Ionic Ozonides of Lithium and Sodium: Circumventive Synthesis by Cation Exchange in Liquid Ammonia and Complexation by Cryptands☆

Nikolaus Korber and Martin Jansen*

Institut für Anorganische Chemie der Universität Bonn,
Gerhard-Domagk-Straße 1, D-53121 Bonn, Germany
Telefax: (internat.) +49(0)228/735660
E-mail: unc420@ibm.rhrz.uni-bonn.de

Received February 28, 1996

Key Words: Ozonides / Sodium ozonide / Lithium ozonide / Cation exchange

Concentrated solutions of the ozonides LiO_3 and NaO_3 in anhydrous liquid ammonia were obtained for the first time by using an ion exchange reaction that starts from CsO_3. No solid LiO_3 or NaO_3 can be precipitated. Upon removal of the solvent, the ozonide anion oxidises ammonia, resulting in the precipitation of LiOH and NaOH, respectively. This behaviour is in sharp contrast to that of solutions of KO_3, RbO_3 and CsO_3. Proof of the existence of LiO_3 and NaO_3 in the solutions is provided by complexation of the cations with cryptands, which leads to solid $(Li[2.1.1])O_3$ and $(Na[2.2.2])O_3$. Crystal structure analysis shows that these are ionic solids containing the V-shaped O_3^- anion.

The ozonides of the heavier alkali metals, KO_3, RbO_3 and CsO_3, have now been available for some time[1]. They are synthesised by ozonisation of the respective hyperoxides under precise temperature control, a process which has been further optimised by introducing microprocessor-controlled cooling equipment. This new synthetic route, which was introduced by Schnick and Jansen in 1985[2], has replaced the traditional method of ozonising the respective hydroxides[3]. Both routes rely on dry liquid ammonia as a solvent for the extraction and crystallistion of the ozonides. We estimate that, over the years, more than one kilogram of CsO_3 has been prepared in our laboratory for the use in various synthetic projects.

However, while we were able to obtain new ozonides by metathesis[4] and complexation[5] reactions, we were unable to extend the ozonisation reaction itself beyond compounds of potassium, rubidium and caesium. Judging from chemical similarity arguments (ratio of charge-to-radius, chemical hardness etc.), the most likely candidates for such an extension are compounds of the remaining alkali metals, namely sodium and lithium, and of barium, the heaviest alkaline earth metal. The successful preparation of NaO_3[6] and $Ba(O_3)_2$[7] was claimed several times in the literature, and there exists a single publication on $[Li(NH_3)_4]O_3$ by Solomon et al.[8]. Of special interest is the case of NaO_3, which seems to be the most probable candidate for the fourth binary ozonide due to the usually small difference between the properties of most potassium and sodium salts. The reports on the properties of NaO_3 from the literature, however, are extremely contradictory[6], which caused Salomon et al. to suggest different modifications of this compound to account for the widely ranging reported colours, thermal stabilities and solubilities in liquid ammonia. Further investigations seemed to be necessary.

Results

Sodium Ozonide

We found that our ozonisation process, which generates almost quantitative yields in the case of the ozonides of the heavier alkali metals[1], produces only negligible amounts of NaO_3, regardless whether we started from NaO_2, Na_2O_2 or NaOH. In all of the experiments we conducted under varying temperature regimes, we never observed more than a passing orange colouring (ionic ozonides are red) of the sodium compounds used as starting materials. Only weakly orange solutions of liquid ammonia could be extracted, containing almost no solute.

We were able, however, to arrive at concentrated solutions of pure sodium ozonide by circumventing the ozonisation reaction, using "prefabricated" O_3^- taken from CsO_3 instead. To this end, we employed the recently developed ion exchange method in liquid ammonia[9], which uses a macroreticular ion exchange resin made from highly crosslinked sulfonated polystyrene. This very stable resin proved to be resistant to oxidation as well as to the rigorous drying procedures, which are necessary when working with ionic ozonides. The selectivity coefficient (data measured for a similar resin[10]) favours the uptake of Cs^+ ions over that of Na^+ (or Li^+) ions. Therefore, a simple batch process with a fifteenfold excess of Na^+-loaded resin should assure complete ion exchange.

