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Structure of Lead(II) Nitrite Monohydrate

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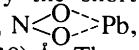
Abstract. $Pb(NO_2)_2.H_2O$, $M_r = 317·2$, monoclinic, $P2_1/c$, $a = 9·194$ (4), $b = 11·806$ (5), $c = 12·210$ (5) Å, $\beta = 130·64$ (2)°, $V = 1005·7$ (8) Å^3, $Z = 8$, $D_x = 4·19$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 33·74$ mm^{-1}, $F(000) = 1104$, $T = 295$ (1) K, final $R = 0·062$ for 1809 observed unique reflections. The yellow color of the crystal is caused by the short contact between Pb^{2+} and nitrite O atoms,  $\mathrm{N}{<}\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}{>}\mathrm{Pb}$, the mean Pb···O distance being 2·645 (20) Å. There are two independent Pb^{2+} ions in a unit cell. Pb(1) is surrounded by seven nitrite O, two N and a water O atom and Pb(2) by seven nitrite O, one N and a water O atom with distances ranging from 2·543 (20) to 3·212 (24) Å.

Introduction. Colorations of the post-transition-metal nitrites are due to a spin-orbital enhancement of the spin-forbidden triplet ← singlet transition of the NO_2^- ion (McGlynn, Azumi & Kumar, 1981). Structural investigations have not been carried out except for $AgNO_2$ (Ohba & Saito, 1981). The structure of $Pb(NO_2)_2.H_2O$ has been determined to reveal the arrangement of Pb^{2+} with respect to the nitrite ions.

Experimental. Yellow plate-like crystals grown from filtrate of a mixture of $PbCl_2$ and $AgNO_2$ aqueous solutions, not hygroscopic. Spherical crystal of 0·462 (7) mm diameter ground with a piece of sandpaper. Rigaku AFC-5 four-circle diffractometer, graphite monochromator. Laue group $2/m$, systematic absences $h0l$ with l odd and $0k0$ with k odd; cell parameters refined by least squares for 20 2θ values ($20 < 2\theta < 30°$); intensity measurement performed to $2\theta = 55°$ (h 0→11, k −15→15, l −15→15), ω scan, scan speed 6° min^{-1} (θ). Mean ratio of structure factors of four standard reflections $0·976 \leq (|F_o|/|F_o|_{\rm initial})/4 \leq 1·003$. 4781 reflections measured, 3465 observed reflections with $|F_o| > 3\sigma(|F_o|)$, 1809 unique ($R_{\rm int} = 0·032$). Corrections for Lorentz–polarization and for absorption ($\mu r = 7·80$, $0·0019 < A < 0·0109$). Positions of two independent Pb atoms determined by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), non-H atoms except one nitrite O atom found on Fourier synthesis, the remaining one fixed on difference synthesis. Coordinates and anisotropic thermal parameters of non-H atoms refined with full-matrix least-squares program *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979). Large anisotropic thermal ellipsoids of N and O atoms of two nitrite ions, $NO_2(3)$ and $NO_2(4)$ (see Fig. 1), with abnormal geometries: $1·04\ (6) \leq$ N—O $\leq 1·18\ (3)$ Å, O—N—O 123 (2) and 152 (4)°. Shape and size of the cavities for four NO_2^- ions defined as the concave space limited by the envelope surface of the neighboring atomic spheres (Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1981) were rather similar. This observation suggested partial disorder for two nitrite ions. Positions of $NO_2(3)$, and $NO_2(4a)$ and $NO_2(4b)$ with half weights deduced from Fourier synthesis were fixed with isotropic thermal parameters. No water H atoms found on difference synthesis. $\sum w||F_o| - |F_c||^2$ minimized, $w^{-1} = \sigma^2(|F_o|) + (0·015|F_o|)^2$, final $R = 0·062$, $wR = 0·050$, $S = 1·52$ for 1809 unique reflections.* Smallest secondary-extinction correction factor (F_o^2/F_c^2) 0·68 for $02\bar{1}$. Reflection/parameter (refined) ratio 17·9, $\Delta/\sigma < 0·38$, max. and min. heights in final difference synthesis 4·2 and −4·3 e Å^{-3}. Complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations performed on the FACOM M-380R of this university.

