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A Neutron Crystallographic Study of Lead Nitrate*

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A neutron diffraction investigation of powdered lead nitrate at temperatures up to 300° C. has been undertaken to determine whether there is any significant rotation of the nitrate group about its symmetry axis. If a cosine-like potential is assumed, the potential barrier for hindered rotation is at least $V_0 > 16kT$. Revised parameters for the room-temperature data lead to an N–O bond length of 1·267 Å ($\sigma = 0{\cdot}021$ Å), a value somewhat greater than that previously reported for the compound. It is suggested that disorder or dislocation phenomena can account for the somewhat irreversible changes in the intensities of the most intense reflections which occur on heating or vigorous grinding of the sample.

1. Introduction

Studies of the metallic nitrates are of interest in connection with the general phenomenon of rotating groups in crystals. The nitrate group is reported to undergo 'free' rotation, either about the symmetry axis or spherically, in a number of compounds. The transition to free rotation, which is often accompanied by a phase change, usually takes place in the temperature range 150–175° C. (See, for example, Finbak & Hassel, 1937; Kracek, Posnjak & Hendricks, 1931; and Hendricks, Posnjak & Kracek, 1932.)

Early X-ray results were interpreted (Kracek, Hendricks & Posnjak, 1931) as indicating that the nitrate group in lead nitrate is rotating at room temperature. However, other work resulted in the assignment of fixed positions to the oxygen atoms (Vegard, 1922; Vegard & Bilberg, 1932). Although no phase change is observed on heating the compound to 300° C., it has been postulated that there might be a gradual transition to free rotation such as one would expect if there were a low potential barrier (Vegard & Roer, 1941). No determination of structure has been attempted at the higher temperatures, Vegard & Roer (1941) having observed only reflections with lead contributions for the purpose of determining lattice constants. Neutron diffraction would appear to be more suitable than X-ray diffraction for a closer examination of the structure because of the comparable magnitudes of the neutron scattering factors for Pb, N, and O (b = 0·957, 0·940, $0{\cdot}58\times10^{-12}$ cm., respectively (Hughes & Harvey, 1955)). It is to be noted, however, that accurate information concerning light-atom positions could in principle be obtained from the X-ray data, despite the disparity in scattering factors, as the lead atoms contribute only to reflections with unmixed indices.

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2. The structure

Lead nitrate crystallizes in the cubic system, space group $Pa3$, $a_0 = 7{\cdot}84$ Å, $Z = 4$. The lead atoms are in a face-centered arrangement (special positions (a) of $Pa3$ in the *International Tables*, 1952). The oxygen atoms occupy general positions and the nitrogen atoms the eightfold positions (c) of the *International Tables*.*

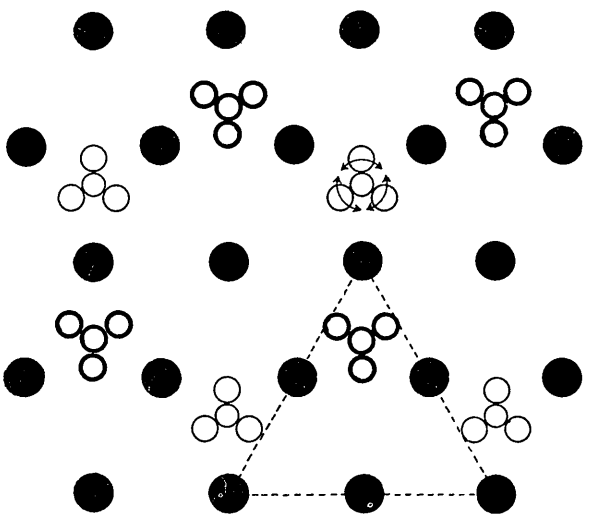

Fig. 1. The (111) plane of lead nitrate showing arrangement of nitrate groups. The filled-in circles are lead atoms. The nitrate groups drawn with heavy lines lie 0·27 Å above the plane of the lead atoms, the ones drawn with light lines an equal distance below. The broken lines are the lines of intersection of the plane with the faces of a unit cube. Arrows on one of the nitrate groups indicate the direction of the postulated rotation.

The structure may be visualized as a face-centered array of lead atoms with every octahedral site in the

* Vegard & Bilberg (1932) give the following values for the parameters: (d): $x = 0{\cdot}266$, $y = 0{\cdot}219$, $z = 0{\cdot}467$; (c): $u = 0{\cdot}344$. This leads to an N–O bond length of 1·22 Å.

