

### 11.3.7 Oxoacids, oxoanions and oxoacid salts of nitrogen

Nitrogen forms numerous oxoacids, though several are unstable in the free state and are known only in aqueous solution or as their salts. The principal species are summarized in Table 11.12; of these by far the most stable is nitric acid and this compound, together with

its salts the nitrates, are major products of the chemical industry (p. 466).

#### Hyponitrous acid and hyponitrites<sup>(131)</sup>

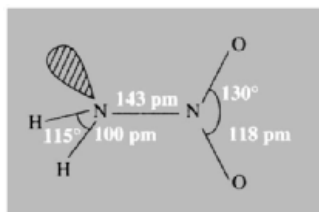
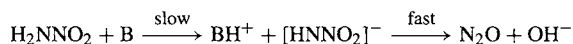
Hyponitrous acid crystallizes from ether solutions as colourless crystals which readily decompose

<sup>131</sup> M. N. HUGHES, *Q. Rev.* **22**, 1–13 (1968).

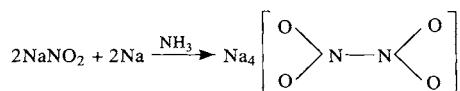
**Table 11.12** Oxoacids of nitrogen and related species

Formula	Name	Remarks
H <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	Hyponitrous acid	Weak acid HON=NOH, isomeric with nitramide, H <sub>2</sub> N–NO <sub>2</sub> ; <sup>(a)</sup> salts are known (p. 460)
{HNO}	Nitroxyl	Reactive intermediate (p. 461), salts are known (see also p. 453).
H <sub>2</sub> N <sub>2</sub> O <sub>3</sub>	Hyponitric acid [trioxodinitric(II) acid]	Known in solution and as salts, e.g. Angeli's salt Na <sub>2</sub> [ON=NO <sub>2</sub> ] (p. 460)
H <sub>4</sub> N <sub>2</sub> O <sub>4</sub>	Nitroxylic (hydronitrous) acid	Explosive; sodium salt known Na <sub>4</sub> [O <sub>2</sub> NNO <sub>2</sub> ] <sup>(b)</sup>
HNO <sub>2</sub>	Nitrous acid	Unstable weak acid, HONO (p. 461); stable salts (nitrites) are known
HOONO	Peroxonitrous acid	Unstable, isomeric with nitric acid; some salts are more stable <sup>(c)</sup>
HNO <sub>3</sub>	Nitric acid	Stable strong acid HONO <sub>2</sub> ; many stable salts (nitrates) are known (p. 465)
HNO <sub>4</sub>	Peroxonitric acid	Unstable, explosive crystals, HOONO <sub>2</sub> ; no solid salts known. (For "orthonitrates", NO <sub>4</sub> <sup>3-</sup> , i.e. salts of the unknown orthonitric acid H <sub>3</sub> NO <sub>4</sub> , see p. 471–2)

<sup>(a)</sup>The structure of nitramide is as shown, the dihedral angle between NH<sub>2</sub> and NNO<sub>2</sub> is 52°. Nitramide is a weak acid pK<sub>1</sub> 6.6 (K<sub>1</sub> 2.6 × 10<sup>-7</sup>) and it decomposes into N<sub>2</sub>O and H<sub>2</sub>O by a base-catalysed mechanism:

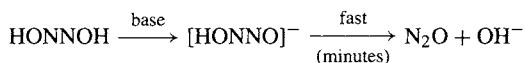


<sup>(b)</sup>Sodium nitroxylate can be prepared as a yellow solid by reduction of sodium nitrite with Na/NH<sub>3</sub>(liq.):



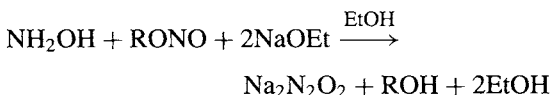
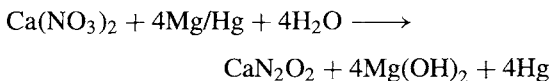
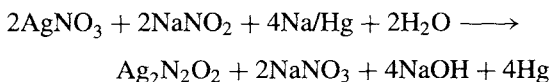
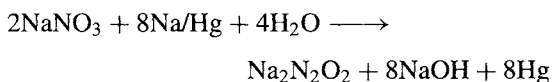
<sup>(c)</sup>Peroxonitrous acid is formed as an unstable intermediate during the oxidation of acidified aqueous solutions of nitrites to nitrates using H<sub>2</sub>O<sub>2</sub>; such solutions are orange-red and are more highly oxidizing than either H<sub>2</sub>O<sub>2</sub> or HNO<sub>3</sub> alone (e.g. they liberate Br<sub>2</sub> from Br<sup>-</sup>). Alkaline solutions are more stable but the yellow peroxonitrites M[OONO] have not been isolated pure. The chemistry of peroxonitrites has recently been reviewed J. O. EDWARDS and R. C. PLUMB, in K. D. KARLIN (ed). *Progr. Inorg. Chem.* **41**, 599–635 (1994).

(explosively when heated). Its structure has not been determined but the molecular weight indicates a double formula  $\text{H}_2\text{N}_2\text{O}_2$ , i.e.  $\text{HON}=\text{NOH}$ ; consistent with this the compound yields  $\text{N}_2\text{O}$  when decomposed by  $\text{H}_2\text{SO}_4$ , and hydrazine when reduced. The free acid is obtained by treating  $\text{Ag}_2\text{N}_2\text{O}_2$  with anhydrous  $\text{HCl}$  in ethereal solution. It is a weak dibasic acid:  $\text{p}K_1$  6.9,  $\text{p}K_2$  11.6. Aqueous solutions are unstable between pH 4–14 due to base catalysed decomposition via the hydrogen-hyponitrite ion:



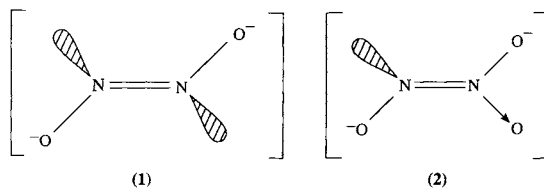
At higher acidities (lower pH) decomposition is slower ( $t_{1/2}$  days or weeks) and the pathways are more complex. The stoichiometry, kinetics and mechanisms of several other reactions of  $\text{H}_2\text{N}_2\text{O}_2$  with, for example,  $\text{NO}$  and with  $\text{HNO}_2$  have also been studied.<sup>(132)</sup>

Hyponitrites can be prepared in variable (low) yields by several routes of which the commonest are reduction of aqueous nitrite solutions using sodium (or magnesium) amalgam, and condensation of organic nitrites with hydroxylamine in  $\text{NaOEt}/\text{EtOH}$ :

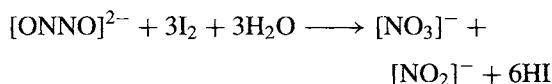


Vibrational spectroscopy indicates that the hyponitrite ion has the *trans*- ( $C_{2h}$ ) configuration (1) in the above salts.

As implied by the preparative methods employed, hyponitrites are usually stable towards

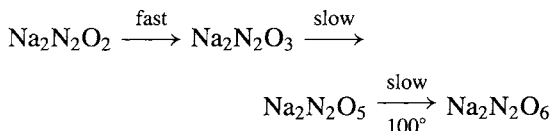


reducing agents though under some conditions they can be reduced (p. 434). More frequently they themselves act as reducing agents and are thereby oxidized, e.g. the analytically useful reaction with iodine:



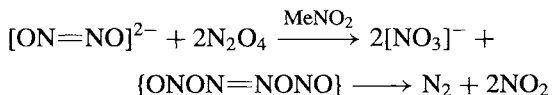
There is also considerable current environmental interest in hyponitrite oxidation because it is implicated in the oxidation of ammonia to nitrite, an important step in the nitrogen cycle (p. 410). Specifically, it seems likely that the oxidation proceeds from ammonia through hydroxylamine and hyponitrous acid to nitrite (or  $\text{N}_2\text{O}$ ).

