Synthesis and Crystal Structure of $M([12]\text{crown-4})_2O_3 \cdot 1.5\ NH_3$ with M = K, Rb

Hanne Nuss and Martin Jansen

Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany

Reprint requests to Prof. Dr. Martin Jansen. Fax: +49 711 689 1502. E-mail: m.jansen@fkf.mpg.de

Z. Naturforsch. **2009**, *64b,* 1325 – 1328; received September 26, 2009

Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

The two new ozonide compounds $K([12]\text{crown-4})_2O_3 \cdot 1.5\ NH_3$ (**1**) and $Rb([12]\text{crown-4})_2O_3 \cdot 1.5\ NH_3$ (**2**) were synthesized from the binary alkali metal ozonides and [12]crown-4 in liquid ammonia. The air- and temperature-sensitive red, needle-shaped compounds crystallize isostructurally in the non-centrosymmetric space group *Fdd*2 (no. 43) with 16 formula units per unit cell. The lattice parameters are a = 26.917(8), b = 43.25(1), c = 7.823(2) Å, V = 9108(5) Å^3; and a = 26.730(6), b = 44.70(1), c = 7.739(2) Å, V = 9245(4) Å^3 for **1** and **2**, respectively. The structure comprises rod-like $[([M([12]\text{crown-4})_2(NH_3)]O_3)_2(NH_3)]$ supramolecular units, forming a fishbone pattern parallel to (001). The ozonide anions are separated from the metal cations and interact only weakly with two ammonia molecules *via* N–H$\cdots$O hydrogen bonds.

Key words: Ionic Ozonides, Hydrogen Bonds, Crown Ether, Liquid Ammonia, Crystal Structure Determination

Introduction

Ionic ozonides are able to build a broad variety of structural arrangements in the solid state [1]. The binary alkali metal ozonides form structures related to common ionic structure types, *e. g.* NaO_3 (NaCl type) [2] or KO_3 and RbO_3 (CsCl type) [3, 4], whereas the crystal structures of ozonides with organic cations, especially in the presence of solvent molecules (usually NH_3), are mainly determined by C–H$\cdots$O and N–H$\cdots$O hydrogen bonds (*e. g.* $(Me_3N(CH_2)_3NMe_3)(O_3)_2 \cdot 3\ NH_3$ [5]). Recently, we have managed to broaden the family of ozonide structures by synthesizing the first supramolecular compound $Cs_5([12]\text{crown-4})_2(O_3)_5$ [6]. The structure of this compound consists of ${}^1_\infty\{Cs_8(O_3)_{10}\}^{2-}$ rods, which are pseudo-tetragonally packed and separated by $[Cs([12]\text{crown-4})_2]^+$ units. The polarizability of the $O_3{}^-$ anion in combination with its angular molecular structure makes different "binding modes" possible. Several structural investigations show that the ozonide ion is able to act as a bidentate ligand for alkali and alkaline earth metal cations. In $Cs_2Ba(O_3)_4 \cdot 2\ NH_3$, for example, the four $O_3{}^-$ ions surround the Ba^{2+} cation with all of their terminal oxygen atoms pointing to the metal center at a distance of about 2.87 Å [7]. Another example is the series of compounds $M([18]\text{crown-6})O_3 \cdot x\ NH_3$ (M = K, Rb, Cs and x = 2, 1, 8), in which the ozonide ions are pointing towards the respective metal with their terminal oxygen atoms at distances of 2.77, 2.88 and 3.16 Å [8].

In the two new ozonide compounds of the composition $M([12]\text{crown-4})_2O_3 \cdot 1.5\ NH_3$ (M = K, Rb) presented here, the coordination sphere of the alkali metal is completely shielded by two crown ether ligands and one ammonia molecule, respectively. The ozonide anions therefore are separated from the metal and accept hydrogen bonds from ammonia resulting in virtually linear building blocks.

