

## Noble-Gas Complexes: Theoretical Investigation of Multicenter Polynuclear Species

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*Ab initio* calculations at the MP2 level of theory disclose the conceivable existence of neutral complexes containing four or five distinct noble gases (Ng) each bound to a distinct Be-atom. These multicenter polynuclear Ng molecules are formally obtained by replacing the H-atoms of CH<sub>4</sub> and but-2-yne with –NBeNg moieties, which behave as independent monovalent ‘functional groups’. Our investigated complexes include the five homotetranuclear [C(NBeNg)<sub>4</sub>] complexes **1–5** (Ng = He–Xe), the five heterotetranuclear complexes [CN<sub>4</sub>Be<sub>4</sub>(He)(Ne)(Ar)(Kr)] (**6**), [CN<sub>4</sub>Be<sub>4</sub>(He)(Ne)(Ar)(Xe)] (**7**), [CN<sub>4</sub>Be<sub>4</sub>(He)(Ne)(Kr)(Xe)] (**8**), [CN<sub>4</sub>Be<sub>4</sub>(He)(Ar)(Kr)(Xe)] (**9**), and [CN<sub>4</sub>Be<sub>4</sub>(Ne)(Ar)(Kr)(Xe)] (**10**), and the heteropentanuclear complex [HC<sub>4</sub>N<sub>3</sub>Be<sub>5</sub>(He)(Ne)(Ar)(Kr)(Xe)] (**11**). We also investigated the five model complexes [H<sub>3</sub>CNBeNg] (Ng = He–Xe) containing a single –NBeNg moiety. The geometries and vibrational frequencies of all these species, invariably characterized as minimum-energy structures, were computed at the MP2(full)/6-31G(d,p)/SDD level of theory, and their stability with respect to the loss of the various Ng-atoms was evaluated by single-point calculations at the MP2(full)/6-311G(d)/SDD level of theory. The beryllium–Ng binding energies range from *ca.* 17 (Ng = He) to *ca.* 63 (Ng = Xe) kJ/mol, and the results of natural-bond-orbital (NBO) and atoms-in-molecules (AIM) analysis reveal that the Be–Ng interaction is essentially electrostatic for helium, neon, argon, and krypton, and has probably a small covalent contribution for xenon.

**Introduction.** – Since *Bartlett's* discovery of ‘Xe<sup>+</sup>PtF<sub>6</sub><sup>–</sup>’ [1][2], the chemistry of the noble gases (Ng) revealed a fascinating field of experimental and theoretical research [3–6]. In recent years, the study of the ‘inert’ elements is enjoying a ‘renaissance’ [7][8], driven by an impressive burst of startling evidence concerning a variety of Ng compounds [9–17]. Particularly relevant for the present investigation is the progress made recently in the study of polynuclear Ng complexes. Following previous experimental and theoretical evidence for gaseous [AuXe]<sup>+</sup> and [XeAuXe]<sup>+</sup> [18][19], a salt containing a tetranuclear xenon cation, [AuXe<sub>4</sub>]<sup>2+</sup>[Sb<sub>2</sub>F<sub>11</sub>]<sub>2</sub><sup>–</sup> [20], has been isolated in the solid state. Recently, numerous polynuclear Ng complexes have also been observed by low-temperature matrix IR spectroscopy. In particular, *Andrews* and co-workers have shown [21] that the neutral CUO molecule trapped in solid noble-gas matrices is coordinated not only by a single but also by multiple Ng-atoms (Ng = Ne–Xe). These first examples of neutral metal–polynuclear Ng complexes include the homonuclear species [CUO(Ng)<sub>n</sub>] (Ng = Ne, Ar, Kr, Xe; *n* = 2, 3, 4), and a variety of heteronuclear species such as [CUO(Ar)<sub>4–n</sub>(Kr)<sub>n</sub>] and [CUO(Ar)<sub>4–n</sub>(Xe)<sub>n</sub>] (*n* = 2, 3, 4). They invariably consist of two or more Ng-atoms which surround the U atom of CUO, and the detailed electronic structure of their ground-state carries on lots of debate in the scientific community [22][23]. Subsequent studies [21e] have shown that other actinide metal oxides such as UO<sub>2</sub> and UO<sub>2</sub><sup>+</sup> are also coordinated by multiple noble-gas atoms. Following these reports, *Zhou* and co-workers observed, in cold matrices, the neutral dinuclear complexes [VO<sub>2</sub>(Ng)<sub>2</sub>] (Ng = Ar, Xe) [24a], and a

series of ionic homo- and heteropolynuclear complexes such as  $[\text{ScO}(\text{Ng})_5]^+$  ( $\text{Ng} = \text{Ar}, \text{Kr}, \text{Xe}$ ),  $[\text{YO}(\text{Ng})_6]^+$  ( $\text{Ng} = \text{Ar}, \text{Kr}$ ),  $[\text{ScO}(\text{Ar})_{5-n}(\text{Kr})_n]^+$  ( $n = 1-5$ ),  $[\text{YO}(\text{Ar})_{5-n}(\text{Kr})_n]^+$  ( $n = 1-6$ ), and  $[\text{YO}(\text{Ar})_{5-n}(\text{Xe})_n]^+$  ( $n = 1-4$ ) [24b]. According to theoretical calculations, these species feature Ng-atoms electrostatically bound to the V, Sc, or Y atoms of  $\text{VO}_2$ ,  $\text{ScO}^+$ , and  $\text{YO}^+$ . Also the binding of two Ar-, Kr-, and Xe-atoms to Pd- and Pt-atoms with formation of homo- and heterodinuclear species has recently been investigated by *ab initio* methods [25]. Therefore, the ability of the noble gases, especially argon, krypton, and xenon, to form polynuclear complexes around a single coordinating atom is currently well recognized. In the present theoretical study, we explore the conceivable existence of complexes which contain four or five noble-gas atoms, including the lightest helium and neon, each bound to a distinct coordinating center of the same molecule. This investigation extends our recent study [26] on neutral polyhelium complexes, including the tetranuclear  $[\text{C}(\text{NBeHe})_4]$ , formally obtained by replacing the H atoms of parent molecules such as  $\text{CH}_4$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$  with  $-\text{NBeHe}$  monovalent ‘functional groups’. Most of these poly-He compounds were characterized as true minima on the singlet surface, stable by nearly 21 kJ/mol with respect to helium loss. Assuming that any  $-\text{NBeNg}$  moiety ( $\text{Ng} = \text{He}-\text{Xe}$ ) behaves as an independent ‘functional group’, it is possible to predict ‘mixed’ complexes such as  $[\text{CN}_4\text{Be}_4(\text{He})(\text{Ne})(\text{Ar})(\text{Ng})]$  ( $\text{Ng} = \text{Kr}, \text{Xe}$ ) and even ‘all together’ Ng compounds containing five distinct  $-\text{NBeNg}$  groups ( $\text{Ng} = \text{He}-\text{Xe}$ ). Our calculations confirm these predictions and disclose periodic trends in the structure, stability, and bonding properties of these multicenter homo- and heteropolynuclear complexes of the noble gases.

**Computational Details.** – The *ab initio* calculations were performed with the Unix version of the Gaussian03 [27] set of programs installed on an *HP-Proliant-DL585* machine. The geometries of the  $[\text{H}_3\text{CNBeNg}]$ , of the  $[\text{C}(\text{NBeNg})_4]$  **1–5**, of the  $[\text{CN}_4\text{Be}_4(\text{Ng}_1)(\text{Ng}_2)(\text{Ng}_3)(\text{Ng}_4)]$  **6–10** ( $\text{Ng} = \text{He}-\text{Xe}$ ), and of  $\text{HC}_4\text{N}_5\text{Be}_5(\text{He})(\text{Ne})(\text{Ar})(\text{Kr})(\text{Xe})$  (**11**)<sup>1)</sup> were optimized by analytical-gradient techniques at the

