Acta Cryst. (1971). B**27**, 1233

The Crystal Structure of 1,2-Bis-(2-methylpyridinium)ethane Tetracyanonickelate(II) Trihydrate

BY L. D. C. BOK, S. S. BASSON, J. G. LEIPOLDT AND G. F. S. WESSELS

Department of Chemistry, University of the O.F.S. Bloemfontein, South Africa

(*Received* 15 *September* 1970)

The crystal structure of the title compound ($C_{18}H_{18}N_6Ni.3H_2O$) has been determined by three-dimensional X-ray analysis. The space group is *Pnnm*, and the cell dimensions are: a = 7·02, b = 19·31 and c = 15·53 Å, and Z = 4. The structure determination was based on intensities of 1612 independent reflexions obtained with Cu $K\alpha$ radiation at room temperature using the multiple-film method. The structure was refined by a least-squares method to a conventional R index of 13·3%. The $Ni(CN)_4^{2-}$ ion is square-planar and the bond lengths are: Ni–C = 1·86 and C–N = 1·15 Å (average). The centre of the 1,2-bis-(2-methylpyridinium)ethane ion lies on a twofold axis. The methyl groups in position 2 of the pyridine rings are arranged *cis* to one another with a C· · ·C distance of 3·94 Å. The bond lengths in the pyridine rings agree well with those in pyridine. The distance between the nitrogen atoms in the 1,2-bis-(2-methylpyridinium)ethane ion is 3·74 Å, which is approximately the distance between the positive charges in the divalent cation. Each water molecule is strongly hydrogen-bonded to two other water molecules and one nitrogen atom of the $Ni(CN)_4^{2-}$ ion.

Introduction

The crystal structure of 1,2-bis-(2-methylpyridinium)ethane tetracyanonickelate(II) trihydrate has been determined as part of a program for the study of the structures of complex cyanide compounds with different types of cations. The distance between the two positively charged nitrogen atoms in the 4,4′-dipyridinium ion (Basson, Bok & Leipoldt, 1969) is 7·05 Å and in the 1,2-bis-(*N*-methyl-4-pyridinium)ethylene ion (Leipoldt, Basson & Bok, 1970) it is 9·27 Å. The structures clearly show that the distance between the positive charges on the divalent cation largely determines the arrangement of the cation with respect to the anion. The distance between the positive charges in the 1,2-bis-(2-methylpyridinium)ethane ion is much shorter than in the former two ions so that quite another type of arrangement is to be expected.

Experimental

1,2-Bis-(2-methylpyridinium)ethane bromide was prepared by heating 1,2-ethane dibromide with a slight excess of 2-picoline in an ethanol medium for about three hours under reflux. On cooling, a white crystalline salt was obtained. An aqueous solution of the bromide was added to a concentrated solution containing an equivalent amount of $Tl_2Ni(CN)_4$. The precipitated insoluble TlBr was removed by filtration. The solution was evaporated until fine needle-like crystals of 1,2-bis-(2-methylpyridinium)ethane tetracyanonickelate(II) were obtained. To obtain well-formed single-crystals the salt was allowed to crystallize very slowly from a dilute aqueous solution. In this way long, light-yellow needle-like crystals were obtained whose cross-section varied from approximately 0·2 to 0·3 mm and the length from approximately 20 to 30 mm.

Since the crystals tended to lose their water of crystallization in the atmosphere, they were covered with a thin layer of oil and sealed in a Lindemann glass tube.

The Weissenberg camera was standardized with NaCl, a = 5·63 Å. The density was determined by the flotation method using di-iodomethane and diluting it with benzene. The orthorhombic unit-cell dimensions determined using Co $K\alpha$, λ = 1·789 Å, radiation were as follows: a = 7·02 ± 0·01, b = 19·31 ± 0·02 and c = 15·53 ± 0·02 Å. Formula weight = 431·1, Z = 4; d_e = 1·35 and d_c = 1·36 g.cm^{-3}. According to the systematic absences $h0l$ for $h+l=2n+1$, $0kl$ for $k+l=2n+1$, the space group is *Pnnm* or *Pnn*2. The former is centrosymmetrical.

The intensity data were obtained from a crystal with the dimensions 0·5 × 0·23 × 0·23 mm^3 (cut off from a longer crystal) with the a axis as oscillation axis. The intensities were determined for layer lines 0–5 using the multiple-film method. A Stoë Weissenberg camera was used with Cu $K\alpha$ radiation and Ilford industrial G, X-ray films. The intensities were estimated using a calibrated standard strip. According to this scale the intensities varied from 1 to approximately 2800. A total of 1612 reflexions were obtained of which about 20% were weaker than the background. A value of $\frac{1}{3}$ of the minimum value was assigned to the latter in accordance with Hamilton (1955). The usual correction factors, *i.e.* Lorentz, polarization, spot shape and $\alpha_1-\alpha_2$ splitting, were applied. No correction was made for absorption as the crystal was much smaller than the optimum size (Buerger, 1942) (μ = 15·24 cm^{-1} and $\mu\ R$ = 0·1714).

Determination and refinement of the structure

If the space group *Pnnm* is assumed to be correct, it follows that the centres of both the organic cation and the $Ni(CN)_4^{2-}$ ion must be situated on a special position since there are only four formula units per unit cell. The corrected intensities were used for the calculation of a three-dimensional Patterson function. The positions of the Ni atom and of the C and N atoms of the $Ni(CN)_4^{2-}$ ion could be determined from the Patterson function. The Ni atom lies in the special position (*g*) with point symmetry *m*. Two cyanide groups are also situated on the same mirror plane. The coordinates of the atoms of the $Ni(CN)_4^{2-}$ ion which were obtained from the Patterson function, were used for the calculation of a three-dimensional Fourier function, from which the positions of all the remaining C, N and O atoms could be determined .There are only two independent water oxygen atoms, one lying on the special position (*g*) with point symmetry *m*. These coordinates were used for refining the structure.

The coefficients of the isotropic temperature factors were originally taken as 3·0 Å^2. The structure was first

Table 1. *Observed and calculated structure factors*

The data are separated into groups having common values of *h*. The four columns in each group list values of *k*, *l*, F_o and F_c in that order.

