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Registry No. 4-MeImH, 822-36-6; *N*-MeIm, 616-47-7; ImH, 288-32-4; HisH⁻, 80448-37-9; Bz⁻, 766-76-7; *cis*-Co(en)₂Cl(*N*-MeIm)²⁺, 60314-39-8; *cis*-Co(en)₂Cl(4-MeImH)²⁺, 88657-81-2; *cis*-Co(en)₂Cl(ImH)²⁺, 60314-38-7; Co(en)Cl(HisH)⁺, 88657-78-7; *cis*-[Co(en)₂Cl(NO₂Im)]Cl·H₂O, 136537-78-5; *cis*-[Co(en)Cl(NO₂His)]·H₂O, 136568-96-2; *cis*-Co(en)₂Cl(NO₂-4-MeImH)²⁺, 136537-79-6; *cis*-Co(en)₂Cl(NO₂-*N*-MeIm)²⁺, 136537-80-9; *cis*-[Co(en)₂Cl(Cl-ImH)]Cl₂, 136537-81-0; *cis*-[Co(en)₂Cl(py)]Cl₂, 21409-63-2; *cis*-[Co(en)₂Cl(benz-ImH)](ClO₄)₂, 136537-82-1; CoAsBz²⁺, 30931-77-2; methyl *m*-nitrobenzoate, 618-95-1; *m*-nitrobenzoic acid, 121-92-6; methyl benzoate, 93-58-3.

Supplementary Material Available: Tables listing positional parameters and their estimated standard deviations for hydrogen atoms and Tables 8-12, listing bond angles about the cobalt and ethylenediamine ligands and bond angles in the attached imidazole ligands, bond lengths to hydrogen in the attached ligands, and selected mean plane angles in the benzimidazole, pyridine, and chloroimidazole complexes (22 pages); tables of observed and calculated structure factors for bis(ethylenediamine)(benzimidazole)chlorocobalt(III) perchlorate, bis(ethylenediamine)(pyridine)chlorocobalt(III) chloride, bis(ethylenediamine)(4-nitroimidazolato)chlorocobalt(III) chloride hydrate, bis(ethylenediamine)(4-chloroimidazole)chlorocobalt(III) chloride, and (ethylenediamine)(4-nitrohistidinato-*O,N,N'*)chlorocobalt(III) hydrate (170 pages). Ordering information is given on any current masthead page.

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New Ionic Ozonides: Syntheses, Structures, and Properties of N(CH₃)₄O₃ and N(C₂H₅)₄O₃

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In contrast to the known alkali-metal ozonides, tetraalkylammonium ozonides can not be synthesized by reaction of ozone with the respective hyperoxides due to the oxidizability of the cation. Therefore, N(CH₃)₄O₃ and N(C₂H₅)₄O₃ have been synthesized via a new route by double reaction of their hyperoxides with alkali-metal ozonides in liquid ammonia. N(CH₃)₄O₃ crystallizes in the orthorhombic space group *Pmmn* (No. 59) with *a* = 850.96 (25) pm, *b* = 689.95 (32) pm, *c* = 544.39 (16) pm, and *Z* = 2. N(C₂H₅)₄O₃ crystallizes in the trigonal space group *P3₁21* (No. 152) with *a* = 706.60 (15) pm, *c* = 1752.60 (43) pm, and *Z* = 3. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer using Mo K α radiation. Whereas the structure of N(CH₃)₄O₃ shows a relationship with the CsCl type of structure, atomic arrangement in the N(C₂H₅)₄O₃ structure derives from the NaCl type of structure. C-H...O hydrogen bonds were found in both structures and were also evidenced by IR investigations. The decomposition of these two compounds has been studied by mass spectroscopy and DTA/TG methods. Two different mechanisms of decomposition, caused by the absence or the presence of β -hydrogen atoms, are observed for N(CH₃)₄O₃ and N(C₂H₅)₄O₃. N(CH₃)₄O₃ is surprisingly stable, only decomposing above 75 °C. As a consequence of their higher solubilities in commonly used solvents (e.g. acetonitrile), these new ozonides are of interest in developing a preparative chemistry involving ionic ozonides.

Introduction

In the past, ionic ozonides, salts which contain the paramagnetic bent molecular anion O₃⁻, were reported only in combination with alkali-metal cations.¹ Attempts to synthesize ionic ozonides with alternative cations (NH₄⁺, N(CH₃)₄⁺, Sr²⁺, Ba²⁺) had been unsuccessful.²⁻⁵ Due to their metastability and extreme sensitivity toward moisture and CO₂, the preparation of ionic ozonides is challenging. Therefore, it was not until 1985 that a general synthetic route for the preparation of pure, crystalline samples of alkali-metal ozonides in gram amounts was developed.⁶ This preparative route, involving the reaction between alkali-metal hyperoxides and gaseous ozone, proved to be unsuccessful for the preparation of ozonides other than those of the alkali metals. In the present case, the oxidizability of the tetraalkylammonium cations by ozone hampered the synthesis of such ozonides. Thus, the formation of tetraalkylammonium ozonides must be carried out under very mild and nonoxidizing conditions. In the current method, the O₃⁻ anions are introduced via an exchange reaction between an alkali-metal ozonide and a salt of the desired cation. Recently N(CH₃)₄O₃ was synthesized by double reaction of KO₃ with N(CH₃)₄O₂ in liquid ammonia.⁷ We have now been suc-

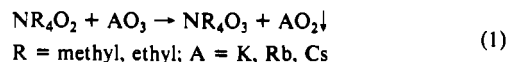
cessful in preparing N(C₂H₅)₄O₃ by reaction of CsO₃ with N(C₂H₅)₄O₂; therefore, this route to ozonides of non-alkali-metal cations should prove to be general. In this paper, we report the syntheses of these two tetraalkylammonium ozonides, as well as of the reagents necessary for the preparation. Structural characterization and investigation of the thermal decomposition of N(CH₃)₄O₃ and N(C₂H₅)₄O₃ are described.

