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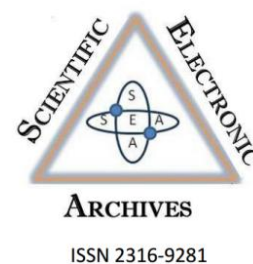
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Preparation and thermal decomposition of solid state chelates of ethylenediaminetetraacetic acid with manganese

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Abstract. Solid state of general formula $H_2[Mn(EDTA)].3,5H_2O$, where EDTA is ethylenediaminetetraacetate, were prepared. Thermogravimetry derivative thermogravimetry (TG-DTG), differential scanning calorimetry (DSC) and other methods of analysis have been used to characterize and to study the thermal stability and thermal decomposition of this complex.

Keywords: Manganese (II), EDTA, Thermal behavior

Introduction

The use of Ethylenediaminetetraacetic acid (EDTA) started in 1946, and it has become one of the most important reagents used in analytical chemistry. There are many studies about EDTA described in literature (Flaschka, 1964; Skoog et al., 2014), but most in solution.

Some metals chelates of ethylenediaminetetraacetic acid in the solid state using thermoanalytical have been reported. Wendlandt et al., (1960) have published a study of the thermal properties of a number of EDTA complexes.

Charles (1966), Bhat and Krishna Iyer (1967), Mercadante et al., (1993), Spirandeli Crespi and co-workers (1993) and Guinesi et al., (2002) studied the thermal decomposition of solid chelates of ethylenediaminetetraacetic acid by Thermogravimetry (TG) and Differential Thermal Analysis (DTA). Moitinho et al., (2004), studied chelates of EDTA with alkalis earth metals by TG and DSC (differential scanning calorimetry) and Ribeiro and co-worker (2006) studied the kinetic of thermal decomposition of complex of titanium (IV) with EDTA.

The principle interest in these studies are with respect to preparation and establishment of the stoichiometry as well as to verify the thermal stability and the thermal decomposition.

Furthermore, Giante et al., (2014) suggested that in the lanthanum to samarium chelates the EDTA acts as pentadentate ligand and as hexadentate one for the europium to lutetium and yttrium from the study the thermal behavior of trivalent lanthanides and yttrium(III) chelates of EDTA using TG-DSC coupled to infrared spectroscopy (FTIR).

In this study, solid chelate of manganese with EDTA was prepared and investigated by complexometry; infrared spectroscopy (IR); X-ray powder (XRD), and thermoanalytical techniques, thermogravimetry- derivative thermogravimetry (TG-DTG) and differential scanning calorimetry (DSC) in air and CO_2 atmosphere using platinum and alumina crucibles.

Methods

Ethylenediaminetetraacetic acid (EDTA) chelates of manganese (II) was obtained by slow addition, with stirring, of stoichiometry quantities of

respective metal carbonate to EDTA solution. The partially dissolved mixture was heated to $\sim 70^{\circ}\text{C}$ to facilitate evolution of CO_2 . After cooling, the solution was evaporated in a water bath and kept in a desiccator over anhydrous calcium chloride.

The metal content of the compound was determined by complexometric titration with standard EDTA solution, after samples of the compounds had been ignited to the metal oxide and dissolved in diluted hydrochloric solution (Flaschka, 1964).

Metal content was also determined from the TG curves. The water and EDTA contents were determined from the TG curves.

The TG-DTG and DSC curves were obtained using a Mettler TA-4000 thermoanalyser system with air or CO_2 flowing at a rate of about 150

mLmin^{-1} and a heating of $10^{\circ}\text{C min}^{-1}$, with samples weighing about 7 mg. Alumina or platinum crucibles were used to obtain the TG-DTG curves and aluminum crucibles to DSC curves.

X-ray power was obtained with an HGZ 4/B horizontal diffractometer (GDR) equipped with a proportional counter and pulse height discriminator (Bragg, 1962). The Bragg Brentano arrangement was adopted using $\text{CuK}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$) and a setting of 38 kV and 20 mA.

Results and discussion

The Table 1 presents the analytical and thermoanalytical data for the prepared compound. These results as well as acid-base titration data establish the formula $\text{H}_2[\text{Mn}(\text{EDTA})\text{H}_2\text{O}]\cdot 3,5\text{H}_2\text{O}$ (EDTA = ethylenediaminetetraacetate).

