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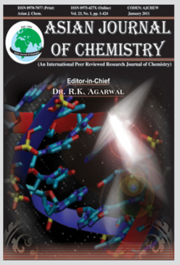

Synthesis and Characterization of Iron(III) Complex Derived from Benzilmonoxime

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The reaction between benzilmonoxime and iron(III)acetylacetonate in presence of potassium acetate in methanol yielded an orange precipitate. The electronic spectral data for this compound in DMF is in agreement with the octahedral coordination of iron(III). The IR data show that, bidentate ligand benzilmonoximate is bound to iron(III) through the oxygen atom of the carbonyl group and the nitrogen atom of the oxime group. The structure of the complex was determined by X-ray diffraction, cofirmed with an octahedral *facial* configuration.

Key Words: Iron(III) complex, Electronic and infrared spectra, Benzilmonoxime, *Facial* isomer, X-ray diffraction.

INTRODUCTION

Benzilmonoxime is known to be a chelating ligand, frequently used in extractive and analytical chemistry[1], for molybdenum, tungsten, vanadium and cobalt[2-4]. Benzilmonoximes are of special interest owing to their biological activities and semiconducting properties[5,6].

In order to extend the range of benzilmonoximate complexes, we decided to synthesize and characterize a complex of iron(III).

EXPERIMENTAL

All chemicals were of analytical grade. Solvents were purified and dried according to standard procedures[7]. The reaction progress and the purity were checked by TLC on silica gel. Benzilmonoxime was synthesized according to the literature method[8].

Preparation of *tris*(benzilmonoximato)iron(III) complex: A solution of iron(III)acetylacetonate (705 mg, 2 mmol) in a minimum quantity of methanol was added to a solution of benzilmonoxime (1.35 g, 6 mmol) in hot methanol (35 mL). The mixture was heated under reflux for 1.5 h until a clear solution was obtained. To this, potassium acetate (0.65 g) was added and the mixture was heated for 6 h to ensure completion of the reaction. The solution was then placed in ice-water container to give an orange precipitate, which was filtered off and washed with hot water and a small quantity of methanol. The product was further purified by recrystallization from DMF-methanol (40:60 v/v). m.p. 183 °C; (1.37 g, 88 % yield). UV-Vis (DMF) λ_{max} (ε): 305 (880), 380 (1250), 428 (95), 516 nm (84); IR (KBr, ν_{max}, cm^{-1}): 1550, 1460, 1220, 570, 680; Anal. calcd. for $Fe(C_{14}H_{10}NO_2)_3$: C 69.25, H 4.12, N 5.77, Fe 7.67; found C 69.67, H 4.22, N 5.89, Fe 7.86.

The elemental analysis was obtained on a Heraeus Carlo Erba1108 elemental analyzer. The electronic spectra were recorded in DMF solution with a Shimadzu UV-160 spectrophotometer. Magnetic susceptibility measurements were done with a 155 Allied Research vibrating sample magnetometer at room temperature. Melting points were measured using an Electrothermal Buchi 512 melting point apparatus. Molecular weights were measured on a Knauer Vapour Pressure Osmometer in $CHCl_3$ solution at room temperature. Iron was determined by use of an AA-670 Shimadzu atomic absorption-flame emission spectrophotometer.

Crystal data and refinement details: $C_{42}H_{30}N_3O_6Fe$, M 727.85, monoclinic, space group P21/c, with cell dimensions of a = 1.7158(3) nm, b = 1.2455(3) nm, c = 1.8023(1) nm, α = 90°, β = 98.65(2)°, γ = 90°, V = 3.2772(6) nm^3, $D_{calcd.}$ (Z = 4) 2.287 Mg/m^3, F(000) 472, μ (MoK_α) 11.706 mm^{-1}, crystal size: 0.3 mm × 0.3 mm × 0.3 mm, Maximum and minimum transmission 0.9621 and 0.2333, R = 0.0344, Rw = 0.0946.

