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Syntheses, crystal structures, and vibrational spectroscopic properties of $MgCN_2$, $SrCN_2$, and $BaCN_2$

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Abstract

The alkaline-earth metal cyanamides $MgCN_2$, $SrCN_2$, and $BaCN_2$ were prepared by the reaction of melamine with the metal nitrides (Mg_3N_2, Sr_2N, Ba_3N_2) at temperatures between 740 °C and 850 °C. $MgCN_2$ was structurally characterized by X-ray analysis using powder methods ($R\bar{3}m$, $Z=3$, $a=327.34(1)$ pm, $c=1412.82(5)$ pm). The crystal structures of $SrCN_2$ and $BaCN_2$ were determined from X-ray single crystal data ($SrCN_2$: $Pnma$, $Z=4$, $a=1241.0(2)$ pm, $b=396.3(2)$ pm, $c=538.9(2)$ pm, $BaCN_2$: $R\bar{3}c$, $Z=18$, $a=1528.2(2)$ pm, $c=701.3(2)$ pm). All compounds consist of the respective cations and CN_2^{2-}-anions with an increasing degree of distortion of the coordination polyhedra with increasing radii of the cations. The structural features are correlated with vibrational spectroscopic data.

1. Introduction

Cyanamide (H_2CN_2) and its salts are well known compounds with a versatile field of applications. Numerous synthetic routes have been proposed for metal cyanamides, however, their preparation in a pure and well-defined state has not been unambiguously achieved. Additionally, reliable structural data are only available for $CaCN_2$ [1].

Strid and co-workers obtained $SrCN_2$ [2] and $BaCN_2$ [3] by the reaction of the respective carbonates with hydrogen cyanide at temperatures between 600 °C and 650 °C, but they were unable to solve the crystal structures completely. For $MgCN_2$ no structural data have been reported.

Here we present a novel simple procedure leading to pure and crystalline cyanamides, and we succeeded in growing single crystals of $SrCN_2$ and $BaCN_2$. To our surprise, the crystallographic data we obtained are not in agreement with those reported by Strid.

2. Experimental details

2.1. *Syntheses*

$MgCN_2$, $SrCN_2$, and $BaCN_2$ were prepared by the reaction of the respective nitrides (Mg_3N_2, Sr_2N, Ba_3N_2) with an excess of melamine [$C_3N_3(NH_2)_3$]. After homogenization in a ball mill, the reaction mixture is heated in a tungsten crucible under argon atmosphere for two days at 220 °C, then for another two days at higher temperatures ($MgCN_2$: 750 °C, $SrCN_2$: 850 °C, $BaCN_2$: 740 °C). Under these conditions the products are yielded as colourless powders. Single crystals of $SrCN_2$ were obtained by increasing the temperature to 980 °C; for the crystal growth of $BaCN_2$ the microcrystalline product was annealed at 740 °C for five days.

The nitrides have been synthesized by reaction of the metals (Mg: 99.995% Alfa Ventron, Sr: 99.95% ABCR, Ba: 99.95% ABCR) with pure nitrogen (Sr_2N, Ba_3N_3) or ammonia (Linde 3.8, Mg_3N_2). Melamine (p.a., Janssen) was purified by sublimation.

The purity of all products was checked by elemental analyses (only metals) and X-ray diffraction; the absence of amide and imide contamination was proved by infrared (IR) spectroscopy.

To exclude moisture and oxygen, all operations have been performed using Schlenk techniques under a purified argon atmosphere.

