

The Crystal Structure of Calcium Tetracyanonickelate(II) Pentahydrate

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The crystal structure of calcium tetracyanonickelate(II) pentahydrate has been solved from Patterson and heavy-atom Fourier syntheses, and refined by full-matrix least squares methods using three-dimensional photographic X-ray diffraction data. The final R factor is 0.073.

The crystals are orthorhombic, space group $Pcab$, with $a=17.185 \pm 0.007$ Å, $b=18.859 \pm 0.008$ Å, $c=6.774 \pm 0.005$ Å, and with eight units of $\text{CaNi}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$ in the cell.

Although the coordination of the nickel ions is approximately square planar and the Ni—C—N atoms are approximately colinear, there are significant deviations, probably imposed by crystal packing effects, from these ideals. The $\text{Ni}(\text{CN})_4^{2-}$ ions form stacked columns along the c axis. The ions in any one stack are approximately parallel to each other, but the normals to the planes of ions in adjacent stacks make angles of $\pm 6^\circ 10'$ with the c axis. The nickel-nickel distances are 3.387 ± 0.003 Å. The lines joining the Ni—C—N atoms in each $\text{Ni}(\text{CN})_4^{2-}$ ion are rotated with respect to the corresponding lines in neighbouring ions of a stack by $26^\circ 56'$ (mean value). Each calcium ion has eight nearest neighbours, six water oxygen atoms, two of which are shared, and two cyano-nitrogen atoms, arranged in a distorted square Archimedean antiprism.

$\text{CaPd}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$ and $\text{CaPt}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$ are isomorphous with the nickel analogue.

Investigations of the crystallographic properties of tetracyano compounds of nickel(II), palladium(II) and platinum(II) with a variety of cations were made by Brasseur, de Rassenfosse and collaborators over the period 1933 to 1943.¹⁻⁸ These were extended much later with two further crystal structure analyses by Fontaine^{9,10} and Vannerberg.¹¹ More recently, interest in the structural details of these compounds has been renewed in this laboratory during a programme of research on the measurement and interpretation of

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the single crystal polarized spectra of square planar transition metal compounds. As part of this, Ballhausen, Bjerrum, Dingle, Eriks and Hare,¹² in experiments on the absorption spectra of several tetracyanonickelate(II) crystals, observed a band at $22\,500\text{ cm}^{-1}$ which was apparently unique to the barium salt only. Subsequent experiments¹³ suggested that this was due to a magnetic dipole transition and that its appearance arose from some unique feature of the crystal structure of this material. To discover this feature, then, the existing crystallographic data have been re-examined, in some cases re-measured, and extended with further observations. The earlier work indicates that, although the compounds with monovalent cations are isomorphous, the packing of those with divalent cations is apparently critically dependent upon the nature of the cations. Structure analyses of the sodium (and, hence, the potassium, rubidium, ammonium, and lithium), strontium, and barium salts, all in hydrated form, had been made,^{7,8,5,6} but the accuracies of these were limited so that re-determinations were necessary, the first of these being for the barium salt.¹⁴

The crystal structure analysis of calcium tetracyanonickelate(II) pentahydrate, $\text{CaNi}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$, is the subject of this communication. A single projection each of the structures of $\text{CaPd}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$ and $\text{CaPt}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$, both isomorphous with $\text{CaNi}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$, was studied by Fontaine.⁹ However, the analysis of $\text{CaNi}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$ described below and also a low accuracy investigation extending the original analyses¹⁰ have shown that the atomic parameters originally published are incorrect due to an origin indeterminacy in the projection.

EXPERIMENTAL SECTION

Pale yellow, single crystals of $\text{CaNi}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$ grow from slowly-evaporating aqueous solution as large, very elongated, well-formed, rectangular prisms or thick plates. When viewed perpendicular to the prism faces in polarized light, the crystals are yellow and nearly colourless when the electric vector is parallel and perpendicular, respectively, to the elongation direction. Under crossed Nicol prisms there is sharp, parallel extinction in these faces.

Preliminary oscillation and Weissenberg photographs showed that the crystals are orthorhombic, the space group being uniquely determined from the systematically absent reflections. The unit cell dimensions (see Crystal Data) were measured from zero layer Weissenberg photographs, taken about the b and c crystallographic axes, each calibrated with a superimposed copper powder diffraction pattern. The crystal density was determined by flotation in a mixture of ethylene dibromide and bromobenzene.

Three-dimensional, multiple-film and multiple-exposure equi-inclination Weissenberg photographic diffraction data were collected for layers 0 to 6, inclusive, with rotation axis c and 0 to 5, inclusive, with rotation axis b , using $\text{CuK}\alpha$ radiation. Their intensities were measured visually by comparison with a standard scale, corrections for variation in spot shape and size being estimated empirically. Lorentz, polarization and Tunell factors were applied, after which inter-film, inter-layer and inter-axis scale factors were calculated using the least squares method of Hamilton, Rollett and Sparks,¹⁵ and applied. No absorption corrections were made, the maximum dimension of the three approximately cubic crystals used in the data collection having been 0.15 mm. Thus, the data were reduced to a set of 2085 independent, non-zero, structure amplitudes. These data were used in the structure analysis. 522 independent reflections had been observed on data from both axes. A measure of the agreement of the individual observations of these common reflections, defined as

$$R_{cb} = 2\sum||F_c| - |F_b|| / \sum(|F_c| + |F_b|)$$

where $|F_c|$ and $|F_b|$ are the scaled structure amplitudes for reflections with common indices recorded on data photographed about the c and b axes, respectively, was calculated to be 0.067.

