

Crystal Structure of $K_2Pb(NO_2)_3(NO_3) \cdot H_2O$

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Crystals of $K_2Pb(NO_2)_3(NO_3) \cdot H_2O$ are orthorhombic (Pbca) with unit-cell dimensions: $a = 6.766(5)$, $b = 11.999(7)$, $c = 26.61(2)$ Å, $Z = 8$. The structure has been determined from diffractometer data by the heavy-atom technique and refined by full-matrix least-squares to an R value of 7.13% for 1285 independent reflections. The lead atom is surrounded by nine ligating atoms belonging to nitrate and nitrite groups. The NO_3^- ion and two NO_2^- ions are chelating to metal in a bidentate fashion through their oxygen atoms, while the third NO_2^- ion acts as a bridge through two metal centers involving in coordination all its three atoms. The two K^+ ions are in different structural environments which differ by the number and the arrangement of the ligating atoms.

Introduction

Lead nitrites and lead nitrito-nitrates of alkaline metals can be obtained by crystallization at room temperature from aqueous solutions containing the components in different ratios. It has been shown that the composition of the compounds mainly depends on the preparation ratios [1]. A noteworthy feature of these compounds is given by the yellow-orange colour they show both in solution and in solid state, this colour being probably due to an increase in intensity of the lowest energy singlet-triplet transition of NO_2^- , brought about by spin-orbit coupling to Pb [2].

With the aim of giving a structural basis to clarify this aspect of lead chemistry, the X-ray crystal analysis of the title compound was undertaken. The results of our analysis confirm the chemical formula previously obtained by conventional chemical methods as well as the preliminary crystallographic data [1].

Experimental

Crystals of $K_2Pb(NO_2)_3(NO_3) \cdot H_2O$ were obtained as yellow-orange prisms following the method previously described. Weissenberg photographs, taken using $CuK\alpha$ radiation, showed the crystals to be

TABLE I. Crystallographic Data.

$K_2Pb(NO_2)_3(NO_3) \cdot H_2O$	$M = 503.4$, orthorhombic
$a = 6.766(5)$, $b = 11.999(7)$, $c = 26.61(2)$ Å; $V = 2160(3)$ Å ³ ;	
$Z = 8$; $D_o = 3.019$, $D_c = 3.095$ g cm ⁻³ ; $F(000) = 1840$;	
MoK α radiation, $\lambda = 0.71069$ Å; $\mu(\text{MoK}\alpha) = 165.6$ cm ⁻¹	
Space group <i>Pbca</i> .	

orthorhombic with systematic extinctions ($hk0$, $h = 2n + 1$; $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$) uniquely defining the space group *Pbca*. The lattice constants were refined by least-squares calculations on the basis of 2θ values for 13 strong reflections ($10^\circ < \theta < 26^\circ$) measured on an on-line Siemens AED single-crystal diffractometer. Table I lists the most significant crystallographic data. Intensity measurements were made at room temperature from a prismatic crystal of approximate dimensions $0.32 \times 0.16 \times 0.13$ mm³ using niobium-filtered MoK α radiation at a takeoff angle of 4° . The moving counter-moving crystal scan technique was used, with a drive speed related to the number of counts on the peak. The pulse height discriminator was set in such a way that 90% of the diffracted intensity was counted. Attenuation filters were used in order to stay in the linear zone of counting. For intensities and background the 'five-points' measuring procedure [3] was employed. A total of 2528 independent reflections were collected up to $\theta_{\text{max}} = 28^\circ$ and of these only 1285 were used in the subsequent calculations having $I > 2\sigma(I)$. A standard reflection (3 8 1) was remeasured after every twenty reflections to detect long-term drift in the equipment or changes in the crystal. The intensity of this reflection as a function of X-ray exposure showed only random deviations from its mean value (maximum deviation 3.2%). Corrections to the structure amplitudes were made for Lorentz and polarization factors, while the absorption effects were neglected ($\mu\bar{r} = 1.19$). The absolute scale was obtained by refining the scale factor for the structure amplitudes as a variable parameter in the least-squares refinement.