k	l	F_o	F_c
		H = 0	
0	2	44.2	-35.9
0	8	154.0	173.8
0	10	122.9	129.9
0	12	11.7	-10.3
0	14	108.2	102.8
0	16	51.1	47.2
0	18	28.7	29.3
2	0	29.7	19.3
6	0	96.0	-102.8
10	0	103.1	100.8
12	0	87.5	-85.8
14	0	60.3	-59.0
16	0	42.8	36.3
18	0	18.5	12.0
20	0	6.1	-6.6
22	0	42.5	-34.5
1	3	68.7	65.9
1	5	132.2	147.7
1	7	22.5	22.5
1	9	81.1	85.1
1	11	52.9	48.7
1	13	50.8	40.4
1	15	28.4	23.6
1	17	29.5	25.8
1	19	15.6	19.4
2	2	2.0	7.4
2	6	3.3	1.3
2	8	41.2	29.5
2	10	14.4	-9.5
2	12	5.6	3.5
2	14	6.1	7.8
2	16	6.1	3.0
3	1	48.2	-59.6
3	3	50.1	42.5
3	5	65.6	50.5
3	7	83.1	-88.1
3	9	15.5	8.2
3	11	5.3	-10.8
3	13	5.9	-2.2
3	15	27.4	-19.5
4	2	30.7	-26.1
4	6	67.2	-73.7
4	8	64.7	-63.5
4	10	53.6	-50.3
4	12	5.7	0.5
4	14	27.2	-26.9
4	16	30.3	-32.2
5	1	37.5	-35.1
5	3	31.0	-28.6
5	5	34.2	-88.6
5	7	20.7	6.2
5	9	46.7	-39.6
5	11	46.0	-36.9
5	13	24.7	-21.5
5	15	10.7	-11.2
6	2	[illegible]	36.0
6	6	21.1	-20.0
6	10	23.3	-16.0
6	12	17.5	14.9
6	14	6.2	-9.3
6	16	12.4	-12.3
7	1	56.7	53.5
7	5	16.1	-14.5
7	7	63.4	57.6
7	9	17.3	13.3
7	11	9.8	-4.9
7	13	10.6	14.2
7	15	10.7	9.0
8	2	36.3	43.4
8	4	95.9	99.8
8	6	70.6	70.4
8	8	35.7	34.8
8	10	79.6	79.7
8	12	29.5	20.2
8	14	32.2	25.6
8	16	26.3	27.1
8	18	15.2	14.7
9	1	117.5	131.8
9	3	3.9	0.9
9	5	89.1	95.7
9	7	67.7	60.5
9	9	71.9	63.3
9	11	35.4	28.8
9	13	33.9	27.8
9	15	43.3	35.6
9	17	14.9	12.4
10	2	34.6	-21.0
10	4	21.3	18.4
10	6	4.8	6.2
10	8	38.8	30.8
10	10	39.0	31.8
10	12	10.7	-13.6
10	14	16.8	15.0
10	16	13.9	13.4
11	1	4.3	1.9
11	3	16.5	-9.9
11	5	28.9	26.6
11	7	32.8	-25.8
11	9	15.7	13.8
11	11	16.7	-15.0
11	13	10.7	9.4
12	2	31.5	-28.2
12	4	20.9	-16.9
12	6	53.4	-50.8
12	8	40.8	-34.8
12	10	34.9	-31.0
12	12	10.7	-11.8
12	14	29.6	-24.8
12	16	22.8	-20.4
13	1	101.5	-102.8
13	3	45.9	-44.7
13	5	42.7	-38.3
13	7	95.7	-90.8
13	9	54.5	-48.3
13	11	38.8	-33.7
13	13	25.9	-24.3
13	15	37.8	-32.9
14	2	42.2	-32.1
14	4	30.2	-21.1
14	6	42.5	-35.7
14	8	33.2	-26.5
14	10	43.0	-36.9
14	12	10.4	-8.3
15	1	5.6	-5.5
15	3	32.6	28.0
15	5	54.8	-48.5
15	7	54.8	44.1
15	9	25.2	-20.8
16	2	26.9	23.6
16	4	20.7	-17.5
16	6	41.1	35.4
16	8	22.8	19.2
17	1	43.1	35.6
17	3	6.1	7.2
17	5	28.3	20.8
17	7	20.1	18.4
17	9	27.6	21.7
17	11	17.3	16.9
18	2	22.7	20.4
18	4	6.2	-5.4
18	6	22.7	17.3
18	8	10.3	10.7
19	1	6.2	1.2
19	3	10.7	10.7
19	5	6.1	9.1
19	7	5.8	-2.4
19	9	5.2	1.4
19	11	16.4	14.4
20	2	6.1	-5.3
20	4	5.9	-0.7
20	6	5.6	-7.6
21	1	31.5	-31.3
21	3	24.7	-21.2
21	5	17.2	-15.0
21	7	27.4	-27.8
21	9	17.9	-19.8
22	2	26.8	-24.9
22	4	15.8	-14.1
22	6	28.5	-24.1
22	8	23.7	-23.7
		H = 1	
0	5	77.6	89.3
0	7	38.9	34.3
0	9	68.2	69.6
0	11	91.1	94.4
0	13	6.9	-2.6
0	15	33.8	32.2
0	17	38.6	39.3
0	19	17.5	18.9
2	0	28.5	-29.8
3	0	10.0	7.5
4	0	17.0	-18.1
6	0	33.7	28.0
7	0	46.9	46.8
8	0	9.9	8.4
10	0	3.6	-6.4
11	0	25.8	-23.4
12	0	25.7	22.3
13	0	54.3	-52.6
14	0	35.2	30.4
15	0	4.9	3.1
16	0	35.6	33.3
17	0	45.9	50.2
18	0	5.4	-3.8
19	0	38.7	37.5
20	0	5.3	-5.7
21	0	40.0	-38.4
1	1	11.8	4.8
1	3	19.2	6.7
1	4	27.0	22.3
1	5	8.0	1.6
1	6	99.2	103.1
1	7	12.6	6.2
1	8	50.0	48.2
1	9	3.9	-6.9
1	10	39.6	37.3
1	11	13.8	-11.8
1	12	54.4	56.1
1	13	11.0	7.4
1	14	5.3	6.6
1	15	5.4	-5.9
1	16	41.1	36.1
1	17	8.4	-6.0
2	1	7.6	-5.8
2	2	64.5	-64.4
2	3	3.7	-4.6
2	4	29.1	-19.7
2	5	48.7	-36.6
2	6	55.2	-44.9
2	7	19.0	16.7
2	8	30.7	-27.4
2	9	23.7	-18.0
2	10	25.7	-22.7
2	11	24.0	20.7
2	12	25.6	-23.4
2	13	29.8	-22.4
2	14	5.4	-6.8
2	15	5.4	7.9
2	16	19.4	-16.5
2	17	5.9	3.6
3	1	53.2	-47.9
3	3	55.5	-55.9
3	4	97.4	-108.7
3	5	32.5	-29.3
3	6	54.6	-45.7
3	7	39.6	-32.0
3	8	35.5	-32.4
3	9	31.0	-25.6
3	10	57.2	-51.8
3	11	38.7	-34.9
3	12	49.4	-50.7
3	13	5.2	-1.9
3	14	5.4	0.1
3	15	16.3	-15.5
3	16	22.2	-22.7
3	17	16.5	-15.3
3	18	17.4	-19.0
4	1	79.7	-96.0
4	2	19.6	-17.3
4	3	40.3	30.2
4	4	23.1	19.5
4	5	72.4	-79.8
4	6	30.7	-24.4
4	7	7.4	-7.6
4	8	12.2	-10.6
4	9	62.9	-63.7
4	10	4.4	1.6
4	11	44.8	-43.7
4	12	5.0	-6.0
4	13	9.1	10.8
4	14	5.4	-6.7
4	15	35.1	-34.3
4	16	5.2	-6.6
4	17	21.5	-21.2
5	1	39.6	38.8
5	2	9.6	-20.7
5	3	15.1	-9.7
5	4	43.9	-49.6
5	5	29.1	24.2
5	6	62.9	-63.6
5	7	10.8	11.4
5	8	36.8	-34.7
5	9	26.2	-20.4
5	10	47.4	-49.8
5	11	4.8	-1.1
5	12	21.5	-21.7
5	13	5.3	5.8
5	14	20.9	-18.3
5	15	5.4	6.7
5	16	25.0	-23.4
6	1	57.2	-61.5
6	2	31.7	32.0
6	3	59.0	-62.3
6	4	49.8	47.7
6	5	3.2	-2.3
6	6	22.5	18.8
6	7	70.8	-60.8
6	8	15.5	13.8
6	9	30.8	-25.6
6	10	33.9	27.9
6	11	37.0	-30.4
6	12	17.8	15.6
6	13	5.3	-1.3
6	14	9.4	2.8
6	15	9.3	-12.3
6	16	8.7	8.4
6	17	20.4	-21.0
7	1	38.8	38.3
7	2	30.4	22.2
7	3	10.6	-4.6
7	4	53.1	53.8
7	5	16.7	14.4
7	6	3.6	8.4
7	7	23.4	19.6
7	8	20.4	17.2
7	9	21.8	19.4
7	10	41.8	38.1
7	11	5.0	7.2
7	12	12.8	8.8
7	13	5.4	0.1
7	14	6.6	0.2
7	15	6.5	10.3
7	16	10.4	11.3
7	17	4.3	6.3
7	18	10.5	14.1
8	1	84.2	97.0
8	2	3.2	1.6
8	3	9.8	13.7
8	4	11.1	12.4
8	5	27.3	24.9
8	6	4.7	5.6
8	7	70.5	72.5
8	8	4.3	-2.0
8	9	42.9	42.0
8	10	4.9	6.7
8	11	31.9	27.7
8	12	5.3	3.2
8	13	5.4	6.5
8	14	5.4	-0.2
8	15	32.4	29.1
8	16	4.7	-0.1
8	17	17.4	19.1
9	1	3.3	3.3
9	2	81.1	89.4
9	3	7.5	6.8
9	4	44.8	44.6
9	5	3.8	0.8
9	6	46.4	42.8
9	7	4.3	1.4
9	8	25.9	19.9
9	9	4.8	-0.5
9	10	48.9	45.1
9	11	5.2	-1.8
9	12	41.4	42.0
9	13	5.4	-1.9
9	14	5.4	-5.4
9	15	5.0	-3.2
9	16	31.4	28.4
9	17	3.9	-1.7