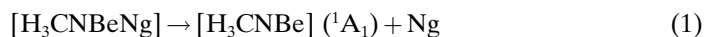
<sup>1)</sup> Systematic names of the noble-gas complexes are:  $[\text{H}_3\text{CNBeHe}]$ , [(methanaminato(2–)beryllium)helium(*Be-He*);  $[\text{H}_3\text{CNBeNe}]$ , [(methanaminato(2–)beryllium)neon(*Be-Ne*);  $[\text{H}_3\text{CNBeAr}]$ , [(methanaminato(2–)beryllium)argon(*Ar-Be*);  $[\text{H}_3\text{CNBeKr}]$ , [(methanaminato(2–)beryllium)krypton(*Be-Kr*);  $[\text{H}_3\text{CNBeXe}]$ , [(methanaminato(2–)beryllium)xenon(*Be-Xe*);  $[\text{C}(\text{NBeHe})_4]$  (**1**),  $\{\{\mu_4\text{-}[\text{methanetetraminato}(8\text{-})\text{-}\kappa\text{N}:\kappa\text{N}':\kappa\text{N}'':\kappa\text{N}''']\}\text{tetraberyllium}\}\text{tetrahelium}(4\text{Be-He})$ ;  $[\text{C}(\text{NBeNe})_4]$  (**2**),  $\{\{\mu_4\text{-}[\text{methanetetraminato}(8\text{-})\text{-}\kappa\text{N}:\kappa\text{N}':\kappa\text{N}'':\kappa\text{N}''']\}\text{tetraberyllium}\}\text{tetraneon}(4\text{Be-Ne})$ ;  $[\text{C}(\text{NBeAr})_4]$  (**3**),  $\{\{\mu_4\text{-}[\text{methanetetraminato}(8\text{-})\text{-}\kappa\text{N}:\kappa\text{N}':\kappa\text{N}'':\kappa\text{N}''']\}\text{tetraberyllium}\}\text{tetraargon}(4\text{Ar-Be})$ ;  $[\text{C}(\text{NBeKr})_4]$  (**4**),  $\{\{\mu_4\text{-}[\text{methanetetraminato}(8\text{-})\text{-}\kappa\text{N}:\kappa\text{N}':\kappa\text{N}'':\kappa\text{N}''']\}\text{tetraberyllium}\}\text{tetra-krypton}(4\text{Be-Kr})$ ;  $[\text{C}(\text{NBeXe})_4]$  (**5**),  $\{\{\mu_4\text{-}[\text{methanetetraminato}(8\text{-})\text{-}\kappa\text{N}:\kappa\text{N}':\kappa\text{N}'':\kappa\text{N}''']\}\text{tetraberyllium}\}\text{tetra-xenon}(4\text{Be-Xe})$ ;  $[\text{CN}_4\text{Be}_4(\text{He})(\text{Ne})(\text{Ar})(\text{Kr})]$  (**6**), argonhelium $\{\{\mu_4\text{-}[\text{methanetetraminato}(8\text{-})\text{-}\kappa\text{N}:\kappa\text{N}':\kappa\text{N}'':\kappa\text{N}''']\}\text{tetraberyllium}\}\text{neonkrypton}(\text{Ar-Be})(\text{Be-He})(\text{Be-Kr})(\text{Be-Ne})$ ;  $[\text{CN}_4\text{Be}_4(\text{He})(\text{Ne})(\text{Ar})(\text{Xe})]$  (**7**), argonhelium $\{\{\mu_4\text{-}[\text{methanetetraminato}(8\text{-})\text{-}\kappa\text{N}:\kappa\text{N}':\kappa\text{N}'':\kappa\text{N}''']\}\text{tetraberyllium}\}\text{neonxenon}(\text{Ar-Be})(\text{Be-He})(\text{Be-Ne})(\text{Be-Xe})$ ;  $[\text{CN}_4\text{Be}_4(\text{He})(\text{Ne})(\text{Kr})(\text{Xe})]$  (**8**), heliumkrypton $\{\{\mu_4\text{-}[\text{methanetetraminato}(8\text{-})\text{-}\kappa\text{N}:\kappa\text{N}':\kappa\text{N}'':\kappa\text{N}''']\}\text{tetraberyllium}\}\text{neonxenon}(\text{Be-He})(\text{Be-Kr})(\text{Be-Ne})(\text{Be-Xe})$ ;  $[\text{CN}_4\text{Be}_4(\text{He})(\text{Ar})(\text{Kr})(\text{Xe})]$  (**9**), argonheliumkrypton $\{\{\mu_4\text{-}[\text{methanetetraminato}(8\text{-})\text{-}\kappa\text{N}:\kappa\text{N}':\kappa\text{N}'':\kappa\text{N}''']\}\text{tetraberyllium}\}\text{xenon}(\text{Ar-Be})(\text{Be-He})(\text{Be-Kr})(\text{Be-Xe})$ ;  $[\text{CN}_4\text{Be}_4(\text{Ne})(\text{Ar})(\text{Kr})(\text{Xe})]$  (**10**), argonkrypton $\{\{\mu_4\text{-}[\text{methanetetraminato}(8\text{-})\text{-}\kappa\text{N}:\kappa\text{N}':\kappa\text{N}'':\kappa\text{N}''']\}\text{tetraberyllium}\}\text{neonkrypton}(\text{Ar-Be})(\text{Be-Kr})(\text{Be-Ne})(\text{Be-Xe})$ ;  $[\text{HC}_4\text{N}_5\text{Be}_5(\text{He})(\text{Ne})(\text{Ar})(\text{Kr})(\text{Xe})]$  (**11**), argon $\{\{\mu_4\text{-}[\text{but-2-yne-1,1,1,4,4-pentaminato}(10\text{-})\text{-}\kappa\text{N}^1:\kappa\text{N}^1:\kappa\text{N}^1:\kappa\text{N}^1:\kappa\text{N}^4]\}\text{pentaberyllium}\}\text{heliumkryptonneonxenon}(\text{Ar-Be})(\text{Be-He})(\text{Be-Kr})(\text{Be-Ne})(\text{Be-Xe})$ .

second-order *Møller–Plesset* level of theory with inclusion of the inner electrons, MP2(full) [28], by means of the 6-31G(d) and 6-311G(d,p) basis sets [29] (5D/7F functions). For the Xe-atom, the Stuttgart/Dresden (SDD) basis set with relativistic effective core potential [30] was employed. The obtained structures were characterized as true minima on the potential-energy surface by calculating their MP2(full)/6-31G(d)/SDD vibrational frequencies, used also to obtain the zero-point vibrational energies (ZPE). The MP2(full)/6-31G(d)/SDD geometries of the various complexes and of the fragments arising from the loss of a single Ng-atom (Ng = He–Xe) were used to perform single-point calculations at the MP2(full)/6-311G(d,p)/SDD level of theory. The Ng-loss energies at 0 K obtained in this way were corrected for the basis-set-superposition error (BSSE) by the method of *Boys and Bernardi* [31]. The atomic charges were calculated by natural-bond-orbital (NBO) analysis [32], and the chemical-bonding analysis was based on the theory of atoms-in-molecules (AIM) [33] as implemented in the AIM2000 program package [34]. In particular, we calculated, at the MP2(full)/6-31G(d)/SDD-optimized geometries, the MP2(full)/6-311G(d,p)/SDD charge density  $\rho$ , the *Laplacian* of the charge density  $\nabla^2\rho$ , and the energy density  $H$  at the bond critical points (bcp), intended as the points on the attractor interaction lines where  $\nabla\rho = 0$ .

**Results and Discussion.** – The presently investigated noble-gas complexes include the five homotetranuclear  $[\text{C}(\text{NBeNg})_4]$  complexes **1–5** (Ng = He–Xe), the five heterotetranuclear complexes  $[\text{CN}_4\text{Be}_4(\text{He})(\text{Ne})(\text{Ar})(\text{Kr})]$  (**6**),  $[\text{CN}_4\text{Be}_4(\text{He})(\text{Ne})(\text{Ar})(\text{Xe})]$  (**7**),  $[\text{CN}_4\text{Be}_4(\text{He})(\text{Ne})(\text{Kr})(\text{Xe})]$  (**8**),  $[\text{CN}_4\text{Be}_4(\text{He})(\text{Ar})(\text{Kr})(\text{Xe})]$  (**9**), and  $[\text{CN}_4\text{Be}_4(\text{Ne})(\text{Ar})(\text{Kr})(\text{Xe})]$  (**10**), and the heteropentanuclear complex  $[\text{HC}_4\text{N}_5\text{Be}_5(\text{He})(\text{Ne})(\text{Ar})(\text{Kr})(\text{Xe})]$  (**11**)<sup>1</sup>. We also investigated the five  $[\text{H}_3\text{CNBeNg}]$  complexes (Ng = He–Xe) as model complexes containing a single –NBeNg moiety. Our optimized geometries, harmonic vibrational frequencies, and thermochemical data, as well as the results of NBO and AIM analysis, are reported in *Figs. 1–4* and in *Tables 1–7*.

$[\text{H}_3\text{CNBeNg}]$  (Ng = He–Xe). The relevant data on the structure and stability of the  $[\text{H}_3\text{CNBeNg}]$  complexes (Ng = He–Xe) are collected in *Tables 1* and *2* and in *Fig. 1*. With both the 6-31G(d)/SDD and the 6-311G(d,p)/SDD basis set, all these species revealed true minima of  $C_{3v}$  symmetry on the singlet MP2(full) potential-energy surface. From *Table 1* it is seen that their computed geometries and harmonic frequencies are only little sensitive to the basis set, and the MP2(full)/6-311G(d,p) bond distances of  $[\text{H}_3\text{CNBeHe}]$ ,  $[\text{H}_3\text{CNBeNe}]$ , and  $[\text{H}_3\text{CNBeAr}]$  are also nearly coincident with the CCSD(T)/6-311G(d,p) parameters obtained in our previous work [35]. The Be–N and C–N distances of any  $[\text{H}_3\text{CNBeNg}]$  (Ng = He–Xe) are invariably computed to be around 1.37 and 1.42 Å, respectively, and the frequencies of the three motions involving the C–N–Be moiety occur at typical values of *ca.* 1700 ( $\tilde{\nu}(\text{Be–N})$ ), 1000 ( $\tilde{\nu}(\text{C–N})$ ), and 300  $\text{cm}^{-1}$  ( $\delta(\text{C–N–Be})$ ), respectively. On the other hand, passing from  $[\text{H}_3\text{CNBeHe}]$  to  $[\text{H}_3\text{CNBeXe}]$ , the Be–Ng distance increases from *ca.* 1.5 to *ca.* 2.3 Å, and the corresponding stretching frequency decreases from *ca.* 530 to *ca.* 200  $\text{cm}^{-1}$  (the force constants decrease in the same order, ranging from 67.9 to 18.6 N/m). The N–Be–Ng bending motions, computed at around 160  $\text{cm}^{-1}$  for  $[\text{H}_3\text{CNBeHe}]$ , red-shift by almost 60  $\text{cm}^{-1}$  on passing to the four heaviest congeners.

*Table 1* shows that at both the MP2(full)/6-31G(d)/SDD and MP2(full)/6-311G(d,p)/SDD//MP2(full)/6-31G(d)/SDD level of theory and at 0 K, all the singlet  $[\text{H}_3\text{CNBeNg}]$  are stable with respect to the dissociation of *Eqn. 1*.



