must therefore have a centre of symmetry.

The structure was derived from a study of the [010] and [100] projections. The two platinum atoms were shown to be linked by the two –SCN– groups, each platinum atom being bound to the sulphur atom of one –SCN– group and the nitrogen atom of the other. All the atoms in the molecule, except for those of the six propyl groups, are coplanar, within experimental error. The Pt–P bond length (2·16 Å) is very much shorter, and Pt–S (2·44 Å) is longer, than expected. This can be accounted for by strong double-bonding between platinum and phosphorus, together with a '*cis* influence' of the phosphorus atom operating through the $d(xy)$-type orbitals.

1. Introduction

Two compounds with the composition

$$[Pt_2(SCN)_2Cl_2(P(C_3H_7)_3)_2]$$

have been isolated (Chatt & Hart, 1952). The α-isomer (yellow, m.p. 144–152°) is slowly converted to the more stable β-isomer (pale yellow, m.p. 173–174·5°) in boiling benzene. They were at first thought to be the structural isomers, Figs. 1(*a*) and (*b*), but later infra-red studies (Chatt & Duncanson, 1956) led to the conclusion that the thiocyanate groups must lie in the bridge between the two metal atoms in both isomers. It was therefore suggested that they might be the geometrical isomers, Figs. 1(*c*) and (*d*). X-ray studies of other thiocyanate complexes (Zhdanov & Zvonkova, 1953; Lindqvist, 1957) have shown that it is also possible for a thiocyanate group to be bonded to two metal atoms by the sulphur and nitrogen atoms. The X-ray study of the structures of these two isomers was therefore undertaken, and in this paper that of the α-isomer is described. The principal structural results have been referred to in a preliminary communication (Chatt, Duncanson, Hart & Owston, 1958).

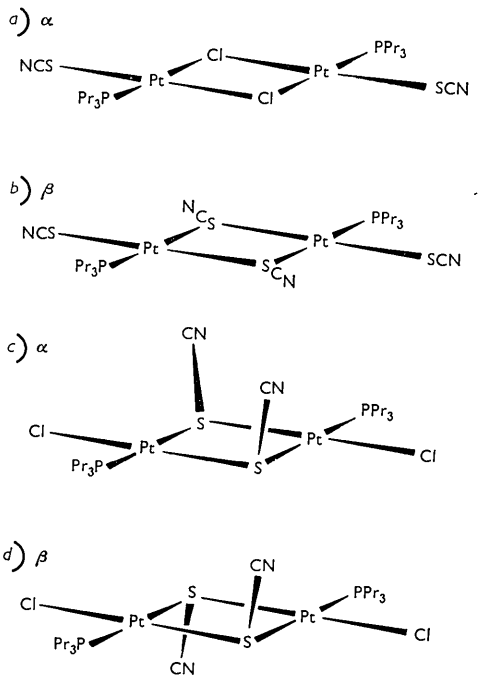

Fig. 1. Possible structures of the two isomers; (*a*) and (*b*) are structural isomers, (*c*) and (*d*) are geometrical isomers.

2. Experimental

The substance was crystallised from acetone, and small crystals with dimensions less than 0·02 mm. were selected. Rotation and Weissenberg photographs about the [010] and [100] axes were taken using Cu $K\alpha$ radiation (mean $\lambda = 1{\cdot}542$ Å), and the crystals found to be monoclinic with the following crystal data:

$$a = 7{\cdot}54 \pm 0{\cdot}02,\ b = 13{\cdot}62 \pm 0{\cdot}03,\ c = 15{\cdot}09 \pm 0{\cdot}03\ \text{Å};\ \beta = 95{\cdot}0°.$$

2 molecules per unit cell.

Density observed 1·937 g.cm.$^{-3}$, calculated 1·930 g.cm.$^{-3}$.

Systematic absences: $0k0$ with k odd.
$h0l$ with $(h+l)$ odd.

Space group: $P2_1/n$.
Molecular symmetry: centre ($\bar{1}$).

