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THERMOANALYTICAL STUDY OF LEAD MONOHYDROXYNITRATE

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ABSTRACT

In this paper we have studied the preparation of lead monohydroxynitrate, obtained from a 0.75 M solution of lead nitrate at 0°C with ammonia. The progressive calcination of the precipitate obtained leads to anhydrous lead monoxynitrate and to other oxynitrates with molar ratios $PbO/Pb(NO_3)_2 = 1.4$ and 2.2. All these precipitates have been studied by chemical analysis, thermogravimetry, differential thermal analysis, infrared spectroscopy and X-ray diffraction, whose results permit us to assign it the formula $Pb(NO_3)_2 \cdot Pb(OH)_2$.

INTRODUCTION

The preparation of basic lead nitrates by reaction of lead nitrate solutions with an alkali (NaOH, NH_4OH) or with a lead nitrate suspension (β-PbO) has been studied by numerous authors from the end of the last century [1] until now. They have assigned different forms to them: if n = nitrate/oxide, n is generally a whole number, 1, 2, 3, 4 or 5. The only other nitrate/oxide relations known are 3/1 and 1/9 of Berton [2], 2/5 of Kwestroo et al. [3] and 3/7 of Brusset et al. [4].

In most studies the chemical composition of the precipitates obtained has been established by calorimetric, conductometric or potentiometric measurements. The interpretation of such measurements is difficult, even if the inflexion points have the characteristics required to suggest a defined compound, as Byé [5], Heubel [6] and Franchèrre [7] opportunely note.

This point illustrates the difficulty of obtaining basic lead nitrates and explains the controversy among authors about the stoichiometry of these compounds.

It has already been established that the nature of the precipitate obtained depends on the operating conditions and, in particular, on temperature, concentration of lead nitrate solution and reagents, duration of contact between aqueous nitrate solution and reagent, and, according to Pauley and Testerman [8], even the addition rate of the reagent.

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Besides, the imprecision of nitrate analysis and the fact that the atomic weight of Pb is much greater than the molecular weight of NO_3^- and H_2O have contributed to the difficulty of determining the stoichiometry of the precipitates obtained. Finally, we have to say that the basic nitrates determined transform in an open atmosphere, also contributing to the difficulty of determining the stoichiometry of these oxynitrates.

Basic lead nitrates are of great technical interest due to their use as catalyzers and pigments.

In this paper we study the obtainment of a lead monohydroxynitrate and the transformations carried out during its progressive calcination. The basic nitrate does not suffer any transformation when left in an open atmosphere even after two years, contrary to what happens with other basic nitrates, as we have shown in the case of lead pentoxynitrate.

This compound has been studied by different authors. All of them use NaOH as precipitant, but we have employed NH_4OH to avoid the possible formation of sodium plumbite. These authors disagree about the formula given to this compound. Pauley and Testerman [8], Byé [5], Kwestroo et al. [3] and Narita et al. [9], assign it the formula $Pb(NO_3)_2 \cdot Pb(OH)_2$, while Heubel [6], Brusset et al. [4] and Michell [10], assign it the formula $Pb(NO_3)_2 \cdot PbO \cdot xH_2O$ ($x = 1, 1.5, 2$). Finally, Cram and Davies [11], by studies of Raman and IR spectroscopy, suggest that the compound $Pb(NO_3)_2 \cdot PbO \cdot 2H_2O$ should be written as $Pb_4(OH)_4(NO_3)_4 \cdot 2H_2O$.

This study was carried out employing the following techniques: thermogravimetry, differential thermal analysis, X-ray powder diffraction and IR spectroscopy.

Thermogravimetry allows the amounts of water and nitrates of the precipitate to be determined with better precision than methods proposed until now. This technique also gives information about the formation of different compounds during heating of the precipitate. Differential thermal analysis completes the thermogravimetric data.

EXPERIMENTAL

Products

$(NO_3)_2Pb$, Merck, r.a.; NH_4OH, Merck, r.a.

