Available online at www.sciencedirect.com

ScienceDirect

Chemical Physics Letters 450 (2008) 228–231

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

Packing atomic metal cations with C_{60}: Mass spectrometric observation of $M^+(C_{60})_n$ with M = Sr and Mo and $n = 0$–4

Gregory K. Koyanagi [a], Jianxun Xu [b], Diethard K. Bohme [a,*]

[a] *Department of Chemistry, Centre for Research in Mass Spectrometry, Centre for Research in Earth and Space Science, York University, Toronto, Ontario, Canada M3J 1P3*
[b] *Department of Chemistry, Peking University, Beijing 100871, China*

Received 5 July 2007; in final form 13 November 2007
Available online 22 November 2007

Abstract

The atomic cations of Sr and Mo have been observed to add sequentially up to four molecules of C_{60} in helium at 0.35 Torr and room temperature in the flow tube of a modified inductively coupled plasma/selected-ion flow tube (ICP/SIFT) tandem mass spectrometer. The available center-of-mass energy in collision-induced dissociation experiments of approximately 1.3 eV failed to remove C_{60} from $M^+(C_{60})_4$. A structure is proposed for $M^+(C_{60})_4$ cations in which the bonding involves η^6 interaction of the metal with the C_{60} ligands and η^2-to-η^2 interactions between the C_{60} ligands.

1. Introduction

Gas-phase interactions of metal atoms and ions with the buckminsterfullerene C_{60} molecule have been of interest since the mass spectrometric discovery of C_{60} [1]. The formation of both endohedral and exohedral metallofullerenes by the incorporation of metal atoms *within* C_{60} and the *outside* coverage of C_{60} with metal atoms, respectively, has been demonstrated experimentally [2,3]. Multi-layer metal coverage of gas-phase fullerene molecules was reported for Ca, Sr and Ba in 1994 with the mass spectrometric observation of $C_{60}M_x^+$ with $x = 0$–500 [4]. Observed anomalies in intensity were interpreted in terms of the completion of metal layers around the fullerene molecule with one metal atom situated above each of the 32 rings of the fullerene cage. The doping of bulk C_{60} with metal atoms also has been demonstrated experimentally in the condensed phase with the discovery of superconductivity in K_3C_{60} films and bulk samples at 18 K and other alkali-metal doped films of C_{60} [5,6].

In the meantime, gas-phase mass spectrometric experiments have demonstrated the attachment of metal cations to C_{60} [7,8] and the formation of metallo-dumbbells of C_{60} in which an atomic metal cation is flanked by two C_{60} molecules [9]. Here we release surprising experimental results with a transition metal (Mo^+) and non-transition metal (Sr^+) cation that point to the packing of isolated atomic metal cations with up to four molecules of C_{60} by sequential C_{60} addition in the gas phase. These observations were made possible with the recent development of an ICP/SIFT/QqQ instrument in our laboratory that provides both a versatile source of metal ions and a detection mass spectrometer with a mass range sufficient to identify singly-charged metal adducts with up to four molecules of C_{60}.

2. Experimental

The experiments were performed with the inductively coupled plasma/selected-ion flow tube (ICP/SIFT) tandem mass spectrometer described previously [10], but modified by the replacement of the single quadrupole detector of the SIFT with a triple quadrupole prototype API 4000.

---

[*] Corresponding author.
E-mail address: dkbohme@yorku.ca (D.K. Bohme).

0009-2614/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2007.11.040

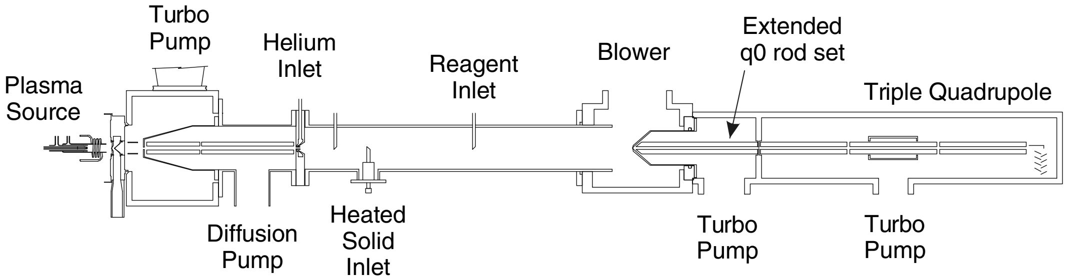

Fig. 1. Schematic view of the ICP/SIFT/QqQ instrument. The atomic ions are derived from the Ar plasma torch at atmospheric pressure, selected by a quadrupole mass filter, injected into the flow tube where they are exposed to helium and a reagent gas, and then sampled, along with product ions, by a triple quadrupole mass spectrometer.

