Crystal and Molecular Structure of a New μ-Oxo-bridged Iron(III) Dimer formed with the Nitrilotriacetate Ligand†

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The molecular structure of the oxo-bridged dimer barium μ-oxo-bis{aqua[nitrilo-κ*N*-triacetato(3−)-κ³*O*,*O*′,*O*″]ferrate(1−)}–water(1/4), $Ba[\{Fe(nta)(H_2O)\}_2O]\cdot4H_2O$, which has an Fe–O–Fe angle of 153.2(6)° has been determined by X-ray crystallography. The iron ions are six-co-ordinate with one tetradentate nta ligand and one water molecule completing the co-ordination sphere. The relationship of this compound to other iron–nta complexes is discussed in the context of the hydrolysis reactions of iron(III) in aqueous solutions.

Oxo-bridged polyiron(III) compounds are ubiquitous and important in nature, ranging from magnetic materials such as γ-Fe_2O_3 to biological molecules such as the iron-storage protein ferritin. The hydrolysis of aqueous solutions of iron(III) salts results in the formation of iron(III) hydroxide, '$Fe(OH)_3$', a polymeric oxo-bridged iron(III) species, the nature of which appears to vary depending on experimental conditions.[1] In the presence of chelating ligands, the conversion of $[Fe(H_2O)_6]^{3+}$ into '$Fe(OH)_3$' can be slowed down and in favourable cases the products formed in the individual steps of the early oligomerisation can be isolated and characterised. Many binuclear oxo-bridged iron compounds have been reported[2–6] as well as molecules containing 3,4,6,8,10 and 11 iron centres.[5,7–10] We have been investigating the factors which influence product formation in the first steps in the hydrolytic polymerisation of iron(III) in the presence of chelating ligands. We report herein our results for the iron(III) and nitrilotriacetic acid [$N(CH_2CO_2H)_3$ = H_3nta] system, including the synthesis and X-ray crystal structure of a new oxo-bridged iron(III)–nta complex. Several compounds of iron and nta formed in aqueous solutions have been reported[11–16] of which two can be regarded as reproducible iron–nta complexes and not mixtures. These are the complex $Na_3[Fe(nta)_2]\cdot5H_2O$, which has been crystallographically characterised[16] and the compound which we formulate as $[Fe(nta)(H_2O)_2]_n$ **1** but the nature of which remains something of a mystery. A compound of this approximate formulation has been reported by Rajabalee,[11] Krishnamurthy and co-workers[12,13] and Mikhailova and co-workers,[14,15] prepared by using methods 1 and 3 below. However, whether or not the three methods we outline for preparing compound **1** are actually all producing the same material is open to question. We detect differences in the magnetic properties of such compounds (EPR and room temperature magnetic susceptibility) which are the subject of further investigation. These differences could be due to metal-containing impurities which may not be present in sufficient quantities to affect analyses. In addition to these two iron–nta complexes, monomeric complexes of iron(III)–nta and bidentate ligands can be isolated from non-aqueous media.[17] These are not of direct relevance to our investigation.

Experimental

All reagents were used as received from Aldrich Chemicals.

Preparation of Compound **1**.—(*a*) *Method 1*. The acid H_3nta (0.96 g, 5 mmol) was dissolved in 0.3 mol dm^{-3} sodium hydroxide solution (0.6 g, 15 mmol) in distilled water (50 cm^3). This solution was added slowly and with stirring to a solution of anhydrous iron(III) chloride (0.81 g, 5 mmol) in distilled water (50 cm^3). The initial pH of the solution was 2.0. After several days a green powder precipitated. This was isolated by filtration through a porosity 4 sintered funnel and washed with water (Found: C, 25.7; H, 3.4; Fe, 19.7; N, 5.1. $C_6H_{10}FeNO_8$ requires C, 25.70; H, 3.60; Fe, 19.90; N, 5.00%).

(*b*) *Method 2*. The acid H_3nta (0.96 g, 5 mmol) was added to a solution of iron(III) nitrate nonahydrate (2.02 g, 5 mmol) in water (50 cm^3). The resulting mixture was stirred for 40 min after which any undissolved H_3nta was removed by filtration. The pH of this resulting solution was 1.2. After approximately 2 h a fine green powder precipitated which was isolated by centrifugation (Found: C, 25.6; H, 3.2; Fe, 19.7; N, 5.0. $C_6H_{10}FeNO_6$ requires C, 25.70; H, 3.60; Fe, 19.90; N, 5.00%).

