

***fac*-Tris(2-ethyl-4-oxo-4*H*-pyran-3-olato- $\kappa^2$ O<sup>3</sup>,O<sup>4</sup>)iron(III) and its aluminium(III) analog**

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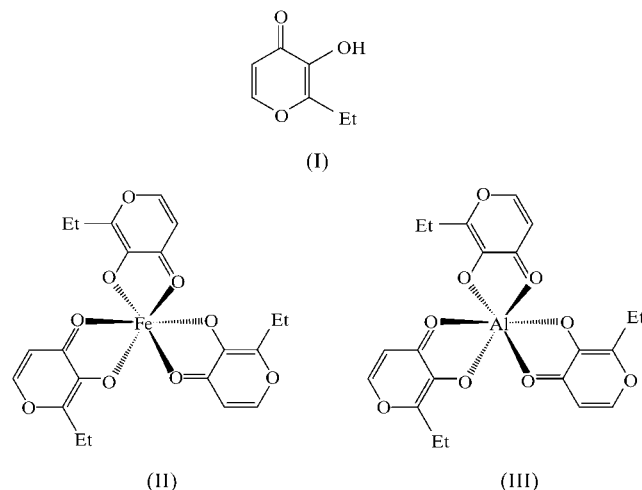
The crystal structures of the title iron(III) and aluminium(III) ethyl maltolate complexes, [Fe(C<sub>7</sub>H<sub>7</sub>O<sub>3</sub>)<sub>3</sub>] and [Al(C<sub>7</sub>H<sub>7</sub>O<sub>3</sub>)<sub>3</sub>], respectively, are isomorphous. In each case, the three bidentate ligand molecules are bound to the metal atom, forming a distorted octahedral coordination geometry in a *fac* configuration.

**Comment**

Pyranone ligands have remarkable properties for clinical purposes. These ligands are relevant to the control of metal levels in the body and have so far been tested for administration for the amelioration of anaemia (Hider *et al.*, 1984*a,b*), and the removal of iron (Kontoghiorghes *et al.*, 1990) and aluminium (Kontoghiorghes, 1995) overload. One of these ligands, *viz.* ethyl maltol (2-ethyl-3-hydroxy-4-pyranone), (I), is suitable for oral administration since it has no toxic effects. It has been tested for the characteristics of iron uptake (Levey *et al.*, 1988; Maxton *et al.*, 1994). In this study, in order to determine the chelating mode of ethyl maltol to the Fe<sup>3+</sup> and Al<sup>3+</sup> ions, we have analyzed the crystal structures of the title complexes, namely *fac*-tris(2-ethyl-4-oxo-4*H*-pyran-3-olato)-iron(III), (II), and *fac*-tris(2-ethyl-4-oxo-4*H*-pyran-3-olato)-aluminium(III), (III), which are isomorphous.

In (II), the Fe atom is bound by the deprotonated hydroxyl and ketone O atoms of three bidentate ligands, forming a distorted octahedral structure (Fig. 1). The chelating O atoms of each ligand form a five-membered chelate ring with the Fe atom. In the ligand molecule, the C—O<sub>keto</sub> bond lengths [O3—C4 = 1.262 (4) Å, O6—C11 = 1.259 (4) Å and O9—C18 = 1.262 (4) Å] are longer than those of free ethyl maltol in the crystal [1.235 (2)–1.256 (6) Å; Brown *et al.*, 1995], and the C—O<sub>OH</sub> bonds [O2—C3 = 1.330 (4) Å, O5—C10 = 1.326 (3) Å and O8—C17 = 1.321 (4) Å] are shorter than those of free ethyl maltol [1.347 (3)–1.356 (6) Å]. This indicates the distinction between the two types of Lewis acid–base inter-

