Ozonides

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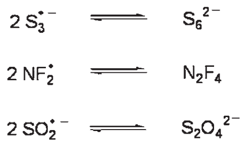
$Cs_5([12]crown\text{-}4)_2(O_3)_5$: A Supramolecular Compound Containing the Confined Ozonide Partial Structure $^1_\infty\{Cs_8(O_3)_{10}\}^{2-}$**

*Hanne Nuss and Martin Jansen**

Over the past twenty years, the chemistry of ionic ozonides has advanced significantly.[1] As an outcome of these efforts, the ozonides of the alkali metals Na–Cs are now accessible in high purities and in gram amounts.[2] This availability has allowed their full structural and basic physical characterization.[3–6] Even more importantly, the alkali-metal ozonides can now be employed as starting materials for the synthesis of ionic ozonides with a broad variety of other (complex) cations by metathesis[7] or ion-exchange reactions in liquid ammonia.[8–10] Whereas liquid ammonia is the only suitable solvent for the alkali-metal ozonides, yielding highly concentrated solutions with long-term stability below 243 K, the ozonides of voluminous organic cations readily dissolve in common solvents, such as tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), or CH_2Cl_2. Ozonide solutions in CH_2Cl_2 are particularly stable and can be stored for weeks at 200 K without any indication of degradation. The availability of such solutions is a crucial requirement for subsequent chemistry involving the ozonide ion (O_3^-) in coordination or main-group molecular chemistry.

One of the most fascinating perspectives of ozonide chemistry is the potential dimerization of the radical ion. In analogy to the known equilibria of isoelectronic species (Scheme 1), two different mechanisms of dimerization, mediated through either the terminal (as for S_3^-) or the central (as for NF_2 and SO_2^-) atoms of the ozonide ion are conceivable. Although no indication of a monomer–dimer equilibrium has been detected in solution, a confinement and reduction in the



Scheme 1. Dimerization equilibria of species isoelectronic to O_3^-.

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[*] Dipl.-Chem. H. Nuss, Prof. Dr. M. Jansen
Max Planck Institute for Solid State Research
Heisenbergstrasse 1, 70569 Stuttgart (Germany)
Fax: (+49) 711-689-1502
E-mail: m.jansen@fkf.mpg.de

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dimensionality of the ozonide partial structure in the solid state might force the ozonide ions to approach one another. Such a reduction in dimensionality could possibly be achieved by employing one of the concepts of crystal engineering, the use of a combination of polar and nonpolar constituents, which tend to occupy separate volumes in the crystal.[11–13]

For cesium ozonide, this goal has been reached through the addition of the crown ether [12]crown-4, which does not match the size of the Cs^+ ion and, thus, coordinates weakly to one side of the ion.[19,20] Indeed, the crystal structure[21] of the transparent, deep red product $Cs_5([12]crown\text{-}4)_2(O_3)_5$ exhibits a one-dimensional host–guest arrangement. As illustrated in Figure 1, the crystal structure can be understood as a distorted tetragonal packing of ${}^1_\infty\{Cs_8(O_3)_{10}\}^{2-}$ rods, which run along the [100] direction and are separated by $[Cs([12]crown\text{-}4)_2]^+$ units.

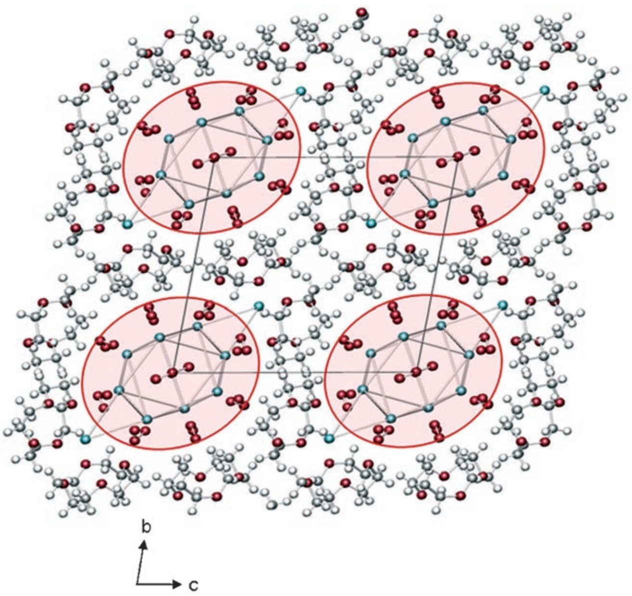

Figure 1. View of the structure of $Cs_5([12]crown\text{-}4)_2(O_3)_5$, showing the distorted tetragonal packing of ${}^1_\infty\{Cs_8(O_3)_{10}\}^{2-}$ rods, which are outlined by red circles. The lines connecting the Cs atoms are to aid visualization. Cs blue, C gray, H white, O red.

