

(*E, E*)*S, S'*-bis(2-benzimidazolymethyl) dithioglyoxime, synthesis and characterization of heterotrinnuclear complexes of and determination of their metal contents by EDXRF analysis

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Abstract

A vicinal dioxime ligand with two 2-benzimidazolymethyl groups, namely *S, S'*-bis(2-benzimidazolymethyl) dithioglyoxime (H_2L) and its axially pyridine and 2,6-dimethyl pyridine bonded Co(III) complexes were prepared according to prior literature [Y. Gök, S.Z. Yıldız, Synth. React. Inorg. Met-Org. Chem. 22 (9) (1992) 1327]. BF_2^+ bridged Co(III) complexes have been synthesized via the hydrogen-bridged Co(III) complexes by using borontrifluoride ethyl ether complex. Heterotrinnuclear complexes have been prepared by the reaction of these more soluble BF_2 -capped Co(III) complexes with stoichiometric amount of $CdCl_2 \cdot H_2O$ and $NiCl_2 \cdot 6H_2O$ salts. Using 1H , ^{13}C NMR, IR and MS spectral data and elemental analysis, the structures of the complexes were identified. Qualitative and quantitative determination of Co, Ni and Cd contents of the heterotrinnuclear complexes have been investigated by energy dispersive X-ray fluorescence (EDXRF) method. An annular 50 mCi ^{241}Am radioactive source emitting 59.543 keV photons was used for excitation and Si(Li) detector having 157 eV FWHM at 5.9 keV was used for intensity measurements.

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1. Introduction

A rapidly growing area of the chemical interest in recent years is the synthesis of heterobinucleating ligands and the coordination chemistry of the heteronuclear complexes prepared such ligands [1]. Homo and hetero polymetallic exchange coupled metal oximates have been recently reviewed in the literature [2]. The heteropolymetallic systems are of interest to both biologist and bioinorganic chemist investigating the structure and function of polynuclear metal centers in proteins and searching for new magnetic materials [3]. Additionally, polynuclear complexes may facilitate electronic transfer studies and serve as mod-

els of relevance to biological process [4]. Using of bimetallic compounds at bioinorganic systems is one of the reasons for the increase in the amount of research on polynuclear compounds [5].

Thioether ligands were investigated as possible selective metal extraction agent for “soft” metal ions such as lead and mercury [6]. Such ligands may have important utility in terms of sequestering agents for treatment of heavy metal poisoning [7]. On the other hand thioethers coordinated to copper ions have been investigated to elucidate the structure of the blue copper proteins, plastocyanines [8] and azurin [9], which have dithioethers coordinated to thallium(I) and mercury(II). The polyazapolitia ligands exhibit intermediate properties between polyaza and polytia ligands as anticipated for the macrocyclic polioxa-politiaether ligands [10]. A variety of ligands containing

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together and benzimidazole groups were synthesized and their complexation works were performed with different transition metal ions [11–14].

Most of these works are about the biological activities and the stability of the complexes [15]. These ligands are potentially tetra dentate N_2S_2 donors and contain benzimidazole groups as well as biologically relevant tioether groups [16]. A large number of octahedral diorganotin halide complexes with benzimidazole containing ligands such as 2-(2-pyridyl) benzimidazole and 2,2'-pyridyl-4-benzimidazoleethyltindichloride were reported to prolong the survival of mice bearing P388 leukemia [17] and to active against a newly characterized renal adenocarcinoma [18].

The chemistry of transition metal complexes with vic-dioximes were well examined and reviewed [19]. These groups of compounds have received considerable attention as model substance to characterize the biofunctions of vitamin B_{12} [20]. Most investigations on transition metal complexes of vic-dioximes have been concerned only with the (*E,E*)-isomer [21]. The mildly acidic hydroxyl groups and slightly basic nitrogen atoms make vic-dioximes amphoteric ligands, which form octahedral complexes with Co(III) as central atom. The metal dioximates undergo facile axial ligation with monodentate N-donors without affecting the planar arrangement around central metal atom, and the relevant chemical analogies with vitamin B_{12} resides in the reactivity of the axial position of these macrocycles [22,23].

The bridging protons of the vic-dioximato Co(III) complexes have been replaced by BF_2^+ groups and the stability studies of the complexes have been investigated [24–26]. The substitution markedly enhanced the stability of the dioxygen adduct by removing the labile acidic protons from the ligand [27].

Atomic absorption spectrometry, neutron activation analysis and X-ray fluorescence spectrometry are some elemental analysis methods. X-ray fluorescence (XRF) methods can be divided into two, namely, the wavelength and energy dispersive. Energy dispersive X-ray fluorescence (EDXRF) spectrometry offers several unique advantages over other analytical methods. It allows simultaneous detection and determination of several elements, it requires none or simple sample preparation. It is sensitive and reproducible [28]. In principle, all kinds of XRF can be used for the determination of metals: excitation by X-rays from different X-ray tubes, excitation by X- or γ -rays (or other radiation) from various radionuclides, measurement of the fluorescence radiation by wavelength dispersion, and measurement of the fluorescence radiation by energy dispersive detectors such as scintillation counters or Si(Li), Ge(Li) and HPGe semiconductor counters [29]. In addition, EDXRF method gives a possibility of trace analysis of chemical complexes.