The centre of symmetry required in the molecule immediately excludes the structure suggested in Fig. 1(*c*). The infra-red spectrum (Chatt & Duncanson, 1956) also indicates that the molecule is centrosymmetric.

The intensities of the 146 *h*0*l* and 180 0*kl* reflections were estimated visually, and the usual Lorentz and polarization corrections applied. No correction was made for absorption, since the linear absorption coefficient is 214 cm.$^{-1}$, and absorption in the very small crystals used was therefore negligible.

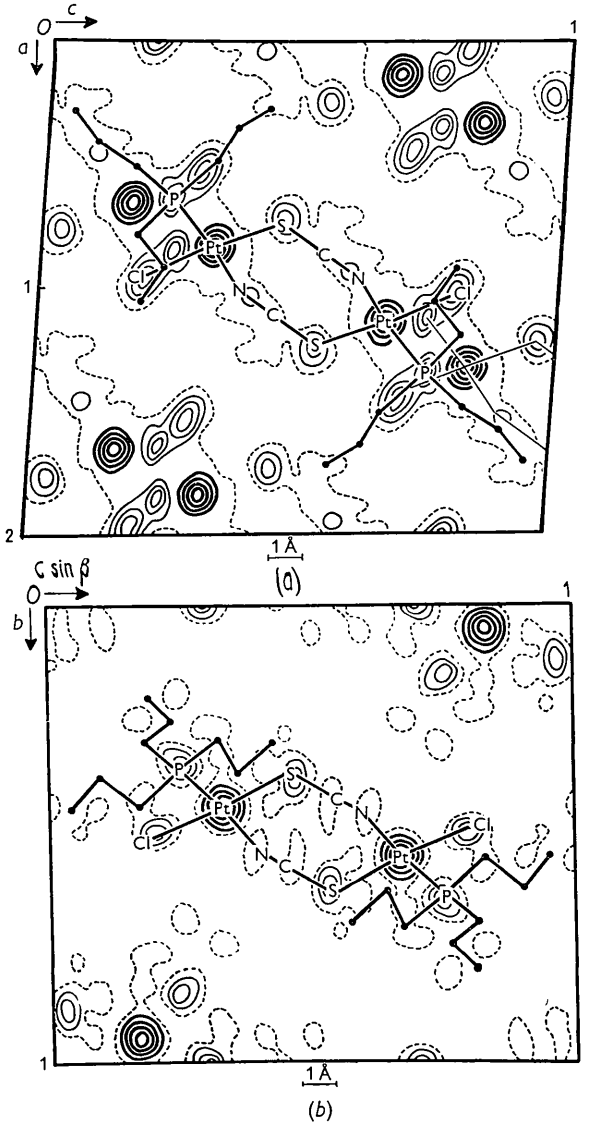

Fig. 2. Electron-density projections where the observed structure factors have the signs of their platinum atom contribution. The carbon atoms of the propyl chains are represented by full circles, and part of one molecule, which overlaps in the [010] projection, has been outlined. Contours are at every 25 e.Å^{-2} round platinum, 5 e.Å^{-2} elsewhere: 5 e.Å^{-2} contour broken. (*a*) [010] projection. (*b*) [100] projection.

3. Method of analysis and results

The position of the platinum atom was found from Patterson syntheses, and the positions of the other atoms by the systematic use of difference syntheses (Alderman, Owston & Rowe, 1960; Owston, Partridge & Rowe, 1960). The carbon atoms in the propyl groups were found by trial and error, with the help of models. The refinement was continued until the value of $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ fell to 0·11 for the [010] and 0·10 for the [100] projection, and the r.m.s. electron densities in the final difference maps were 1·42 e.Å^{-2} for the [010] and 1·65 e.Å^{-2} for the [100] projections.

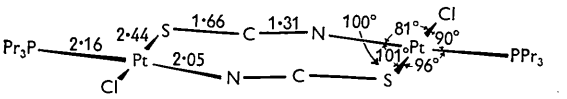

Fig. 3. Molecular configuration with principal bond lengths (in Å) and angles.

