Inorganica Chimica Acta 444 (2016) 141–149

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Syntheses, structural, spectroscopic and magnetic properties of polynuclear Fe(III) complexes containing N and O donor ligands

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ARTICLE INFO

Article history:
Received 20 November 2015
Received in revised form 16 January 2016
Accepted 21 January 2016
Available online 30 January 2016

Keywords:
Dinuclear
Tetranuclear
Iron(III)
Carboxylate bridge
Phenoxo bridge
Magnetochemistry

ABSTRACT

Syntheses, X-ray structural and spectroscopic properties are reported for $[\{Fe(L)_2\}_3Fe]$ (**1**), $[Fe_2(L)_2(ClCH_2COO)_2(H_2O)]$ (**2**) and $[Fe(L)(HL)]_2$ (**3**) [H_2L = a tridentate ONO-donor ligand N-(2-hydroxyphenyl)salicylidenimine]. For (**2**) and (**3**), variable temperature magnetic susceptibilities have been measured and modeled. Both are antiferromagnetic overall. Compound **1** has a tetranuclear Fe_4O_6 core with Fe(III) species at the vertices of a triangle and the fourth Fe(III) at the center of the triangle. The central Fe(III) is surrounded by six phenoxo bridges that connect it to the three peripheral Fe(III) centres. In complex **2**, the two six-coordinate Fe(III) centers are bridged by a chloroacetate and two phenoxy oxygens. The remaining three coordination sites on each iron are occupied by a terminal phenoxy oxygen, an imino nitrogen and, in one case, by a water oxygen while in the other by a terminal chloroacetate oxygen. Comparison of **2** with compounds of similar core structure reveals transition between antiferromagnetic and ferromagnetic coupling occurs at a bridgehead angle between ~97° and ~102°. The asymmetric unit of compound **3** consists of two symmetry-independent mononuclear species ($Z' = 2$) joined by two statistically equivalent short (2.429(2) and 2.432(2) Å) $O\cdots H\cdots O$ bridges, each involving two phenolic oxygens and a strongly bound H atom. Unprecedented weak antiferromagnetic coupling between the two high spin Fe(III) species via these very strong hydrogen bonds was detected.

1. Introduction

Iron is one of the most important microelements in nature and it is an essential element in the majority of biological systems. For example, oxo- hydroxo- and carboxylato-bridged polynuclear iron (III) units have been found in many non-heme metalloproteins and metalloenzymes [1–12]. Hemerythrin (a dioxygen carrier) and ribonucleotide reductase (a tyrosyl radical generator) contain an oxo- and carboxylato-bridged diiron(III) unit, and methane monooxygenase (a catalyst for the conversion of methane to methanol) in its oxidized resting state contains a dihydroxy- and carboxylato-bridged diiron(III) unit. Observation of these and other roles of iron(III) in biology has stimulated examination of the structural, magnetic, spectroscopic and redox properties of oxo- and carboxylato-bridged polynuclear iron(III) complexes as model compounds of biological systems [13–28].

The paramagnetic nature of iron in its common oxidation states generates interesting magnetic properties in its polynuclear clusters. As a result, these are attracting magnetochemists to study structure–magnetism relationships in non-heme iron-containing enzymes [29,30], interactions in spin-coupled systems [31], possibilities for generating polynuclear clusters with large spin values in their ground state [21,32] and new examples of single molecule magnets. Although interactions between Fe(III) ions are generally antiferromagnetic, some clusters experience spin frustration or display particular Fe_x topological arrangements that can result in ground states with reasonably large spins. Previous reports concerning di- and higher nuclearity iron(III) systems have shown that organic oxygen bridge atoms of all types provide weak antiferromagnetic coupling between irons whereas oxo bridges provide stronger coupling, but other details of the influence of structure remain poorly defined. There is, therefore, a continuing search for

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http://dx.doi.org/10.1016/j.ica.2016.01.036
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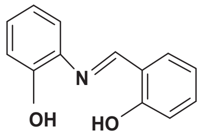
synthetic procedures that yield new types of polynuclear iron compounds having novel chemical and physical properties.

