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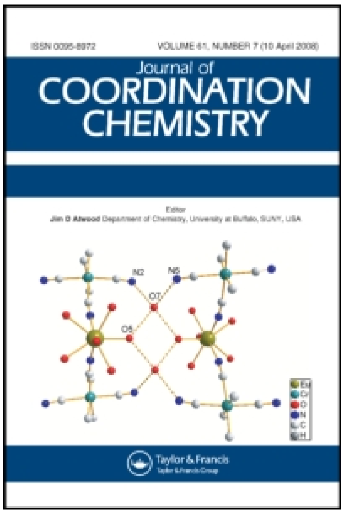

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Synthesis and characterization of a new dioxime: thermal and magnetic behavior of its heterotrinuclear -capped complexes

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Synthesis and characterization of a new dioxime: thermal and magnetic behavior of its heterotrinuclear BF_2^+-capped complexes

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New heterotrinuclear complexes have been obtained from dinuclear Fe(III) oxygen-bridged *N*,*N*′-bis(salicylidene)ethylenediamine (salenH_2) and bis(salicylidene)-*o*-phenylenediamine (salophH_2) and Co(II), Ni(II), Cu(II) salts. Then, heterotrinuclear *vic*-dioxime complexes containing BF_2^+ caps have been synthesized. The complexes have been characterized as low-spin distorted octahedral Fe(III) bridged by COO^- groups. The structure of dioxime and its complexes were identified by using elemental analysis, magnetic susceptibility, thermal analysis, ICP-AES, ^{1}H-NMR, and IR spectral data.

Keywords: BF_2^+-capped complex; *vic*-dioximes; Transition metal complexes; Salen/saloph

1. Introduction

Polydentate coordination of ligands leads to the formation of homo or heteropolynuclear complexes with cations in the metallo-macrocyclic cavity, opening design of macrocycle ligands containing additional donors within the N_4 chain and hydroxyimino nitrogen donors of dioximes. The incorporation of *vic*-dioximes onto the macrocycle provides an efficient binding site for the transition metal cations by the formation of an MN_4 core with two additional hydrogen bridges [1–3]. The presence of mildly acidic hydroxyl groups and slightly basic nitrogens causes *vic*-dioximes to be amphoteric ligands which form corrin-type square-planar, square-pyramidal, and octahedral complexes with transition metal cations such as Ni(II), Cu(II), and Co(II) [4–7].

Synthetic macrocycles have been known for over 75 years, although many publications in this area occurred in the late 1960s [8, 9] when more than 5000 macrocyclic compounds were reported; since then the number has increased markedly from year to year. Some of these compounds were recognized as promising analytical reagents [10, 11]. One of the best strategies for designing and preparing polynuclear

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species is to use mononuclear complexes as ligands which contain potential donor sites for other metal ions.

Magnetochemical properties of the μ-oxo-bridged complexes [{Fe(salen)}$_2$O] (salenH$_2$ = *N*,*N*′-bis(salicylidene)ethylenediamine) and [{Fe(saloph)}$_2$O] [saloph-H$_2$ = bis(salicylidene)-O-phenylenediamine] have been proven, and their properties and X-ray studies are published [12–18].

Gök *et al.* [19–21] recently reported studies of the coordinating ability of new *vic*-dioximes containing macrocyclic units. We are currently interested in the design of new ligands and ligand complexes which can serve as efficient chelating agents toward metal cations [22–24]. In our previous studies, we synthesized and characterized BF_2^+-capped heterotrinuclear complexes, tripodal [Fe(salen/salophen)]-capped melamine-based trinuclear complexes [25–29].

We are also interested in heterotrinuclear systems formed by 4-carboxyanilinophenylglyoxime bridges because no satisfactory work dealing with this bridge and associated data have appeared in the literature. We have prepared an amino *vic*-dioxime containing a diaza-dioxa macrocyclic unit and some of its heterotrinuclear complexes.

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2. Experimental

Acetophenone **1** and all solvents were purchased from Merck. *ω*-Isonitrosoacetophenone **2** [30], *anti*-phenylglyoxime **3** [31], *anti*-chlorophenylglyoxime **4** [30], [{Fe(saloph)}$_2$O], and [{Fe(salen)}$_2$O] [32] were synthesized according to the literature procedures.

