Journal of Saudi Chemical Society (2014) **18**, 762–773

King Saud University

Journal of Saudi Chemical Society

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Investigation of the oxygen affinity of manganese(II), cobalt(II) and nickel(II) complexes with some tetradentate Schiff bases

Adel A.A. Emara [a,b,*], **Ali M. Ali** [c], **Ahmed F. El-Asmy** [d], **El-Sayed M. Ragab** [d]

[a] *Department of Chemistry, University College in Mekkah, Umm Al-Qura University, Mekkah 21955, Saudi Arabia*
[b] *Department of Chemistry, Faculty of Education, Ain Shams University, Roxy, Cairo 11711, Egypt*
[c] *Department of Chemistry, Faculty of Science, Al-Azhar University, Cairo, Egypt*
[d] *Department of Chemistry, Faculty of Science, Mansoura University, Mansoura, Egypt*

Received 12 June 2011; accepted 2 August 2011
Available online 10 August 2011

KEYWORDS

Tetradentate Schiff bases;
Oxygen affinity;
Oxygen carriers;
Transition metal complexes

Abstract Oxygen absorption–desorption processes for square planar Mn(II), Co(II) and Mn(II) complexes of tetradentate Schiff base ligands in DMF and chloroform solvents were investigated. The tetradentate Schiff base ligands were obtained by condensation reaction of ethylenediamine with salcyldehyde, *o*-hydroxyacetophenone or acetylacetone in the molar ratio 1:2. The square planar complexes were prepared by the reaction of the Schiff base ligands with Mn(II) acetate, Co(II) nitrate and Ni(II) nitrate in dry ethanol under nitrogen atmosphere. The sorption processes were undertaken in the presence and absence of (pyridine) axial-base in 1:1 M ratio of (pyridine:metal(II) complexes). Complexes in DMF indicate significant oxygen affinity than in chloroform solvent. Cobalt(II) complexes showed significant sorption processes compared to Mn(II) and Ni(II) complexes. The presence of pyridine axial base clearly increases oxygen affinity.

© 2011 Production and hosting by Elsevier B.V. on behalf of King Saud University.
Open access under CC BY-NC-ND license.

1. Introduction

Schiff base compounds have potential applications in their ability to reversibly bind oxygen (Martell and Clavin, 1952). Since the 1970s, many reports have been published on studies to achieve oxygen absorption–desorption functions similar to those of such natural hemes using synthetic porphinato-iron(II), lacunars (Cairns et al., 2007), Schiff base and macrocyclic complexes of different transition metals (Collman, 1977; Basolo et al., 1975). Recently, this field span the gamut, in

---

[*] Corresponding author at: Department of Chemistry, University College in Mekkah, Umm Al-Qura University, 21955 Mekkah, Saudi Arabia. Tel.: +966 5 92188087; fax: +9662 5566401.
E-mail address: adelaaemara@yahoo.com (A.A.A. Emara).
Peer review under responsibility of King Saud University.

ELSEVIER Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.jscs.2011.08.002

1319-6103 © 2011 Production and hosting by Elsevier B.V. on behalf of King Saud University. Open access under CC BY-NC-ND license.

applications of the artificial oxygen carrier complexes, such as their use as catalysts for the oxidation of unsaturated organic compounds (Khandar et al., 2005; Lu et al., 2000; Li et al., 2007), and inorganic–organic hybrid membrane for oxygen/nitrogen separation containing a cobalt(II) Schiff base complex as oxygen carrier (Kuraoka et al., 2000) and also, in finding new ligands with different substituents to encourage the complexes to bind with the dioxygen in a higher rate (Li et al., 2006; Huber et al., 2005; Comuzzi et al., 2002).

Oxygen absorption properties of cobalt(II) complexes of *N*,*N*′-*bis*(salicylidene)-2,2′-dimethyl-1,3-propanediimine ligand derivatives, termed CoSaldmpr, were reported (Park et al., 1998). The complexes gave significant results in 1-methyl-2-pyrrolidinone (NMP) solution. The complexes with 2 M 2-cyanopyridine axial base, loading of Co(3-methoxy-Saldmpr), measured in (g O_2/g solution) remains about 35% higher than Co(3-methoxy-Salen) for at least four absorption/desorption cycles.

In our laboratory, the oxygen absorption–desorption properties for the square pyramide Mn(II), Co(II) and Ni(II) complexes of pentadentate Schiff bases derived from diethylenetriamine with salicylaldehyde or *o*-hydroxyacetophenone, in the molar ratio 1:2, were investigated (Emara et al., 2008). It was clear that, Co(II) complex is a better oxygen carrier than Ni(II) and Mn(II).

In the present work, some Mn(II), Co(II) and Ni(II) complexes in square planar arrangements were synthesized. The square planar complexes are formed through the reactions of the metal ions with some tetradentate Schiff base ligands under nitrogen atmosphere. The tetradentate Schiff base ligands were obtained by condensation reaction of ethylenediamine with salcyldehyde, *o*-hydroxyacetophenone or acetylacetone. The oxygen absorption–desorption properties for the square planar Mn(II), Co(II) and Ni(II) complexes were investigated in DMF and chloroform. The sorption processes were undertaken in the presence and absence of (pyridine) axial-base. The molar ratio of the axial-base:metal(II) complexes were 1:1. Although the solubility of the Ni(II) and Mn(II) complexes were significant in both solvents, the oxygen affinities of these particular ions were not significant. On the other hand, cobalt(II) complexes showed significant absorption and desorption processes, which the color of the Co(II) complexes terns red after the absorption of the oxygen at −10 °C in both DMF and chloroform solvents and turned back to its original brown color by releasing the absorbed oxygen starting from 60 °C until 80 °C. Comparing the two solvents with the oxygen affinity, it is noted that in case of chloroform the oxygen affinity is decreased more than in case of DMF solvent. The presence of pyridine axial base clearly increases oxygen affinity. This may be ascribed to the electron-donating nature of the base which strengthens the cobalt–dioxygen interaction.

