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Synthesis, characterization and thermogravimetric study of EU(III), Tm(III), Fe(III), Cr(II), Ni(II), Co(II), Cu(II), Pb(II) and Hg(II) coordination compounds with hexamethylenetetraamine

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SYNTHESIS, CHARACTERIZATION AND THERMOGRAVIMETRIC STUDY OF EU(III), Tm(III), Fe(III), Cr(II), Ni(II), Co(II), Cu(II), Pb(II) AND Hg(II) COORDINATION COMPOUNDS WITH HEXAMETHYLENETETRAAMINE

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The coordination compounds $\text{EuCl}_3 \cdot 1.5\text{hmta} \cdot \text{H}_2\text{O}$, $\text{TmCl}_3 \cdot \text{hmta} \cdot \text{H}_2\text{O}$, $\text{Cr}(\text{CH}_3\text{COO})_2 \cdot 2\text{hmta}$, $\text{FeCl}_3 \cdot \text{hmta} \cdot 3\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 3\text{hmta}$, $\text{CuSO}_4 \cdot 3\text{hmta}$, $\text{PbCl}_2 \cdot 0.5\text{hmta} \cdot 5\text{H}_2\text{O}$, $\text{HgCl}_2 \cdot \text{hmta}$ and $\text{NiCl}_2 \cdot \text{hmta} \cdot \text{H}_2\text{O}$ (hmta = hexamethylenetetraamine) were synthesized and characterized by elemental analysis, infrared spectroscopy and thermogravimetry. The infrared data are in agreement with coordination through nitrogen. For the hydrated compounds, a first mass-loss step, associated with the release of water molecules, followed by release of an hmta molecule was observed. The anhydrous adducts exhibit a first single-mass loss associated with the release of hmta. For $\text{Cr}(\text{CH}_3\text{COO})_2 \cdot 2\text{hmta}$, the first mass-loss step is due to release of hmta, and the second is due to the acetate, consistent with the proposed structural formula.

Keywords: Hexamethylenetetraamine; Lanthanide; Transition metals

INTRODUCTION

Thermal techniques such as thermogravimetry, differential scanning calorimetry and solution calorimetry have been used extensively to study, from an energetic viewpoint, the interaction between chemical species of biological interest and model molecules, exhibiting N, O and/or S as coordination sites, with transition metal cations from groups 3 to 12 of the periodic table. Caffeine [1] and imidazole [2,3] interactions with zinc group halides are the most recent examples of such investigation. Ethyleneurea, ethylenethiourea and propyleneurea have also been used for the synthesis of a series of adducts with Zn(II), Cd(II), Cu(II), Co(II), Sn(II), Ni(II) and Ce(IV) [4–12]. The interaction of ethyleneurea with V(V) in an octahedral environment was also investigated, through the synthesis and characterization of the first $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$

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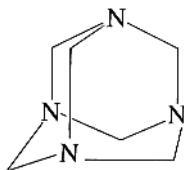


FIGURE 1 Structural formula for hmta.

intercalation compound prepared with both host and guest molecules in the solid state at room temperature [13]. Furthermore, it was recently shown [14] by empirical correlations and equations that thermogravimetric, calorimetric and infrared data are very closely related for coordination compounds.

This work describes the synthesis, characterization and thermogravimetric study of the coordination compounds $\text{EuCl}_3 \cdot 1.5\text{hmta} \cdot \text{H}_2\text{O}$, $\text{TmCl}_3 \cdot \text{hmta} \cdot \text{H}_2\text{O}$, $\text{Cr}(\text{CH}_3\text{COO})_2 \cdot 2\text{hmta}$, $\text{FeCl}_3 \cdot \text{hmta} \cdot 3\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 3\text{hmta}$, $\text{CuSO}_4 \cdot 3\text{hmta}$, $\text{PbCl}_2 \cdot 0.5\text{hmta} \cdot 5\text{H}_2\text{O}$, $\text{HgCl}_2 \cdot \text{hmta}$ and $\text{NiCl}_2 \cdot \text{hmta} \cdot \text{H}_2\text{O}$ (hmta = hexamethylenetetramine). hmta, or urotropine, whose structural formula is shown in Fig. 1, has a cage structure, with four nitrogen atoms free of steric hindrance, and is a well-known antibacterial agent. It is used in the preparation of the well-known explosive RDX and has been shown to be a corrosion inhibitor for copper in bromide medium [15].

