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Coordination Modes of Polydentate Ligands.
4. The Crystal and Molecular Structure of an Oxo-bridged Iron(III) Complex Containing a Pentadentate Imino–Alkoxy Ligand

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Abstract

In the presence of Fe^{3+}, template condensation of the fluorinated keto-alcohol $CH_3C(O)CH_2C(CF_3)_2OH$ with the triamine $CH_3C(CH_2NH_2)_3$ leads to two products: a fully condensed, imino–alkoxy, iron(III) complex, $Fe\{CH_3C[CH_2N{=}C(CH_3)CH_2C(CF_3)_2O]_3\}$, and a partially condensed iron(III) complex, $O\{FeCH_3C[CH_2N{=}C(CH_3)CH_2C(CF_3)_2O]_2(CH_2NH_2)\}_2$, in which two six-coordinate iron(III) centers are linked by an oxide ion. A complete crystal and molecular structure determination of the latter has been made.

Crystals are monoclinic, space group *C2/c*, $a = 13.886(4)$; $b = 23.206(5)$; $c = 15.241(4)$ Å; $\beta = 106.55(2)°$; $V = 4708$ Å^3; $Z = 4$. Least-squares refinement on F of 322 variables using 2627 observations converged at a conventional agreement factor of 3.8%. The Fe to bridging oxide distance is 1.811(1) Å, the Fe–Fe distance 3.468 Å, and the Fe–O–Fe angle 146.6(2)°. A comparison is made between this structure and those of natural hemerythrin systems.

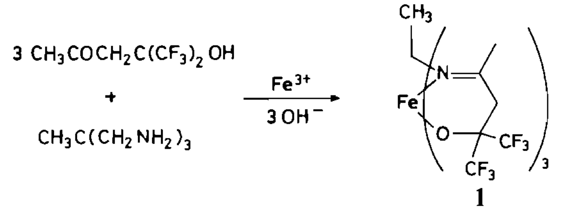
Introduction

We have previously demonstrated the application of template condensation processes in the formation of imino–alkoxy Schiff-base type complexes of a variety of metals by the reaction of hexafluorodiacetone-alcohol, $CH_3C(O)CH_2C(CF_3)_2OH$ (HFDA), with primary amines in the presence of metal ions [1–3].

$$R{-}NH_2 + CH_3C(O)CH_2C(CF_3)_2OH \xrightarrow[OH^-]{M^{2+}} \overline{RN{=}C(CH_3)CH_2C(CF_3)_2O{-}M}/2$$

With Cu^{2+} and monofunctional primary amines, the complexes are *trans*-four-coordinate [4]. The use of difunctional amines $H_2N(CH_2)_nNH_2$ with small values of n (2 or 3) leads to complexes containing linked, six-membered, chelate rings in *cis*-geometry, but amines of larger chain lengths ($n \geqslant 5$) give dinuclear[§] complexes in which two *trans*-coordinated, non-interactive, metal centres are linked by the $(-CH_2-)_n$ chains [5, 6]. By use of diamines containing additional $-CH_2-NH-CH_2-$ or $-CH_2-O-CH_2-$ donor sites within a long chain, we have been able to characterize mononuclear, neutral or cationic, complexes in which the metal ion (Co^{2+}, Co^{3+}, Ni^{2+}, or Cu^{2+}) is complexed by a multidentate, dinegative, ligand [2].

It was clearly of interest to extend this study to a condensation reaction using a triamine of suitable geometry to give a trinegative, hexadentate, imino–alkoxy ligand surrounding a tripositive metal ion, and tris(aminomethyl)ethane, $CH_3C(CH_2NH_2)_3$ (TAME), seemed the most suitable starting material. Out of a variety of trivalent metal ions investigated (lanthanides, Co^{3+}), iron(III) proved most suitable for the template condensation process, and the fully condensed product **1** was obtained.



1

However, the yield was poor, and it was apparent that other products were formed in which condensation was incomplete. The most readily isolated of these was shown by complete structural determina-

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[§] We use the terms mononuclear and dinuclear with reference to the number of metal atoms in one unit of the complex.

