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Synthesis of polar unique 3d metal-imine complexes of salicylidene anthranilate sodium salt. Homogeneous catalytic and corrosion inhibition performance

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Three polar Ni(II)-, Cu(II)- and Zn(II)-complexes (M-SSA) of salicylidene anthranilate sodium salt ligand were synthesized. The ligand (H_2SSA) and its corresponding metal-complexes are characterized by alternative physico-chemical tools in which H_2SSA acts as tridentate bi-basic chelating agent. Catalytic potential of M-SSA was investigated in the homogenous oxidation of 1,2-cyclohexene at 80 °C in acetonitrile, water or under solvent-free condition. M-complexes exhibit high catalytic reactivity with high chemoselectivity in acetonitrile. Cu-SSA shows the highest catalytic potential for the oxidation of 1,2-cyclohexene than Ni-SSA or Zn-SSA. The lowest yield of the epoxy-product was obtained in water due to the hydrolysis ring opening reaction affording 1,2-cyclohexanediol. The inhibition performance of H_2SSA and M-SSA on the carbon steel corrosion (CS) in HCl was studied using electrochemical techniques. The inhibition capability was increased with increasing inhibitor dose. The adsorption of inhibitors on the surface of CS obeyed the Langmuir isotherm paradigm. Surface characterizations (SEM/EDX) revealed that the investigated compounds adsorbed on CS surface and form protective layer that shield the surface from direct corrosion attack. The experimental data have been completed by density functional theory treatment. The obtained theoretical results are exceedingly in agreement with empirical results catalytically and inhibitory.

1. Introduction

Imines, as Schiff base derivatives, are well known as high coordinated ligands with various transition metals of low and high valents. Specific chemical features of steric demand, bite angles and the nature donor centers of imines could control their reactivity towards complex formation [1,2]. Tridentate imine ligands with hard donor atoms, alternatively, oxygen and/or nitrogen atoms as strong σ- and π-donors are widely applied in complexation 3d transition metals [3,4], which form very stable and defined stoichiometric structures [5–7]. Complexes of imines are particularly advantageous because of their ready high applicability in many fields, *e.g.* biological [2], pharmacological [8] and anticancer [6]. They act as containing enzymes and oxidation catalysts [9,10]. The type of the central metal ion in the imine complexes has a remarkable effect on their reactivity of towards catalytic redox processes and steel corrosion inhibition [11]. Hence, synthesis of novel complexes with the modified ligands of low cost, high coordinately active and greener reagents [11], is the motivation in inorganic chemistry [12]. High applicability of transition metal complexes as catalysts for redox processes of alkenes in the organic synthesis is the main object industrially and in laboratories [13]. High sufficiency and chemoselectivity of metal complexes as catalysts for such redox processes is the reason for many researchers to design new classes of metal complexes, especially with cheap and easily synthesized ligands, *e.g.* imine-salicylidene ligands [14]. Type of central metal ion has a remarkable influence in its complex catalytic activity towards oxidation of alkenes and alcohols [15], which is the challenge to present the catalytic potential of some various 3d metal ions in the (ep)oxidation of 1,2-cyclohexene.

Corrosion of carbon steel (CS) processes is highlighted in research and industry, recently, especially in acid solutions due to the increased industrial implementations [11]. For example, the crude oil refining products in an assortment of corrosive situations [16]. Generally, refinery corrosion could take place by the attacking of equipment surface with a strong acid [17]. The other fundamental fields of enforcements are petrochemical processes, acid

