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# Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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# Thermo-Chemical Study on Complexes of Nickel (II)-, Chromium (III)- and Europium (III)- Tricarballylic acid (TCA) Moiety of Mycotoxin Natural Products

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# Thermo-Chemical Study on Complexes of Nickel (II)-, Chromium (III)- and Europium (III)- Tricarballylic acid (TCA) Moiety of Mycotoxin Natural Products

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The coordination behavior of nickel (II) chromium (III) and europium (III) with tricarballylic acid (TCA) is described. Three new compounds Ni(II)-TCA, Cr(III)-TCA and Eu(III)-TCA were obtained and characterized of the species by elemental analysis, thermal behavior of TGA, DTA, DSC, IR and magnetic susceptibility.

Keywords chromium(III)-TCA, europium(III)-TCA, nickel(II)-TCA, tricarballylic acid

#### **INTRODUCTION**

Tricarballylic acid (TCA) has attracted the attention of several research groups because it was found as a fragment in mycotoxin, fumonisins  $B_1$  and  $B_2$  (**1a,b**)<sup>[1]</sup>, isolated from the corn pathogen fusarium moliniforme, which have been linked to human esophageal cancer in parts of China and southern Africa.<sup>[2]</sup> In particular TCA has found also as a fragment in the AAL Toxin TA (**2**) and Actinoplanic acid (**3**), (Scheme 1). The TCA side chains become play an important role in the resistant to any chemical treatment of this fungs (Fumonisins and Toxins).<sup>[3]</sup> The occurrence and biological activity of the TCA molecule has been studied extensively.<sup>[4]</sup>

One of the most studied topics in the stereochemistry of TCA is the development of a reliable method for determining the absolute configuration of carboxylic acids containing a stereogenic center at C(3) of the TCA derivatives.<sup>[5,6]</sup> Previous syntheses of both enantiomers of tricarballylic anhydrides, imides and 4-(5-nonyloxycarbonyl)-3-substituted butanoic acids, methyl esters

were described by our groups.<sup>[7-9]</sup> In this context, the study of the interaction between nickel (II), chromium (III) and europium (III) and tricarballylic acid (1,2,3-propanetricarboxylic acid, TCA), has been performed to prepare three new nickel (II)-TCA, chromium (III)-TCA and europium(III)-TCA complexes. The family of metal carboxylate has drawn much attention owing to the diversity of the binding modes of carboxylate groups, a wide range of structural diversities and potential applications as molecule-based materials.<sup>[10]</sup> Among them, the majority of these reports have still focused on the metal carboxylate with rigid carboxylate-containing ligands.<sup>[10-12]</sup> Recently, increasing attention has also been paid to construction of frameworks with the flexibility of carboxylate ligands, the conformational freedoms of which may offer various possibilities for unique structures and special properties.<sup>[13,14]</sup> The polycarboxylic acid TCA is a small biomimetic ligand due to its participation in the zinc excretion through the interaction and chelation with this metal ion<sup>[1-5]</sup> it is suggested that it is partly responsible for the deficiency of Zn. There are few reports about the study of metal complexes with TCA and related polycarboxylic acids.<sup>[16-19]</sup> In contrast to the aromatic tricarboxylate compounds,<sup>[11]</sup> the aliphatic tricarboxylate (CH(COO<sup>-</sup>)(CH<sub>2</sub>COO<sup>-</sup>)<sub>2</sub>, TCA) has been less studied as building blocks in the construction of MOFs though the flexible TCA ligand, with the coordination versatility by six potentially O-donor atoms, is a proper candidate to acquire various polymeric structures with functional characters different of the reported MOFs constructed from aliphatic carboxylates.<sup>[12]</sup> Particularly, variable bridging modes of multiple carboxylate of TCA with metal cations may involve interesting magnetic interaction among them. A few interesting structure of metal-TCA complexes were reported. For example, ternary complexes of Zn(II) with TCA and Lewis bases (1,10-phenanthroline, 4,4'-bipyridine or 1,2bis(4-pyridine) ethane),<sup>[20]</sup> where TCA behaves as a  $\mu_5$ -and  $\mu_2$ -bridging ligand, respectively. Also, coordination polymer of Ce(III)<sup>[20]</sup> and Mn(II) has been reported.<sup>[21]</sup> Here in, we report the synthesis of  $(\pm)$  Ni(II)-TCA,  $(\pm)$  Cr(III)-TCA,  $(\pm)$  Eu(III)-TCA, infrared spectrum (Figures 8-11), Calorimetric study (DSC), (Figures 5-7), thermo-gravimetric analysis (TGA) and