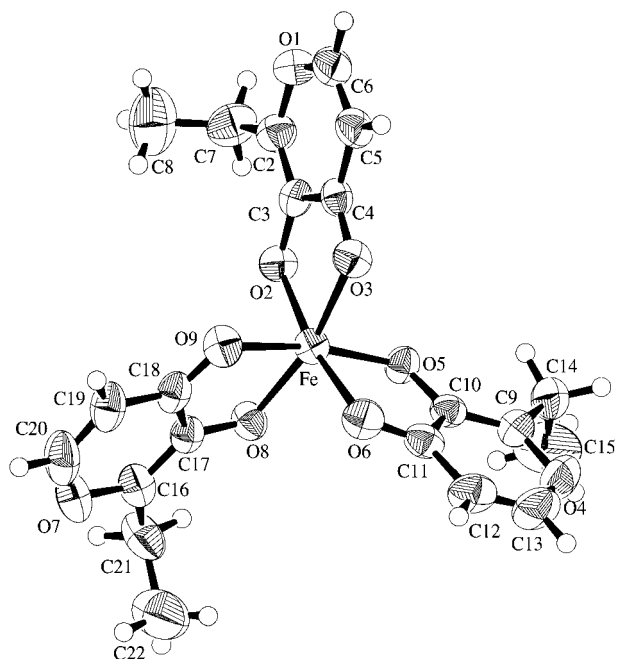
actions. The Fe atom lies in a trigonally distorted octahedral environment, coordinated to the six O atoms of three bidentate ligands in a *fac* configuration, that is, the three longer Fe—O<sub>keto</sub> bonds (Fe—O3, Fe—O6 and Fe—O9) are *cis* to each other, and the three shorter Fe—O<sub>OH</sub> bonds (Fe—O2, Fe—O5 and Fe—O8) are also *cis*. The distortion of the octahedral environment is due to the differences found in the Fe—O bond lengths [Fe—O<sub>keto</sub> = 2.074 (2)–2.090 (2) Å and Fe—O<sub>OH</sub> = 1.960 (2)–1.969 (2) Å]. This situation is similar to that in the crystal structure of the maltolate–Fe<sup>3+</sup> complex (Ahmet *et al.*, 1988). The differences between the Fe—O<sub>keto</sub> and Fe—O<sub>OH</sub> bond lengths are due to the negative charge at the deprotonated O atom.



In (III), coordination about the Al atom is similar to that in (II). The Al atom is surrounded by six O atoms of three bidentate ligands in a *fac* configuration, resulting in a distorted octahedral environment (Fig. 2). In the ligand molecule, the C—O<sub>keto</sub> bond lengths [O3—C4 = 1.274 (6) Å, O6—C11 = 1.263 (6) Å and O9—C18 = 1.268 (6) Å] are longer than those of free ethyl maltol and the C—O<sub>OH</sub> bonds [O2—C3 = 1.315 (5) Å, O5—C10 = 1.329 (5) Å and O8—C17 = 1.321 (5) Å] are shorter than those of the free molecule. The overall conformational tendency of (III) is similar to that in the crystal structures of previously reported maltolate–Al<sup>3+</sup> complexes (Finnegan *et al.*, 1986; Yu *et al.*, 2002).

Despite the conformational similarity of the crystal structures of (II) and (III), the bite angles, O—M—O, of the ethyl maltolate ligands are different. Those for the Fe<sup>3+</sup> complex [range 80.39 (9)–80.79 (9)°] are smaller than those for the Al<sup>3+</sup> complex [range 84.3 (1)–84.6 (1)°]. This correlates with the M—O bond lengths [Fe—O = 1.960 (2)–2.090 (2) Å and Al—O = 1.860 (3)–1.956 (4) Å], *viz.* the steric constraint imposed by the ionic radii (0.79 Å for Fe<sup>3+</sup> and 0.68 Å for Al<sup>3+</sup>; Shannon, 1976).

