

**682. Tetrahedral Nickel(II) Complexes and the Factors Determining Their Formation. Part V.\* The Tetrahedral Co-ordination of Nickel in Dichlorobistriphenylphosphinenickel.**

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The molecule  $(\text{Ph}_3\text{P})_2\text{NiCl}_2$  is shown by X-ray analysis to contain a tetrahedrally co-ordinated nickel atom with the angles P-Ni-P  $117^\circ$  and Cl-Ni-Cl  $123^\circ$ .

COMPOUNDS  $(\text{Ph}_3\text{P})_2\text{NiX}_2$  (X = Cl, Br, or I) do not have the *trans*-planar configuration commonly found among nickel compounds of similar composition. They have large dipole moments and are paramagnetic.<sup>1</sup> Molecular weights could not be determined satisfactorily but the evidence from dipole moments is not easily reconciled with dimerisation or more complex association. The observations could be explained by either tetrahedral or *cis*-planar structures of a monomer. Either of these would be unusual and, there being no chemical method of distinguishing them, a crystal-structure determination was undertaken.

*Complex*  $(\text{Ph}_3\text{P})_2\text{NiCl}_2$ .  $\text{C}_{26}\text{H}_{30}\text{Cl}_2\text{NiP}_2$ ,  $M = 654$ , monoclinic prisms,  $a = 11.70$ ,  $b = 8.31$ ,  $c = 17.59 \pm 0.05$  Å,  $\beta = 108^\circ \pm 0.5^\circ$ ,  $V = 1627$  Å<sup>3</sup>,  $D_m = 1.348$  g./c.c. (pycnometer),  $Z = 2$ ,  $D_c = 1.33$  g./c.c. Space group  $P2/c$  ( $C_{2h}^2$ , No. 13) or  $Pc$  ( $C_s^2$ , No. 7). Cu- $K_\alpha$  radiation, single-crystal oscillation and Weissenberg photographs. Implied molecular symmetry  $2(C_2)$  for space group  $P2/c$ , shown to be correct by the subsequent structure analysis.

*Complex*  $(\text{Ph}_3\text{P})_2\text{NiBr}_2$ .  $\text{C}_{36}\text{H}_{30}\text{Br}_2\text{NiP}_2$ ,  $M = 742$ , monoclinic needles,  $a = 10.3$ ,  $b = 9.1$ ,  $c = 39.2 \pm 0.1$  Å,  $\beta = 111^\circ \pm 1^\circ$ ,  $V = 3452$  Å<sup>3</sup>,  $D_m = 1.44$  g./c.c. (flotation),  $Z = 4$ ,  $D_c = 1.426$  g./c.c.

*Complex*  $(\text{Ph}_3\text{P})_2\text{NiI}_2$ .  $\text{C}_{36}\text{H}_{30}\text{NiP}_2\text{I}_2$ ,  $M = 837$ , monoclinic plates,  $a = 19.6$ ,  $b = 10.3$ ,  $c = 18.2 \pm 0.05$  Å,  $\beta = 112^\circ \pm 0.5^\circ$ ,  $V = 3407$  Å<sup>3</sup>,  $D_m = 1.64$  g./c.c. (pycnometer),  $Z = 4$ ,  $D_c = 1.628$ . Space group  $P2/c$  ( $C_{2h}^2$ , No. 13) or  $Pc$  ( $C_s^2$ , No. 7). Cu- $K_\alpha$  radiation, single-crystal oscillation and Weissenberg photographs. Implied molecular symmetry  $1(C_1)$ .

*Structure of*  $(\text{Ph}_3\text{P})_2\text{NiCl}_2$ .—The crystal structure, so far as the immediate surroundings of the nickel atom are concerned, was determined from projections along the three unit-cell axes. Zero-layer Weissenberg photographs were taken about the three principal axes and the intensities of the reflections were measured by visual comparison with a standard intensity scale.

The systematic absences indicate space group  $Pc$  or  $P2/c$ . The latter centrosymmetric

\* Part IV, *J.*, 1962, 693.