Table 1: Analytical and thermoanalytical data of $\text{H}_2[\text{Mn}(\text{EDTA})]\cdot 3,5\text{H}_2\text{O}$

Ligand loss (%)		Metal content (%)			Water content (%)		Final Residue
Calc.	TG	Calc.	TG	TIT. EDTA	Calc.	TG	Mn_3O_4
65,87	65,79	13,45	13,82	13,63	15,45	15,03	

*EDTA- ethylenediaminetetraacetate anion; Calc. –calculated value; TIT. EDTA- determined by EDTA titration

The X-ray powder diffraction patterns are shown in Figure 1. The compound has a crystalline structure, without evidence for formation of an amorphous series. The TG-DTG curves of the compound are shown in Figure 2 in the sequence: air-Pt, air- Al_2O_3 and in Figure 3, in the sequence, CO_2 -Pt and CO_2 - Al_2O_3 . The compound loses mass in several steps. The curves also show the influence of the crucibles and the atmosphere used during the thermal decomposition of this compound. The anhydrous compound in CO_2 atmosphere was more stable than that in air. For the same atmosphere, the final thermal decomposition temperature in an alumina crucible was higher than that in a platinum crucible. A great similarity in the curves was also

observed for the same atmosphere in both kinds of crucibles.

For the compound, the TG-DTG curves show a first mass loss due to dehydration. The thermal decomposition of the resulting anhydrous compound is similar in air and CO_2 atmosphere and the temperature at which the partial thermal decomposition occurs is lower for air than for CO_2 atmosphere. For the air atmosphere, up to 400°C (Pt) and 450°C (α - Al_2O_3) occur formation of Mn_3O_4 , and for the CO_2 atmosphere up to 770°C in both kinds of crucibles MnO is observed. The residues observed in air and CO_2 atmosphere were confirmed by X-ray powder diffraction (Figure 4 and 5).

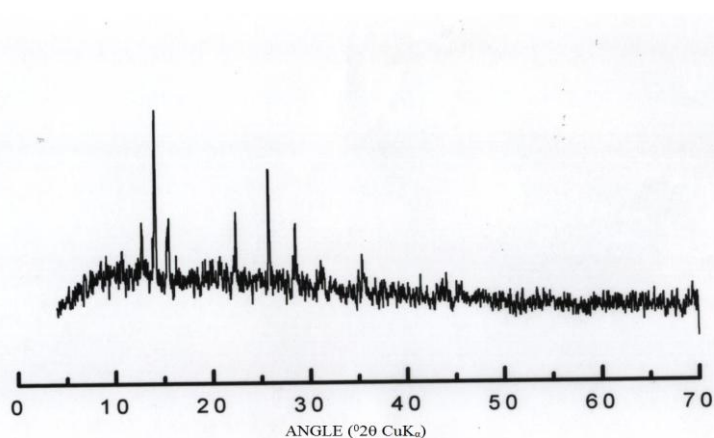


Figure 1: X-ray powder diffraction patterns of the complex $\text{H}_2[\text{Mn}(\text{EDTA})]\cdot 3,5\text{H}_2\text{O}$

