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Cesium and barium as honorary *d* elements: CsN_7Ba as an example

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Abstract. Quantum chemical calculations suggest that inverse sandwich compounds with the general formula MN_7M', where M is an alkali metal (K,Rb,Cs), N_7 is a ten-π-electron ring, and M' is an alkaline-earth metal (Ca,Sr,Ba), are local C_{7v} minima. Among these systems, the CsN_7Ba molecule is the stablest of all and presents a barrier of 35 kcal/mol to dissociation towards CsNBa and three N_2 molecules. Substantial 5*d* character is found in the bonding. Possible ways of making these high-energy compounds are discussed.

Keywords: Cesium – Barium – Honorary *d* elements
B3LYP – CASSCF

1 Introduction

The alkali and alkaline-earth metals are usually seen as rather boring counterion elements whose bonding is essentially electrostatic and whose consequent ionic radii are rather well defined [1]. In interalkali molecules, such as Cs_2, the bonding obviously is covalent. The relevant ionic and covalent radii are discussed later. We now combine the old observation that the atoms, molecules, and solids containing Ca, Sr, and Ba possess increasing *d* character in their bonds (a summary from 1979 is given in Ref. [2]) with the striking recent observation [3] that a system like $CsN{\equiv}Ba$ actually contains a well-defined triple bond between the Ba 5*d* and N 2*p* orbitals, with a Ba–N bond length far below any normal range. We now give a broader view on the *d* phenomenon and expand the discussion to recently discussed aromatic nitrogen ring systems. These can be used on one hand as sample η^n ligands and they may also have applications as future high-energy compounds.

The isolation of stable salts of the N_5^+ cation, the first new all-nitrogen bulk species to be made in a century [4, 5] has put the spotlight on the search for other stable polynitrogen species. Here we refer to N_2, N_3^- and N_5^+; actually it should be added that both N_2^{2-} and N_2^{4-} are thought to exist in solids [6].

Related work using quantum chemical calculations has predicted the possible existence of the ScN_7 molecule [7], which contains a new structural group, the η^7-N_7^{3-} ten-π-electron ring, isoelectronic with the experimentally known η^7-$(C_7H_7)^{3-}$ ligand, and has a relatively low energy of formation of 36 kcal/mol per N_2 unit, above a Sc atom and N_2. A $Fe(N_5)_2$ ferrocene analogue has been suggested independently by Lein et al. [8]. Pentazole metal compounds, like NaN_5, KN_5, $Mg(N_5)_2$, $Ca(N_5)_2$, and $Zn(N_5)_2$, have also been predicted recently by Burke et al. [9].

We then predicted the possible existence of some sandwich compounds with the general formula N_5MN_7 [10] ($M = $ Ti,Zr,Hf,Th). N_5ThN_7 is the stablest of all and has an energy of formation of 22 kcal/mol per N_2 unit above a Th atom and N_2. As part of a project to investigate new mixed metal–nitrogen species, compounds with the general formula MN_7M' containing one central η^7-N_7^{3-} ten-π-electron ring and a group 1 (K,Rb,Cs) and group 2 (Ca,Sr,Ba) metal atom are now considered (Fig. 1). They were found to be locally stable with all frequencies real. The formation/dissociation mechanism of such systems was also investigated and it seems that the building blocks to form MN_7M' (or the dissociation products) are a MNM' moiety and three N_2 molecules. This is of interest because first of all it has allowed the prediction of the existence of the MNM' triatomic molecules never investigated before neither experimentally nor theoretically, [3].

