Electron microprobe analysis of the $SmZn_{12}$ crystallites in the zinc matrix of the alloys described above indicates variation in the composition of these crystals and gives an average stoichiometry of $SmZn_{10.9}$. Some variation in lattice constants was also indicated by X-ray powder diffraction data. Consideration of the single-crystal data obtained indicates a probable Zn/Sm ratio of $11 \cdot 0 \pm 0 \cdot 5$. The electron microprobe data indicate a similar range in composition; however, whether this is the result of an actual variation in composition or of the uncertainty in the analysis is not known.

A similar type of disordered structure was observed by Johnson & Smith (1967) for $CeMg_{10 \cdot 3}$. They started with a basic Th_2Ni_{17} type structure in which the disorder occurred by the occasional substitution of a pair of light atoms for a heavy atom. It is interesting to note that if in the hexagonal $SmZn_{12}$ structure all the pairs of zinc atoms in the Sm(1) rows along the z axis are replaced by samarium atoms, the resulting stoichiometry is Sm_2Zn_{17}. Disorder of a similar type very probably also occurs in $CeZn_{5 \cdot 25}$ ($D2_d$ type) which exists with a composition range of 70·4 to 71·1 wt.% zinc (Lott & Chiotti, 1966).

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The Crystal Structure of 1,2-Bis-(*N*-methyl-4-pyridinium)ethylene Tetracyanonickelate(II)

By J. G. Leipoldt, S. S. Basson and L. D. C. Bok

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

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The crystal structure of the title compound ($C_{18}H_{16}N_6Ni$) was determined by means of three-dimensional X-ray analysis. The space group is $P2_1/n$ (C_{2h}^5), and the cell dimensions are $a = 6 \cdot 864$, $b = 12 \cdot 96$, $c = 10 \cdot 05$ Å, $\beta = 107 \cdot 0°$. The corresponding Pd and Pt compounds are isomorphous with the Ni compound. The Ni atoms lie on a centre of symmetry so that the $Ni(CN)_4^{2-}$ ion is centrosymmetric. The $Ni(CN)_4^{2-}$ ion is square planar and the bond lengths are: Ni–C 1·85 and C–N 1·16 Å (average). The centre of the 1,2-bis-(*N*-methyl-4-pyridinium)ethylene ion also lies on a centre of symmetry, so that the two rings are approximately coplanar, while the bond lengths in the ion agree very well with those in pyridine. The distance between the N atoms in the 1,2-bis-(*N*-methyl-4-pyridinium)ethylene ion is 9·27 Å, which is thus approximately the distance between the two positive charges on the divalent cation.

Introduction

The complex cyanides previously studied were mainly those with simple monovalent and divalent cations, *e.g.* K^+ and Ca^{2+}. The structure of 1,2-bis-(*N*-methyl-4-pyridinium)ethylene tetracyanonickelate(II) has been determined as part of a programme for the study of complex cyanides with varying types of cation to find the effect of the cation structure on that of the complex formed. When the two positive charges on the cation are separated, as in this case, the complex is expected to assume a different structure to that of the complexes of simple cations. In the 4,4′-dipyridinium ion (Basson, Bok & Leipoldt, 1969) the distance between the two positively charged N atoms is 7·05 Å and in the dipyridiniumethylene ion the distance is much greater, so that a different type of configuration with respect to the $Ni(CN)_4^{2-}$ can be expected.

Experimental

1,2-Bis-(*N*-methyl-4-pyridinium)ethylene di-iodide was prepared by refluxing 1,2-bis-(4-pyridyl)ethylene for two hours with an excess of methyl iodide in a methanol medium. On cooling brownish red crystals were formed. An aqueous solution of the iodide was added to a dilute solution of $K_2Ni(CN)_4$. Clear orange crystals of 1,2-bis-(*N*-methyl-4-pyridinium)ethylene tetracyanonickelate(II) were obtained after slow crystallization. The compound is only slightly soluble in cold water, but is reasonably soluble in hot water. There is a strong tendency for the formation of twinned crystals. To obtain well formed single crystals the compound was crystallized very slowly from a solution containing equal quantities of water and dimethylformamide. The corresponding Pd and Pt compounds were prepared similarly.

The cell dimensions and space group were determined from oscillation and Weissenberg photographs taken with Co $K\alpha$ radiation. The camera was standardized with NaCl, $a=5·63$ Å. Densities were determined by means of the flotation method using diiodomethane and diluting it with benzene. The crystal data for the Ni compound, as well as for the Pd and Pt compounds which are isomorphous with the Ni compound, are given in Table 1. The space group was determined as $P2_1/n$ from the following systematic extinctions: $h0l$ for $h+l=2n+1$; $0k0$ for $k=2n+1$.

The intensity data were obtained from a crystal with the dimensions $0·25\times0·25\times0·24$ mm^3 with the a axis as the oscillation axis. The intensities were determined for layers 0–5 along the a axis by the multiple-film method and a Stoe integrating Weissenberg camera with Cu $K\alpha$ radiation. Ilford industrial G X-ray films were used. The intensities were estimated by the use of a calibrated standard strip. According to this scale, the intensities varied from 1 to approximately 2000. A total of 1303 reflexions were obtained, of which about 15% were weaker than the background. To the latter reflexions a value of $\frac{1}{3}$ of the minimum value was allocated (Hamilton, 1955). The usual correction factors, *e.g.* Lorentz, polarization, spot shape, and α_1–α_2 splitting, were applied. No correction was made for absorption as the crystal was much smaller than the optimum size ($\mu=16·81$ cm^{-1} and $\mu R=0·202$).

Table 1. *Crystal data*

	$C_{18}H_{16}N_6Ni$	$C_{18}H_{16}N_6Pd$	$C_{18}H_{16}N_6Pt$
M	375·06	422·75	511·44
a (Å)	6·864	6·890	6·894
b (Å)	12·96	13·14	13·14
c (Å)	10·05	10·14	10·17
β (°)	107·0	106·0	105·0
V (Å^3)	855	882	889
D_e (g.cm^{-3})	1·46	1·58	1·92
D_c (g.cm^{-3})	1·46	1·59	1·91
Z	2	2	2

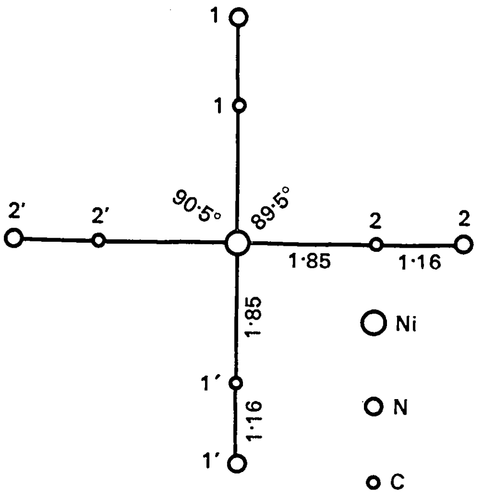

Fig. 1. Bond lengths and angles in the $Ni(CN)_4^{2-}$ ion.

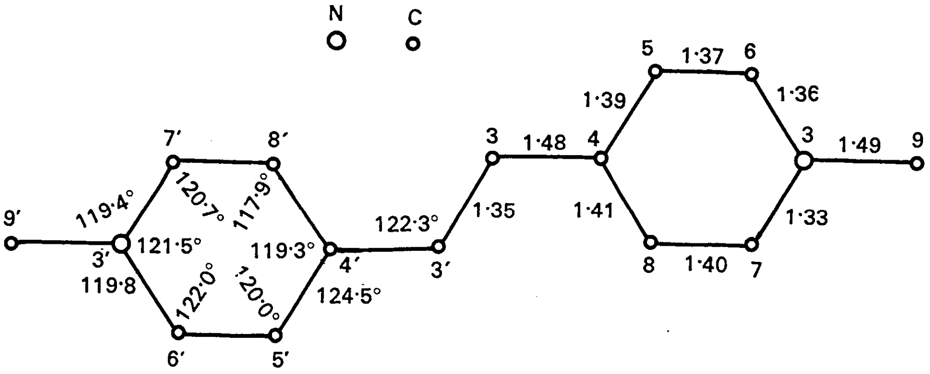

Fig. 2. Bond lengths and angles in the 1,2-bis-(*N*-methyl-4-pyridinium)ethylene ion.

