

M(CN)₂ Species (M = Be, Mg, Ca, Sr, Ba): Cyanides, Nitriles, or Neither?

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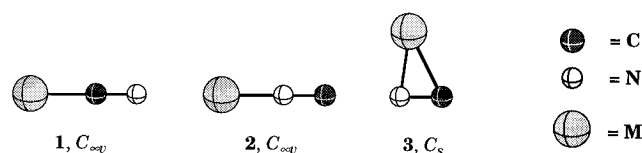
The “cyanide” salts of the group 2 (alkaline earth) metals exhibit remarkable structural variations: CN[−] binds to the metals via the carbon, via the nitrogen, and via bridged arrangements. The most stable geometries of the beryllium and the magnesium salts are linear (CNBeNC and NCMgCN, respectively), but CaC₂N₂, SrC₂N₂, and BaC₂N₂ prefer twisted, bridged structures. However, several stationary points of the bridged complexes are close in energy, and considerable fluxionality is to be expected. These theoretical predictions (MP4SDTQ/6-311+G-(2d)//MP2(fu)/6-31+G*, Ca, Sr, Ba: 5s5p3d1f//5s5p3d basis sets and 10 valence electron pseudopotentials) invite experimental verification.

Introduction

In contrast to the alkali metal cyanides,¹ little is known about the corresponding alkaline earth metal compounds² although they have some importance in organic synthesis³ and in technical chemistry.⁴ While the patent literature in the last decade concerning the industrial uses of alkaline earth metal cyanides is extensive, comprehensive theoretical or experimental studies have not been undertaken. The solid state structure of beryllium cyanide—first purely synthesized in 1963—was assumed to be polymeric with tetracoordinated beryllium atoms.⁵ Computations on a hypothetical Be(CN)₂ solid state structure were performed to evaluate the material properties,⁶ while calculations of linear Be(NC)₂ and Mg(CN)₂ molecules gave geometries, ionization potentials, and heats of formation.^{7,8} However, no complete investigations of the potential energy surfaces at high theoretical levels have been reported and the heavier alkaline earth metal cyanides have not been considered.

Some compounds of the heavier group 2 metals (Ca, Sr, Ba) adopt nonlinear geometries,⁹ contrary to the VSEPR rules. The influence of core polarization on the coordination chemistry of calcium, strontium, and barium is now well established,¹⁰ as well as the increasing importance of d-orbital participation in

Chart 1



the small covalent contributions to the metal–ligand bonds.^{9a–c} These two explanations are complementary; detailed discussions of the alkaline earth metal coordination are given by Bytheway et al.¹⁰ and Kaupp et al.¹¹ While barium compounds are rather strongly bent, strontium analogs possess smaller linearization barriers, and calcium derivatives are linear or almost so (quasi-linear). The bending is increased by greater substituent electronegativity but decreases by π donation. Consequently, CH₃ groups result in the largest bending.^{9c}

Furthermore, the different structures of the alkali metal cyanide complexes are also noteworthy. The minima can be bridged (**3**) as well as linear nitrile (**2**) and linear isonitrile (**1**) forms (Chart 1). The preferred geometry of these ionic complexes depends on the alkali metal.¹ Lithium nitrile (**2**) is favored over the bridged form (**3**) and lithium isonitrile (**1**), but neither the sodium nor the potassium nitrile is a minimum. Instead, the bridged isomers **3** (M = Na, K) have the lowest energies.

Consequently, complexes of CN[−] anions and alkaline earth metal cations can be expected to have many structural possibilities, e.g. linear or bent forms corresponding to **1–3**. Hence, we computed the potential energy surfaces of the M(CN)₂ compounds of all group 2 elements at high ab initio levels in order to locate the global minima.

