

## Eight-co-ordinate Iron(III) Complex: Crystal Structure of Tetraphenylarsonium Tetranitratoferrate(III)

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**Summary** The tetranitratoferrate(III) anion possesses essentially dodecahedral ( $D_{2d}$ ) symmetry and is the first example of an eight-co-ordinate iron(III) species of crystallographically established structure.

THE  $\text{Fe}(\text{NO}_3)_4^-$  anion is found to be the dominant species in the anhydrous nitrate chemistry of iron(III).<sup>1</sup> On the basis of i.r. spectra of several salts of this anion, a structural similarity to  $\text{Co}(\text{NO}_3)_4^{2-}$ , which possesses four unsymmetrically bidentate nitrate groups,<sup>2</sup> was suggested.<sup>1</sup> We

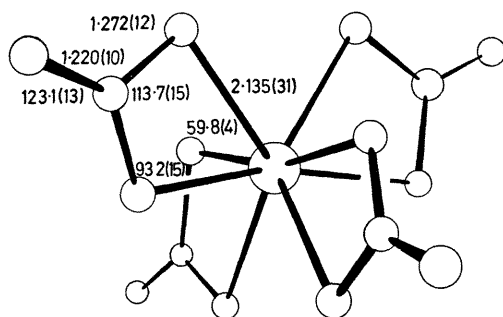


FIGURE. Structure of the tetranitratoferrate(III) anion indicating average bond lengths (in Å) and angles (in degrees) for the  $\text{FeO}_2\text{NO}$  unit. Root mean square deviations, in units of the least significant digit, are given in parentheses.

now report the crystal structure of  $\text{Ph}_4\text{As}[\text{Fe}(\text{NO}_3)_4]$ . This compound (prepared by a method similar to that of Straub *et al.*<sup>3</sup> by reaction of an equimolar mixture of  $\text{FeCl}_3$  and  $\text{Ph}_4\text{AsCl}$  with  $\text{AgNO}_3$  in MeCN) crystallises from nitromethane as dark red tablets. Oscillation and equi-inclination Weissenberg photographs ( $\text{Cu-K}\alpha$ ) showed that the unit cell is monoclinic, space group  $P2_1/c$ , containing four

molecules. *Crystal data:*  $a = 13.412 \pm 0.010$ ,  $b = 13.963 \pm 0.010$ ,  $c = 21.667 \pm 0.015$  Å,  $\beta = 136.42 \pm 0.15^\circ$ ,  $U = 2789$  Å<sup>3</sup>,  $D_m = 1.65$ ,  $Z = 4$ ,  $D_c = 1.66$ . Intensity measurements were made on 2578 independent reflections on the layers  $hk0-hk17$  using a Hilger and Watts linear diffractometer. Solution of the structure was by normal Patterson and Fourier methods. Least-squares refinement (using Ahmed's block-diagonal programme) converged at  $R = 0.078$  with all the atoms (except hydrogen) treated anisotropically.

The structure consists of discrete  $\text{Ph}_4\text{As}^+$  and  $\text{Fe}(\text{NO}_3)_4^-$  ions. The anion (see Figure) is in the form of a flattened tetrahedron, approximating to  $D_{2d}$  symmetry, with a dodecahedral arrangement of eight oxygen atoms around iron, arising from four almost symmetrically bidentate nitrate groups. Average dimensions for the  $\text{FeO}_2\text{NO}$  unit are given in the Figure. Although it was suggested (on the basis of i.r. and Mössbauer data) that disodium diethylenetriaminepenta-acetatoferrate(III) contains eight-co-ordinate iron(III)<sup>4</sup> and the crystal structure of an eight-co-ordinate iron(II) complex, tetrakis-(1,8-naphthyridine)iron(II) perchlorate, was reported recently,<sup>5</sup> to our knowledge, the complex  $\text{Fe}(\text{NO}_3)_4^-$  is the first example of eight-co-ordinate iron(III) to be authenticated by X-ray studies.

The  $\text{Fe}(\text{NO}_3)_4^-$  anion has essentially the same geometry as  $\text{Ti}(\text{NO}_3)_4$ ,<sup>6</sup>  $\text{Sn}(\text{NO}_3)_4$ ,<sup>7</sup> and the isoelectronic  $\text{Mn}(\text{NO}_3)_4^{2-}$ .<sup>8</sup> This may be related to the spherically symmetrical distribution of non-bonding metal electrons in these four tetranitratospecies<sup>9</sup> and contrasts with the less symmetrical arrangement of nitrate groups in the presence of *e.g.* a  $d^7$ , high-spin, non-bonding configuration as observed<sup>2</sup> in  $\text{Co}(\text{NO}_3)_4^{2-}$ .

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