nature chemistry

Infrared spectrum and structure of the homochiral serine octamer-dichloride complex

Jongcheol Seo^{1*}, Stephan Warnke¹, Kevin Pagel^{1,2}, Michael T. Bowers³ and Gert von Helden^{1*}

¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany. ²Freie Universität Berlin, Institute of Chemistry and Biochemistry, Takustrasse 3, 14195 Berlin, Germany. ³Department of Chemistry and Biochemistry, University of California Santa Barbara, Santa Barbara, California 93106, USA. *e-mail: jseo@fhi-berlin.mpg.de; helden@fhi-berlin.mpg.de





Abhijit Nag 28/07/2018

Introduction

- Clusters of atoms or molecules with unusually high relative intensities in mass spectra are termed 'magic'.
- In many instances, these 'magic' clusters can be assigned to specific structures, often of high symmetry.
- In the case of C₆₀, the initial observation of magic numbers in mass spectra eventually led to the discovery of a new group of materials and a new form of carbon.
- After electrospray of solutions containing serine, it was first observed that a cluster with the composition (Ser₈H)⁺ dominated the mass spectrum.
- For anionic clusters, a deprotonated octamer has not been reported to show signs of special behaviour. However, octamer clusters containing two halide ions, such as (Ser₈Cl₂)^{2–} and (Ser₈Br₂)^{2–}, are found to be abundant in mass spectra.

C₆₀: Buckminsterfullerene

H. W. Kroto^{*}, J. R. Heath, S. C. O'Brien, R. F. Curl & R. E. Smalley

Rice Quantum Institute and Departments of Chemistry and Electrical Engineering, Rice University, Houston, Texas 77251, USA

Metallo-Carbohedrenes $[M_8C_{12}^+ (M = V, Zr, Hf, and Ti)]$: A Class of Stable Molecular Cluster lons

B. C. Guo, S. Wei, J. Purnell, S. Buzza, A. W. Castleman, Jr.*

Findings of magic peaks corresponding to $M_8C_{12}^+$ (M = V, Zr, and Hf) formed from reactions of the respective metals with various small hydrocarbons, in conjunction with recent findings for the titanium system, establish metallo-carbohedrenes as a stable general class of molecular cluster ions. A dodecahedral structure of T_h point symmetry accounts for the stability of these ionic clusters.

Fig. 3 Time-of-flight mass spectra of carbon clusters prepared by laser vaporization of graphite and cooled in a supersonic beam. Ionization was effected by direct one-photon excitation with an ArF excimer laser (6.4 eV, 1 mJ cm⁻²). The three spectra shown differ in the extent of helium collisions occurring in the supersonic nozzle. In c, the effective helium density over the graphite target was less than 10 torr-the observed cluster distribution here is believed to be due simply to pieces of the graphite sheet ejected in the primary vaporization process. The spectrum in b was obtained when roughly 760 torr helium was present over the graphite target at the time of laser vaporization. The enhancement of C₅₀ and C₇₀ is believed to be due to gas-phase reactions at these higher clustering conditions. The spectrum in a was obtained by maximizing these cluster thermalization and cluster-cluster reactions in the 'integration cup' shown in Fig. 2. The concentration of cluster species in the especially stable C60 form is the prime

experimental observation of this study.



Fig. 1. Time-of-flight mass spectrum of vanadium-carbon cluster cations. The labeled magic peak is $V_8C_{12}^+$. Note that there are other prominent peaks proceeding the magic $M_8C_{12}^+$ which are precursors involved in the mechanism of formation of the cage-like metallo-carbohedrenes. Species with one- and two-carbon atoms attached to $M_8C_{12}^+$ are also visible, where some carbons remain on the magic structure upon its closing (9). Other precursors to the magic peak are seen, such as (7, 12).



а

Chiroselective Self-Directed Octamerization of Serine: Implications for Homochirogenesis

R. Graham Cooks,* Duxi Zhang, and Kim J. Koch

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Fabio C. Gozzo and Marcos N. Eberlin

Institute of Chemistry, State University of Campinas, CP 6154 Campinas SP 13083-970, Brazil



Figure 1. Mass spectrum of a 0.01 M L-serine solution prepared in a methanol-water (1:1) mixture and recorded by positive ion ESI/MS using a $5-\mu$ L loop injection.

Serine Octamers: Cluster Formation, Reactions, and Implications for Biomolecule Homochirality**

Sergio C. Nanita and R. Graham Cooks*

he emergence of homochirality continues to be one of the most challenging topics associated with the origin of life. One possible scenario is that aggregates of amino acids might have been involved in a sequence of chemical events that led to chiral biomolecules in selfreplicating systems, that is, to homochirogenesis. Serine is the amino acid of principal interest, since it forms "magic-number" ionic clusters composed of eight amino acid units, and the clusters have a remarkable preference for homochirality. These serine octamer clusters (Ser₈) can be generated under simulated prebiotic conditions and react selectively with other biomolecules. These observations led to the hypothesis that serine reactions were responsible for the first chiral selection in nature which was then passed through chemical reactions to other amino acids, saccharides, and peptides. This Review evaluates the chemistry of Ser₈ clusters and the experimental evidence that supports their possible role in homochirogenesis.

Synthesis of clusters using D, L thiol and their racemic mixtures. Now, they will have different types of interactions in the unit cell depending upon their orientations. Other way, IM MS study can be conducted on this system.

Synthesis of $Au_{25}(SR)_{18}^{1-}$ using optically active SR ligands. Here, we can study on the polymer by IM MS and gas phase IR.

