

Experimental Section

2: Compound **1** (0.20 g 0.18 mmol) was suspended in dry toluene (4 mL) containing neopentanol (2.0 g 22.7 mmol). The minimum volume of toluene necessary to dissolve all the alcohol at room temperature was used. Stirring the solution for 24 h at room temperature allowed complete dissolution of the basic Fe carboxylate **1**, giving a red solution. Dark red single crystals of **2** suitable for X-ray study were deposited during the next 7 d (yield ca. 50%). No other product was deposited from the solution. Crystals of **2** lose solvent on drying under a stream of nitrogen and analyze as the ditoluene solvate: found: C 57.9, H 5.0%; calcd for $C_{132}H_{132}O_{36}Fe_8$: C 57.8, H 4.8%.

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- [8] X-ray structural analysis of **2** ($C_{146}H_{148}O_{36}Fe_8$): $M_r = 2925.53$, dark red crystals, dimensions $0.20 \times 0.20 \times 0.15$ mm, monoclinic, space group $P2_1/n$ (no. 14); $a = 18.379(1)$, $b = 16.264(1)$, $c = 24.122(1)$ Å, $\beta = 103.756(1)^\circ$, $V = 7000.3(6)$ Å³; $Z = 2$, $\rho_{\text{calcd}} = 1.39$ g cm⁻³; $2\theta_{\text{max}} = 58.2^\circ$; $F_{000} = 3040$, $T = 123$ K; Nonius Kappa CCD, graphite-monochromated MoK_{α} radiation ($\lambda = 0.71069$ Å), data corrected for Lorentzian polarization ($\mu(MoK_{\alpha}) = 8.80$ cm⁻¹); of 17312 independent reflections, 10570 were observed ($I \geq 3\sigma(I)$) and used in the full-matrix least-squares refinement of 856 variables; $R = 0.053$, $R_w = 0.052$ (refined against $|F|$); max./min. residual electron peaks were $1.18/-1.04$ e⁻ Å⁻³. Non-hydrogen atoms were refined with anisotropic thermal parameters, hydrogen atoms were included but not refined. Neutral atom scattering factors were employed. Crystal structural solution and refinement was performed using the teXsan analysis package (Molecular Structure Corporation, **1992**). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-134640. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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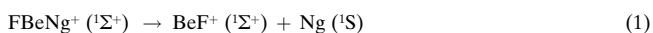
FBeNg⁺ (Ng = He, Ne, Ar): Suitable Cations for Salts of the Lightest Noble Gases?*

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Since the isolation by Bartlett of the first stable compound containing xenon,^[1] numerous ionic and covalent species of this element and certain analogues of krypton have been synthesized and characterized.^[2,3] It is also well known that helium, neon, and argon form quite stable species in the gas phase,^[4] but no “true” chemical compounds of these elements have ever been prepared. Therefore, overcoming the chemical inertness of the lightest noble gases still remains a fascinating challenge of great experimental and theoretical interest.

The ArF⁺ cation has been suggested^[5] as being suitable for the preparation of salts like ArF⁺AuF₆⁻ and ArF⁺SbF₆⁻. We report here computational results on the structure, stability, and thermochemistry of the FBeNg⁺ cations (Ng = He, Ne, Ar), which open the challenging but not unrealistic perspective that not only FBeAr⁺ but also FBeNe⁺ and even FBeHe⁺ could form stable salts. Our calculations have been inspired by results reported on the neutral complexes between the BeO molecule and the noble gases.^[6,7] All the OBeNg complexes, including OBeHe, were predicted^[6] to be stable with respect to dissociation into ground-state BeO (¹Σ⁺) and Ng (¹S). The heaviest members in this series—OBeAr, OBeKr, and OBeXe—have actually been observed in low-temperature matrix-isolation experiments.^[7] The OBe–Ng bond energies were calculated to range from about 3 kcal mol⁻¹ for Ng = He to about 13 kcal mol⁻¹ for Ng = Xe.^[6] It is plausible that, in its singlet ground state ¹Σ⁺,^[8,9] the positively charged BeF⁺ could fix noble gases even more efficiently than the neutral, isoelectronic BeO.

The results of our calculations (Table 1) fully meet, and perhaps exceed, this qualitative expectation. In fact, all the FBeNg⁺ species proved to be stable with respect to dissociation into BeF⁺ (¹Σ⁺) and Ng (¹S). The enthalpy changes (at 298.15 K) of reaction (1) were computed, at the Gaussian 3



(G3)^[10] level of theory, to be 10.6 (Ng = He), 16.0 (Ng = Ne), and 34.5 kcal mol⁻¹ (Ng = Ar). These values are indeed

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Table 1. Optimized geometries, vibrational frequencies, and G3 total energies of FBeNg⁺, BeF⁺, and Ng.