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The authors gratefully acknowledge the Professor Dr. Thomas R. Hoye University of Minnesota, USA for providing us the TCA acid material as well as the useful comment, "Figure 1. The TGA curves of tricarballylic acid (TCA) 4."

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SCH. 1.

differential thermal analysis (DTA) (Figures 1–4) of a unique complexes.

In order to understand the nature of the changes involved; thermogravimetric and differential thermal analysis (TGA and DTA) of a few Cu(II) and Ni(II) amine complexes had been carried out and the preliminary results reported in earlier papers.<sup>[22,23]</sup> Since then, a detailed study of TGA and DTA of a variety of amine complexes of different Cu(II) salts was undertaken.<sup>[24]</sup> The results of Zinc complexes on *trans*-aconitic acid (H<sub>3</sub>L) and 1,10-phenanthroline<sup>[25]</sup> and Zinc complexes



FIG. 1. The TGA curves of tricarballylic acid (TCA) 4.

with tricarballylic acid (TCA) and Lewis bases such as 1,10phenanthroline [4,4-bipyridine and 1,2-bis(4-pyridine)ethane with zero and two dimensional structures complexes of Zn(II) nitrate are found to lead to an understanding of the roles of the ligand and the counter anion in determining the nature of thermal decomposition of such complexes.<sup>[26]</sup> Reports<sup>[27–30]</sup> on thermal analysis of some of the systems studied in the present work dealing with certain limited aspects are found in literatures which are duly referred to at appropriate stages in the discussion part.

#### **RESULTS AND DISCUSSION**

## Chemistry: Characterization of the Solid Compounds

#### Characterization

The observed percentage weights of various elements were fitted with those calculated on the basis of different possible metal to ligand stochiometries (1:1; 1:2, etc.) together with probable numbers of water molecules of crystallization (0, 0.5, 1, 2, etc.) for deducing the molecular/empirical formulae of the complexes. The molecular formulae so obtained the complexes indicate that all of the present complexes exhibit 1:1 (metal:ligand) stoichiometry. The TCA complexes of Ni(II), Cr(III) and Eu(III) hydroxide appear as hydrated to different extents. These features as well as the infrared and electronic spectral data on the complexes are in good agreement with the reported<sup>[32–35]</sup> ones on similar complexes and are indicative of a distorted octahedral symmetry of the complex cation with the four oxygen atoms from two ligand molecules

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forming a square planar arrangement around the central metal ion.

The Chromium is coordinated by four *trans* oxygen atoms from TCA species and the two oxygen atoms from two water molecules to form a slightly distorted CrO6 octahedron. However, the Cr1 adopts a highly distorted octahedral geometry and is coordinated by a water oxygen atom, as outlined in Scheme 2.

## Thermogravimetric Analysis and Diffuse Reflectance Spectra

As shown in the TGA curve of Tricarballylic acid (TCA) in Scheme 1, the melting point of TCA was 162–163°C. The TCA started to lose weight above 160°C, and it lost 5.5% of its original weight at 200°C.