Results and Discussion

The reaction of the alkali metal ozonides KO_3 and RbO_3 with [12]crown-4 in liquid NH_3 leads to complex compounds with different ammonia contents, depending on the crystallization conditions. In the case of potassium, for instance, a slow crystallization at 195 K yields an ammonia-free ozonide [9], whereas allowing faster crystallizations at slightly higher temperatures (213 K), compounds of the composition M([12]-

0932–0776 / 09 / 1100–1325 \$ 06.00

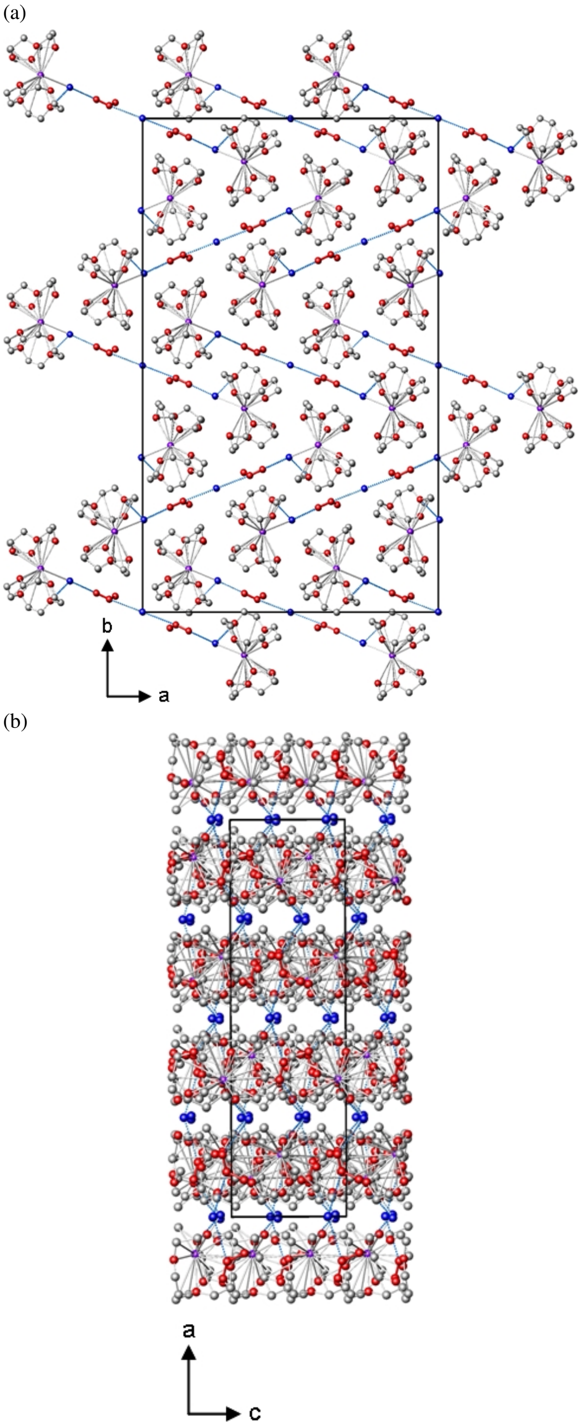

Fig. 1. Crystal structures of **1** and **2**: (a) view along [001] illustrating the fishbone pattern of the [([M([12]crown-4)$_2$-(NH$_3$)]O$_3$)$_2$(NH$_3$)] units; (b) view along [010] showing alternating layers of [M([12]crown-4)$_2$(NH$_3$)]O$_3$ units and ammonia molecules.

Table 1. Crystal structure data for **1** and **2**.