Interestingly, square planar Co(II) complexes in the presence of pyridine axial base have greater oxygen affinity than pentadentate Co(II) complexes (Emara et al., 2008). Investigations on the effect of concentration of the metal complex with the oxygen affinity indicate that the decrease in the concentration of the carrier complex results in a decrease in the absorption of the dioxygen.

2. Materials and methods

2.1. Materials

$Mn(OAc)_2{\cdot}4H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ were purchased from Merck; salicylaldehyde, *o*-hydroxyacetophenone, acetylacetone and ethylenediamine from BDH or Merck. Ethyl alcohol (95%), acetone, diethylether, methanol and absolute ethanol were used after purification (Vogel, 1978; Verlag and Wissenschaften, 1977).

2.2. Synthesis of the tetradentate Schiff base ligands

Although high precautions were undertaken to avoid either air-oxygen or moisture in the reaction conditions in obtaining the tetradentate Schiff base ligands, *N,Ń*-ethylene-*bis*(salicylideneimine); H_2Salen, *N,Ń*-ethylene-*bis*(*o*-hydroxyaceto-phenoneimine); H_2O-Hacen and *N,Ń*-ethylene-*bis*(acetylacetoneimine); H_2Acacen, the literature method of preparation of the ligands (under air atmosphere) was used (Campbell and Nyuyen, 2001). The apparatus, materials and super-dry ethanol as a solvent were housed in a glove bag flushed with nitrogen gas for 30 min before performing each individual reaction. Filtration, washing the products with dry ethanol and dry diethylether were performed inside the glove bag. Recrystallization was also undertaken after isolation of the ligands and performed in air-atmosphere. The products were left in a dissecator containing dry $CaCl_2$, filled with nitrogen gas for drying until used. The physical and analytical data of the Schiff base ligands are summarized as follows:

H_2Salen (i)*:* Yellow. Yield: 88%; M.P.: 120 °C. FT-IR (KBr, cm^{-1}): 3300 ν(OH), 3050 ν(CH), 1636 ν(–C=N–), 1318 ν(C–N), 1284 ν(C–O). ^1H NMR (200.13 MHz, DMSO-d_6): 3.94 (s, 4H, CH_2), 9.35 (s, 2H, C*H*), 6.89 and 7.26 (m, 8H, Ar–*H*), 13.22 (s, 2H, Ar–O*H*). Anal. Calcd. for $C_{16}H_6N_2O_2$: C, 71.62; H, 6.01; N, 10.04. Found: C, 71.68; H, 6.09; N, 9.89. UV (DMF, nm): 267 and 316 (π–π^* phenyl ring), 337 (π–π^* azomethine) and 424 (n–π^* nitrogen and oxygen).

H_2o-Hacen (ii): Yellow. Yield: 86%; M.P.: 200 °C. FT-IR (KBr, cm^{-1}): 3568 ν(OH), 3054 ν(CH), 1612 ν(–C=N–), 1314 ν(–C=N–), 1240 ν(C–O). ^1H NMR (200.13 MHz, DMSO-d_6): 2.90 (s, 3H, C$\boldsymbol{H_3}$), 3.04 (s, 3H, C$\boldsymbol{H_3}$), 3.96 (s, 4H, C$\boldsymbol{H_2}$), 6.87 and 7.33 (m, 8H, Ar–***H***), 13.72 (s, 2H, Ar–O***H***). Anal. Calcd. for $C_{18}H_{20}N_2O_2$: C, 72.92; H, 6.80; N, 9.51. Found: C, 72.07; H, 6.81; N, 10.04. UV (DMF, nm): 267 and 316 (π–π^* phenyl ring), 334 (π–π^* azomethine) and 398 (n–π^* nitrogen and oxygen).

H_2Acacen (iii): Pale brown. Yield: 74%; M.P.: 125 °C. FT-IR (KBr, cm^{-1}): 3400 ν(OH), 3086 ν(CH), 2948 ν(CH_3), 1622 ν(–C=N–), 1372 ν(C-N), 1292 δ(CCN), 1162 ν(C-O). e268 (π–* carbonyl), 286 (π–π^* azomethine) and 334 (n–π^* nitrogen and oxygen). ^1H NMR (200.13 MHz, DMSO-d_6)): 2.23 (s, 6H, CH_3), 2.44 (s, 6H, CH_3), 3.84 (s, 4H, CH_2), 4.35 (s, 2H, C*H*), 9.82 (s, 2H, Ar–O*H*). Anal. Calcd. for $C_{12}H_{20}N_2O_2$: C, 64.20; H, 8.92; N, 12.48. Found: C, 64.23; H, 8.63; N, 12.74. UV–visible (DMF, nm): 268 (π–π^* C=O carbonyl), 286 (π–π^* azomethine) and 334 (n–π^* nitrogen and oxygen).

Download English Version:

https://daneshyari.com/en/article/229601

Download Persian Version:

https://daneshyari.com/article/229601

Daneshyari.com