The batch equilibration between CsO_3 and the Na^+-loaded resin in liquid ammonia was performed in a reaction vessel in which the solution could be separated from the resin by filtration through a glass frit. The resulting clear solution was deep red and seemed to be in no way different from solutions of ozonides of the heavier alkali metals. Upon removal of the solvent, however, only a yellow powder remained. The very broad lines in the X-ray powder

0009–2940/96/0707–0773 $ 15.00+.25/0

diffractogram of this powder correspond to the literature data of NaOH (JCPDS 35–1009); no other lines were detected. Especially important is the absence of any lines of caesium compounds, which proves that a complete cation exchange took place. A Raman spectrum of the powder shows a single weak band at 1150 cm^{-1}, which agrees well with the value reported for the symmetric stretching vibration of O_2^- in NaO_2 (1156 cm^{-1}[11]). Obviously, a small amount of NaO_2 was formed as a by-product of the reaction, which accounts for the yellow colour of the powder.

Since we are certain that the solutions in question contain pure NaO_3 (see below) and because no other solids were detected as main products besides NaOH, an oxidation of ammonia by the ozonide anion resulting in the evolution of nitrogen and oxygen is the most probable explanation (1):

$$3\,Na^+ + 3\,O_3^- + NH_3 \rightarrow 3\,NaOH + 0.5\,N_2 + 3\,O_2 \qquad (1)$$

This decomposition is completely analogous to the well-known and violent reaction of ionic ozonides with water, during which water is oxidised to elemental oxygen[1]. However, we never observed such an attack on ammonia while dealing with the ozonides of the heavier alkali metals, solutions of which may be stored for at least six weeks at 230 K.

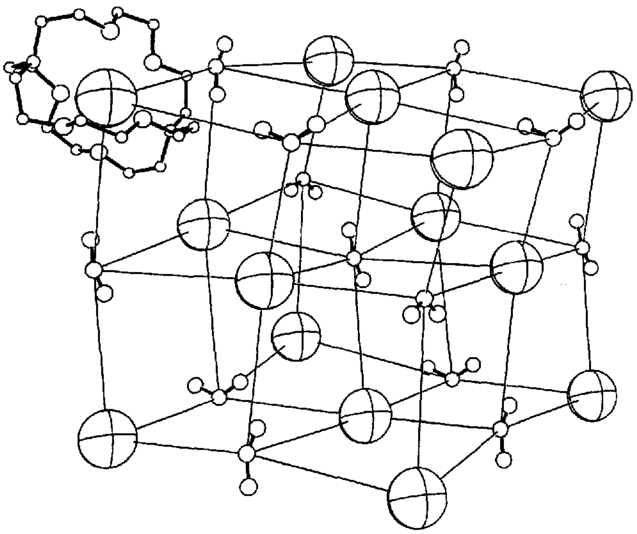
The presence of pure sodium ozonide in the solutions was unequivocally proven by complexing the cation with cryptand [2.2.2]. Slow evaporation of ammonia gave $(Na[2.2.2])O_3$, the first reported derivative of sodium ozonide. It is a red, rather unstable crystalline substance, that **explodes violently at 17°C** (DTA/TG results). The compound obtained from ammonia consisted of large (0.5–2 mm) hexagonal rods that turned opaque immediately upon removal of the solvent, indicating the presence of ammonia of solvation in the crystals. Single crystals which were suitable for an X-ray structure analysis were grown from anhydrous methylamine.

The crystal structure of $(Na[2.2.2])O_3$ is built from Na^+ ions, which are completely encapsulated by the cryptand, and O_3^- ions (Figure 1). The very roughly spherical $Na^+[2.2.2]$ complexes form a heavily distorted cubic close packing with the ozonide ions residing in the "octahedral" sites. Figure 1 indicates the analogy of this arrangement to the rock salt structure. The ozonides of the heavier alkali metals, having far smaller cations, are all derived from the caesium chloride structure. The cavity formed by six complexed cations is rather large for the ozonide anion, leading to large atomic displacement parameters for this species; crystallographically it behaves more like a small solvent molecule embedded into a molecular structure. Nevertheless, bond lengths and angles of the two crystallographically inequivalent O_3^- ions are in agreement with previously determined values.

