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SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF OXO-BRIDGED BINUCLEAR IRON(III) COMPLEX $[Fe(phen)_2PhCOO]_2OCl_2 \cdot 7H_2O$

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Abstract—An oxo-bridged binuclear iron(III) complex, $[Fe(phen)_2PhCOO]_2OCl_2 \cdot 7H_2O$, was synthesized and the crystal structure indicated that two octahedrally coordinated iron(III) ions bridged with oxygen atoms formed a non-linear complex. The bond angle of Fe—O—Fe is 155.6°. The studies of magnetic properties showed that there was strong antiferromagnetic superexchange coupling ($J = -80.8$ cm^{-1}) between two $S = 5/2$ iron(III) ions.

The first oxo-bridged binuclear iron(III) complex, $[Fe(salen)]_2O$, was prepared by Pferiffer *et al.* 1933.[1] The magnetic exchange interaction between two iron(III) ions has earlier been reviewed.[2-4] Most oxo-bridged Fe^{III} dimers appear to have strong antiferromagnetic superexchange coupling ($-J = 122$–146 cm^{-1}).[5] A series of binuclear iron(III) complexes in which phen acts as a terminal ligand has been reported.[6] In this paper, we report the synthesis, crystal structure and magnetic properties of $[Fe(phen)_2PhCOO]_2OCl_2 \cdot 7H_2O$.

EXPERIMENTAL

THF, MeOH and CH_3CN were used as received. Elemental analyses for carbon, hydrogen and nitrogen were performed on a Perkin–Elmer 240C analyser. The variable-temperature (74–300 K) magnetic susceptibility of crystal line samples of the title complex (26.74 mg) was obtained on a Shimadzu-MB-2 magnetic balance at 1.2 T magnetic field. IR spectra were obtained on a Nicolet FT 1703X spectrometer using KBr pellets.

Preparation of materials

Synthesis of $[Fe(phen)_2PhCOO]_2OCl_2 \cdot 7H_2O$. $(NEt_4)_2[Fe_2OCl_6]$ was prepared following ref. 7. $(NEt_4)_2[Fe_2OCl_6]$ (0.207 g) and PhCOONa (0.1 g) were dissolved in acetonitrile (3.5 cm^3) with stirring for 2 h, and then an acetonitrile solution of phenanthroline (0.136 g) was added. The colour of the solution turned dark brown, and was then stirred for 5 h, filtered and the red–brown filtrate was vapourized in air for several weeks before the single crystal was obtained, yield: 78%. Found: C, 57.6; H, 3.9; N, 8.8. Calc. for $[Fe(phen)_2 PhCOO]_2OCl_2 \cdot 7H_2O$: C, 57.8; H, 4.4; N, 8.7%. IR data: 3372(s) H_2O, 3054(w), 1613(s), 1575(m), 1516(s), 1425(s), 1337(vs), 1225(w), 1141(m), 1104(m), 848(s), 817(s), 723(vs), 6721w), 573(w) cm^{-1}.

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X-ray crystallography

A prismatic red–black crystal ($0.32 \times 0.30 \times 0.30$ mm) was used for X-ray diffraction at 293 K using graphite-monochromated Mo-K_α(0.71069 Å) radiation and ω–2θ scan mode in the range $3 \leqslant 2\theta \leqslant 50°$. Of the 5444 unique reflections, 3509 with $|F| \geqslant 4\sigma|F|$ were used in the structure calculation. The structure was solved using direct methods and difference-Fourier syntheses, and refined by the full-matrix least-squares technique using anisotropic temperature factors. Hydrogen atoms were calculated as riding on carbon atoms at 0.96 Å and refined using isotropic temperature factors. Lorentz, polarization and semi-empirical absorption corrections were applied. Crystal data for $[Fe(phen)_2PhCOO]_2OCl_2 \cdot 7H_2O$: $M = 1287.7$, monoclinic, $C2/c$ (No. 15), $a = 18.784(4)$, $b = 16.563(4)$, $c = 20.407(4)$Å, $\beta = 109.99(1)°$, $V = 5966(2)$Å^3, $Z = 4$, $F(000) = 2664$, $D_x = 1.434$ g cm^{-3}, $\mu = 0.65$ mm^{-1}, $0 \leqslant h \leqslant 22$, $0 \leqslant k \leqslant 21$, $-25 \leqslant l \leqslant 24$, the final $R = 0.044$ and $R_w = 0.0586$. $R = \Sigma||F_0| - |F_c||/|F_0|$; $R_w = [[\Sigma\omega^2(|F_0| - |F_c|)^2]/\Sigma\omega^2|F_0|^2]^{1/2}$.

