Two Different Terminal Nitrate Bonding Modes in $[Fe_2O(NO_3)_4(C_7H_7N_3)_4]$

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Treatment of $Fe(NO_3)_3\cdot 9H_2O$ with 1-methylbenzotriazole in EtOH–$CH(OEt)_3$ gave the unique, oxo-bridged complex $[Fe_2O(NO_3)_4(C_7H_7N_3)_4]$; crystal structure and Mössbauer studies showed that the molecule has both bidentate and monodentate nitrates and possesses an $S = 0$ ground state, respectively.

Research into iron nitrate complexes ranges from catalysis[1] to bioinorganic[2,3] and environmental chemistry.[2,4] For example, iron(III) nitrate complexes containing hexamethylphosphoric triamide as a co-ligand catalyse the aerobic oxidation of cyclohexene to cyclohex-1-en-3-one and cyclohex-1-en-3-ol.[1] Recently, we have developed an interest in iron nitrates, an area that has been relatively unexplored[2,5] for this otherwise well studied metal and we report herein the preparation and characterization of $[Fe_2O(NO_3)_4(C_7H_7N_3)_4]$, a dinuclear complex possessing both monodentate and bidentate nitrates.

In a typical reaction † $CH(OEt)_3$ was refluxed with $Fe(NO_3)_3\cdot 9H_2O$ in anhydrous EtOH and $C_7H_7N_3$ added to yield $[Fe_2O(NO_3)_4(C_7H_7N_3)_4]$. Crystals suitable for a crystal structure analysis were obtained by slow cooling of a hot concentrated solution of the complex in $MeNO_2$. Similar reactions in strictly anhydrous media and in reaction mixtures containing relatively high H_2O concentrations yielded the complexes $[Fe(NO_3)_3(C_7H_7N_3)_2]$ and $[Fe_2O(NO_3)_4(H_2O)_2(C_7H_7N_3)_4]$, respectively, which are currently under investigation.

The crystal structure of $[Fe_2O(NO_3)_4(C_7H_7N_3)_4]$ ‡ (Fig. 1) consists of isolated dinuclear molecules. The bridging oxo atom lies on a crystallographically imposed centre of symmetry. The two iron(III) atoms are six-co-ordinate, bonded to an oxo atom, two monodentate $C_7H_7N_3$ and one bidentate and one monodentate nitrate groups. Although a few iron(III) nitrate complexes have been structurally characterized,[1,2,8–10] $[Fe_2O(NO_3)_4(C_7H_7N_3)_4]$ represents the first example of an iron complex containing two different types of nitrate co-ordination. The Fe(1)–O(27) bond *trans* to the oxo bridge [2.278(2) Å] is longer than its counterpart in the *cis* position [2.103(2) Å] as a result of the powerful *trans* influence of the short Fe–(μ-O) bond.[11] The Fe $\cdots$ Fe and Fe–μ-O distances of 3.538(1) and 1.769(1) Å are typical for singly μ-oxo-bridged iron(III) complexes.[12,13] The non-bonding Fe(1) $\cdots$ O(5) distance is 3.048(2) Å. Using the criteria of Reedijk and co-workers,[14] the chelating nitrato group is considered to be 'bidentate' not 'anisobidentate'.

The co-ordination environment of the iron atom is distorted octahedral, the severe distortion being due to the restricted 'bite' of the chelating nitrate ligand, with an angle at the metal of 59.0°. The two bulky, planar $C_7H_7N_3$ ligands are *trans* to each other to minimize steric interactions; the $C_7H_7N_3$ groups in *syn* positions are nearly parallel, the angle between their best planes being 7.8°. There appear to be intradimer stacking interactions between these ligands on the two sides of the molecule [closest interatomic separation, C(15) $\cdots$ C(25), between opposite $C_7H_7N_3$ ligands within the dimer is 3.367(4) Å] and such interactions aid in stabilizing the dinuclear structure.[15,16] Compared with other six-co-ordinate, singly μ-oxo linearly bridged diiron(III) complexes,[9,13,17,18] $[Fe_2O(NO_3)_4(C_7H_7N_3)_4]$ appears to have the smallest Fe $\cdots$ Fe separation.