Lithium Ozonide

The next logical step was to investigate the behaviour of solutions of lithium ozonide prepared by the same method. In the single publication in the literature that deals with LiO_3, Kacmarek, McDonough and Solomon describe the preparation of $Li(NH_3)_4O_3$ by ozonisation of LiOH in the presence of NH_3 at 161 K[8]. They extracted the red product with liquid ammonia and detected the ozonide anion by its characteristic UV band.

Figure 1. A projection of the structure of $(Na[2.2.2])O_3$ that demonstrates the analogy to the rock salt structure. In order to improve clarity only one of the cryptands is drawn

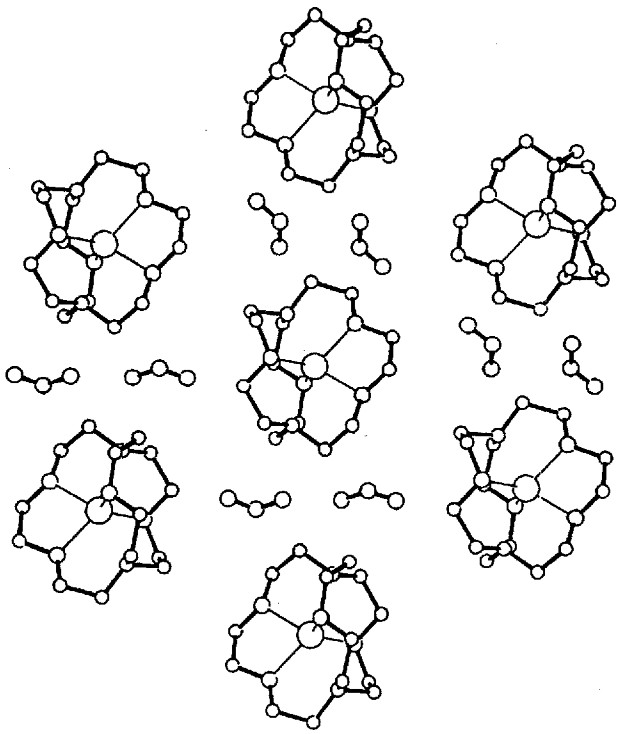


We did not try to reproduce the ozonisation reaction, but rather used the ion exchange route to arrive at concentrated solutions of LiO_3 in liquid ammonia starting from Li^+-loaded resin and CsO_3. The solutions were of the same aspect and the same concentration (ca. 0.1 $moll^{-1}$) as those of NaO_3. Upon removal of the solvent at 213 K, a red solid precipitated; it was extremely unstable and decomposed even at this low temperature with evolution of gases to give a white powder. The X-ray diffractogram showed this powder to be amorphous, but after annealing at 423 K for 1 d, the lines of LiOH (JCPDS 32-564) appeared. Thus, the decomposition by oxidation of NH_3 to elemental nitrogen, which we formulated for the solutions of NaO_3, also applies to LiO_3. No evidence for the formation of NO_2^- and NO_3^-, which were reported as decomposition products by Solomon et al.[8], was detected by Raman spectroscopy or in the X-ray powder pattern.

In analogy to the treatment of the solutions of NaO_3, we proceeded to complex the compound by using an appropriate ligand for Li^+. The cryptand that best fits the Li^+ ion is the [2.1.1] cryptand[12]. Accordingly, we obtained $(Li[2.1.1])O_3$ after removal of ammonia; the product crystals again seemed to incorporate ammonia. Subsequent recrystallisation from methylamine gave red, transparent crystals, which were very unstable and tended to decompose violently even at temperatures below 273 K.

