Synthesis, Characterization, and Thermal Analysis of Two Polymeric Chromium Ternary Complexes with Nitrilotriacetic Acid and Alanine or Glycine

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ABSTRACT: Two chromium ternary complexes with nitrilotriacetic acid as a primary ligand and alanine or glycine as secondary ligand were prepared in slightly acidic medium. The structure of these two complexes was characterized using elemental, thermal analysis, FTIR spectra, and the two complexes mass spectra. The spectroscopy data suggest that these two complexes were in polymeric form and have the monomeric unit $H[Cr(HNTA)(Hala)(SO_4)]$ and $H[Cr(HNTA)(Gly)(SO_4)]$ in which sulfate group act as a bidentate ligand linked between each monomeric unit for the same complex. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 1976–1980, 2012

Key words: chromium; ternary complex; nitrilotriacetic acid; alanine; glycine

INTRODUCTION

Polymers of amino acid compounds have found wide application in a number of area such as photo resistance, coatings, and antibodies.[1–4] Besides possessing good thermal properties. These polymers also exhibit variability of electro conductivity due to one free amino group per repeat unit on the polymers and potentially wide applicability.[5–13] These compounds have emerged as a new generation materials with tremendous potentials in fields like superconductivity and heat stability material.[14]

Chromium, which is an abundant element in the earth crust, has many applications in both industrial and pharmaceutical fields. It is used in industry for plating and in chrome steels, ceramics, catalysis, and many other applications.[15–19] It is also present in many pharmaceutical products due to its ability to stabilize blood sugar level.[20] For these reasons many scientists keep trying to prepare novel compounds that containing chromium, especially coordination compounds.[21–26]

Aminocarboxylate chelating agent (Nitrilotriacetic acid, for example) can be considered one of the most important ligands which we can use to prepare a coordination compound. Aminocarboxylate chelates strongly with most metals, this chelation change metal bioavailability and mobility in the environment.[27] These complexes may be used as laundry detergent builders, boiler scale inhibitors, in metal plating and cleaning operation, in textile manufacture, and in paper and cellulose production.[28,29]

Amino acid is one of the most important biological substances, therefore, the study of ternary complexes which containing amino acid as a secondary ligand was and is still one of the most interesting points of research because it reveals the role of the metal ion on the molecular level.[30–33]

In this work, preparation and characterization of new chromium ternary complexes with nitrilotriacetic acid glycine or alanine as secondary ligand are studied.

EXPERIMENTAL

General procedure for complexes preparation

Two solutions were prepared, the first contains 10^{-3} mole of the $Cr_2(SO_4)_3 \cdot 15 H_2O$ salt in 100 mL water and the second one containing a mixture of 10^{-3} mole of nitrilotriacetic acid and 10^{-3} mole of alanine (complex I) or glycine (complex II) in 100 mL water. The two solutions were mixed and heated nearly to boiling to ensure complete reaction. The solution was left on a water bath until the volume was reduced to about 50 mL. The solid complexes were obtained after heating by adding 96% ethanol, and then the solid complexes filtered off and washed several times with ethanol following by 1 mL of diethyl ether. The prepared complexes were kept in vacuum desiccator under silica gel.

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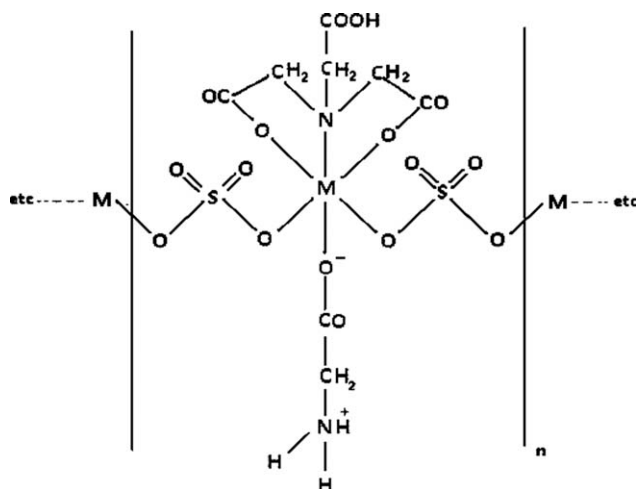
Figure 1 The proposed structure of the polymer complex.