In this paper

- They presented results from a study on serine cluster anions in which they coupled ion mobility spectrometry-mass spectrometry (IMS-MS) with infrared (IR) spectroscopy.
- IMS-MS gives the absolute, angle-averaged collision cross-section (CCS) of specific clusters, and this value can be used to determine the overall size of the cluster and to judge if particular calculated structures are compatible with experiments.
- Furthermore, IMS-MS can be used to prepare samples for gas-phase IR spectroscopy.
- The results allow the identification of a unique structure for (Ser₈Cl₂)²⁻ that is highly symmetric, very stable and homochiral and whose calculated properties match those observed in experiments.

ARTICLES



Figure 1 | IMS-MS of serine cluster anions. a–c, TOF mass spectra of aqueous solutions of L-Ser in HCl (**a**), a 1:1 mixture of L- and D-Ser in HCl (**b**) and a 1:1 mixture of D-Ser and L-Ser* in HCl, where L-Ser* is L-serine-D₃, ${}^{13}C_3$, ${}^{15}N_1$ (**c**). Notations: n^{z-} stands for $[nSer+zCl]^{z-}$; $(n+m)^{z-}$ stands for $[(L-Ser^*)_n + (D-Ser)_m + z \cdot Cl]^{z-}$. The distributions of serine clusters complexed with two and three chloride ions are marked by dashed lines in the drift time versus m/z plots. **d–f**, Drift-time-selected TOF mass spectra highlighting octamer-dichloride complexes with three drift time windows: 5.8–6.0 ms (**I**), 6.3–6.5 ms (**II**) and 6.6–6.8 ms (**III**).

NATURE CHEMISTRY DOI: 10.1038/NCHEM.2821



Figure 2 | Size- and conformer-selected infrared spectra of serine cluster-dichloride complexes. **a**-**c**, Arrival time distributions and corresponding CCSs of $(Ser_{12}Cl_2)^{2^-}$ (**a**), $(Ser_{10}Cl_2)^{2^-}$ (**b**) and $(Ser_8Cl_2)^{2^-}$ (**c**). Red and blue traces denote the results from L-Ser only and racemic Ser, respectively. For $(Ser_8Cl_2)^{2^-}$, the smaller (CCS = 189 Å²) and larger (CCS = 201 Å²) conformers are annotated with **I** and **II**, respectively. **d**-**f**, Infrared spectra of $(Ser_{12}Cl_2)^{2^-}$ (**d**), $(Ser_{10}Cl_2)^{2^-}$ (**e**) and $(Ser_8Cl_2)^{2^-}$ (**f**). Grey dots are data points from two repeated scans and the lines denote averaged results. a.u., arbitrary units.

NATURE CHEMISTRY DOI: 10.1038/NCHEM.2821

ARTICLES



Figure 3 | Theoretical structure of the homochiral serine octamer-dichloride complex. a, Proposed symmetric (D_4 point group) homochiral structure of the serine octamer-dichloride complex. The chloride anions are omitted from the chemical structure on the left for clarity, but shown on the right panel. The red arrows emphasize the two rings of four Ser molecules **b**, Theoretical infrared bands of the proposed structure compared with the experimental results. Symmetric and antisymmetric stretching vibrations (ν_{sym} and ν_{as}) of the carboxylate groups (-COO⁻) as well as deformations (δ) of protonated amine groups (-NH₃⁺) are assigned. Notations 'umb' and 'scis' indicate umbrella and scissoring modes. a.u., arbitrary units. **c**,**d**, Detailed views of the octamer from the side (**c**) and top (**d**). Atom colour code: C, grey; O, red; N, blue; H, white; Cl, green. The ionic size of the chloride anion is indicated by the larger pale green circle.



The Structure of the Protonated Serine Octamer

Valeriu Scutelnic,^{†,‡} Marta A. S. Perez,^{†,§} Mateusz Marianski,^{⊥,#} Stephan Warnke,^{‡,⊥} Aurelien Gregor,[§] Ursula Rothlisberger,[§][®] Michael T. Bowers,^{||} Carsten Baldauf,[⊥][®] Gert von Helden,[⊥][®] Thomas R. Rizzo,[‡][®] and Jongcheol Seo^{*,⊥}[®]

[‡]Laboratory of Molecular Physical Chemistry, Ecole Polytechnique Fédérale de Lausanne, Station 6, CH-1015 Lausanne, Switzerland [§]Laboratory of Computational Chemistry and Biochemistry, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Department of Chemistry and Biochemistry, University of California Santa Barbara, Santa Barbara, California 93106, United States



Received: February 21, 2018 Published: April 11, 2018



pubs.acs.org/JACS

Conclusion

- They investigated anionic serine octamers coordinated with two chloride ions using a novel technique coupling ion mobility spectrometry–mass spectrometry with infrared spectroscopy, in combination with theoretical calculations.
- The results allowed the identification of a unique structure for (Ser₈Cl₂)²⁻ that is highly symmetric, very stable and homochiral and whose calculated properties match those observed in experiments.



Figure 2. Schematic drawing of the drift-tube ion mobility-mass spectrometry experimental setup for mobility-selective gas-phase IR spectroscopy. Laser light coming from the free electron laser is coupled linearly into the setup using evacuated/nitrogen-flushed beamlines.



Figure 2. Comparison between two different structures, both of D4 symmetry, however with different interaction patterns. Predicted IR spectra of the present structure (a) and the less stable structure with intramolecular H-bonds between OH and COO^- (b). The red line is the experimental IRMPD spectrum of Ser₈Cl₂²⁻. The observed IR band positions are diagnostic for the proposed lower energy structure.