Species	Symmetry	Be–Ng [Å] ^[a]	Be–F [Å] ^[a]	ν_1 (σ) [cm ^{−1}] ^[b]	ν_2 (σ) [cm ^{−1}] ^[b]	ν_3 (π) [cm ^{−1}] ^[b]	E [Hartree] ^[c]
FBeHe ⁺	¹ Σ ⁺	1.481 1.493	1.339 1.334	1504.0 (273.8)	673.3 (1.8)	183.9 (130.5)	−117.13518
FBeNe ⁺	¹ Σ ⁺	1.668 1.706	1.340 1.334	1494.7 (279.2)	405.0 (10.8)	135.1 (182.8)	−243.11376
FBeAr ⁺	¹ Σ ⁺	1.930 1.946	1.344 1.341	1496.7 (354.3)	384.0 (19.5)	155.2 (142.1)	−641.63995
BeF ⁺	¹ Σ ⁺		1.337 1.333	1448.9 (223.2)			−114.21809
He	¹ S						−2.90093
Ne	¹ S						−128.87092
Ar	¹ S						−527.36780

[a] The upper values were calculated at the MP2(FULL)/6-31G(d) level of theory and the lower values at CCSD(T)/6-311+G(d). [b] Infrared intensities [kmol^{−1}] are given in parentheses. [c] At 298.15 K.

remarkable and allow the prediction that FBeNg⁺ complexes are stable species in the gas phase, even at relatively high temperatures.^[11]

The large energy difference between the ¹Σ⁺ ground state of BeF⁺ and its first excited state ³Π (5.5 eV)^[8,9] and the large difference between the ionization potential (IP) of BeF (ca. 9 eV)^[12] and that of He (24.587 eV), Ne (21.565 eV), and Ar (15.759 eV) suggest that the FBeNg⁺ ions should be well described by single-configuration approaches. We have, however, checked for conceivable artifacts in the MP2(FULL)/6-31G(d) structures used to perform the G3 calculations by repeating the geometry optimizations of the FBeNg⁺ ions at the coupled cluster level of theory. As shown in Table 1, we found only minor differences between the CCSD(T)/6-311+G(d) and MP2(FULL)/6-31G(d) geometries. The structure of FBeHe⁺ obtained at the multiconfigurational quasi-degenerate perturbation level of theory (MCQDPT/6-311+G(d)) also proved to be quite similar (Be–F 1.330, Be–He 1.510 Å). In addition, the MCQDPT results concerning FBeHe⁺ confirmed the validity of a single-configuration description for the FBeNg⁺ cations.

We combined the experimental enthalpy of formation of gaseous BeF⁺ (168 kcal mol^{−1})^[13] with the calculated (G3) enthalpy changes of reaction (1) to estimate the enthalpies of formation of FBeNg⁺: 157.4 (Ng = He), 152.0 (Ng = Ne), and 133.5 kcal mol^{−1} (Ng = Ar). In addition, the results of CCSD(T)/6-311+G(d) calculations revealed that none of the neutral FBeNg compounds are bound species with respect to ground-state BeF (²Σ⁺) and Ng. Therefore, the electron affinities (EAs) of FBeHe⁺, FBeNe⁺, and FBeAr⁺ are predicted to be 198.0 kcal mol^{−1} (8.6 eV), 192.6 kcal mol^{−1} (8.4 eV), and 174.1 kcal mol^{−1} (7.5 eV), respectively (the enthalpy of formation of BeF is −40.6 kcal mol^{−1}). These estimated EAs are of considerable interest since they allow the prediction that a number of anions, including those with a relatively low IP, could form salts FBeAr⁺X[−], FBeNe⁺X[−], and even FBeHe⁺X[−] that are stable with respect to electron transfer. For example, the IP of NO₂[−] is about 2.3 eV, and the stabilization of solid FBeNg⁺NO₂[−] requires lattice energies larger than around

145, 141, and 120 kcal mol^{−1} for Ng = He, Ne, and Ar, respectively.

With the equation of Kapustinskii^[14] and the thermochemical radius^[15] of NO₂[−] (1.55 Å), and under the assumption that the thermochemical radii of FBeNe⁺ and FBeAr⁺ are similar to those of the isoelectronic CNO[−] (1.59 Å) and CNS[−] (1.95 Å), the lattice energies of FBeNe⁺NO₂[−] and FBeAr⁺NO₂[−] are estimated to be about 163 and 148 kcal mol^{−1}, respectively. Therefore, even though the thermochemical radius of FBeHe⁺ is assumed to be identical to that of FBeNe⁺, the lattice energies of all the FBeNg⁺NO₂[−] salts, including FBeHe⁺NO₂[−], appear in principle to be large enough to ensure stabilization with respect to electron transfer between gaseous FBeNg⁺ and NO₂[−].