2 The hybridization of Ca–Ba

The alkaline earths are basically *ns* elements. The *np* orbitals come in as their polarization functions. The

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Contribution to the Björn Honorary Issue

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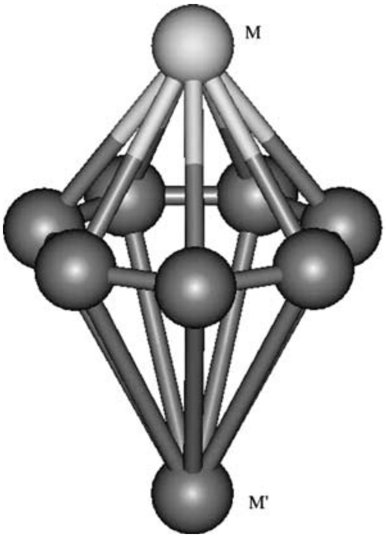

Fig. 1. The calculated structure of the local minimum of CsN_7Ba. The other MN_7M' ($M = K$, Rb; $M' = Ca$, Sr) systems have similar structures

evidence for increasing (n-1)d- character in Ca–Ba was summarized in Ref. [2] and comprises both atomic, molecular, and solid-state data. The atomic ground states at multiconfiguration level are a mixture of s^2, p^2, and d^2 configurations. In molecules, the classical example is the bent shapes of the heavier alkaline-earth dihalides (SrF_2 and BaX_2; $X = F - Br$). They are partially due to a transition from metal *sp* hybridization to metal *sd* hybridization; the situation has just been summarized by Kaupp [11]. In the MH^+ or MH_2 hydrides, the calculated d character increased along $M = Ca - Ba$. Nonrelativistically it would increase further to $M = Ra$, while relativistically a decrease was found (Fig. 1 in Ref. [2]). Later calculations on CsH and BaH^+ using large Slater basis sets [12] indicated that the 5*d* character of the latter was larger than the 6*s* character.

As a particular example of *d* character, consider the diatomic oxides *M*O; $M = Ca - Ba$. The experimental R_e are 182, 192, and 194 pm, and the D_e are 4.76, 4.88, and 6.91 eV, respectively [13]. Note the unusual rising trend of the latter. Ab initio calculations including *d* functions reproduce this trend [14,15]. The increasing *d* character along the series $M = Ca - Ba$ was explicitly discussed by Fuentealba and Savin [15].

Note the two differences between the $\sigma^2\pi^4$ triple bonds of Ba≡O and C≡O in groups 2 and 14, respectively: Ba uses for the σ bonds its valence *ns*, while C uses its (hybridized) 2*p*. Secondly, Ba uses for the π bond its 5*d*, while C uses its 2*p*.

Finally, the crystal structures of the elements (face-centered cubic for Ca, Sr; body-centered cubic for Ba; not hexagonal close packed for any of them) suggest the importance of the *d* orbitals [2]. A recent summary is given in Ref. [16]. In the three-dimensional solid *M*O, $M = Ca - Ba$, most of the *d* character remains in empty conduction bands [17]. In the nearest neighbor of Ba, metallic cesium, the high-pressure isostructural phase transformation at about 4.3 GPa is attributed to a transition from a predominant *s* bonding orbital to a predominant *d* bonding orbital; for the latest summary, see Ref. [18]. For the analogous phenomenon in metallic Sr and Ba, see Ref. [19]. Strong hybridization of the Cs 5*d* shells in solid CsAu was found by Hasegawa and Watabe [20].

The known binary solid nitrogen compounds of the group 1 and 2 elements comprise the nitrides of Li, and possibly Na [21], the nitrides of Be, Mg, and Ca, the subnitrides M_2N, $M = Ca$, Sr, Ba [22], and the binary azides of Li–Cs and Be–Ra. In addition there are ternary nitrides such as Li*M*N; $M = Be - Sr$.

Effectively a $\sigma^2\pi^4$ triple bond between Ba and N was found in both CsNBa and the diatomic BaN^-, isoelectronic to BaO [3]. The Ba–N equilibrium bond distance was calculated to be 2.05 Å in CsNBa, 2.17 Å in BaN^-, and 2.00 Å in BaO.

A further simple way to obtain insight into the bonding character of the present elements is to compare their observed or calculated bond lengths with those resulting from a system of additive covalent radii. We use the particular system based on Pauling's halogen radii and it is summarized in Table 1.