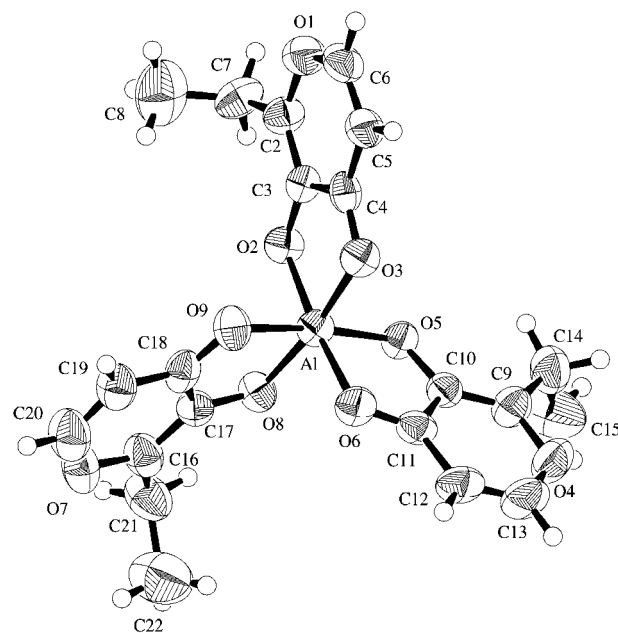
Until now, the crystal structures of the Sn<sup>4+</sup> (Lu *et al.*, 1999; Alshehri *et al.*, 2000), Ti<sup>4+</sup> (Alshehri *et al.*, 2000) and Bi<sup>3+</sup> (Burgess *et al.*, 1994) complexes of ethyl maltol have been reported. In these complexes, similar to (II) and (III), the metal atoms are bound by bidentate ligand molecules which form five-membered chelate rings. These structures, except for



**Figure 1**  
ORTEP (Johnson, 1976) drawing of (II), with the atomic numbering scheme. Ellipsoids for non-H atoms are shown at the 50% probability level.

the  $Ti^{4+}$  complex, show the same trends with regard to the increasing radius of the metal ion, *i.e.* the  $M-O$  bond lengths increase and the  $O-M-O$  bond angles decrease with increasing ionic radius.

Comparing the two title complexes with the corresponding maltolate complexes shows that all four crystal structures are similar in the fact that the metal atoms are bound by six O



**Figure 2**  
ORTEP (Johnson, 1976) drawing of (III), with the atomic numbering scheme. Ellipsoids for non-H atoms are shown at the 50% probability level.

atoms of bidentate ligand molecules to form distorted octahedral structures, but are different with regard to their geometrical isomerism properties. In the ethyl maltolate complexes, the ligand molecules are coordinated in a *fac* configuration, in contrast with the maltolate complexes, which exhibit a *mer* configuration. This may be due to the bulky hydrophobic ethyl groups of the ethyl maltolate ligand molecules.

## Experimental

For the preparation of (II), ethyl maltol and  $Fe(NO_3)_3 \cdot 9H_2O$  (8:1 molar ratio) were dissolved in ethanol–water (4:6). Red pillar-shaped crystals of (II) were obtained by slow evaporation at room temperature. For the preparation of (III), ethyl maltol and  $Al(NO_3)_3 \cdot 9H_2O$  (3:1 molar ratio) were dissolved in ethanol–water (1:1). The pH of this solution was raised to about 8 by the addition of ammonia solution, and the resulting solution was then heated for a few minutes and cooled to room temperature. Colorless plate-shaped crystals of (III) were obtained by slow evaporation.