9	18	10.1	13.1
10	1	58.5	63.4
10	2	35.3	-29.6
10	3	23.5	15.5
10	4	21.3	-18.6
10	5	35.1	32.7
10	6	16.5	-14.8
10	7	49.5	42.7
10	8	12.8	-11.8
10	9	30.7	25.3
10	10	21.7	-18.5
10	11	33.0	30.0
10	12	11.4	-13.8
10	13	5.4	-1.0
10	14	5.3	-1.0
10	15	26.6	22.5
10	16	12.9	-11.6
10	17	12.4	14.2
11	1	37.3	-34.2
11	2	16.6	-17.4
11	3	15.5	-13.8
11	4	4.1	3.4
11	5	12.9	-11.5
11	6	4.5	0.1
11	7	34.3	-30.5
11	8	30.4	-31.3
11	9	18.6	-14.4
11	10	5.2	-0.2
11	11	18.6	-15.7
11	12	5.4	-1.5
11	13	5.4	-2.7
11	14	5.1	-2.5
11	15	15.0	-13.6
11	16	4.0	-5.1
11	17	6.8	-8.8
12	1	55.0	-52.3
12	2	15.4	-10.1
12	3	22.2	-20.2
12	4	4.4	-1.0
12	5	78.5	-79.7
12	6	4.7	-1.6
12	7	10.3	8.5
12	8	6.2	7.8
12	9	58.4	-54.7
12	10	9.2	-6.7
12	11	31.1	-24.9
12	12	5.4	-7.2
12	13	17.0	-14.6
12	14	4.9	5.5
12	15	16.8	-15.9
12	16	3.7	-5.0
13	1	4.4	5.2
13	2	38.6	-37.6
13	3	9.6	10.3
13	4	64.8	-64.1
13	5	28.6	24.8
13	6	32.9	-33.4
13	7	19.6	-14.6
13	8	22.1	-20.1
13	9	18.4	15.0
13	10	52.0	-50.6
13	11	5.4	2.1
13	12	29.2	-26.7
13	13	5.0	6.2
13	14	4.6	-7.2
13	15	4.0	-2.2
13	16	18.7	-20.3
14	1	58.4	-52.7
14	2	4.7	2.0
14	3	26.2	-26.8
14	4	16.9	14.6
14	5	19.3	-17.0
14	6	5.1	5.0
14	7	54.2	-52.3
14	8	14.6	14.4
14	9	18.7	-19.2
14	10	6.6	9.8
14	11	31.0	-26.8
14	12	5.1	1.2
14	13	4.7	-4.4
14	14	4.2	6.1
14	15	19.8	-19.0
15	1	25.6	23.2
15	2	5.0	4.3
15	3	10.6	13.8
15	4	5.1	3.8
15	5	29.7	25.4
15	6	5.3	-2.0
15	7	5.3	5.8
15	8	5.4	7.1
15	9	24.8	21.9
15	10	5.4	0.9
15	11	11.0	9.8
16	1	21.8	19.5
16	2	9.0	10.2
16	3	29.9	29.4
16	4	24.1	23.0
16	5	50.5	51.3
16	6	18.6	15.1
16	7	16.2	-14.5
16	8	16.3	13.6
16	9	32.3	30.1
16	10	16.8	16.2
16	11	25.4	23.2
17	1	18.4	15.9
17	2	5.3	1.4
17	3	5.3	6.4
17	4	20.8	18.9
17	5	6.6	8.7
17	6	6.6	8.0
17	7	16.2	12.7
17	8	26.3	22.4
17	9	6.3	9.6
17	10	20.8	19.3
18	1	29.6	27.3
18	2	5.4	-2.9
18	3	5.4	7.7
18	4	5.4	2.3
18	5	5.4	10.8
18	6	5.4	-1.1
18	7	25.9	20.1
18	8	5.1	-3.6
18	9	17.8	17.1
19	1	5.4	-7.4
19	2	5.4	-1.9
19	3	5.4	-7.9
19	4	5.4	9.5
19	5	5.3	-7.0
19	6	17.8	17.9
19	7	5.0	-4.0
19	8	4.7	3.6
19	9	4.4	-5.6
19	10	18.5	15.0
20	1	5.3	-3.3
20	2	5.2	2.8
20	3	11.0	-11.0
20	4	5.1	4.5
21	1	4.9	5.9
21	2	5.9	-8.2
21	3	4.8	5.7
21	4	11.4	-10.5
21	5	5.5	7.8
21	6	16.6	-15.1
21	7	4.0	3.0
21	8	15.6	-14.3
22	1	23.0	-22.7
22	2	4.4	2.9
22	3	10.5	-9.7
22	4	7.1	6.6
22	5	22.6	-21.2
		H = 2	
0	4	6.3	20.8
0	6	65.8	69.9
0	8	62.3	60.8
0	10	62.6	62.7
0	12	39.4	-33.7
0	14	49.9	51.0
0	16	20.0	18.6
0	18	4.8	8.2
5	0	43.2	37.7
6	0	87.3	-81.0
7	0	66.7	62.1
8	0	65.1	72.4
9	0	30.9	-26.0
10	0	79.3	78.8
11	0	80.5	-81.8
12	0	63.7	-60.9
13	0	11.3	-5.5
14	0	28.0	-26.5
15	0	26.5	21.0
16	0	33.1	31.9
17	0	5.4	0.9
18	0	23.2	17.7
19	0	34.0	-29.0
20	0	5.1	2.5
21	0	5.8	-8.1
22	0	17.8	-14.8
1	1	33.4	27.8
1	2	29.1	19.6
1	3	24.8	18.7
1	4	7.8	1.6
1	5	36.4	30.7
1	6	33.2	-33.6
1	7	11.4	0.9
1	8	36.3	-35.0
1	9	28.8	22.3
1	10	26.9	-21.2
1	11	8.3	9.5
1	12	6.2	6.5
1	13	6.5	7.9
1	14	21.1	-22.4
1	15	5.5	8.1
1	16	9.0	-10.5
2	1	57.4	-52.4
2	2	7.8	-8.1
2	3	28.0	-29.7
2	4	55.1	-44.5
2	5	64.2	-65.5
2	6	34.6	-25.7
2	7	18.4	-14.0
2	8	4.7	-8.6
2	9	41.7	-41.4
2	10	27.1	-23.6
2	11	30.2	-27.7
2	12	5.1	-3.4
2	13	24.5	-23.3
2	14	11.6	-12.3
2	15	13.4	-11.5
2	16	5.1	-5.2
2	17	12.6	-14.7
3	1	87.7	-94.2
3	2	24.6	-25.9
3	3	24.7	-19.7
3	4	40.4	-42.3
3	5	9.1	-12.1
3	6	68.8	-73.5
3	7	83.9	-86.4
3	8	76.4	-76.5
3	9	25.5	-23.2
3	10	48.8	-44.9
3	11	29.3	-22.6
3	12	5.1	-5.1
3	13	14.7	-15.9
3	14	39.0	-39.3
3	15	28.3	-24.5
3	16	23.3	-22.3
3	17	14.7	-15.3
3	18	11.5	-13.9
4	1	25.4	-16.7
4	2	62.5	-68.8
4	3	49.3	-44.7
4	4	40.6	-40.4
4	5	70.1	-69.1
4	6	76.1	-93.3
4	7	31.5	27.2
4	8	70.0	-71.5
4	9	39.7	-35.0
4	10	58.6	-55.7
4	11	22.6	-21.0
4	12	15.5	-15.6
4	13	13.2	-12.7
4	14	32.8	-32.5
4	15	5.4	-2.0
4	16	30.2	-30.1
4	17	5.5	-8.3
5	1	58.1	-63.9
5	2	52.4	52.6
5	3	40.2	-44.8
5	4	42.9	43.2
5	5	84.2	-89.1
5	6	44.9	37.8
5	7	18.8	-13.1
5	8	17.5	16.1
5	9	46.7	-48.3
5	10	36.7	34.1
5	11	37.8	-32.0
5	12	17.0	16.4
5	13	28.1	-26.0
5	14	5.5	6.4
5	15	16.1	-15.0
5	16	12.1	12.9
5	17	11.9	-13.3
6	1	59.2	62.9
6	2	21.6	11.0
6	3	3.1	6.1
6	4	16.9	-14.5
6	5	23.3	22.2
6	6	25.7	-20.4
6	7	52.0	51.6
6	8	19.5	-14.7
6	9	23.6	21.6
6	10	26.5	-23.4
6	11	21.6	19.0
6	12	5.3	3.9
6	13	11.5	13.8
6	14	9.5	-10.3
6	15	20.4	18.0
6	16	8.4	-10.2
6	17	7.3	9.2
7	1	3.1	3.7
7	2	11.0	12.5
7	3	28.0	-15.1
7	4	4.2	6.7
7	5	29.7	-27.8
7	6	23.3	23.5
7	7	30.4	22.5
7	8	24.1	23.7
7	9	4.7	-5.4
7	10	30.9	28.7
7	11	9.0	-7.0
7	12	5.4	0.6
7	13	5.5	3.3
7	14	5.5	9.3
7	15	5.2	-1.0
7	16	16.2	16.6
8	1	23.1	20.1
8	2	3.4	7.2
8	3	12.2	11.1
8	4	39.2	38.0
8	5	28.4	27.7
8	6	36.7	34.8
8	7	4.3	4.6
8	8	7.9	8.5
8	9	8.4	12.0
8	10	43.0	42.4
8	11	9.1	10.3
8	12	6.6	5.6
8	13	5.5	6.5
8	14	14.8	12.4
8	15	5.0	4.2
8	16	13.5	15.8
9	1	74.3	78.4
9	2	19.0	-16.1
9	3	3.8	1.7
9	4	35.8	-31.5
9	5	54.3	59.2
9	6	22.2	-17.5
9	7	38.2	36.9
9	8	10.0	-9.3
9	9	44.7	38.7
9	10	20.1	-18.3
9	11	26.2	22.6
9	12	9.4	-11.8
9	13	13.4	14.3
9	14	11.2	-9.5
9	15	26.6	25.9
9	16	4.3	-4.8
9	17	7.5	8.8
10	1	63.6	-66.9
10	2	4.8	-4.7
10	3	13.0	-15.2
10	4	13.4	12.2
10	5	38.7	-34.2
10	6	16.5	14.0
10	7	46.7	-45.6
10	8	32.9	28.9
10	9	37.5	-35.0
10	10	29.0	24.3
10	11	14.8	-14.4

