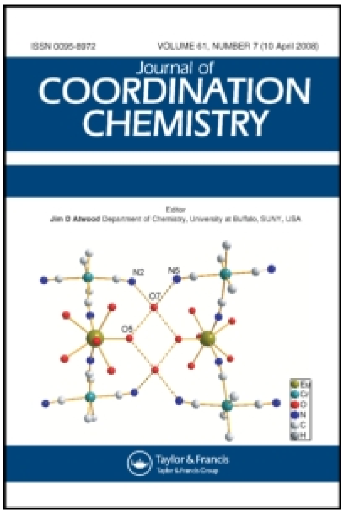

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Mixed ligand complexes of <i>β</i>-diketones and pseudohalides of Iron nitrosyl

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Mixed ligand complexes of β-diketones and pseudohalides of Iron nitrosyl

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Reactions of pentapseudohalonitrosyl ferrate(II) with β-diketones formed complexes of the type, $[Fe(X)_3(NO)(L–L)]$ where $X = CN^-$, NCO^- and N_3^- and L–L = acetylacetonate(acac) and benzoylacetonate (bzac). These compounds have been characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, IR, electronic spectra and thermal gravimetric analysis. Molecular modeling studies have been carried out for structural analysis of some complexes using Hyperchem release 7.52 professional version.

Keywords: Pentapseudohalonitrosyl; Acetylacetonate; Benzoylacetonate; Molecular modeling

1. Introduction

Study of β-diketonate complexes has interest due to their role in the polymer industry, solvent extraction and as shift reagents in NMR spectroscopy [1]. These complexes have diverse stereochemistries and stoichiometeries depending on the nature and coordination ability of metal ions and sometimes on the nature of substituted groups on the β-diketones [2–6]. A number of complexes formed by Ni(II) β-diketonates with various donors have been reported [7–11].

Emmert *et al*. synthesized β-diketonates of di and tri-valent iron and observed that ferrous acetylacetonate is oxidized by air in alcoholic medium to give $Fe(acac)_2$ or whereas $Fe(acac)_3$ is reduced by phenylhydrazine to ferrous acetylacetonate coordinated to two molecules of phenylhydrazine [12, 13].

Complexes of the type $[(NC)_5Fe^{II}–NC–Fe^{II}(CN)_4L]^{n-}$ where $L = H_2O$, pyridine, isonicotinamide and 4-cyanopyridine have been reported [14]. β-diketonates with different metal ions have been synthesized [15] and with sandwich complexes of the type Cp_2TiCl_2 have been characterized by X-ray crystallography [16]. Some physical data

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regarding Cu(II) complexes with non-flourinated β-diketonates have been proposed in the temperature range 90–150°C.

This paper describes the synthesis and characterization of complexes of pseudohalonitrosyl iron(II) with β-diketone.

2. Experimental

2.1. *Reagents and reaction conditions*

Ferrous sulphate (BDH), sodium azide (BDH), sodium nitroprusside (Thomas Baker), potassium cyanate (BDH), hydroxylamine hydrochloride (SRL), acetylacetone (SDS) and benzoylacetone were used as supplied. The solvents were dried before use by conventional methods. The analysis of iron was carried out gravimetrically [17]. Carbon, hydrogen and nitrogen analyses were done by microanalytical method. Molar conductivity was measured for 10^{-3} M solutions in DMF/DMSO at room temperature by Elico conductivity Bridge, type CM82T having conductivity cell with cell constant of 0.74. The IR spectra of the complexes were recorded on FTIR-spectrophotometer-Vector 22 using KBr discs over the region of 4000–400 cm^{-1}. The thermogravimetric analyses (TGA/DTA) of some of the complexes were recorded on TGA 60 thermoanalyzer at a heating rate of 10°C min^{-1}.

2.2. *Preparation of pentapseudohalonitrosyl iron(II) complexes*

2.2.1. Synthesis of $K_2[Fe(NCO)_5NO]$. To an aqueous solution (25 mL) of $FeSO_4 \cdot 7H_2O$ (0.01 mol, 2.78 g), KCNO (0.05 mol, 4.05 g) in water (25 mL) and $NH_2OH \cdot HCl$ (0.01 mol, 0.694 g) in water (10 mL) were added with stirring. A reddish brown product obtained immediately was stirred for about two hours. The precipitates so obtained were allowed to cool in a refrigerator overnight, filtered, washed several times with ice cold water and dried *in vacuo* (yield: 70%). Analytical data: Found (%): C 15.98; N 22.00 and Fe 14.84; Calcd (%): C 16.05; N 22.45 and Fe 14.93.

