



Formation of Singly Bonded Fullerene Dimers in Electrospray Mass Spectrometry

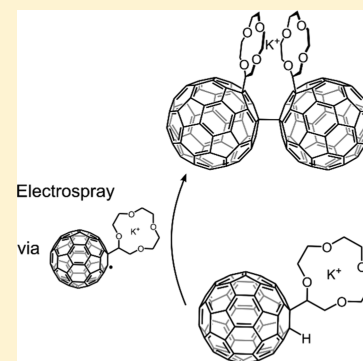
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S Supporting Information

ABSTRACT: The K^+ adducts of the crown ether–[60]fullerene conjugate of the form $(12cr4 - H)-C_{60}-H$ are investigated by electrospray mass spectrometry (ESI-MS), focusing on the dimeric species produced from two different solvent mixtures. A singly bonded fullerene dimer of the type $(12cr4 - H)-C_{60}-C_{60}-(12cr4 - H)K^+$ is generated in aprotic solvents, while in protic solvents, a metal-bridged, noncovalently bound dimer predominates. The dimerization reaction is proposed to occur during the ESI process via the radical intermediate $(12cr4 - H)-C_{60}^\bullet$. The fragmentation behavior of the different dimers is studied by collision-induced dissociation (CID), showing characteristic product ions for each species.



INTRODUCTION

Dumbbell-shaped fullerene dimers are regarded as simplest model for the pearl necklace type of fullerene polymers.^{1–3} The covalent connection between the fullerenes can take various forms. Laser irradiation for instance leads to the connection of two C_{60} molecules via $[2 + 2]$ cycloaddition.^{4,5} Other fullerene dimers are connected by oxo- or methylene-bridges,^{6–8} or by various functionalized spacers.³ Evidence for the formation of singly bonded fullerene dimers of the general structure $RC_{60}-C_{60}R$ was first provided by Morton et al. after EPR measurements of alkylated fullerene radicals.⁹ The increased intensity of the EPR signal at higher temperature was ascribed to an equilibrium between the RC_{60}^\bullet radicals and their diamagnetic dimer in solution.^{9–11} Since their pioneering work, various synthetic routes to singly bonded fullerene dimers have been devised.^{12–20} A recent review by Tzirakis and Orfanopoulos gives a comprehensive overview of the various methods.²¹ While several X-ray structures of singly bonded fullerene dimers have been published,^{14–16} mass spectrometric analysis of the dimers has proven to be challenging. Because of the weak central $C_{60}-C_{60}$ bond,^{10–12} only the monomeric radical was observed in most cases.^{15,18} To the best of our knowledge, a dimer was detected using atmospheric pressure chemical ionization (APCI)¹⁴ and matrix-assisted laser desorption/ionization (MALDI).²⁰

The authors have recently investigated the adducts of crown ether fullerenes $C_{60}H(cr - H)$ (Scheme 1),²² regarding their ability to form ions in ESI and MALDI-MS.²³ Wilson and Wu synthesized the first crown ether-fullerene conjugate in which

the crown ether was linked via a methylene bridge to the fullerene and showed the applicability of electrospray ionization to investigate these adducts.²⁴ The present compounds are a new type of crown ether–fullerene conjugate in which the crown ether is directly attached via a C–C single bond to the C_{60} , which also attains a hydrogen atom as second substituent to the former fullerene double bond. The current study focuses on the unprecedented formation of dimeric species produced in ESI. Apart from the expected metal-bridged dimer $[C_{60}H(cr - H)]_2M^+$, we also observed a dimer at two mass units lower, consistent with the formula $[C_{60}(cr - H)]_2M^+$. We propose the formation of a $C_{60}-C_{60}$ single bond under formal loss of two hydrogen atoms during the electrospray process (Scheme 1). As the dimer formation can be controlled by the choice of solvent, the different dimers could be studied separately in collision-induced dissociation (CID) experiments. The different dissociation products in turn provide evidence for the different bonding of the dimers.