As seen from this table, the isoelectronic diatomics BaN^- and BaO have bond lengths far inside the sum of the single-bond radii. Numerous η^5 complexes of cyclopentadienyl (Cp, C_5H_5) or its derivatives are experimentally known [23, 24]. The typical distances are compared with predictions in the table. We are tacitly assuming the five carbons of Cp occupy one coordination site. The predicted *M*–C(Cp) distances are on the high side, again suggesting more multiple bonding character than in the average reference case for obtaining the r_{cov}[C(Cp)]. Finally it is seen that the calculated Ba–N distance in $Cs(N_7)Ba$ is over 30 pm shorter than the typical Ba–C(Cp) distances, again suggesting strong multiple bonding.

3 Computational details

The calculations were carried out at the density functional theory (DFT) level, using the B3LYP exchange–correlation functional. In all cases the 6–31g* basis sets [10s4p2d]/(3s2p1d) was used for the nitrogen atom. The various basis sets for the metal atoms are summarized in Table 2.

Table 1. Predicted *M–L* distances for single-bond radii and observed or ab initio calculated *M–L* bond lengths in picometers for group 1 and 2 metals (Metal radii K 166, Rb 179, Cs 191; Ca 152, Sr 169, Ba 185. Single-bond ligand radii C(η^5 Cp) 125, N 73, O 73.) Radii from Table VI Ref. [33]. Experimental distances for organometallic compounds from Refs. [23, 24]

M–L	System	Predicted	Exp./Calc.
Ca–C	$Ca(Cp)_2$	277	261–264
Sr–C	$Sr(Cp)_2$	294	275
Ba–C	$Ba(Cp)_2$	310	294–303
Ba–N	$Cs(N_7)Ba$		265
Ba–N	BaN^-	258	217[a]
Ba–O	BaO	258	200[a], 1.939692[b]

[a] From Ref. [3]

[b] From Ref. [13]

Table 2. Contracted basis sets

KN_7Ca[a]	RbN_7Sr[b]	CsN_7Ba[c]
BS1 3s2p1d	BS1 5s4p; 4s4p2d	BS1 5s4p; 4s4p2d1f
BS2 5s3p2d	BS2 5s4p2d; 4s4p2d	BS2 5s4p2d1f; 4s4p2d1f
BS3 8s7p3d1f	BS3 5s4p5d; 4s4p5d	BS3 5s4p5d1f; 4s4p5d1f
BS4 8s7p5d1f	BS4 5s4p5d1f; 4s4p5d1f	BS4 5s4p5d3f; 4s4p5d3f
BS5 8s7p7d1f		

[a] 6-31g* type both on K and Ca

[b] Valence basis accompanying the Stuttgart effective care potentials for Rb and Sr, respectively

[c] Valence basis accompanying the Stuttgart effective care potentials for Cs and Ba, respectively

Table 3. B3LYP bond lengths (angstroms) and angles (degrees) in the KN_7Ca and RbN_7Sr molecules with various basis sets. The CASSCF bond distances for KN_7Ca (basis sets of atomic natural orbital, *ANO*, type) are given in *parentheses*

MN_7M'	R_{M-N}	$R_{N-M'}$	R^{a}_{N-N}
KN_7Ca BS1	2.805	2.440	1.382
BS1	(2.913)	(2.475)	(1.339)
BS2	2.780	2.356	1.376
BS3	2.803	2.352	1.368
BS4	2.813	2.358	1.377
BS5	2.814	2.359	1.376
RbN_7Sr BS1	3.038	2.502	1.374
BS2	2.967	2.508	1.374
BS3	2.974	2.512	1.376
BS4	2.978	2.520	1.372

[a] In N_7^{3-} B3LYP $R_{N-N} = 1.374$ Å

Table 4. B3LYP bond lengths (angstroms) and angles (degrees) in CsN_7Ba, BaN_7Ba^+, BaN_7^-, and $Cs(CH)_7Ba$, with various basis sets. The CASSCF bond distances for CsN_7Ba (basis sets of atomic natural orbital type) are given in *parentheses*