All the computations described were performed on an IBM 7090 computer using modifications of programmes written by Hamilton, Rollett and Sparks¹⁵ (data reduction and scaling), Sly, Shoemaker and van den Hende¹⁶ (Patterson, electron density and difference electron density maps), Busing, Martin and Levy^{17,18} (full matrix least squares refinement and molecular geometry) and Watson¹⁹ (data and weighting scheme analyses). In the calculation of structure factors from postulated structural parameters, the following X-ray atomic scattering factors were used: Watson and Freeman²⁰ for Ni⁺, Freeman²¹ for Ca²⁺, Hoerni and Ibers²² for O, N, and C. The Ni⁺ and Ca²⁺ scattering factors were corrected for the real part of the anomalous dispersion effect.²³

CRYSTAL DATA

Calcium tetracyanonickelate(II) pentahydrate; $\text{CaNi}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$; $M=292.94$. Orthorhombic, $a=17.185 \pm 0.007$ Å, $b=18.859 \pm 0.008$ Å, $c=6.774 \pm 0.005$ Å, $U=2195 \pm 3$ Å³. $D_m=1.774 \pm 0.008$ g·cm⁻³, $Z=8$, $D_c=1.771 \pm 0.004$ g·cm⁻³. Linear absorption coefficient for X-rays [$\lambda(\text{CuK}\alpha)=1.5418$ Å], $\mu=65$ cm⁻¹.²⁴ Number of electrons per unit cell, $F(000)=1520$. Systematically absent reflections: $-hk0$ when k odd, $h0l$ when h odd, $0kl$ when l odd; space group $Pcab$ (D_{2h}^{15} , No. 61).²⁵ Developed faces on all crystals studied were $\{110\}$ and $\{001\}$. Elongation direction parallel to c .

STRUCTURE DETERMINATION²⁶

The characteristic feature of the three-dimensional Patterson map computed from the scaled observed data is that all the large peaks, which were assumed to correspond to Ni—Ni, Ni—Ca, and Ca—Ca vectors, are on, or are within 0.7 Å of, the mirror planes perpendicular to c at $z/c=0, 1/2, 1$, etc. Thus, it was concluded that the Ni and Ca ions lie very nearly in the same planes which are almost perpendicular to c and are separated by $c/2$. Analysis of the Harker sections and lines, although complicated by this high peak density and the difficulty of resolving single-weight Ni—Ni vectors and double weight Ni—Ca vectors, provided four possible solutions for the Ca and Ni coordinates. Two of these, although apparently less likely because the expected Ca—Ca peaks are very low, correspond in x/a and y/b parameters with the initial solution,⁹ subsequently revised,¹⁰ given by Fontaine for the Ca and Pd (and Pt) ions in the 001 projection of the structures of the compounds $\text{CaPd}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$ and $\text{CaPt}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$, which are isomorphous with $\text{CaNi}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$.

The Ni—C and Ni—N vectors were clearly seen and identified as two pairs of peaks, corresponding to approximately linear Ni—C—N atoms, near the Patterson origin and again very nearly in the ab plane, but since there is a two-fold ambiguity in the C and N real space coordinates (x/a for Ni is 0.250), neither their contributions nor those of the water molecules, for which no search was made, were included in the initial structure factor calculations based on each of the above Ca and Ni solutions. The structure factors based on the solutions agreeing with Fontaine⁹ were computed first and were used

to calculate three-dimensional, heavy-atom-phased electron density maps. These are very similar, differing only in the z/c coordinates of the peaks, but these peaks are of irregular height in positions corresponding to the superposition of several apparently feasible structures. There are several spurious peaks and hollows. Since Fontaine's solution⁹ was at this time assumed basically correct, structure factors for trial postulates based on various combinations of coordinates of calcium and tetracyanonickelate(II) ions were computed. None of the trials produced the anticipated agreement with the observed data, the lowest R factor²⁷ being 0.51.

Structure factor contributions from the Ni and Ca ions with coordinates of the third solution were computed and a heavy-atom electron density map plotted. Here the peaks are very distinct and an unambiguous solution for all fifteen non-hydrogen atoms was immediately found. The highest remaining peak on this map, apart from diffraction ripple near the heavy atoms, is only $0.8 \text{ e}/\text{\AA}^3$. The correctness of the solution was demonstrated when a structure factor calculation, with all atoms included with individual isotropic thermal parameters postulated by comparison with other, similar structures, gave an R factor of 0.24.

REFINEMENT

Two rounds of full matrix least squares refinement, minimizing $\sum \omega (|F_o| - G|F_c|)^2$, where ω is the weight accorded each observation and G is a variable overall scaling factor, with individual atomic isotropic temperature factors and positions varied, and with equal weights for all data, reduced R to 0.131. At this stage, an analysis to find a suitable data weighting function was made by plotting $\langle 1/||F_o| - |F_c||^2 \rangle$ against $\langle |F_o| \rangle$ for the data arranged in twenty groups of increasing $|F_o|$. As has been pointed out,^{27,28} when there are no systematic errors, the resulting graph should indicate the appropriate variation of ω with $|F_o|$. A function of the type

$$\begin{aligned} \omega &= 1 \text{ for } |F_o| < F^* \\ \omega &= (F^*/|F_o|)^2 \text{ for } |F_o| \geq F^* \end{aligned}$$

where $F^* = 18.75$ electrons, gave reasonable agreement, except possibly at very low $|F_o|$, with the plotted curve, and this weighting scheme was used in the next stage of the refinement.

All the main features of a difference Fourier synthesis also computed at this point indicated vibrational anisotropies of the postulated atoms, so refinement continued with a further two cycles of full matrix least squares computation including parameters for these effects. The R factor dropped to 0.110.

The data were then re-checked for gross and systematic errors. It was found that the ratio $|F_o|/|F_c|$ increased very markedly to an average value of 1.40 for very weakly observed data. These had been given maximum weight in the refinement along with reflections of medium intensity. The original intensity data were re-examined and, as a result, all those independent reflections which were measured only once at the low end of the relative intensity

Table 1. Atomic coordinates. The general equivalent positions are $\pm(x,y,z)$; $\pm(\frac{1}{2}-x, \frac{1}{2}+y, -z)$; $\pm(\frac{1}{2}+x, -y, \frac{1}{2}-z)$; $\pm(-x, \frac{1}{2}-y, \frac{1}{2}+z)$. The estimated standard deviations ($\times 10^4$) of the coordinates are given in parentheses.