2.2. *X-ray structure determination and structure calculation*

For intensity data collection $MgCN_2$ powder and single crystals of $SrCN_2$ and $BaCN_2$ were sealed under dry argon in glass capillaries. The crystal structure of $MgCN_2$ was determined from X-ray powder diffraction data collected on a Stoe Stadi P diffractometer. The

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TABLE 1. Crystallographic data for $MgCN_2$, $SrCN_2$ and $BaCN_2$

	$MgCN_2$	$SrCN_2$	$BaCN_2$
Data collected from	powder	single crystal	single crystal
Space group (No.)	$R\bar{3}m$(166)	$Pnma$(62)	$R\bar{3}c$(167)
Unit cell dimensions (pm)	$a=327.34(1)$ $c=1412.82(5)$	$a=1241.0(2)$ $b=396.3(2)$ $c=538.9(2)$	$a=1528.2(2)$ $c=701.3(2)$
Volume (pm × 10^6)	131.10(1)	265.0(2)	1418.4(5)
Formula weight	64.3	127.7	177.4
Density calc. (g cm^{-3})	2.445	3.199	3.738
Z	3	4	18
Absorption coefficient (mm^{-1})	4.6	20.0	12.3
Diffractometer used	Stoe Stadi P	Nonius CAD4	Siemens P4
Radiation (pm)	$CuK\alpha_1=154.056$	$MoK\alpha=71.069$	$MoK\alpha=71.069$
Monochromator	Germanium	Graphite	Graphite
2θ-range	3–104	2–64	2–60
Scan type	Debye–Scherrer	ω	ω
Reflections collected	5053 datapoints	1881	2682
Independent reflections	28	497(R_{int}: 4.33%)	649(R_{int}: 2.34%)
Observed reflections	28($>4\sigma$)	422($>3\sigma$)	585($>3\sigma$)
Solution and refinement	Rietveld method Full profile [4]	Patterson method SHELXS-86 [5] SHELX-76 [6]	Patterson method SHELX TL-PLUS [7]
Number of parameters refined	7	26	24
Final R values	$R_{I,hkl}=4.5\%$ $R_{pro}=10.8\%$	$R=4.96\%$ $wR=4.04\%$	$R=4.40\%$ $wR=3.85\%$

structure was refined by using the Rietveld full-profile technique.

Intensity measurements of $SrCN_2$ and $BaCN_2$ were performed on four-circle diffractometers, in both cases the structures were solved using Patterson's method.

Further details of data collection and the results of the X-ray structure determination are shown in Table 1.

2.3. *Vibrational spectroscopic investigations*

Infrared spectra were recorded on a Bruker IFS 113 v vacuum spectrometer equipped with two deuterated triglycin sulfat (DTGS) detectors, measuring a range from 150 cm^{-1} to 4000 cm^{-1}. $MgCN_2$ and $SrCN_2$ were measured as CsI pellets, $BaCN_2$ was mixed with KBr. To avoid broad and extremely tailed bands through the Christiansen effect caused by the hardness of the cyanamides, the salts have been ground in a micro ball mill before mixing with CsI or KBr.

The Raman spectra were excited by an argon ion laser (Amko, Coderg LRT 800) at a wavelength of 514.5 nm. In this case the pure probes were sealed in glass capillaries.

All preparation procedures have been performed in a glove-box under a dry argon atmosphere ($H_2O<0.2$ ppm, $O_2<1$ ppm).

3. Results

3.1. *The crystal structure of $MgCN_2$*

The crystal structure of magnesium cyanamide has to be considered as an ionic layer structure isostructural to the high temperature (or β) phase of NaN_3 [8] and $CaCN_2$. The cations as well as the anions form close-packed arrangements in the unit cell with each ion coordinated by six counterions. The terminal nitrogen atoms surround the Mg^{2+}-ions as a regular octahedron (Fig. 1), whereas the coordination polyhedron around the CN_2^{2-}-ion (C–N: 124.8(2) pm, NCN: 180°) can be regarded either as an elongated octahedron or as a trigonal antiprism.

The central C-atom of the anion occupies a centre of symmetry, the two nitrogen atoms are generated by only one crystallographic site resulting in $D_{\infty h}$ symmetry of the anion. The positional and isotropic displacement parameters for $MgCN_2$ are shown in Table 2, bond lengths, interatomic distances and bond angles are summarized in Table 3.