In the present paper, our goal is to prepare some heteronuclear complexes, bearing Cd(II), Ni(II), and BF_2^+ bridges by using bis [*S,S'*-bis (2-benzimidazolylmethyl)

dithio glyoximato] Co(III) complexes with axial ligands such as pyridine and 2,6-dimethyl pyridine. The metal contents of the complexes have been qualitatively and quantitatively determined by using EDXRF method as an alternative method to atomic absorption spectroscopy. All the other conventional spectroscopic methods such as FT-IR, 1H NMR, ^{13}C NMR, MS and elemental analysis have been used to identify the complexes.

2. Experimental

2.1. General procedure

The vicinal dioxime ligand, “*S,S'*-bis (2-benzimidazolylmethyl) dithioglyoxime” (H_2L) (**1**) and its Co(III) complexes with pyridine (**2**) and 2,6-dimethylpyridine (**3**) were prepared according to the prior literature [16]. All the other reagents are commercially available in sufficient purity.

Infrared spectra were recorded in KBr pellets on a Perkin Elmer 1600 FT-IR spectrophotometer. 1H and ^{13}C NMR spectra were recorded on a Varian-Oxford 200-MHz FT-NMR at Karadeniz Technical University Department of Chemistry, Trabzon, Turkey. FAB (positive, matrix: m-nitro benzyl alcohol) was recorded on an EI-FAB Krotos MS-50 Triple Analyzer at York University, Department of Chemistry, Ontario, Canada.

Quantitative determination of Co, Ni and Cd in the complexes has been investigated using EDXRF method at Karadeniz Technical University Department of Physics, Trabzon-Turkey. An annular 50 mCi ^{241}Am radioactive source emitting 59.543 keV FWHM for 5.9 keV photons was used for intensity measurements. A Tennelec TC 244 amplifier and PCA multichannel analyzer 2048 channels of the MCA were employed in data acquisition. Data reduction was accomplished by means of a PCA software program. The data were collected for 2000 s of real time. The block diagram of the counting system is shown in Fig. 1 [30].

Standard calibration method was used for quantitative determination of Co, Ni and Cd amounts in the samples. Co, Ni and Cd standards were prepared in solid phase by using chloride salts of related metal and starch as filler. The quantitative metal contents of the standards were

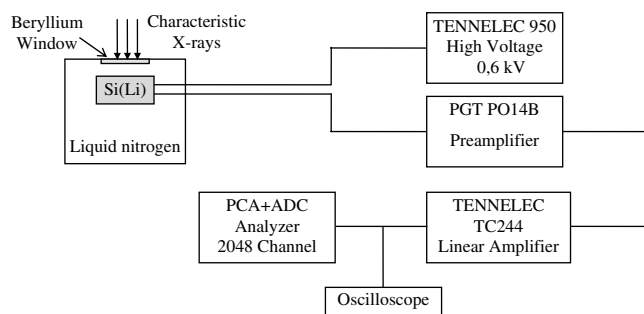


Fig. 1. The block diagram of the counting system.

measured by EDXRF to prepared the calibration graphics, which are given in Fig. 2.

2.2. Synthesis of BF_2^+ -capped Co(III) complexes

To a suspension of Co(III)-pyridine (**2**) or 2,6-dimethyl pyridine (**3**) complex (1.3 mmol) [(**2**): 1.30 g or (**3**): 1.33 g] in freshly distilled acetonitrile (80 mL) was added $BF_2\text{-Et}_2O$ complex (0.62 g; 4.3 mmol) (0.55 mL) in acetonitrile (10 mL). The final mixture was heated up to reflux temperature under a dry argon atmosphere by using Schlenk system. The reaction was maintained for 6 h. and cooled to room temperature. The reaction mixture converted to a red-brown solution during the reflux. After the solution evaporated to 15 mL volume, diethylether (10 mL) was diffused and the mixture was allowed to stand in a refrigerator for several days. The tiny crystals were collected by filtration and dried in vacuo over P_4O_{10} .