Atom	x/a	y/b	z/c
Ni	0.2504 (1)	0.1688 (1)	0.0495 (2)
Ca	0.4122 (1)	0.4200 (1)	0.0385 (2)
O(1)	0.3310 (3)	0.4017 (2)	-0.2709 (8)
O(2)	0.4934 (2)	0.4928 (2)	-0.2139 (6)
O(3)	0.4718 (3)	0.3552 (3)	0.3029 (8)
O(4)	0.3244 (3)	0.4456 (2)	0.3232 (7)
O(5)	0.4903 (3)	0.3386 (2)	-0.1485 (8)
N(1)	0.1571 (3)	0.0342 (3)	0.0144 (9)
N(2)	0.3971 (3)	0.0831 (3)	0.0070 (9)
N(3)	0.3334 (3)	0.3090 (3)	0.0802 (9)
N(4)	0.1045 (3)	0.2550 (3)	0.0775 (10)
C(1)	0.1931 (3)	0.0857 (3)	0.0269 (9)
C(2)	0.3420 (4)	0.1173 (3)	0.0240 (9)
C(3)	0.3039 (3)	0.2543 (3)	0.0698 (9)
C(4)	0.1587 (3)	0.2210 (3)	0.0676 (9)

scale (these corresponded to just-visible reflections) were omitted from the intensity set, which was then re-reduced as before. There was a marked change of film-to-film scale factors towards expected values. Although 419 reflections were omitted, there were still 12.4 observations per varied parameter.

With the revised data, the anisotropic least squares refinement was resumed, and completed, with two cycles of computation. For these, F^* in the above

Table 2. Mean square vibration amplitude tensors, U_{ij}^a ($\times 10^4$) in \AA^2 .

The estimated standard deviations ($\times 10^4$) of the U_{ij} are given in parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{31}
Ni	52 (2)	32 (2)	107 (2)	-21 (1)	-2 (2)	-1 (1)
Ca	23 (2)	15 (2)	79 (3)	-3 (1)	2 (2)	-2 (2)
O(1)	120 (10)	80 (8)	165 (11)	-8 (8)	7 (8)	30 (9)
O(2)	65 (8)	55 (7)	98 (9)	2 (6)	-6 (7)	-4 (6)
O(3)	117 (10)	122 (10)	209 (14)	-58 (8)	64 (9)	-73 (9)
O(4)	114 (9)	86 (8)	136 (11)	11 (8)	9 (8)	30 (8)
O(5)	92 (8)	81 (8)	176 (11)	-28 (7)	2 (8)	7 (8)
N(1)	125 (12)	69 (10)	168 (14)	-57 (9)	1 (10)	-3 (10)
N(2)	85 (11)	130 (12)	153 (14)	19 (10)	37 (11)	26 (9)
N(3)	123 (11)	84 (11)	150 (13)	-50 (9)	-0 (9)	-9 (10)
N(4)	111 (12)	112 (11)	186 (16)	7 (10)	-23 (11)	-29 (10)
C(1)	83 (11)	61 (11)	100 (12)	-8 (9)	-10 (9)	11 (9)
C(2)	88 (12)	84 (11)	100 (13)	-17 (9)	16 (10)	12 (10)
C(3)	70 (10)	60 (10)	109 (13)	-22 (9)	14 (10)	-1 (9)
C(4)	78 (11)	86 (11)	120 (14)	-12 (9)	0 (10)	-8 (10)

^a The U_{ij} are derived from the b_{ij} 's of the anisotropic temperature factor term $\exp\left\{-\left(\sum_{i=1}^3 \sum_{j=1}^3 b_{ij} h_i h_j\right)\right\}$ using the relations $b_{ij} = 2\pi^2 U_{ij} a_i^* a_j^*$ where a_i and a_j are the appropriate unit cell dimensions.

Table 3. Continued.