Instrumentation

Elemental analysis of the prepared complexes were carried out on Vario Elementary instrument. The percentage of Cr was found by titration against EDTA. FTIR spectra of the solid complexes were recorded on Jasco FTIR-300 E Fourier transform infrared spectrometer, using KBr pellets over the range 4000–400 cm^{-1} and CsI pellets over the range 600–200 cm^{-1}. Thermogravimetric analysis of these prepared complexes under nitrogen atmosphere and at a heating rate 10°C min^{-1} were carried out using a Perkin–Elmer 7 series thermal analyzer. Magnetic susceptibilities of these paramagnetic chromium complexes were measured using a magnetic susceptibility balance Johnson Matthey, Alfa products; model No. MKI at room temperature. Mass spectra were recorded at 350°C and 70 eV on a GL/MS Finnegan mat SSQ 7000 apparatus.

Energy-dispersive X-ray spectroscopy (EDX analysis), The SEM/EDX data presented here were collected using the Hitachi S4500 field emission SEM (Nissei Sangyo, Ltd., Tokyo, Japan) equipped with a EDAX CDU LEAP Detector(EDAX, Mahwah, NJ) with a light element.

RESULTS AND DISCUSSION

The two prepared complexes were crystallized at pH about 2.8–4. At this pH range the predominating species are $HNTA^{2-}$ and Hala or Hgly in their zwitter form. At this pH, $HNTA^{2-}$ has three coordination sites (N and two COO^-) while Hala or Hgly coordinate in slightly acid medium via its carboxylic oxygen after being converted into the zwitter ion form (H_3N^+ CH_2COO^-). This means that under the reaction condition used in this study, the amino acids coordinated as monodentate ligand. Accordingly, the metal coordinates to six sites to form an octahedral structure, two oxygen of two half sulfate groups which coordinate to metals as bridged bidentate ligand.[34] The proposed structure of the polymer complex is shown in Figure 1.

Now, the two complexes should contain Cr^{3+}, $HNTA^{2-}$, SO_4^{2-}, and Hala or Hgly, this mean that this combination should have a net charge −1. We found that our complexes are slightly acidic due to protonated amine group of glycine or alanine (second ligand) which give weak effervescence with sodium carbonate salt. We can use FTIR spectra to explain the above suggestions. The free sulfate ion belongs to the high-symmetry point group T_d. Of the four fundamentals, only ν_3 and ν_4 are infrared active. If the symmetry of the ion is lowered by complex formation, the degenerate vibrations split and Raman-active appear in the infrared spectrum. The lowering of symmetry comes from different coordination modes as unidentate or bidentate metal complexes.[35]

In complex I, ν_1 appeared at 911 cm^{-1}, while ν_2 appeared at 412 cm^{-1}. ν_3 split into 1045, 1138, 1201 cm^{-1}, and also ν_4 split into 596, 616, 642 cm^{-1}. By the same way for complex II, ν_1 appeared at 911 cm^{-1}, ν_2 at 408 cm^{-1}, ν_3 at 1042,1129,1189 cm^{-1} and finally ν_4 at 607, 617, 644 cm^{-1}.

Now from these FTIR bands, we can conclude that the symmetry of SO_4^{2-} ion was reduced from T_d to C_{2v} which mean that each SO_4^{2-} group in these complexes forms a bridge bidentate ligand connecting to two chromium metal complexes[35] for each sulfate group. There are many bands in the FTIR spectra which support the suggested structure of the two

TABLE I
Characteristic FTIR Bands and *m/e* Values of the Mass Spectra Represent the Molecular Ion Peaks of the Prepared Complexes

Complex	ν_{NH}	ν_{OH}	ν_{COOH}	ν_{COOM}	ν_{M-O}	ν_{M-N}	*m/e*
H[Cr(HNTA)(Hala)(SO$_4$)]	3086	3372 (m,br)	1734 (vs)	1644 (s) 1514 (vs) 1392 (m)	399 (s)	507 (m)	422
H[Cr(HNTA)(Hgly)(SO$_4$)]	3103	3442 (m,br)	1744 (vs)	1546 (s) 1514 (m) 1463 (m)	408 (s)	497 (m)	410
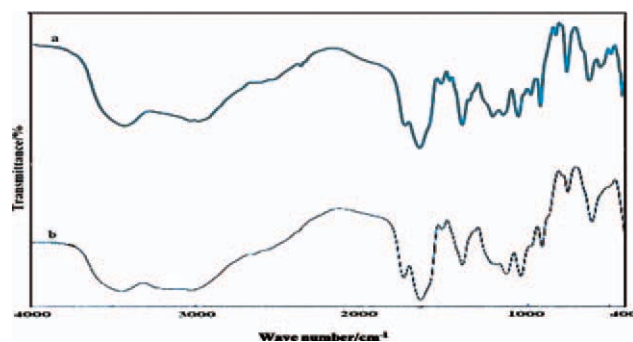
Figure 2 FTIR spectra of (a) H[Cr(HNTA)(Hala)(SO₄)] and (b) H[Cr(HNTA)(Hgly)(SO₄)]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