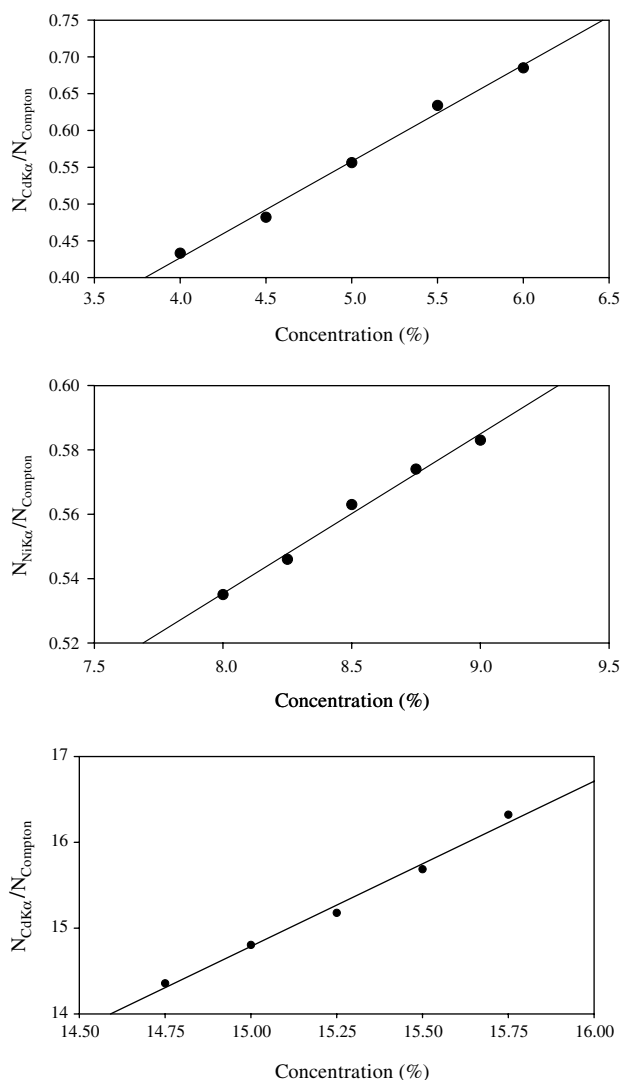


Fig. 2. Standard calibration graphics for Co, Ni and Cd.

2.2.1. $[Co(III)(L)_2(BF_2)_2PyCl]$ (**4**)

Dark reddish-brown crystals. Yield: 1.01 g, 71%, m.p.: 285 °C. IR (KBr pellets, cm^{-1}): 3438 (N–H), 3112 ($C-H$)_{arom.}, 2830 ($C-H$)_{aliph.}, 1633 (C=N), 1590 (C=C), 956 (N–O). 1H NMR (DMSO- d_6) δ : 8.47–7.80 (m, 5H, $C-H$ _{arom.}), 7.72 (s, 4H, NH), 7.23–6.80 (m, 16H, $C-H$ _{arom.}), 4.33 (s, 8H, $C-H$ _{aliph.}). ^{13}C NMR (DMSO- d_6) δ : 148.97; 144.47; 134.72; 130.43; 128.67; 128.15; 123.65; 123.17; 116.28; 114.54; 27.43. Elemental analysis for $C_{41}H_{33}N_{13}O_4S_4B_2F_4CoCl$: Calc.: H, 3.05; C, 45.09; N, 16.67; Co, 5.40. Found: H, 3.18; C, 45.02; N, 16.58; Co, 5.53% (by EDXRF). Co K α (6.95 keV), Co K β (7.62 keV).

2.2.2. $[Co(III)(L)_2(BF_2)_2Py(CH_3)_2Cl]$ (**5**)

Reddish-brown crystals. Yield: 1.2 g, 83%, m.p.: 270 °C. IR (KBr pellets, cm^{-1}): 3425 (N–H), 3096 ($C-H$)_{arom.}, 2952 ($C-H$)_{aliph.}, 1635 (C=N), 1595 (C=C), 962 (N–O). 1H NMR (DMSO- d_6) δ : 7.92 (s, 4H, NH), 7.50–7.35 (m, 3H, $C-H$ _{arom.}), 7.26–6.81 (m, 16H, $C-H$ _{arom.}), 4.41 (s, 8H, $C-H$ _{aliph.}), 2.42 (s, 6H, $C-H$ _{aliph.}). ^{13}C NMR (DMSO- d_6) δ : 148.55; 143.98; 134.72; 131.46; 128.54; 128.23; 123.18; 122.97; 115.20; 114.50; 34.25, 27.40. Elemental analysis for $C_{43}H_{37}N_{13}O_4S_4B_2F_4CoCl$: Calc.: H, 2.46; C, 46.11; N, 16.26; Co, 5.26. Found: H, 2.28; C, 46.18; N, 15.97; Co, 5.38% (by EDXRF). Co K α (6.95 keV), Co K β (7.62 keV).

2.3. Synthesis of heterotrinnuclear BF_2^+ -capped Co(III) complexes

The $[Co(III)(L)_2(BF_2)_2(L')Cl]$ complexes (0.3 mmol) [$L' = Py$ (0.33 g) or $L' = Py(CH_3)_2$ (0.34 g)] was dissolved in ethanol (50 mL). After the solution was heated up to reflux temperature, related metal salt (0.65 mmol) [$NiCl_2 \cdot 6H_2O$ (0.15 g) or $CdCl_2 \cdot H_2O$ (0.13 g)] solution in hot ethanol (15 mL) was added. The final solution was refluxed for 30 h. and the volume was reduced to 15–20 mL by evaporation. The mother liquor was allowed to stand in a refrigerator for overnight. The appeared precipitate was collected by filtration and washed with excess water, ethanol and diethylether, respectively and then dried in vacuo.