Computational Details

All structures were fully optimized within the chosen symmetries, first at Hartree–Fock and then at the electron-correlated MP2 level of

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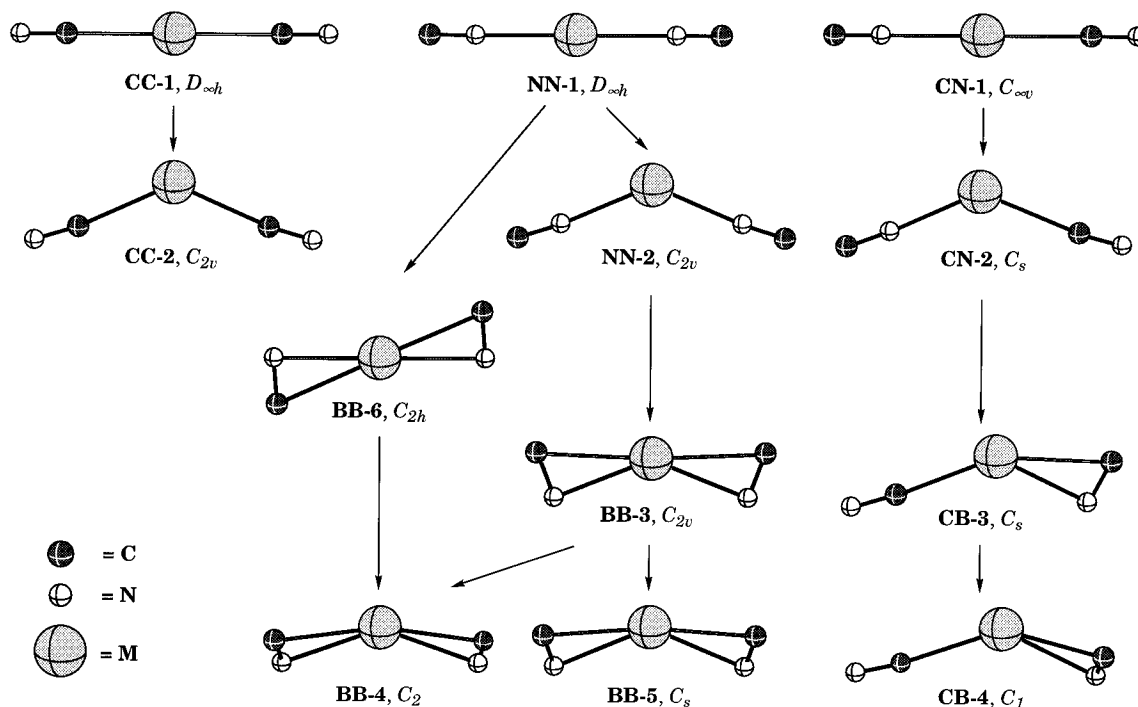


Figure 1. Schematic representations of the MC_2N_2 ($M = Be, Mg, Ca, Sr, Ba$) structures considered.

theory.¹² Frequency calculations at both levels gave zero-point vibrational energies and the number of imaginary frequencies (which characterize the nature of the stationary points). The GAUSSIAN series of programs was employed using the 6-31+G* standard basis set for the elements C, N, Be, and Mg.^{13,14} Quasirelativistic pseudopotentials (ECP) replaced the core electrons of heavier group 2 elements:¹⁵ 10 valence electron ECP together with 6s6p5d basis sets contracted to 5s5p3d.¹¹ MP4SDTQ single-point calculations were performed at the stationary points to include higher level electron correlation.¹⁶ The 6-311+G(2d) basis set was used for C, N, Be, and Mg,¹⁷ while the Ca, Sr, and Ba basis sets were augmented by an additional f function.¹¹ The natural atomic charges and bond orders discussed are based on Reed and Weinhold's natural population analysis (NPA).¹⁸

Three main types of CN^- coordination to the alkaline earth metals are possible: both ligands may be coordinated via the nitrogen atoms (NN), via the carbon atoms (CC), and via mixed C/N coordination (CN). These linear structures were chosen as starting points of the potential energy hypersurface scan ($D_{\infty h}$ and $C_{\infty v}$). Analysis of the negative eigenvectors then helped to locate other stationary points (Figure 1).

Results

BaC₂N₂ and SrC₂N₂. The energy differences between the structures are greatest and the largest variety of isomers occurs for the heaviest group 2 metal compounds. An overview of the BaC₂N₂ and SrC₂N₂ hyperfaces is given in Figure 1 (see Table 1 for the bond lengths). All linear structures (CC-1, NN-1, CN-1) are second-order saddle points (NIMAG = 2); the molecules bend toward C_{2v} symmetry. These findings are in line with extensive previous investigations of other alkaline earth metal derivatives.^{9,11} The bent end-on isomers (CC-2, NN-2, CN-2) are minima at the Hartree-Fock level—but at the electron-correlated MP2 level this is true only for CC-2. The MP2 geometry optimization of NN-2 led to a bridged complex in C_{2v} symmetry, which is denoted BB-3. The N-coordinated CN^- moiety of CN-2 also bent resulting in CB-3 with C_s geometry.

