ACTA CHEMICA SCANDINAVICA 18 (1964) 2385–2391

The Crystal Structure of $K_2Ni(CN)_4$

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The crystal structure of $K_2Ni(CN)_4$ has been determined. The elementary cell is monoclinic with $a = 4.294$ Å, $b = 7.680$ Å, $c = 13.03$ Å and $\beta = 87° 16'$. The space group is $P2_1/c$ No. 14. The structure consists of isolated potassium ions and square planar tetracyano nickelate ions.

Crystal structures of mononuclear nickel(II)cyanide complexes have previously been determined by Brasseur and Rassenfosse,[1,2] [$Na_2Ni(CN)_4 \cdot 3H_2O$, $BaNi(CN)_4 \cdot 4H_2O$] and by Lambot[3] [$SrNi(CN)_4 \cdot 5H_2O$]. The structures of the water free compounds have not been determined. The potassium compound $K_2Ni(CN)_4$ has been investigated by magnetic and spectrographic methods but not by X-ray methods.

EXPERIMENTAL

Potassium tetracyanonickelate(II) was prepared according to a method given by Fernelius and Burbage.[4] Nickel cyanide was precipitated from a nickel salt solution by the calculated amount of potassium cyanide. The grayish-green precipitate was washed carefully and eventually dissolved in a solution of potassium cyanide. From this solution potassium tetracyanonickelate(II)-1-water crystallized in orange-red monoclinic crystals. The water of crystallisation was removed by heating the crystals to 110°C. The crystals were orange yellow monoclinic and of suitable quality.

Crystallographic data

The X-ray data were obtained from Weissenberg and powder diffraction photographs. A well developed single crystal was rotated about its crystallographic a-axis and the zones detectable with Cu$K\alpha$ radiation were registered. Multiple film technique was used. The intensities were estimated visually by comparison with known scales. It was found necessary to apply a correction for the varying size of the spots.

With the aid of the elementary cell dimensions obtained from the single crystal data, the powder diffraction pattern could be indexed (Table 1). From the powder pattern the following cell dimensions were obtained

$$a = 4.294 \pm 0.004 \text{ Å}$$
$$b = 7.680 \pm 0.008 \text{ Å}$$
$$c = 13.03 \pm 0.01 \text{ Å}$$
$$\beta = 87° 16' \pm 10'$$

Table 1. Powder diffraction data for $K_2Ni(CN)_4$, $CuK\alpha$-radiation.

h	k	l	$\sin^2\Theta_o \times 10^4$	$\sin^2\Theta_c \times 10^4$	I_o
0	1	1	136	136	m
0	0	2		140	
0	1	2	241	241	w
1	0	0	327	323	m
0	2	0	403	403	m
0	1	3	418	417	st
1	0	2	446	443	m
$\bar{1}$	1	1	468	469	vst
$\bar{1}$	0	2	480	483	m
1	1	2	546	544	w
$\bar{1}$	1	2	585	584	vw
0	1	4	662	661	m
1	1	3	708	710	vw
0	2	3	717	719	vvw
$\bar{1}$	1	3	767	770	w
1	2	2	844	846	st
$\bar{1}$	2	2	888	886	msv
1	0	4	923	924	m
0	2	4	962	963	vvw
0	1	5	972	978	vw
1	2	3	1008	1012	w
0	3	2	1045	1047	w
$\bar{1}$	2	3	1072	1072	w
0	3	3	1218	1223	m
0	0	6	1265	1262	m
$\bar{1}$	3	1	1272	1275	w
$\bar{1}$	2	4	1324	1327	w
2	1	1		1408	
2	1	0	1403	1393	w
2	0	2		1392	
$\bar{2}$	1	1	1442	1448	vw
$\bar{2}$	0	2	1468	1472	vw
$\bar{2}$	1	2	1573	1573	vw
1	3	3		1576	
0	4	0	1613	1612	vvw
$\bar{2}$	1	3	1651	1649	w
1	0	6		1645	
2	1	3	1763	1768	w
2	2	2	1792	1794	vw
0	3	5		1784	
$\bar{2}$	2	2	1872	1875	w
2	1	4		1874	
1	2	6	1928	1928	w
$\bar{2}$	0	4		1933	
$\bar{2}$	1	4	2030	2034	w
2	1	5		2170	
2	2	4	2174	2176	w
0	3	6		2169	
$\bar{1}$	1	7	2213	2212	w
2	0	6	2430	2434	vvw
1	3	6		2432	
2	3	3	2464	2455	w
2	2	5		2472	
2	1	6	2536	2535	vw
1	4	4		2536	
0	3	7	2635	2625	vw
0	5	2	2659	2659	vvw
2	2	6		2838	w
$\bar{2}$	3	4	2843	2839	
0	5	1	2869	2867	w
0	4	6		2874	