2.3.1. $[Co(III)(L)_2(BF_2)_2PyNi_2Cl]Cl_4$ (**6**)

Obtained product is brown. Yield: 0.15 g, 37%, m.p.: 165 °C. IR (KBr pellets, cm^{-1}): 3435 (N–H), 3105 ($C-H$)_{arom.}, 2950 ($C-H$)_{aliph.}, 1621 (C=N), 1595 (C=C), 955 (N–O). Mass spectra (FAB, positive) m/z : 1229 [$M^+ + H_2O + 1$], 1131 [$M^+ - Py + 1$]. Elemental analysis for $C_{41}H_{33}N_{13}O_4S_4B_2F_4CoNi_2Cl_5$: Calc.: H, 2.46; C, 36.44; N, 13.43; Co, 4.36; Ni, 8.69. Found: H, 2.38; C, 36.20; N, 13.38; Co, 4.61 (by EDXRF); Ni, 8.56% (by EDXRF). Co K α (6.95 keV), Co K β (7.62 keV), Ni K α (7.51 keV), Ni K β (8.26 keV).

2.3.2. $[Co(III)(L)_2(BF_2)_2Py(CH_3)_2Ni_2Cl]Cl_4$ (**7**)

Obtained product is brown. Yield: 0.23 g, 54%, m.p.: 158 °C. IR (KBr pellets, cm^{-1}): 3424 (N–H), 3110

(C–H)_{arom.}, 2953 (C–H)_{aliph.}, 1623 (C=N), 1593 (C=C), 963 (N–O). Mass spectra (FAB, positive) m/z : 1238 [M⁺+1], 1208 [M⁺–2CH₃+1], 1130 [M⁺–Py(CH₃)₂]. Elemental analysis for C₄₃H₃₇N₁₃O₄S₄B₂F₄CoNi₂Cl₅: Calc.: H, 2.70; C, 37.45; N, 13.20; Co, 4.27; Ni, 8.51. Found: H, 2.54; C, 37.28; N, 13.18; Co, 4.23 (by EDXRF); Ni, 8.80% (by EDXRF). Co K α (6.95 keV), Co K β (7.62 keV), Ni K α (7.51 keV), Ni K β (8.26 keV).

2.3.3. [Co(III)(L)₂(BF₂)₂Py Cd₂Cl]Cl₄ (8)

Obtained product is dark brown. Yield: 0.15 g, 36%, m.p.: 200 °C. IR (KBr pellets, cm⁻¹): 3436 (N–H), 3113 (C–H)_{arom.}, 2950 (C–H)_{aliph.}, 1620 (C=N), 1590 (C=C), 960 (N–O). ¹H NMR (DMSO-*d*₆) δ : 7.90 (s, 4H, NH), 8.20–7.78 (m, 5H, C–H_{arom.}), 7.32–6.6.92 (m, 16H, C–H_{arom.}), 4.32 (s, 8H, C–H_{aliph.}). ¹³C NMR (DMSO-*d*₆) δ : 148.50; 144.57; 134.72; 130.45; 128.63; 128.20; 123.25; 122.93; 115.22; 114.48; 27.38. Mass spectra (FAB, positive) m/z : 1336 [M⁺+H₂O+1], 1240 [M⁺–Py+2]. Elemental analysis for C₄₁H₃₃N₁₃O₄S₄B₂F₄CoCd₂Cl₅: Calc.: H, 2.28; C, 33.76; N, 12.48; Co, 4.04; Cd, 15.41. Found: H, 2.27; C, 33.61; N, 12.63; Co, 4.10 (by EDXRF); Cd, 15.30% (by EDXRF). Co K α (6.95 keV), Co K β (7.62 keV), Cd K α (23.13 keV), Cd K β 1 (26.16 keV) Cd K β 2 (26.68 keV).

2.3.4. [Co(III)(L)₂(BF₂)₂Py(CH₃)₂Cd₂Cl]Cl₄ (9)

Obtained product is dark reddish brown. Yield: 0.21 g, 47%, m.p.: 224 °C. IR (KBr pellets, cm⁻¹): 3425 (N–H), 3120 (C–H)_{arom.}, 2955 (C–H)_{aliph.}, 1625 (C=N), 1592 (C=C), 963 (N–O). ¹H NMR (DMSO-*d*₆) δ : 7.92 (s, 4H, NH), 7.54–7.32 (m, 3H, C–H_{arom.}), 7.32–6.90 (m, 16H, C–H_{arom.}), 4.34 (s, 8H, C–H_{aliph.}) 2.64 (s, 6H, C–H_{aliph.}). ¹³C NMR (DMSO-*d*₆) δ : 148.63; 142.02; 134.70; 130.43; 128.51; 127.86; 123.20; 122.95; 115.22; 114.32; 33.90; 27.51. Mass spectra (FAB, positive) m/z : 1345 [M⁺], 1257 [M⁺–Py(CH₃)₂+H₂O+1]. Elemental analysis for C₄₃H₃₇N₁₃O₄S₄B₂F₄CoCd₂Cl₅: Calc.: H, 2.51; C, 34.74; N, 12.25; Co, 3.96; Cd, 15.12. Found: H, 2.42; C, 34.77; N, 12.13; Co, 3.78 (by EDXRF); Cd, 15.07% (by EDXRF). Co K α (6.95 keV), Co K β (7.62 keV), Cd K α (23.13 keV), Cd K β 1 (26.16 keV) Cd K β 2 (26.68 keV).