2.2.2. Synthesis of $Na_2[Fe(N_3)_5NO]$. To an aqueous solution (25 mL) of $FeSO_4 \cdot 7H_2O$ (0.01 mol, 2.78 g), NaN_3 (0.05 mol, 3.25 g) in water (25 mL) and $NH_2OH \cdot HCl$ (0.01 mol, 0.694 g) in water (10 mL) were added with stirring. A blood red solution obtained immediately was stirred for 3–4 h. Precipitates so obtained were allowed to cool in a refrigerator overnight. The precipitates were filtered, washed several times with water and dried *in vacuo* (yield: 68%). Analytical data: Found (%): N 61.29; Fe 16.00; Calcd (%): N 61.40; Fe 16.32.

2.3. *Preparation of complexes*

2.3.1. $[Fe(CN)_3NO(L–L)]$ (where L–L = acacor bzac). To an aqueous solution (100 mL) of $Na_2[Fe(CN)_5(NO)] \cdot 2H_2O$ (0.01 mol, 2.97 g) was added 0.01 mol ligand (acacH 1.00 g or bzacH 1.62 g) dissolved in 25 mL of ethanol. The pH of the resulting solution was maintained at 8 by adding sodium hydroxide solution. The resulting solution was refluxed for 3–4 h, when a shiny blue product appeared. The precipitates so obtained were allowed to cool in a refrigerator overnight. The precipitates were filtered, washed several times with water and ethanol and then dried *in vacuo*. The same product was obtained by mixing reactants at pH 3–4 under similar conditions.

2.3.2. [Fe(NCO)$_3$NO(L–L)] (where L–L = acac or bzac). K$_2$[Fe(NCO)$_5$(NO)] (0.01 mol, 3.73 g) was dissolved in 100 mL of hot water. To this was added 0.01 mol ligand (acacH 1.0 g or bzacH 1.62 g) in 25 mL of ethanol. The reaction mixture was refluxed for 2–3 h (table 1) when a reddish brown product appeared in each case. The precipitates so formed were allowed to cool overnight, filtered, washed several times with hot water and ethanol and dried *in vacuo*.

2.3.3. [Fe(N$_3$)$_3$NO(L–L)] (where L–L = acac or bzac). To a solution (100 mL) of Na$_2$[Fe(N$_3$)$_5$NO] (0.01 mol, 3.42 g) in DMF, was added 0.01 mol ligand (acacH 1.0 g or bzacH 1.62 g) in 25 mL of ethanol. The resulting solution was refluxed for 2–3 h (table 1) when a brown product appeared in each case. The precipitates so obtained were allowed to cool overnight, filtered, washed several times with water followed by ethanol and dried *in vacuo*.

Table 1. Physical data of [Fe(X)$_3$(NO)(L–L)].

No.	Complex	Formula	Formula wt. (g mol^{-1})	Colour	Conductance (Ohm^{-1} cm^2 mol^{-1})	μ_{eff} (B.M.)
1	[Fe(CN)$_3$NO(acac)]	$C_8H_7N_4O_3Fe$	263.01	Blue	38	1.89
2	[Fe(CN)$_3$NO(bzac)]	$C_{13}H_9N_4O_3Fe$	325.08	Blue	41	1.80
3	[Fe(NCO)$_3$NO(acac)]	$C_8H_7N_4O_6Fe$	311.01	Reddish brown	32	5.78
4	[Fe(NCO)$_3$NO(bzac)]	$C_{13}H_9N_4O_3Fe$	373.08	Reddish brown	42	5.90
5	[Fe(N$_3$)$_3$NO(acac)]	$C_5H_7N_{10}O_3Fe$	311.02	Brown	30	5.84
6	[Fe(N$_3$)$_3$NO(bzac)]	$C_{10}H_9N_{10}O_3Fe$	373.09	Brown	39	5.96

Table 2. Analytical data of [Fe(X)$_3$(NO)(L–L)].

