The Structure of a Five-co-ordinate Complex of Iron; the Penta-azidoiron(III) Ion, $Fe(N_3)_5^{2-}$

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Summary The penta-azidoiron(III) ion, $Fe(N_3)_5^{2-}$ contains a five-co-ordinate metal atom with trigonal bipyramidal geometry.

ALTHOUGH both preparative and structural aspects of five-co-ordination chemistry continue to attract attention, still comparatively few molecules or ions containing five equivalent ligands have been characterised. In the case of the transition elements, therefore, little is known of the way in which the ground state geometry is influenced by the number of (formally non-bonding) *d*-electrons.

There have been to date eight structure determinations on first row transition-element species of the type ML_5 and in five of those, M has the d^8-electronic configuration.[1] The most interesting of these species is probably the penta-cyanonickelate ion $Ni(CN)_5^{3-}$, for which two different geometries have been found in the same crystal.[1d] Three pentahalogeno-complex ions $CuCl_5^{3-}$ [2c] (d^9), $MnCl_5^{2-}$ [1e] (d^4), and the "$NiCl_5$" unit in $Ni_2Cl_8^{4-}$ [1f] (d^8), have respectively trigonal bipyramidal, square pyramidal, and square pyramidal geometries.

In an attempt to extend the series of ML_5 complexes and provide more information on the co-ordination geometry, we have undertaken a structure analysis of the recently reported penta-azidoiron(III) ion,[2] in the form of its tetraphenylarsonium salt. The electronic configuration of the metal is d^5 and the complex ion is high-spin with $\mu_{eff} =$ 6·0 B.M. According to Gillespie,[3] therefore, treating the *d*-electrons as a non-bonding shell, the stereochemistry should be trigonal bipyramidal with the axial metal–ligand bonds slightly longer than the equatorial bonds. The preliminary results of the structure analysis reported here are in agreement with these predictions.

The compound crystallises in space group *C*2/*c* with four formula units, $[(Ph_4As)_2Fe(N_3)_5]$, per unit cell, and the penta-azido-ion is crystallographically required to possess two-fold symmetry. The structure has been determined from *ca.* 2300 intensity data measured on a manual diffractometer using Mo-K_α radiation and the moving crystal-moving counter technique. The conventional *R*-value at the present level of refinement with anisotropic thermal parameters for the iron and arsenic atoms is 0·09.

Electron density and difference Fourier maps indicated disorder in one of the azide ions, about the two-fold axis and the model which has been found to refine most successfully (with isotropic thermal parameters for all nitrogen atoms) is that in which only the co-ordinated nitrogen atom is constrained to lie on the two-fold axis. In view of the anticipated non-linear Fe–N–N system, this model is then also chemically reasonable. The complex ion viewed down the *a* axis of the unit cell and illustrating the nature of the disorder in the azide group close to the two-fold axis, is depicted in the Figure. The co-ordination polyhedron comes very close to the idealised symmetry D_{3h} of the trigonal bipyramid, although the complex ion itself has no symmetry. The pertinent dimensions, with standard deviations in parentheses are as follows: Fe–N(11), 1·963(42) Å; Fe–N(21), 2·041(15) Å; Fe–N(31), 1·971(14) Å; N(11)–Fe–N(21), 93·1(1·4)°; N(11)–Fe–N(31), 118·3(1·4)°; N(21)–Fe–N(31) 88·2(1·3)°; N(21)–Fe–N(31)′ 88·9(1·3)°; N(31)–Fe–N(31)′ 123·5(1·5)°, and N(21)–Fe–N(21)′ 178·0 (1·5)°.

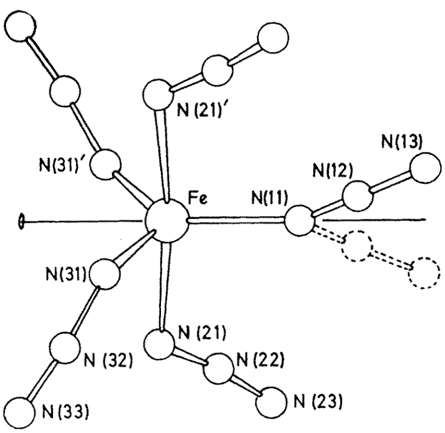

FIGURE. *Structure of the penta-azidoiron*(III) *ion viewed down the crystallographic* a *axis.*

The azide ions are symmetrical and almost linear, the average N–N distance being 1·16(3) Å with only N(11)–N(12) marginally significantly different from the mean. The Fe–N–N angles are 124·8 and 125·1° respectively for the N(2*n*) and N(3*n*) ions and are as anticipated for a trigonally hybridised nitrogen. The Fe–N(11)–N(12) angle is however much larger (146·0°) but is subject to considerable uncertainty because of the disorder present in this ion.

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