EXPERIMENTAL SECTION

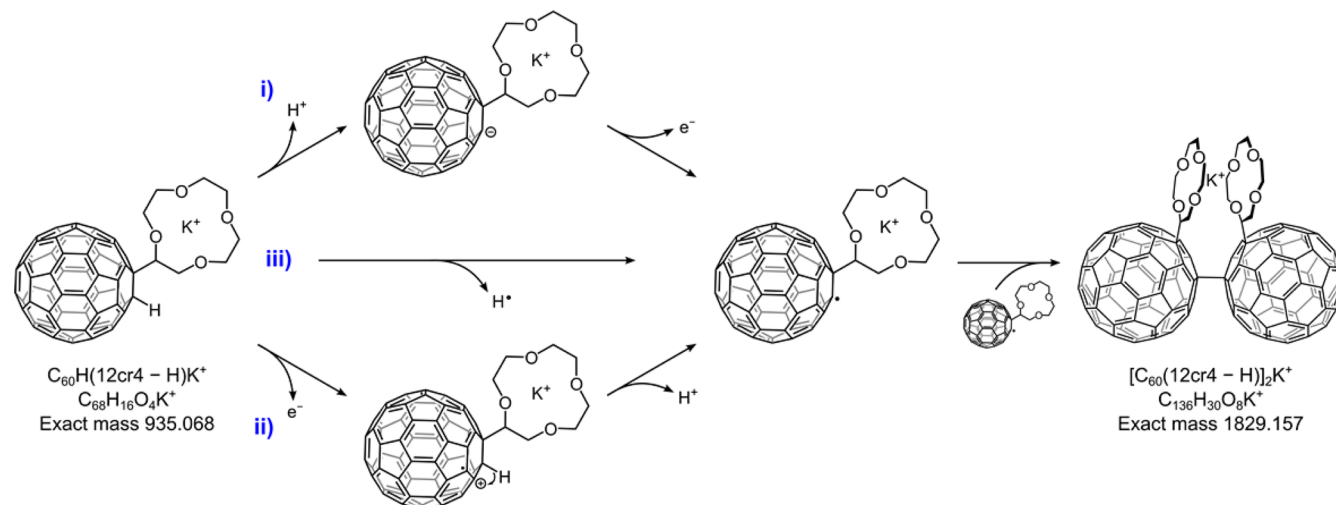
The experiments were performed with two different instruments. The high resolution mass spectra were acquired with a quadrupole time-of-flight (QTOF) instrument (mircOTOF-Q II, Bruker Daltonics). For its ESI source a flow rate of 180 $\mu\text{L h}^{-1}$ was used, the temperature of the nitrogen counter flow was

Received: September 25, 2014

Revised: November 19, 2014

Published: November 25, 2014



Scheme 1. Possible Mechanisms of the Formation of the Covalent Dimer $[C_{60}(12cr4 - H)]_2K^+$ During the Electrospray Process

set to 180 °C and between the needle and the spray shield a voltage of -4 kV was applied. The transfer region of this instrument consists of two ion guide funnels.

The quadrupole ion trap (QIT) instrument (esquire6000, Bruker Daltonics) was used for the hydroquinone experiment and the MS/MS spectra. As its source geometry is slightly different, a flow rate of $240 \mu\text{L h}^{-1}$ was used and the nitrogen temperature was set to 300 °C. A voltage of -3.5 kV was applied to the spray shield, while the needle is grounded. After passing a glass capillary, the ions have to pass through a skimmer into the next vacuum stage. Between the capillary and the skimmer a voltage gradient of 40 V is applied to accelerate the ions. Compared to the above-mentioned ion guide funnels, the skimmer system provides in general a harsher transfer region, in which collisions may lead to dissociations of more labile ions.

All solvents used were of HPLC grade purity. The crown ether fullerene adduct was dissolved in dichloromethane (DCM) and then diluted with either acetonitrile (ACN) to give a 1:1 (volume: volume) mixture, or with MeOH in a 3:5 (v:v) ratio. The mixing ratios were chosen to achieve a stable spray in the ESI source. KCl was dissolved in MeOH at a concentration of 1 g L^{-1} , so only small volumes of this solution had to be added to the $C_{60}H(12cr4 - H)$ samples. The concentration of the crown ether fullerene adduct in the final solution was in the range of $2\text{--}7 \times 10^{-5} \text{ mol L}^{-1}$ with at least a 2-fold molar excess of KCl. For the mixing experiment, $C_{60}H(12cr4 - H)$ and $C_{60}H(15cr5 - H)$ were individually dissolved in DCM. These solutions were mixed in a 1:1 (molar: molar) ratio, then diluted as above with ACN. NaCl (1 g L^{-1} in MeOH) was added in at least a 2-fold molar excess to the crown ether fullerenes.

Hydroquinone (>99%) was purchased from Fluka Chemie AG and used without further purification. It was initially dissolved in MeOH at a concentration of 100 g L^{-1} . Small volumes of this solution were added to the $C_{60}H(12cr4 - H)/\text{KCl}$ -sample so that the resulting concentration of hydroquinone was 0.1 mol L^{-1} .