Some reactions were carried out under dry argon. Melting points were measured using a Buchi SMP-20 melting point apparatus. Elemental analyses (C, H, and N) were determined using a Leco, CHNS-932 model analyzer. ^{1}H-NMR spectra were recorded on a Bruker DPX-400 400 MHz high-performance digital FT-NMR and IR spectra on a Perkin-Elmer 1605 FT-IR spectrometer in KBr pellets (4000–440 cm^{-1}). Thermal analyses were performed on Shimadzu DTA 50 and TG 50 H models using 10 mg samples. The differential thermal analysis (DTA) and thermal gravimetric analysis (TG) curves were obtained at a heating rate of 10°C min^{-1} from 22°C to 750°C under dry nitrogen. The magnetic susceptibilities of metal samples were determined using a Sheerwood Scientific MX Gouy magnetic susceptibility apparatus and magnetic measurements were carried out using the Gouy method with Hg[Co(SCN)$_4$] as calibrant. The effective magnetic moments, μ_{eff}, per metal were calculated from the expression: $\mu_{\mathrm{eff}} = 2.84\sqrt{\chi_{\mathrm{M}}T}$ B.M., where χ_{M} is the molar susceptibility. The metal and boron contents of each complex were determined on a Varian, Vista AX CCD simultaneous model ICP-AES spectrophotometer. The product mixture at the end of the reaction was separated using Combi Flash Chromotography.

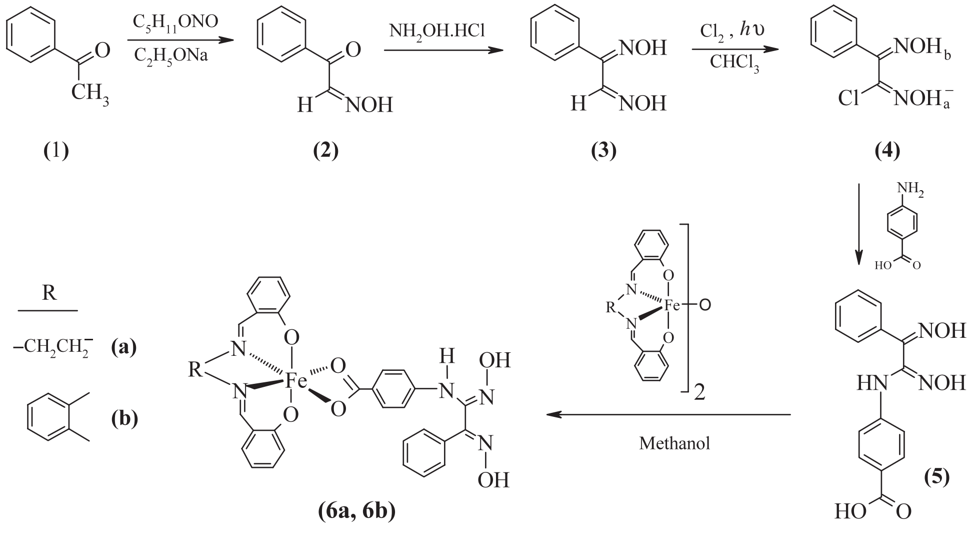
2.1. *4-Carboxyanilinophenylglyoxime (H_3L)*

A solution of 4-carboxyanilin (1.4 g, 10.0 mmol) dissolved in 10 mL of benzene was added dropwise to a suspension of chlorophenylglyoxime (2.0 g, 10.0 mmol) dissolved in

10 mL of benzene, and the mixture was stirred for 40 h under argon. The solvent was evaporated and the precipitated solid product was filtered and dried. LC-MS (ESI^+) $m/z = 299.09$ [100%, 4-carboxyanilinophenylglyoxime (H_3L)]. Molecular peaks of the compounds are observed with the same isotope distribution as the theoretical ones.