## Compound (II)

### Crystal data

$[Fe(C_7H_7O_3)_3]$   
 $M_r = 473.23$   
 Monoclinic,  $P2_1/n$   
 $a = 7.878$  (3) Å  
 $b = 8.818$  (4) Å  
 $c = 30.721$  (2) Å  
 $\beta = 90.80$  (2)°  
 $V = 2133.9$  (13) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.473$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 12.8$ – $14.3^\circ$   
 $\mu = 0.76$  mm<sup>-1</sup>  
 $T = 296.2$  K  
 Pillar, red  
 $0.40 \times 0.10 \times 0.10$  mm

### Data collection

Rigaku AFC-5R diffractometer  
 $\omega$  scans  
 5604 measured reflections  
 4911 independent reflections  
 2768 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.026$   
 $\theta_{max} = 27.5^\circ$

$h = 0 \rightarrow 10$   
 $k = 0 \rightarrow 11$   
 $l = -39 \rightarrow 39$   
 3 standard reflections  
 every 150 reflections  
 intensity decay: 0.1%

### Refinement

Refinement on  $F^2$   
 $R(F) = 0.042$   
 $wR(F^2) = 0.135$   
 $S = 0.99$   
 4911 reflections  
 283 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0624P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.001$   
 $\Delta\rho_{max} = 0.41$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.32$  e Å<sup>-3</sup>

**Table 1**  
Selected geometric parameters (Å, °) for (II).

Fe–O2	1.969 (2)	O2–C3	1.330 (4)
Fe–O3	2.085 (2)	O3–C4	1.262 (4)
Fe–O5	1.960 (2)	O5–C10	1.326 (3)
Fe–O6	2.074 (2)	O6–C11	1.259 (4)
Fe–O8	1.967 (2)	O8–C17	1.321 (4)
Fe–O9	2.090 (2)	O9–C18	1.262 (4)
O2–Fe–O3	80.79 (9)	O8–Fe–O9	80.39 (9)
O5–Fe–O6	80.71 (8)		

Compound (III)

Crystal data

[Al(C<sub>7</sub>H<sub>7</sub>O<sub>3</sub>)<sub>3</sub>]  
*M<sub>r</sub>* = 444.36  
 Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 7.897 (4) Å  
*b* = 8.696 (9) Å  
*c* = 30.801 (4) Å  
 $\beta$  = 91.40 (3)°  
*V* = 2115 (2) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.395 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 10 reflections  
 $\theta$  = 10.4–11.8°  
 $\mu$  = 0.15 mm<sup>-1</sup>  
*T* = 296.2 K  
 Plate, colorless  
 0.20 × 0.20 × 0.10 mm

Data collection

Rigaku AFC-5R diffractometer  
 $\omega$  scans  
 Absorption correction:  $\psi$  scan  
 (North *et al.*, 1968)  
*T<sub>min</sub>* = 0.952, *T<sub>max</sub>* = 0.999  
 5552 measured reflections  
 4868 independent reflections  
 1804 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.127  
 $\theta_{\text{max}}$  = 27.5°  
*h* = 0 → 10  
*k* = 0 → 11  
*l* = -39 → 40  
 3 standard reflections  
 every 150 reflections  
 intensity decay: 7.3%

Refinement

Refinement on *F*<sup>2</sup>  
*R*(*F*) = 0.064  
*wR*(*F*<sup>2</sup>) = 0.228  
*S* = 0.94  
 4868 reflections  
 280 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.1054P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.37 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.42 \text{ e \AA}^{-3}$

Table 2

Selected geometric parameters (Å, °) for (III).

Al—O2	1.872 (3)	O2—C3	1.315 (5)
Al—O3	1.956 (3)	O3—C4	1.274 (5)
Al—O5	1.858 (3)	O5—C10	1.329 (5)
Al—O6	1.949 (3)	O6—C11	1.263 (6)
Al—O8	1.874 (3)	O8—C17	1.321 (5)
Al—O9	1.952 (3)	O9—C18	1.268 (6)
O2—Al—O3	84.6 (1)	O8—Al—O9	84.3 (1)
O5—Al—O6	84.6 (1)		

The intensity decay of standard reflections for (III) was 7.3%, which was corrected. For both compounds, all H atoms were generated geometrically and refined as riding atoms (C—H = 0.93–0.96 Å).

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell

refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2000); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1104). Services for accessing these data are described at the back of the journal.

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