

## The Crystal Structure of Barium Tetracyanonickelate(II) Tetrahydrate

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The crystal structure of barium tetracyanonickelate(II) tetrahydrate,  $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ , has been redetermined using automatically collected counter data and refined to an  $R$ -value of 4.6 %. The space group is  $C2/c$  (No. 15) with  $a=12.07_6$ ,  $b=13.61_0$ ,  $c=6.72_8$ ,  $\beta=107^\circ.54$ .

The square planar tetracyanonickelate groups are stacked along the  $c$ -axis. Adjacent groups are turned  $45^\circ$  with respect to each other. This makes the short nickel-nickel distance of 3.36 Å compatible with usual van der Waals' distances of carbon and nitrogen.

The barium ion is tenfold coordinated. It is surrounded by six oxygen and four nitrogen atoms.

Crystals of  $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$  have an unusually sharp absorption band at  $222\,000\text{ cm}^{-1}$  according to Ballhausen, Bjerrum, Eriks, Dingle and Hare.<sup>1</sup> This band does not show up in analogous compounds containing Ca, Sr, Na, or K instead of Ba. Neither is it observed in aqueous solutions.

Professor Ballhausen suggested that we carry out an accurate structure analysis of the barium salt in order to correlate spectral and structural data. Brasseur and de Rassenfosse<sup>2,3</sup> have previously investigated crystallographic properties of  $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$  and suggested a structure which is correct in principle. However, precise location of the light atoms C, N, and O in the presence of heavy atoms such as Ba and Ni was not possible at the time of the investigation of Brasseur and de Rassenfosse. Our aim was the location of all atoms except hydrogen.

### EXPERIMENTAL

*Unit cell and space group.* Large well developed crystals (several  $\text{mm}^3$ ) were supplied by Professor Ballhausen.

A sphere of 0.13 mm diameter was ground in a "Bond sphere grinder".<sup>4</sup> The spherical crystal was mounted along the  $c$ -axis and investigated by oscillation, Weissenberg, precession, and retigraph methods using  $\text{CuK}\alpha$  radiation.

The linear absorption coefficient for  $\text{CuK}\alpha$ -radiation is  $349.5 \text{ cm}^{-1}$ , for  $\text{MoK}\alpha$ -radiation  $60.0 \text{ cm}^{-1}$ .

The X-ray photographs showed that  $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$  is monoclinic in agreement with the results of Brasseur and de Rassenfosse.<sup>2,3</sup>

*Data collection and reduction.* Three dimensional data were measured with a linear diffractometer designed by Arndt and Phillips<sup>4</sup> and manufactured by Hilger and Watts.

Mo-Radiation was employed. Balanced filters  $\text{SrO}$ ,  $\text{ZrO}_2$  in conjunction with a pulse height discriminator simulated a practically monochromatic  $\text{MoK}\alpha$  beam.

The intensities measured were symmetry related in pairs. The diffractometer output was processed by a GIER computer using an ALGOL program<sup>6</sup> which evaluated intensities, calculated averages of symmetry related reflexions, applied  $L_p$  corrections and gave the standard deviations. 1452 of the 1840 independent reflexions showed intensities greater than twice their standard deviation estimated as the square root of the total number of counts in an intensity measurement. Reflexions within 0.1 reciprocal units from the spindle axis were omitted and for computational convenience only reflexions with  $\sin\theta/\lambda < 0.75$  were used. This reduced the number of reflexions used to 1264.

### STRUCTURE DETERMINATION

The coordinates of Ba and Ni were determined from a three dimensional Patterson function calculated using a program written by Lauesen.<sup>7</sup> A three dimensional Fourier synthesis was calculated with signs obtained from the Ba and Ni positions. C, N, and O atoms were located from this Fourier synthesis. The space group  $C2/c$  was assumed in all calculations.

Least squares analysis was carried out using the diagonal approximation and isotropic temperature factors. The program was written by Danielsen<sup>8</sup> and modified by one of us. Convergence was reached at  $R=10.26 \%$ . Refinement continued using another least squares program. The program<sup>9</sup> employs anisotropic temperature factors and a block diagonal approximation using  $3 \times 3$  and  $6 \times 6$  matrices. Convergence was reached at  $R=4.7 \%$ .