Table 2. *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.

H = 0			
0	4	36.1	38.6
0	6	18.0	17.1
0	8	18.4	17.0
0	10	14.2	10.7
0	12	6.1	4.4
4	0	31.2	35.7
6	0	50.0	62.2
8	0	41.7	42.0
10	0	21.8	16.0
12	0	9.1	3.0
14	0	10.7	4.7
1	1	22.4	31.0
1	2	29.4	30.9
1	4	18.3	-15.8
1	5	21.6	22.1
1	6	24.7	-23.9
1	7	36.0	34.1
1	8	13.1	-12.0
1	9	14.4	12.0
1	10	6.3	-4.9
1	11	11.0	8.1
1	12	2.7	-2.9
2	2	32.1	34.7
2	3	16.5	13.8
2	4	25.5	25.1
2	5	26.7	-24.8
2	6	16.3	17.7
2	7	2.3	0.2
2	8	17.0	16.3
2	9	2.6	1.5
2	10	16.7	15.0
2	11	8.6	-7.9
3	1	10.6	10.9
3	3	22.1	22.7
3	4	15.1	12.0
3	5	7.9	7.3
3	6	2.1	-0.9
3	7	25.5	25.5
3	8	20.3	-17.6
3	9	12.9	11.9
3	10	2.6	1.5
4	1	44.6	46.0
4	3	33.7	30.8
4	4	32.8	34.4
4	5	2.0	-2.1
4	6	25.5	22.8
4	8	14.2	10.8
4	9	10.2	8.9
4	10	7.6	4.6
4	11	5.0	-5.1
5	1	17.4	19.5
5	2	1.5	-3.4
5	3	43.0	49.3
5	4	10.1	7.9
5	5	33.7	33.8
5	6	2.3	-0.6
5	7	6.1	4.2
5	8	15.1	-13.3
5	9	17.0	14.1
5	10	4.2	4.4
5	11	10.3	9.7
6	1	25.8	22.4
6	2	25.3	25.0
6	3	1.8	2.7
6	4	37.3	38.4
6	5	10.0	7.5
6	6	19.9	18.7
6	7	9.9	8.4
6	8	16.5	15.4
6	9	2.6	-3.7
6	10	9.7	8.2
7	1	6.3	1.8
7	2	1.9	-2.6
7	3	37.2	36.7
7	4	19.0	16.4
7	5	33.7	34.5
7	6	13.0	-11.7
7	7	26.4	23.8
7	8	4.6	-2.9
7	9	9.8	10.2
7	10	2.1	-3.3
7	11	5.3	7.5
8	1	12.5	-10.3
8	2	24.1	25.0
8	3	2.2	1.6
8	4	40.9	40.6
8	5	10.4	8.3
8	6	13.4	11.8
8	7	19.4	18.7
8	8	13.5	11.8
8	9	2.4	0.0
8	10	12.2	13.4
9	1	25.9	26.1
9	2	6.8	-4.9
9	3	29.7	28.3
9	4	9.5	8.0
9	5	15.4	13.3
9	6	4.6	-3.2
9	7	32.2	31.5
10	1	11.7	-9.2
10	2	14.6	11.9
10	3	12.3	-8.4
10	4	26.1	21.7
10	5	13.7	-10.9
10	6	17.7	17.1
10	7	12.6	9.2
10	8	12.7	12.4
10	9	4.5	4.9
11	1	14.6	13.9
11	2	6.3	-1.9
11	3	7.8	6.2
11	4	10.2	-9.6
11	5	7.2	5.5
11	6	4.5	2.6
11	7	13.7	11.7
11	8	15.6	-18.2
11	9	7.3	7.1
12	1	5.6	-5.7
12	2	2.6	1.7
12	3	6.5	5.1
12	4	12.0	10.5
12	5	4.4	2.7
12	6	14.4	12.5
12	7	10.8	9.5
12	8	11.4	13.8
13	1	27.3	22.0
13	2	2.6	2.9
13	3	5.5	2.5
13	4	4.4	-4.6
13	5	14.6	13.0
13	6	2.1	-0.8
13	7	7.5	5.9
14	1	2.5	-2.5
14	2	20.5	16.6
14	3	2.4	3.5
14	4	16.6	13.6
14	5	1.9	-1.9
15	1	18.0	16.4
15	2	5.1	-3.3
15	3	10.1	7.7
15	4	3.0	-2.9
15	5	6.9	8.5
H = 1			
0	3	26.3	27.1
0	5	25.7	25.9
0	7	17.4	18.0
0	9	10.1	7.5
0	11	10.3	10.9
1	1	33.4	-34.7
1	2	23.9	23.8
1	3	43.8	-42.5
1	4	44.8	49.3
1	5	20.3	-18.2
1	6	18.6	18.0
1	7	8.6	-7.4
1	8	15.9	15.2
1	9	1.6	-3.1
1	10	8.0	8.2
2	1	27.3	25.6
2	2	44.2	-42.4
2	3	28.1	30.0
2	4	4.8	-3.2
2	5	29.8	33.2
2	6	7.1	5.4
2	7	26.1	27.0
2	8	13.1	-12.4
2	9	15.9	17.2
2	10	1.4	-0.7
2	11	5.7	7.2
3	1	18.5	15.1
3	2	2.0	8.4
3	3	3.9	-2.3
3	4	38.5	41.4
3	5	32.3	-28.9
3	6	20.4	20.9
3	7	2.5	2.3
3	8	27.3	27.0
3	9	2.7	-4.2
3	10	12.6	15.3
4	1	39.9	40.6
4	2	5.1	-8.0
4	3	29.7	32.8
4	4	22.6	19.9
4	5	16.9	16.5
4	6	17.3	14.6
4	7	11.3	10.1
4	8	8.5	-8.3
4	9	14.5	15.2
4	10	1.3	-1.5
5	1	8.7	9.5
5	2	41.3	37.8
5	3	3.7	3.7
5	4	2.0	3.3
5	5	23.0	-21.2
5	6	25.4	24.4
5	7	7.0	5.5
5	8	15.7	16.2
5	9	1.5	1.7
5	10	7.0	6.3
6	1	44.3	47.5
6	2	6.1	6.4
6	3	30.5	31.1
6	4	5.3	6.4
6	5	20.9	20.7
6	6	1.5	-0.9
6	7	17.8	16.8
6	8	2.7	2.7
6	9	11.0	11.7
7	1	21.8	18.2
7	2	42.9	45.1
7	3	10.6	-10.1
7	4	33.5	32.9
7	5	5.0	-4.3
7	7	10.8	-8.9
7	8	12.7	13.0
7	10	4.6	5.1
8	1	45.5	47.2
8	2	17.1	12.4
8	3	18.9	15.5
8	4	21.2	20.0
8	5	20.1	19.1
8	6	1.5	3.0
8	7	21.8	21.5
8	8	4.1	-4.4
9	1	10.1	8.9
9	2	18.5	15.6
9	3	3.0	-3.5
9	4	40.1	42.1
9	5	30.8	-29.5
9	6	4.3	-4.7
9	7	7.0	-7.3
9	8	9.5	9.1
10	1	30.1	27.3
10	2	18.0	-14.1
10	3	23.1	21.4
10	4	14.4	12.3
10	5	16.4	16.5
10	6	8.2	7.2
10	7	8.3	7.0
10	8	8.4	-9.2
11	1	12.1	-11.5
11	2	8.4	6.4
11	3	5.4	5.1
11	4	23.1	19.8
11	5	26.9	-24.8
11	6	15.1	13.0
11	7	5.5	5.4
11	8	10.9	11.6
12	1	15.7	14.6
12	2	1.6	2.3
12	3	23.1	19.3
12	4	13.5	10.7
12	5	18.2	16.3
12	6	9.8	9.7
12	7	5.6	3.7
13	1	4.2	-4.4
13	2	17.7	15.0
13	3	1.5	2.4
13	4	12.2	9.2
13	5	5.4	5.1
13	6	8.3	8.9
14	1	16.4	13.5
14	2	1.4	-1.8
14	3	5.8	5.0
14	4	6.2	5.4
14	5	7.7	7.8
14	6	4.5	7.4
15	1	4.7	-3.2
15	2	11.4	9.6
15	3	9.5	-8.5
15	4	12.5	11.3
16	1	8.7	9.1
16	2	4.5	-3.6
3	0	27.7	23.9
4	0	40.0	37.7
5	0	49.8	56.8
6	0	1.0	3.8
7	0	45.3	45.4
9	0	33.7	31.9
10	0	14.8	-11.2
11	0	10.5	8.5
12	0	8.5	6.9
13	0	6.6	3.7
14	0	1.5	2.6
15	0	11.1	10.0
1	-1	25.3	19.8
2	-1	48.0	49.5
3	-1	46.6	53.3
5	-1	1.5	1.6
6	-1	27.0	27.7
7	-1	1.1	-1.6
8	-1	27.8	26.8
9	-1	5.8	-3.7
10	-1	16.7	11.6
11	-1	7.4	-1.1
12	-1	1.6	1.3
13	-1	3.8	3.9
14	-1	19.2	15.4
15	-1	4.8	-2.6
16	-1	5.1	4.8
1	-2	19.6	24.3
2	-2	50.0	-51.0
3	-2	10.3	-5.3
4	-2	49.6	45.3
5	-2	13.5	15.0
6	-2	21.9	19.0
7	-2	1.9	5.3
8	-2	12.8	-11.4
9	-2	21.3	22.3
10	-2	14.6	-12.9
11	-2	14.7	14.6
12	-2	5.4	-5.8
13	-2	22.6	21.4
14	-2	1.4	-2.2
15	-2	17.4	15.9
1	-3	13.5	7.9
3	-3	16.1	11.4
4	-3	31.0	31.3
5	-3	4.3	-2.5
6	-3	50.7	51.6
7	-3	3.5	5.2
8	-3	39.4	36.7
9	-3	3.4	1.7
10	-3	16.0	14.1
11	-3	1.5	-1.0
13	-3	2.6	1.7
14	-3	7.6	4.2
15	-3	1.1	-1.8
1	-4	27.8	33.1
2	-4	21.3	21.7
3	-4	29.3	27.9
4	-4	28.5	-24.0
5	-4	19.2	20.0
6	-4	20.7	-17.3
7	-4	2.2	2.1
8	-4	7.8	6.2
9	-4	21.6	22.4
10	-4	3.2	4.5
11	-4	11.4	10.5
12	-4	2.7	4.8
13	-4	19.0	18.3
14	-4	1.3	2.3
15	-4	13.9	14.0
1	-5	26.6	-23.0
2	-5	18.8	21.4
