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A novel access to ionic superoxides and the first accurate determination of the bond distance in O_2^-

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The compound $[C_6H_4(NMe_3)_2\text{-}1,3][O_2]_2\cdot 3NH_3$ was prepared from $[NMe_4][O_2]$ *via* cation-exchange in liquid ammonia; the bond length of the superoxide anion was determined by X-ray crystallographic analysis to be 134(3) pm.

Among the solids supposed to contain isolated superoxide anions only the alkali-metal superoxides MO_2 (M = Na, K, Rb and Cs)[1] and $[NMe_4][O_2]$[2] have been unambiguously confirmed with respect to their identity. Though having been investigated thoroughly using X-ray or neutron diffraction studies no reliable O–O bond distance could be determined. The values reported so far, range from 119 pm (CsO_2 in phase 2)[3] through 128 pm (α-KO_2),[4] 132 pm (NaO_2 in phase 4) and 137 pm (NaO_2 in phase 1).[3] This wide spread of bond lengths lacks any physical or chemical meaning and seems to be an artefact caused by crystallographic problems resulting from dynamic or, at low temperatures, static disorder[5,6] of the superoxide ion.

In this paper we report on the use of bulky, non-spherical cations in order to force the O_2^- group into an ordered position. As most complex cations or at least their side chains are oxidizable, all high-temperature routes for the synthesis of the respective superoxides are not viable. Cation-exchange in liquid ammonia[7] has been developed as a versatile and efficient route to ionic superoxides containing the bulky cations mentioned. Starting with $[NMe_4][O_2]$, which is the only superoxide known to readily dissolve in liquid ammonia, we have succeeded in synthesising a number of superoxides with quaternary and bis(quaternary) ammonium counter ions. The compound $[C_6H_4(NMe_3)_2\text{-}1,3][O_2]_2\cdot 3NH_3$ **1** was obtained by treating a solution of $[NMe_4][O_2]$ with an approximately 20-fold excess of the dication of 1,3-bis(trimethylammonium)benzene, loaded onto a thoroughly dried cation exchange resin, under diffusion control. This yielded large, pale yellow crystals of compound **1**.‡ Applying an inert oil matrix to select and mount the crystals, a single-crystal structure analysis of the compound was performed.§ Two crystallographically independent superoxide anions were observed in this structure showing bond lengths of 133.5(3) pm [O(1)–O(2)] and 134.5(3) pm [O(3)–O(4)], respectively, which are equal within the limits of experimental error (three times the estimated standard deviation). They are in good agreement with the bond length proposed for NaO_2 in phase 4.[3] The O_2^- group is held in a fixed position by N–H · · · O hydrogen bonds from the solvent ammonia molecules as well as C–H · · · O hydrogen bonds of the cation (see