Discussion. Final atomic coordinates and interatomic distances and bond angles are presented in Tables 1 and 2. The crystal structure is shown in Fig. 1. The preferred orientation of the metal cations to the nitrite ion is expected to coincide with the direction of the lone-pair electrons. Fig. 2 shows the arrangement of metal cations and water molecules around the nitrite ions in $LiNO_2.H_2O$ (Hermansson & Thomas, 1983), $Sr(NO_2)_2.H_2O$ (Abrahams, Marsh, Liminga & Lundgren, 1983), $Ba(NO_2)_2.H_2O$ (Kvick, Liminga & Abrahams, 1982) and $Pb(NO_2)_2.H_2O$, where the shifts of the metal ions or H_2O are less than 0·5 Å from the NO_2 plane. In $NaNO_2$ (Kay & Frazer, 1961) and $AgNO_2$ (Ohba & Saito, 1981), the N atom and metal

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42292 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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cations lie on a twofold axis with the arrangement $M\cdots\mathrm{N}\!<\!\substack{\mathrm{O}\\ \mathrm{O}}\!>\!M$. There are three types of approach for the metal cation to the nitrite ion: (1) on a bridge position between the two O atoms of NO_2, (2) close to one of the nitrite O atoms, where $M\cdots$O—N—O is *trans*, and (3) close to the N atom, where $M\cdots$N—O is nearly 120°. Types (2) and (3) seem to indicate the directions of the lone-pair electrons of the O and N atoms. The $M\cdots$O—N angles in type (2) are in the range 121·0 (1) to 137·0 (1)°, suggesting sp^2 hybridization of the nitrite O atoms. This is in good accord with the difference synthesis of $LiNO_2.H_2O$ at 120 K (Ohba, Kikkawa & Saito, 1985). Fig. 3 compares the distribution of the direction of the metal cations around NO_2^- ions in types (1) and (2) with those around HCO_2^- ions in the crystals of $LiHCO_2.H_2O$ (Thomas, Tellgren & Almlöf, 1975), $NaHCO_2$ (Fuess & Bats, 1982), $Mg(HCO_2)_2.2H_2O$ (orthorhombic; Malard, Pezerat, Herpin & Toledano, 1982), $Mg(HCO_2)_2.2H_2O$ (monoclinic; De With, Harkema & van Hummel, 1976), α-$Ca(HCO_2)_2$ (Watanabé & Matsui, 1978), β-$Ca(HCO_2)_2$ (Matsui & Watanabé, 1980), α-$Sr(HCO_2)_2$ and $Ba(HCO_2)_2$ (Watanabé & Matsui, 1978), $Fe(HCO_2)_2.2H_2O$ (Weber, 1980*b*) and $Cd(HCO_2)_2$ (Weber, 1980*a*), the $M\cdots$O—N angles in type (2) being 119·4 (6) to 170·3 (2)°.

Table 1. *Positional parameters* [×10⁴; *for* Pb ×10⁵; *for* N(3), O(31), O(32), N(4*a*), O(41*a*), O(42*a*), N(4*b*), O(41*b*), O(42*b*) ×10²] *and isotropic temperature factors* (*Hamilton*, 1959)