<sup>1</sup> Venanzi, *J.*, 1958, 719.

space group was first assumed and subsequent refinement of the structure has proved this assumption to be valid. Cell dimensions were obtained from copper-calibrated Weissenberg photographs. There are two molecules per unit cell and the nickel atoms therefore occupy special positions. In  $P2/c$  there are two types of special position. In one of these the point symmetry is  $\bar{1}$  and in the other the symmetry is 2. Patterson projections obtained with  $F^2_{0kl}$  and  $F^2_{hk0}$  confirm that the nickel atoms occupy either position (e) or (f) of space group  $P2/c$  having point symmetry 2. These positions are identical but for a change of origin.

The Patterson synthesis with  $F^2_{hol}$ , sharpened by a Wäser-Schomaker sharpening function corresponding to point atoms at rest, showed the positions of the phosphorus and chlorine atoms. A Fourier  $F_{hol}$  synthesis, phased on these positions of the nickel,

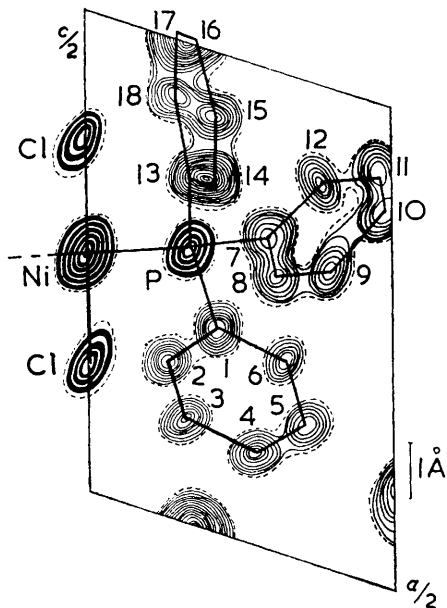


FIG. 1. Electron-density projection on (010) of  $(\text{Ph}_3\text{P})_2\text{NiCl}_2$ . Broken contours are drawn at zero  $e/\text{Å}^2$ , others at intervals of 1  $e/\text{Å}^2$ ; but at ten times this interval round the nickel, phosphorus, and chlorine atoms.

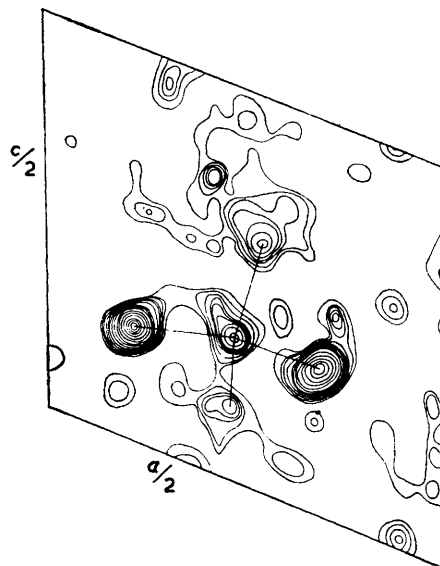


FIG. 2. Electron-density projection on (010) of  $(\text{Ph}_3\text{P})_2\text{NiCl}_2$ . Contours are drawn at arbitrary equal intervals.

phosphorus, and chlorine showed the eighteen carbon atoms disposed around the phosphorus atom in three benzene rings.

Co-ordinates  $x$  and  $y$  of the heavy atoms and of most of the carbon atoms in this projection were refined by a series of electron-density syntheses and finally by difference syntheses. The scattering factor for the nickel atom was corrected for anomalous dispersion, and individual isotropic temperature factors were applied to all the atoms. The final difference synthesis indicated a slight thermal anisotropy, but this was not taken into account in the calculation of structure factors. The final  $F_{\text{obs}}$  synthesis is shown in Fig. 1.

The two other Patterson projections gave  $y$  co-ordinates for the three heavy atoms. For the carbon atoms the  $y$  co-ordinates were provisionally estimated from a model. Electron-density and difference syntheses were used to refine the atomic positions. The co-ordinates of several of the carbon atoms are less accurate than others owing to overlap, which occurs in both projections.

The final parameters of the twenty-one atoms are shown in Table 1. The significant bond distances and angles are: Ni-Cl = 2.27, Ni-P = 2.28 Å; Cl-Ni-Cl = 123°, P-Ni-P = 117°. The structure factors are in Table 2. The *R* values are: for *h0l*, 22.5; for

TABLE 1.  
Final atomic parameters for  $(\text{Ph}_3\text{P})_2\text{NiCl}_2$ .