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC
22	32	30															
23	26	-29															
			6,K,2			2 46 47			9 38 -42			12 24 -22			21 25 27		
						3 16 -13			10 109 -104			13 21 16					
			0 208 -249			4 11 -11			11 38 34			14 30 -27			6,K,3		
			1 84 94			5 84 -93			13 20 19			16 40 -40					
			2 44 -40			6 176 -195			14 55 51			17 40 -39			0 14 9		
			3 70 71			7 89 96			16 10 10			18 19 -18			2 36 -34		
			4 97 100			10 30 29						19 45 -41			3 30 -29		
			5 38 -40			12 21 18			16,K,2			20 19 16			4 57 56		
			6 20 -17			13 22 23						22 21 22			5 12 -8		
			7 76 74			14 53 58			0 19 -18						6 15 -15		
			8 81 87			17 60 -58			2 60 -62			2,K,3			7 19 18		
			11 109 -115			18 101 -102			3 22 20						8 35 34		
			12 167 -186			19 48 47			4 26 -23			0 74 68			9 52 50		
			13 57 55						5 51 48			1 64 63			10 15 -15		
			14 24 -24			11,K,2			6 76 78			2 47 46			13 26 -25		
			15 22 23						7 32 -31			3 115 119			14 24 -22		
			16 24 25			2 49 52			9 19 -19			4 76 -71			15 19 -19		
			17 18 -17			3 31 -29			10 40 -37			5 30 31			16 16 14		
			18 18 -17			4 57 -63			11 18 17			6 44 -42			20 12 12		
			19 38 35			5 34 33			12 18 16			7 57 -51			21 13 13		
			20 38 35			8 55 52			13 21 -21			8 45 -40					
						9 29 -29			14 43 -45			9 71 -68			7,K,3		
			7,K,2			12 22 21			15 22 24			10 56 57					
			1 38 -35			14 23 21						11 45 -45			1 56 -55		
			2 38 -30			15 37 -42			17,K,2			12 46 42			2 33 32		
			3 75 75			16 80 -88						15 26 24			3 14 13		
			4 155 -168			17 40 39			1 26 -24			17 37 33			4 34 34		
			5 60 64			20 34 33			2 27 -25			18 38 -36			5 33 31		
			6 15 11						3 44 41			20 13 -11			6 26 -23		
			7 40 42			12,K,2			4 64 56			21 14 -14			7 16 12		
			8 89 -96						5 28 -24						8 22 -16		
			9 38 -37			0 108 117			7 20 -20			3,K,3			10 49 -44		
			10 64 -63			1 70 -68			8 50 -47						11 55 -52		
			11 14 14			2 31 -32			9 43 38			1 86 -90			12 23 -22		
			12 28 27			3 22 -20			10 48 49			2 81 77			13 48 -51		
			13 27 -27			4 58 -64			11 34 -34			3 53 -51			14 19 16		
			14 44 -46			5 33 35			13 11 -12			4 32 -31			15 19 -17		
			15 66 73			6 21 23			14 24 -25			5 37 -38			16 19 18		
			16 34 30			7 23 -22						6 18 14			18 14 12		
			17 18 15			8 73 77			18,K,2			7 26 27			19 22 21		
			18 14 13			9 47 47			9 43 38			8 40 -34			20 22 -20		
			19 46 41			11 23 21			0 87 -83			9 31 30			21 14 17		
			20 46 41			12 56 59			1 31 29			10 21 -18					
			21 13 -15			13 35 -30			2 16 -14			11 17 -15			8,K,3		
			22 11 -13			16 26 -25			3 27 25			13 19 -14					
						15 17 -17			4 35 29			14 21 18			0 33 -33		
			8,K,2			18 12 -12			7 18 18			15 22 21			1 20 -18		
			0 42 46			19 16 -16			8 44 42			18 20 -21			2 26 -21		
			1 17 -19						9 16 -17			8 40 -34			3 45 -40		
			2 59 -62			13,K,2			11 41 -43			20 24 -23			4 19 19		
			4 58 -59						12 70 -85						5 57 -56		
			5 27 28			1 24 -24						4,K,3			6 35 31		
			6 70 63			2 65 -63			19,K,2						8 32 31		
			7 59 -52			3 45 47						0 12 -8			9 52 51		
			8 65 -63			4 77 71			3 35 -33			1 26 26			10 26 22		
			10 49 -47			5 46 -46			4 63 -67			2 76 75			11 37 35		
			11 28 27			7 50 -49			5 25 22			3 61 58			12 28 -28		
			12 25 21			8 73 -75			7 23 23			5 26 25			13 31 -33		
			14 62 -63			9 48 50			8 49 49			6 31 -33			14 47 -49		
			15 34 30			12 17 -17			9 13 -13			7 21 -20			15 54 -56		
			16 18 -17			14 28 -26						8 53 -50			16 38 32		
			17 37 34			15 41 38			20,K,2			9 54 -50			17 28 -23		
			18 64 63			16 63 67						10 20 16			18 19 19		
			19 33 31			17 30 -32			0 69 69			11 30 -25			20 35 34		
			20 18 -17			18 11 12			1 36 -34			12 18 15					
									2 20 -18			13 21 19			9,K,3		
			9,K,2			14,K,2			4 28 -26			14 57 57					
			1 74 -77			0 60 -62			7 9 -9			15 69 73			1 60 -58		
			2 136 -145			1 49 48			8 17 -21			16 27 -23			2 29 27		
			3 88 93			2 37 35						17 34 36			3 16 -14		
			4 51 50			3 24 -24			21,K,2			19 25 -23			4 37 -34		
			5 22 -23			5 43 -41						20 45 -45			5 27 -24		
			7 18 -20			6 60 -68			1 26 -30			21 55 -54			8 18 -14		
			8 46 -50			7 33 33			2 57 -65			22 14 14			9 20 18		
			9 50 54			8 20 20			3 23 27						15 16 15		
			10 83 85			11 30 -29			4 6 -7			5,K,3			16 18 -17		
			11 41 -39			12 70 -70									18 23 -23		
			13 54 -56			13 54 55			1,K,3			1 19 -18			19 21 -19		
			14 71 -75			16 22 -22						2 29 31					
			15 41 38			17 12 -14			1 50 46			4 35 35			10,K,3		
			18 32 -30						2 50 -44			5 11 -10					
			19 15 16			15,K,2			3 11 10			6 18 -16			0 61 -64		
			21 30 32						4 69 -62			7 15 -14			1 27 -24		
						1 35 35			5 60 -63			10 51 -52			3 49 -46		
			10,K,2			2 80 81			6 41 -40			11 40 -42			4 40 41		
			0 43 -44			3 24 -22			7 71 -71			12 35 -37			5 34 -33		
			1 42 45			5 13 -12			8 67 65			13 43 -43			6 35 34		
						7 19 -20			9 25 -23			16 35 33			8 21 20		
									10 34 32			19 17 14			9 38 38		

Table 3. Continued.