In this work, we report preparations for new chloroacetato- and phenoxo-bridged polynuclear Fe(III) compounds with ONO donor ligands based on the species H_2L shown below as well as structural, spectroscopic and variable temperature magnetic studies of these complexes.



H_2L

2. Experimental

2.1. Chemicals and materials

All chemicals were of reagent grade and were used without further purification. Salicylaldehyde and 2-aminophenol were purchased from Sigma–Aldrich. Chloroacetic acid, $NaHCO_3$, anhydrous ferric chloride, $Fe(ClO_4)_3{\cdot}6H_2O$ and perchloric acid (70%) were supplied by Spectrochem Pvt. Ltd. (India). Solvents were used as received. We have previously reported preparation of the precursor oxo-centered trinuclear iron(III) complex, $[Fe_3(\mu_3\text{-}O)(O_2CCH_2Cl)_6(H_2O)_3]ClO_4$, [33].

2.2. Synthesis of N-(2-hydroxyphenyl)salicylidenimine (H_2L)

The ligand, H_2L, was prepared by modification of the procedure of Westland et al. [34]. A solution of 2-aminophenol (1.10 g, 10.1 mmol) in methanol (20 ml) was added slowly to a solution of salicylaldehyde (1.22 g, 9.99 mmol) in the same solvent (20 ml) with stirring. The resulting mixture was stirred for 3 h. During this time an orange-red microcrystalline precipitate gradually separated. This was removed by filtration, washed several times with ethanol then diethyl ether and dried in air. Yield: 1.54 g (72.3%), *Anal.* Calc. for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57. Found: C, 73.02; H, 5.04; N, 6.42%. MS: (m/z) 214 ($[M+1]^+$, 100%).

2.3. Synthesis of iron(III)complexes

2.3.1. $[\{Fe(L)_2\}_3Fe]$ (**1**) and $[Fe_2(L)_2(ClCH_2COO)_2(H_2O)]$ (**2**)

To a stirred solution of the precursor complex $[Fe_3(\mu_3\text{-}O)(O_2CCH_2Cl)_6(H_2O)_3]ClO_4$ (450 mg, 0.501 mmol) in CH_3CN (30 ml), a solution of the ligand H_2L (160 mg, 0.750 mmol) in the same solvent (20 ml) was added drop-wise. The color of the solution changed from orange to dark reddish-brown during the addition. The solution was stirred for 30 min and filtered to remove undissolved solids and the filtrate was allowed to evaporate 30% of its volume over two days at room temperature during which a black crystalline precipitate of (**1**) was deposited. The precipitate was collected by filtration, washed with Et_2O and dried in air. Yield: 310 mg (55.4% based on Fe). Layering a 40 mg sample of **1** dissolved in CH_3CN (15 ml) with diethyl ether gave, after sitting undisturbed for several days, X-ray quality black crystals.

The filtrate from which the black crystals had initially been obtained was again, at room temperature, allowed to evaporate slowly a further 40% of its initial volume. This resulted in precipitation of a mixture of **1** and **2** that was separated by filtration and discarded. The remaining filtrate was again, at room temperature, allowed to evaporate very slowly a further 20% of its initial volume. A precipitate of X-ray quality dark brown crystals of **2** was deposited and then collected by filtration, washed with Et_2O, and dried in air. Yield: 90 mg (16.2% based on Fe). *Anal.* Calc. for $C_{78}H_{54}Fe_4N_6O_{12}$ (**1**): C, 62.84; H, 3.65; N, 5.64. C: Found: 62.65; H, 3.49; N, 5.48%. IR (KBr, cm^{-1}): 3427 (w, br), 1604 (s), 1580 (s), 1538 (s), 1463 (s), 1440 (m), 1379 (s), 1299 (w, br), 1146 (w, br), 839 (s), 751 (s), 612 (w), 524 (m) (for **1**). UV–Vis [CH_3CN, λ_{max}, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$)]: 223 (sh), 296 (86,639), 340 (sh), 388 (83,310) and 495 (12,635) (for **1**). *Anal.* Calc. for $C_{30}H_{24}Cl_2Fe_2N_2O_9$ (**2**): C, 48.75; H, 3.27; N, 3.79; Cl, 9.59. Found: C, 48.24; H, 3.20; N, 4.15; Cl, 9.54%. IR (KBr, cm^{-1}): 3427 (w, br), 1604 (s), 1580 (s), 1570 (s), 1538 (s), 1463 (s), 1440 (m), 1379 (s), 1303 (s), 1256 (s), 1151 (m), 839 (s), 751 (s), 620 (m), 524 (m) (for **2**). UV–Vis [CH_3CN, λ_{max}, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$)]: 227 (sh), 315 (58,424), 345 (sh), 379 (51,120) and 490 (15,420) nm (for **2**).

