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Preparation and characterization of homoleptic and ethoxy-bridged nitronato iron(III) complexes

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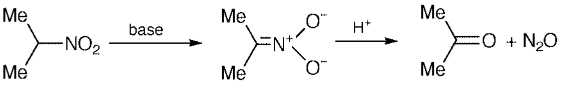
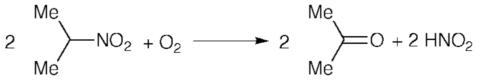
Iron(III) chloride reacts with potassium 2-propanenitronate to give the homoleptic tris(2-propanenitronato-*O,O*)iron(III) complex which in ethanol transfoms to an ethoxy-bridged diiron(III) 2-propanenitronate complex.

The conversion of nitro compounds to aldehydes and ketones is one of the most important functional group transformations.[1] It can be achieved conveniently by the Nef reaction, where conjugate bases of nitro compounds are treated with sulfuric acid leading to the hydrolysis of the C=N bond [eqn. (1)].[2]



$$\mathrm{Me_2CHNO_2} \xrightarrow{\text{base}} \mathrm{Me_2C{=}N^+(O^-)_2} \xrightarrow{H^+} \mathrm{Me_2C{=}O} + \mathrm{N_2O} \qquad (1)$$

Alternative oxidative methods also exist for this reaction in the literature resulting in better yields and fewer side reactions.[3] Biological organisms can also transform aliphatic nitro compounds to the corresponding oxo species and nitrite ion [eqn. (2)]. Oxygenated flavoenzyme species,[4] glucose oxidase, D- and L-amino acid oxidase,[5] extracts of *Neurospora crassa*[6] pea seedlings and those from the hyphae of a nitrifying strain of *Aspergillus flavus*[7] and the intracellular enzyme 2-nitropropane dioxygenase of *Hansenula mraki*[8] oxidatively degrade nitroalkanes. The latter is believed to contain iron ions at its active center. Recently we demonstrated the facile copper-assisted oxygenation of nitroalkanes according to eqn. (2) and proposed a mechanism for the reaction.[3,9]

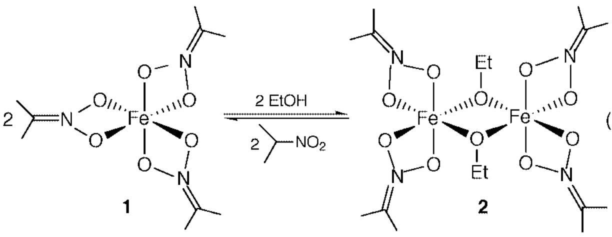


$$2\,\mathrm{Me_2CHNO_2} + \mathrm{O_2} \longrightarrow 2\,\mathrm{Me_2C{=}O} + 2\,\mathrm{HNO_2} \qquad (2)$$

In order to understand the coordination of alkanenitronates to iron and their conversion to oxo compounds, we now describe the first fully characterised 2-propanenitronato-*O,O*–Fe(III) complexes and their oxygenation reaction.

Treatment of $FeCl_3$ with an equimolar amount of potassium 2-propanenitronate in benzene at room temperature for 4 h yielded the red–brown crystalline complex $[Fe(C_3H_6NO_2)_3]$ **1** in 24% yield.† If the reaction was carried out in a mixture of benzene and ethanol or **1** was recrystallised from ethanol the red crystalline complex $[Fe_2(C_3H_6NO_2)_4(C_2H_5O)_2]$ **2** was obtained in 27% yield.† In ethanol complex **1** undergoes ligand exchange, ethanolate displaces the nitronate ligand and bridges the two iron(III) ions to form **2** in an equilibrium [eqn. (3)].

The IR spectra of **1** and **2**, obtained as KBr pellets, reveal a particularly diagnostic absorption [ν(C=N)] at 1639 and 1644 cm^{-1}, respectively. The relative intensity of this absorption suggests a similar mode of coordination for both complexes and implies considerable carbon–nitrogen double bond character.[10] Magnetic measurements gave values of μ_B = 5.87 per Fe(III) for **1** and 7.29 per 2Fe(III) for **2** accord with high spin Fe(III) centers, with a slight antiferromagnetic interaction in complex **2**. The Mössbauer spectra, recorded at 80 K, reflect the different coordination of Fe(III) in complexes **1** and **2**. Although the identical isomer shift values (δ_1 = 0.48 mm s^{-1} and δ_2 = 0.48 mm s^{-1}) reveal the same electron density on the iron in both compounds, the quadrupole splittings (Δ_1 = 0.90 mm s^{-1} and Δ_2 = 0.53 mm s^{-1}) differ significantly owing to different ligand contributions to the electric field gradient (EFG). The trigonal distortion of complex **1** makes the EFG rather large; however, this is considerably reduced upon dimerisation, when the local environment of the iron becomes closer to octahedral.



