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# **Synthesis and structural characterizations of chromium(III)–thiamine chelation: Eco-friendly procedure for preparation of nanometric Cr<sub>2</sub>O<sub>3</sub> by bio-precursor at elevated temperature**

*Mohammed Alsawat*

*Department of Chemistry, Faculty of Science, Taif University, Al-Haweiah, P.O. Box 888, Zip Code 21974, Taif, Saudi Arabia  
Email: mosawat@tu.edu.sa; dr.alsawat@gmail.com*

## **Abstract**

Synthesis, spectral assignments, and magnetic susceptibility of a new chromium(III) complex were described. This complex was prepared via the reaction of chromium chloride (CrCl<sub>3</sub>·6H<sub>2</sub>O) with thiamine hydrochloride (thiOH·HCl) in an alkaline media to afford the new complex [Cr(thiO)<sub>2</sub>(Cl)(H<sub>2</sub>O)]·4H<sub>2</sub>O in which thiO<sup>-</sup> is a deprotonated hydroxyl group in the thiamine chelate. The Cr(III) complex was characterized by molar conductance, infrared (IR) and electronic spectroscopic methods, magnetic moment, X-ray diffraction (XRD), and elemental analysis. The magnetic moment for the complex was equal to 3.87 B.M. with an octahedral environment around the chromium atom. The synthesized Cr(III) complex was used as a suitable eco-friendly bio-precursor for the preparation of Cr<sub>2</sub>O<sub>3</sub> nanoparticles via the calcination method at annealed temperature of 800 °C. IR spectroscopy, powder XRD, transmission electron microscopy (TEM), and energy-dispersive X-ray (EDX) techniques were used to characterize the solid Cr<sub>2</sub>O<sub>3</sub> product. TEM and XRD results showed that the resulting Cr<sub>2</sub>O<sub>3</sub> nanoparticles had a high degree of crystallinity with an average size of 30 nm.

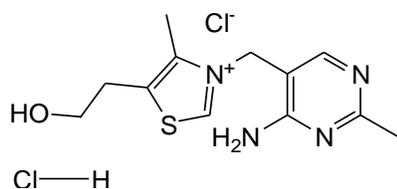
**Keywords:** thiamine hydrochloride; complex; nanoparticles; calcination; EDX; XRD.

## **1. INTRODUCTION**

Thiamine hydrochloride (thiOH·HCl) is an eco-friendly, inexpensive, non-toxic, stable chemical compound. Its chemical structure is given in [Figure 1](#), which indicates that it includes thiazole and a pyrimidine rings attached via a methylene bridge. Thiamine is a member of a wider group of

water-soluble nutrients and is commonly known as vitamin B1. The human body cannot synthesis vitamin B1, so it must be acquired through dietary sources [1]. Thiamine and its compounds have an essential role in many biological systems and as a coenzyme for many enzymes, such as like transketolase and carboxylase, which catalyze the formation