3	-5	25.1	-26.1
4	-5	33.1	33.5
5	-5	2.1	3.9
6	-5	21.0	19.0
7	-5	1.4	2.3
8	-5	16.6	18.1
9	-5	3.2	3.9
10	-5	9.3	9.3
11	-5	1.6	1.6
12	-5	1.5	1.7
13	-5	1.4	-1.4
14	-5	14.2	14.4
1	-6	42.3	46.2
2	-6	7.6	-7.2
3	-6	17.1	17.3
4	-6	18.4	-17.1
5	-6	30.2	31.3
6	-6	2.4	-1.4
7	-6	24.3	23.2
8	-6	1.5	1.2
9	-6	21.6	20.0
10	-6	4.3	4.9
11	-6	4.2	3.2
12	-6	2.5	-2.7
1	-7	2.3	4.0
2	-7	19.3	17.6
3	-7	6.6	-7.1
4	-7	20.4	21.9
5	-7	6.8	-5.4
6	-7	23.3	24.8
7	-7	12.4	-12.1
8	-7	28.2	28.0
9	-7	4.7	-5.9
10	-7	14.5	13.7
11	-7	5.0	6.8
12	-7	4.9	5.9
1	-8	16.1	15.1
2	-8	12.1	12.3
3	-8	5.7	4.8
4	-8	1.5	-1.3
5	-8	22.8	23.7
6	-8	8.5	-7.1
7	-8	21.3	22.1
8	-8	2.7	-4.7
9	-8	9.8	9.0
10	-8	6.9	6.6
11	-8	4.3	3.9
4	-9	11.5	12.2
5	-9	1.6	2.5
6	-9	8.9	8.5
7	-9	10.9	10.5
8	-9	7.2	7.5
9	-9	1.3	2.9
10	-9	9.6	10.4
0	-5	38.5	42.2
0	-7	27.0	28.6
H = 2			
0	2	27.7	30.2
0	4	23.1	26.7
0	6	12.5	10.4
0	8	21.3	19.9
0	10	17.2	-18.4
1	1	47.7	54.9
1	2	26.6	-23.0
1	3	18.9	19.4
1	4	13.4	-9.7
1	5	20.0	23.3
1	6	3.0	-2.1
1	7	15.7	13.4
1	8	8.0	6.5
1	9	22.0	24.9
1	10	4.6	5.0
1	11	8.2	10.0
2	1	13.5	-8.2
2	2	51.7	53.0
2	3	18.5	12.7
2	4	36.1	41.7
2	5	19.8	-18.6
2	6	24.3	25.9
2	7	3.2	-1.1
2	8	17.1	15.5
2	9	9.5	-8.1
3	1	48.5	52.0
3	2	48.6	-40.5
3	3	25.7	29.4
3	4	6.8	2.3
3	5	41.3	43.3
3	6	8.3	-7.1
3	7	23.8	24.3
3	8	3.3	-1.5
3	9	18.7	19.6
3	10	4.3	3.6
4	1	28.5	24.8
4	2	19.1	19.8
4	3	22.0	19.5
4	4	19.0	16.9
4	5	15.7	-12.0
4	6	24.1	24.4
4	7	3.3	-2.3
4	8	8.9	6.5
4	9	5.2	5.5
4	10	8.1	8.4
5	1	5.1	1.4
5	2	26.6	-27.5
5	3	34.9	34.5
5	4	6.7	5.4
5	5	23.6	22.5
5	6	3.2	3.0
5	7	13.9	10.7
5	8	3.2	1.0
5	9	14.1	13.8
6	1	2.3	1.6
6	2	20.8	21.9
6	3	5.6	5.7
6	4	28.1	28.2
6	5	8.4	7.2
6	6	18.6	17.6
6	7	7.0	5.8
6	8	8.7	7.8
6	9	8.7	10.1
7	1	36.4	36.6
7	2	6.5	-6.3
7	3	21.4	20.4
7	4	20.9	-17.5
7	5	20.6	19.0
7	6	7.0	6.3
7	7	9.8	8.9
7	8	3.0	3.6
7	9	9.5	9.3
8	1	16.5	15.2
8	2	26.3	25.1
8	3	6.4	7.1
8	4	29.2	29.3
8	5	8.9	-6.7
8	6	3.3	1.5
8	7	3.2	-0.7
8	8	7.6	5.3
8	9	3.7	-4.5
9	1	43.6	45.1
9	2	37.5	-35.9
9	3	9.5	-7.6
9	4	10.5	-9.8
9	5	15.1	13.1
9	6	3.2	5.7
9	7	5.2	4.4
9	8	2.5	1.0
9	9	5.5	5.0
10	1	15.4	14.0
10	2	20.0	18.3
10	3	9.8	8.9
10	4	10.6	9.6
10	5	11.9	-10.9
10	6	3.1	-0.0
10	7	2.7	1.2
10	8	11.0	10.3
11	1	28.8	26.4
11	2	30.1	-28.4
11	3	24.1	19.0
11	4	6.9	6.3
11	5	15.4	14.1
11	6	2.8	-0.7
11	7	7.9	7.4
12	1	11.4	10.1
12	2	17.8	15.5
12	3	14.7	12.9
12	4	9.3	7.3
12	5	2.8	1.9
12	6	5.0	4.2
13	1	14.6	10.9
13	2	7.7	7.4
13	3	11.5	11.5
13	4	2.7	4.4
13	5	2.3	2.1
13	6	4.2	-3.5
14	1	5.0	4.5
14	2	8.2	7.9
14	3	10.6	11.0
14	4	8.7	7.8
15	1	12.7	11.9
1	0	54.5	-48.0
2	0	39.8	38.5
3	0	7.2	-4.4
4	0	32.6	35.8
5	0	9.1	8.6
6	0	33.7	38.8
7	0	6.7	-4.5
8	0	21.3	17.0
9	0	2.9	-3.9
10	0	24.7	22.8
11	0	6.9	6.8
12	0	26.7	23.7
13	0	7.9	5.8
14	0	6.2	5.7
15	0	9.9	-8.4
16	0	4.4	4.4
1	-1	28.1	22.3
2	-1	48.5	-43.1
3	-1	10.9	15.2
4	-1	10.9	-11.6
5	-1	32.8	31.0
6	-1	2.2	3.8
7	-1	45.5	44.7
8	-1	16.0	13.1
9	-1	16.6	14.5
10	-1	16.1	-13.4
11	-1	8.9	6.1
12	-1	5.7	1.0
13	-1	15.8	14.0
14	-1	5.1	-1.2
15	-1	10.0	8.7
16	-1	3.5	-2.4
1	-2	39.0	-34.6
2	-2	26.6	25.0
3	-2	11.1	7.9
4	-2	35.5	33.3
5	-2	8.2	8.1
6	-2	42.8	42.9
7	-2	16.0	14.8
8	-2	41.0	41.0
9	-2	6.2	6.8
10	-2	25.9	27.0
11	-2	10.5	-10.9
12	-2	17.5	15.8
13	-2	3.2	-3.3
14	-2	11.3	10.4
15	-2	4.2	-2.8
16	-2	8.1	9.0
1	-3	53.9	55.7
2	-3	15.0	14.8
3	-3	25.4	24.8
4	-3	27.6	25.4
5	-3	43.8	43.2
6	-3	2.3	3.4
7	-3	39.5	41.4
8	-3	3.4	5.3
9	-3	24.8	28.1
10	-3	13.4	-11.2
11	-3	9.8	8.8
12	-3	8.0	6.7
13	-3	5.5	4.1
14	-3	2.8	0.9
15	-3	11.2	10.6
1	-4	8.3	4.0
2	-4	46.4	47.1
3	-4	31.9	33.2
4	-4	47.9	58.0
5	-4	4.9	6.4
6	-4	22.6	24.9
7	-4	2.7	0.2
8	-4	20.8	21.7
9	-4	3.1	-1.1
10	-4	11.2	8.7
11	-4	3.3	0.4
12	-4	3.2	0.8
13	-4	3.1	3.9
14	-4	12.6	11.4
1	-5	11.3	18.1
2	-5	34.5	-32.5
3	-5	6.8	-5.8
4	-5	24.2	26.5
5	-5	5.4	10.1
6	-5	12.0	11.7
7	-5	5.0	7.7
8	-5	9.2	-9.3
9	-5	14.1	14.3
10	-5	13.3	-13.5
11	-5	11.3	12.1
12	-5	5.5	-5.0
13	-5	15.9	16.9
14	-5	2.4	-1.4
1	-6	9.4	8.1
2	-6	49.5	52.5
3	-6	12.5	11.8
4	-6	20.7	20.7
5	-6	2.8	-2.6
6	-6	34.8	32.6
7	-6	5.3	6.6
8	-6	25.3	25.8
9	-6	3.3	2.4
10	-6	11.4	9.7
11	-6	3.2	-1.4
1	-7	20.7	23.2
2	-7	5.9	6.8
3	-7	21.5	25.0
4	-7	8.8	-9.0
5	-7	13.4	15.0
6	-7	10.9	-10.4
7	-7	3.2	1.8
8	-7	3.3	2.6
9	-7	13.9	14.7
10	-7	3.2	1.4
11	-7	5.3	6.3
12	-7	2.7	3.5
13	-7	11.3	12.4
1	-8	14.9	-14.0
2	-8	10.6	11.1
3	-8	12.1	-13.3
4	-8	14.5	15.7
5	-8	3.2	2.3
6	-8	10.6	11.7
7	-8	3.3	1.5
8	-8	9.8	10.6
3	-9	9.8	10.3
4	-9	8.0	-8.7
5	-9	14.5	16.3
6	-9	3.3	-0.4
7	-9	13.1	12.4
8	-9	3.1	2.4
9	-9	11.1	11.9
6	-10	13.1	14.0
7	-10	7.1	-8.4
8	-10	13.3	16.6
0	-2	29.1	23.1
0	-4	31.1	31.5
H = 3			
0	1	36.5	34.2
0	3	10.0	11.3
0	5	29.4	30.6
0	7	25.0	-24.4
0	9	8.3	8.8
1	2	29.1	28.4
1	3	1.2	1.0
1	4	19.4	19.0
1	5	13.5	12.0
1	6	33.6	35.0
1	7	3.0	4.9
1	8	15.9	16.5
1	9	1.4	-2.2
1	10	2.1	-5.0
2	1	46.6	49.9
2	2	27.5	-23.8
2	3	31.0	32.1
2	4	1.4	-1.4
2	5	25.4	25.6
2	6	8.8	-7.7
2	7	1.7	-0.9
2	8	15.3	16.1
2	9	2.4	3.6
2	10	0.9	-1.2
3	1	5.3	0.2
3	2	50.8	54.9
3	3	14.4	-11.0
3	4	33.6	32.8
3	5	2.8	-2.1
3	6	23.2	23.0
3	7	3.0	3.7
3	8	17.2	15.5
3	9	1.4	-3.1
4	1	25.2	23.0