The crystal structure again shows a close packing of the Li^+-ligand complexes reminiscent of a cubic close packing; the relatively small ozonide anion is completely isolated in interstitial sites (Figure 2). The anion is surrounded by six neighbouring complexes (distance of the central oxygen atom of O_3^- to Li between 5.49 and 6.71 Å). It has an average O–O bond length of 1.23 Å, which is a bit short if compared to previous data from other ozonides[9] but consistent with the well-known apparent shortening of bonds due to large atomic displacement parameters. The bond angle is 121°. The structure of the complex between Li^+ and cryptand [2.1.1] is very similar to that of the complex in (Li[2.1.1])I[13], the only other crystal structure reported so far for this combination. The cryptand adopts the endo-endo conformation; Li^+ is coordinated by four short Li–O and two slightly longer Li–N contacts. It should be mentioned that the overall packing of the molecular ions in the structure of (Li[2.1.1])I shows no similarity to that of $(Li[2.1.1])O_3$.

Figure 2. A projection of a section of the close packed plane of $Li[2.1.1]^+$ in $(Li[2.1.1])O_3$. The ozonide anions are situated in interstitial sites below and above the plane



Discussion

Obviously, the properties of the ozonides of lithium and sodium differ markedly from those of the ozonides of the heavier alkali metals. Two important questions need to be addressed: why does the ozonisation reaction fail in the case of sodium ozonide, and if ozonides of the lighter alkali metals are produced by a circumventive route in liquid ammonia, why does an oxidation of ammonia take place upon precipitation of the products?

A plausible answer to the first question makes use of the known or estimated thermodynamical data of the ozonisation process. This process may be described as the transfer of a monooxygen diradical •O• from ozone to the hyperoxide anion O_2^-. The necessary separation of ozone into the dioxygen molecule and this radical is endothermic ($O_3 \rightarrow O_2 + {}^\bullet O^\bullet$ $\Delta H = 107$ kJ · mol^{-1}[14]), which explains our observation that a minimum temperature (ca. 5 °C) is needed to start the ozonisation reaction. On the other hand, ozonides are metastable compounds, and the thermal stability of the alkali metal ozonides decreases with decreasing size of the cation[1]. This conflict, which is further aggravated by the fact that the ozonisation reaction itself is exothermic[15], may be resolved in the case of potassium ozonide by precise temperature control. Sodium ozonide, however, which has a smaller cation and is consequently less stable, seems to have a decomposition temperature that is below the temperature necessary to start the dissociation of ozone. Thus, we have the unfortunate situation that the decomposition temperature of solid NaO_3 lies below its potential temperature of formation.

An answer to the second question concerning the reason for the oxidation reaction with ammonia may be derived from the hypothesis of Solomon et al.[8], who suggest that lithium ozonide precipitates from liquid ammonia as the ammine $[Li(NH_3)_4]O_3$. Given the well-known occurrence of $Li(NH_3)_4^+$ in solutions of lithium salts in liquid ammonia[16], this hypothesis is plausible. The bonding between lithium and ammonia in this tetraammine complex is stronger than that in the ammines of the remaining alkali metals, a fact which is demonstrated by the symmetric stretching vibration of the complex in solution (Raman spectroscopy, $\nu_{sym} = 249$ cm^{-1}; the analogous frequencies of the ammines of K^+, Rb^+ and Cs^+ are far smaller[17]). The bonding interaction makes the ammonia molecules of the first ligand sphere susceptible to an oxidative attack by the ozonide, which occurs only when the solvent separating the complex and the anion in solution is removed upon precipitation. This "activation" of ammonia by ion-dipole interaction seems to be a necessary precondition for this oxidation reaction, since solid ozonides were prepared in which free ammonia molecules (that is, not bonded to a metal ion) of solvation are in close contact to the ozonide anion[18]. The same explanation probably holds true for the decomposition of NaO_3 upon precipitation from solution. While ammines of Na^+ were detected[16], none were as stable or as well characterised as $Li(NH_3)_4^+$, which may account for our observation that no red solid formed in this case at all. Still, the formation energy for ammine complexes of Li^+ and Na^+ seems to be favourable enough to prevent the precipitation of the pure binary ozonides from solutions in liquid ammonia. In contrast, K^+, Rb^+ and Cs^+ have a lower tendency to form ammines, which permits the recrystallistion of the binary compounds.