The systematic extinctions were $h0l$, absent when $l = 2n + 1$, and $0k0$ absent when $k = 2n + 1$, thus the space group must be $P2_1/c$, No. 14. There are two formula units in the elementary cell.

The structure determination

From a three-dimensional Patterson synthesis the positions of the nickel and potassium atoms were found. A Fourier synthesis based on the signs calculated from the nickel and potassium parameters revealed the positions of all atoms. The unreliability index R became 0.24. After a difference synthesis the R-factor dropped to 0.15. An isotropic temperature factor $B = 1.7$ Å^2 was used for all atoms. The structure was not refined by least square analysis as this was thought to overtask the intensity material.

The final parameters can be found in Table 3; a comparison of observed and calculated structure factors in Table 2. The standard deviations were calculated with Chruickshank's [5] method.

Table 2. Observed and calculated structure factors for $K_2Ni(CN)_4$.

h	*k*	*l*	F_o	F_c
0	0	2	15.3	+ 21.0
		4	10.7	−10.8
		6	26.7	+ 17.9
		12	9.1	+ 12.8
0	1	1	12.9	+ 13.0
		2	11.2	+ 9.5
		3	38.9	+ 44.5
		4	27.5	−25.3
		5	11.1	+ 11.6
		6	7.0	− 7.2
		8	4.8	+ 6.7
		9	20.1	+ 19.3
		11	6.6	+ 6.1
0	2	0	29.6	+ 27.0
		1	2.7	+ 0.7
		2	7.6	+ 8.5
		3	10.1	+ 8.4
		4	5.2	+ 7.5
		5	6.5	+ 6.2
		6	23.9	+ 26.4
		7	8.1	− 9.0
		8	13.7	+ 13.9
		9	5.7	− 5.8
		10	3.4	+ 2.3
		11	4.7	+ 4.6
		12	6.1	+ 8.0
		14	3.0	+ 3.9
0	3	1	5.5	+ 6.3
		2	19.2	+ 17.5
		3	34.6	+ 33.2
		4	3.1	− 3.1
		5	6.3	+ 5.5
		6	3.7	− 3.9
		7	2.6	+ 1.3
		8	5.5	+ 6.6
		9	12.4	+ 14.8
		11	4.7	+ 6.0
0	4	0	21.2	+ 16.4
		1	24.5	−17.8
		2	9.8	+ 8.3
		4	11.5	+ 11.5
		5	14.3	+ 14.9
		6	16.7	+ 17.1
		7	4.7	− 6.8
		8	4.5	+ 4.7
		11	4.6	+ 6.0
		12	4.0	+ 5.1
		13	2.6	− 3.3
		14	2.2	+ 3.4
0	5	1	10.8	+ 10.4
		2	11.9	+ 12.0
		3	10.2	+ 9.9
		4	6.6	− 6.8
		5	11.7	+ 11.7
		6	2.5	− 2.0
		7	3.5	+ 5.5
		8	4.6	+ 6.2
		10	2.6	− 4.2
		11	2.4	+ 3.2
		12	2.2	− 2.4
0	6	0	8.9	+ 8.9
		1	8.1	− 8.0
		2	8.2	+ 8.7
		3	4.6	− 5.2
		4	4.3	+ 6.8
		5	4.0	+ 4.6
		6	3.6	+ 3.5
		8	2.4	+ 3.3
		9	2.3	− 2.2
		10	2.9	+ 4.1
		11	1.9	+ 2.8
		12	1.5	+ 2.8
0	7	1	4.3	+ 4.6
		2	3.9	+ 3.7
		3	2.4	+ 2.6
		4	5.9	− 6.8
		5	4.2	+ 4.9
		7	4.1	+ 6.4
		8	3.9	+ 5.1
		9	2.9	+ 3.2
		11	1.9	+ 1.8
0	8	1	3.8	− 3.0
		2	5.0	+ 5.2
		4	3.9	+ 4.8
		5	4.5	+ 4.5
		8	2.7	+ 3.9
0	9	1	7.1	+ 5.7
		2	1.8	+ 1.3
		5	2.1	+ 1.7
1	0	14	9.3	+ 7.8
		12	5.9	− 0.8
		10	10.2	+ 8.9
		8	31.1	+ 25.3
		4	6.2	− 6.0
		2	23.3	+ 23.7
		$\bar{2}$	27.6	+ 30.1
		$\bar{4}$	42.6	+ 42.0
		$\bar{6}$	19.5	+ 16.1
		$\bar{8}$	6.9	− 3.7
		$\overline{10}$	13.5	+ 10.6
		$\overline{12}$	9.8	+ 8.6
1	1	11	14.4	+ 14.2
		10	7.8	+ 4.6
		5	37.4	+ 34.6
		3	10.0	+ 9.9
		2	14.7	−10.1
		0	10.8	− 9.5
		$\bar{1}$	47.7	+ 54.7
		$\bar{2}$	12.1	−11.0
		$\bar{3}$	19.4	+ 16.6
		$\bar{5}$	8.6	− 6.6
		$\bar{6}$	8.6	+ 8.2