(*c*) *Method 3*. The acid H_3nta (0.96 g, 5 mmol) was added to a suspension of iron(III) hydroxide [obtained by the addition of a solution of sodium hydroxide (0.6 g, 15 mmol) in water (10 cm^3) to a solution of iron(III) nitrate nonahydrate (2.02 g, 5 mmol) in water (20 cm^3)]. A yellow precipitate formed after stirring at ambient temperature for approximately 4 h. This was isolated by filtration through a porosity 4 sintered funnel (Found: C, 25.7; H, 3.0; Fe, 19.7; N, 5.0. $C_6H_{10}FeNO_8$ requires C, 25.70; H, 3.60; Fe, 19.90; N, 5.00%).

Preparation of $Ba[\{Fe(nta)(H_2O)\}_2O]\cdot4H_2O$ **2**.—In an average experiment the free acid H_3nta (0.96 g, 5 mmol) was dissolved in a 0.5 mol dm^{-3} sodium hydroxide solution (0.8 g, 20 mmol) in distilled water (40 cm^3). This solution was added slowly and with continuous stirring to a solution of anhydrous iron(III) chloride (0.81 g, 5 mmol) in distilled water (40 cm^3). To this a solution of barium(II) chloride dihydrate (1.22 g, 5 mmol) in distilled water (20 cm^3) was added. The initial pH of this solution was 4.2. After a few hours a fine red–pink powder of $Ba[\{Fe(nta)(H_2O)\}_2O]\cdot4H_2O$ had precipitated. This was isolated by filtration through a porosity 4 sintered funnel (Found: C, 19.1; H, 3.1; Fe, 14.8; N, 3.7. $C_{12}H_{24}BaFe_2N_2O_{19}$ requires C, 19.25; H, 3.25; Fe, 14.90; N, 3.75%).

Crystallisation.—Compound **2** (0.71 g, ≈1 mmol) and hydrated sodium acetate (0.07 g, 0.5 mmol) were dissolved, with

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

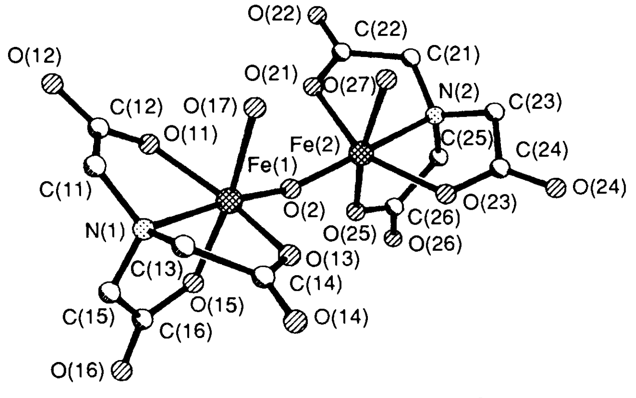

Fig. 1 Molecular structure of $[\{Fe(nta)(H_2O)\}_2O]^{2-}$

heating, in distilled water (20 cm^3). The resulting solution was dark red, pH 4.12. After 2 d a powder precipitate of $Ba[\{Fe(nta)(H_2O)\}_2]\cdot 4H_2O$ had formed. The solution was then reheated to dissolve this and sodium acetate (0.07 g, 0.5 mmol) was added. The pH of the solution was now 4.60. This process was repeated twice. First after a further day had elapsed, when sodium acetate (0.14 g, 0.1 mmol) was added and secondly after 5 d, when another 0.1 mmol of sodium acetate was added. The pH of these solutions was 5.06 and 5.30 respectively. This solution was left in a beaker covered with a watchglass. After 2 weeks small red needle crystals of compound **2** formed on the base of the beaker. The crystals were isolated by filtration and washed with water. They proved to be stable to air. The acetate appears to have a buffering effect and is not incorporated in the crystals. In spite of many attempts it was not possible to grow crystals any bigger than the one used for the structure determination. IR spectra and microanalysis revealed these crystals to be the same compound as the red powder (Found: C, 19.1; H, 3.1; Fe, 14.8; N, 3.7. $C_{12}H_{24}BaFe_2N_2O_{13}$ requires C, 19.25; H, 3.25; Fe, 14.90; N, 3.75%).

