Synthesis and Characterization of Monomeric and Dimeric Dihydroxo-Bridged Complexes of Iron(II) with α-Benzilmonoxime

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The reaction of α-benzilmonoxime(BMOH) with $Fe(CH_3COO)_2 \cdot 4H_2O$ in the presence of CH_3COONa as a base gives the mononuclear Fe(II) complex, $Na[Fe(BMO)_3]$ (**1**). Treatment of **1** with a methanolic solution of NaOH at room temperature leads to a dinuclear Fe(II)-Fe(II) complex, $Na_2[Fe(BMO)_2OH]_2$ (**2**). The complexes were characterized on the basis of their elemental analysis, mass, infrared and electronic spectra. The infrared studies were useful in assigning the coordination mode of the benzilmonoxime ligand to the iron(II) ion. In addition, the presence of a hydroxo-bridge in the dimeric complex **2** is inferred from the infrared spectral studies. The electronic spectra of the complexes revealed two bands due to *d-d* transitions and one band assignable to an oxygen $(p_\pi) \rightarrow Fe(e_{g*})$ LMCT transition observed in both complexes. An additional charge-transfer transition, assignable to μ-hydroxo$(p_\pi) \rightarrow Fe(e_{g*})$, was only observed for the dimeric complex **2**. The splitting energy (Δ_O) and ligand field stabilization energy are found to be 16825 and -6730 cm^{-1} for complex **1** and 16200 and -6480 cm^{-1} for complex **2**, respectively.

Key Words: Iron(II) complexes, α-Benzilmonoxime, Dihydroxo bridge complexes, IR and electronic spectra of iron(II).

INTRODUCTION

The importance of iron as an essential element can be estimated by the wide range of iron proteins and enzymes playing different roles in biological systems. Proteins containing non-heme iron centers are widely spread in nature. They perform a broad range of functions, especially activating molecular oxygen for the oxidation of various substrates[1]. Dinuclear iron complexes in particular have biological relevance since they give valuable information about the binding mode of dioxygen to the iron sites of proteins involved in its transport and activation. They provide structural models for dinuclear sites in several proteins involved in oxygen storage of hemerythrin and oxygen activation of methanemonooxygenase[2]. Efforts to model these proteins have simulated the study of complexes containing $[Fe(\mu\text{-}O)_2Fe]$ and $[Fe(\mu\text{-}OH)_2Fe]$ cores[3,4]. Attia *et al.*[5,6] reported presently the synthesis and characterization of dinuclear chromium and molybdenum complexes containing oxo and hydroxo bridged ligands. In the present work, we describe the preparation and characterization of two new iron(II) complexes of the α-benzilmonoxime ligand. The coordination properties of the complexes were studied using IR and electronic techniques.

EXPERIMENTAL

$Fe(CH_3COO)_2 \cdot 4H_2O$, methanol, sodium acetate, sodium hydroxide and benzil (Merck) were used as received. Methanol was distilled prior to use. The α-benzilmonoxime ligand was synthesized by a modified procedure given in previous work[7]. The elemental analyses (C, H and N) were performed using a Perkin-Elmer 2400 analyzer. Iron and sodium were determined by spectrophotometeric method on an AA-670 Shimadzu atomic absorption-flame emission spectrophotometer. Mass spectra were recorded on a Varian 711 and VG Zapspec spectrometer. The IR spectra (4000-400 cm^{-1}) were recorded on a Perkin-Elmer model 377 spectrometer using KBr disks. The electronic absorption spectra (200-1100 nm) were recorded in DMSO solution with a Shimadzu UV-160 spectro-photometer.