2.2. *Synthesis for [H_2Lsalen/saloph]Fe(III) complexes (6a,6b)*

A solution of 4-carboxyanilinophenylglyoxime (0.30 g, 1.00 mmol) dissolved in 10 mL of absolute methanol was added dropwise to a suspension of [{Fe(salen)}$_2$O] (0.33 g, 0.50 mmol) or [{Fe(saloph)}$_2$O] (0.38 g, 0.50 mmol) dissolved in 10 mL of absolute methanol, and the mixture was stirred and refluxed for 2 h under argon. A distinct change in color and decrease in pH (2.5–2.8) was observed. While an equivalent of methanolic solution of NaOH (0.1 M) was added dropwise to adjust pH to 5.5, the mixture was stirred and heated to 60°C on a water bath for 2 h. The precipitated solid product was cooled to room temperature and filtered, washed with water, ethanol, and diethylether, and dried in a vacuum cabinet. LC-MS (ESI^+) $m/z = 619.85$ [100%, **6a**], MS (ESI^+) $m/z = 667.85$ [100%, **6b**]. Molecular peaks of the cations are observed with the same isotope distribution as the theoretical ones.



2.3. *Synthesis for Ni(II), Cu(II) and Co(II) complexes of (6a,6b)*

A suspension of (**6a**, **6b**) (1.24–1.34 g, 2.00 mmol) was prepared in hot ethanol (20 mL). Solution of 1.00 mmol $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $CoCl_2 \cdot 6H_2O$ in 10 mL ethanol was added dropwise with stirring to the suspension. The pH of the reaction mixture was

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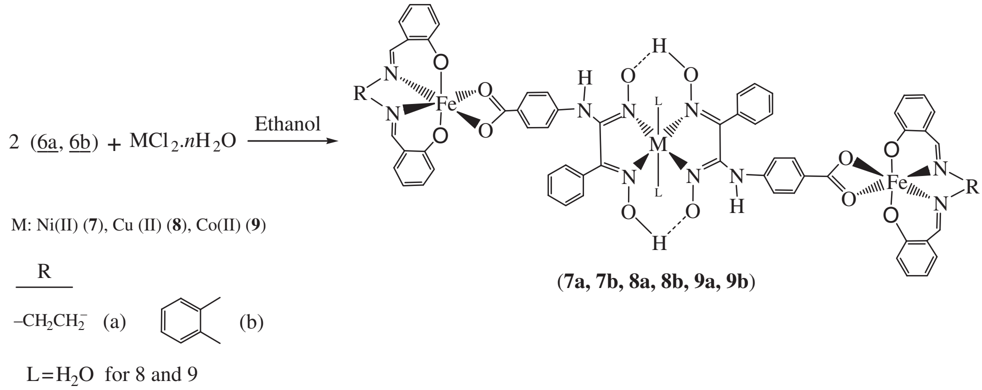
3.5–4.0 and was then adjusted to 5.5–6.0 by adding 1% NaOH solution. The precipitated complex was kept on a water bath at 60°C for 1 h to complete precipitation. The precipitated solid product was cooled to room temperature, filtered, washed with water, ethanol and diethylether, and dried in vacuum. LC-MS (ESI$^+$) $m/z = 1392.39$ [100%, **7b**], LC-MS (ESI$^+$) $m/z = 1337.25$ [100%, **8a**], and LC-MS (ESI$^+$) $m/z = 1428.63$ [100%, **9b**]. Molecular peaks of the cations are observed with the same isotope distribution as the theoretical ones.



(7a, 7b, 8a, 8b, 9a, 9b)

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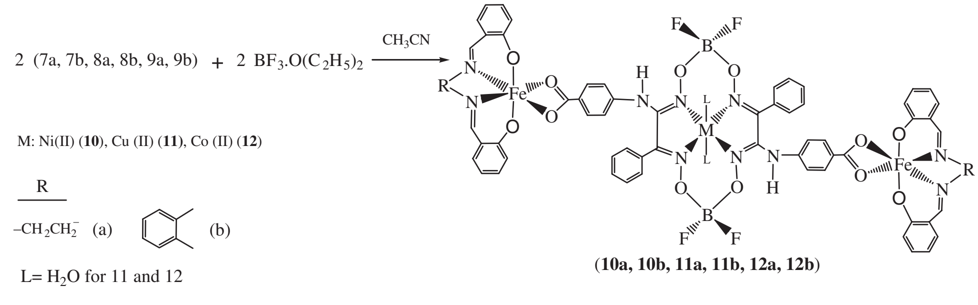
2.4. *Synthesis of [Fe(III)(BF$_2$Lsalen/saloph)$_2$Ni(II)/Cu(II)/CoII)] complexes (10a, 10b, 11a, 11b, 12a, 12b)*