RESULTS AND DISCUSSION

In the ESI spectra of $C_{60}H(12cr4 - H)$ with added KCl in a 1:1 (v:v) mixture of DCM and ACN, the K^+ adduct of the analyte is the most prominent peak at m/z 935 (Figure 1a). In the

higher mass region a mixture of dimeric species is observed (Figure 1a,b). Visible, but comparatively low in intensity at m/z 1831 is the expected dimer of the intact molecule, $[C_{60}H(12cr4 - H)]_2K^+$. In this dimer the alkali-metal ion is sandwiched between the two crown ether moieties, noncovalently binding to the oxygens in both crowns. The majority of the detected signals, however, belongs to a dimer that has formally lost two hydrogen atoms, appearing two mass units lower at m/z 1829. The most reasonable explanation for this would be a covalently bound dimer $[C_{60}(12cr4 - H)]_2K^+$, in which both C_{60} crown adducts lost the hydrogen atom bound to the fullerene core and instead form a single bond between the fullerenes (Scheme 1). Both crown ether units in this dimer may be bridged by the potassium ion, similar to the noncovalently bound dimer.

An interesting observation can be made when the solvent is changed from the aprotic DCM/ACN mixture to DCM/MeOH (3:5 v/v) (Figure 1c). No longer is the covalently bound dimer the most abundant, but the metal-bridged dimer $[C_{60}H(12cr4 - H)]_2K^+$ dominates the higher mass region of the spectrum. Obviously, the dimer formation can be controlled by choice of solvent, indicating that the covalent bond between the monomeric units is either formed during the ESI process or it is a byproduct of the compound's synthesis and dissociates in the protic solvent mixture. To prove that the covalently bound dimer is indeed generated during the electrospray process, solutions of two different crown ether fullerenes, $C_{60}H(12cr4 - H)$ and $C_{60}H(15cr5 - H)$, were mixed. After addition of NaCl, the ESI spectrum clearly shows the formation of a covalently bound heterodimer $[C_{60}(12cr4 - H)C_{60}(15cr5 - H)]Na^+$ (see Supporting Information). As there is no inducement for the crown ether fullerenes to simply react in solution, the covalently bound dimer must be formed due to the high electric field inherent to the electrospray process.

Singly bonded fullerene dimers of the structure $RC_{60}-C_{60}R$ are reportedly formed by dimerization of the corresponding radicals RC_{60}^\bullet .^{12–21} This also seems to be a plausible mechanism in this case. A radical mechanism would explain the dependency on the solvent mixture. While the aprotic solvents DCM and ACN apparently do not influence the radical reaction, MeOH has been shown to transfer hydrogen atoms to fullerene radicals in the gas phase.²⁵ MeOH could therefore react with the radical $C_{60}(12cr4 - H)K^+$, restoring