The standard deviations given by the counting statistics  $\sigma(F^2)_c$  were modified for use as weights in the least squares refinements. The weights used were  $w=1/(\mu F)^2$  where  $\mu F = \sqrt{\sigma(F^2)_c + kF^2} - F$ . The constant  $k$  was adjusted to give an average of  $w|F_o - F_c|^2$  which is nearly independent of the size of  $F$ . A best fit was obtained for  $k=1.053$ .

When these computations were finished the program system "X-Ray 63" by Stewart<sup>10</sup> became available to us. Computations using this system were carried out at NEUCC in Lundtofte. Corrections for absorption were applied and dispersion corrections were introduced for the barium and nickel atoms. An  $R$ -value of  $4.6 \%$  was reached at the end of the refinement. Bond lengths and angles were computed and nickel-carbon and carbon-nitrogen distances were corrected for thermal vibration assuming "riding-motion" of outer atoms with respect to inner atoms.

A difference Fourier synthesis was calculated after refinement was ended. It showed fluctuations between  $\pm 1 \text{ e}/\text{\AA}^3$  near the barium atom and  $\pm 0.5 \text{ e}/\text{\AA}^3$  elsewhere. Hydrogen atoms could not be located.

During refinement it was assumed that the carbon atom of the cyanide group was attached to nickel. This hypothesis was tested the following way: After convergence was reached with isotropic temperature factors carbon and nitrogen were interchanged in the calculations and a few least squares

cycles were computed. The  $R$ -value increased to 10.75 %. The temperature factors of the alleged nitrogen-atoms increased and those of alleged carbon atoms are smallest in both models. Since the atom which is located between the nickel atom and one other atom of the cyanide group probably has the smallest temperature factor, we consider the structure with carbon directly linked to nickel to be the most probable one.

CRYSTAL DATA

Using a unit cell with  $a=12.07_6 \text{ \AA}$ ,  $b=13.61_0 \text{ \AA}$ ,  $c=6.72_8 \text{ \AA}$ ,  $\beta=107^\circ 54'$ , the following extinctions were found:

$$hkl: h+k=2n+1, h0l: l=2n+1 (h=2n+1), 0k0: (k=2n+1).$$

This indicates the space groups  $Cc$  or  $C2/c$ . No piezoelectricity could be detected using the Giebe-Scheibe method. The density calculated for four formula units per cell is  $2.32 \text{ g/cm}^3$ . Brasseur and de Rassenfosse found experimentally  $2.38 \text{ g/cm}^3$ . Geometric and thermal parameters are given in Table 1. Table 2 gives bond lengths and angles and Table 3 observed and calculated structure factors.

Table 1a. Geometric parameters as fractions of cell edges. Standard deviations times  $10^4$  in parentheses.

Atom	$x$	$\sigma x$	$y$	$\sigma y$	$z$	$\sigma z$
Ba	0		0.37049	(.4)	0.2500	
Ni	0		0		0	
C1	0.0641	(6)	0.1250	(5)	0.0557	(11)
C2	0.1475	(6)	-0.0563	(5)	0.0905	(11)
N1	0.0997	(6)	0.2032	(5)	0.0914	(11)
N2	0.2393	(6)	-0.0924	(6)	0.1439	(11)
O1	0.3588	(5)	0.1896	(4)	0.3431	(9)
O2	0.4018	(4)	0.0551	(4)	0.0562	(8)

Table 1b. Temperature factor parameters with standard deviations times  $10^4$ . The expression used is  $\exp-(h^2b_{11} + \dots 2hkb_{12} + \dots)$ .

Atom	$b_{11}$	$\sigma b_{11}$	$b_{22}$	$\sigma b_{22}$	$b_{33}$	$\sigma b_{33}$	$b_{12}$	$\sigma b_{12}$	$b_{13}$	$\sigma b_{13}$	$b_{23}$	$\sigma b_{23}$
Ba	48.1	(.5)	18.5	(.3)	133	(1)	0		31.6	(.6)	0	
Ni	26.2	(.9)	18.7	(.6)	159	(3)	-0.1	(.5)	10	(1)	-5	(1)
C1	30	(5)	26	(4)	183	(16)	2	(3)	15	(7)	-4	(6)
C2	39	(5)	24	(4)	180	(16)	-8	(4)	15	(8)	-6	(6)
N1	55	(6)	28	(4)	271	(19)	3	(4)	39	(8)	-20	(7)
N2	34	(5)	41	(4)	248	(18)	4	(4)	13	(8)	7	(7)
O1	49	(5)	34	(3)	233	(14)	9	(3)	19	(7)	11	(5)
O2	37	(4)	36	(3)	180	(12)	0	(3)	21	(6)	14	(5)

Table 2. Interatomic distances with  $10^3 \times$  standard deviations in parentheses.