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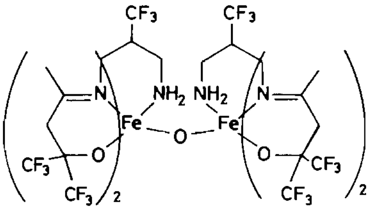
tion to be the dinuclear, neutral, complex 2 in which two Fe^{3+} centers are oxide-bridged, each being surrounded by two iminoalkoxy ligands and one uncondensed NH_2 function:



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This compound, in view of its relevance to the hemerythrin systems, was of greater interest than the fully condensed product, and its structure is described in this paper.

Experimental

Synthesis

General techniques and the preparation of HFDA have been described previously [1]. The triamine TAME, as the trihydrochloride $CH_3C(CH_2NH_2)_3\cdot 3HCl$, was prepared from the corresponding triol by the azide reduction route [7].

In a typical experiment, $FeCl_2\cdot 4H_2O$ (1.32 g, 6.62 mmol), HFDA (4.45 g, 19.9 mmol), and TAME·3HCl (1.50 g, 6.62 mmol) were dissolved in ethanol and ethanolic KOH (1.86 g, 33.1 mmol) added slowly with stirring, allowing free access of air. The solution rapidly became orange–brown in color, with precipitation of KCl. After 1 h, it was filtered, evaporated to dryness, and the product recrystallized from ethanol, giving a brown powder. Microscopic examination showed it to contain two components; the same result was obtained when an excess of HFDA was used in the reaction. The mixture was separated by fractional crystallization using methanol, yielding two products;

(i) Fully condensed iron(III) complex, 1, $Fe\{CH_3C[CH_2N{=}C(CH_3)CH_2C(CF_3)_2O]_3\}$ (less soluble; major fraction), tan powder. *Anal.* Found: C, 34.90; H, 3.25; N, 5.60. Calcd. for $C_{23}H_{24}F_{18}FeN_3O_3$: C, 35.04; H, 3.07; N, 5.33%. Mass spectrum, parent ion, *m/e* 788, strong peak at *m/e* 719 (loss of CF_3). The visible spectrum (acetone solution) showed a strong C.T. peak at 334 nm (ϵ = 1950).

(ii) Partially condensed iron(III) complex, 2, $O\{FeCH_3C\ [CH_2N{=}C\ (CH_3)\ CH_2C\ (CF_3)_2O]_2\ (CH_2NH_2)\}_2$ (more soluble; minor fraction) orange–brown crystals. *Anal.* Found: C, 34.67; H, 3.51; N, 7.12. Calcd. for $C_{34}H_{42}F_{24}Fe_2N_6O_5$: C, 34.54; H, 3.58; N, 7.10%. Mass spectrum, heaviest peaks at *m/e* 599 and 583 (cleavage at one Fe–O bond). Visible spectrum similar to 1, but the C.T. peak was weaker and broader (330–350 nm, ϵ = 660 per Fe centre, acetone solution).

Infrared spectra of 1 and 2 were very similar, with C=N absorption at 1640 cm^{-1} and strong C–F absorption at 1150–1200 cm^{-1}. However, the partially condensed complex 2 could be distinguished by the presence of sharp N–H absorptions (absent in 1) at 3135, 3240, and 3348 cm^{-1}.

Structural Determination

Crystals of complex 2 were grown by slow evaporation from methanol.

X-ray collection and reduction

Diffraction experiments were performed on a four-circle Syntex $P2_1$ diffractometer with graphite-monochromatized Mo Kα radiation. The orientation matrix was obtained from 15 machine-centered reflections selected from a rotation photograph. These data were used to determine the crystal system. Partial rotation photographs around each axis were consistent with a monoclinic crystal system. Machine parameters, crystal data, and data collection parameters are summarized in Table I.

The observed extinctions were consistent with the space groups *C2/c* or *Cc*. $\pm h, -k, -l$ data were collected in three shells ($4.5 < 2\theta < 35.0°$, $35.0 < 2\theta < 45.0°$, $45.0 < 2\theta < 50°$). Three standard reflections were recorded every 197 reflections; their intensities showed no statistically significant change over the duration of data collection. The data were processed by using the SHELX-76 program package on the