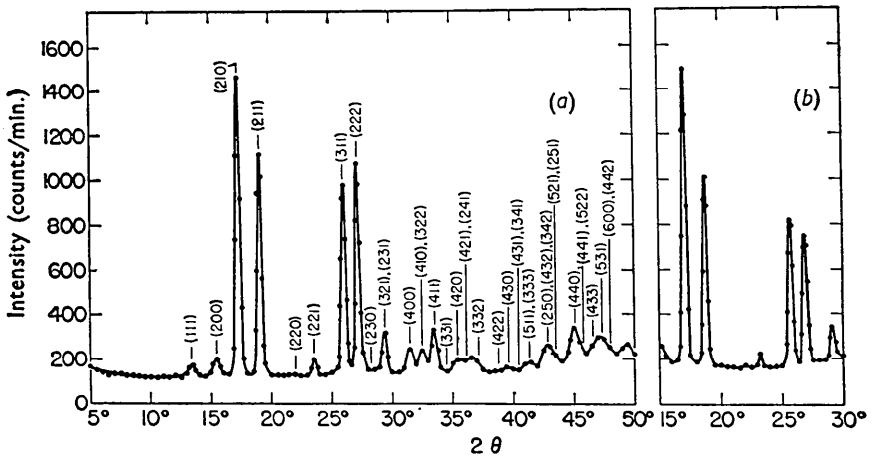

Fig. 2. Typical neutron diffraction patterns for lead nitrate: (*a*) room temperature; (*b*) one sample at 45° C.

lattice occupied by two nitrate groups in the staggered configuration, the axes of the groups lying along ⟨111⟩ crystallographic axes. The oxygen atoms lie nearly along the Pb–Pb lines, so that every lead atom is bonded to twelve oxygen atoms (possibly in two unequal sets of six). The arrangement of the nitrate groups is such that every (111) plane contains an equal number of nitrogen atoms (see Fig. 1).

3. Experimental

Analytical grade $Pb(NO_3)_2$ was ground in an agate mortar to a fine powder which was placed in glass- or quartz-walled sample holders for the measurement of the diffraction pattern. A cylindrical sample holder about one inch in diameter and wrapped with quartz insulated nichrome wire was used for the measurements at elevated temperatures. A chromel–alumel thermocouple immersed in the powder controlled a thermostat which regulated the temperature to ±5° C. For the room-temperature runs, a larger sample-holder of rectangular cross section, one-half inch thick and intercepting a neutron beam two inches square, was used. Runs made with the sample-holders empty showed that any inhomogeneities in their scattering did not significantly affect the intensities of the more intense reflections. The nichrome-wrapped cylindrical holder did, however, create some unevenness in the background which made accurate intensity measurements on the weaker reflections impossible. Only the data from the flat sample-holder were used for the final refinement of parameters.

The neutron spectrometer used was that described by Corliss, Hastings & Brockman (1953). Integrated intensities were derived from the total counts received as the counter revolved at a constant angular velocity of 1°, 2° or 4° per hour. The values of F^2 were calculated from the intensities in the usual way (Bacon 1955). The linear absorption coefficient was determined experimentally by transmission measurements on the flat sample. The neutron wavelength was 1·07 Å.

Initial experiments on heating of the sample indicated that above 300° C. there was some evolution of nitrogen oxides, and continued heating at higher temperatures led to complete decomposition, as witnessed by the complete disappearance of the characteristic diffraction pattern. This is in qualitative agreement with published data by Neumann & Sonntag (1933), who found dissociation pressures of 6 mm., 87 mm., and 767 mm. at temperatures of 266, 320, and 359° C. At lower temperatures, however, and for all samples which are discussed below, no appreciable decomposition took place.*

4. Results

The diffraction pattern at room temperature is shown in Fig. 2(*a*). The calculated intensities are in general quite sensitive to oxygen positions, especially to the angle of rotation out of the equilibrium configuration. Fig. 3 exhibits the calculated variation with angle of rotation of the structure factors for the most intense reflections, (210), (211), (311), and (222). It was immediately obvious from comparison of observed and calculated intensities that any departure from the zero position (oxygen equidistant from two lead atoms) must be small. The assumption was then made that there is a rotation-hindering, cosine potential function with minima at the three equivalent zero positions. Intensities were calculated for models with classical distributions of degree of rotation as determined by the potential barrier, i.e., the probability of the nitrate