MN_7M'	R_{M-N}	$R_{N-M'}$	R^{a}_{N-N}
CsN_7Ba BS	3.208	2.651	1.371
BS1	(3.249)	(2.685)	(1.333)
BS2	3.104	2.663	1.371
BS2	(3.201)	(2.690)	(1.333)
BS3	3.103	2.666	1.3713
BS4	3.095	2.657	1.370
BaN_7Ba^+ BS1	2.766	2.766	1.375
BaN_7^- BS1		2.618	1.369
BS1 (ANO)		(2.638)	(1.332)
$Cs(CH)_7Ba$ BS1	3.242	2.767	1.441
$Cs(CH)_7Ba$ BS2	3.132	2.773	1.441

[a] In N_7^{3-} B3LYP $R_{N-N} = 1.374$ Å

In the KN_7Ca case, a series of basis sets for K and Ca were used, from the 3s2p1d basis of 6–31g* type, up to the 8s7p7d1f basis. In the RbN_7Sr and CsN_7Ba cases, effective core potentials (ECPs) were used. The energy-adjusted Stuttgart ECPs were used for this purpose [25]. The number of valence electrons is 9 for *M* and 10 for *M′*. The basis sets accompanying the ECPs were used to describe them [26], Rb [7s6p]/(5s4p), Sr [6s6p5d]/(4s4p2d), Cs [7s6p]/(5s4p), Ba [6s6p5d1f]/(4s4p2d1f), BS1. Comparative calculations were also performed by adding two d functions and one f function to the Cs valence basis (d exponents 0.133 and 0.404 from Ref. [27], and the f exponent 0.6970 was taken from the Ba valence basis set) and two d functions to the Rb valence basis (with exponents 0.226 and 0.695 [27]), BS2. The valence basis sets were also extended up to 5s4p5d1f for Rb, 4s4p5d1f for Sr, 5s4p5d3f for Cs, and 4s4p5d3f for Ba, respectively. (We do not report all the exponents but they are available upon requests.) The program Gaussian98 was employed.

Equilibrium geometries and harmonic frequencies were computed for all species. The calculations were performed using the ultrafine (99, 590) grid having 99 radial shells and 590 angular points per shell. At the same time the weighting scheme of Becke was used for numerical integrations.

Comparative geometry optimizations were performed at the multiconfigurational self-consistent-field level, CASSCF [28], for KN_7Ca and CsN_7Ba, using atomic natural orbital type basis sets [29] on N [10s6p3d]/(3s2p1d), K, and Ca atoms [17s12p4d]/(4s3p2d), and the same ECPs as previously mentioned for Cs and Ba. The program MOLCAS-5.2 [30] was employed. In the CASSCF calculations an active space formed by ten electrons in seven orbitals was used. These molecular orbitals (MOs) are one σ, two, two δ, and two ϕ linear combinations of the nitrogen p_z atomic orbitals. The σ, π, and δ MOs are bonding to barium, while the ϕ MOs are nonbonding and essentially localized on the N_7 ring. Extra CASSCF calculations were performed, in which five antibonding orbitals were added, with the same symmetry as the bonding MOs, one σ, two π, and two δ. The two active spaces give equivalent results.

While performing these calculations it was found that the valence basis set of the barium atom present in the library of the programs Gaussian98 and MOLCAS-5.2 had the wrong contraction. For the correct valence basis set we recommend downloading it directly from http://www.theochem.uni-stuttgart.de/.

4 Results

The structures of the KN_7Ca, RbN_7Sr, and CsN_7Ba molecules obtained with the various basis sets are reported in Tables 3 and 4. In all cases they were found to be local minima in C_{7v} symmetry, in their singlet ground state. The calculations were also carried out with lowered C_s symmetry and the same C_{7v} structures were obtained. We checked the stability of the triplet for CsN_7Ba and it was found to lie 40 kcal/mol higher in energy than the singlet with BS1.

As seen from Tables 3 and 4, the larger basis sets give closely similar results, which we interpret as a sign for basis-set saturation. It is seen that the effect of adding more than one d function on the alkali atom has a negligible effect for K but shortens the Cs–N distance by about 0.1 Å. A larger basis on the alkaline-earth atom has a similar effect on Ca. Surprisingly this effect on $R_{N-M'}$ decreases for Sr and Ba, for which the other evidence for d participation becomes greater (Fig. 2).