The experimentally determined TGA and DTA curves for all the 3 complexes are presented in Figures 2–4 and briefly described below. The observed percentage weight losses corresponding to various steps in all the TGA curves were compared with those calculated on the assumption of possible compositions of the expelled groups,<sup>[36-38]</sup> and those showing the best agreement with the former are incorporated in Figures 2-4. These TGA patterns indicate that the thermal decomposition of these complexes broadly involves three stages; viz dehydration (in case of hydrated ones), decarboxylation and deanionation. The dehydration process is generally found to spread over somewhat large temperature intervals resulting in broad steps; while the decarboxylation steps in practically all the cases are quite steep ranging over an interval of only a few °C. In all the cases, the last steps comprising of deanionation with simultaneous oxidation M to MO(NiO, Cr<sub>2</sub>O<sub>3</sub>, Eu<sub>2</sub>O<sub>3</sub>) are found to be very broad in nature. However, in the majority of the cases, all these steps are not generally isolated but overlap to varying extents and frequently result in fractional losses of the constituent moieties. The DTA curves of all these complexes exhibit a weak and somewhat broad endothermic peak in the lower temperature region just prior to or accompanying the first weight loss step in the corresponding TGA curve. Since the latter corresponds to the loss of crystal water (in case of the hydrated complexes) or the ligand (in case of anhydrous complexes); the endothermic nature of these DTA peaks implies some kind



FIG. 2. Thermograms TGA and DTA curves of Cr(III)TCA complexes 7.

of phase change associated with an absorption of the required latent heat. The DTA peaks corresponding to the dehydration steps in TGA are found endothermic and broad, while those for decarboxylation, deanionation and conversion of metallic M to MO processes are all exothermic in nature. However, there is no distinct peak corresponding to the last process of oxidation of metallic M to MO since it occurs almost simultaneously with the deanionation process. The TGA steps corresponding to decarboxylation involving sudden weight loss are accompanied by relatively sharp peaks in DTA. In case of the DTA peaks corresponding to the phase change of a complex prior to any actual dissociation, the TGA curves obviously exhibit no weight loss steps. In all the cases, the DTA peaks for the M to MO process are rather weak and spread over a wide temperature range  $(\sim 300-600^{\circ}C)$ . The TGA plot of the TCA complexes of Ni(II), Cr(III) and Eu(III) exhibit a steep step accompanied by sudden weight loss. This appears to be due to a chain type highly explosive reaction because of simultaneous presence of an oxidizing group (OH) and a reducing group (TCA) in the same complex molecule. Similar explosive effect<sup>[39,40]</sup> is reported in the case of thermal decomposition of some amine complexes of Ni(II) nitrate. All these observations are in close agreement with those reported in literature.<sup>[41]</sup>

#### **Calorimetric Study**

As outlined in the DSC curve of the three complexes presented in Figures 5–7. In the dynamic curing process the degree of conversion by DSC ( $\alpha_{DSC}$ ) was calculated as follows:

$$\alpha_{DSC} = \frac{\Delta H_T}{\Delta H_{dyn}}$$
[1]

Where  $\Delta H_T$  is the heat released up to a temperature T, obtained by integration of the calorimetric signal up to this temperature, and  $\Delta H_{dyn}$  is the total reaction heat associated with the complete conversion of all reactive groups. The  $T_g$  was measured as the half-way point of the jump in the heat capacity when the material changed from the glassy to the rubbery state at 10C/min. In order to establish the relations  $T_g - \alpha$  we performed a series of non-isothermal scans from 20°C to several temperatures, below 225°C, at a heating rate of 10°C/min. Then, the samples were immediately quenched and a second scan from 100°C to 225°C at a heating rate of 10°C/min was registered to determine the  $T_g$  value and the residual heat. The degree of conversion was calculated on the basis of residual heat taking into account the total reaction heat. The kinetic analysis was carried out using an integral isoconversional method as we



FIG. 3. Thermograms TGA and DTA curves of Ni(II)TCA complex 6.

will explain next. The basic assumption of this method is that the reaction rate at given conversion is only a function of the temperature.<sup>[42,43]</sup> Isoconversional methods make it possible to easily determine the dependence of E on the degree of conversion in complex processes. The kinetics often here action is usually described by the following rate equation:

$$\frac{d\alpha}{dt} = Af(\alpha)\exp\left(-\frac{E}{RT}\right)$$
[2]