2.4. Quantitative determination of the metals in the complexes

2.4.1. Preparation and measurement of the standart

The related metal salts CoCl₂·6H₂O (for Co), NiCl₂·6H₂O (for Ni) and CdCl₂·H₂O (for Cd) were mixed with certain amount of purified starch to give the mixtures containing the metals as percentage in the determination range. The ingredients of the mixtures are listed in the table (Table 1). The measured and the calculated metal amount of the standards are also given as percentage. The mixture was ground in to a fine homogeny mixture in an agate mortar. The final mixture was weighted as 30 mg

Table 1
The ingredient of prepared standards and theirs measured metal percentage

Substance metal salt	Additive		Percentage of the metal	
	Amount (mg)	Substance	Amount (mg)	Calculated (measured)
CoCl ₂ ·6H ₂ O	48.42	Starch	151.57	6.00 (5.97)
CoCl ₂ ·6H ₂ O	44.39	Starch	155.61	5.50 (5.48)
CoCl ₂ ·6H ₂ O	40.36	Starch	159.64	5.00 (5.02)
CoCl ₂ ·6H ₂ O	36.32	Starch	163.68	4.50 (4.50)
CoCl ₂ ·6H ₂ O	32.29	Starch	167.71	4.00 (3.96)
NiCl ₂ ·6H ₂ O	72.85	Starch	127.17	9.00 (8.99)
NiCl ₂ ·6H ₂ O	70.83	Starch	129.17	8.75 (8.73)
NiCl ₂ ·6H ₂ O	68.80	Starch	131.20	8.50 (8.51)
NiCl ₂ ·6H ₂ O	66.78	Starch	133.22	8.25 (8.26)
NiCl ₂ ·6H ₂ O	64.75	Starch	135.25	8.00 (8.00)
CdCl ₂ ·H ₂ O	56.41	Starch	143.59	15.75 (15.76)
CdCl ₂ ·H ₂ O	55.52	Starch	144.48	15.50 (15.48)
CdCl ₂ ·H ₂ O	54.62	Starch	145.38	15.25 (15.26)
CdCl ₂ ·H ₂ O	53.73	Starch	146.27	15.00 (15.00)
CdCl ₂ ·H ₂ O	52.83	Starch	147.17	14.75 (14.74)

and pressed by light pressure (1500 kg/cm²) to make pellet. The pellet was put on a mylar film, which was shown in Fig. 3, to determine the standard metal quantity. The standard metal concentrations were plotted on the standard calibration graphics as percentage against to the calculated absorption areas (Fig. 2).

2.4.2. Preparation and measurements of the samples

The sample, which was demanded to determine the metal content quantitatively, was put into an agate mortar and ground into the same particle size with the standard samples. The sample was weighted as 30 mg and pressed by light pressure (1500 kg/cm²) to make pellet. The pellet was put on the same apparatus (Fig. 3) [30], which was used to measure the standards. The metal concentration was determined by using related calibration graphics.

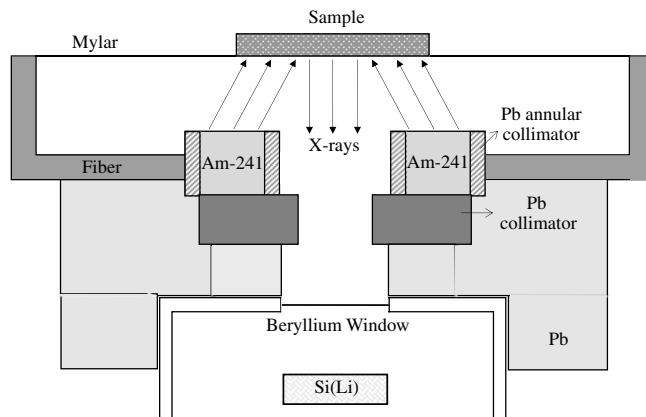
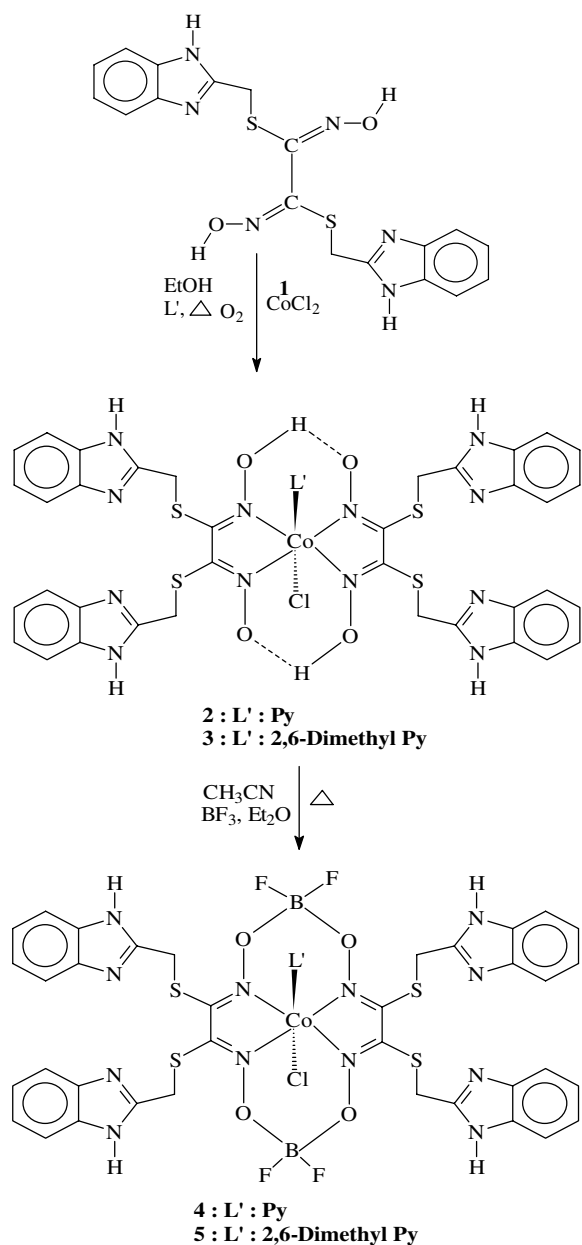


