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The Crystal Structure of Barium Tetracyanonickelate(II) Tetrahydrate

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The crystal structure of barium tetracyanonickelate(II) tetrahydrate, $BaNi(CN)_4,4H_2O$, 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 $a=12.07_6$, $b=13.61_0$, $c=6.72_8$, $\beta=107°.54$.

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 $BaNi(CN)_4$, $4H_2O$ have an unusually sharp absorption band at 22 000 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 $BaNi(CN)_4,4H_2O$ 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 mm^3) 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 Cu$K\alpha$ radiation.

The linear absorption coefficient for Cu$K\alpha$-radiation is 349.5 cm^{-1}, for Mo$K\alpha$-radiation 60.0 cm^{-1}.

The X-ray photographs showed that $BaNi(CN)_4,4H_2O$ 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 Phillips [5] 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 Mo$K\alpha$ beam.

The intensities measured were symmetry related in pairs. The diffractometer output was processed by a GIER computer using an ALGOL program [6] which evaluated intensities, calculated averages of symmetry related reflexions, applied Lp 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 Danielsen [8] and modified by one of us. Convergence was reached at $R=10.26$ %. Refinement continued using another least squares program. The program [9] 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 Stewart [10] 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 ±1 e/Å^3 near the barium atom and ±0.5 e/Å^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, $\beta=107°54'$, 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 10^4 in parentheses.

Atom	x	σx	y	σy	z	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 10^4. The expression used is $\exp-(h^2b_{11}+ \ldots 2hkb_{12}+ \ldots)$.

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

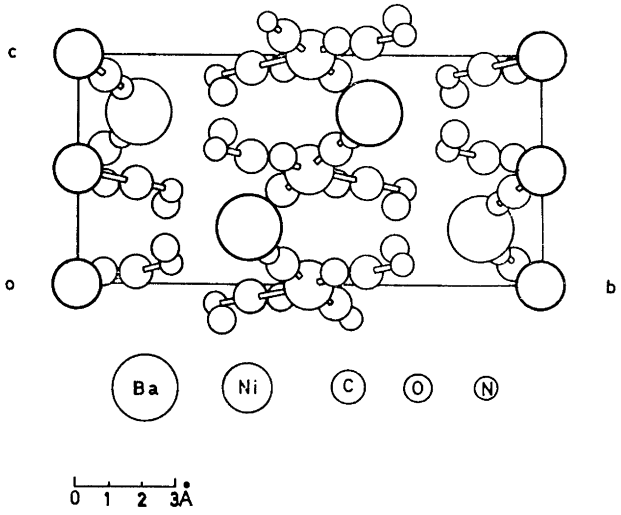

Fig. 1. Projection of a unit cell along the *a*-axis.

Table 3. Observed and calculated structure factors.

