[3] A. W. Sleight, J. L. Gillson, P. E. Bierstedt, *Solid State Commun. 17* (1975) 27.

[4] H. G. von Schnering, L. Walz, M. Schwarz, W. Becker, M. Hartweg, T. Popp, B. Hettich, P. Müller, G. Kämpf, *Angew. Chem. 100* (1988) 604; *Angew. Chem. Int. Ed. Engl. 27* (1988) 574.

[5] A. Simon, *Chem. Unserer Zeit 22* (1988) 1; A. Simon, *Angew. Chem. 99* (1987) 602; *Angew. Chem. Int. Ed. Engl. 26* (1987) 579.

[6] M. Jansen, *Angew. Chem. 99* (1987) 1136; *Angew. Chem. Int. Ed. Engl. 26* (1987) 1098.

[7] *Synthesis*: Intimate mixtures of Ag_2O (prepared according to Ref. [8]) and "Bi_2O_5" (prepared according to Ref. [9]) in the ratio Ag:Bi 25:3 were allowed to react with H_2O (2 mL) in silver crucibles in a stainless steel autoclave at an O_2-pressure of 10 MPa. After a reaction time of 1–2d, black crystals are formed.

[8] G. Brauer (Ed.): *Handbuch der Präparativen Anorganischen Chemie*, Enke, Stuttgart 1962, p. 912.

[9] G. Gattow, W. Klippel, *Z. Anorg. Allg. Chem. 470* (1980) 25.

[10] The ratio of the metals was determined by energy dispersive microanalysis (EDX PV9800) (calcd. Ag. 89.3 Bi 10.7%, obs. Ag. 90.1, Bi 9.9%).

[11] Crystal data: $Ag_{25}Bi_3O_{18}$ crystallizes trigonally. Space group $P\bar{3}$ (No. 147) with $a = 1158.9(1)$, $c = 623.9(1)$ pm (Guinier data, standard α-quartz; $a = 491.3$, $c = 540.5$ pm), $Z = 1$, $\mu(Mo_{K\alpha}) = 344.16\ cm^{-1}$. 8430 reflections measured (four-circle diffractometer Enraf-Nonius CAD-4 with $Mo_{K\alpha}$ graphite monochromator), $\omega/2\theta$ scan, 1409 independent reflections ($2\theta_{max} = 60°$). Absorption and extinction corrections. Solution of structure by direct methods and subsequent difference Fourier syntheses (SHELX-76 and SHELXS-86) [12]. Refinement of the parameters with anisotropic temperature factors (least squares method) gave for 1369 reflections with $I > 2\sigma(I)$ $R = 3.9\%$, $R_w = 3.4\%$ ($w = 3.857/\sigma^2(F)_o$). Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-55253, the names of authors, and the journal citation.

[12] G. Sheldrick: *SHELX-76/SHELXS-86-Programmsystem*, Cambridge (UK) and Göttingen (FRG) universities.

[13] The decomposition was monitored by simultaneous thermal analysis (STA 429, Pt/Rh crucible, purged with Ar, heating rate 5 K min^{-1}) between 20 and 550°C.

[14] The measurement was carried out on a pellet (silver contact) of 9 mm diameter and 1 mm thickness in the temperature range 10–298 K.

[15] M. Bortz, M. Jansen, K. Syassen, H. Wilhelm, unpublished.