Experimental Section

General Comments. All manipulations were carried out under an atmosphere of dry argon by using Schlenk techniques. Infrared spectra were recorded by a Bruker IFS 113 spectrometer on pressed KBr disks. Pressing was effected by using a Perkin-Elmer minipellet press. The collection of Raman data was attempted by use of a Coderg LRT 800 spectrophotometer using 514.5-nm excitation of an Ar ion laser.

Thermal decomposition was studied by MS and DTA/TG investigations. MS spectra were recorded on a Kratos MS 50 high-resolution spectrometer. The ozonides were placed in a "hot box" and the evaporated gaseous products were detected. Combined DTA/TG measurements were undertaken with a NETZSCH STA 429 thermoanalyzer.

Syntheses. The synthesis of the tetraalkylammonium ozonides is depicted in eq 1. The alkali-metal ozonides were prepared as described elsewhere in a special glass apparatus⁸ by reaction of gaseous ozone/



oxygen mixtures with alkali-metal hyperoxides, obtained by direct oxidation of alkali metals with molecular oxygen.⁹ Extraction by and recrystallization from liquid ammonia led to pure, hyperoxide-free ozonides. The most effective method of synthesizing N(CH₃)₄O₃ is the novel solid-state exchange reaction between tetramethylammonium hydroxide

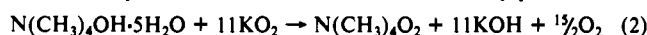
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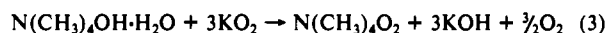
Table I. Data for Crystal Structure Analysis

| | N(CH ₃) ₄ O ₃ | N(C ₂ H ₅) ₄ O ₃ |
|---|---|---|
| formula | C ₄ H ₁₂ NO ₃ | C ₈ H ₂₀ NO ₃ |
| <i>M</i> | 122.14 | 178.25 |
| cryst syst | orthorhombic | trigonal |
| space group | <i>Pmmn</i> (No. 59) | <i>P3₁21</i> (No. 152) |
| <i>a</i> /pm | 850.96 (25) | 706.60 (15) |
| <i>b</i> /pm | 689.95 (32) | |
| <i>c</i> /pm | 544.39 (16) | 1752.60 (43) |
| <i>V</i> /pm ³ × 10 ⁶ | 319.63 | 758.16 |
| <i>Z</i> | 2 | 3 |
| cryst size/mm | 0.3 × 0.15 × 0.05 | 0.4 × 0.4 × 0.4 |
| <i>D_c</i> /g·cm ⁻³ | 1.269 | 1.171 |
| μ(Mo Kα)/cm ⁻¹ | 0.69 | 0.53 |
| <i>T</i> /°C | -90 | -70 |
| λ/pm | 71.069 | 71.069 |
| 2θ range/deg | 2 < 2θ < 52 | 2 < 2θ < 52 |
| no. of data measd | 1336 | 2406 |
| no. of unique reflns | 344 | 2406 (no merging) |
| no. of obsd data | 219 | 1437 |
| with <i>F_o</i> > 2σ(<i>F_o</i>) | | |
| merging <i>R</i> value (<i>R_i</i>) | 0.045 | |
| no. of params refined | 38 | 100 |
| <i>R</i> | 0.078 | 0.046 |
| <i>R_w</i> ; <i>w</i> = 1/σ ² (<i>F</i>) | 0.035; <i>k</i> = 2.39 | 0.025; <i>k</i> = 3.29 |

and potassium hyperoxide, followed by subsequent extraction with liquid ammonia (eq 2).¹⁰ We have modified this method by previous vacu-



um-drying of the tetramethylammoniumhydroxide pentahydrate stepwise at 20, 40, and 75 °C (1 day at each step), forming a monohydrate. Obviously, reaction of this monohydrate with KO₂ does not demand such an excess of KO₂ (eq 3). The tetramethylammoniumhydroxide mono-



hydrate and potassium hyperoxide were stirred at room temperature for 3–4 days, and O₂ was removed daily by vacuum. Exhaustive extraction with liquid ammonia resulted in nearly quantitative yields of pure N(CH₃)₄O₂, as identified by powder X-ray investigations and Raman spectroscopy. In contrast to the high solubility of N(CH₃)₄O₂, KO₂ and KOH are nearly insoluble in liquid ammonia. Thus, only traces of soluble KOH·H₂O were occasionally found as an impurity in the samples of N(CH₃)₄O₂. In the case of the N(C₂H₅)₄⁺ compound a 20 wt % solution of N(C₂H₅)₄OH in water was evaporated to dryness, and the formed N(C₂H₅)₄OH hydrate was dried at 20 °C for 12 h (10⁻³ mmHg). Reaction with KO₂ to form N(C₂H₅)₄O₂ was conducted in a manner identical with that used to yield the N(CH₃)₄⁺ compound.

One millimole each of alkali-metal ozonide and tetraalkylammonium hyperoxide were placed in separate sides of a H-tube connected by a frit. Subsequently, liquid ammonia was condensed onto each substance. The red AO₃ solution and the colorless NR₄O₂ solution were mixed, and immediately AO₂ precipitation was observed. The cloudy solution was stirred for a few minutes to complete the precipitation. The formed red NR₄O₃ solution was decanted through the frit of the H tube to separate it from the poorly soluble AO₂. Slow evaporation of ammonia led to transparent crystals of NR₄O₃ in nearly quantitative yield. N(CH₃)₄O₃ is bright orange-red, and N(C₂H₅)₄O₃ is bright ruby red in color.