The modified instrument is shown in Fig. 1. The rf-only q0 stage was extended 4 cm to position the rod tips near the down-stream side of the sampling nose cone to increase ion gathering efficiency. Three turns were removed from the inductors of the quadrupole rf-power supply to balance the added capacitance of the extended q0 rod. The collision gas system on the commercial instrument was bypassed using a 1 l reservoir and a 15-turn, micro-metering needle valve (Parker Hannifin, part number 4F-H1A-V-SS-TC). In this way the selection of collision gas is not limited to nitrogen seconded from the interface region. Also, finite, as opposed to stepped, adjustment of the collision gas pressure is available. The down-stream triple quadrupole is controlled by the Analyst™ software package supplied with the instrument.

Atomic strontium and molybdenum cations were generated in the argon plasma at atmospheric pressure from a solution (50 ppm plasma calibration standard) sprayed into a Scott-type sprayer. Computations of Boltzmann state distributions indicate that 90% and 72% of the Sr^+ and Mo^+ ions, respectively, formed within the plasma at 5500 K, are initially in the ground electronic state [11].

Gas-phase C_{60} (SES Research, Houston) was introduced into the flow tube using a heated solid inlet probe located in the side of the flow tube which is flushed with helium at 0.35 Torr in the usual way [10]. Sufficient C_{60} vapour was generated when the sample reservoir in the probe was heated to 600 °C. The absolute flow of the C_{60} is not known and this precluded the measurement of reaction rate coefficients.

3. Results and discussion

3.1. Mass spectra

Fig. 2 (top) shows a mass spectrum recorded with the addition of C_{60} vapour into the flow tube when Sr^+ is selected from the ICP upstream. Adducts of the type $Sr^+(C_{60})_n$ with $n = 1$–4 were observed and their peak intensities show a geometric decline with increasing n. The $^{98}Mo^+$ cation does almost the exact same thing as Sr^+ (see Fig. 2 (bottom)); it also adds four C_{60} molecules, but with slightly different intensity ratios and a decline in the intensities that is a bit curved, tailing off for the 4th adduct. Notably, the mass range is insufficient to rule out the existence of a 5th adduct or even higher-order clusters. A higher mass range, or experiments with a doubly charged metal species, is required to add clarity. Presumably the adduct ions that were observed were formed by sequential addition reactions of type (1) with He acting as the stabilizing third body

$$M^+(C_{60})_n + C_{60} + He \rightarrow M^+(C_{60})_{n+1} + He$$

3.2. Collision-induced dissociation

We attempted to investigate the N_2 collision products of the $M^+(C_{60})_n$ clusters in the downstream triple quadrupole, but none of the clusters were observed to dissociate. Apparently the available center-of-mass energy was too low. The available lab-frame collision voltage (130 V) provides a lower limit to the binding energy of the fourth C_{60} molecule of approximately 1.3 eV (30 kcal mol^{-1}). However, as has been pointed out by the reviewer, the lifetime of $M^+(C_{60})_4$ for dissociation at threshold could easily be

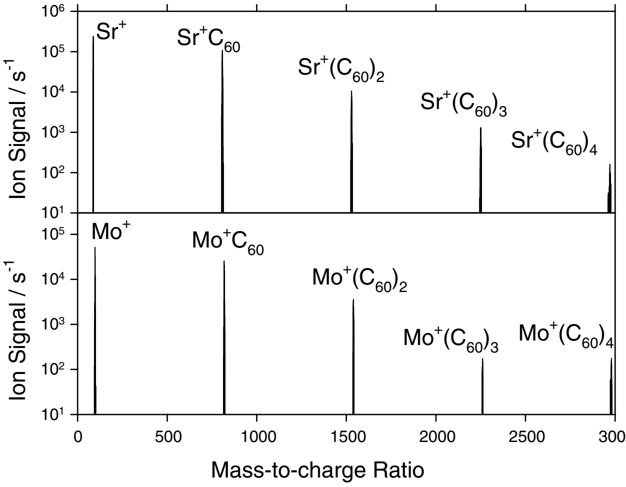

Fig. 2. Product mass spectra for Sr^+ reacting with C_{60}, top, and Mo^+ reacting with C_{60}, bottom, in the selected-ion flow tube in He buffer gas at 0.35 Torr and room temperature.

very long, pushing the observable threshold much higher than the thermodynamic threshold.

3.3. Possible structures of $M^+(C_{60})_n$

In a study of the polarizability of fullerenes, Moore et al. [12] comment that no aromaticity was observed for neutral C_{60}. For this reason ion-molecule interactions with C_{60} are believed to follow an η-2 motif. $M^+(C_{60})_n$ cluster structures, revealed as bond distances and fullerene orientation, are controlled by two principal factors: the force of electrostatic interaction with M^+, controlled by multipole moments, and the directed nature of the conjugated double-bond structure of the fullerene.