Table 2 (*cont.*)

4	2	18.0	-14.0
4	3	35.1	32.8
4	4	6.2	-3.3
4	5	16.0	14.2
4	6	7.9	7.8
4	7	14.5	14.0
4	8	1.6	-2.2
4	9	7.6	8.9
5	1	1.2	2.4
5	2	24.3	25.0
5	3	4.7	4.5
5	4	19.5	15.9
5	5	2.9	0.3
5	6	20.0	19.6
5	7	7.8	8.7
5	8	17.5	17.0
6	1	36.9	37.0
6	2	14.3	12.7
6	3	22.7	21.4
6	4	9.4	7.3
6	5	12.2	11.1
6	6	14.0	14.0
6	7	1.7	-3.8
6	8	2.5	-2.4
7	1	28.5	-25.4
7	2	23.1	21.8
7	3	11.2	10.8
7	4	14.3	12.3
7	5	3.0	4.3
7	6	13.2	13.2
7	7	1.6	-0.6
7	8	9.7	11.3
8	1	31.6	31.3
8	2	11.9	-8.5
8	3	1.7	0.7
8	4	1.7	-1.6
8	5	9.4	8.3
8	6	5.8	-4.9
8	7	1.5	0.5
8	8	1.1	-0.4
9	1	12.1	-11.3
9	2	16.0	15.7
9	3	7.6	7.6
9	4	9.0	7.9
9	5	1.7	0.2
9	6	9.0	7.8
9	7	2.3	-3.5
10	1	11.1	10.4
10	2	11.9	-10.3
10	3	5.2	2.7
10	4	2.9	3.4
10	5	14.3	14.5
10	6	1.4	-1.1
11	1	5.2	6.0
11	2	13.3	13.8
11	3	1.7	-0.4
11	4	11.2	10.6
11	5	1.4	1.2
11	6	7.1	8.3
12	1	9.7	9.9
12	2	1.7	2.4
12	3	7.7	6.7
12	4	1.4	1.4
12	5	13.0	14.3
12	6	4.3	-6.2
13	1	1.6	1.0
13	2	1.5	1.8
13	3	5.2	-5.1
13	4	9.8	10.5
14	1	7.6	8.2
14	2	2.1	3.6
1	0	15.9	14.4
3	0	31.8	32.5
4	0	21.7	17.7
5	0	39.5	37.5
6	0	13.4	13.7
7	0	21.2	19.9
8	0	7.7	10.6
9	0	9.3	-8.6
10	0	10.2	8.9
11	0	24.3	21.6
12	0	15.0	14.5
13	0	10.8	12.7
14	0	11.5	13.4
15	0	1.0	1.2
1	-1	24.0	-19.0
2	-1	61.4	58.1
3	-1	42.2	-38.6
4	-1	21.2	20.3
5	-1	26.1	-23.7
6	-1	17.0	17.7
7	-1	7.6	-7.3
8	-1	23.6	25.7
9	-1	34.4	-34.2
10	-1	16.8	16.2
11	-1	27.2	-26.1
12	-1	11.8	11.3
13	-1	4.5	4.7
14	-1	4.9	6.4
15	-1	1.1	1.3
1	-2	45.0	43.9