Endohedral Cluster Compounds: Inclusion of Helium within $C_{60}^{\bullet\oplus}$ and $C_{70}^{\bullet\oplus}$ through Collision Experiments[**]

By *Thomas Weiske, Diethard K. Böhme, Jan Hrušák, Wolfgang Krätschmer*, and *Helmut Schwarz*[*]

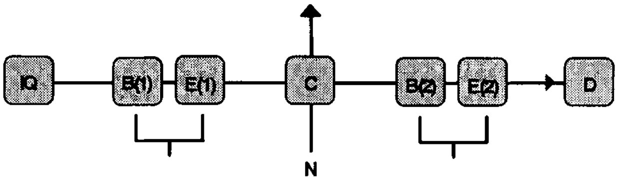
Dedicated to Dr. Curt Brunnée

Of all the C_x carbon clusters,[1] the fullerene C_{60} (the "third allotropic form of carbon"[2]) is currently of greatest interest, largely because it can be produced in macroscopic quantities with the convenient method developed by *Krätschmer, Huffman*, et al.[3] Not long thereafter sufficient experimental evidence had been reported[1–3] to verify the visionary suggestion[4, 5] that C_{60} was the celebrated icosahedron of the I_h-point group.

What are the physico-chemical properties of C_{60}? Early results suggest, for example, that doped C_{60} can be regarded as a three-dimensional organic superconductor,[6] that it can be hydrogenated by the Birch-reduction to produce $C_{60}H_{36}$,[7] and that up to 24 methyl groups can be added to the polyanions of C_{60} as has just been reported.[8] Is an "endohedral chemistry", i.e. a chemistry which proceeds inside the cage of C_{60} or its radical cation, $C_{60}^{\bullet\oplus}$ also possible? While theory has postulated a variety of endohedral cluster compounds for C_{60} with interesting properties,[9] experimental findings for the production of C_xM-clusters ($x \geq 60$; M = La, Cu, Ba, Sr) from the laser-induced vaporization of a mixture of salt and graphite have been interpreted more diversely: *Smalley* et al.[10] indicate that their experimental results point to the production of a spherically-constructed C_x cluster with a metal atom inside it; on the other hand, *Kaldor* et al.[11] are of the opinion that $C_{60}La$, for example, is an empty C_{60} cluster which has "custody" of the metal on its outside surface.

Here we report results of a molecular-beam experiment in which mass-selected ions of $C_{60}^{\bullet\oplus}$ and $C_{70}^{\bullet\oplus}$ produced by electron-impact ionization at 70 eV collide with a stationary neutral gas N; products are observed which are dependent on the nature of the collision gas and which leave no doubt about the incorporation of N.[12]

Earlier experiments have already shown[13] that highly accelerated $C_{60}^{\bullet\oplus}$ and $C_{70}^{\bullet\oplus}$ ions lose C_2 unimolecularly and even-numbered C_n units ($n = 2, 4, 6$ etc.) upon collisional activation (CA);[14] however, nothing has been reported about the incorporation of N. Perhaps this is a consequence of the limited performance parameters of the mass spectrometers which have been employed, which do not allow certain experiments to be performed. The four-sector machine used by us (Scheme 1) records measurements which demonstrate the incorporation of N according to the collision-induced reaction [Eq. (a)].



Scheme 1. Sketch of the tandem mass spectrometers used in this study: IQ = ion source, B = magnetic sector, C = collision chamber, E = electric sector, D = ion detector, N = neutral gas. For a complete description of the machine see Ref. [15].

$$C_x^{\bullet\oplus}\ (8\ \text{keV}) + N \longrightarrow [C_{x-n} + N]^{\bullet\oplus} + C_n \qquad \text{(a)}$$

$$x = 60, 70 \quad n = 2, 4, 6, \ldots$$

For this purpose $C_x^{\bullet\oplus}$ ions ($x = 60$ or 70) were accelerated up to 8 keV, were mass-selected in the B(1)E(1) sector (resolution $m/\Delta m = 1500$), and then were allowed to react with various gases N in the collision cell C with ca. 75% reduction of the primary ion beam. The products of this high-energy

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[**] This research was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. *D. K. B.* is grateful to the Alexander von Humboldt Foundation for a Senior Scientist Award.