Preparation of the samples

The sample is obtained by precipitation at 0°C of a 0.75 M solution of lead nitrate with concentrated ammonia. For 60 ml of lead nitrate solution, 5 ml of ammonia are added at a rate of 0.4 ml min^{-1}. The solution is stirred quickly during the addition of ammonia. The precipitate obtained is filtered by means of an N.4 coarse filter, washed with ethanol, and dried in an open atmosphere. The rate of addition must be strictly controlled, otherwise mixtures of monohydroxynitrate and hydrated dioxynitrate are obtained.

The composition of the precipitate has been determined by quantitative chemical analysis: NO_3^-, Perkin-Elmer 240 analyzer; Pb^{2+}, complexometric titration with EDTA, indicator Eriochrome Black T.

Apparatus

TG apparatus

Chevenard thermobalance (model 93) from Adamel. Photographic recording. Heating rate: 300°C h^{-1}.

DTA apparatus

Constructed in the laboratory using a vertical furnace and a temperature regulation system, both Adamel. A differential chromel/alumel thermocouple was used. Heating rate: 300°C h^{-1}.

X-ray powder diffraction

Siemens D-500 diffractometer. Graphite monochromater. K 805 generator. Cu $K\alpha_1$ radiation.

Infrared spectroscopy

Perkin-Elmer 599B; the samples were prepared as a mull using fluorolube as mulling agent for the region 4000–1500 cm^{-1}, and KBr pellets for the region 1500–200 cm^{-1}.

RESULTS AND DISCUSSION

Thermal and X-ray diffraction studies

In Table 1 we give the X-ray diffraction pattern of the lead monohydroxynitrate.

Figure 1 gives the TG and DTA curves of lead monohydroxynitrate. The TG curve (Fig. 1.1) presents six steps, the first and second steps (80–200°C) correspond to the loss of the hydroxyls. Between 200 and 375°C there is a plateau, which corresponds to $Pb(NO_3)_2 \cdot PbO$, whose X-ray diffraction pattern is given in Table 2.

Above 375°C, four steps are observed which are badly defined in the TG curve but well defined in the DTA curve (Fig. 1.2).

Determination of the composition of the intermediate compounds is possible with the help of thermograms of samples taken at predetermined points on the DTA curve.

TABLE 1

X-ray data corresponding to $Pb(NO_3)_2 \cdot Pb(OH)_2$

d_{obs} (Å)	d_{calc} (Å)	I/I_0	h	k	l	d_{obs} (Å)	d_{calc} (Å)	I/I_0	h	k	l
6.553	6.556	29	−1	0	1	2.572	2.572	14	−3	3	1
6.320	6.313	100	1	0	1	2.514	2.511	10	−2	4	1
5.453	5.455	8	2	0	0	2.473	2.478	15	2	3	2
4.875	4.792	17	2	0	1	2.416	2.411	9	3	2	3
4.815	4.792	17				2.354	2.351	10	1	2	3
4.160	4.147	5	2	1	1	2.281	2.293	11	−4	0	2
3.823	3.789	19	−1	0	2	2.253	2.252	9	−4	1	2
3.782	3.779	12	0	1	2	2.186	2.185	5	−3	0	3
3.638	3.636	10	3	0	0	2.153	2.154	11	1	3	3
3.600	3.613	24	−1	1	2	2.128	2.126	12	−5	0	1
3.573	3.575	28	0	3	1	2.113	2.109	15	2	5	1
3.513	3.530	10	1	1	2	2.099	2.105	11	3	0	3
3.427	3.415	36	−1	3	1	2.025	2.026	20	2	3	3
3.377	3.379	7	1	3	1	1.946	1.946	5	−5	0	2
3.270	3.259	46	3	0	1	1.922	1.921	7	−5	1	2
3.192	3.204	10	−1	2	2	1.883	1.882	6	5	0	2
3.151	3.145	27	3	1	1	1.860	1.859	7	5	1	2
3.063	3.053	9	2	1	2	1.846	1.847	7	2	0	4
2.996	3.001	38	0	4	0	1.829	1.833	6	−2	6	1
2.958	2.966	14	2	3	1	1.815	1.818	5	6	0	0
2.891	2.893	22	−1	4	0	1.802	1.802	6	4	5	0
2.860	2.864	9	3	2	1	1.762	1.765	7	−1	5	3
2.779	2.794	10	2	2	2	1.749	1.749	7	1	3	4
2.758	2.751	18	−1	3	2	1.744	1.746	6	−4	3	3
2.732	2.737	39	−4	0	0	1.685	1.687	6	6	2	1
2.623	2.629	5	2	4	0	1.664	1.663	7	−6	1	2
						1.650	1.648	7	−1	4	4