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
Ni	0	0.197	0.250	C5	0.357	0.871	0.142	C12	0.386	0.171	0.393
P	0.174	0.053	0.289	C6	0.325	0.996	0.200	C13	0.179	0.925	0.376
Cl	0.008	0.327	0.138	C7	0.300	0.204	0.329	C14	0.213	0.767	0.367
C1	0.215	0.934	0.213	C8	0.310	0.354	0.295	C15	0.217	0.668	0.433
C2	0.137	0.816	0.170	C9	0.405	0.469	0.325	C16	0.187	0.731	0.007
C3	0.170	0.725	0.111	C10	0.490	0.434	0.389	C17	0.153	0.890	0.015
C4	0.278	0.754	0.097	C11	0.480	0.285	0.423	C18	0.150	0.986	0.450

TABLE 2.  
Structure factors for  $(\text{Ph}_3\text{P})_2\text{NiCl}_2$ .

<i>h</i>	<i>l</i>	<i>F</i> <sub>obs.</sub>	<i>F</i> <sub>calc.</sub>	<i>h</i>	<i>l</i>	<i>F</i> <sub>obs.</sub>	<i>F</i> <sub>calc.</sub>	<i>h</i>	<i>l</i>	<i>F</i> <sub>obs.</sub>	<i>F</i> <sub>calc.</sub>	<i>h</i>	<i>l</i>	<i>F</i> <sub>obs.</sub>	<i>F</i> <sub>calc.</sub>
<i>h0l</i> zone ( <i>R</i> = 22.5%)															
0	2	-28.4	-24.2	3	-4	-14.1	-12.0	7	0	17.9	12.9	10	-16	8.2	7.9
	4	-15.4	-18.1		-8	21.8	17.9		2	-7.3	-5.7		-18	-8.1	-5.4
	8	10.6	12.1		-10	-17.5	-16.3		4	2.5	0.8	11	0	2.6	4.4
	10	4.2	5.1		-12	2.3	0.9		6	9.7	9.4		2	2.5	4.2
	12	-5.4	-6.7		-14	-10.9	-9.5		8	-2.7	-3.8		4	5.3	1.9
	14	9.1	5.5		-16	2.7	7.6		10	-2.6	-3.8		6	-5.4	-7.9
	16	4.6	5.0		-18	-7.2	-10.8		12	2.4	-0.8		8	14.3	12.2
	18	3.4	1.7		-20	3.1	6.9		14	-10.9	-10.2		-2	-9.3	-8.8
	20	1.9	2.9						-2	-15.0	-10.4		-4	-2.7	-2.5
				4	0	13.0	12.1		-4	12.5	9.3		-6	-2.7	-0.7
	0	25.7	24.9		2	-22.2	-22.2		-6	-10.8	-4.9		-8	9.3	15.2
	2	3.5	0.9		4	-1.8	-3.7		-8	16.1	12.3		-10	2.6	1.3
	4	6.5	8.5		6	-12.3	-12.8		-10	-13.4	-8.4		-12	-6.3	-6.6
	6	12.6	12.1		8	13.9	16.1		-12	9.9	12.5		-14	2.4	1.1
	8	13.1	12.6		10	-13.3	-9.7		-14	-3.8	-7.6		-16	4.3	1.8
	10	-9.6	-13.4		12	6.0	9.3	8	0	6.4	2.8		-18	-6.0	-11.4
	12	-5.5	-8.9		14	2.6	1.1		2	-2.5	-0.5	12	0	8.4	7.2
	14	-2.7	-4.9		16	2.3	0.4		4	-12.7	-17.9		2	-6.4	-12.9
	16	7.5	2.8		-2	12.4	10.5		6	2.7	3.9		4	-2.0	-1.8
	18	-2.3	-2.0		-4	-8.3	-3.7		8	2.7	6.2		-2	2.5	4.4
	20	3.3	3.4		-6	-13.0	-18.6		10	-6.0	-10.1		-4	8.1	9.3
	-2	-19.7	-22.9		-8	2.4	6.4		12	4.6	5.8		-6	-8.1	-7.1