The IPs of anions X[−] such as NO₃[−], CNO[−], CN[−], and N₃[−] are larger than that of NO₂[−], and we have invariably calculated lattice energies of the corresponding salts FBeNg⁺X[−], including FBeHe⁺X[−], which far exceed the difference between the EA of FBeNg⁺ and the IP of X[−]. Salts like FBeNg⁺AlF₄[−] and FBeNg⁺AuF₆[−] are predicted to be stable with respect to electron transfer, even when unrealistically low lattice energies are assumed. In fact, the charge exchange between FBeNg⁺ and X[−] is practically thermoneutral for AlF₄[−] (whose IP was recently theoretically estimated to be about 8.0 eV^[16]) and even largely endothermic for AuF₆[−] (IP > 10.0 eV). Of course, the IP of the anion is not the only limiting factor to the stabilization of salts FBeNg⁺X[−], which could be severely affected by the various exothermic reactions that gaseous FBeNg⁺ ions are able to undergo with X[−]. In the absence of thermochemical data for the conceivably formed species, we cannot determine whether reactions of FBeNg⁺ with anions like NO₂[−], NO₃[−], CN[−], CNO[−], and N₃[−] could make the formation of corresponding FBeNg⁺X[−] salts prohibitive. We can, however, use the enthalpy of formation of gaseous BeF₂ (−190.2 kcal mol^{−1}) to estimate the conceivable influence of the transfer of fluoride on the stability of salts FBeNg⁺MF_{*n*}[−]. For example, the gas-phase transfer of fluoride from AlF₄[−] to FBeNg⁺ with formation of BeF₂ and Ng is exothermic by 161, 156, and 137 kcal mol^{−1} for Ng = He, Ne, and Ar, respectively. Whereas the lattice energies required to stabilize FBeHe⁺AlF₄[−] and FBeNe⁺AlF₄[−] are probably exceedingly large, that required to stabilize FBeAr⁺AlF₄[−] does not appear as prohibitive. Thus, with the equation of Kapustinskii and a thermochemical radius of AlF₄[−] similar to that of AsF₄[−] (2.1 Å), the lattice energy of FBeAr⁺AlF₄[−] is estimated to be about 130 kcal mol^{−1}.

In conclusion, our calculations suggest that a number of quite common anions X[−] could form salts FBeNg⁺X[−], including FBeHe⁺X[−], that are stable with respect to electron transfer. Exothermic reactions other than the charge exchange could, however, severely limit the formation of these ionic species and make their experimental preparation challenging. Nonetheless, any successful effort along this direction would result in the unprecedented preparation of stable compounds of the lightest noble gases.

Computational Details

We have used Unix versions of the Gaussian 94^[17] and Gamess USA^[18] programs installed on an Alphaserber 1200 Compaq machine. The geometry optimizations and frequency calculations performed at the second-order Møller–Plesset^[19] level of theory (including the inner shell electrons for the correlation) were based on analytical gradients and second derivatives, whereas the geometry optimizations performed at the coupled cluster^[20] level of theory (including the contribution of single and double excitations, and an estimate of connected triples) were based on the algorithm by Fletcher and Powell.^[21] The optimization of FBeHe⁺ performed at the MCQDPT level of theory^[22] was based on a numerical grid of 0.05 Å size. The reference wavefunction, expanded on RHF orbitals within the C_{2v} Abelian subgroup, was derived from an active space of 12 electrons in 10 orbitals. The MP2(FULL)/6-31G(d) geometries were used to calculate the G3 total energies following the procedure described in the literature.^[10] With respect to the previous G2 theory,^[23] G3 significantly improves the calculation of the thermochemical properties of molecules such as CF₄, SiF₄, and NF₃. Therefore, the G3 thermochemical properties of the FBeNg⁺ adducts should be accurate to within less than 2 kcal mol⁻¹.

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Self-Assembly of Rotaxane-Like Complexes with Macrocycles Containing Reversible Coordinate Bonds**

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Remarkable advances in noncovalent and covalent chemistry have led to the efficient synthesis of various interlocked and intertwined supramolecular species with new functions.^[1] Rotaxanes are supermolecules composed of two distinct molecular components—a beadlike molecule and a dumbbell-shaped molecule—which possess mutual recognition motifs that exert weak intermolecular forces when they are assembled in a threading mode. The beadlike components used for the synthesis of rotaxanes to date are all covalently bonded macrocycles such as cyclodextrins, crown ethers, cucurbituril, and cationic or neutral cyclophanes.^[1] Although a variety of transition metal bridged macrocycles were reported over the last decade,^[2] none has been employed yet for the construction of rotaxanes.^[3] This is possibly due to the lack of driving forces for the formation of rotaxane-like assemblies, or because of self-aggregation into other supramolecular species such as catenanes.^[4] When macrocycles that are bridged by coordinate bonds are employed as bead molecules instead of conventional covalent macrocycles, an additional feature of the resulting rotaxanes is that the formation and dissociation might be reversibly controlled under certain conditions. In addition, the kinetic stability of rotaxanes could also be controlled by modifying the coordination sites of the ligands or by selecting an appropriate combination of transition metal and ligand. Here we report for the first time the reversible formation of rotaxane-like complexes from macrocycles that contain weak coordinate bonds.

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