



(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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tioether 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-dioximate 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 heterotrinnuclear complexes, bearing Cd(II), Ni(II), and BF_2^+ bridges by using bis [*S,S'*-bis (2-benzimidazolylmethyl)

dithio glyoximate] 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

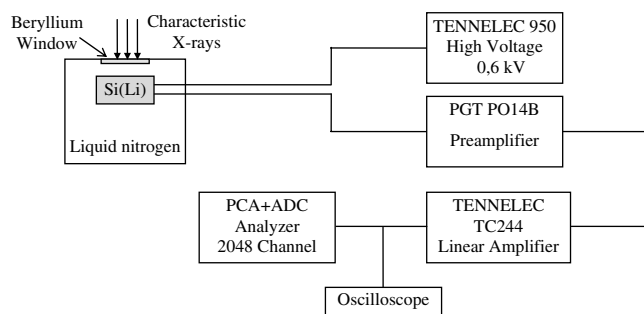


Fig. 1. The block diagram of the counting system.

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