X-ray Analysis. A single crystal of each compound (NR₄O₃; R = methyl, ethyl) was wedged in a capillary tube under dry argon. After flame sealing, each tube was mounted on an Enraf-Nonius CAD 4 diffractometer. Further crystallographic data collection parameters are given in Table I. The space group of N(CH₃)₄O₃ was unambiguously determined by interpretation of systematic absences and an *E*-value statistic.

In the case of N(C₂H₅)₄O₃, 00*l* reflections with *l* = 3*n* + 1 are systematically absent. From the possible Laue groups of the hexagonal crystal system $\bar{3}$, $3m\bar{1}$, $31m$, $6/m$, and $6/mmm$ the last three were ruled out by data reduction (high *R_i*). The possible space groups with Laue symmetries $\bar{3}$ and $3m\bar{1}$ are thus

$$\begin{array}{cc} P3_1 & P3_121 \\ P3_2 & P3_221 \end{array}$$

The pairs of acentric space groups with the same Laue symmetry differ only in the direction of their screw axes. Because of low atomic weights for the elements present in these compounds, there is no anomalous

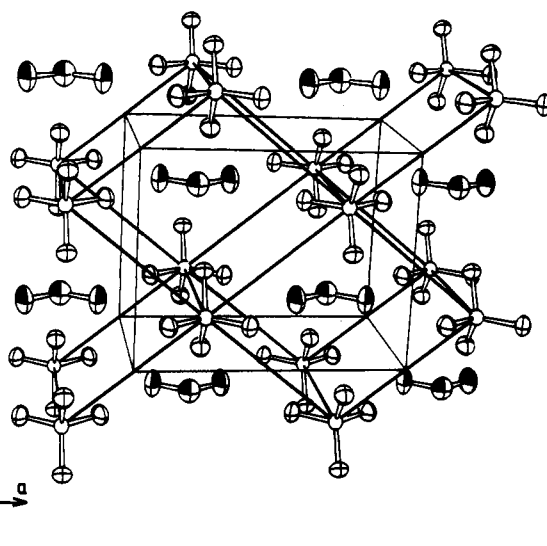


Figure 1. Perspective drawing of the crystal structure of N(CH₃)₄O₃ (H atoms omitted). Selected bond distances (Å) and angles (deg): N–C = 1.497 (4), 1.500 (4); C–N–C = 109.1 (4)–109.9 (4); O–O = 1.288 (3); O–O–O = 119.6(4); shortest intermolecular O–O = 4.388 (3).

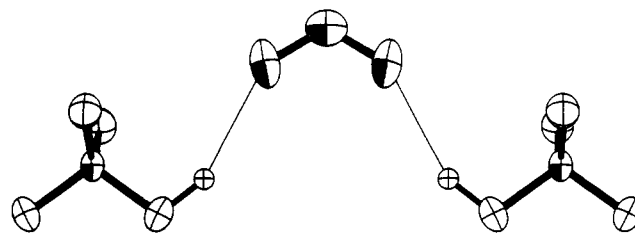


Figure 2. Hydrogen bonds in N(CH₃)₄O₃. Selected bond distances (Å) and angles (deg): O–C = 3.344 (4), O–H = 2.370 (9); O–H–C = 156.4 (8).

dispersion, and the absolute configuration of the crystal structure cannot be determined. Thus, the structure was refined in each of two space groups: *P3₁*; and *P3₁21* (vide infra).

The structures were solved by direct methods (SHELXS program).¹¹ Subsequent refinements used the SHELX-76 program.¹² All non-hydrogen atoms were refined anisotropically until convergence. The hydrogen atoms were found from difference Fourier maps and refined isotropically. No absorption correction was made.

In order to determine accurate lattice constants, the X-ray powder diffraction patterns of these two compounds were recorded by using a Guinier–Simon camera and monochromated Cu Kα₁ radiation (λ = 154.056 pm). The patterns were indexed as shown in Table II; all observed *d* spacings and intensities are in good agreement with the values calculated from the results of the single-crystal investigations.

Results and Discussion

Crystal Structure of N(CH₃)₄O₃. The crystal structure of N(CH₃)₄O₃ contains ordered N(CH₃)₄⁺ cations and O₃⁻ anions. Atomic positional parameters are listed in Table III; selected bond distances and angles are given in Figures 1 and 2 (see also supplementary material).

The cation/anion packing is closely related to the CsCl structure (Figure 1). The ozonide groups are arranged in a strictly ordered manner forming layers parallel to (010). In contrast to the alkali-metal ozonides, the O₃⁻ dipoles in N(CH₃)₄O₃ are arranged in an antiferroelectric sense, with shortest intermolecular O–O distances (438.8 pm) between terminal oxygen atoms. The negatively polarized terminal O atoms are directed toward the center of the N(CH₃)₄⁺ tetrahedra. The shortest contacts between terminal O atoms and H atoms are 237 pm, which are typical values for C–H···O hydrogen bonds¹³ (compare with Figure 2).