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC
17 ₂ K, 3			6 35 ⁻	-35		8 18	14		13 ₂ K, 4			2 ₂ K, 5			4 56	60	5 22	19		
1 39	-39		7 73	81		9 86	-97		1 21	20		0 29	28		5 33	33	6 26	-28		
2 22	19		11 37	-40		16 28	-26		3 54	56		2 16	15		8 44	-45	8 24	-26		
4 32	29		13 42	46		17 57	52		4 42	39		4 36	-34		10 29	-30	9 15	-14		
5 23	19		14 45	42		19 37	40		5 45	-42		6 27	-27		14 13	15	10 12	14		
6 14	11		15 64	-57		20 18	19		7 52	-44		7 36	-37		16 32	32	11 13	-14		
7 17	13		16 22	24					8 41	-36		8 29	-26		17 12	13	12 35	41		
8 24	-23		17 50	-48					9 25	21		9 19	-17		18 21	23				
10 27	-27		18 29	-25		8 ₂ K, 4			13 18	18		10 17	18		15 ₂ K, 5					
11 22	-23		19 38	39		0 14	11		15 56	56		11 15	-15		8 ₂ K, 5					
12 23	-25					1 50	-53		16 24	30		12 43	42		0 54	-62	1 26	23		
18 ₂ K, 3			3 ₂ K, 4			14 ₂ K, 4			3 ₂ K, 5			16 ₂ K, 5			17 ₂ K, 5					
1 20	-18		1 99	110		0 20	-19		1 29	27		11 22	22		0 36	38				
2 13	-16		2 48	49		1 58	57		2 20	-19		12 37	-37		3 14	13				
3 25	-22		3 98	-102		2 13	13		3 13	13		13 39	-36		4 10	-11				
4 25	22		4 78	-88		3 23	23		4 28	28		14 28	24		5 9	9				
5 15	15		5 52	-52		4 28	28		5 38	-35		15 24	21		6 16	17				
6 15	15		6 73	77		5 38	-35		6 29	-27		16 36	-38		7 9	9				
7 19	18		7 72	77		6 45	47		7 51	44		17 15	14		8 8	-9				
8 21	20		8 36	34		7 67	-72		8 28	28		18 36	-38		9 9	9				
9 24	23		9 41	-38		8 28	28		9 38	-35		19 16	15		10 8	-9				
11 9	10		10 23	-40		9 19	-17		10 43	-40		8 26	27		11 8	10				
			11 73	80		11 28	29		11 46	-45		9 15	16		12 8	10				
			12 40	-48		13 62	-59		12 21	-21		10 22	22		13 8	-10				
						16 20	18		13 29	26		11 22	22		14 8	-10				
						17 45	46		15 19	-23		12 37	-37		15 8	-10				
						19 43	-48		15 23	26		13 36	-38		16 8	-10				
												14 28	24		17 8	-12				
												15 24	21		18 8	-12				
												17 15	14		19 8	-12				
												18 36	-38		20 8	-12				
												19 16	15		21 8	-12				
												8 20	-18		22 8	-12				
												9 25	26		23 8	-12				
												11 18	18		24 8	-12				
												13 12	12		25 8	-12				
												15 13	12		26 8	-12				
												16 25	24		27 8	-12				
												17 37	36		28 8	-12				
												18 14	13		29 8	-12				
												19 14	15		30 8	-12				
												8 20	-18		31 8	-12				
												9 25	26		32 8	-12				
												11 18	18		33 8	-12				
												13 12	12		34 8	-12				
												15 13	12		35 8	-12				
												16 25	24		36 8	-12				
												17 37	36		37 8	-12				
												18 14	13		38 8	-12				
												19 14	15		39 8	-12				
												8 20	-18		40 8	-12				
												9 25	26		41 8	-12				
												11 18	18		42 8	-12				
												13 12	12		43 8	-12				
												15 13	12		44 8	-12				
												16 25	24		45 8	-12				
												17 37	36		46 8	-12				
												18 14	13		47 8	-12				
												19 14	15		48 8	-12				
												8 20	-18		49 8	-12				
												9 25	26		50 8	-12				
												11 18	18		51 8	-12				
												13 12	12		52 8	-12				
												15 13	12		53 8	-12				
												16 25	24		54 8	-12				
												17 37	36		55 8	-12				
												18 14	13		56 8	-12				
												19 14	15		57 8	-12				
												8 20	-18		58 8	-12				
												9 25	26		59 8	-12				
												11 18	18		60 8	-12				
												13 12	12		61 8	-12				
												15 13	12		62 8	-12				
												16 25	24		63 8	-12				
												17 37	36		64 8	-12				
												18 14	13		65 8	-12				
												19 14	15		66 8	-12				
												8 20	-18		67 8	-12				
												9 25	26		68 8	-12				
												11 18	18		69 8	-12				
												13 12	12		70 8	-12				
												15 13	12		71 8	-12				
												16 25	24		72 8	-12				
												17 37	36		73 8	-12				
												18 14	13		74 8	-12				
												19 14	15		75 8	-12				
												8 20	-18		76 8	-12				
												9 25	26		77 8	-12				
												11 18	18		78 8	-12				
												13 12	12		79 8	-12				
												15 13	12		80 8	-12				
												16 25	24		81 8	-12				
												17 37	36		82 8	-12				
												18 14	13		83 8	-12				
												19 14	15		84 8	-12				
												8 20	-18		85 8	-12				
												9 25	26		86 8	-12				
												11 18	18		87 8	-12				
												13 12	12		88 8	-12				
												15 13	12		89 8	-12				
												16 25	24		90 8	-12				
												17 37	36		91 8	-12				
												18 14	13		92 8	-12				
												19 14	15		93 8	-12				
												8 20	-18		94 8	-12				
		</																		

Table 3. Continued.