TABLE I. Summary of Crystal Data, Intensity Collection and Structure Refinement

Formula	$C_{34}H_{42}Fe_2F_{24}O_5O_6$
M	1181
a (Å)	13.886(4)
b (Å)	23.206(5)
c (Å)	15.241(4)
β (°)	106.55(2)
Crystal system	monoclinic
Space group	*C2/c*
V (Å^3)	4708(2)
D_c (g/cm^3)	1.67
Z	4
Crystal dimensions (mm)	0.13 × 0.27 × 0.35
Absorption coefficient (cm^{-1})	6.94
Radiation	Mo Kα (λ = 0.71069 Å)
Scan speed (deg/min)	2.0–5.0 ($\theta/2\theta$ scan)
Scan range (deg)	1.0° below Kα_1, 1.1° above Kα_2
Background/scan time ratio	0.5
Data collected	2θ of 4.5–50° $\pm h, -k, -l$
Unique data ($F_o^2 > 3\sigma F_o^2$)	2627
Number of variables	322 (2 blocks)
R (%)	3.83
R_w (%)	4.28

computing facilities at the University of Windsor. Of the 4217 reflections measured, a total of 2627 reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement.

Structure Solution and Refinement

Non-hydrogen atomic scattering factors were taken from the tabulation of Cromer and Waber [8, 9]. The Fe atom position was determined by the heavy atom (Patterson) method. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. Refinement was carried out using full-matrix least-squares techniques on F, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ where the weight w is defined as $4F_o^2/\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles, block diagonal least-squares refinement was used, with all non-hydrogen atoms were assigned anisotropic temperature factors. The hydrogen atom contributions were included, C–H bond lengths of 1.08 Å were assumed, and hydrogen atom temperature factors were fixed at 1.20 times the isotropic temperature factor of the bonded carbon atom. This gave $R_1 = \Sigma||F_o| - |F_c|/F_o| = 0.0383$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2} = 0.0428$. The maximum Δ/σ on any of the parameters in the final cycles was 0.013. A final difference Fourier map calculation showed no peaks of chemical significance; the largest peak was 0.75 electrons and was associated with the bridging oxygen atoms. The following data are tabulated: positional parameters (Table II); interatomic distances and angles (Table III). See also 'Supplementary Material'.

TABLE II. Positional Parameters[a]

Atom	x	y	z
Fe	991(1)	1482(1)	2018(1)
F1	2797(2)	2589(1)	1260(2)
F2	3783(2)	2691(1)	2596(2)
F3	2877(3)	3395(1)	1953(3)
F4	3003(2)	2678(2)	4020(2)
F5	1428(2)	2713(2)	3748(2)
F6	2226(3)	3435(1)	3444(3)
F7	2066(2)	−279(1)	3477(2)
F8	2088(2)	−430(1)	2110(2)
F9	3459(2)	−236(1)	3148(3)
F10	3996(2)	596(2)	4464(2)
F11	2554(2)	572(1)	4686(2)
F12	3107(3)	1355(1)	4297(2)
O1	2079(2)	2028(1)	2510(2)
O2	1606(2)	853(1)	2886(2)
O_B	0	1706(1)	2500
N1	623(2)	2034(1)	799(2)
N2	2(2)	824(1)	1214(2)
N5	1946(2)	1063(1)	1171(2)
C1	111(3)	1011(2)	−1239(3)
C2	429(3)	1156(2)	−204(3)
C3	369(3)	1804(2)	−146(3)
C4	714(3)	2586(2)	893(3)
C5	535(4)	3009(2)	99(4)
C6	1007(3)	2836(2)	1843(3)
C7	2027(3)	2609(2)	2455(3)
C8	2880(3)	2829(2)	2072(4)
C9	2171(4)	2862(2)	3419(4)
C10	−314(3)	853(2)	206(3)
C11	1511(3)	945(2)	184(3)
C12	2830(3)	876(2)	1554(3)
C13	3506(3)	588(2)	1078(3)
C14	3235(3)	948(2)	2575(3)
C15	2570(3)	660(2)	3121(3)
C16	2552(3)	8(2)	2973(3)
C17	3061(3)	798(2)	4135(3)

[a] $\times 10^4$.

