

Preparation and Crystal Structure of the Complex between Rubidium Ozonide and 18-Crown-6

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The preparation of the 1 : 1 complex between rubidium ozonide and 18-crown-6 in liquid ammonia introduces a novel route to ionic ozonides soluble in typical organic solvents; the crystal structure and the thermal properties of this compound are determined.

Since ionic ozonides of the type MO_3 ($M = \text{K}, \text{Rb}, \text{Cs}$) became available in gram amounts *via* a new general synthetic route¹ the investigation of the scarcely studied chemical properties of the unique O_3^- ion has now become possible. It is, however, desirable to be able to use a wide range of solvents especially

with respect to reactions with organic or organometallic compounds. Because the choice of solvent in the case of the alkali metal ozonides is limited to liquid ammonia, different ionic ozonides with more lipophilic cations had to be prepared. A first effort in this direction resulted in the synthesis of tetramethyl- and tetraethyl-ammonium ozonides,^{2,3} which show the desired solubilities but are difficult and somewhat dangerous to prepare on a larger scale. We now report the general route to gram amounts of crystalline complexes of alkali metal ozonides with crown ethers or cryptands and the crystal structure of the prototypical $([\text{18-crown-6}]\text{Rb})\text{O}_3 \cdot \text{NH}_3$. These complexes are easily soluble in typical organic solvents such as CH_2Cl_2 , THF or MeCN; a 0.01 mol dm^{-3} solution of $([\text{benzo-18-crown-6}]\text{K})\text{O}_3$ in dry THF is stable for at least 24 h at -78°C .

Complexes between crowns or cryptands and alkali metal ozonides are prepared by adding a solution of the ozonide in liquid ammonia to a suspension of an equimolar amount of the ligand in the same solvent which then dissolves rapidly. Slow evaporation of ammonia leads to red, crystalline products. As ionic ozonides are invariably highly sensitive substances extreme care has to be taken to avoid contact with air, moisture or oxidizable materials. Complexes have been prepared using cryptand[2.2.2], benzo-18-crown-6, dibenzo-18-crown-6, 18-crown-6 and KO_3 , RbO_3 , CsO_3 . DTA/TG measurements show that these compounds decompose exothermically with loss of weight above room temperature; typical decomposition temperatures are: $([\text{18-crown-6}]\text{Rb})\text{O}_3$ 34°C , $([\text{18-crown-6}]\text{Cs})\text{O}_3$ 35°C , $([\text{2.2.2}]\text{Rb})\text{O}_3$ 28°C . At -36°C and sealed under argon they can be stored for over two months without perceptible change.

The crystal structure of $([\text{18-crown-6}]\text{Rb})\text{O}_3 \cdot \text{NH}_3$ is shown in Fig. 1.† It is the first reported structure of a 1 : 1 complex of