h	k	l	Fobs	Fcalc
-14	0	0	720	726
-12	0	0	1036	1067
-10	0	0	1139	1137
-8	0	0	1860	1954
-6	0	0	1567	1562
-4	0	0	1548	1641
-13	1	0	192	93
-11	1	0	256	-265
-9	1	0	268	-293
-7	1	0	268	-282
-5	1	0	303	-395
-14	2	0	208	219
-12	2	0	411	394
-10	2	0	417	390
-8	2	0	542	494
-6	2	0	547	456
-4	2	0	1079	948
-2	2	0	820	702
-15	3	0	546	556
-13	3	0	711	712
-11	3	0	739	711
-9	3	0	1097	1059
-7	3	0	1904	2007
-5	3	0	2000	2208
-3	3	0	1666	1816
-14	4	0	213	-174
-12	4	0	251	-271
-8	4	0	343	-393
-6	4	0	425	-475
-4	4	0	1151	-1187
-2	4	0	810	-820
0	4	0	1171	-1263
-15	5	0	352	349
-13	5	0	395	429
-11	5	0	1015	990
-9	5	0	1111	1096
-7	5	0	1155	1188
-5	5	0	1265	1268
-3	5	0	1831	1967
-1	5	0	1657	1732
-14	6	0	373	367
-12	6	0	352	319
-10	6	0	523	526
-8	6	0	613	559
-6	6	0	1068	1011
-4	6	0	793	685
-2	6	0	1273	1214
0	6	0	830	767
-13	7	0	188	-125
-11	7	0	167	-132
-9	7	0	254	-288
-7	7	0	373	-413
-5	7	0	549	-558
-3	7	0	423	-421
-1	7	0	407	-433
-14	8	0	537	579
-12	8	0	732	719
-10	8	0	942	943
-8	8	0	967	970
-6	8	0	1458	1467
-4	8	0	2072	2313
-2	8	0	1944	2056
0	8	0	1325	1348
-11	9	0	155	108
-9	9	0	252	-235
-5	9	0	218	-270
-1	9	0	293	229
-12	10	0	184	125
-8	10	0	250	247
-4	10	0	342	279
-2	10	0	151	78
0	10	0	400	332
-11	11	0	752	779
-9	11	0	1020	1022
-7	11	0	892	890
-5	11	0	1247	1217
-3	11	0	1461	1476
-1	11	0	1389	1361
-10	12	0	223	-257
-8	12	0	208	-238
-6	12	0	249	-275
-4	12	0	160	-189
-2	12	0	676	-674
0	12	0	769	-775
-9	13	0	530	498
-7	13	0	685	687
-5	13	0	714	702
-3	13	0	673	633
-1	13	0	753	734
-8	14	0	483	458
-6	14	0	506	515
-4	14	0	613	588
-2	14	0	740	706
0	14	0	721	692
-7	15	0	253	-282
-5	15	0	381	-356
-3	15	0	349	-345
-1	15	0	304	-310
-6	16	0	700	762
-4	16	0	667	653
-2	16	0	905	960
0	16	0	1060	1087
-1	17	0	170	56
-3	19	0	538	580
-1	19	0	680	698
-15	1	1	276	-297
-13	1	1	282	-274
-11	1	1	639	-629
-9	1	1	1045	-1041
-7	1	1	871	-829
-5	1	1	769	-748
-3	1	1	1206	-1126
-1	1	1	1271	-1320
3	1	1	1979	-2228
5	1	1	1221	-1221
7	1	1	481	-501
9	1	1	336	-355
11	1	1	628	-618
13	1	1	250	-303
-16	2	1	369	363
-14	2	1	200	307
-12	2	1	615	618
-10	2	1	714	683
-8	2	1	1285	1296
-6	2	1	1456	1468
-4	2	1	2264	2566
-2	2	1	1546	1684
0	2	1	1602	1781
2	2	1	1325	1329
4	2	1	1676	1801
6	2	1	1150	1134
8	2	1	964	953
10	2	1	738	736
12	2	1	605	610
14	2	1	437	419
-15	3	1	367	-348
-13	3	1	302	-324
-11	3	1	404	-404
-9	3	1	716	-686
-7	3	1	923	-881
-5	3	1	1031	-996
-3	3	1	734	-765
-1	3	1	1199	-1254
1	3	1	939	-874
3	3	1	1615	-1683
5	3	1	1009	-996
7	3	1	783	-778
11	3	1	392	-418
13	3	1	195	-210
15	3	1	313	-258
-14	4	1	200	-108
-10	4	1	301	-344
-8	4	1	270	258
-6	4	1	369	337
-4	4	1	568	-552
-2	4	1	1734	-1669
0	4	1	704	596
2	4	1	645	571
4	4	1	259	-255
6	4	1	379	-409
10	4	1	230	-159
-15	5	1	255	264
-9	5	1	530	565
-11	5	1	702	724
-9	5	1	568	605
-7	5	1	668	642
-5	5	1	1001	1005
