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The Crystal Structure of Calcium Cyanamide

NILS-GÖSTA VANNERBERG

Department of Inorganic Chemistry, Chalmers University of Technology, Göteborg, Sweden

The crystal structure of calcium cyanamide has been reinvestigated using threedimensional X-ray data. The bond length C—N was found to be 1.22 ± 0.02 Å.

To be able to study the solubility of calcium cyanamide in calcium carbide it is necessary to know the dimensions of the cyanamide ion accurately. The crystal structure of calcium cyanamide was first investigated by X-ray methods by Dehlinger [1]. He found that the compound had rhombohedral symmetry with $a = 5.11$ Å and $\alpha = 43°50'$. The C—N bond distance was found to be about 1.6 Å, an improbable large distance. Bredig [2] some years later confirmed the rhombohedral symmetry but found the unit cell edge to be 5.40 Å, while the interaxial angle was 39°55′. Moreover, the C—N distance was determined to 1.16 ± 0.08 Å, in agreement with the known bond lengths in isoelectronic groups, for instance in N_3^-, NCO^- or CO_2 (Ref.[3]). The figure is very little accurate, as the author also observes. The investigation was based on a sample which contained only 70 % calcium cyanamide. Only 13 powder diffraction lines were registered. A refinement of the structure of calcium cyanamide seemed consequently to be desirable.

PREPARATION OF THE COMPOUND

Calcium cyanamide was prepared from calcium carbonate and hydrogen cyanide [4]. A mixture of nitrogen and hydrogen cyanide vapor was led over pure calcium carbonate at a temperature of about 800°C.

$CaCO_3(s) + 2HCN(g) \rightleftharpoons CaCN_2(s) + CO(g) + H_2(g) + CO_2(g)$ The sample which contained 96 % calcium cyanamide and had very small crystallite size, was then heated to 1300°C in a nitrogen atmosphere. The preparation did not lose any nitrogen under this treatment. It melted or at least sintered and the product contained well developed crystals suited for single crystal work.

The nitrogen content was in all cases determined by the Kjeldahl method.

DETERMINATION OF THE CRYSTAL STRUCTURE

The elementary cell dimensions were determined with the aid of X-ray powder photographs using the Guinier technique; NaCl was used as internal

Table 1. Powder diffraction data for $CaCN_2$. $a = 5.347 \pm 0.004$ Å $\alpha = 40°26' \pm 10'$.

hkl	$10^4\sin^2\Theta_{obs}$	$10^4\sin^2\Theta_{calc}$	I_{obs}
111	248	247	w
110	688	690	vs
211	1018	1020	m
221	1262	1267	s
$1\bar{1}0$	1740	1740	s
322	1926	1926	m
210	1982	1988	m
332	2338	2338	w
200	2426	2430	m
321	2725	2729	w
220	2753	2756	w
433	3328	3327	w
331	3658	3666	w
444	3960	3955	w
432		3965	
$2\bar{1}1$	4169	4171	w
320	4753	4748	vw

Table 2. Parameter values for $CaCN_2$. Space group $R\bar{3}m$.

Atom	Position	Number	*x*	*y*	*c*
Ca	*a*	1	0	0	0
C	*b*	1	½	½	½
N	*c*	2	0.4168	0.4168	0.4168

standard. A comparison of calculated and determined $\sin^2\Theta$ values can be found in Table 1.

The unit cell was found to be rhombohedral

$$a = 5.347 \pm 0.004 \text{ Å}$$
$$\alpha = 40°26' \pm 10'$$

The structural investigation was based on single crystal methods. The single crystals were mounted inside capillary tubes in order to prevent atmospheric attack. Filtered Mo$K\alpha$ radiation was used. The crystals were rotated about $[1\bar{1}0]$ and all zones detectable with Mo radiation were registered using an integrating Weissenberg camera and a multiple film technique. The intensities were estimated by visual comparison with known scales, and corrected by Lorentz and polarization factors. The absorption could be neglected as the crystals were very small, about 0.1 mm, while the radiation was hard.

No systematic extinctions were found. The space group was assumed to be $R\bar{3}m$. The atomic parameters, Table 2, were calculated from a threedimensional Fourier synthesis using a Besk electronic computer [5,6]. The observed and calculated structure factors can be found in Table 3. The errors in the atomic parameters were calculated by Cruichkshank's method.

