

The Basic Lead Nitrates

I. Compounds Formed by the Reaction of Orthorhombic Lead Monoxide with Cold Aqueous Lead Nitrate^a

E. W. John Michell

Associated Lead Manufacturers Ltd., Research Laboratories, 7 Wadsworth Road, Perivale, Greenford, Middlesex UB6 7JQ

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Solid products of the reaction between orthorhombic lead monoxide and cold aqueous lead nitrate solutions in the range of molar proportions 1 : 3 to 3 : 1 PbO : Pb(NO₃)₂ have been studied by X-ray powder diffraction (X.R.P.D.). Three distinct crystalline phases were recognised.

Reasonably pure samples of monobasic lead nitrate dihydrate [dilead (II) monoxide dinitrate dihydrate], PbO.Pb(NO₃)₂.2H₂O, were obtained at temperatures below 20 °C when the reactants were in the range of molar proportions 1 : 3 to 1 : 1 PbO : Pb(NO₃)₂. This compound seems to be stable below 20 °C, but it partially dehydrates at higher temperatures. It does not seem to have been reported elsewhere. Monobasic lead nitrate monohydrate [dilead (II) monoxide dinitrate monohydrate], PbO.Pb(NO₃)₂.H₂O, was formed in isolation at temperatures between 25 and 30 °C when the reactants were in the range of molar proportions 1 : 3 to 1 : 1 PbO : Pb(NO₃)₂. This compound is stable at room temperatures, and is identical to phases which have been reported by other authors. Mixtures of these two substances were obtained at temperatures between 20 and 25 °C. Tribasic lead nitrate trihydrate [tetra lead (II) trioxide dinitrate trihydrate], 3PbO.Pb(NO₃)₂.3H₂O, was formed in isolation at all temperatures in the range 15 to 30 °C when the reactants were in the molar proportion 3 : 1 PbO : Pb(NO₃)₂. This compound seems to be stable at room temperatures and has been reported elsewhere. When the reactants were in the molar proportion 2 : 1 PbO : Pb(NO₃)₂, mixtures of tribasic lead nitrate trihydrate with one or other (or both, depending on the temperature) of the monobasic lead nitrate hydrates were obtained.

X.R.P.D. data are given for these three compounds, and a critical assessment is made of all the results in the cases of the two compounds for which published data already exists. Also, it is suggested that compounds of stoichiometries intermediate between that of a monobasic lead nitrate hydrate and that of a tribasic lead nitrate hydrate (and which have been described in the literature) can be only metastable in contact with water. The nomenclature used in this paper follows common industrial practise in naming basic lead compounds. However, scientific names are also given in parentheses when necessary.

1. Introduction

No X-ray powder diffraction (X.R.P.D.) work on basic lead nitrates seems to have been reported before 1967. In 1967, two independent X.R.P.D. studies of basic lead nitrates were published, one by a group of Dutch workers¹ and the other by a group

^a Reactants in the range of molar proportions 1 : 3 to 3 : 1 PbO : Pb(NO₃)₂.

of French workers.² Agreement between results described in these two papers is not altogether satisfactory. For example, despite the fact that both groups of workers prepared their compounds by adding sodium hydroxide solutions to aqueous lead nitrate solutions, each paper claims the existence of species which are not reported in the other paper. Also, X.R.P.D. data for corresponding substances do not agree precisely. Further, one paper states "lead oxide did not react with a solution of lead nitrate".¹ This conflicts with previous statements made in the literature to the effect that "monobasic lead nitrate can be made by heating lead monoxide with an aqueous solution of lead nitrate"^{3,4} and also with the present author's experience.

In the hope that some of the confusion which evidently surrounds the basic lead nitrates will be removed, it is the aim of this and subsequent papers to describe investigations of these compounds which have been carried out in these laboratories. The results obtained fall into groups according to the method of preparation and also according to the experimental products. This paper describes crystalline compounds formed by the reaction of orthorhombic lead monoxide with cold aqueous lead nitrate solutions in the range of molar proportions 1 : 3 to 3 : 1 PbO : Pb(NO₃)₂. Another paper will describe compounds formed when the reactants were in molar ratios greater than 3 : 1 PbO : Pb(NO₃)₂. It is hoped to discuss the basic lead nitrates formed in hot aqueous suspensions, and those compounds formed when other reactants are used, subsequently.