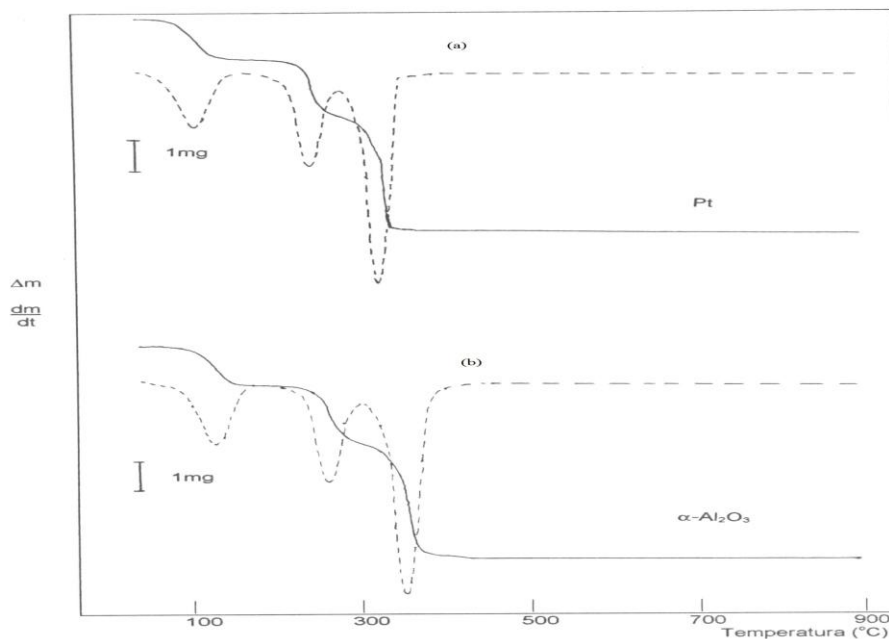


Figura 2: TG and DTG curves of the complex $H_2[Mn(EDTA)].3,5H_2O$ in air atmosphere (150 mL min^{-1}): a- Platine crucible (7,392mg); b- alumina crucible (7,736 mg); $30 \leq \Delta T \leq 900^\circ\text{C}$, $\beta = 20^\circ\text{C}$,

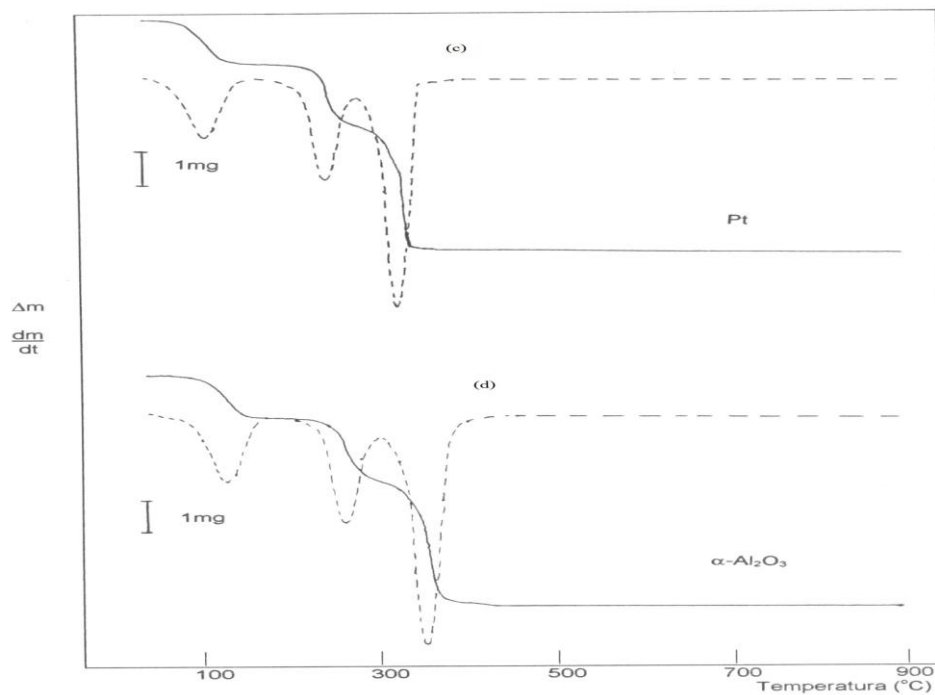


Figura 3: TG and DTG curves of the complex $H_2[Mn(EDTA)].3,5H_2O$ in CO_2 atmosphere (150 mL min^{-1}): a- Platine crucible (7,276 mg); b- alumina crucible (7,582 mg).; $30 \leq \Delta T \leq 900^\circ\text{C}$, $\beta = 20^\circ\text{C}$, CO_2 flow = 150 mL min^{-1}

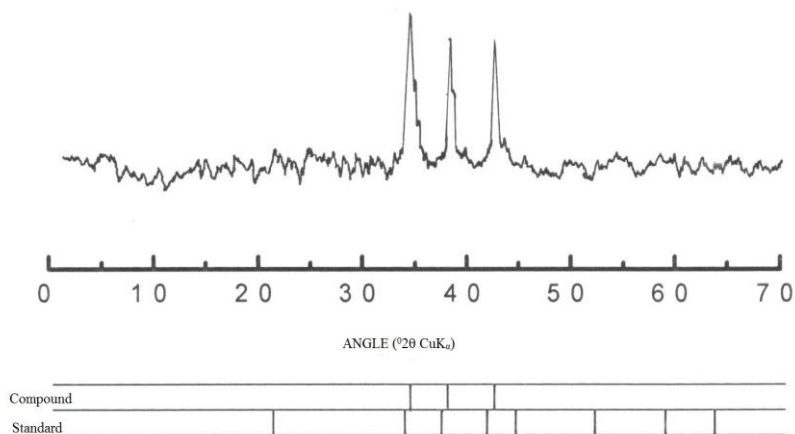


Figura 4: X-ray power diffraction patterns of residue (Mn_3O_4) of the complex $H_2[Mn(EDTA)].3,5H_2O$ obtained in air atmosphere