Where *t* is time, *A* is the pre exponential factor, *E* is the activation energy, *T* is the absolute temperature, *R* is the gas constant, and *f* ( $\alpha$ ) is the differential conversion function. By integrating the rate equation, Eq. (2), under non-isothermal conditions and using the Coats–Redfern<sup>[44]</sup> approximation to solve the so-called temperature integral and considering that 2RT/ E is much lower than 1, the Kissinger–Akahira–Sunose (KAS) equation may be written<sup>[45]</sup>:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left[\frac{AR}{g(\alpha)E}\right] - \frac{E}{RT}$$
[3]

Where  $\beta$  is the heating rate and  $g(\alpha)$  is the integral conversion function. For each conversion degree, the linear plot

of  $\ln(\beta/T^2)$  versus 1/T enables *E* and  $\ln[AR/g(\alpha)E]$  to be determined from the slope and the intercept. If the reaction model,  $g(\alpha)$ , is known, for each conversion the corresponding pre-exponential factor can be calculated for every activation energy. In this study, we used the reduced master curves procedure of Criado,<sup>[46]</sup> described else where, to assign a reaction model to the systems studied.<sup>[47]</sup> Different kinetic models have been studied: diffusion  $(D_1-D_4)$ , Avrami–Erofeev  $(A_2-A_4)$ , power law, phase -boundary- controlled reaction  $(R_2 \text{ and } R_3)$ , autocatalytic (n m = 2 and 3) and order n (n = 1–3).We found that all systems studied follow a kinetic model of the surface-controlled reaction type, R2, with  $g(\alpha) = [1-(1\alpha)^{1/2}]$ . The rate constant, *k*, was calculated with *E* and *A* determined at conversion of 0.5, using the Arrhenius equation.

#### **Magnetic Properties**

As well known, Trimeric complexes can be classified as linear or nonlinear according to the arrangements of the metal centers, and most of them linked by two, three or four simple and/or intricate bridging ligands, such as hydroxide, chloride.<sup>[42]</sup> On the other hand, only a minority of them have the M3 (M = metal cations) core bridged by a single organic ligand.<sup>[48]</sup> The structure represents the new example of "inorganic" metal



FIG. 4. Thermograms TGA and DTA curve of Eu(III)TCA complex 6.

carboxylate chain interconnected by tricarboxylate ligands with out the presence of any hydroxyl groups.<sup>[49]</sup> Compounds similar to those complexes will be crucial to an understanding of bonding and magnetic interactions between proximate metal centers and metal chains. Variable temperature magnetic susceptibility of Ni(II)-TCA, Eu(III)-TCA, Cr(III)-TCA complexes were measured on powdered sample at room temperature. The magnetic susceptibility above 15 K obeys the Curie-Weiss law this being further evidence supporting the antiferromagnetic ordering of those complexes. These features are indicative of antiferromagnetic ordering behavior below 3.0 K, confirmed the effect of this structural arrangement on the magnetism of complexes. Since the Ni(II), Cr(III) and Eu(III) chains in complexes are well separated by the long linkers of TCA bridges, the antiferromagnetic behavior can be suggested to arise from intra-chain magnetic interactions of the adjacent trimers. According to the chain topology, there are two sets of magnetic exchange pathways within the chain: one consists of one carboxylate bridges and a  $\mu_2$ -O bridge from the  $\mu_3$ -carboxylate group ( $J_1$ ); the other mainly consists of two syn-syn carboxylate bridges  $(J_2)$ , as outlined in Scheme 3.

However, the metal adopts a highly distorted octahedral geometry and is coordinated by water oxygen atom and carboxylate oxygen atoms from TCA ligand. Each TCA is coordinated to metal ions through one  $1,1,3-\mu_3$ -bridging carboxylate group and two similar  $1,3-\mu_2$ -bridging carboxylate groups, as shown in Scheme 4.