Consequently, our failure to produce solid LiO_3 or NaO_3 by cation exchange does not mean that these compounds do not exist, but only that they may not be obtained from solutions of liquid ammonia. A different solvent, which is less oxidisable and less prone to form complexes with cations, may still lead to the binary compounds. Our own first attempt to prevent the oxidation of ammonia and to prepare the first derivatives of LiO_3 and NaO_3 was considerably more drastic, since we exchanged the ammonia solvent sphere for cryptands, which are less susceptible to oxidation. Unfortunately, they also form much more stable complexes; thus it is impossible to regain the binary ozonides from them.

The crystallisation of metal ozonides as ammines is a more general problem that affects solutions of the ozonides of Ba^{2+}, Sr^{2+}[19] and Ag^{+}[20] in liquid ammonia as well. All of these ozonides may be easily prepared from CsO_3 by ion exchange in liquid ammonia, but all of them decompose by oxidation of the solvent upon removal of the solvent.

Experimental

All manipulations were carried out under dry argon in all-glass reaction and handling vessels that were dried in vacuo. Ammonia (Bayer AG) was made anhydrous by distilling it first from sodium, then from potassium; it was stored as a potassium-ammonia solution at 195 K. CsO_3 was produced according to the procedure given in the literature[21]. The ion exchange resin (Amberlyst 15) was purchased in its acidic form, loaded in water by reaction with LiOH and NaOH, respectively, dried according to ref. 9 and stored under argon. Cryptand [2.2.2] (4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosan) and Cryptand [2.1.1] (4,7,13,16-Tetraoxa-1,10-diazabicyclo-[8.5.5]eicosan) (both from Merck) were purified by sublimation and stored under argon. Methylamine was made anhydrous by distilling it from a mixture of potassium and 18-crown-6 (molar ratio 1:1). Elemental analyses were performed by Pascher Microanalytical Laboratory, Remagen, Germany. The Raman spectra were recorded with a Coderg LRT 800 using a Spectra Physics Ar^+ laser. DTA/TG measurements were performed with Netzsch STA 429. Powder patterns were obtained on a Stoe STADI P diffractometer.

General Procedure for the Preparation of Solutions of LiO_3 and NaO_3: Into an H-shaped reaction vessel, fitted with a glass frit (porosity 3) separating the two arms, 0.1 g ($5.5 \cdot 10^{-4}$ mol) of CsO_3 and 2 g (corresponding to ca. $9.2 \cdot 10^{-3}$ mol of Li^+ or Na^+ on the exchange resin, the maximal capacity of the resin was $4.6 \cdot 10^{-3}$ mol g^{-1}) of the loaded resin were placed into the same arm while the vessel was cooled to 195 K. Approximately 30 ml of ammonia was frozen in the same arm of the vessel at 77 K. The mixture was allowed to warm to 195 K. The equilibration was finished after 2 h, and the dark red solution was separated from the resin by pouring it through the cooled glass frit. The resulting solutions of NaO_3 and LiO_3 may be stored without apparent change for several days at 230 K.

General Procedure for the Preparation of $(Li[2.1.1])O_3$ and $(Na[2.2.2])O_3$:

WARNING! These ozonides are violently explosive.

The procedure is the same as that described above, except that now an equimolar amount of cryptand was placed into the opposite arm of the reaction vessel ($5.5 \cdot 10^{-4}$ mol, 0.158 g for [2.1.1] and 0.207 g for [2.2.2]). After the equilibration, the ozonide solution was poured through the frit onto the cryptand. The complexation took place at 233 K. Cryptand [2.2.2] dissolved within 30 min, while [2.1.1] (combined with the solution of LiO_3) took 6 h to dissolve completely. The solvent was removed by distillation in vacuo, while the temperature of the reaction vessel was kept below 220 K. Red, non-transparent hexagonal rods of $(Na[2.2.2])O_3$ and needles of $(Li[2.1.1])O_3$ remained, respectively. The product was placed into a Schlenk-type vessel with cooling and recrystallised from anhydrous methylamine. Transparent crystals shaped like blocks resulted for both $(Li[2.1.1])O_3$ and $(Na[2.2.2])O_3$. The products were stored in sealed glass ampoules under argon at 77 K. $C_{18}H_{36}O_9N_2Na$ (447.49): calcd. C 48.30, H 8.11, N 6.26, Na 5.14; found C 47.63, H 8.11, N 6.30, Na 5.42. Due to the thermal instability of $(Li[2.1.1])O_3$, no elemental analysis could be performed for this compound. Suitable single crystals for the X-ray structure analysis were selected in a stream of cooled nitrogen and wedged into Lindemann glass capillaries.