	x	y	z	B/B_{eq}(Å^2 × 10)
Pb(1)	93351 (10)	31638 (6)	36150 (7)	20 (1)
Pb(2)	40421 (10)	35269 (6)	33649 (8)	22 (1)
O(*W*1)	4711 (20)	3782 (11)	8757 (15)	26 (6)
O(*W*2)	7900 (18)	4668 (10)	1630 (14)	20 (6)
N(1)	3947 (25)	2896 (14)	862 (18)	27 (8)
O(11)	5409 (19)	3261 (15)	2017 (17)	36 (7)
O(12)	2526 (19)	2839 (14)	810 (16)	32 (7)
N(2)	9346 (24)	2257 (14)	1219 (16)	21 (7)
O(21)	7841 (22)	2185 (13)	983 (16)	33 (7)
O(22)	10733 (17)	2614 (12)	2452 (13)	21 (5)
N(3)	83	7	35	43 (4)
O(31)	90	0	32	60 (5)
O(32)	66	5	29	60 (5)
N(4*a*)	27	48	54	34 (7)
O(41*a*)	14	51	54	79 (12)
O(42*a*)	25	46	43	90 (17)
N(4*b*)	28	51	53	41 (9)
O(41*b*)	21	50	59	55 (9)
O(42*b*)	20	45	42	57 (10)

Table 2. *Interatomic distances* (Å) *and angles* (°)

N(1)—O(11)	1·230 (19)	N(4*a*)—O(41*a*)	1·25
N(1)—O(12)	1·268 (34)	N(4*a*)—O(42*a*)	1·25
O(11)—N(1)—O(12)	113·4 (23)	N(41*a*)—N(4*a*)—O(42*a*)	126
N(2)—O(21)	1·219 (33)	N(4*b*)—O(41*b*)	1·26
N(2)—O(22)	1·253 (17)	N(4*b*)—O(42*b*)	1·25
O(21)—N(2)—O(22)	114·7 (22)	O(41*b*)—N(4*b*)—O(42*b*)	114
N(3)—O(31)	1·24		
N(3)—O(32)	1·24		
O(31)—N(3)—O(32)	113		
Pb(1)—O(*W*2)	2·570 (13)	Pb(2)—O(*W*1^{v})	2·767 (13)
Pb(1)—O(11)	2·770 (15)	Pb(2)—O(11)	2·661 (25)
Pb(1)—O(12^{i})	2·636 (12)	Pb(2)—O(12)	2·583 (18)
Pb(1)—N(2^{ii})	3·212 (24)	Pb(2)—O(21^{ii})	2·929 (12)
Pb(1)—O(21)	2·793 (18)	Pb(2)—O(22^{vi})	2·691 (16)
Pb(1)—O(22)	2·543 (20)	Pb(2)—O(31^{vii})	2·75
Pb(1)—N(3)	3·04	Pb(2)—O(32^{vii})	2·64
Pb(1)—O(41*a*^{iii})	2·68	Pb(2)—N(4*a*^{iii})	3·04
Pb(1)—O(41*a*^{iv})	2·86	Pb(2)—O(42*a*)	2·65
Pb(1)—O(42*a*^{iv})	2·98	Pb(2)—N(4*b*^{iii})	2·75
Pb(1)—O(41*b*^{iii})	2·79	Pb(2)—O(42*b*)	2·90
Pb(1)—O(42*b*^{iv})	2·59		

Symmetry code

(i) $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$	(v) $x, \frac{1}{2} - y, -\frac{1}{2} + z$
(ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$	(vi) $-1 + x, y, z$
(iii) $1 - x, 1 - y, 1 - z$	(vii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
(iv) $1 + x, y, z$	(viii) $-1 + x, \frac{1}{2} - y, -\frac{1}{2} + z$

If there is some covalency in the $Pb^{2+}\cdots NO_2^-$ interaction (McGlynn *et al.*, 1981), the interatomic distance will be shorter than the sum of the ionic radii. The radii of the metal cations, r_M, can be estimated using a list of ionic radii tabulated as functions of coordination number (CN) (Shannon & Prewitt, 1969). However, the ionic radii for the O and N atoms are not available. The effective radius of the N atom, $r_{\rm N}$, in Fig. 4 was defined as $\overline{d_{M\cdots\rm N}}$(type 3) − r_M(CN). The CN of the cation M in each crystal was estimated, where the CN of the two O atoms of a nitrite ion bound to one metal ion was assumed to be 1·5. The effective radii of the O atom, $r_{\rm O}$(type 1) and $r_{\rm O}$(type 2), were calculated separately because of significant differences in the mean interatomic distances, $\overline{d_{M\cdots\rm O}}$(type 1) and $\overline{d_{M\cdots\rm O}}$(type 2). For $Pb(NO_2)_2.H_2O$, the interatomic distances involving the two disordered nitrite ions were not included in the calculation. $r_{\rm N}$ and $r_{\rm O}$(type 2) for $Pb(NO_2)_2.H_2O$ are larger than those for alkali and alkaline-earth metal salts, and $r_{\rm O}$(type 1) is *ca* 0·1 Å shorter. It was revealed that the Pb^{2+} ions which induce the yellow color of the title compound lie on a bridge position between the two O atoms, in contrast to large Ag—N covalency in the pale-yellow $AgNO_2$ crystals.