Determination of the structure: An orange diffraction-quality crystal was grown at room temperature by slow evaporation of a DMF-methanol solution. Intensity data was measured at 293 K on an Enra-Nonius CAD4 diffractometer by use of graphite monochromated MoK_α radiation (λ = 0.71073 Å). Accurate unit cell parameters and an orientation matrix for data collection were obtained from least-squares refinement. Intensities of 12255 unique reflections [4063 independent (R_{int} 0.049)] were measured, 3789 of which, with $I > 2\sigma(I)$, were used in the refinement. The structure was determined by direct methods and difference Fourier maps and refined on F^2

by a full-matrix least-squares procedure with anisotropic displacement parameters.

Positions of the hydrogen atoms in the complex were idealized and included in the calculations of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotopic thermal parameter. The final difference density map showed a maximum peak and hole of 3.032 and -2.625 e/Å^3. Corrections for Lorentz and polarization effects as well as an empirical correction for absorption using the SADABS programs were applied. All the structural calculations were carried out using a PDP-11/23+ computer equipped with the SDP-PLUS program package[9,10].

RESULTS AND DISCUSSION

The reaction of iron(III)acetylacetonate with the sodium salt of benzilmonoxime (prepared *in situ* by the reaction of potassium acetate with benzilmonoxime in 1:1 molar ratio in refluxing methanol) in 1:3 molar ratio led to the formation of the iron(III) complex. The reaction was found to be quite facile.

This iron(III) complex was characterized on the basis of satisfactory elemental analysis and molecular weight determination. The analytical data are consistent with the proposed molecular formula, $Fe(C_{14}H_{10}NO_2)_3$, for the iron(III) complex. The molecular weight determination in $CHCl_3$ solution showed the monomeric nature of the iron(III) complex at room temperature. This compound is sparingly soluble in water and methanol but soluble in $CHCl_3$ and DMF.

IR spectra: A broad band of medium intensity is observed at 3450 cm^{-1} in the spectrum of the free ligand of benzilmonoxime, which is due to ν(N-OH)[11]. This band is absent in the spectrum of the iron(III) complex, suggesting the deprotonation of the hydroxyl group in the oxime in the complex formation[12].

Also, the IR spectrum of benzilmonoxime shows bands in the regions 1650 and 1580 cm^{-1}, assignable to ν(C=O) of the carbonyl group and ν(C=N) of the imine group, respectively[13]. These bands were shifted to 1550 and 1460 cm^{-1} in the iron(III) complex. The band due to the ν(C=O) of the carbonyl group, which is observed at 1650 cm^{-1} in benzilmonoxime is shifted to a lower energy at 1550 cm^{-1} in its iron(III) complex, indicating the participation of the carbonyl group in coordination. Also the band at 1580 cm^{-1} due to ν(C=N) in benzilmonoxime is observed at a lower frequency at 1460 cm^{-1} in the iron(III) complex, indicating the involvement of the C=N group in the coordination[14]. This fact is further supported by the appearance of new bands in the regions 570 and 680 cm^{-1} in the iron(III) complex, which were assigned to the ν(Fe-O) and ν(Fe-N) stretching vibrations, respectively. The band at 1220 cm^{-1} in the IR spectrum of benzilmonoxime, which is also observed unaltered in the IR spectrum of the iron(III) complex was assigned to the ν(N-O) stretching mode[15], indicating no participation of oxygen atom of the N-O group in coordination.

Electronic spectra and magnetic moment: The electronic spectra for benzilmonoxime and the iron(III) complex in DMF exhibit a broad absorption band at 305 nm with a high molar extinction coefficient that can be assigned to $\pi \rightarrow \pi^*$ intra ligand charge transfer[16]. This absorption band has a high intensity since it obeys the Lapport selection rule. In addition to the above band, three other bands were also observed in the electronic spectrum of the iron(III) complex with wavelengths at 380, 428 and 516 nm (Fig. 1).