Preparation of α-benzilmonoxime: To 1.05 g (5 mmol) of benzil in 30 mL of warm methanol, were added 410 mg (5 mmol) of sodium acetate and 342 mg (5 mmol) of hydroxyl-amine hydrochloride in 25 mL of 50 % aqueous methanol. The reaction mixture was refluxed for 6 h. The solution was then cooled in a beaker containing ice-water to get a white precipitate. The solid obtained was filtered off and washed

with cold water. The yield is 1.03 g (91 %), the crude material was then recrystallized from ethanol. $C_{14}H_{11}NO_2$ (m.w. = 225): C, 74.67; H, 4.89; N, 6.22. Found: C, 74.91; H, 4.751; N, 6.03. IR (KBr, ν_{max}, cm^{-1}): 3450, 1685, 1580, 1220. ^{1}H NMR (200 MHz, DMSO-d_6) δ 10.20 (s, 1H, C=N-OH), 7.2-7.8 (m, 10H, 2×ArH). UV (DMSO) λ_{max} (log ε) 286 (2.9), 410 nm (1.6).

Synthesis of sodium*tris*(benzilmonoximato)ferrate(II), Na[Fe(BMO)₃]: A solution of Fe(CH₃COO)₂·4H₂O (0.411 g, 1.67 mmol) in a minimum quantity of methanol was added to a solution of α-benzilmonoxime (1.125 g, 5 mmol) in hot methanol (25 mL). The mixture was heated under reflux for 1.5 h until a clear solution was obtained. To this, sodium acetate (0.55 g) was added and the mixture was heated for 15 h to ensure completion of the reaction. The solution was then placed in an ice-water container to give a purple precipitate, which was filtered off and washed with cold water and methanol. The product was further purified by recrystallization from CH₂Cl₂-methanol [40:60] (m.p. 223 ºC; yield, 88 %). Anal. calcd. for $C_{42}H_{30}FeN_3NaO_6$ (m.w. = 750.85): C, 67.12; H, 4.00; Fe, 7.44; N, 5.59; Na, 3.06. Found: C, 67.35; H, 4.12; Fe, 7.17; N, 5.65; Na, 3.25. IR (KBr, ν_{max}, cm^{-1}): 1640, 1550, 1222, 602, 690. ^{1}H NMR (200 MHz, DMSO-d_6) δ 7.4-8.4 (m, 10H, 2×ArH). UV (DMSO) λ_{max} (log ε) 300 (4.4), 485 (3.3), 575 (1.9), 615 nm (2.0).

Synthesis of sodiumμ-dihydroxo*bis*{*bis*(benzilmonoximato)ferrate(II)}, Na₂[Fe(BMO)₂(μ-OH)]₂: To a solution of Na[Fe(BMO)₃] (0.60 g, 0.8 mmol) in 10 mL CH₃OH was added 5 mL CH₃OH solution of NaOH (0.032 g, 0.8 mmol) and the mixture was stirred for 48 h. The colour of the solution turned red and was dried in vacuum. The residue was washed with hot ethanol (95 %) to remove sodium benzilmonoximate (BMONa). Then the residue was further purified by recrystallization from CH₂Cl₂-ethanol [80:20] (m.p. 258 ºC; yield, 76 %). Anal. calcd. for $C_{56}H_{42}Fe_2N_4Na_2O_{10}$ (m.w. = 1087.7): C, 61.78; H, 3.86; Fe, 10.27; N, 5.14; Na, 4.23. Found: C, 61.98; H, 4.08; Fe, 10.03; N, 5.37; Na, 4.51. IR (KBr, ν_{max}, cm^{-1}): 1642, 1554, 1224, 960, 910, 692, 605. ^{1}H NMR (200 MHz, DMSO-d_6) δ 6.7-8.8 (m, 10H, 2×ArH). UV (DMSO) λ_{max} (log ε) 302 (4.2), 490 (3.4), 560 (3.4), 605 (1.9), 630 nm (1.8).

RESULTS AND DISCUSSION

The stoichiometric reaction between α-benzilmonoxime (BMOH) and Fe(CH₃COO)₂ in the presence of CH₃COONa as a base has yielded the monomeric complex Na[Fe(BMO)₃] (**1**). Addition of OH⁻ to complex **1** at room temperature afforded the dimeric product **2**. Chromatographic analyses of both complexes have indicated one isomeric form for each complex.