Fig. 3. Geometry of the experimental setup.

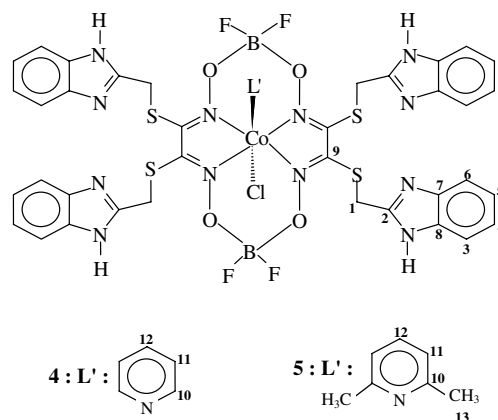
3. Results and discussion

The synthesis of the ligand and the Co(III) complexes with pyridine and 2,6-dimethyl pyridine were performed according to the previous literature [16] shown in Scheme 1. The BF₂-capped Co(III) complexes (4) and (5) have been templately synthesized by adding BF₃–OEt₂ complex to acetonitrile solutions of (2) and (3), and refluxing under an argon atmosphere.

In the formation of (4) and (5) the O–H···O bridged protons of the pseudomacrocycles complexes of (2) and (3) were replaced by BF₂⁺ groups. In the ¹H NMR spectra of the BF₂-capped complexes the signals at δ = 17.40 and δ = 17.30, which belonged to O–H···O bridged protons of (2) and (3), respectively [15], disappeared. Moreover,



Scheme 1.

Fig. 4. Chemical structures of BF₂-capped Co(III) complexes (4) and (5).

all the other chemical shifts correspond to the proposed formulation (Fig. 4) of (4) and (5). In the IR spectra of (4) and (5), the weak vibrations at 1698 and 1725 cm⁻¹, which belonged to hydrogen bridged complexes of (2) and (3), respectively, disappeared as well. In contrast to the literature [31] the BF₂-capped complexes exhibit mostly not shifts in the other stretching vibrations. The proton-decoupled ¹³C NMR spectra for these complexes are inconsistent with the formulas (Table 2).

In addition, elemental analysis results of C, H and N of (4) and (5) support to the proposed formulas. EDXRF analysis technique has been used for qualitative and quantitative determination of Co(III) ion (Fig. 5) in the complexes. The obtained results are in a good agreement with the structure (Table 3).

The BF₂-capped heterotrinnuclear nickel complexes (6) and (7) have been prepared by refluxing the solutions of (4) and (5) in ethanol with the nickel chloride solution in ethanol. The same method has been used to prepare heterotrinnuclear cadmium complexes (8) and (9) using cadmium chloride instead of nickel chloride (Scheme 2). The ¹H and ¹³C NMR spectra of (6) and (7) have not been able to record. These results illustrate that the Co(III) complexes (4) and (5) give paramagnetic tetrahedral trinuclear Ni(II)

Table 2
The ¹³C NMR spectra data for (4) and (5)

Compound (4)		Compound (5)	
Carbons	δ (ppm)	Carbons	δ (ppm)
C ₁	27.43	C ₁	27.40
C ₂	144.47	C ₂	143.98
C ₃	114.54	C ₃	114.50
C ₄	116.28	C ₄	115.20
C ₅	123.17	C ₅	122.97
C ₆	123.65	C ₆	123.18
C ₇ –C ₈	134.72	C ₇ –C ₈	134.72
C ₉	148.97	C ₉	148.55
C ₁₀	130.43	C ₁₀	131.46
C ₁₁	128.15	C ₁₁	128.23
C ₁₂	128.67	C ₁₂	128.54
		C ₁₃	34.25