* Analysis for lead in the three samples in Table 2 gave 62·6%, 62·5%, 62·7%; calculated for $Pb(NO_3)_2$, 62·5%. The sample which appeared from the diffraction pattern to be completely decomposed gave 82% Pb; calculated for PbO_2, 86·5%. The diffraction patterns for the other samples showed no evidence of anomalous lines or increased background scattering which would be expected from decomposition products.

group being rotated to an angle φ is proportional to $\exp[-b(1-\cos 3\varphi)]$. Fig. 4 shows plots of the ratios $R_1 = I(210)/I(211)$ and $R_2 = I(311)/I(222)$ as functions of $b = V_0/2kT$, where V_0 is the height of the potential barrier, k is the Boltzmann constant, and T is the absolute temperature. The observed values were 1·43 and 0·89 with estimated *maximum* errors of 0·08 and 0·06. The condition on R_2 alone leads one to the conclusion that the absolute minimum value of b is 3, or $V_0 > 6kT$.

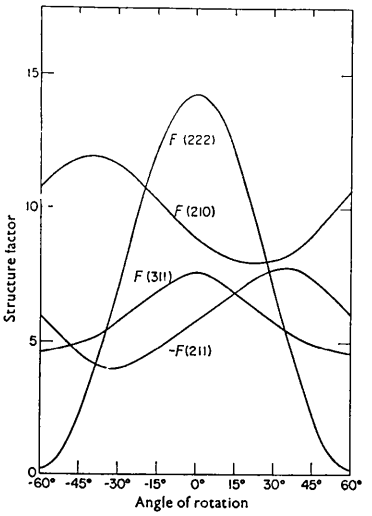

Fig. 3. Structure factors for four intense reflections as functions of rotation of nitrate group from zero position defined by $x = y$. Negative angles defined so that $x > y$. $u = 0{\cdot}353$, $B = 0{\cdot}1608$ Å^2, $r_{N-O} = 0{\cdot}1608$ Å.

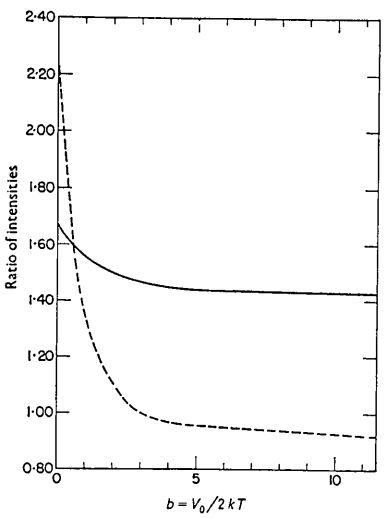

Fig. 4. Intensity ratios as functions of potential-barrier height, $b = V_0/2kT$. Unbroken line: $R_1 = I(210)/I(211)$; broken line: $R_2 = I(311)/I(222)$. Observed values were 1·43 and 0·89.

In order to obtain a better estimate of the height of the potential barrier, $1/b$* was included as a parameter in a series of least-squares adjustments† which also included the four parameters determining the oxygen and nitrogen positions. The first iteration indicated that any departure of the nitrate group from planarity or any deviation from the condition $x = y$ (all Pb–O distances equal) is less than the corresponding standard deviation.‡ Hence in the succeeding iterations only two structural parameters, the N–O bond length and the nitrogen parameter u, were included together with $1/b$, a scale factor (K), and an isotropic temperature factor (B).

The results of the final iteration were as follows:

$$\begin{aligned} u &= 0{\cdot}3535, & \sigma &= 0{\cdot}0013; \\ r_{N-O} &= 0{\cdot}1617, & \sigma &= 0{\cdot}0027; \\ 2B &= 1{\cdot}45, & \sigma &= 1{\cdot}06; \\ 1/b &= 0{\cdot}00, & \sigma &= 0{\cdot}06; \\ K &= 1{\cdot}00, & \sigma &= 0{\cdot}06. \end{aligned}$$

From the values of u and r_{N-O} may be derived

$$\begin{aligned} x = y &= 0{\cdot}2875, & \sigma &= 0{\cdot}0013; \\ z &= 0{\cdot}4856, & \sigma &= 0{\cdot}0022. \end{aligned}$$

The σ's in each case are marginal standard deviations derived from the least-squares error matrix. It will be noted that the error in the temperature-factor determination is quite large, $2B$ not being significantly different from 0 at the 5% level of acceptance. This arises because the reflections used in the least-squares treatment occur at relatively small Bragg angles. With the exception of (440) with $(\sin\theta/\lambda)^2 = 0{\cdot}129$, all reflections used had $(\sin\theta/\lambda)^2 < 0{\cdot}07$.