1) Fe(CH₃COO)₂ + 3 BMOH + CH₃COONa ⟶

        Na[Fe(BMO)₃] + 3 CH₃COOH

        1

2) 2 Na[Fe(BMO)₃] + 2 NaOH ⟶ (−2 BMONa)

$$Na_2\left[(BMO)_2Fe \begin{array}{c} O \\ H \\ \diamond \\ O \\ H \end{array} Fe(BMO)_2\right]$$

2
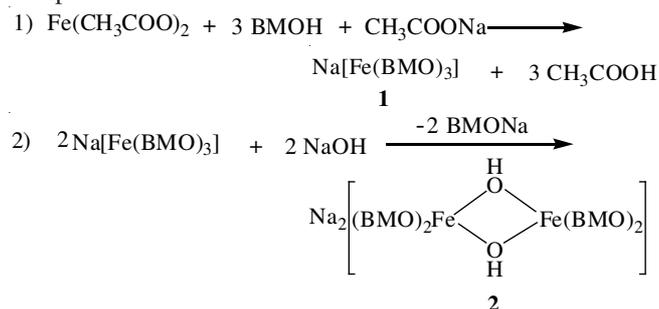
The complexes were initially characterized on the basis of their elemental analyses and mass spectra. The parent ion peaks (m/z) were observed in the mass spectra at 751 and 1088 for complexes **1** and **2**, respectively.

The primary ligand, α-benzilmonoxime, showed characteristic IR bands at 3450, 1580 and 1220 cm^{-1} due to the OH, C=N and N-O stretching vibrations of the oxime group (C=N-OH), respectively and at 1685 cm^{-1} for C=O stretching vibration of the carbonyl group (Table-1).

The band due to ν(O-H) of oxime group is absent in complexes **1** and **2** suggesting the deprotonation of the hydroxyl group of the oxime in the complex formation[8]. The band due to the ν(C=O) of the carbonyl group, which is observed at 1685 cm^{-1} in α-benzilmonoxime is shifted to a lower energy and appear at 1640 and 1642 cm^{-1} in complexes **1** and **2**, indicating the participation of the carbonyl group in coordination. Also the band at 1580 cm^{-1} due to ν(C=N) in α-benzilmonoxime is observed at a lower frequency at 1550 and 1554 cm^{-1} in the complexes **1** and **2**, which shows the involvement of the C=N group in the coordination[9,10].

This fact is further supported by the appearance of new bands in the regions 605-602 and 692-690 cm^{-1} in both complexes, which were assigned to the ν(Fe-O) and ν(Fe-N) stretching vibrations, respectively. The band observed at 1220 cm^{-1} in the IR spectrum of α-benzilmonoxime, appears almost in the same frequencies in complexes **1** at 1222 cm^{-1} and **2** at 1224 cm^{-1} which was assigned to the ν(N-O) stretching mode[11], indicating no participation of oxygen atom of the N-O group in coordination.

The infrared spectrum of complex **2** revealed two strong absorptions at 910 and 960 cm^{-1} that are not present in the spectrum of the monomeric complex Na[Fe(BMO)₃]. In addition, no band between 800 and 850 cm^{-1} attributable to an oxo bridged structural unit is observed[12] in the IR spectrum of the dimeric complex Na₂[Fe(BMO)₂OH]₂. Furthermore, the similarity in the absorption peaks due to coordinated benzilmonoxime ligand in both the monomeric and the dimeric complexes rules against any type of benzilmonoximate bridging in the dimer. Therefore, the bands at 910 and 960 cm^{-1} in the Na₂[Fe(BMO)₂OH]₂ dimer are assigned to vibrational mode associated with the [Fe(μ-OH)₂Fe]$^{2+}$ structural unit. Consistent with this assignment, IR spectra of [Fe(pic)₂OH]₂ showed[13] bands due to [Fe(μ-OH)₂Fe]$^{2+}$ at 950 cm^{-1}.

