

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 $a = 12.07$, $b = 13.61$, $c = 6.72$, $\beta = 107^\circ.54$.

The square planar tetracyanonickelate groups are stacked along the c -axis. Adjacent groups are turned 45° 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 $22\ 000\ \text{cm}^{-1}$ according to Ballhausen, Bjerrum, Eriks, Dingle and Hare.¹ 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^{2,3} 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 mm³) were supplied by Professor Ballhausen.

A sphere of 0.13 mm diameter was ground in a "Bond sphere grinder".⁴ 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 cm^{-1} , for $\text{MoK}\alpha$ -radiation 60.0 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.^{2,3}

Data collection and reduction. Three dimensional data were measured with a linear diffractometer designed by Arndt and Phillips⁴ and manufactured by Hilger and Watts.

Mo-Radiation was employed. Balanced filters SrO , 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 program⁵ 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.⁷ 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 Danielsen⁸ and modified by one of us. Convergence was reached at $R=10.26\%$. Refinement continued using another least squares program. The program⁹ employs anisotropic temperature factors and a block diagonal approximation using 3×3 and 6×6 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 Stewart¹⁰ 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 $a=12.07_6$ Å, $b=13.61_0$ Å, $c=6.72_8$ Å, $\beta=107^{\circ}54'$, 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 g/cm³. Brasseur and de Rassenfosse found experimentally 2.38 g/cm³. 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 10⁴ in parentheses.

Atom	<i>x</i>	σx	<i>y</i>	σy	<i>z</i>	σz
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 10⁴. The expression used is $\exp - (h^2 b_{11} + \dots + 2hkb_{12} + \dots)$.

Atom	b_{11}	σb_{11}	b_{22}	σb_{22}	b_{33}	σb_{33}	b_{12}	σb_{12}	b_{13}	σb_{13}	b_{23}	σb_{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 Ni(CN)₄ group (Å).

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

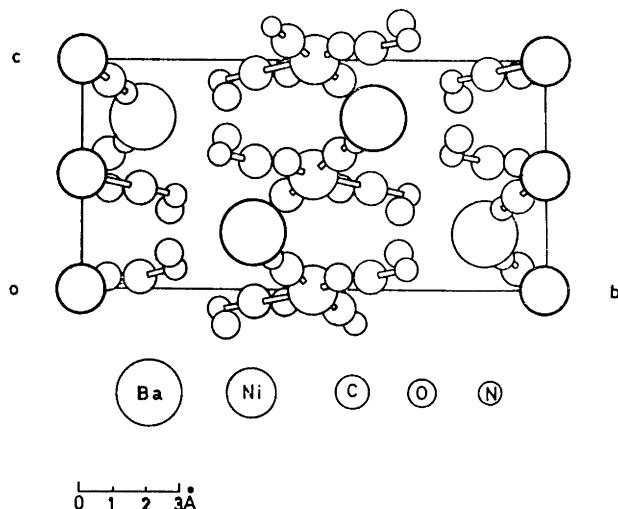
Fig. 1. Projection of a unit cell along the *a*-axis.

Table 3. Observed and calculated structure factors.