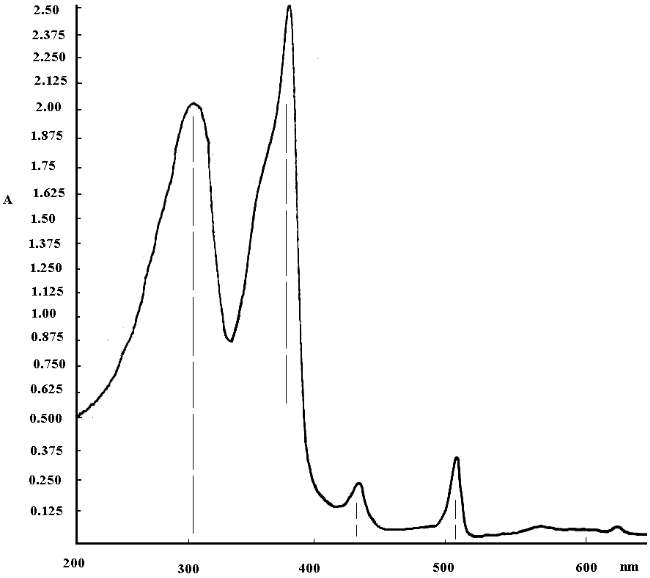

Fig. 1. UV-Visible spectrum for *tris*(benzilmonoximato)iron(III) in DMF (2.5×10^{-3} M)

Since there are no spin-allowed $d \rightarrow d$ transitions for the high spin d^5 configuration, the bands at the regions 380 and 428 nm with molar extinction coefficients lower than 100 M^{-1} cm^{-1} can be assigned to the ligand field transitions for iron(III) with $(t_{2g})^5$ configuration[17].

The low spin configuration of the Fe(III) complex is further confirmed by magnetic susceptibility measurement. At ambient temperature, the Fe(III) complex exhibit effective magnetic moment of 1.98 BM. This magnetic moment value confirm that Fe(III) complex remain low spin (S = 1/2) with $(t_{2g})^5$ configuration. Mononuclear Fe(III) complexes $[CpFe(dppe)\text{-}SR]PF_6$ and $[Fe(pyAS)_2]Bph_4$ with a low spin d^5 configuration have been reported to exhibit magnetic moment at 1.93 and 1.97 BM, respectively[18,19].

According to the Tanabe-Sugano diagram for d^5 configuration, the bands at the regions 516 nm (19380 cm^{-1}) and 428 nm (23360 cm^{-1}) were assigned to the $^2T_{2g} \rightarrow (^2A_{2g}$ or $^2T_{1g})$ and $^2T_{2g} \rightarrow {}^2E_g$ transitions, respectively[20].

The absorption band at 380 nm (26320 cm^{-1}) with the molar extinction coefficient of about 1250 M^{-1} cm^{-1} could be assigned to the charge transfer from the filled π-orbit of benzilmonoximate to the empty e_g^* orbit of iron(III) in the complex[21], which has a high intensity (Lapport selection rule).

The molar extinction coefficient of the ligand field transitions for trigonal prismatic complexes is more than 250 M^{-1} cm^{-1} due to the lack of a center of symmetry. However, the molar extinction coefficient of the ligand field transitions for the iron(III) complex was lower than 100 M^{-1} cm^{-1}. This behaviour indicates that the *tris*(benzilmonoximato)iron(III) complex has an octahedral geometry.

