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%.

Received: October 1, 1999 [Z 14086]
Revised: February 14, 2000

[1] K. S. Hagen, *Angew. Chem.* **1992**, *104*, 1036; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1010.

[2] A. K. Powell, *Struct. Bonding (Berlin)* **1997**, *88*, 1.

[3] D. Gatteschi, A. Caneschi, R. Sessoli, A. Cornia, *Chem. Soc. Rev.* **1996**, *25*, 101.

[4] K. L. Taft, S. J. Lippard, *J. Am. Chem. Soc.* **1990**, *112*, 9629; K. L. Taft, C. D. Delfs, G. C. Papaefthymiou, S. Foner, D. Gatteschi, S. J. Lippard, *J. Am. Chem. Soc.* **1994**, *116*, 823.

[5] C. Benelli, S. Parsons, G. A. Solan, R. E. P. Winpenny, *Angew. Chem.* **1996**, *108*, 1967; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1825.

[6] S. M. Gorun, G. C. Papaefthymiou, R. B. Frankel, S. J. Lippard, *J. Am. Chem. Soc.* **1987**, *109*, 3337.

[7] R. Papiernik, L. G. Hubert-Pfalzgraf, J. Vaissermann, M. C. H. B. Goncalves, *J. Chem. Soc. Dalton Trans.* **1998**, 2285.

[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, $\beta = 103.756(1)^\circ$, $V = 7000.3(6)$ Å^3; $Z = 2$, $\rho_{calcd} = 1.39\ g\,cm^{-3}$; $2\theta_{max} = 58.2^\circ$; $F_{000} = 3040$, $T = 123$ K; Nonius Kappa CCD, graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å), data corrected for Lorentzian polarization ($\mu(Mo_{K\alpha}) = 8.80\ cm^{-1}$); 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 CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[9] J. M. McCusker, J. B. Vincent, E. A. Schmitt, M. L. Mino, K. Shin, D. K. Coggin, P. M. Hagen, J. C. Huffman, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1991**, *113*, 3012.

[10] S. M. Gorun, S. J. Lippard, *Inorg. Chem.* **1988**, *27*, 149.

[11] A. B. Blake, L. R. Fraser, *J. Chem. Soc. Dalton Trans.* **1975**, 193.

[12] K. Wieghardt, K. Pohl, I. Jibril, G. Huttner, *Angew. Chem.* **1984**, *96*, 66; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 77.

[13] C. Delfs, D. Gatteschi, L. Pardi, R. Sessoli, K.Wieghardt, D. Hanke, *Inorg. Chem.* **1993**, *32*, 3099; A.-L. Barra, P. Debrunner, D. Gatteschi, C. E. Schultz, R. Sessoli, *Europhys. Lett.* **1996**, *35*, 133.

[14] W. Wernsdorfer, R. Sessoli, *Science* **1999**, *284*, 133.

[15] V. S. Nair, K. S. Hagen, *Inorg. Chem.* **1994**, *33*, 185.

[16] R. G. Raptis, I. P. Georgaki, D. C. R. Hockless, *Angew. Chem.* **1999**, *111*, 1751; *Angew. Chem. Int. Ed.* **1999**, *38*, 1632.

[17] J. H. Satcher, Jr., M. M. Olmstead, M. W. Droege, S. R. Parkin, B. C. Noll, L. May, A. L. Balch, *Inorg. Chem.* **1998**, *37*, 6751.

[18] I. M. Atkinson, C. Benelli, M. Murrie, S. Parsons, R. E. P. Winpenny, *Chem. Commun.* **1999**, 285.