h	k	l	F_o	F_c
		$\bar{7}$	24.4	−23.9
		$\bar{8}$	7.2	+ 5.2
		$\bar{9}$	14.2	+ 13.6
		$\bar{13}$	7.4	+ 7.6
1	2	14	5.5	+ 7.7
		8	19.5	+ 23.2
		6	9.5	+ 10.2
		5	6.4	− 6.7
		4	4.8	+ 6.1
		3	20.3	−17.6
		2	37.4	+ 46.4
		1	24.9	+ 21.7
		0	11.4	+ 12.1
		$\bar{1}$	13.6	+ 13.1
		$\bar{2}$	14.9	−10.4
		$\bar{3}$	22.2	−20.5
		$\bar{4}$	26.4	+ 27.5
		$\bar{6}$	9.1	+ 10.2
		$\bar{7}$	4.9	+ 5.6
		$\bar{10}$	13.7	+ 17.1
		$\bar{12}$	7.0	+ 8.7
1	3	12	4.8	− 5.0
		10	5.1	+ 6.5
		9	4.8	+ 6.0
		7	8.5	+ 10.8
		6	11.7	−13.7
		5	22.3	+ 19.9
		4	12.7	+ 11.7
		3	7.7	+ 8.7
		2	13.6	+ 11.1
		1	6.9	+ 6.7
		0	14.7	−13.0
		$\bar{1}$	23.8	+ 19.1
		$\bar{2}$	11.9	+ 10.1
		$\bar{3}$	16.2	+ 17.0
		$\bar{5}$	6.8	+ 8.4
		$\bar{6}$	12.2	−13.9
		$\bar{7}$	11.5	+ 13.9
		$\bar{8}$	5.0	+ 4.6
		$\bar{9}$	8.3	+ 7.6
		$\bar{13}$	4.3	+ 6.3
1	4	14	4.0	+ 5.5
		13	2.6	+ 2.5
		8	8.5	+ 6.8
		7	8.4	+ 8.7
		6	2.7	+ 4.8
		4	12.8	+ 12.2
		3	5.8	− 5.7
		2	25.6	+ 21.6
		1	9.4	+ 8.2
		0	10.2	+ 10.4
		$\bar{3}$	10.4	−10.2
		$\bar{4}$	15.5	+ 14.4
		$\bar{5}$	3.8	+ 3.3
		$\bar{6}$	11.4	+ 13.0
		$\bar{7}$	3.0	+ 5.9
		$\bar{8}$	4.3	+ 5.6