		Analysis							
		% Found				% Calcd			
No.	Complex	Fe	C	H	N	Fe	C	H	N
1	[Fe(CN)$_3$NO(acac)]	21.19	36.48	2.61	21.24	21.23	36.53	2.68	21.30
2	[Fe(CN)$_3$NO(bzac)]	17.08	47.96	2.71	17.18	17.17	48.03	2.79	17.23
3	[Fe(NCO)$_3$NO(acac)]	17.88	30.81	2.20	17.04	17.95	30.89	2.26	18.01
4	[Fe(NCO)$_3$NO(bzac)]	14.89	41.79	2.39	14.91	14.96	41.85	2.43	15.01
5	[Fe(N$_3$)$_3$NO(acac)]	17.94	18.29	2.20	45.09	17.95	19.30	2.26	45.03
6	[Fe(N$_3$)$_3$NO(bzac)]	14.89	32.11	2.39	37.49	14.96	32.19	2.43	37.54

3. Results and discussion

The physical and analytical data (tables 1 and 2) revealed that all the complexes are monomers having general formula, $[Fe(X)_3(NO)(L–L)]$ where $X = CN^-$, NCO^- and N_3^- and L–L = acetylacetonate (acac) and benzoylacetonate (bzac). All the complexes are coloured solids, stable to air at room temperature and insoluble in water but soluble in DMF/DMSO.

3.1. *Infrared spectra*

In the IR spectra of $[Fe(X)_3(NO)(L–L)]$ the absorptions at 1580–1605 and 1520–1540 cm^{-1} are due to $\upsilon(C{=}O)$ and $\upsilon(C{=}C)$, respectively. The absorption bands due to $\upsilon(C{=}O)$ shift to lower wave number by 10–30 cm^{-1} in the complexes compared to the ligand, suggesting that the bonding takes place through both carbonyl oxygens of the β-diketones. A broad absorption band at 2800–3100 cm^{-1} in the IR spectra of β-diketones due to $\upsilon(O–H)$ is absent in the spectra of the complexes indicating deprotonation of the ligands upon complex formation. The absorption bands in the region 1645–1690 cm^{-1} are assigned to $\upsilon(N{=}O)$ indicating linear NO.

The IR spectra of $[Fe(CN)_3(NO)(L–L)]$ show a strong band in the region 2140–2240 cm^{-1} assigned to $\upsilon(CN)$. A positive shift in these values as compared to 2080 cm^{-1} in free cyanides indicates coordination of –CN group through carbon [18–25].

In the IR spectra of $[Fe(NCO)_3(NO)(L–L)]$, a strong band in the region 2170–2210 cm^{-1} corresponds to $\upsilon(CN)$ of –NCO indicating that the cyanate group is N-bonded. Bending of $\delta(NCO)$ shows a negative shift in the complexes, around 605–650 cm^{-1}, further supporting N-bonded NCO.

The bands at 2045 and 2080 cm^{-1}, 1360 and 1340 cm^{-1} in $[Fe(N_3)_3(NO)(L–L)]$ can be assigned to asymmetric and symmetric stretching vibrations of azide. The principal IR bands of the complexes are given in table 3.

3.2. *Molar conductance and magnetic studies*

The molar conductivities of the complexes lie in the range 30–42 $Ohm^{-1} cm^2 mol^{-1}$ which indicates that all the complexes are non-electrolytic. The molar conductance values of the complexes are listed in table 1.

Table 3. Principal IR bands (cm^{-1}) of $[Fe(X)_3(NO)(L–L)]$.

No.	Complex	$\upsilon(Fe–X)$ X = N, S or O	$\upsilon(C–N)/\upsilon(C{\equiv}N)$	$\upsilon(N{=}N–N)$	$\upsilon(N{=}O)$	$\upsilon(C{=}O)$	$\upsilon(C{=}C)$
1	$[Fe(CN)_3(NO)(acac)]$	590, 465	2240	–	1690	1605	1537
2	$[Fe(CN)_3(NO)(bzac)]$	600, 472	2140	–	1672	1580	1540
3	$[Fe(NCO)_3(NO)(acac)]$	592, 468	2170	–	1670	1549	1526
4	$[Fe(NCO)_3(NO)(bzac)]$	576, 459	2210	–	1675	1585	1520
5	$[Fe(N_3)_3(NO)(acac)]$	580, 450	–	2045, 1360	1660	1595	1525
6	$[Fe(N_3)_3(NO)(bzac)]$	575, 458	–	2080, 1340	1645	1590	1528

The observed effective magnetic moments of the cyanide complexes lie in the range 1.80–1.89 B.M (table 1) which corresponds to one unpaired electron, suggesting low spin distorted octahedral geometry around iron(III) in these complexes. The cyanate and azide complexes show magnetic moments in the range 5.78–5.96 B.M corresponding to five unpaired electrons in a high spin distorted octahedral geometry around iron(III).