To achieve non-compensation in spin moments within such a chain, the interaction through the two sets of bridges must be anti-ferromagnetic (AF). The interactions alternate according to an AF–AF–AF repeating sequence to yield the spin topology that corresponds to a new homo-metallic anti-ferromagnetic chain system with alternating interactions  $J_1J_1J_2$ .<sup>[13,14]</sup> To



SCH. 3. Spin states of the metal –carboxylate chain in the ground state overlaid onto the molecular structure.



SCH. 4. Coordination mode of TCA ligand with metal ions.

evaluate the magnetic interactions in the 3D networks of complexes, neglected weaker mediators of  $\sigma$ -bonding ditopic linkers among the chains, may allow us to fit of the observed magnetic data based on the theoretical expression of 1D Heisenberg anti-ferromagnetic chains with alternating interactions  $J_1J_1J_2$ , proposed by Escuer et al.<sup>[50]</sup>

#### **Transmission IR Properties**

The characteristic bands of the free ligand (TCA) at 1730.8 (vs), 1722 (vs) and 1703 (vs) cm<sup>-1</sup>, assigned to them  $\nu$ (C=O) stretching mode of the carboxylic group -(COOH), disappear upon carboxyl-ate formation.

In the nickel(II)-TCA.12H<sub>2</sub>O complex the spectrum shows two new components corresponding to antisymmetric and symmetric stretching modes of the carboxylate moiety, one strong and broad band at 1576.2 cm<sup>-1</sup>( $\nu$  as COO-) and the other at 1413.2 cm<sup>-1</sup> ( $\nu$  s COO-) as it is expected for the presence of the carboxylate group in its ionic form.<sup>[51]</sup> At 1718.8 cm<sup>-1</sup>, one band related to the characteristic  $\nu$ (C=O) stretching mode remains unchanged. General broadening is observed, surely enhanced by the presence of  $\delta$ (H<sub>2</sub>O) vibrations at1637.3 cm<sup>-1</sup>, which are expected to lie between 1600 and 1650 cm<sup>-1</sup>.<sup>[52]</sup>

In the Europium(II)-TCA.12H<sub>2</sub>O complex the spectrum shows two new components corresponding to antisymmetric and symmetric stretching modes of the carboxylate moiety, one strong and broad band at 1509 cm<sup>-1</sup>(vas COO-) and the other at 1399.7 cm<sup>-1</sup> (vs COO-) as it is expected for the presence of the carboxylate group in its ionic form. At 1651.1 cm<sup>-1</sup>, one band related to the characteristic  $\nu$ (C=O) stretching mode remains unchanged. General broadening is observed, surely enhanced by the presence of  $\delta$ (H<sub>2</sub>O) vibrations at 1631.2 cm<sup>-1</sup>, which are expected to lie between 1600 and 1650 cm<sup>-1</sup>.

In the chromium (II)-TCA. 16H<sub>2</sub>O complex the spectrum shows two new components corresponding to antisymmetric and symmetric stretching modes of the carboxylate moiety, one



FIG. 5. Differential scanning calorimetry (DSC) of Cr(III)TCA complex 7.



FIG. 6. Differential scanning calorimetry (DSC) of Ni(II)TCA complex 5.

strong and broad band at 1508.2 cm<sup>-1</sup>(vas COO-) and the other at 1448.5 cm<sup>-1</sup> (vs COO-) as it is expected for the presence of the carboxylate group in its ionic form. At 1718.7 cm<sup>-1</sup>, one band related to the characteristic  $\nu$ (C=O) stretching mode remains unchanged. General broadening is observed, surely enhanced by the presence of  $\delta$ (H<sub>2</sub>O) vibrations at 1626 cm<sup>-1</sup>, which are expected to lie between 1600 and 1650 cm<sup>-1</sup>.