However, these **planar** side-on coordinated complexes are not minima! BB-3 is a second-order saddle point and CB-3 a transition state. Instead, the side-on ligands prefer to twist out of the molecular plane: the C_1 minimum with the mixed C/N coordination has no symmetry (CB-4), while the minimum of the double side-on coordinated complex adopts point group C_2 (BB-4). In the C_s transition state BB-5, both cyanide substituents bend from the molecular plane in the same direction. A second possible path from the linear NN-1 toward BB-4 involves the C_{2h} symmetric BB-6, but this is a second-order saddle point rather than a true transition structure.

The differences in energy between the various structures of BaC₂N₂ and SrC₂N₂ are quite similar.¹⁹ Two trends are clear (Table 2): First, coordination via nitrogen atoms is preferred

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- (19) All compounds are extremely stable toward homolytic dissociation in the gas phase and should therefore be observable. ΔE_{Diss} according to $M(CN)_2 \rightarrow M + 2CN^\bullet$: Be 255, Mg 215, Mg 237, Ca 237, and Ba 332 kcal/mol (vs the most stable $M(CN)_2$ isomer; MP4SDTQ/MP2 + ZPE; see text). These values are only an estimation of the stabilities, since the energy of the CN^\bullet radical cannot be calculated exactly by the Møller-Plesset perturbation theory, due to large spin contamination (calc, 101.9 kcal/mol; exp, 88.1 kcal/mol): (a) Baker, J. *J. Chem. Phys.* **1989**, *91*, 1789. (b) Baker, J. *Chem. Phys. Lett.* **1988**, *152*, 227.

Table 1. Selected MP2 Geometry Parameters (Å; deg) (See Figure 1)

| | M(CN) ₂ | NC | CM | MN | NC | M...C ^a | ∠XMY ^b | ∠NCM | ∠MNC | ∠NMNC ^c |
|-------------|-------------------------|-------|-------|-------|-------|--------------------|-------------------|--------|--------|--------------------|
| <i>Be</i> | CC-1 | 1.187 | 1.644 | | | | | | | |
| | NN-1 | | | 1.524 | 1.195 | | | | | |
| | CN-1 | 1.187 | 1.644 | 1.522 | 1.195 | | | | | |
| <i>Mg</i> | CC-1 | 1.188 | 2.044 | | | | | | | |
| | NN-1 | | | 1.927 | 1.195 | | | | | |
| | BB-3 | | | 2.033 | 1.203 | 2.243 | 151.5° | | 83.5° | |
| | BB-4 | | | 2.051 | 1.203 | 2.209 | 156.3° | | 80.9° | 44.8° |
| | BB-6 | | | 2.048 | 1.203 | 2.221 | | | 81.7° | |
| | CN-1 | 1.188 | 2.039 | 1.928 | 1.195 | | | | | |
| | CB-3 | 1.188 | 2.042 | 2.051 | 1.203 | 2.219 | 164.0° | 179.9° | 81.5° | |
| <i>Ca</i> | CC-1 | 1.193 | 2.385 | | | | | | | |
| | NN-1 | | | 2.239 | 1.198 | | | | | |
| | BB-3 | | | 2.349 | 1.202 | 2.510 | 149.9° | | 83.3° | |
| | BB-4 | | | 2.353 | 1.202 | 2.497 | 157.7° | | 82.4° | 46.9° |
| | BB-6 | | | 2.356 | 1.202 | 2.500 | | | 82.4° | |
| | CN-1 | 1.193 | 2.385 | 2.239 | 1.198 | | | | | |
| | CB-3 | 1.193 | 2.377 | 2.360 | 1.202 | 2.502 | 162.6° | 179.2° | 82.4° | |
| <i>Sr</i> | CC-1 | 1.194 | 2.565 | | | | | | | |
| | CC-2 | 1.194 | 2.542 | | | | 147.6° | 173.2° | | |
| | NN-1 | | | 2.409 | 1.199 | | | | | |
| | <i>NN-2^d</i> | | | 2.402 | 1.166 | | 158.0° | | 179.3° | |
| | BB-3 | | | 2.514 | 1.201 | 2.698 | 148.7° | | 85.4° | |
| | BB-4 | | | 2.521 | 1.201 | 2.680 | 155.4° | | 84.2° | 45.2° |
| | BB-5 | | | 2.512 | 1.201 | 2.689 | 145.2° | | 85.0° | 29.9° |
| | BB-6 | | | 2.532 | 1.201 | 2.678 | | | 83.6° | |
| | CN-1 | 1.194 | 2.564 | 2.409 | 1.199 | | | | | |
| | <i>CN-2^d</i> | 1.150 | 2.588 | 2.392 | 1.166 | | 156.0° | 177.2° | 179.8° | |
| CB-3 | 1.194 | 2.550 | 2.519 | 1.202 | 2.703 | 155.7° | 177.2° | 85.4° | | |
| CB-4 | 1.194 | 2.544 | 2.521 | 1.201 | 2.679 | 151.7° | 174.0° | 84.1° | 48.9° | |
| <i>Ba</i> | CC-1 | 1.195 | 2.768 | | | | | | | |
| | CC-2 | 1.195 | 2.707 | | | | 131.0° | 171.8° | | |
| | NN-1 | | | 2.604 | 1.199 | | | | | |
| | <i>NN-2^d</i> | | | 2.563 | 1.166 | | 133.7° | | 174.7° | |
| | BB-3 | | | 2.673 | 1.201 | 2.943 | 137.5° | | 90.7° | |
| | BB-4 | | | 2.678 | 1.201 | 2.906 | 139.9° | | 88.5° | 60.3° |
| | BB-5 | | | 2.682 | 1.201 | 2.892 | 135.2° | | 87.6° | 45.7° |
| | BB-6 | | | 2.725 | 1.201 | 2.885 | | | 85.2° | |
| | CN-1 | 1.195 | 2.770 | 2.602 | 1.200 | | | | | |
| | <i>CN-2^d</i> | 1.150 | 2.755 | 2.550 | 1.166 | | 133.2° | 173.0° | 174.8° | |
| | CB-3 | 1.194 | 2.721 | 2.641 | 1.202 | 2.975 | 132.7° | 173.2° | 93.9° | |
| CB-4 | 1.194 | 2.715 | 2.683 | 1.202 | 2.880 | 135.1° | 172.4° | 86.9° | 65.6° | |

