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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Uysal, Şaban , Coşkun, Ahmet , Erdem Koç, Ziya and İsmet Uçan, H.(2008) 'Synthesis and Characterization of a New Dioxime and Its Heterotrinary BF_2^+ Capped Complexes', Journal of Macromolecular Science, Part A, 45: 9, 727 — 732

To link to this Article: DOI: 10.1080/10601320802222616

URL: <http://dx.doi.org/10.1080/10601320802222616>

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Synthesis and Characterization of a New Dioxime and Its Heterotrinnuclear BF_2^+ Capped Complexes

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Received November, 2007, Accepted December, 2007

ω -Isonitrosoacetophenone (1), phenylglyoxime (2), chlorophenylglyoxime (1), dopaminophenylglyoxime (3) and $[(\text{salen}/\text{saloph})\text{Fe}]_2\text{O}$ (4) have been synthesized as described in the literature procedure. $[\text{Fe}(\text{III})(\text{salen}/\text{saloph})\text{dopaminophenylglyoxime}]$ (starting complexes) have been synthesized from dopaminophenylglyoxime and tetradentate schiff bases which contain dinuclear Fe(III) oxygen-bridges $\text{N,N}'$ -bis(salicylidene)ethylenediamine (salenH_2) and bis(salicylidene)-*o*-phenylenediamine (salophH_2). The new heterotrinnuclear complexes have been obtained from starting complexes and Co(II), Ni(II), Cu(II) salts. Then, heterotrinnuclear *vic*-dioxime complexes containing BF_2^+ capped have been synthesized. The complexes have been characterized as low-spin distorted octahedral Fe(III) bridged by *o*-hydroxyphenolic groups. The *o*-hydroxyphenolic groups play a role as bridges for weak antiferromagnetic intramolecular exchange. The structure of dioxime and its complexes were identified by using elemental analysis, ICP-AES, ¹H-NMR and IR spectral data.

Keywords: BF_2^+ -capped complex; *vic*-dioximes; transition metal complexes; salen; saloph

1. Introduction

The polydentate coordination mode of the ligands leads to the formation of homo or heteropolynuclear complexes with cations in the metallo-macrocyclic cavity. This opens the attractive perspective of the design of macrocycle ligands containing additional donor atoms within the N_4 chain and hydroxyimino nitrogen donor atoms of dioximes. The incorporation of *vic*-dioxime unit onto the macrocycle provides an efficient binding site for the transition metal cations by the formation of an MN_4 core with additional two hydrogen bridges (5–7). The presences of mildly acidic hydroxyl groups and slightly basic nitrogen atoms causes *vic*-dioximes to be amphoteric ligands which forms corrin type square-planar, square-pyramidal and octahedral complexes with transition metal cations such as Ni(II), Cu(II) and Co(II) as central atoms (8–11).

Synthetic macrocycles have been known for over 75 years, although a real spate of publications in this area occurred in the late 1960's (12, 13). In that period, more than 5000 macrocyclic compounds were reported, and since then their number has increased markedly from year to year. Some of these compounds were recognized as promising analytical reagents in early 1970 (14, 15). One of the best strategies for designing and preparing

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

Schiff bases of Fe(III) have been known since 1938 (16). The magnetochemical properties of the μ -oxo-bridged complexes $[\{\text{Fe}(\text{salen})\}_2\text{O}]$ ($\text{salenH}_2 = \text{N,N}'$ -bis(salicylidene) ethylenediamine) and $[\{\text{Fe}(\text{saloph})\}_2\text{O}]$ [$\text{salophH}_2 = \text{bis}(\text{salicylidene})\text{-O-phenylenediamine}$] particularly have been proven, and their properties and X-ray studies are mentioned in numerous works (17–23).

Gök et al., recently reported results of the studies of the coordinating ability of new *vic*-dioximes containing macrocyclic units (24–26). We are currently interested in the design of new ligand and ligand-complexes which can serve as efficient chelating agents towards metal cations of a different nature (27–29).

We are also interested in heterotrinnuclear systems formed by the dopaminophenylglyoximes bridges since no satisfactory work dealing with this bridge and associated data have appeared in the literature. We have then prepared a novel amino *vic*-dioxime containing a diaza-dioxia macrocyclic unit and some of its heterotrinnuclear complexes.