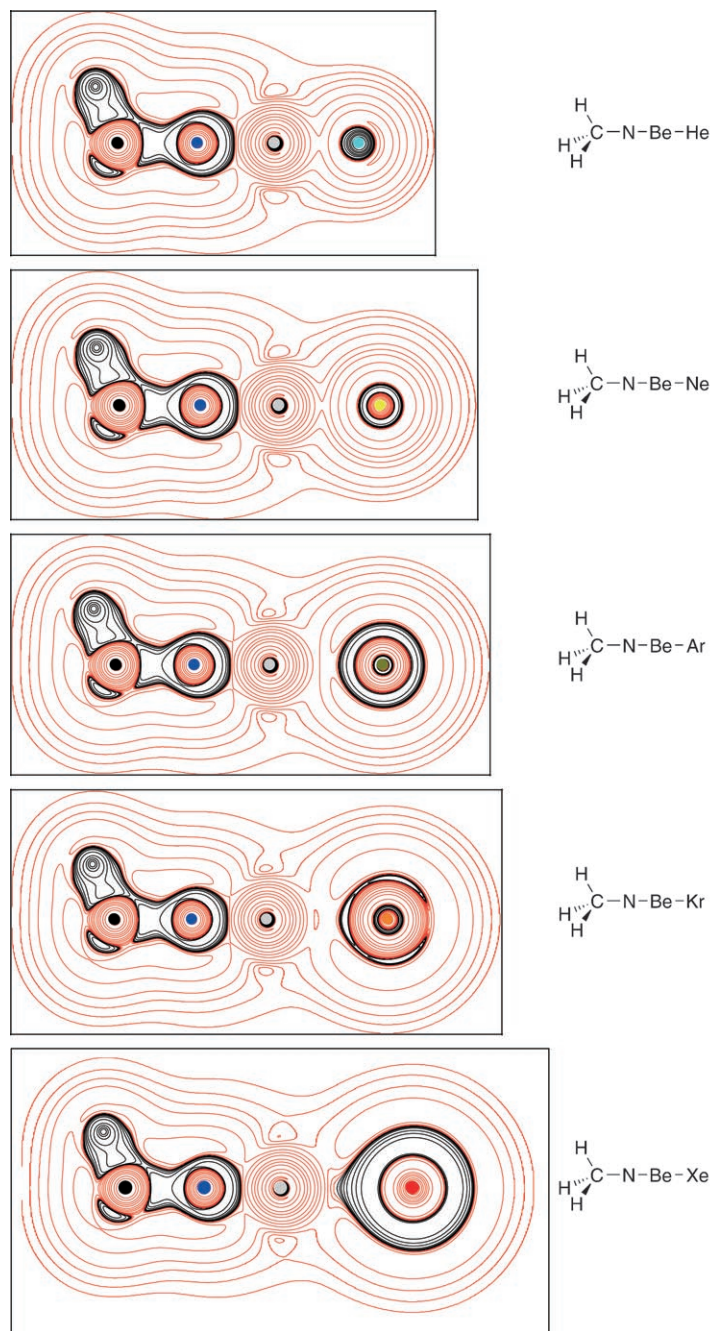


Fig. 1. Contour line diagrams of the MP2(full)/6-311G(d,p)/SDD Laplacian of the electronic charge density  $-\nabla^2\rho(\mathbf{r})$  in the  $\sigma_v$  plane of  $[H_3CNBeNg]$  ( $Ng = He - Xe$ ). Red lines are in regions of charge depletion ( $-\nabla^2\rho(\mathbf{r}) < 0$ ) and black lines in regions of charge concentration ( $-\nabla^2\rho(\mathbf{r}) > 0$ ).

Table 1. *MP2(full) Bond Distances [Å]<sup>a)</sup>, Harmonic Vibrational Frequencies [cm<sup>-1</sup>]<sup>b)</sup>, and Dissociation Energies [kJ/mol] at 0 K of the [H<sub>3</sub>CNBeNg] Complexes (Ng = He–Xe)*

Basis set	Be–Ng	Be–N	C–N	$\bar{\nu}(\text{Be–Ng})$	$\bar{\nu}(\text{Be–N})$	$\delta(\text{N–Be–Ng})$	$\bar{\nu}(\text{C–N})$	$\delta(\text{C–N–Be})$	$\Delta E^c$
Ng = He	1.50	1.37	1.42	528.7 (A <sub>1</sub> , 1.4)	1709.4 (A <sub>1</sub> , 30.2)	156.8 (E, 9.4)	1012.7 (A <sub>1</sub> , 9.1)	294.8 (E, 12.5)	13.8 (18.8)
	1.49	1.37	1.42	532.0 (A <sub>1</sub> , 0.03)	1695.9 (A <sub>1</sub> , 13.0)	165.3 (E, 13.2)	1003.3 (A <sub>1</sub> , 13.5)	286.5 (E, 12.4)	19.2 (23.0) <sup>d)</sup>
Ng = Ne	1.78	1.37	1.42	275.1 (A <sub>1</sub> , 3.4)	1718.3 (A <sub>1</sub> , 65.6)	101.5 (E, 0.4)	1008.4 (A <sub>1</sub> , 3.2)	280.2 (E, 13.8)	20.1 (39.7)
	1.82	1.37	1.42	241.9 (A <sub>1</sub> , 2.8)	1711.6 (A <sub>1</sub> , 43.1)	110.8 (E, 0.4)	995.3 (A <sub>1</sub> , 4.4)	278.5 (E, 18.0)	9.6 (28.5) <sup>d)</sup>
Ng = Ar	2.04	1.37	1.42	256.0 (A <sub>1</sub> , 5.1)	1715.6 (A <sub>1</sub> , 105.3)	102.5 (E, 1.3)	1013.9 (A <sub>1</sub> , 0.2)	295.8 (E, 13.3)	32.6 (48.1)
	2.05	1.37	1.42	257.4 (A <sub>1</sub> , 4.2)	1706.5 (A <sub>1</sub> , 86.0)	109.6 (E, 2.2)	1006.5 (A <sub>1</sub> , 0.5)	283.8 (E, 14.8)	34.3 (53.1) <sup>d)</sup>
Ng = Kr	2.22	1.37	1.42	206.7 (A <sub>1</sub> , 1.8)	1706.2 (A <sub>1</sub> , 90.3)	91.6 (E, 1.3)	1007.8 (A <sub>1</sub> , 1.3)	294.1 (E, 11.9)	42.7 (59.0)
	2.21	1.37	1.42	214.7 (A <sub>1</sub> , 1.9)	1696.4 (A <sub>1</sub> , 81.3)	102.3 (E, 2.2)	1001.0 (A <sub>1</sub> , 1.0)	283.7 (E, 13.5)	45.6 (56.9) <sup>d)</sup>
Ng = Xe	2.38	1.38	1.42	197.8 (A <sub>1</sub> , 0.5)	1694.4 (A <sub>1</sub> , 84.3)	79.1 (E, 2.5)	1004.3 (A <sub>1</sub> , 1.8)	296.3 (E, 9.8)	54.8 (62.8)
	2.37	1.38	1.42	201.8 (A <sub>1</sub> , 0.3)	1683.5 (A <sub>1</sub> , 70.0)	91.3 (E, 3.2)	996.9 (A <sub>1</sub> , 2.4)	281.6 (E, 11.2)	58.6 (68.2) <sup>f)</sup>

<sup>a)</sup> The C–H bond distances and the H–C–H bond angles are invariably computed at *ca.* 1.1 Å and 107.3°, respectively. <sup>b)</sup> The –CH<sub>3</sub> motions are not included. Symmetries (point group: C<sub>3v</sub>) and IR intensities [km/mol] are given in parentheses. <sup>c)</sup> Energy change of the reaction of *Eqn. 1*. The values in parentheses are not corrected for the BSSE. <sup>d)</sup> At the MP2(full)/6-31G(d) optimized geometry. <sup>e)</sup> SDD basis set with relativistic effective core potential for Xe. <sup>f)</sup> At the MP2(full)/6-31G(d)/SDD-optimized geometry.

Table 2. *MP2(full)/6-311G(d,p)/SDD//MP2(full)/6-31G(d)/SDD NBO Atomic Charges  $q$  [e] and AIM Analysis of the  $[H_3CNBeNg]$  Complexes (Ng=He–Xe). The AIM charge density  $\rho$  [ $e/\text{\AA}^3$ ], the Laplacian of the charge density  $\nabla^2\rho$  [ $e/\text{\AA}^3$ ], and the energy density  $H$  [hartree/ $\text{\AA}^3$ ] are calculated at the bond critical point [bcp] on the specified bond.*

Ng	$q(H)$	$q(C)$	$q(N)$	$q(Be)$	$q(Ng)$	Bond	$r(X)^a$	$\rho$	$\nabla^2\rho$	$H$
He	0.164	−0.340	−1.523	1.324	0.048	C–H	0.70	1.842	−22.149	−1.861
						C–N	0.54	1.868	−18.816	−2.412
						Be–N	0.49	1.004	30.832	−0.260
						Be–He	0.63	0.207	8.206	0.086
Ne	0.160	−0.336	−1.560	1.368	0.047	C–H	0.70	1.839	−22.071	−1.857
						C–N	0.54	1.872	−18.984	−2.404
						Be–N	0.49	1.006	30.940	−0.264
						Be–Ne	0.65	0.173	6.147	0.051
Ar	0.158	−0.334	−1.547	1.308	0.098	C–H	0.70	1.837	−22.019	−1.855
						C–N	0.54	1.878	−19.132	−2.399
						Be–N	0.50	1.005	30.347	−0.269
						Be–Ar	0.65	0.236	5.468	0.003
Kr	0.159	−0.335	−1.539	1.290	0.108	C–H	0.70	1.836	−21.984	−1.852
						C–N	0.54	1.879	−19.138	−2.402
						Be–N	0.50	1.002	30.146	−0.269
						Be–Kr	0.67	0.210	4.169	−0.009
Xe	0.159	−0.335	−1.526	1.257	0.128	C–H	0.70	1.835	−21.975	−1.852
						C–N	0.54	1.881	−19.173	−2.406
						Be–N	0.50	0.997	29.812	−0.267
						Be–Xe	0.68	0.216	3.350	−0.028

<sup>a</sup>) Distance [ $\text{\AA}$ ] of the bcp from the X-atom of any X–Y bond.