3.2. *The crystal structure of $SrCN_2$*

In strontium cyanamide, Sr^{2+}-ions and nearly linear CN_2^{2-}-groups have been found. The N–C–N angle (178.8(9)°) may be regarded as 180° with respect to the standard deviation, the C–N bond lengths (122.8(10),

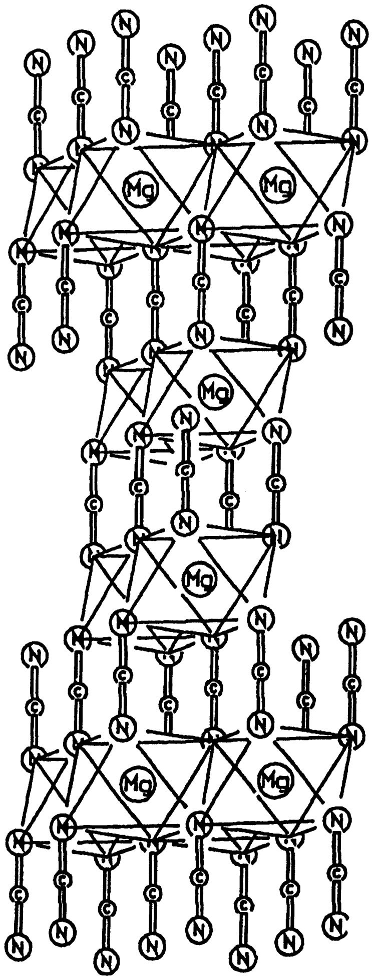

Fig. 1. A view of the layer structure of $MgCN_2$ with the MgN_6-octahedra along [210].

122.2(11) pm) are nearly equal despite two crystallographically independent sites of nitrogen.

Anions in two orientations built up layers parallel to the *a–c* plane of the unit cell. The cations also belong to these layers, forming distorted octahedra around the anions visualized as an Ortep plot in Fig. 2. Distorted nitrogen octahedra centred by Sr^{2+}-ions are connected by corner sharing and by NCN-bridges. A view of the structure is depicted in Fig. 3.

Atomic sites and anisotropic displacement parameters are listed in Table 2, important bond lengths and bond angles are shown in Table 3.

3.3. *The crystal structure of* $BaCN_2$

In barium cyanamide no layer structure occurs, but a three-dimensional arrangement of Ba^{2+}-ions and CN_2^{2-}-groups (C–N: 119.2(11) pm) has been found. The CN_2^{2-}-anion is crystallographically generated by one site of carbon and nitrogen each leading to an N–C–N bond angle of 177.2(18)°. However, the sig-

TABLE 2. Positional and anisotropic displacement parameters for $MgCN_2$, $SrCN_2$ and $BaCN_2$

Compound	Atom	Site	x^a	y^a	z^a	$U_{11}{}^b$	$U_{22}{}^b$	$U_{33}{}^b$	$U_{12}{}^b$	$U_{13}{}^b$	$U_{23}{}^b$
$MgCN_2$	Mg	3a	0	0	0	21.8(1) Uiso					
	C	3b	0	0	1/2	22.4(1) Uiso					
	N	6c	0	0	5883(1)	24.8(1) Uiso					
$SrCN_2$	Sr	4c	1309(1)	1/4	1144(1)	13(1)	11(1)	10(1)	0	1(1)	0
	C	4c	3765(6)	1/4	1160(14)	12(3)	11(2)	12(2)	0	9(4)	0
	N(1)	4c	3273(6)	1/4	−819(12)	16(3)	22(3)	10(3)	0	0(2)	0
	N(2)	4c	4236(6)	1/4	3152(13)	17(3)	19(3)	11(2)	0	−1(2)	0
$BaCN_2$	Ba	18e	1947(1)	0	1/4	32(1)	37(1)	22(1)	19(1)	1(1)	3(1)
	C	18e	7691(9)	0	1/4	27(4)	37(7)	116(11)	19(4)	−9(4)	−18(8)
	N	36g	1995(9)	−591(11)	−1219(11)	53(5)	101(9)	51(3)	40(6)	−4(4)	−9(5)

[a] Atomic coordinates (*10⁴).
[b] The U_{ij} are defined as $\exp\{-2\pi^2(U_{11}h^2a^{*2}+\ldots+2U_{23}klb^*c^*)\}$ in pm^2*10^{-1}.