$FBeNg^+$ ($Ng = He, Ne, Ar$): Suitable Cations for Salts of the Lightest Noble Gases?[**]

Massimiliano Aschi* and Felice Grandinetti*

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 $ArF^+AuF_6^-$ and $ArF^+SbF_6^-$. 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 ($^1\Sigma^+$) 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 $^1\Sigma^+$,[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^+ ($^1\Sigma^+$) and Ng (^1S). The enthalpy changes (at 298.15 K) of reaction (1) were computed, at the Gaussian 3

$$FBeNg^+\ (^1\Sigma^+) \rightarrow BeF^+\ (^1\Sigma^+) + Ng\ (^1S) \qquad (1)$$

(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

---

[*] Dr. M. Aschi
Dipartimento di Chimica
Università di Roma "La Sapienza"
P.le A. Moro, 5, 00185 Roma (Italy)
E-mail: aschi@caspur.it

Prof. F. Grandinetti
Dipartimento di Scienze Ambientali
Università della Tuscia
Via S.C. De Lellis, 01100 Viterbo (Italy)
Fax: (+39)0761-357179
E-mail: fgrandi@unitus.it

[**] This work was supported by the Italian Ministero dell' Università e della Ricerca Scientifica e Tecnologica (MURST) and the Consiglio Nazionale delle Ricerche (CNR).

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]
$FBeHe^+$	$^1\Sigma^+$	1.481	1.339	1504.0	673.3	183.9	– 117.13518
		1.493	1.334	(273.8)	(1.8)	(130.5)	
$FBeNe^+$	$^1\Sigma^+$	1.668	1.340	1494.7	405.0	135.1	– 243.11376
		1.706	1.334	(279.2)	(10.8)	(182.8)	
$FBeAr^+$	$^1\Sigma^+$	1.930	1.344	1496.7	384.0	155.2	– 641.63995
		1.946	1.341	(354.3)	(19.5)	(142.1)	
BeF^+	$^1\Sigma^+$		1.337	1448.9			– 114.21809
			1.333	(223.2)			
He	^1S						– 2.90093
Ne	^1S						– 128.87092
Ar	^1S						– 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 [$km\,mol^{-1}$] 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 $^1\Sigma^+$ ground state of BeF^+ and its first excited state $^3\Pi$ (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 ($^2\Sigma^+$) 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 NO_2^- is about 2.3 eV, and the stabilization of solid $FBeNg^+NO_2^-$ 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 NO_2^- (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 $FBeNe^+NO_2^-$ and $FBeAr^+NO_2^-$ 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 $FBeNg^+NO_2^-$ salts, including $FBeHe^+NO_2^-$, appear in principle to be large enough to ensure stabilization with respect to electron transfer between gaseous $FBeNg^+$ and NO_2^-.

The IPs of anions X^- such as NO_3^-, CNO^-, CN^-, and N_3^- are larger than that of NO_2^-, 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 $FBeNg^+AlF_4^-$ and $FBeNg^+AuF_6^-$ 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 AlF_4^- (whose IP was recently theoretically estimated to be about 8.0 eV[16]) and even largely endothermic for AuF_6^- (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 NO_2^-, NO_3^-, CN^-, CNO^-, and N_3^- could make the formation of corresponding $FBeNg^+X^-$ salts prohibitive. We can, however, use the enthalpy of formation of gaseous BeF_2 (– 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 AlF_4^- to $FBeNg^+$ with formation of BeF_2 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 $FBeHe^+AlF_4^-$ and $FBeNe^+AlF_4^-$ are probably exceedingly large, that required to stabilize $FBeAr^+AlF_4^-$ does not appear as prohibitive. Thus, with the equation of Kapustinskii and a thermochemical radius of AlF_4^- similar to that of AsF_4^- (2.1 Å), the lattice energy of $FBeAr^+AlF_4^-$ 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.

0570-0833/00/3909-1691 $ 17.50+.50/0

Computational Details

We have used Unix versions of the Gaussian 94[17] and Gamess USA[18] programs installed on an Alphaserver 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 CF_4, SiF_4, and NF_3. Therefore, the G3 thermochemical properties of the FBeNg$^+$ adducts should be accurate to within less than 2 kcal mol^{-1}.

Received: November 17, 1999 [Z14290]

---

[1] N. Bartlett, *Proc. Chem. Soc. London* **1962**, 18.