The sample taken at 440°C is white in colour; its thermogram shows that the ratio $PbO/(NO_3)_2Pb$ is 1.4, on an average of four determinations. Its X-ray diffraction pattern is given in Table 3.

Sometimes the transformation $Pb(NO_3)_2 \cdot PbO \rightarrow Pb(NO_3)_2 \cdot 1.4PbO$, appears in the DTA curve (Fig. 1.2) as two endothermic peaks.

The X-ray diffraction of a sample taken at 410°C, after the first peak, shows that the transformation is continuing; in the diagram, lines of both $Pb(NO_3)_2 \cdot 1.4PbO$ and $Pb(NO_3)_2 \cdot PbO$ appear.

The thermogram of the sample taken at 470°C shows that for this compound the ratio $PbO/(NO_3)_2Pb$ is 2.2, on an average of four determinations. The X-ray diffraction pattern is given in Table 4.

The X-ray diagram of the sample taken at 505°C corresponds to a mixture of $Pb(NO_3)_2 \cdot 5PbO$ and red PbO.

Finally, the X-ray diagram of the sample taken at 600°C corresponds to yellow PbO.

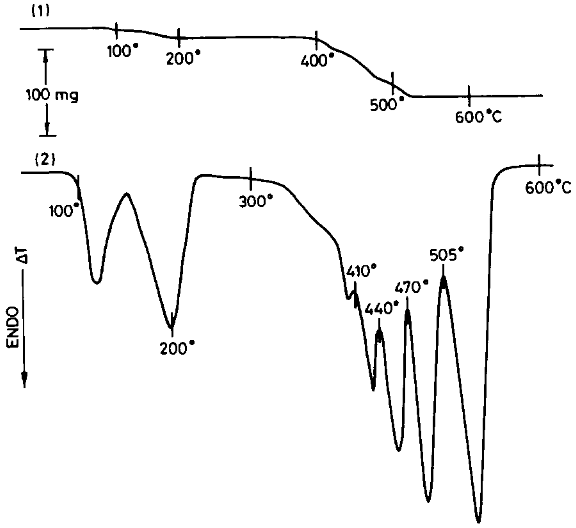

Fig. 1. TG (1) and DTA (2) curves. Sample weight: 354.9 mg.

The crystalline parameters of the compounds obtained were adjusted by the least-squares method using the sub-program PARAM of the general program X-ray L-SUCRE [12]. These data are shown in Table 5.