a) Side-on structures. b) X, Y = N, C. c) Dihedral angle. d) HF-geometries (shown in italics) are given for forms which are not stationary points at MP2.

in linear structures. For BaC₂N₂, each N coordination is favored by about 2.8 kcal/mol over C coordination (Sr: ~2.3 kcal/mol). Second, the most stabilizing effect involves side-on coordinated CN⁻ fragments; out-of-plane twisting is of minor importance. The side-on **BB-3** is 5.9–6.7 kcal/mol more stable than the linear end-on **NN-1** for both metals. The side-on coordination of a single CN⁻ anion is stabilized by 4.5 kcal/mol (Ba) and by 3.1 kcal/mol (Sr), respectively (**CB-1** → **CB-3**). However, the energy differences among the second-order saddle points **BB-3** and **BB-6**, the transition state **BB-5**, and the minimum structure **BB-4** are very small: 0.0–0.8 kcal/mol for BaC₂N₂ and 0.2–0.3 kcal/mol for SrC₂N₂. The same is true for the

isomers with mixed C/N coordination: the C₁ symmetric **CB-4** is 0.4 kcal/mol more stable than the planar **CB-3** (Ba), while both conformers have almost the same energy for the strontium compound.

Bending, e.g. in going from end-on **CC-1** (*D_{∞h}*) to end-on **CC-2** (*C_{2v}*), results in only a small energy gain; this is found generally.^{9,11} The linearization barrier of the barium compound is larger than that of the strontium compound (Ba, 2.8 kcal/mol; Sr, 0.3 kcal/mol).