TABLE II. Fractional Atomic Coordinates ($\times 10^4$ for Pb and K, and $\times 10^3$ for O and N).

	x	y	z
Pb	1628(2)	2287(1)	961(1)
K(1)	2372(11)	4997(5)	-440(3)
K(2)	722(13)	4584(7)	3019(3)
N(1)	-284(6)	254(4)	121(1)
O(1)	-171(4)	342(2)	123(1)
O(2)	-196(4)	173(2)	108(1)
N(2)	249(4)	-33(2)	92(1)
O(3)	87(4)	9(2)	102(1)
O(4)	374(4)	35(3)	79(1)
N(3)	-30(4)	247(2)	-12(1)
O(5)	20(4)	322(2)	13(1)
O(6)	20(3)	152(2)	8(1)
N(4)	168(4)	243(4)	218(1)
O(7)	224(5)	329(2)	191(1)
O(8)	148(7)	256(4)	260(1)
O(9)	144(5)	165(1)	191(1)
O(10)	55(4)	32(2)	293(1)

The structure was solved by the heavy-atom technique, the Pb–Pb vectors being identified in a three-dimensional Patterson map. A least-squares refinement of the Pb coordinates led to a conventional R index ($\sum \|F_o| - |F_c| \| / \sum |F_o|$) of 21.46%. A Fourier difference map, based upon the phases assigned from this refinement, clearly showed the positions of all non-hydrogen atoms. Two cycles of full-matrix refinement with isotropic thermal parameters lowered R to 13.50%, while with the introduction of anisotropic thermal parameters (154 variables over 1285 data), the index dropped to 7.13%. The function minimized was $\sum w(F_o - F_c)^2$, where the weight for each reflection was unity at first, while in the last cycles the weighting scheme $w = [\sigma^2(F_o^2 + 0.005 F_c^2)]^{-1}$, based on counting statistics, was employed. At the end of the refinement a difference Fourier map was calculated and found to contain only two relevant residual peaks of $\sim 5 \text{ e } \text{\AA}^{-3}$, approximately 0.9 Å from lead, symmetrically situated with respect to it. No attempt was made to locate the hydrogen atoms from the water molecule since their peaks would be indistinguishable from background.

Atomic scattering factors (neutral atoms) were taken from Cromer & Mann [4]. Real and imaginary dispersion corrections for lead scattering factor were also applied ($\Delta f' = -4.133$, $\Delta f'' = 10.102$) [5].

Final atomic coordinates are listed in Table II. Observed and calculated structure factors and thermal parameters have been deposited with the Editor. All calculations were carried out on the Cyber 76 Computer of Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia

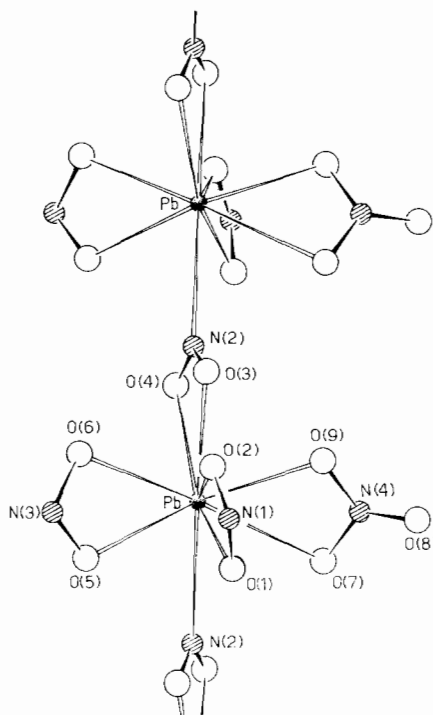


Fig. 1. Projection of the structure along [100] showing the linking of lead coordination polyhedra.

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Results and Discussion

As shown in Fig. 1 the coordination around lead is nine-membered and involves the nitrate group, which behaves as unsymmetrical bidentate chelating ligand, and the three nitrite groups. Two of these coordinate to metal through both their oxygen atoms, while the third one bridges two metal centers, one through the two oxygens, and the other through the nitrogen. This last interaction, which produces the linking of the coordination polyhedra in chains running along [010], could explain the enhanced intensity of the singlet–triplet transition of NO_2^- , which is responsible for the colour of the compound*.

*The electronic spectrum of aqueous solutions containing KNO_2 and $\text{Pb}(\text{NO}_3)_2$ shows two relevant bands, one at ca. 355 nm, the other at ca. 440 nm. The position of these bands remains unchanged even if the ratio $\text{KNO}_2/\text{Pb}(\text{NO}_3)_2$ is varied from 1/1 to 1/5. The band at ca. 355 nm is due to the NO_2^- free ions as is found also in the aqueous solutions of KNO_2 [6]. The small broad band at ca. 440 nm is responsible for the colour of the compound and corresponds to that found for the aqueous solutions of TlNO_2 [7].

