Synthesis and crystal structure determination of sodium ozonide

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So-far-unknown ionic ozonides are accessible by a new method of synthesis; the new binary compound NaO_3 crystallizes isostructural to $NaNO_2$.

Recently, the alkali metal ozonides KO_3,[1] RbO_3[2] and CsO_3[3] have become available as bulk and pure materials, and a generally applicable route for the syntheses of ionic ozonides with relatively bulky organic group-15-'onium' cations has been developed.[4] All ozonides known so far are metastable and decompose *via* exothermal reactions.[5] Within the group of the alkali metal ozonides the stability decreases with decreasing diameter of the respective cation. As a consequence, unlike KO_3, RbO_3 and CsO_3, the lithium and sodium ozonides are not accessible *via* direct ozonisation of their peroxides or hyperoxides. However, solutions of LiO_3 and NaO_3 in liquid ammonia can be obtained by ion exchange. From these solutions the solid ozonides Li[2.2.1]O_3 and Na[2.2.2]O_3 precipitate after complexation of the cations by the appropriate cryptands.[6] In the absence of a cryptand, NaO_3 decomposes into a mixture of solid NaOH and NaO_2 upon removing the solvent. Presumably, in an initial step a proton is transferred to the ozonide anion from ammonia, which shows an increased acidity because of its coordination to the smaller and thus more strongly polarizing sodium cation, compared to K^+, Rb^+ and Cs^+. In order to circumvent this complication, we have added methylamine, which, being a stronger base than ammonia, would be the preferred ligand for the coordination of sodium, and at the same time, is less proton acidic. When evaporating the solvent mixture at -78 °C, first ammonia is removed, and upon increasing the temperature slowly up to -20 °C, pure sodium ozonide precipitates. The intensively red, air sensitive polycrystalline samples decompose slowly at room temperature into solid NaO_2 and oxygen. However, at a temperature of -18 °C, NaO_3 can be stored undecomposed for months. Surprisingly, the temperature at which rapid spontaneous decomposition starts is slightly higher for NaO_3 (37 °C) than for KO_3 (35 °C).[1]

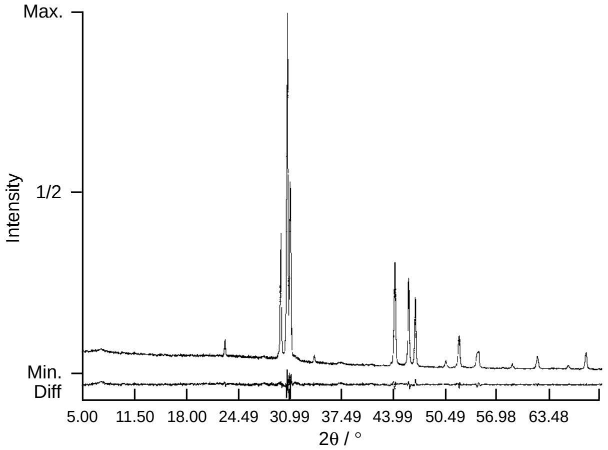

Fig. 1 Measured and calculated powder diffraction pattern of sodium ozonide and difference plot

According to a crystal structure determination by Rietveld's technique of refinement of X-ray powder data[7] (Fig. 1), NaO_3 is isostructural to sodium nitrite.‡ Thus, sodium ozonide is the first alkali metal ozonide exhibiting a ferroelectric arrangement of the anions. Generally, the crystal structure of NaO_3 can be related to the rock salt type of structure (*cf.* Fig. 2), each sodium being surrounded octahedrally by six ozonide groups. However, six negatively polarized terminal oxygen atoms belonging to only five complex anions coordinate sodium at a distance (242–244 pm) as would be expected for the first coordination sphere[8–10] (*cf.* Fig. 3). The ozonide ion exhibits the longest O–O bonds and the smallest O–O–O angle that have been seen so far. The newly determined data confirm the trend that with decreasing ionic radius of the cation the bond lengths increase and the bond angles decrease within the ozonide ion (see Table 1). Note that the differences among these values are rather close to the limits of experimental error. However, they are consistent with considerations based on Walsh's rules.[11] As in KO_3 (300.5