Factors affecting Product Formation.—First, the pH of the reaction affects the product formed. The product which forms at low pH is the compound $[Fe(nta)(H_2O)_2]_n$. At higher pH, the dimeric $[\{Fe(nta)(H_2O)\}_2O]^{2-}$ forms and once the pH exceeds about 7, $Fe(OH)_3$ precipitates. The relative solubilities of compounds **1** and **2** mean that unless a suitable counter ion is supplied in order to precipitate the highly soluble $[\{Fe(nta)(H_2O)\}_2O]^{2-}$ complex, this species is only stable with respect to the precipitation of compound **1** or $Fe(OH)_3$ between pH 5 and 5.5. Thus, solutions containing Fe^{3+}, H_3nta and NaOH but no Ba^{2+} yield compound **1** at pH lower than 5; no precipitates are formed at all between pH 5 and 5.5 even after 3 months; and solutions with a pH of more than 5.5 give $Fe(OH)_3$. However, the rather insoluble barium salt of the dimer can be isolated from reaction solutions with pH 4–7. Secondly, the concentration of the ligand affects the species formed. Solutions containing Fe^{3+} and nta^{3-} in a 1:1 ratio yield compound **1** or **2** up to pH 7 as discussed above. With a 1:2 ratio the seven-co-ordinate complex $[Fe(nta)_2]^{3-}$ (ref. 16) forms even from solutions of pH 10, demonstrating the ability of excess ligand to suppress the hydrolysis of iron(III).

X-Ray Crystallography.—A red needle crystal of compound 7 having approximate dimensions of 0.050 × 0.050 × 0.250 mm was mounted on a glass fibre. Because of the small size of the crystal all measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Cu-Kα radiation and a 12 kW rotating-anode generator at the University of Manchester.

Crystal data. $C_{12}H_{24}BaFe_2N_2O_{19}$, $M = 749.35$, triclinic, space group $P\bar{1}$, $a = 12.481(3)$, $b = 13.576(4)$, $c = 7.088(2)$ Å, $\alpha = 103.04(2)$, $\beta = 105.20(2)$, $\gamma = 87.29(2)^\circ$, $U = 1129.0(6)$ Å^3 (obtained from a least-squares refinement using the setting angles of 22 carefully centred reflections in the range $75.19 < 2\theta < 79.57^\circ$), $Z = 2$, $D_c = 2.204$ g cm^{-3}, $\lambda = 1.541\,78$ Å for Cu-Kα radiation, $F(000) = 740$, $\mu = 248.02$ cm^{-1}.

Data collection and reduction. The data were collected at a temperature of 23 ± 1 °C using the ω–2θ scan technique to a maximum 2θ value of 120.5°. Scans of width $(1.31 + 0.30 \tan \theta)^\circ$ were made at a speed of 32.0° min^{-1} in ω with weak reflections $[I < 10.0\sigma(I)]$ rescanned (maximum of 2 rescans) and counts accumulated to assure good counting statistics. Of the 3526 reflections collected 3338 were unique ($R_{int} = 0.096$). The intensities of three representative reflections which were measured after every 100 reflections declined quite significantly by −26.00%. A linear correction factor was applied to the data to account for this phenomenon. This decay was accompanied by a small distortion of the unit cell. The final cell parameters were used in all calculations. An empirical absorption correction, using the program DIFABS,[18] was applied which resulted in transmission factors ranging from 0.77 to 1.50. The data were corrected for Lorentz and polarization effects.