The alkali atom is at a greater distance from the N_7 ring than the alkaline-earth atom. In KN_7Ca, the K–N distance is 0.37 Å longer than the Ca–N distance with BS1, and is 0.42 Å longer with BS5. In RbN_7Sr the Rb–N distance is 0.54 Å longer than the Sr–N distance with BS1 and 0.46 Å longer with BS4. In CsN_7Ba (Table 4) the Cs–N distance is 0.56 Å longer than the Ba–N distance with BS1 and 0.44 Å longer with BS4.

The structure of the BaN_7Ba^+ cation, isoelectronic to CsN_7Ba, is also reported in Table 4. The Ba–N bond distance of 2.76 Å is 0.1 Å longer than in CsN_7Ba.

For comparison the CASSCF bond distances of KN_7Ca and CsN_7Ba are also reported. The CASSCF calculations were performed in order to understand the MOs involved in the bonding. The bonding σ, π, and δ CASSCF MOs of CsN_7Ba are reported in Figs. 3, 4, and 5. Ba forms five bonds with the N_7 ring, while Cs is a separated entity. The Ba–N_7 bonds should not only be interpreted as ionic interactions; it is striking to see how Ba in its formal valence of +2 can interact so strongly with the N_7 ring, by forming σ, π, and δ bonds, similarly to what is observed for transition metals such as Sc [7] and Ti–Hf [10]. The 5*d* orbitals of Ba take an active role in the formation of this multiple bond, intervening especially in the δ bond. The MOs of KN_7Ca look rather similar to those of CsN_7Ba, with a preferential Ca–N_7 interaction; however, the bonding σ and π MOs have small potassium character. The analogous cesium participation is completely absent in CsN_7Ba. In the lighter homologue KN_7Ca, the character of the δ MOs is also small on the alkaline-earth metal (Ca) and rests mainly on the N_7 ring.

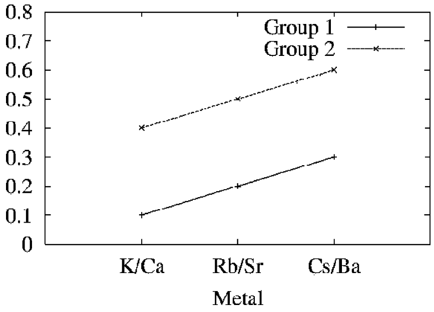

Fig. 2. The Mulliken *d* character along group 1 and group 2 metals

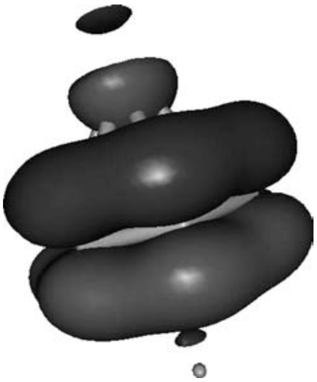

Fig. 3. The bonding σ molecular orbital in CsN_7Ba at the CASSCF level

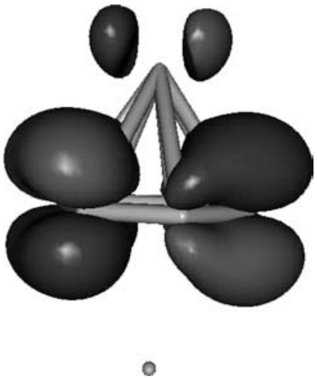

Fig. 4. One component of the two bonding π molecular orbitals in CsN_7Ba at the CASSCF level

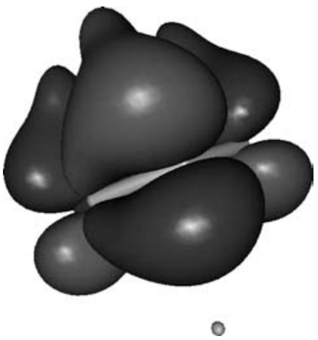

Fig. 5. One component of the two bonding δ molecular orbitals in CsN_7Ba at the CASSCF level