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Table II. Observed and Calculated X-ray Powder Pattern for $N(CH_3)_4O_3$ ($T = -80^\circ C$) and $N(C_2H_5)_4O_3$ ($T = -20^\circ C$)

| $N(CH_3)_4O_3$ | | | | | $N(C_2H_5)_4O_3$ | | | | |
|----------------|----------------------|----------------------|----------------------|----------------------|------------------|----------------------|----------------------|----------------------|----------------------|
| <i>hkl</i> | <i>d_c</i> | <i>d_o</i> | <i>I_c</i> | <i>I_o</i> | <i>hkl</i> | <i>d_c</i> | <i>d_o</i> | <i>I_c</i> | <i>I_o</i> |
| 001 | 5.446 | 5.450 | 1.1 | 5 | 100 | 6.138 | 6.108 | 14.4 | 15 |
| 101 | 4.584 | 4.580 | 9.4 | 10 | 003 | 5.863 | 5.874 | 11.5 | 10 |
| 011 | 4.277 | 4.281 | 9.9 | 15 | 101 | 5.795 | 5.790 | 49.6 | 50 |
| 200 | 4.245 | 4.245 | 24.8 | 10 | 012 | 5.033 | 5.043 | 100.0 | 100 |
| 111 | 3.820 | 3.820 | 100.0 | 20 | 014 | 3.575 | 3.583 | 68.6 | 70 |
| 020 | 3.454 | 3.450 | 32.4 | 40 | 111 | 3.474 | 3.477 | 20.0 | 20 |
| 211 | 3.013 | 3.015 | 3.4 | 10 | 112 | 3.287 | 3.289 | 67.5 | 70 |
| 121 | 2.759 | 2.760 | 25.6 | 30 | 200 | 3.069 | 3.071 | 6.7 | 10 |
| 220 | 2.679 | 2.678 | 0.5 | 5 | 105 | 3.052 | 3.056 | 14.8 | 15 |
| 102 | 2.593 | 2.592 | 6.0 | 10 | 113 | 3.033 | 3.035 | 4.7 | 10 |
| 012 | 2.533 | 2.533 | 9.5 | 10 | 114 | 2.759 | 2.763 | 18.9 | 20 |
| 301 | 2.511 | 2.511 | 10.3 | 10 | 203 | 2.719 | 2.718 | 7.0 | 10 |
| 131 | 2.058 | 2.059 | 4.3 | 5 | 016 | 2.645 | 2.642 | 8.8 | 10 |
| | | | | | 204 | 2.517 | 2.516 | 5.3 | 10 |
| | | | | | 115 | 2.497 | 2.500 | 2.2 | 5 |
| | | | | | 205 | 2.312 | 2.310 | 1.4 | 5 |
| | | | | | 121 | 2.299 | 2.297 | 1.4 | 5 |
| | | | | | 116 | 2.259 | 2.255 | 3.1 | 5 |
| | | | | | 122 | 2.243 | 2.248 | 6.7 | 10 |
| | | | | | 123 | 2.157 | 2.157 | 7.9 | 10 |
| | | | | | 214 | 2.052 | 2.050 | 4.4 | 5 |
| | | | | | 126 | 1.8192 | 1.8179 | 2.0 | 5 |
| | | | | | 208 | 1.7873 | 1.7889 | 5.1 | 5 |
| | | | | | 217 | 1.7045 | 1.7031 | 1.6 | 5 |

Table III. Positional Parameters and U_{ij} 's for $N(CH_3)_4O_3$

| atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|------|-------------|--------------|-------------|-------------|-------------|-------------|--------------|--------------|----------|
| N1 | 0.25 | 0.25 | 0.0065 (7) | 0.0184 (21) | 0.0242 (26) | 0.0307 | 0 | 0 | 0 |
| C1 | 0.25 | 0.0724 (6) | 0.84867 (7) | 0.0364 (20) | 0.0343 (20) | 0.0426 (23) | -0.0086 (21) | 0 | 0 |
| H11 | 0.3411 (22) | 0.0817 (27) | 0.7511 (41) | 0.0440 (40) | | | | | |
| H12 | 0.25 | -0.0513 (46) | 0.9739 (57) | 0.0440 (40) | | | | | |
| C2 | 0.3936 (4) | 0.25 | 0.166 (5) | 0.0285 (21) | 0.0418 (23) | 0.0402 (23) | 0 | -0.0041 (23) | 0 |
| H21 | 0.3891 (23) | 0.1371 (26) | 0.2775 (43) | 0.0440 (40) | | | | | |
| H22 | 0.4862 (33) | 0.25 | 0.0554 (48) | 0.0440 (40) | | | | | |
| O1 | 0.25 | 0.75 | 0.4531 (6) | 0.0651 (29) | 0.0681 (34) | 0.0408 (27) | 0 | 0 | 0 |
| O2 | 0.3808 (3) | 0.75 | 0.3342 (5) | 0.0315 (16) | 0.0889 (22) | 0.0786 (22) | 0 | 0.0114 (19) | 0 |