2. Experimental

2.1. Reactants

"Canary litharge", orthorhombic (yellow) lead monoxide was used in all the experiments described in this paper. Lead nitrate was made by dissolving Canary litharge in A.R. grade nitric acid diluted to about 20% with deionised water, crystallising the solid from hot solution, and then recrystallising three times from solutions made with fresh deionised water (specific resistance > 2 M Ω cm). U.v. emission spectroscopy did not reveal any significant differences between the trace impurity contents of the Canary litharge⁵ and those impurities in the lead nitrate made from it.

2.2. Procedure

Solutions containing 33.12 g (0.1 mols), 66.24 g (0.2 mols) or 99.36 (0.3 mols) of lead nitrate in about 250 ml deionised water were added to suspensions of 22.32 g (0.1 mols), 44.64 g (0.2 mols) or 66.96 g (0.3 mols) of orthorhombic lead monoxide in about 250 ml deionised water. In all of these experiments the lead monoxide suspensions were stirred for about 1 h before adding the lead nitrate solutions, after which stirring was continued for various periods of time up to about ten days (240 h).

In one series of experiments the vessels containing the reaction mixtures were partially immersed in a bath of cold running tap water, and the mixtures were agitated with glass stirrers driven by variable speed electric motors. It was found that the temperatures of these reaction mixtures varied between 15 and 20 °C. In a second series of experiments, the reaction mixtures were agitated using electrically controlled

magnetic-stirrer assemblies and small bar magnets coated with P.T.F.E. The temperatures in these experiments usually varied between 25 and 30 °C (being higher than ambient due to heat generated in the magnetic-stirrer assembly).

All reaction products were filtered and the solids were washed with cold deionised water. Drying was achieved at "room temperature" by washing with acetone followed by prolonged suction at the filter pad.

2.3. Examination of the products

All solid products of these experiments were examined in transmission with monochromatic CuK_α X-radiation using a Nonius Guinier-de Wolff quadruple focussing camera. For this purpose the dry powders were mounted on adhesive coated cellulose tape.

All single phase solid products were chemically analysed for total lead content by E.D.T.A. titrations, for nitrate content by ion exchange titrations, and for water by the gravimetric method using anhydrous magnesium perchlorate as the absorbant. (In the ion exchange titrations, the sparingly soluble basic lead nitrates were stirred in aqueous suspension with an appropriate ion-exchange resin until all lead was exchanged for hydrogen ion. After filtering to remove the ion exchange resin, the resulting free nitric acid was titrated against standard sodium hydroxide solution). Results were then expressed as stoichiometric formulae of the type $m\text{PbO} \cdot n\text{Pb}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$.

Many single phase solid products were studied in detail to obtain characteristic X.R.P.D. data. For this purpose samples of these products were mounted in specimen segments adjacent to normal lead nitrate, the X.R.P.D. spectra being recorded simultaneously using the Guinier-de Wolff quadruple focusing camera. Long exposures were employed so that faint diffraction lines could be detected. Line positions in the photographic spectra were measured with a Vernier scale reading to 0.05 mm. In each case, a calibration graph was prepared from the lead nitrate spectrum, plotting d_{observed} against $\Delta d = d_{\text{true}} - d_{\text{observed}}$, and using the most accurately known data for lead nitrate.⁶ These calibration graphs were then used to correct the observed sets of data for the various basic lead nitrate samples. Relative intensities were estimated visually on the scale 0–10.

3. Results

In marked contrast to the bright yellow colour of the initial reaction mixtures the solid products of all of these experiments were white. For each molar proportion 1 : 3, 1 : 2, 1 : 1, 2 : 1, 3 : 1 $\text{PbO} : \text{Pb}(\text{NO}_3)_2$, several experiments were performed at temperatures between 15 and 20 °C, varying the periods for which the reaction mixtures were stirred between 40 and 240 h. At each molar ratio essentially identical results were obtained. Corresponding experiments were performed at temperatures between 25 and 30 °C, varying the duration of stirring from 20 to 240 h. Again identical results were obtained at each molar proportion. In all, one hundred experiments were conducted over a period of about three calendar years.

Three single phase solid products were obtained.

(a) Monobasic lead nitrate dihydrate [dilead (II) monoxide dinitrate dihydrate], $\text{PbO} \cdot \text{Pb}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, was formed in a reasonably pure state at temperatures below 20°C when the reactants were in the molar proportions 1 : 3 to 1 : 1 $\text{PbO} : \text{Pb}(\text{NO}_3)_2$. This compound seemed to be stable at temperatures below 20°C , but it partially dehydrated at temperatures much above 20°C .