Table 3. Observed and calculated structure factors for $CaCN_2$.

hkl	F_o	F_c	*hkl*	F_o	F_c
200	32.3	31.4	$32\bar{1}$	13.0	11.1
300	9.0	11.1	$42\bar{1}$	11.9	10.3
400	9.1	9.7	222	14.7	17.1
500	9.1	8.3	322	30.2	29.4
101	46.7	48.1	422	15.2	15.6
201	18.9	17.7	522	8.0	9.4
301	14.0	15.0	622	9.8	12.1
401	13.0	13.0	323	19.9	20.1
$10\bar{1}$	49.3	43.2	423	14.4	13.5
$20\bar{1}$	6.4	6.1	523	16.7	17.6
$30\bar{1}$	13.8	16.5	723	11.9	11.1
202	18.7	18.7	424	19.3	21.0
302	16.9	18.3	524	8.7	4.8
402	10.2	8.6	624	13.5	15.4
502	10.6	10.1	$22\bar{4}$	9.8	8.7
$20\bar{2}$	19.3	20.3	525	13.8	17.0
303	9.5	9.6	725	9.8	9.8
403	11.3	12.5	626	9.7	10.5
503	8.8	8.1	$23\bar{1}$	13.0	11.4
$30\bar{3}$	10.5	11.4	$33\bar{1}$	9.2	11.4
505	9.4	8.9	$33\bar{2}$	9.0	7.1
211	29.3	26.1	333	15.5	17.2
311	21.3	23.6	433	24.9	26.7
411	8.1	9.6	434	6.7	6.2
511	8.7	11.1	534	22.3	22.8
$11\bar{1}$	4.9	6.6	734	10.8	11.5
$21\bar{1}$	26.0	23.7	635	12.8	14.6
$31\bar{1}$	9.7	9.7	735	11.3	6.3
$41\bar{1}$	9.0	8.8	636	8.3	7.1
212	35.1	34.3	$44\bar{1}$	9.2	8.1
312	13.4	13.6	444	25.5	28.6
412	15.8	17.0	544	6.2	5.5
512	10.6	10.1	644	13.4	16.5
$11\bar{2}$	22.6	24.2	744	8.2	7.1
$21\bar{2}$	8.2	4.6	844	12.0	6.7
$31\bar{2}$	12.5	13.0	545	15.7	19.4
313	20.4	21.4	645	9.3	9.0
413	12.5	13.0	745	9.1	9.0
513	9.9	8.3	646	10.8	10.1
613	11.8	11.2	746	10.9	10.1
$11\bar{3}$	7.6	4.1	555	9.4	10.4
414	8.4	9.3	655	9.5	11.4
514	14.2	13.8	755	9.6	11.2
714	10.9	9.5	656	10.8	12.8
116	9.3	6.6	756	9.4	7.1
316	11.8	12.9			
417	10.9	9.7			

Table 3. cont.

hkl	F_o	F_c	*hkl*	F_o	F_c
856	9.7	9.2	867	10.3	6.3
757	9.6	10.0	868	10.6	10.0
857	10.7	7.1	877	11.6	11.0
666	8.2	8.0	888	19.1	11.5
766	11.3	11.4			
767	8.9	8.7			

DISCUSSION

The structure is built up by calcium and cyanamide CN_2^{2-} ions. Each calcium ion is octahedrally surrounded by six nitrogen atoms belonging to six different cyanamide ions, and each cyanamide ion is octahedrally surrounded by six calcium ions. The distance between the nitrogen atom and a calcium ion is 2.461 ± 0.016 Å. The cyanamide ion is linear as are all the isoelectronic species, for instance the carbon dioxide molecule and the azide ion. The cyanamide ion has a somewhat lower nuclear charge so its interatomic distances are somewhat longer than in the mentioned species. This distance between the nitrogen and carbon atom is 1.224 ± 0.016 Å. It is worth while to compare the bond distances in the three isoelectronic species N_2, CN^- and C_2^{2-} with the corresponding distances in N_3^-, CN_2^{2-} and C_3^{4-}.

Species	Electronic structure	Bond distances
N_2	:N:::N:	1.095 Å
CN^-	:C:::$\bar{N}$:	1.168 Å
C_2^{2-}	:$\bar{C}$:::$\bar{C}$:	1.20 Å
N_3^-	$^{-}$:$\ddot{N}$::$^{+}$N::$\ddot{N}$:$^{-}$	1.17 Å
CN_2^{2-}	$^{-}$:$\ddot{N}$::C::$\ddot{N}$:$^{-}$	1.224 Å
C_3^{4-}	:$\bar{\bar{C}}$::C::$\bar{\bar{C}}$:	1.309 Å

The values for the bond lengths were taken from Ref.[3] In some cases the bond lengths for the corresponding hydrides were used.

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