The largest and most significant of the correlation coefficients is the one between r_{N-O} and $1/b$. This implies that a decrease in N–O bond length must be accompanied by an increase in the torsional oscillation to give the most satisfactory fit to the data. When $1/b$ is omitted from the least-squares treatment, the errors in bond lengths and atomic positions are almost halved.

If we accept 2σ as the limit of error in the determination of $1/b$, we have $0 < 1/b < 0{\cdot}12$, or $b > 8$. This corresponds to $V_0 > 16kT$. At this value of b, the average value of $|\varphi|$ is about 6°, so that the motion of the oxygen atoms may be approximately represented by an anisotropic temperature factor with the long axis of the ellipsoid perpendicular to the N–O bond and lying in the plane of the nitrate group.

If it is assumed that $a_0 = 7{\cdot}84$ Å (Vegard & Roer, 1941), the following interatomic distances may be derived:

* The structure factors vary approximately linearly with $1/b$.

† The starred reflections in Table 1 were used in these adjustments, and weights were assigned inversely proportional to the variance of the individual measurements.

‡ These values were $\sigma(x-y) = 0{\cdot}003$ and $\sigma(x+y+z-3u) = 0{\cdot}004$.

$$r_{N-O} = 1{\cdot}268 \text{ Å}, \quad \sigma = 0{\cdot}021 \text{ Å};$$
$$r_{Pb-O} = 2{\cdot}805 \text{ Å}, \quad \sigma = 0{\cdot}011 \text{ Å}.$$

The value of the N–O distance is significantly different from the value of 1·22 Å reported by Vegard & Bilberg (1932) for this compound, but is not incompatible with N–O bond lengths in other compounds; values ranging from 1·22 to 1·28 Å have been reported for various nitrates (see, for example, Wyckoff (1948)). The shortest O–O contact between nitrate groups is 3·20 Å, so it would appear that Pb–O interactions play the major role in determining the packing of the ions.

The observed intensities (averages over three runs with different samples) are presented in Table 1,

Table 1. *Observed and calculated intensities*

$$I = \frac{jF^2 \exp[-\mu h \sec\theta] \exp[-1{\cdot}45 (\sin\theta/\lambda)^2]}{10 \sin^2\theta} \times 10^{24} \text{ cm}^2.$$

I_o: observed value; I_H: present results; I_V: Vegard & Bilberg (1932).

(*hkl*)	I_o	I_H	I_V
111*	9	17	42
200*	19	18	56
210*	614	612	638
211*	428	429	387
220	< 10	0	51
221	22	2	104
311*	410	402	315
222*	463	456	438
230	< 10	3	0
321, 231	92	90	121
400*	49	62	89
410*, 322*	59	90	29
411*	124	115	157
331	< 20	2	0
420	15	14	6
421, 241	50	76	32
332	37	37	33
422	< 20	13	0
430	< 20	1	43
431, 341	< 20	12	20
511, 333	53	30	83
250, 432, 342	152	142	214
521, 251	64	37	33
440*	298	300	238
441, 522	35	6	66
433	88	67	68
531	145	143	149
600, 442	54	72	35

* Starred reflections were used in the least-squares adjustments.

together with those calculated for the parameters derived here and for those of Vegard & Bilberg (1932). The same temperature factor has been used in both sets of calculated intensities. The internal estimate of the standard deviation of an individual intensity measurement is about 10 for the well-resolved reflections and naturally somewhat greater for the poorly resolved higher-angle reflections. The value of the reliability factor $R = \Sigma||F_o| - |F_c|| \div \Sigma|F_o|$ for all single reflections is 0·039, and for the reflections used in the least-squares treatment 0·019.

5. Effects of heating

The effects obtained on heating the sample were somewhat unexpected. Some of the results are given in Table 2, Samples 1 and 2. A typical diffraction pattern

Table 2. *Results of heating and grinding*

$R_1 = I(210)/I(211)$, $R_2 = I(311)/I(222)$.