Table 1 (*cont.*)

k	l	F_o	F_c	k	l	F_o	F_c	k	l	F_o	F_o	k	l	F_o	F_c	k	l	F_o	F_c	k	l	F_o	F
10	12	6.7	-7.1	19	7	4.8	3.2	4	6	40.7	-36.2	11	12	4.5	-0.1	5	0	65.3	59.4	7	13	5.3	2.7
10	13	21.1	-18.1	19	8	17.4	-18.1	4	7	3.4	-8.5	11	13	4.2	-4.2	6	0	3.6	0.9	7	14	23.0	25.9
10	14	16.8	15.1	19	9	4.2	6.3	4	8	17.8	-14.9	11	14	3.8	6.1	7	0	102.0	104.8	7	15	3.5	-4.1
10	15	17.1	-18.2	19	10	9.1	-11.1	4	9	33.6	-25.7	11	15	20.4	-22.9	8	0	3.4	1.9	7	16	13.5	25.8
10	16	11.0	12.5	19	11	11.0	13.4	4	10	4.1	2.3	12	1	19.2	-19.5	9	0	14.5	-10.9	8	1	45.0	40.4
10	17	9.6	-12.7	20	1	8.9	-12.5	4	11	29.0	-31.7	12	2	32.1	-32.7	10	0	32.1	30.2	8	2	4.2	-5.1
11	1	4.1	1.0	20	2	5.1	-0.7	4	12	7.8	-8.1	12	3	4.0	-2.4	11	0	58.0	-60.1	8	3	25.2	21.9
11	2	15.3	-15.6	20	3	5.0	-4.1	4	13	5.6	7.4	12	4	15.9	-16.2	12	0	23.9	-23.5	8	4	4.5	-6.3
11	3	4.3	-2.5	20	4	4.9	6.5	4	14	4.6	-7.8	12	5	35.6	-38.8	13	0	4.3	-0.2	8	5	51.9	46.1
11	4	44.9	-43.6	20	5	13.0	-11.7	4	15	17.5	-19.4	12	6	18.3	-16.4	14	0	4.4	-3.5	8	6	4.9	7.1
11	5	15.4	15.4	20	6	4.6	-1.9	4	16	11.7	-8.8	12	7	15.3	13.5	15	0	39.8	38.6	8	7	16.0	13.4
11	6	33.6	-30.5	20	7	4.3	-2.3	5	1	51.7	48.8	12	8	4.5	0.1	16	0	4.5	2.9	8	8	5.2	-10.1
11	7	18.0	-14.4	20	8	4.0	1.2	5	2	3.1	-1.3	12	9	25.0	-22.9	17	0	4.5	1.4	8	9	31.5	31.1
11	8	30.4	-28.1	20	9	12.4	-11.5	5	3	16.0	-10.8	12	10	17.7	-19.3	18	0	4.2	-2.2	8	10	4.5	3.5
11	9	11.1	11.2	21	1	8.1	-11.7	5	4	2.8	-5.0	12	11	4.5	-8.7	19	0	25.5	-25.7	8	11	17.5	15.7
11	10	35.4	-38.0	21	2	4.6	2.5	5	5	41.4	37.8	12	12	14.9	-16.6	1	1	55.5	27.7	8	12	4.5	-2.0
11	11	5.5	-7.2	21	3	7.9	-9.2	5	6	23.9	-22.9	12	13	4.0	-3.1	1	2	2.2	-2.1	8	13	14.7	16.2
11	12	5.5	-6.3	21	4	4.4	1.5	5	7	10.4	12.1	12	14	3.5	6.1	1	3	10.4	4.6	8	14	3.9	-1.2
11	13	6.5	7.5	21	5	4.2	-0.4	5	8	14.4	-11.1	12	15	3.0	-5.2	1	5	5.2	-6.8	8	15	10.9	12.3
11	14	11.6	-18.7	21	6	4.0	-0.3	5	9	39.4	35.5	12	16	7.9	-11.7	1	6	43.0	-41.0	9	1	13.9	11.8
11	15	4.4	-1.1	21	7	15.8	-14.4	5	10	21.7	-18.8	13	1	5.0	-9.5	1	7	38.1	38.4	9	2	17.8	-14.7
11	16	13.6	-14.2	22	1	5.1	6.8	5	11	4.4	4.5	13	2	4.1	-3.9	1	8	39.3	-37.3	9	3	4.6	4.2
12	1	44.9	-42.8	22	2	14.2	-12.8	5	12	4.5	-2.9	13	3	4.2	-4.7	1	9	4.0	-1.4	9	4	16.3	-15.3
12	2	10.9	-13.2	22	3	4.0	3.0	5	13	12.5	11.1	13	4	20.9	-20.1	1	10	31.1	-25.9	9	5	13.7	10.7
12	3	11.1	7.9	22	4	3.8	-2.2	5	14	4.6	-6.2	13	5	26.1	26.1	1	11	5.4	7.9	9	6	15.1	-12.9
12	4	13.9	-11.9	22	5	3.6	-3.9	5	15	16.5	15.2	13	6	4.4	-5.4	1	12	5.5	4.5	10	1	44.1	-44.3
12	5	43.6	-42.5	22	6	12.9	-11.6	5	16	6.6	-12.3	13	7	38.2	-39.2	1	13	4.5	-0.5	10	2	3.8	6.8
12	6	31.8	-30.2	22	7	12.4	12.6	6	1	3.2	-6.2	13	8	4.6	4.1	1	14	24.1	-26.8	10	3	4.8	-7.1
12	7	6.2	-6.5	22	8	8.6	-11.8	6	2	68.9	68.0	13	9	17.7	16.8	1	15	9.9	12.8	10	4	4.0	[illegible]
12	8	27.1	-22.6					6	3	13.9	-10.2	13	10	13.7	-17.2	1	16	6.1	-11.0	10	5	16.7	-12.5
12	9	33.4	-32.2			H = 3		6	4	74.9	76.5	14	1	4.3	-7.2	2	2	72.9	64.7	10	6	12.7	12.3
12	10	18.3	-18.9					6	5	32.1	30.2	14	2	4.3	-4.7	2	3	15.3	-16.4	10	7	38.4	-35.9
12	11	5.5	0.4	0	1	15.6	13.1	6	6	46.8	46.2	14	3	4.4	-4.5	2	4	9.7	10.4	10	8	17.2	14.9
12	12	5.4	-3.1	0	3	26.7	20.7	6	7	35.2	-30.7	14	4	17.1	16.6	2	5	43.9	-40.3	10	9	23.4	-19.6
12	13	15.3	-15.5	0	5	42.2	38.6	6	8	36.9	37.9	14	5	4.5	2.7	2	6	24.3	18.5	11	1	4.0	-1.5
12	14	16.1	-15.8	0	7	17.5	-16.5	6	9	4.0	6.0	14	6	4.5	-2.1	2	7	31.4	-26.8	11	2	4.0	-0.5
12	15	10.0	-11.1	0	9	22.4	27.1	6	10	55.1	55.1	14	7	7.9	-12.3	2	8	11.4	8.8	11	3	4.1	3.3
12	16	10.0	-10.7	0	11	25.4	21.2	6	11	4.4	-6.5	14	8	15.9	16.6	2	9	37.7	-37.8	11	4	14.4	-15.5
13	1	56.3	-58.7	0	13	4.5	0.1	6	12	32.4	35.8	14	9	4.6	2.6	2	10	4.3	4.7	11	5	4.3	-5.0
13	2	22.2	19.4	0	15	4.4	2.5	6	13	4.6	4.4	14	10	13.2	13.4	2	11	13.7	-18.4	11	6	23.4	-20.2
13	3	20.2	-19.5	1	0	15.0	3.4	6	14	7.8	12.3	15	1	29.8	33.7	2	12	23.4	25.1	11	7	4.4	2.9
13	4	26.6	-16.8	2	0	62.2	-52.8	6	15	4.2	-2.4	15	2	4.5	5.6	2	13	20.0	-21.1	11	8	14.3	-16.0
13	5	7.5	-3.7	4	0	32.2	-27.7	6	16	20.2	25.6	15	3	12.3	15.8	2	14	4.4	-7.2	11	9	4.5	0.5
13	6	19.3	17.9	5	0	53.5	-53.2	6	17	3.8	-8.1	15	4	4.5	5.4	2	15	13.0	-13.6	11	10	26.0	-26.2
13	7	56.6	-58.6	6	0	59.2	59.9	7	1	69.7	75.6	15	5	33.4	36.9	2	16	4.3	9.2	12	1	33.9	-33.7
13	8	5.3	2.3	7	0	53.6	48.5	7	2	11.3	-9.6	15	6	4.6	-1.7	2	17	9.7	-13.5	12	2	4.2	6.8
13	9	24.3	-24.2	8	0	3.7	10.0	7	3	18.1	18.2	15	7	4.6	5.3	3	1	2.8	-3.9	12	3	12.7	11.3
13	10	6.7	-6.2	9	0	10.5	12.9	7	4	23.2	21.3	15	8	4.0	-3.1	3	2	3.0	-5.5	12	4	4.3	-6.0
13	11	16.4	-14.1	10	0	25.5	-29.2	7	5	40.0	39.6	15	9	30.6	34.3	3	3	25.7	22.3	12	5	35.6	-35.2
13	12	5.2	7.0	11	0	16.3	13.9	7	6	3.5	3.1	15	10	4.2	2.2	3	4	30.4	-28.4	12	6	4.4	-2.0
13	13	10.5	-10.9	12	0	12.6	10.6	7	7	49.6	47.1	15	11	11.7	15.0	3	5	20.9	13.6	12	7	4.5	-2.5
13	14	4.3	-0.3	13	0	4.1	-8.9	7	8	8.4	11.4	16	1	4.5	4.8	3	6	44.8	-46.0	12	8	4.5	-7.5
13	15	17.0	-17.4	14	0	31.5	34.2	7	9	45.4	43.8	16	2	4.5	3.4	3	7	3.6	-3.7	12	9	27.2	-26.7
14	1	17.0	15.2	15	0	9.4	-12.8	7	10	13.0	15.0	16	3	5.6	10.0	3	8	47.7	-48.7	13	1	7.5	-5.0
14	2	12.1	-10.7	16	0	39.3	44.7	7	11	29.0	29.2	16	4	23.8	25.7	3	9	4.1	0.8	13	2	13.0	13.6
14	3	21.2	18.0	17	0	17.7	19.0	7	12	4.6	-3.0	16	5	19.4	20.6	3	10	39.3	-38.5	13	3	4.4	-0.9