Table IV. Positional Parameters and U_{ij} 's for $N(C_2H_5)_4O_3$

| atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} |
|------|--------------|--------------|------------|-------------|-------------|-------------|--------------|--------------|-------------|
| N1 | 0.4024 (3) | 0 | 0.8333 | 0.0359 (8) | 0.0253 (12) | 0.0261 (8) | 0.0012 (11) | 0.0006 (6) | 0.0126 (6) |
| C1 | -0.1882 (3) | 0.1862 (3) | 0.1365 (1) | 0.0294 (8) | 0.0289 (9) | 0.0420 (9) | -0.0041 (8) | -0.0040 (8) | 0.0059 (7) |
| C2 | 0.0835 (3) | 0.5650 (3) | 0.1007 (1) | 0.0342 (9) | 0.0413 (9) | 0.0300 (8) | 0.0108 (8) | 0.0020 (8) | 0.0141 (8) |
| C3 | -0.1183 (3) | 0.0722 (3) | 0.0795 (1) | 0.0522 (9) | 0.0434 (9) | 0.0420 (9) | -0.0104 (8) | -0.0056 (8) | 0.0253 (7) |
| C4 | 0.2644 (4) | 0.7913 (4) | 0.1227 (1) | 0.0486 (9) | 0.0387 (9) | 0.0563 (10) | 0.0165 (8) | -0.0042 (9) | 0.0100 (8) |
| O3 | 0.4518 (5) | 0.3097 (4) | 0.0437 (2) | 0.0680 (11) | 0.0429 (10) | 0.0387 (10) | -0.0009 (10) | 0.0061 (10) | 0.0285 (9) |
| O2 | 0.5366 (6) | 0.4096 (6) | 0.0347 (3) | 0.1064 (11) | 0.0981 (11) | 0.0670 (11) | 0.0197 (11) | -0.0161 (11) | 0.0614 (10) |
| O1 | 0.5302 (6) | 0.5035 (2) | 0.0129 (2) | 0.1074 (11) | 0.0589 (11) | 0.0622 (12) | 0.0217 (10) | -0.0142 (10) | 0.0482 (10) |
| H11 | -0.2963 (11) | 0.2196 (11) | 0.1123 (8) | 0.0643 (10) | | | | | |
| H12 | -0.2648 (11) | 0.0861 (11) | 0.1862 (8) | 0.0643 (10) | | | | | |
| H21 | -0.0521 (11) | 0.5705 (11) | 0.0811 (8) | 0.0643 (10) | | | | | |
| H22 | 0.1556 (11) | 0.5059 (11) | 0.0587 (8) | 0.0643 (10) | | | | | |
| H31 | -0.0365 (11) | 0.1668 (11) | 0.0332 (8) | 0.0643 (10) | | | | | |
| H32 | -0.2558 (11) | -0.0689 (11) | 0.0591 (8) | 0.0643 (10) | | | | | |
| H33 | -0.0314 (11) | 0.0054 (11) | 0.0984 (7) | 0.0643 (10) | | | | | |
| H41 | 0.2952 (11) | 0.8830 (11) | 0.0807 (8) | 0.0643 (10) | | | | | |
| H42 | 0.2140 (11) | 0.8663 (11) | 0.1645 (8) | 0.0643 (10) | | | | | |
| H43 | 0.3974 (10) | 0.7950 (11) | 0.1427 (8) | 0.0643 (10) | | | | | |

These hydrogen bonds cause a shortening of the O—O bond length and an increase of the bond angle in the ozonide ion.

Crystal Structure of $N(C_2H_5)_4O_3$. The crystal structure of $N(C_2H_5)_4O_3$ was solved in both space groups $P3_1$ and $P3_121$. In the latter case, thermal ellipsoids of the ozonide groups were abnormally large (Figure 3a), while the cations were completely ordered with normal thermal ellipsoids. Structure solution in space group $P3_1$ differs only in oxygen sites. Ozonide groups are unsymmetrical with respect to the 2-fold axis in the [110] direction. Therefore, two different explanations are possible to understand the real structure.

1. Ozonide groups in $N(C_2H_5)_4O_3$ are disordered in such a way that the arrangement shown in Figure 3b is statistically distributed through the crystal. This possibility leads to an overall symmetry with a 2-fold axis and, therefore, to space group $P3_121$.

2. The crystal is twinned in domains with one "extreme position" of the O_3^- site in every domain. These domains are ordered in such a way that they may be transmitted into one another via a 2-fold axis in the [110]-direction; thus, the space group of every domain is $P3_1$.

Structure refinements for both models (twinned structure was refined with the program SFLS¹⁴) show that the statistical dis-

(13) Green, R. D. *Hydrogen Bonding by C-H-Groups*; Macmillan: New York, 1974.

(14) Eitel, M.; Bärnighausen, H. SFLS. Program version for refinement of twinned crystals. University of Karlsruhe 1986.

Table V. Geometry of the Ozonide Group in Known Ionic Ozonides

| | KO ₃ ^{15a} | RbO ₃ ^{15a} | CsO ₃ ^{15b} | N(CH ₃) ₄ O ₃ | N(C ₂ H ₅) ₄ O ₃ |
|-----------------|--------------------------------|---------------------------------|---------------------------------|---|---|
| O1-O2/pm | 134.6(2) | 134.1(6) | 133.3(9) | 128.8(3) | 129.5(5) |
| O1-O3/pm | | 134.4(7) | 133.2(8) | | 130.9(4) |
| O2-O1-O2(3)/deg | 113.5(1) | 113.7(5) | 114.6(6) | 119.6(4) | 118.4(4) |

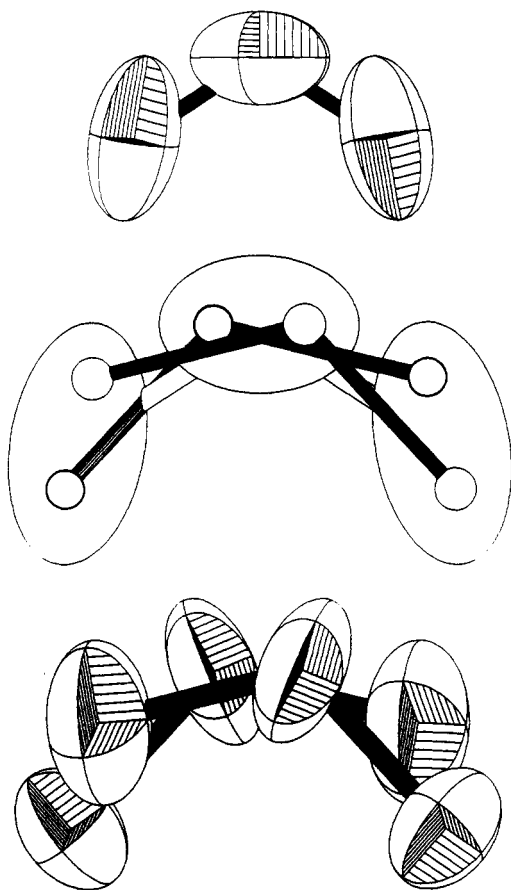


Figure 3. Ozonide group in N(C₂H₅)₄O₃: (a, top) thermal ellipsoids for an ordered O₃⁻ ion (P3₁21); (b, middle) O sites in space group P3₁ projected over thermal ellipsoids of structure a; (c, bottom) disordered O₃⁻ ions (P3₁21).

ordered model with space group P3₁21 is more probable. Figure 3c shows the thermal ellipsoids of the disordered O₃⁻ groups. Resulting atomic positional parameters are listed in Table IV; selected bond distances and angles are given in Figure 4 (see also supplementary material).