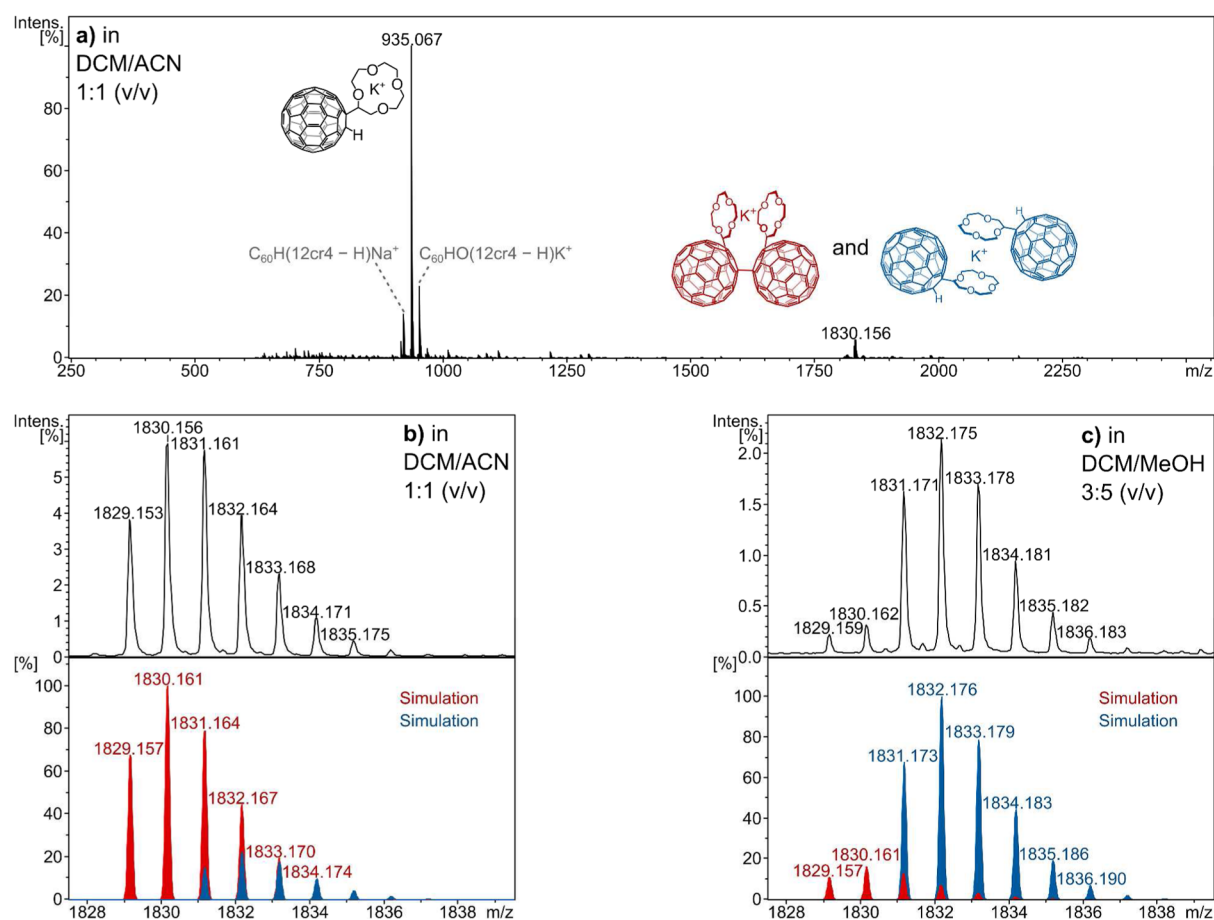


Figure 1. (a) ESI spectrum of $C_{60}H(12cr4 - H)$ with KCl in DCM/ACN. In the lower mass region the metalated $C_{60}H(12cr4 - H)K^+$ dominates the spectrum (m/z 935). In the high mass region, both the covalently (m/z 1829) and the noncovalently bound dimer (m/z 1831) can be observed. In a DCM/ACN mixture, the formation of the covalently bound dimer is preferred (b), while in DCM/MeOH the noncovalently bound dimer is more pronounced (c).

the intact crown ether fullerene, $C_{60}H(12cr4 - H)K^+$, and preventing further reaction to the covalently bound dimer.

Raji et al. observed a covalently bound dimer of pterostilbene during their ESI analysis.²⁶ By intentionally adding a radical scavenger to the sample solution, they successfully verified the involvement of radicals in the reaction mechanism. We tried the same approach with the crown ether C_{60} adducts, adding hydroquinone to the sample solution (DCM/ACN) and monitoring the change in relative abundance of the two dimeric species. If the dimerization proceeds via the radical $C_{60}(12cr4 - H)^{\bullet}$, the hydroquinone should react with it to regenerate $C_{60}H(12cr4 - H)$, preventing the formation of the covalently bound dimer. As hydroquinone does not dissolve in DCM or ACN, but very well in MeOH, it had to be added as a methanolic solution to the sample. The alcohol itself, however, can suppress the formation of the covalently bound dimer as shown above. Hence a highly concentrated hydroquinone stock solution was prepared so only very small amounts of MeOH had to be added to the sample, reducing the effect of the protic solvent. The results of this experiment are shown in Figure 2. The reference solution contained only DCM/ACN (Figure 2a), consequently the covalently bound dimer is formed predominately. At high hydroquinone concentration (Figure 2b) the intensity of the covalently bound dimer does indeed decrease compared to the noncovalently bound species. Note that despite the excess of hydroquinone, the overall appearance of

the spectrum does not change (data not shown). To eliminate the possibility that the decrease in covalently bound dimer is only due to the minute amount of added MeOH, the reference solution was mixed with an appropriate amount of pure MeOH without hydroquinone. Figure 2c shows that the alcohol is not responsible for the change in this case, the radical scavenger alone is accountable. The hydroquinone therefore does prevent the formation of $[C_{60}(12cr4 - H)]_2K^+$, proving that radicals are involved in the dimerization.