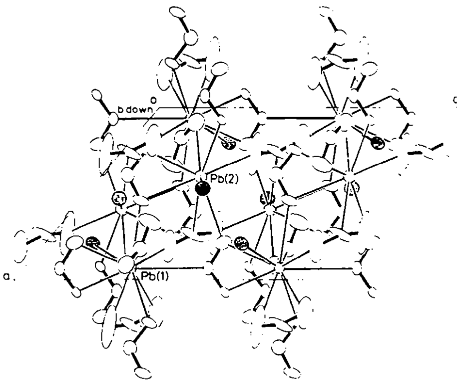

Fig. 1. Projection of the structure along **b**. The dotted and shaded ellipsoids represent the Pb and hydrate O atoms, respectively.

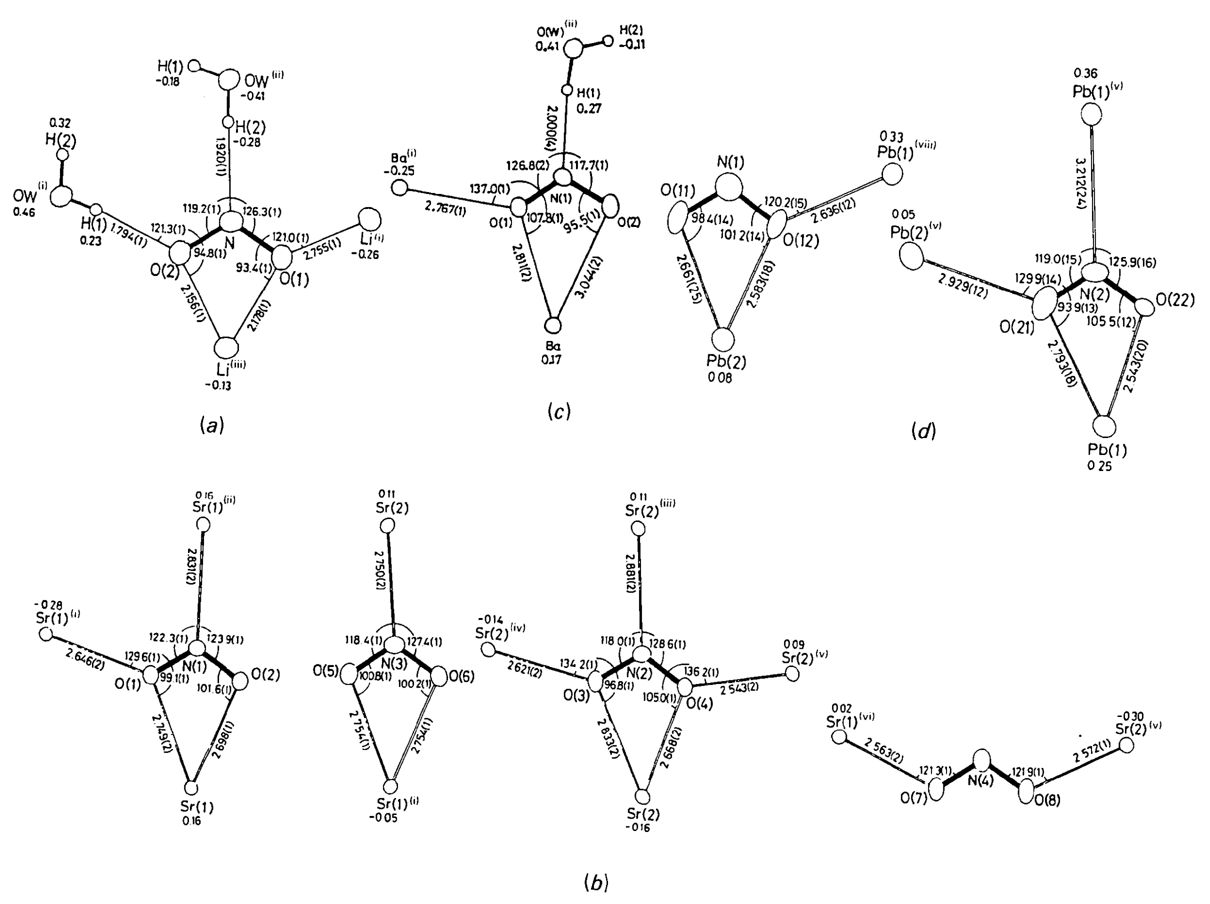

Fig. 2. Arrangement of metal cations and water molecules around the NO_2^- ions with distances from the ONO plane less than 0·5 Å in (*a*) $LiNO_2.H_2O$, (*b*) $Sr(NO_2)_2.H_2O$, (*c*) $Ba(NO_2)_2.H_2O$, and (*d*) $Pb(NO_2)_2.H_2O$. There are no neighboring Ba^{2+} or H_2O nearly coplanar with O(3)N(2)O(4) in $Ba(NO_2)_2.H_2O$. A numeral below the atom numbering indicates a deviation of the atom from the NO_2 plane (Å). Symmetry code: (*a*) (i) $1-x, 1-y, 1-z$; (ii) $1+x, y, z$; (iii) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (*b*) (i) $-x, \frac{1}{2}+y, -z$; (ii) $-x, \frac{1}{2}+y, 