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Aqua complex of iron(III) and 5-chloro-3-(2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hydrazinyl)-2-hydroxybenzenesulfonate: Structure and catalytic activity in Henry reaction

Kamran T. Mahmudov [a,b], Maximilian N. Kopylovich [a,*], Matti Haukka [c], Gunay S. Mahmudova [a,b], Espandi F. Esmaeila [b,d], Famil M. Chyragov [b], Armando J.L. Pombeiro [a,*]

[a] Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Technical University of Lisbon, Av. Rovisco Pais, 1049–001 Lisbon, Portugal
[b] Baku State University, Department of Chemistry, Z. Xalilov Str. 23, Az 1148 Baku, Azerbaijan
[c] University of Jyväskylä, Department of Chemistry, P.O. Box 35, FI-40014 University of Jyväskylä, Finland
[d] Independent Islam University, Garaj Filial, Tehran, Iran

HIGHLIGHTS

- New aqua soluble Fe^{III} complex with arylhydrazone of 5,5-dimethylcyclohexane-1,3-dione.
- Intermolecular charge-assisted halogen bonding.
- The complex acts as a catalyst in the nitroaldol (Henry) reaction.

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ABSTRACT

A water-soluble iron(III) complex $[Fe(H_2O)_3(L)]\cdot 5H_2O$ (**1**) was prepared by reaction of iron(III) chloride with 5-chloro-3-(2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hydrazinyl)-2-hydroxy-benzenesulfonic acid (H_3L). The complex was characterized by IR, ^1H NMR and ESI-MS spectroscopies, elemental and X-ray crystal structural analyses. The coordination environment of the central iron(III) is a distorted octahedron, three sites being occupied by L^{3-} ligand, which chelates in O,N,O fashion, while three other sites are filled with the water molecules. The uncoordinated water molecules are held in the channels of the overall 3D supramolecular structure by the carbonyl and sulfonyl groups of L^{3-} and the ligated waters. Apart from the multiple hydrogen bonds, an intermolecular charge-assisted O···Cl halogen bonding with 3.044 Å distance was described. **1** acts as an effective catalyst in the Henry reaction producing nitroaldols from nitroethane and various aldehydes with yields up to 90% and *threo/erythro* diastereoselectivity ranging from 3:1 to 1:1.

1. Introduction

Arylhydrazones of β-diketones (AHBD) are versatile intermediates in organic chemistry [1]; the coordination chemistry of AHBD is also of interest [2]. The AHBD ligands interact with many metal ions in various fashions, thus allowing one to create different confined and overall geometries in solution and in solid phase. Different types of complexes can be easily prepared depending on the position of substituents in AHBD and on the nature of metal ions [2–12]. It was demonstrated, that in solution the stabilities of metal complexes with AHBDs increase in the order $Ca^{II} < Mg^{II} < Mn^{II} < Cd^{II} < Zn^{II} < Co^{II} < Ni^{II} < UO_2^{II} < Cu^{II} < Fe^{III}$ and are higher than those of metal complexes with simple β-diketones [2]. In spite of the fact that in solution iron(III) forms the most stable complexes with AHBD ligands, only two such complexes were isolated in solid state and structurally characterized [8]. It was demonstrated that these complexes perform high catalytic activity in peroxidative oxidation of cycloalkanes [8]. The catalytic activity of the complexes can be related to the fact that the central Fe^{III} ion is, on the one hand, protected by the chelating AHBD ligand, and, on the other hand, possesses labile sites with coordinated water molecules [8]. Similar Zn(II) complexes were found to be catalytically active in another type of reaction, namely C—C bond formation [5]. Thus, it worth to extend a number of the structurally characterized Fe(III)-AHBD complexes and check their catalytic activity in other relevant reactions.

The selective and efficient functionalization of C—H bonds has attracted much attention from both academia and industry.

* Corresponding authors.
E-mail addresses: kopylovich@yahoo.com (M.N. Kopylovich), pombeiro@ist.utl.pt (A.J.L. Pombeiro).

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Although great progress has been made in this area, more effective processes for the construction of C—C bonds starting from C—H bonds are still highly desirable. The synthesis of 2-nitroalcohols from an enolizable nitroalkane and a carbonyl compound, known as Henry or nitroaldol reaction, is an important synthetic tool for the creation of C—C bond [13]. The development of new catalysts and procedures for the Henry reaction has been constantly elaborated in view of the reduction of toxic by-products and the increase of yield and diastereoselectivity. Several organic and inorganic catalysts have been described for the reaction [14–20], however, the catalytic activity of Fe(III)-AHBD complexes has not yet been reported.

Taking in mind all the above considerations, in this contribution we describe the synthesis and structural details of the iron(III) complex with 5-chloro-3-(2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hydrazinyl)-2-hydroxybenzenesulfonic acid (H_3L) and evaluate its activity and diastereoselectivity in production of 2-nitroalcohols by the Henry reaction.