Structure solution and refinement. The structure was solved by a combination of the Patterson method and direct methods.[19] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms except those attached to water molecules were placed in calculated positions. The final cycle of full-matrix least-squares refinement was based on 2115 observed reflections $[I > 3.00\sigma(I)]$ and 325 variable parameters and converged (largest parameter shift was 0.01 times its e.s.d.) with unweighted and weighted agreement factors of $R\ (= \Sigma||F_o| - |F_c||/\Sigma|F_o|) = 0.065$ and $R'\ \{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}}\} = 0.067$. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$, with the weighting scheme, $w = 4F_o^2/\sigma^2(F_o^2)$, based on counting statistics and including a factor, $p = 0.03$ $\{\sigma^2(F_o^2) = [S^2(C + R^2B + (pF_o^2)^2]/L_p^2$, S = scan rate, C = total integrated peak count, R = ratio of scan time to background-counting time, B = total background count and L_p = Lorentz-polarization factor$\}$, to downweight the intense reflections. The maximum and minimum peaks on the final Fourier difference map corresponded to 1.15 and −1.11 e Å^{-3}, respectively. Neutral-atom scattering factors were taken from ref. 20. Anomalous dispersion factors were included in F_{calc},[21] the values for $\Delta f'$ and $\Delta f''$ were those from ref. 22. All calculations were performed using the TEXSAN–TEXRAY crystallographic software package.[23]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Infrared Spectra.—Infrared spectra were measured in the solid state as KBr discs. The samples were all dried for 2d in an evacuated desiccator to remove excess water. All spectra were run for 16 scans at a resolution of 4 cm^{-1} over the range 4000–400 wavenumbers on a Mattson Sirius spectrometer utilising a Michelson interferometer.

Results and Discussion

Crystal Structure of $Ba[\{Fe(nta)(H_2O)\}_2O]\cdot 4H_2O$.—The atomic coordinates are given in Table 1, selected bond lengths in Table 2 and Fig. 1 shows the structure of the anion. The structure consists of discrete $[\{Fe(nta)(H_2O)\}_2O]^{2-}$ units. Each unit consists of two chemically (but not crystallographically) equivalent six-co-ordinate Fe^{III} ions. This is in contrast to the seven-co-ordinate $[Fe(nta)_2]^{3-}$ anion. The geometry shows deviations from octahedral with bond angles ranging from 78.1(4) [O(11)–Fe(1)–N(1)] to 103.5(5)° [O(11)–Fe(1)–O(2)]. The distorted octahedral NO_5 donor sets are composed of a bridging oxide ion O(2), one water molecule O(17) and a tetradentate nitrilotriacetic acid ligand N(1), O(11), O(13) and O(15) for Fe(1) and O(2), O(27), N(2), O(21), O(23) and O(25) for Fe(2). The Fe–O–Fe angles are found to be in the range 114–180° for binuclear oxo-bridged compounds,[2–6] but in many

Table 1 Atomic coordinates for $Ba[\{Fe(nta)(H_2O)\}_2O]\cdot 4H_2O$ **2**

Atom	x	y	z
Ba	0.162 48(8)	0.049 07(7)	0.058 1(1)
Fe(1)	−0.226 5(2)	0.206 8(2)	−0.532 7(3)
Fe(2)	0.057 7(2)	0.275 8(2)	−0.364 8(3)
C(11)	−0.464(1)	0.258(1)	−0.648(2)
C(12)	−0.396(2)	0.301(1)	−0.791(3)
C(13)	−0.427(1)	0.171(1)	−0.402(2)
C(14)	−0.324(2)	0.133(1)	−0.267(2)
C(15)	−0.429(1)	0.075(1)	−0.731(2)
C(16)	−0.327(1)	0.018(1)	−0.787(2)
C(21)	0.223(1)	0.431(1)	−0.332(2)
C(22)	0.136(1)	0.431(1)	−0.514(2)
C(23)	0.252(1)	0.358(1)	−0.031(2)
C(24)	0.201(1)	0.275(1)	0.022(2)
C(25)	0.303(1)	0.262(1)	−0.326(2)
C(26)	0.249(1)	0.169(1)	−0.476(2)
O(2)	−0.076 8(8)	0.218 4(7)	−0.494(1)
O(3)	−0.029 9(8)	0.025 2(7)	−0.294(1)
O(4)	−0.049 6(8)	0.140 2(6)	0.106(1)
O(5)	0.561(1)	0.439(1)	0.798(2)
O(6)	−0.111(1)	0.351 2(8)	−0.907(2)
O(11)	−0.291(1)	0.276 3(8)	−0.761(2)
O(12)	−0.446(1)	0.361(1)	−0.891(2)
O(13)	−0.230 2(9)	0.150 1(8)	−0.299(1)
O(14)	−0.336(1)	0.089 3(8)	−0.143(2)
O(15)	−0.233 3(8)	0.066 8(7)	−0.710(1)
O(16)	−0.335 8(8)	−0.067 8(8)	−0.888(2)
O(21)	0.055 1(9)	0.372 0(8)	−0.546(1)
O(22)	0.145 8(8)	0.488 0(8)	−0.623(2)
O(23)	0.117 1(8)	0.229 5(7)	−0.107(1)
O(24)	0.237(1)	0.255 2(8)	0.188(1)
O(25)	0.140 3(8)	0.165 9(8)	−0.514(1)
O(26)	0.301 3(8)	0.103 3(8)	−0.557(1)
O(27)	0.003 5(8)	0.403 5(7)	−0.172(1)
O(17)	−0.255 0(8)	0.354 4(7)	−0.352(2)
N(1)	−0.408(1)	0.174 9(9)	−0.596(2)
N(2)	0.230(1)	0.339 2(8)	−0.248(2)