TABLE 3. Selected bond distances (pm) and bond angles (°) (standard deviations in parentheses) of $MgCN_2$, $SrCN_2$, and $BaCN_2$

	$MgCN_2$	$SrCN_2$	$BaCN_2$
Distances			
C–N	124.8(2)	122.8(10)N1 122.2(11)N2	119.2(11)
M–N	219.0(1)	262.2(4)N1 265.7(8)N1 260.1(8)N2 264.3(5)N2	277.3(9) 284.2(9) 286.7(12)
M–M	327.34(1)	396.3(1) 400.0(1) 446.4(1)	435.1(1) 459.9(1)
Bond angles			
N=C=N	180.00(8)	178.8(9)	177.2(18)

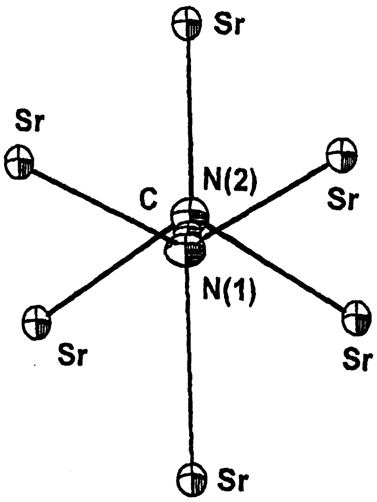

Fig. 2. Coordination around the CN_2^{2-}-ion in $SrCN_2$ (ellipsoids drawn at 50% probability).

nificance of this deviation from linearity has to be analysed by vibrational spectroscopic investigations (*cf.* Section 3.4).

The Ba^{2+}-cations are coordinated in the crystal structure by six different anions in a rather irregular way (Fig. 4). The polyhedron formed by the cations around the CN_2^{2-}-group represents a twisted trigonal prism shown as an Ortep plot in Fig. 5. The observed N–C–N bond angle of 177.2(18)° suggests a reduction of the anion's symmetry from $D_{\infty h}$ to C_{2v}.

Table 2 contains the atomic sites and the anisotropic displacement parameters of the compound. Selected bond lengths, interatomic distances and bond angles are summarized in Table 3.

3.4. *Vibrational spectroscopic properties*

The vibrational spectra of alkaline-earth metal cyanamides show the typical band sequence of a linear three-atomic arrangement with $D_{\infty h}$ symmetry (Fig. 6). As expected by the selection principle for molecules containing an inversion centre, the asymmetric stretching and the deformation vibration of the CN_2^{2-}-group are allowed in IR spectra, whereas the symmetric stretching mode is Raman active. If the symmetry of a three atomic ion is lowered from $D_{\infty h}$ to C_{2v}, as assumed for the cyanamide anion in $BaCN_2$, the sym-