Suspensions of [Fe(III)(HLsalen/saloph)$_2$Ni(II)/Cu(II)/CoII)] (1.00 mmol) in 40 mL of dry acetonitrile were stirred at room temperature in argon for 30 min and an equivalent of boron-trifluoride etherate (0.82 mL) was added with continuous stirring to this suspension, which changed to yellow color immediately. After stirring for 2 h, during which color changed to dark red, the solvent was evaporated to dryness. The dark red crude products were dissolved in 10 mL dry diethyl ether and allowed to stand in a refrigerator at −18°C overnight, whereupon the compounds precipitated from the solution. The dark red powders were collected by filtration, washed with cold diethyl ether and then dried in vacuum. LC-MS (ESI$^+$) $m/z = 1391.97$ [100%, **10a**], LC-MS (ESI$^+$) $m/z = 1528.83$ [100%, **11b**], and LC-MS (ESI$^+$) $m/z = 1428.21$ [100%, **12a**]. Molecular peaks of the cations are observed with the same isotope distribution as the theoretical ones.



(10a, 10b, 11a, 11b, 12a, 12b)

3. Results and discussion

3.1. *^{1}H NMR spectrum interpretation of ligands*

The target ligand **5** was synthesized in a four-step sequence from acetophenone. The conversion of **1** to the keto oxime derivative **2** was accomplished in 74% yield [30]. In the ^{1}H-NMR spectrum of **2**, the presence of singlets at $\delta = 8.40$ and 11.50 ppm showed the keto oxime. This compound was easily converted to the glyoxime derivative **3** by the reaction with hydroxylamine [31] in 92% yield. ^{1}H-NMR spectra of **3** with two singlets at $\delta = 11.6$ and 11.4 ppm showed glyoxime. Chlorophenylglyoxime [30] **4** was obtained from the reaction with chlorine in 86% yield. In the ^{1}H-NMR spectrum of **4**, the absence of a singlet at $\delta = 8.40$ ppm showed the formation of chlorophenylglyoxime. 4-Carboxyanilinophenylglyoxime, **5**, was prepared by reacting 4-aminobenzoic acid with chlorophenylglyoxime. Resonances at 11.62 and 11.23 ppm are the OH protons of the oxime groups. These two deuterium-exchangeable singlets correspond to two nonequivalent OH, indicating that the *anti*-configuration of OH groups are relative to each other [33, 34]. In ^{1}H-NMR spectra of **5**, a broad signal at 13.08 ppm was assigned to the acidic OH. The NH proton was at 8.52 ppm and the aromatic C–H protons were at 6.61–7.63 ppm. ^{1}H-NMR spectrum of the complexes could not be taken because of their paramagnetic character. NMR spectra are in good agreement with the previous reports [35, 36].

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3.2. *FT-IR spectrum interpretation of ligands and complexes*

In FT-IR spectra of **5** bands at 3375, 3268, 1644, 1410, and 998 cm^{-1} were, respectively, assigned to (NH), (O–H), (C=N), (COO$^-$), and (N–O) stretching vibrations [37–42]. In **6a** and **6b**, vibrations at 1572–1583, 1635–1628, and 993–997 cm^{-1} were assigned to ν(C=N) (for $N_2O_2O_2$ compartment) [38, 39], $(C{=}N)_{oxime}$, and (N–O) vibrations, respectively. In FT-IR spectra of **7a**, **7b**, **8a**, **8b**, **9a**, and **9b**, shift of the N–O band to higher frequency indicates the formation of bonds between metal and nitrogen of the dioximes [43]. In **7a**, **7b**, **8a**, **8b**, **9a**, and **9b**, N–H stretching vibrations were observed at 3337–3343 cm^{-1} [38]; downward shifts of 23 cm^{-1} for the C=N absorption indicated coordination through nitrogen [38, 39, 43, 44]. It seems that salen (or saloph) has been linked from carboxylate of the ligand. In all complexes, peaks at 1320–1360 cm^{-1} (phenolic C–O stretching vibrations) of salen and saloph ligands are seen at 1286–1288 cm^{-1} [38, 39]. The BF_2^+-bridged complexes (**10a**, **10b**, **11a**, **11b**, **12a**, and **12b**) exhibited a shift to about 1658 cm^{-1} for the $(C{=}N)_{oxime}$ absorption and to about 1065 cm^{-1} for the N–O absorption. The broad band at 1715–1723 cm^{-1} assigned to the O–H $\cdots$ O bending vibrations disappeared upon the insertion of the BF_2^+ with the simultaneous appearance of peaks at 1171–1175 and 872–875 cm^{-1} for B–O and B–F resonances, respectively. Broad bands at 3511–3525 cm^{-1} were attributed to the H_2O bands as axial ligands for Co(II) and Cu(II) complexes. These absorption data are in good harmony with those previously reported for substituted *vic*-dioximes [33–36, 43, 44] (table 1).