	-4	13.1	16.5		-10	-11.9	-7.1		14	-4.3	-10.1		-8	8.4	7.3
	-6	-9.9	-6.1		-12	-2.4	-3.1		-2	2.3	3.6		-10	-2.5	-2.4
	-8	19.9	21.1		-14	-10.0	-5.4		-4	7.4	5.4		-12	-5.8	-5.4
	-10	-14.1	-12.9		-16	14.7	9.8		-6	-22.1	-19.0	13	0	10.0	8.3
	-12	5.8	4.9		-18	-9.3	-11.8		-8	19.3	13.1		-2	-5.3	-7.2
	-14	8.6	13.2	5	0	30.4	28.5		-10	-18.0	-17.9		-4	7.2	7.7
	-16	2.7	6.4		2	-4.4	-7.0		-12	10.0	11.2		-6	-7.6	-5.2
	-18	-2.5	-4.5		4	5.8	3.5		-14	-5.4	-3.6		-8	7.2	4.8
					6	-11.7	-6.7						-10	-6.2	-4.5
2	0	-12.4	-14.2		8	25.7	22.8	9	0	-2.6	-3.0	14	-2	1.6	1.6
	2	-2.9	-5.5		10	-14.0	-11.2		2	-13.9	-15.0		-4	1.8	0.8
	4	-5.6	-4.2		12	-2.7	-1.8		4	9.3	14.1		-6	-5.9	-6.8
	6	-1.7	-3.5		14	6.0	9.3		6	2.7	1.8		-8	6.4	4.7
	8	10.5	8.6		-2	-15.7	-11.8		8	-2.5	-4.3		-10	-6.0	-10.8
	10	-10.0	-10.6		-4	-1.7	-1.2		10	-7.6	-11.8				
	12	-2.6	-1.4		-6	6.3	4.7		12	1.6	1.7				
	14	-9.5	-10.9		-8	11.7	11.7		-2	2.5	0.9				
	16	8.5	11.8		-10	-2.2	-3.7		-4	-11.3	-8.9				
	18	-14.8	-12.4		-12	-8.3	-8.8		-6	-5.1	-1.9				
	-2	-4.1	-0.2		-14	7.4	1.5		-8	12.2	9.5				
	-4	-11.4	-10.1		-16	9.7	5.9		-10	-13.2	-15.5				
	-6	-13.8	-14.9		-18	-9.6	-11.3		-12	2.7	0.5	0	1	43.8	53.7
	-8	19.9	22.3						-14	2.7	6.9		2	-33.8	-39.4
	-10	-23.2	-26.4						-16	8.7	9.3		3	18.6	20.5
	-12	14.7	13.1	6	0	36.6	40.1		-18	-8.0	-11.4		7	-14.6	-12.1
	-14	2.6	2.2		2	-9.8	-7.9						8	-13.9	-18.1
	-16	-2.7	-2.2		4	8.0	5.3						10	-10.6	-4.4
	-18	-6.2	-1.6		6	-4.2	-3.9	10	0	12.3	13.7	1	1	20.6	32.0
					8	6.4	7.5		2	-13.0	-12.4		2	-23.9	-28.1
					10	-2.7	-0.2		4	8.5	4.6		3	18.6	22.6
3	0	-12.3	-9.0		12	-2.6	-3.0		6	-8.7	-6.7		6	13.9	8.2
	2	-23.0	-23.3		14	4.9	5.0		8	7.0	8.4		7	-14.6	-19.9
	4	-3.6	-0.8		-2	-20.7	-13.7		10	-4.1	-0.6		8	-11.9	-13.7
	6	4.6	2.9		-4	-1.9	-1.0		-2	-2.7	-3.2		10	7.3	4.5
	8	-2.2	-0.1		-6	4.8	2.7		-4	-10.6	-11.4	2	0	-22.6	-28.3
	10	-13.8	-15.0		-8	18.9	16.7		-6	2.7	1.8		1	-45.2	-54.4
	12	9.3	13.4		-10	2.3	0.8		-8	-2.7	-0.1		2	21.2	-16.6
	16	-2.4	-3.4		-12	-11.1	-13.4		-10	2.7	4.0		3	-13.3	-14.2
	18	-5.1	-5.6		-14	9.5	6.2		-12	2.7	1.0				
	-2	-21.8	-24.4		-16	6.0	8.6		-14	-7.3	-5.2				

TABLE 2. (Continued.)