17 25 -24	6,K,6	3 43 44	13,K,6	4,K,7	12,K,7	5 19 18
		4 20 -23				
3,K,6	0 17 13	9 39 38	3 34 33	0 32 33	0 13 13	5,K,8
	1 54 52	11 42 -40	5 47 -49	2 14 12	2 7 8	
1 64 69	3 39 40	13 42 -45	7 42 -47	3 13 -10	5 7 -7	1 17 17
2 13 -12	5 14 -12	14 18 15	8 16 17			2 20 19
3 48 -51	6 27 25		9 23 22	5,K,7	13,K,7	3 18 17
5 13 -11	7 41 39	10,K,6	10 9 -9			5 22 -24
7 30 -30	9 42 -42			2 21 19	1 5 -6	
8 16 -12	10 39 -36	0 16 16	14,K,6	3 16 -14		6,K,8
9 58 -59	11 68 -65	1 22 21		5 27 -26		
10 16 12	13 40 40	3 30 -29	0 11 9		0,K,8	0 24 25
11 59 62	14 18 -19	4 23 -23	1 25 24	6,K,7	0 48 -49	1 35 33
13 56 55	15 32 35	5 52 -51	2 17 -18	5 16 -16	1 27 -25	3 24 26
15 26 -24		7 49 53	5 24 -24		2 23 23	
16 14 13	7,K,6	8 30 -33	6 11 12	7,K,7	3 42 -47	7,K,8
		9 32 31	7 23 25			
4,K,6	1 17 -18	10 15 14			1,K,8	1 18 -20
	2 14 -14	11 16 13	15,K,6	2 32 31		2 16 -16
0 16 -15	3 49 -53	12 18 17		5 14 -13	1 15 -14	3 14 -13
1 25 -22	4 16 16	13 20 18	1 35 40		3 24 24	5 26 32
2 24 -24	5 46 48		3 28 -31	8,K,7	5 13 -13	
3 42 41	7 45 43	11,K,6	5 12 -15			8,K,8
5 57 64	9 39 -38			0 29 -28	2,K,8	
7 60 -61	10 16 12	3 43 -44	16,K,6	1 11 10		0 10 -11
8 16 13	11 19 16	5 32 36		2 15 -14	0 23 23	1 10 -10
11 32 31	12 29 -28	7 21 20	0 11 -13	5 11 -9	1 13 10	2 8 9
13 30 -28	13 21 -20	9 33 -33	1 10 -10		2 25 -24	3 10 12
15 34 36	14 15 -11	10 15 13	2 7 -6	9,K,7	3 12 -11	
17 33 44	15 45 -48	12 15 17			5 25 -28	
			1,K,7	1 14 -12		
5,K,6	8,K,6	12,K,6		3 26 -25	3,K,8	
			2 38 -34	5 9 -9		
2 33 36	1 29 -30	1 59 -62	3 19 -16		1 38 38	
3 58 55	3 22 21	2 18 17		10,K,7	2 37 -35	
4 14 -13	5 51 52	3 43 -43			3 16 -15	
5 40 -41	7 51 -54	5 19 19	2,K,7	0 31 -29	5 14 -14	
7 43 -43	11 33 28	6 17 -18		1 9 9		
9 43 43	13 18 -17	7 17 -15	0 50 49	2 21 -20	4,K,8	
10 16 -14	15 27 27	9 39 41	2 24 23			
11 27 -25		10 13 -14	3,K,7	11,K,7	0 20 -20	
12 22 22	9,K,6	11 35 43			1 9 -8	
15 35 35			3 37 -34		3 21 23	
	1 58 -62			1 9 -10		
	2 17 17			2 35 -34		
				3 10 -10		

weighting scheme was changed to 30.00 electrons in accordance with the results of a second weighting scheme analysis. The final R factor was 0.073. Tables 1 and 2 list the final atomic coordinates and the final thermal parameters (in the form of the mean-square-amplitude tensors, U_{ij}), respectively. From these parameters, a terminal set of structure factors, listed with the observed data in Table 3, was computed.

The assumption that a crystal structure analysis is free from systematic errors, both of data and of postulated model, is never satisfied. As a result the final structural parameters may differ significantly (in terms of their standard deviations, which themselves will be in error if calculated from the usual formulae) and in an unknown manner from their "true" values. These differences may be accentuated by inaccurate data weighting, the choice of which again usually neglects systematic errors. In an effort to test the reliability of the present results and data, the final stages of the least squares refinement were repeated with each of two weighting schemes differing from that deduced during the analysis. The first was an arbitrary scheme giving equal weight to all observations. The other was an "observational" function (in the sense that it accounts for random errors of intensity measurement) of the form

$$\omega = 1/[1 - \{(|F_o| - a)/b\}^2]$$

where a and b , 20.7 electrons and 2.52 electrons, respectively, were chosen to give close fit to a plot of $\langle 1/||F_c| - |F_b||^2 \rangle$ against $|F_o|$ for the re-examined and corrected data set. This scheme was similar to that used in the original refinement for medium and strong observations, but gave lower weight to the weak reflections.

The following comparative results were obtained:

i) the final R factors were 0.073 (original refinement), 0.074 (equal weights), and 0.083 (observational function).

ii) the overall scale factors differed by 15%. This sensitivity of scale factor to weighting is of importance in connection with experimental determination of "residual" electron density from diffraction data.

iii) in no case did the differences between corresponding positional coordinates exceed three times their respective estimated standard deviations. In general they were much less than this.

iv) the estimated standard deviations of the positional coordinates from the unit weight refinement were about 1.5 times the corresponding figures for the other refinements.

v) the thermal parameters, although showing the same general features, differed markedly in numerical value for the respective refinements. For the equal weights refinement the parameters for one atom (Ca) became non-positive definite.

Thus, the general conclusions from these experiments are that the data are relatively free from serious systematic error (although some evidence of extinction may be seen in Table 3), that the weighting scheme used in the initial refinement was probably satisfactory, that the use of unit weights was clearly inappropriate, that the positional parameters are reliable and that only qualitative information is provided by the thermal parameters.

No attempt was made to locate the hydrogen atoms in the structure, although it is probable that several of the significant features of a difference electron density map plotted from the final data are due to these. The maximum peak height on this map is $0.85 \text{ e}/\text{\AA}^3$.

Table 4. Least squares plane through the $\text{Ni}(\text{CN})_4^{2-}$ ion. Plane given by $-0.0281x + 0.1036y - 0.9942z + 0.1005 = 0$, where x , y , and z are expressed parallel to a , b , and c , respectively.

Atom	Deviation (\AA)	Atom	Deviation (\AA)
Ni	-0.024	C(3)	-0.020
C(1)	-0.006	N(3)	0.003
N(1)	-0.006	C(4)	0.000
C(2)	0.003	N(4)	0.026
N(2)	0.024		

Table 5. Some inter-atomic distances (Ångströms). The estimated standard deviations ($\times 10^3$) of the distances are given in parentheses.