prepared complexes. In the beginning one can observe a band at 1734 cm⁻¹ (complex I), and 1744 cm⁻¹ (complex II) this band is also present in the spectra of the H₃NTA itself at 1730 cm⁻¹. This band is corresponding to the free carboxylic group. Another band which is not found on the spectra of the free H₃NTA spectra at 1644 cm⁻¹ (complex I), and 1546 cm⁻¹ (complex II) can be assigned to the stretching vibration $\nu(CO)$ of the coordinated carboxylate group, COOM also we found broad band at 3086 cm⁻¹ (complex I) and 3103 cm⁻¹ (complex II) which corresponding to free NH group.[36]

These bands support the assumption that H₃NTA at the pH used to prepare the two complexes acts as a tridentate ligand (one from nitrogen and two from dissociated carboxylate groups) and there is still one undissociated carboxylic group. The νMO frequencies of complex I and complex II is at 399 cm⁻¹ and 408 cm⁻¹ respectively. On the other hand the νMN frequencies of complex I and complex II is at 507 cm⁻¹ and 497 cm⁻¹ respectively. The important FTIR bands are presented in Table I and FTIR spectra are shown in Figure 2.

The empirical formula of the two complexes may be H[Cr(HNTA)(Hala)(SO₄)] and H[Cr(HNTA)(Hgly) (SO₄)] for complex I and complex II respectively. As more evidence that SO_4^{2-} ion group isn't counter ion by adding $0.1M$ BaCl₂ to complex I or complex II solution give no white precipitate indicating that there is no free SO_4^{2-} ion in the complex

solutions. The elemental analysis, physical and chemical properties of the two prepared complexes are found in Table II.

Thermal analysis

The thermogravimetric analysis (TGA) of the two complexes, Figure 3 were carried out under nitrogen atmosphere, Table III From literature the (TGA) curve for H₃NTA was suggested, its thermal decomposition gives glycine and maleic acid[37–40] while alanine[34] may decomposes into CO₂, NH₃, and H₂C=CH₂.
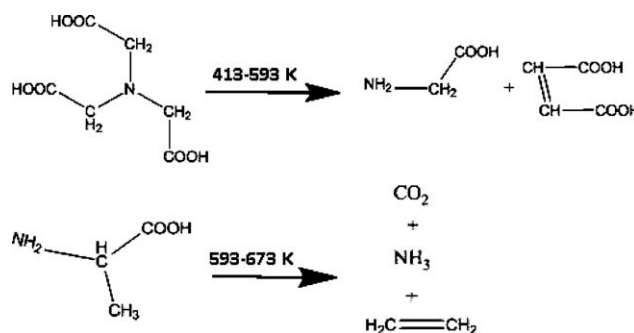
Complex I decomposed in two steps. At the first, the complex loss about 29.6% of its mass at temperature 417 K, this loss can be interpreted to the loss of one H₂S molecule, one NH₃ molecule from alanine and one glycine molecule come from the decomposition of H₃NTA. This result is agreement with the theoretical value 29.65%. The second mass loss is about 44.42% at temperature 574 K, one can interpret this loss as an overlapping between different organic compounds and gases coming from the decomposition of maleic acid (the remaining part of H₃NTA) and the remaining part of alanine, this loss is also in agreement with the theoretical value which is 44.24%. Finally, under these evolved reducing gases and as the analysis took place under nitrogen atmosphere a reducing reaction was happened in which the Cr^{3+} reduced to Cr^{2+} and also SO_4^{2-} reduced to SO_2^{2-} the leaving residue was Cr (SO₂).