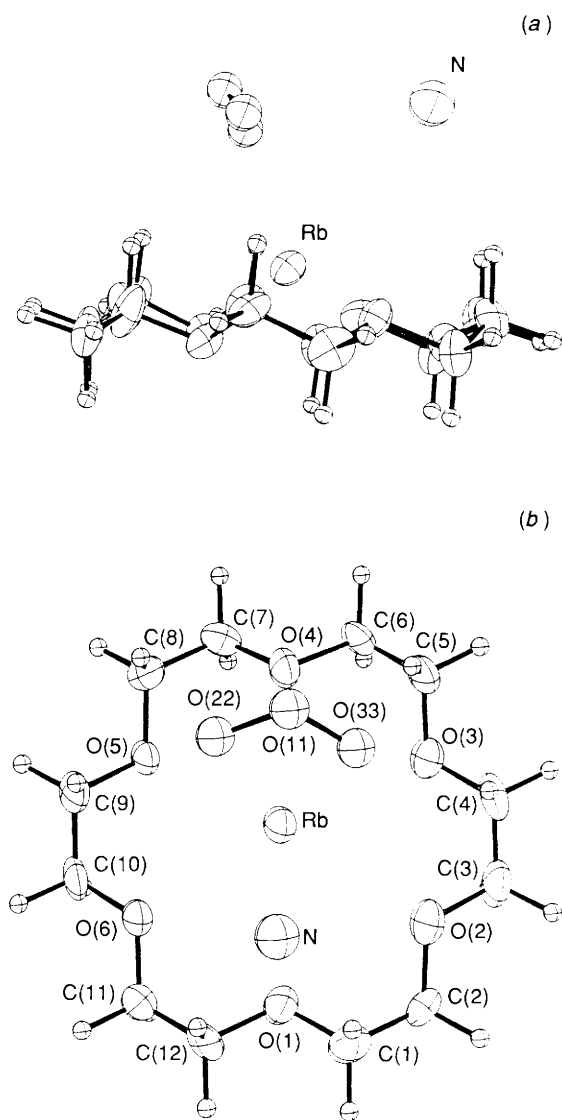


Fig. 1 ORTEP⁸-plots of $([\text{18-crown-6}]\text{Rb})\text{O}_3 \cdot \text{NH}_3$ viewed along a direction in the mean plane (a) and in a direction normal to the mean plane (b). Thermal ellipsoids are drawn at 50% probability level; H atoms, O atoms of the ozonide group and the N atom of the ammonia of crystallisation were assigned arbitrary radii. Selected atomic distances and bond lengths (pm): $\text{Rb} \cdots \text{O}(1)$, 300.4(9); $\text{Rb} \cdots \text{O}(2)$, 293.4(9); $\text{Rb} \cdots \text{O}(3)$, 302.8(8); $\text{Rb} \cdots \text{O}(4)$, 291.6(1.0); $\text{Rb} \cdots \text{O}(5)$, 305.8(9); $\text{Rb} \cdots \text{O}(6)$, 290.5(9); $\text{Rb} \cdots \text{O}(22)$, 290(1.6); $\text{Rb} \cdots \text{O}(33)$, 284.0(2.2); $\text{Rb} \cdots \text{N}$, 376.8(2.3); $\text{O}(1) - \text{C}(1)$, 141.8(2.0); $\text{C}(1) - \text{C}(2)$, 151.6(2.1).

† *Crystal data*: $\text{C}_{12}\text{H}_{27}\text{NO}_9\text{Rb}$, $M = 414.81$, orthorhombic, space group $P2_12_12_1$, $a = 822.1(3)$, $b = 1309.2(5)$, $c = 1724.3(5)$ pm, $V = 1.855(1)$ nm³, $Z = 4$, $D_c = 1.48$ g cm⁻³, $F(000) = 850$, $\mu(\text{Mo-K}\alpha) = 26.28$ cm⁻¹. No. of independent data measured 2497, no. of observed data with $|F_0| > 2\sigma|F_0|$ 1575, no. of parameters 209. The lattice constants were determined by a CAD-4 indexing program and refined by a least-squares routine with the angular settings of 25 reflections ($2\theta > 40^\circ$). Diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 71.073$ pm) at -60°C to $2\theta_{\text{max}} = 56^\circ$. Three intensity control reflections were measured every hour, showing a decay of 45% during the collection of the unique data set. Intensity data were corrected for linear isotropic decay, Lorentz and polarisation effects. The structure was solved by a combination of direct methods (SHELXS-86⁶) and Fourier techniques, and refined by full-matrix least squares analysis (SHELX-76⁷). Non-hydrogen atoms were refined anisotropically, with the hydrogen atoms at calculated positions (C-H 108 pm) riding on the carbon atoms with one common isotropic thermal parameter. The final R value was 0.065 (unit weights). Both possible enantiomorphs were refined separately, showing a difference of 1.1% in R values. The maximum and minimum residues in the final ΔF synthesis were 0.012 e pm⁻³ and -0.010 e pm⁻³ in the neighbourhood of the Rb atom. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

a rubidium compound with 18-crown-6.⁴ The crown ether displays effective D_{3d} symmetry; the rubidium ion, being too large for the central cavity, is displaced by about 100 pm from the mean plane of the ligand. Two Rb \cdots O contacts by the ozonide and a Rb \cdots N contact by an ammonia molecule complete the coordination of the cation. Large thermal parameters for oxygen in the ozonide anion indicate that it is somewhat disordered, which is a common feature for the anion in this type of complexes,⁵ since close packing of the complexed cation still leaves large cavities for the much smaller counter ion. The O–O bond length [130(2) and 129(3) pm] and the bond angle [117(2) $^\circ$] of the ozonide are, however, in good agreement with previously determined values.^{2,3} The presence of ammonia was additionally proved by chemical means (testing for gaseous ammonia upon hydrolysis) and elemental analysis. The N \cdots O distance between the nitrogen atom and the terminal oxygen atoms of the ozonide anion [335(3) and 338(3) pm] suggests weak hydrogen bonding; this would be a novel and rather unexpected feature of ionic ozonides because one of the major decomposition routes involves protonation.

Crystal preparation and isolation were severely hampered by the tendency of the substance to lose ammonia; it was

necessary to develop an apparatus that allowed crystal isolation in Lindemann capillaries in a cooled atmosphere of ammonia; details will be published in a later report.

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