of  $\alpha$ -ketols or the decarboxylation of  $\alpha$ -ketoacids [2,3]. Malandrinoset *al.*[4] did a detailed study of the mechanism of thiamine enzymatic actions in the presence of bivalent metal ions. In the literature, several thiamine complexes generated with bivalent metals as ionic salts of the types  $[\text{ThH}]^{2+}[\text{MX}_4]^{2-}$  (M: Zn, Co, Cd or Hg) have been reported [5–8] and include  $[\text{ThH}]^{2+}([\text{MX}_3])_2$  (M: Pt or Pd) [9] and  $([\text{Th}]^+)_2[\text{MX}_4]^{2-}$  (M: Pt or Pd) [9–11], which do not have direct metal-ligand bonding. Th was assigned to the positive charge location on the thiamine molecule and facilitates protonation of the  $\text{NH}_2$  in the pyrimidine ring [12]. Hadjiladis *et al.*[9] reported that the thiamine molecule formed metal complexes with Pd(II) and Pt(II) ions through a M-S linkage. Hu *et al.*[13] reported that organic–inorganic hybrid compounds were formed from the interaction of the polymeric halogen cadmate anions with the thiaminium cation. Synthesis of nanoparticles using sustainable synthetic methods provide benign alternatives to removing or reducing the production and use of the hazardous chemicals and substances. Wine phenols, tea, vitamin C, and vitamins B2 and B1 act as both capping and reducing agents [14–17]. These compounds offer extremely simple one-pot green synthetic approaches for producing bulk quantities of metal nanoplates, nanoballs, aligned nanobelts, nanowires, nanorods, and nanospheres in water without the need for large amounts of insoluble templates [14–19]. Considerable attention has been focused on the preparation of metal oxides in the nanoscale range due to their unusual properties and potential applications in magnetic, catalytic, and electronic materials [20, 21]. Several techniques, such as thermal decomposition, alcohol reduction, micro-emulsion, solvent extraction, and photolytic, have been reported for the preparation of nanostructured metal oxides [22–27]. Recently, chromium sesquioxide ( $\text{Cr}_2\text{O}_3$ ), which is an important technological material, has attracted much interest due to its properties and applications such as catalysis, humidity sensing, and advanced colorant [28–30]. Based on the interesting properties of thiamine metal complexes, two results are reported: (1) the synthesis and spectral characterization of a new Cr(III)–thiamine complex using conductance, magnetic moment, IR, and electronic spectroscopy, powder XRD, and elemental analysis techniques and (2) the decomposition of the synthesized Cr(III) complex at 800 °C to produce a high-quality nanostructured  $\text{Cr}_2\text{O}_3$ , which was characterized by IR, powder XRD, TEM, and EDX physical methods.

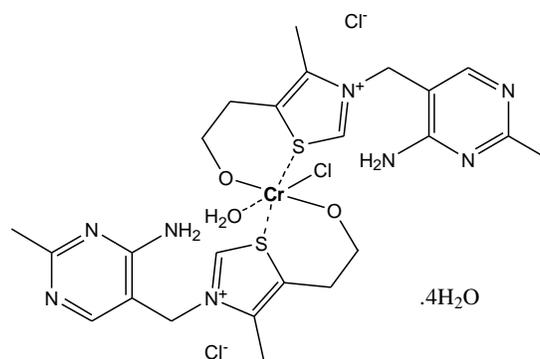


**Figure 1.** Chemical structure of thiOH·HCl.

## 2. EXPERIMENTAL/MATERIALS AND METHODS

### 2.1. Chemicals and Preparations

All chemicals used in this work were Sigma-Aldrich (USA) Chemical Company products and were of analytical grades reagents. Synthesis of the Cr(III) thiamine complex was performed as follows: A 25 mL methanolic solution containing one mmole of Cr(III) chloride hexahydrate was mixed well with a 25 mL methanolic solution containing two mmole of thiamine hydrochloride (thiOH·HCl). The mixture solution was adjusted at pH = 8, filtered to remove any solids, and then heated at reflux (65° C) for 3 hours. The resulted leaf green precipitate of  $[\text{Cr}(\text{thiO})_2(\text{Cl})(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$  was collected by filtration and washed several times with methanol. Elemental analysis results for the product;  $\text{C}_{24}\text{H}_{42}\text{Cl}_3\text{CrN}_8\text{O}_7\text{S}_2$  (yield 78%); Found: C, 36.97; H, 5.38; N, 14.31; Cr, 6.60%. Cal.: C, 37.09; H, 5.45; N, 14.42; Cr, 6.69%. **Figure 1** showed the proposed chemical structure of the product. Preparation of the  $\text{Cr}_2\text{O}_3$  nanoparticles was performed as follows: the  $[\text{Cr}(\text{thiO})_2(\text{Cl})(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$  complex was annealed at 800° C in air for 3 hours, and then the resulted oxide was left to cool at room temperature to form the green  $\text{Cr}_2\text{O}_3$  nanoparticles.



**Figure 2.** Proposed chemical structure of  $[\text{Cr}(\text{thiO})_2(\text{Cl})(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$  complex.