h	k	l	Obs.	Calc.	h	k	l	Obs.	Calc.	h	k	l	Obs.	Calc.	h	k	l	Obs.	Calc.	h	k	l	Obs.	Calc.	h	k	l	Obs.	Calc.		
-12	0	0	170	725	-2	2	1	194	1624	11	11	1	227	-175	6	2	471	408	12	2	3	317	-311	-13	2	3	491	469			
-12	0	0	186	167	2	2	1	132	1329	-1	12	1	508	-231	10	2	320	254	-10	2	3	494	466	11	2	3	504	473			
-10	0	0	1139	1137	4	2	1	1676	1801	2	12	1	428	-121	-11	7	2	594	-449	-9	3	3	504	473	12	2	3	504	473		
-8	0	0	1860	1954	6	2	1	1150	1134	2	12	1	555	-556	11	7	2	949	899	-7	3	3	504	473	11	2	3	504	473		
-6	0	0	1567	1562	8	2	1	943	953	4	12	1	207	-152	-9	7	2	1156	1126	-5	3	3	504	473	10	2	3	504	473		
-4	0	0	1264	1261	10	2	1	739	735	6	12	1	248	-12	7	2	1366	1325	-5	3	3	504	473	11	2	3	504	473			
-13	1	0	192	93	12	2	1	605	610	8	12	1	209	-233	5	7	2	1436	1479	1	3	3	504	473	11	2	3	504	473		
-9	1	0	256	-265	14	2	1	637	419	-9	13	1	638	624	-5	7	2	1736	1734	1	3	3	504	473	11	2	3	504	473		
-7	1	0	262	-253	15	3	1	591	-348	-7	13	1	675	700	-1	7	2	1694	1587	3	3	3	504	473	11	2	3	504	473		
-1	1	0	263	262	11	3	1	604	594	1	13	1	545	559	3	7	2	1693	1674	5	3	3	504	473	11	2	3	504	473		
-14	2	0	303	-595	11	3	1	604	-164	11	13	1	606	677	3	7	2	1692	1674	2	4	3	504	473	11	2	3	504	473		
-12	2	0	208	219	7	3	1	676	-686	-1	13	1	716	721	5	7	2	1310	1272	9	3	3	496	466	11	2	3	504	473		
-12	2	0	811	564	7	3	1	523	-681	11	13	1	714	528	7	7	2	869	792	11	2	3	345	358	11	2	3	345	358		
-10	2	0	417	593	5	3	1	595	-596	11	13	1	673	695	11	7	2	897	828	11	2	3	345	358	11	2	3	345	358		
-8	2	0	942	493	5	3	1	595	-596	11	13	1	724	765	11	7	2	694	667	-6	4	3	345	358	11	2	3	345	358		
-6	2	0	947	456	-1	3	1	1139	-1254	7	13	1	293	379	11	7	2	567	587	-6	4	3	345	358	11	2	3	345	358		
-4	2	0	1879	943	9	3	1	599	-574	9	12	1	410	370	-12	6	2	250	266	-1	4	3	345	358	11	2	3	345	358		
-2	2	0	702	549	9	3	1	1493	1493	1	12	1	414	344	9	8	2	269	221	-1	4	3	345	358	11	2	3	345	358		
-15	3	0	946	556	5	3	1	1009	-996	-6	13	1	718	797	-11	8	2	710	711	-1	4	3	345	358	11	2	3	345	358		
-13	3	0	711	712	7	3	1	783	-778	-1	13	1	810	784	-6	8	2	275	273	197	-1	4	3	345	358	11	2	3	345	358	
-11	3	0	729	711	11	3	1	592	-618	-1	13	1	714	751	-1	8	2	242	291	203	2	4	3	345	358	11	2	3	345	358	
-9	3	0	187	192	11	3	1	593	-596	11	13	1	674	574	11	7	2	930	896	275	2	4	3	345	358	11	2	3	345	358	
-7	3	0	1904	2007	15	3	1	513	-258	2	13	1	696	-709	0	8	2	708	724	-1	6	4	3	345	358	11	2	3	345	358	
-5	3	0	2000	208	-14	4	1	200	-108	4	14	1	625	-605	6	14	1	602	-503	2	8	2	359	401	-13	5	3	345	358		
-3	3	0	1666	1816	14	4	1	301	-344	6	14	1	624	-604	6	14	1	601	-502	6	8	2	359	401	211	-2	3	345	358		
-1	3	0	1747	1747	14	4	1	595	-596	6	14	1	623	-603	6	14	1	600	-501	6	8	2	359	401	211	-2	3	345	358		
-12	4	0	251	-271	-6	4	1	569	-337	-7	13	1	237	159	10	8	2	269	221	-1	4	3	345	358	11	2	3	345	358		
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-4	4	0	1657	1732	3	5	1	100	-1005	1	17	1	577	571	7	9	2	645	599	-1	4	3	345	358	11	2	3	345	358		
-2	4	0	373	367	5	5	1	1433	1451	1	17	1	558	578	9	9	2	643	625	1444	-1	4	3	345	358	11	2	3	345	358	
-1	6	0	122	1263	5	5	1	152	-152	1	17	1	510	533	10	10	2	346	336	1336	1350	-1	4	3	345	358	11	2	3	345	358
-8	6	0	1068	1011	5	5	1	960	902	1	13	1	505	508	12	10	2	482	427	1020	-1027	-1	4	3	345	358	11	2	3	345	358
-6	6	0	1747	1747	7	3	1	950	950	1	13	1	497	443	12	10	2	346	336	1146	1112	-1	4	3	345	358	11	2	3	345	358
-4	6	0	1273	1214	7	3	1	765	744	1	13	1	247	267	1	10	2	346	336	1146	1112	-1	4	3	345	358	11	2	3	345	358
-2	6	0	820	767	11	3	1	305	264	1	13	1	246	271	1	10	2	346	336	1146	1112	-1	4	3	345	358	11	2	3	345	358
-1	7	0	188	-125	15	3	1	247	240	-12	13	1	241	241	-10	10	2	346	336	1146	1112	-1	4	3	345	358	11	2	3	345	358
-1	7	0	155	-125	15	3	1	247	240	-12	13	1	241	241	-10	10	2	346	336	1146	1112	-1	4	3	345	358	11	2	3	345	358
-1	7	0	254	-288	15	3	1	247	240	-12	13	1	241	241	-10	10	2	346	336	1146	1112	-1	4	3	345	358	11	2	3	345	358
-1	7	0	373	-415	15	3	1	247	240	-12	13	1	241	241	-10	10	2	346	336	1146	1112	-1	4	3	345	358	11	2	3	345	358
-1	7	0	467	-533	15	3	1	1072	-1116	6	12	2	670	-666	10	12	2	265	223	-7	7	3	518	-508	1146	1112	-1	4	3	345	358
-1	7	0	537	-579	15	3	1	1115	1155	8	12	2	597	-601	10	12	2	265	223	518	-508	1146	1112	-1	4	3	345	358			
-1	7	0	723	719	15	3	1	1163	1043	-15	1	2	575	570	-11	12	2	409	360	518	-508	1146	1112	-1	4	3	345	358			
-1	7	0	242	235	15	3	1	247	240	-15	1	2	575	570	-11	12	2	409	360	518	-508	1146	1112	-1	4	3	345	358			
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-1	7	0	1067	1067	15	3	1	247	240	-15	1	2	575	570	-11	12	2	409	360	518	-508	1146	1112	-1	4	3	345	358			
-1	7	0	170	-169	15	3	1	247	240	-15	1	2	575	570	-11	12	2	409	360	518	-508	1146	1112	-1	4	3	345	358			
-1	7	0	760	760	15	3	1	247	240	-15	1	2	575	570	-11	12	2	409	360	518	-508	1146	1112	-1	4	3	345	358			
-1	7	0	721	692	15	3	1	941	-935	1	13	1	247	240	-15	12	2	346	336	518	-508	1146	1112	-1	4	3	345	358			
-1	7	0	476	476	15	3	1	247	240	-15	1	2	575	570	-11	12	2	409	360	518	-508	1146	1112	-1	4	3	345	358			
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-1	7	0	349	-345	15	3	1	785	-813	-14	13	2	683	659	-11	12	2	346	336	518	-508	1146	1112	-1	4	3	345	358			
-1	7	0	314	-310	15	3	1	927	-936	11	12	2	620	596	-11	12	2	346	336	518	-508	1146	1112	-1	4	3	345	358			
-1	7	0	657	653	15	3	1	1099	1113	12	12	2	428	-421	-11	7	2	594	549	-11	3	3	515	562	1146</td						