Crystal Data and Structure Refinement for $(Li[2.1.1])O_3$[22]: $C_{14}H_{28}LiN_2O_7$, $M = 343.32$, red blocks, crystal size ca. $0.3 \cdot 0.2 \cdot 0.2$ mm³, monoclinic, space group $P2_1/c$ (Nr. 14), $a = 12.977(5)$, $b = 8.744(2)$, $c = 16.625(7)$ Å, $\beta = 112.12(2)°$, $V = 1747(1)$ Å³, $Z = 4$, $D_c = 1.305$ g · cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 0.102$ mm^{-1}, $F(000) = 740$ electr. No. of measured reflections 3062, no. of independent reflections 2415 ($R_{int} = 0.049$), no. of observed reflections with $I > 2\sigma(I)$ 1420, no. of parameters 218. The lattice parameters were determined by a CAD4 indexing programme and refined by a least-squares routine with the angular settings of 25 reflections ($12° < \Theta < 15°$). Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) at 213(2) K to $\Theta_{max} = 23°$ by using ω-BPB scans. Three intensity control reflections were measured every hour, showing a total decay of 30% during 52 h. Intensity data were corrected for linear isotropic decay, Lorentz and polarisation effects. The structure was solved by direct methods (SHELXS-86[23]) and refined on F^2 using all 2415 independent reflections (SHELXL-93[24]). The hydrogen atoms were inserted at calculated positions and not refined. All other atoms were refined anisotropically. The final wR_2 value was 0.196 [corresponding to a conventional R value of 0.073 by using only reflections with $I > 2\sigma(I)$]. The largest peak and hole in the final difference Fourier map were 0.31 and -0.37 eÅ^{-3} respectively.

Crystal Data and Structure Refinement for $(Na[2.2.2])O_3$[22]: $C_{18}H_{36}N_2NaO_9$, $M = 447.49$, red blocks, crystal size ca. $0.2 \cdot 0.1 \cdot 0.1$ mm³, monoclinic, space group $P2_1$ (Nr. 4), $a = 15.617(9)$, $b = 10.326(4)$, $c = 15.392(8)$ Å, $\beta = 116.09(2)°$, $V = 2229(2)$ Å³, $Z = 4$, $D_c = 1.333$ g · cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 0.121$ mm^{-1}, $F(000) = 964$ electr. No. of measured reflections 4435, no. of independent reflections 4256 ($R_{int} = 0.024$), no of observed reflections with $I > 2\sigma(I)$ 2330, no. of parameters 537. The lattice parameters were determined by a CAD4 indexing programme and refined by a least-squares routine with the angular settings of 25 reflections ($11° < \Theta < 13°$). Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) at 213(2) K to $\Theta_{max} = 25°$ by using ω-BPB scans. Three intensity control reflections were measured every hour, showing a total decay of 38% during 62 h. Intensity data were corrected for linear isotropic decay, Lorentz and polarisation effects. The structure was solved by direct methods (SHELXS-86[23]) and refined on F^2 using all 4256 independent reflections (SHELXL-93[24]). The hydrogen atoms were inserted at calculated positions and not refined. All other atoms were refined anisotropically. The final wR_2 value was 0.16 [corresponding to a conventional R value of 0.055 by using only reflections with $I > 2\sigma(I)$]. The largest peak and hole in the final difference Fourier map were 0.45 and -0.35 eÅ^{-3} respectively.

---

[*] Dedicated to Professor *H. G. von Schnering* on the occasion of his 65th birthday.

[1] W. Hesse, M. Jansen, W. Schnick, *Prog. Solid State Chem.* **1990**, *19*, 47.