The Fe–O–Fe antisymmetric stretch[11–13,19,20] occurs at 851 cm^{-1} in the IR spectrum (Nujol mull); this absorption is clearly absent from the spectra of other, $C_7H_7N_3$-containing transition-metal nitrate complexes.[21] The symmetric Fe–O–Fe stretch is located at 384 cm^{-1} in the FT Raman spectrum on the basis of literature reports[9,11,13,20] and its shift to 375 cm^{-1} upon ^{18}O substitution [use of $Fe(NO_3)_3\cdot nH_2{}^{18}O$ as starting material]. The solid-state electronic spectrum (330–1200 nm) of $[Fe_2O(NO_3)_4(C_7H_7N_3)_4]$ displays a strong absorption at 370 nm and three weaker bands at 530, 718 and 1120 nm which are assigned[11,20,22] to the $O^{2-} \longrightarrow Fe^{III}$ charge-transfer, $^6A_1 \longrightarrow [^4A_1, {}^4E]$ (^4G) ligand-field, $^6A_1 \longrightarrow {}^4T_2(^4G)$ ligand-field and/or a forbidden oxo ligand-to-metal charge-transfer, and $^6A_1 \longrightarrow {}^4T_1(^4G)$ ligand-field transitions, respectively (ligand-field assignments are based on ideal octahedral symmetry).

The room-temperature magnetic moment of this complex is

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† To an orange solution of $Fe(NO_3)_3\cdot 9H_2O$ (1.50 g, 3.7 mmol) in anhydrous EtOH (10 cm^3) was added $CH(OEt)_3$ (2.2 cm^3) (the amount of this dehydrating agent is less than that required to remove all the water content from the reaction mixture). This was refluxed for 30 min and to the resulting pale brown solution was added $C_7H_7N_3$ (1.70 g, 7.5 mmol) in anhydrous EtOH (10 cm^3). After stirring for 45 min at room temperature, the flask was stored in a refrigerator (5 °C) overnight. The resultant crystalline orange solid was collected by filtration, washed with Et_2O and dried *in vacuo* over P_4O_{10}; yield *ca.* 55% (Found: C, 36.8; H, 3.20; N, 24.3. $C_{28}H_{28}Fe_2N_{16}O_{13}$ requires C, 37.0; H, 3.10; N, 24.7%).

‡ Crystal data. $C_{28}H_{28}Fe_2N_{16}O_{13}$, $M = 908.32$, monoclinic, space group $P2_1/n$, $a = 11.647(5)$, $b = 11.414(4)$, $c = 14.018(6)$ Å, $\beta = 99.25(1)°$, $U = 1839.22$ Å^3 (by least-squares refinement on diffractometer angles for 42 automatically centred reflections, $\lambda = 0.710\,69$ Å), $Z = 2$, $F(000) = 928$, $D_c = 1.64$ g cm^{-3}, $T = -175$ °C, orange crystals, 0.25 × 0.30 × 0.30 mm, $\mu = 8.71$ cm^{-1}. Intensity data, collected on a Picker four-circle diffractometer, were corrected for Lorentz and polarization effects, $6 \leqslant 2\theta \leqslant 45°$, scan speed 8.0 ° min^{-1}, scan width 2.0° + dispersion; 3499 reflections measured, 2407 unique, giving 2238 with $F > 2.33\sigma(F)$ (R for averaging = 0.021). The structure was solved by a combination of direct methods[6] and Fourier techniques and refined by full-matrix least squares. The non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were visible in a subsequent Fourier difference map and were included in the final least-squares refinement. A final Fourier difference map was featureless, the largest peak being 0.17 e Å^{-3}. Final R $(= \Sigma||F_o| - |F_c||/\Sigma|F_o|)$ and R' $\{= \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, where $w = 1/\sigma^2(|F_o|)\}$ values are 0.0277 and 0.0347, respectively. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