[2] a) K. Seppelt, D. Lenz, *Prog. Inorg. Chem.* **1982**, *29*, 167; b) H. Selig, J. T. Holloway, *Top. Curr. Chem.* **1984**, *124*, 33.

[3] F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, **1987**.

[4] *Ion and Cluster Ion Spectroscopy and Structure* (Ed.: J. P. Maier), Elsevier, Amsterdam, **1989**.

[5] G. Frenking, W. Koch, C. A. Deakyne, J. F. Liebman, N. Bartlett, *J. Am. Chem. Soc.* **1989**, *111*, 31.

[6] a) W. Koch, J. R. Collins, G. Frenking, *Chem. Phys. Lett.* **1986**, *132*, 330; b) W. Koch, G. Frenking, J. Gauss, D. Cremer, J. R. Collins, *J. Am. Chem. Soc.* **1987**, *109*, 5917; c) A. Veldkamp, G. Frenking, *J. Am. Chem. Soc.* **1994**, *226*, 11, and references therein.

[7] C. A. Thompson, L. Andrews, *J. Am. Chem. Soc.* **1994**, *116*, 423.

[8] H. Partridge, S. R. Langhoff, C. W. Bauschlicher, Jr., *J. Chem. Phys.* **1986**, *84*, 4489.

[9] F. R. Ornellas, F. B. C. Machado, O. Roberto-Neto, *Mol. Phys.* **1992**, *77*, 1169.

[10] L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, J. A. Pople, *J. Chem. Phys.* **1998**, *109*, 7764.

[11] Using the MP2(FULL)/6-31G(d) vibrational frequencies and moments of inertia, the change in free energy for reaction (1) (Ng = He) is computed to be negative up to about 400 K.

[12] Unless stated otherwise, all thermochemical data have been taken from: *NIST Chemistry Webbook, NIST Standard Reference Database Number 69* (Eds.: W. G. Mallard, P. J. Linstrom), National Institute of Standards and Technology, Gaithersburg, MD, USA, **1998** (http://webbok.nist.gov).

[13] S. G. Lias, J. A. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, W. G. Mallard, *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

[14] a) T. C. Waddington, *Adv. Inorg. Chem. Radiochem.* **1959**, *1*, 157; b) J. E. Huheey, *Inorganic Chemistry: Principles of Structure and Reactivity*, Harper and Row, New York, **1978**.

[15] For a detailed discussion of the concept of thermochemical radius, see ref. [14a], p. 179. The presently employed values of thermochemical radii have been taken from ref. [14b].

[16] G. L. Gutsev, P. Jena, R. J. Bartlett, *Chem. Phys. Lett.* **1998**, *292*, 289.

[17] Gaussian 94, Revision E.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Pittsburgh, PA, **1995**.

[18] M. W. Schmidt, K. K. Baltridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, *J. Comput. Chem.* **1993**, *14*, 1347.

[19] C. Møller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618.

[20] K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479.

[21] R. Fletcher, M. J. D. Powell, *Comput. J.* **1963**, *6*, 163.

[22] H. Nakano, *J. Chem. Phys.* **1993**, *99*, 7983.

[23] L. A. Curtiss, K. Raghavachari, G. W. Trucks, J. A. Pople, *J. Chem. Phys.* **1991**, *94*, 7221.

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

Kyu-Sung Jeong,* Jeung Soon Choi, Sung-Youn Chang, and Hong-Young Chang

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.

---

[*] Prof. K.-S. Jeong, J. S. Choi, S.-Y. Chang, H.-Y. Chang
Department of Chemistry, Yonsei University
Seoul 120-749, (South Korea)
Fax: (+82) 2-364-7050
E-mail: ksjeong@alchemy.yonsei.ac.kr

[**] This work was supported by the Korea Science and Engineering Foundation (1999-2-123-001-3). We thank Professor Moon-Gun Choi for help in X-ray crystallography, and Professor Weontae Lee for assistance with EXSY experiments.

Supporting information for this article is available on the WWW under http://www/wiley-vch.de/home/angewandte/ or from the author.