

Tris[2-(2-oxazolin-2-yl)phenolato]-
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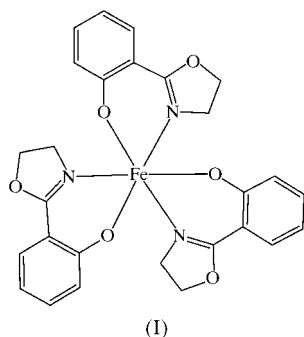
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The title compound, tris[2-(4,5-dihydrooxazol-2-yl- κ N)-phenolato- κ O]iron(III), [Fe(C₉H₈NO₂)₃], is disordered over a non-crystallographic twofold rotation axis perpendicular to the crystallographic threefold rotation axis. The disorder can be a pure rotational disorder of an iron complex in the facial configuration, or the consequence of a mixture of facial and meridional configurations. In the latter case, at least 25% of the iron complexes must adopt the facial configuration in order to obtain the disorder ratio observed in the crystal.

Comment

The title compound, (I), was prepared in the course of our investigation aimed at producing new epoxidation catalysts (Hoogenraad *et al.*, 2002). The crystal structure, abbreviated as Fe(phox)₃, shows the Fe^{III} ion located on a crystallographic threefold rotation axis. The distribution of the Fe^{III} ions over the unit cell follows space group $P\bar{3}m1$, which is a supergroup of $P\bar{3}$, the actual space group of (I). The higher symmetry holds only for the iron substructure.



The phox ligand is found to be disordered over two orientations, hereafter denoted *A* [occupancy factor refined to 0.758 (5)] and *B* [occupancy factor 0.242 (5)]. Orientations *A* and *B* are related by a non-crystallographic twofold rotation

axis perpendicular to the crystallographic threefold rotation axis. In Fig. 1, a displacement ellipsoid plot of the major component is given. Fig. 2 shows both orientations of the ligand as a ball-and-stick model.

The crystal packing can accommodate both orientations of the ligand in the ratio found during refinement. Only when the contact ligands of two neighbouring complexes are in the minor disorder component orientation (*B*) are interatomic distances shorter than the van der Waals radii found.

An exact analysis of the configuration of the coordinating phox ligands to the central cation is very difficult due to the presence of disorder in the crystal structure. We expected Fe(phox)₃ to assume the meridional configuration, as found in all other previously reported Fe^{III}N₃O₃ species [Cambridge Structural Database (CSD), February 2002 update; Allen & Kennard, 1993]; the only exceptions are the mixed-valence Fe^{II}/Fe^{III} complex (Mashuta *et al.*, 1992) and the related manganese(III) complex Mn(phox)₃ (Hoogenraad *et al.*, 1998). A complex in the meridional configuration would have its three phox ligands in an *AAB* orientation. The threefold crystallographic symmetry would generate the permutations *ABA* and *BAA*, resulting in an occupancy of $\frac{2}{3}$ for the major component. However, the Fe(phox)₃ complex, as a whole, can also be rotated by the local twofold axis that causes the disorder, resulting in the *BBA* orientation of the ligands (and permutations thereof). The observed occupation factor of component *A* could therefore lie between the values $\frac{2}{3}$ and $\frac{1}{3}$, depending on the amount of disorder of the complete molecule over the local twofold rotation axis.

The observed value of 0.758 (5) for the occupancy of *A* clearly lies outside of the expected range. If this is not an artifact caused by effects unaccounted for in the present model,¹ the high value found for the occupancy of the major component would suggest that at least $\frac{1}{4}$ of the molecules have their three ligands in the *AAA* (or *BBB*) configuration. *AAA* represents a structure with the facial configuration of the ligands. The disorder model can also be interpreted as consisting of 75.8% *AAA* configuration and 24.2% *BBB* configuration, *i.e.* 100% facial configuration distributed over two orientations which are related by the disorder operation. It should be noted that, according to the CSD, the facial configuration only occurs if the ligands are forced by covalent or coordinating bonds to adopt this orientation. Since the facial configuration has not been corroborated by other techniques, further study is necessary to unequivocally assign this configuration to a part of the complex molecules present in the crystal.