$h$	$k$	$F_{\text{obs.}}$	$F_{\text{calc.}}$	$h$	$k$	$F_{\text{obs.}}$	$F_{\text{calc.}}$	$h$	$l$	$F_{\text{obs.}}$	$F_{\text{calc.}}$	$h$	$l$	$F_{\text{obs.}}$	$F_{\text{calc.}}$
2	4	-8.6	-13.0	9	1	13.9	8.5	1	9	-15.6	-5.8	4	5	17.8	20.3
	6	11.9	20.8		2	-17.9	-14.9		10	12.8	8.6		6	-16.6	-8.5
	8	-15.3	-14.9						11	10.4	12.9		7	-10.0	-17.4
3	0	-21.9	-17.9	10	0	24.2	27.5		14	10.4	9.2		11	-11.8	-4.6
	1	-25.2	-30.3					2	0	-33.8	-39.4		13	-17.2	-26.8
	2	-31.9	-35.4	11	0	5.3	8.7		1	28.2	23.9		15	-23.1	-26.1
	3	-15.9	-14.7		5	-6.0	-9.9		2	-17.4	-17.3	5	2	-16.2	-22.4
	4	-7.3	-16.7	12	0	15.9	14.3		3	16.1	28.2		3	18.5	15.1
	5	8.6	20.5		1	7.3	3.5		4	26.6	29.7		4	-13.8	-10.0
	6	27.9	38.3						5	-46.7	-42.7		5	-12.0	-10.8
	8	13.9	6.7	13	0	20.0	16.7		7	7.1	11.1		6	-9.6	-16.9
4	0	23.2	24.2		2	-6.0	-6.0		8	-34.2	-34.6		8	-8.1	-6.5
	1	-30.5	-35.0						9	14.9	16.5		9	8.3	14.7
	2	-35.8	-42.6						10	18.9	18.0		10	-8.5	-8.0
	3	18.6	18.7						12	-22.6	-32.4		11	8.6	10.6
	4	10.0	5.2						13	-13.2	-12.8		12	14.9	6.9
	7	-13.9	-12.0						14	12.1	8.0		14	-12.9	-24.2
				$Ok$ zone ( $R = 29.8\%$ )											
				0	2	-55.8	-48.4	3	0	18.6	20.5	6	1	-18.2	-15.5
					4	-30.7	-36.1		2	4.9	10.6		3	19.4	22.3
					8	20.8	24.1		3	-10.3	-6.2		6	11.7	3.8
					10	8.3	10.2		4	-9.4	-3.6		7	10.3	4.6
					12	-10.9	-13.3		5	17.1	10.4		9	-8.6	-7.1
					14	18.9	11.1		7	6.4	2.7		10	-10.5	-20.6
					16	8.6	10.0		8	-10.7	-17.9				
				1	0	54.2	53.7		9	13.4	18.2	7	0	-13.4	-12.1
					1	-37.0	-35.2		10	9.3	11.2		1	-18.9	-19.7
					2	-33.5	-27.9		11	-14.9	-22.3		4	-13.6	-9.4
					3	37.6	37.3		12	-22.7	-34.1		5	10.5	9.6
					4	28.6	35.6		14	29.3	35.9		7	10.5	14.1
					5	-18.8	-7.6								
					6	-7.0	-2.6	4	1	5.8	4.9	8	0	-16.0	-18.1
					7	12.1	13.0		2	-2.6	-1.8		2	14.8	20.6
					8	-10.2	-2.5		4	13.3	4.8				

$hk0$ , 23.4; and for  $Ok$ , 29.8. The values of  $F_{\text{calc.}}$  are based on atomic scattering factors for nickel, phosphorus, chlorine, and carbon given by Thomas and Umeda.<sup>2</sup> They were corrected for anomalous dispersion by the method of Dauben and Templeton.<sup>3</sup> The isotropic temperature factors,  $B$ , used in the final structure factor calculations were for Ni 1.5, P 2.0, Cl 2.5, and C 3 Å<sup>2</sup>.

In two zones,  $hk0$  and  $Ok$ , the number of reflections is small. The high  $R$  values are due to lack of refinement, particularly of the carbon atom positions. The  $h0l$  projection uses 212 terms and resolves nearly all the atoms. Some refinement of carbon positions, which was possible in this projection, brought the  $R$  value to 22.3%. This constitutes the main evidence for the proposed structure. The other projections give further information concerning the co-ordinates of the nickel, chlorine, and phosphorus atoms.