2. Experimental

Acetophenone **1** and all solvents were purchased from Merck. ω -Isonitrosoacetophenone **2** (1), *anti*-phenylglyoxime **3** (2),

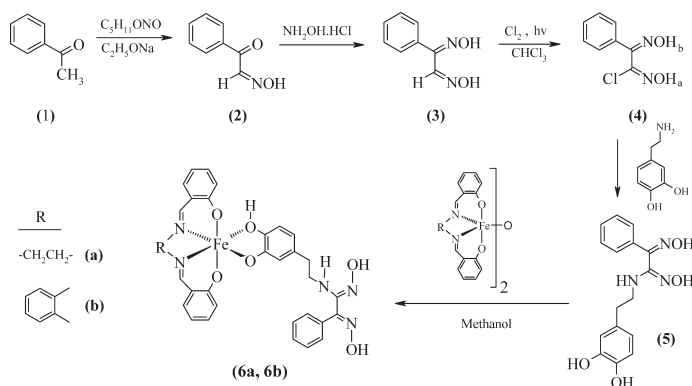
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anti-chlorophenylglyoxime **4** (1), dopaminophenylglyoxime (**H₄L**) **5** (3), [$\text{Fe}(\text{saloph})_2\text{O}$] and [$\text{Fe}(\text{salen})_2\text{O}$] (**4**) were synthesized according to literature procedures.

Some of the reactions were carried out under dry argon atmosphere. Melting points were measured using a Buchi SMP-20 melting point apparatus. Elemental analyses (C, H, N) were determined using a Leco, CHNS-932 model analyzer. The ^1H -NMR spectra were recorded on a Bruker DPX-400 400 MHz high performance digital FT-NMR, IR spectra on a Perkin-Elmer 1605 FT-IR spectrometer in KBr pellets ($4000\text{--}440\text{ cm}^{-1}$). The thermal analyses were performed on a Shimadzu DTA 50 and TG 50 H models using 10 mg samples. The DTA and TG curves were obtained at a heating rate of $10^\circ\text{C min}^{-1}$. In all cases, the $22\text{--}750^\circ\text{C}$ temperature range was studied under dry nitrogen atmosphere. 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 $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. The effective magnetic moments, μ_{eff} , per metal atom was calculated from the expression: $\mu_{\text{eff}} = 2.84\sqrt{\chi_M TB.M.}$, 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 occurred at the end of the reaction and separated using Combi Flash Chromatography.

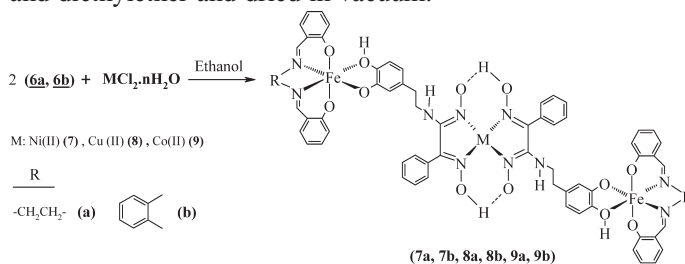
2.1 The Synthesis Procedure for [$\text{H}_2\text{LSalen}/\text{Saloph}$] $\text{Fe}(\text{III})$ Complexes (**6a**, **6b**)

A solution of dopaminophenylglyoxime (0.32 g, 1.00 mmol) dissolved in 10 mL of absolute methanol was added dropwise to a suspension of [$\text{Fe}(\text{salen})_2\text{O}$] (0.33 g, 0.50 mmol) or [$\text{Fe}(\text{saloph})_2\text{O}$] (0.38 g, 0.50 mmol) dissolved in 10 mL of absolute methanol, and the mixture stirred and refluxed for a 2 h period under an nitrogen atmosphere. A distinct change in color and a decrease in pH (2.5–2.8) was observed. While an equivalent amount of methanolic solution of NaOH (0.1 M) was adding dropwise to adjust a pH value of about 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. The precipitated complexes were washed with water, ethanol and diethylether and dried in a vacuum cabinet.