The reaction of a distonic ion $C_{60}(12cr4 - H)K^{+\bullet}$ and a neutral radical $C_{60}(12cr4 - H)^{\bullet}$ would afford the observed dimer (Scheme 1). Its formation is also possible via dimerization of two neutral radicals and subsequent capture of a potassium ion. This, however, seems highly unlikely as it would necessitate an additional reaction step and a chance encounter of the neutral dimer and K^+ in the latter stages of the electrospray process, possibly in the gas phase. The high intensity of the $[C_{60}H(12cr4 - H)]K^+$ signal, the base peak in all our ESI spectra, confirms the implausibility of this option. Because of the excess of KCl in the sample solution, at least parts of the crown ether fullerenes should exist as potassium ions in solution. Their transfer into the gas phase gives rise to our base peak, and it is probably also the source of the distonic ions. The neutral radical may stem from the remaining uncomplexed crown ether adducts in the solution. As the

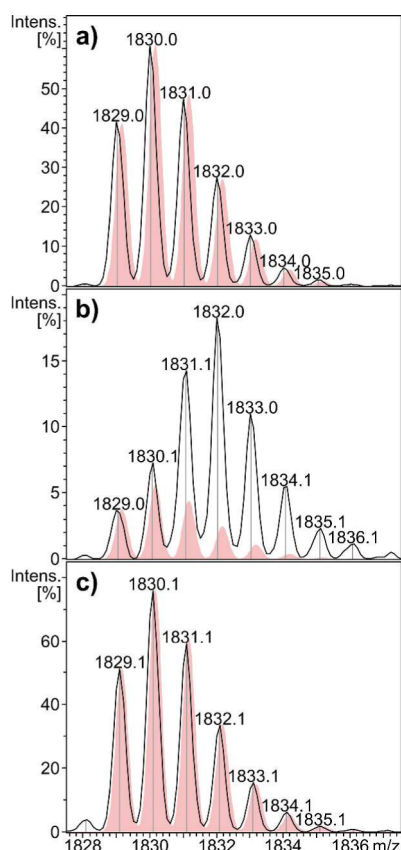


Figure 2. (a) ESI spectrum of the reference solution of $C_{60}H(12cr4-H)$ with KCl in DCM/ACN, showing only the covalently bound dimer $[C_{60}(12cr4-H)]_2K^+$. (b) After addition of hydroquinone (in MeOH), the intensity of the covalently bound dimer is reduced in favor of the noncovalent, metal-bridged dimer $[C_{60}H(12cr4-H)]_2K^+$. (c) As a control experiment the same amount of pure alcohol is added to the reference solution. No change is observed. (a–c) The red overlay in all three spectra is a simulation of the isotope pattern of the covalently bound dimer.

bond between K^+ and the 12cr4 moiety is easily broken,^{23,27,28} it might also be generated by loss of the potassium ion.

The exact mechanism for the generation of the radicals remains unclear, but it is probable that they are formed under the influence of the high electric field inherent to the electrospray ionization method.^{29–32} Taking into account the properties of the crown ether fullerene adducts, three possible pathways come to mind (cp. Scheme 1): (i) Oxidation of the anion $C_{60}(12cr4-H)^-$ or the zwitterion $C_{60}(12cr4-H)^-K^+$, respectively. (ii) One-electron oxidation of the intact molecule and subsequent loss of a proton. (iii) Homolytic cleavage of the C_{60} –H bond or H^\bullet abstraction by radicals generated in the source. These three possibilities shall be discussed in the following.

- (i) As the hydrogen atom attached directly to the fullerene is acidic,^{13,23,33–36} the anion $C_{60}(12cr4-H)^-$ or the zwitterion $C_{60}(12cr4-H)^-K^+$ could already be present in solution. The deprotonated conjugate $C_{60}(12cr4-H)^-$ is readily observed in negative-ion mode ESI spectra.²³ In the high electric field penetrating the needle, one-electron oxidation would afford the radical $C_{60}(12cr4-H)^\bullet$ or $C_{60}(12cr4-H)K^{\bullet+}$. The oxidation of the anion to the radical was reportedly used by various research groups in the synthesis of singly bonded

fullerene dimers.²¹ The applied oxidants included I_2 ,^{13,14,19} *N*-chlorosuccinimide¹⁹ and O_2 , presumably singlet oxygen.¹⁷

- (ii) The electron abstraction from the fullerene core might also be the first step of the reaction mechanism, resulting in a rather unstable, doubly charged radical ion. The repulsion between the two charged sites, however, should be comparatively small as the positive charge on the potassium ion is localized and insulated by the surrounding crown ether. In a subsequent step, the loss of the fullerenyl hydrogen as a proton would afford a more stable singly charged radical. A similar mechanism was suggested by Yamamoto and co-workers for their synthesis of fullerene dimers catalyzed by $Cu(OAc)_2$.¹⁶
- (iii) The third possible pathway is the homolytic cleavage of the C_{60} –H bond or H^\bullet abstraction by radicals generated in the source. The occurrence of OH^\bullet radicals in positive-ion mode ESI, for example, is generally attributed to corona discharge events.^{37–40} If the potential between the needle and the counter electrode is high enough, the nebulizer gas (here: N_2) can be ionized, forming a plasma containing radical cations and free electrons. The electrons are accelerated toward the needle and collide with solvent or analyte molecules, inducing homolytic cleavage.⁴⁰ Though corona discharge is often associated with rather harsh conditions in the electrospray source,^{37–39} Konermann and co-workers provided evidence of its occurrence even under typical conditions used in commercial instruments and without visible light emission.⁴⁰ The crown ether fullerene radicals $C_{60}(12cr4-H)K^{\bullet+}$ in our case could therefore be generated by corona discharge-induced events like high energy collisions with free electrons formed in the plasma. The generation of a solvent radical in a first step and its subsequent abstraction of a hydrogen radical from a crown ether fullerene adduct seems less likely. In both cases, however, the C_{60} –H bond should not be broken selectively, the cleavage of the C_{60} –crown ether bond should be equally probable. The resulting fragment $(12cr4-H)K^{\bullet+}$ was not observed in any of the ESI spectra, though.