TABLE III. Selected Distances (Å) and Angles ($^\circ$).

a) Lead Environment			
Pb-O(1)	2.74(2)	Pb-O(5)	2.67(2)
Pb-O(2)	2.54(2)	Pb-O(6)	2.69(2)
Pb-O(3)	2.69(2)	Pb-O(7)	2.83(3)
Pb-O(4)	2.77(3)	Pb-O(9)	2.64(2)
Pb-N(2 ⁱ)	2.92(2)		
O(1)-Pb-O(2)	46	O(3)-Pb-O(7)	113
O(1)-Pb-O(3)	108	O(3)-Pb-O(9)	69
O(1)-Pb-O(4)	153	O(3)-Pb-N(2 ⁱ)	178
O(1)-Pb-O(5)	73	O(4)-Pb-O(5)	114
O(1)-Pb-O(6)	96	O(4)-Pb-O(6)	76
O(1)-Pb-O(7)	71	O(4)-Pb-O(7)	115
O(1)-Pb-O(9)	82	O(4)-Pb-O(9)	86
O(1)-Pb-N(2 ⁱ)	72	O(4)-Pb-N(2 ⁱ)	135
O(2)-Pb-O(3)	63	O(5)-Pb-O(6)	45
O(2)-Pb-O(4)	107	O(5)-Pb-O(7)	128
O(2)-Pb-O(5)	82	O(5)-Pb-O(9)	154
O(2)-Pb-O(6)	71	O(5)-Pb-N(2 ⁱ)	69
O(2)-Pb-O(7)	98	O(6)-Pb-O(7)	167
O(2)-Pb-O(9)	76	O(6)-Pb-O(9)	135
O(2)-Pb-N(2 ⁱ)	117	O(6)-Pb-N(2 ⁱ)	112
O(3)-Pb-O(4)	44	O(7)-Pb-O(9)	44
O(3)-Pb-O(5)	113	O(7)-Pb-N(2 ⁱ)	66
O(3)-Pb-O(6)	69	O(9)-Pb-N(2 ⁱ)	109
σ are 1° .			
b) Potassium Environment			
K(1)-O(5)	3.00(2)	K(2)-O(8)	2.72(5)
K(1)-O(6 ⁱ)	2.82(2)	K(2)-O(10 ⁱ)	2.69(3)
K(1)-O(2 ⁱⁱ)	2.71(3)	K(2)-O(1 ^v)	2.99(2)
K(1)-O(3 ⁱⁱⁱ)	2.83(3)	K(2)-O(3 ^{vi})	2.83(2)
K(1)-O(6 ⁱⁱⁱ)	2.80(2)	K(2)-O(9 ^{vi})	2.88(3)
K(1)-O(4 ⁱⁱⁱ)	2.66(3)	K(2)-O(10 ^{vi})	2.80(3)
K(1)-O(1 ^{iv})	2.87(2)	K(2)-O(7 ^{vii})	2.83(3)
K(1)-O(5 ^{iv})	2.88(2)		
c) Nitrite Groups			
N(1)-O(1)	1.31(5)	N(1)-O(2)	1.20(5)
N(2)-O(3)	1.24(4)	N(2)-O(4)	1.22(4)
N(3)-O(5)	1.18(3)	N(3)-O(6)	1.31(3)
O(1)-N(1)-O(2)	112(4)	O(3)-N(2)-O(4)	114(3)
O(5)-N(3)-O(6)	111(3)		
Pb-O(1)-N(1)	94(2)	Pb-O(2)-N(1)	107(3)
Pb-O(3)-N(2)	108(3)	Pb-O(4)-N(2)	99(2)
Pb-O(5)-N(3)	105(2)	Pb-O(6)-N(3)	99(2)
d) Nitrate Group			
N(4)-O(7)	1.30(5)	N(4)-O(8)	1.14(4)
N(4)-O(9)	1.19(5)		
O(7)-N(4)-O(8)	117(5)	O(7)-N(4)-O(9)	110(3)
O(8)-N(4)-O(9)	133(5)		
Pb-O(7)-N(4)	96(2)	Pb-O(9)-N(4)	110(3)

TABLE III. (continued)

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

The geometry around lead is quite irregular and its shape does not exhibit the characteristics of the ideal polyhedra for nine-coordinate complexes, *i.e.* the tricapped trigonal prism (D_{3h}) and the mono-capped square antiprism (C_{4v}) [5]. The irregularity is a consequence of the presence of a large empty region, which seems to be caused by the presence of the lone-pair, on the side opposite to the N(1)O(1)-O(2) nitrite group. If the presence of the lead lone-pair is taken into account, the arrangement around the metal may approach a bicapped severely distorted square antiprism or, in a better way, a distorted octahedron, if the nitrite and nitrate ions are considered as occupying each only one stereochemical position.