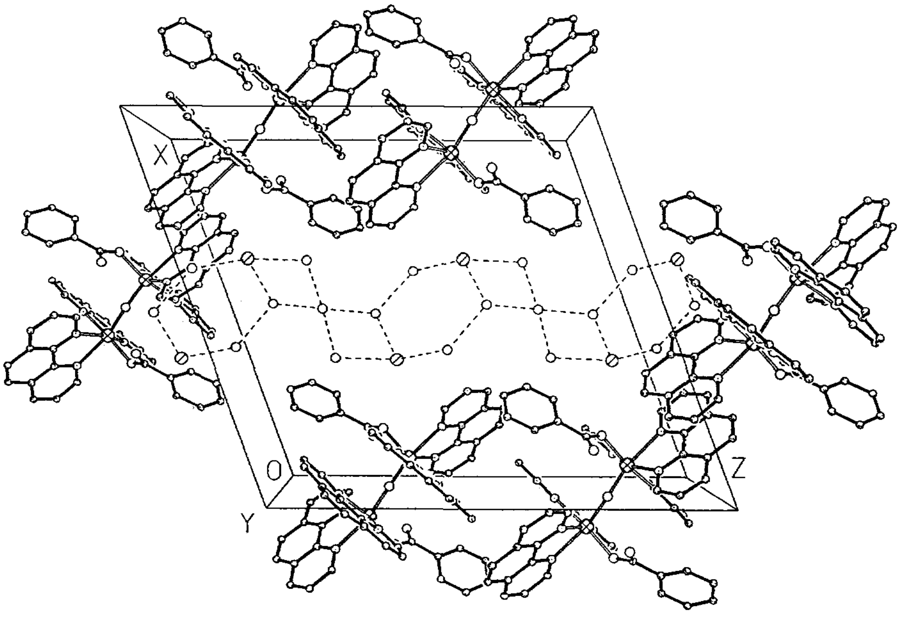
Fractional atomic coordinates and thermal parameters, together with observed and calculated structure factors, have been deposited with editor, from whom copies are available on request. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Center.

RESULTS AND DISCUSSION

Description of the structure

The cation complex of $\{[Fe(phen)_2PhCOO]_2O\}^{2+}$ has a C_2 symmetry axis through the bridged O(1) atom. The title complex consists of a binuclear iron(III) cation complex, $\{[(phen)_2PhCOOFe]_2O\}^{2+}$, seven water molecules and two chloride anions. The structure of the binuclear iron(III) cation complex is shown in Fig. 1. Selected bond distances and angles are listed in Table 1.

The iron atoms are surrounded by four nitrogen and two oxygen atoms to form a distorted octahedral geometry. Four nitrogen atoms from two phenanthrolines are perpendicular to each other. Two parts of the binuclear iron(III) cation complex are bridged by the atom O(1). Benzoic acid coordinates to the Fe^{III} ion as a monodentate ligand, and the Fe—O(carboxylate) distance is 1.956(3)Å, which is shorter than that (2.048 Å) in the complex $Fe_2O(CH_3COO)_2(HBPz_3)_2$[8](here, CH_3COO^- acts as a bidentate ligand.) The Fe—O(1) distance (1.789 Å) is in accordance with that of $(FeL)_2O \cdot$solvate[9] (1.76–1.82 Å). The bond angle of Fe—O(1)—Fe is 155.6°, which is less than that of the other dinuclear iron(III) complex (165–175°).[4] The bond angle of Fe—O(1)—Fe is of particular interest. It depends on the electronic repulsion between the ligands, for example, the Fe—O—Fe