Sample	T (°C.)	R_1	R_2	Notes*
1	25	1·36	0·88	(*a*)
	100	1·72	1·04	—
	210	1·76	1·18	—
	260	1·39	1·10	—
	310	1·25	0·96	—
	25	1·30	0·79	—
2	25	1·39	0·89	(*a*)
	35	1·64	1·01	—
	45	1·59	1·04	—
	55	1·49	1·02	—
	25	1·59	1·05	—
	25	1·44	0·80	(*b*)
3	25	1·12	0·70	(*c*)
	35	1·00	0·55	—
	25	1·17	1·20	—
	25	1·14	1·45	—
	50	1·46	1·55	(*b*)
	25	1·30	1·38	—
	25	1·44	0·77	(*d*)
	25	1·41	0·80	—

* (*a*): Cured at least one week after grinding.
(*b*): 24 hr. later.
(*c*): Immediately after grinding.
(*d*): One week later.

(Sample 2 at 45° C.) over the region including the four intense reflections is shown in Fig. 2(*b*). The runs listed in the table were made immediately following one another unless otherwise noted. It will be observed that the results were not strictly reproducible and that recovery to room-temperature values was slow and imperfect. The behavior is not at all that to be expected for excitation of internal degrees of freedom; indeed, it was impossible to account, even in a qualitative way, for the changes in intensity on the basis of a hindered-rotation model. It would seem that the effects could best be explained by some sort of dislocation or disorder phenomenon.

Some weight is lent to this interpretation by the behavior of Sample 3, on which the diffraction pattern was run immediately after severe grinding in a mortar. The ratios of intensities here, both in the cold and heated samples, were completely out of agreement with earlier results. However, one day later R_1 had recovered its correct value, and after a week R_2 was more nearly correct.

No attempt will be made here to determine the exact nature of the disorder. It is plausible that there is some disorder in the location of the nitrate groups (such disorder would involve only small changes in average oxygen positions) or that there are numerous stacking faults in the lead lattice, which in the perfect crystallite may be described as cubic closest packed.

Qualitative estimates of the intensity changes which would accompany such disorder indicate that either of these explanations is plausible. However, in connection with the latter suggestion, it may be noted that no appreciable peak broadening or peak shift was observed.

The samples used for refinement of parameters at room temperature had of course been ground, but the diffraction patterns were run a few weeks later. The question arises whether the values of the intensities in the cured sample are indeed the correct ones for an ideally imperfect crystal. It may be noted in this connection that the changes in intensity summarized in Table 2 have relatively little effect on atomic positions. A least-squares treatment similar to that described above was carried out on one of the worst samples described here (Sample 3, line 4 in Table 2), and the parameter values obtained lay within one standard deviation of those obtained above. However, the fit to the data is here rather poor, the estimates of error being about four times as great as those derived above. This would seem to add further weight to the disorder hypothesis suggested, i.e. the intensities cannot be fitted well on the basis of variation in atomic positions and temperature factors alone. The goodness of the fit in the least-squares treatment in § 4 would seem to indicate that the samples there are more nearly perfect. However, it would perhaps be best not to have complete confidence in the parameter values derived there until they are confirmed by measurements on a single, unstrained crystal. This investigation was undertaken not for precise determination of atomic positions (the standard deviations quoted are evidence of this) but rather to shed some light on the rotation of the nitrate groups.

The author would like to express his appreciation to Dr L. M. Corliss and Dr J. M. Hastings for helpful discussions and to Dr R. W. Stoenner for performing the lead analyses.

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Investigation of Hexamethylene Tetramine by Neutron Diffraction

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Hexamethylene tetramine has been re-investigated by neutron diffraction in order to determine the exact positions of the hydrogen atoms. The space group is found to be $I\bar{4}3m$, and the parameters lead to C–H bonds of lengths 1·13 Å forming angles of 110° 6′. An anisotropic temperature factor is introduced, based on the assumption of the molecule rotating as a rigid constellation. This leads to a remarkably good agreement between observed and calculated structure factors.

Introduction

Despite the fact that hexamethylene tetramine was one of the first organic structures to be solved (Dickinson & Raymond, 1923), reports of new investigations have appeared at regular intervals. The main reasons for this continuing interest have been the location of the hydrogen atoms, which are assumed to play an important part in the structure and determine the space group, and lack of agreement between observed and calculated intensities.

Hexamethylene tetramine, $C_6N_4H_{12}$, crystallizes, as far as the C and N atoms are concerned, in a body-centred cubic lattice with $a = 7{\cdot}02$ Å. The 6 C atoms