Crystal and molecular structure: The crystal structure of the iron(III) complex was determined by X-ray diffraction. Crystal data collection and refinement parameters are given in Table-1. Selected bond lengths and bond angles are given in Tables 2 and 3, respectively.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR *TRIS*(BENZILMONOXIMATO)IRON(III)

Empirical formula	$C_{42}H_{30}N_3O_6Fe$
Crystal colour	Orange
Formula weight	727.85
Temperature (K)	293
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	
a (Å)	17.158(3)
b (Å)	12.455(3)
c (Å)	18.023(1)
α (°)	90
β (°)	98.65(2)
γ (°)	90
V (Å^3)	3277.2(6)
Z	4
D_{calc} (Mg/m^3)	2.287
Absorption coefficient (mm^{-1})	11.706
F(000)	472
Crystal size (mm)	0.3 × 0.3 × 0.3
Index ranges	$-20 < h \leq 20$, $-12 \leq k \leq 12$, $-15 < l \leq 15$
Number of reflections collected	12255
Independent reflections	4063 [R_{int}=0.0492]
Maximum and minimum transmission	0.9621 and 0.2333
Refinement method	Full matrix least-squares on F^2
Goodness-of-fit on F^2	1.088
Final R indices [for 3789 reflections with I > 2σ(I)]	$R_1 = 0.0344$, $wR_2 = 0.0946$
R indices (all data)	$R_1 = 0.0368$, $wR_2 = 0.0946$
Largest difference peak and hole (e/Å^3)	3.032 and -2.625

TABLE-2
SELECTED BOND LENGTHS (Å) FOR *TRIS*(BENZILMONOXIMATO)IRON(III)

Fe-O1	1.943(2)	Fe-N1	1.891(3)
Fe-O2	1.953(3)	Fe-N2	1.878(3)
Fe-O3	1.938(2)	Fe-N3	1.901(3)
N1-O6	1.256(4)	C1-C2	1.428(4)
N2-O4	1.268(4)	C3-C4	1.444(5)
N3-O5	1.278(4)	C5-C6	1.434(4)
O1-C2	1.282(4)	C1-N2	1.332(4)
O3-C4	1.301(4)	C3-N1	1.364(4)
O2-C6	1.301(4)	C5-N3	1.330(4)

Three oxygen atoms from carbonyl groups are bound to iron give the bond lengths of Fe-O1 [1.943(2) Å], Fe-O2 (1.953(3) Å] and Fe-O3 [1.938(2) Å]; none of the Fe-O bond lengths differs significantly from the mean value of 1.945 Å, which is in the range shown by related species such as tris(oxalato)iron(III)[22].

As expected, the three nitrogen atoms of oxime group give stronger coordination bonds. The bond lengths for Fe-N1 [1.891(3) Å], Fe-N2 [1.878(3) Å] and Fe-N3 [1.901(3) Å] are not significantly different [mean 1.890 Å] and shorter than those in related compounds (2.13 -2.18 Å)[23]. The bond lengths for C1-C2 [1.428(4) Å], C3-C4 [1.444(5) Å] and C5-C6 [1.434(4) Å] are shorter than normal C-C bond length but longer than C=C bond length, suggesting delocalization of electrons in the coordinated ligand systems.

TABLE-3
SELECTED BOND ANGLES (°) FOR *TRIS*(BENZILMONOXIMATO)IRON(III)

O1-Fe-O2	93.28(2)	N1-Fe-O1	85.92 (1)
N3-Fe-O2	87.43(1)	N1-Fe-N3	93.38(2)
N1-Fe -N2	91.79(4)	N2-Fe-N3	93.91(1)
N2-Fe-O2	90.48(1)	O1-Fe-N2	86.36(1)
N1-Fe-O3	86.47(1)	N3-Fe-O3	86.30 (2)
O2-Fe-O3	91.26(1)	O1-Fe-O3	93.43(9)
N3-Fe-O1	176.74(1)	C2-O1-Fe	112.30(2)
N1-Fe-O2	174.25(1)	C4-O3-Fe	111.30(2)
N2-Fe-O3	177.42(2)	C6-O2-Fe	111.00(2)
C1-N2-O4	121.10(3)	O4-N2-Fe	122.70(2)
C1-N2-Fe	116.10(2)	O6-N1-C3	120.50(3)
O6-N1-Fe	123.90(2)	C3-N1-Fe	115.50(3)
O5-N3-C5	123.30(3)	O5-N3-Fe	119.80(2)
C5-N3-Fe	116.50(2)	N2-C1-C2	110.90(3)
N2-C1-C13	119.30(3)	C2-C1-C13	129.70(3)
O1-C2-C1	117.70(3)	O1-C2-C7	114.80(3)
N1-C3-C19	122.10(3)	N1-C3-C4	109.00(3)
O3-C4-C3	119.00(3)	O3-C4-C25	115.10(3)
N3-C5-C31	120.50(3)	N3-C5-C6	111.00(3)
O2-C6-C5	118.80(3)	O2-C6-C37	116.40(3)
C1-C2-C7	127.50(3)	C4-C3-C19	128.10(3)
C3-C4-C25	125.80(3)	C6-C5-C31	128.20(3)
C5-C6-C37	124.90(3)	–	–