The approximate stereochemistry of the molecule is immediately apparent from the Fourier maps (Figs. 2(*a*) and (*b*)), and the final results after refinement are given in Tables 1–4 and Fig. 3. The standard deviations in Tables 1 and 3 were calculated from the diagonal terms only of the least-squares matrix, and may not be true measures of accuracy. No estimate of accuracy has been made for the carbon atoms in the propyl groups, since their parameters were not exhaustively refined; the standard deviations of their coordinates will be similar to those for the C and N atoms of the thiocyanate group.

4. Discussion

This type of bridging of two metal atoms by two –SCN– groups, forming an 8-membered ring, appears to have been found previously only in two complexes

Table 1. *Final atomic co-ordinates (decimal) and standard deviations*

	x	y	z	$a\sigma(x)$ (Å)	$b\sigma(y)$ (Å)	$c\sigma(z)$ (Å)
Pt	0·1553	0·0540	0·1688	0·0047	0·0066	0·0038
Cl	0·048	−0·010	0·300	0·024	0·041	0·023
S	0·250	0·134	0·036	0·027	0·042	0·024
P	0·352	0·138	0·249	0·027	0·043	0·027
N	−0·023	0·453	0·113	0·148	0·201	0·123
C	−0·125	0·425	0·043	0·148	0·190	0·113
C_1	0·717	0·196	0·073			
C_2	0·637	0·128	0·138			
C_3	0·510	0·209	0·170			
C_4	−0·060	0·299	0·300			
C_5	0·073	0·247	0·258			
C_6	0·210	0·198	0·315			
C_7	0·720	0·053	0·453			
C_8	0·587	0·125	0·400			
C_9	0·497	0·057	0·327			

Best molecular plane: $-0{\cdot}6825X+0{\cdot}7230Y+0{\cdot}1075Z=0$
where $X=ax\sin\beta$; $Y=by$; $Z=cz+ax\cos\beta$.

Table 2. *Temperature factors*

Atom	Projection [100]	Projection [010]
Pt	$\exp -[0{\cdot}0039h^2+0{\cdot}0032l^2-0{\cdot}0002kl]$	$\exp -[0{\cdot}0249h^2+0{\cdot}0043l^2-0{\cdot}0027hl]$
Cl, S and P	$\exp -[4{\cdot}0\ (\sin^2\theta)/\lambda^2]$	
N, C, CH_2 and CH_3	$\exp -[6{\cdot}0\ (\sin^2\theta)/\lambda^2]$	

Table 3. *Bond lengths and angles, with standard deviations*

Bond	Calculated length d	$\sigma(d)$	Sum of atomic radii	Angle	θ	$\sigma(\theta)$
Pt–P	2·16 Å	0·06 Å	2·44 Å	N–Pt–S	101·0°	8·1°
Pt–S	2·44	0·06	2·36	S–Pt–P	96·0	2·1
Pt–Cl	2·37	0·05	2·30	P–Pt–Cl	89·7	2·0
Pt–N	2·05	0·28	2·06	Cl–Pt–N	80·7	8·0
S–C	1·66	0·28	1·81*	Pt–S–C	100·7	9·7
C–N	1·31	0·39	1·51*	S–C–N	167·8	24·6
				Pt–N–C	147·7	22·9
$P–C_3$	2·01					
$P–C_6$	1·73			$Pt–P–C_3$	109·2	
$P–C_9$	1·89			$Pt–P–C_6$	98·3	
Mean P–C	1·88		1·87	$Pt–P–C_9$	111·8	
$C_3–C_2$	1·57			$P–C_3–C_2$	104·7	
$C_2–C_1$	1·51			$P–C_6–C_5$	108·7	
$C_6–C_5$	1·45			$P–C_9–C_8$	106·7	
$C_5–C_4$	1·42					
$C_9–C_8$	1·55			$C_3–C_2–C_1$	93·3	
$C_8–C_7$	1·57			$C_6–C_5–C_4$	117·3	
Mean C–C	1·51		1·54	$C_9–C_8–C_7$	102·2	

* Single-bond distances.