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descaling, acid pickling, industrial cleaning and oil well acid in oil recovery [18]. Among the acid solutions, HCl is one of the most exceedingly utilized agents [19]. According to the immersion of carbon steels in aggressive media, they are liable to various corrosion types; subsequently, the applied corrosion inhibitors, to protect the steel surfaces from dissolution, will be unavoidable [20]. Numerous of organic compounds containing N, O and S donor centers have been applied for protection of metals and alloys from corrosion. The presence of $-C = N-$ linkage (azomethine) in the imine moiety, as Schiff bases, in the organic compounds, improves their effective corrosion inhabitation [21]. Imines could be adsorbed on the metal surface and spontaneously form a monolayer on its surface, therefore, they display good inhibitive properties [22]. Some imines were used to prevent the corrosion attack, *e.g.* amino acid derivatives [11,16] and polydentate imines, which contain donor nitrogen centers [23]. The high inhibiting potential of imines could be interpreted by their adsorption on the steel/solution interface. However, little works about metal complexes with imines, coordinated ligands, as corrosion inhibitors for CS in acidic environments have been reported previously [24,25]. Various Zn(II)-, Ni(II)-, Sn(II)- and Co(II)-imines complexes demonstrated good corrosion inhibiting performance for steel alloy in different aggressive solution at different temperatures [26]. Abdel-Gaber et al. studied the corrosion inhibition of CS in H_2SO_4 by various doses (50 to 200 ppm) of a bulky Co(III) Schiff base complex [27]. Transition metal-imine complexes are predictable to supply better efficiency because of their compactness, larger size and the synergistic effect of metal–organic blends [28]. They display improved inhibiting performance more than their coordinated free ligands [29].

Quantum chemical calculations have become widely used as an important method for supported both mechanisms of corrosion inhibition and catalytic oxidation of organic compounds [30,31]. The relationships between structural parameters and their inhibition and efficiencies would be investigated in these studies, as well as, the HOMO and LUMO would be used to study the catalytic potential of metal-complexes in the oxidation processes.

The present study aims to present novel metal-imine complexes as homogenous oxidation catalysts and corrosion inhibitors. The advantages of these compounds include synthesized from comparatively cheap raw materials, water soluble and green. Synthesis and characterization of three novel complexes of Ni(II), Cu(II) and Zn(II) ions with salicylidene anthranilate sodium salt (H_2SSA) (Fig. 1) would be studied. The catalytic performance of Ni-SSA, Cu-SSA and Zn-SSA could be examined in the homogenous oxidation of 1,2-cyclohexene by an aqueous H_2O_2 or *tert*-butyl hydroperoxide (TBHP or *t*BuOOH) at 80 °C in acetonitrile, water or under solvent-free condition. The ability of H_2SSA and their Ni(II)-, Cu(II)- and Zn(II)-complexes as inhibiting agents for the corrosion of CS in acidic chloride media using electrochemical (EIS and PDP) and surface characterization (SEM and EDX) methods could be investigated. DFT approaches are performed on the synthesized compounds to emphasize empirical results.

2. Experimental part

2.1. Materials and instruments

All applied reagents and materials are supplied from Sigma-Aldrich and Acros. They are used without further purification or treatment. Micro-analyses were accomplished by a GMBH VarioEl model V2.3 CHNS machine. Nuclear magnetic resonating spectra were evaluated on a multinuclear FT-NMR spectrometer Bruker ARX400 at 400.1 for H-proton and 100.6 MHz for C-nucleus at room temperature. The ^1H and ^{13}C chemical shifts d are given in ppm. J_{HH} and J_{CC} refer to coupling constants between H and C nuclei in the NMR. Electronic spectrums were done with 10 mm quartz cells in a thermostatted holder of a Jasco UV–vis spectrophotometer (model V-570) in the range from 190 to 800 nm. IR spectra (as KBr discs) are estimated by Shimadzu FTIR-8101 Fourier Transform Infrared spectrophotometer from 4000 to 400 cm^{-1}. Conductivity values of the polar current complexes were measured using a Jenway conductivity meter model 4320, connected with an epoxy bodied conductivity cell (two electrodes, shiny) and cell constant calibration from 0.01 to 19.99 at 25 °C. Magnetic susceptibility of Ni-SSA and Cu-SSA were determined by a Gouy's balance, the diamagnetic correction was achieved within Pascal's contents and $Hg[Co(SCN)_4]$ as a calibrant. Electrospray ionization mass spectroscopy (EIS-MS) was performed on a Waters API Quatroo Micro Triple Quadrupole electrospray ionization mass spectrophotometer in the positive and negative modes. All chemical reactions were taken place with a magnetically stirrer and kept at the specific temperatures using a thermostated oil bath.