In order to investigate the peculiar Ba–N_7 interactions, B3LYP and CASSCF calculations were also performed on the BaN_7^- anion. The Ba–N bond distance is 0.03 (0.05) Å shorter in BaN_7^- than in CsN_7Ba at the B3LYP (CASSCF) level, respectively, and the N–N distance is virtually unaffected (about 0.002 Å shorter in the anion). The bonding MOs are again one σ, two π, and two δ, as in the neutral species. The Ba–N interaction is slightly stronger in the anion than in the neutral molecule, but overall this suggests the hypothesis that CsN_7Ba is essentially formed by Cs^+ and BaN_7^- entities. Given the preferential interaction between Ba, formally in the +2 oxidation state, and N_7, we wondered if BaN_8 could also be stable. This would correspond to Ba^{2+} and the 10 π N_8^{2-} ring. This system however is unstable as a local minimum, and presents two imaginary frequencies corresponding to the N_8 ring bending. BaN_7^- is isoelectronic with the previously studied LaN_7 species [7], which has a La–N bond of 2.486 Å.

Comparative B3LYP calculations were also performed on $Cs(CH)_7Ba$, isoelectronic to CsN_7Ba, with both the BS1 and BS2 basis sets. The Cs–C and Ba–C bond distances are 0.03 and 0.12 Å longer than the Cs–N and Ba–N bond distances in CsN_7Ba respectively.

The harmonic frequencies of the MN_7M' species, obtained with the largest basis sets of each series, are reported together with their IR intensities in Table 5. For comparison the frequencies of BaN_7^- and N_7^{3-} are also reported. The isolated N_7^{3-} anion is however unlikely to exist (the calculated electron affinity of N_7^{2-} has a negative value of −10.31 eV). All frequencies are

Table 5. B3LYP harmonic frequencies (cm^{-1}) and their IR intensities ($km\ mol^{-1}$) in *parentheses* for KN_7Ca, SrN_7Rb, CsN_7Ba, BaN_7^-, and N_7^{3-} obtained with the largest basis sets in each case

Normal mode	KN_7Ca BS5	RbN_7Sr BS4	CsN_7Ba BS4	BaN_7^- BS1	N_7^{3-} 6-31g*
$\nu_1(e)$ M-N_7	104.5 (25)	90.1 (28)	76.6 (26)		
$\nu_2(a)$ M-N_7 stretch	196.7 (39)	138.9 (15)	114.8 (13)		
$\nu_3(e)$ M'-N_7 bend	263.5 (6)	225.9 (5)	205.2 (4)	211.9 (9)	
$\nu_4(e)$ N_7 out of plane bend	385.0 (0)	312.0 (134)	406.8 (0)	390.8 (0)	324.2 (0)
$\nu_5(a)$ M'-N_7 stretch	390.0 (148)	394.0 (0)	287.7 (148)	289.7 (51)	
$\nu_6(e)$ N_7 out of plane bend	426.9 (0)	429.7 (0)	432.2 (0)	428.8 (0)	475.0 (0)
$\nu_7(e)$ N_7 out of plane bend	459.7 (0)	479.5 (0)	474.0 (0)	484.7 (0)	504.7 (0)
$\nu_8(a)$ N_7 in plane breathing	763.2 (5)	767.7 (3)	771.5 (3)	778.3 (4)	769.6 (0)
$\nu_9(e)$ N_7 in plane asymmetric stretch	894.4 (0)	913.3 (0)	925.9 (0)	937.3 (0)	934.2 (0)
$\nu_{10}(e)$ N_7 in plane deformation	887.8 (89)	898.9 (79)	901.7 (74)	909.5 (88)	892.2 (134)
$\nu_{11}(e)$ N_7 in plane asymmetric deformation	973.2 (0)	986.4 (0)	984.7 (0)	987.8 (0)	1063.4 (0)
$\nu_{12}(e)$ N_7 in plane asymmetric deformation	1178.2 (0)	1204.7 (0)	1206.4 (0)	1200.2 (0)	1316.9 (0)