reaction were detected and identified with a combined momentum and energy analysis ("linked scan": B(2)/E(2) = constant[16l]). With H_2, D_2, Ar, and SF_6, the experiments show exclusive production of fragments in which C_n ($n = 2, 4, 6, 8$) or, less likely,[13b] multiple units of C_2 have been splitt off. A typical example is shown in Figure 1 for N = D_2. The same processes were observed for the other gases, but the relative intensities are somewhat different because of differences in "center-of-mass" energy, E_{cm}.[17]

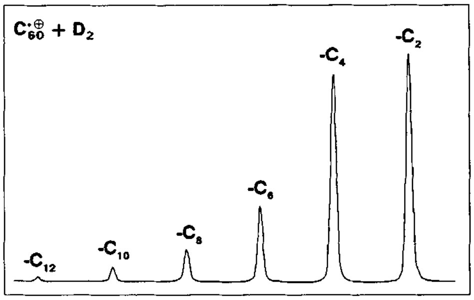

Fig. 1. CA mass spectrum for $C_{60}^{\cdot\oplus}/D_2$; $E_{cm} = 44.2$ eV.

A fundamentally different result is obtained when helium is used as a collision gas (Fig. 2). New signals appear at *higher* masses at all signals, corresponding to the loss of C_n; the mass difference Δm is equal to 4 when ^4He is used (Fig. 2, top) and 3 when ^3He is used (Fig. 2, bottom). The differences which appear with D_2 and He cannot be accounted for by energy since E_{cm} is identical for these two gases; other factors (presumably size and shape of N) must be responsible. Totally analogous results are obtained with $C_{70}^{\cdot\oplus}$: while helium is incorporated (appearance of $[C_{70-n}He]^{\cdot\oplus}$), the other collision partners only lead to collision-induced elimination (loss of C_n). The observation that the $C_{60}^{\cdot\oplus}$/He fragment arises from $C_{70}^{\cdot\oplus}$/He (Fig. 4) is particularly noteworthy. If *Smalley*'s argument[5d] that loss of C_2 units is accompanied by a "repair" of the cluster-cage applies, this $C_{60}^{\cdot\oplus}$/He is the fullerene-noble gas complex which has been sought for a long time.[18]

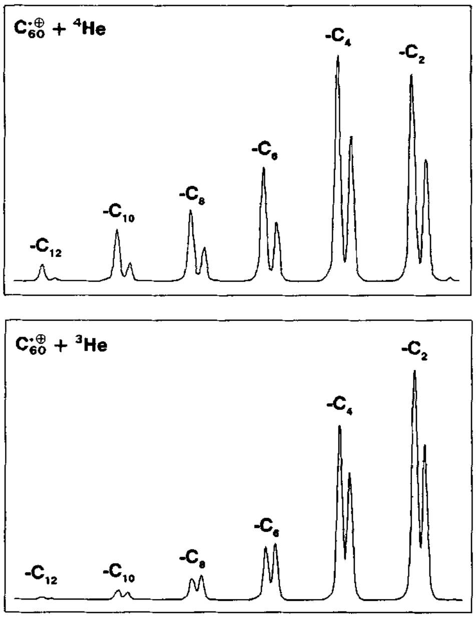

Fig. 2. CA mass spectra for $C_{60}^{\cdot\oplus}$ with ^4He($E_{cm} = 44.2$ eV) (top) and ^3He($E_{cm} = 33.2$ eV) (bottom).

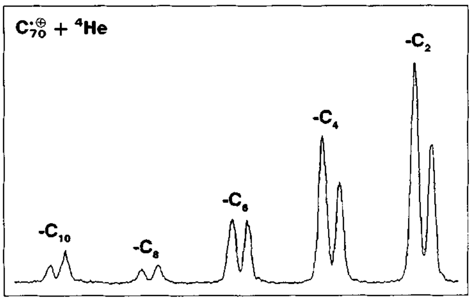

Fig. 3. CA mass spectrum for $C_{70}^{\cdot\oplus}$ with ^4He ($E_{cm} = 37.9$ eV).