Since the triplet  $[H_3CNBe]$  ( $^3A''$ ) is less stable than the singlet ground-state  $^1A_1$  by *ca.* 17 kJ/mol [35], all the  $[H_3CNBeNg]$  adducts (Ng=He–Xe) are predicted to be thermochemically stable with respect to dissociation into  $[H_3CNBe]$  and Ng. As to the trend of their stability, the polarizability of the noble gases regularly increases from He to Xe [36], and one expects that the  $\Delta E$  of the reaction of *Eqn. 1* increases from  $[H_3CNBeHe]$  to  $[H_3CNBeXe]$ . As a matter of fact, at both the *MP2(full)/6-31G(d)/SDD* and *MP2(full)/6-311G(d,p)/SDD//MP2(full)/6-31G(d)/SDD* level of theory, if not corrected for the BSSE, the computed  $\Delta E$ s follow this expected trend and range from *ca.* 21 kJ/mol for  $[H_3CNBeHe]$  to *ca.* 63 kJ/mol for  $[H_3CNBeXe]$ . However, if one includes the BSSE, the  $[H_3CNBeAr]$ ,  $[H_3CNBeKr]$ , and  $[H_3CNBeXe]$  complexes are still more stable than  $[H_3CNBeNe]$ , but the dissociation energy of the latter species drastically reduces and becomes lower than that of  $[H_3CNBeHe]$  by nearly 8 kJ/mol at the *MP2(full)/6-311G(d,p)//MP2(full)/6-31G(d)* level of theory. At this stage of experience, however, this apparently anomalous trend is not surprising. In fact, *Frenking* and co-workers noted so far [37] that the *MP4(SDTQ)/6-311G(2df,2pd)* stabilities of the  $[OBeNg]$  adducts (Ng=He–Ar) increased in the unexpected order  $[OBeNe] < [OBeHe] < [OBeAr]$  when the BSSE correction was included. Similarly, we have more recently found [35] that, once corrected for the BSSE, the *CCSD(T)/6-311G(d,p)* and *CCSD(T)/6-311++G(2df,2p)* dissociation energy of  $[HNBeNe]$  is lower than that of  $[HNBeHe]$  by *ca.* 6 kJ/mol. As already noted previously [37], these

anomalous trends could reflect the at least partial inadequacy of the counterpoise method to correct for the BSSE, and the results of *Table 1* do not support a safe conclusion as to which of  $[\text{H}_3\text{CNBeHe}]$  and  $[\text{H}_3\text{CNBeNe}]$  is actually more stable. We note also that, while rather big, the 6-311++G(2df,2p) basis set is not ideally suited to describe very weak interactions, crucially affected by correlation energy. Therefore, especially for the neon-containing species, one cannot safely rule out that the involved curves can be very well dissociative. In any case, from the quantitative point of view, the stability of any  $[\text{H}_3\text{CNBeNg}]$  is quite similar to the corresponding  $[\text{OBeNg}]$  [37][38], thus suggesting a comparable type of beryllium–noble-gas interaction. The NBO and AIM analyses of  $[\text{H}_3\text{CNBeNg}]$  (Ng=He–Xe), performed at a level of theory comparable to that employed in the previous investigation of  $[\text{OBeNg}]$  [37][38], confirm this expectation. The data reported in *Fig. 1* and in *Table 2* indicate in fact that, similarly to  $[\text{OBeNg}]$  (Ng=He–Kr), the  $\text{H}_3\text{CNBe–Ng}$  bond of  $[\text{H}_3\text{CNBeHe}]$ ,  $[\text{H}_3\text{CNBeNe}]$ ,  $[\text{H}_3\text{CNBeAr}]$ , and  $[\text{H}_3\text{CNBeKr}]$  is essentially a charge-induced dipole electrostatic interaction, while the  $\text{H}_3\text{CNBe–Xe}$  bond has a small covalent contribution comparable to the  $\text{OBe–Xe}$  bond. From *Fig. 1*, the contour line diagrams of the *Laplacian* distribution  $-\nabla^2\rho(\mathbf{r})$  of  $[\text{H}_3\text{CNBeHe}]$  and  $[\text{H}_3\text{CNBeNe}]$  indicate that the field of He and Ne is essentially identical with that of the isolated atoms. However, inspection of the red contour lines suggests that the electron density of He and Ne is polarized toward  $\text{H}_3\text{CNBe}$ , indicative of charge-induced dipole interactions. Consistently, from *Table 2*, at the bond critical points (bcp) located on the attractor interaction lines corresponding to the  $\text{H}_3\text{CNBe–He}$  and  $\text{H}_3\text{CNBe–Ne}$  bonds, the charge density  $\rho$  is as low as *ca.*  $0.2 \text{ e}/\text{\AA}^3$ , the *Laplacian*  $\nabla^2\rho$  is positive, as typical for closed-shell interactions, and the energy density  $H$  is also positive. Positive values of  $H$  are usually associated with ionic and *van der Waals* interactions, while negative values of  $H$  indicate covalent bonds [39]. Passing to  $[\text{H}_3\text{CNBeAr}]$ , the contour lines of the *Laplace* distribution around Ar reveal a slight deformation of the valence sphere, but the positive value of  $H$  at the bcp on the  $\text{H}_3\text{CNBe–Ar}$  bond still confirms the predominance of electrostatic forces. Passing to  $[\text{H}_3\text{CNBeKr}]$ , the *Laplace* distribution around Kr is clearly oval-shaped, and, in  $[\text{H}_3\text{CNBeXe}]$ , it is possible to note a droplet-like appendix of electron concentration from the xenon towards the Be-atom. This deformation is only slightly less pronounced than in  $[\text{OBeXe}]$  [38], and the value of  $H$  at the bcp on the  $\text{H}_3\text{CNBe–Xe}$  bond,  $-0.028 \text{ hartree}/\text{\AA}^3$ , is also quite similar to that on the  $\text{OBe–Xe}$  bond,  $-0.033 \text{ hartree}/\text{\AA}^3$  [38]. It is, therefore, clear that along the trend from He to Xe, the *Laplace* distribution, the total-energy density at the Be–Ng critical point, and the value of the *Laplacian* change considerably and may overall suggest the conceivable onset of covalent bonding, particularly in  $[\text{H}_3\text{CNBeXe}]$ . However, any definitive conclusion on this point is difficult. In general, the kind of interaction between noble gases and closed-shell compounds, whether ionic or covalent or both, raises animated debate in the literature. For example, for Ng=Ar, Kr, and Xe, the  $\text{Au}^+\text{–Ng}$  complexes were theoretically predicted to be mainly covalent-like [18]. This suggestion was, however, subsequently rejected by arguments based on higher-order multipoles to describe induced polarization effects [40]. The inclusion of these terms significantly reduces the amount of covalent interaction and supports the conclusion that ‘the need to invoke covalency within the  $\text{Au}^+\text{–Ng}$  bond appears to be unproven, even for diffuse species such as Xe’ [40]. It is also known that, for elements as heavy as

xenon, the use of the effective core potential and the consequent absence of an explicit representation of the core electron density makes the corresponding topological analysis problematical [41]. In any case, from *Table 2*, the NBO charges of the Ng-atoms of  $[\text{H}_3\text{CNBeNg}]$  increase in the order  $\text{He} \approx \text{Ne} < \text{Ar} < \text{Kr} < \text{Xe}$  and confirm a larger charge transfer from Ng to  $\text{H}_3\text{CNBe}$  passing from  $[\text{H}_3\text{CNBeHe}]$  to  $[\text{H}_3\text{CNBeXe}]$ . In addition, as already noted for  $[\text{OBeNg}]$  (Ng = He–Xe) [37][38] and  $[\text{HNBeNg}]$  (Ng = He–Ar) [35], the charge of the Be-atom of  $[\text{H}_3\text{CNBeNg}]$  is invariably computed as large as *ca.* +1.30 e. Therefore, we explain the stable attachment of Ng to  $[\text{H}_3\text{CNBe}]$  by assuming that, due to the small radius of the Be-atom, any approaching Ng experiences an electric field large enough to allow its fixation into a relatively deep potential-energy well.

$[\text{C}(\text{NBeNg})_4]$  **1–5** (Ng = He–Xe). The five  $[\text{C}(\text{NBeNg})_4]$  structures **1–5** (Ng = He–Xe) of  $T_d$  symmetry, formally obtained by replacing the H-atoms of  $\text{CH}_4$  with  $-\text{NBeNg}$  groups, were invariably located as true minima on the MP2(full)/6-31G(d)/SDD potential-energy surface. The data reported in *Fig. 2* and in *Tables 3* and *4* indicate that, irrespective of the Ng, the structural and bonding features of the various  $-\text{NBeNg}$  moieties are quite similar to those of the mononuclear complexes  $[\text{H}_3\text{CNBeNg}]$  (Ng = He–Xe).