real. The same also holds when smaller basis sets are used. The lowest three modes, ν_1, ν_2, ν_3, together with ν_5, corresponding to some M–N_7 and M'–N_7 motions have nonzero IR intensity. The N_7 ring modes ν_4 and ν_6–ν_{12} all have zero intensity, with the exception of ν_{10}. The correspondence between the N_7 ring modes in the bare ring and in the metal–ring complexes is rather straightforward. The modes of BaN_7^- are virtually unaffected by the presence of Cs^+ in CsN_7Ba.

The partial charges on the M, N_7, and M' moieties, obtained by a Mulliken population analysis, are reported in Table 6. Formally they correspond to M^+, N_7^{3-}, and M'^{2+}. With BS1 K and Rb have a partial charge of about +0.85, while Cs has a partial charge of +0.90, which is closer to the formal value of +1. With BS2 the partial charges on Rb and Cs become +0.80 and +0.77, respectively. Among the group 2 metal, Ba has the smallest partial charge of all, +1.12, instead of the formal value of +2. This combination of the Cs and Ba charges confirms that in CsN_7Ba, preferential interaction occurs between N_7 and Ba, while Cs is an isolated moiety with more pronounced ionic character, as suggested by the MOs analysis. The partial positive charge on Ba decreases by about 0.2 in the BaN_7^-anion. The total dipole moments for the neutral species are also reported. KN_7Ca has the largest dipole moment of all, with a value of 2.77 D.

The *d* character of the heavier MN_7M' systems at the Mulliken level is summarized in Fig. 2. An increase of the *d* character occurs along the group 1 and group 2 series. For the heaviest species, CsN_7Ba, the alkali–metal *d* character rises to about half of that of the alkaline–earth metal. If the Cs d functions were omitted, the Cs–N bond length would increase from 3.104 to 3.208 Å at the DFT level.

Table 6. Partial charges on M, N_7, and M' and total dipole moment (debye)

MN_7M'	δ_M	δ_{N_7}	$\delta_{M'}$	Dipole
KN_7Ca BS1	+0.85	−2.10	+1.25	2.77
KN_7Ca BS5	+0.59	−1.64	+1.05	0.28
RbN_7Sr BS1	+0.86	−2.02	+1.16	1.00
RbN_7Sr BS2	+0.80	−1.96	+1.16	0.47
RbN_7Sr BS4	+0.62	−1.56	+0.93	1.06
CsN_7Ba BS1	+0.90	−2.02	+1.12	1.49
CsN_7Ba BS2	+0.77	−1.90	+1.13	1.33
CsN_7Ba BS4	+0.71	−1.62	+0.91	1.72
BaN_7Ba^+ BS1	+1.40	−2.80	+1.40	
BaN_7^- BS1		−1.81	+0.81	

A possible dissociation mechanism was investigated for the three molecules, in analogy with what was previously done for ScN_7 [7], by considering the opening of the N_7 ring and finding a transition state (TS) (Fig. 6). The TS for KN_7Ca occurs when the N–N bond opens to 2.51 Å, and lies 14.8 kcal/mol higher in energy than the local minimum. The TS for RbN_7Sr has an open N–N bond of 2.30 Å and it lies 28.4 kcal/mol above the local minimum. The TS for CsN_7Ba has an open N–N bond of 2.45 Å and it lies 34.5 kcal/mol above the local minimum. For ScN_7 the analogous energy barrier is 20 kcal/mol, and the TS occurs when the N–N bond opens to 2.10 Å. With BS2 the TS for CsN_7Ba has an open N–N bond of 2.40 Å and lies 33.3 kcal/mol above the local minimum. All these values for the barriers are zero-point-energy corrected.