With liquid  $\text{N}_2\text{O}_4$  stepwise oxidation of hyponitrites occurs to give  $\text{Na}_2\text{N}_2\text{O}_x$  ( $x = 3-6$ ):



Angeli's salt  $\text{Na}_2\text{N}_2\text{O}_3$  has been shown by vibration spectroscopy to contain the trioxodinitrate(II) anion structure (2). Its decomposition and reactions in aqueous solutions have been extensively studied by  $^{15}\text{N}$  nmr spectroscopy and other techniques.<sup>(133)</sup>

In contrast to the stepwise oxidation of sodium hyponitrite in liquid  $\text{N}_2\text{O}_4$ , the oxidation goes rapidly to the nitrate ion in an inert solvent of high dielectric constant such as nitromethane:



<sup>132</sup> M. N. HUGHES *et al.*, *Inorg. Chem.* **24**, 1934–5 (1985); *J. Chem. Soc., Dalton Trans.*, 527–32 and 533–7 (1989).

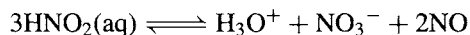
<sup>133</sup> M. J. AKHTAR, C. A. LUTZ and F. T. BONNER, *Inorg. Chem.* **18**, 2369–75 (1979). F. T. BONNER, H. DEGANI and M. J. AKHTAR, *J. Am. Chem. Soc.* **103**, 3739–42 (1981). D. A. BAZYLINSKI and T. C. HOLLOCHER, *Inorg. Chem.* **24**, 4285–8 (1985).

More recently it has been found that the hyponitrite ion can act as a bidentate ligand in either a bridging or a chelating mode. Thus, the controversy about the nature of the black and red isomers of nitrosyl pentammine cobalt(III) complexes has been resolved by X-ray crystallographic studies which show that the black chloride  $[\text{Co}(\text{NH}_3)_5\text{NO}]\text{Cl}_2$  contains a mononuclear octahedral  $\text{Co}^{\text{III}}$  cation with a linear  $\text{Co}-\text{N}-\text{O}$  group whereas the red isomer, in the form of a mixed nitrate-bromide, is dinuclear with a bridging *cis*-hyponitrite- $(\text{N},\text{O})$  group as shown in Fig. 11.15.<sup>(134)</sup> The *cis*-configuration is probably adopted for steric reasons since this is the only configuration that allows the bridging of two  $\{\text{Co}(\text{NH}_3)_5\}$  groups by an ONNO group without steric interference between them. The *cis*-chelating mode  $(\text{O},\text{O})$  was found in the air-sensitive yellow crystalline complex  $[\text{Pt}(\text{O}_2\text{N}_2)(\text{PPh}_3)_2]$  which has already been mentioned on p. 446. The presence of the *cis*-configuration in this complex invites speculation as to whether *cis*- $[\text{ON}-\text{NO}]^{2-}$  can also exist in simple hyponitrites. Likely candidates appear to be the "alkali metal nitrosyls"  $\text{MNO}$  prepared by the action of  $\text{NO}$  on  $\text{Na}/\text{NH}_3$ ; infrared data suggest they are not  $\text{M}^+[\text{NO}]^-$  and might indeed contain the *cis*-hyponitrite ion. They would therefore not be salts

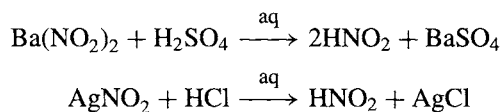
of nitroxyl  $\text{HNO}$  which has often been postulated as an intermediate in reactions which give  $\text{N}_2\text{O}$  and which is well known in the gas phase. Nitroxyl can be prepared by the action of atomic  $\text{H}$  or  $\text{HI}$  on  $\text{NO}$  and decomposes to  $\text{N}_2\text{O}$  and  $\text{H}_2\text{O}$ . As expected, the molecule is bent (angle  $\text{H}-\text{N}=\text{O}$   $109^\circ$ ). See also Fig. 11.14(b), p. 453.

### Nitrous acid and nitrites

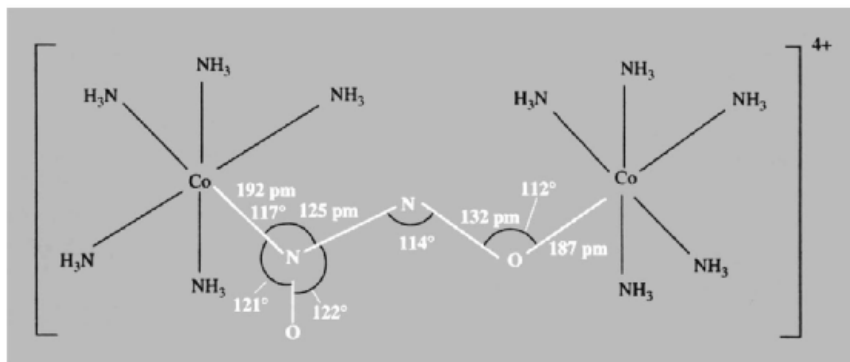
Nitrous acid,  $\text{HNO}_2$ , has not been isolated as a pure compound but it is a well known and important reagent in aqueous solutions and has also been studied as a component in gas-phase equilibria. Solutions of the free acid can readily be obtained by acidification of cooled aqueous nitrite solutions but even at room temperature disproportionation is noticeable:



It is a fairly weak acid with  $\text{p}K_a$  3.35 at  $18^\circ\text{C}$ , i.e. intermediate in strength between acetic (4.75) and chloroacetic (2.85) acids at  $25^\circ$ , and very similar to formic (3.75) and sulfanilic (3.23) acids. Salt-free aqueous solutions can be made by choosing combinations of reagents which give insoluble salts, e.g.:



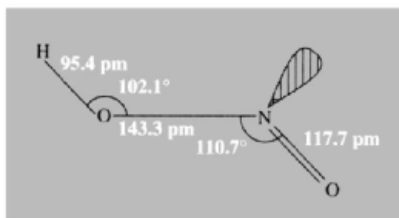
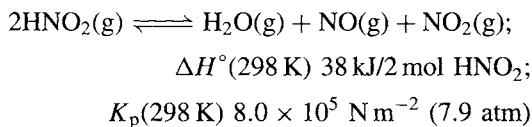
<sup>134</sup> B. F. HOSKINS, F. D. WHILLANS, D. H. DALE and D. C. HODGKIN, *J. Chem. Soc., Chem. Commun.*, 69–70 (1969).



**Figure 11.15** Structure of the dinuclear cation in the red isomer  $[\{\text{Co}(\text{NH}_3)_5\text{NO}\}_2](\text{Br})_{2.5}(\text{NO}_3)_{1.5} \cdot 2\text{H}_2\text{O}$ ; (mean  $\text{Co}-\text{NH}_3$   $194 \pm 2$  pm, mean angle  $90 \pm 4^\circ$ ).

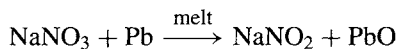
When the presence of salts in solution is unimportant, the more usual procedure is simply to acidify  $\text{NaNO}_2$  with hydrochloric acid below  $0^\circ$ .

In the gas phase, an equilibrium reaction producing  $\text{HNO}_2$  can be established by mixing equimolar amounts of  $\text{H}_2\text{O}$ ,  $\text{NO}$  and  $\text{NO}_2$ :

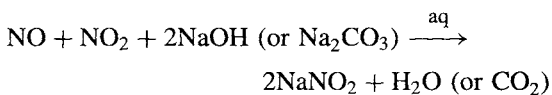


Microwave spectroscopy shows that the gaseous compound is predominantly in the *trans*-planar ( $C_s$ ) configuration with the dimensions shown. The differences between the two N–O distances is notable. Despite the formal single-bond character of the central bond the barrier to rotation is  $45.2 \text{ kJ mol}^{-1}$ . Infrared data suggest that the *trans*-form is  $\sim 2.3 \text{ kJ mol}^{-1}$  more stable ( $\Delta G^\circ$ ) than the *cis*-form at room temperature.