Compared with the  $[\text{H}_3\text{CNBeNg}]$  species, the Be–Ng, Be–N, and C–N bond distances of **1–5** show largest elongations of only 0.01 Å, and the frequencies of the motions involving the  $-\text{NBeNg}$  moieties of **1–5** are only slightly lower than for  $[\text{H}_3\text{CNBeNg}]$ . We note in particular from *Table 3* the two groups of Be–N and C–N stretching frequencies around 1600 and 750/1030  $\text{cm}^{-1}$ , respectively, the N–Be–Ng bending motions around 150  $\text{cm}^{-1}$ , the Be–He stretching frequencies of **1** around 450  $\text{cm}^{-1}$ , and the Be–Ng stretching frequencies of **2–5** in the range between 100 and 200  $\text{cm}^{-1}$ . The AIM analysis of **1–5** confirms that they consist of essentially independent  $-\text{NBeNg}$  building blocks which retain the bonding features of  $[\text{H}_3\text{CNBeNg}]$  (Ng = He–Xe). Thus, irrespective of Ng, the charge density  $\rho$ , the Laplacian  $\nabla^2\rho$ , and the energy density  $H$  calculated at the bcp on the various C–N, Be–N, and Be–Ng bonds (see *Table 4*) are quite similar to those predicted for the corresponding  $[\text{H}_3\text{CNBeNg}]$ . Consistently, the contour line diagrams of the Laplacian distributions around the  $-\text{NBeNg}$  moieties of the various  $[\text{C}(\text{NBeNg})_4]$  (not shown in detail) are quite similar to those reported in *Fig. 1*. Therefore, we suggest that, in the complexes **1–4**, the beryllium–noble-gas interaction is essentially electrostatic, with a probable small covalent contribution in  $[\text{C}(\text{NBeXe})_4]$  (**5**). Comparing *Table 2* with *Table 4*, we note also that the atomic charge of the Be- and the Ng-atoms of any  $[\text{C}(\text{NBeNg})_4]$  is slightly lower than that of the corresponding  $[\text{H}_3\text{CNBeNg}]$ . Consistently, according to *Table 3*, irrespective of the Ng, the MP2(full)/6-311G(d,p)/SDD//MP2(full)/6-31G(d)/SDD energy change at 0 K of the dissociation of *Eqn. 2* is slightly lower than that of the dissociation of *Eqn. 1*. We note also that the  $\Delta E$  of the reaction of *Eqn. 2* regularly increases from  $[\text{C}(\text{NBeHe})_4]$  (**1**) to  $[\text{C}(\text{NBeXe})_4]$  (**5**) and follows the same periodic trend already noted for  $[\text{H}_3\text{CNBeNg}]$  (we note again the anomalous BSSE effect on the stability of  $[\text{C}(\text{NBeNe})_4]$  (**2**)).





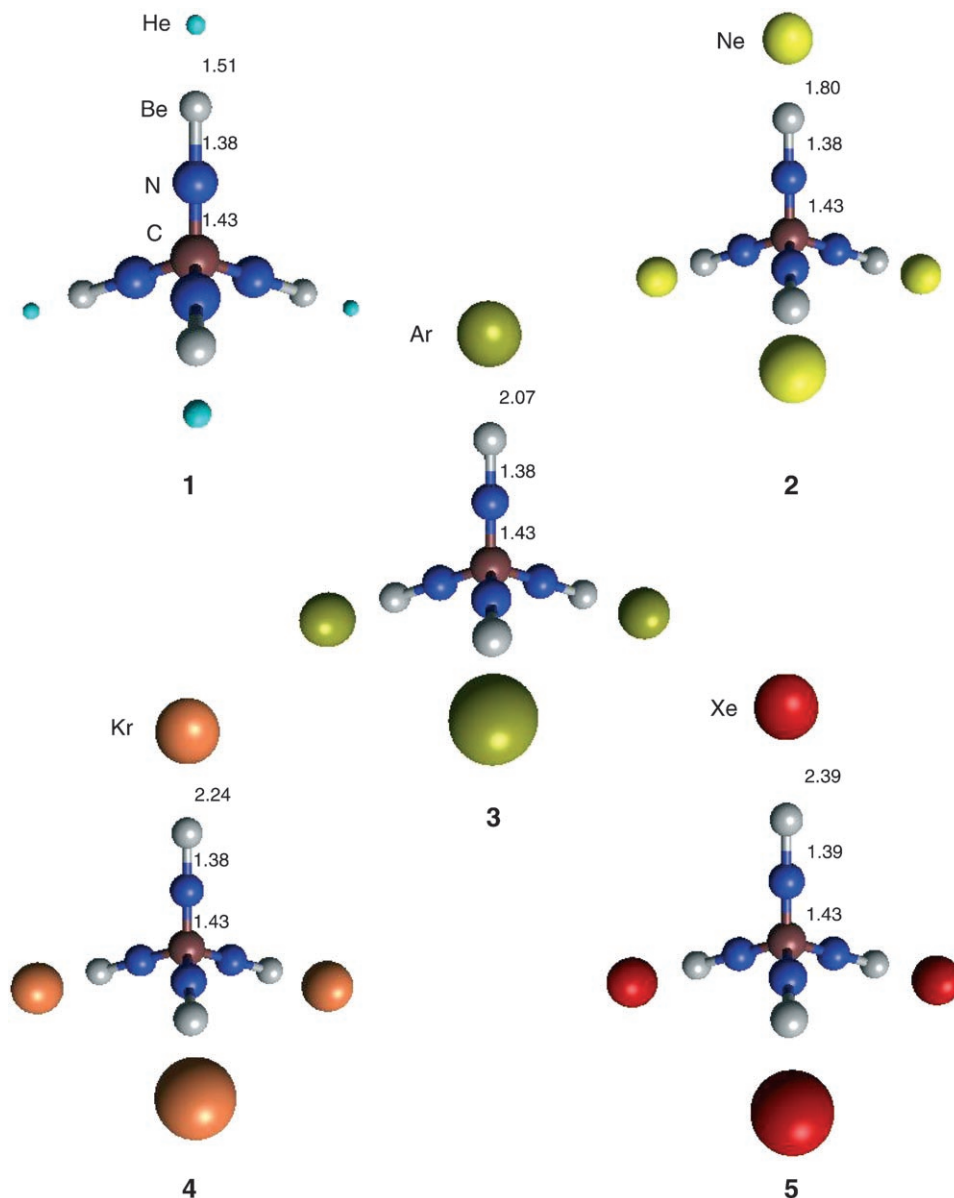


Fig. 2. *MP2(full)/6-31G(d)/SDD-Optimized bond distances [Å] of the  $[C(NBeNg)_4]$  complexes 1–5 (Ng = He–Xe). The point group is  $T_d$ .*

$[CN_4Be_4(Ng_1)(Ng_2)(Ng_3)(Ng_4)]$  **6–10** (Ng<sub>*i*</sub> = He–Xe). Having ascertained the stability of the homopolynuclear complexes  $[C(NBeNg)_4]$  **1–5** containing four identical  $-NBeNg$  groups, we investigated the five heterotetranuclear complexes **6–10**, formally obtained by replacing the H atoms of  $CH_4$  with four distinct  $-NBeNg$  groups

Table 3. *MP2(full)/6-31G(d)/SDD Harmonic Vibrational Frequencies [cm<sup>-1</sup>]<sup>a</sup>, and *MP2(full)/6-311G(d,p)/SDD//MP2(full)/6-31G(d)/SDD Dissociation Energies [kJ/mol] at 0 K of the [C(NBeNg)<sub>4</sub>] complexes 1–5* (see Fig. 2)*