There are *facial* and *meridonial* isomers for *tris*-bidentated octahedral complex with unsymmetrical ligands. The present ligand (benzilmonoximate) is an unsymmetrical one. Now the question is whether the iron(III) complex has a *facial* or *meridonial* configuration. The molecular structure of the iron(III) complex is shown in Fig. 2. As can be seen, the coordination number of iron in the complex is six, with three

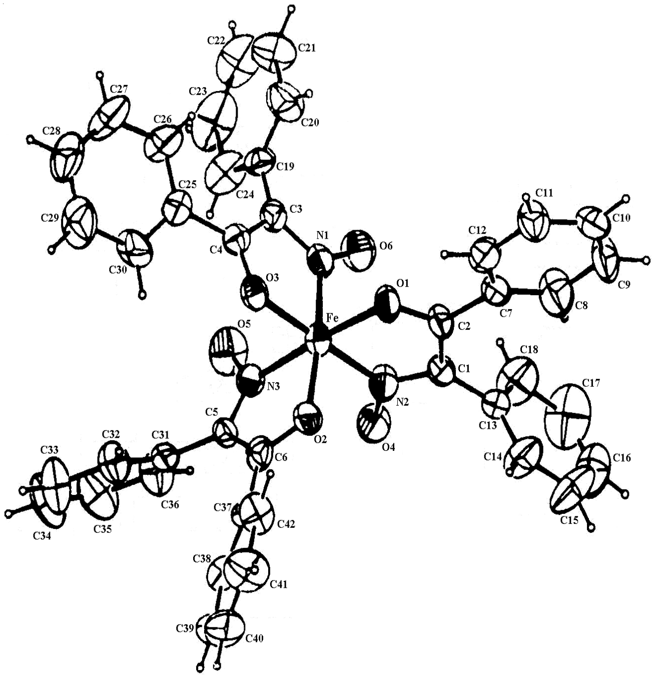

Fig. 2. Crystal structure of *tris*(benzilmonoximato)iron(III)

nitrogen atoms of the imine group [N1, N2, N3] and three oxygen atoms of the carbonyl group [O1, O2, O3], thus giving an octahedral configuration. Therefore, three unsymmetrical bidentate ligands are arranged in *facial* configuration around the metal ion.

Conclusion

The IR spectra of *tris*(benzilmonoximato)iron(III) show that the bidenate ligand of benzilmonoxime is bonded to iron(III) through the oxygen atom of the carbonyl group and the nitrogen atom of the oxime group.

The molar extinction coefficient of the ligand field transitions for trigonal prismatic complexes is more than 250 $M^{-1} cm^{-1}$ due to the lack of a center of symmetry. However, the molar extinction coefficient of the ligand field transitions for the iron(III) complex was lower than 100 $M^{-1} cm^{-1}$. This behaviour indicates that the *tris*(benzilmonoximato)iron(III) complex has an octahedral geometry.

The X-ray diffraction of the *tris*(benzilomonoximato)-iron(III) complex shows that it is a *facial* isomer, having octahedral configuration, with the unsymmetrical bidenate ligand of benzilmonoximate.

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