The location of the helium atom in the $[C_{x-n}He]^{\cdot\oplus}$ clusters of course cannot be determined with the experiments described here, but there are indirect indications that we are almost certainly dealing with intra-cavity bonding rather than with cluster ions in which helium is fixed to the outer wall. The process $C_{60}^{\cdot\oplus} \rightarrow C_{58}^{\cdot\oplus} + C_2$ requires at least 4–5 eV according to *Lifshitz* et al.[13e] and *Smalley* et al.,[19] while the binding energy of He to $C_6H_6^{\cdot\oplus}$, for example, is less than 0.2 eV acoding to ab initio MO calculations.[20] If the helium was not incorporated by the cage during the collision process, it would have had to leave the complex on energetic and kinetic grounds before a C_2 unit splits off. Accordingly an increase in mass, $\Delta m = 3$ and 4, would not have appeared. Furthermore mass-selected $[C_xHe]^{\cdot\oplus}$ ions lose not He, but C_2 unimolecularly.

How much energy is required to bring a helium atom inside the $C_x^{\cdot\oplus}$ cages ($x = 60, 70$)? We have obtained an upper limit of less than 10 eV in model calculations in which He is forced through a C_6H_6 or $C_6H_6^{\cdot\oplus}$ plane.[20] This energy barrier,[21] whose accuracy should not be overemphasized, is clearly smaller than the kinetic energy of greater than 30 eV which is available to the collision complexes $C_x^{\cdot\oplus}$/He ($x = 60, 70$). Consequently, the inclusion of a helium atom into the cluster is energetically possible. *There is no doubt that a He atom is incorporated into the* $C_x^{\cdot\oplus}$ ($x = 60, 70$) *cluster in the course of the collision.*

The experiments and thoughts presented here provide a first item in the cornucopia of endohedral bonded (ionized) C_x fullerenes.[2, 9, 22]

Received: May 23, 1991
German version: *Angew. Chem. 103* (1991) 898

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[1] Review: W. Weltner, Jr., R. J. Van Zee, *Chem. Rev. 89* (1989) 1713.

[2] a) J. F. Stoddart, *Angew. Chem. 103* (1991) 71; *Angew. Chem. Int. Ed. Engl. 30* (1991) 70, and references cited therein; b) F. Diederich, R. L. Whetten, *ibid. 103* (1991) 695 and *30* (1991) 678.

[3] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *Nature (London) 347* (1990) 354.

[4] E. Osawa, *Kagaku* (Kyoto) **25** (1970) 85.

[5] a) H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature (London) 318* (1985) 162; c) For "the story of buckminsterfullerenes" see: R. E. Smalley, *The Sciences (N.Y.) 31* (1991), No. 2, p. 22.

[6] A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, A. R. Kortan, *Nature (London) 350* (1991) 600.

[7] R. E. Haufler, J. Conceicao, L. P. F. Chibante, Y. Chai, N. E. Byrne, S. Flanangan, M. M. Haley, S. C. O'Brien, C. Pan, Z. Xiao, W. E. Billups, M. A. Cinfolini, R. H. Hauge, J. L. Margrave, L. J. Wilson, R. F. Curl, R. E. Smalley, *J. Phys. Chem. 94* (1990) 8634.

[8] J. W. Bausch, G. K. Surya Prakash, G. A. Olah, D. S. Tse, D. C. Lorents, Y. K. Bae, R. Malkotra, *J. Am. Chem. Soc. 113* (1991) 3205.

[9] a) J. Cioslowski, *J. Am. Chem. Soc. 113* (1991) 4139; b) J. Cioslowski, E. D. Fleischmann, *J. Chem. Phys. 94* (1991) 3730; c) A. H. H. Chang, W. C. Ermler, R. M. Pitzer, *ibid. 94* (1991) 5004.