	1	**2**
Formula	$C_{16}H_{36.5}O_{11}N_{1.5}K$	$C_{16}H_{36.5}O_{11}N_{1.5}Rb$
M_r	465.07	511.44
Crystal size, mm^3	0.15 × 0.08 × 0.08	0.2 × 0.02 × 0.02
Crystal system	orthorhombic	orthorhombic
Space group	$Fdd2$ (no. 43)	$Fdd2$ (no. 43)
a, Å	26.917(8)	26.730(6)
b, Å	43.25(1)	44.70(1)
c, Å	7.823(2)	7.739(2)
V, Å^3	9108(5)	9245(4)
Z	16	16
D_{calcd}, g cm^{-3}	1.36	1.47
μ(MoK_α), cm^{-1}	2.9	22.0
F(000), e	4000	4264
hkl range	$-25 \le h \le +25$ $-41 \le k \le +41$ $-7 \le l \le +7$	$-29 \le h \le +29$ $-46 \le k \le +48$ $--6 \le l \le +8$
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	0.48	0.48
Refl. measured	11453	8504
Refl. unique	2137	2712
R_{int}	0.0742	0.1514
Param. refined	267	268
$R_1(F_o^2)^a$	0.0597	0.1253
$wR(F_o^2)^b$ (all refls)	0.1310	0.1380
a, b^b	0.084, 23.23	0.054, 0
x(Flack)	0.00(9)	0.03(2)
GoF $(F^2)^c$	1.033	1.010
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.33 / −0.20	0.54 / −0.59

[a] $R_1 = \|F_o| - |F_c\|/\Sigma|F_o|$; [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [c] $\mathrm{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

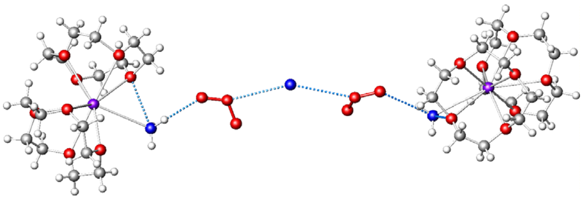

Fig. 2. [([M([12]crown-4)$_2$(NH$_3$)]O$_3$)$_2$(NH$_3$)] supramolecular building block: dashed lines indicate N–H···O bonds.

crown-4)$_2$O$_3$ · 1.5 NH$_3$ (with M = K (**1**), M = Rb (**2**)) are formed. They crystallize isostructurally in the non-centrosymmetric space group $Fdd2$ (no. 43) with 16 formula units per unit cell (Table 1, Fig. 1). As a prominent feature of the structure, each two ion pairs [M([12]crown-4)$_2$(NH$_3$)]O$_3$ are linked by an additional solvent molecule, forming rod-like supramolecular units (Fig. 2). Within the (001) layer, such building blocks are tilted by approximately ± 25° from the a axis, leading to a fishbone pattern (Fig. 1a). The alkali metal cations are sandwiched between two [12]crown-4 molecules, with the angle between the centers of each

Table 2. Selected bond lengths (Å) and angles (deg) for **1** and **2** with estimated standard deviations in parentheses.

	1	**2**
Distances		
M–O2	2.73(1)	2.88(1)
M–O7	2.78(1)	2.88(1)
M–O8	2.78(1)	2.89(1)
M–O3	2.80(1)	2.94(1)
M–O6	2.81(1)	2.99(1)
M–O1	2.82(1)	3.00(1)
M–O4	2.83(1)	3.02(1)
M–O5	2.86(1)	3.03(1)
M–N1	3.90(1)	3.35(1)
O11–O12	1.31(1)	1.31(1)
O12–O13	1.29(1)	1.31(1)
N1···O11	3.26(1)	3.16(2)
O12···N2	3.32(1)	3.37(1)
Angles		
O11–O12–O13	117.6(7)	118.0(1)