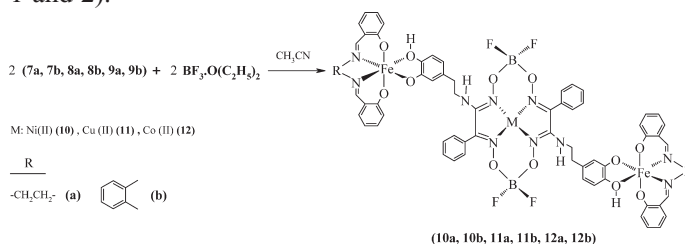
2.2 The Synthesis Procedure for $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$ and $\text{Co}(\text{II})$ Complexes of (**6a**, **6b**)

A suspension of (**6a–b**) (1.28–1.38 g, 2.00 mmol) was prepared in hot ethanol (20 mL). Then the solution of 1.00 mmol $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in 10 mL ethanol was added dropwise with stirring to the suspension. The pH of the reaction mixture was around 3.5–4.0, and then was adjusted to 5.5–6.0 by adding a 1% NaOH solution. The precipitated complex was kept on a water bath at 60°C for 1 h in order to complete the precipitation. The precipitated solid product was cooled to room temperature and filtered. The precipitated complexes were washed with water, ethanol and diethylether and dried in vacuum.



2.3 The Synthesis Procedure for [$\text{Fe}(\text{III})(\text{BF}_2\text{LSalen}/\text{Saloph})_2\text{Ni}(\text{II})/\text{Cu}(\text{II})/\text{Co}(\text{II})$] Complexes (**10a**, **10b**, **11a**, **11b**, **12a**, **12b**)

A suspension of [$\text{Fe}(\text{III})(\text{HLSalen}/\text{Saloph})_2\text{Ni}(\text{II})/\text{Cu}(\text{II})/\text{Co}(\text{II})$] (1.00 mmol) in 40 mL of dry acetonitrile were stirred at room temperature in argon atmosphere for 30 min. An equivalent amount of boron-trifluoride etherate complex (0.82 mL) was added with continuous stirring to this suspension, which changed its color to yellow immediately. After stirring for 2 h, the solvent, which color changed to dark red, was evaporated to dryness. Then the dark red crude product was dissolved in 10 mL dry diethyl ether and allowed to stand in a refrigerator at -18°C overnight, whereupon the compound crystallized from the solution. The dark red crystallized product was collected by filtration, washed with cold diethyl ether and then dried in vacuum (Tables 1 and 2).



3. Results and Discussion

The target ligand **5** was synthesized (**3**) in a four-step sequence from acetophenone. The conversion of **1** to the keto oxime derivative **2** was accomplished in 74% yield (**1**). In the ^1H -NMR spectrum of **2**, the presence of singlet at

Table 1. The elemental analysis data and physical properties of ligand and complexes