3.3. *Electronic spectra*

Because of greater oxidizing power of Fe(III), ligand to metal charge transfer bands often obscure the very low intensity d–d absorptions.

In the spectra of **1** and **2** a band at 592 and 599 nm, respectively, of low intensity may be assigned to d–d transitions whereas sharp bands at 375 and 344 nm may be assigned to M → ligand charge transfer transitions.

In the high spin complexes of Fe(III) (3–6) the absorption features in the spectra are primarily charge transfer in origin. A sharp band in the region 342–385 nm can be assigned to M → L charge transfer. The d–d transitions being spin forbidden are masked by charge-transfer transitions though a weak band appears in the region 550–625 nm. The electronic spectra of all the complexes are given in table 4.

3.4. *TGA/DTA*

Thermal analyses of [Fe(CN)$_3$(NO)(acac)] and [Fe(NCO)$_3$(NO)(bzac)] have been carried out.

In [Fe(CN)$_3$(NO)(acac)] decomposition starts with an initial weight loss of 10.16% (Calcd 11.40%) corresponding to loss of NO around 125°C; the three CN$^-$ groups are lost around 185°C (% weight loss: found 30.08, Calcd 29.66). Thereafter continuous weight loss is observed to 585°C corresponding to loss of acac (% weight loss: found 39.58, Calcd 38.06) leading to the formation of stable oxide, FeO$_{1.5}$ (½Fe$_2$O$_3$).

TGA/DTA curve for this complex shows two DTA peaks. The first endothermic DTA peak around a temperature of 115°C corresponds to loss of NO and the second exothermic DTA peak around 350°C indicates formation of Fe$_2$O$_3$.

In [Fe(NCO)$_3$(NO)(bzac)] the decomposition starts with an initial weight loss of 8.32% (Calcd 8.04%) around 130°C, probably due to loss of NO and formation

Table 4. Electronic spectra of the complexes (nm).

No.	Complex	d–d Transitions	M → L
1	[Fe(CN)$_3$(NO)(acac)]	592	375
2	[Fe(CN)$_3$(NO)(bzac)]	599	344
3	[Fe(NCO)$_3$(NO)(acac)]	623	362
4	[Fe(NCO)$_3$(NO)(bzac)]	625	385
5	[Fe(N$_3$)$_3$(NO)(acac)]	598	372
6	[Fe(N$_3$)$_3$(NO)(bzac)]	615	342

Table 5. Thermal data of the complexes.

No.	Complex	Decomp. temp (°C)	% Wt. loss obs. (Calcd)	Residue compound	$-E_a$ (kJ mol^{-1})	Z (s^{-1})	$-\Delta S^*$ (JK^{-1} mol^{-1})
1	$[Fe(CN)_3(NO)(acac)]$	585	69.08 (69.66)	Fe_2O_3	24.37	2019	113.7
2	$[Fe(NCO)_3(NO)(bzac)]$	600	78.57 (78.68)	Fe_2O_3	36.43	2560	121.6

of $[Fe(NCO)_3(bzac)]$ as an intermediate. Further decomposition starts around 180°C with the loss of three –NCO groups (% weight loss: found 34.01, Calcd 33.78). Thereafter, continuous weight loss is observed to 600°C corresponding to loss of bzac (weight loss: found = 42.98%, Calcd = 43.47%) leading to the formation of stable oxide, $FeO_{1.5}$ ($\frac{1}{2}Fe_2O_3$).

Two DTA peaks are observed in TGA/DTA curve. The first endothermic DTA peak around 100°C corresponds to loss of NO and the second exothermic DTA peak around 360°C indicates the formation of Fe_2O_3.