Table 3. Continued.

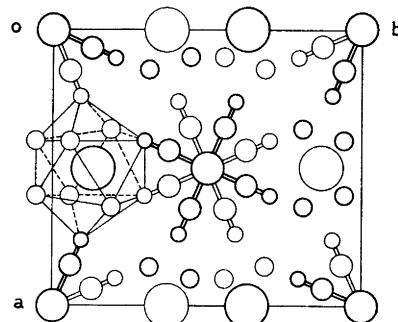


Fig. 2. Projection of a unit cell along the *c*-axis.

DISCUSSION

The nickel atoms are located in (0,0,0). This means that the tetracyano-nickelate groups are stacked in the *c* direction with a separation of $c/2 = 3.364 \text{ \AA}$ 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_{\pm} \AA . The correction for "riding motion" yields a mean value of 1.16_{\pm} \AA . Neither value differs significantly from C—N distances in other cyanides including HCN. An extensive review of cyanide distances is given by Britton.¹¹

The normal to the $\text{Ni}(\text{CN})_4$ plane forms an angle of $4^{\circ}46'$ with the *c*-axis. Simon and Toussaint¹² 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° 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.

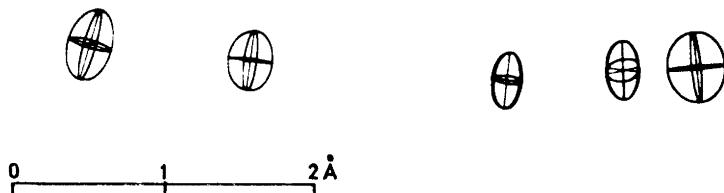


Fig. 3. Projection of principal vibration axes of $\text{Ni}(\text{CN})_4$ group on (100) plane.