14	4	5.1	0.8	18	0	23.7	-23.6	7	13	5.6	7.2	16	6	13.7	15.4	3	11	5.4	10.7	13	4	7.7	-9.1
14	5	9.0	-10.2	19	0	17.6	16.8	7	14	4.4	5.7	16	7	4.5	-8.0	3	12	4.5	2.9	13	5	15.5	15.4
14	6	20.4	-15.3	20	0	27.8	-31.7	7	15	24.3	27.6	16	8	15.2	13.5	3	13	4.5	4.1	13	6	15.6	14.9
14	7	33.5	32.5	21	0	19.7	-20.7	7	16	3.5	2.5	16	9	4.2	9.6	3	14	27.1	-30.5	13	7	21.5	-20.3
14	8	5.4	-8.3	1	1	27.4	-17.2	8	1	31.3	26.9	16	10	20.3	22.1	3	15	4.0	-0.6	14	1	32.6	30.0
14	9	5.5	-2.5	1	2	45.3	43.3	8	2	5.4	5.8	16	11	7.6	11.7	3	16	14.0	-16.4	14	2	4.5	-5.3
14	10	16.9	-16.6	1	3	7.0	-11.3	8	3	3.2	7.3	17	1	5.6	9.4	4	1	17.6	-9.8	14	3	24.5	27.9
14	11	19.4	16.7	1	4	34.1	30.0	8	4	14.2	12.0	17	2	5.6	8.0	4	2	3.2	3.8	14	4	5.5	7.3
15	1	5.1	3.5	1	5	21.2	-17.0	8	5	3.5	7.0	17	3	4.6	-5.9	4	3	17.6	-16.6	14	5	4.5	-1.8
15	2	28.2	24.8	1	6	31.8	23.7	8	6	16.8	12.4	17	4	7.9	13.4	4	4	3.7	-0.7	14	6	4.5	-6.8
15	3	28.3	20.8	1	7	3.2	0.0	8	7	23.2	19.4	17	5	4.6	-4.2	4	5	47.5	-44.4	14	7	39.9	44.4
15	4	6.4	-9.5	1	8	13.4	11.3	8	8	4.1	-0.8	17	6	4.5	5.6	4	6	3.5	-2.2	14	8	4.5	-1.1
15	5	32.0	-32.5	1	9	22.4	-21.7	8	9	14.7	16.4	17	7	10.6	12.1	4	7	29.3	25.3	14	9	4.3	5.5
15	6	28.0	26.6	1	10	15.5	16.3	8	10	13.2	13.6	17	8	12.4	12.9	4	8	4.8	-6.1	14	10	4.0	-3.1
15	7	43.2	42.6	1	11	29.3	-27.7	8	11	9.6	10.2	17	9	3.9	1.9	4	9	30.4	-26.2	14	11	18.1	17.7
15	8	17.7	15.5	1	12	24.2	22.5	9	1	17.0	-14.8	17	10	6.2	11.1	5	1	3.4	5.4	15	1	4.5	-6.1
15	9	6.7	-11.0	1	13	12.4	11.5	9	2	44.3	43.6	18	1	17.7	17.3	5	2	41.4	41.5	15	2	33.2	33.8
15	10	6.5	9.9	1	14	4.6	-3.3	9	3	3.4	-1.1	18	2	19.3	-18.4	5	3	18.6	13.7	15	3	4.5	1.2
16	1	30.4	28.8	1	15	7.7	-13.1	9	4	18.4	15.7	18	3	5.5	6.6	5	4	37.9	39.1	15	4	4.5	5.2
16	2	20.6	19.1	1	16	7.0	10.7	9	5	20.1	-16.8	18	4	10.8	-13.1	5	5	17.4	-13.2	15	5	23.5	-25.9
16	3	20.7	20.7	2	1	41.1	32.4	9	6	27.4	25.2	18	5	4.3	1.4	5	6	46.7	42.7	15	6	36.7	35.3
16	4	6.6	-6.9	2	2	113.4	-108.4	9	7	4.0	-3.1	18	6	7.3	-13.4	5	7	19.7	21.2	15	7	17.1	15.5
16	5	21.0	21.7	2	3	12.3	-11.4	9	8	21.7	21.1	18	7	20.9	20.2	5	8	29.4	26.1	15	8	24.4	25.2
16	6	29.9	28.3	2	4	41.0	-39.5	9	9	14.1	-11.7	18	8	17.9	-18.3	5	9	4.2	-6.5	15	9	12.1	-11.6
16	7	20.1	20.9	2	5	3.3	7.6	9	10	20.5	16.4	18	9	3.5	6.4	5	10	30.3	35.9	15	10	17.1	18.6
16	8	16.4	17.5	2	6	72.2	-73.8	9	11	5.6	-4.1	18	10	14.4	-15.3	5	11	4.5	8.2	15	11	3.3	-6.8
16	9	15.9	16.7	2	7	21.0	16.9	9	12	19.4	20.6	19	1	26.0	-29.6	5	12	17.5	16.2	15	12	11.6	12.8
16	10	5.0	8.0	2	8	48.6	-49.2	9	13	4.5	-5.6	19	2	4.3	-1.6	5	13	4.5	-2.8	16	1	33.3	34.5
16	11	18.2	20.5	2	9	4.6	7.4	9	14	4.2	0.8	19	3	24.3	-26.6	5	14	14.6	16.2	16	2	7.8	-10.3
17	1	36.4	37.5	2	10	43.0	-42.4	9	15	3.7	-5.1	19	4	4.1	-0.6	5	15	4.6	3.5	16	3	20.7	17.8
17	2	16.3	13.8	2	11	4.3	3.2	9	16	12.2	15.3	19	5	24.1	-27.0	5	16	12.5	17.2	16	4	7.8	-10.7
17	3	5.4	9.3	2	12	39.9	-43.8	10	1	35.7	34.1	19	6	4.7	9.6	6	1	77.7	83.0	16	5	26.8	27.4
17	4	5.5	4.0	2	13	5.6	-5.6	10	2	52.0	-57.2	19	7	14.8	-18.6	6	2	35.3	32.4	16	6	5.3	-3.1
17	5	31.4	27.0	2	14	4.6	-7.1	10	3	26.6	23.0	19	8	3.4	-0.8	6	3	37.5	36.5	16	7	22.9	20.0
17	6	5.5	6.2	2	15	5.4	7.7	10	4	39.3	-41.4	19	9	19.7	-23.5	6	4	3.3	-6.0	16	8	4.0	-3.6
17	7	16.3	18.8	2	16	29.5	-32.0	10	5	38.4	42.1	20	1	4.0	-2.8	6	5	51.0	49.6	16	9	23.2	24.0
17	8	5.2	5.5	3	1	70.6	-66.5	10	6	31.0	-31.5	20	2	4.8	-9.8	6	6	14.3	14.7	16	10	3.4	-3.0
17	9	27.4	25.7	3	2	70.9	-67.6	10	7	14.4	9.3	20	3	3.9	-6.2	6	7	62.5	62.6	16	11	16.8	18.7
17	10	5.7	7.7	3	3	77.6	-74.3	10	8	26.9	-23.2	20	4	4.6	-9.7	6	8	18.7	20.1	17	1	4.5	7.4
17	11	12.9	15.2	3	4	29.6	-21.9	10	9	24.3	24.1	20	5	3.6	-2.6	6	9	42.5	43.8	17	2	5.5	10.6
18	1	21.2	-21.8	3	5	41.8	-40.4	10	10	33.3	-35.6	20	6	12.6	-15.7	6	10	4.4	-4.5	17	3	7.6	-13.0
18	2	26.0	24.8	3	6	28.9	-23.3	10	11	26.3	23.2	20	7	3.2	-2.2	6	11	34.9	32.6	17	4	4.3	7.6
18	3	13.4	-14.1	3	7	51.1	-50.4	10	12	25.0	-25.0	20	8	14.0	-14.4	6	12	5.5	8.4	17	5	7.3	10.4
18	4	15.0	10.9	3	8	10.7	-10.4	10	13	4.3	6.2					6	13	25.5	25.3	17	6	4.1	2.6
18	5	9.4	-10.2	3	9	36.8	-36.7	10	14	4.0	-1.2			H = 4		6	14	4.1	4.2	17	7	3.9	-8.0
18	6	20.6	20.1	3	10	19.9	-13.8	10	15	6.1	10.5					6	15	23.8	27.3	17	8	3.6	4.6
18	7	17.8	-19.0	3	11	52.0	-55.9	10	16	17.4	-20.1	0	2	34.7	-25.3	7	1	9.5	-7.0	17	9	5.8	9.0
18	8	14.7	14.6	3	12	29.9	-30.2	11	1	59.2	-65.4	0	4	2.7	1.7	7	2	41.6	41.3	17	10	8.8	8.3
18	9	13.9	-13.9	3	13	4.6	1.3	11	2	11.2	-11.2	0	6	17.8	14.7	7	3	17.4	18.1	18	1	18.0	-18.9
18	10	12.8	14.4	3	14	5.6	7.0	11	3	30.3	-33.7	0	8	3.8	-2.5	7	4	41.8	45.2	18	2	4.2	0.7
18	11	4.7	-7.5	3	15	27.9	-25.1	11	4	13.6	12.1	0	10	23.2	23.1	7	5	3.6	-5.8	18	3	5.1	-13.5
18	12	12.4	13.1	3	16	12.9	-14.3	11	5	30.4	-31.0	0	12	16.5	-17.2	7	6	50.9	50.5	18	4	4.9	6.9
19	1	5.4	7.5	3	17	18.8	-24.6	11	6	5.1	6.1	0	14	5.4	10.6	7	7	4.0	5.0	18	5	3.9	-3.4
19	2	18.7	-17.8	4	1	50.0	-45.0	11	7	49.3	-52.2	0	16	4.3	6.2	7	8	48.6	48.9	18	6	3.7	-1.3
19	3	13.1	12.1	4	2	28.4	-24.5	11	8	4.4	-7.5	1	0	115.9	-120.5	7	9	4.3	-4.4	18	7	21.0	-25.1
19	4	9.1	-8.8	4	3	6.7	-5.7	11	9	30.2	-31.7	2	0	58.5	-44.7	7	10	47.0	49.6	18	8	3.2	-2.3
19	5	8.9	13.0	4	4	31.6	24.3	11	10	4.6	6.4	3	0	142.5	-144.1	7	11	4.5	5.8	18	9	9.2	-9.7
19	6	21.1	-19.6	4	5	46.2	-44.5	11	11	31.7	-31.6	4	0	25.9	-19.5	7	12	14.7	13.9	19	1	3.9	-4.9