3.4. $M^+(C_{60})$, $M^+(C_{60})_2$

A previous assessment of the mode of bonding in $Fe^+(C_{60})$ with comparative chemical reactivity studies using SIFT techniques [8] has indicated a two-electron donating ability for C_{60}, M^+([η-2]-C_{60}), similar to that for ethylene. It is proposed here that, in the absence of any covalent interaction, Sr^+ and Mo^+ will bind to a C–C edge in an η-2 manner in both the C_{60} adduct ion and the bis complex.

3.5. $M^+(C_{60})_3$

The most logical structures for this ion are trigonal planar or trigonal pyramidal, the controlling factors being the balance between the strength of the fullerene–fullerene interaction and the orientation of the valence orbitals of the central metal. Both of the metal cations studied have spherical outer shell symmetry: Sr^+ and Mo^+ have valence electron configurations of $5s^1$ and $4d^5$, respectively, and therefore have spherical symmetry. Presumably if the fullerene–fullerene interaction is non-zero then the structure will be trigonal pyramidal. Several possible structures for the $M^+(C_{60})_3$ cluster are illustrated in Fig. 3.

3.6. $M^+(C_{60})_4$

C_{60} is a highly symmetric molecule, belonging to the point group I_h. Remarkably the symmetry of C_{60} lends itself well to binding preferentially in the face-centered-cubic (fcc) crystal structure [13]. There are 12 pentagon(5)-faces in C_{60} in which each vertex of a 5-face connects along a 6–6 edge to another pentagon-face. Therefore, there are 30 ($5 \times 12 = 60$ divided by 2 for sharing) 5-to-5 C–C bridge bonds. These are broken into five sets of six 5-to-5 C–C bonds arranged in an octahedral (propellered) conformation, one such set is illustrated in orange in Fig. 4. We shall take this orientation as a base for further discussion. Remarkably, there are two sets of four 6-faces arranged tetrahedrally, which point at the tetrahedral interstices of the fcc crystal structure, one set being illustrated in green in Fig. 4. It is interesting to note from the crystal structure [13] that the 5–6 edges (single

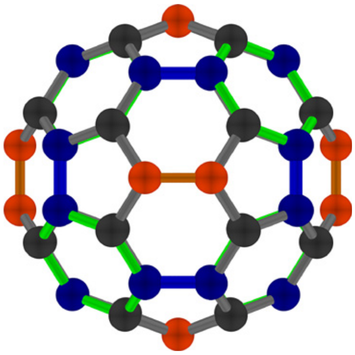

Fig. 4. A color-coded C_{60} molecule illustrating the C═C bonds oriented in synergy with the fcc structure of solid C_{60}. Orange carbons illustrate octahedral oriented η-2 bonds directed towards octahedral intersticial voids. They lie along the unit cell axis. Green bonds illustrate an η-6 face (3 × η-2) directed towards tetrahedral intersticial voids. Blue bonds illustrate C–C bonds oriented towards nearest neighbors and bisect pairs of unit cell axes. The upper right face highlighted in green lies approximately in the (1,1,1) plane. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

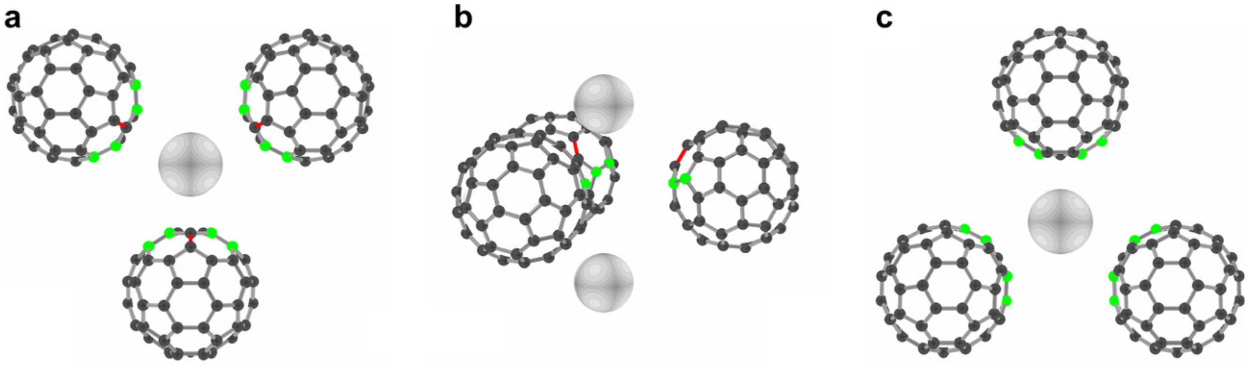

Fig. 3. Two possible structures for $M^+(C_{60})_3$: (a) from above showing metal binding to electron-rich 5–5 bridge bonds (b) from the side showing metal above or below plane of fullerene molecules and (c) from below showing binding via η-6 to the fullerenes. With the metal in the upper location the metal cation is bound η-2 (red bonds) to fullerenes, while in the bottom position it is bound η-6 to the fullerenes. In both cases the fullerenes are interacting with each other via η-2 binding (green carbons). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