	1 Ng = He	2 Ng = Ne	3 Ng = Ar	4 Ng = Kr	5 Ng = Xe
$\tilde{\nu}(\text{Be-Ng})$	445.8 (A <sub>1</sub> , 0) 457.8 (T <sub>2</sub> , 0.4)	200.7 (A <sub>1</sub> , 0) 237.2 (T <sub>2</sub> , 2.2)	158.4 (A <sub>1</sub> , 0) 219.7 (T <sub>2</sub> , 2.3)	104.6 (A <sub>1</sub> , 0) 194.0 (T <sub>2</sub> , 0.2)	85.9 (A <sub>1</sub> , 0) 192.7 (T <sub>2</sub> , 0.1)
$\tilde{\nu}(\text{Be-N})$	1618.8 (A <sub>1</sub> , 0) 1636.1 (T <sub>2</sub> , 107.1)	1627.9 (A <sub>1</sub> , 0) 1641.1 (T <sub>2</sub> , 181.8)	1624.7 (A <sub>1</sub> , 0) 1636.8 (T <sub>2</sub> , 254.8)	1609.7 (A <sub>1</sub> , 0) 1625.5 (T <sub>2</sub> , 225.0)	1586.5 (A <sub>1</sub> , 0) 1609.8 (T <sub>2</sub> , 198.0)
$\delta(\text{N-Be-Ng})$	108.4 (T <sub>1</sub> , 0) 161.7 (E, 0) 167.7 (T <sub>2</sub> , 0.1)	58.0 (T <sub>1</sub> , 0) 141.7 (E, 0) 143.6 (T <sub>2</sub> , 1.3)	63.8 (T <sub>1</sub> , 0) 154.0 (T <sub>2</sub> , 0.3) 157.8 (E, 0)	53.6 (T <sub>1</sub> , 0) 132.6 (T <sub>2</sub> , 0.1) 152.2 (E, 0)	40.5 (T <sub>1</sub> , 0) 124.8 (T <sub>2</sub> , 2.1) 149.9 (E, 0)
$\omega(\text{N-Be-Ng})^b$	72.9 (E, 0) 83.5 (T <sub>2</sub> , 49.2)	26.4 (E, 0) 33.1 (T <sub>2</sub> , 12.1)	18.9 (E, 0) 26.1 (T <sub>2</sub> , 9.8)	11.5 (E, 0) 17.4 (T <sub>2</sub> , 5.8)	7.5 (E, 0) 12.4 (T <sub>2</sub> , 4.2)
$\tilde{\nu}(\text{C-N})$	751.4 (A <sub>1</sub> , 0) 1036.1 (T <sub>2</sub> , 240.2)	712.7 (A <sub>1</sub> , 0) 1028.8 (T <sub>2</sub> , 184.4)	721.0 (A <sub>1</sub> , 0) 1035.2 (T <sub>2</sub> , 190.0)	714.2 (A <sub>1</sub> , 0) 1028.8 (T <sub>2</sub> , 256.1)	714.8 (A <sub>1</sub> , 0) 1021.3 (T <sub>2</sub> , 355.2)
$\delta(\text{C-N-Be})$	257.8 (T <sub>1</sub> , 0)	240.2 (T <sub>1</sub> , 0)	261.2 (T <sub>1</sub> , 0)	261.2 (T <sub>1</sub> , 0)	264.4 (T <sub>1</sub> , 0)
$\delta(\text{N-C-N})$	485.6 (E, 0) 623.9 (T <sub>2</sub> , 8.8)	473.6 (E, 0) 574.1 (T <sub>2</sub> , 4.8)	482.8 (E, 0) 583.3 (T <sub>2</sub> , 19.6)	482.7 (E, 0) 579.7 (T <sub>2</sub> , 15.6)	481.9 (E, 0) 579.3 (T <sub>2</sub> , 19.2)
$\Delta E^c$	17.6 (21.3)	4.2 (23.4)	26.4 (45.2)	34.3 (45.6)	48.1 (58.6)

<sup>a</sup>) Symmetries and IR intensities [km/mol] are given in parentheses. <sup>b</sup>) (NgBeN)–C–(NBeNg) bending motion. <sup>c</sup>) Energy change of the reaction of Eqn. 2. The values in parentheses are not corrected for the BSSE.

Table 4. *MP2(full)/6-311G(d,p)/SDD//MP2(full)/6-31G(d)/SDD NBO Atomic Charges q [e] and AIM Analysis of the [C(NBeNg)<sub>4</sub>] Complexes 1–5* (see Fig. 2). The AIM charge density  $\rho$  [e/Å<sup>3</sup>], the Laplacian of the charge density  $\nabla^2\rho$  [e/Å<sup>3</sup>], and the energy density  $H$  [hartree/Å<sup>3</sup>] are calculated at the bond critical point on the specified bond.

Ng	$q(\text{C})$	$q(\text{N})$	$q(\text{Be})$	$q(\text{Ng})$	Bond	$r(\text{X})^a$	$\rho$	$\nabla^2\rho$	$H$	
1	He	0.538	–1.455	1.274	0.046	C–N	0.57	1.905	–19.877	–2.288
						Be–N	0.50	0.970	29.484	–0.245
						Be–He	0.63	0.201	8.147	0.088
2	Ne	0.550	–1.492	1.310	0.045	C–N	0.57	1.897	–19.700	–2.266
						Be–N	0.50	0.971	29.722	–0.245
						Be–Ne	0.66	0.160	5.904	0.005
3	Ar	0.546	–1.473	1.246	0.091	C–N	0.57	1.897	–19.682	–2.264
						Be–N	0.50	0.971	29.235	–0.249
						Be–Ar	0.65	0.215	5.277	0.011
4	Kr	0.540	–1.460	1.224	0.101	C–N	0.57	1.899	–19.695	–2.269
						Be–N	0.50	0.966	28.947	–0.249
						Be–Kr	0.67	0.195	4.169	–0.001
5	Xe	0.531	–1.431	1.187	0.111	C–N	0.57	1.904	–19.770	–2.285
						Be–N	0.50	0.959	28.486	–0.246
						N–Xe	0.68	0.205	3.468	–0.021

<sup>a</sup>) Distance [Å] of the bcp from the X atom of any X–Y bond.

(Ng = He–Xe) (Fig. 3). All these species revealed true minima on the *MP2(full)/6-31G(d)/SDD* potential-energy surface, with the positive harmonic frequencies listed in Table 5. The optimized bond lengths of the various –NBeNg moieties are nearly

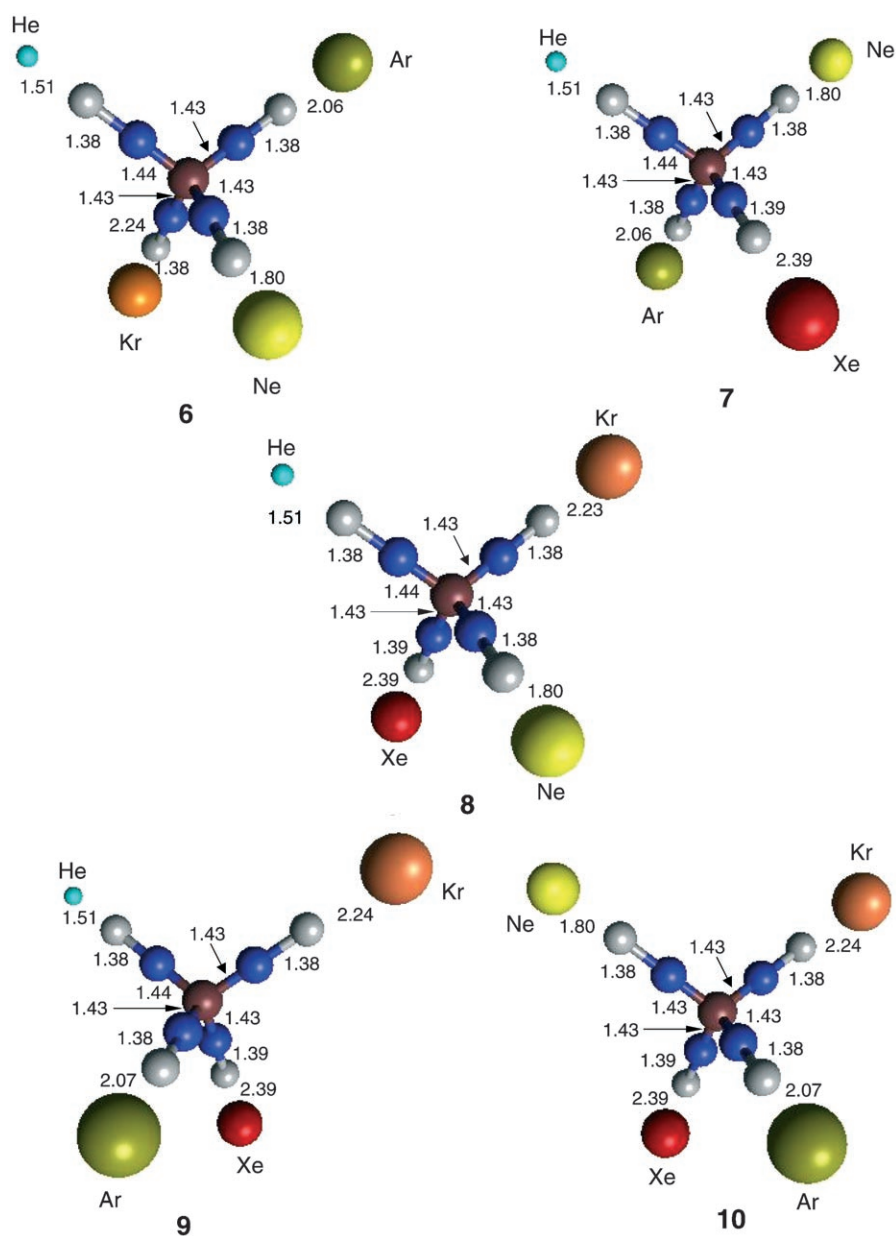


Fig. 3. *MP2(full)/6-31G(d)/SDD-Optimized bond distances [Å] of the  $[CN_4Be_4(Ng_1)(Ng_2)(Ng_3)(Ng_4)]$  complexes 6–10 ( $Ng_i = \text{He–Xe}$ ).*

identical with those of the  $[C(NBeNg)_4]$  complexes and are only slightly elongated with respect to the  $[H_3CNBeNg]$  species. All the Be–N and C–N distances are in fact computed at *ca.* 1.43 and 1.38 Å, respectively, and the Be–Ng distances at *ca.* 1.50

Table 5. *MP2(full)/6-31G(d)/SDD Harmonic Vibrational Frequencies [cm<sup>-1</sup>]<sup>a</sup> of the Heteropolynuclear Ng Complexes **6–10** (see Fig. 3)*