	Uncorrected	Corrected for thermal vibration assuming that second atom rides on first.
Ni—C1	1.859 (7)	1.861 (7)
Ni—C2	1.861 (7)	1.863 (7)
C1—N1	1.145 (10)	1.159 (10)
C2—N2	1.163 (10)	1.178 (10)
Ba—O1	2.864 (8)	
Ba—O2	2.860 (8)	
Ba—O2	2.910 (8)	
Ba—N1	2.926 (8)	
Ba—N2	3.049 (8)	
O1—O2	2.822 (8)	

Angles with standard deviations (degrees).

Ni—C1—C2	90.8 (0.3)
C1—Ni—N1	177.3 (0.8)
C2—Ni—N2	178.8 (0.7)

Distances from least squares plane through  $\text{Ni}(\text{CN})_4$  group (Å).

Ni	0.00
C1	-0.011
C2	0.008
N1	0.007
N2	-0.005

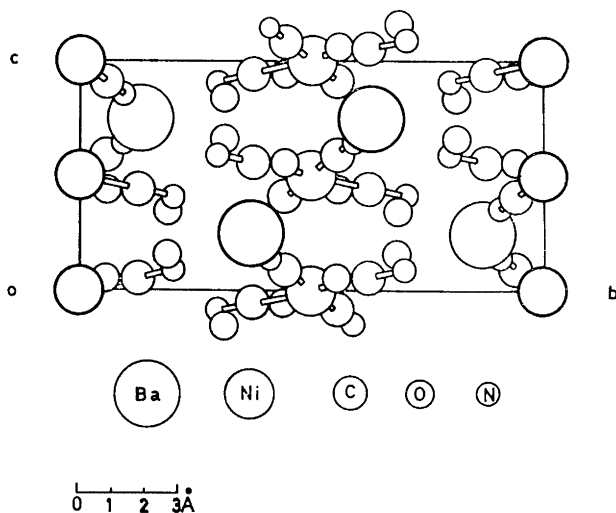


Fig. 1. Projection of a unit cell along the  $a$ -axis.

BARIUM TETRACYANONICKELATE (II)

Table 3. Observed and calculated structure factors.

Table with multiple columns containing observed and calculated structure factors for various h k l reflections. The table is organized into groups based on the reflection indices.



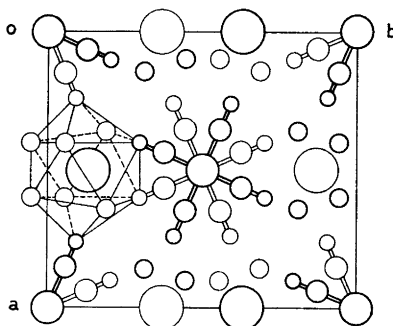


Fig. 2. Projection of a unit cell along the  $c$ -axis.

### DISCUSSION

The nickel atoms are located in  $(0,0,0)$ . This means that the tetracyanonickelate groups are stacked in the  $c$  direction with a separation of  $c/2=3.364$  Å between the nickel atoms.

A projection on  $(100)$  is shown in Fig. 1 and a projection on  $(001)$  in Fig. 2. Fig. 3 and Fig. 4 show projections on  $(100)$  and  $(001)$ , respectively, of vibrational principal axes.

Four cyanide groups are attached to each nickel atom. The  $\text{Ni}(\text{CN})_4^{2-}$  group is planar and quadratic within the experimental uncertainty. The uncorrected mean distance of the cyanide groups is  $1.15_4$  Å. The correction for "riding motion" yields a mean value of  $1.16_9$  Å. Neither value differs significantly from C—N distances in other cyanides including HCN. An extensive review of cyanide distances is given by Britton.<sup>11</sup>

The normal to the  $\text{Ni}(\text{CN})_4$  plane forms an angle of  $4^\circ 46'$  with the  $c$ -axis. Simon and Toussaint<sup>12</sup> have investigated the anisotropy of the diamagnetism of  $\text{BaNi}(\text{CN})_4 \cdot 4\text{H}_2\text{O}$ . One of the principal axes of the magnetic tensor ellipsoid must be parallel to the  $b$ -axis. One of the other principal axes was found to form an angle of  $3^\circ$  with the crystallographic  $c$ -axis. This result is in good agreement with our structural results.