Though possible in general, radical generation via corona discharge-induced events is therefore unlikely in our case. The other two mechanisms, namely one-electron oxidation of the anion and proton loss after the abstraction of one electron, seem more likely. Which of these mechanisms is actually responsible for the radical generation, however, cannot be elucidated at this point.

In all three possible mechanisms the radical is formed in the immediate vicinity of the crown ether substituent, at C1 for (i) and (ii) and at C3 or C3' for (iii) (Figure 3). According to the EPR measurements of Morton et al. on RC_{60}^\bullet radicals, the unpaired electron is not delocalized over the whole fullerene, but is restricted to C1, C3 and C3', the carbon atoms with the highest spin density.^{11,41} Since the crown ether substituent is rather large, the addition of another $C_{60}(12cr4-H)^\bullet$ radical at C1 cannot occur, but should be possible at C3 or C3', leading to different isomers of the covalently bound dimer.

Collision-induced dissociation (CID) of the two dimeric species provides further evidence of their individual structures. The MS/MS spectra shown in Figure 4 were acquired using a quadrupole ion trap (QIT) instrument, as its harsher transfer

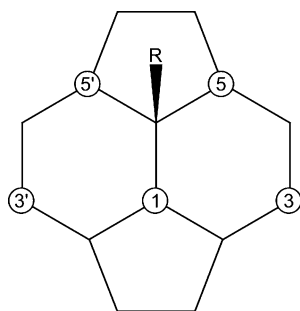


Figure 3. Atom numbering in the relevant part of the RC_{60}^{\bullet} radicals.

conditions enhance the solvent dependency shown before (cp. Figure 1). The less stable, noncovalently bound dimer is not observed at all in DCM/ACN on the ion trap (Figure 2a). The covalently bound dimer can therefore be generated exclusively simply by choice of the solvent. In the DCM/MeOH mixture the covalently bound dimer is still formed, but fortunately only in very small abundance compared to the noncovalent, metal-bridged dimer. As this dimer is more stable than the noncovalently bound dimer, careful control of the applied fragmentation amplitude results in dissociation of the metal-bridged dimer, while the covalently bound one remains largely intact. Figure 4a shows the resulting MS/MS spectrum. Upon activation, the interaction between the potassium ion and one of the crown ether moieties breaks. The noncovalently bound dimer fragments into one metalated crown ether fullerene adduct via loss of the unmetalated counterpart. The enhancement of the lower mass region (Figure 4b) shows the intact monomer $\text{C}_{60}\text{H}(\text{12cr4} - \text{H})\text{K}^+$ at m/z 935.

The CID spectrum of the covalently bound dimer shows two fragments at m/z 934 and m/z 1109 in almost equal abundance (Figure 4c). The lower mass fragment (Figure 4d) corresponds to the distonic ion $\text{C}_{60}(\text{12cr4} - \text{H})\text{K}^+$, generated by homolytic cleavage of the $\text{C}_{60}\text{--C}_{60}$ bond and subsequent loss of the radical $\text{C}_{60}(\text{12cr4} - \text{H})^{\bullet}$. This dissociation is not surprising, as singly bonded fullerene dimers are at equilibrium with their monomeric radicals in solution^{9–16,21} and the $\text{C}_{60}\text{--C}_{60}$ bond should therefore be one of the weakest bonds in the dimer. The origin of the fragment at m/z 1109, on the other hand, is less obvious. It appears exactly 720 mass units lower compared to the precursor (m/z 1829), signifying the loss of a neutral C_{60} and requiring the dissociation of two covalent bonds. The charged fragment would therefore consist of a fullerene with two crown ether moieties and a potassium ion, corresponding to the formula $\text{C}_{60}(\text{12cr4} - \text{H})_2\text{K}^+$. The proposed mechanism for this dissociation is shown in Scheme 2. Even after homolytic cleavage of the $\text{C}_{60}\text{--C}_{60}$ bond, the potassium ion could retain its bonds to both of the crown ether units, holding the radicals in a kind of template complex. Delocalization of an unpaired electron close to the $\text{C}_{60}\text{--crown ether}$ bond could induce homolytic cleavage of this bond forming a new double bond on the fullerene and a crown ether radical. The stability of the resulting, intact C_{60} might be the driving force of this reaction. The crown ether radical $(\text{12cr4} - \text{H})^{\bullet}$ formed in this dissociation remains bound to the potassium ion and thereby close to the radical $\text{C}_{60}(\text{12cr4} - \text{H})^{\bullet}$ generated in the first step of the reaction. Recombination of these two radicals could then afford $\text{C}_{60}(\text{12cr4} - \text{H})_2\text{K}^+$, an even electron fullerene adduct with two crown ethers bound to one core. A similar mechanism of C_{60} -loss from a singly bonded fullerene dimer and