EXPERIMENTAL

Europium, thulium, iron, chromium, lead, nickel and mercury chlorides and cobalt nitrates, copper sulfate, chromium acetate and hmta (Aldrich) were of analytical grade and were used without further purification.

The chromium compound was prepared by dissolving stoichiometric amounts (1:4 mol: mol) of chromium acetate and hmta separately in methanol (methanol was added dropwise and the addition was sustained for a short time after the hmta and chromium acetate dissolutions) and then the prepared solutions were mixed together immediately. The solvent was then removed by a rotary evaporator and the solid obtained was washed with dichloroethane and then dried at room temperature for 24 h. The other coordination compounds were prepared similarly by dissolving stoichiometric amounts (1:4 mol: mol) of the transition metal salts and hmta in methanol under magnetic stirring, and then the solutions were mixed together at once. For iron and zinc compounds, precipitation of brown and white powders, respectively, was observed. Pb and Hg produced white precipitates, and the Tm compound was a light yellow color. For Co and Cu, pink and green precipitates were obtained, respectively. The solvent was removed by using a rotary evaporator. The compounds were filtered off, washed with water (Eu), methanol (Fe) or chloroform (Ni) and then dried under vacuum at room temperature for 24 h.

C, H and N analyses were performed on a CHN Perkin-Elmer instrument. Infrared spectra were obtained in the range $4000\text{--}400\text{ cm}^{-1}$ from powders in KBr disks by using a Brookman instrument. Thermogravimetric curves were obtained under nitrogen at a heating rate of $10^\circ\text{C min}^{-1}$ on a Shimadzu TGA-50.

TABLE I Elemental analyses for the hexamethylenetetraamine compounds

<i>Proposed formula</i>	<i>Found (Calculated) (%)</i>		
	<i>C</i>	<i>H</i>	<i>N</i>
EuCl ₃ ·1.5hmta·H ₂ O	22.4 (22.2)	4.3 (4.1)	16.9 (17.3)
TmCl ₃ ·hmta·H ₂ O	16.4 (16.6)	3.1 (3.2)	12.8 (12.9)
Cr(CH ₃ COO) ₂ ·2hmta	42.6 (42.7)	7.2 (6.6)	28.0 (24.9)
FeCl ₃ ·hmta·3H ₂ O	20.5 (20.2)	5.5 (5.1)	15.0 (15.7)
Co(NO ₃) ₂ ·3hmta	34.8 (35.8)	6.8 (6.0)	32.1 (32.5)
CuSO ₄ ·3hmta	37.4 (37.3)	6.3 (6.2)	29.1 (29.0)
PbCl ₂ ·0.5hmta·5H ₂ O	8.3 (8.2)	2.5 (3.7)	5.9 (6.4)
HgCl ₂ ·hmta	17.9 (17.5)	3.4 (2.9)	13.3 (13.6)
NiCl ₂ ·hmta·H ₂ O	25.3 (25.0)	7.3 (4.9)	19.7 (19.5)