Ni —C(1)	1.859 (6)	O(1) —O(2)	3.299 (6)
Ni —C(2)	1.858 (6)	O(1) —O(5)	3.097 (6)
Ni —C(3)	1.860 (6)	O(1) —N(1)	3.050 (7)
Ni —C(4)	1.863 (6)	O(1) —N(3)	2.952 (8)
C(1) —N(1)	1.154 (8)	O(2) —O(2')	2.920 (8)
C(2) —N(2)	1.152 (9)	O(2) —O(5)	2.942 (6)
C(3) —N(3)	1.152 (7)	O(2) —N(1)	3.020 (7)
C(4) —N(4)	1.133 (8)	O(2') —O(3)	2.991 (6)
Ca —O(1)	2.541 (5)	O(2') —O(4)	3.421 (6)
Ca —O(2)	2.599 (4)	O(2') —N(1)	3.251 (7)
Ca —O(2')	2.599 (4)	O(3) —O(4)	3.057 (7)
Ca —O(3)	2.398 (5)	O(3) —O(5)	3.090 (8)
Ca —O(4)	2.495 (5)	O(3) —N(3)	2.948 (7)
Ca —O(5)	2.401 (5)	O(4) —N(1)	2.849 (8)
Ca —N(1)	2.487 (5)	O(4) —N(3)	3.062 (7)
Ca —N(3)	2.509 (5)	O(5) —N(3)	3.159 (7)

DISCUSSION

The tetracyanonickelate(II) ions are approximately square planar, but there are significant deviations from this (Table 4 lists the distances of atoms from the least squares planes through the ions, and further geometry is given in Tables 5 and 6, which record the important inter-atomic distances and angles in the structure). They are stacked in columns parallel to the *c* axis. Although in any one column the ions are approximately parallel to each other, their planes are not perpendicular to this axis, the normals to them making angles of $\pm 6^\circ 10'$ with *c*, almost in the *bc* plane (the calculated deviation is $1^\circ 35'$),

Table 6. Some inter-atomic angles (degrees). The estimated standard deviations ($\times 10$) of the angles are given in parentheses.

C(1) —Ni —C(2)	90.0 (3)	O(2') —O(3) —O(5)	82.9 (2)
C(2) —Ni —C(3)	92.4 (3)	O(5) —O(3) —N(3)	63.1 (2)
C(3) —Ni —C(4)	87.4 (3)	N(3) —O(3) —O(4)	61.3 (2)
C(4) —Ni —C(1)	90.2 (3)	O(4) —O(3) —O(2')	68.9 (2)
Ni —C(1) —N(1)	179.4 (6)	N(3) —O(4) —O(3)	57.6 (2)
Ni —C(2) —N(2)	177.3 (6)	O(3) —O(4) —O(2')	54.6 (1)
Ni —C(3) —N(3)	176.4 (5)	O(2') —O(4) —N(1)	61.7 (2)
Ni —C(4) —N(4)	177.4 (6)	N(1) —O(4) —N(3)	93.2 (2)
O(2) —O(1) —O(5)	54.7 (1)	O(2) —O(5) —O(3)	92.9 (2)
O(5) —O(1) —N(3)	62.9 (2)	O(3) —O(5) —N(3)	56.3 (2)
N(3) —O(1) —N(1)	91.5 (2)	N(3) —O(5) —O(1)	56.3 (2)
N(1) —O(1) —O(2)	56.6 (2)	O(1) —O(5) —O(2)	66.2 (1)
O(2') —O(2) —O(5)	86.8 (2)	O(2) —N(1) —O(2')	55.3 (2)
O(5) —O(2) —O(1)	59.2 (1)	O(2') —N(1) —O(4)	67.9 (2)
O(1) —O(2) —N(1)	57.5 (2)	O(4) —N(1) —O(1)	88.2 (2)
N(1) —O(2) —O(2')	66.3 (2)	O(1) —N(1) —O(2)	65.9 (2)
O(2) —O(2') —O(3)	95.5 (2)	O(3) —N(3) —O(5)	60.7 (2)
O(3) —O(2') —O(4)	56.5 (1)	O(5) —N(3) —O(1)	60.8 (2)
O(4) —O(2') —N(1)	50.5 (1)	O(1) —N(3) —O(4)	86.2 (2)
N(1) —O(2') —O(2)	58.3 (2)	O(4) —N(3) —O(3)	61.1 (2)

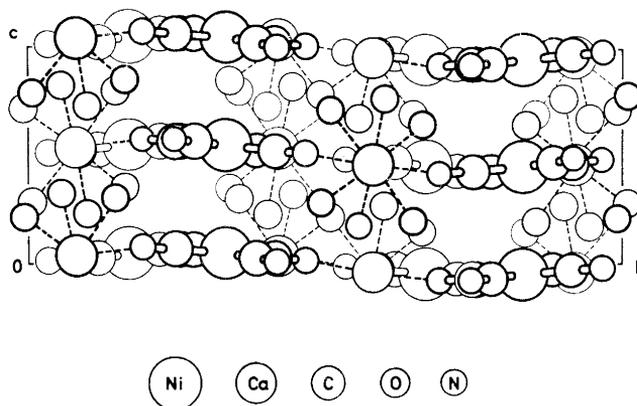


Fig. 1. A view of the crystal structure projected on to the bc plane.

the \pm indicating that alternate columns of the ions are deviated in opposite senses (see Fig. 1). Within any one column, the projections of the Ni—C—N lines of one tetracyanonickelate(II) ion, each of which is nearly straight, make angles of $\pm 26^{\circ}56'$ with the corresponding projections from the two neighbouring ions (see Fig. 2). These angles are 0° and 45° , respectively, in the analogous strontium⁸ and barium compounds.¹⁴ Their variation must be due wholly to the effects of the different ionic radii of the cations (although in the case of the barium salt there is also a different hydration state).