Compound (empirical formular)	μ_B	M.p. ($^{\circ}\text{C}$)	Yield g (%)	Contents				Calculated/ Found (%)				
				C	N	H	Fe	Ni	Cu	Co	B	F
$\text{C}_{32}\text{H}_{30}\text{FeN}_5\text{O}_6$ (6a)	1.86	210 ^a	0.42; 65	60.33 60.13	11.00 10.92	4.71 4.68	8.77 8.73	—	—	—	—	—
$\text{C}_{36}\text{H}_{30}\text{FeN}_5\text{O}_6$ (6b)	1.86	230 ^a	0.46; 68	63.11 62.99	10.23 10.12	4.38 4.32	8.16 8.09	—	—	—	—	—
$\text{C}_{64}\text{H}_{58}\text{Fe}_2\text{N}_{10}\text{O}_{12}\text{Ni}$ (7a)	1.86	>300	0.88; 66	57.76 57.61	10.53 10.39	4.36 4.29	8.40 8.35	4.42 4.33	—	—	—	—
$\text{C}_{72}\text{H}_{58}\text{Fe}_2\text{N}_{10}\text{O}_{12}\text{Ni}$ (7b)	1.83	>300	0.90; 63	60.60 60.47	9.82 9.73	4.07 3.98	7.83 7.74	4.05 4.02	—	—	—	—
$\text{C}_{64}\text{H}_{58}\text{Fe}_2\text{N}_{10}\text{O}_{12}\text{Cu}$ (8a)	1.75	>300	0.87; 65	57.55 57.42	10.49 10.37	4.35 4.28	8.37 8.28	—	4.76 4.68	—	—	—
$\text{C}_{72}\text{H}_{58}\text{Fe}_2\text{N}_{10}\text{O}_{12}\text{Cu}$ (8b)	1.80	>300	0.96; 67	60.39 60.03	9.79 9.69	4.05 4.01	7.81 7.70	—	4.44 4.38	—	—	—
$\text{C}_{64}\text{H}_{58}\text{Fe}_2\text{N}_{10}\text{O}_{12}\text{Co}$ (9a)	1.88	>300	0.87; 65	57.75 57.68	10.53 10.44	4.36 4.24	8.39 8.31	—	—	4.43 4.32	—	—
$\text{C}_{72}\text{H}_{58}\text{Fe}_2\text{N}_{10}\text{O}_{12}\text{Co}$ (9b)	1.97	>300	0.93; 65	60.59 60.42	9.82 9.71	4.07 4.02	7.73 7.65	—	—	4.13 4.08	—	—
$\text{C}_{64}\text{H}_{56}\text{Fe}_2\text{N}_{10}\text{O}_{12}\text{NiB}_2\text{F}_4$ (10a)	1.75	160 ^a	0.70; 49	53.88 53.54	9.82 9.71	3.93 3.88	7.84 7.72	4.12 4.06	—	—	1.52 1.51	5.33 5.30
$\text{C}_{72}\text{H}_{56}\text{Fe}_2\text{N}_{10}\text{O}_{12}\text{NiB}_2\text{F}_4$ (10b)	1.88	165 ^a	0.72; 47	56.79 56.51	9.20 9.11	3.68 3.63	7.39 7.24	3.86 3.79	—	—	1.42	4.99
$\text{C}_{64}\text{H}_{56}\text{Fe}_2\text{N}_{10}\text{O}_{12}\text{CuB}_2\text{F}_4$ (11a)	1.80	183 ^a	0.75; 52	53.70 53.59	9.79 9.68	3.92 3.86	7.71 7.69	—	4.44 4.36	—	1.51 1.48	5.31 5.26
$\text{C}_{72}\text{H}_{56}\text{Fe}_2\text{N}_{10}\text{O}_{12}\text{CuB}_2\text{F}_4$ (11b)	1.85	185 ^a	0.68; 44	56.61 56.41	9.17 9.08	3.67 3.54	7.32 7.22	—	4.16 4.10	—	1.42 1.38	4.98 4.93
$\text{C}_{64}\text{H}_{56}\text{Fe}_2\text{N}_{10}\text{O}_{12}\text{CoB}_2\text{F}_4$ (12a)	1.77	160 ^a	0.85; 57	53.87 53.66	9.82 9.71	3.93 3.82	7.84 7.76	—	—	4.13 3.98	1.52 1.45	5.33 5.21
$\text{C}_{72}\text{H}_{56}\text{Fe}_2\text{N}_{10}\text{O}_{12}\text{CoB}_2\text{F}_4$ (12b)	1.83	170 ^a	0.88; 56	56.78 56.60	9.20 9.06	3.68 3.57	7.34 7.25	—	—	3.87 3.76	1.42 1.40	4.99 4.87

^aDec.