CaC₂N₂ and MgC₂N₂. Although there are significant differences in the structural chemistry of calcium and magnesium compounds,²⁰ the same stationary points occur in both the

Table 2. MP4SDTQ/MP2 Total and Relative Energies, MP2 Zero-Point Vibrational Energies (ZPE), and Number of Imaginary Frequencies (NIMAG) (au; and kcal/mol) (See Figure 1)

| M(CN) ₂ | | total energy | ZPE | NIMAG | relative energy (incl. ZPE ^a) |
|-------------------------|-------------------------|--------------|------------|-------|---|
| <i>Be</i> | CC-1 | -200.04826 | 10.62 | 0 | 3.87 |
| | NN-1 | .05434 | 10.57 | 0 | 0.00 |
| | CN-1 | .05176 | 10.71 | 0 | 1.75 |
| <i>Mg</i> | CC-1 | -385.01556 | 9.22 | 0 | 0.00 |
| | NN-1 | .01417 | 8.99 | 0 | 0.66 |
| | BB-3 | .00989 | 7.96 | 1 | 2.40 |
| | BB-4 | .01006 | 8.08 | 0 | 2.39 |
| | BB-6 | .00957 | 7.92 | 1 | 2.56 |
| | CN-1 | .01494 | 9.11 | 0 | 0.29 |
| | CB-3 | .01304 | 8.47 | 0 | 0.89 |
| <i>Ca</i> | CC-1 | -222.14500 | 7.46 | 0 | 8.60 |
| | NN-1 | .15193 | 7.65 | 0 | 4.42 |
| | BB-3 | .15852 | 7.53 | 1 | 0.17 |
| | BB-4 | .15900 | 7.67 | 0 | 0.00 |
| | BB-6 | .15844 | 7.54 | 1 | 0.23 |
| | CN-1 | .14843 | 7.51 | 0 | 6.48 |
| | CB-3 | .15221 | 7.60 | 0 | 4.20 |
| <i>Sr</i> | CC-1 | -215.96501 | 7.02 | 2 | 10.55 |
| | CC-2 | .96607 | 7.42 | 0 | 10.26 |
| | NN-1 | .97267 | 7.15 | 2 | 5.87 |
| | <i>NN-2^b</i> | .97978 | 8.18 | 0 | 7.76 |
| | BB-3 | .98180 | 7.17 | 2 | 0.16 |
| | BB-4 | .98229 | 7.33 | 0 | 0.00 |
| | BB-5 | .98185 | 7.24 | 1 | 0.20 |
| | BB-6 | .98158 | 7.16 | 2 | 0.29 |
| | CN-1 | .96879 | 7.12 | 2 | 8.28 |
| | <i>CN-2^b</i> | .96617 | 8.42 | 0 | 10.87 |
| | CB-3 | .97395 | 7.24 | 1 | 5.15 |
| | CB-4 | .97413 | 7.37 | 0 | 5.16 |
| | <i>Ba</i> | CC-1 | -210.67687 | 6.84 | 2 |
| CC-2 | | .68200 | 7.25 | 0 | 9.54 |
| NN-1 | | .68585 | 6.78 | 2 | 6.69 |
| <i>NN-2^b</i> | | .68723 | 8.05 | 0 | 6.74 |
| BB-3 | | .69624 | 6.97 | 2 | 0.34 |
| BB-4 | | .69702 | 7.13 | 0 | 0.00 |
| BB-5 | | .69699 | 7.10 | 1 | 0.00 |
| BB-6 | | .69544 | 6.95 | 2 | 0.82 |
| CN-1 | | .68127 | 6.82 | 2 | 9.59 |
| <i>CN-2^b</i> | | .68231 | 8.35 | 0 | 10.10 |
| CB-3 | | .68886 | 7.10 | 1 | 5.09 |
| CB-4 | | .68938 | 7.23 | 0 | 4.70 |

Values of 'free' CN⁻: -92.67974 a.u. and 2.85 kcal/mol (ZPE). ^a) Calibrated by 0.92. ^b)MP4SDTQ/HF-energies (shown in italics) are given for forms which are not stationary points at MP2.

Ca and Mg potential energy surfaces (Figure 1, Table 1). However, the relative energies of the stationary points are completely different (Table 2).¹⁹

All linear CaC₂N₂ and MgC₂N₂ structures are minima, even at the MP2 level of theory (**CC-1**, **NN-1**, **CN-1**). Bent minima **NN-2**, **CN-2**, and **CC-2** do not exist; optimization led to linear geometries. Nevertheless, a few species with side-on coordi-

nated CN⁻ ligands could be located at MP2, but the number of stationary points was less compared with BaC₂N₂ and SrC₂N₂. The *C*_{2h} **BB-6** and the *C*_{2v} **BB-3** are transition states (instead of second-order saddle points for M = Ba, Sr), and **BB-5** is not a stationary point. However, the *C*₂ **BB-4** again is the "side-on minimum". The diminished out-of-plane twisting also is reflected in the structures with mixed C/N coordination: **CB-3** is a minimum (*C*_s); no *C*₁ **CB-4** isomer exists.