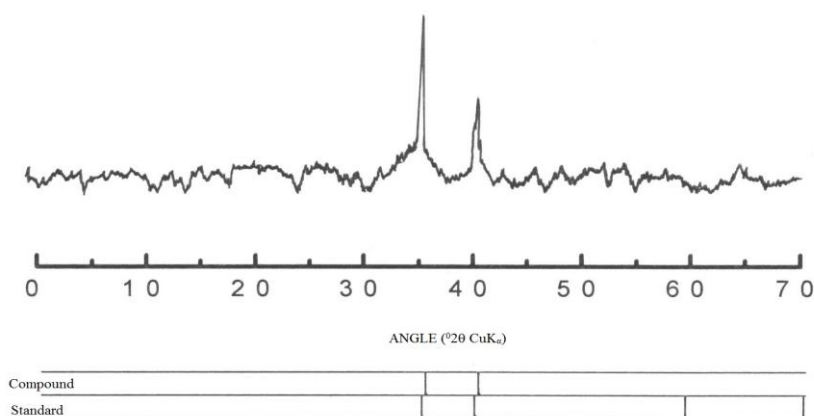


Figura 5: X-ray power diffraction patterns of residue (MnO) of the complex $H_2[Mn(EDTA)].3,5H_2O$ obtained in CO_2 atmosphere

The mass losses and the corresponding temperature ranges for the partial thermal decomposition of the compound are shown in Table 2. The DSC curves of the compound in air and CO_2 atmosphere are shown in Figure 6 and 7. This curve show endothermic and exothermic peaks that are in accord with the mass losses of the TG and DTG curves up to $600^{\circ}C$.

The DSC curves in air atmosphere (Figure 6) exhibit endothermic peak at $160^{\circ}C$, attributed to dehydration, in agreement with mass losses observed in TG and DTG curves. The second endothermic peak is attributed to partial thermal decomposition of compound and the broad exotherm in the range $314-520^{\circ}C$ with maximum in

$360^{\circ}C$ and $388^{\circ}C$ are ascribed to the final pyrolysis with formation of oxide, as residue. The peak at $388^{\circ}C$ suggest a change in oxidation state intermolecular of binder.

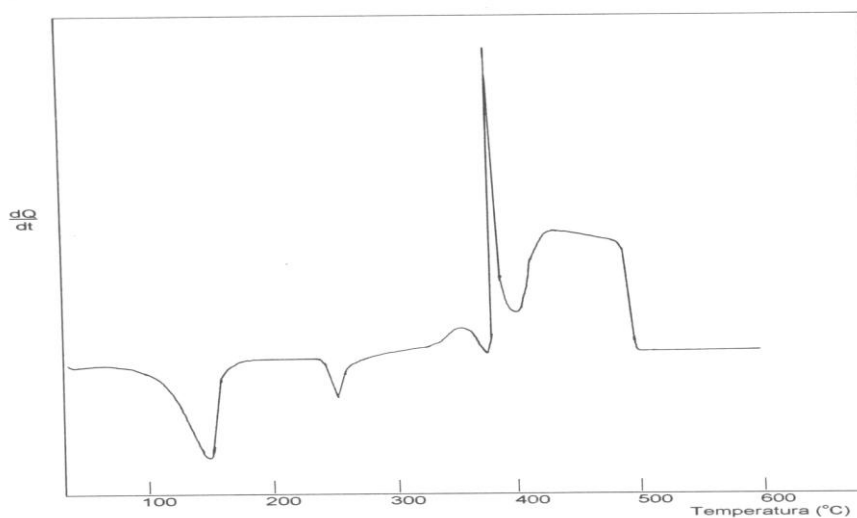
For CO_2 atmosphere (Figure 7) the DSC curve also exhibit endothermic peak due to dehydration ($150^{\circ}C$) and it is observed at the same temperature that in air atmosphere. The endothermic peaks observed at $260^{\circ}C$ and $380^{\circ}C$ are attributed to the thermal decomposition of anhydrous compounds. These are in agreement with the steps mass loss observed in the TG and DTG curves.