In projection neither  $F_{\text{obs.}}$  nor  $F_{\text{diff.}}$  syntheses allow further progress. Refinement of the structure would require three-dimensional methods. The co-ordinates determined for the immediate neighbourhood of the nickel atom are sufficiently accurate for the present purpose; it is not intended to collect three-dimensional data for the purpose of establishing accurate carbon positions.

The details of the structure of  $(\text{Ph}_3\text{P})_2\text{NiCl}_2$  show three interesting features: (1) the Ni-Cl and Ni-P bond distances, 2.27 and 2.28 Å, respectively, are very close to the sum of the covalent radii (Ni-Cl 2.24 Å, and Ni-P 2.30 Å, calculated from Ni-metal, Cl<sub>2</sub> and  $[\text{PH}_4]^+$ ); (2) the Cl-Ni-Cl and P-Ni-P bond angles, 123° and 117°, respectively, are larger than tetrahedral; (3) the angle Cl-Ni-Cl is larger than the angle P-Ni-P.

One of us<sup>1</sup> earlier attributed the formation of complexes of nickel(II) with tetrahedral structure to a combination of electronic and steric effects. The field-inducing capacity of the halide and triphenylphosphine ligands was thought to be too low to cause the formation of diamagnetic square-planar complexes, while the bulk of the triphenylphosphine prevented polymerisation of  $(\text{Ph}_3\text{P})_2\text{NiCl}_2$  to form an octahedrally co-ordinated nickel

<sup>2</sup> Thomas and Umeda, *J. Chem. Phys.*, 1957, **26**, 293.

<sup>3</sup> Dauben and Templeton, *Acta Cryst.*, 1955, **8**, 841.

with an arrangement of donor atoms similar to that found in  $\text{Py}_2\text{CoCl}_2$ .<sup>4</sup> This view receives general support from the present structure determination.

Dunitz and Orgel<sup>5</sup> have pointed out that the Jahn-Teller effect operates in tetrahedral complexes of nickel(II). Thus, the distortions of bond angles observed in  $(\text{Ph}_3\text{P})_2\text{NiCl}_2$  could be attributed to this cause. More recently, however, Liehr and Ballhausen<sup>6</sup> have suggested that, as a result of spin-orbit coupling, the ground state of the nickel(II) atom is not orbitally degenerate and, thus, no Jahn-Teller distortion should be observed. In that case the large bond angles now found could be attributed to the steric requirements of triphenylphosphine which might cause a general widening of angles.

The simplest explanation for the difference in P-Ni-P and Cl-Ni-Cl bond angles is provided by the general stereochemical rule governing the magnitude of interelectronic repulsions between bonded pairs and lone pairs: the lone-pair repulsions of the chlorine atoms are expected to be larger than the bond-pair repulsions of the phosphine.

*Structure of  $(\text{Ph}_3\text{P})_2\text{NiI}_2$ .*—No detailed structural study of this compound was undertaken. From a Patterson projection for [010] iodine atoms were readily located and, these being known, the map could be further interpreted to give positions for the nickel and phosphorus atoms. A first electron-density map (Fig. 2), phased on the heavy atom positions, shows an arrangement consistent with tetrahedral co-ordination. The atoms I-Ni-I and P-Ni-P depart noticeably from linearity. If this were ignored and a planar structure were assumed, the molecule would be of the *trans*-form; this is incompatible with the observed dipole moment of 9.0 D, and, therefore, it is concluded that, like  $(\text{Ph}_3\text{P})_2\text{NiCl}_2$ , the iodo-complex is tetrahedral.

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<sup>4</sup> Dunitz, *Acta Cryst.*, 1957, **10**, 307.

<sup>5</sup> Dunitz and Orgel, *J. Phys. Chem. Solids*, 1957, **3**, 20.

<sup>6</sup> Liehr and Ballhausen, *Ann. Phys.*, 1959, **6**, 134.

<sup>7</sup> Mills and Rollett, "Computing Methods and the Phase Problem in X-Ray Crystal Analysis," Pergamon, London, 1961, p. 107.