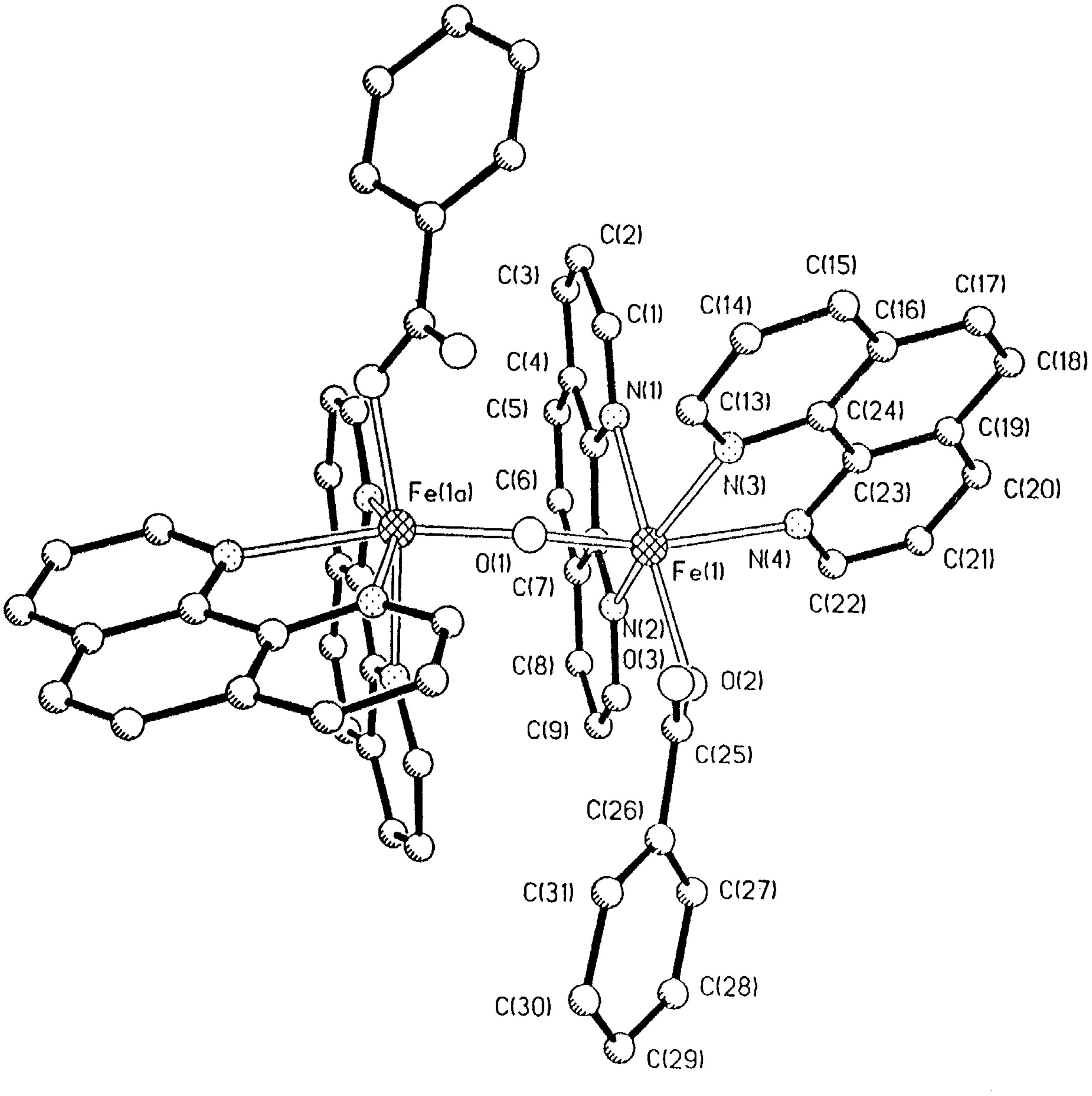


Fig. 1. Structure diagram of the $\{[Fe(phen)_2PhCOO]_2O\}^{2+}$ cation.

angle is *ca* 180° in $(FeTPP)_2O$[4] and 164(2)° and 175(1)° in $[Fe(sal\text{-}N\text{-}m\text{-}C_3H_7)_2]_2O$ and $[Fe(sal\text{-}N\text{-}p\text{-}Cl\text{-}C_6H_4)_2]_2O$,[4] respectively. The larger the R group, the stronger the electronic repulsion and the larger the bond angle of the complex. In the title complex benzoic acid is a monodentate ligand, the electronic repulsion between the ligands is rather weak, and so the bond angle of Fe—O(1)—Fe is less than the above values. The O(3)—O(1w) distance is 2.719 Å. This means that a strong hydrogen bond exists there. The O(1w)—O(4w) and O(3w)—O(4w) distances are 2.790 and 2.922 Å, respectively, and weak interactions are present there.