1-z$; (iii) $1-x, -\frac{1}{2}+y, 1-z$; (iv) $1-x, -\frac{1}{2}+y, 2-z$; (v) $x, y, -1+z$; (*c*) (i) $1+x, 1-x+y, \frac{1}{6}+z$; (ii) $x-y, x, -\frac{1}{6}+z$; (*d*) see Table 2.

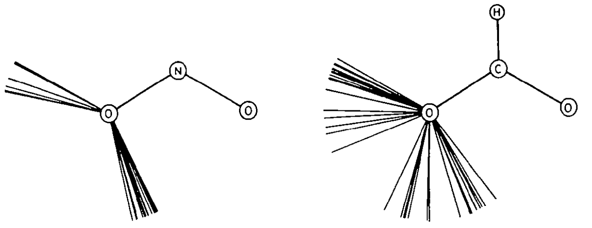

Fig. 3. Directions of the metal cations neighboring the O atoms with the shift from the ONO or HCO_2 plane less than 0·5 Å.

Polymorphism of lead nitrite crystals grown from aqueous solutions was observed. $Pb(NO_2)_2$, hexagonal plates (001), orthorhombic, $Pca2_1$, $a = 8{\cdot}858$ (2), $b = 11{\cdot}785$ (2), $c = 22{\cdot}708$ (3) Å, $V = 2370{\cdot}5$ (6) $Å^3$, $Z = 24$, $D_x = 5{\cdot}03$ Mg m^{-3}, μ(Mo $K\alpha$) = 42·9 mm^{-1}, $T = 299$ (1) K. Intensity measurement up to $2\theta = 55°$,