	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>	<b>10</b>
$\tilde{\nu}(\text{Be–He})$	450.0 (1.2)	449.6 (1.2)	450.1 (1.2)	449.9 (1.0)	
$\tilde{\nu}(\text{Be–Ne})$	234.1 (2.0)	234.6 (2.1)	233.3 (1.8)		233.9 (2.3)
$\tilde{\nu}(\text{Be–Ar})$	209.2 (1.1)	208.7 (1.0)		214.5 (1.9)	210.5 (1.6)
$\tilde{\nu}(\text{Be–Kr})$	127.9 (0.6)		187.1 (0.03)	191.9 (0.04)	188.9 (0.02)
$\tilde{\nu}(\text{Be–Xe})$		119.6 (2.5)	116.3 (2.5)	115.3 (2.0)	114.2 (1.2)
$\tilde{\nu}(\text{Be–N})$	1615.6 (12.5)	1608.9 (45.8)	1607.4 (36.2)	1606.2 (24.5)	1605.7 (54.9)
	1628.8 (151.8)	1621.9 (125.0)	1621.4 (134.3)	1620.0 (131.3)	1623.3 (181.9)
	1637.3 (181.1)	1636.1 (156.7)	1629.3 (204.6)	1628.0 (201.1)	1632.7 (179.7)
	1641.2 (248.0)	1640.9 (247.0)	1638.0 (175.5)	1638.3 (251.9)	1636.8 (236.6)
$\delta(\text{N–Be–Ng})$	43.4 (9.9)	39.9 (8.6)	37.8 (8.5)	37.4 (8.0)	23.6 (8.2)
	46.0 (9.8)	45.1 (9.2)	42.3 (8.2)	43.3 (9.0)	25.2 (7.1)
	59.7 (0.1)	55.6 (0.4)	51.4 (0.1)	55.5 (0.4)	47.7 (0.01)
	82.8 (12.7)	80.4 (12.4)	79.1 (12.6)	77.5 (12.3)	53.2 (0.03)
	84.5 (12.9)	84.5 (12.7)	82.0 (12.3)	81.4 (12.0)	56.9 (0.01)
	144.8 (0.3)	143.8 (0.3)	127.5 (0.6)	131.8 (1.1)	126.7 (0.2)
	151.2 (0.5)	149.7 (0.4)	147.8 (0.3)	149.7 (0.04)	142.7 (0.2)
	154.0 (0.2)	152.8 (0.3)	149.7 (0.6)	153.2 (0.2)	150.0 (0.03)
	161.3 (0.4)	160.5 (0.2)	158.8 (0.1 <sub>5</sub> )	153.5 (0.3)	152.8 (0.03)
	174.5 (0.3)	172.1 (0.4)	168.0 (0.3)	173.5 (0.3)	161.7 (0.3)
$\omega(\text{N–Be–Ng})^{\text{b}}$	19.0 (2.2)	16.1 (2.3)	13.0 (1.7)	12.5 (1.6)	12.0 (1.1)
	23.8 (2.7)	21.3 (3.4)	20.6 (2.5)	16.6 (1.8)	15.1 (0.7)
	28.9 (10.0)	27.8 (9.1)	24.6 (8.7)	21.8 (8.3)	20.6 (7.4)
$\tilde{\nu}(\text{C–N})$	726.5 (1.9)	726.1 (1.7)	724.7 (0.6)	726.6 (1.6)	715.4 (1.2)
	1021.1 (237.0)	1020.9 (249.1)	1020.7 (250.9)	1019.7 (276.1)	1022.7 (284.3)
	1033.6 (225.1)	1029.8 (273.7)	1030.1 (278.1)	1031.9 (290.6)	1027.3 (250.3)
	1042.1 (188.0)	1040.0 (193.8)	1035.3 (236.4)	1040.1 (207.2)	1035.2 (194.5)
$\delta(\text{C–N–Be})$	252.4 (0.01)	252.2 (0.004)	252.0 (0.03)	259.2 (0.01)	253.6 (0.08)
	253.7 (0.03)	254.6 (0.2)	254.3 (0.2)	260.9 (0.05)	255.0 (0.3)
	260.3 (0.02)	261.1 (0.1)	261.0 (0.06)	262.0 (0.07)	262.2 (0.1)
$\delta(\text{N–C–N})$	481.1 (0.04)	480.7 (0.06)	480.5 (0.07)	483.1 (0.01)	479.8 (0.1)
	481.4 (0.1)	481.0 (0.1)	481.0 (0.2)	483.2 (0.01)	479.9 (0.1)
	579.7 (11.9)	579.5 (12.3)	579.0 (12.7)	580.8 (16.2)	577.6 (11.6)
	582.1 (15.7)	582.0 (16.5)	580.1 (13.3)	583.4 (20.5)	578.6 (12.4)
	607.8 (9.3)	607.3 (9.7)	606.9 (9.5)	608.7 (12.4)	580.8 (17.3)

<sup>a</sup>) Symmetries and IR intensities [km/mol] are given in parentheses. <sup>b</sup>) (NgBeN)–C–(NBeNg) bending motion.

(Ng = He), 1.80 (Ng = Ne), 2.10 (Ng = Ar), 2.22 (Ng = Kr), and 2.40 Å (Ng = Xe). We also repeated the geometry optimization of **6–10** at the MP2(full)/6-311G(d,p)/SDD level of theory, but we found only minor differences with the MP2(full)/6-31G(d)/SDD parameters (*i.e.*, practically unchanged Be–N and C–N distances, and largest changes of only 0.05 Å in the Be–Ng distances). In addition, as shown in *Table 5*, the vibrational motions of **6–10** occur at wavenumbers quite similar to those of [H<sub>3</sub>CNBeNg] and [C(NBeNg)<sub>4</sub>]. We note in particular the four Be–N stretchings around 1610–1640 cm<sup>-1</sup>, the four C–N stretchings around 730 and 1030 cm<sup>-1</sup>, a group of ten N–Be–Ng bending motions up to *ca.* 170 cm<sup>-1</sup>, and the four Be–Ng stretchings

between *ca.* 110 and 450  $\text{cm}^{-1}$ . The various  $-\text{NBeNg}$  building blocks of **6–10** are also clearly recognizable in terms of charge distribution and topological features of the electron density. The relevant NBO and AIM data are collected in *Table 6*.

Table 6. *MP2(full)/6-311G(d,p)/SDD//MP2(full)/6-31G(d)/SDD NBO Atomic Charges  $q$  [e] of the Heteropolynuclear Ng Complexes 6–10 (see Fig. 3)*

	Group	$q(\text{C})$	$q(\text{N})$	$q(\text{Be})$	$q(\text{Ng})$
<b>6</b>	C–N–Be–He	0.543	–1.445	1.247	0.046
	C–N–Be–Ne		–1.489	1.306	0.045
	C–N–Be–Ar		–1.478	1.259	0.102
	C–N–Be–Kr		–1.467	1.237	0.102
<b>7</b>	C–N–Be–He	0.541	–1.444	1.247	0.046
	C–N–Be–Ne		–1.489	1.306	0.045
	C–N–Be–Ar		–1.477	1.260	0.093
	C–N–Be–Xe		–1.443	1.199	0.115
<b>8</b>	C–N–Be–He	0.540	–1.443	1.247	0.046
	C–N–Be–Ne		–1.488	1.306	0.045
	C–N–Be–Kr		–1.465	1.238	0.103
	C–N–Be–Xe		–1.443	1.200	0.115
<b>9</b>	C–N–Be–He	0.539	–1.441	1.242	0.046
	C–N–Be–Ar		–1.474	1.256	0.092
	C–N–Be–Kr		–1.463	1.233	0.102
	C–N–Be–Xe		–1.441	1.196	0.114
<b>10</b>	C–N–Be–Ne	0.542	–1.484	1.296	0.044
	C–N–Be–Ar		–1.473	1.251	0.092
	C–N–Be–Kr		–1.462	1.228	0.101
	C–N–Be–Xe		–1.438	1.190	0.113

Taking for example the C–N–Be–He group of the complexes **6–9**, the charge density  $\rho$ , the Laplacian  $\nabla^2\rho$ , and the energy density  $H$  calculated at the bcp on the C–N, Be–N, and Be–He bonds are essentially independent on the complex (*Table 7*) and quite similar to those computed for the corresponding homonuclear  $[\text{C}(\text{NBeHe})_4]$ . A similar consideration holds true for all the other C–N–Be–Ng groups (Ng = Ne–Xe). The total charges of the various  $-\text{NBeNg}$  groups of complexes **6–10** are also quite similar to the homonuclear complexes  $[\text{C}(\text{NBeNg})_4]$ , thus suggesting quite similar Be–Ng interactions. The thermochemical data listed in *Table 7* confirm this expectation.

For any complex **6–10**, we calculated the  $\text{MP2}(\text{full})/6\text{-}311\text{G}(\text{d},\text{p})/\text{SDD}//\text{MP2}(\text{full})/6\text{-}31\text{G}(\text{d})/\text{SDD}$  energy change at 0 K for the loss of the various noble gases (*Table 8*). For any Ng, the obtained values are nearly identical to the energy change of the reaction of *Eqn. 2* and amount to *ca.* 16 kJ/mol for Ng = He, *ca.* 3 kJ/mol for Ng = Ne (the BSSE uncorrected value is, however, *ca.* 22.0 kJ/mol), *ca.* 25 kJ/mol for Ng = Ar, *ca.* 36 kJ/mol for Ng = Kr, and *ca.* 50 kJ/mol for Ng = Xe. Once again, these values regularly increase in the expected order from He to Xe.

$[\text{HC}_4\text{N}_5\text{Be}_5(\text{He})(\text{Ne})(\text{Ar})(\text{Kr})(\text{Xe})]$  (**11**). Our last investigated structure, **11**, is shown in *Fig. 4*. It is formally obtained by replacing five H-atoms of but-2-yne with five

Table 7. *MP2(full)/6-311G(d,p)/SDD//MP2(full)/6-31G(d)/SDD AIM Analysis of the Heteropolynuclear Ng Complexes 6–10* (see Fig. 3). The AIM charge density  $\rho$  [ $e/\text{\AA}^{-3}$ ], the Laplacian of the charge density  $\nabla^2\rho$  [ $e/\text{\AA}^5$ ], and the energy density  $H$  [hartree/ $\text{\AA}^3$ ] are calculated at the bond critical point [bcp] on the specified bond.