TABLE 2

X-ray data corresponding to $Pb(NO_3)_2 \cdot PbO$

d_{obs} (Å)	d_{calc} (Å)	I/I_0	h	k	l	d_{obs} (Å)	d_{calc} (Å)	I/I_0	h	k	l
9.302	9.330	18	−1	0	1	2.653	2.629	7	−4	0	3
7.369	6.990	8	–	–	–	2.569	2.572	5	4	0	1
7.019	6.990	18	1	0	1	2.396	2.399	6	−1	1	4
5.862	5.730	7	−2	0	1	2.367	2.367	57	−4	1	0
4.548	4.545	100	2	0	1	2.335	2.336	14	3	1	2
4.223	4.328	9	–	–	–	2.299	2.298	8	−1	0	5
4.107	4.042	11	–	–	–	2.264	2.262	29	−5	0	0
3.922	3.920	34	3	0	1	1.963	1.963	12	−2	2	2
3.693	3.691	5	0	0	3	1.891	1.892	5	5	1	1
3.520	3.495	8	–	–	–	1.845	1.845	5	0	0	6
3.250	3.250	16	1	0	3	1.801	1.801	17	1	2	3
3.173	3.173	27	−2	1	2	1.756	1.756	17	−2	1	6
3.124	3.119	41	1	1	2	1.706	1.706	5	3	2	2
2.882	2.882	36	−1	0	4	1.601	1.602	9	5	1	3
2.825	2.827	7	4	0	0	1.511	1.511	9	−5	0	7
2.776	2.774	30	3	0	2						

TABLE 3

X-ray data corresponding to $Pb(NO_3)_2 \cdot 1.4PbO$

d_{obs} (Å)	d_{calc} (Å)	I/I_0	h	k	l	d_{obs} (Å)	d_{calc} (Å)	I/I_0	h	k	l
9.817	9.830	24	0	2	0	2.650	2.650	40	−4	2	3
8.999	9.027	32	0	0	1	2.572	2.570	51	−6	3	1
8.418	8.422	100	−1	2	0	2.537	2.537	33	−4	3	3
8.073	8.055	38	−1	1	1	2.499	2.497	27	2	7	1
6.651	6.649	91	0	2	1	2.460	2.460	16	1	4	3
5.063	5.063	31	−3	1	1	2.428	2.425	33	2	6	2
4.237	4.240	67	3	0	1	2.354	2.353	20	2	8	0
4.149	4.145	43	3	1	1	2.328	2.326	15	1	8	1
4.064	4.062	46	1	4	1	2.252	2.253	32	−7	3	1
3.894	3.894	20	3	2	1	2.194	2.194	17	−4	1	4
3.767	3.770	35	−4	2	0	2.083	2.083	18	−2	9	1
3.609	3.607	74	2	0	2	2.039	2.039	20	−8	1	2
3.545	3.543	36	−2	5	0	1.992	1.991	34	−7	5	2
3.457	3.461	62	−4	0	2	1.979	1.981	23	−6	7	1
3.373	3.374	70	−1	4	2	1.903	1.902	18	−5	8	2
3.288	3.286	49	−5	1	1	1.868	1.868	36	2	9	2
3.186	3.189	89	2	5	1	1.824	1.825	17	−7	7	1
3.087	3.085	85	−3	4	2	1.802	1.802	17	0	10	2
3.007	3.009	54	0	0	3	1.773	1.773	14	−4	10	1
2.976	2.974	83	0	1	3	1.751	1.752	23	−1	11	1
2.924	2.923	47	−5	3	0	1.692	1.692	22	6	7	2
2.812	2.812	97	4	4	1	1.657	1.657	17	−2	11	2
2.688	2.688	45	−6	2	1	1.627	1.627	21	10	1	0

TABLE 4

X-ray data corresponding to $Pb(NO_3)_2 \cdot 2.2PbO$

d_{obs} (Å)	d_{calc} (Å)	I/I_0	h	k	l	d_{obs} (Å)	d_{calc} (Å)	I/I_0	h	k	l
9.796	9.809	100	0	0	1	3.466	3.469	8	3	2	2
8.648	8.665	50	1	0	1	3.273	3.270	19	0	0	3
8.378	8.396	96	0	1	1	3.220	3.220	34	1	0	3
6.180	6.161	9	3	0	0	3.078	3.081	53	6	0	0
4.965	4.967	8	3	1	1	2.962	2.962	25	2	4	2
4.918	4.908	13	3	2	2	2.839	2.844	40	3	1	3
4.223	4.216	21	2	3	1	2.736	2.733	13	5	4	0
3.604	3.605	17	5	1	0	2.679	2.679	17	1	5	2
3.559	3.566	12	1	3	2	2.453	2.452	16	0	0	4
						2.333	2.335	17	4	6	0