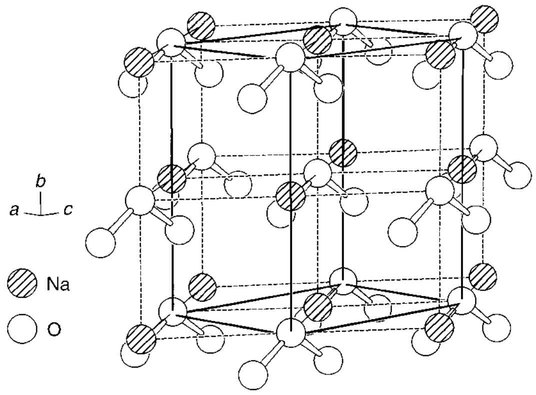

Fig. 2 Perspective view of the crystal structure of NaO_3. Bold lines: conventional unit cell, dashed lines emphasize the relation to the rock salt type of structure.

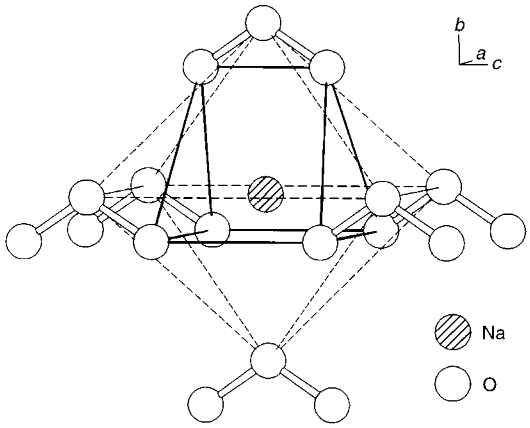

Fig. 3 Trigonal prismatic coordination of the sodium cation by six terminal oxygen atoms (bold lines), octahedral surrounding by six ozonide anions (dashed lines)

Table 1 Selected bond lengths and angles for ionic ozonides

	O–O/Å	O–O–O/°
NaO_3	135.3(3)	113.0(2)
KO_3[a]	134.6(2)	113.5(1)
RbO_3[a]	134.3(7)	113.7(5)
CsO_3[b]	133.3(9)	114.6(6)

[a] Ref. 2. [b] Ref. 13.

pm),[12] the shortest distances between different anions in NaO_3 are 301.5 pm. In contrast, for the first time the nearest oxygen atoms of different ozonide groups are terminal and negatively polarized,[13] instead of one terminal and one less negatively polarized bridging atom like in the other alkali ozonides.

Somewhat unexpectedly, the difficulties in preparing pure NaO_3 are not caused by its supposed higher intrinsic instability as compared with, *e.g.* KO_3, but probably by a stronger activation of ammonia with respect to a proton transfer when coordinated to sodium instead of potassium. Thus the synthesis method employed here might represent a general procedure for the synthesis of so far unknown ozonides. According to preliminary results $Ba(O_3)_2$ seems to be accessible *via* this novel route.

Notes and References

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‡ X-Ray structure determination of NaO_3: space group *Im*2*m* (no. 44), $a = 3.5070(2)$, $b = 5.7703(3)$, $c = 5.2701(3)$ Å, $U = 106.777(1)$ Å^3, $Z = 2$, $D_c = 2.2078$ g cm^{-3}, X-ray scattering experiments were carried out on a Stoe Stadi P diffractometer with germanium monochromated Cu-Kα_1 radiation, small PSD, $2\theta = 5$–70°, $T = -60$ °C. The crystal structure was refined supposing the structure model of $NaNO_2$ with the CSD program package[7] by application of Rietveld method: no. of observed reflections 19, no. of parameters 8, Na, O(1) on 2a, O(2) on 4d, $R_\text{int} = 0.0371$, $R_\text{prof} = 0.0922$. Atomic parameters are listed in Table 2.

Table 2 Atomic parameters for NaO_3

	x	*y*	*z*	B_eq/Å^2
Na	0	0.5074(3)	0	2.20(5)
O(1)	0	0.0106(6)	0	4.97(8)
O(2)	0	−0.1189(3)	0.2139(4)	2.87(6)

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