As can be seen from Table III, which lists the most significant distances and angles, the distances Pb-O range from 2.54 to 2.83 Å. These values are in a quite good agreement with those found in 2,4,6-tris(2-pyrimidyl)1,3,5-triazinedilead(II) nitrate dihydrate (2.644, 2.748, 2.564, 2.637 Å being the values concerning the bidentate nitrates) [9], in $Pb(NO_3)_2$ (2.805 Å) [10] as concerns the NO_3 group, and in $K_2PbCu(NO_2)_6$ (2.793 Å) [11] and in $K_2PbNi(NO_2)_6$ (2.773 Å) [12] as concerns the NO_2 group. No comparison can be made for the Pb-N $_{NO_2}$ distance as this compound seems to be, to our knowledge, the first nitrite lead complex of known structure, in which a similar interaction occurs.

As clearly pointed out by Klanderman, Hamilton and Bernal [13] the nitrite ion can bind a metal in several ways, which can be summarized as follows: *i*, unidentate through nitrogen; *ii*, unidentate through one of its oxygens; *iii*, bidentate to a single metal atom through the two oxygens; *iv*, bidentate bridging to two metal centers, in a symmetrical fashion, through the oxygen atoms; *v*, bidentate bridging to two metal centers, in an asymmetric fashion, through nitrogen and one of its oxygens. In the present compound one more way of behaviour for this ion is found, as all its atoms are involved in coordination.

There are two crystallographically independent potassium ions in the unit cell. They are both surrounded by oxygen atoms, but the number of ligating atoms as well as their arrangement around the potassium ions is different. K(1) is bonded to eight oxygen atoms, all belonging to nitrite groups, while K(2) has seven oxygen neighbours, two from NO_2^- groups, three from NO_3^- groups, and two from water

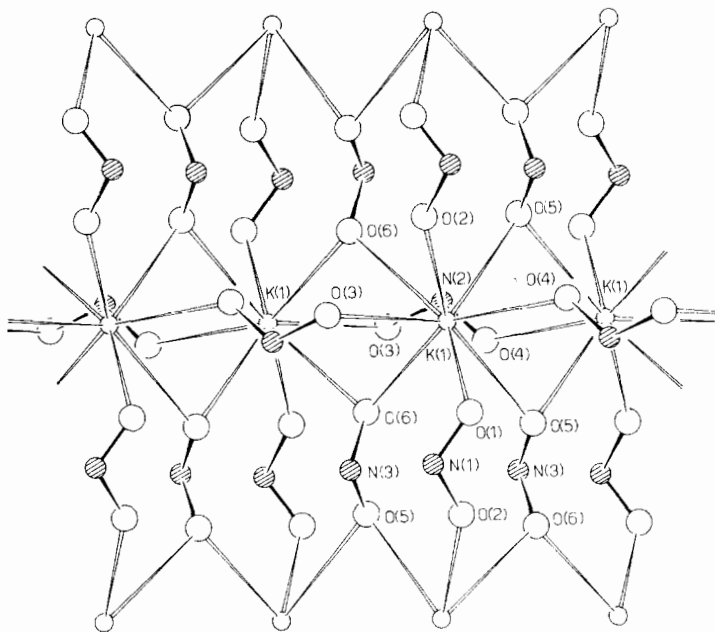


Fig. 2. A projection of the structure along $[001]$ showing the relationships between K(1) and the nearest oxygen atoms.

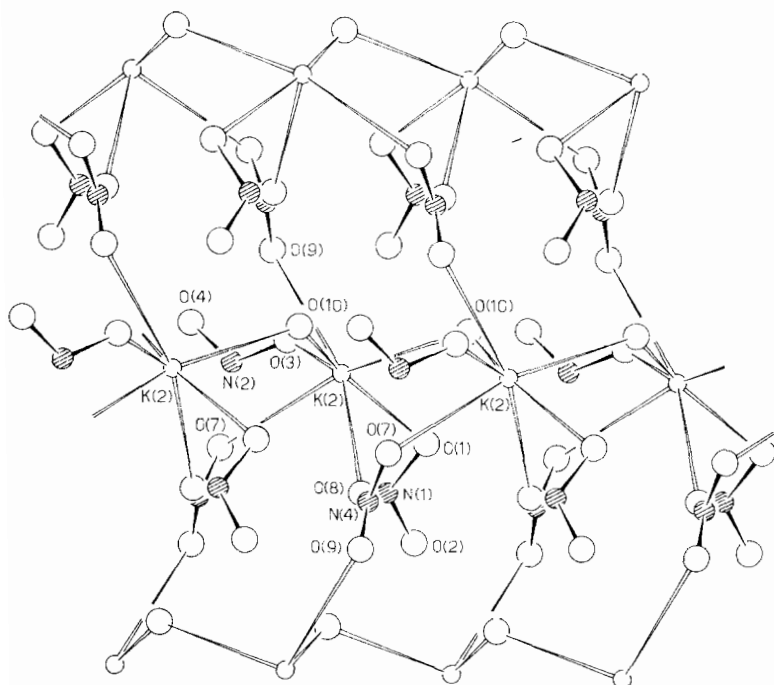


Fig. 3. A projection of the structure along $[001]$ showing the relationships between K(2) and the nearest oxygen atoms.