The formation/dissociation of these MN_7M' molecules is likely to occur stepwise. By following the opening

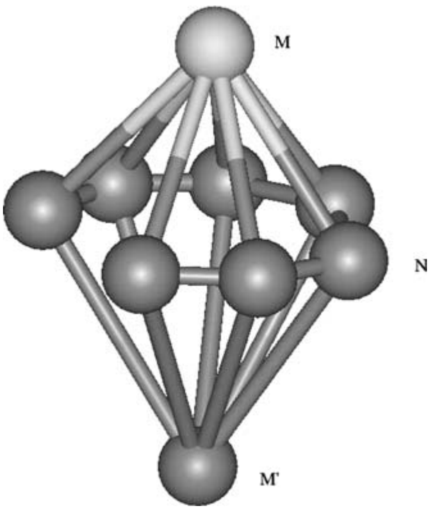

Fig. 6. The calculated structure of the transition state of CsN_7Ba. The other MN_7M' transition states have similar structures

of the N–N bond in CsN_7Ba with the BS1 basis set, it seems that CsN_7Ba can either dissociate to $CsNBa + 3N_2$ (reaction A), or to $BaN_2 + CsN_3 + N_2$ (reaction B). The products of reaction A lie 66.9 kcal/mol lower in energy than CsN_7Ba, or 22.3 kcal/mol per N_2 molecule. The products of reaction B lie 22.7 kcal/mol lower in energy than CsN_7Ba, which, per N_2 molecule, is the same amount of energy as reaction A. The existence of CsNBa has just been predicted by us [3] with a Cs–N and Ba–N bond distance of 2.827 and 2.051 Å respectively, at the B3LYP level, while BaN_2 has been prepared in a crystal by Vajenine et al. [31]. We performed B3LYP calculations on BaN_2 which turned out to be stable as a linear molecule (BaNN), with all real frequencies (lowest mode of $= 158\,\mathrm{cm}^{-1}$) and a N–N and Ba–N bond distances of 1.147 and 2.545 Å respectively.

The analogous products of reaction A for KN_7Ca lie 63.5 kcal/mol lower in energy (21.2 kcal/mol per N_2 molecule) than KN_7Ca, and those for SrN_7Rb are 64.5 kcal/mol lower (21.5 kcal/mol per N_2 molecule). It thus seems that the three molecules have similar reactivity, even if the dissociation reaction presumably starts with more difficulties in CsN_7Ba than in the other species, because of the much higher activation barrier.

5 Conclusions[1]

We presented the results of a study on some complexes with general formula MN_7M', where M is an alkaline metal (K,Rb,Cs) and M' is an alkaline-earth metal (Ca,Sr,Ba). These compounds are C_{7v} local minima, and are characterized by preferential N_7–M' interactions. This is mainly enhanced in the system containing Cs and Ba in which a quintuple bond occurs between Ba and N_7. One σ, two π, and two δ) bonding MOs are identifiable, with a substantial 5*d* Ba character in the δ bonds. Along the group 1 and group 2 series an increase of *d* character is identifiable.

CsN_7Ba is also the most stable of all. It presents a barrier to dissociation of 35 kcal/mol, corresponding to the breaking of a N–N bond in the N_7 ring, and lies only 67 kcal/mol above $CsNBa + 3N_2$, or 22 kcal/(mol N_2). CsN_7Ba also lies 23 kcal/(mol N_2) above $BaN_2 + CsN_3 + N_2$. This study suggests possible ways of forming mixed metal–polynitrogen compounds, by reacting new species such as CsNBa and BaN_2 with N_2. These compounds will, however, be highly endothermic and it may be difficult to prepare them experimentally. An extension of CsN_7Ba chemistry from a single molecule to the solid state could be considered and the question could be raised whether in molecular or solid CsN_7Ba separate Cs and BaN_7 can still be distinguished.

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[1] After the original submission of this paper, Sitzmann et al. [32] reported the new compound ^{4}CpBaCotBa^{4}Cp (^{4}Cp = CH(CHMe)$_4$, Cot = cyclooctatetraene) with a very short Ba–C bond of 240 pm between a barium atom and the centroid of Cot. That independent experimental observation may be due to very similar bonding mechanisms as the present short bonds between Ba and the N_7^{3-} ring, and thereby provides indirect experimental support for our predictions