Table 2. Characteristic FT-IR bands (cm^{-1}) of complexes^a

Compound (empirical formular)	FT-IR data of compounds ($\nu_{\text{max}}/\text{cm}^{-1}$)											
	C=N _{ox}	C=N	N-H	CH _{Ar}	OH _{ph}	CH _{aliph}	OH-O	N-O	Fe-N	Fe-O	B-O	B-F
C ₃₂ H ₃₀ FeN ₅ O ₆ (6a)	1632	1580	3345	3015	3260	2860 2970	1710	993–3608	536	475		
C ₃₆ H ₃₀ FeN ₅ O ₆ (6b)	1630	1585	3344	3020	3263	2864	1712	997–3610	535	474		
C ₆₄ H ₅₈ Fe ₂ N ₁₀ O ₁₂ Ni (7a)	1636	1585	3343	3020	3262	2866 2967	1712	1031	532	471		
C ₇₂ H ₅₈ Fe ₂ N ₁₀ O ₁₂ Ni (7b)	1635	1580	3345	3018	3261	2865	1714	1029	533	472		
C ₆₄ H ₅₈ Fe ₂ N ₁₀ O ₁₂ Cu (8a)	1638	1581	3344	3017	3260	2861 2963	1712	1032		473		
C ₇₂ H ₅₈ Fe ₂ N ₁₀ O ₁₂ Cu (8b)	1639	1584	3343	3020	3262	2863	1718	1026	537	475		
C ₆₄ H ₅₈ Fe ₂ N ₁₀ O ₁₂ Co (9a)	1632	1585	3343	3021	3261	2861 2964	1719	1028	535	476		
C ₇₂ H ₅₈ Fe ₂ N ₁₀ O ₁₂ Co (9b)	1640	1588	3343	3021	3260	2860	1720	1025	535	473		
C ₆₄ H ₅₆ Fe ₂ N ₁₀ O ₁₂ NiB ₂ F ₄ (10a)	1653	1584	3344	3020	3268	2861 2964		1063	537	475	1175	872
C ₇₂ H ₅₆ Fe ₂ N ₁₀ O ₁₂ NiB ₂ F ₄ (10b)	1653	1584	3345	3020	3267	2863		1061	537	475	1172	873
C ₆₄ H ₅₆ Fe ₂ N ₁₀ O ₁₂ CuB ₂ F ₄ (11a)	1654	1584	3344	3020	3266	2863 2965		1061	537	475	1172	873
C ₇₂ H ₅₆ Fe ₂ N ₁₀ O ₁₂ CuB ₂ F ₄ (11b)	1655	1584	3344	3020	3269	2863		1065	534	473	1177	874
C ₆₄ H ₅₆ Fe ₂ N ₁₀ O ₁₂ CoB ₂ F ₄ (12a)	1653	1582	3347	3020	3268	2863 2965		1063	537	475	1175	872
C ₇₂ H ₅₆ Fe ₂ N ₁₀ O ₁₂ CoB ₂ F ₄ (12b)	1655	1582	3345	3020	3268	2862		1064	538	474	1172	871

^aKBr pellet.

$\delta = 8.40$ ppm and $\delta = 11.50$ ppm showed that keto oxime had occurred. This compound was easily converted to the glyoxime derivative **3** by reaction with hydroxylamine, and the yield of the conversion reaction (2) was very high 92%. The $^1\text{H-NMR}$ spectra of **3**, the presence of two singlet at $\delta = 11.6$ and $\delta = 11.4$ ppm showed that glyoxime had occurred. Chlorophenylglyoxime (1) **4** was obtained from reacting with chlorine gases in a 75% yield. In the $^1\text{H-NMR}$ spectrum of **4**, the absence of singlet at $\delta = 8.40$ ppm showed that chlorophenylglyoxime had occurred. Dopaminophenylglyoxime **5** was prepared by reacting dopamine hydrochloride with chlorophenylglyoxime. Two peaks are present in the ligands for the OH protons of the oxime groups. These two deuterium-exchangeable singlets correspond to two non-equivalent OH protons which also indicate the *anti*-configuration of the OH groups relative to each other (30, 31). In the $^1\text{H-NMR}$ spectra of **5**, two peaks (11.60, 11.20 ppm) are present for the OH protons because of the difference in the neighboring oxime groups. The signal at 6.10 ppm was assigned to the phenolic OH protons. The NH proton was observed at 8.55 ppm, the aromatic C-H protons at 6.63–7.60 ppm. $^1\text{H-NMR}$ spectrum of all the complexes could not be taken because of their paramagnetic character. All these values are in agreement with the previously reported (32, 33).