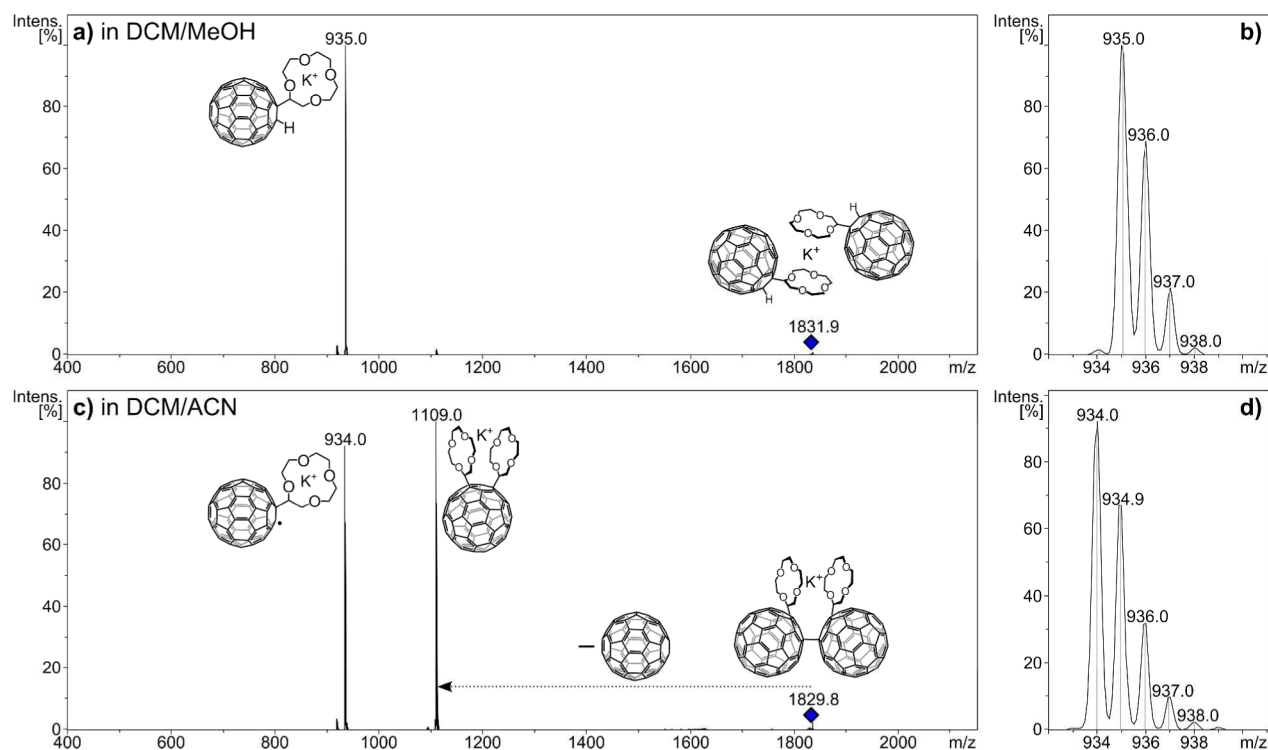
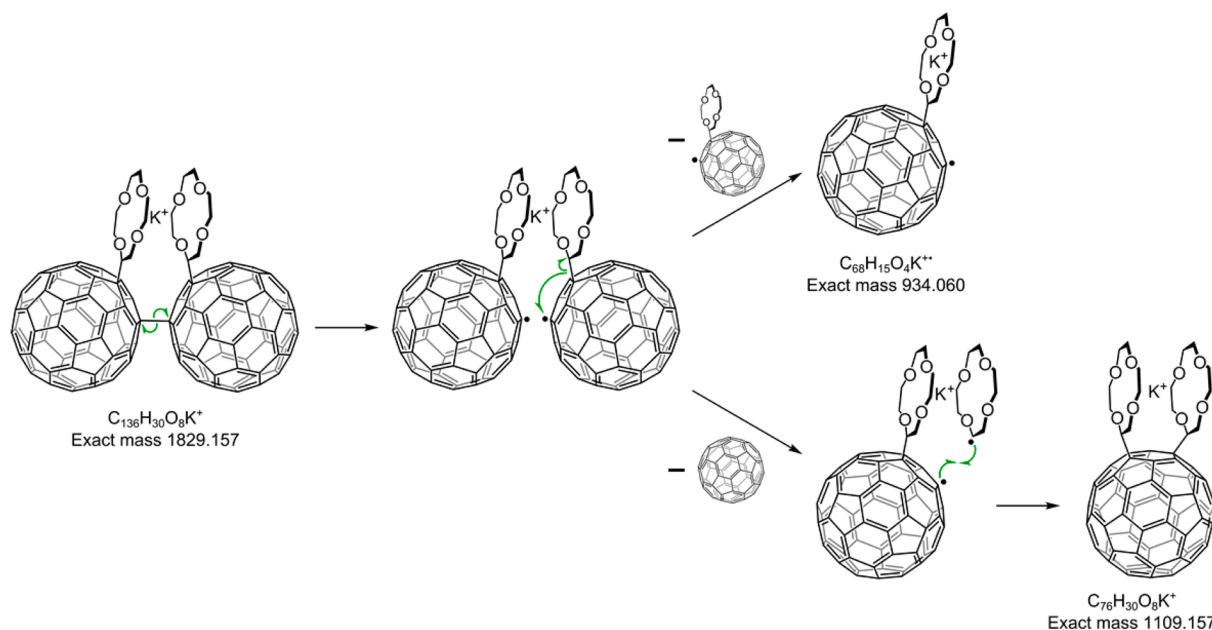