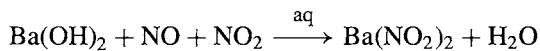
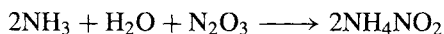
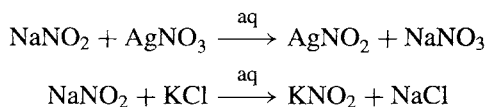
Nitrites are usually obtained by the mild reduction of nitrates, using C, Fe or Pb at moderately elevated temperatures, e.g.:



On the industrial scale, impure  $\text{NaNO}_2$  is made by absorbing “nitrous fumes” in aqueous alkali or carbonate solutions and then recrystallizing the product:

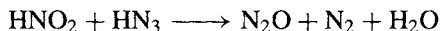
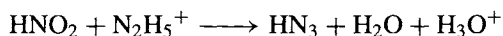


The sparingly soluble  $\text{AgNO}_2$  can be obtained by metathesis, and simple variants yield the other stable nitrites, e.g.:

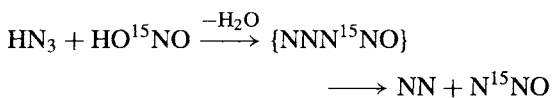


Many stable metal nitrites (Li, Na, K, Cs, Ag,  $\text{Tl}^I$ ,  $\text{NH}_4$ , Ba) contain the bent  $[\text{O}-\text{N}-\text{O}]^-$  anion (p. 413) with N–O in the range 113–123 pm and the angle  $116\text{--}132^\circ$ . Nitrites of less basic metals such as Co(II), Ni(II) and Hg(II) are often highly coloured and are probably essentially covalent assemblages. Solubility (g per 100 g  $\text{H}_2\text{O}$  at  $25^\circ$ ) varies considerably, e.g.  $\text{AgNO}_2$  0.41,  $\text{NaNO}_2$  (hygroscopic) 85.5,  $\text{KNO}_2$  (deliquescent) 314. Thermal stability also varies widely: e.g. the alkali metal nitrites can be fused without decomposition (mp  $\text{NaNO}_2$   $284^\circ$ ,  $\text{KNO}_2$   $441^\circ\text{C}$ ), whereas  $\text{Ba}(\text{NO}_2)_2$  decomposes when heated above  $220^\circ$ ,  $\text{AgNO}_2$  above  $140^\circ$  and  $\text{Hg}(\text{NO}_2)_2$  above  $75^\circ$ . Such trends are a general feature of oxoacid salts (pp. 469, 863, 868).  $\text{NH}_4\text{NO}_2$  can decompose explosively.

The aqueous solution chemistry of nitrous acid and nitrites has been extensively studied. Some reduction potentials involving these species are given in Table 11.4 (p. 434) and these form a useful summary of their redox reactions. Nitrites are quantitatively oxidized to nitrate by permanganate and this reaction is used in titrimetric analysis. Nitrites (and  $\text{HNO}_2$ ) are readily reduced to  $\text{NO}$  and  $\text{N}_2\text{O}$  with  $\text{SO}_2$ , to  $\text{H}_2\text{N}_2\text{O}_2$  with  $\text{Sn}(\text{II})$ , and to  $\text{NH}_3$  with  $\text{H}_2\text{S}$ . Hydrazinium salts yield azides (p. 432) which can then react with further  $\text{HNO}_2$ :

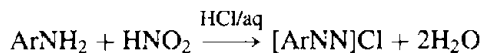


This latter reaction is most unusual in that it simultaneously involves an element (N) in four different oxidation states. Use of  $^{15}\text{N}$ -enriched reagents shows that all the N from  $\text{HNO}_2$  goes quantitatively to the internal N of  $\text{N}_2\text{O}$ .<sup>(135)</sup>

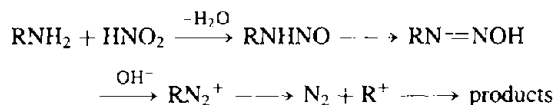


<sup>135</sup> K. CLUSIUS and H. KNOFF, *Chem. Ber.* **89**, 681–5 (1956).

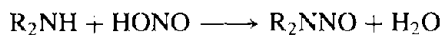
$\text{NaNO}_2$  is mildly toxic (tolerance limit  $\sim 100$  mg/kg body weight per day, i.e. 4–8 g/day for humans).  $\text{NaNO}_2$  (or a precursor such as  $\text{NaNO}_3$ , which is itself harmless) has been much used for curing meat and for treating preserved foods stuffs to prevent bacterial spoilage and consequent poisoning by the (often deadly) toxins produced by *Clostridium botulinum* etc., (normal dietary intake of  $\text{NO}_2^-$  10–15  $\mu\text{g}$  per day).  $\text{NaNO}_2$  is used industrially on a large scale for the synthesis of hydroxylamine (p. 431), and in acid solution for the diazotization of primary aromatic amines:



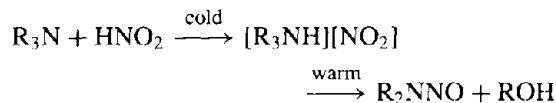
The resulting diazo reagents undergo a wide variety of reactions including those of interest in the manufacture of azo dyes and pharmaceuticals. With primary *aliphatic* amines the course of the reaction is different:  $\text{N}_2$  is quantitatively evolved and alcohols usually result:



The reaction is generally thought to involve carbonium-ion intermediates but several puzzling features remain.<sup>(136)</sup> Secondary aliphatic amines give nitrosamines without evolution of  $\text{N}_2$ :

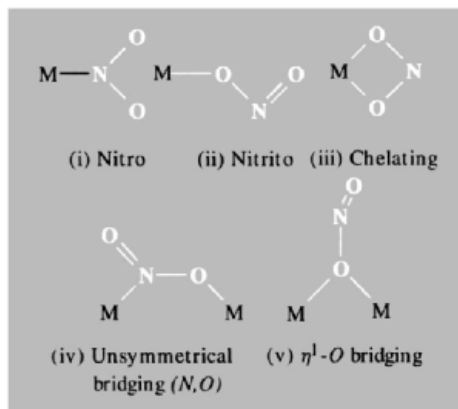


Tertiary aliphatic amines react in the cold to give nitrite salts and these decompose on warming to give nitrosamines and alcohols:



In addition to their general use in synthetic organic chemistry, these various reactions afford the major route for introducing  $^{15}\text{N}$  into organic compounds by use of  $\text{Na}^{15}\text{NO}_2$ .

The nitrite ion,  $\text{NO}_2^-$ , is a versatile ligand and can coordinate in at least five different ways (i)–(v):



Nitro-nitrito isomerism (i), (ii), was discovered by S. M. Jørgensen in 1894–9 and was extensively studied during the classic experiments of A. Werner (p. 912); the isomers usually have quite different colours, e.g.  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$ , yellow, and  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ , red. The nitrito form is usually less stable and tends to isomerize to the nitro form. The change can also be effected by increase in pressure since the nitro form has the higher density. For example application of 20 kbar pressure converts the violet nitrito complex  $[\text{Ni}(\text{en})_2(\text{ONO})_2]$  to the red nitro complex  $[\text{Ni}(\text{en})_2(\text{NO}_2)_2]$  at 126°C, thereby reversing the change from nitro to nitrito which occurs on heating the complex from room temperature at atmospheric pressure.<sup>(137)</sup> An X-ray study of the thermally induced nitrito  $\rightarrow$  nitro isomerization and the photochemically induced nitro  $\rightarrow$  nitrito isomerization of Co(III) complexes has shown that both occur intra-molecularly by rotation of the  $\text{NO}_2$  group in its own plane, probably via a 7-coordinated cobalt intermediate.<sup>(138)</sup> Similarly, the base-catalysed nitrito  $\rightarrow$  nitro isomerization of  $[\text{M}^{\text{III}}(\text{NH}_3)_5(\text{ONO})]^{2+}$  ( $\text{M} = \text{Co}$ ,

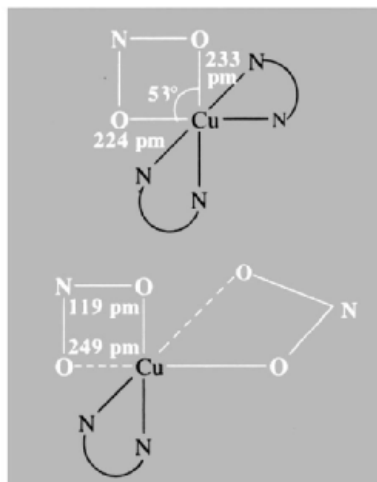
<sup>137</sup> J. R. FERRARO and L. FABBRIZZI, *Inorg. Chim. Acta* **26**, L15–L17 (1978).

<sup>138</sup> I. GRENTHE and E. NORDIN, *Inorg. Chem.* **18**, 1109–16 and 1869–74 (1979).

<sup>136</sup> C. J. COLLINS, *Acc. Chem. Res.* **4**, 315–22 (1971).