TABLE II
Elemental Analysis, Physical and Chemical Properties of the Prepared Complexes

Complex	Calculated molar mass	Color	Elemental analysis Found (calculated) (%)				
			C	H	N	S	Cr
H[Cr(HNTA)(Hala)(SO₄)]	425	blue-viloet	25.74 (25.41)	4.45 (3.53)	6.14 (6.58)	6.31 (7.50)	12.20 (12.24)
H[Cr(HNTA)(Hgly)(SO₄)]	411	blue-viloet	22.68 (23.35)	4.31 (4.31)	6.64 (6.69)	6.60 (7.78)	12.44 (12.65)
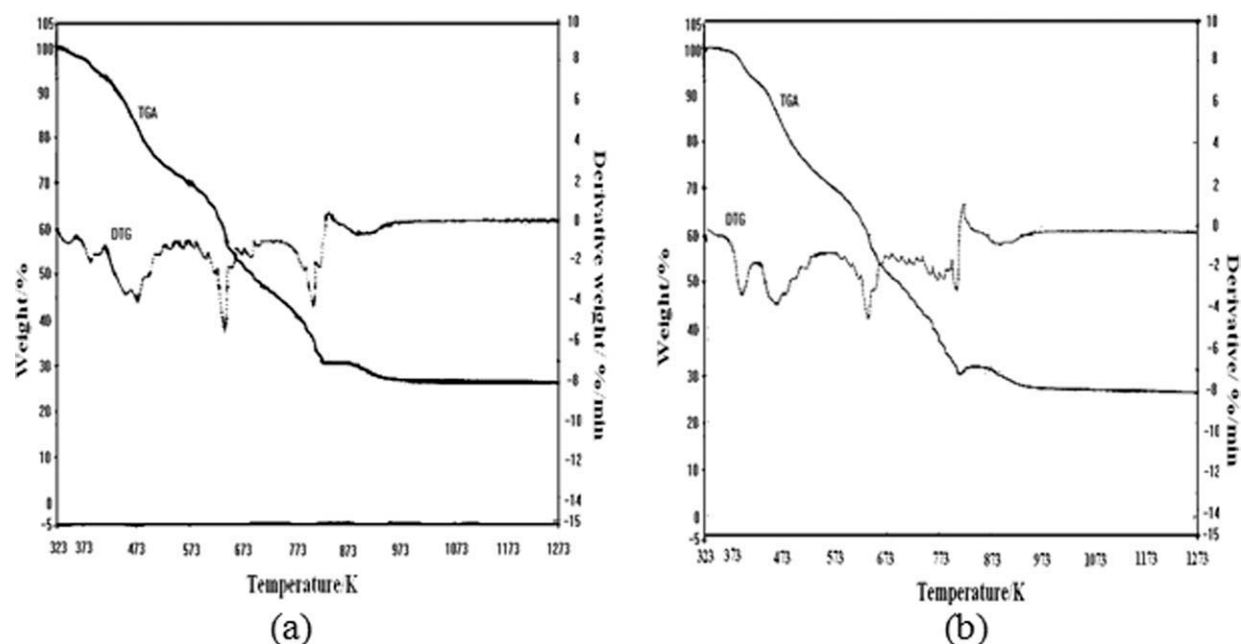
Figure 3 TGA and DTG of (a) H[Cr(HNTA)(Hala)(SO$_4$)] and (b) H[Cr(HNTA)(Hgly)(SO$_4$)].

H[Cr (HNTA) (Hala) (SO$_4$)]$_n$

↓ glycine + H$_2$S + NH$_3$

[Cr (Maleic acid) (Hala) (SO$_4$)]$_n$

↓ Maleic acid + H$_2$C══CH$_2$ + CO$_2$

[Cr (SO$_2$)]
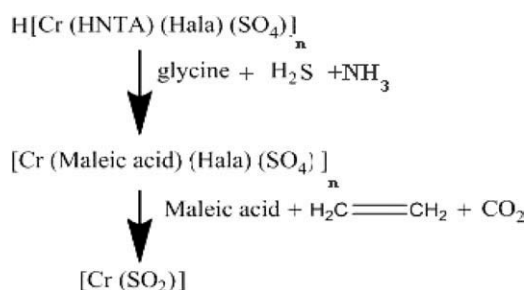
For complex II, nearly the same three mass losses were appeared. The first one is about 30.060% at temperature 427 K, which corresponds to three water molecules and one glycine molecule. The theoretical weight loss is 30.65%. The second one which is equal to 43.381% at temperature 571 K may correspond to the loss of one maleic acid molecule (the remaining part of H$_3$NTA) and the remaining part of glycine (methan gas and CO$_2$ gas). The theoretical value of this loss is 43.07%. For the same reasons which we mentioned above, the Cr^{3+} reduced

to Cr^{2+} and also SO$_4^{2-}$ reduced to SO$_2^{2-}$ the remaining residue was Cr (SO$_2$)