In the Ni(II)TCA.12H<sub>2</sub>O and Cr(III)TCA.16H<sub>2</sub>O complexes exhibit various interesting and important changes in the middle region of the spectrum. Some aspects of the performed assignments are commented: At 1718 cm<sup>-1</sup>, one band related to the characteristic  $\nu$ (C=O) stretching mode remains unchanged. At lower frequencies, the disappearance of two bands related to -COOH stretching and the appearance of a set of new bands located at 1637.3(vs), 1626(s) 11576.7 (s), cm<sup>-1</sup> are observed, confirming the participation of two carboxylate group in the coordination sphere. Hence, the spectral splitting is probably caused by the presence of non-equivalent carboxylate groups. Similar changes are observed in Eu(III)TCA 12H<sub>2</sub>O complex with the splitting of the bands related to the free carboxylic group 1651.1, 1631.2 and 1509, 1399.7 cm<sup>-1</sup>. This band is strongly dependent on the coordination geometry of the complexes, being displaced to higher energies after coordination.<sup>[53]</sup> Furthermore, the new bands located at 3416.8, 3421.3, 3380 and 598.8, 623.8, 668.2 cm<sup>-1</sup> assigned to  $\nu$ (OH),  $\delta ip$ (CH) and  $\delta$ (ring), respectively, have been taken as an evidence of the presence of TCA in the metal environment.<sup>[54]</sup>

### **EXPERIMENTAL PART**

#### General

All manipulations were carried out in air. Metal salts and organic ligands were purchased from Aldrich. All the reactions were performed at refluxing temperature in aqueous medium recommended Green chemistry and not special conditions were demanded.

#### Instrumentation

All chemicals were of reagent grade and were used as purchased. IR spectra were recorded in the range 4000–400  $cm^{-1}$  on Perkin-Elmer PE Spectrum One FT/IR spectrometer using a KBr pellet. Elemental analyses (C, H) were performed on a Perkin-Elemer PE 2400 II CHN elemental analyzer. Thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) were performed on a Shimadzu system (models TG-50 and DTA-50, respectively), working in an oxygen flow



FIG. 7. Differential scanning calorimetry (DSC) of Eu(III)TCA complex 6.

(60 mL/min) at a heating rate of  $10^{\circ}$ C/min. Sample quantities ranged between 10 and 20 mg. Al<sub>2</sub>O<sub>3</sub> was used as a DTA standard. Differential scanning calorimetry (DSC)-821e thermal analyzer in covered Al pans under N<sub>2</sub> at 2, 5, 10 and 15°C/min of the samples weighed approximately 7–9 mg.

#### Characterization

The percentage weights of various elements (C, H, and O) in all the complexes were first determined on the basis of elemental microanalysis (C and H), estimation of oxygen by the following standard procedures.<sup>[31]</sup> For determining their empirical/molecular formulae, the complexes were further examined by their infra-red and electronic absorption spectra (in the form of their nujol mulls and methanolic solutions) to understand the nature of coordination of the ligands and the stereochemistry about the central Ni(II), Cr(III) and Eu(III), respectively.

#### Thermal Analysis

A Mettler TG50 and DTA-50 thermobalance was used for thermal analysis. The samples were heated from room temperature ( $25^{\circ}$ C) to a specified temperature at a rate of  $10^{\circ}$ C/min with a continuous nitrogen flow rate of 10 ml/min. The sample size for the TGA and DTA experiments was approximately 9 mg, as shown in Figures 1–4.

#### Differential Scanning Calorimetry (DSC)

Calorimetric studies were carried out on a Mettler DSC-821e thermal analyzer in covered Al pans under N<sub>2</sub> at 2, 5, 10 and  $15^{\circ}$ C/min. The calorimeter was calibrated using an indium standard (heat flow calibration) and an indium –lead –zinc standard (temperature calibration). The samples weighed approximately 7–9 mg, as outlined in Figures 5–7.