Table 2 Selected bond lengths (Å) for $Ba[\{Fe(nta)(H_2O)\}_2O]\cdot 4H_2O$ **2**

Fe(1)–N(1)	2.23(1)	Fe(2)–N(2)	2.23(1)
Fe(1)–O(2)	1.83(1)	Fe(2)–O(2)	1.81(1)
Fe(1)–O(11)	2.02(1)	Fe(2)–O(21)	2.02(1)
Fe(1)–O(13)	1.99(1)	Fe(2)–O(23)	2.01(1)
Fe(1)–O(15)	2.02(1)	Fe(2)–O(25)	2.03(1)
Fe(1)–O(17)	2.19(1)	Fe(2)–O(27)	2.15(1)

cases other bridging ligands are present. For singly μ-oxo-bridged binuclear iron(III) complexes, the most favourable arrangement is expected to be linear and deviations from 180° are often attributed to crystal-packing forces. In this dimer the Fe(1)–O(2)–Fe(2) angle is 153.2(6)°. As in other $[Fe_2O]^{4+}$ complexes, the Fe–O bonds in the bridge are significantly shorter than the Fe–O (carboxylate) bonds and Fe–O(water) bonds. The Fe(1)–O(2) and Fe(2)–O(2) bond distances are equivalent within their standard deviations [1.83(1) and 1.81(1) Å] and lie in or on the extremes of the range reported for other $[Fe_2O]^{4+}$ complexes (1.73–1.82 Å).[2] The iron–nta Fe–O and Fe–N bond lengths are comparable with those found for the $[Fe(nta)_2]^{3-}$ complex,[16] with both the Fe–N [Fe(1)–N(1) and Fe(2)–N(2)] distances of 2.23(1) Å being significantly longer than the Fe–O bond lengths. We attribute this to the greater affinity of iron for oxygen than for nitrogen. This has been observed for other complexes of mixed N–O donating ligands.[16,17,24,25] The Ba^{2+} ion lies within 3.0 Å of ten O atoms, four lattice water molecules and six carboxylate O atoms derived from both ligands, with distances ranging from 2.78(1) to 2.99(1) Å.

It is feasible that compound **1** might possess a loosely bound polymeric structure involving one or more bridging carboxylate groups from the nta ligand as is the case for the 1:1 complexes formed from Co^{II}, Zn^{II} or Cu^{II} with nta.[26–28]

Infrared Spectra.—The spectrum of compound **2** has a broad band in the 3600–3000 cm^{-1} region which is due to the presence of co-ordinated and lattice water. The two carboxylate antisymmetric and symmetric stretching frequencies are located at 1619 and 1415 cm^{-1} respectively. The Fe–O–Fe antisymmetric stretch occurs at 826 cm^{-1}. This absorption is clearly absent from the spectrum of compound **1** which is otherwise similar to that of compound **2** in the region 2000–400 cm^{-1}. A very broad absorption in the OH stretching region between 3600 and 2400 cm^{-1} for compound **1** is perhaps indicative of co-ordinated water involved in a hydrogen-bonding network.[29]

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