Group	C–N			Be–N			Be–Ng						
	$r(\text{C})^a$	$\rho$	$\nabla^2\rho$	$H$	$r(\text{Be})^a$	$\rho$	$\nabla^2\rho$	$H$	$r(\text{Be})^a$	$\rho$	$\nabla^2\rho$	$H$	
<b>6</b>	C–N–Be–He	0.57	1.875	–19.317	–2.240	0.50	0.966	29.401	–0.242	0.63	0.199	8.139	0.089
	C–N–Be–Ne	0.57	1.895	–19.635	–2.262	0.50	0.969 <sub>5</sub>	29.700	–0.244	0.66	0.158	5.869	0.052
	C–N–Be–Ar	0.57	1.915	–20.010	–2.294	0.50	0.972	29.212	–0.251	0.65	0.219	5.326	0.010
<b>7</b>	C–N–Be–Kr	0.57	1.914	–19.994	–2.295	0.50	0.969	28.982	–0.242	0.67	0.197	4.164	–0.002
	C–N–Be–He	0.57	1.877	–19.354	–2.248	0.50	0.966	29.390	–0.242	0.63	0.199	8.122	0.089
	C–N–Be–Ne	0.57	1.895	–19.641	–2.263	0.50	0.969 <sub>5</sub>	29.687	–0.244	0.66	0.159	5.885	0.052
<b>8</b>	C–N–Be–Ar	0.57	1.915	–19.999	–2.293	0.50	0.972	29.202	–0.251	0.65	0.219	5.324	0.010
	C–N–Be–Xe	0.57	1.913	–19.972	–2.295	0.50	0.963	28.643	–0.249	0.68	0.207	3.451	–0.022
	C–N–Be–He	0.57	1.877	–19.352	–2.245	0.50	0.965	29.376	–0.242	0.63	0.199	8.134	0.089
<b>9</b>	C–N–Be–Ne	0.57	1.896	–19.660	–2.265	0.50	0.969	29.675	–0.244	0.66	0.159	5.895	0.052
	C–N–Be–Kr	0.57	1.916	–20.010	–2.297	0.50	0.969	28.963	–0.251	0.67	0.198	4.174	–0.003
	C–N–Be–Xe	0.57	1.914	–19.975	–2.296	0.50	0.963	28.630	–0.249	0.68	0.207	3.460	–0.022
<b>10</b>	C–N–Be–He	0.57	1.872	–19.253	–2.237	0.50	0.965	29.362	–0.242	0.63	0.199	8.133	0.089
	C–N–Be–Ar	0.57	1.911	–19.927	–2.288	0.50	0.971	29.192	–0.250	0.65	0.218	5.306	0.010
	C–N–Be–Kr	0.57	1.911	–19.917	–2.289	0.50	0.968	28.964	–0.250	0.67	0.197	4.171	–0.002
<b>10</b>	C–N–Be–Xe	0.57	1.910	–19.906	–2.290	0.50	0.963	28.640	–0.248	0.68	0.206	3.460	–0.022
	C–N–Be–Ne	0.57	1.885	–19.437	–2.244	0.50	0.968	29.657	–0.243	0.66	0.157	5.862	0.052
	C–N–Be–Ar	0.57	1.905	–19.821	–2.278	0.50	0.971	29.190	–0.250	0.65	0.216	5.289	0.011
<b>10</b>	C–N–Be–Kr	0.57	1.904	–19.799	–2.279	0.50	0.967	28.957	–0.250	0.67	0.196	4.164	–0.002
	C–N–Be–Xe	0.57	1.902	–19.762	–2.278	0.50	0.962	28.623	–0.247	0.68	0.205	3.467	–0.021

<sup>a</sup>) Distance [ $\text{\AA}$ ] of the bcp from the specified atom.

Table 8. *MP2(full)/6-311G(d,p)/SDD//MP2(full)/6-31G(d)/SDD* Dissociation Energies [kJ/mol] at 0 K of the Ng Complexes **6–10** (see Fig. 3)

$\Delta E^a$	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>	<b>10</b>
He	16.3 (20.1)	16.3 (20.1)	16.3 (20.1)	15.9 (19.7)	
Ne	3.3 (22.6)	3.3 (22.6)	3.3 (22.6)		2.5 (21.8)
Ar	25.5 (44.4)	25.5 (44.4)		24.3 (43.1)	23.0 (42.7)
Kr	36.8 (48.1)		36.8 (48.1)	36.0 (47.3)	35.1 (46.4)
Xe		50.2 (60.7)	50.2 (60.7)	44.4 (59.8)	48.5 (59.0)

<sup>a</sup>) Energy change for the loss of the specified Ng-atom. The values in parentheses are not corrected for the BSSE.

distinct –NBeNg groups (Ng = He–Xe), so to obtain the probably first example of a molecular species containing all these noble gases in the same structure. The geometry of **11** was first optimized at the *MP2(full)/6-31G(d)/SDD* level of theory, and the corresponding harmonic frequencies invariably resulted in positive values. However, since some lowest frequencies were below 20 cm<sup>-1</sup>, with a first one of only 4 cm<sup>-1</sup>, we repeated the geometry optimization and the frequencies calculations by using the larger basis set *6-311G(d,p)/SDD*. The obtained wavenumbers were nearly identical to those obtained with the smaller basis set, and only the intensities of few selected frequencies showed non-negligible differences. This confirms the identification of **11** as a true minimum on the potential-energy surface.

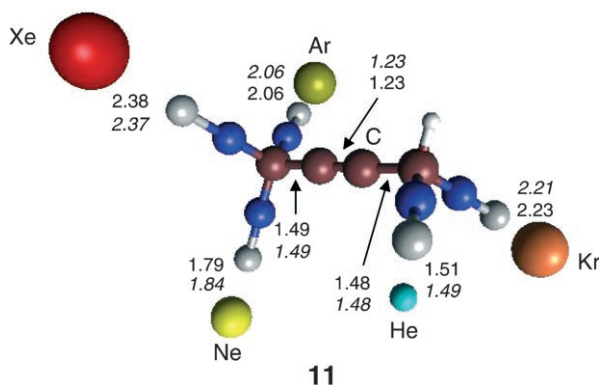
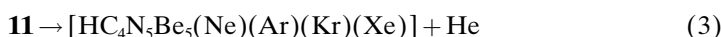


Fig. 4. *MP2(full)/6-31G(d)/SDD-Optimized* and *MP2(full)/6-311G(d,p)/SDD-optimized* (italics) bond distances [Å] of the complex  $[HC_4N_3Be_5(He)(Ne)(Ar)(Kr)(Xe)]$  (**11**)

Similarly to all the other investigated Ng complexes, the Be–Ng bond distances of **11**, as well as the C–N and Be–N distances (not shown in Fig. 4), were only little sensitive to the basis set and also quite similar to the corresponding values of the complexes **1–5** (see Fig. 2) and **6–10** (see Fig. 3). Based on these strong structural similarities, we suggest that in complex **11**, the interaction between the Be- and the various Ng-atoms is qualitatively and also quantitatively similar to that predicted for **1–5** and **6–10**. A first evidence in this regard came from the evaluated stability of **11** with respect to helium loss. We computed in particular the *MP2(full)/6-311G(d,p)/*

SDD//MP2(full)/6-31G(d)/SDD energy change at 0 K of the dissociation of *Eqn. 3*. The obtained value of 17.6 kJ/mol (including the BSSE) is quite similar to the  $\Delta E$  of the reactions of *Eqns. 1* and *2* for Ng=He, both computed as nearly 17 kJ/mol, thus suggesting that the energy change for the loss of the other Ng-atoms from **11** (Ng = Ne–Xe) should also be similar to that of the dissociations of complexes **2–5** and **6–10**. Due to the relatively large size and low symmetry of the species involved in these dissociations of **11**, we refrained from performing the time-consuming calculations required to obtain the quantitative estimates. In any case, the atomic charges and the topological features of the electron density of any –NBeNg moiety of **11** were quite similar to those predicted for the complexes **2–5** and **6–10**.



**Conclusions.** – Searching for novel compounds of the noble gases still remains a fascinating experimental challenge, and theory is invited to explore still uncovered molecules and ions. The present theoretical investigation was initiated by the recognition that any –NBeNg moiety (Ng=He–Xe) behaves as a monovalent ‘functional group’ able to replace the H-atoms of parent molecules such as CH<sub>4</sub> and but-2-yne, thus forming homonuclear and heteronuclear complexes such as [C(NBeNg)<sub>4</sub>], [CN<sub>4</sub>Be<sub>4</sub>(Ng<sub>1</sub>)(Ng<sub>2</sub>)(Ng<sub>3</sub>)(Ng<sub>4</sub>)] (Ng<sub>*i*</sub>=He–Xe), and [HC<sub>4</sub>N<sub>5</sub>Be<sub>5</sub>(–He)(Ne)(Ar)(Kr)(Xe)]. These species were characterized as minimum-energy structures, featuring beryllium–noble-gas binding energies which range from *ca.* 17 (Ng=He) to *ca.* 63 (Ng=Xe) kJ/mol. The Be–Ng interaction is essentially electrostatic for helium, neon, argon, and krypton, and has probably a small covalent contribution for xenon. Although our investigated molecules are probably very exotic and have little chance to become ever synthesized, they yet reveal a still little explored feature of noble-gas chemistry, namely the conceivable existence of multicenter homo- and heteropolynuclear complexes.

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