TABLE III. Selected Interatomic Distances and Angles

Distances (Å)			
Fe–O1	1.952(2)	O1–C7	1.351(5)
Fe–O2	1.991(2)	O2–C15	1.359(4)
Fe–O_B	1.811(1)	N1–C4	1.289(5)
Fe–N1	2.195(3)	N1–C3	1.482(5)
Fe–N2	2.184(3)	N2–C10	1.474(5)
Fe–N3	2.313(3)	N3–C11	1.477(5)
Fe–Fe′	3.468(1)	N3–C12	1.277(4)
C1–C2	1.549(6)	C12–C13	1.501(7)
C2–C3	1.510(6)	C12–C14	1.502(6)
C2–C10	1.521(6)	C14–C15	1.558(6)
C2–C11	1.529(5)		
C4–C5	1.523(7)		
C4–C6	1.504(6)		
C6–C7	1.549(5)		
Angles (deg)			
O1–Fe–O2	94.7(1)	Fe–O1–C7	127.1(2)
O1–Fe–O3	104.6(1)	Fe–O2–C15	128.4(3)
O1–Fe–N1	85.0(1)	Fc–O_B–Fe′	146.6(2)
OI–Fe–N2	165.0(1)	Fe–N3–C12	120.9(3)
O1–Fe–N3	89.1(1)	Fe–N3–C11	120.9(2)
O2–Fe–O_B	99.9(1)	Fe–N2–C10	120.3(3)
O2–Fe–N1	160.6(1)	Fe–N1–C4	119.6(3)
O2–Fe–N2	86.8(1)	Fe–N1–C3	123.1(2)
O2–Fe–N3	81.8(1)	O1–C7–C6	113.6(3)
O_B–Fe–N1	98.9(1)	C7–C6–C4	113.4(4)
O_B–Fe–N2	89.9(1)	C6–C4–C5	116.9(4)
O_B–Fe–N3	166.0(1)	C5–C4–N1	124.2(4)
N1–Fe–N2	88.6(1)	N1–C3–C2	114.4(3)
N1–Fe–N3	78.7(1)	C3–C2–C10	112.4(4)
N2–Fe–N3	76.3(1)	C3–C2–C11	111.1(3)
		C2–C10–N2	114.6(3)
C1–C2–C3	105.7(3)	C2–C11–N3	114.0(3)
C1–C2–C10	106.7(3)	N3–C12–C13	125.4(4)
C1–C2–C11	106.8(3)	N3–C12–C14	117.8(4)
C3–N1–C4	117.1(3)	C12–C14–C15	113.5(3)
C11–N3–C12	117.9(3)	C14–C15–O2	114.0(3)

Results and Discussion

Synthesis and Characterization

The condensation reaction of HFDA with the triamine TAME did not proceed as smoothly as similar reactions which we had previously studied. Using trivalent lanthanide ions, it was clear that reaction was occurring, but no well-defined products could be characterized, neither were we successful in preparing a cobalt(III) complex. Better results were achieved with iron(III), but yields were poor (<10%) and $Fe(OH)_3$ precipitated during the condensation reaction. This problem is presumably the result of the steric hindrance to coordination in the complex where the pyramidal nature of the amine requires the three bulky $-C(CF_3)_2O^-$ to be in a facial configuration. As a result, template condensation is slow, and the highly insoluble nature of $Fe(OH)_3$ induces its irreversible precipitation from the reaction mixture.

Both the fully-condensed product 1 and the partially-condensed product 2 were produced whenever the reaction was carried out, and their relative proportions were not much affected by changes in the ratio of HFDA to TAME in the reaction mixture. Once formed, these products were stable; they could be separated by repeated crystallization, and showed no tendency to interconversion or disproportionation. Compound 1 was the expected reaction product; it was characterized by elemental analysis and mass spectrum and shown to be fully condensed by the absence of N–H absorptions in the infrared spectrum.

The second product, compound 2, appeared from the presence of both N–H and C=N bands in the infrared spectrum to contain uncondensed amino groups as well as the imino-alkoxy system. Since it formed well-defined crystals, a complete structural investigation was undertaken in order to establish the degree of condensation within the ligand, and its mode of coordination to the metal ion.

Crystallographic Study

An X-ray diffraction study of 2 revealed that the crystals were made up of monoclinic unit cells each containing four neutral molecules. Each of these molecules are oxo-bridged iron dimers possessing a crystallographically imposed two-fold axis of symmetry through the central oxygen atom. Each iron of this dimer is coordinated to a pentadentate ligand in which two alkoxy-oxygen atoms, two imino-nitrogen atoms and an amino nitrogen atom bond to the metal. Thus it is clear that condensation of the HFDA with two of the three amino groups of TAME has taken place. Selected bond distances and angles derived from this crystallographic study are given in Table III and an ORTEP drawing of the entire molecule is shown in Fig. 1. The geometry of each iron atom is pseudo-octahedral. Each oxygen donor atom is *trans* to a nitrogen atom. This facial arrangement is dictated by the geometric constraints of the ligand. The slight distortions from octahedral symmetry about the Fe atom, in particular the O1–Fe–N2 angle, can be attributed to steric interactions between the CF_3 groups of one half of the molecule with the ligand on the other iron. The Fe–N and Fe–O bond