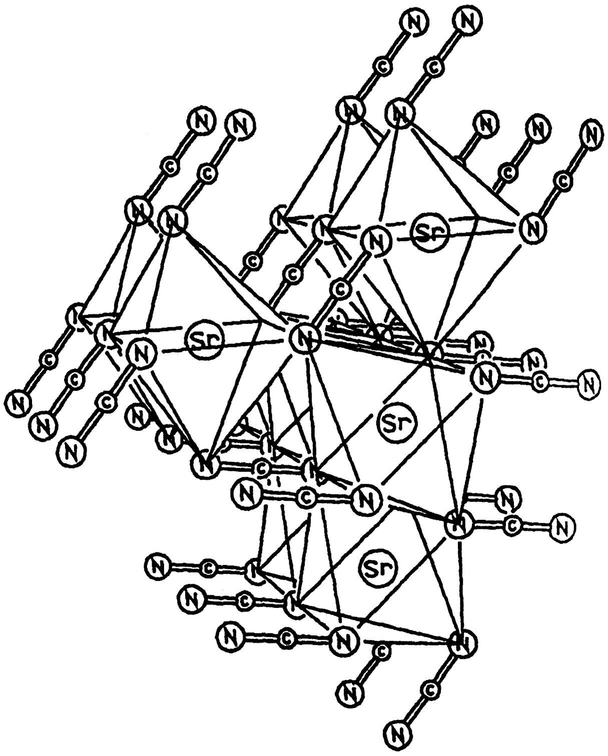

Fig. 3. The view of the $SrCN_2$ structure along [010] with the coordination polyhedra around the cations.

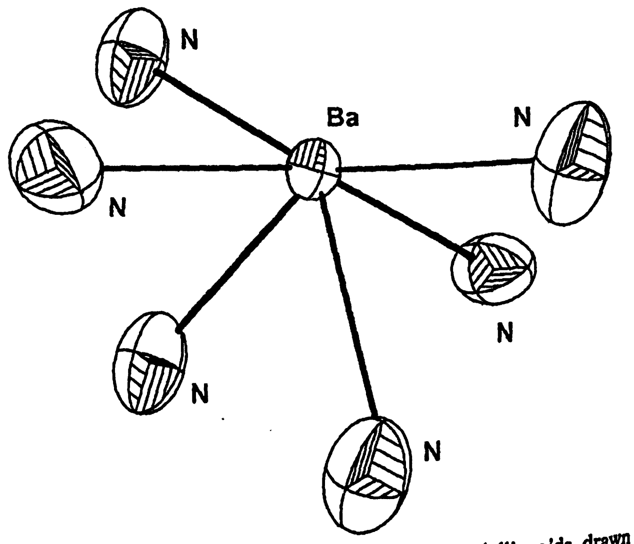

Fig. 4. Coordination sphere of Ba in $BaCN_2$ (ellipsoids drawn at 50% probability).

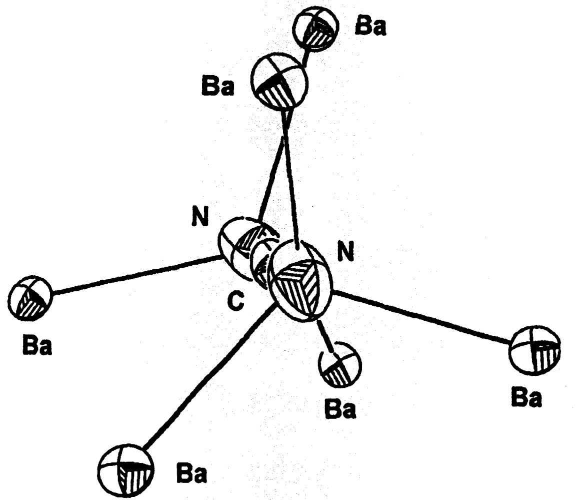

Fig. 5. The twisted trigonal prismatic coordination of the CN$_2$$^{2-}$-group in BaCN$_2$ by the barium cations (ellipsoids drawn at 50% probability).