(b) Monobasic lead nitrate monohydrate [dilead (II) monoxide dinitrate monohydrate], $\text{PbO} \cdot \text{Pb}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, was formed in isolation at temperatures above 25°C when the reactants were in the molar proportions 1 : 3 to 1 : 1 $\text{PbO} : \text{Pb}(\text{NO}_3)_2$. This compound was found to be stable at room temperatures (samples stored in screw capped bottles for longer than four years have not changed significantly, as judged by chemical analyses and X.R.P.D. examinations).

(c) Tribasic lead nitrate trihydrate [tetralead (II) trioxide dinitrate trihydrate] $3\text{PbO} \cdot \text{Pb}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, was formed in isolation at all temperatures in the range 15 to 30°C when the reactants were in the molar ratio 3 : 1 $\text{PbO} : \text{Pb}(\text{NO}_3)_2$. This compound was found to be relatively stable at room temperature, and samples stored in screw-capped bottles for longer than four years have not changed significantly.

Chemical analyses are quoted for these three compounds in Table 1 and X.R.P.D. data are given in Tables 2-4. Experiments which did not give pure samples gave mixtures containing these three substances. No other crystalline phases were observed in these experiments.

TABLE 1. Chemical analyses

Sought by analysis	Monobasic lead nitrate dihydrate $\text{PbO} \cdot \text{Pb}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	Monobasic lead nitrate monohydrate $\text{PbO} \cdot \text{Pb}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	Tribasic lead nitrate trihydrate $3\text{PbO} \cdot \text{Pb}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$
	(%)	(%)	(%)
Pb found (theoretical)	69.3-71.55 (70.19)	72.50-72.90 (72.40)	78.20-79.00 (78.57)
$(\text{NO}_3)_2$ found (theoretical)	19.98-21.30 (21.00)	20.90-21.52 (21.66)	11.56-12.22 (11.76)
H_2O found (theoretical)	5.15-6.74 (6.10)	3.01-3.26 (3.14)	5.10-5.37 (5.12)

Notes: (a) for each compound the range of analytical results obtained from ten independent products is quoted; (b) the overall precision of analysing individual products was such that, when expressed as %PbO plus % $\text{Pb}(\text{NO}_3)_2$ plus % H_2O , the determined values gave totals within the range $100.0 \pm 0.5\%$, and in many cases the totals were found to lie in the comparatively narrow range $100.0 \pm 0.1\%$.

TABLE 2. X.R.P.D. data for monobasic lead nitrate dihydrate [dilead (II) monoxide dinitrate dihydrate], $\text{PbO} \cdot \text{Pb}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$

I/I_{10}	d (Å)	I/I_{10}	d (Å)	I/I_{10}	d (Å)
$\frac{1}{2}$	8.22	6	6.77	1	5.71
4	7.47	$\frac{1}{2}?$	6.64	2	5.53
$\frac{1}{4}$	7.29	1?	6.40	4	5.34
1	7.02	8	6.29	$\frac{1}{2}$	5.18
10	6.93	4	6.10	1	4.90