Figure 4. MS/MS spectra of the noncovalently (a) and the covalently bound dimer (c). The enlargements on the right show the low mass region, confirming the dissociation into $\text{C}_{60}\text{H}(\text{12cr4} - \text{H})\text{K}^+$ for the noncovalently bound dimer (b) and into $\text{C}_{60}(\text{12cr4} - \text{H})\text{K}^+$ for the covalently bound dimer (d).

Scheme 2. Proposed Mechanism of the Dissociation of the Covalently Bound Dimer $[C_{60}(12cr4 - H)]_2K^+$ 

recombination of the radicals was proposed by Wang and co-workers for their synthesis of a fullerene-bisadduct.¹⁸

Comparison of the CID spectra of the two dimers shows characteristic fragmentations, confirming the difference in their respective structures. The only product ion from the non-covalently bound dimer is the intact, metalated crown ether fullerene adduct $C_{60}H(12cr4 - H)K^+$, while one fragment of the other, covalently bound dimeric species is the radical, metalated ion $C_{60}(12cr4 - H)K^{+\bullet}$ as expected from a singly bonded fullerene dimer. The other product ion of the covalently bound dimer, $C_{60}(12cr4 - H)_2K^+$, is probably only feasible because of the release of a stable C_{60} molecule and aided by stabilization through the crown–metal ion–crown sandwich complex. The latter reaction represents one of two possible mechanistic routes to form a bisadduct from a pure monoadduct, that is via a dimeric intermediate. For the other alternative of ligand release from one and transfer to the other monoadduct, we have recently published an example using MALDI.⁴²

CONCLUSIONS

In the present study, we have provided evidence of the formation of a covalently bound fullerene dimer during the electrospray process. Its composition and structure has been proven by high resolution mass spectra and characteristic fragmentation products compared to the noncovalently bound dimer. The involvement of radical ions in the generation of the dimer has been proven by suppression of the reaction after addition of a radical scavenger or changing of the solvent mixture. Though the exact mechanism for the radical formation remains unclear, two plausible pathways have been proposed.

A detailed study is in progress covering the possible stabilization afforded by the crown–metal ion–crown sandwich complex and the influence of the respective sizes of the alkali-metal cation and the crown ether cavity on the formation and dissociation of both dimeric species.

ASSOCIATED CONTENT

Supporting Information

Positive-ion mode ESI spectrum of the heterodimer $[C_{60}(12cr4 - H)C_{60}(15cr5 - H)]Na^+$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank the Deutsche Forschungsgemeinschaft (DFG) – SFB 953 “Synthetic Carbon Allotropes” for financial support.

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