2	-2	13.2	8.8
3	-2	45.9	44.3
4	-2	19.9	18.5
5	-2	2.0	3.8
6	-2	4.4	-2.9
7	-2	31.1	30.7
8	-2	4.9	5.9
9	-2	35.5	37.4
10	-2	12.0	12.4
11	-2	28.0	27.4
12	-2	7.5	7.9
13	-2	11.7	10.2
14	-2	1.4	3.1
15	-2	9.1	10.0
1	-3	30.6	-27.7
2	-3	34.8	35.0
3	-3	7.9	-4.5
4	-3	27.4	29.4
5	-3	10.2	9.3
6	-3	31.3	34.8
7	-3	1.4	1.0
8	-3	17.2	15.5
9	-3	4.0	-3.9
10	-3	20.8	19.7
11	-3	5.2	7.0
12	-3	25.1	23.2
13	-3	6.2	7.7
14	-3	4.7	5.9
15	-3	5.8	-7.0
1	-4	17.3	19.3
2	-4	28.5	-26.3
3	-4	18.3	19.3
4	-4	10.1	-9.1
5	-4	19.7	20.5
6	-4	1.4	1.9
7	-4	31.0	33.4
8	-4	8.2	9.7
9	-4	10.8	10.8
10	-4	9.4	-9.5
11	-4	5.6	4.6
12	-4	1.7	-0.5
13	-4	9.9	10.6
14	-4	1.3	-0.5
15	-4	4.5	6.2
1	-5	22.5	-20.2
2	-5	20.5	19.2
3	-5	1.2	1.1
4	-5	20.1	20.7
5	-5	7.2	5.5
6	-5	27.4	29.4
7	-5	8.6	9.5
8	-5	25.1	27.7
9	-5	1.7	3.5
10	-5	20.9	21.3
11	-5	7.8	-8.3
12	-5	13.3	13.6
13	-5	1.4	-1.7
14	-5	4.4	6.0
1	-6	28.9	29.7
2	-6	9.8	8.8
3	-6	17.4	18.1
4	-6	11.7	12.5
5	-6	24.9	25.1
6	-6	1.6	2.3
7	-6	24.0	29.3
8	-6	1.7	3.4
9	-6	18.9	20.2
10	-6	9.4	-9.0
11	-6	7.9	7.1
12	-6	3.7	5.0
13	-6	3.8	3.7
1	-7	3.6	-1.5
2	-7	33.2	32.5
3	-7	15.0	17.5
4	-7	33.3	37.7
5	-7	6.6	7.9
6	-7	15.6	17.9
7	-7	1.7	1.6
8	-7	13.7	13.9
9	-7	1.7	1.0
10	-7	5.4	4.8
11	-7	1.5	1.6
1	-8	7.1	9.8
2	-8	20.1	-18.5
3	-8	6.4	-6.6
4	-8	11.2	13.5
5	-8	1.7	4.3
6	-8	7.0	6.8
7	-8	5.2	6.3
8	-8	7.2	-6.7
9	-8	5.0	7.0
2	-9	26.2	28.9
3	-9	6.7	9.1
4	-9	11.2	11.3
5	-9	1.7	-1.6
6	-9	16.7	17.5
7	-9	1.7	5.7
8	-9	12.8	15.5
9	-9	1.5	2.4
10	-9	5.0	5.4
5	-10	8.1	8.9

0	-3	26.7	27.0
0	-5	16.2	16.1
0	-7	15.6	18.0
		H = 4	
0	0	9.5	10.4
0	2	40.1	37.5
0	4	30.5	-27.9
0	6	15.1	13.5
0	8	8.2	9.8
1	1	24.6	22.3
1	2	19.5	16.6
1	3	42.8	41.1
1	4	2.1	3.0
1	5	24.0	22.8
1	6	1.9	-1.8
1	7	3.2	-4.5
1	8	2.7	0.9
1	9	6.6	8.2
2	1	1.3	-1.3
2	2	36.5	32.9
2	3	5.3	-4.7
2	4	1.8	-1.6
2	5	23.9	22.8
2	6	1.9	2.4
2	7	3.9	-3.7
2	8	5.3	5.9
2	9	1.0	-1.4
3	1	39.0	35.0
3	2	1.5	-1.5
3	3	23.1	21.7
3	4	4.4	3.1
3	5	26.3	25.8
3	6	4.6	-3.9
3	7	9.4	9.7
4	1	8.0	-3.6
4	2	23.1	21.3
4	3	9.2	8.9
4	4	21.8	19.5
4	5	5.2	-2.8
4	6	10.3	10.5
4	7	2.2	-4.3
5	1	23.0	19.6
5	2	1.7	0.1
5	3	23.1	23.5
5	4	10.2	11.4
5	5	24.7	25.4
5	6	3.2	3.8
5	7	12.0	14.2
5	8	4.1	-6.0
6	1	9.6	6.8
6	2	13.3	11.9
6	3	14.6	16.4
6	4	1.9	-2.4
6	5	1.9	-3.6
6	6	16.4	15.4
6	7	1.6	-1.8
6	8	5.4	7.2
7	1	13.3	13.0
7	2	3.2	4.5
7	3	14.6	15.4
7	4	4.0	-3.5
7	5	14.5	14.5
7	6	1.7	1.7
7	7	3.9	3.8
8	1	1.8	-2.7
8	2	9.8	10.4
8	3	5.7	-4.0
8	4	2.3	2.0
8	5	1.8	0.9
8	6	9.5	11.4
8	7	1.2	0.8
9	1	10.4	10.0
9	2	1.9	-0.5
9	3	11.3	10.2
9	4	6.4	-5.5
9	5	15.6	15.5
9	6	1.4	-1.7
10	1	5.2	5.1
10	2	17.6	17.1
10	3	1.8	-0.3
10	4	13.9	14.8
10	5	1.5	3.1
11	1	12.0	12.3
11	2	1.8	0.6
11	3	10.6	10.9
11	4	1.5	0.5
11	5	6.5	6.6
12	1	1.7	0.1
12	2	14.2	15.1
12	3	6.1	-6.6
13	1	10.5	12.2
13	2	3.9	-2.7
13	3	3.2	4.2
1	0	7.6	4.5
2	0	34.6	30.7
3	0	17.4	-12.2
4	0	38.5	35.3
5	0	5.7	5.1
6	0	19.3	19.9