-3	5	1	1433	1451
-1	5	1	1545	1558
1	5	1	1456	1512
3	5	1	960	982
5	5	1	921	950
7	5	1	939	951
9	5	1	765	744
11	5	1	345	321
13	5	1	247	240
15	5	1	219	224
-16	6	1	311	-276
-14	6	1	357	-345
-12	6	1	500	-508
-10	6	1	697	-714
-8	6	1	1072	-1116
-6	6	1	1131	-1155
-4	6	1	1368	-1403
-2	6	1	1588	-1689
0	6	1	1783	-1937
2	6	1	1195	-1237
4	6	1	903	-925
6	6	1	903	-911
8	6	1	942	-961
10	6	1	796	-785
12	6	1	515	-519
14	6	1	237	-291
-13	7	1	467	441
-11	7	1	429	413
-9	7	1	250	263
-7	7	1	535	514
-5	7	1	767	779
-3	7	1	529	537
-1	7	1	1068	1072
1	7	1	971	981
3	7	1	658	621
5	7	1	388	378
7	7	1	850	867
9	7	1	418	410
11	7	1	212	163
-10	8	1	197	227
-8	8	1	215	215
-6	8	1	473	483
-4	8	1	263	224
0	8	1	294	260
2	8	1	691	672
4	8	1	224	191
6	8	1	178	158
10	8	1	169	170
-13	9	1	490	-489
-11	9	1	495	-497
-9	9	1	526	-511
-7	9	1	781	-817
-5	9	1	958	-935
-3	9	1	977	-971
-1	9	1	1012	-1030
1	9	1	1258	-1290
3	9	1	786	-813
5	9	1	937	-930
7	9	1	767	-785
9	9	1	580	-599
11	9	1	195	-210
13	9	1	264	-298
-12	10	1	389	386
-10	10	1	552	557
-8	10	1	677	715
-6	10	1	1018	1033
-4	10	1	1070	1072
-2	10	1	1239	1267
0	10	1	1099	1113
2	10	1	949	943
4	10	1	710	732
6	10	1	818	851
8	10	1	727	726
10	10	1	595	576
12	10	1	403	387
-11	11	1	317	-337
-9	11	1	325	-310
-7	11	1	296	-279
-5	11	1	308	-313
-3	11	1	395	-371
-1	11	1	539	-525
1	11	1	630	-618
3	11	1	509	-518
5	11	1	334	-337
7	11	1	307	-307
9	11	1	274	-233
11	11	1	227	-175
-8	12	1	304	-231
-6	12	1	508	-526
0	12	1	428	-421
2	12	1	556	-556
4	12	1	207	-152
6	12	1	248	-212
8	12	1	209	-233
-9	13	1	638	624
-7	13	1	675	700
-5	13	1	561	589
-3	13	1	686	677
-1	13	1	714	721
1	13	1	923	928
3	13	1	877	895
5	13	1	795	815
7	13	1	393	379
9	13	1	410	370
-8	14	1	410	-454
-6	14	1	778	-797
-4	14	1	810	-784
-2	14	1	751	-760
0	14	1	572	-582
2	14	1	696	-709
4	14	1	625	-605
6	14	1	602	-585
8	14	1	411	-444
-7	15	1	227	159
-3	15	1	313	314
-1	15	1	217	211
1	15	1	192	200
3	15	1	369	352
5	15	1	341	384
-4	16	1	403	368
-2	16	1	407	418
0	16	1	268	252
4	16	1	242	271
6	16	1	289	295
-5	17	1	452	-447
-3	17	1	577	-571
-1	17	1	577	-571
1	17	1	558	-578
3	17	1	532	566
5	17	1	510	-513
-2	18	1	505	508
0	18	1	407	443
2	18	1	487	464
-1	19	1	267	-98
1	19	1	241	-126
-12	0	2	506	-528
-8	0	2	595	564
-6	0	2	1283	-1294
-4	0	2	1541	-1465
2	0	2	1310	-1270
4	0	2	804	842
6	0	2	670	-666
8	0	2	597	-601
10	0	2	285	-234
-15	1	2	577	630
-13	1	2	836	837
-11	1	2	792	730
-9	1	2	1075	1014
-7	1	2	1366	1303
-5	1	2	2189	2185
-3	1	2	2308	2247
1	1	2	1473	1415
3	1	2	1641	1589
5	1	2	1435	1381
7	1	2	1502	1433
9	1	2	842	751
11	1	2	714	681
13	1	2	465	495
15	1	2	402	438
-14	2	2	323	315
-12	2	2	304	274
-10	2	2	561	495
-8	2	2	954	847
-6	2	2	1196	1050
-4	2	2	350	299
-2	2	2	452	427
2	2	2	1503	1344
4	2	2	822	716
6	2	2	456	429
8	2	2	443	417
10	2	2	448	391
12	2	2	416	401
14	2	2	267	252
