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Seaborgium Hexacarbonyl Sg(CO)6:
First Carbonyl Complex of a Superheavy Element

The Scientific Article

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The first author is Dr. Julia Even, postdoctoral researcher at the Helmholtz Institute Mainz, a joint daughter of the GSI Helmholtzzentrum in Darmstadt and the Johannes Gutenberg University Mainz. From the beginning on, she was one of the leading persons of the carbonyl-project, which started in 2010 at the research reactor TRIGA Mainz. Further experiments took place at the gas-filled recoil separator TASCA at GSI. Dr. Even was responsible for the planning and organization of the beamtime in Japan. Together with the team, she developed the gas-jet system and was responsible for the analysis of the chemistry data. For her work, she received the ARCEBS-14 young scientist award in January 2014 in Kolkata, India.

Protons, Neutrons, Atoms, Elements... The Basic

Matter around us consists of atoms. Every atom consists of a small atomic nucleus, which comprises almost the total mass of the atom, and an extended electron shell. The nucleus is built up from (positively charged) protons and (neutral) neutrons, whereas the shell consists of (negatively charged) electrons. The electrons surround the nucleus in certain orbitals. Atoms with the same number of protons belong to the same element. The elements up to uranium (element 92) exist in nature (except technetium). The elements heavies than uranium are man-made. All these elements are arranged in the periodic table of the elements. Their positions in the periodic correspond to their proton number and electron shell structure and thus provide information on their chemical behavior. In neutral atoms, the proton number and the electron number is the same.

Atoms with the same number of protons belong to the same element. Atomic nuclei with the same number of protons and different numbers of neutrons are called isotopes. The elements up to uranium (element 92) exist in nature (except for technetium). The elements heavier than uranium are man-made.

All elements are arranged in the periodic table of the elements. Their positions in the periodic table correspond to their proton number; elements in the same column (i.e., in the same group) feature similar and electronic shell structure, which characterizes the chemical behavior of an element. An element's position in the periodic table and thus provides information on its chemical behavior, e.g., as a metal or an inert gas.

The electron configuration characterizes the chemical behavior of an element. Thus, it behaves e.g. like a metal or like an inert gas.

If atoms undergo chemical reactions their electron shells interact. For example they can donate electrons to other atoms and thus form ionic pairs of positively and negatively charged ions. In contrast, if their electron orbitals overlap, they can form a covalent bond. In coordination complexes, a central atom (in most cases a metal) and molecules – the so-called ligands - coordinating around the central atom form a molecule, Ligands donate electron density into the empty orbitals of the metal or vice versa.

The Radioactive Decay

If atomic nuclei have too many protons (all of which repel each other) or have an this ratio is unfavorable proton to neutron ratio, the nuclei are not stable but undergo radioactive decay.

- One important decay mode is α decay, where an α particle consisting of two protons and two neutrons is emitted.
- Spontaneous fission is α decay in which the nucleus splits into two fragments.
- In β-decay, a neutron is converted into a proton (under emission of an electron; β^--decay) or a proton converts into a neutron (under emission of a positron, the positively charged antiparticle of the electron; β^+-decay). Thus, the number of nucleons remains the same in β-decay processes. Both β-decay processes are accompanied by the emission of a (anti)neutrino.

Production and Stability of the Heaviest Elements

The elements heavier than uranium are man-made. The elements up to the element fermium (which has atomic number 100) can be produced at research reactors by irradiating a target of a heavy element with neutrons. The target atoms capture a neutrons and subsequently decay through β^--emission, thus forming an element with the next higher proton number. This process can be repated, up to fermium.

As there are no isotopes of fermium which decay through β^--emission, no elements with higher proton number can be synthesized by this method.

Heavy ion induced fusion reactions give access to yet heavier elements. Target foils containing the element to be irradiated are bombarded with ions from an accelerator such as the UNILAC at GSI or the RILAC at RIKEN

If a projectile at the right energy hits an atomic nucleus of the target centrally, the two nuclei may fuse, forming an excited compound nucleus. Ideally, if this compound nucleus deexcites by the evaporation of neutrons, an atom of anew heavy element is formed. Most often, though, the nucleus fissions into two lighter fragment. Therefore, the production rates for the heaviest elements are very small: between a few atoms minute or per hour down to a single atom per month.