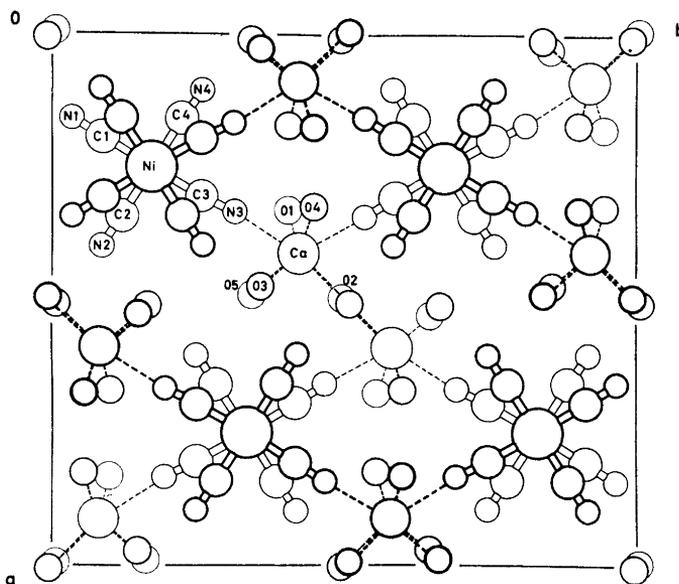


Fig. 2. A view of the crystal structure projected on to the ab plane.

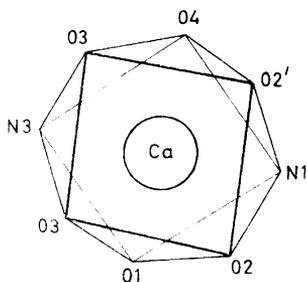


Fig. 3. The coordination polyhedron surrounding each calcium ion, as seen in projection on to the bc plane.

The nickel ions are separated by 3.387 ± 0.003 Å ($\sim c/2$). It is interesting to note that this distance is 3.364 Å in the barium analogue, but 3.64 Å in the compounds with strontium and the monovalent cations (Na^+ , K^+ , Rb^+ , Li^+ , NH_4^+). Again this is presumably a result of the balancing of packing constraints and its variation lends support to the conclusion¹³ that there is little interaction between neighbouring tetracyanonickelate(II) ions.

The calcium ions are eight-fold coordinated, the coordinated atoms lying at the corners of distorted square Archimedean antiprisms (Fig. 3). Six of the nearest neighbours of each calcium ion are oxygen atoms of the waters of crystallization and the other two are nitrogens (N(1) and N(3)) from the tetracyanonickelate(II) ions of two stacks, one on either side of the calcium ion (Figs. 1 and 2). In addition to these linkages between the anions and cations, the structure is further stabilized by the sharing of one edge (O(2) to its symmetry-equivalent, O(2')) by each pair of adjacent calcium coordination polyhedra.

The tetracyanonickelate(II) ions and the calcium ions form "undulating" sheets, approximately parallel to the ab plane, between which the oxygen atoms of the waters of crystallization are packed. There is a similar arrangement in strontium tetracyanonickelate(II) pentahydrate. There is also a "thick" sheet of water oxygen atoms parallel to the bc plane at $x/a=1/2$.

All the bond lengths of the structure agree very well with accepted values. The inter-bond angles of each tetracyanonickelate(II) ion, however, show statistically highly significant deviations from those of an ideally square planar ion with linear Ni—C—N bonds. The most marked of these are on the ligands whose nitrogen atoms are in calcium polyhedra. Thus, the angles C(3)—Ni—C(4) (87.4°) and Ni—C(3)—N(3) (176.4°) both result from a distortion of the ligands from the "ideal" in the same sense. There is also a significant out-of-plane bending of the C—N bonds. Likewise, the other "bound" ligands, Ni—C(1)—N(1), are bent. It is less obvious why the angles at the carbon atoms of the "unbound" ligands (C(2) and C(4)) are not 180° . As was noted above the existence of unaccounted systematic data errors may lead to unusual geometrical results (and certainly under-estimated standard deviations of these), but would be unlikely to produce features of the magnitude observed here. Also, it has often been shown that angular distortions, rather than bond length changes, result from dense packing of matter. When these points are considered with the consistent bond lengths obtained here, the

angular deviations from the ideal square plane must be regarded as real. These geometrical characteristics almost surely arise from a general balancing of packing forces imposed by the bonding of the nickel and calcium ions.

No detailed analysis of the thermal vibrations has been made but, although there are large variations, it is fairly clear from the U_{ij} values (Table 2) that, as expected, the major axes of vibrations of the atoms of the tetracyanonickelate(II) ions are approximately perpendicular to their planes, and the higher vibration amplitudes of the nitrogen atoms lead to the speculation that the ions may be undergoing rigid body motion in these directions. The vibrations of the shared oxygen atoms (O(2)) are significantly lower than the others.

It is interesting that quite large changes of structure result in progressing through the series of compounds with Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} cations (the crystal structure of the magnesium salt is not known in detail but preliminary data show that it is not isomorphous with any of the other three). For the monovalent cation species, however, where the effective ionic radii vary over an even larger range, no such changes occur. This supports the conclusion reached above that the units of structure in these latter compounds are less "tightly" packed.

Preliminary information (cell dimensions, space groups, *etc.*) has been obtained for a number of other compounds in this series. With the exception, possibly, of the magnesium salts, the data are in basic agreement with the earlier results. In all cases, crystals of a group containing Ni(II), Pd(II), and Pt(II) with a given cation are isomorphous.

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26. The authors are grateful for the assistance given in the structure determination by Dr. E. N. Maslen, Department of Physics, University of Western Australia, who pointed out the existence of four possible solutions of the Patterson map for the Ni and Ca ions, after assumption of the correctness of Fontaine's⁹ solution had led to difficulties.
27. Defined, as usual, as $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$ where F_o and F_c are the observed and calculated structure factors.
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