-11	3	2	186	-242
-7	3	2	199	-229
-5	3	2	627	-625
-3	3	2	308	-374
-1	3	2	750	-741
1	3	2	1114	-1055
3	3	2	315	-379
5	3	2	301	219
9	3	2	285	-297
11	3	2	170	-93
13	3	2	688	659
-12	4	2	1130	1081
-10	4	2	1406	1357
-8	4	2	1789	1774
-6	4	2	1752	1753
-4	4	2	2058	2106
-2	4	2	2163	2231
0	4	2	2220	2377
2	4	2	2076	2089
4	4	2	1880	1901
6	4	2	1710	1691
8	4	2	1286	1279
10	4	2	959	963
12	4	2	626	630
14	4	2	510	473
-5	5	2	246	-289
-3	5	2	187	-211
-1	5	2	582	-571
1	5	2	399	372
3	5	2	454	-458
5	5	2	232	237
-12	6	2	304	290
-10	6	2	268	209
-8	6	2	313	279
-6	6	2	197	-211
-4	6	2	786	699
-2	6	2	644	555
0	6	2	312	256
2	6	2	268	183
4	6	2	491	432
6	6	2	471	408
8	6	2	320	254
10	6	2	249	248
-13	7	2	594	549
-11	7	2	949	899
-9	7	2	1150	1126
-7	7	2	1446	1425
-5	7	2	1496	1479
-3	7	2	1736	1734
-1	7	2	1604	1587
1	7	2	1973	2034
3	7	2	1682	1674
5	7	2	1310	1272
7	7	2	869	792
9	7	2	893	852
11	7	2	634	687
13	7	2	567	587
-12	8	2	250	-206
-10	8	2	587	-572
-8	8	2	710	-711
-6	8	2	246	-273
-4	8	2	242	-291
-2	8	2	906	-905
0	8	2	704	-724
2	8	2	359	-401
4	8	2	655	-621
6	8	2	553	-553
8	8	2	269	-221
10	8	2	278	-225
12	8	2	224	-206
-13	9	2	424	424
-11	9	2	657	650
-9	9	2	813	789
-7	9	2	805	782
-5	9	2	1074	989
-3	9	2	1118	1057
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1	9	2	1292	1249
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0 12 7	189	174
-5 13 7	312	-315
-3 13 7	285	-303
-1 13 7	265	-331
-12 0 8	477	455
-10 0 8	622	580
-8 0 8	703	712
-6 0 8	608	582
-4 0 8	557	526
-2 0 8	501	508
0 0 8	514	497
2 0 8	415	446
-7 1 8	205	-220
-5 1 8	173	-224
-1 1 8	187	-162
-12 2 8	219	133
-8 2 8	164	193
-4 2 8	131	205
-2 2 8	124	79
-13 3 8	420	399
-11 3 8	496	486
-9 3 8	499	492
-7 3 8	351	373
-5 3 8	504	501
-3 3 8	592	590
-1 3 8	599	573
1 3 8	518	481
3 3 8	505	504
-12 4 8	245	-244
-10 4 8	319	-312
-8 4 8	364	-348
-6 4 8	345	-347
-4 4 8	344	-353
-2 4 8	325	-308
0 4 8	267	-258
2 4 8	202	-170
4 4 8	208	-164
-11 5 8	406	360
-9 5 8	376	353
-7 5 8	539	467
-5 5 8	451	444
-3 5 8	477	438
-1 5 8	434	389
1 5 8	473	435
3 5 8	297	351
-10 6 8	233	224
-8 6 8	274	252
-6 6 8	205	188
-4 6 8	229	186
-2 6 8	287	281
0 6 8	242	223
2 6 8	200	182
-9 7 8	212	-208
-7 7 8	181	-190
-5 7 8	211	-243
-3 7 8	225	-178
-1 7 8	256	-206
1 7 8	259	-229
-10 8 8	485	506
-8 8 8	586	594
-6 8 8	556	552
-4 8 8	542	554
-2 8 8	578	561
0 8 8	594	502
2 8 8	578	594
-5 11 8	414	458
-3 1 9	225	-228
-1 1 9	241	-201
-3 1 9	256	-304
-1 1 9	222	-240
1 1 9	225	-212
-10 2 9	374	387
-8 2 9	333	349
-6 2 9	255	344
-4 2 9	333	418
-2 2 9	327	347
0 2 9	364	327
-9 3 9	183	-208
-7 3 9	251	-257
-5 3 9	373	-402
-3 3 9	247	-273
-1 3 9	289	-274
-9 5 9	348	299
-7 5 9	288	307
-5 5 9	290	337
-3 5 9	320	291
-1 5 9	257	251
-8 6 9	196	-227
-6 6 9	360	-365
-4 6 9	339	-282
-2 6 9	278	-279
-5 7 9	176	191