The heavier an atom is, the more protons are contained in its nucleus. With increasing proton number, the repulsive force of these protons will eventually lead to immediate disintegration of the nucleus. The elements with a proton number higher than 103 can only exist due to nuclear shell effects and are called the superheavy elements. A topic of intense research concerns the question of the heaviest possible element. To date, all elements up to element 112 as well as elements 114 and 116 are officially recognized as discovered, and reports about the observation also of element 113, 115, 117, and 118 are also published. It is currently not clear, which element is the heaviest one that can exist.

In our work, we studied the element with atomic number 106, seaborgium, with chemical symbol Sg. The isotope ^{265}Sg containing 106 protons and 159 neutrons was synthesized in the nuclear fusion reaction

$^{248}\mathrm{Cm} + {}^{22}\mathrm{Ne} \rightarrow {}^{270}\mathrm{Sg}^{*} \rightarrow {}^{265}\mathrm{Sg}$ + 5 neutrons

The production of ^{265}Sg and its separation in GARIS was perfected in preparatory work led by Dr. Hiromitsu Haba from RIKEN Nishina Center (RNC) and his team. In this nuclear reaction, a few Sg atoms per hour can be produced.

^{265}Sg has two isomeric states which both decay through α-emission with half-lives of 8.4 s and 14.4 s into ^{261}Rf.

Also ^{261}Rf has two isomers. One decays with a half-life of 68 s by emission of an α-particle into ^{259}No, which is an α-emitter with 24.5 s half-life. The other isomer of ^{261}Rf has a half-life of 2.6 s and decays through α- emission or, more frequently, spontaneous fission. Thus, ^{265}Sg can be identified by correlated α and spontaneous fission events.

Chemical Properties of the Superheavy Elements - The Influence of Einstein's Relativity Theory

In the periodic table of elements, all elements with atomic number ≥ 104 follow the actinide series, which ends with lawrencium (element 103). The first transactinides, up to element 111, are transition metals, while the heaviest known elements belong to the main groups with element 118 standing in the group of the noble gases.

The heavier an element, the higher theo positive charge of its nucleus, which attracts the negatively charged electrons in the electron shells. The velocities, with which electrons move, are directly related to this force, meaning that electrons which are near the atomic nucleus of a superheavy element are accelerated to high velocities – to about 80% of the speed of light. Here is where the influence of the special theory of relativity comes in: according to this theory, objects that are moving become heavier than if they are at rest. While the effect is too small in daily life where velocities are typically very small compared to the speed of light, this is different for the electrons in superheavy elements, and the mass increase is of the order of 50% of the rest mass. This is called the "direct relativistic effect", which acts most pronouncedly on electrons in orbitals with a high probability density near the atomic nucleus, e.g., electrons in s orbitals. These orbitals are therefore relativistically contracted in space and energetically stabilized by the direct relativistic effect.

As a consequence of the contraction of, e.g., the s orbitals, electrons occupying d or f orbitals, which are never near the atomic nucleus, are better screened from the latter, thus feeling less attraction. They thus expand in space and are energetically destabilized by this "indirect relativistic effect". Finally, a third effect, the "spin-orbit splitting" lifts the energetic equivalence of orbitals in a single subshell (like the 6 electrons that can occupy a p orbital) and splits each such subshell into two different levels. The best example is the p orbital, which, in a relativistic description, falls into a $p_{1/2}$ and a $p_{3/2}$ orbital, which accommodate 2 and 4 electrons, respectively.

As the influence of relativistic effects increases roughly with the square of the atomic number, the transactinide elements are the best suited laboratory for the study of their influence on chemical properties.

To date, using gas-phase chemical methods, which profit from being faster than liquid phase studies, have been conducted for all elements up to hassium (element 108) as well as for copernicium (112) and flerovium (114). In liquid phase chemical studies, rutherfordium (104), dubnium (105), and seaborgium (106) were studied. So far only a limited number of volatile compounds of transactinide elements has been synthesized, including oxides, oxyhydroxides, halides and oxyhalides. These are simple inorganic compounds, where the transactinide binds to the other atoms by forming covalent bonds. They thus donate an electron to each bond. In all molecules studied to date, all the valence electrons were thus engaged in a chemical bond, which the chemists refer to as the metal being in its highest oxidation state. The influence of relativistic effects was not expressed pronouncedly in most of these systems. However, they were still present, as follows from the good agreement between experimental data and theoretical calculations that include the effects of relativity fully (so called fully-relativistic quantum chemical calculations, as, e.g., performed by Dr. Valeria Pershina (from our group) and Dr. Josef Anton from the University of Ulm. Apparently, these effects were masked in many of these systems.