### 2.2. Measurements

A Magnetic Susceptibility Balance model (Sherwood Scientific, Cambridge Science Park Cambridge, England) was used to calculate the magnetic data at room temperature. A Bruker FT-IR Spectrophotometer ( $4000\text{--}400\text{ cm}^{-1}$ ) was applied to record the IR spectra, where the electronic spectra were recorded with a UV2 Unicam UV/Vis Spectrophotometer. A Jenway 4010 conductivity meter was used to determine the molar conductivity of freshly prepared solutions with concentrations of  $1.0 \times 10^{-3}\text{ M}$  in DMSO, where contents in (%) of nitrogen, hydrogen and carbon were collected with a Perkin Elmer CHN 2400. A X'Pert PRO PANalytical with copper target was applied to scan the XRD spectrum of the prepared  $\text{Cr}_2\text{O}_3$  nanoparticles, where the transmission electron microscopy (TEM) images of these particles were pictured with a JEOL 100s microscopy equipment.

### 3. RESULTS AND DISCUSSION

#### 3.1. Molar conductance data and magnetic susceptibility

The obtained elemental data of the Cr(III) complex were in good consistent with the proposed formula. The probable structure for the Cr(III) complex, according to the elemental data; it suggests the presence of the neutral structure for the  $[\text{Cr}(\text{thiO})_2(\text{Cl})(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$  complex. The magnetic moment value ( $\mu_{\text{eff}}$ ) of the complex is equal to 3.87 B.M, and this value was close to the predicted value for three unpaired electrons in the metal ion, and suggests the octahedral geometry for the synthesized Cr(III) complex [31]. Molar conductivity was performed to observe the geometrical structure of the prepared Cr(III) complex. The molar conductance ( $\Lambda_M$ ) of the complex dissolved in DMSO ( $1 \times 10^{-3}$  M) was obtained, and the value was equal to  $18 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  in consistent with a non-electrolyte property [32]. This outcome proposed that the synthesized Cr(III) complex behaves as a 1:2 non-electrolyte having one chloride ion inside the coordination sphere.

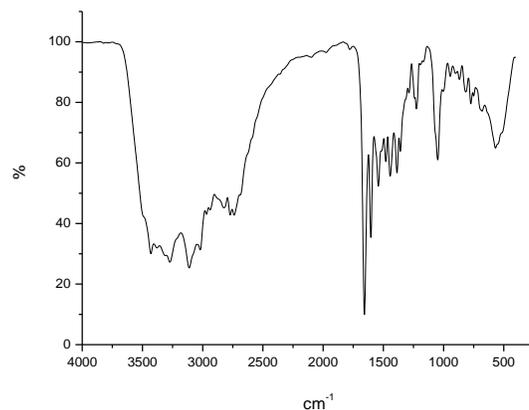
#### 3.2. Electronic and IR spectra of the Cr(III) complex