^{1}H NMR spectra of benzilmonoxime and complexes **1** and **2** show a multiplet due to the phenyl group in the aromatic region at 6.7-7.80 ppm. The singlet peak due to the N-OH proton at 10.20 ppm in benzilmonoxime is absent in both complexes, suggesting the deprotonation of the hydroxyl group of the oxime ligand[14].

The electronic absorption spectra are also recorded for the two complexes and the parent ligand as well in DMSO solution over the range 200-1100 nm which are summarized in Table-2.

α-Benzilmonoxime ligand displayed two absorptions at 286 and 410 nm corresponding to π→π* and n–π* intra-ligand charge transfer transitions, respectively[7]. The electronic spectra of complexes **1** and **2** are characterized by a band at 300 nm that can be assigned to a ligand-based π→π* transition, which

TABLE-1
IMPORTANT IR SPECTRAL BANDS (cm^{-1}) AND THEIR ASSIGNMENTS FOR α-BENZILMONOXIME AND COMPLEXES **1** AND **2**

Vibration modes	ν(O-H)	ν(C=O)	ν(C=N)	ν(N-O)	ν(Fe-OH-Fe)	ν(Fe-O)	ν(Fe-N)
α-Benzilmonoxime	3450	1685	1580	1220	–	–	–
Na[Fe(BMO)$_3$] (**1**)	–	1640	1550	1222	–	602	690
Na$_2$[Fe(BMO)$_2$OH]$_2$ (**2**)	–	1642	1554	1224	910, 960	605	692

TABLE-2
ELECTRONIC ABSORPTION DATA (nm) FOR BENZILMONOXIME AND ITS IRON(II) COMPLEXES **1** AND **2** RECORDED IN DMSO.
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Transition type	Intra-ligand charge transfer		Ligand to metal charge transfer		Ligand field transfer	
	π→π*	n→π*	p$_\pi$(O)→e$_g$*(Fe)	p$_\pi$(OH)→e$_g$*(Fe)	^{5}T$_2$g→^{5}B$_1$g	^{5}T$_2$g→^{5}A$_1$g
α-Benzilmonoxime	286 (2.9)	410 (1.6)	–	–	–	–
Na[Fe(BMO)$_3$] (**1**)	300 (4.4)	–	485 (3.3)	–	575 (1.9)	615 (2.0)
Na$_2$[Fe(BMO)$_2$OH]$_2$ (**2**)	302 (4.2)	–	490 (3.4)	560 (3.4)	605 (1.9)	630 (1.8)

is normally the most intense band in the higher energy region of the spectra[15].

Both complexes displayed a band that can be assigned to a charge-transfer transition from p$_\pi$ orbitals of the carbonyl oxygen atom to the e$_g$* orbitals of the Fe(II) ion[15,16]. This band is observed at 485 nm for monomeric complex **1** and at 490 nm for dimeric complex **2**. The red shift of this charge-transfer band for the dimeric complex with respect to the monomeric complex may explain the colours of the DMSO solutions of the two complexes (solutions of complexes **1** and **2** have purple and red colours, respectively).

Two low energy transitions (log ε ≤ 2) were also observed in the spectra of both complexes and most probably are due to spin allowed *d-d* transitions. An electronic transition from type ^{5}T$_{2g}$→^{5}E$_g$ is expected for iron(II) with high spin d^6 configuration[17]. Appearance of two absorption bands with near energy show that excited sate of ^{5}E$_g$ term due to Jahn-Teller effect is splitted to partial terms ^{5}A$_{1g}$ and ^{5}B$_{1g}$. Therefore absorption bands at 615 nm (16260 cm^{-1}) and 575 nm (17390 cm^{-1}) for monomeric complex **1** and at 630 nm (15870 cm^{-1}) and 605 nm (16530 cm^{-1}) for dimeric complex **2** are attributed to the ^{5}T$_{2g}$→^{5}A$_{1g}$ and ^{5}T$_{2g}$→^{5}B$_{1g}$ transitions, respectively[18].