RESULTS AND DISCUSSION

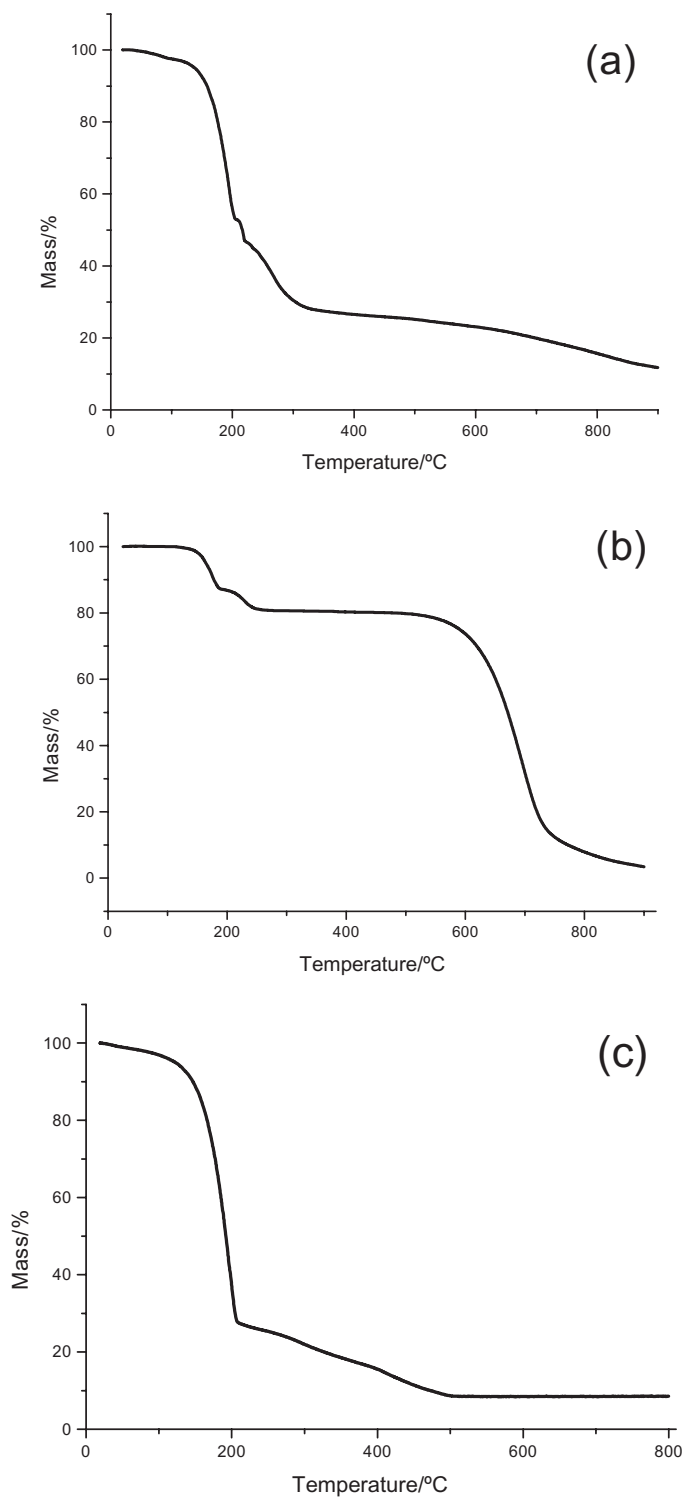
The elemental analyses, summarized in Table 1, are in good agreement with the proposed formulas. As a 1:4 (mol:mol) metal salt/hmta stoichiometric ratio was used, and none of the synthesized compounds has four hmta molecules, the adducts formed have the most stable stoichiometry at room temperature (27°C) and pressure (1 atm). Compounds with a half-ligand, as observed for Eu and Pb, indicate that hmta is a tetradentate ligand, and a cross-linking agent.

For all compounds, minor positive or negative shifts of the frequencies associated with the C–N stretching vibrations (two strong bands at 1125 and 1000 cm⁻¹) are observed. The IR spectra obtained for all of the adducts can be almost superimposed on the IR spectrum of the uncoordinated ligand. This is a characteristic previously observed for hmta adducts [16,17], and the IR data are in agreement with coordination involving the nitrogen atoms, as expected.