The Cremer & Pople (1975) total puckering amplitude amounts to 0.077 (9) Å for the oxazolinyl ring and to 0.020 (10) Å for the phenyl ring of the major disorder component, indicating that the former ring deviates slightly more from planarity than the latter. For the minor disorder component, the puckering parameters are 0.05 (2) and 0.03 (3)

¹ There is no indication of twinning over one of the symmetry elements of the supergroup of the iron substructure, as is illustrated by the averaging index R_{int} , which amounts to 0.359 for $P\bar{3}m1$ as opposed to 0.057 for $P\bar{3}$. Systematic deviations of F_{calc} from F_{obs} , another indicator of twinning, were not found.

for the oxazolanyl and phenyl rings, respectively, showing a less pronounced difference. The acute angles between the least-squares planes of the oxazolanyl and phenyl rings are 6.1 (4) and 3.0 (12)° for the major and minor disorder components, respectively. The six-membered chelate rings deviate significantly from planarity, as is indicated by a total puckering amplitude of 0.167 (6) Å for the major and 0.263 (18) Å for the minor disorder component.

The crystal structure of (I) displays a close C—H···O contact for each disorder component (Table 2). These inter-

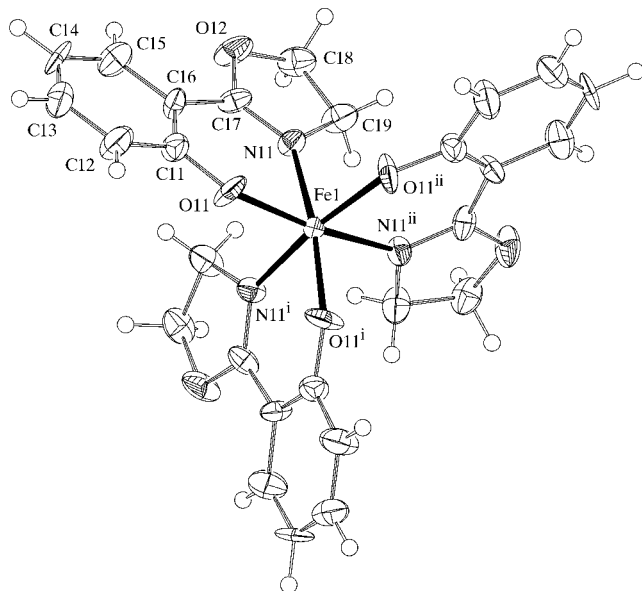


Figure 1
View of [Fe(phox)₃] with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. The minor disorder component has been omitted for clarity. The labels for the minor disorder component are obtained by replacing the first digit of the atom label by '2'. [Symmetry codes: (i) 1 - y, x - y, z; (ii) 1 - x + y, 1 - x, z.]

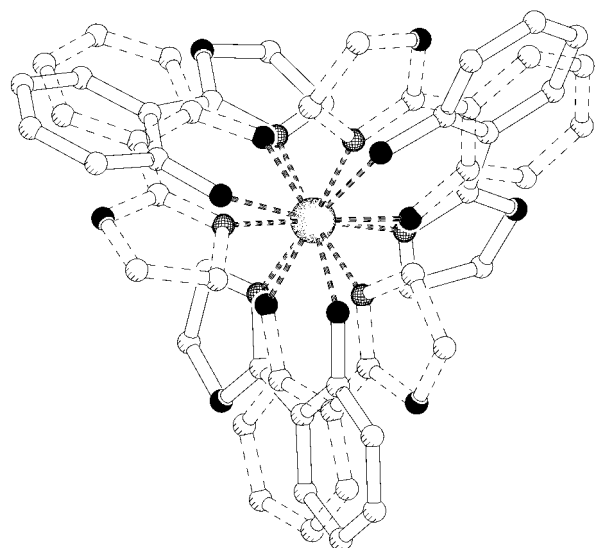


Figure 2
The major (solid lines) and minor (dashed lines) disorder components of [Fe(phox)₃], which are related by a non-crystallographic twofold rotation axis. H atoms have been omitted for clarity.

actions link the molecules into infinite chains parallel to *c*. An illustration is given in Fig. 3.