The splitting energy (Δ_O) of complexes are equal to average energy of two near bands. So splitting energy of complexes **1** and **2** are found to be 16825 and 16200 cm^{-1}, respectively. Also, using this value, the ligand field stabilization energy for complexes **1** and **2** are found to be -6730 and -6480 cm^{-1}, respectively[19].

The dominant feature of the spectrum of the dimeric complex **2** is an intense transition observed at 560 nm (log ε = 3.4), which is absent in the spectra of both the monomeric complex and the parent ligand itself. This transition can be assigned to a charge transfer transition from p$_\pi$ orbitals of the hydroxo bridged oxygen atom to e$_g$* orbitals of the Fe(II) ion. Consistence with this assignment, a similar transition was observed for a number of dihydroxo bridged Fe(II) complexes[20,21].

REFERENCES

1. L. Que Jr. and R.Y. Ho, *Chem. Rev.*, **96**, 2607 (1996).
2. R.E. Stenkamp, L.C. Sieker and L.H. Jesen, *J. Am. Chem. Soc.*, **116**, 618 (1994).
3. B.J. Kennedy, K.S. Murray, P.R. Zwack, H. Homborg and W. Kalz, *Inorg. Chem.*, **24**, 3302 (1985).
4. Y. Zang, Y. Dong and L. Que Jr., *J. Am. Chem. Soc.*, **117**, 1169 (1995).
5. A.S. Attia, S.F. El-Mashtoly and M.F. El-Shahat, *Polyhedron*, **22**, 895 (2003).
6. A.S. Attia, S.F. El-Mashtouly and M.F. El-Shahat, *Synth. React. Inorg. Met.-Org. Chem.*, **32**, 509 (2002).
7. E. Soleimani, *J. Chem. Soc. Pak.*, **31**, 434 (2009).
8. M.S. Singh and P. Narayan, *Synth. React. Inorg. Met.-Org. Chem.*, **31**, 149 (2001).
9. K. Nakamoto, Infrared and Raman Spectroscopy of Inorganic and Coordination Compounds, Wiley-Interscience, New York, p. 374 (1978).
10. N.S. Biradar, V.B. Mahale and V.H. Kulkarni, *J. Inorg. Nucl. Chem.*, **35**, 2656 (1973).
11. R.T. Morrison and R.N. Boyd, Organic Chemistry, New York University, edn. 6, p. 897 (1992).
12. C.S. Wu, G.R. Rossman, H.B. Gray, G.S. Hammond and H.J. Schugar, *Inorg. Chem.*, **11**, 990 (1972).
13. H.J. Schugar, G.R. Rossman and H.B. Gray, *J. Am. Chem. Soc.*, **91**, 4564 (1969).
14. M.S. Singh, B.K. Singh and K. Tawade, *Indian J. Chem.*, **40A**, 1295 (2001).
15. M. Satake, Y. Matsumura and T. Fujinaga, *Talanta*, **25**, 718 (1978).
16. L. Borer, L. Thalken, J.H. Zhang and W.M. Reiff, *Inorg. Chem.*, **22**, 3174 (1983).
17. B.P. Gaber, V. Miskowski and T.G. Spiro, *J. Am. Chem. Soc.*, **96**, 6868 (1974).
18. D.F. Shriver, P.W. Atkins and C.H. Langford, in ed.: W.H. Freeman, Inorganic Chemistry, Oxford University Press, Oxford, edn. 3, p. 298 (1999).
19. J.E. Huheey, Inorganic Chemistry, Harper & Row, New York, edn. 3, p. A26 (1983).
20. B.E. Douglas, D.H. McDaniel and J.J. Alexander, Concepts and Models of Inorganic Chemistry, John Wiley and Sons, Inc., New York, edn. 3, p. 233 (1994).
21. L. Lopes, J. DeLaat and B. Legube, *Inorg. Chem.*, **41**, 2505 (2002).