TABLE 5

Crystallographic data

Compound	System	Parameters (Å)
$Pb(NO_3)_2 \cdot Pb(OH)_2$	Monoclinic	$a = 10.918 \pm 0.007$
	$\alpha = \gamma = 90°$	$b = 12.008 \pm 0.012$
	$\beta = 92°14'$	$c = 7.969 \pm 0.010$
$Pb(NO_3)_2 \cdot PbO$	Monoclinic	$a = 11.783 \pm 0.005$
	$\alpha = \gamma = 90°$	$b = 4.328 \pm 0.002$
	$\beta = 106°19'$	$c = 11.537 \pm 0.003$
$Pb(NO_3)_2 \cdot 1.4PbO$	Monoclinic	$a = 16.803 \pm 0.003$
	$\alpha = \gamma = 90°$	$b = 19.660 \pm 0.003$
	$\beta = 103°38'$	$c = 9.289 \pm 0.002$
$Pb(NO_3)_2 \cdot 2.2PbO$	Orthorhombic	$a = 18.484 \pm 0.001$
	$\alpha = \beta = \gamma = 90°$	$b = 16.233 \pm 0.001$
		$c = 9.809 \pm 0.0004$

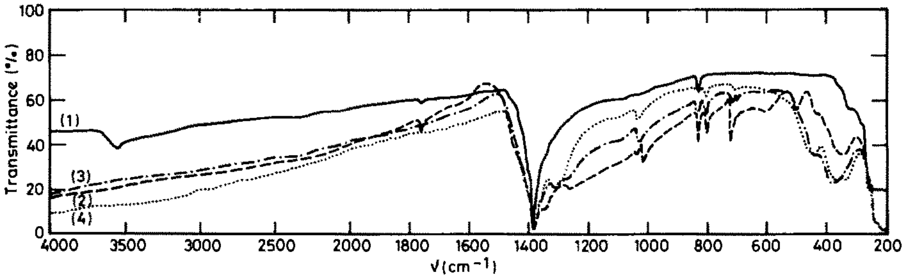

Fig. 2. IR spectra.

Infrared spectroscopy

Figure 2 shows the spectra of $Pb(NO_3)_2 \cdot Pb(OH)_2$, $Pb(NO_3)_2 \cdot PbO$, $Pb(NO_3)_2 \cdot 1.4PbO$ and $Pb(NO_3)_2 \cdot 2.2PbO$, curves 1–4, respectively.

In curve 1 the H–O–H bending motion does not appear in the region 1600–1650 cm^{-1}, so the band in the region 3200–3700 cm^{-1} is only due to the hydroxyl group.

Also observed in this curve are two characteristic bands of nitrates in the regions 1380–1320 (ν_3) and 810–830 cm^{-1} (ν_2), and the weak band of nitrates at 1760 cm^{-1}.

Curves 2, 3 and 4 are similar. The characteristic bands of nitrates appear in all of them: 1380–1270 (ν_3), 810–830 (ν_2), 1040 (ν_1) and the weak band at 1760 cm^{-1}.

CONCLUSION

The study carried out in the present paper allows us to establish the following stages in the thermical transformation of the $Pb(NO_3)_2 \cdot Pb(OH)_2$ obtained by precipitation:

$$Pb(NO_3)_2 \cdot Pb(OH)_2 \rightarrow Pb(NO_3)_2 \cdot PbO \rightarrow$$

$$Pb(NO_3)_2 \cdot 1.4PbO \rightarrow Pb(NO_3)_2 \cdot 2.2PbO \rightarrow$$

$$Pb(NO_3)_2 \cdot 5PbO + (\text{red})\ PbO \rightarrow (\text{yellow})\ PbO$$

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