The rods have a diameter of approximately 1 nm and exhibit symmetry corresponding to rod group $p\bar{1}$ (no. 2).[22] They consist of stacks of tetragonal antiprisms of Cs^+ ions (with an average Cs···Cs distance of 456 pm), which are each centered by one ozonide ion and surrounded by four other crystallographically independent ozonide ions (Figure 2). The eight-fold coordination environment of the central ozonide ion is reminiscent of the situation in α-CsO_3 and β-CsO_3; however, in these CsCl-type structures, the ozonide ions are surrounded by Cs^+ ions in a cubic arrangement.[2e,f] The bond lengths and angles of the ozonide ions lie within the expected ranges. Those outside of the antiprisms are more distorted than the central ozonide ions, which have nearly perfect C_{2v} symmetry.

Furthermore, the structural restrictions imposed by this packing arrangement lead to the shortest intermolecular O···O distance yet observed between ozonide ions in the solid state. The distance between the central oxygen atoms of two adjacent ozonide ions within the stacks of antiprisms is 275.3(8) pm (indicated by the red dotted lines in Figure 2). Previous investigations on alkali-metal ozonides showed that the arrangement of adjacent ozonide ions is mainly determined by dipole–dipole interactions between the negatively polarized terminal atoms and the positively polarized central atoms.[2] This interaction mode does not occur in the structure of $Cs_5([12]crown\text{-}4)_2(O_3)_5$. Apart from the rather short intermolecular distance described above, the next closest contacts of 347–368 pm occur between the terminal oxygen atoms of adjacent ozonide anions outside of the stacks of antiprisms. We ascribe these features to the structural confinement of the ${}^1_\infty\{Cs_8(O_3)_{10}\}^{2-}$ substructure by the nonpolar shell of $[Cs([12]crown\text{-}4)_2]^+$ units.

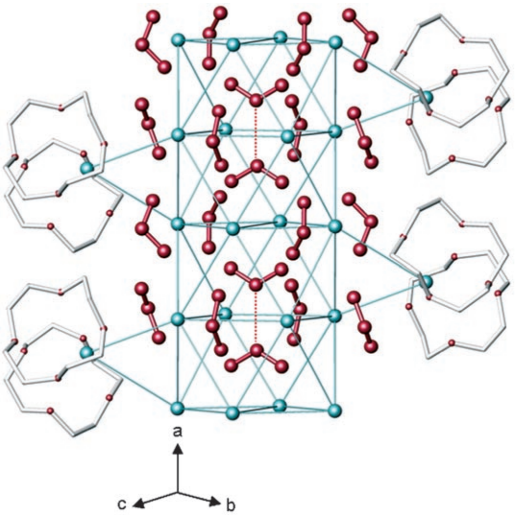

Figure 2. Side view of a ${}^1_\infty\{Cs_8(O_3)_{10}\}^{2-}$ rod and surrounding $[Cs([12]crown\text{-}4)_2]^+$ units. The short intermolecular distance (275.3(8) pm) between the central atoms of adjacent O_3^- ions is indicated by a red dotted line. The lines connecting the Cs atoms are to aid visualization. Geometry of the O_3^- ions: mean O–O distance 131(4) pm, O-O-O angles 115.5(4)–121.7(4)°. Cs blue, C gray, O red; H atoms are omitted for clarity.

The Cs^+ ions of the $[Cs([12]crown\text{-}4)_2]^+$ units are coordinated by two crown ether molecules in a sandwich-like arrangement. The mean distance between the oxygen-atom planes of the crown ether molecules and the coordinated Cs^+ ions is 252 pm, and the tilt angle (the angle between the normals of these planes) is 135°. The IR spectrum of $Cs_5([12]crown\text{-}4)_2(O_3)_5$ demonstrates that the interaction between the Cs^+ ions and the [12]crown-4 molecules is weak: the five characteristic stretching modes of free [12]crown-4 in the fingerprint region, which have been shown to be sensitive to M^+–O interactions, are not shifted.[23,24]

The 19-valence-electron anion O_3^- exhibits the rarely encountered p-electron magnetism, which arises from the one unpaired electron. Ionic ozonides usually display Curie–Weiss paramagnetism, with a tendency towards antiferromagnetic ordering, depending on the intermolecular O···O distance and the type of interaction between the ozonide ions (terminal–terminal, terminal–central, or central–central). The mean