of cadmium (Zhdanov & Zvonkova, 1953; Calvalca, Nardelli & Fava, 1959), where the metal atoms are linked to form infinite chains. The bonding appears to be much stronger in this platinum complex, where reasonably stable discrete molecules exist both in the solid and in solution. Unlike the ($Cd_2(SCN)_2$) ring, the ($Pt_2(SCN)_2$) ring is planar, and interaction between the *d*-electrons of platinum and the π-electrons of the –SCN– groups can therefore confer a kind of 'aromatic character' on the 8-membered ring, resulting in additional stability. The distances of the atoms from the best molecular plane are all within experimental error with the possible exception of chlorine:

Pt 0·002, Cl 0·139, S 0·075 Å,
P 0·066, N 0·164, C 0·038 Å.

The Pt–P bond is very much shorter than expected from the sum of the atomic radii (Table 3), presumably due to strong double-bonding. As would be expected, this is much more marked than in *trans*-$[Pt(PEt_3)_2HBr]$ where two phosphorus atoms must share the same *d*-orbitals to form double bonds, and the Pt–P bond length is 2·26 Å (Owston *et al.*, 1960). The Pt–N bond, which is *trans* to the Pt–P bond, is of normal length, but the Pt–S bond length is greater than the sum of the atomic radii and considerably greater than the lengths of 2·30 and 2·27 Å reported in *cis*- and *trans*-$[Pt(NH_3)_2(SCN)_2]$ (Bleidelis, 1957; Bleidelis & Bokii, 1957). The Pt–Cl bond, which is also *cis* to the Pt–P bond, is a little longer than usual, though the difference is not highly significant. These results can be explained if the platinum *d*(*xy*)-orbital takes part in the strong double-bonding between platinum and phosphorus, and interacts so strongly with the phosphorus *d*-orbitals that it is less readily available than usual for forming double bonds with the atoms *cis* to phosphorus. This '*cis*-influence' of the phosphorus atom will act most strongly on bonds which normally have most double-bond character, and in this example therefore the Pt–S bond is more affected than the Pt–Cl bond.

The bond angle Pt–S–C is similar to those found in *cis*- and *trans*-$[Pt(NH_3)_2(SCN)_2]$, where the average value is 106°. The standard deviations of the positions of the light atoms are so large that little chemical significance can be attached to the values obtained for the S–C–N and Pt–N–C bond angles. Since our main purpose was to establish the approximate stereochemistry of the molecule no further study of these more detailed points is proposed.

The authors are indebted to Dr J. Chatt for suggesting the problem and for helpful discussion, to Dr F. A. Hart for providing the material, to Miss F. R. Harper for experimental assistance, and to Miss G. G.