Rh, Ir) is intramolecular and occurs without  $^{18}\text{O}$  exchange of the coordinated  $\text{ONO}^-$  with  $\text{H}_2^{18}\text{O}$ ,  $^{18}\text{OH}^-$  or "free"  $\text{N}^{18}\text{O}_2^-$ .<sup>(139)</sup> However, an elegant  $^{17}\text{O}$  nmr study using specifically labelled  $[\text{Co}(\text{NH}_3)_5(^{17}\text{ONO})]^{2+}$  and  $[\text{Co}(\text{NH}_3)_5(\text{ON}^{17}\text{O})]^{2+}$  established that spontaneous intramolecular O-to-O exchange in the nitrite ligand occurs at a rate comparable to that of the spontaneous O-to-N isomerization.<sup>(140)</sup>

A typical value for the N-O distance in nitro complexes is 124 pm whereas in nitrito complexes the terminal N-O (121 pm) is shorter than the internal N-O(M)  $\sim 129$  pm. In the bidentate chelating mode (iii) the 2 M-O distances may be fairly similar as in  $[\text{Cu}(\text{bipy})_2(\text{O}_2\text{N})]\text{NO}_3$  or quite different as in  $[\text{Cu}(\text{bipy})(\text{O}_2\text{N})_2]$ :



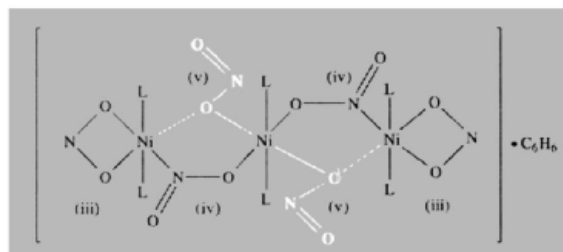
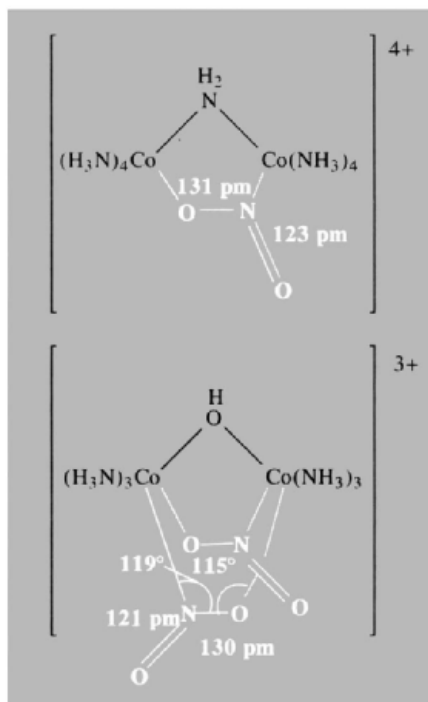
Examples of the unsymmetrical bridging mode (iv) are shown in the top diagram.

The oxygen-bridging mode (v) is less common but occurs together with modes (iii) and (iv) in the following centrosymmetrical trimeric Ni complex and related compounds.<sup>(141)</sup>

<sup>139</sup> W. G. JACKSON, G. A. LAWRENCE, P. A. LAY and A. M. SARGESON, *Inorg. Chem.* **19**, 904-10 (1980).

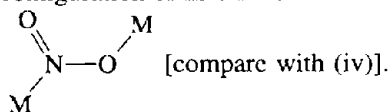
<sup>140</sup> W. G. JACKSON, G. A. LAWRENCE, P. A. LAY and A. M. SARGESON, *J. Chem. Soc., Chem. Commun.*, 70-2 (1982).

<sup>141</sup> D. M. L. GOODGAME, M. A. HITCHMAN, D. F. MARSHAM, P. PHAVANANTHA and D. ROGERS, *Chem. Commun.*, 1383-4 (1969); see also *J. Chem. Soc. A*, 259-64 (1971).



It is possible that a sixth (symmetrical bridging) mode  $\text{M}-\text{O}-\text{N}-\text{O}-\text{M}$  occurs in

some complexes such as  $\text{Rb}_3\text{Ni}(\text{NO}_2)_5$  but this has not definitely been established; an unsymmetrical bridging mode with a *trans*-configuration of metal atoms is also possible, i.e.



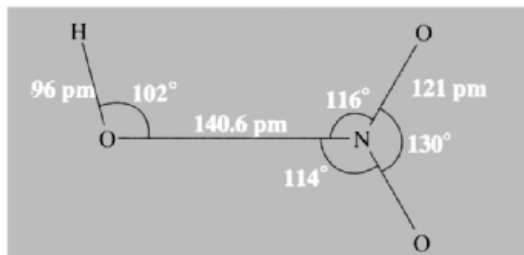
The familiar problem of misleading stoichiometries, and the frequent impossibility of deducing the correct structural formula from the empirical composition is well illustrated by the

recent synthesis of the novel alkali metal oxide nitrites  $\text{Na}_4\text{N}_2\text{O}_5$  (yellow) and  $\text{K}_4\text{N}_2\text{O}_5$  (red).<sup>(142)</sup> These compounds are made by heating powdered mixtures of  $\text{M}_2\text{O}$  and  $\text{MNO}_2$  at  $340^\circ$  for 8 days in a silver crucible and have an anti- $\text{K}_2\text{NiF}_4$  type structure,  $[(\text{NO}_2)_2\text{OM}_4]$ , i.e.  $\text{M}_4\text{O}(\text{NO}_2)_2$ , with N–O 122.1 pm, angle O–N–O  $114.5^\circ$  and octahedrally coordinated  $\text{O}^{2-}$  (i.e.  $\text{OM}_6$  with K–O 260 pm.

### Nitric acid and nitrates

Nitric acid is one of the three major acids of the modern chemical industry and has been known as a corrosive solvent for metals since alchemical times in the thirteenth century.<sup>(143,144)</sup> It is now invariably made by the catalytic oxidation of ammonia under conditions which promote the formation of NO rather than the thermodynamically more favoured products  $\text{N}_2$  or  $\text{N}_2\text{O}$  (p. 423). The NO is then further oxidized to  $\text{NO}_2$  and the gases absorbed in water to yield a concentrated aqueous solution of the acid. The vast scale of production requires the optimization of all the reaction conditions and present-day operations are based on the intricate interaction of fundamental thermodynamics, modern catalyst technology, advanced reactor design, and chemical engineering aspects of process control (see Panel). Production in the USA alone now exceeds 7 million tonnes annually, of which the greater part is used to produce nitrates for fertilizers, explosives and other purposes (see Panel).

Anhydrous  $\text{HNO}_3$  can be obtained by low-pressure distillation of concentrated aqueous nitric acid in the presence of  $\text{P}_4\text{O}_{10}$  or anhydrous  $\text{H}_2\text{SO}_4$  in an all-glass, grease-free apparatus in the dark. The molecule is planar in the gas phase



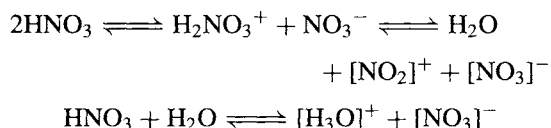
with the dimensions shown (microwave). The difference in N–O distances, the slight but real tilt of the  $\text{NO}_2$  group away from the H atom by  $2^\circ$ , and the absence of free rotation are notable features. The same general structure obtains in the solid state but detailed data are less reliable. Physical properties are shown in Table 11.13. Despite its great thermodynamic stability (with respect to the elements) pure  $\text{HNO}_3$  can only be obtained in the solid state; in the gas and liquid phases the compound decomposes spontaneously to  $\text{NO}_2$  and this occurs more rapidly in daylight (thereby accounting for the brownish colour which develops in the acid on standing):



**Table 11.13** Some physical properties of anhydrous liquid  $\text{HNO}_3$  at  $25^\circ\text{C}$

MP/ $^\circ\text{C}$	–41.6	Vapour pressure/mmHg	57
BP/ $^\circ\text{C}$	82.6	Density/ $\text{g cm}^{-3}$	1.504
$\Delta H_f^\circ/\text{kJ mol}^{-1}$	–174.1	$\eta/\text{centipoise}$	7.46
$\Delta G_f^\circ/\text{kJ mol}^{-1}$	–80.8	$\kappa/\text{ohm}^{-1}\text{cm}^{-1}$ ( $20^\circ$ )	$3.72 \times 10^{-2}$
$S^\circ/\text{J K}^{-1}\text{ mol}^{-1}$	155.6	Dielectric constant $\epsilon$ ( $14^\circ$ )	$50 \pm 10$

In addition, the liquid undergoes self-ionic dissociation to a greater extent than any other nominally covalent pure liquid (cf.  $\text{BF}_3 \cdot 2\text{H}_2\text{O}$ , p. 198); initial autoprotolysis is followed by rapid loss of water which can then react with a further molecule of  $\text{HNO}_3$ :



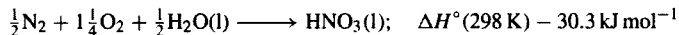
<sup>142</sup> W. MULLER and M. JANSEN, *Z. anorg. allg. Chem.* **610**, 28–32 (1992).