[10] a) J. R. Heath, S. C. O'Brien, Q. Zhang, Y. Lin, R. F. Curl, H. W. Kroto, F. K. Tittel, R. E. Smalley, *J. Am. Chem. Soc. 107* (1985) 7779; b) F. D. Weiss, J. L. Elkind, S. C. O'Brien, R. F. Curl, R. E. Smalley, *J. Am. Chem. Soc. 110* (1988) 4464.

[11] a) D. M. Cox, D. J. Trevor, K. C. Reichmann, A. Kaldor, *J. Am. Chem. Soc. 108* (1986) 2457; b) D. M. Cox, K. C. Reichmann, A. Kaldor, *J. Chem. Phys. 88* (1988) 1588; c) A. Rosén, B. Wästberg, *J. Am. Chem. Soc. 110* (1988) 8701.

[12] Presented for the first time: D. K. Böhme, T. Weiske, J. Hrušák, W. Krätschmer, H. Schwarz, *37th Annu. Conference on Mass Spectrom. and Allied Top. (ASMS)*, Nashville, TN, USA, May 21, 1991.—We have heard from Dr. M. M. Ross, Naval Research Laboratories, Washington, D.C., that he has repeated our experiment after the ASMS conference and obtained the same results.

[13] a) P. P. Radi, M. T. Hsu, J. Brodbelt-Lustig, M. Kincon, M. T. Bowers, *J. Chem. Phys. 92* (1990) 4817; b) A. B. Young, L. M. Cousins, A. G. Harrsion, *Rapid Commun. Mass Spectrom. 5* (1991) 226; c) D. R. Luffer, K. H. Schram, *ibid. 4* (1990) 552; d) P. P. Radi, M.-T. Hsu, M. E. Rincon, P. R. Kemper, M. T. Bowers, *Chem. Phys. Lett. 174* (1990) 223; e) C. Lifshitz, M. Iraqi, T. Peres, J. E. Fischer, *Int. J. Mass Spectrom. Ion Processes*, in press; f) C. Lifshitz, M. Iraqi, T. Peres, J. E. Fischer, *Rapid Commun. Mass Spectrom. 5* (1991) 238; g) D. Schröder, D. Sülzle, *J. Chem. Phys. 94* (1991), 6933; h) R. J. Doyle, Jr., M. M. Ross, *J. Phys. Chem.*, in press.

[14] Reviews: a) R. G. Cooks (Ed.): *Collision Spectroscopy*, Plenum, New York 1978; b) K. Levsen, H. Schwarz, *Mass Spectrom. Rev. 2* (1983) 77; c) J. Bordas-Nagy, K. R. Jennings, *Inst. J. Mass Spectrom. Ion Processes 100* (1990) 105.

[15] a) R. Srinivas, D. Sülzle, T. Weiske, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes*, in press; b) R. Srinivas, D. Sülzle, W. Koch, C. H. DePuy, H. Schwarz, *J. Am. Chem. Soc.*, in press.

[16] J. R. Chapman: *Practical Organic Mass Spectrometry*, Wiley, Chichester, England 1985, Chapter 6.

[17] The "center of mass"-energy (E_{cm}) determines the maximum energy which can be transferred in a collision of a projectile A with a stationary particle N. The following relationship holds: $E_{cm} = E_A[m_N/(m_N + m_A)]$, where E_A = kinetic energy of A (corresponding to 8000 eV in the experiments described here) and m_i the masses of A and N.

[18] Direct production of $C_{60}^{\bullet\oplus}$/He or $C_{70}^{\bullet\oplus}$/He according to Equation (a) in a high-energy collision experiment is fundamentally impossible on kinematic grounds. However, we are planning experiments with "slow" $C_x^{\bullet\ominus}$ ions. Furthermore, we intend to expose the $C_x^{\bullet\oplus}$/He species to a neutralization–reionization (NRMS) experiment. The experiment (which has not yet been performed because of insufficient intensities) will answer the question about the existence of neutral C_xHe clusters.

