Inorganic Chemistry Communications 12 (2009) 21–25

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

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

Synthesis, characterization and catalytic study of a novel iron(III)-tridentate Schiff base complex in sulfide oxidation by UHP

Mojtaba Bagherzadeh *, Mojtaba Amini

Chemistry Department, Sharif University of Technology, Azadi Avenue, P.O. Box 11155-3615, Tehran, Iran

ARTICLE INFO

Article history:
Received 26 July 2008
Accepted 26 October 2008
Available online 5 November 2008

Keywords:
Sulfoxide
Iron complex
Schiff base
Catalytic oxidation
UHP

ABSTRACT

An hydrazone Schiff base-iron(III) complex using salicylidene benzoyl hydrazine (L) as ligand has been synthesized and characterized by elemental analyses, IR, ^{1}H and ^{13}C NMR and UV–Vis spectroscopy. Oxidation of sulfides to sulfoxides in one-step was conducted by this complex catalyst using urea hydrogen peroxide (UHP) in mixture of CH_2Cl_2/CH_3OH (1:1) under air at room temperature. The effect of the reaction conditions on the oxidation of methylphenylsulfide was studied by varying the amount of the catalyst, reaction temperature, reaction time and the amount of UHP. The results showed that using this system in the oxidation of sulfides, sulfoxides were obtained as the main products, together with variable amounts of sulfones (⩽9%), depending on the nature of the substrate.

Sulfoxides and sulfones play important roles in synthetic organic chemistry and are important bioactive compounds [1]. Furthermore, sulfoxidation catalysis has assumed special relevance in the deep desulfurization of fuels, due to environmental constraints [2]. The finding of efficient catalysts for the selective insertion of one oxygen atom from oxygen donors, like iodosylbenzene, dioxygen, hydrogen peroxide, alkylhydroperoxide, or sodium hypochlorite into various organic molecules, under mild conditions, remains a difficult challenge in the fields of chemical and biological catalysis [3,4]. The oxidation of hydrocarbons by transition metal complexes has been studied extensively [5–15]. Among the inorganic mimics of enzymes, metal complexes containing porphyrin, salen (salen = *N*,*N*′-ethylenebis(salicylideneaminato)), and phthalocyanine ligands have been investigated as possible alternative catalysts in many oxidation and hydroxylation reactions [16–20].

In analytical chemistry hydrazones find application by acting as multidentate ligands [21,22] with metals (usually from the transition group). Various studies have also shown that the azomethine group having a lone pair of electrons in either a p or sp^2 hybridized orbital on trigonally hybridized nitrogen has considerable biological importance [23]. Hydrazone complexes of Cu(II), Ni(II), Pd(II) [24] and Co(II) [25–27] and benzoylhydrazone complexes of copper(II) [28], vanadium [29,30], and ruthenium(II) [31] have been studied.

In this paper we report the synthesis and characterization of the ligand, obtained in the reaction of benzhydrazide with salicylaldehyde, and its iron complex by physico-chemical methods. There has been interest in the design, synthesis and application of non-symmetric Schiff base ligand (Scheme 1). This has been stimulated from the awareness that in many metalloproteins the metals are contained in non-symmetrical environments and also by an interest in the potential modification of the properties of complexes derived from ligands having present non-symmetrical mixed sets of donor atoms [32,33].

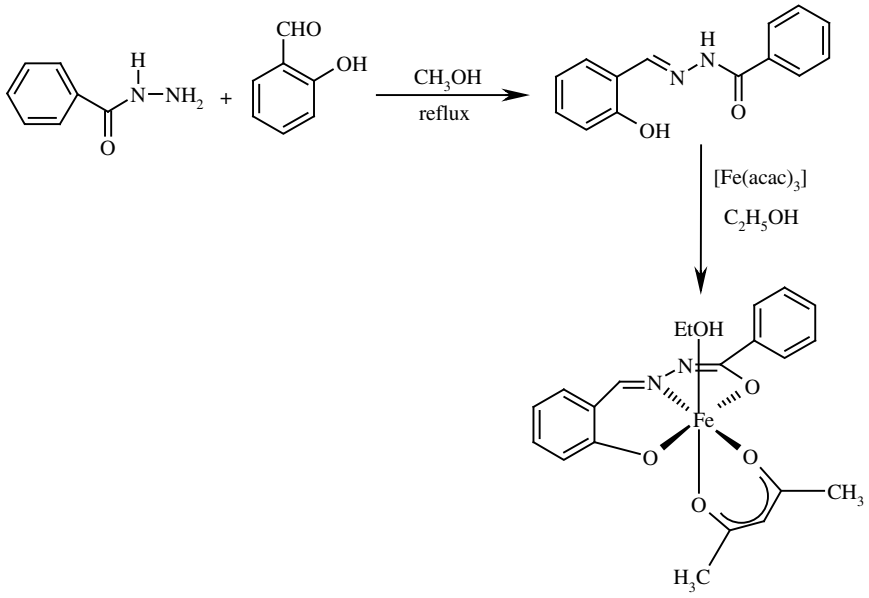
Here, we also report the catalytic performance of the Schiff base complex of iron, [Fe(L)(acac)(EtOH)] in the oxidation of sulfides with UHP (urea hydrogen peroxide) in mixture of CH_2Cl_2/CH_3OH as solvent system (Scheme 2).