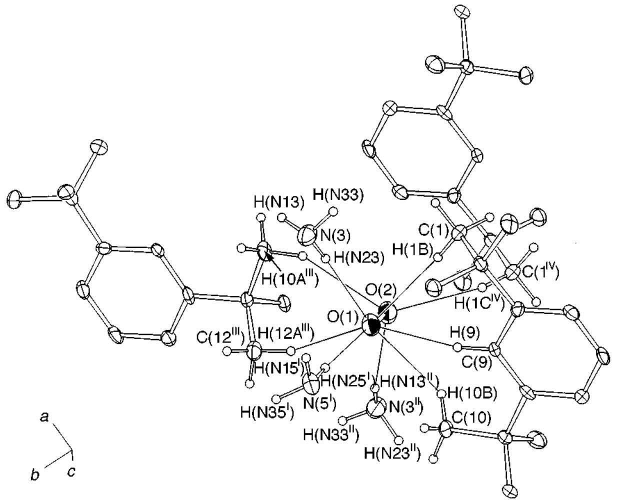

Fig. 1 An ORTEP[10] plot of the chemical environment of the superoxide anion O(1)–O(2) (50% probability ellipsoids). Possible hydrogen bonds are marked by thin lines. Selected interatomic distances (pm) and angles (°): O(1)–O(2) 133.5(3), O(1)–HN(23) 219(5), O(1)–N(3) 312.9(4), O(1)–H(1B) 241.3(8), O(1)–C(1) 334.2(4), O(1)–H(9) 233.3(4), O(1)–C(9) 327.1(4), O(1)–H(10B) 263(2), O(1)–C(10) 316.9(4), O(1)–HN(25^{I}) 230(5), O(1)–N(5^{I}) 313.3(4), O(1)–H($12A^{III}$) 250(1), O(1)–C(12^{III}) 335.6(4), O(2)–H($10A^{III}$) 250(1), O(2)–C(10^{III}) 339.3(4), O(2)–H($1C^{IV}$) 241(2), O(2)–C(1^{IV}) 331.0(4), O(2)–HN(13^{II}) 241(2), O(2)–N(3^{II}) 322.9(4); O(1)–HN(23)–N(3) 163(3), O(1)–H(1B)–C(1) 158(1), O(1)–H(9)–C(9) 169.29(9), O(1)–H(10B)–C(10) 115(1), O(1)–HN(25^{I})–N(5^{I}) 164(4), O(1)–H($12A^{III}$)–C(12^{III}) 162.4(5), O(2)–H($10A^{III}$)–C(10^{III}) 150.9(4), O(2)–H($1C^{IV}$)–C(1^{IV}) 152.1(4), O(2)–HN(13^{II})–N(3^{II}) 159(4). Symmetry operators used to generate equivalent atoms: I x, $y + 1$, z; II $x - 0.5$, $-y + 1.5$, $-z$; III $x + 0.5$, $-y + 1.5$, $-z$; IV $-x$, $-y + 1$, $-z$

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‡ Preparation of $[C_6H_4(NMe_3)_2\text{-}1,3][O_2]_2\cdot 3NH_3$: ion-exchange resin (1.5 g) loaded with the dication of 1,3-bis(trimethylammonium)benzene was placed in one side of a U-shaped vessel equipped with a glass sieve (porosity 3) at the lowest position. The compound $[NMe_4][O_2]$ (*ca.* 150 mg, *ca.* 1.4×10^{-3} mol), prepared by a method described elsewhere,[2] was placed in the other side of the vessel. After cooling (ethanol–dry ice), ammonia was condensed into the vessel until the glass sieve was completely covered. The reaction mixture was stored at 230 K, and allowed to react by slow diffusion for ten days. The precipitated air- and moisture-sensitive pale yellow crystals were removed from the liquid ammonia, transferred into an inert oil mixture (3:1 perfluorpolyether RS3000, Riedel de Haën–perfluorpolyether 216, Riedel de Haën) which was cooled with a nitrogen stream to 233 K, and picked up using a glass capillary.

§ Crystal data for compound **1**: $C_{12}H_{22}N_2O_4\cdot 3NH_3$, $M = 309.42$, pale yellow prisms, orthorhombic, space group *Pbca* (no. 61), $a = 1116.7(1)$, $b = 1566.3(2)$, $c = 1933.9(3)$ pm, $U = 3382.6(7) \times 10^6$ pm^3, $D_c = 1.215$ g cm^{-3}, $Z = 8$, μ(Mo-Kα) = 0.091 mm^{-1}, no. of measured reflections 6273, no. of independent reflections 2978, no. of observed reflections with $(I) > 2\sigma(I)$ 1950, no. of parameters 232. Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 71.073 pm) at 113(2) K with ω–θ scans to $\theta_{max} = 25°$. The structure was solved by direct methods and refined by full-matrix least-squares analysis on F^2.[8,9] The hydrogen atoms of the ammonia molecules were located by Fourier-difference synthesis and refined with isotropic atomic displacement parameters; $wR2 = 0.1373$ for all reflections, $R1 = 0.0593$ for 1950 reflections. CCDC reference number 186/895.