(3)

The crystal structure of **1**,‡ shown in Fig. 1 together with selected data, shows a distorted octahedral geometry around the

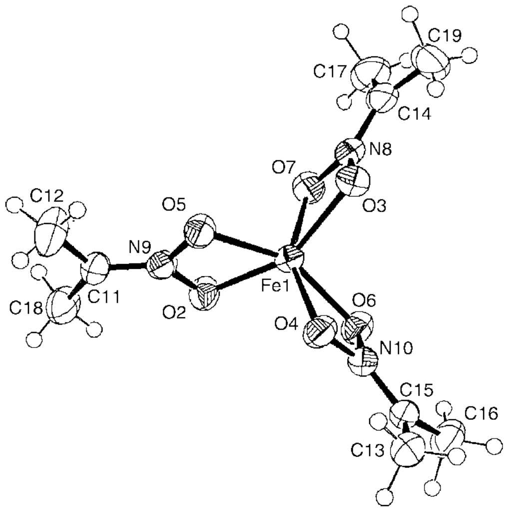


Fig. 1 Molecular structure of $[Fe(C_3H_6NO_2)_3]$ **1**. Selected distances (Å) and angles (°): Fe(1)–O(2) 2.021(3), Fe(1)–O(3) 2.026(3), Fe(1)–O(4) 2.016(3), Fe(1)–O(5) 2.016(2), Fe(1)–O(6) 2.019(3), Fe(1)–O(7) 2.013(3), O(2)–N(9) 1.342(4), O(3)–N(8) 1.342(4), O(4)–N(10) 1.338(4), O(5)–N(9) 1.346(4), O(6)–N(10) 1.344(4), O(7)–N(8) 1.339(4), N(8)–C(14) 1.293(5), N(9)–C(11) 1.283(4), N(10)–C(15) 1.288(5); O(2)–Fe(1)–O(5) 66.0(1), O(3)–Fe(1)–O(7) 66.0(1), O(4)–Fe(1)–O(6) 65.9(1), O(3)–N(8)–O(7) 110.3(3), O(2)–N(9)–O(5) 109.8(3), O(4)–N(10)–O(6) 109.9(3). Displacement ellipsoids are shown at 50% probability level.

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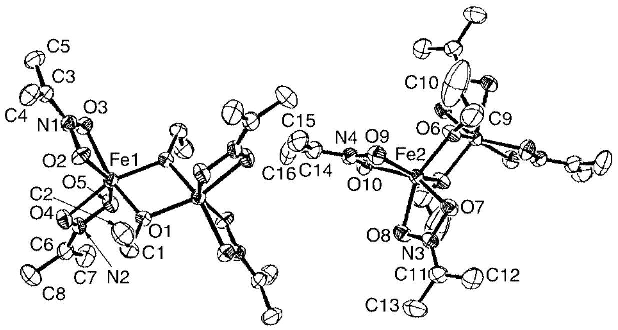

Fig. 2 Molecular structure of $[Fe_2(C_3H_6NO_2)_4(C_2H_5O)_2]$ **2**. Selected distances (Å) and angles (°): O(4)–N(2) 1.335(3), O(5)–N(2) 1.338(3), Fe(2)–O(6) 1.958(2), Fe(2)–O(6) 1.964(2), Fe(2)–O(7) 2.030(2), Fe(2)–O(10) 2.040(2), Fe(2)–O(8) 2.048(2), Fe(2)–O(9) 2.053(2), O(6)–Fe(2) 1.958(2), O(7)–N(3) 1.341(3), O(8)–N(3) 1.335(3), O(9)–N(4) 1.331(4), O(10)–N(4) 1.337(3), O(1)–Fe(1)–O(1) 77.65(8), O(2)–Fe(1)–O(3) 65.28(8), O(5)–Fe(1)–O(4) 65.13(8), Fe(1)–O(1)–Fe(1) 102.35(8), O(3)–N(1)–O(2) 110.6(2), O(4)–N(2)–O(5) 110.3(2), O(6)–Fe(2)–O(6) 77.43(10), O(7)–Fe(2)–O(8) 65.13(8), O(10)–Fe(2)–O(9) 4.85(9), Fe(2)–O(6)–Fe(2) 102.58(10), O(8)–N(3)–O(7) 110.2(20), O(9)–N(4)–O(10) 110.7(2). Displacement ellipsoids are shown at 50% probability level.