The elemental analyses and spectral data of the ligand, salicylidene benzoyl hydrazine (L) [34] and [Fe(L)(acac)(EtOH)] complex [36] are listed in Table 1.

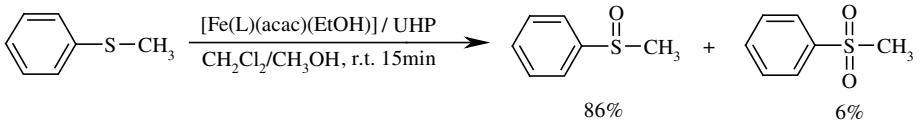
The C, H, N and selected spectroscopic data presented in Table 1 confirm the assigned composition of the ligand and complex. The ligand showed stretching bands attributed to C=O, C=N and N–H at 1671, 1639 and 3265 cm^{-1}, respectively. In addition a strong band found at 1617 cm^{-1} is attributed to >C=N–N=C< group. This IR evidence has been registered earlier for the similar class of ligands that behave as tridentate dibasic ligands upon enolization [37]. On complexation, the υ(C=N) band was shifted to lower frequency in the 1625 cm^{-1} range indicating the coordination of the azomethine nitrogen atom to the central metal ion [25,26]. The bands due to υ(CO) and υ(NH) were absent in the complex. This suggests occurrence of keto-imine tautomerization of the ligand during complexation [38]. The >C=N–N=C<, framework seen at 1617 cm^{-1} in the ligand shifted to 1602 cm^{-1} upon coordination to Fe atom [38]. Very broad O–H vibration at 3415 cm^{-1} in [Fe(L)(acac)(EtOH)], is probably due to the adsorbed ethanol molecule.

* Corresponding author. Tel.: +98 21 661 65354; fax: +98 21 66012983.
E-mail address: bagherzadehm@sharif.edu (M. Bagherzadeh).

1387-7003/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.inoche.2008.10.023



Scheme 1.



Scheme 2.

Table 1
Microanalytical and spectral data for ligand (L) and [Fe(L)(acac)(EtOH)].

Ligand/complex	UV–Vis		C, H, N			IR (cm^{-1})		^{1}H NMR (δ, ppm)	^{13}C NMR
	Solvent	λ (nm) (ε, M^{-1} cm^{-1})	C (%)	H (%)	N (%)				
$C_{14}H_{12}N_2O_2$ (L)	CH_3OH	290 (3941)	69.65	5.00	11.61	υ(C=O)	1671 (s)	11.51 (1H, s)	163.71,
FW = 240.26		331 (10,649)	(70.0)	(5.03)	(11.66)	υ(C=N)	1639 (s)	11.16 (1H, s)	158.47,
Mp = 172 °C						υ(N–H)	3265 (s)	8.18 (1H, s)	150.11,
						υ(>C=N–N=C<)	1617 (s)	7.52 (2H, d)	133.15,
								7.12 (1H, t)	132.06,
								7.04 (2H, t)	131.41,
								6.85 (2H, q)	130.74,
								6.51 (1H, d)	128.54,
								6.46 (1H, t)	127.92,
									119.29,
									118.26,
									116.90.
[Fe(L)(acac)(EtOH)]	CH_3OH	270 (4398)	56.8	5.20	6.31	υ(C=O)	Absent		
$C_{21}H_{23}N_2O_5Fe$		317 (6970)	(57.42)	(5.28)	(6.38)	υ(C=N)	1625		
FW = 439.26		364 (6350)				υ(N–H)	Absent		
		460 (970)				υ(>C=N–N=C<)	1602(s)		

The UV–Vis spectra of complex [Fe(L)(acac)(EtOH)] was obtained in methanol solution. The complex shows a weak d–d band around 460 nm regions. In addition, the complex exhibit intense bands in the 364 nm regions, which are attributed to a charge-transfer (CT) transition [39]. Also an absorption band at about 317 nm is attributed to a phenolate (p_π) → iron(III) (d_σ^*) charge-transfer transition [40–43]. The intense higher-energy bands at around 270 nm can be attributed to intraligand $\pi \rightarrow \pi^*$ transitions [38].

The oxidation of sulfides to sulfoxides has been extensively studied due to the importance of sulfoxides as useful intermediates in organic synthesis, and some of them play key roles in the activation of enzymes. There are several reagents and oxidative procedures available for this transformation. However, many result in over-oxidation to sulfones. Therefore, controlling the reaction conditions, that is, time, temperature and the relative amount of oxidants, plays an important role to avoid forming oxidative side products, however, these requirements are often hard to meet. Thus, there is still considerable interest in the development of selective oxidants for this transformation.

In order to find the optimum conditions for the oxidation of sulfides, Oxidation of methylphenylsulfide in various conditions was studied and listed in Table 2 [44]. With the increase of the amount of UHP to 0.4 mmol, sulfoxide reached the highest yield. However, more excess of UHP led to a slightly decreasing yield (Table 2, entries 6–10). It may be pointed out that the addition of catalyst led