In contrast to all other known ozonides, the atomic arrangement in solid N(C₂H₅)₄O₃ is related to the NaCl type of structure. This structural difference may be explained by the increasing size of the cation in the sequence K-Rb-Cs-N(CH₃)₄-N(C₂H₅)₄. The ratio of the cation/anion radii of the first four ozonides lies between 0.747 (KO₃) and 1.483 (N(CH₃)₄O₃). In this range the lowest lattice energy (-U_g) results from coordination number 8 (CsCl type). Only in N(C₂H₅)₄O₃ is coordination number 6 (NaCl type) favored, due to the large value of the ratio of the cation/anion radii (2.185). The trigonal unit cell in Figure 4 exhibits three different layers of cations and anions in the distorted cubic closest packed structure. Hydrogen bonds between terminal O atoms of O₃⁻ anions and hydrogen atoms of the cations are found in N(C₂H₅)₄O₃ as well as in N(CH₃)₄O₃. The geometry of the ozonide group in each compound is changed slightly as compared to that present in the alkali-metal ozonides (Table V).

Thermal Decomposition Studies. Thermal stability and decomposition processes were investigated by DTA/TG and MS

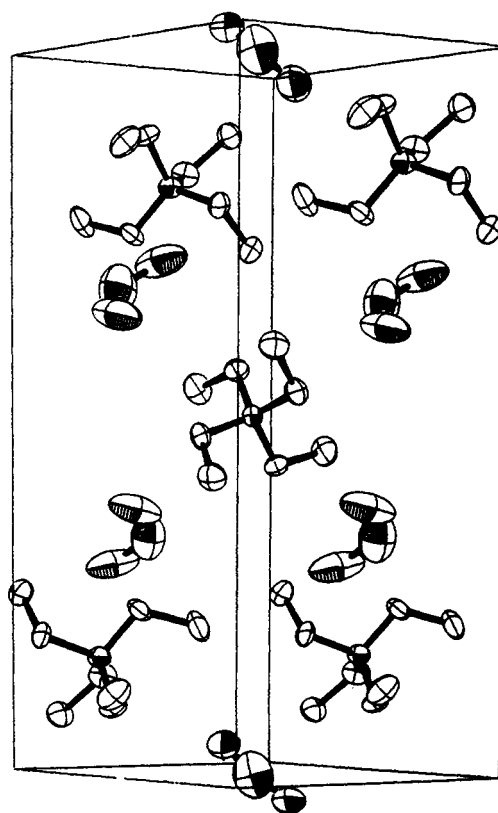


Figure 4. Unit cell of N(C₂H₅)₄O₃ (H atoms omitted). Selected bond distances (Å) and angles (deg): N-C = 1.534 (3), 1.525 (3), C-C = 1.513 (3), 1.516 (3), O-O = 1.295 (5), 1.309 (4); O-O-O = 118.4 (4).

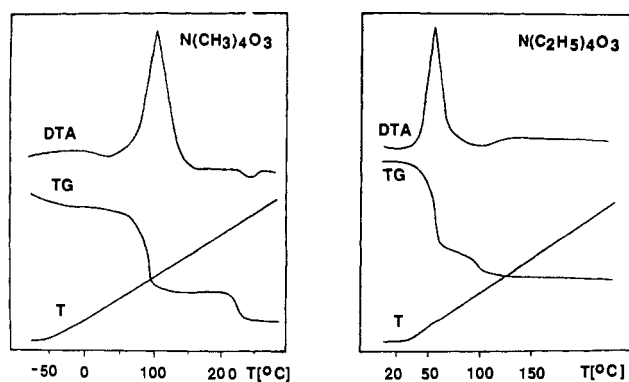


Figure 5. DTA/TG diagrams of N(CH₃)₄O₃ and N(C₂H₅)₄O₃. Heating rate: 1 K/min.

Table VI. Decomposition Temperatures of Ionic Ozonides

| N(C ₂ H ₅) ₄ O ₃ | KO ₃ ^{15a} | RbO ₃ ^{15a} | CsO ₃ ¹⁶ | N(CH ₃) ₄ O ₃ |
|---|--------------------------------|---------------------------------|--------------------------------|---|
| 30 °C | 35 °C | 38 °C | 53 °C | 75 °C |

measurements. From temperature-dependent X-ray powder photographs, decomposition temperatures of N(CH₃)₄O₃ and N(C₂H₅)₄O₃ were determined to be 75 and 30 °C, respectively. The thermograms of these two compounds are shown (Figure 5). Strong exothermic peaks at ca. 100 °C for N(CH₃)₄O₃ and 50 °C for N(C₂H₅)₄O₃ demonstrate the metastability of these ozonides. Extrapolations to a heating rate of 0 °C/min lead to the same decomposition temperatures as determined by Guinier methods (vide supra). The decomposition temperatures of all