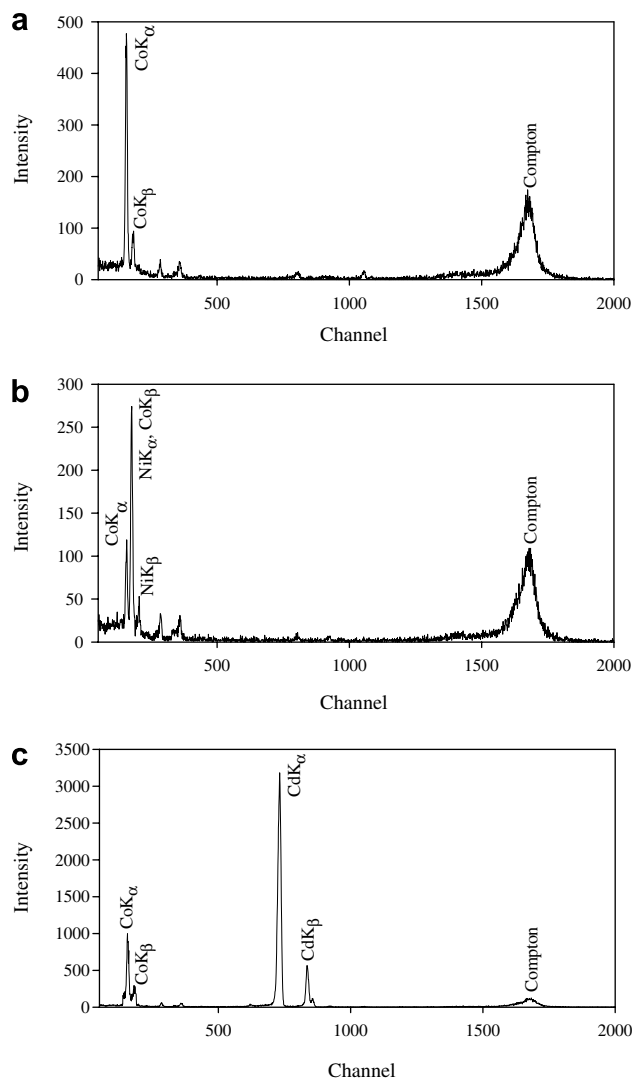
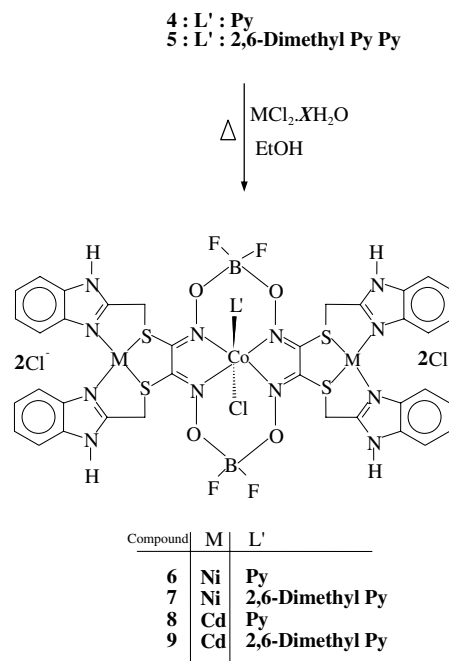


Fig. 5. EDXRF spectra of complexes: (a) for (4), (5); (b) for (6) and (8); (c) for (7) and (9).



Scheme 2.

complexes (6) and (7) (Fig. 6) with the N_2S_2 cores of the molecules. According to the literature [32,33], azomethyn ($\text{C}=\text{N}$) nitrogen atom is used in such complexions. Approximately, 12 cm^{-1} down field shift has been observed for the $\text{C}=\text{N}$ stretching vibration in the IR spectra of the trinuclear Ni(II) complexes is in accord with the literature. However, having little shifts at N–H stretching vibrations, which belong to imidazole ring, in the IR spectra of (6) and (7) by comparing with IR spectra of (4) and (5) contribute to the proposed structure. The mass spectra of (6) and (7) are also in good agreement with the formula having $m/z = 1229 [\text{M}^+ + 2\text{H}_2\text{O} + 1]$ and $m/z = 1238 [\text{M}^+ + 1]$ values,

Table 3
Analytical data for the heteronuclear complexes

Complex	Colour	Yield (%)	Found (calc.) / %			M (measured by EDXRF)	K_{α} , $\text{K}_{\beta 1}$, $\text{K}_{\beta 2}$ (keV)
			C	H	N		
[Co(III)(L) ₂ (BF ₂) ₂ PyCl] (4)	Dark reddish-brown	71	45.02 (45.09)	3.18 (3.05)	16.58 (16.67)	Co: 5.53 (5.40)	Co: 6.95; 7.62
[Co(III)(L) ₂ (BF ₂) ₂ Py(CH ₃) ₂ Cl] (5)	Reddish-brown	83	46.18 (46.11)	2.28 (2.46)	15.97 (16.26)	Co: 5.38 (5.26)	Co: 6.95; 7.62
[Co(III)(L) ₂ (BF ₂) ₂ PyNi ₂ Cl]Cl ₄ (6)	brown	37	36.20 (36.44)	2.38 (2.46)	13.38 (13.43)	Co: 4.61 (4.36) Ni: 8.56 (8.69)	Co: 6.95; 7.62 Ni: 7.51; 8.26
[Co(III)(L) ₂ (BF ₂) ₂ Py(CH ₃) ₂ Ni ₂ Cl]Cl ₄ (7)	Brown	54	37.28 (37.45)	2.54 (2.70)	13.18 (13.20)	Co: 4.23 (4.27) Ni: 8.80 (8.51)	Co: 6.95; 7.62 Ni: 7.51; 8.26
[Co(III)(L) ₂ (BF ₂) ₂ PyCd ₂ Cl]Cl ₄ (8)	Dark brown	36	33.61 (33.76)	2.27 (2.28)	12.63 (12.48)	Co: 4.10 (4.04) Cd: 15.30 (15.41)	Co: 6.95; 7.62 Cd: 23.13; 16.16; 26.68
[Co(III)(L) ₂ (BF ₂) ₂ Py(CH ₃) ₂ Cd ₂ Cl]Cl ₄ (9)	Dark reddish-brown	47	34.77 (34.74)	2.42 (2.51)	12.13 (12.25)	Co: 3.78 (3.96) Cd: 15.07 (15.12)	Co: 6.95; 7.62 Cd: 23.13; 16.16; 26.68

