The $N_4O_6^{2+}$ Group: *X*-Ray Crystal Structure of $Fe(NO_3)_3,1{\cdot}5N_2O_4$

By C. CLIFFORD ADDISON,* LESLIE J. BLACKWELL, BRIAN HARRISON, DAVID H. JONES, NORMAN LOGAN, ERNEST K. NUNN, and STEPHEN C. WALLWORK

(*Department of Chemistry, The University, Nottingham* NG7 2RD)

Summary The crystal structure of the adduct $Fe(NO_3)_3$,$1{\cdot}5N_2O_4$ indicates that it should be represented as $3NO^+,NO_3^-,2[Fe(NO_3)_4^-]$; vibrational spectroscopy provides evidence for interaction between the NO_3^- and $3NO^+$ ions, and the properties are correlated in terms of a weakly bonded $N_4O_6^{2+}$ group which may also be present in solutions of N_2O_4, or the adduct, in pure nitric acid.

THERE is no reference to the group $N_4O_6^{2+}$ in the literature, but we have now obtained evidence for its existence both in crystalline solids and in solution in pure nitric acid, and a number of apparent inconsistencies can be correlated on the basis of such a group. Adducts of metal nitrates with dinitrogen tetroxide are usually formed in the ratio 1 : 1 [*e.g.* $Cu(NO_3)_2,N_2O_4$] or 1 : 2 [*e.g.* $Zn(NO_3)_2,2N_2O_4$]. However, vapour pressure studies have established that with the iron compound the adduct with 1 : 1·5 ratio, *i.e.* $Fe(NO_3)_3,1{\cdot}5N_2O_4$, is stable. Because of the unusual nature of the i.r. and Raman spectra, and the difficulty in formulating the compound in terms of known units, we have carried out an *X*-ray crystallographic determination of the structure of this 1 : 1·5 adduct. The compound separates from liquid dinitrogen tetroxide as pale yellow-brown crystals;[1] these lose their crystalline form when removed from the liquid, and the *X*-ray data were obtained from crystals sealed into capillaries containing a small amount of the liquid tetroxide.

The crystals are monoclinic, space group $P2_1/c$, and each asymmetric unit has the composition $2Fe(NO_3)_3,3N_2O_4$. The positions of the two crystallographically independent iron atoms were deduced from a three-dimensional Patterson synthesis, and a Fourier electron density synthesis phased on the iron positions revealed some of the nitrato-groups co-ordinated to the iron atoms. During further cycles of structure-factor calculation and Fourier synthesis, the rest of the light atom positions became apparent, and it was recognised that the adduct had the formulation $3NO^+,NO_3^-,[Fe(NO_3)_4^-{}_2]$. The tetranitratoferrate(III) anions have the same flattened tetrahedral structure as is found[2] in $(Ph_4As^+)[Fe(NO_3)_4^-]$. The relative dispositions of the $3NO^+$ and NO_3^- ions are shown in the Figure. The NO^+ distances are of the order already reported for this ion (1·062 Å; 0·94—1·03 Å),[3,4] and are being refined. The numbers shown for each NO^+ ion represent distances of the N or O atoms above and below the NO_3^- plane. One NO^+ axis lies nearly in this plane, one is about 110° out of this plane, and the third is in an intermediate orientation. Within these $N_4O_6^{2+}$ groups, one end of each NO^+ ion (presumably nitrogen) lies approximately on the bisector of each nitrate ONO angle.

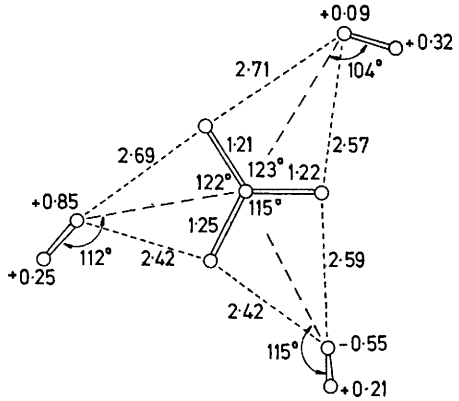

FIGURE. *Structure of the* $N_4O_6^{2+}$ *group.* (*Interatomic distances in* Å. *Distances in* Å *above or below the* NO_3 *plane signified by* + *or* — .)

The crystallographic results indicate a fairly symmetrical $N_4O_6^{2+}$ group with weak interaction between the NO^+ and the NO_3^- ions. Other evidence, however, indicates that this interaction (though largely coulombic) is significant.

(i) The 1 : 1·5 adduct can be prepared from the 1 : 1 adduct. In the process

$$2Fe(NO_3)_3 \xrightarrow{2N_2O_4} 2NO^+[Fe(NO_3)_4]^-$$

$$\xrightarrow{N_2O_4} 3NO^+,NO_3^-,[Fe(NO_3)_4^-]_2$$

the complete ionic dissociation of N_2O_4 in the first step is due to the stability of the tetranitrato-complex thereby produced. The complete dissociation of the N_2O_4 molecule in the second step is unusual, and must be related to the stability of the complex cation so formed.

(ii) The vibrations characteristic of a free NO_3^- ion are not observed. The 831 cm^{-1} out-of-plane rocking mode is absent in the i.r., and the characteristic NO_2 stretch at 1390 cm^{-1} is absent in the Raman and i.r. spectra.

(iii) In the 1 : 1 adduct, the vibrational mode of "free" NO^+ in an environment of $[Fe(NO_3)_4]^-$ anions appears at 2298 cm^{-1} (i.r.) and 2302 cm^{-1} (Raman). In the 1·5 adduct the NO^+ vibration energy is lowered to 2235 cm^{-1} (i.r.) and 2250 cm^{-1} (Raman).

This evidence indicates appreciable association between the units shown in the Figure. The NO^+ ion in liquid dinitrogen tetroxide systems corresponds to H^+ in aqueous systems, and the association discussed above may have a significance resembling that of the hydrogen bond.

The $N_4O_6^{2+}$ group may also occur in solution. Solutions of N_2O_4 in pure nitric acid show anomalously low NO^+ bands in the i.r. (2220 cm^{-1}) and Raman (2240 cm^{-1}) spectra. These were attributed[5] to the presence of $N_2O_3^+$, though the diamagnetic nature of the solutions was not consistent with this.[6] The presence of the "dimer" $N_4O_6^{2+}$ overcomes this inconsistency, and it is of interest that the NO^+ frequencies for solutions of $Fe(NO_3)_3,1{\cdot}5N_2O_4$ in nitric acid are close to those for solutions of N_2O_4. Magnetic evidence also conflicted with our earlier formulations of the 1 : 1·5 adduct as $N_2O_3^+[Fe(NO_3)_4]^-$. However, the existence of a dimeric $N_4O_6^{2+}$ group as a cluster of diamagnetic ions is in accord with the negligible change in magnetic moment on treating the 1 : 1 adduct with N_2O_4.

The 1·5 adduct has particular importance in that it sometimes separates from liquid N_2O_4 which has been stored in steel vessels, and can be responsible for the failure of rockets used in space vehicles. It seems possible that such separation may be encouraged in conditions which favour the formation of the $N_4O_6^{2+}$ group.

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