Table 2—continued

I/I_{10}	d (Å)	I/I_{10}	d (Å)	I/I_{10}	d (Å)
1	4.83	4	2.520	$\frac{1}{2}$	1.785
$\frac{1}{2}$	4.74	$\frac{1}{2}$	2.493	1	1.775
1	4.66	$\frac{1}{2}$	2.480	$\frac{1}{4}$	1.761
6	4.53	$\frac{1}{2}$	2.467	$\frac{1}{2}$	1.753
$\frac{1}{4}$	4.27	$\frac{1}{4}$	2.449	2b	1.741
3	4.22	1	2.430	$\frac{1}{4}$	1.732
1	4.15	3	2.393	1	1.725
2	4.08	1	2.379	2	1.710
4	3.91	$\frac{1}{4}$	2.365	1	1.701
2	3.89	1	2.359	$\frac{1}{4}$	1.687
$\frac{1}{4}$	3.84	1	2.328	$\frac{1}{4}$	1.683
2	3.80	1	2.314	1	1.659
4	3.76	$\frac{1}{2}$ b	2.292	3	1.654
4	3.73	$\frac{1}{2}$	2.264	1	1.646
$\frac{1}{2}$	3.69	$\frac{1}{2}$	2.260	$\frac{1}{2}$ b	1.640
1	3.65	3	2.237	1	1.615
$\frac{1}{2}$	3.62	3	2.219	$\frac{1}{2}$ b	1.599
4	3.60	2	2.199	$\frac{1}{4}$	1.589
$\frac{1}{2}$	3.55	$\frac{1}{2}$	2.177	2	1.582
2b	3.48	$\frac{1}{2}$	2.163	$\frac{1}{2}$	1.571
1	3.42	$\frac{1}{2}$	2.149	1	1.564
4	3.41	1	2.132	1	1.560
4	3.36	$\frac{1}{4}$	2.110	1	1.550
3	3.32	2	2.103	3	1.532
1?	3.30	$\frac{1}{4}$	2.096	$\frac{1}{2}$	1.525
1	3.25	$\frac{1}{4}$	2.079	4	1.513
$\frac{1}{2}$	3.24	$\frac{1}{2}$	2.067	$\frac{1}{4}$	1.505
2	3.19	$\frac{1}{4}$	2.052	1b	1.492
1	3.17	$\frac{1}{2}$	2.040	$\frac{1}{2}$ b	1.479
$\frac{1}{2}$	3.13	$\frac{1}{2}$	2.030	$\frac{1}{2}$	1.469
$\frac{1}{2}$	3.10	$\frac{1}{2}$ b	2.005	$\frac{1}{2}$ b	1.458
4	3.07	1	1.993	$\frac{1}{2}$	1.446
1	3.05	$\frac{1}{2}$	1.986	$\frac{1}{2}$	1.435
4	3.02	$\frac{1}{2}$ b	1.961	$\frac{1}{2}$	1.428
2	2.986	$\frac{1}{4}$	1.953	$\frac{1}{2}$	1.412
6	2.967	2	1.940	$\frac{1}{2}$	1.409
2	2.948	$\frac{1}{2}$	1.929	$\frac{1}{2}$ b	1.401
$\frac{1}{2}$	2.920	3	1.918	$\frac{1}{2}$ b	1.385
$\frac{1}{4}$	2.898	1	1.903	1	1.378
$\frac{1}{2}$	2.864	$\frac{1}{2}$	1.894	{ $\frac{1}{4}$	1.359
1	2.849	$\frac{1}{2}$	1.883	{ $\frac{1}{4}$	1.355
1	2.804	$\frac{1}{2}$ b	1.868	$\frac{1}{4}$	1.348
$\frac{1}{4}$	2.785	$\frac{1}{2}$	1.862	1b	1.334
1b	2.754	$\frac{1}{2}$	1.846	$\frac{1}{4}$	1.325
4	2.725	3	1.840	$\frac{1}{4}$	1.318
3	2.679	1	1.826	$\frac{1}{4}$	1.313
$\frac{1}{2}$	2.658	1	1.820	$\frac{1}{2}$	1.307
$\frac{1}{2}$	2.598	$\frac{1}{2}$	1.812	1	1.299
6b	2.577	1	1.799		
1	2.537	$\frac{1}{4}$	1.792		

(Plus lines to $d = 1.1$ Å)

Note: some lines in this pattern may be attributable to very small amounts of monobasic lead nitrate monohydrate, $\text{PbO} \cdot \text{Pb}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, formed by the slow and partial dehydration of the monobasic lead nitrate dihydrate. These lines have been indicated by the symbol "?".

(See also Note to Table 3.)

TABLE 3. X.R.P.D. data for monobasic lead nitrate monohydrate, [dilead (II) monoxide dinitrate monohydrate], $\text{PbO} \cdot \text{Pb}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$