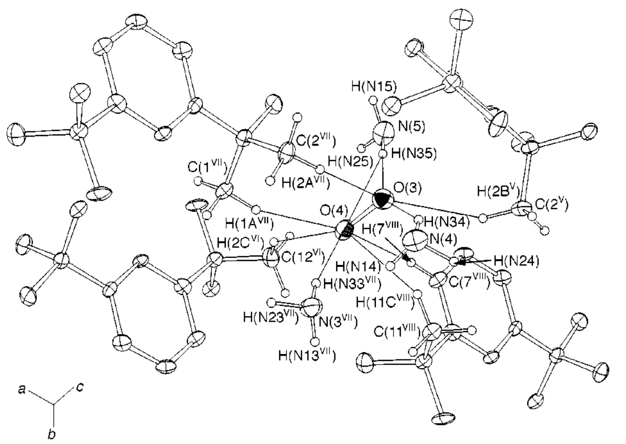

Fig. 2 An ORTEP plot of the chemical environment of the superoxide anion O(3)–O(4) (50% probability ellipsoids). Possible hydrogen bonds are marked by thin lines. Selected interatomic distances (pm) and angles (°): O(3)–O(4) 134.5(3), O(3)–HN(34) 264(5), O(3)–N(4) 336.4(4), O(3)–HN(35) 222(7), O(3)–N(5) 319.9(4), O(3)–H(2B^{V}) 247(2), O(3)–C(2^{V}) 338.9(4), O(3)–H(2A^{VII}) 245(2), O(3)–C(2^{VII}) 339.0(4), O(4)–HN(35) 248(7), O(4)–N(5), 339.6(4), O(4)–H(12C^{VI}) 245.5(6), O(4)–C(12^{VI}) 324.9(4), O(4)–HN(33^{VII}) 231(5), O(4)–N(3^{VII}) 319.5(4), O(4)–H(1A^{VII}) 232(2), O(4)–C(1^{VII}) 326.2(4), O(4)–H(11C^{VIII}) 250(2), O(4)–C(11^{VIII}) 338.4(4), O(4)–H(7^{VIII}) 229.0(4), O(4)–C(7^{VIII}) 323.4(4); O(3)–HN(34)–N(4) 149(4), O(3)–HN(35)–N(5) 173(5), O(3)–H(2B^{V})–C(2^{V}) 156.1(7), O(3)–H(2A^{VII})–C(2^{VII}) 160.9(3), O(4)–HN(35)–N(5) 155(5), O(4)–H(12C^{VI})–C(12^{VI}) 138.0(8), O(4)–HN(33^{VII})–N(3^{VII}) 166(4), O(4)–H(1A^{VII})–C(1^{VII}) 160.1(4), O(4)–H(11C^{VIII})–C(11^{VIII}) 150.7(9), O(4)–H(7^{VIII})–C(7^{VIII}) 172.3(1). Symmetry operators used to generate equivalent atoms: V $-x, y - 0.5, -z + 0.5$; VI $x + 0.5, -y + 0.5, -z$; VII $-x + 0.5, y - 0.5, z$; VIII $-x - 0.5, y - 0.5, z$

Figs. 1 and 2). The N···O distances range from 312.9 to 339.6 pm and the N–H···O angles from 148.58 to 172.78°; the C···O distances from 316.9 to 339.3 pm and the C–H···O angles from 114.97 to 172.25°. These geometries of the hydrogen bonds allow them to be classified as being extremely weak.[11,12]

The ion-exchange technique in liquid ammonia opens up a feasible and general route to the synthesis of new superoxides with various counter ions, and offers the opportunity to settle the discrepancies concerning the geometry of the superoxide anion in the solid state. Decreasing the charge of the diatomic species from O_2^+ to O_2^{2-} step-by-step, the O–O distance continuously increases from 112 (O_2^+) through 121 (O_2) and 134 pm (O_2^-) to 149 pm (O_2^{2-}),[13] and the bond distance of O_2^- determined in this work fits well into the observed trend.

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