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# Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: [www.elsevier.com/locate/saa](http://www.elsevier.com/locate/saa)

## Development of a C<sub>3</sub>-symmetric benzohydroxamate tripod: Trimetallic complexation with Fe(III), Cr(III) and Al(III)

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### ARTICLE INFO

#### Article history:

Received 14 July 2015

Received in revised form 26 January 2016

Accepted 28 February 2016

Available online 2 March 2016

#### Keywords:

Spectrophotometric

Potentiometric

Hydroxamate

Formation constants

Protonation constants

### ABSTRACT

The design, synthesis and physicochemical characterization of a C<sub>3</sub>-symmetry Benzene-1,3,5-tricarboxylhydroxamate tripod, noted here as BTHA, are described. The chelator was built from a benzene as an anchor, symmetrically extended by three hydroxamate as ligating moieties, each bearing O, O donor sites. A combination of absorption spectrophotometry, potentiometry and theoretical investigations are used to explore the complexation behavior of the ligand with some trivalent metal ions: Fe(III), Cr(III), and Al(III). Three protonation constants were calculated for the ligand in a pH range of 2–11 in a highly aqueous medium (9:1 H<sub>2</sub>O: DMSO). A high rigidity in the molecular structure restricts the formation of 1:1 (M/L) metal encapsulation but shows a high binding efficiency for a 3:1 metal ligand stoichiometry giving formation constant (in β unit) 28.73, 26.13 and 19.69 for [M<sub>3</sub>L]; M=Fe(III), Al(III) and Cr(III) respectively, and may be considered as an efficient Fe-carrier. The spectrophotometric study reveals of interesting electronic transitions occurred during the complexation. BTHA exhibits a peak at 238 nm in acidic pH and with the increase of pH, a new peak appeared at 270 nm. A substantial shifting in both of the peaks in presence of the metal ions implicates a s coordination between ligand and metal ions. Moreover, complexation of BTHA with iron shows three distinct colors, violet, reddish orange and yellow in different pH, enables the ligand to be considered for the use as colorimetric sensor.

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### 1. Introduction

Hydroxamic acids, R<sub>1</sub>C(O)N(R<sub>2</sub>)OH, where R<sub>1</sub> = alkyl/aryl and R<sub>2</sub> = alkyl/aryl or H are ubiquitously known ligands in coordination chemistry for their high binding affinity for wide range of transition metal ions, and have received much attention in biological, analytical, chemical, medical and industrial field offering broad applications, particularly as clinical iron removing agents [1–3]. They form stable chelates with various metal ions attributing to their inhibitory action against enzymes having metalloprotein as their functional group [2–4]. The solutions of these organic molecules produce intense color complexes contributing widely in analytical chemistry as well as spectrophotometry for determination of metals [5–7]. Moreover, a significant adsorption of metals (mainly iron) by hydroxamate may play a beneficial role in recovery of metals from ground/waste water. Such as, excess metals dissolved in water caused toxic concentration as in acid mine drainage, posing multiple health problems such as high accumulation of iron in body, causing hemochromatosis [8]. Moreover, Al(III) a non-essential element, is involved in causing dialysis dementia in patients and

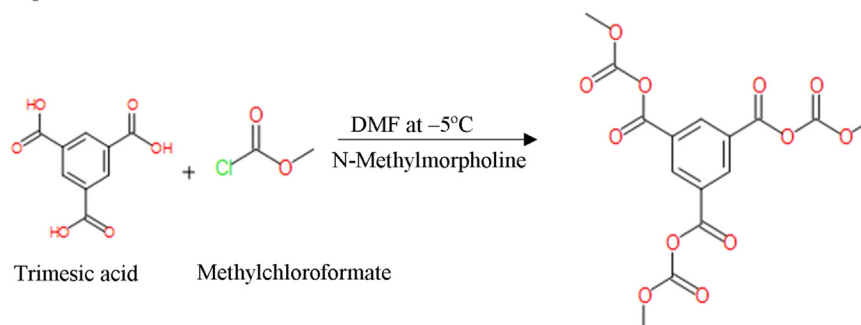
affecting the central nervous system that causes different disorders such as amyotrophic lateral sclerosis [9–10]. The only approved drug, desferrioxamine B (iron chelator) for hemochromatosis is posing several drawbacks and side effects [11]. Although Cr<sup>+3</sup> is absorbed by biological system, still, a high instance of occupational exposure to this trivalent metal pertained with respiratory problems like coughing, wheezing and dyspnea. Dermal exposure to chromium has also been demonstrated to produce irritant and allergic contact dermatitis [12]. Moreover, industrial effluents also have high concentration of dissolved chromium which causes chromium toxicity in nearby water resources. So, to deal with such situations, some molecules are under necessity to reduce overload of Fe(III), Cr(III) and Al(III) ions in an eco-friendly manner.