CaC₂N₂ behaves like its heavier congeners. N coordination is preferred by about 2.1 kcal/mol for each CN⁻ group. Side-on coordination sharply lowers the energy by about 2.3 kcal/mol for a single CN⁻ (**CN-1** → **CB-3**), and 4.2 kcal/mol for

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Table 3. Natural Atomic Charges (NAC) and Bond Orders (NPA/NLMO) of the MP4SDTQ//MP2 CI One-Particle Density (See Figure 1)

| M(CN) ₂ | Natural atomic charges | | | | | NPA bond orders | | | | | |
|--------------------|-------------------------|-------------|-------------|--------------|---------------|-----------------|--------------|-------------|-------------|--------------|------|
| | N | C | M | N | C | NC | CM | MN | NC | M...C | |
| <i>Be</i> | CC-1 | -285 | -470 | 1.510 | | | 2.705 | .236 | | | |
| | NN-1 | | | 1.712 | -1.244 | .388 | | | .103 | 1.591 | |
| | CN-1 | -299 | -468 | 1.612 | -1.249 | .403 | 2.694 | .228 | .137 | 1.578 | .035 |
| <i>Mg</i> | CC-1 | -383 | -472 | 1.710 | | | 2.612 | .137 | | | |
| | NN-1 | | | 1.866 | -1.212 | .279 | | | .060 | 1.705 | |
| | BB-3 | | | 1.754 | -856 | -.021 | | | .075 | 2.048 | .097 |
| | BB-4 | | | 1.747 | -827 | -.047 | | | .074 | 2.078 | .101 |
| | BB-6 | | | 1.750 | -838 | -.037 | | | .075 | 2.066 | .099 |
| | CN-1 | -385 | -481 | 1.791 | -1.208 | .283 | 2.609 | .130 | .065 | 1.702 | .023 |
| | CB-3 | -389 | -472 | 1.730 | -831 | -.038 | 2.604 | .136 | .077 | 2.069 | .100 |
| <i>Ca</i> | CC-1 | -452 | -487 | 1.878 | | | 2.543 | .064 | | | |
| | NN-1 | | | 1.941 | -1.182 | .212 | | | .029 | 1.770 | |
| | BB-3 | | | 1.854 | -843 | -.085 | | | .044 | 2.097 | .064 |
| | BB-4 | | | 1.852 | -836 | -.091 | | | .044 | 2.104 | .065 |
| | BB-6 | | | 1.854 | -837 | -.090 | | | .044 | 2.104 | .065 |
| | CN-1 | -457 | -488 | 1.912 | -1.185 | .219 | 2.537 | .057 | .033 | 1.764 | |
| | CB-3 | -456 | -481 | 1.863 | -835 | -.092 | 2.537 | .066 | .043 | 2.105 | .064 |
| <i>Sr</i> | CC-1 | -481 | -476 | 1.914 | | | 2.515 | .047 | | | |
| | CC-2 | -480 | -470 | 1.899 | | | 2.515 | .055 | | | |
| | NN-1 | | | 1.960 | -1.161 | .181 | | | .021 | 1.800 | |
| | <i>NN-2^a</i> | | | <i>1.956</i> | <i>-1.141</i> | <i>.163</i> | | | <i>.023</i> | <i>1.823</i> | |
| | BB-3 | | | 1.889 | -853 | -.091 | | | .036 | 2.096 | .054 |
| | BB-4 | | | 1.887 | -844 | -.100 | | | .035 | 2.105 | .055 |
| | BB-5 | | | 1.886 | -850 | -.093 | | | .037 | 2.098 | .055 |
| | BB-6 | | | 1.888 | -840 | -.104 | | | .036 | 2.100 | .054 |
| | CN-1 | -486 | -476 | 1.939 | -1.165 | .181 | 2.509 | .043 | .024 | 1.794 | |
| | <i>CN-2^a</i> | <i>-494</i> | <i>-461</i> | <i>1.929</i> | <i>-1.146</i> | <i>.172</i> | <i>2.503</i> | <i>.048</i> | <i>.027</i> | <i>1.814</i> | |
| | CB-3 | -484 | -470 | 1.898 | -852 | -.092 | 2.511 | .051 | .036 | 2.096 | .051 |
| CB-4 | -484 | -468 | 1.894 | -843 | -.099 | 2.510 | .055 | .037 | 2.104 | .055 | |
| <i>Ba</i> | CC-1 | -509 | -463 | 1.944 | | | 2.488 | .035 | | | |
| | CC-2 | -502 | -455 | 1.913 | | | 2.494 | .053 | | | |
| | NN-1 | | | 1.972 | -1.138 | .152 | | | .016 | 1.828 | |
| | <i>NN-2^a</i> | | | <i>1.957</i> | <i>-1.119</i> | <i>.141</i> | | | <i>.024</i> | <i>1.844</i> | |
| | BB-3 | | | 1.912 | -882 | -.074 | | | .033 | 2.070 | .044 |
| | BB-4 | | | 1.906 | -867 | -.086 | | | .034 | 2.084 | .046 |
| | BB-5 | | | 1.903 | -862 | -.090 | | | .035 | 2.088 | .048 |
| | BB-6 | | | 1.913 | -847 | -.109 | | | .030 | 2.111 | .043 |
| | CN-1 | -515 | -460 | 1.959 | -1.143 | .159 | 2.482 | .033 | .019 | 1.822 | |
| | <i>CN-2^a</i> | <i>-516</i> | <i>-443</i> | <i>1.935</i> | <i>-1.126</i> | <i>.150</i> | <i>2.581</i> | <i>.047</i> | <i>.027</i> | <i>1.835</i> | |
| | CB-3 | -508 | -453 | 1.915 | -903 | -.050 | 2.487 | .048 | .037 | 2.043 | .046 |
| CB-4 | -508 | -452 | 1.908 | -857 | -.092 | 2.487 | .050 | .038 | 2.090 | .049 | |