		$\bar{9}$	4.6	− 6.5
		$\bar{10}$	3.1	+ 6.2
1	5	11	3.9	+ 6.3
		6	8.1	− 9.7
		5	11.2	+ 10.7
		4	9.1	+ 7.7
		3	11.6	+ 11.0
		1	7.7	+ 7.3
		0	12.6	−10.9
		$\bar{1}$	14.4	+ 14.2
		$\bar{2}$	9.5	+ 9.3
		$\bar{3}$	9.4	+ 9.2
		$\bar{4}$	5.5	+ 5.9
		$\bar{5}$	6.2	+ 8.0
		$\bar{6}$	9.3	−11.2
		$\bar{7}$	8.7	+ 11.9
		$\bar{9}$	4.2	+ 4.7
1	6	10	4.3	+ 5.6
		9	3.9	− 5.6
		8	4.5	+ 4.6
		7	7.1	+ 8.0
		6	5.1	+ 6.4
		5	3.0	+ 3.1
		4	6.6	+ 7.1
		3	13.8	−12.8
		2	5.5	+ 3.6
		1	4.5	+ 3.4
		0	7.7	+ 9.4
		$\bar{2}$	10.5	+ 11.1
		$\bar{3}$	9.8	− 9.7
		$\bar{4}$	6.0	+ 7.4
		$\bar{5}$	6.6	+ 7.6
		$\bar{6}$	6.6	+ 6.9
		$\bar{7}$	4.2	+ 5.3
		$\bar{9}$	2.8	− 6.5
1	7	9	3.7	+ 4.4
		7	6.5	+ 7.5
		4	5.5.	+ 5.5
		3	6.6	+ 7.8
		1	7.4	+ 10.1
		0	8.1	− 8.7
		$\bar{3}$	5.1	+ 3.8
		$\bar{4}$	5.5	+ 4.7
		$\bar{5}$	4.5	+ 6.2
		$\bar{6}$	4.0	− 3.0
		$\bar{9}$	3.9	+ 4.8
1	8	6	3.5	− 5.9
		0	4.5	+ 5.5
		$\bar{2}$	6.5	+ 6.5
		$\bar{3}$	4.1	− 2.6
1	9	$\bar{1}$	4.8	+ 4.8
		$\bar{3}$	4.5	+ 4.9
		$\bar{5}$	3.9	+ 5.4
2	0	10	21.6	+ 17.4
		8	13.4	+ 12.0
		4	30.5	+ 31.5
		2	3.2	+ 6.8
		$\bar{2}$	32.3	+ 35.4
		$\bar{4}$	28.4	+ 27.7