2. Experimental

2.1. Materials and instrumentation

The ^1H and ^{13}C NMR spectra were recorded at room temperature on a Bruker Avance II + 300 (UltraShield™ Magnet) spectrometer operating at 300.130 and 75.468 MHz for proton and carbon-13, respectively. The chemical shifts are reported in ppm using tetramethylsilane as the internal reference. The infrared spectra (4000–400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. Carbon, hydrogen, and nitrogen elemental analyses were done using a "2400 CHN Elemental Analyzer" by Perkin Elmer. Electrospray mass spectra (ESI-MS) were run with an ion-trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer) equipped with an electrospray ion source. For electrospray ionization, the drying gas and flow rate were optimized according to the particular sample with 35 p.s.i. nebulizer pressure. Scanning was performed from *m/z* 100 to 1200 in methanol solution. The compounds were observed in the positive mode (capillary voltage = 80–105 V).

2.2. Syntheses of *1*

About 373 mg (1 mmol) of H_3L was dissolved in 15 mL water (pH 2), then 270 mg (1 mmol) of $FeCl_3{\cdot}6H_2O$ was added at room temperature giving (after *ca.* 2 d) a brown precipitate of the product. The precipitate was filtered off and recrystallized from ethanol giving brown crystals suitable for X-ray structural analysis.

$[Fe(H_2O)_3(L)]{\cdot}5H_2O$(1). Yield, 50% (based on Fe). Calcd. for $C_{14}H_{28}ClFeN_2O_{14}S$ (M = 571.74): C 29.41, H 4.94, N 4.90. Found C 29.13, H 4.63, N 4.74. MS (ESI): *m/z*: 428.01 $[M–8H_2O + H]^+$. IR (KBr), cm^{-1}: 3323 and 3082 (s, br) ν(OH), 1659 (s) ν(C=O) and δ(OH), 1562 (s) ν(C=N). 1H NMR (300.13 MHz, DMSO-d_6) δ: 1.06 CH_3, 4.11 CH_2, 7.43–7.54 (2H, C_6H_2).

2.3. X-ray measurements

The crystals of **1** was immersed in cryo-oil, mounted in a Nylon loop, and measured at the temperature of 100 K. The X-ray diffraction data was collected on a Bruker Smart Apex II [21] diffractometer using Mo Kα radiation (λ = 0.71073 Å). The *APEX2* program package was used for cell refinements and data reductions. The structures were solved by direct methods using the *SHELXS-97* program with the *WinGX* graphical user interface [22–24]. A semi-empirical multi-scan absorption correction based on equivalent reflections (*SADABS*) [25] was applied to all data. Structural refinements were carried out using *SHELXL-97* [23]. The H_2O hydrogen atoms were located from the different Fourier map but constrained to ride on their parent atom with U_{iso} = 1.5 U_{eq}(parent atom). Other hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms with U_{iso} = 1.2–1.5 U_{eq} (parent atom). The crystallographic details are summarized in Table 1. CCDC 919328 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.4. General procedure for the reaction of nitroethane and various aldehydes

The solvent (2 mL) was added to a flask which contained the Fe(III) catalyst **1** (typically 3.01 mol%) and the mixture was agitated for 5 min. Then aldehyde (1 mmol) and nitroethane (4 mmol) were added and the reaction mixture was stirred for the appropriate amount of time, after which the solvent was evacuated. The residue was dissolved in DMSO-d_6 and analyzed by ^1H NMR [5,19]. The yield of β-nitroalkanol was related to the amount of aldehydes; the adequacy of this procedure was verified by blank ^1H NMR analyses with 1,2-dimethoxyethane as an internal reference. The *threo* and *erythro* isomers were distinguished from the values of vicinal coupling constants between the α-N—C—*H* and the α-O—C—*H* protons, being *J* = 7–9 or 3.2–4 Hz for the *threo* or *erythro* isomers, respectively [5,19].

3. Results and discussion

3.1. Synthesis and characterization of *1*

The synthesis and characterization of 5-chloro-3-(2-(4,4-dimethyl-2,6-dioxocyclo-hexylidene)hydrazinyl)-2-hydroxybenzenesulfonic acid (H_3L) was reported earlier [8] and hence will not be discussed herein. Treatment of Fe^{III} chloride hexahydrate with H_3L in water (pH 2) with the subsequent work-up led to the brown compound $[Fe(H_2O)_3(L)]{\cdot}5H_2O$ (**1**, Scheme 1) in 50% yield. The IR spectrum of **1** displays 3323 and 3082 (s, br) ν(OH), 1659 (s) ν(C=O) and δ(OH), 1562 (s) ν(C=N) lines, the peaks are significantly shifted in relation to the spectrum of free ligand (3504 ν(OH), 3385 ν(NH), 1647 ν(C=O), 1597 ν(C=N)) [8]. The proton signals of the

Table 1
Crystal data and structure refinement for **1**.

Empirical formula	$C_{14}H_{28}ClFeN_2O_{14}S$
Formula weight	571.74
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	11.0372(19)
b (Å)	11.2243(19)
c (Å)	11.2715(17)
α (°)	67.357(7)
β (°)	78.198(7)
γ (°)	89.434(7)
Volume ($Å^3$)	1257.8(4)
Z	2
Density (mg/m^3)	1.510
Absorption coefficient	0.854 mm-1
Goodness-of-fit on F^2	1.021
Final *R* indices [I > 2sigma(I)]	*R*1[a] = 0.0421, w*R*2[b] = 0.0984
R indices (all data)	*R*1 = 0.0686, w*R*2 = 0.1112
Largest diff. peak and hole	1.274 and −0.318 e $Å^{-3}$

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.