molecules. The overall geometry of the K(1) coordination can be described as a distorted square antiprism. As depicted in Fig. 2 these antiprisms form chains running along $[100]$ and the chains are joined together in layers lying on (010) by N(1)O(1)O(2)

bridges. The coordination polyhedron around K(2) does not exhibit the shape of any of the classical polyhedra, but this is rather common in potassium stereochemistry [13, 14]. Figure 3 shows the K(2) polyhedra joined in chains running along $[100]$ and

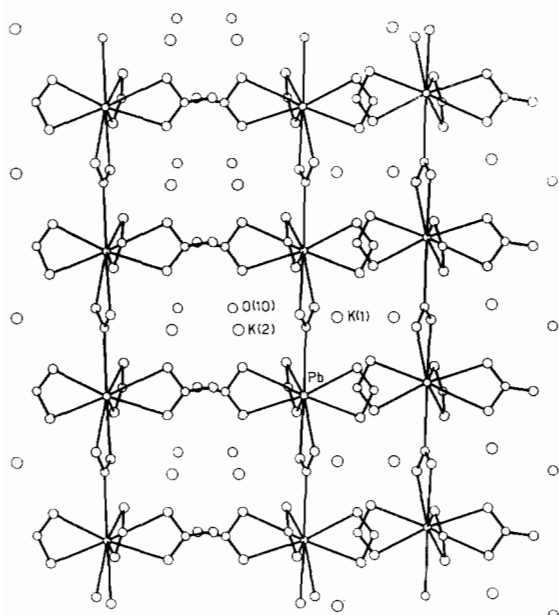


Fig. 4. Molecular packing viewed along [100].

the chains linked in layers by NO_3^- bridges. The K–O interatomic distances are listed in Table III, they range from 2.66 to 3.00 Å, in a good agreement with the values observed in related structures for this kind of interactions [12, 13, 14].

The water molecule interacts uniquely with the K(2) ion.

Figure 4 gives a complete view of the molecular packing; the closest significant approaches are as

follows: $Pb \cdots K(1) = 4.210(7)$ Å; $Pb \cdots K(2) = 4.518(9)$ Å, $K(1) \cdots K(1) = 3.973(11)$ Å; $K(1) \cdots K(2) = 4.328(12)$ Å; $K(2) \cdots K(2) = 4.367(12)$ Å.

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References

- 1 M. Nardelli, L. Cavalca and A. Braibanti, *Gazz. Chim. Ital.*, **85**, 1535 (1955).
- 2 H. J. Maria, A. T. Armstrong and S. P. McGlynn, *J. Chem. Phys.*, **48**, 4694 (1968).
- 3 W. Hoppe, *Acta Cryst.*, **A25**, 67 (1969).
- 4 D. T. Cromer and J. B. Mann, *Acta Cryst.*, **A24**, 321 (1968).
- 5 'International Tables for X-Ray Crystallography', vol. IV; The Kynoch Press, Birmingham, England, 1974, p. 150.
- 6 G. Kortüm, *Z. phys. Chem.*, **B43**, 418 (1939).
- 7 M. Nardelli, A. Braibanti and I. Chierici, *Gazz. Chim. Ital.*, **87**, 510 (1957).
- 8 E. L. Muetterties and C. M. Wright, *Quart. Reviews*, **21**, 109 (1967).
- 9 E. I. Lerner and S. J. Lippard, *Inorg. Chem.*, **16**, 1537 (1977).
- 10 W. C. Hamilton, *Acta Cryst.*, **10**, 103 (1957).
- 11 D. L. Cullen and E. C. Lingafelter, *Inorg. Chem.*, **10**, 1264 (1971).
- 12 S. Tagaki, M. D. Joesten and P. G. Lenhart, *Acta Cryst.*, **B31**, 1968 (1975).
- 13 K. A. Klanderman, W. C. Hamilton and I. Bernal, *Inorg. Chim. Acta*, **23**, 117 (1977).
- 14 L. F. Power, J. A. King and F. H. Moore, *J. Chem. Soc. Dalton*, 93 (1976).