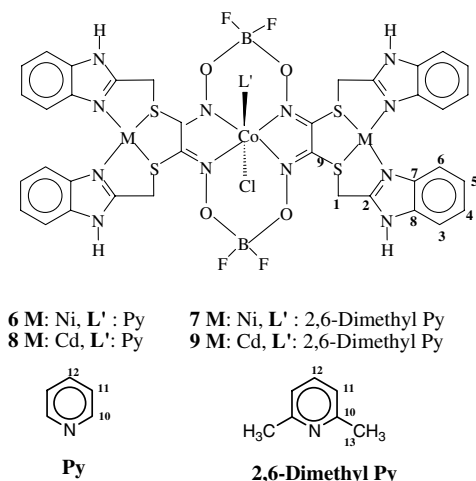


Fig. 6. Chemical structures of trinuclear $[\text{Co(III)(L)}_2(\text{BF}_2)_2(\text{L}_0)\text{M}_2\text{Cl}]\text{Cl}_4$ complexes (6) and (7).

respectively. Finally, elemental analysis and quantitative EDXRF results of (6) and (7) support the trinuclear $[\text{Co(III)(L)}_2(\text{BF}_2)_2(\text{L}')\text{Ni}_2\text{Cl}]\text{Cl}_4$ structure, as well (Table 3).

Since Cd(II) has closed shell with the d^{10} ionic structure, which gives tetrahedral complexes with the N_2S_2 cores of the molecule, ^1H and ^{13}C NMR spectra of its trinuclear complexes (8) and (9) have been recorded. In the ^1H NMR spectrum of (8) the deuterium exchangeable singlet at $\delta = 7.90$ is attributed to NH proton of imidazole ring. There is a little up field shift when the chemical shift values of NH groups of (4) and (8) are compared. However, there is no significant differences in the infrared spectra of (4) and (8) from the aspect of the NH stretching vibrations appeared at 3438 and 3436, respectively. The little up field shift in the ^1H NMR of (8) is due to withdrawing of the imidazole ring electrons by the cadmium ion. These results exhibit that nitrogen atom of $\text{C}=\text{N}$ group in the imidazole ring system is used in the formation of trinuclear Cd(II) complexes (8). The mass spectra of (8) also support to the structure with the $m/z = 1336$ $[\text{M}^+ + \text{H}_2\text{O} + 1]$ value. There are no differences between the chemical shift values of NH groups of the mononuclear complex (5) and the trinuclear complex (9). The NH groups show up at 7.92 ppm for both compounds (5) and (9). In the IR spectrum of (9), there is no also significant difference when it compares with the IR spectrum of (5). However, the mass spectrum (FAB) for (9) is in good agreement with the trinuclear structure having $m/z = 1345$ $[\text{M}^+]$ value. On the other hand, elemental analysis and qualitative and quantitative EDXRF results (Table 3) support to the trinuclear structure of (9) (Fig. 5).

^{13}C NMR spectra of (8) and (9) have been able to record due to the electronic structure of Cd(II). The ^{13}C NMR values of (8) and (9) listed in Table 4 contribute to the structure of complexes.

EDXRF technique was used for quantitative determination of metal amount of the prepared complexes. Standard calibration method was performed for quantitative determi-

Table 4
The ^{13}C NMR spectra data for (8) and (9)

Compound (8)		Compound (9)	
Carbons	δ (ppm)	Carbons	δ (ppm)
C ₁	27.38	C ₁	27.51
C ₂	141.57	C ₂	142.02
C ₃	114.48	C ₃	114.32
C ₄	115.22	C ₄	115.22
C ₅	122.93	C ₅	122.95
C ₆	123.25	C ₆	123.20
C ₇ –C ₈	234.72	C ₇ –C ₈	134.70
C ₉	148.50	C ₉	148.63
C ₁₀	130.45	C ₁₀	130.43
C ₁₁	128.20	C ₁₁	127.89
C ₁₂	128.63	C ₁₂	128.51
		C ₁₃	33.90

nation. To prepare standards in the determination range, related metal salt ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ for Co, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ for Ni and $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ for Cd) were mixed with a certain amount of natural starch. The starch was chosen due not to cause any absorption in the EDXRF spectra. The obtained calibration graphics by using prepared standards are shown in Fig. 2. Characteristic K_α peak areas of the metal atoms were plotted against the percentage concentrations on the graphics. The peak areas were calculated by using the Nucleus PCA-KLM software. For normalization, K_α peak areas of the standards and samples divided by related Compton peak areas. The metal amounts in the mononuclear and trinuclear complexes were extracted as percentage for each calculated K_α peak areas of the samples by using the standard calibration graphics.

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