I/I_{10}	d (Å)	I/I_{10}	d (Å)	I/I_{10}	d (Å)
$\frac{1}{4}$	7.56	2b	2.583	1b	1.754
8	6.64	1	2.547	1	1.741
10	6.40	1	2.528	1	1.731
10	6.29	1	2.521	$\frac{1}{2}$	1.709
$\frac{1}{4}$	5.74	2b	2.485	1	1.697
1	5.49	1	2.466	2	1.689
$\frac{1}{2}$	4.96	$\frac{1}{2}$	2.446	1	1.673
5	4.90	2	2.427	2	1.666
2	4.82	$\frac{1}{2}$	2.416	1	1.655
$\frac{1}{2}$	4.74	$\frac{1}{4}$	2.387	$\frac{1}{2}$	1.650
3	4.67	1	2.373	$\frac{1}{4}$	1.637
$\frac{1}{2}$	4.58	1	2.358	$\frac{1}{2}$	1.621
$\frac{1}{2}$	4.36	$\frac{1}{4}$	2.346	1	1.614
$\frac{1}{4}$	4.26	1b	2.325	$\frac{1}{4}$	1.604
$\frac{1}{4}$	4.22	$\frac{1}{4}$	2.309	$\frac{1}{2}$ b	1.591
1	4.10	1	2.295	$\frac{1}{4}$	1.582
1	3.87	2	2.284	{ 1b	1.571 }
4	3.84	2	2.260	{ 1b	1.565 }
2	3.78	$\frac{1}{2}$	2.248	1	1.553
$\frac{1}{2}$	3.75	$\frac{1}{2}$	2.242	2	1.543
$\frac{1}{2}$	3.70	$\frac{1}{4}$ b	2.214	1	1.531
1b	3.65	2b	2.194	{ 1b	1.513 }
3	3.62	2	2.156	{ 1b	1.510 }
4	3.58	$\frac{1}{2}$	2.151	2	1.498
1b	3.54	2b	2.138	1	1.477
5	3.45	2	2.121	1	1.461
$\frac{1}{4}$	3.42	2	2.105	$\frac{1}{2}$	1.452
$\frac{1}{2}$	3.39	$\frac{1}{2}$	2.078	$\frac{1}{2}$	1.443
$\frac{1}{2}$	3.34	$\frac{1}{4}$	2.063	$\frac{1}{2}$	1.438
8	3.31	1	2.055	$\frac{1}{4}$	1.428
2	3.21	1	2.046	1	1.421
1	3.19	$\frac{1}{4}$	2.023	$\frac{1}{4}$	1.413
4	3.17	1	2.017	$\frac{1}{4}$ b	1.403
$\frac{1}{4}$	3.15	$\frac{1}{2}$	1.990	1b	1.392
$\frac{1}{4}$	3.13	$\frac{1}{2}$	1.966	1b	1.382
1b	3.08	$\frac{1}{2}$	1.951	$\frac{1}{2}$	1.371
2	3.02	$\frac{1}{4}$	1.940	$\frac{1}{4}$ b	1.364
6	3.00	1b	1.927	$\frac{1}{2}$ b	1.354
2	2.970	$\frac{1}{2}$	1.915	$\frac{1}{4}$	1.342
3	2.928	$\frac{1}{2}$	1.899	1	1.334
2	2.914	1b	1.887		
1	2.873	2b	1.867		
2	2.801	2	1.850		
2	2.772	2	1.835		
4	2.747	1	1.820		
$\frac{1}{2}$	2.711	1b	1.807		
$\frac{1}{4}$	2.693	$\frac{1}{4}$	1.790		
$\frac{1}{4}$	2.670	$\frac{1}{4}$	1.784		
1	2.630	$\frac{1}{4}$	1.772		
$\frac{1}{4}$	2.612	2	1.767		

(Plus lines to $d = 1.1$ Å)

Note: (a) some lines were visibly broad, and these are indicated by the symbol "b"; (b) some pairs or groups of lines were not resolved; these are shown by braces to indicate the range of diffracted intensity.

TABLE 4. X.R.P.D. data for tribasic lead nitrate trihydrate, [tetralead (II) trioxide dinitrate trihydrate], $3\text{PbO} \cdot \text{Pb}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$

I/I_{10}	d (Å)	I/I_{10}	d (Å)	I/I_{10}	d (Å)
$\frac{1}{2}$	7.61	$\frac{1}{4}$	2.290	$\frac{1}{4}$	1.532
$\frac{1}{4}$	7.52	$\frac{1}{4}$	2.249	$\frac{1}{2}$	1.525
$\frac{1}{4}$	7.29	$\frac{1}{2}$	2.196	2	1.516
$\frac{1}{4}$	4.72	$\frac{1}{2}$	2.176	2	1.493
10	4.29	3	2.152	2	1.490
8	4.15	2	2.140	$\frac{1}{2}$	1.432
$\frac{1}{2}$	3.83	3	2.082	3	1.424
$\frac{1}{2}$	3.74	$\frac{1}{4}$	1.942	4	1.408
$\frac{1}{4}$	3.72	3	1.923	$\frac{1}{2}$	1.383
$\frac{1}{4}$	3.66	5	1.915	1	1.359
$\frac{1}{2}$	3.19	3	1.902	2	1.353
$\frac{1}{2}$	3.14	7	1.871	1	1.347
8	3.04	7	1.741	3	1.316
10	2.987	3	1.715	2	1.291
$\frac{1}{4}$	2.871	$\frac{1}{4}$	1.701	2	1.285
$\frac{1}{2}$	2.818	$\frac{1}{4}$	1.670	2	1.259
$\frac{1}{2}$	2.574	$\frac{1}{4}$	1.645	1	1.223
1	2.553	$\frac{1}{4}$	1.639		
$\frac{1}{4}$	2.520	$\frac{1}{4}$	1.612		
$\frac{1}{2}$	2.495	$\frac{1}{4}$	1.595		
8	2.452	$\frac{1}{2}$	1.574		
$\frac{1}{4}$	2.308	$\frac{1}{4}$	1.541		