Table 1. Characteristic FT-IR bands (cm^{-1}) of complexes.[a]

Compound (empirical formula)		FT-IR data of compounds (ν_{max}/cm^{-1})								
		C=N$_{ox}$	C=N	N–H	OHO	N–O	M–N	M–O	B–O	B–F
$C_{31}H_{26}FeN_5O_6$	**(6a)**	1635	1572	3344	1712	993	535	474	–	–
$C_{35}H_{26}FeN_5O_6$	**(6b)**	1628	1583	3346	1713	997	536	475	–	–
$C_{62}H_{50}Fe_2N_{10}O_{12}Ni$	**(7a)**	1612	1582	3343	1715	1035	533	475	–	–
$C_{70}H_{50}Fe_2N_{10}O_{12}Ni$	**(7b)**	1605	1576	3338	1714	1028	535	472	–	–
$C_{62}H_{54}Fe_2N_{10}O_{14}Cu$	**(8a)**	1614	1584	3339	1714	1033	536	476	–	–
$C_{70}H_{54}Fe_2N_{10}O_{14}Cu$	**(8b)**	1606	1587	3337	1716	1029	536	477	–	–
$C_{62}H_{54}Fe_2N_{10}O_{14}Co$	**(9a)**	1613	1586	3343	1718	1035	536	476	–	–
$C_{70}H_{54}Fe_2N_{10}O_{14}Co$	**(9b)**	1608	1589	3342	1722	1027	537	471	–	–
$C_{62}H_{48}Fe_2N_{10}O_{12}NiB_2F_4$	**(10a)**	1657	1585	3342	–	1066	538	477	1172	872
$C_{70}H_{48}Fe_2N_{10}O_{12}NiB_2F_4$	**(10b)**	1658	1584	3339	–	1063	535	474	1171	874
$C_{62}H_{52}Fe_2N_{10}O_{14}CuB_2F_4$	**(11a)**	1654	1586	3340	–	1064	536	476	1172	875
$C_{70}H_{52}Fe_2N_{10}O_{14}CuB_2F_4$	**(11b)**	1657	1587	3338	–	1065	537	472	1175	874
$C_{62}H_{52}Fe_2N_{10}O_{14}CoB_2F_4$	**(12a)**	1656	1585	3345	–	1061	534	478	1173	873
$C_{70}H_{52}Fe_2N_{10}O_{14}CoB_2F_4$	**(12b)**	1658	1583	3344	–	1065	533	473	1175	875

[a] KBr pellet.

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3.3. *Magnetic measurements of complexes*