Despite of ongoing several researches for elucidating hydroxamate behavior, they remain poorly characterized. Possibilities of several conformations depending on concentration, temperature and the nature of the solvent attributes to the biggest challenge in hydroxamic acid characterization. A detailed comparative study is thus required to evaluate the capability of the ligand to serve as a potential chelator. High stability constants of hydroxamic acids with transition metal ions can be considered as an important tool for elucidating chelating (polarizing) power of the ligands. The preferential binding mode in the metal hydroxamic acid complexes is through O, O (bidentate) donors in which

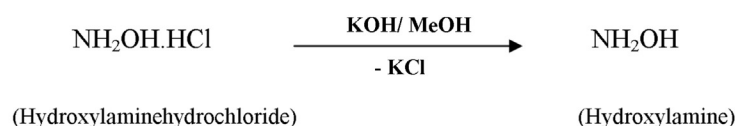
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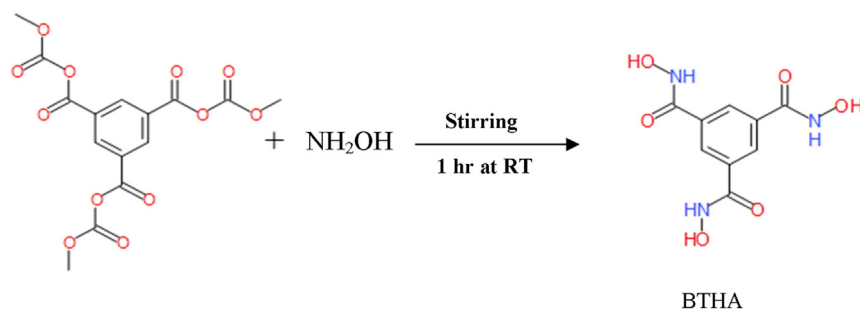
Step 1:



Step 2:



Step 3:



**Scheme 1.** Schematic representation of synthesis of tripodal ligand BTHA.

the ligand is either monobasic (hydroxamate) or dibasic (hydroximato) [13–15].

Hard metals with higher oxidation states preferentially form more stable hydroxamate complexes. Benzohydroxamic acid (Bha), acetohydroxamic acid (Aha), salicylhydroxamic acid and desferrixomine family (derived from *Streptomyces* species) are few hydroxamic acids dominating the coordination chemistry and chemical biology. The Bha is extensively used as an excellent spectrophotometric reagent for determination of metal ions such as Fe, Mo, V, U, and Mn, and could be served as a potential colorimetric reagent [16]. Synthesis and studies of a number of mono benzohydroxamates with various divalent and trivalent metal ions have been documented [17–18]. Trimesic acid coated alumina has been reported as a potent adsorbent for iron [8]. Considering the implications of Bha in analytical chemistry, there arises a burgeoning interest in increasing the substitution and exploring the coordination behavior in relation with the enhanced metal selectivity, efficiency and affectivity.

However, realizing the efficiency of hydroxamic acids as an efficient metal binder, it was thought for a higher substitution on benzohydroxamate which may offer an increased metal chelation in quantity, hence may be served as a potential metal scavenger. Keeping in view of the above, in the present communication we describe the development and complexation studies of a multidentate polyfunctional benzene-1,3,5-tricarbonylhydroxamic acid (BTHA). The potentiometric

and spectrophotometric studies also explore the coordination behavior of the ligand with Fe, Al, and Cr trivalent metal ions in highly aqueous medium,  $\text{H}_2\text{O}:\text{DMSO} = 9:1$ . Due to a rigid molecular framework and the coordination ability of three equally spaced hydroxamate groups, BTHA can serve as a strong metal-chelator and may find its use as a potent in applications in the areas such as acid mine drainage carrying excess dissolved iron at low pH.

## 2. Experimental

### 2.1. Materials and measurements

Ultrapure grade reagents such as trimesic acid, methylchloroformate, and N-methylmorpholine were purchased from Sigma Aldrich for the synthesis as well as titration purposes and used directly without further purification unless otherwise mentioned. Analytical grade solvents: dimethylformamide, methanol, tetrahydrofuran and dimethylsulphoxide were purchased from Qualigens and SD Fine Chemicals Limited and distilled over appropriate drying agents as per standard procedures prior to use. Melting points were determined on MICROSIL digital melting point apparatus and were uncorrected.

The progress of the reaction and the purity were monitored by thin layer chromatography (TLC), performed on silica gel glass plates using 8:2 hexane and ethylacetate mixture and were visualized in iodine

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