(Plus lines to $d = 1.1$ Å)

(See Note to Table 3.)

4. Discussion

4.1. Experimental techniques

Merits of Guiner-de Wolff multiple focusing cameras have been described elsewhere.⁷ Here it is sufficient to mention that the high resolution and spectral clarity obtained by using focused monochromatic X-radiation, coupled with the multiple exposure feature and the ease of specimen preparation, were of immense value in this research.

Determination of lead by E.D.T.A. titrations is probably the most accurate method available at the present time, and results such as $70.0 \pm 0.1\%$ can be quoted with confidence. The method of determining nitrate is fundamentally the same as that which has been described in the literature for analysing "insoluble" compounds,⁸ and has been used for several years in these laboratories. It is rapid and precise, and nitrate contents such as $20.0 \pm 0.1\%$ can be obtained with confidence. At 300°C it appeared that all water combined in these basic lead nitrate hydrates was evolved and could be absorbed on anhydrous magnesium perchlorate in a simple gas analysis train. The precision of these gravimetric determinations was such that results better than $5.0 \pm 0.1\%$ can be quoted. The overall precision of analysing individual compounds in this work was found to be high (better than $100.0 \pm 0.5\%$).

4.2. Solid products of the reaction between orthorhombic lead monoxide and cold aqueous lead nitrate solutions in the range of molar proportions

1 : 3 to 3 : 1 $\text{PbO} : \text{Pb}(\text{NO}_3)_2$

The X.R.P.D. data of Table 2 for monobasic lead nitrate dihydrate [dilead (II) monoxide dinitrate dihydrate], $\text{PbO} \cdot \text{Pb}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, completely distinguish this

phase from all other basic lead nitrates observed in these laboratories and from all basic lead nitrates for which X.R.P.D. data have been reported elsewhere.^{1,2} Hence it seems that this compound has not been observed by other workers.

The X.R.P.D. data of Table 3 for monobasic lead nitrate monohydrate [dilead (II) monoxide dinitrate monohydrate], $\text{PbO} \cdot \text{Pb}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, agree sufficiently well with data reported by the Dutch authors¹ for their monobasic lead nitrate hydrate $\text{Pb}(\text{NO}_3)_2 \cdot \text{Pb}(\text{OH})_2$, for there to be no doubt that these two phases are identical. However, there are differences between the precise values of corresponding interplanar (d -) spacings in these two sets of data which will be discussed in the next section of this paper.

The X.R.P.D. data of Table 3 for monobasic lead nitrate monohydrate also agree sufficiently well with data published by the French authors² for the monobasic lead nitrate which they formulate as $\text{Pb}(\text{NO}_3)_2 \cdot \text{PbO} \cdot 1\frac{1}{2}\text{H}_2\text{O}$ for there to be no doubt that these phases are identical. In the present work it was found very difficult to dry the experimental products at room temperature, even when the utmost care was taken in rinsing with acetone and prolonged suction at the filter pad. However, in the French work "drying was effected, either in free air, or over calcium chloride in a dessicator". For this reason, it is felt that the water content given by the French authors² for this monobasic lead nitrate cannot be valid, and it would seem that their quoted stoichiometry $\text{Pb}(\text{NO}_3)_2 \cdot \text{PbO} \cdot 1\frac{1}{2}\text{H}_2\text{O}$ should be altered to $\text{Pb}(\text{NO}_3)_2 \cdot \text{PbO} \cdot \text{H}_2\text{O}$.

The X.R.P.D. data of Table for tribasic lead nitrate trihydrate [tetralead (II) trioxide dinitrate trihydrate] $3\text{PbO} \cdot \text{Pb}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, agree sufficiently well with the data reported by the Dutch authors¹ for their tribasic lead nitrate hydrate $\text{Pb}(\text{NO}_3)_2 \cdot 3\text{Pb}(\text{OH})_2$ for there to be no doubt that these two compounds are identical. Again there are discrepancies between corresponding d -values which will be discussed in the next section of this paper.