In the IR spectrum of [Fe(phox)₃], the effect of complexation on the C=N bond is demonstrated by the shift from 1644 cm⁻¹ in the free ligand to 1617 cm⁻¹ in the complex. The UV-vis-NIR spectrum (NIR is near IR) of the solid compound shows a broad absorption in the range between 700

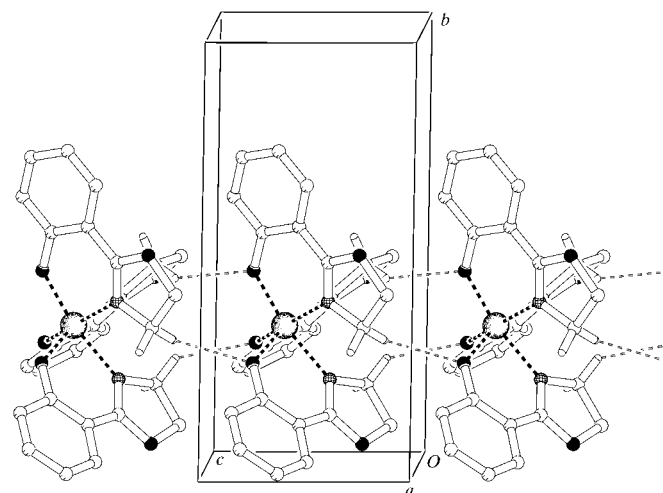


Figure 3
The C—H···O interactions in [Fe(phox)₃]. H atoms, with the exception of those of the oxazolanyl CH₂ moieties involved in the interactions, have been omitted for clarity. Only the major disorder component is shown.

and 230 nm. The UV-vis-NIR spectrum of [Fe(phox)₃] in methanol shows an absorption band at 461 nm, which can be assigned to the phenolate-to-Fe^{III} ligand-to-metal charge-transfer (LMCT) band. Bands observed at 307 and 222 nm, which are also present in the free ligand, can be assigned to $\pi \rightarrow \pi^*$ transitions of the ligand. The magnetic moment of [Fe(phox)₃] (5.70 μ_B) is close to the spin-only value of 5.92 μ_B expected for an $S = \frac{5}{2}$ system of an octahedral high-spin Fe^{III} ion. During variable-temperature measurements, the compound shows a strict Curie-Weiss behaviour, indicating an isolated paramagnetic ion, as the plot of $1/\chi$ against T can be extrapolated to zero.

Experimental

For the synthesis of [Fe(phox)₃], FeCl₃·6H₂O (0.27 g, 1.0 mmol), dissolved in water (10 ml), was added to a stirred solution of Hphox (0.49 g, 3.0 mmol) and triethylamine (0.30 g, 3.0 mmol) in methanol (10 ml). A dark-red product precipitated within a few days and was collected by filtration. The complex was recrystallized from acetonitrile to yield 0.40 g (0.74 mmol, 74%) of [Fe(phox)₃]. X-ray quality crystals were obtained by recrystallization from MeOH/MeCN (3:1). IR (cm⁻¹): 1617 (s), 1589 (w), 1545 (m), 1470 (s), 1441 (m), 1390 (m), 1336 (m), 1260 (m), 1239 (m), 1154 (m), 1071 (m), 947 (w), 928 (w), 856 (m), 759 (m), 688 (m), 660 (w), 601 (w). Analysis calculated for C₂₇H₂₄FeN₃O₆: C 59.80, H 4.46, N 7.75%; found: C 59.38, H 4.63, N 7.75%. ES-MS: *m/z*: 543 {[Fe(phox)₃] + H⁺}, 380 {[Fe(phox)₂]⁺}, 164 {Hphox + H⁺}. Electronic absorption spectrum in MeOH, λ_{\max}/nm ($\epsilon/M^{-1} \text{ cm}^{-1}$): 461 (4.1×10^3), 307 (1.4×10^4), 222 (5.1×10^4). $\mu_{\text{eff}} = 5.70 \mu_B$ (at 290.6 K).