H[Cr (HNTA) (Hgly) (SO$_4$)]$_n$

↓ glycine + H$_2$S + NH$_3$

[Cr (Maleic acid) (Hgly) (SO$_4$)]$_n$

↓ Maleic acid + CH$_4$ + CO$_2$
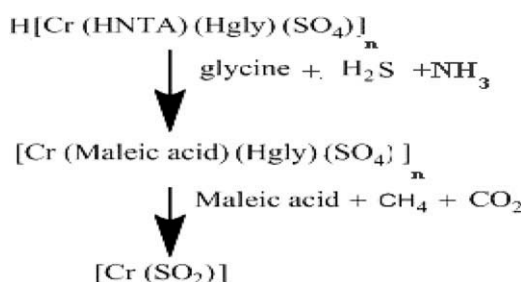
[Cr (SO$_2$)]

Energy-dispersive X-ray spectroscopy (EDX analysis) was used to prove the suggested chemical composition of the residue obtained from the TGA analysis. This analysis was in agreement with the Cr (SO$_2$)formula that we suggested. Figure 4 contains the EDX chart of the residue obtained from TGA analysis of complex I, and Figure 5 presented scanning electron microscope (SEM) of this residue.

TABLE III
Temperature Values for the Decomposition Along with the Species Lost in Each Step

Complex	Temperature (K)	Mass loss (%)		Significance
		Calculated	Found	
H[Cr(HNTA)(Hala)(SO$_4$)]	417	29.65	29.60	H$_2$S+NH$_3$+ glycine
	574	44.24	44.417	Maleic acid+ ethylene +CO$_2$
	Above 574	27.29	25.99	Residue Cr(SO$_2$)
H[Cr(HNTA)(Hgly)(SO$_4$)]	427	30.86	30.06	H$_2$S+NH$_3$+ glycine
	571	42.82	43.38	Maleic acid+ CH$_4$ +CO$_2$
	Above 571	28.22	26.56	Residue Cr(SO$_2$)
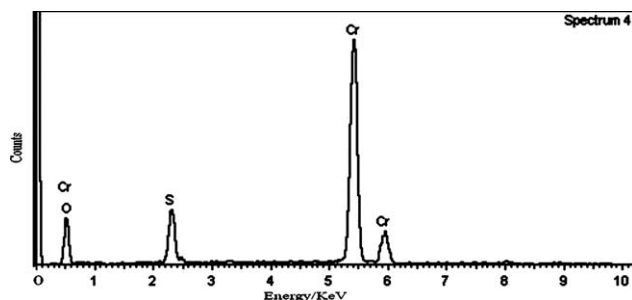
Figure 4 Typical EDX spectrum of the thermal analysis residue from complex I.
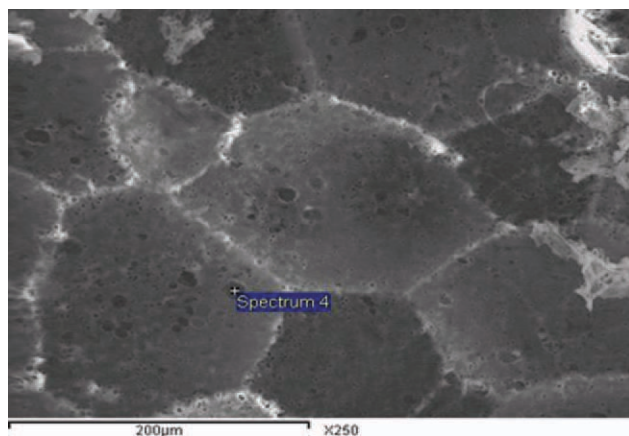
Figure 5 Scanning electron microscope image (SEM) of the thermal analysis residue from complex I. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Mass spectra

The mass spectra of the two complexes were recorded. The molecular ion peaks of the two complexes obtained from the mass spectra were very close with the suggested molecular weight. In complex I the molecule ion peak at $m/z = 422$ while the suggested molecular weight is 425. In complex II the molecular ion peak at $m/z = 410$ and the suggested molecular weight is 411.

CONCLUSIONS

The reaction of chromium sulfate with nitrilotriacetic acid and alanine or glycine in acidic medium yields polymeric coordination compounds in which nitrilotriacetic acid acts as a tridentate ligand and the amino acid (alanine or glycine) acts as a monodentate ligands and finally the sulfate ions plays the role of the connection between the polycomplexes and acts as a bridge bidentate ligand.

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