7	0	12.9	12.9
8	0	1.8	-0.6
9	0	8.3	8.1
10	0	6.2	5.1
11	0	1.9	-0.2
12	0	8.2	8.0
13	0	5.4	-5.6
1	-1	29.9	27.1
2	-1	26.8	-21.9
3	-1	49.8	50.3
4	-1	14.6	-10.7
5	-1	19.5	21.1
6	-1	14.5	15.3
7	-1	20.7	18.7
8	-1	10.2	-8.2
9	-1	14.8	15.1
10	-1	8.1	-7.1
11	-1	9.2	10.5
12	-1	1.8	2.5
13	-1	1.6	1.2
1	-2	9.3	4.0
2	-2	42.7	43.3
3	-2	2.0	-2.1
4	-2	25.8	25.0
6	-2	34.3	36.3
7	-2	25.8	-26.4
8	-2	25.2	25.6
9	-2	10.2	-10.6
10	-2	9.3	9.0
11	-2	3.3	4.3
12	-2	8.9	10.1
13	-2	3.4	-2.2
14	-2	5.5	6.7
1	-3	6.0	8.5
2	-3	22.0	15.5
3	-3	26.4	27.7
4	-3	11.0	10.2
5	-3	31.7	30.9
6	-3	15.9	16.6
7	-3	12.8	14.3
8	-3	9.3	11.1
9	-3	6.1	-6.8
10	-3	7.0	7.4
11	-3	17.6	19.4
12	-3	10.9	13.6
13	-3	8.2	11.8
1	-4	14.5	-11.1
2	-4	43.1	43.9
3	-4	28.0	-25.9
4	-4	16.6	17.1
5	-4	14.0	-14.1
6	-4	10.2	11.4
7	-4	7.1	-6.7
8	-4	17.0	20.5
9	-4	24.4	-25.7
10	-4	10.9	11.4
11	-4	16.5	-19.3
12	-4	4.3	5.8
13	-4	1.5	3.0
1	-5	29.1	27.3
2	-5	5.4	-5.8
3	-5	28.8	28.6
4	-5	6.8	9.3
5	-5	7.5	5.8
6	-5	5.2	-4.5
7	-5	18.7	20.0
8	-5	1.9	-1.3
9	-5	21.8	24.6
10	-5	6.6	8.9
11	-5	18.3	22.7
12	-5	4.1	5.3
13	-5	5.9	7.5
1	-6	8.7	-12.1
2	-6	21.2	23.2
3	-6	4.8	-3.7
4	-6	19.6	19.3
5	-6	5.6	7.3
6	-6	19.8	24.1
7	-6	1.9	3.3
8	-6	10.4	11.7
9	-6	1.9	-3.4
10	-6	12.3	14.0
1	-7	10.1	12.6
2	-7	12.6	-14.0
3	-7	13.0	14.8
4	-7	5.4	-5.7
5	-7	10.1	11.6
6	-7	1.9	1.1
7	-7	15.1	20.4
8	-7	1.9	5.9
9	-7	5.1	6.4
10	-7	3.1	5.3
2	-8	9.0	10.7
3	-8	1.9	-1.4
4	-8	8.0	10.5
5	-8	1.9	3.8
6	-8	10.7	16.8
7	-8	1.9	6.0
8	-8	10.4	15.7
9	-8	1.8	1.1

0	-4	25.6	20.9
0	-6	17.0	16.9
		H = 5	
0	1	29.6	-25.0
0	3	17.0	16.2
0	5	14.4	14.3
0	7	11.0	11.1
1	1	1.8	-0.6
1	2	28.0	25.4
1	3	2.2	-0.8
1	4	4.0	-2.4
1	5	2.3	1.3
1	6	13.8	12.6
1	7	2.2	1.2
2	1	3.3	-2.6
2	2	28.5	26.2
2	3	2.7	-0.3
2	4	9.4	-6.8
2	5	12.0	9.5
2	6	2.2	-1.8
2	7	9.7	9.5
3	1	3.4	2.1
3	2	34.1	33.9
3	3	5.5	-4.3
3	4	13.3	12.5
3	5	2.3	-2.3
3	6	12.0	10.9
3	7	1.7	0.4
4	1	24.4	21.6
4	2	3.8	-1.8
4	3	11.5	9.7
4	4	5.7	-4.8
4	5	14.7	15.0
4	6	2.0	-0.4
4	7	6.1	7.1
5	1	12.1	12.0
5	2	29.9	30.9
5	3	2.3	0.5
5	4	18.8	18.3
5	5	10.2	-8.3
5	6	10.3	8.9
5	7	6.3	-6.3
6	1	2.2	0.3
6	2	5.6	-4.6
6	3	20.1	17.7
6	4	6.2	-3.3
6	5	10.5	9.3
6	6	5.3	-4.7
7	1	6.9	-6.0
7	2	17.5	15.4
7	3	2.3	1.6
7	4	6.7	4.7
7	5	3.4	-3.6
7	6	2.7	1.6
8	1	5.7	3.0
8	2	2.3	2.5
8	3	12.9	13.8
8	4	2.1	1.4
8	5	7.2	5.6
9	1	8.9	-6.7
9	2	19.9	18.8
9	3	2.1	-1.8
9	4	7.6	8.1
10	1	15.4	15.5
10	2	2.1	4.9
10	3	12.7	13.7
10	4	3.8	3.6
11	1	2.0	0.2
11	2	7.8	6.7
11	3	3.8	-4.0
12	1	12.6	14.3
1	0	40.0	37.4
2	0	2.1	0.2
3	0	16.8	15.5
4	0	8.8	7.8
5	0	21.9	22.4
6	0	13.5	15.1
7	0	14.1	14.4
8	0	4.0	-1.8
9	0	12.7	10.9
10	0	2.3	0.1
11	0	12.0	11.5
12	0	7.8	-6.1
13	0	5.8	5.1
1	-1	17.9	16.1
2	-1	30.5	31.7
3	-1	1.7	0.8
4	-1	24.7	23.6
5	-1	2.0	0.6
6	-1	10.9	9.7
7	-1	3.8	3.8
8	-1	10.5	10.2
9	-1	2.3	-0.5
10	-1	16.8	16.6
11	-1	2.2	0.1
12	-1	13.3	13.0
13	-1	4.5	-3.0
1	-2	21.9	20.9

2	-2	1.4	-0.4
3	-2	28.8	28.6
4	-2	5.3	-2.8
5	-2	20.4	19.5
6	-2	5.1	4.3
7	-2	10.1	10.6
8	-2	2.3	-3.0
9	-2	9.8	9.5
10	-2	4.9	5.2
11	-2	12.1	11.4
12	-2	3.4	-1.1
13	-2	11.3	11.5
1	-3	7.6	5.3
2	-3	24.0	23.0
3	-3	12.4	-9.6
4	-3	29.6	29.8
5	-3	3.4	4.3
6	-3	13.1	14.1
7	-3	12.7	12.4
8	-3	2.3	-1.4
9	-3	7.0	6.7
10	-3	6.9	6.0
11	-3	2.2	-0.2
12	-3	7.5	7.4
13	-3	4.5	-4.9
1	-4	21.9	20.0
2	-4	15.0	-15.1
3	-4	31.2	33.9
4	-4	7.3	-5.0
5	-4	13.6	13.6
6	-4	11.7	13.6
7	-4	11.6	12.2
8	-4	2.3	-6.0
9	-4	12.7	11.6
10	-4	4.8	-3.1
11	-4	4.6	6.0
12	-4	3.2	2.2
13	-4	1.4	0.5
1	-5	1.8	-0.4
2	-5	27.8	29.7
3	-5	3.3	-2.9
4	-5	18.5	21.1
5	-5	5.8	-5.5
6	-5	21.7	27.9
7	-5	19.0	-21.7
8	-5	15.0	16.2
9	-5	6.9	-8.6
10	-5	6.1	6.0
11	-5	2.1	2.1
12	-5	6.7	8.1
13	-5	4.5	-4.0
1	-6	3.4	3.1
2	-6	9.6	9.9
3	-6	16.1	18.7
4	-6	4.6	4.5
5	-6	19.2	20.4
6	-6	11.2	14.6
7	-6	6.3	7.6
8	-6	7.5	9.3
9	-6	2.8	-4.4
10	-6	4.6	5.1
11	-6	11.4	14.3
12	-6	7.8	10.9
1	-7	7.5	-6.2
2	-7	22.1	26.9
3	-7	14.9	-15.2
4	-7	10.7	11.2
5	-7	7.4	-7.0
6	-7	5.7	5.6
7	-7	4.9	-5.3
8	-7	11.5	13.2
9	-7	13.7	-16.2
10	-7	6.8	6.6
11	-7	9.0	-12.0
1	-8	14.2	14.4
2	-8	2.3	-3.6
3	-8	14.4	15.6
4	-8	2.3	3.5
5	-8	6.9	4.6
6	-8	4.0	-4.3
7	-8	9.6	10.4
8	-8	4.6	-4.3
9	-8	11.3	13.5
10	-8	2.9	5.2
2	-9	10.6	12.3
3	-9	2.3	-2.9
4	-9	10.5	10.6
5	-9	3.9	4.9
6	-9	11.2	14.1
7	-9	2.1	3.2
8	-9	5.6	7.5
9	-9	1.9	-2.6
5	-10	6.1	5.8
6	-10	1.9	0.7
7	-10	8.3	10.8
0	-1	38.0	34.6
0	-3	9.7	8.5
0	-5	32.9	28.8
0	-7	15.4	13.4

Determination and refinement of the structure

As there are only two molecules per unit cell, *e.g.* only two Ni(CN)$_4^{2-}$ ions, the Ni atoms must be in a special position, which is a centre of symmetry for the space group $P2_1/n$. This is in agreement with the measured intensities, since the reflexions of the type $h+k+l=2n$ are much stronger than reflexions of the type $h+k+l=2n+1$. This is particularly noticeable for the Pd and Pt compounds since Pd and Pt have a much greater scattering power than Ni. There are also only two 1,2-bis-(*N*-methyl-4-pyridinium)ethylene ions, which means that there must be a centre of symmetry between the two carbon atoms of the ethylene group.