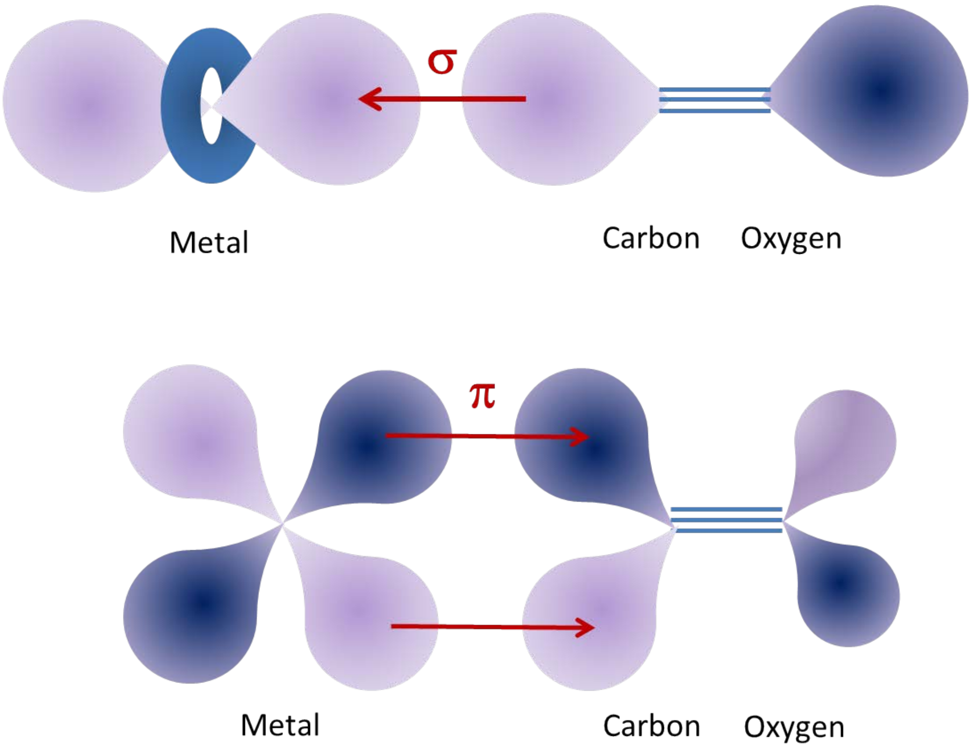
Thus, we were looking for a new compound class, where the transition metal binds to other atoms through different types of bonds. So far, nobody had achieved the synthesis of such a chemical compound.

Seaborgium hexacarbonyl – Why is it so special ?

Carbon monoxide (CO) is known to form complexes with many transition metals. In 1890, Ludwig Mond, Carl Langer and Friedrich Quincke reported of the first synthesis of a carbonyl complex – nickeltetracarbonyl ($Ni(CO)_4$). In this compound, the nickel (Ni) atom is surrounded by 4 carbon monoxide molecules (CO).

In this type of molecule, coordination bonds (rather than covalent bonds) form between the metal and the carbon monoxide.

The carbon monoxide ligands bind to the metal by forming a so-called σ-donation bond, and a π-backbond from the metal to the carbon monoxide ligand establishes. In the σ-donation bond the highest occupied molecular orbital (HOMO) of the CO donates electron density into the σ-symmetric orbitals of the metal (s or $p_{1/2}$ or d_{z2} orbitals). In the π-backbonding, electron density for the π-symmetric d-orbital is donated to the lowest unoccupied molecular orbital (LUMO) of the CO-ligand. The σ-donation bond is the strongest bond, while the π-backbond is slightly weaker.



Schematic drawing of the σ-donation bond of the HOMO of the CO-ligand to the σ-symmetric d_{z^2}-orbital of the metal (upper graphic) and the schematic drawing of the π-backbond from the π-symmetric d orbitals to the LUMO of the CO-ligand.