In the FT-IR spectra of **5** bands at 3370, 3263, 3600, 1640 and 997 cm^{-1} were respectively assigned to (NH), (O-H), (OH)_{arom.}, (C=N) and (N-O) stretching vibrations. In the FT-IR spectra of the complexes (**6a** and **6b**), vibrations in the 1580–1585, 1632–1630, 993–997, 3608–3610 and $3260\text{--}3263\text{ cm}^{-1}$ range were assigned to ν (C=N) (for $\text{N}_2\text{O}_2\text{O}_2$ compartment), (C=N)_{oxime}, (N-O)_{bend}, (N-O)_{strec} and (O-H)_{arom} cm^{-1} stretching vibrations respectively. In the FT-IR spectra of the complexes (**7a**, **7b**, **8a**, **8b**, **9a**, **9b**) shift of the vibration corresponding to the N-O band to higher frequency indicates the formation of coordination bonds between metal and the nitrogen atoms of the dioximes (34). A downward shifts of 20 cm^{-1} for the C=N absorption in the complexes indicated coordination through the N atoms (34, 35). In the FT-IR spectrum of (**7a**, **7b**, **8a**, **8b**, **9a**, **9b**), the O-H_{arom} and N-H stretching vibrations were observed at $3260\text{--}3262$ and $3343\text{--}3345\text{ cm}^{-1}$ as broad absorptions band. It seems that, salen (or saloph) had been linked from phenolic OH of the ligand. This BF_2^+ -bridged complexes (**10a**, **10b**, **11a**, **11b**, **12a**, **12b**) exhibited an upward shift to about 1653 cm^{-1} for the (C=N)_{oxime} absorption and an upward shift to about 1063 cm^{-1} for the N-O absorption. The broad band at $1712\text{--}1720\text{ cm}^{-1}$ assigned to the O-H...O bending vibrations, disappeared upon insertion of the BF_2^+ groups with the simultaneous appearance of peaks at $1172\text{--}1177$ and $871\text{--}874\text{ cm}^{-1}$ for the B-O and B-F resonances, respectively. These absorption data are in agreements with those previously reported for substituted *vic*-dioximes (30–35).

Best evidence for the proposed structures of the heteronuclear complexes comes from magnetic measurements. Where the starting $[\text{H}_2\text{LSalen/Saloph}]\text{Fe(III)}$ complexes are octahedral d^5 (paramagnetic) and any magnetic moment of the

heteronuclear species should arise from occupation of $\text{N}_2\text{O}_2\text{O}_2$ compartment. On this assumption, the observed magnetic moments for the heterotrinnuclear complexes are those for isolated d^5 systems. Thus, heterotrinnuclear complexes of (**7a**, **7b**, **8a**, **8b**, **9a**, **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). The values of $1.86\text{--}1.83\text{--}1.75\text{--}1.88$ B.M. for (**7a**, **7b**, **10a**, **10b**), respectively, which are same as the starting complexes (1.86 B.M.) of magnetic measurement of per Fe(III) atom of heterotrinnuclear complexes, shows that the Ni(II) containing compounds are represented by the structure of square-planar d^8 (diamagnetic). The values of $1.75\text{--}1.80$, $1.88\text{--}1.97$, $1.80\text{--}1.85$ and $1.77\text{--}1.83$ for (**8a**, **8b**, **9a**, **9b**, **11a**, **11b**, **12a**, **12b**), respectively, of magnetic measurement of per atom of heterotrinnuclear complexes shows that the Cu(II) and Co(II) containing compounds are represented only in the low spin state for Co(II) and in the structures of d^7 for Co(II) and d^9 for Cu(II) in this case. The magnetic data of the Cu(II) and Co(II) complexes agree with the d^9 and d^7 metal ion in square-planar for complexes of either Cu(II) or Co(II) with starting complexes (36). Magnetic susceptibility measurements of the complexes provide information regarding to their structures and are presented in the Experimental section.

The thermal analyses (TG, DTA) of complex **12a** showed a weight loss of 6.3% in the temperature range $75\text{--}175^\circ\text{C}$, corresponding to the loss of BF_2^+ molecules. Thermal decomposition of the anhydrous $[\{\text{Fe}(\text{salen})\}_2\text{O}]$ complexes of the **12a** starts in the range of $200\text{--}400^\circ\text{C}$ by weight loss of 41.6%, and organic groups completes in the range of $450\text{--}550^\circ\text{C}$ by weight loss of 40.4%. The final decomposition products were metal oxides. The observed weight losses for **12a** complexes are in good agreement with the calculated values (37).

4. Conclusions

In this work, we have synthesized and characterized new heterotrinnuclear BF_2^+ -capped complexes containing *vic*-dioxime.

5. Acknowledgment

The authors would please to acknowledge the Scientific Research Projects (BAP) of Selçuk University for a grant with the grant number of 2005/5201005.

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