The positions of all the atoms could be determined from a three-dimensional Patterson synthesis which was calculated by means of the centrosymmetrical Fourier program of P. Gantzel and H. Hope. The Ni atoms were placed at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. From the Patterson synthesis it then followed that the centres of the 1,2-bis-(*N*-methyl-

Table 3. *Atomic parameters with their standard deviations*

	x/a	y/b	z/c	$\sigma(x/a)$	$\sigma(y/b)$	$\sigma(z/c)$	B	σB
Ni	0·5000	0·5000	0·5000				2·96 Å^2	0·05 Å^2
C(1)	0·3988	0·6335	0·4747	0·0011	0·0005	0·0007	2·20	0·12
C(2)	0·2419	0·4475	0·4204	0·0011	0·0005	0·0007	2·06	0·12
C(3)	0·4163	−0·0248	0·4614	0·0011	0·0005	0·0007	2·07	0·12
C(4)	0·2195	0·0283	0·4025	0·0011	0·0005	0·0006	1·67	0·11
C(5)	0·1902	0·1336	0·4098	0·0012	0·0005	0·0007	2·21	0·13
C(6)	0·0014	0·1750	0·3525	0·0012	0·0006	0·0008	2·61	0·14
C(7)	−0·1352	0·0127	0·2750	0·0012	0·0005	0·0007	2·34	0·13
C(8)	0·0536	−0·0348	0·3333	0·0011	0·0005	0·0007	1·96	0·12
C(9)	−0·3628	0·1597	0·2224	0·0013	0·0006	0·0008	2·92	0·15
N(1)	0·3353	0·7170	0·4583	0·0011	0·0005	0·0007	3·12	0·13
N(2)	0·0804	0·4144	0·3658	0·0011	0·0005	0·0007	2·89	0·13
N(3)	−0·1577	0·1135	0·2867	0·0009	0·0004	0·0005	1·82	0·10

4-pyridinium)ethylene ions must be at $0\frac{1}{2}0$ and $\frac{1}{2}0\frac{1}{2}$. The coordinates obtained from the Patterson synthesis were used for the calculation of a three-dimensional Fourier synthesis. More accurate coordinates were obtained from the Fourier synthesis and were used for the refinement of the structure.

The coefficient of the isotropic temperature factors was initially taken as 3·0 Å^2. The structure was refined by means of three full-matrix least-squares cycles using the Fortran program *ORFLS* of Busing, Martin & Levy (1962). In the first cycle in which only the scale factors were refined, R was brought to 20·3%, where $R = \Sigma|F_o - F_c|/\Sigma|F_o|$. In the two further cycles in which the scale factors, the positional and the temperature parameters were refined, R was decreased to 12·9%. It was found that some of the strongest reflexions had F_o values consistently low compared with F_c, and a total of 15 such reflexions were excluded from the refinement. After this another two full-matrix least-squares cycles reduced R to 11·1%. The mean shift/error ratio for the positional and temperature parameters was less than 0·1.

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

The values of F_o and F_c are given in Table 2. The final positional and temperature parameters with their standard deviations are given in Table 3.

Description of the structure and discussion

The dimensions of the $Ni(CN)_4^{2-}$ ion and of the 1,2-bis-(*N*-methyl-4-pyridinium)ethylene ion are given in Figs. 1 and 2, and in Tables 4 and 5. The mean bond lengths in the rings of the latter ion (mean C–C distance = 1·39 Å and mean C–N distance = 1·35 Å) agree well with the bond lengths in pyridine (Palmer, 1967) and with the bond lengths in the dipyridinium ion (Basson, Bok & Leipoldt, 1969). The angles between the bonds joining the atoms in the rings are also approximately the same as in pyridine and in the dipyridinium ion. The bond length between the carbon atoms of the ethylene group, C(3)–C(3′) = 1·35 Å, is slightly greater than that of an ordinary double bond [C–C = 1·33 Å (Pauling, 1960)]. The opposite was found for diphenyl (Pauling, 1960, p. 291) and for the dipyridinium ion (Basson, Bok & Leipoldt, 1969) where the C–C distance between the two rings is slightly shorter than in a normal single bond [1·54 Å, and 1·504 Å when corrected for adjacent bent-bond effect (Pauling, 1960, p. 236)]. The $C(sp^2)$–$C(sp^2)$ single bond length found for C(3)–C(4) in the present structure is 1·48 Å which is slightly less than the latter value given by Pauling quoted above. The deviation from the normal single or double bond distance can be regarded as a result of the conjugated systems present in the compounds mentioned. The C–C=C angle of 122·3° at the ethylene carbon atoms [C(3′)–C(3)–C(4)] agrees with the C–C=C angle in many other unsaturated compounds (Pauling, 1960, p. 138).

Table 4. *Interatomic distances*

Ni —C(1)	1·85 Å	C(6)–N(3)	1·36 Å
Ni —C(2)	1·85	N(3)–C(7)	1·33
Ni —N(1)	3·01	C(7)–C(8)	1·40
Ni —N(2)	3·01	C(8)–C(4)	1·41
C(1)–N(1)	1·16	N(3)–C(9)	1·49
C(2)–N(2)	1·16	N(3)–C(4)	2·74
C(1)–C(2)	2·63	N(3)–N(3′)	9·27
N(1)–N(2)	4·29	N(1)–N(3)	3·84
C(3)–C(3′)	1·35	N(1)–N(3′)	4·00
C(3)–C(4)	1·48	N(2)–N(3)	3·85
C(4)–C(5)	1·39	N(2)–N(3′)	4·21
C(5)–C(6)	1·37	C(9)–C(9′)	12·25
N(1)–N(2) of the next $Ni(CN)_4^{2-}$ ion	4·31 Å		
Ni —Ni of the next $Ni(CN)_4^{2-}$ ion	8·31		
C(8)–C(9) of the next cation	5·02		

On all of the above the estimated standard deviation is 0·01 Å.

The least-squares equation for the best plane through the atoms in the ring of the 1,2-bis-(*N*-methyl-4-pyridinium)ethylene ion and the deviations from the plane are given in Table 6. It follows that the rings are approximately planar as in benzene. Since the ion is centrosymmetric it follows that the rings are coplanar as in the dipyridinium ion for which the equation for the best plane for the atoms of the ring together with their deviations from the plane are given in Table 7. In both ions the largest deviation of the atoms from the plane is too small to be of significance. Since the 1,2-bis-(*N*-methyl-4-pyridinium)ethylene ion is centrosymmetric, the H atoms bound to the ethylene carbon atoms are situated *trans* to one another.

The Ni–C distance (mean 1·85 Å) is in good agreement with the Ni–C separation in $K_2Ni(CN)_4$ (Vannerberg, 1964) and in dipyridiniumnickel cyanide (Basson, Bok & Leipoldt, 1969). The C–N bond length in the cyanide groups (mean 1·16 Å) is the same as in many other complex cyanides, *e.g.* $K_3Co(CN)_6$ (Curry & Runciman, 1959) and also in the $Ni(CN)_4^{2-}$ ion (Vannerberg, 1964; Basson, Bok & Leipoldt, 1969).