The fractional weight loss (α) and the corresponding $(1-\alpha)^n$ values have been calculated from the TG curves at different temperatures, where n is the order of reaction and $\alpha = (W_0 - W_t)/(W_0 - W_f)$. The weighted least square method (LSM) was used for obtaining the best linear fit. Kinetic parameters have been calculated (table 5) by Coats-Redfern method [26] which assumes a rate law of the type,

$$\frac{d\alpha}{dt} = k(1-\alpha)^n$$

and an Arrhenius equation of the type

$$k = z\exp^{-Ea/RT}$$

where, α stands for the fraction transformed, n for reaction order, k for rate constant, E_a for activation energy, R the gas constant, z for frequency factor, T the temperature and β the heating rate. The thermoanalytical data of some of the complexes are given in table 5.

3.5. *Molecular modeling*

Since single crystals could not be grown for these complexes obtained structural information through molecular modeling. The molecular modeling calculations for $[Fe(CN)_3(NO)(acac)]$ and $[Fe(CN)_3(NO)(bzac)]$ have been carried out using Hyperchem release 7.52 professional version [27] that allows for rapid structural building, geometry optimization and molecular display.

Energy values obtained for the complexes indicate a distorted octahedral geometry. Figures 1(a–c) and 2(a–c) show the energy minimized structures for the complexes, $[Fe(CN)_3(NO)(acac)]$ and $[Fe(CN)_3(NO)(bzac)]$ with energy values 25.359 and 31.983 K cal mol^{-1}, respectively. Selected bond lengths (Å) and bond angles (°) obtained from the energy minimized structures are given in tables 6 and 7.

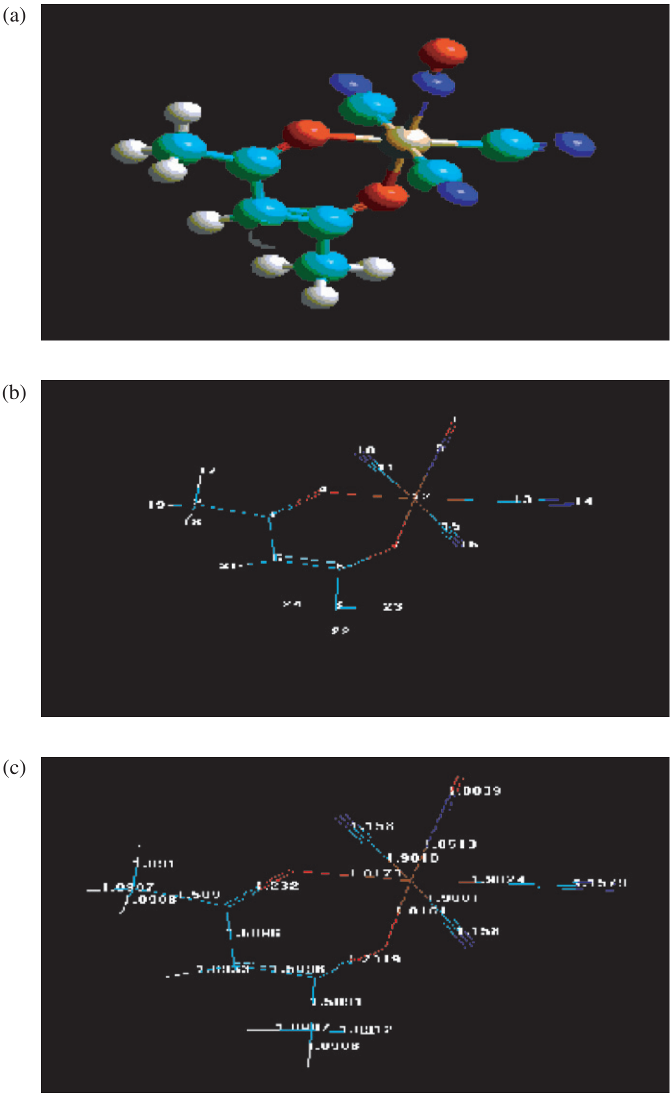

Figure 1. (a) Energy minimized structure of complex, [Fe(CN)$_3$NO(acac)]; (b) atomic labeling; (c) bond length.
Color codes for atoms H = white, O = red, N = blue, C = cyano, Fe = brown.