given two cycles of full-matrix least-squares refinement by using the Fortran program *ORFLS* of Busing, Martin & Levy (1962). In the first cycle only the scale factors were varied, while the scale factors together with the positional and temperature parameters were varied in the second cycle. The value of the residual index R, where $R = \sum |F_o| - |F_c| / \sum |F_o|$, was at this stage $= 0{\cdot}17$. The program which was used minimizes the quantity $\sum w(F_o - F_c)^2$. A weight $w = 1$ was given to all the observed and non-observed reflexions. After the value of F_o was re-estimated for a number of reflexions and some of the strongest reflexions (which could not be measured with sufficient accuracy) were omitted, the structure was isotropically refined for three further cycles. This caused the value of R to decrase to 0·153.

As a result of the comparatively high value of R which was obtained, the possibility of the non-centrosymmetric space group *Pnn*2 was investigated. The atomic coordinates as obtained from the Fourier function were converted according to the equivalent positions of the space group *Pnn*2. All the atoms were now placed in the general position, 4(*c*). The *c* coordinate of

Table 1 (*cont.*)

19	2	20.0	-21.3	19	0	3.0	0.3	3	9	24.0	-22.2	7	4	10.7	-8.4	10	10	17.1	-20.5	14	7	3.9	2.5
19	3	3.8	-3.9	1	1	34.3	-25.9	3	10	14.2	14.8	7	5	36.8	36.0	10	11	4.6	-4.9	14	8	11.1	13.0
19	4	3.7	-4.2	1	2	31.7	-24.3	3	11	26.9	-30.4	7	6	12.4	-9.7	10	12	6.0	-13.3	14	9	3.5	4.3
19	5	3.5	-3.0	1	3	22.3	-18.8	3	12	4.1	-8.2	7	7	40.0	44.1	11	1	30.6	-30.3	14	10	12.1	13.9
19	6	18.0	-20.7	1	4	15.8	10.5	3	13	3.9	1.4	7	8	4.1	-5.4	11	2	13.8	-17.2	15	1	30.4	32.0
19	7	3.0	-5.1	1	5	30.7	-28.4	3	14	10.6	14.6	7	9	32.8	32.5	11	3	15.5	-13.9	15	2	4.1	-1.9
19	8	15.3	-18.3	1	6	21.1	-20.9	3	15	13.9	-16.3	7	10	4.2	-4.9	11	4	4.1	8.4	15	3	22.6	21.1
20	1	18.1	-18.7	1	7	3.6	-4.2	4	1	13.2	5.0	7	11	28.6	34.1	11	5	21.3	-21.5	15	4	4.1	-4.0
20	2	3.4	-7.9	1	8	14.7	-14.2	4	2	16.8	-10.1	7	12	13.5	-14.0	11	6	4.1	-4.2	15	5	26.4	29.2
20	3	3.3	-7.5	1	9	24.8	-24.0	4	3	10.3	6.8	8	1	22.6	-20.2	11	7	14.4	-15.2	15	6	3.8	-6.1
20	4	3.2	0.1	1	10	4.1	-3.4	4	4	3.2	4.2	8	2	22.1	16.9	11	8	4.1	-4.0	15	7	14.8	15.0
20	5	12.7	-14.3	1	11	22.7	-24.9	4	5	3.3	-3.0	8	3	12.5	-11.7	11	9	22.4	-22.5	15	8	13.3	-14.8
				1	12	4.1	-2.9	4	6	20.4	-18.8	8	4	3.7	2.9	11	10	3.9	2.8	15	9	24.2	26.0
		H = 5		1	13	4.0	5.3	4	7	13.7	8.2	8	5	14.8	-18.8	11	11	14.6	-18.3	16	1	12.0	-12.4
				1	14	3.6	-3.6	4	8	4.8	-8.8	8	6	16.7	15.5	12	1	4.1	3.5	16	2	9.8	9.4
0	3	32.1	-25.8	1	15	9.4	-12.0	4	9	12.1	10.4	8	7	14.8	-13.3	12	2	15.0	-13.9	16	3	11.8	-5.8
0	5	7.6	5.8	2	1	25.0	19.5	5	1	21.9	17.6	8	8	4.1	4.0	12	3	4.1	4.8	16	4	17.6	16.9
0	7	37.3	-39.2	2	2	71.9	-66.8	5	2	22.0	17.3	8	9	10.2	-10.9	12	4	5.0	-12.0	16	5	6.4	-7.5
0	9	4.0	-0.8	2	3	23.9	-21.7	5	3	3.1	1.4	8	10	7.2	9.6	12	5	5.1	-9.4	16	6	15.1	16.6
0	11	19.0	-20.6	2	4	33.8	-29.8	5	4	11.4	10.4	8	11	8.6	-11.0	12	6	7.2	-8.9	16	7	3.3	-7.1
0	13	4.9	7.0	2	5	16.5	12.6	5	5	25.4	20.6	9	1	14.8	-15.7	12	7	5.1	11.6	16	8	11.9	11.6
0	15	11.6	-14.4	2	6	41.4	-40.1	5	6	3.6	5.1	9	2	14.3	-11.7	12	8	5.0	-5.4	16	9	12.4	-12.9
1	0	17.2	-15.5	2	7	3.6	1.0	5	7	3.8	-1.0	9	3	3.8	2.0	12	9	4.8	0.3	17	1	3.7	7.6
2	0	26.9	-24.4	2	8	29.6	-31.8	5	8	4.0	5.0	9	4	20.0	-19.8	12	10	9.0	-13.5	17	2	3.7	1.3
3	0	50.7	48.7	2	9	15.4	13.1	5	9	23.4	18.6	9	5	24.6	-22.4	13	1	4.1	-5.1	17	3	3.6	1.0
4	0	19.5	-18.9	2	10	26.5	-29.7	6	1	3.1	2.1	9	6	17.1	-11.2	13	2	4.1	7.1	17	4	3.5	-4.2
5	0	11.7	-9.7	2	11	5.1	-7.1	6	2	55.5	57.2	9	7	5.0	3.3	13	3	4.1	-6.2	17	5	4.1	-7.4
6	0	41.6	44.8	2	12	27.8	-32.7	6	3	3.3	-0.2	9	8	5.1	-4.6	13	4	4.1	-1.3	17	6	3.2	-4.9
7	0	17.0	19.3	2	13	4.0	3.0	6	4	44.4	39.5	9	9	16.1	-18.0	13	5	13.5	13.3	17	7	13.0	17.7
8	0	3.5	6.7	2	14	3.6	1.1	6	5	19.6	22.0	9	10	13.4	-16.8	13	6	4.1	2.8	18	1	3.4	-2.7
9	0	17.8	-14.3	2	15	3.1	7.4	6	6	37.7	41.4	10	1	16.2	-13.3	13	7	22.5	-22.9	18	2	3.4	-1.7
10	0	22.8	-23.0	2	16	15.6	-25.5	6	7	15.8	-15.8	10	2	25.8	-23.3	13	8	6.8	11.9	18	3	3.3	-2.9
11	0	11.8	15.4	3	1	43.1	-35.4	6	8	34.0	35.4	10	3	10.7	-11.0	13	9	6.4	8.7	18	4	5.4	-9.1
12	0	7.0	-7.7	3	2	16.4	-17.0	6	9	4.1	9.5	10	4	20.6	-23.0	14	1	5.1	5.6	18	5	9.6	-12.9
13	0	7.1	9.9	3	3	32.4	-29.1	6	10	34.5	35.0	10	5	7.0	14.5	14	2	10.2	13.2	19	1	15.4	-17.4
14	0	14.4	14.4	3	4	22.3	18.6	6	11	4.1	4.1	10	6	15.8	-13.3	14	3	4.2	-3.0	19	2	2.9	-1.9
15	0	23.8	-24.3	3	5	21.1	-19.6	6	12	23.0	27.6	10	7	27.7	-32.1	14	4	16.1	16.9	19	3	8.4	-9.5
16	0	29.6	33.0	3	6	3.5	1.6	7	1	54.7	58.2	10	8	14.4	-18.6	14	5	4.1	0.3	19	4	2.6	-7.1
17	0	13.0	-14.0	3	7	34.3	-28.6	7	2	31.3	-32.0	10	9	4.1	1.8	14	6	4.1	3.5	19	5	12.5	-16.4
18	0	8.4	-12.5	3	8	14.2	11.9	7	3	35.9	35.8												

the Ni atom was kept = 0 and was also not changed during the refinement. The structure was refined for four cycles according to the non-centrosymmetric space group. In the first three cycles only the positional parameters were varied while the temperature parameters were also varied in the fourth cycle. The final *R* value was 0·15.

The decrease in the value of *R* (from the centrosymmetric to the non-centrosymmetric space group) is not statistically significant according to the test of Hamilton (1965). Furthermore the calculated interatomic distances according to the non-centrosymmetric refinement agree very poorly with the interatomic distances in the $Ni(CN)_4^{2-}$ ion according to other refinements (Leipoldt, Basson & Bok, 1970), *e.g.* the Ni–C distances vary between 1·78 and 1·92 Å. The small decrease in the value of *R* could thus rather be ascribed to the larger number of variables than to the possibility of the structure being non-centrosymmetric. The space group *Pnnm* was thus assumed to be correct.