4.3. X.R.P.D. data (Tables 2-4)

Lead nitrate is a good compound for calibrating X.R.P.D. photographs. It is not expensive and very pure samples can be made by recrystallisation from aqueous solutions. It gives twenty useful powder lines with CuK_α X-radiation in the spectral range of the Nonius Guinier-de Wolff quadruple focusing camera (up to $90^\circ 2\theta$), and it has an accurately known cubic lattice parameter, $a = 7.8568 \text{ \AA}$ at 25°C .⁶ The only drawback of using lead nitrate as a calibration standard is that the lowest angle X.R.P.D. line arises from the 111 crystal lattice planes of d -spacing 4.537 \AA and occurs at $19.57^\circ 2\theta$ for CuK_α X-radiation. Hence, calibration of d -values higher than this (which occur at lower angles) must be effected by extrapolation. In the present work the calibration graphs d_{observed} versus $\Delta d = d_{\text{true}} - d_{\text{observed}}$ were essentially linear and extrapolation was easy.

Assuming an error of $\pm 0.05 \text{ mm}$ in measuring spectral line positions with a Vernier scale reading to 0.05 mm , there was a consequent error $\Delta 2\theta = \pm 0.025^\circ$ (spectral dispersion $1^\circ 2\theta = 2 \text{ mm}$ for the Nonius Guinier-de Wolff quadruple focusing camera) and a corresponding error Δd in the interplanar spacing which can be calculated from a differentiated form of Bragg's equation.⁹

Thus,

$$\mp \Delta d = \pm d \cot \theta \Delta \theta$$

whence (for the assumed error $\Delta 2\theta = \pm 0.025^\circ$) if $d = 10.0 \text{ \AA}$ ($8.84^\circ 2\theta$ for CuK_α) $\Delta d = \mp 0.028 \text{ \AA}$, and if $d = 3.00 \text{ \AA}$ ($29.78^\circ 2\theta$ for CuK_α) $\Delta d = \mp 0.0025 \text{ \AA}$. Hence, it was felt justifiable to quote d -spacings to two decimal places in the range 10.00–3.00 \AA , and to three decimal places for values below 3.00 \AA , in Tables 2–4.

Taking into consideration the calibration procedure, and the measurement errors, described above, it is felt that the X.R.P.D. data of Tables 2–4 are reliable. Now it is of some interest to compare these data with sets of data for corresponding compounds which have been published in the Dutch¹ and French² papers on basic lead nitrates.

Interplanar spacings (d -values) published by the Dutch workers¹ for the monobasic lead nitrate hydrate $\text{Pb}(\text{NO}_3)_2 \cdot \text{Pb}(\text{OH})_2$ are somewhat higher than corresponding values given in Table 3 for monobasic lead nitrate monohydrate. This discrepancy is largest (about 1%) for the higher d -values, and decreases (to about $\frac{1}{2}\%$) for the lowest recorded d -values. Unfortunately the Dutch authors state only "X-ray diagrams were taken with a Philips X-ray powder diffractometer using CuK_α radiation".¹ However it is possible that this instrument was not precisely aligned, and a constant misalignment of about $0.2^\circ 2\theta$ low would account for the observed variable percentage difference.

Evidence in favour of the values given in Table 3 has been provided by measurements on the X.R.P.D. spectrum of monobasic lead nitrate monohydrate conducted in these laboratories using a Siemens (model F) X-ray powder diffractometer. This instrument was carefully aligned and checked against a gold calibration standard. The d -values then obtained were slightly lower than (but in generally close agreement with) the data of Table 3, and significantly lower than the Dutch¹ data for $\text{Pb}(\text{NO}_3)_2 \cdot \text{Pb}(\text{OH})_2$.

Interplanar spacings (d -values) published by the Dutch authors¹ for their tribasic lead nitrate hydrate $\text{Pb}(\text{NO}_3)_2 \cdot 3\text{Pb}(\text{OH})_2$, are somewhat higher than corresponding values given in Table 4 for tribasic lead nitrate trihydrate. Although these discrepancies are not as great as those already noted for the monobasic lead nitrate hydrates, it is thought that the Dutch angular measurements were again consistently low.