Table 4. *Observed and calculated structure factors*

[010] projection

h	k	l	$\lvert F_o\rvert$	F_c
0	0	0	—	856
		2	217	−243
		4	63	−66
		6	207	209
		8	131	−135
		10	73	−70
		12	90	101
		14	85	−78
		16	18	− 8
		18	15	22
1	0	$\bar{19}$	18	22
		$\bar{17}$	<12	0
		$\bar{15}$	66	−70
		$\bar{13}$	112	107
		$\bar{11}$	40	−31
		$\bar{9}$	71	−75
		$\bar{7}$	226	226
		$\bar{5}$	144	−128
		$\bar{3}$	182	−183
		$\bar{1}$	334	338
		1	178	−175
		3	37	38
		5	107	111
		7	88	−80
		9	106	−104
		11	117	112
		13	58	−65
		15	36	−27
		17	40	46
		19	6	−14
2	0	$\bar{18}$	<10	0
		$\bar{16}$	28	−28
		$\bar{14}$	87	76
		$\bar{12}$	33	−24
		$\bar{10}$	41	−45
		$\bar{8}$	144	157
		$\bar{6}$	90	−58
		$\bar{4}$	182	−186
		$\bar{2}$	99	98
		0	89	−76
		2	202	−244
		4	186	185
		6	48	−50
		8	110	−102
		10	154	167
		12	39	−33
		14	26	−24
		16	62	53
		18	13	−22
3	0	$\bar{17}$	< 9	−13
		$\bar{15}$	44	38
		$\bar{13}$	<14	− 5
		$\bar{11}$	57	−84
		$\bar{9}$	81	91
		$\bar{7}$	54	−38
		$\bar{5}$	135	−131
		$\bar{3}$	132	116
		$\bar{1}$	47	−45
		1	133	−143
		3	240	233
		5	95	−108
		7	54	−44
		9	124	134
		11	44	−26
		13	24	−26
		15	40	49
		17	21	−25
4	0	$\bar{16}$	12	14
		$\bar{14}$	13	− 2
		$\bar{12}$	53	−70
		$\bar{10}$	77	78
		$\bar{8}$	42	−38
		$\bar{6}$	62	−56
		$\bar{4}$	134	127
		$\bar{2}$	37	−18
		0	75	−74
		2	196	197
		4	65	−46
		6	41	−48
		8	55	47
		10	24	−19
		12	48	−52
		14	47	42
		16	20	−19
5	0	$\bar{17}$	7	16
		$\bar{15}$	<12	5
		$\bar{13}$	41	−46
		$\bar{11}$	60	64
		$\bar{9}$	<14	− 5
		$\bar{7}$	24	−21
		$\bar{5}$	80	87
		$\bar{3}$	<12	2
		$\bar{1}$	79	−91
		1	92	99
		3	44	−32
		5	58	−69
		7	58	53
		9	<14	−13
		11	52	−65
		13	55	54
		15	15	−16
6	0	$\bar{16}$	< 5	6
		$\bar{14}$	<12	−14
		$\bar{12}$	42	37
		$\bar{10}$	<14	− 6
		$\bar{8}$	26	−28
		$\bar{6}$	63	45
		$\bar{4}$	<14	7
		$\bar{2}$	74	−102
		0	74	62
		2	30	−23
		4	60	−75
		6	74	71
		8	<14	− 5
		10	37	−37
		12	45	54
7	0	$\bar{13}$	< 9	10
		$\bar{11}$	<12	6
		$\bar{9}$	25	−40
		$\bar{7}$	30	17
		$\bar{5}$	<13	7
		$\bar{3}$	52	−63
		$\bar{1}$	62	57
		1	<12	− 9
		3	39	−37
		5	47	57
		7	<13	− 7
		9	36	−18
		11	33	33
8	0	$\bar{12}$	< 1	13
		$\bar{10}$	<11	−23
		$\bar{8}$	26	29
		$\bar{6}$	<12	0
		$\bar{4}$	34	−21
		$\bar{2}$	40	40
		0	<13	8
		2	30	−18
		4	36	28
		6	<12	2
		8	< 9	−23
9	0	$\bar{7}$	<15	1
		$\bar{5}$	< 9	− 1
		$\bar{3}$	<11	9
		$\bar{1}$	<11	12
		1	15	−22
		3	26	16
		5	< 7	− 2

[100] projection

h	k	l	$\lvert F_o\rvert$	F_c
0	0	0	—	856
		2	248	−246
		4	66	−69
		6	224	218
		8	129	−145
		10	85	−76
		12	130	110
		14	128	−90
		16	44	−15
0	1	1	207	161
		2	83	−87
		3	206	−193
		4	36	28
		5	76	76
		6	30	− 2
		7	116	123
		8	64	−87
		9	178	−163
		10	41	41
		11	44	46
		12	52	0
		13	56	45
		14	54	−27
		15	106	−88
		16	50	22
0	2	0	254	221
		1	261	−317
		2	83	−81
		3	21	−14
		4	95	−103
		5	76	77
		6	193	191
		7	121	−130
		8	102	−103
		9	34	−23
		10	40	−23
		11	72	79
		12	55	67
		13	88	−82
		14	57	−42
		15	53	22
		16	52	−17
0	3	1	30	−18
		2	148	−157
		3	88	−106
		4	179	219
		5	27	− 2
		6	29	−33
		7	68	70
		8	130	−121
		9	60	−65
		10	106	92
		11	54	58
		12	53	−16
		13	57	34
		14	54	−55
		15	55	−45
		16	49	52
0	4	0	46	34
		1	193	−172
		2	88	−98
		3	25	23
		4	58	−25
		5	190	183
		6	53	72
		7	168	−200
		8	52	−69
		9	36	20
		10	52	35
		11	109	89
		12	56	16
		13	81	−82
		14	56	8
		15	51	10
0	5	1	40	−21
		2	173	−141
		3	29	31
		4	203	213
		5	51	−56
		6	33	14
		7	35	− 6
		8	94	−86
		9	41	15
		10	117	37
		11	55	2
		12	54	−20
		13	57	13
		14	53	−59
		15	53	4
0	6	0	69	−53
		1	130	−111
		2	31	20
		3	30	− 5
		4	57	51
		5	169	172
		6	100	−71
		7	128	−151
		8	50	22
		9	41	39