#### Synthesis of the Complexes

#### Preparative Cr(III) complex

The complex was prepared by mixed aqueous solutions of  $CrCl_3.6H_2O$  (5 mmol) dissolved in 10 ml water and to this a 1M NaOH was added until the formation of the hydrated  $Cr(OH)_3$  was completed. The mixture was centrifuged and the solid was washed thoroughly with water. The wet solid was dispersed in 30 ml distilled water containing (5 mmol, 0.88 g) tricarballylic acid under continuously stirring. Afterwards, the solution was refluxed for 8h during which the color of the solution was turned to blue. The reaction solution was cooled and filtered to separate







FIG. 9. Transmission IR spectra of Ni(II)TCA complex 5.



FIG. 10. Transmission IR spectra of Eu(III)TCA complex 6.

the excess of Cr(OH)<sub>3</sub>. The filtrate was concentrated to about 10 ml. The solid complex was obtained by scratching with addition of ethanol, then dried at 80°C for 2h and it was dried in vacuo and kept in desiccators (silica gel), Yield: 65%. IR data (KBr): 3416.8 vs, [ $\nu$ (O–H)], 1718.7m, [ $\nu$ (C=O)]; 1626sb, [ $\nu_{as}$ (CO<sub>2</sub>)] 1449m [ $\nu_s$ (CO<sub>2</sub>)], 1561sh, 1319, 598, 637m,br. *Anal. calc.* for Cr(TCA).16H<sub>2</sub>O [C<sub>6</sub>H<sub>40</sub>CrO<sub>22</sub>]; (516.36) C, 13.96%; H, 7.81%; Cr 10.07%.; Found: C, 13.47%; H, 7.29%. Cr,10.10%.

#### Preparative Ni (II) complex

The complex was prepared by mixing aqueous solutions of NiCO<sub>3</sub>.Ni(OH)<sub>2</sub>.H<sub>2</sub>O (5 mmole) and (5 mmol, 0.88 g)of TCA in 30 ml water and refluxed for 8h. Afterwards, the reaction mixture was concentrated to  $^{1}/_{4}$  of its original volume. Addition of 20 ml ethanol and scratching the solution lead to solid residue. The solid complex washed several times with ethanol and dried in vacuo at 80°C for 2h and kept in desiccator (silica gel) to Yield 75%. IR (KBr) 3421vs, 1719m, 1632s, 1576s, 1413m, 1323, 1205W, 889, 598, 624 m,br. *Anal. calc.* for Ni(TCA).12H<sub>2</sub>O [C<sub>6</sub>H<sub>30</sub>NiO<sub>18</sub>]; 4(48.99) C, 16.05%; H, 6.73%; Ni 13.07%.; Found: C, 16.02%; H, 5.80%. Ni,13.8%.

#### Preparative Eu (III) complex

The complex was prepared by mixing aqueous solutions of  $Eu(NO_3)_{3.5}$  H<sub>2</sub>O (5 mmol) and (5 mmol, 0.88 g) of TCA in 30 ml water and refluxed for 8h. Afterwards, the reaction mixture was concentrated to  $^{1}/_{4}$  of its original volume. Addition of 20 ml ethanol and scratching the solution lead to solid residue. The solid complex washed several times with ethanol and dried

in vacuo at 80°C for 2h and kept in desiccator (silica gel) to yield 80%. IR (KBr), 3400 m, 1shoulder, 1597vs, 1623sh, 1420m, 1319. *Anal. calc.* for Eu(TCA).12H<sub>2</sub>O [C<sub>6</sub>H<sub>30</sub>EuO<sub>18</sub>]; (542.26) C, 13.29%; H, 5.58%. Eu, 28.02%.; Found: C, 13.23%; H, 5.88%; Eu 27.94%.

#### **CONCLUSIONS**

In summary, we have successfully synthesized a new coordination polymer aliphatic tricarballylic acid ligand, featuring linear trimeric nickel(II), chromium(III), europium(III)-based, metal carboxylate chains, which exhibit a low-dimensional ferro or anti-ferromagnetic behaviur. Literature reported results further support the idea that judiciously assembling "metal-chains" with anisotropic shapes from other metal centers and long  $\sigma$ bonding ditopic linkers.<sup>[55]</sup>

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