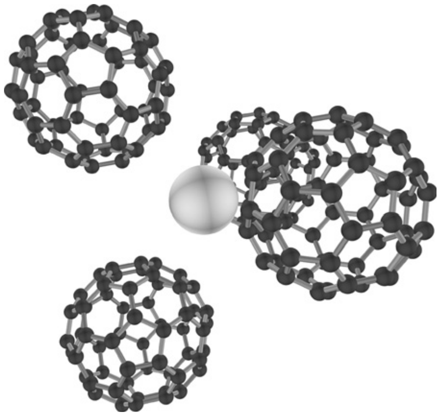

Fig. 5. Proposed structure for $M^+(C_{60})_4$ cations. Binding is characterized by η^6 interaction of the metal with the C_{60} ligands (illustrated clearly in the lower left) and by η^2-to-η^2 binding of the ligands to one another (as illustrated by the left-most pair of ligands).

bond C–C) bisecting all pairs of the octahedrally oriented bonds and pointing toward 12 nearest neighbors (in fcc crystal) are not capable of forming aligned η-2 interactions.

Intuitively, the proposed structure for $M^+(C_{60})_4$ cations is taken as a sub-element of the fcc structure of solid C_{60} as shown in Fig. 5. Binding in the proposed structure is characterized by a η^6 interaction of the metal with the C_{60} ligands (illustrated clearly in the lower left) and by η^2-to-η^2 binding of the ligands to one another (as illustrated by the left-most pair of ligands).

4. Conclusions

At least four C_{60} molecules are able to add sequentially to Mo^+ and Sr^+ in helium bath gas at 0.35 Torr and room temperature and form moderately stable $M^+(C_{60})_4$ cluster ions.

The structure of the fourth adduct generated in the gas phase is proposed to be dominated by η-2 binding between fullerenes and by multiple η-2 binding in metal–fullerene interactions. While physical limitations (mass range) precluded the observation of the fifth or sixth adducts, they cannot be ruled out. For the case of the fifth adduct a trigonal bipyramidal geometry could be envisioned, given the suspected bond distance in the fourth adduct. For the case of the sixth adduct, one could further envision simply placing the metal at an octahedral intersticial site of the fcc subunit.

Acknowledgements

Continued financial support from the Natural Sciences and Engineering Research Council of Canada is greatly appreciated. Also, we acknowledge support from the National Research Council, the Natural Science and Engineering Research Council and MDS SCIEX in the form of a Research Partnership grant. As holder of a Canada Research Chair in Physical Chemistry, D.K.B. thanks the contributions of the Canada Research Chair Program to this research.

References

[1] H.W. Kroto, J.R. Heath, S.C. O'Brian, R.F. Curl, R.E. Smalley, Nature 318 (1985) 162.

[2] E.G. Gillan, C. Yeretzian, K.S. Min, M.M. Alvarez, R.L. Whetten, R.B. Kaner, J. Phys. Chem. 96 (1992) 6869.

[3] H.R. Rose, I.G. Dance, K.J. Fisher, D.R. Smith, G.D. Willet, M.A. Wilson, J. Chem. Soc., Chem. Commun. (1993) 1361.

[4] U. Zimmermann, N. Malinofski, U. Näher, S. Frank, T.P. Martin, Phys. Rev. Lett. 72 (1994) 3542.

[5] R.C. Haddon et al., Nature 350 (1991) 320.

[6] A.F. Hebard et al., Nature 350 (1991) 600.

[7] L.M. Roth, Y. Huang, J.T. Schwedler, C.J. Cassidy, D. Ben-Amotz, B. Kahr, B.S. Freiser, J. Am. Chem. Soc. 113 (1991) 6298.

[8] .V. Baranov, D.K. Bohme, Int. J. Mass Spectrom Ion Processes 149/150 (1995) 543.

[9] Y. Huang, B.S. Freiser, J. Am. Chem. Soc. 113 (1991) 8186.

[10] G.K. Koyanagi, V.V. Lavrov, V. Baranov, D. Bandura, S. Tanner, J.W. McLaren, D.K. Bohme, Int. J. Mass Spectrom. 194 (2000) L1.

[11] V.V. Lavrov, V. Blagojevic, G.K. Koyanagi, G. Orlova, D.K. Bohme, J. Phys. Chem. A 108 (2004) 5610.

[12] C.E. Moore, B.H. Cardelino, X.Q. Wang, J. Phys. Chem. 100 (1996) 4685.

[13] P.A. Heiney et al., Phys. Rev. Lett. 66 (1991) 2911.