Best evidence for the proposed structures of the heteronuclear complexes comes from magnetic measurements. For Fe(III) complexes such as (salen or salophen)Fe(III), magnetic moments depend greatly upon the axial ligands. Many reports state that Fe(III) exhibits high spin ($S = 5/2$), if only one oxygen donor coordinates to Fe(III) of salen or salophen complexes [32, 45]. We report here that if COO^- ion coordinates to Fe(III) of salen or salophen through both oxygens, Fe(III) exhibits low spin ($S = 1/2$) [25–29, 46–48]. Where the starting complexes [H_2Lsalen/saloph]Fe(III) are octahedral d^5 (paramagnetic), any magnetic moment of the heteronuclear species should arise from the occupation of $N_2O_2O_2$ compartment [25]. On this assumption, the observed magnetic moments for the heterotrinuclear complexes are those for isolated d^5 systems ($S = 1/2$). Thus, heterotrinuclear complexes **7a**, **7b**, **8a**, **8b**, **9a**, and **9b** 1 : 2 (metal : starting complexes) ratio were obtained throughout the reaction of starting complexes (**6a, 6b**) with Ni(II), Co(II), and Cu(II). Values of 1.85–1.84–1.85–1.86 B.M. for **7a**, **7b**, **10a**, and **10b**, respectively, which are same as the starting complexes (1.85 B.M.) for magnetic measurement per Fe(III), shows that the Ni(II) compounds are square-planar d^8 ($S = 0 \times 1/2$) (diamagnetic). The values of 1.74–1.76 and 1.72–1.74 B.M. for **8a, 8b**, **11a**, and **11b**, respectively, show that the Cu(II) containing compounds have $t_{2g}^6e_g^3$ ($S = 1/2$). The values of 3.55–3.61 and 3.49–3.57 B.M. for **9a**, **9b**, **12a**, and **12b**, respectively, of magnetic measurement per atom of heterotrinuclear complexes show that Co(II) containing compounds are represented by the electronic structure $t_{2g}^5e_g^2$ ($S = 3/2$). The magnetic data for the Cu(II) and Co(II) complexes show good harmony with the d^9 and high-spin d^7 distorted octahedral metal ion for the complexes of both Cu(II) and Co(II) [25–29, 46–48]. Magnetic susceptibility measurements are presented in table 2. This conclusion is supported by elemental analyses, suggesting that trinuclear Co(II) and Cu(II) complexes also have octahedral, while trinuclear Ni(II) complexes have two octahedral and a square-planar structure.

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Table 2. The elemental analysis data and physical properties of ligand and complexes.

Compound (empirical formula)	μ_B	m.p. (°C)	Yield % [M_w]	Contents calculated/Found% C	N	H	Fe	Ni	Cu	Co	B	F
$C_{31}H_{26}FeN_5O_6$ **(6a)**	1.85	230[a]	75	60.01	11.29	4.20	9.01	–	–	–	–	–
			[619.85]	**59.17**	**10.81**	**4.18**	**8.87**					
$C_{35}H_{26}FeN_5O_6$ **(6b)**	1.85	255[a]	70	62.89	10.48	3.89	8.36	–	–	–	–	–
			[667.85]	**62.75**	**10.22**	**3.70**	**8.23**					
$C_{62}H_{50}Fe_2N_{10}O_{12}Ni$ **(7a)**	1.85	>300	69	57.39	10.80	3.86	8.62	4.53	–	–	–	–
			[1296.39]	**56.98**	**10.64**	**3.65**	**8.57**	**4.42**				
$C_{70}H_{50}Fe_2N_{10}O_{12}Ni$ **(7b)**	1.84	>300	68	60.33	10.05	3.59	8.02	4.22	–	–	–	–
			[1392.39]	**59.86**	**9.53**	**3.39**	**7.81**	**4.10**				
$C_{62}H_{54}Fe_2N_{10}O_{14}Cu$ **(8a)**	1.74	>300	66	55.64	10.47	4.04	8.35	–	4.75	–	–	–
			[1337.25]	**55.17**	**10.07**	**3.93**	**8.18**		**4.49**			
$C_{70}H_{54}Fe_2N_{10}O_{14}Cu$ **(8b)**	1.76	>300	70	58.61	9.77	3.77	7.79	–	4.43	–	–	–
			[1433.25]	**57.72**	**9.32**	**3.63**	**7.57**		**4.36**			
$C_{62}H_{54}Fe_2N_{10}O_{14}Co$ **(9a)**	3.55	>300	72	55.83	10.51	4.05	8.38	–	–	4.42	–	–
			[1332.63]	**54.95**	**10.18**	**4.01**	**8.10**			**4.21**		
$C_{70}H_{54}Fe_2N_{10}O_{14}Co$ **(9b)**	3.61	>300	75	58.80	9.80	3.78	7.82	–	–	4.13	–	–
			[1428.63]	**57.92**	**9.58**	**3.55**	**7.71**			**4.10**		
$C_{62}H_{48}Fe_2N_{10}O_{12}NiB_2F_4$ **(10a)**	1.85	167[a]	66	53.45	10.06	3.45	8.03	4.21	–	–	1.55	5.46
			[1391.97]	**53.21**	**10.01**	**3.37**	**7.90**	**3.95**			**1.50**	**5.38**
$C_{70}H_{48}Fe_2N_{10}O_{12}NiB_2F_4$ **(10b)**	1.86	169[a]	65	56.45	9.41	3.23	7.51	3.94	–	–	1.45	5.11
			[1487.97]	**56.02**	**9.19**	**3.15**	**7.32**	**3.70**			**1.40**	**4.93**
$C_{62}H_{52}Fe_2N_{10}O_{14}CuB_2F_4$ **(11a)**	1.72	161[a]	52	51.93	9.77	3.63	7.80	–	4.44	–	1.51	5.30
			[1432.83]	**51.91**	**9.32**	**3.46**	**7.60**		**4.20**		**1.21**	**4.85**
$C_{70}H_{52}Fe_2N_{10}O_{14}CuB_2F_4$ **(11b)**	1.74	165[a]	58	54.94	9.16	3.40	7.31	–	4.16	–	1.41	4.97
			[1528.83]	**54.72**	**9.06**	**3.21**	**7.19**		**4.10**		**1.38**	**4.84**
$C_{62}H_{52}Fe_2N_{10}O_{14}CoB_2F_4$ **(12a)**	3.49	142[a]	67	52.09	9.80	3.64	7.82	–	–	4.13	1.51	5.32
			[1428.21]	**51.11**	**9.32**	**3.49**	**7.62**			**3.89**	**1.35**	**5.10**
$C_{70}H_{52}Fe_2N_{10}O_{14}CoB_2F_4$ **(12b)**	3.57	163[a]	70	55.11	9.19	3.41	7.33	–	–	3.87	1.42	4.99
			[1524.21]	**55.08**	**9.01**	**3.24**	**7.11**			**3.70**	**1.31**	**4.81**