h	*k*	*l*	F_o	F_c
		$\bar{7}$	23.0	+ 20.1
		$\overline{10}$	15.2	+ 13.5
2	1	7	27.6	+ 23.1
		5	9.3	+ 9.0
		4	10.1	+ 8.9
		3	5.5	− 3.3
		2	11.7	− 8.2
		1	32.0	+ 28.8
		0	8.0	+ 3.1
		$\bar{1}$	22.5	+ 22.7
		$\bar{4}$	17.1	− 18.4
		$\bar{5}$	18.8	+ 20.0
		$\bar{7}$	12.0	+ 12.9
		$\bar{8}$	10.0	+ 8.8
		$\overline{11}$	11.6	+ 11.0
		$\overline{31}$	10.8	+ 11.9
2	2	10	13.5	+ 13.9
		9	9.8	+ 10.2
		6	6.1	+ 5.0
		5	10.2	− 9.4
		4	26.5	+ 24.6
		2	16.9	+ 16.9
		0	7.7	+ 9.4
		$\bar{2}$	20.9	+ 22.9
		$\bar{3}$	6.7	+ 3.4
		$\bar{4}$	10.5	+ 13.4
		$\bar{7}$	7.2	− 5.2
		$\bar{8}$	8.9	+ 9.1
		$\overline{10}$	10.1	+ 11.8
2	3	13	4.2	+ 6.7
		8	6.8	− 6.8
		7	16.4	+ 19.2
		6	4.3	+ 4.1
		5	15.1	+ 15.8
		2	10.5	− 8.8
		1	26.5	+ 24.0
		0	11.1	+ 9.4
		$\bar{1}$	11.4	+ 11.1
		$\bar{2}$	10.3	+ 9.9
		$\bar{3}$	6.3	+ 4.9
		$\bar{4}$	8.0	− 8.9
		$\bar{5}$	14.0	+ 15.2
		$\bar{7}$	8.7	+ 15.2
		$\bar{8}$	4.9	+ 6.1
2	4	12	5.4	+ 5.4
		11	5.9	− 8.1
		10	7.9	+ 12.1
		5	12.7	− 14.6
		4	13.8	+ 13.0
		3	10.9	+ 9.0
		2	16.3	+ 14.2
		1	15.3	+ 14.3
		0	6.6	+ 7.2
		$\bar{1}$	14.2	− 14.0
		$\bar{2}$	12.8	+ 14.6
		$\bar{3}$	5.4	+ 3.3
		$\bar{4}$	7.9	+ 10.2
		$\bar{5}$	6.8	+ 9.3
		$\bar{7}$	7.4	− 10.7
		$\bar{8}$	6.8	+ 11.5
		$\overline{10}$	4.2	+ 7.6
		$\overline{11}$	3.8	+ 5.9
2	5	13	4.3	+ 5.3
		11	3.8	+ 6.2
		10	4.1	+ 2.1
		9	7.1	+ 8.5
		8	6.8	− 6.7
		7	6.8	+ 4.8
		6	6.8	+ 6.9
		4	4.3	+ 4.2
		3	8.4	+ 9.6
		2	14.7	− 14.4
		1	12.3	+ 10.0
		0	4.1	+ 2.4
		$\bar{1}$	8.1	+ 8.5
		$\bar{2}$	7.5	+ 8.9
		$\bar{3}$	7.8	+ 9.5
		$\bar{4}$	7.3	− 7.1
		$\bar{5}$	6.2	+ 8.1
		$\bar{7}$	7.5	+ 10.0
		$\bar{8}$	4.3	+ 5.3
		$\bar{9}$	4.2	+ 7.5
		$\overline{10}$	3.8	− 6.8
2	6	6	7.2	+ 8.3
		4	7.9	+ 7.4
		3	7.9	+ 6.3
		2	7.2	+ 7.3
		1	4.3	+ 1.5
		0	6.1	+ 6.1
		$\bar{1}$	11.4	− 11.4
		$\bar{2}$	6.1	+ 5.0
		$\bar{3}$	6.4	+ 7.2
		$\bar{4}$	6.0	+ 6.1
		$\bar{5}$	5.9	+ 9.0
		$\bar{7}$	4.1	− 3.8
		$\bar{8}$	3.7	+ 6.5
		$\overline{10}$	3.1	+ 3.3
2	7	8	5.5	− 6.9
		7	3.7	+ 2.8
		6	5.4	+ 4.1
		5	6.2	+ 7.0
		4	6.3	+ 6.4
		3	7.6	+ 8.4
		2	7.6	− 6.5
		1	6.5	+ 6.0
		$\bar{1}$	7.1	+ 7.9
		$\bar{2}$	4.2	+ 3.1
		$\bar{3}$	6.3	+ 7.8
		$\bar{4}$	6.2	− 7.5
2	8	6	7.1	+ 8.3
		5	6.0	− 5.3
		0	6.6	+ 10.1
		$\bar{6}$	4.5	+ 7.6