[19] S. C. O'Brien, J. R. Heath, R. F. Curl, R. E. Smalley, *J. Chem. Phys. 88* (1988) 220.

[20] The ab initio MO calculations were performed at the MP2/6-31G**// MP2/3-21G* level of theory. We expect that calculations with larger basis sets will lead to *smaller* values for the binding energy of $C_6H_6^{\bullet\oplus}$/He as well as for the energy required to pass He through a C_6H_6 or $C_6H_6^{\bullet\oplus}$ plane.

[21] For MNDO calculations of the barrier for the *endo* → *exo* migration of $Li^{\oplus}$ in C_x clusters see: D. Bakowies, W. Thiel, *J. Am. Chem. Soc. 113* (1991) 3704.

[22] Note added in proof (12 June 1991): First experiments with $C_{60}^{\bullet\oplus}$ and Ne (E_{CM} = 216 eV) show that this noble gas can also be incorporated into the cavity (appearance of $[C_{60-n}Ne]^{\bullet\oplus}$, $n = 2 - 10$), but the "yield" is a factor 10 smaller than in the case of He.

BOOK REVIEWS

Book Reviews are written by invitation from the editor. Suggestions for books to be reviewed and for book reviewers are welcome. Publishers should send brochures or (better) books to the following address: Redaktion Angewandte Chemie, Postfach 10 11 61, D-6940 Weinheim, Federal Republic of Germany. The editor reserves the right of selecting which books will be reviewed. Uninvited books not chosen for review will not be returned.

Comprehensive Medicinal Chemistry. The Rational Design, Mechanistic Study and Therapeutic Application of Chemical Compounds. Six volumes. Edited by *C. Hansch, P. G. Sammes* and *J. B. Taylor*. Pergamon, Oxford 1990. Hardcover $ 1995.00. (Individual volume: $ 350.00 each).— ISBN 0-08-032530-0 (complete work)

Volume 1: General Principles. Volume Editor: *P. D. Kennewell.* xv, 811 pp.—ISBN 0-08-037057-8

The first section of this volume is very heterogeneous in content; it sets out to describe the development of medicinal chemistry by giving a chronology of drug introductions and tracing the history of the pharmaceutical industry. It shows how the different initial conditions and environments existing in German-speaking countries, in Great Britain and in the USA have led to the industry developing in different ways. The important role of legislation and of public regulatory agencies such as the FDA in imposing quality standards is emphasized, and it is shown how this led to a strengthening of the German and North American pharmaceutical companies even before the First World War.

The account of drug introductions is not in chronological order, nor is it complete. Admittedly it would not be possible to cover this subject exhaustively within the space allowed, but it is surprising that some important milestones such as the introduction of antihyperlipidemic aryloxycarboxylic acids ("Fibrates"), HMG-CoA-reductase inhibitors ("Lovastatin") and calcium antagonists of the dihydropyridine type are not included. On the other hand the space devoted to compounds such as LSD, tetrahydrocannabinol and chloramin-T is disproportionately large in relation to their importance. Antibacterial agents and their development are discussed in detail, but only penicillins and cephaalosporins are covered. Neither quinolones nor carbapenemes are mentioned. The important contribution of the azoles in antifungal therapy is also ignored. This not entirely successful historical introduction ends with brief accounts of Egyptian, Greek and Arabic medicine, plus two separate chapters on traditional Chinese and Indian medicine.

The second section on "Targets of Biological Active Molecules" follows a logical sequence, starting with the essentials of anatomy and physiology and proceeding via cell architecture to the identification of specific macromolecular targets. Principles of general pharmacology, such as the receptor theory, are derived in the course of the discussion.

Although the introduction to anatomy and physiology is pleasingly concise, this means that the non-biologists for whom this chapter is mainly intended will find that their needs are not fully satisfied here; it would have been useful to include references to suitable books covering these topics.