The structure was then anisotropically refined for two cycles (isotropic temperature factors were converted to anisotropic temperature factors) by using the parameters as obtained from the last centrosymmetric refinement. This made the value of *R* decrease to 0·133. The mean shift/error ratio for all the parameters was less than 0·1. Lingafelter & Donohue (1966) showed that refinement with full anisotropic parameters has no significance if the layer lines have not been experimentally scaled. The introduction of anisotropic thermal motion is, however, justified in the light of the general improvement of the structure as could be seen in comparing the results of the isotropic and anisotropic refinements.

The atomic scattering factors for C, N, O and Ni^{2+} were obtained from the work of Cromer & Waber (1965), while that for N^- (for the cyanide nitrogen) was taken from *International Tables for X-ray Crystallography* (1962).

The final values of F_o and F_c are given in Table 1. The final atomic coordinates are given in Table 2 and the anisotropic temperature coefficients are given in Table 3.

Table 2. *Positional parameters as obtained from the last anisotropic refinement*

The standard deviation is given in parentheses.

	x/a	y/b	z/c
Ni	0·0601 (2)	0·1160 (1)	0·0000
C(1)	0·0551 (13)	0·1154 (4)	0·1187 (5)
C(2)	0·2026 (17)	0·0338 (6)	0·0000
C(3)	−0·0608 (17)	0·2014 (6)	0·0000
C(4)	0·6001 (11)	0·0191 (4)	0·2206 (6)
C(5)	0·5439 (14)	0·1239 (4)	0·1409 (6)
C(6)	0·5146 (13)	0·1932 (5)	0·1334 (6)
C(7)	0·4963 (13)	0·2338 (4)	0·2033 (6)
C(8)	0·5092 (13)	0·2032 (5)	0·2841 (6)
C(9)	0·5399 (12)	0·1328 (4)	0·2923 (6)
C(10)	0·5627 (19)	0·0993 (6)	0·3763 (6)
N(1)	0·0451 (12)	0·1115 (4)	0·1928 (5)
N(2)	0·2806 (14)	−0·0181 (5)	0·0000
N(3)	−0·1260 (16)	0·2565 (5)	0·0000
N(4)	0·5595 (9)	0·0943 (3)	0·2189 (4)
O(1)	0·5816 (12)	0·4367 (4)	0·1398 (5)
O(2)	0·5592 (15)	0·3498 (5)	0·0000

Description of the structure and discussion

The dimensions of the $Ni(CN)_4^{2-}$ ion and the 1,2-bis-(2-methylpyridinium)ethane ion are given in Figs. 1 and 2 and in Tables 4 and 5. The mean bond lengths in the pyridine rings of the 1,2-bis-(2-methylpyridinium)-ethane ion (mean C–C distance = 1·37 Å and mean C–N distance = 1·36 Å) agree well with the bond lengths in the 1,2-bis-(*N*-methyl-4-pyridinium)ethylene ion (Leipoldt, Basson & Bok, 1970). The bond angles between the atoms in the rings of the two ions are equal within the experimental error. The bond lengths between the carbon atoms of the ethane group, C(4)–C(4′) = 1·59 ± 0·012 Å, are much longer than the normal single bond length (*i.e.* 1·54 Å) between two carbon atoms. A similar value was, however, found for the C–C dis-

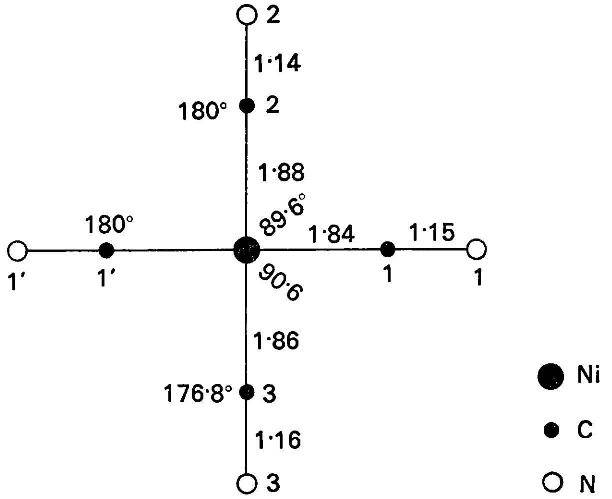

Fig. 1. Bond lengths and angles in the $Ni(CN)_4^{2-}$ ion.

tance in 10,10'-dianthranil, C(10)–C(10') = 1·60 ± 0·05 Å (Ehrenberg, 1967).

The least-squares equation for the best plane through the atoms of the pyridine ring and the carbon atoms of the methyl and ethane groups, together with the deviations from the plane, are given in Table 6. From this it follows that the rings are approximately planar just as in the case of pyridine. Since the centre of the cation is situated on a twofold axis which is nearly parallel to the planes of the pyridine rings (see Fig. 3), it follows that the planes through the two rings of the cation are approximately parallel to one another. From this it also follows that the two methyl groups in the 2-position of the ring are situated *cis* to one another with a C–C distance = 3·94 Å. This distance is about the same as that which the van der Waals radius for a methyl group allows (Pauling, 1960).

Although one can not attach much importance to the anisotropic temperature factors, since the layer

Table 3. *Thermal movement parameters as obtained from the last refinement* (*all* × 10^4)

The standard deviation is given in parentheses. b_{ij} is defined by
$T = e - (b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ni	142 (5)	20 (1)	26 (1)	6 (1)	—	—
C(1)	148 (25)	13 (2)	27 (4)	8 (4)	−2 (7)	−2 (2)
C(2)	118 (32)	18 (3)	13 (4)	−20 (7)	—	—
C(3)	126 (33)	16 (3)	26 (5)	−13 (7)	—	—
C(4)	42 (19)	13 (2)	40 (4)	−2 (5)	10 (7)	−2 (2)
C(5)	179 (27)	18 (2)	30 (4)	−2 (6)	19 (8)	4 (2)
C(6)	85 (23)	23 (3)	48 (4)	−1 (5)	33 (7)	2 (3)
C(7)	76 (23)	19 (2)	52 (5)	−2 (5)	5 (8)	−3 (3)
C(8)	100 (23)	22 (2)	46 (4)	−5 (5)	19 (8)	−14 (3)
C(9)	110 (23)	18 (2)	30 (4)	6 (5)	4 (8)	−8 (2)
C(10)	475 (41)	33 (4)	18 (4)	16 (9)	21 (10)	6 (3)
N(1)	264 (24)	20 (2)	28 (4)	8 (5)	1 (7)	−4 (2)
N(2)	74 (26)	16 (3)	38 (5)	13 (6)	—	—
N(3)	178 (30)	16 (3)	42 (5)	15 (7)	—	—
N(4)	90 (17)	13 (2)	25 (3)	−1 (4)	13 (5)	−6 (2)
O(1)	342 (24)	37 (3)	36 (4)	26 (6)	−5 (7)	2 (3)
O(2)	270 (31)	30 (3)	45 (5)	21 (7)	—	—

Table 4. *Interatomic distances* (Å)

(*a*) In the $Ni(CN_4)^{2-}$ ion.

Ni–C(1)	1·84 ± 0·009	C(1)–N(1)	1·15 ± 0·012
Ni–C(2)	1·87 ± 0·011	C(2)–N(2)	1·14 ± 0·016
Ni–C(3)	1·86 ± 0·008	C(3)–N(3)	1·16 ± 0·009

(*b*) In the 1,2-bis(2-methylpyridinium)ethane ion

C(4)–C(4')	1·59 ± 0·016	C(8)——C(9)	1·38 ± 0·012
C(4)–N(4)	1·48 ± 0·010	C(9)——C(10)	1·46 ± 0·016
N(4)–C(5)	1·34 ± 0·012	C(9)——N(4)	1·37 ± 0·011
C(5)–C(6)	1·36 ± 0·013	C(10)···C(10')	3·94 ± 0·019
C(6)–C(7)	1·35 ± 0·013	N(4)····N(4')	3·74 ± 0·013
C(7)–C(8)	1·39 ± 0·013		

(*c*) Other

N(1)···N(4)	3·65 ± 0·011	O(1)···O(2)	2·75 ± 0·014
N(1)···N(4'')	3·45 ± 0·011	O(2)···N(3)	2·86 ± 0·012
O(1)···O(1''')	2·70 ± 0·012	O(1)···N(1)	2·77 ± 0·012

' Related to one another by a twofold axis.
'' Adjacent cell.
''' Related to one another by a mirror plane.

lines have not been experimentally scaled (Lingafelter & Donohue, 1966), it is noticeable that the ratio of the highest b_{ii} to the lowest b_{ii} is greatest for $i=1$. This is especially noticeable for C(10), which indicates a high thermal vibration in the direction of the a axis. According to the packing of the cation (Fig. 3) it is clear that the methyl group, C(10), is not bound in the direction of the a axis which thus explains the relatively high thermal vibration in this direction.

The interatomic distance in the Ni(CN)$_4^{2-}$ ion (mean Ni–C distance = 1·86 Å and mean C–N distance = 1·15 Å) agree well with the corresponding distances in the dipyridinium (Basson, Bok & Leipoldt, 1969). The Ni(CN)$_4^{2-}$ ion is square-planar within experimental error as can be expected as a result of the dsp^2 hybridization obtained. The Ni–C–N bonds are in a straight line but the N(1)···Ni···N(''') and N(2)···Ni···N(3) angles (both = 174·5°) show significant deviations from a linear geometry. The least-squares equation for the best plane through the Ni(CN)$_4^{2-}$ ion is given in Table 6. The deviation from a plane is too small to be of significance.