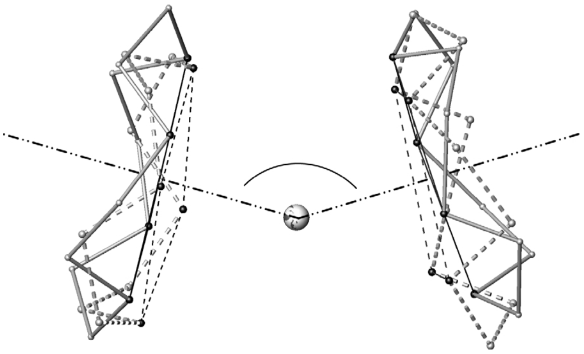

Fig. 3. Superimposed complex cations [K([12]crown-4)$_2$]$^+$ (dashed lines) and [Rb([12]crown-4)$_2$]$^+$ (full lines): the angle between the oxygen planes and the metal center (dash-dotted line) is about 155° in both cases.

four oxygen atoms and the metal amounting in both cases to approximately 155° (Fig. 3). As expected due to the different cation radii, potassium fits better to the small crown ether [12]crown-4 (diameter about 1.20–1.50 Å) than rubidium, manifesting itself in the 5 % shorter M–O bond lengths (see Table 2). In fact, one of the crown ether ligands in **2** shows statistical disorder, indicated by large anisotropic displacement parameters of the carbon atoms. However, applying a split model to the respective carbon atom positions did not improve the refinement. The M–N1 distance of the ammonia molecule close to the metal center is about 14 % longer in the potassium than in the rubidium compound, for which the coordination sphere of the alkali metal needs to be expanded.

Parallel to (100), layers of [M([12]crown-4)$_2$]$^+$-O$_3{}^-$ ion pairs alternate with ammonia molecules (Fig. 1b). In this arrangement, half of the [12]crown-4 ligands of adjacent [((M([12]crown-4)$_2$(NH$_3$))]O$_3$)$_2$-(NH$_3$)] building blocks flock together, forming more unpolar, “organic” layers parallel to (010). The resulting separate layers of weakly bonded NH$_3$ explain the easy loss of ammonia and the pronounced temperature sensitivity of these compounds that need to be handled below 240 K in order to prevent decomposition.

While in the crown ether–ozonide compounds of the type M([18]crown-6)O$_3 \cdot x$ NH$_3$ (with M = K (x = 2); Rb (x = 1) and Cs (x = 8)) [8], the ozonide anions are coordinating the respective metal as a bidentate ligand, the ozonide anions of the title compounds appear “isolated”, being just connected to ammonia *via* weak hydrogen bonds (Fig. 2). Unfortunately, the thermal instability of this type of compounds often hampers structural analyses and, in this very case, is thwarting the determination of hydrogen positions from Fourier density maps. Therefore the discussion of hydrogen bonding is only based on donor-acceptor distances and on the influence of hydrogen bonding on the molecular structure of the ozonide anion. In Table 2, N···O distances between ammonia and the ozonide anions are given. In terms of the ‘bond length-bond strength’ picture, in both cases the interaction of O$_3{}^-$ with the NH$_3$ molecule (N1) coordinated to the respective metal is slightly stronger than that with the bridging ammonia molecule (N2). Both distances are longer than 2.9 Å, which is the sum of the van-der-Waals radii between donor and acceptor (nitrogen and oxygen). Following Steiner [10] and Jeffrey [11], respectively, donor-acceptor distances of about 3.2 Å indicate moderate to weak hydrogen bonds of mainly electrostatic nature. Ozonide anions are highly polarizable, and would deform easily as the electron density in the SOMO (singly occupied molecular orbital) is changed by external influences, in accordance to the Walsh model of triatomic molecules. The O–O bond lengths and the O–O–O bond angle of the O$_3{}^-$ ions in **1** and **2** are given in Table 2. In comparison to the alkali metal ozonides KO$_3$ (d(O–O) = 1.346(2) Å; ∠(O–O–O) = 113.5(1)°) [3] and RbO$_3$ (d(O–O) = 1.341(6), 1.344(6) Å; ∠(O–O–O) = 113.7(5)°) [4] the slight shortening of the bonds and the increase in the bond angle might indicate a certain removal of electron density from the antibonding 2b$_1$-MO, due to contributing to an N–H···O hydrogen bond. However, the difficulties in the structure determination and the flexibility of the molecular frame of the ozonide anion, indicated by a broad minimum in the energy surface around the so-called ‘best estimate' of 1.35±0.03 Å and 114.5±1.0° [8b, 12], suggest that only the angle deviation might be regarded as a significant indicator for decrease in electron density in the anti-bonding orbitals, as was previously shown for the M([18]crown-6)O$_3 \cdot x$ NH$_3$ type of compounds [8].