4. Conclusions

The analytical and spectroscopic data indicate [Fe(X)$_3$(NO)(L–L)] where X = CN$^-$, NCO$^-$ and N$_3^-$; L–L = acac and bzac. IR spectra of the complexes indicate the bidentate nature of acac and bzac coordinating through carbonyl oxygens. The studies suggest an oxidation state of +3 for iron and the behavior of the complexes as non-electrolytes is indicated by their molar conductance values. The TGA/DTA studies show that the complexes undergo thermal decomposition through first order

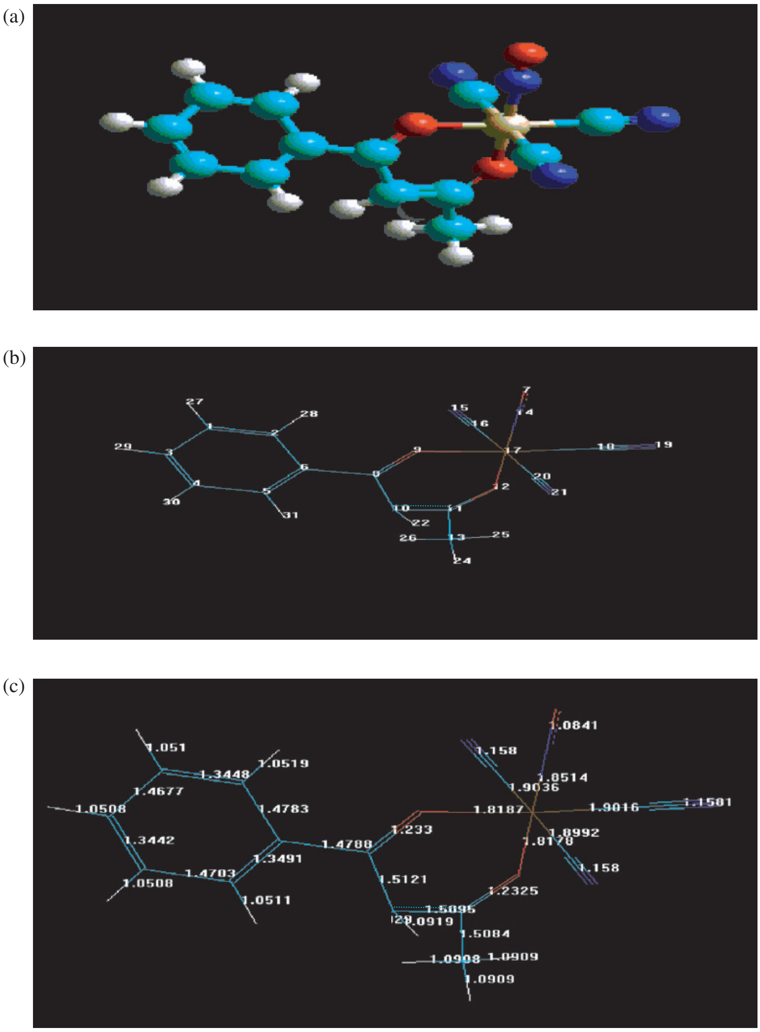

Figure 2. (a) Energy minimized structure of complex, [Fe(CN)$_3$NO(bzac)]; (b) atomic labeling; (c) Bond length.
Color codes for atoms H = white, O = red, N = blue, C = cyano, Fe = brown.

Table 6. Selected bond lengths (Å) and bond angles (°) of [Fe(CN)$_3$(NO)(acac)].

O(1)–N(9)	1.8039	N(9)–Fe(12)–C(13)	89.44
N(9)–Fe(12)	1.8513	C(13)–Fe(12)–C(15)	91.16
Fe(12)–C(13)	1.9024	C(15)–Fe(12)–O(7)	91.12
C(13)–N(14)	1.1579	O(7)–Fe(12)–O(4)	97.08
Fe(12)–C(15)	1.9001	O(4)–Fe(12)–C(11)	87.64
C(15)–N(16)	1.158	C(11)–Fe(12)–N(9)	90.23
Fe(12)–O(7)	1.8161	O(1)–N(9)–Fe(12)	179.66
O(7)–C(6)	1.2319	Fe(12)–C(13)–N(14)	179.52
Fe(12)–O(4)	1.8173	Fe(12)–O(4)–C(3)	126.86
O(4)–C(3)	1.232	Fe(12)–O(7)–C(6)	126.87
Fe(12)–C(11)	1.9028		
C(11)–N(10)	1.158		

Table 7. Selected bond lengths (Å) and bond angles (°) of $[Fe(CN)_3(NO)(bzac)]$.