The exothermic peak at $428^{\circ}C$ probably is due to the internal oxidation-reduction that occur during the thermal decomposition of the binder.

Table 2: Thermoanalytical data of solid state chelate of ethylenediaminetetraacetic acid with manganese (II).

Compound /m _i (mg) /condition	Mass loss (mg)	Temp. range (°C)	Atribution	Mass loss Obs. (%)	Mass loss. Calc.(%)
H ₂ [Mn(EDTA)].3,5 H ₂ O	1,111	30 - 120	3,5 H ₂ O	15,03	15,45
7,392	1,632	175-266	CO ₂ ; CO; 1H ₂ O	22,08	22,06
Pt Ar	3,231	266-400	Pyrolysis of binder with formation of Mn ₃ O ₄	43,71	43,81
H ₂ [Mn(EDTA)].3,5 H ₂ O	1,163	30 - 138	3,5 H ₂ O	15,03	15,45
7,736	1,697	175-287	CO ₂ ; CO; 1H ₂ O	21,94	22,06
α-Al ₂ O ₃ Ar	3,389	287-450	Final thermal decomposition of the compound with formation of Mn ₃ O ₄	43,81	43,81
H ₂ [Mn(EDTA)].3,5 H ₂ O	1,100	30 - 132	3,5 H ₂ O	15,12	15,45
7,276	1,608	200-294	CO ₂ ; CO; 1H ₂ O	22,10	22,06
Pt CO ₂	1,533	294-393	CO ₂ ; (-CH ₂ NCH ₂)	21,06	21,09
	1,721	393-770	Thermal decomposition of the compound with formation of MnO	23,65	24,04
H ₂ [Mn(EDTA)].3,5 H ₂ O	1,156	30 - 150	3,5 H ₂ O	15,25	15,45
7,582	1,669	200-320	CO ₂ ; CO; 1H ₂ O	22,01	22,06
α-Al ₂ O ₃ CO ₂	1,593	320-400	CO ₂ ; (-CH ₂ NCH ₂ -)	21,01	21,09
	1,807	400-750	Thermal decomposition of the compound with formation of MnO	23,83	24,04

Temp: temperature; Obs.: observed; Calc.: calculated

**Figure 6:** DSC curve of the complex H₂[Mn(EDTA)].3,5H₂O in air atmosphere (150 mL min⁻¹); 30 ≤ ΔT ≤ 900°C, β = 20°C, perforated aluminum 1 mm crucible.

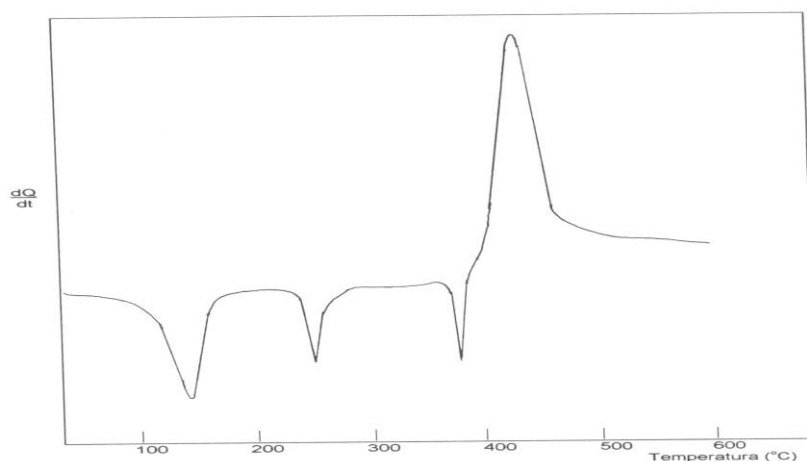


Figure 7: DSC curves of the complex $H_2[Mn(EDTA)].3,5H_2O$ in CO_2 atmosphere ($150 mL min^{-1}$); $30 \leq \Delta T \leq 900^\circ C$, $\beta = 20^\circ C$, perforated aluminum 1 mm crucible.

Conclusions

The TG-DTG curves permitted to establish the general formula of the compound in the solid state and provided information about the thermal decomposition of the manganese complex with ethylenediaminetetraacetic acid.

In addition, the thermal decomposition of these compound have been reported for the first time.

Acknowledgment

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