<sup>143</sup> J. W. MELLOR, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 8, pp. 555–8, Longmans, Green, London, 1928.

<sup>144</sup> T. K. DERRY and T. I. WILLIAMS, *A Short History of Technology from the Earliest Times to AD 1900*, Oxford University Press, Oxford, 1960, 782 pp.

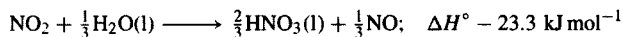
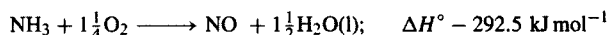
### Production and Uses of Nitric Acid<sup>(56,145,146)</sup>

Before 1900 the large-scale production of nitric acid was based entirely on the reaction of concentrated sulfuric acid with  $\text{NaNO}_3$  and  $\text{KNO}_3$  (p. 407). The first successful process for making nitric acid directly from  $\text{N}_2$  and  $\text{O}_2$  was devised in 1903 by E. Birkeland and S. Eyde in Norway and represented the first industrial fixation of nitrogen:

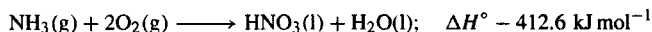


The overall reaction is exothermic but required the use of an electric arc furnace which, even with relatively cheap hydroelectricity, made the process very expensive. The severe activation energy barrier, though economically regrettable, is in fact essential to life since, in its absence, all the oxygen in the air would be rapidly consumed and the oceans would be a dilute solution of nitric acid and its salts. [Dilution of  $\text{HNO}_3(\text{l})$  to  $\text{HNO}_3(\text{aq})$  evolves a further  $33.3 \text{ kJ mol}^{-1}$  at  $25^\circ\text{C}$ .]

The modern process for manufacturing nitric acid depends on the catalytic oxidation of  $\text{NH}_3$  over heated Pt to give NO in preference to other thermodynamically more favoured products (p. 423). The reaction was first systematically studied in 1901 by W. Ostwald (Nobel Prize 1909) and by 1908 a commercial plant near Bochum, Germany, was producing 3 tonnes/day. However, significant expansion in production depended on the economical availability of synthetic ammonia by the Haber–Bosch process (p. 421). The reactions occurring, and the enthalpy changes per mole of N atoms at  $25^\circ\text{C}$  are:

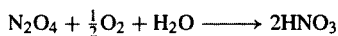


Whence, multiplying the second and third reactions by  $\frac{3}{2}$  and adding:



In a typical industrial unit a mixture of air with 10% by volume of  $\text{NH}_3$  is passed very rapidly over a series of gauzes (Pt, 5–10% Rh) at  $\sim 850^\circ\text{C}$  and 5 atm pressure; contact time with the catalyst is restricted to  $\leq 1$  ms in order to minimize unwanted side reactions. Conversion efficiency is  $\sim 96\%$  (one of the most efficient industrial catalytic reactions known) and the effluent gases are passed through an absorption column to yield 60% aqueous nitric acid at about  $40^\circ\text{C}$ . Loss of platinum metal from the catalyst under operating conditions is reduced by alloying with Rh but tends to increase with pressure from about 50–100 mg/tonne of  $\text{HNO}_3$  produced at atmospheric pressure to about 250 mg/tonne at 10 atm; though this is not a major part of the cost, the scale of operations means that about 0.5 tonne of Pt metals is lost annually in the UK from this cause and more than twice this amount in the USA.

Concentration by distillation of the 60% aqueous nitric acid produced in most modern ammonia-burning plants is limited by the formation of a maximum-boiling azeotrope ( $122^\circ$ ) at 68.5% by weight; further concentration to 98–99% can be effected by countercurrent dehydration using concentrated  $\text{H}_2\text{SO}_4$ , or by distillation from concentrated  $\text{Mg}(\text{NO}_3)_2$  solutions. Alternatively 99% pure  $\text{HNO}_3$  can be obtained directly from ammonia oxidation by incorporating a final oxidation of  $\text{N}_2\text{O}_4$  with the theoretical amounts of air and water at  $70^\circ\text{C}$  and 50 atm over a period of 4 h:



The largest use of nitric acid ( $\sim 75\%$ ) is in the manufacture of  $\text{NH}_4\text{NO}_3$  and of this, about 75% is used for fertilizer production. Many plants have a capacity of 2000 tonnes/day or more and great care must be taken to produce the  $\text{NH}_4\text{NO}_3$  in a readily handleable form (e.g. prills of about 3 mm diameter); about 1% of a “conditioner” is usually added to improve storage and handling properties.  $\text{NH}_4\text{NO}_3$  is thermally unstable (p. 469) and decomposition can become explosive. For this reason a temperature limit of  $140^\circ\text{C}$  is imposed on the neutralization step and pH is strictly controlled. The decomposition is catalysed by many inorganic materials including chloride, chromates, hypophosphites, thiosulfates and powdered metals (e.g. Cu, Zn, Hg). Organic materials (oil, paper, string, sawdust, etc.) must also be rigorously excluded during neutralization since their oxidation releases additional heat. Indeed, since the mid-1950s  $\text{NH}_4\text{NO}_3$  prills mixed with fuel oil have been extensively used as a direct explosive in mining and quarrying operations (p. 469) and this use now accounts for up to 15% of the  $\text{NH}_4\text{NO}_3$  produced.

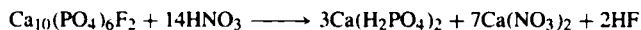
*Panel continues*

<sup>145</sup>C. KELETI (ed), *Nitric Acid and Fertilizer Nitrates*, Marcel Dekker, N.Y. 1985, 392 pp.

<sup>146</sup>S. I. CLARKE and W. J. MAZZAFRO Nitric acid, in *Kirk–Othmer Encyclopedia of Chemical Technology*, 4th edn., Vol. 17, pp. 80–107 (1996).



Some 8–9% of  $\text{HNO}_3$  goes to make cyclohexanone, the raw material for adipic acid and  $\epsilon$ -caprolactam, which are the monomers for nylon-6,6 and nylon-6 respectively. A further 7–10% is used in other organic nitration reactions to give nitroglycerine, nitrocellulose, trinitrotoluene and numerous other organic intermediates. Minor uses (which still consume large quantities of the acid) include the pickling of stainless steel, the etching of metals, and its use as the oxidizer in rocket fuels. In Europe nitric acid is sometimes used to replace sulfuric acid in the treatment of phosphate rock to give nitrophosphate fertilizers according to the idealized equation:



Another minority use is in the manufacture of nitrates (other than  $\text{NH}_4\text{NO}_3$ ) for use in explosives, propellants, and pyrotechnics generally; typical examples are:

explosives: gun powder,  $\text{KNO}_3/\text{S}/\text{powdered C}$  (often reinforced with powdered Si)

white smokes:  $\text{ZnO}/\text{CaSi}_2/\text{KNO}_3/\text{C}_2\text{Cl}_6$

incendiary agents:  $\text{Al}/\text{NaNO}_3/\text{methylmethacrylate}/\text{benzene}$

local heat sources:  $\text{Al}/\text{Fe}_3\text{O}_4/\text{Ba}(\text{NO}_3)_2$ ;  $\text{Mg}/\text{Sr}(\text{NO}_3)_2/\text{SrC}_2\text{O}_4/\text{thiokol polysulfide}$

photoflashes:  $\text{Mg}/\text{NaNO}_3$

flares (up to 10 min):  $\text{Mg}/\text{NaNO}_3/\text{CaC}_2\text{O}_4/\text{polyvinyl chloride}/\text{varnish}$ ;  $\text{Ti}/\text{NaNO}_3/\text{boiled linseed oil}$

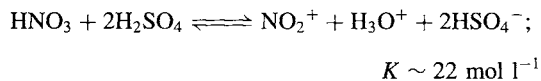
coloured flares:  $\text{Mg}/\text{Sr}(\text{NO}_3)_2/\text{chlorinated rubber (red)}$ ;  $\text{Mg}(\text{Ba}(\text{NO}_3)_2)/\text{chlorinated rubber (green)}$ .