^a) MP4SDTQ//HF-values (shown in italics) are given for forms which are not stationary points at MP2.

two CN⁻'s (**NN-1** → **BB-3**). Again the energy differences between the side-on complex (**BB-3**, **BB-4**, **BB-6**) stationary points are small (0.2 kcal/mol).

The preferences reverse completely for MgC₂N₂ (Table 2): coordination to the carbon atoms is about 0.3 kcal/mol for each CN⁻ group more favorable than N coordination, and linear structures are more stable than side-on complexes. Accordingly, **CC-1** is the absolute minimum. However, the stationary points with side-on coordinated ligands are only somewhat higher in energy (**CB-3**, ~0.9 kcal/mol; **BB-4**, ~2.4 kcal/mol), and the same is true for the transition states **BB-3** and **BB-6** (*C*_{2v} and *C*_{2h}, respectively).

BeC₂N₂. The least complex hyperface was found for BeC₂N₂ (Figure 1, Tables 1 and 2).¹⁹ All starting geometries optimized to the linear minima. The CN–Be–NC isomer (*D*_{∞h}) **NN-1** is 1.75 and 3.9 kcal/mol more stable than **CN-1** and **CC-1**, respectively.

Discussion

The nitriles follow the patterns for other derivatives of the group 2 metals investigated earlier.^{9,11} Bent (Sr, Ba) or linear (Ca, Mg, Be) end-on geometries are found—but only at the Hartree–Fock level. Upon MP2 optimization, the N-coordinated CN⁻ groups favor side-on arrangements not only for Sr

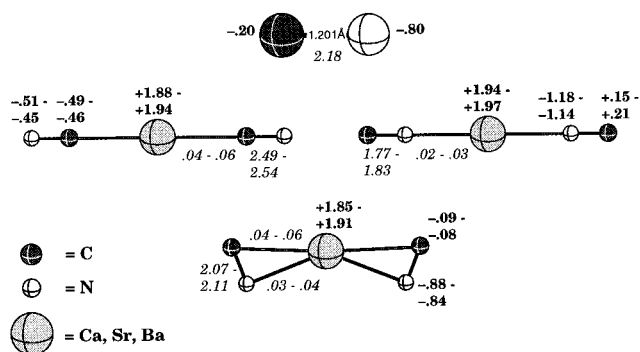


Figure 2. Natural atomic charges (**bold**) and NPA bond orders (*italic*) of free CN^- and average values for calcium, strontium, and barium isonitriles, nitriles, and bridged complexes at MP4SDTQ/MP2.

and Ba but also for Ca and Mg. On the other hand, the bent **CC-2** form is a minimum for $\text{Sr}(\text{CN})_2$ and for $\text{Ba}(\text{CN})_2$, although the end-on N-coordinated isomers (with NIMAG = 2!) are more stable. What is responsible for the different behavior of the nitriles at Hartree-Fock and the electron correlated levels?