The electronic spectrum of the Cr(III) complex in DMSO solution exhibited intra-ligand transitions in the UV-region and d-d transitions in the visible region [32]. The  $d^3$  Cr(III) ion in agreement with an octahedral geometry is expected to have three absorption bands due to the electron transitions from  ${}^4A_{2g}$  as the electronic ground state, and to the  ${}^4T_{2g}$ ,  ${}^4T_{1g}(\text{F})$  and  ${}^4T_{1g}(\text{P})$  as the excited states. The d-d bands generating from  ${}^4A_{2g} \rightarrow {}^4T_{1g}(\text{P})$  fall in the in the UV region, and from  ${}^4A_{2g} \rightarrow {}^4T_{1g}(\text{F})$  and  ${}^4A_{2g} \rightarrow {}^4T_{2g}$ , found in the visible region [32]. The Cr(III) complex had an octahedral geometry with a lower symmetry than normal octahedral. Therefore, the splitting of the orbitally degenerate terms could be possible. Accordingly, the lower symmetry of the Cr(III) complex led to the observation of three bands in the UV-Vis spectrum at 275, 285 and 392 nm. The assignments of IR spectrum of the free thiamine HCl chelate (Table 1) included some characteristic bands for the stretching vibration motions of ethyl alcoholic group ( $-\text{CH}_2-\text{OH}$ ) at  $1066 \text{ cm}^{-1}$ ,  $(685, 699, 752) \text{ cm}^{-1}$ ,  $(1247, 1287, 1380) \text{ cm}^{-1}$ , and  $3630 \text{ cm}^{-1}$  which were attributed to the  $\nu(\text{C}-\text{O})$ , out-of-plane bending, in-plane bending, and  $\nu(\text{O}-\text{H})$  vibrations, respectively [33]. Bands observed at  $(1031, 1044) \text{ cm}^{-1}$ ,  $1650 \text{ cm}^{-1}$ ,  $3266 \text{ cm}^{-1}$ , and  $(3431, 3497) \text{ cm}^{-1}$  were attributed to the  $\nu(\text{C}-\text{N})$ ,  $\delta(\text{NH}_2)$ ,  $\nu_s(\text{N}-\text{H})$  and  $\nu_{\text{as}}(\text{N}-\text{H})$  vibrations of amino group ( $-\text{NH}_2$ ), respectively [33]. The stretching vibration bands of  $\nu(\text{C}-\text{S})$ ,  $\nu(\text{C}=\text{C})$ , and  $\nu(\text{C}=\text{N})$  were located at  $773 \text{ cm}^{-1}$ ,  $1464 \text{ cm}^{-1}$  and  $(1660, 1607, 1544) \text{ cm}^{-1}$ , respectively [32]. Regarding the IR spectrum of the  $[\text{Cr}(\text{thiO})_2(\text{Cl})(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$  complex (Figure 3 and Table 1), the stretching vibration bands due to the  $\nu(\text{C}-\text{O})$  and  $\nu(\text{O}-\text{H})$  of hydroxyl group were no longer observed. The stretching and bending vibration motions of the  $-\text{NH}_2$  group;  $\nu_{\text{as}}(\text{N}-\text{H})$ ,  $\nu_s(\text{N}-\text{H})$ ,  $\delta(\text{NH}_2)$  and  $\nu(\text{C}-\text{N})$  were unshifted, suggests that the  $-\text{NH}_2$  group didn't participated in the coordination with Cr(III) ion. The vibration band due to the  $\nu(\text{C}-\text{S})$  vibration of thiazole ring was not observed in IR spectrum of the

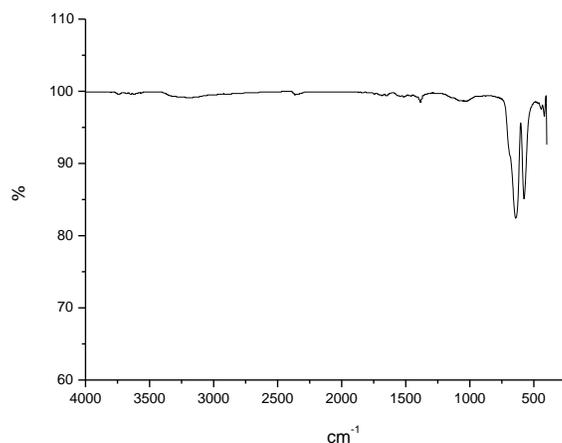
complex, suggests that the C-S participated in the celeration process. The new vibration bands appeared at  $679$  and  $565 \text{ cm}^{-1}$  are due to the  $\nu(\text{Cr}-\text{O})$  vibrations [33]. These results confirmed that the coordination occurs between Cr(III) metal ion and thiamine through oxygen and sulfur atoms of hydroxyl group and thiazole ring.