The experimental mass losses observed in the TG curves are in good agreement (±5%) with the proposed formulas based on the elemental analyses. As illustrative examples, the TG curves for PbCl₂·0.5hmta·5H₂O and Cr(CH₃COO)₂·2hmta are shown in Fig. 2. For hydrated compounds, such as PbCl₂·0.5hmta·5H₂O, the first mass-loss step is associated with the release of water molecules, followed by hmta release. Anhydrous adducts, such as CuSO₄·3hmta, exhibit a first mass-loss of hmta and a second one due to the sublimation and/or thermal degradation of the metal salt. On the other hand, for a compound with two kind of ligands, such as Cr(CH₃COO)₂·2hmta, the first mass-loss step is due to the release of hmta and the second to the acetate, as follows: Cr(CH₃COO)₂·2hmta (s) → Cr(CH₃COO)₂ (s) + 2hmta (g); Cr(CH₃COO)₂ (s) → 2(CH₃COO) (g) + Cr (s). The compound prepared exhibits a blue color, in agreement with the ‘common’ color for Cr(II) compounds.

For this last compound, a structure can be proposed (Fig. 3) in which the acetate anions are located at equatorial positions, and the hmta molecules are along the z axis, with longer bond lengths consistent with first release of hmta when the compound is heated. In the proposed structure, hmta is a monodentate ligand, as it is necessary to have two hmta molecules for each chromium acetate unit.

For the chromium compound, a dimeric formula, [Cr(OAc)₂·hmta]₂, could be proposed. However, the monomeric compound with a total organic mass of 88.5% and the dimer with a total organic mass of 83.3% indicate that the monomer is

FIGURE 2 TG curves for (a) $\text{CuSO}_4 \cdot 3\text{hmta}$, (b) $\text{PbCl}_2 \cdot 0.5\text{hmta} \cdot 5\text{H}_2\text{O}$ and (c) $\text{Cr}(\text{CH}_3\text{COO})_2 \cdot 2\text{hmta}$.

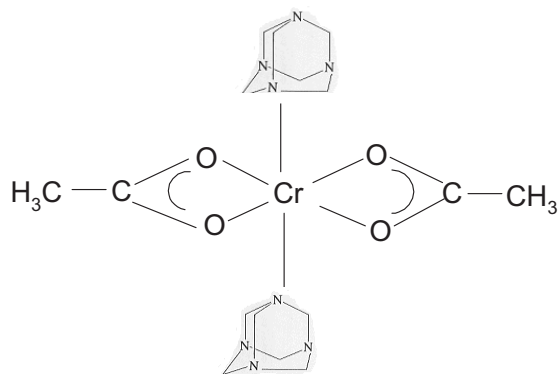


FIGURE 3 Proposed structure (not to scale) for the compound $\text{Cr}(\text{CH}_3\text{COO})_2 \cdot 2\text{hmta}$.

in better agreement (after thermal degradation) with the experimental final residue of 8.9%.

Similar considerations indicate that in $\text{PbCl}_2 \cdot 0.5\text{hmta} \cdot 5\text{H}_2\text{O}$, one hmta molecule is bonded to two Pb cations, forming a bridge. For the compounds with three hmta molecules, $\text{Co}(\text{NO}_3)_2 \cdot 3\text{hmta}$ and $\text{CuSO}_4 \cdot 3\text{hmta}$, two 'terminal' hmta molecules and one 'bridging' hmta molecule are likely. These hypotheses are in agreement with previously reported spectroscopic data for hmta monoadducts with Mn, Co, Ni, Zn and Cd sulfates [16] as well as for bidentate hmta adducts with Mn, Co, Ni, Cu, Zn and Cd thiocyanates [17]. For such compounds hmta, although potentially a tetradentate ligand, acts only as a terminal monodentate ligand or as a bidentate ligand bridging between two metal ions.

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