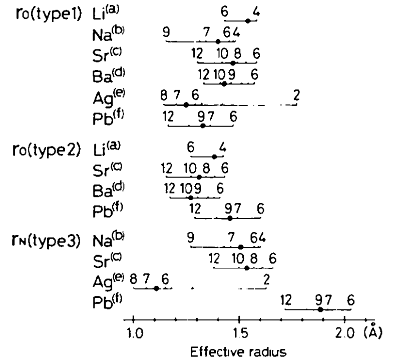

Fig. 4. Effective radii of the nitrite O and N atoms in (*a*) $LiNO_2.H_2O$, (*b*) $NaNO_2$, (*c*) $Sr(NO_2)_2.H_2O$, (*d*) $Ba(NO_2)_2.H_2O$, (*e*) $AgNO_2$, and (*f*) $Pb(NO_2)_2.H_2O$. Bars are the range of the effective radii estimated using the ionic radius of the metal with different coordination numbers (CN). Points on the bars show the values corresponding to the estimated CN.

slight decay of the crystal. Positions of six independent Pb atoms were determined by direct methods ($R = 0{\cdot}15$). $Pb(NO_2)_2.2H_2O$(?), triangular or trapezoidal plates, rapid decay of the crystals by X-ray irradiation, orthorhombic(?), $a = 11{\cdot}884$ (3), $b = 38{\cdot}988$ (37), $c = 9{\cdot}201$ (2) Å, $V = 4263$ (4) Å^3, $Z = 28$ (?).

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Structure (Neutron) of Potassium Iodate at 100 and 10 K

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Abstract. KIO_3, $M_r = 214{\cdot}001$, $P1$, $Z = 4$, neutron powder diffraction (Rietveld method), $\lambda = 1{\cdot}9090$ (1) Å, $F(000) = 320$, $D_m(300\ \mathrm{K}) = 3{\cdot}89\ \mathrm{g\ cm^{-3}}$; at $T = 100$ K: $a = 7{\cdot}6982$ (4), $b = 7{\cdot}6597$ (2), $c = 7{\cdot}6912$ (5) Å, $\alpha = 108{\cdot}999$ (5), $\beta = 109{\cdot}745$ (2), $\gamma = 109{\cdot}085$ (5)°, $V = 351{\cdot}60$ (2) Å^3, $D_x = 4{\cdot}04\ \mathrm{g\ cm^{-3}}$, $R_I = 8{\cdot}12\%$ for 799 integrated Bragg intensities; at $T = 10$ K: $a = 7{\cdot}6818$ (5), $b = 7{\cdot}6504$ (3), $c = 7{\cdot}6896$ (5) Å, $\alpha = 109{\cdot}062$ (5), $\beta = 109{\cdot}786$ (2), $\gamma = 109{\cdot}012$ (5)°, $V = 350{\cdot}22$ (3) Å^3, $D_x = 4{\cdot}06\ \mathrm{g\ cm^{-3}}$, $R_I = 7{\cdot}95\%$ for 786 integrated Bragg intensities. The previously reported phase transitions to phase IV (below 263 K) and phase V (below 83 K) [Herlach (1961). *Helv. Phys. Acta*, **34**, 305–330] are found not to involve significant atomic-scale change to the room-temperature phase III triclinic structure. The observed marked variations in the ferroelectric behaviour that prompted the transitions proposal are considered to originate from domain- or twin-scale changes within the sample.

Introduction. At atmospheric pressure, potassium iodate has been reported (from nuclear quadrupole resonance, dielectric constant, and X-ray powder diffraction measurements) to undergo phase transitions with temperature change:

$$\mathrm{V} \xleftrightarrow{83\mathrm{K}} \mathrm{IV} \underset{263\mathrm{K}}{\overset{255\mathrm{K}}{\rightleftarrows}} \mathrm{III} \xleftrightarrow{343\mathrm{K}} \mathrm{II} \xleftrightarrow{485\mathrm{K}} \mathrm{I}$$

and all phases, except I, are ferroelectric (Herlach, 1961).

Recently the room-temperature phase III has been shown by neutron diffraction to have a triclinic structure, with very pronounced pseudorhombohedral symmetry (Lucas, 1984). No structural information on the reported lower-temperature phases (IV and V) has been published to date and therefore the present study was made to investigate this, using the neutron powder profile method.

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