The elements of group 6, chromium (Cr), molybdenum (Mo) and tungsten (W), are known to form volatile hexacarbonyl complexes, where the metal atom binds to six carbon monoxide molecules. Hence, the question arose if also the heaviest element in this group –seaborgium (Sg) would form such a hexacarbonyl complex. Theoretical calculations (see Nash and Bursten, J. Am Chem. Soc, 121, 10830 (1996); Nash and Bursten, New. J. Chem. 19, 669, (1995)) predicted seaborgium hexacarbonyl to be stable. However, due to the direct relativistic effect the σ-donation bond is predicted to become weaker. The s and $p_{1/2}$ orbitals shrink, so that the overlap with the HOMO is weaker. Due to the indirect relativistic effect, the d-orbitals diffuse and the overlapping with the LUMO becomes larger. Thus the π-backbond will be stronger.
Measuring the characteristics of the metal-carbon bond would thus be highly interesting. However, as a first step, the compound has to be synthesized in the first place, and this is what we have now achieved.

Carbonyl complexes are normally synthesized at high CO pressure (around 300 bar). At the research reactor TRIGA Mainz and at TASCA, we developed a technique to synthesize carbonyl complexes with single atoms at pressure conditions around 1 atm. Short-lived isotopes were produced in the nuclear fission of californium-249 at the TRIGA Mainz reactor. The recoiling fission products were stopped in CO-conatining atmosphere. Thus, the free atom can react directly with the CO-molecules without applying high pressure conditions (needed in classical approaches with macroamounts to drive the carbon monoxide into the bulk metal to give individual atoms a chance to find six neighboring molecules).

To test this technique under conditions relevant for an experiment with superheavy elements, short-lived isotopes of W, Os, Re, and Ir, were synthesized in ^{24}Mg induced nuclear fusion reactions. These studies took place at the UNILAC at GSI behind the gas-filled separator TASCA, where TASCA was used as a physical preseparator. The fusion products were separated in magnetic fields form the primary beam and the unwanted by-products. W, Os, Re, and Ir were stopped at the end of TASCA in a carbon-monoxide gas containing chamber under ambient conditions (pressure around 1 bar, room temperature) and formed volatile carbonyl complexes.

Synthesis of carbonyl complexes with fusion products directly behind the target in a CO-containing atomosphere is not possible, as the primary beam would pass the gas and create a plasma. This would destroy the CO molecules. Therefore, only our new approach to perform chemical experiments behind a separator like TASCA or GARIS allows the synthesis and study of this compound class.

Our Experiment

Our experiment took place at the RILAC accelerator at RIKEN Nishina Center (RNC) and was based on the experience gained in the nuclear synthesis experiments of ^{265}Sg at GARIS and the carbonyl chemistry experiments at TASCA. The aim was the investigation of $Mo(CO)_6$, $W(CO)_6$ and $Sg(CO)_6$, all in the same setup, to make sure that no influence of even just slightly different conditions would affect our interpretation of the data.

The short-lived isotopes were produced in the following nuclear fusion reactions:

^{nat}Zn + ^{24}Mg → ^{87,88}Mo + x neutrons

^{144}Sm + ^{24}Mg → ^{163,164}W + 4 to 5 neutrons

^{248}Cm + ^{22}Ne → ^{265}Sg + 5 neutrons

To suppress the main beam and the nuclear reaction by-products, the experiment was performed at Gas-filled Recoil Ion Separator the GARIS.

GARIS is a magnetic separator consisting of a dipole magnet followed by two identical quadrupole magnets and another dipole magnet. Within the first dipole magnet the wanted fusion products were separated from the main beam and by-products. Afterwards the fusion products were focused by the two quadrupole magnets to the final dipole magnet, which provided the final separation, and then to the end of GARIS. Here, they passed a thin plastic foil and entered a gas-filled chamber, which was filled with a mixture of helium and carbon monoxide. The photo below shows Dr. Julia Even and Dr. Hiro Haba mounting the plastic window and the chamber.

Mo, W and Sg were completely stopped in the gas. The free atoms reacted with the carbon monoxide and formed volatile carbonyl complexes. The gas volume, called recoil transfer chamber was continuously flushed with the gas mixture. Thus, the volatile species were transported in the gas stream to a chemistry laboratory, where our gas chromatography and detection system was installed.