M_w, molecular weight. Found values are given in bold.

[a] Decreasing.

3.4. *Thermal analysis interpretation of complexes*

Complex **12b** was selected for the investigation of thermal properties. The thermal analyses (TG, DTA) of **12b** showed weight loss of 6.25% in the temperature range 75–180°C, corresponding to the loss of BF_2^+. The thermal decomposition of **12b** starts in the range of 210–390°C by the weight loss of 5.74% from CO_2, and organic group decomposition is complete in the range of 440–580°C by the weight loss of 61.63%. The final decomposition products were metal oxides. The observed weight loss for **12b** is in good harmony with calculated values [26–29, 46].

3.5. *Mass spectral data interpretation of complexes of all ligand and complexes*

Some complexes were investigated by LC-MS (ESI^+) spectra. The calculated molecular weights of all ligand and complexes have been given in table 2. The molecular peaks of the cations are observed with the same isotope distribution as calculated, theoretically. That is, from the investigation of LC-MS spectra of the compounds, it has been seen that the molecular weights of ligands and complexes are in good harmony with the intensity of observed values in LC-MS spectra.

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4. Conclusions

Heterotrinuclear BF_2^+-capped complexes containing *vic*-dioxime were synthesized. Synthetic strategy for preparing heterotrinuclear BF_2^+-capped complexes uses a complex as a "ligand" that contains a potential donor capable of coordinating to the other ligand. We have chosen $[\{Fe(salen/saloph)\}_2O]$ as "ligand complexes" because they can coordinate to the other ligand. These complexes are examples of heterotrinuclear BF_2^+-capped complexes bridged by carboxylate anions to the iron centers. Their structures were characterized by elemental analysis, ^1H NMR, FT-IR spectroscopy, LC-MS, thermal analyses, and magnetic susceptibility measurements. The magnetic data for the complexes show d^5–d^8–d^5 ($S = 1/2–0–1/2$), d^5–d^9–d^5 ($S = 1/2–1/2–1/2$), and d^5–d^7–d^5 ($S = 1/2–3/2–1/2$) metal ion in octahedral–octahedral–octahedral structures for Cu(II) and Co(II), octahedral–square planar–octahedral structures for Ni(II). The other characterization methods, ^1H NMR, FT-IR spectroscopy, LC-MS, and thermal analyses confirm the suggested structures.

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