These equilibria effect a rapid exchange of N atoms between the various species and only a single  $^{15}\text{N}$  nmr signal is seen at the weighted average position of  $\text{HNO}_3$ ,  $[\text{NO}_2]^+$  and  $[\text{NO}_3]^-$ . They also account for the high electrical conductivity of the “pure” (stoichiometric) liquid (Table 11.13), and are an important factor in the chemical reactions of nitric acid and its non-aqueous solutions see below.

The phase diagram  $\text{HNO}_3\text{--H}_2\text{O}$  shows the presence of two hydrates,  $\text{HNO}_3\cdot\text{H}_2\text{O}$  mp  $-37.68^\circ$ , and  $\text{HNO}_3\cdot 3\text{H}_2\text{O}$  mp  $-18.47^\circ$ . A further hemihydrate,  $2\text{HNO}_3\cdot\text{H}_2\text{O}$ , can be extracted into benzene or toluene from 6 to 16 M aqueous solutions of nitric acid, and a dimer hydrate,  $2\text{HNO}_3\cdot 3\text{H}_2\text{O}$ , is also known, though neither can be crystallized. The structure of the two crystalline hydrates is dominated by hydrogen bonding as expected; e.g. the monohydrate is  $[\text{H}_3\text{O}]^+[\text{NO}_3]^-$  in which there are puckered layers comprising pyramidal  $[\text{H}_3\text{O}]^+$  hydrogen bonded to planar  $[\text{NO}_3]^-$  so that there are 3 H bonds per ion. The trihydrate forms a more complex three-dimensional H-bonded framework. (See also p. 468 for the structure of hydrogen-nitrates.)

The solution chemistry of nitric acid is extremely varied. Redox data are summarized in Table 11.4 and Fig. 11.9 (pp. 434–8). In

dilute aqueous solutions (<2 M) nitric acid is extensively dissociated into ions and behaves as a typical strong acid in its reactions with metals, oxides, carbonates, etc. More concentrated aqueous solutions are strongly oxidizing and attack most metals except Au, Pt, Rh and Ir, though some metals which react at lower concentrations are rendered passive, probably because of the formation of an oxide film (e.g. Al, Cr, Fe, Cu). Aqua regia (a mixture of concentrated hydrochloric and nitric acids in the ratio of  $\sim 3:1$  by volume) is even more aggressive, due to the formation of free  $\text{Cl}_2$  and  $\text{ClNO}$  and the superior complexing ability of the chloride ion; it has long been known to “dissolve” both gold and the platinum metals, hence its name. In concentrated  $\text{H}_2\text{SO}_4$  the chemistry of nitric acid is dominated by the presence of the nitronium ion (pp. 458, 465):



Such solutions are extensively used in aromatic nitration reactions in the heavy organic chemicals industry. See also pp. 457–8.

Anhydrous nitric acid has been studied as a nonaqueous ionizing solvent, though salts tend to be rather insoluble unless they produce  $\text{NO}_2^+$  or

$\text{NO}_3^-$  ions.<sup>(147)</sup> Addition of water to nitric acid at first diminishes its electrical conductivity by repressing the autoprotolysis reactions mentioned above. For example, at  $-10^\circ$  the conductivity decreases from  $3.67 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$  to a minimum of  $1.08 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$  at 1.75 molal  $\text{H}_2\text{O}$  (82.8%  $\text{N}_2\text{O}_5$ ) before rising again due to the increasing formation of the hydroxonium ion according to the acid-base equilibrium



By contrast, Raman spectroscopy and conductivity measurements show that  $\text{N}_2\text{O}_4$  ionizes almost completely in anhydrous  $\text{HNO}_3$  to give  $\text{NO}^+$  and  $\text{NO}_3^-$  and such solutions show no evidence for the species  $\text{N}_2\text{O}_4$ ,  $\text{NO}_2^+$  or  $\text{NO}_2^-$ .<sup>(126)</sup>  $\text{N}_2\text{O}_5$  is also extremely soluble in anhydrous nitric acid in which it is completely ionized as  $\text{NO}_2^+ \text{NO}_3^-$ .

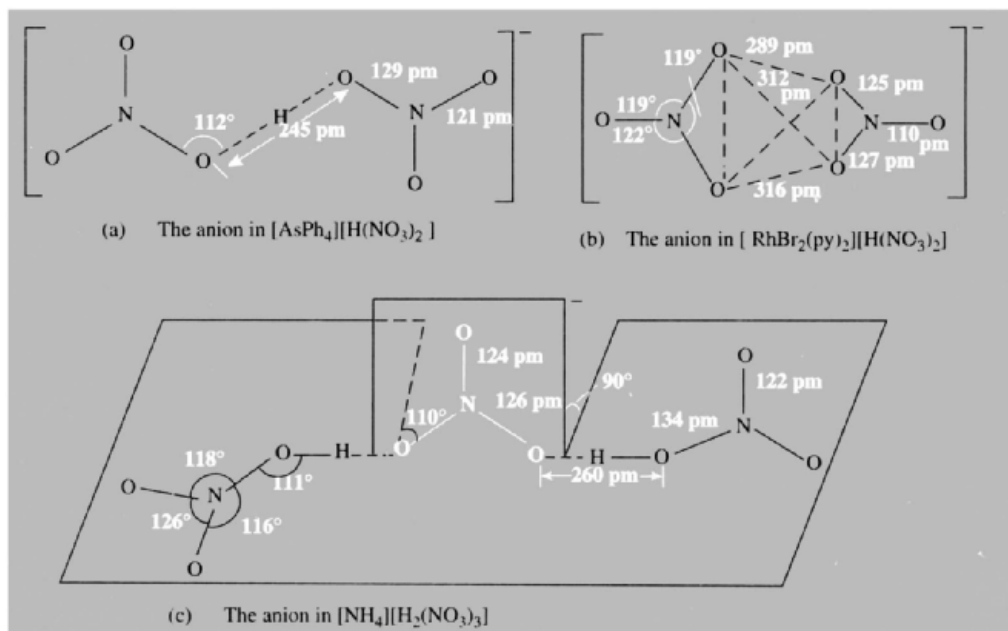
Nitrates, the salts of nitric acid, can readily be made by appropriate neutralization of the acid, though sometimes it is the hydrate which crystallizes from aqueous solution. Anhydrous

nitrates and nitrate complexes are often best prepared by use of donor solvents containing  $\text{N}_2\text{O}_4$  (p. 456). The reaction of liquid  $\text{N}_2\text{O}_5$  with metal oxides and chlorides affords an alternative route, e.g.:



Many nitrates are major items of commerce and are dealt with under the appropriate metal (e.g.  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{NH}_4\text{NO}_3$ , etc.). In addition, various hydrogen dinitrates and dihydrogen trinitrates are known of formula  $\text{M}[\text{H}(\text{NO}_3)_2]$  and  $\text{M}[\text{H}_2(\text{NO}_3)_3]$  where M is a large cation such as K, Rb, Cs,  $\text{NH}_4$  or  $\text{AsPh}_4$ . In  $[\text{AsPh}_4][\text{H}(\text{NO}_3)_2]$  2 coplanar  $\text{NO}_3^-$  ions are linked by a short H bond as shown in (a) whereas  $[\text{trans-RhBr}_2(\text{py})_4][\text{H}(\text{NO}_3)_2]$  features a slightly distorted tetrahedral group of 4 oxygen atoms in which the position of the H atom is not obvious [structure (b)]. In  $[\text{NH}_4][\text{H}_2(\text{NO}_3)_3]$  there is a more extended system of H bonds in which 2 coplanar molecules of  $\text{HNO}_3$  are symmetrically bridged by an  $\text{NO}_3^-$  ion at right angles as shown in (c).