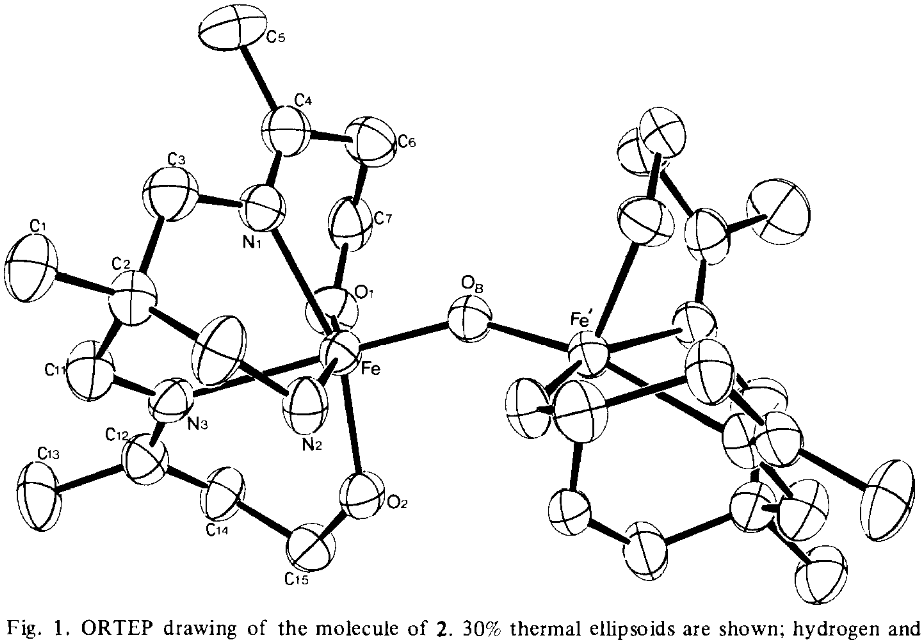

Fig. 1. ORTEP drawing of the molecule of 2. 30% thermal ellipsoids are shown; hydrogen and fluorine atoms are omitted for clarity.

distances are typical of those found in other Fe(III) compounds [12–18]. The short Fe–O_B bond (*versus* the Fe–O1 and Fe–O2 bonds) is consistent with bridging oxide, O^{2-}. The Fe–N3 bond which is *trans* to the Fe–O_B bond is longer than the other two Fe–N bonds. This is rationalized on the basis of simple *trans*-influence arguments. The Fe–O_B–Fe angle is 146.6°. This angle dictates an Fe–Fe distance of 3.468(1) Å. These data are similar to those found for other oxo-bridged iron dimers containing Schiff-base type ligands [10–16].

The nature of this iron dimer is reminiscent of the iron site of azido-hemerythrin. X-ray data for the metazido forms of hemerythrin from *Themiste dyscritum* [17] and *Themiste zostericola* [18] have shown that the coordination sphere of the one iron consists of three histidines, two carboxylate oxygens and a bridging oxygen atom, while the other iron atom is bound to two histidines, two carboxylate oxygens, the azide and the oxo bridge. The present compound has the same donor atom set and thus in that sense is a model compound. In recent reports, Armstrong *et al.* [19, 20] have described the model systems $[HBpz_3)FeO(O_2CR)Fe(HBpz_3)]$, which provide the same donor atom set yet with ligands which better resemble the biological system. Interestingly when carboxylate groups also bridge the metal atoms the Fe–O–Fe′ angle is reduced to about 124° and the Fe–Fe′ distance becomes 3.15 Å [19]. The larger angle and Fe–Fe′ distance in the present compound may arise from the lack of the additional bridging groups, as well as the presence of the sterically demanding CF_3 groups.

Supplementary Material

Temperature factors (Table S-I), Hydrogen atom parameters (Table S-II), Interatomic distances and angles associated with the CF_3 groups (Table S-III), angles and values of $10|F_o|$ and $10|F_c|$ (Table S-IV) have been deposited with the Editor-in-Chief.

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