Table 3. Fractional atomic parameters for $K_2Ni(CN)_4$.

Atom	Position	x	y	z
Ni	a	0	0	0
K	e	0.281	0.046	0.341
C_1	e	0.167	0.207	0.055
C_2	e	0.849	0.382	0.390
N_1	e	0.261	0.338	0.082
N_2	e	0.764	0.300	0.327

Table 4. Bond distances in $K_2Ni(CN)_4$.

Ni(1)$-C_1$(1)	1.90 ± 0.03 Å
Ni(1)$-C_2$(4)	1.84 ± 0.03
Ni(3)$-C_2$(5)	3.96 ± 0.03
Ni(1)$-C_1$(5)	3.95 ± 0.03
Ni(1)$-$Ni(5)	4.294
$C_1(1)-N_1(1)$	1.15 ± 0.05
$C_2(1)-N_2(1)$	1.11 ± 0.05
K(3) $-N_1$(1)	2.96 ± 0.04
K(3) $-N_1$(5)	2.76 ± 0.04
K(3) $-N_2$(1)	2.91 ± 0.04
K(1) $-N_2$(1)	2.85 ± 0.04
K(3) $-N_2$(3)	2.87 ± 0.04
K(1) $-N_1$(4)	3.26 ± 0.04

A_1(1) denotes atom A_1 in position x, y, z
A_1(2) » » » » » x, y, z
A_1(3) » » » » » $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$
A_1(4) » » » » » $x, \frac{1}{2}-y, \frac{1}{2}+z$
A_1(5) » » » » » $1+x, y, z$

Table 5. Bond angles in $K_2Ni(CN)_4$.

Ni(1)$-C_1(1)-N_1$(1)	175 ± 6°
Ni(1)$-C_2(4)-N_2$(4)	175 ± 6°
C_2(4)$-$Ni(1)$-C_1$(1)	88 ± 3°
C_2(4)$-$Ni(1)$-C_1$(2)	92 ± 3°
C_1(1)$-$Ni(1)$-C_1$(2)	180°
C_2(4)$-$Ni(1)$-C_2$(3)	180°

DESCRIPTION OF THE STRUCTURE

The nickel atoms are surrounded by four cyanide groups situated in the same plane. Within the limits of error the coordination is square planar. The tetracyanonickelate ions are then packed in such a way that the nickel atoms have four carbon atoms at distances about 3.95 Å. These carbon atoms belong to complex ions situated in the neighbouring elementary cells in the a-axis direction. The distance between two adjacent nickel atoms is 4.294 Å (the length of the a-axis). A potassium ion is surrounded by six nitrogen atoms which form an octahedron. Bond distances can be found in Table 4, bond angles in Table 5.

Each complex ion has six potassium ions as nearest neighbours. These six atoms form a distorted octahedron. Two of the faces of this octahedron are parallel to the (100) plane. Each potassium ion has three complex ions as nearest neighbours. The coordination is accordingly similar to that in the rutile structure.

DISCUSSION

The structure is built up of potassium ions and isolated tetracyanonickelate ions. The distances between a nickel atom and the non-metallic atoms in the other complex ions are too large to allow anything but weak van der Waals bonds. The distance between two nickel atoms in adjacent complex ions, 4.294 Å, is much longer than the 3.245 Å found in crystalline nickel dimethylglyoxime where there can be weak nickel-nickel interactions. The average bond distances nickel-carbon, 1.86 Å, and carbon-nitrogen 1.13 Å, are in good agreement with those found in $SrNi(CN)_4 \cdot 5H_2O$,[3] 1.85 Å and 1.18 Å, respectively, but deviate appreciably from those found in $Na_2Ni(CN)_4 \cdot 3H_2O$,[2] 1.95 Å and 1.30 Å, respectively.

Acknowledgements. I thank Mrs. Margareta Biéth for her skilful assistance.

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Received September 5, 1964.