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Table VII. IR Frequencies and Assignments for Ionic Ozonides (Observed Frequency, cm^{-1})^a

| KO ₃ | RbO ₃ | CsO ₃ | NMe ₄ O ₃ | NEt ₄ O ₃ | assignments | | |
|-------------------|----------------------------|----------------------------|--------------------------------------|--|-------------------------------------|-----------------------------|-------------------------|
| | | | | | O ₃ ⁻ | R ₄ ⁺ | |
| | | | 461 m | 419 w 465 vw | | } fundamentals | |
| 620 s 816 vs | 607 s 800 } vs 830 } | 593 } w 606 } 808 vs | 588 m 782 vs | ... | ν_2 ν_3 | | |
| 1020 w | 1020 vw | 1019 w | 926 sh 951 s | 1003 s | ν_1 | | |
| 1235 w | 1240 m | 1240 s | 1060 vw 1074 vw | 1053 w 1072 w 1099 vw | | | |
| 1405 w | 1400 | 1385 | 1181 vw 1226 s 1295 vw | 1191 s 1231 s 1303 vw | $2\nu_2$ | | } C-H deformation modes |
| | | | 1414 m 1447 w 1493 s | 1398 s 1441 m 1494 s | $\nu_2 + \nu_3$ | | |
| | | 1565 m 1593 m | 1569 w 1608 m | 1580 sh 1613 m | $2\nu_3$ | | |
| 1793 w 2165 vw | 1805 m 2165 w | 1795 w 2160 m | 1770 m 2143 m | 1748 vw 1769 vw 2145 m | $\nu_1 + \nu_2$ $2\nu_2 + \nu_3$ | | |
| | | | 2854 w 2924 m 2964 m 3028 s | 2899 sh 2926 sh 2953 sh 2981 s 3006 sh 3504 | | | |
| | | | | | | | } C-H stretching modes |
| | | | | | | } OH stretching mode | |

^aw = weak; m = medium; s = strong; vw = very weak; vs = very strong; sh = shoulder.

currently known ionic ozonides are given (Table VI).

Metastable compounds do not have definite decomposition points, since they always slowly decompose at lower temperatures. Therefore, the above values serve only for comparison of onset temperatures of rapid decomposition. In the sequence KO₃-RbO₃-CsO₃, thermal stability increases with increasing cation radii. Alkali-metal ozonides decompose in an exothermic reaction, forming the respective hyperoxides and oxygen. The most probable mechanism involves transfer of monooxygen from an O₃⁻ ion to a neighboring hyperoxide group.

Intermolecular O-O distances in N(CH₃)₄O₃ are much longer than those in CsO₃. Therefore, this type of reaction is suppressed, and N(CH₃)₄O₃ is surprisingly stable. Instead, decomposition via an oxidative attack on the cation is observed by MS techniques. Above ca. 100 °C, N(CH₃)₄O₃ decomposes into gaseous products, identified as N(CH₃)₃, CO, O₂, H₂O, CH₃OCH₃, CH₃OH, and C₃H₇NO (Figure 6a). Thus, the oxidizability of the cation is the limiting factor of thermal stability in this case.

The previously known decomposition mechanism of alkali-metal ozonides is suppressed also in the case of N(C₂H₅)₄O₃. Here the presence of β -hydrogen atoms is responsible for a lowered stability. A decomposition reaction like a Hofmann elimination demands only a low activation energy, and the O₃⁻ ion acts as a base. Above 30-40 °C, elimination products (N(C₂H₅)₃, ethylene, and O₂) were identified by mass spectrometry (Figure 6b). Small amounts of oxidation products also are observed, produced from further reactions of initially formed hydroxyl radicals.

Vibrational Spectra. IR spectra of all five known ionic ozonides were recorded. The spectra of N(CH₃)₄O₃ and N(C₂H₅)₄O₃ are shown (Figure 7a). The observed frequencies and their assignments are summarized (Table VII). The O₃⁻ group with C_{2v} symmetry present in ionic ozonides has three fundamentals according to group theory: a symmetric stretching mode ν_1 (A₁), a symmetric deformation mode ν_2 (A₁), and an antisymmetric stretching mode ν_3 (B₂). All three fundamentals are, in principle, Raman and IR active, but their intensities should differ very strongly. Whereas ν_1 should be very intense in the Raman spectrum, owing to the large change in polarizability, ν_3 should

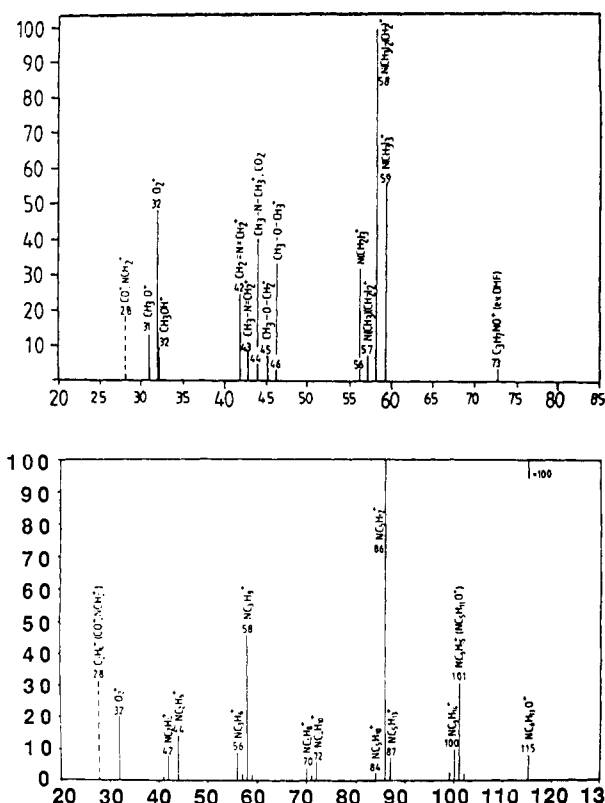


Figure 6. (a) Top: Mass spectrum for decomposition products of N(CH₃)₄O₃. (b) Bottom: Mass spectrum for decomposition products of N(C₂H₅)₄O₃.

be very intense in the IR spectrum on account of the large change in dipole moment. The intensity of the ν_2 mode is expected to lie between these two extremes. In earlier Raman investigations on alkali-metal ozonides, only ν_1 was observed^{16,17} centered between