Crystal data

| | |
|--|---|
| [Fe(C ₉ H ₈ NO ₂) ₃] | Mo K α radiation |
| $M_r = 542.34$ | Cell parameters from 25 reflections |
| Trigonal, $P\bar{3}$ | $\theta = 10.2\text{--}15.3^\circ$ |
| $a = 14.882(2) \text{ \AA}$ | $\mu = 0.66 \text{ mm}^{-1}$ |
| $c = 6.4052(11) \text{ \AA}$ | $T = 150 \text{ K}$ |
| $V = 1228.5(3) \text{ \AA}^3$ | Block, dark red |
| $Z = 2$ | $0.30 \times 0.15 \times 0.05 \text{ mm}$ |
| $D_x = 1.466 \text{ Mg m}^{-3}$ | |

Data collection

| | |
|--|------------------------------|
| Enraf–Nonius CAD-4 Turbo diffractometer | $\theta_{\max} = 25.0^\circ$ |
| ω scans (with $\Delta\omega = 1.26 + 0.35 \tan\theta$) | $h = -19 \rightarrow 17$ |
| 1686 measured reflections | $k = -17 \rightarrow 19$ |
| 1448 independent reflections | $l = -8 \rightarrow 0$ |
| 970 reflections with $I > 2\sigma(I)$ | 3 standard reflections |
| $R_{\text{int}} = 0.057$ | frequency: 60 min |
| | intensity decay: 3% |

Refinement

| | |
|-------------------------------|---|
| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2) + (0.0615P)^2 + 1.78P]$ |
| $R(F) = 0.074$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.168$ | $(\Delta/\sigma)_{\max} < 0.001$ |
| $S = 1.19$ | $\Delta\rho_{\max} = 0.51 \text{ e \AA}^{-3}$ |
| 1448 reflections | $\Delta\rho_{\min} = -0.53 \text{ e \AA}^{-3}$ |
| 161 parameters | |
| H-atom parameters not refined | |

Table 1

Selected geometric parameters (\AA , $^\circ$).

| | | | |
|---------------------------|------------|---------------------------|------------|
| Fe1—O11 | 1.940 (7) | O22—C27 | 1.35 (3) |
| Fe1—N11 | 2.132 (7) | O22—C29 | 1.44 (3) |
| Fe1—O21 | 1.870 (19) | N11—C17 | 1.313 (13) |
| Fe1—N21 | 2.10 (2) | N11—C18 | 1.476 (11) |
| O11—C11 | 1.338 (12) | N21—C27 | 1.30 (3) |
| O12—C17 | 1.343 (10) | N21—C28 | 1.47 (3) |
| O12—C19 | 1.448 (11) | C18—C19 | 1.505 (14) |
| O21—C21 | 1.35 (3) | C28—C29 | 1.49 (3) |
| O11—Fe1—N11 | 83.7 (3) | O21—Fe1—N21 | 85.6 (8) |
| O11—Fe1—O11 ⁱ | 98.8 (3) | O21—Fe1—O21 ⁱ | 105.9 (9) |
| O11—Fe1—N11 ⁱ | 93.4 (3) | O21—Fe1—N21 ⁱ | 162.3 (9) |
| O11—Fe1—N11 ⁱⁱ | 167.0 (3) | O21—Fe1—N21 ⁱⁱ | 83.0 (10) |
| N11—Fe1—N11 ⁱ | 83.4 (3) | N21—Fe1—N21 ⁱ | 82.5 (9) |

Symmetry codes: (i) $1 - y, x - y, z$; (ii) $1 - x + y, 1 - x, z$.

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

| $D\text{---}H\cdots A$ | $D\text{---}H$ | $H\cdots A$ | $D\cdots A$ | $D\text{---}H\cdots A$ |
|-------------------------------------|----------------|-------------|-------------|------------------------|
| C18—H18A \cdots O11 ⁱ | 0.99 | 2.52 | 3.313 (11) | 137 |
| C28—H28A \cdots O21 ⁱⁱ | 0.99 | 2.58 | 3.36 (3) | 136 |

Symmetry codes: (i) $1 - x + y, 1 - x, z - 1$; (ii) $1 - y, x - y, 1 + z$.

The phox ligand was found to be disordered over two positions related by a non-crystallographic twofold rotation axis. The smallest angle between the disorder axis and a translation axis is approximately 9° . The coordinates of both components and their occupation ratio were refined. Corresponding distances and 1–3 distances of the disorder components were restrained to be equal within an s.u. of 0.02 \AA . H atoms were included in the model in calculated positions, riding on their carrier atoms. The minor component non-H atoms were refined with isotropic displacement parameters. The isotropic displacement parameters of the H atoms bonded to C atoms were coupled to the equivalent isotropic displacement parameter of their carrier atoms by a fixed factor of 1.2.

Data collection: locally modified *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *SET4* (de Boer & Duisenberg, 1984); data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1649). Services for accessing these data are described at the back of the journal.

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