Carbon steel (CS) with the composition (in wt%): 0.04% (S), 0.15% (C),0.70% (Mn), 0.19% (Si), 0.011% (Cr), 0.011% (Ni) and Fe (rest) was utilized as working electrode (WE) for one time. HCl (1.0 M, Merck 37%) was prepared in deionized water. H_2SSA and its corresponding complexes of Ni-SSA, Cu-SSA and Zn-SSA were dissolved in bi-distilled at the concentration range 50 to 300 ppm.

2.2. Synthesis of H_2SSA (2-[(2-Hydroxy-5-sodium sulfonate-benzylidene)-amino]-benzoate)

In 30 mL water, 5.0 mmol of sodium salicylaldehyde-5-sulfonate was mixed with 5.0 mmol of anthranilic acid in 30 mL ethanol at room temperature. A yellow color in the reaction media was observed just after addition. The reaction mixture was kept with stirring for 3 h at 25 °C. The reaction was monitored by thin layer chromatography (TLC). The solvent was removed by vacuum and the residual washed many times with diethyl ether and dried in oven. The pure ligand was obtained by recrystallization in water–ethanol (1:1) to award yellow crystalline solid with yield 1.20 g (70%).

^1H NMR (DMSO-d_6, 400 MHz): δ 6.50 (t, $^3J = 6.9$ and 7.2 Hz, 1H), 6.74 (d, $^3J = 8.2$ Hz, 1H), 6.94 (dd, $^3J = 8.0$ and 8.3 Hz, 1H), 7.22 (t, $^3J = 7.0$ and 7.4 Hz, 1H), 7.70 (dd, $^3J = 7.7$ Hz, 2H), 7.92 (s, 1H), 10.26 (s, 1H, phenolic-OH), 10.82 ppm (s br, 1H, CH = N).

^{13}C NMR (100 MHz, DMSO-d_6, dept-135): δ 110.18 (C_q), 115.05 (CH), 116.83 (CH), 116.96 (CH), 121.48 (CH), 126.92 (CH), 131.61 (CH), 134.20 (CH), 140.72 (C_q), 151.94 (C_q), 161.15 (C_q), 169.99 (C_q), 192.11 ppm (CH, CH = N). (^{1}HNMR, ^{13}CNMR and dep135, Figs. S1–S3, Supplementary materials).

2.3. Synthesis of metal-complexes (M-SSA)

An aqueous solution (20 mL) of copper acetate monohydrate, nickel acetate hexahydrate or zinc acetate dihydrate (5.0 mmol) was added dropwisely to an aqueous solution of H_2SSA at 25 °C. The reaction mixture was warming up 70 °C for 3 h with stirring. The color was changed gradually to the corresponding complex color. The solvent was removed in vacuum and the residual was washed many times with diethyl ether and dried in oven. The pure complexes were recrystallized in water–methanol mixture (1:1).

2.3.1. NMR spectra of Zn-SSA

^1H NMR (DMSO-d_6, 400 MHz): δ 1.82 (s, 6H, crystalline $3H_2O$), 3.29 (s, 2H, coordinated H_2O, overlapped with H_2O of the solvent), 6.58 (d, $^3J = 8.7$ Hz, 1H), 7.29 (dd, $^3J = 7.4$, 6.7 Hz, 2H), 7.47 (m, 2H), 7.64 (d, $^4J = 1.9$ Hz, 1H), 7.89 (d, $^3J = 7.0$ Hz, 1H), 8.42 ppm (s br, 1H, CH = N).

^{13}C NMR (100 MHz, DMSO-d_6, dept-135): δ 115.04 (CH), 116.97 (CH), 121.49 (C_q), 127.20 (C_q), 131.76 (CH), 132.52 (C_q), 133.85 (CH), 134.24 (CH), 156.11 (C_q), 168.55 (C_q), 192.40 ppm (CH, CH