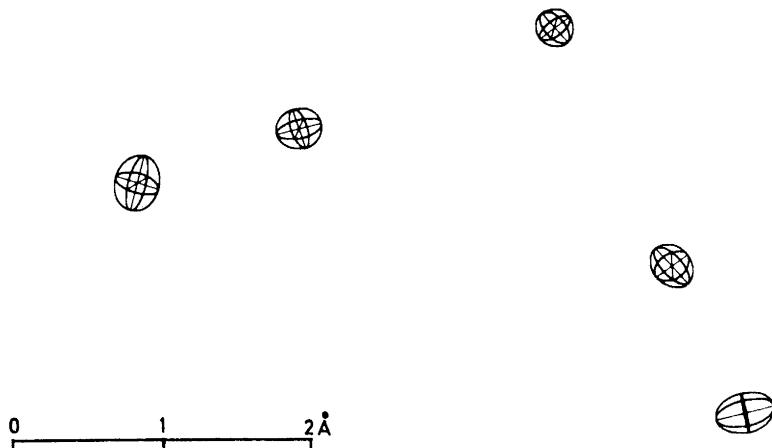


Fig. 4. Projection of principal vibration axes of $\text{Ni}(\text{CN})_4$ group on (001) plane.

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.¹³

The barium ion is also tenfold coordinated in BaHCl ,¹⁴ in BaC_2 ,¹⁵ and in hexagonal BaTiO_3 .¹⁶ Coordination numbers of 6, 8, 9, and 12 are reported in other crystalline barium compounds.

The cyanide groups of adjacent anions are turned 45° 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.¹⁷ The preliminary results of Brasseur and de Rassenfosse^{2,3} indicate a Ni—Ni distance of 3.7 Å in $\text{SrNi}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$. Vannerberg¹⁸ reports a Ni—Ni distance of 4.29 Å in $\text{K}_2\text{Ni}(\text{CN})_4$.

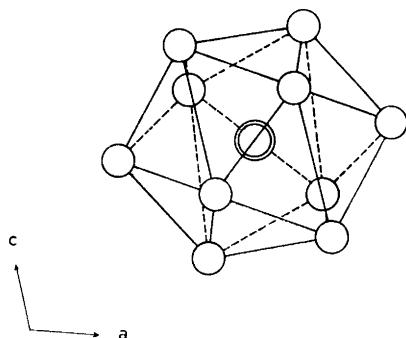


Fig. 5. Projection of barium co-ordination polyhedron on (010).

Other short Ni—Ni distances in planar, diamagnetic complexes are 3.25 Å in nickel dimethylglyoxime¹⁹ and 2.65 Å in tris-mercaptoethyl phosphine nickel.²⁰

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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REFERENCES

1. Ballhausen, C. J., Bjerrum, N., Eriks, K., Dingle, R. and Hare, C. *Inorg. Chem.* **4** (1965) 514.
2. Brasseur, H. and de Rassenfosse, A. *Mem. Acad. Roy. Belg.* **16** (1937) 1.
3. Brasseur, H. and de Rassenfosse, A. *Bull. Soc. Franc. Mineral.* **61** (1938) 129.
4. Bond, W. L. *Rev. Sci. Instr.* **22** (1951) 344.
5. Arndt, U. W. and Phillips, D. C. *Acta Cryst.* **14** (1961) 807.
6. Grønbæk, R. *Algol program G* (4) printed in this Department.
7. Lauesen, S. *Fourier program*, GIER machine code printed at Regnecentralen.
8. Danielsen, J. *Algol program D* (28) printed in this Department.
9. Grønbæk, R. *Algol program G* (3) printed in this Department.
10. Stewart, J. *X-Ray 63*, University of Maryland.
11. Britton, D. In Dunitz, J. D. and Ibers, J. A. *Perspectives in Structural Chemistry*, Vol. 1 (1967).
12. Simon, J. and Toussaint, J. *Bull. Soc. Roy. Sci. Liège* **32** (1963) 881.
13. Cundy, H. M. and Rollett, A. P. *Mathematical Models*, Oxford 1961.
14. Wells, A. F. *Structural Inorganic Chemistry* (1962) 329.
15. Wells, A. F. *Structural Inorganic Chemistry* (1962) 761.
16. Wells, A. F. *Structural Inorganic Chemistry* (1962) 495.
17. Holt, E. M. and Watson, K. J. *Acta Chem. Scand.* **23** (1969) 14.
18. Vannerberg, N.-G. *Acta Chem. Scand.* **18** (1964) 2385.
19. Godycki, L. and Rundle, R. E. *Acta Cryst.* **6** (1953) 487.
20. Grønbæk, R. *Submitted to Helv. Chim. Acta*.

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