One final comment must be made about the Dutch X.R.P.D. patterns. Occasionally two d -values are recorded when only one corresponding value is given in Table 3 or Table 4. It seems that the Dutch workers¹ used X-ray powder diffractometer operating conditions which permitted higher spectral resolution than was achieved in the present studies.

The French authors² publish relatively few d -values for each of the compounds which they report. They used an X-ray powder diffractometer and it seems that the specimens were examined in transmission with CuK_α X-radiation reflected from a curved quartz crystal monochromator. This contrasts with the normally adopted Seeman–Bohlin parafocusing geometry¹⁰ with filtering or monochromating facilities in the diffracted beam, and it is possible that the spectral intensities and resolution observed by these French workers would have been comparatively low.

5. Conclusions

Results described in this paper show that orthorhombic (yellow) lead monoxide reacts with cold aqueous lead nitrate solutions in the range of molar proportions 1 : 3 to 3 : 1 $\text{PbO} : \text{Pb}(\text{NO}_3)_2$ to give white solid products. The reaction took from 20 to 40 h to reach equilibrium depending on the precise temperature (in the range 15 to 30 °C), and three distinct crystalline phases were observed. Monobasic lead nitrate dihydrate [dilead (II) monoxide dinitrate dihydrate], $\text{PbO} \cdot \text{Pb}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, does not seem to have been reported elsewhere. Monobasic lead nitrate monohydrate [dilead (II) monoxide dinitrate monohydrate], $\text{PbO} \cdot \text{Pb}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, is identical to substances reported by Dutch¹ and French² authors. Tribasic lead nitrate trihydrate [tetralead (II) trioxide dinitrate trihydrate], $3\text{PbO} \cdot \text{Pb}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ has also been reported by the Dutch authors.¹

It is particularly interesting that the monobasic lead nitrate monohydrate formed in the present experiments is identical to the substance $\text{Pb}(\text{NO}_3)_2 \cdot \text{Pb}(\text{OH})_2$ reported by the Dutch workers¹ because these Dutch authors state "lead oxide did not react with a solution of lead nitrate". In the present work, unreacted orthorhombic lead monoxide gave intense yellow colours to the aqueous suspensions for long periods of time before the reactions went to completion, and it seems that the Dutch workers could have been misled if they used colour change as an assessment of reaction.

Compounds of other stoichiometries were not observed in the present experiments, and it seems that the above three phases are the only compounds with compositions in the range of molar ratios 1 : 3 to 3 : 1 $\text{PbO} : \text{Pb}(\text{NO}_3)_2$ which are stable in contact with water at room temperature. Hence, other phases having compositions intermediate between that of a monobasic lead nitrate hydrate and that of a tribasic lead nitrate hydrate, and which have been reported by the Dutch¹ and French² authors, can only be metastable in contact with water. In this connection it is interesting to note that the X.R.P.D. for one such "compound" made by "steeping another product [thought to be of the stoichiometric composition $\text{Pb}(\text{NO}_3)_2 \cdot 2\text{PbO} \cdot 2\text{H}_2\text{O}$] in water and drying in air" and reported by the French authors as having the stoichiometry $\text{Pb}(\text{NO}_3)_2 \cdot 2\text{PbO} \cdot 2\frac{1}{2}\text{H}_2\text{O}$,² can be interpreted as arising from a mixture of monobasic lead nitrate monohydrate, $\text{PbO} \cdot \text{Pb}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, with tribasic lead nitrate trihydrate, $3\text{PbO} \cdot \text{Pb}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$.

As implied above, various sets of X.R.P.D. data published by the Dutch¹ and French² authors are in sufficient agreement with sets of data given in this paper for positive identifications to be made. However, there are small but significant differences between these sets of data which appear to originate in the examination techniques. Thus, *d*-values quoted by the Dutch authors¹ are high compared with values obtained in these laboratories, which can be explained if the Dutch goniometer was misaligned so that the angular measurements were low. The French authors² publish rather few *d*-values in all of their quoted sets of data, presumably due to low spectral intensity and resolution achieved in their technique. Further, these French authors quote a seemingly wrong water content for their monobasic lead nitrate hydrate, apparently due to the analysis of a wet material. (A consideration of their drying procedures suggests that this criticism may well apply to other chemical analysis results published by these

French workers.) It is important to be aware of such discrepancies now that data from these Dutch¹ and French² papers have been incorporated in the "Inorganic Powder Diffraction File", particularly as this latter is a work used by many as a source of reliable information.

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