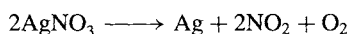
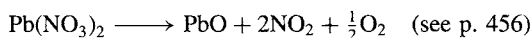
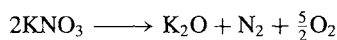
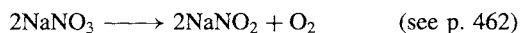
<sup>147</sup> W. H. LEE, in J. J. LAGOWSKI (ed.), *The Chemistry of Non-aqueous Solvents*, Vol. 2, pp. 151–89, Academic Press, New York, 1967.



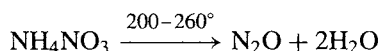
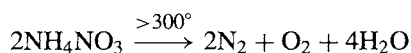
As with the salts of other oxoacids, the thermal stability of nitrates varies markedly with the basicity of the metal, and the products of decomposition are equally varied.<sup>(148)</sup> Thus the nitrates of Group 1 and 2 metals find use as molten salt baths because of their thermal stability and low mp (especially as mixtures). Representative values of mp and the temperature ( $T_d$ ) at which the decomposition pressure of  $O_2$  reaches 1 atm are:

M	Li	Na	K	Rb	Cs	Ag	Tl
MP of $MNO_3/^\circ C$	255	307	333	310	414	212	206
$T_d/^\circ C$	474	525	533	548	584	-	-

The product of thermolysis is the nitrite or, if this is unstable at the temperature employed, the oxide (or even the metal if the oxide is also unstable):<sup>(149)</sup>



As indicated in earlier sections,  $NH_4NO_3$  can be exploded violently at high temperatures or by use of detonators (p. 466), but slow controlled thermolysis yields  $N_2O$  (p. 443):



The presence of organic matter or other reducible material also markedly affects the thermal stability of nitrates and the use of  $KNO_3$  in gunpowder has been known for centuries (p. 645).

The nitrate group, like the nitrite group, is a versatile ligand and numerous modes of coordination have been found in nitrate complexes.<sup>(150)</sup> The "uncoordinated"  $NO_3^-$  ion (isoelectronic with  $BF_3$ ,  $BO_3^{3-}$ ,  $CO_3^{2-}$ , etc.) is planar with N-O near 122 pm; this value

increases to 126 pm in  $AgNO_3$  and 127 pm in  $Pb(NO_3)_2$ . The most common mode of coordination is the symmetric bidentate mode Fig. 11.16a, though unsymmetrical bidentate coordination (b) also occurs and, in the limit, unidentate coordination (c). Bridging modes include the *syn-syn* conformation (d) (and the *anti-anti* analogue), and also geometries in which a single O atom bridges 2 or even 3 metal atoms (e), (f). Sometimes more than one mode occurs in the same compound.

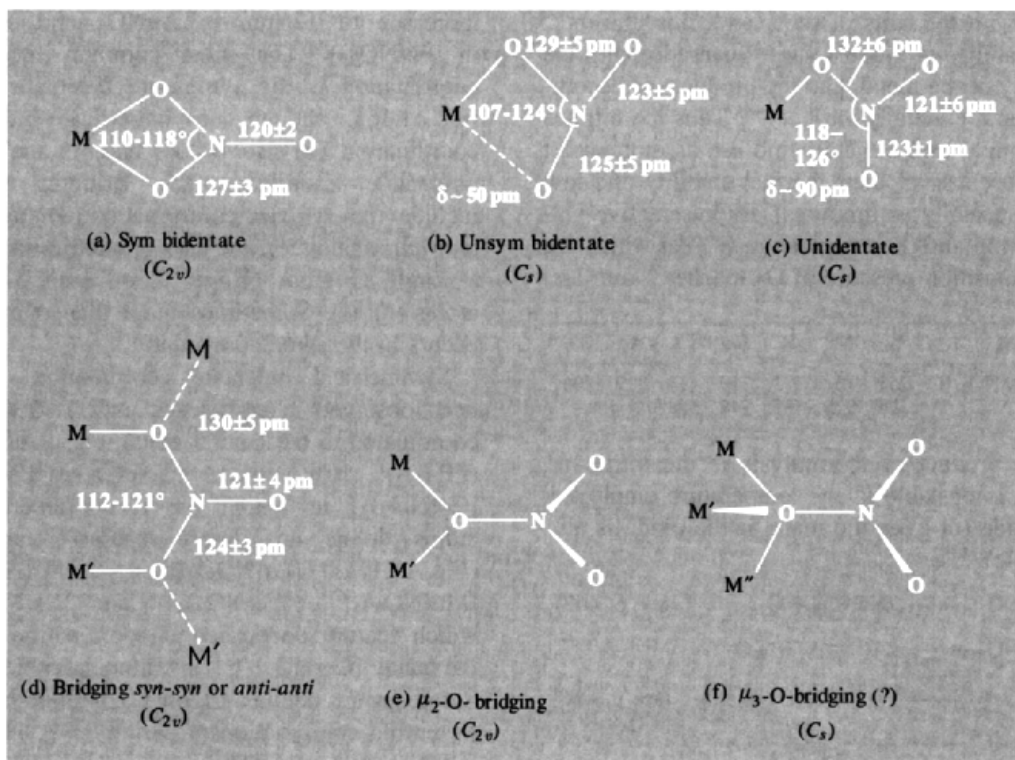
Symmetrical bidentate coordination (a) has been observed in complexes with 1-6 nitrates coordinated to the central metal, e.g.  $[Cu(NO_3)_2(PPH_3)_2]$ ;  $[Cu(NO_3)_2]$ ,  $[Co(NO_3)_2(OPMe_3)_2]$ ;  $[Co(NO_3)_3]$  in which the 6 coordinating O atoms define an almost regular octahedron (Fig. 11.17a),  $[La(NO_3)_3(bipy)_2]$ ;  $[Ti(NO_3)_4]$ ,  $[Mn(NO_3)_4]^{2-}$ ,  $[Fe(NO_3)_4]^-$  and  $[Sn(NO_3)_4]$ , which feature dodecahedral coordination about the metal;  $[Ce(NO_3)_5]^{2-}$  in which the 5 bidentate nitrate groups define a trigonal bipyramid leading to tenfold coordination of cerium (Fig. 11.17b);  $[Ce(NO_3)_6]^{2-}$  and  $[Th(NO_3)_6]^{2-}$ , which feature nearly regular icosahedral (p. 141) coordination of the metal by 12 O atoms; and many lanthanide and uranyl  $[UO_2]^{2+}$  complexes. It seems, therefore, that the size of the metal centre is not necessarily a dominant factor.

Unsymmetrical bidentate coordination (Fig. 11.16b) is observed in the high-spin  $d^7$  complex  $[Co(NO_3)_4]^{2-}$  (Fig. 11.17c), in  $[SnMe_2(NO_3)_2]$  and also in several  $Cu^{II}$  complexes of formula  $[CuL_2(NO_3)_2]$ , where L is MeCN,  $H_2O$ , py or 2-MeC<sub>5</sub>H<sub>4</sub>N ( $\alpha$ -picoline). An example of unidentate coordination is furnished by  $K[Au(NO_3)_4]$  as shown in Fig. 11.18(a), and further examples are in *cis*- $[Pd(NO_3)_2(OSMe_2)_2]$ ,  $[Re(CO)_5(NO_3)]$ ,  $[Ni(NO_3)_2(H_2O)_4]$ ,  $[Zn(NO_3)_2(H_2O)_4]$  and several  $Cu^{II}$  complexes such as  $[CuL_2(NO_3)_2]$  where L is pyridine *N*-oxide or 1,4-diazacycloheptane. It appears that a combination of steric effects and the limited availability of coordination sites in these already highly coordinated late-transition-metal complexes restricts each nitrate group to one coordination site. When more

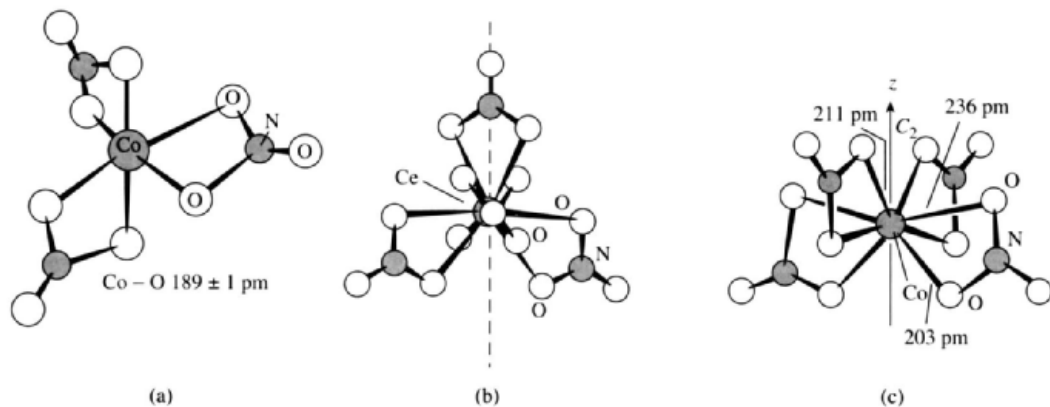
<sup>148</sup> B. O. FIELD and C. J. HARDY, *Q. Rev.* **18**, 361-88 (1964).