#### 3.3. IR spectrum of the $\text{Cr}_2\text{O}_3$ material

The thermal decomposition of the  $[\text{Cr}(\text{thiO})_2(\text{Cl})(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$  complex at  $800^\circ \text{C}$  led to the production of nanostructured  $\text{Cr}_2\text{O}_3$ . The IR spectrum of  $\text{Cr}_2\text{O}_3$  nanoparticles is shown in Figure 4. The weak broad absorption bands appeared at  $3190$ ,  $1670$  and  $1045 \text{ cm}^{-1}$  in the IR spectrum of the complex were resulted from the bending and stretching vibrations of the water molecules absorbed by the samples. The stretching vibrations mode of Cr-O exhibited two strong bands at  $640$  and  $580 \text{ cm}^{-1}$ .



**Figure 3.** IR spectrum of the  $[\text{Cr}(\text{thiO})_2(\text{Cl})(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$  complex.



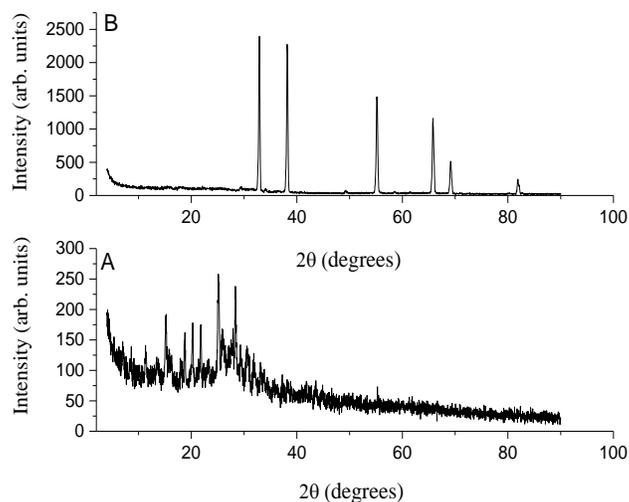
**Figure 4.** IR spectrum of  $\text{Cr}_2\text{O}_3$ .

**Table 1.** IR band assignments of free thiOH·HCl and [Cr(thiO)<sub>2</sub>(Cl)(H<sub>2</sub>O)]·4H<sub>2</sub>O complex.

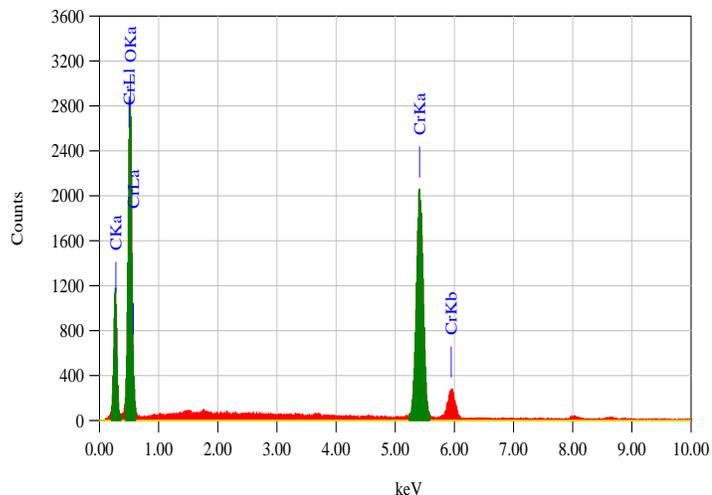
thiOH·HCl	[Cr(thiO) <sub>2</sub> (Cl)(H <sub>2</sub> O)]·4H <sub>2</sub> O	Assignments
3630 1380, 1287, 1249 752, 699, 685 1066	-- 1385, 1224 -- --	$\nu(\text{O-H})$ ; alcoholic group -OH; in-plane bending -OH; out-of-plane bending $\nu(\text{C-O})$
3497, 3431 3266 1650 1044, 1031	3434 3275 1658 1055	$\nu_{\text{asym.}}(\text{NH})$ ; NH <sub>2</sub> $\nu_{\text{sym.}}(\text{NH})$ ; NH <sub>2</sub> $\delta(\text{NH}_2)$ $\nu(\text{C-N})$
1660, 1607, 1544, 1464	1604, 1544	$\nu(\text{C=C}) + \nu(\text{C=N})$
773	--	$\nu(\text{C-S})$
--	679, 565	$\nu(\text{Cr-O})$