[2] W. Schnick, M. Jansen, *Rev. Chim. Miner.* **1987**, *24*, 446.

[3] First mentioned by C. A. Wurtz, *Dictionnaire de Chimie pure et appliqué* **1868**, *Vol. II*, 721.

[4] W. Hesse, M. Jansen, *Inorg. Chem.* **1991**, *30*, 4380.

[5] N. Korber, M. Jansen, *J. Chem. Soc., Chem. Commun.* **1990**, 1654.

[6] T. P. Whaley, J. Kleinberg, *J. Am. Chem. Soc.* **1951**, *73*, 79; H. D. McLachlan, M. C. R. Symons, M. U. Townsend, *J. Chem.*

Soc. **1959**, 952; I. J. Solomon, H. J. Kacmarek, *J. Phys. Chem.* **1960**, *64*, 168; S. A. Tokareva, M. S. Dobrolynbova, *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1964**, *4*, 734; I. A. Kazarnovskii, G. P. Nilol'skii, *Dokl. Akad. Nauk. SSSR* **1949**, *64*, 69.

[7] I. I. Vol'nov, A. W. Petrocelli in *Peroxides, Superoxides and Ozonides of Alkali and Alkaline Earth Metals* (Ed. A. W. Petrocelli), Plenum Press, New York, **1966**, chapter 4; I. I. Vol'nov, S. A. Tokareva,V. N. Belevskii, V. I. Klimanov, G. P. Pilipenko, *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1972**, *6*, 1235; I. I. Vol'nov, S. A. Tokareva, G. P. Pilipenko, V. I. Klimanov, V. N. Belevskii, *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1973**, *9*, 2138; I. I. Vol'nov, S. A. Tokareva, V. N. Belevskii, E. I. Latyskeva, V. I. Klimanov, G. P. Pilipenko, *Neorg. Perekisnye Soedin. Dokl. Vses. Soveshch*, Meeting Date **1973** (Pub. **1975**), 110.

[8] A. J. Kacmarek, J. M. McDonough, I. J. Solomon, *Inorg. Chem.* **1962**, *1*, 659.

[9] N. Korber, M. Jansen, *Chem. Ber.* **1992**, *125*, 1383.

[10] A. M. Phipps, D. N. Hume, *Anal. Chem.* **1967**, *39* (14), 1755.

[11] M. Bösch, W. Känzig, *Helv. Phys. Acta* **1975**, *48*, 743.

[12] J.-M. Lehn, M. R. Truter, *Structure and Bonding* **1973**, *16*, 46.

[13] D. Moras, R. Weiss, *Acta Crystallogr.* **1973**, *B29*, 400.

[14] W. Schnick, M. Jansen, Thesis W. Schnick, Hannover **1986**.

[15] G. P. Nikol'skii, Z. A. Bagdasar'yan, I. A. Kazarnovskii, *Dokl. Akad. Nauk. SSSR* **1951**, *77*, 67.

[16] G. Jander, H. Spandau, C. C. Addison, *Anorganische und Allgemeine Chemie in flüssigem Ammoniak,* Friedrich Vieweg und Sohn, Braunschweig, **1966**.

[17] P. Gans, J. B. Bill, *J. Chem. Soc. Dalton Trans.* **1976**, 779.

[18] H. Seyeda, M. Jansen, *Chem. Ber.*, submitted.

[19] W. Assenmacher, M. Jansen, Thesis W. Assenmacher, Bonn **1994**.

[20] N. Korber, M. Jansen, Thesis N. Korber, Bonn **1992**.

[21] M. Jansen, W. Hesse, *Z. Anorg. Allg. Chem.* **1988**, *560*, 47.

[22] Further details of the crystal structure determinations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-404871 ((Na[2.2.2])O_3) and -404870 ((Li[2.1.1])O_3), the names of the authors, and the journal citation.

[23] G. M. Sheldrick, *SHELXS-86, Program for Crystal Structure Determination, University of Göttingen*, **1986**.

[24] G. M. Sheldrick, *SHELXL-93, Program for the Refinement of Structures, University of Göttingen*, **1993**.

[96042]