<sup>149</sup> K. J. MYSELS, *J. Chem. Educ.* **36** 303-4 (1959).

<sup>150</sup> C. C. ADDISON, N. LOGAN, S. C. WALLWORK and C. D. GARNER, *Q. Rev.* **25**, 289-322 (1971).



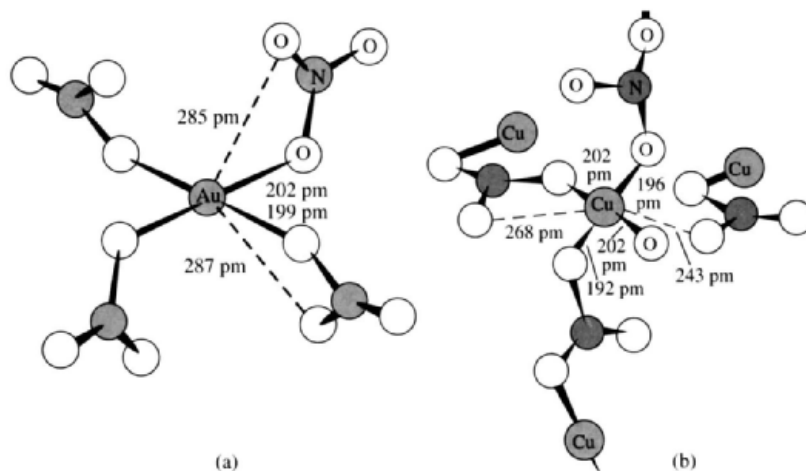
**Figure 11.16** Coordination geometries of the nitrate group showing typical values for the interatomic distances and angles. Further structural details are in ref. 150.



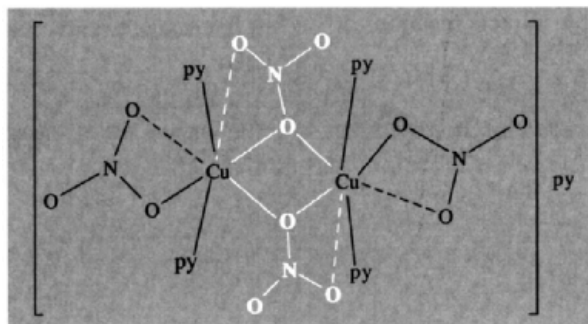
**Figure 11.17** Structures of (a)  $\text{Co}(\text{NO}_3)_3$ , (b)  $[\text{Ce}(\text{NO}_3)_5]^{2-}$  and (c)  $[\text{Co}(\text{NO}_3)_4]^{2-}$

sites become available, as in  $[\text{Ni}(\text{NO}_3)_2(\text{H}_2\text{O})_2]$  and  $[\text{Zn}(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ , or when the co-ligands are less bulky, as in  $[\text{CuL}_2(\text{NO}_3)_2]$ , where L is  $\text{H}_2\text{O}$ ,  $\text{MeCN}$  or  $\text{MeNO}_2$ , then the nitrate

groups become bidentate bridging (mode d in Fig. 11.16) and a further example of this is seen in  $[\alpha\text{-Cu}(\text{NO}_3)_2]$ , which forms a more extensive network of bridging nitrate groups, as



**Figure 11.18** (a) Structure of  $[\text{Au}(\text{NO}_3)_4]^-$ . (b)  $\alpha\text{-Cu}(\text{NO}_3)_2$ .



**Figure 11.19** Schematic diagram of the centrosymmetric dimer in  $[\text{Cu}_2(\text{NO}_3)_4(\text{py})_4]\text{py}$  showing the two bridging nitrate groups each coordinated to the 2 Cu atoms by a single O atom; the dimer also has an unsymmetrical bidentate nitrate group on each Cu.

shown in Fig. 11.18(b). The single oxygen atom bridging mode (e) occurs in  $[\text{Cu}(\text{NO}_3)_2(\text{py})_2]_2\text{py}$  (Fig. 11.19) and the triple-bridge (f) may occur in  $[\text{Cu}_4(\text{NO}_3)_2(\text{OH})_6]$  though there is some uncertainty about this structure and further refinement would be desirable. Finally, the structure of the unique yellow solvate of formula  $[\text{Fe}(\text{NO}_3)_3 \cdot 1\frac{1}{2}\text{N}_2\text{O}_4]$  (p. 457) has been shown<sup>(128)</sup> to be  $[\text{N}_4\text{O}_6]^{2+}[\text{Fe}(\text{NO}_3)_4]^{-2}$ . Each anion has 4 symmetrically bidentate  $\text{NO}_3$  groups in which the coordinating O atoms lie at the corners of a trigonal dodecahedron, as is commonly found in tetrannitrate species (N-O, 120 pm, N-O(Fe) 127 pm, angles O-N-O 113.4° and O-Fe-O

60.0°). The  $[\text{N}_4\text{O}_6]^{2+}$  cation comprises a central planar nitrate group (N-O 123 pm) surrounded by 3 NO groups at distances which vary from 241 to 278 pm (Fig. 11.20); the interatomic distance in the NO groups is very short (90–99 pm) implying  $\text{NO}^+$  and the distances of these to the central  $\text{NO}_3$  group are slightly less than the sum of the van der Waals radii for N and O.

### Orthonitrates, $\text{M}_3\text{NO}_4$

There is no free acid  $\text{H}_3\text{NO}_4$  analogous to orthophosphoric acid  $\text{H}_3\text{PO}_4$  (p. 516), but the alkali metal orthonitrates  $\text{Na}_3\text{NO}_4$  and  $\text{K}_3\text{NO}_4$

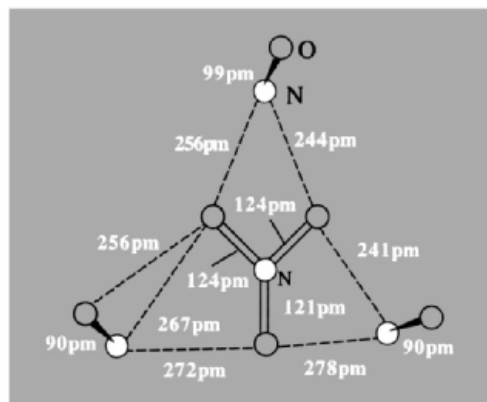
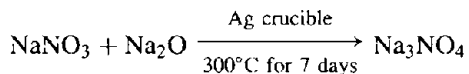


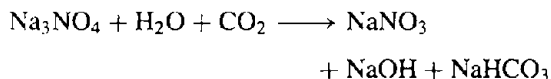
Figure 11.20 The  $\{N_4O_6\}^{2+}$  cation.

have been synthesized by direct reaction at elevated temperatures, e.g.:<sup>(151,152)</sup>

<sup>151</sup> M. JANSEN, *Angew. Chem. Int. Edn. Engl.* **16**, 534 (1977); **18**, 698 (1979).



The compound forms white crystals that are very sensitive to atmospheric moisture and  $\text{CO}_2$ :



X-ray structural analyses have shown that the  $\text{NO}_4^{3-}$  ion has regular  $T_d$  symmetry with the unexpectedly small N-O distance of 139 pm. This suggests that substantial polar interactions are superimposed on the N-O single bonds since the  $d_\pi$  orbitals on N are too high in energy to contribute significantly to multiple covalent bonding. It further implies that  $d_\pi-p_\pi$  interactions need not necessarily be invoked to explain the observed short interatomic distance in the isoelectronic oxoanions  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$  and  $\text{ClO}_4^-$ .

<sup>152</sup> T. BREMM and M. JANSEN, *Z. anorg. allg. Chem.* **608**, 56-9 (1992).