Experimental Section

Attention: Ozonides containing organic ligands 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. 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. The alkali metal ozonides KO_3 and RbO_3 were synthesized according to a literature procedure [3, 4].

An H-shaped reaction vessel with a glass frit (porosity 3) was charged with [12]crown-4 (77.6 mg, 0.44 mmol) and cooled to approximately 200 K using ethanol/dry ice. KO_3 (19.2 mg, 0.22 mmol) and RbO_3 (30.0 mg, 0.22 mmol), respectively, was added, and the reaction vessel was 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 of its volume. After 2 – 3 d at 213 K, red needles were isolated from the solution.

Crystal structure determination

For single-crystal structure determination, the extremely sensitive crystals were handled according to the procedure described by Stalke and Kottke [13]. Intensity data were collected at 100 K on a SMART-APEX CCD X-ray diffractometer (Bruker AXS Inc.) with MoK_α radiation (λ = 0.71073 Å) and a graphite monochromator. A semi-empirical absorption correction was applied using SADABS [14]. The structures were solved with Direct Methods and refined using the program package SHELXTL [15].

CCDC 752899 (**1**) and CCDC 752900 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

The authors thank Ms. A. Müller for her help with the sample preparation.

---

[1] a) W. Hesse, M. Jansen, W. Schnick, *Progr. Solid Sate Chem.* **1989**, *19*, 47 – 110; b) M. Jansen, H. Nuss, *Z. Anorg. Allg. Chem.* **2007**, *633*, 1307 – 1315.

[2] W. Klein, K. Armbruster, M. Jansen, *Chem. Commun.* **1998**, 707 – 708.

[3] W. Schnick, M. Jansen, *Angew. Chem.* **1985**, *97*, 48 – 49, *Angew. Chem.*, Int. Ed. Engl. **1985**, *24*, 54 – 55.

[4] W. Schnick, M. Jansen, *Z. Anorg. Allg. Chem.* **1986**, *532*, 37 – 46.

[5] H. Seyeda, K. Armbruster, M. Jansen, *Chem. Ber.* **1996**, *129*, 997 – 1001.

[6] H. Nuss, M. Jansen, *Angew. Chem.* **2006**, *118*, 8137 – 8140; *Angew. Chem. Int. Ed.* **2006**, *45*, 7969 – 7972.

[7] W. Klein, M. Jansen, *Z. Anorg. Allg. Chem.* **2000**, *626*, 947 – 950.

[8] a) N. Korber, M. Jansen, *J. Chem. Soc., Chem. Commun.* **1990**, 1654 – 1655; b) H. Nuss, J. Nuss, M. Jansen, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1291 – 1295.

[9] H. Nuss, Dissertation, University of Stuttgart, Germany **2007**.

[10] T. Steiner, *Angew. Chem.* **2002**, *114*, 50 – 80; *Angew. Chem. Int. Ed.* **2002**, *41*, 48 – 76.

[11] G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, Oxford, **1997**.

[12] W. Koch, G. Frenking, G. Steffen, D. Reinen, M. Jansen, W. Assenmacher, *J. Chem. Phys.* **1993**, *99*, 1271 – 1277.

[13] T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615 – 619.

[14] G. M. Sheldrick, SADABS (version 2008/1), Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen (Germany) **2008**.

[15] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112 – 122.