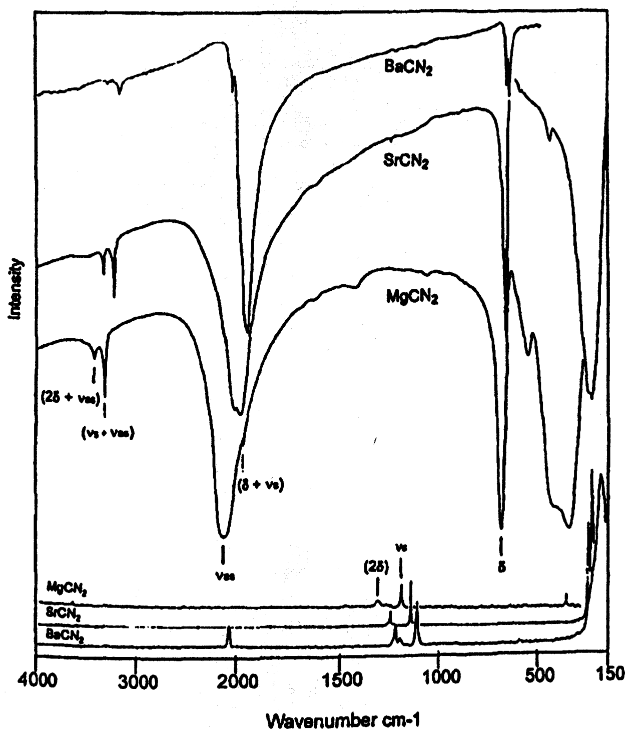

Fig. 6. Infrared and Raman spectra of MgCN$_2$, SrCN$_2$, and BaCN$_2$.

metric stretching vibration is no longer forbidden in the IR spectra and has to be observable. Since there is no hint of a ν_s-vibration in the IR spectrum of BaCN$_2$, we consider the deviation from linearity as determined by X-ray structure analysis not to be significant. So the symmetry of the anion is $D_{\infty h}$ rather than C_{2v}. For SrCN$_2$, the ν_{as}-bond is split as a result of the two crystallographically independent nitrogen atoms of the anion. Nevertheless, even in this spectrum no symmetrical stretching vibration appears which would indicate the lower C_{2v} symmetry of the CN$_2$$^{2-}$-group.

TABLE 4. Vibrational frequencies and force constants

Compound	ν_s [cm^{-1}]	ν_{as} [cm^{-1}]	δ [cm^{-1}]	f_{CN} [Ncm^{-1}]	$f_{CN/CN}$ [Ncm^{-1}]	f_{NCN} [Ncm^{-1}]
MgCN$_2$	1301	2114	681	12.52	1.45	0.57
SrCN$_2$	1251	1989 2023	663 677	11.44	1.48	0.54
BaCN$_2$	1238	1947	662 673	11.02	1.63	0.54

f_{CN}, $f_{CN/CN}$ = valency force constants.
f_{NCN} = deformation force constant.
μ_N, μ_c = reciprocal masses of carbon and nitrogen.
c = constant = $5.891\,46 \times 10^{-7}$.
$(f_{CN} + f_{CN/CN}) \times \mu_N = c \times \nu_s^2$.
$(f_{CN} - f_{CN/CN}) \times (\mu_N + 2\mu_c) = c \times \nu_{as}^2$.
$f_{NCN} \times 2 \times (\mu_N + 2\mu_c) = c \times \delta^2$.

The bands of the deformation vibration are split in the IR spectra of SrCN$_2$ and BaCN$_2$. This may be an effect of the asymmetric coordination of the anions by the cations which leads to the suppression of the degeneracy of the δ-vibration.

The vibrational frequencies and force constants [9] are shown in Table 4.

4. Conclusions

All three alkaline-earth metal cyanamides investigated contain linear CN$_2$$^{2-}$-anions. Though in all three crystal structures the ions are coordinated by six counterions, the crystal structures are not directly related to each other. In MgCN$_2$ we found alternating layers of cations and anions. In SrCN$_2$ the layers contain both ions, and finally in BaCN$_2$ we no longer have a layer structure but a three-dimensional arrangement of the ions in the solid.

With increasing radii of the cations, the regularity of coordination polyhedra of both, anions and cations, decrease. Although the C–N bond lengths in all cyanamides investigated are of comparable lengths, the vibrational frequencies of the ν_{as} and ν_s-bands decrease with increasing radii of the corresponding cations in the same way as the force constant f_{CN} (Table 4). An analogous effect has been observed in the spectroscopic data of orthonitrates [10] and can be explained by the reciprocal relation between the polarization of the nitrogen atoms and the size of the cations. This polarization reduces the repulsion between the lone pairs of the nitrogen atoms. Consequently, the antibonding interactions decrease and the C–N bonding gets stabilized.

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