### 3.4. XRD patterns, EDX and TEM of the Cr<sub>2</sub>O<sub>3</sub> material

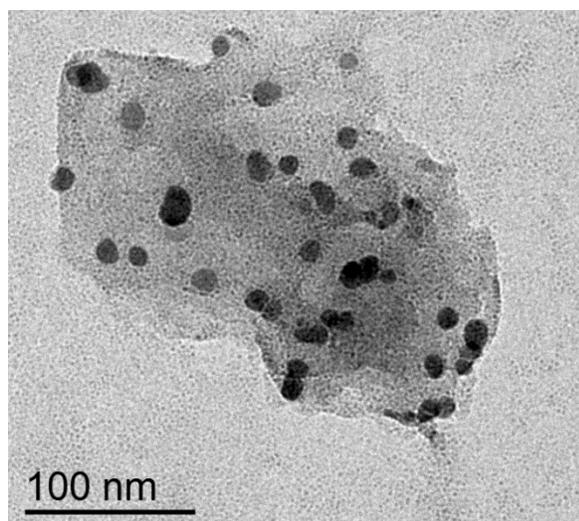
The XRD profiles of the synthesized [Cr(thiO)<sub>2</sub>(Cl)(H<sub>2</sub>O)]·4H<sub>2</sub>O and Cr<sub>2</sub>O<sub>3</sub> are shown in Figure 5. The XRD patterns of the [Cr(thiO)<sub>2</sub>(Cl)(H<sub>2</sub>O)]·4H<sub>2</sub>O complex (Figure 5A) indicated the amorphous nature of the complex. The XRD patterns of Cr<sub>2</sub>O<sub>3</sub> showed the reflection planes (220), (300), (214), (116), (024), (110), (104), and (012) at  $2\theta$  82, 69, 66, 55, 49, 38, 32 and 25, respectively, which indicate the presence of the rhombohedral structure [35]. The Debye-Scherrer's formula ( $D = 0.9\lambda/\beta\cos\theta$ ) was used to calculate the average crystallite diameter ( $D$ ) for Cr<sub>2</sub>O<sub>3</sub> in nanometer, where  $\theta$  is the Bragg angle,  $\beta$  is the line sharpness at half the maximum intensity in radians, and  $\lambda$  is the X-ray wavelength. The calculated average crystallite for Cr<sub>2</sub>O<sub>3</sub> was found to be ~29 nm. To investigate the atomic percentage of the Cr<sub>2</sub>O<sub>3</sub> nanoparticles, the chemical composition was checked by energy dispersive X-ray diffractograms (EDX), and the obtained spectrum is shown in Figure 6. The results show the presence of elements Cr and O, and it confirms the successful synthesis of nanostructure Cr<sub>2</sub>O<sub>3</sub> material. The TEM image of Cr<sub>2</sub>O<sub>3</sub> material synthesized at 800° C revealed the formation of spherical shape particles with nearly uniform morphology, small agglomeration, and an average diameter of ~30 nm (Figure 7).



**Figure 5.** XRD spectra of the synthesized [Cr(thiO)<sub>2</sub>(Cl)(H<sub>2</sub>O)]·4H<sub>2</sub>O complex (A) and Cr<sub>2</sub>O<sub>3</sub> nanoparticles (B).



**Figure 6.** EDX spectrum of the synthesized  $\text{Cr}_2\text{O}_3$  nanoparticles.



**Figure 7.** TEM image of  $\text{Cr}_2\text{O}_3$  nanoparticles.

#### 4. CONCLUSION

A new metal complex containing Cr(III) ion and thiamine;  $[\text{Cr}(\text{thiO})_2(\text{Cl})(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$  was synthesized and characterized by physicochemical and spectroscopic techniques. The direct thermal decomposition of this complex leads to a  $\text{Cr}_2\text{O}_3$  material that had a high degree of crystallinity, rhombohedral structure, and their particles nanoscale-sized ( $\sim 30$  nm).

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