Table 4 (*cont.*)

h k l	$\|F_o\|$	F_c	*h k l*	$\|F_o\|$	F_c	*h k l*	$\|F_o\|$	F_c	*h k l*	$\|F_o\|$	F_c
10	55	36	2	55	52	10	< 54	− 5	3	81	83
11	75	96	3	< 34	4	11	56	−53	4	< 54	−42
12	57	−49	4	83	94	12	< 51	−10	5	57	−57
13	54	−66	5	< 38	18	13	51	−16	6	< 54	− 8
14	55	21	6	106	−138				7	57	−24
			7	< 50	−42	0 10 0	110	−121	8	< 54	27
0 7 1	79	−54	8	55	83	1	< 50	12	9	55	53
2	82	−92	9	< 54	−18	2	58	46			
3	141	160	10	57	25	3	< 51	−11	0 12 0	57	−73
4	119	103	11	< 54	32	4	55	30	1	73	81
5	68	−67	12	74	−74	5	< 53	−43	2	57	16
6	36	− 6	13	< 51	−32	6	75	−75	3	< 57	−16
7	41	−16				7	< 54	25	4	57	21
8	66	−47	0 9 1	63	−59	8	57	22	5	< 57	−34
9	77	67	2	< 38	−26	9	< 54	−28	6	56	−39
10	75	73	3	142	142	10	56	51	7	< 55	52
11	57	−60	4	< 48	21	11	< 51	− 7			
12	54	− 8	5	72	−68	12	73	−63	0 13 1	57	−13
13	55	−20	6	< 51	−34	13	< 46	4	2	< 56	52
14	50	−36	7	55	5				3	56	28
			8	< 54	−21	0 11 1	78	−55	4	< 56	−42
0 8 0	103	−105	9	81	73	2	< 53	29	5	55	−16
1	74	−69									

Reynolds who undertook most of the computing work, including the tedious task of finding the best positions for the light atoms.

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The Structure of the Intermetallic Phase θ(Cr–Al)

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(*Received* 31 *July* 1959)

The monoclinic θ-phase in the chromium–aluminium system has been shown to be isomorphous with α′(V–Al). The structure has been refined and the interatomic distances are discussed and compared with those in α′(V–Al) and with those in two ternary alloy phases containing chromium and aluminium.

1. Introduction

The chromium–aluminium system has been investigated by many workers and the composition of the θ-phase, which is in equilibrium with the primary solid solution, has been shown to be represented by the formula $CrAl_7$ (Raynor & Little, 1945). The phase forms monoclinic crystals and the unit cell given by Hofmann & Wiehr (1941) is:

$$a = 20{\cdot}43,\ b = 7{\cdot}62,\ c = 25{\cdot}31\ \text{Å};\ \beta = 155°\ 10'.$$

This unit cell corresponds to the morphology of the crystals.

The similarity of rotation photographs from θ(Cr–Al) and α′(V–Al) has been reported by Brown (1957). The present analysis of θ(Cr–Al) was undertaken to investigate the relationship between the two phases and in particular the nature of the chromium–aluminium