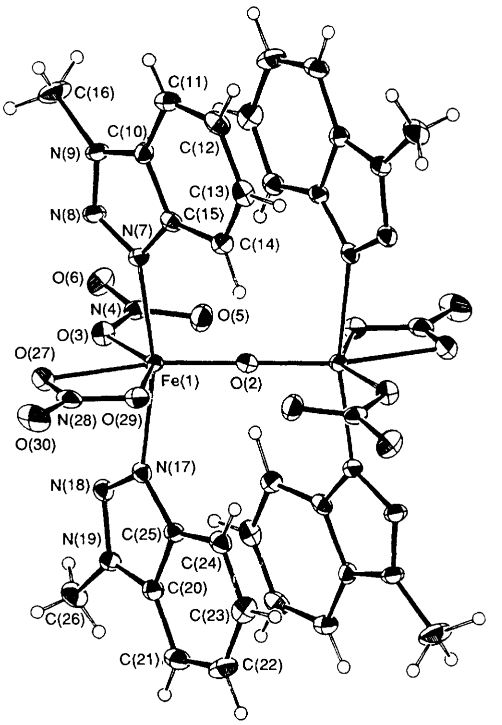

Fig. 1 ORTEP[7] representation of $[Fe_2O(NO_3)_4(C_7H_7N_3)_4]$ at the 50% probability level. Symmetry-related atoms are not labelled; Fe(1)$\cdots$Fe(1') 3.538(1), Fe(1)–O(2) 1.769(1), Fe(1)–O(3) 1.990(2), Fe(1)–O(27) 2.278(2), Fe(1)–O(29) 2.103(2), Fe(1)–N(7) 2.131(2), Fe(1)–N(17) 2.141(2), N(4)–O(3) 1.309(3), N(28)–O(30) 1.221(3) Å, O(2)–Fe(1)–O(3) 118.5(1), O(2)–Fe(1)–O(27) 157.9(1), O(3)–Fe(1)–O(29) 142.6(1), O(3)–Fe(1)–N(7) 88.2(1), O(27)–Fe(1)–O(29) 59.0(1), O(29)–Fe(1)–N(17) 86.3(1), N(7)–Fe(1)–N(17) 165.5(1), O(27)–N(28)–O(29) 115.8(2), O(3)–N(4)–O(5) 118.5(2)°

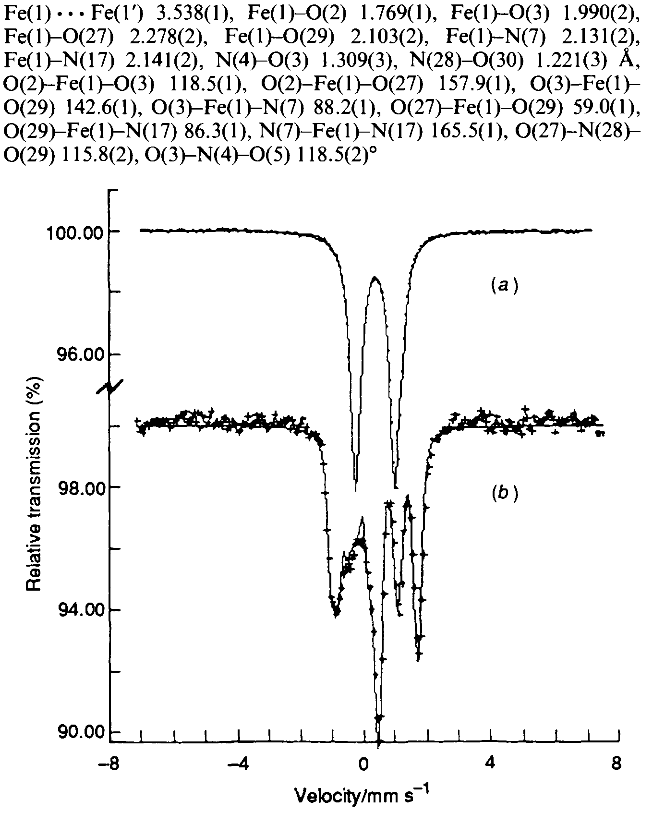

Fig. 2 The 4.2 K ^{57}Fe Mössbauer spectra of a polycrystalline sample of $[Fe_2O(NO_3)_4(C_7H_7N_3)_4]$ in zero (*a*) and in an applied transverse (5.5 T) (*b*) magnetic field. The solid lines through the data are least-squares fits to one iron site

1.97 μ_B ($\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}), indicating an antiferromagnetically coupled high-spin diiron(III) species;[13,17] preliminary data from variable-temperature, solid-state magnetic susceptibility studies give an estimated J value of *ca.* -110 cm^{-1}. The Mössbauer spectrum of the nitrate complex at 4.2 K (Fig. 2) consists of a single quadrupole doublet with $\delta = 0.50$ mm s^{-1} (*vs.* iron foil at room temperature) and $\Delta E_Q = 1.30$ mm s^{-1}. The isomer shift value is well within the range expected for high-spin Fe^{III} in a non-sulfur environment.[23] The large ΔE_Q value is characteristic of an oxo-bridged complex[11,13] and reasonable[24] for a distorted N_2O_4 co-ordination sphere about Fe^{III}. The spectrum recorded in an applied transverse magnetic field of 5.5 T at 4.2 K can be analysed [solid line in Fig. 2(*b*)] assuming only one iron site with the above δ and ΔE_Q values and with a hyperfine field value of 5.5 T. The value of the hyperfine field confirms the diamagnetism of the ground state ($S = 0$).

The compound $[Fe_2O(NO_3)_4(C_7H_7N_3)_4]$ proves to be a useful precursor for the preparation of complexes having the biologically important[13] (μ-oxo)bis(μ-carboxylato)diiron(III) core; for example, its reactions with an excess of carboxylic acid give complexes with the general formula $[Fe_2O(H_2O)_2(O_2CR)_2(C_7H_7N_3)_4][NO_3]_2$. Work in progress on the Fe^{III}–NO_3^-–$C_7H_7N_3$ (and other monodentate N-donors) system also includes the preparation of hydroxo-bridged diiron nitrate species, the study of ligand-exchange reactions, and the preparation and characterization of higher nuclearity iron(III) nitrate clusters.

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