Polarization of the CN^- ligands by the alkaline earth metal cations leads to significant changes in the atomic charges. The natural charges of a "free", uncoordinated CN^- anion are -0.20 (C) and -0.80 (N). Complexation with a heavy group 2 metal cation shifts 0.3–0.4 electron towards the coordinating atom (Table 3 and Figure 2).

For example, the CN^- nitrogen atoms in the N-coordinated ligands are highly negatively charged ($\text{N} \sim -1.15$), while the carbon atoms are positively charged ($\text{C} \sim +0.20$). Due to this charge polarization, the C–N natural bond order (NPA) decreases from ~ 2.2 in free CN^- to ~ 1.8 (Table 3). At electron-correlated levels, geometries with such strong charge separations are not favored. Ligand bending to side-on orientations leads to charge distributions and C–N bond orders similar to those of the free CN^- anion (e.g.: NAC–C -0.09 to -0.11 , NAC–N -0.83 to -0.90 , NPA CN 2.07 to 2.11; Table 3 and Figure 2). Metal cation core polarization twists the side-on ligands out of plane. Small covalent d-orbital contributions for $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ might contribute to this behavior.^{9–11}

In C-coordinated cyano groups the natural charge distribution is more homogeneous ($\text{N} \sim -0.30$ to -0.50 , $\text{C} \sim -0.45$; Table 3 and Figure 2), and the NPA C–N bond orders even exceed those of the free anion (~ 2.5 to ~ 2.7). These end-on structures (bent or linear) are local minima although motion of the ligands

would lead to the more stable side-on complexes. Interestingly, the end-on $\text{C} \cdots \text{M}$ NPA bond orders are not larger than those of the side-on complexes (e.g. C–Ca NPA bond orders 0.064 for **CC-1** vs 0.065 for **BB-4**; Table 3). Hence, these weak covalent interactions do not determine the side-on vs end-on coordination preference.

BeC_2N_2 and MgC_2N_2 also are ionic complexes, although the metal charges are less and the ligand–metal bond orders are slightly higher than in the Ca–Ba compounds (Table 3). However, both metal cations are smaller and side-on coordination is less effective (Mg) or does not occur (Be). While end-on C coordination is preferred for $\text{Mg}(\text{CN})_2$ (stronger covalent $\text{M} \cdots \text{C}$ interactions, "normal" charge distribution in the CN^- ligand), the distance-dependent electrostatic interactions determine the energy preferences of the isomers of the small BeC_2N_2 molecule. Therefore, beryllium cation coordination is best via the strongly negatively charged nitrogen atoms of the CN^- ligands.

Conclusions

Remarkably, the heavier alkaline earth metal MC_2N_2 complexes are neither nitriles nor isonitriles. The global minimum geometries of Ca, Sr, and Ba compounds are side-on complexes with C_2 symmetry, but several transition structures are extremely low in energy (0.0–0.3 kcal/mol). Therefore, the side-on CN^- ligands orbit around the central metal.²¹ Nevertheless, side-on coordination of the CN^- groups is favored; the other geometries are far less stable.

The first member of this series, $\text{CN}^- \text{Be} \text{CN}^-$, forms a linear complex with N-coordinated CN^- groups. MgC_2N_2 also adopts a linear minimum geometry. However, all three possibilities of ligand orientation—nitrile, isonitrile, and mixed coordination—are within 0.7 kcal/mol, and a side-on structure is only 0.9 kcal/mol less stable. These somewhat surprising theoretical results challenge experimental investigations.

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(21) Other CN^- -containing species also reveal significant fluxionality. See for example: Meot-Ner, M.; Cybulski, S. M.; Scheiner, S.; Liebman, J. J. *Phys. Chem.* **1988**, *92*, 2738.