O(1)–N(14)	1.8041	N(14)–Fe(17)–C(18)	90.29
N(14)–Fe(17)	1.8514	C(18)–Fe(17)–C(20)	91.87
Fe(17)–C(18)	1.9016	C(20)–Fe(17)–O(12)	92.80
C(18)–N(19)	1.1581	O(9)–Fe(17)–O(9)	95.31
Fe(17)–C(20)	1.8992	O(9)–Fe(17)–C(16)	86.61
C(20)–N(21)	1.158	C(16)–Fe(17)–N(14)	89.86
Fe(17)–O(12)	1.8178	O(7)–Fe(17)–N(14)	179.53
O(12)–C(11)	1.2325	Fe(17)–C(18)–N(19)	179. 47
Fe(17)–O(9)	1.8187	Fe(17)–O(9)–C(8)	126.93
O(9)–C(8)	1.233	Fe(17)–O(12)–C(11)	126.14
Fe(17)–C(16)	1.9036		
C(16)–N(15)	1.158		

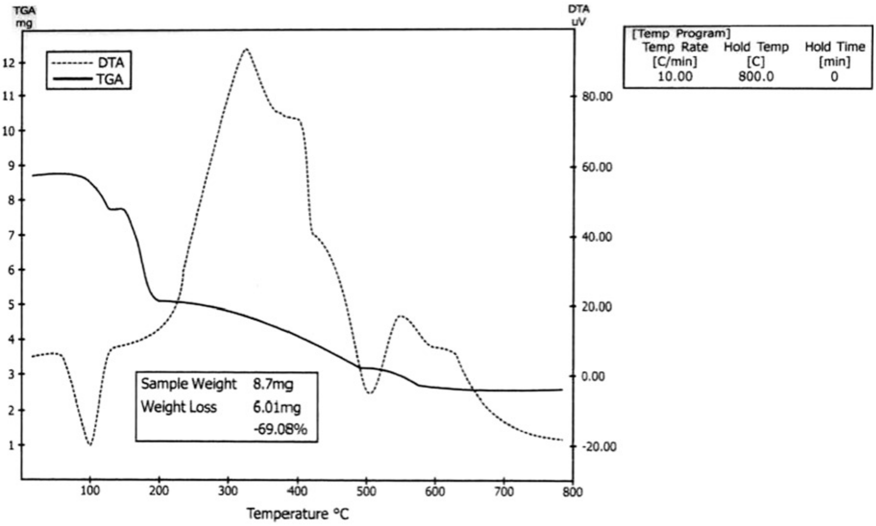

Figure 3. TGA/DTA of $[Fe(CN)_3(NO)(acac)]$.

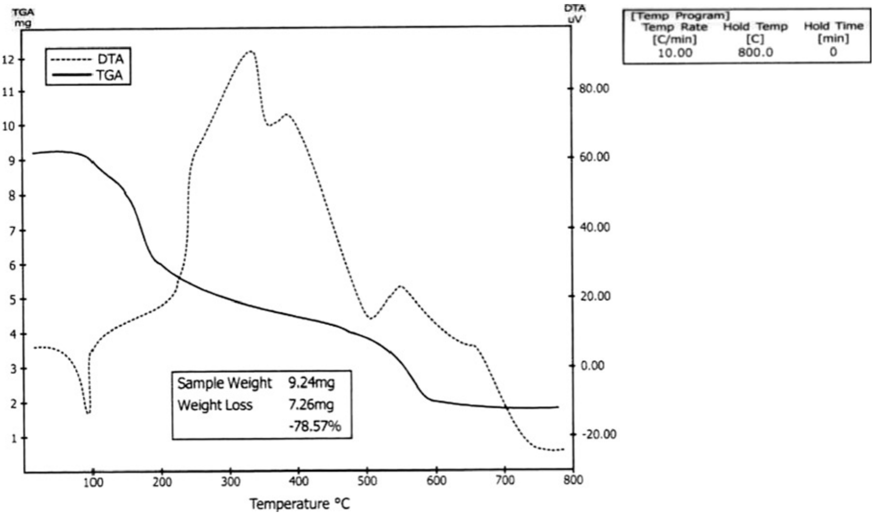

Figure 4. TGA/DTA of $[Fe(NCO)_3(NO)(bzac)]$.

kinetics. The molecular modeling suggests a distorted octahedral structure for the complexes.

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