Dr. Julia Even from the Helmholtz Institute in Mainz, Germany and Dr. Hiromitsu Haba from RIKEN, Wako, Japan prepare the GARIS gas-filled recoil separator for connection to the Recoil Transfer Chamber chemistry interface.
Credit: M. Schädel

We used a gas-chromatography setup optimized for the study of short-lived volatile species, which decay by α or β-decay or by spontaneous fission. It is called Cryo Online Multi detector for Physics and Chemistry of the Transactinoides, COMPACT. The chromatography column consists of radiation detectors suitable for registering the radioactive decay of the seaborgium atoms. The beginning of the channel, where the molecules enter, was kept at room temperature, and the end was cooled down to -135°C. The volatile carbonyl complexes, which are flushed from warm towards cold temperatures along the channel, undergo adsorption-desorption processes on the chromatography column surface (i.e., on the detectors of the COMPACT array). The colder the temperature, the longer the complexes remain adsorbed on the surface. As soon as their adsorption time exceeds the nuclear lifetime of the central seaborgium atoms, the nuclear decay of ^{265}Sg is measured at that position. Our measurement thus allowed the determination, at which temperature the sticking time was longer than the nuclear half-life. This information is sufficient to extract the strength of the chemical bond between the complex and the surface: this strength dominantly determines the sticking time as a function of temperature.

In our experiment, the volatility and adsorption properties of $Mo(CO)_6$, $W(CO)_6$ and $Sg(CO)_6$ on a silicon dioxide surface were directly compared. $Sg(CO)_6$ was synthesized for the first time and could be characterized by its volatility and adsorption properties. As predicted by theoretical calculations, these turned out to be similar to those of $Mo(CO)_6$ and $W(CO)_6$.

The fact that the compound, when contacting a surface like silicon dioxide, behaves similarly to its lighter homolog complexes $Mo(CO)_6$ and $W(CO)_6$ supports our chemical formulation of seaborgium hexacarbonyl, which is also in line with what fully-relativistic theoretical calculations suggest. We are now looking forward to study the chemical properties inside the molecule, e.g., to find out how strong the metal-carbon bond in the complex is.

Practical Implications ?

Our technique can be used to prepare clean sample of single atoms of superheavy elements and thus allows decay spectroscopy und zero-background conditions

Furthermore, the technique of the fast formation of carbonyl complexes and fast transport in a gas stream has been patented. It can be used e.g. for the production, fast separation and transport of nuclides for applications in nuclear medicine, or bears potential for the development of ion beams of radioactive isotopes.

Future Perspectives

Our experiment marks a milestone in superheavy element chemistry. For the first time a bond between a superheavy element and carbon was established. These bonds are typical for organometallic compounds. Our experiment is the first step into the direction of organometallic chemistry of the superheavy elements and we would be fascinated if many more compounds would follow.

The influence of relativity on the seaborgium-carbon monoxide bond will be probed in future experiments. At the moment a method to investigate the stability of this bond in single molecules is under development.

The Collaboration

Our collaboration comprises XX scientists and engineers from XX institutions in XX countries:

- Helmholtz Institute Mainz (HIM), Mainz, Germany
- GSI Helmholzzentrum für Schwerionenforschung GmbH, Darmstadt, Germany
- Johannes Gutenberg University Mainz, Mainz, Germany
- RIKEN, Wako, Saitama, Japan
- Japan Atomic Energy Agency (JAEA), Tokai, Ibaraki, Japan
- University of Bern, Bern, Switzerland
- Paul Scherrer Institute, Villigen, Switzerland
- Institute of Modern Physics (IMP), Chinese Academy of Sciences, Lanzhou, China
- Hiroshima University, Kagamiyama, Higashi-Hiroshima, Japan
- Kyushu University, Higashi-Ku, Fukuoka, Japan
- Niigata University, Niigata, Japan
- University of California, Berkeley, CA, USA
- Lawrence Berkeley National Laboratory (LBNL), Berkeley, CA, USA
- Saitama University, Saitama, Japan

The local superheavy element group from Darmstadt/Mainz working on this experiment comprises:

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- Holger Brand (GSI Darmstadt)
- Antonio Di Nitto (Univ. of Mainz)
- Christoph Düllmann* (Univ. of Mainz, GSI Darmstadt, & HIM Mainz)
- Robert Eichler (Univ. of Bern & PSI, Villigen)
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- Kosuke Morita (RIKEN, Wako, Saitama & Kyushu Univ., Higashi-Ku, Fukuoka)
- Masashi Murakami (RIKEN, Wako, Saitama & Niigata Univ.)
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