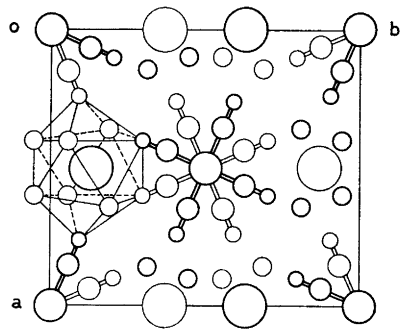

Fig. 2. Projection of a unit cell along the *c*-axis.

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 $Ni(CN)_4^{2-}$ 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.[11]

The normal to the $Ni(CN)_4$ plane forms an angle of 4°46′ with the *c*-axis. Simon and Toussaint [12] have investigated the anisotropy of the diamagnetism of $BaNi(CN)_4,4H_2O$. 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.

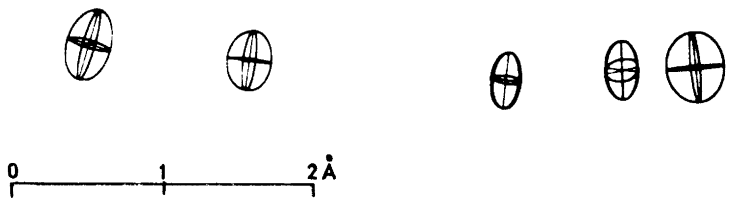

Fig. 3. Projection of principal vibration axes of $Ni(CN)_4$ group on (100) plane.

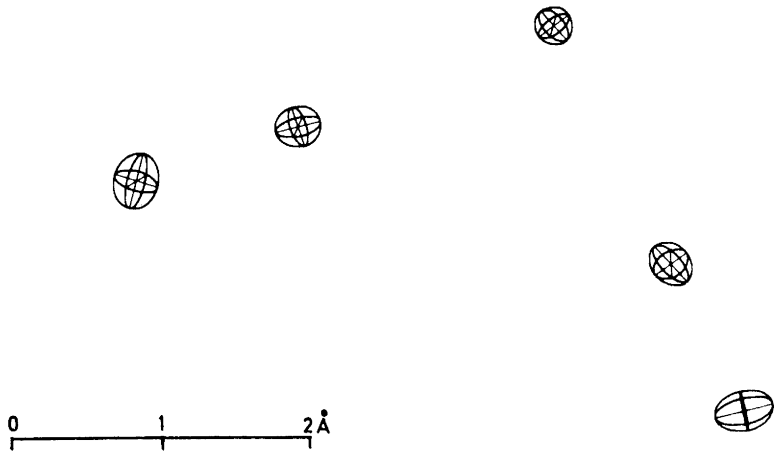

Fig. 4. Projection of principal vibration axes of $Ni(CN)_4$ group on (001) plane.

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 $SrNi(CN)_4,5H_2O$. Vannerberg[18] reports a Ni—Ni distance of 4.29 Å in $K_2Ni(CN)_4$.

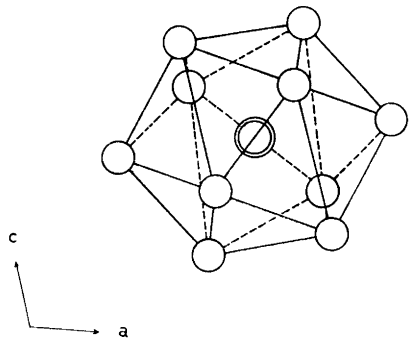

Fig. 5. Projection of barium co-ordination polyhedron on (010).

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

We have prepared a compound $BaK_2(Ni(CN)_4)_2,4H_2O$ 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 $\beta=125°30$.

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