The Crystal Structure of Tris(tropolonato)iron(III) ("Ferric Tropolone")

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Summary *X*-Ray crystallographic analysis of ferric tropolone establishes that the iron co-ordination deviates considerably from octahedral, and, in contrast to the cupric tropolone structure, all C–C bonds, apart from the long C(1)–C(2) bond, have lengths near to the aromatic value.

CO-ORDINATION complexes based on the tropolone anion, X, as bidentate ligand were first reported[1] in 1951 with the preparation of ferric and cupric tropolone, FeX_3 and CuX_2. Recently it has been shown[2] that this ligand is particularly effective in forming high-co-ordinate structures with a wide variety of metal ions. Accurate molecular dimensions have been determined for cupric tropolone[3] and also for the anion, X, in the sodium salt.[4] We have now carried out an *X*-ray structure determination for ferric tropolone, tris(tropolonato)iron(III) which established the structure shown in the Figure.

Crystals of FeX_3, grown from chloroform–ethanol (1 : 1), are trigonal, space group $R\bar{3}c$. Employing hexagonal axes, the unit cell has $a = 10{\cdot}375$, $c = 32{\cdot}68$ Å, $Z = 6$. Three-dimensional intensity data were recorded on integrated equi-inclination Weissenberg photographs using Co-K_α radiation and measured photometrically. The structure was solved by the heavy-atom technique[5] and positional

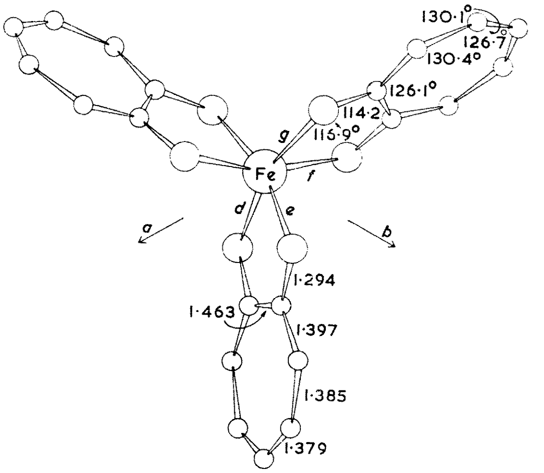
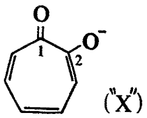


FIGURE. *Drawing of the* FeX_3 *molecule as viewed down the* c-*axis. Bond lengths in* Å, *angles in degrees. Iron co-ordination sphere*: Fe–O 2·008 Å, ∠*de* 77·8°, ∠*df* 91·1°, ∠*ef* 102·6°, ∠*dg* 162.4°.

and anisotropic thermal parameters refined by least-squares (local version of the ORFLS programme[6]). Hydrogen atoms were included in the calculations with fixed co-ordinates. The final value of R is 6·4% for 405 observed structure amplitudes.

Our results are summarised in the Figure which shows one molecule of FeX_3 (six asymmetric units), centred at the special position $(0,0,\frac{1}{2})$ with point symmetry 32 (D_3). Estimated standard deviations are 0·003 Å for Fe–O, 0·005 Å for C–O and about 0·007 Å for C–C lengths; for angles involving iron, 0·1—0·2° and for other angles 0·3—0·7°.



The Fe–O length of 2·008 Å is within the range of values found in comparable six-co-ordinated high-spin Fe^{3+} complexes such as ferric acetylacetonate[7] and iron cupferron[8] (1·99—2·01 Å), and may be compared with the sum of the ionic radii (2·04 Å). The essentially octahedral co-ordination of iron by oxygen deviates considerably from the ideal configuration. The O–Fe–O angle involving oxygen atoms from the same ligand is 77·8° (an apparently necessary consequence of the dimensions of the rigid tropolonate ligand and the effective radius of high-spin Fe^{3+}), with a concomitant increase of other angles above 90°, while overall D_3 symmetry is maintained. It may be noted that a similar co-ordination geometry is adopted by the iron cupferron molecule,[8] but here D_3 symmetry is only approximately maintained.

The C–C bond lengths, apart from the C(1)–C(2) bond, are in good agreement with the standard aromatic value of 1·394 Å.[9] The C(1)–C(2) length of 1·463 Å is significantly greater than this, and only slightly less than the value suggested[10] for the length of the C_{sp^2}–C_{sp^2} single bond (1·48 Å), so that this bond is included in the π-electron delocalisation only to a small extent. Conjugation, however, appears to be virtually complete around the periphery of the tropolone ring and includes the oxygen atoms. This picture of bond dimensions is comparable to that found in the tropolone anion [C(1)–C(2) = 1·487 Å, other C–C bonds, 1·388—1·426 Å]. The differences in bond angles within the tropolone ring ("small" angles of 126·1 and 126·7°, and "large" angles of 130·4 and 130·1°) appear to be real and also follow a pattern similar to that in the tropolone anion (angles at corresponding atoms in the ring: 125·0, 127·3, 131·9, 129·6°).[4]

Each "blade" of the propeller-shaped molecule is planar to within the limits of experimental error, the maximum atomic displacement from the mean plane being 0·009 Å and the r.m.s. displacement 0·006 Å. It is interesting that in the cupric tropolone structure, although the seven carbon atoms of the ring are coplanar, the plane of the copper and oxygen atoms makes an angle of 4·9° with this plane. Consistent with this, the molecule exhibits marked bond-length alternation.[3]

The possibility that bond-length alternation in the ferric tropolone molecule might be concealed by disorder in the crystal packing cannot be entirely excluded. However, since the thermal parameters appear to be normal, and refinement has led to a satisfactory R value, we consider that this is unlikely. Furthermore, there is no packing disorder in the analogous cupric tropolone structure.

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