Fig. 3 shows the structure as seen in the direction of the a axis. The structure is made up of alternating layers of cations and anions as seen in the direction of the a axis. The two nitrogen atoms of the same cation each have a nitrogen atom of two different Ni(CN)$_4^{2-}$ ions (situated on the same mirror plane) as nearest neighbours. This arrangement is repeated by the mirror plane so that a type of ring structure (as seen in the direction of the a axis) is obtained consisting of two cations and two anions.

The negative nitrogen atoms of the cyanide groups tend to take up a position closer to the nitrogen atoms of the pyridine rings than to any of the other atoms of the cation. This is in agreement with the results obtained in the study of the pyridinium ion in solution with the aid of nuclear magnetic resonance. The study showed that the full positive charge is not confined to the nitrogen atom only, but is spread over the whole ring in such a manner that the largest part of the charge is situated on the nitrogen atom (Smith & Schneider, 1961).

Each oxygen atom of the water molecules is surrounded by two other oxygen atoms and one nitrogen atom. The water molecules form fairly large, open hexagonal channels as appear in the direction of the a axis. Similar hexagonal channels are also found in the structure of

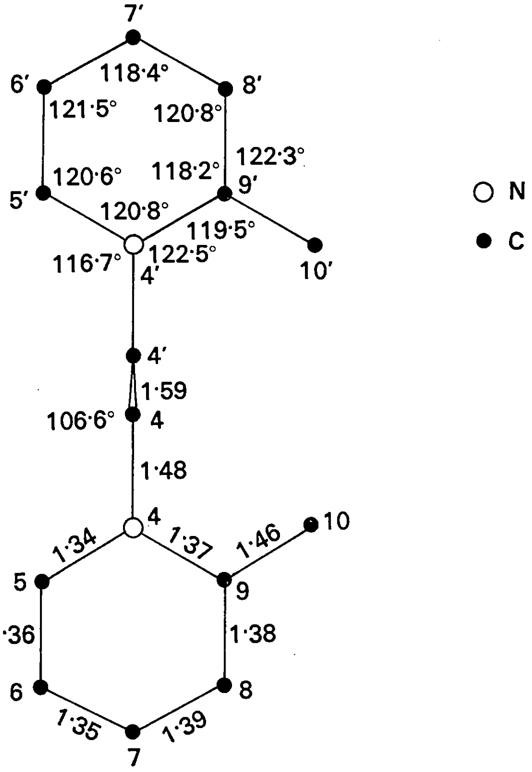

Fig. 2. Bond lengths and angles in the 1,2-bis-(2-methyl-pyridinium)ethane ion.

Table 5. *Bond angles in degrees*

(*a*) In the Ni(CN)$_4{}^{2-}$ ion			
N(1)···Ni···N(2)	89·6 ± 0·3	Ni–C(1)–N(1)	180·0 ± 0·8
N(1)···Ni···N(3)	90·6 ± 0·2	Ni–C(2)–N(2)	180·0 ± 1·1
N(1)···Ni···N(1''')	174·5 ± 0·3	Ni–C(3)–N(3)	176·8 ± 0·5
N(2)···Ni···N(3)	174·5 ± 0·2		
(*b*) In the 1,2-bis-(2-methylpyridinium)ethane ion			
C(6)–C(7)–C(8)	118·4 ± 0·8	N(4)—C(9)C(8)	118·2 ± 0·8
C(5)–C(6)–C(7)	121·5 ± 0·9	N(4)—C(9)–C(10)	119·5 ± 0·8
N(4)–C(5)–C(6)	120·6 ± 0·9	C(10)–C(9)–C(8)	122·3 ± 0·7
C(5)–N(4)–C(9)	120·8 ± 0·7	C(9)—C(8)–C(7)	120·8 ± 0·8
C(4)–N(4)–C(9)	122·5 ± 0·7	N(4)—C(4)–C(4')	106·7 ± 0·6
(*c*) Other			
O(1)···O(1')···O(2)	121·9 ± 0·9		
O(1)···O(2)···O(1')	104·3 ± 0·9		

(The mean standard deviation for the bond angles is as follows: N–Ni–N, 0·4°; Ni–C–N, 0·8°; other, 1·0°.)

' Related to one another by a twofold axis.
''' Related to one another by a mirror plane.

Table 6. *Equation for the best plane through (a) the* $Ni(CN)_4^{2-}$ *ion, and (b) the* 1,2-*bis*-(2-*methylpyridinuim*)*ethane ion*

Equations are expressed in the form $Ax+By+Cz=D$, where D is expressed in Å and x, y and z are fractional coordinates.

(*a*) $A=0{\cdot}8748$, $B=0{\cdot}4791$, $C=0{\cdot}0720$, $D=1{\cdot}5298$

Deviations from the best plane in Å

Ni	−0·0877	C(1)	0·0093
C(2)	0·0278	C(3)	−0·0397
N(1)	−0·0054	N(2)	0·0269
N(3)	0·0687		

(*b*) $A=0{\cdot}9872$, $B=0{\cdot}1598$, $C=0{\cdot}0014$, $D=4{\cdot}1646$

Deviations from the best plane in Å

C(4)	0·0594	C(5)	−0·0083	C(6)	0·0022
C(7)	0·0022	C(8)	−0·0007	C(9)	−0·0053
C(10)	0·0512	N(4)	0·0099		

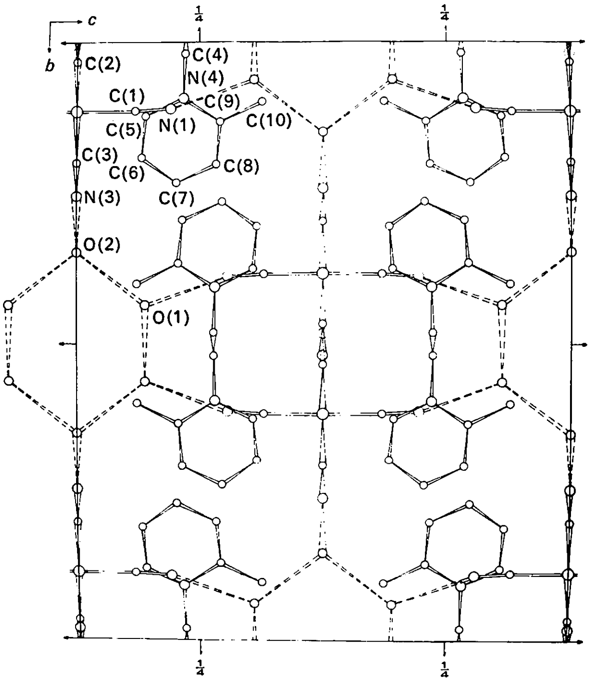

Fig. 3. Projection of the structure along the *a* axis.

ice I (Pauling, 1960). The O···O and O···N distances range between 2·70 and 2·86 Å. This implies strong hydrogen bonds of the type O–H···O and O–H···N. These distances are in agreement with the O···O distance in ice I.

It is noticeable that the structure is bound by strong ionic forces along [100] (the two nitrogen atoms of the $Ni(CN)_4^{2-}$ ion that are not situated on the mirror plane each have two nitrogen atoms of the cation at a distance of 3·45 and 3·65 Å). No ionic forces are, however, active along [010] and [001]. The structure is bound only by hydrogen bonds in the latter two directions. This also explains the tendency of the crystal to grow very rapidly in the direction of the *a* axis. According to the dimensions of the crystals they grow approximately a hundred times more rapidly in the direction of the *a* axis; typical measurements are 25 × 0·25 × 0·25 mm³.

The mean Ni–C distance is noticeable shorter than the sum of the planar radius of Ni and the single-bond radius of C, 1·22 and 0·77 Å respectively (Pauling, 1960). If the partial ionic character of the Ni–C bond is considered, the observed Ni–C distance indicates (according to the method of Pauling) a double-bond character of about 30% for the Ni–C bond. On this basis one can calculate, using Pauling's method, for an equal resonance between all the Ni–C bonds, that each nitrogen atom obtains an effective charge of approximately −0·45 so that the Ni atom has only an effective charge of −0·2. This representation is in good agreement with the principle of electroneutrality since the central atom obtains a very small effective charge. It is also in agreement with all the determined structures since in no case was a tendency found for the positive charge of the cation to come near the Ni atom, although that would be quite possible according to the planar configuration of the $Ni(CN)_4^{2-}$ ion.

Thanks are expressed to Dr G. Gafner of the South African C.S.I.R. for valuable help and for the provision of the program used, and to the C.S.I.R. for financial assistance.

References

Basson, S. S., Bok, L. D. C. & Leipoldt, J. G. (1969). *Acta Cryst.* **B25**, 579.
Buerger, M. J. (1942). *X-ray Crystallography*, New York: John Wiley.
Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS Program.* Report ORNL-TM-305, Oak Ridge National Laboratory, Tennessee.
Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104.
Ehrenberg, M. (1967). *Acta Cryst.* **22**, 482.
Hamilton, W. C. (1955). *Acta Cryst.* **8**, 185.
Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
Leipoldt, J. G., Basson, S. S. & Bok, L. D. C. (1970). *Acta Cryst.* **B26**, 361.
Lingafelter, E. C. & Donohue (1966). *Acta Cryst.* **20**, 321.
Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
Smith, I. C. & Schneider, W. G. (1961). *Canad. J. Chem.* **39**, 1158.