IR spectra

The IR spectrum of the title complex displays the absorption peaks of H_2O at 3372 cm^{-1}(s), and phen at 3054(w), 1575(m), 1516(s), 1425(s), 1225(w), 1141(m) and 1104(m) cm^{-1}. The bands at 1613(s), 1337(s), 723(s), 672(w) and 573(w) cm^{-1} belong to benzoic acid. The difference between the bands at 1613 cm^{-1} and 1337 cm^{-1} is 276 cm^{-1}, which indicates that the benzoic acid coordinates in a monodentate fashion. This is in accordance with X-ray crystal structure analysis data. In all oxo-bridged binuclear iron(III) com-

Table 1. Selected intermolecular distances (Å) and bond angles (°)

Fe(1)—O(1)	1.789(1)	Fe(1)—N(1)	2.221(4)
Fe(1)—N(2)	2.168(3)	Fe(1)—N(3)	2.139(3)
Fe(1)—N(4)	2.270(3)	Fe(1)—O(2)	1.956(3)
O(1)—Fe(1a)	1.789(1)		
Cl(1)—O(1w)	3.059	Cl(1)—O(2w)	3.178
Cl(1)—O(3w)	3.031	O(3)—O(1w)	2.719
O(1w)—O(4w)	2.790	O(3w)—O(4w)	2.922
O(1)—Fe(1)—N(1)	89.9(1)	O(1)—Fe(1)—N(2)	102.9(1)
N(1)—Fe(1)—N(2)	75.1(1)	O(1)—Fe(1)—N(3)	95.7(1)
N(1)—Fe(1)—N(3)	90.5(1)	N(2)—Fe(1)—N(3)	156.2(1)
O(1)—Fe(1)—N(4)	167.4(1)	N(1)—Fe(1)—N(4)	82.3(1)
N(2)—Fe(1)—N(4)	84.7(1)	N(3)—Fe(1)—N(4)	74.5(1)
O(1)—Fe(1)—O(2)	101.9(1)	N(1)—Fe(1)—O(2)	159.9(1)
N(2)—Fe(1)—O(2)	86.2(1)	N(3)—Fe(1)—O(2)	104.4(1)
N(4)—Fe(1)—O(2)	88.5(1)	Fe(1)—O(1)—Fe(1a)	155.6(2)

plexes, the antisymmetric stretch of (Fe—O—Fe) is a strong broad band in the region 820–960[4] and 835 cm^{-1} in $[Fe_2O(Phen)_4]X_n$.[6] Therefore, the band at 817 cm^{-1} could belong to the antisymmetric stretch of Fe—O(1)—Fe.

Magnetic properties

The variable-temperature magnetic moment in the range 78–300 K for a solid sample of the title compound is shown in Fig. 2.

The magnetic moment is strongly temperature dependent and decreases from 3.57 B. M. at 301 K to 1.23 B. M. at 77.8 K. This firmly proves that there is antiferromagnetic coupling across the oxygen bridge. The magnetic behaviour of the title complex could be interpreted using isotropic spin Hamiltonian $H = -2JS_1S_2$, where $S_1 = S_2 = 5/2$, and expression (1).[4] The least-squares fitting of the magnetic susceptibility shown in Fig. 2 leads to $J = -80.8$ cm^{-1} and $g = 2.00$.

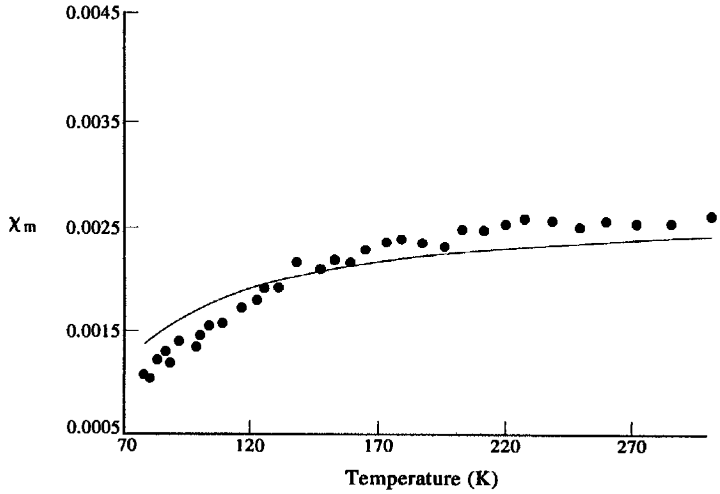


Fig. 2. Plots of the magnetic susceptibility χ_m vs. temperature, T for the title compound, (———) calculated, (● ● ●) experimental.

$$\chi_{\mathrm{Fe}} = \frac{2Ng^2\mu^2[\exp(2x)+5\exp(6x)+14\exp(12x)+30\exp(20x)+55\exp(30x)]}{kT[1+3\exp(2x)+5\exp(6x)+7\exp(12x)+9\exp(20x)+11\exp(30x)]} \tag{1}$$

Here,

$$x = J/kT.$$

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