The barium ion is tenfold coordinated. It is surrounded by six oxygen and four nitrogen atoms. A projection of the barium coordination polyhedron is shown in Fig. 5.

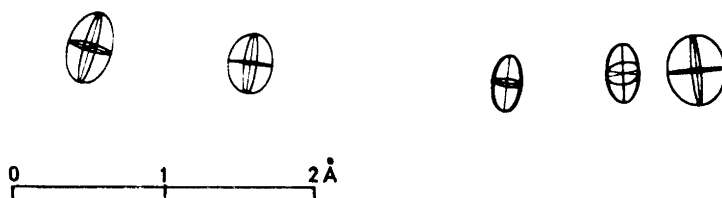


Fig. 3. Projection of principal vibration axes of  $\text{Ni}(\text{CN})_4$  group on  $(100)$  plane.

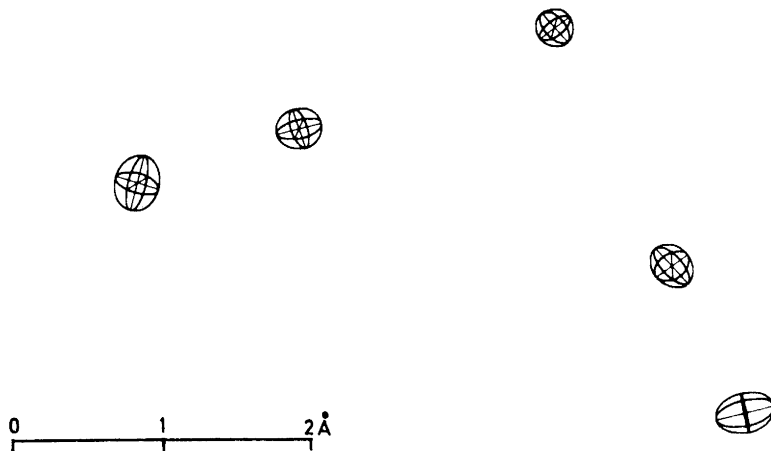


Fig. 4. Projection of principal vibration axes of  $\text{Ni}(\text{CN})_4$  group on (001) plane.

It can be described as a distorted tetragonal antiprism the end planes of which are developed into pyramids. In the case where the sixteen triangular faces were all equilateral triangles the name of the polyhedron would presumably be a heccaidecadeltahedron.<sup>13</sup>

The barium ion is also tenfold coordinated in  $\text{BaHCl}$ ,<sup>14</sup> in  $\text{BaC}_2$ ,<sup>15</sup> and in hexagonal  $\text{BaTiO}_3$ .<sup>16</sup> Coordination numbers of 6, 8, 9, and 12 are reported in other crystalline barium compounds.

The cyanide groups of adjacent anions are turned  $45^\circ$  with respect to each other. This makes the short Ni—Ni distance compatible with reasonable van der Waals' distances between the cyanide groups. In the calcium salt the stacking is different as shown by Watson.<sup>17</sup> The preliminary results of Brasseur and de Rassenfosse<sup>2,3</sup> indicate a Ni—Ni distance of 3.7 Å in  $\text{SrNi}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$ . Vannerberg<sup>18</sup> reports a Ni—Ni distance of 4.29 Å in  $\text{K}_2\text{Ni}(\text{CN})_4$ .

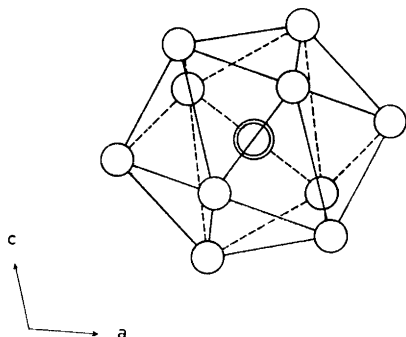


Fig. 5. Projection of barium co-ordination polyhedron on (010).



Other short Ni—Ni distances in planar, diamagnetic complexes are 3.25 Å in nickel dimethylglyoxime<sup>19</sup> and 2.65 Å in tris-mercaptoethyl phosphine nickel.<sup>20</sup>

We have prepared a compound  $\text{BaK}_2(\text{Ni}(\text{CN})_4)_2 \cdot 4\text{H}_2\text{O}$  which probably also has a short Ni—Ni distance. It is monoclinic with space group  $C2/c$  and with  $a=13.02$  Å,  $b=12.54$  Å,  $c=13.49$  Å and  $\beta=125^\circ 30'$ .

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