iron atom, with all coordination sites being occupied by the bidentate 2-nitropropanate ligands. The Fe–O bond distances are in the range 2.013(3)–2.026(3) Å and the bite-angles of the ligands lie in the range 109.8(3)–110.3(3)°. **1** exhibits a propeller-like structure with the iron atom being 0.007 Å out of the plane of the three N atoms of the three ligands. The crystal structure of **2**,‡ shown in Fig. 2 together with selected data, shows that there are two very similar ethoxy-bridged diiron molecules with slightly different bond distances and angles. The geometry around the iron atoms is aproximately octahedral, the six coordination sites being occupied by two ethoxy groups and two bidentate 2-propanenitronate ligands. The average Fe–O (bridging) bond distance is 1.966 Å with an Fe··Fe separation of 3.07 Å. The dimer lies on a crystallographic inversion center, the bridging Fe_2O_2 is perfectly planar with Fe–O–Fe and O–Fe–O angles of 102.35(8), 102.58(10) and 77.65(8), 77.43(10)°, respectively. The Fe–O bond lengths of the nitronato ligands are in the range 2.021(2)–2.053(2) Å while the N–O bond distances average 1.337 Å, only slightly shorter than the N–O single bond and larger than the N=O double bond (N–O 1.40 Å, N=O, 1.21 Å).[11] The carbon–nitrogen bonds in both complexes (1.283–1.291 Å) are essentially double bond in character (C–N 1.47 Å, C=N 1.27 Å).[11]

Complex **1** is very sensitive towards dioxygen and moisture while **2** is reasonably stable to both in the solid state. Preliminary oxygenation reactions of 2-nitropropane in the presence of **1** and **2** in pyridine at 90 °C resulted in the formation of acetone and HNO_2. Conversions of *ca.* 80% could be achieved at substrate : catalyst ratios of 20–40 : 1 during 20 h. The conversion–time profiles of the catalytic reactions were very similar for complexes **1** and **2** indicating that **2** transforms to **1** if an excess of 2-nitropropane is present. To our knowledge, these reactions represent the first examples of iron-catalysed oxygenation of 2-nitropropane resembling enzyme action, and indicating the possible role of iron ion as a cofactor. Further work is in progress for the elucidation of the mechanism of the reaction.

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Notes and references

† Satisfactory elemental analyses were obtained for compounds **1** and **2**.

‡ *Crystal data*: $C_9H_{18}FeO_6N_3$ **1**, M_r = 320.10, monoclinic, space group $P2_1/n$, a = 12.395(1), b = 9.226(1), c = 13.343(1) Å, β = 109.082(1)°, V = 1442.0(4) Å^3, Z = 4, T = 298 K, μ(Mo-Kα) 10.698 mm^{-1}, 4145 reflections measured, 3070 unique (R_{int} = 0.031) which were used in all calculations. The final $wR(F^2)$ was 0.33 (all data).

$C_{16}H_{34}Fe_2N_4O_{10}$ **2**, M_r = 554.16, triclinic, space group $P\bar{1}$, a = 10.1033(4), b = 10.3819(4), c = 13.8442(4) Å, α = 111.60(2), β = 95.66(2), γ = 99.77(1)°, V = 1309.7(2) Å^3, Z = 2, μ(Mo-Kα) 1.15 mm^{-1}, T = 297 K,: 4865 reflections measured, 4324 unique (R_{int} = 0.0318) which were used in all calculations. The final $wR(F^2)$ was 0.1038 (all data).

CCDC 182/1541. See http://www.rsc.org/suppdata/cc/b0/b000408l/ for crystallographic files in .cif format.

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