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magnetic moment is normally close to the spin-only value of 1.73 μ_B.[25] A significant interaction between the unpaired electrons, imposed by the short distance between the oxygen atoms, would lead to spin compensation and, thus, to a magnetic moment that is lower than the spin-only value. To determine whether such a scenario takes place, we investigated the magnetic properties of $Cs_5([12]crown\text{-}4)_2(O_3)_5$ by means of measurements on a superconducting quantum interference device (SQUID) magnetometer. The magnetic susceptibility χ of $Cs_5([12]crown\text{-}4)_2(O_3)_5$ in an applied field of 1 T is plotted against temperature T in Figure 3. The magnetic behavior above approximately 20 K can be described by the Curie–Weiss law $\chi = C/(T-\theta) + \chi_0$, with a temperature-independent contribution of $\chi_0 = 1.08(4)\times10^{-3}$ emu mol^{-1}. The calculated magnetic moment of 1.72 μ_B is close to the spin-only value of 1.73 μ_B expected for a single unpaired electron. Antiferromagnetic ordering occurs below the Néel temperature of $T_N = 4.5$ K (the Weiss parameter is $\theta = -5.1(4)$ K). Apparently, the O···O distance between the ozonide ions is too long to allow a measurable interaction between the unpaired electrons. However, further experiments, in particular, by means of electron paramagnetic resonance (EPR) spectroscopy, seem worthwhile, since the SQUID magnetometer detects only mean values of magnetization, from which the contributions of the interactions between the ozonide ions inside and outside of the stacks of antiprisms cannot be distinguished.

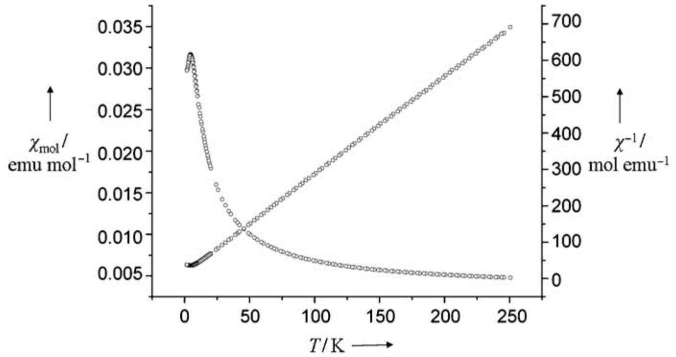

Figure 3. Temperature dependence of the magnetic susceptibility of $Cs_5([12]crown\text{-}4)_2(O_3)_5$ (○) and its inverse (□) in an applied field of 1 T (see Supporting Information for data at 0.1 and 7 T).

By applying the tools of crystal engineering to ionic ozonides, we were able to synthesize the first supramolecular ozonide with a one-dimensional host–guest structure. Structural confinement in this compound leads to a remarkably short intermolecular O···O distance between the ozonide ions. Although no evidence of an electronic interaction between the ions has yet been found, this supramolecular approach appears to be promising for the dimerization of ozonide ions.

Experimental Section

Attention: Ionic ozonides tend to decompose explosively. They should always be handled with care and should only be produced in small amounts.

All experiments were carried out under argon using modified Schlenk techniques or a glovebox (M. Braun; H_2O and O_2 less than 0.1 ppm). Ammonia (3.8, Westfalen AG) was stored as a potassium–ammonia solution at 195 K prior to use. [12]crown-4 (97%, Acros Organics) was used as received. CsO_3 was synthesized according to a literature procedure.[2c]

An H-shaped reaction vessel with a glass frit (porosity 3) was charged with [12]crown-4 (15.6 mg, 8.84×10^{-5} mol) and cooled to approximately 200 K using ethanol/dry ice. CsO_3 (40.0 mg, 2.21×10^{-4} mol) was added, and the reaction vessel was then filled with ammonia (ca. 10 mL) through condensation. The deep red reaction mixture was brought to the boiling point several times, until the crown ether dissolved completely. After 1 h, the deep red solution was filtered and reduced to half its volume. After 5 d at 200 K, red needles were isolated from the solution. For the single-crystal structure determination, the extremely sensitive crystals were handled according to the procedure described by Stalke and Kottke.[26]

Magnetic susceptibilities were determined with a MPMS7 Quantum Design SQUID magnetometer in applied fields of 0.1, 1, and 7 T over the temperature range 2–250 K. Powder samples were sealed under cooling into Suprasil quartz tubes filled with helium gas enabling fast thermal equilibration. Data were corrected for the magnetization of the empty tubes and for the diamagnetic contributions of the samples, using the increment method of Pascal and Pascal and of Gallais and Labarre.[27,28] A Honda–Owen correction was made to account for the contributions of small amounts of ferromagnetic impurities.[29,30]

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