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THERMOANALYTICAL AND STRUCTURAL STUDY OF LEAD TRIOXYNITRATES

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ABSTRACT

A study of lead trihydroxynitrate obtained by precipitation at 0ºC from a solution of lead nitrate 0.75M with concentrated ammonia is carried out.
By progressive calcination of the trihydroxynitrate of lead, different compounds are obtained.

INTRODUCTION

Following the study of lead oxynitrates that we began years ago (1,2),this is a study of the conditions of the formation of lead trioxynitrate.We have assigned it the empirical formula $Pb(NO_3)_2 \cdot 3Pb(OH)_2$.

This compound has been studied by different authors (3)(4)(5)(6).Some of them assign it the empirical formula $Pb(NO_3)_2 \cdot 3Pb(OH)_2$ and others,$Pb(NO_3)_2 \cdot 3PbO \cdot 3H_2O$,but no reason has been given for these formulae.

We obtained the trihydroxynitrate by precipitation from an aqueous solution of lead nitrate with concentrated ammonia.This precipitate was studied by thermal analysis,IR spectroscopy,X-ray powder diffraction and electronic microscopy.

EXPERIMENTAL

Products

$Pb(NO_3)_2$, NH_4OH,Merck,a.r.

Preparation of the samples

The sample is obtained by precipitation at 0°C of a solution of lead nitrate 0.75M with concentrated ammonia.For 60ml of lead nitrate solution,15ml of ammonia are required.These are added in two phases:1)5ml at a rate of 0.4ml/min,and 2)10ml at a rate of 1.3ml/min.The solution is stirred quickly during the addition of the ammonia,and when the precipitation is finished,stirring is continued for 30 minutes.

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The obtained precipitate is filtered and dried in an open atmosphere,and identified by quantitative chemical analysis and IR spectroscopy.

RESULTS AND DISCUSSION

Thermal study

In fig.1 we give the TG and DTA curves of the trihydroxynitrate of lead.

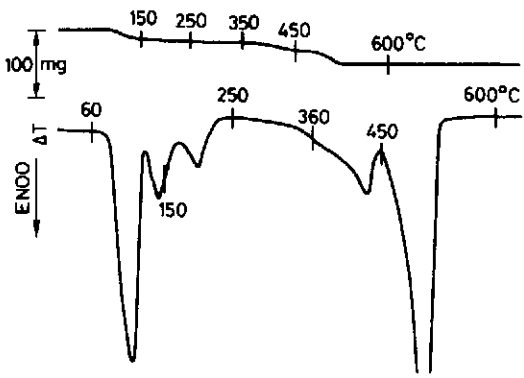

Fig.1.TG and DTA curves

In TG curve,the first release corresponds to the decomposition of lead trihydroxynitrate to anhydrous trioxynitrate. The second release,between 250°C and 550°C,corresponds to the decomposition of anhydrous trioxynitrate to PbO, which occurs in two steps with the intermediate formation of pentoxynitrate of lead,as the X-ray diffraction confirms.

The ATD curve presents 5 endothermic peaks;the three former correspond to the first loss of the TG curve due to the dehydroxylation.

Electronic microscopy

The lead trihydroxynitrate appears as well defined hexagonal crystals,about 2μ(Fig.2).

Infrared spectroscopy

The spectra of $Pb(NO_3)_2 \cdot 3Pb(OH)_2$ and of $Pb(NO_3)_2 \cdot 3PbO$ are shown in Fig.3,curves a) and b).

The samples were prepared as mull using fluorolube as mulling agent for the region between 4000-1500cm^{-1},and potassium bromide pellets for the region between 1500-200cm^{-1}.

In curve a) the H-O-H bending motion does not appear in the region 1600-1650cm^{-1};for this reason we have discarded the formula $Pb(NO_3)_2 \cdot 3PbO \cdot 3H_2O$.

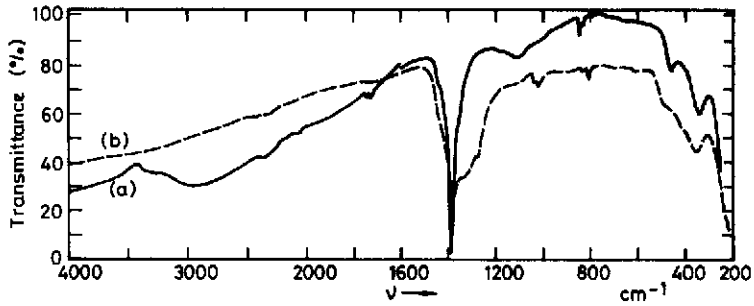

Fig.3.IR spectra

X-ray Diffraction

X-ray powder diffractions of lead trihydroxynitrate and anhydrous trioxynitrate of lead,were carried out.

In Table I we give the X-ray diffraction pattern of the anhydrous trioxynitrate of lead,which is not reported in the literature.

Table I

X-ray data corresponding to $Pb(NO_3)_2.3PbO$

d_{obs}(Å)	d_{cal}(Å)	h k l	I/I_o	d_{obs}(Å)	d_{cal}(Å)	h k l	I/I_o
9.036	8.997	1 1 0	10	2.803	2.803	-2 3 0	11
7.769	7.822	-2 0 0	100	2.760	2.761	-3 0 1	15
6.676	6.715	2 1 0	3	2.710	2.708	1 2 1	11
4.862	4.878	1 2 0	4	2.592	2.589	-3 1 1	16
3.880	3.882	4 1 0	11	2.440	2.439	2 4 0	6
3.806	3.810	-2 2 0	24	1.961	1.961	6 4 0	6
3.246	3.250	0 0 1	25	1.933	1.932	3 5 0	10
3.131	3.129	-5 0 0	90	1.899	1.900	-7 2 0	8
3.061	3.061	1 1 1	21	1.677	1.676	-8 0 1	7
2.878	2.879	5 2 0	6				

The X-ray diffraction pattern of $Pb(NO_3)_2.3Pb(OH)_2$ is identical to that reported by Kwestroo(4) and Michell(5).These authors do not give the crystalline parameters.

The crystalline parameters for both compounds were obtained (7) and these were adjusted by the least squares method using the sub-program PARAM of the general program X-ray L-SUCRE(8).These data are shown in Table II.

Table II

Crystallographic Data

Compound	System	Parameters (Å)
$Pb(NO_3)_2 \cdot 3Pb(OH)_2$	Orthorhombic	a=17.201 b= 8.5556 c= 4.1603
$Pb(NO_3)_2 \cdot 3PbO$	Monoclinic $\alpha = \beta = 90^\circ$ $\gamma = 79^\circ\ 40'$	a=15.915 b= 9.8349 c= 3.2558

CONCLUSIONS

The study carried out, allows us to establish the following stages in the thermal transformation of the trihydroxynitrate of lead obtained by precipitation

$$Pb(NO_3)_2 \cdot 3Pb(OH)_2 \longrightarrow Pb(NO_3)_2 \cdot 3PbO \longrightarrow Pb(NO_3)_2 \cdot 5PbO \longrightarrow PbO$$

We have also determined the crystallographic data of the lead trihydroxynitrate and the anhydrous trioxynitrate, which do not appear in the literature.

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