The CN groups of the $Ni(CN)_4^{2-}$ ion lie at the corners of a square as is found in all the tetra-coordinated compounds of Ni^{II}, Pd^{II}, and Pt^{II} as a result of the dsp^2 hybridization which occurs. The C(1)–Ni–C(2) angle of 89·5° thus indicates a right angle within the experimental errors. The Ni–C–N bonds form a straight line. The least-squares equation for the best plane defined by Ni, C(1), N(1), C(2), and N(2) of the $Ni(CN)_4^{2-}$ ion of the 1,2-bis-(*N*-methyl-4-pyridinium)-ethylene salt together with their deviations from the plane are given in Table 6, and similarly calculated values for the $Ni(CN)_4^{2-}$ ion of the dipyridinium salt are given in Table 7. In both cases the deviation from the plane is too small to be of significance.

The N–N distance in the 1,2-bis-(*N*-methyl-4-pyridinium)ethylene ion is 9·27 Å, which is thus approximately the distance between the positive charges of the divalent cation. This is thus much greater than in the dipyridinium ion where the N–N distance was found to be 7·05 Å (Basson, Bok & Leipoldt, 1969). The mean distance between two opposite N atoms in the $Ni(CN)_4^{2-}$ ion is 6·03 Å, which is thus nearly the distance between the two positive charges on the dipyridinium ion (difference = 1·02 Å), but which differs appreciably from the distance between the two positive charges on the 1,2-bis-(*N*-methyl-4-pyridinium)ethylene ion (difference = 3·24 Å). As a result the arrangement of the latter ion with respect to the $Ni(CN)_4^{2-}$ ion is quite different from that of the dipyridinium salt. The two positive nitrogen atoms of the 1,2-bis-(*N*-methyl-4-pyridinium)ethylene ion do not have two opposite nitrogen atoms of the same $Ni(CN)_4^{2-}$ ion as nearest neighbours (as was found for the dipyridinium salt) but instead two nitrogen atoms of two separate $Ni(CN)_4^{2-}$ ions, so that a chain structure is obtained made up of alternating 1,2-bis-(*N*-methyl-4-pyridinium)ethylene

Table 5. *Bond angles*

C(1) –Ni —C(2)	89·5 ± 0·4°	C(6) –N(3) –C(7)	121·5 ± 0·7°
C(1) –Ni —C(2′)	90·5 ± 0·4	N(3) –C(7) –C(8)	120·7 ± 0·7
Ni——C(1) –N(1)	180·0 ± 0·7	C(7) –C(8) –C(4)	117·9 ± 0·7
Ni——C(2) –N(2)	180·0 ± 0·7	C(8) –C(4) –C(5)	119·3 ± 0·7
C(3′) –C(3) –C(4)	122·3 ± 0·7	C(8) –C(4) –C(3)	116·3 ± 0·7
C(3) –C(4) –C(5)	124·5 ± 0·7	C(6) –N(3) –C(9)	119·8 ± 0·7
C(4) –C(5) –C(6)	120·0 ± 0·8	C(7) –N(3) –C(9)	119·4 ± 0·7
C(5) –C(6) –N(3)	122·0 ± 0·8		

Table 6. *Equation of the best plane through* (i) *the* 1,2-*bis*-(*N*-*methyl*-4-*pyridinium*)*ethylene ion, and* (ii) *the* $Ni(CN)_4^{2-}$ *ion*

$Ax+By+Cz+D=0$

(i) $A=-0·4971$, $B=-0·1356$, $C=0·8570$, $D=3·1096$.

Individual deviations from the best plane (in Å)

C(3)	0·011	C(4)	0·004	C(5)	0·009	C(6)	0·005
C(7)	0·012	C(8)	0·007	C(9)	0·006	N(3)	0·006

(ii) $A=-0·4454$, $B=-0·0307$, $C=0·8948$, $D=3·2361$.

Individual deviations from the best plane (in Å)

Ni	0·009	C(1)	0·003	C(2)	0·028	N(1)	0·002
N(2)	0·017						

Table 7. *Equation of the best plane through* (i) *the dipyridinium ion, and* (ii) *the* $Ni(CN)_4^{2-}$ *ion*

$Ax+By+Cz+D=0$

(i) $A=0·4019$, $B=0·9093$, $C=-0·1083$, $D=0·5803$.

Individual deviations from the best plane (in Å)

C(3)	0·024	C(4)	0·011	C(5)	0·020	C(6)	0·020
C(7)	0·003	C(8)	0·033	N(3)	0·026		

(ii) $A=-0·4106$, $B=0·9037$, $C=0·1211$, $D=-0·0010$.

Individual deviations from the best plane (in Å)

Ni	0·0010	C(1)	0·0004	C(2)	0·0021	N(1)	0·0003
N(2)	0·0013						

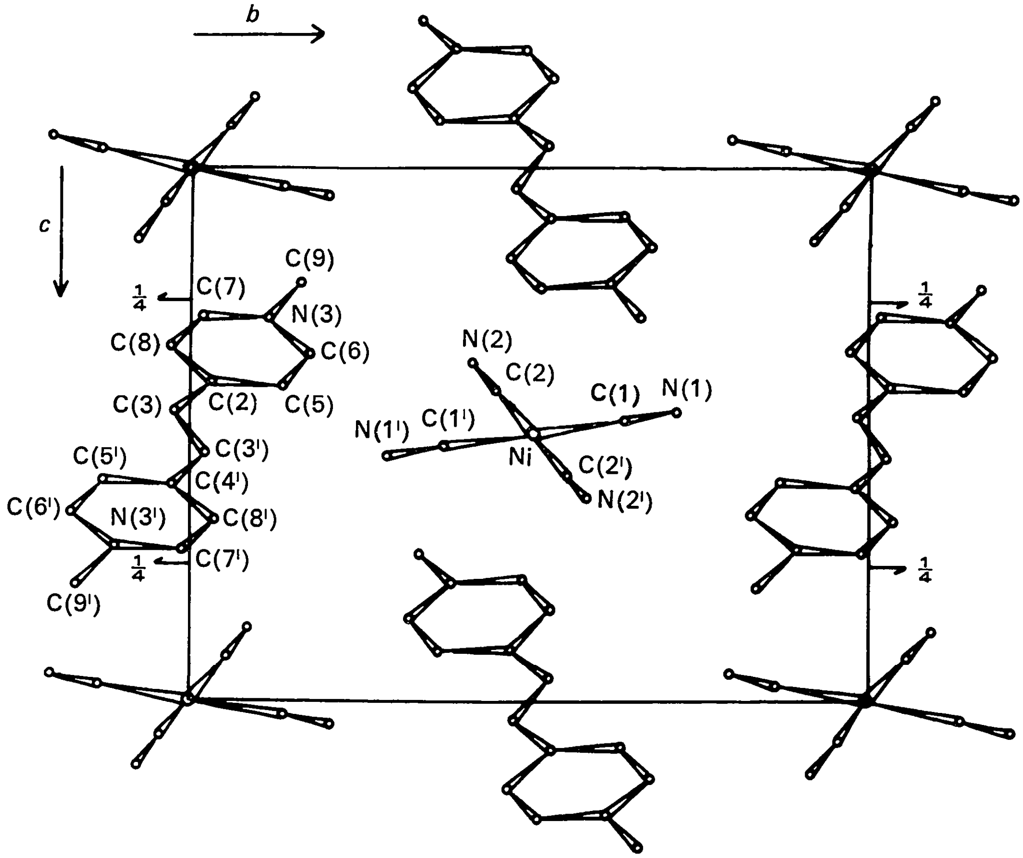

Fig. 3. Projection of the structure along the *a* axis.

ons and $Ni(CN)_4^{2-}$ ions. Fig. 3 gives a sketch of the structure in the direction of the *a* axis. The carbon atoms of the methyl group bound to the pyridine nitrogen atom, C(9), and the carbon atoms of the ethylene group, C(3), which are between the two rings, lie in the same plane as the atoms in the pyridine ring as is shown in Table 6.

It was found that the negative nitrogen atoms of the cyanide group tend to take up a position closer to the nitrogen atoms of the pyridine rings than to the centre of the ion. This was also found for the dipyridinium salt. This is in agreement with the results obtained in the study of the pyridinium ion in solution with the aid of nuclear magnetic resonance which 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).

All the calculations were carried out on an IBM 360 computer.

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