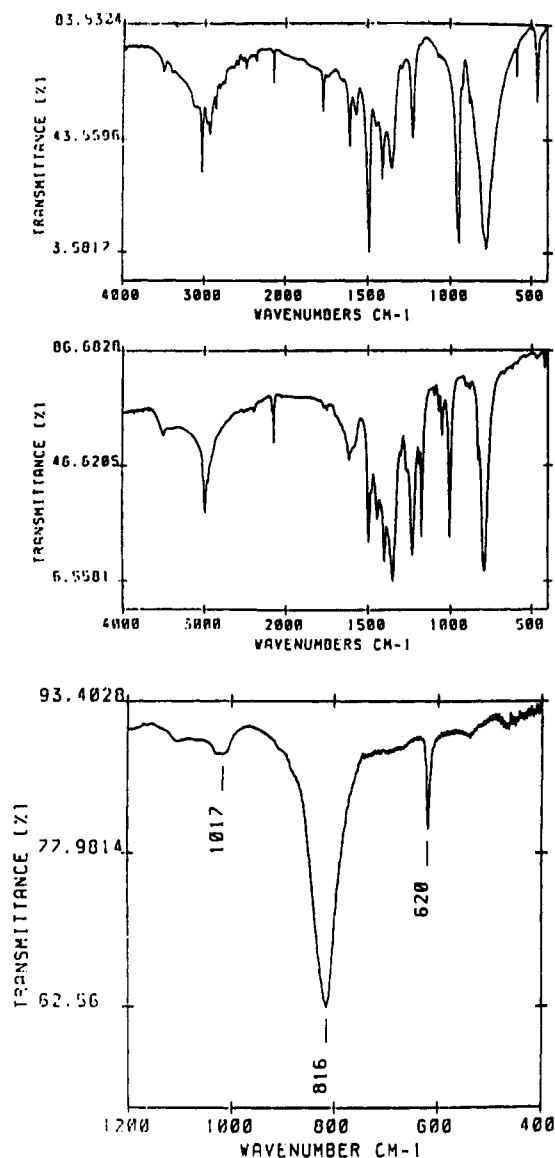


Figure 7. (a) Top: Infrared spectra of N(CH₃)₄O₃ and N(C₂H₅)₄O₃. (b) Bottom: Infrared spectrum of KO₃ in the range 400–1200 cm⁻¹. For assignment of the frequencies, see Table VII.

1008 and 1020 cm⁻¹. We were not able to collect Raman data for N(CH₃)₄O₃ and N(C₂H₅)₄O₃, due to decomposition in the laser beam even at N₂(l) temperatures. The measured IR spectrum of KO₃ exhibits all fundamentals (Figure 7b). We have redetermined the force constants of O₃⁻ on the basis of spectroscopic

data using different ¹⁸O isotopes in Ar matrices and the geometry of the O₃⁻ anion from X-ray work.¹⁶

The spectra of N(CH₃)₄O₃ and N(C₂H₅)₄O₃ exhibit different modes resulting from the cations. The presence of C–H...O–hydrogen bonds, implicated in the X-ray work, also are evidenced in the IR spectra. As Pimentel and McClellan declare,¹⁸ the C–H modes are “the most sensitive, the most characteristic, and one of the most informative manifestations of the hydrogen bond”. Harmon’s work¹⁹ on C–H...X hydrogen bonds in different N-(CH₃)₄⁺ salts is very helpful for comparison of the C–H...O hydrogen bond strength in our ozonides. The presence of C–H...O hydrogen bonds in N(CH₃)₄O₃ and N(C₂H₅)₄O₃ is demonstrated by the following characteristics:

The C–H stretching mode shifts from ca. 3050 cm⁻¹ to lower frequencies (ca. 2980 cm⁻¹) and splits into a structured broad band. The intensity of the δ_{sym} increases and the intensities of the ν_{rock} and the ν_{rot} decrease in the methyl deformation mode range. In the case of N(CH₃)₄O₃, the symmetric NC₄ stretching mode splits into a doublet according to symmetry reduction: thus, in addition to the strong band at 951 cm⁻¹, a weak band appears at 926 cm⁻¹.

Summary. We have accomplished a new synthetic route leading to ionic ozonides without the use of ozone and under exceedingly mild conditions (temperatures below –33 °C). This approach should prove to be general and probably will be useful for the syntheses of ozonides containing other cations (e.g. onium ions such as tetraphenylarsonium). Compared to those for the alkali-metal ozonides, the chemical and physical properties of the tetraalkylammonium ozonides differ strongly in several respects: solubility is extended to polar aprotic solvents like acetonitrile or DMSO, and N(CH₃)₄O₃ is the most thermally stable ozonide known at this time.

These new results and insights should enable one to plan the syntheses of even more stable ionic ozonides with advantageous properties for use in preparative organic or organometallic chemistry.

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Registry No. N(CH₃)₄O₃, 78657-29-1; N(CH₃)₄O₂, 3946-86-9; N-(CH₃)₄OH·5H₂O, 10424-65-4; N(CH₃)₄OH·H₂O, 55605-35-1; N(C₂H₅)₄O₃, 133324-06-8; N(C₂H₅)₄O₂, 54260-53-6; N(C₂H₅)₄OH, 77-98-5; KO₃, 12030-89-6; RbO₃, 12060-04-7; CsO₃, 12053-67-7; KO₂, 12030-88-5.

Supplementary Material Available: Tables of interatomic distances and angles for N(CH₃)₄O₃ and N(C₂H₅)₄O₃ (3 pages); tables of structure factors $F_o/\sigma(F_o)$ (10 pages). Ordering information is given on any current masthead page.

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