2.3.2. $[\{Fe(HL)_2\}\{Fe(L)_2\}]$ (**3**)

To a solution of $Fe(ClO_4)_3{\cdot}6H_2O$ (463 mg, 1.00 mmol) in CH_3CN (10 ml), a solution of H_2L (426 mg, 2.00 mmol) in CH_3CN (10 ml) was added with stirring. The resulting solution turned deep red immediately and a dark brown microcrystalline precipitate appeared within a few minutes. The mixture was stirred for 3 h during which the color of the precipitate gradually changed to yellowish brown. The precipitate was collected by filtration, washed with acetonitrile and diethyl ether and dried in air. Yield: 450 mg (93.8%). Crystals for X-ray analysis were obtained by recrystallization from acetonitrile. *Anal.* Calc. for $C_{52}H_{38}Fe_2N_4O_8$ (**3**): C, 65.15; H, 3.99; N, 5.84. Found: C, 65.02; H, 3.87; N, 6.08%. IR (KBr, cm^{-1}): 3436 (w, br), 3057 (w), 1605 (s), 1580 (s), 1536 (s), 1465 (s), 1438 (s), 1311 (m), 1149 (m), 826 (m), 881 (s), 743 (s), 609 (m), 516(m), 471 (m). UV–Vis [CH_3CN, λ_{max}, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$)]: 230 (sh), 295 (17,500), 345 (sh), 408 (16,500) and 500 (5,100).

2.4. Physical measurements

Elemental analyses were performed by Canadian Microanalytical Service Ltd. (**2**) or by using a Perkin–Elmer 2400 Series II elemental analyzer (H_2L), (**1**) and (**3**). Fourier Transform Infrared (FTIR) spectra (4000–400 cm^{-1}) were recorded using KBr disks on a JASCO FTIR-460 Plus spectrometer. Electronic absorption spectra were recorded at a concentration of $1 \times 10^{-5}\,mol\,L^{-1}$ in acetonitrile on a JASCO V-530 spectrophotometer. Variable temperature (2–300 K) magnetic susceptibility measurements were obtained by using a Quantum Design MPMS SQUID magnetometer at a fixed field strength of 1.00 Tesla. Diamagnetic corrections were estimated by using Pascal's constants [35].

2.5. X-ray crystallography

Single crystals of (**1**) and (**3**) were mounted on glass fibres and coated with perfluoropolyether oil, while (**2**) was coated in oil and mounted on a low temperature MiTeGen loop. Intensity data were collected at 100 K (for **1**), 120 K (for **2**) and 150 K (for **3**) on a Bruker-AXS SMART APEX II diffractometer (**1** and **3**) or a Rigaku Saturn 70 diffractometer (**2**) equipped with a CCD detector and using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data were processed with SAINT [36a] and absorption corrections were made with SADABS [36a] software packages (**1** and **3**), while **2** was processed *via* the Crystal Clear software suite [36b]. The structures were solved by direct methods and refined by full-matrix least-squares analysis based on F^2 using WINGX software of SHELXTL [37a] and SHELX-97 [38] (**1** and **3**), while **2** was also refined using SHELX-97 [38], but *via* the crystal structure [37b] graphical