

Table 3. *Hydrogen-bonding distances, angles, and bond valences*

	H...O (Å)	N—H (Å)	N—H...O (°)	N...O (Å)	Adjusted H...O* (Å)	s† (v.u.)
N(1 ⁱ)—H(2 ⁱ)...O(1)	2.09 (7)	0.87 (8)	170 (6)	2.945 (5)	1.86	0.19
N(2 ⁱⁱ)—H(6 ⁱⁱ)...O(1)	1.88 (7)	1.19 (6)	149 (5)	2.963 (5)	1.96	0.16
N(1 ⁱⁱⁱ)—H(3 ⁱⁱⁱ)...O(2)	2.14 (7)	0.91 (8)	161 (5)	3.010 (5)	1.96	0.16
N(2 ^{iv})—H(6 ^{iv})...O(2)	2.50 (7)	1.19 (6)	114 (5)	3.179 (4)	2.54	0.07
N(2 ^v)—H(5 ^v)...O(3)	2.12 (7)	1.04 (6)	134 (6)	2.939 (5)	2.08	0.13
N(1 ^{vi})—H(1 ^{vi})...O(3)	2.31 (5)	0.79 (7)	150 (7)	3.014 (4)	2.05	0.13
N(2 ^{vii})—H(4 ^{vii})...O(3)	2.26 (8)	0.92 (8)	170 (3)	3.165 (6)	2.08	0.13

Symmetry operators to transform from coordinates in Table 1: (i) $1-x, -y, -z$; (ii) $-x, -y, -z$; (iii) $1-x, 1-y, -z$; (iv) $1+x, 1+y, 1+z$; (v) $1+x, 1+y, z$.

* O...H distance recalculated with consideration of the angle at H to adjust for a 1.1 Å N—H bond (Brown, 1982).

† For the O...N hydrogen bond, 0.02 v.u. are added to the *s* value from the O—H curve (Brown, 1982).

References

- BJORLING, C. O. (1941). *Ark. Kemi Mineral. Geol.* **B15**, No. 2.
- BOND, W. L. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 291–306. Birmingham: Kynoch Press.
- BRITTEN, J. F., LOCK, C. J. L. & PRATT, W. M. C. (1982). *Acta Cryst.* **B38**, 2148–2155.
- BROWN, I. D. (1981). In *Structure and Bonding in Crystals*, Vol. II, ch. 14. New York: Academic Press.
- BROWN, I. D. (1982). Personal communication.
- CALABRESE, J. C. & BURNETT, R. M. (1980). *TAPER*, locally modified for CDC Cyber by Z. TUN, with permission of Nicolet XRD Corporation.
- CRIVEN, B. M. & HALL, D. (1961). *Acta Cryst.* **14**, 475–480.
- CROMER, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1, pp. 149–150. Birmingham: Kynoch Press.
- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B, pp. 99 *ff.* Birmingham: Kynoch Press.
- FAGGIANI, R., HOWARD-LOCK, H. E., LOCK, C. J. L., LIPPERT, B. & ROSENBERG, B. (1982). *Can. J. Chem.* **60**, 529–534.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- KAUFFMAN, G. B. & COWAN, D. O. (1963). *Inorg. Synth.* **7**, 239–245.
- LIU, C. F. & IBERS, J. A. (1970). *Inorg. Chem.* **9**, 773–778.
- LOCK, C. J. L. (1980). *ACS Symp. Ser.* **140**, 209–224.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination and refinement. Univ. of Cambridge, England.
- SHUSTOROVICH, E. M., PORAI-KOSHITS, M. A. & BUSLAEV, YU. A. (1975). *Coord. Chem. Rev.* **17**, 1–98.
- STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1983). **C39**, 1591–1594

The Structure (Neutron) of Phase II Caesium Nitrate at 298 K, CsNO₃

BY B. W. LUCAS

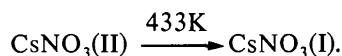
Department of Physics, University of Queensland, St. Lucia, Brisbane, Queensland 4067, Australia

(Received 15 March 1983; accepted 28 July 1983)

Abstract. $M_r = 194.92$, trigonal, $P3_1$ (or its enantiomorph $P3_2$), $a = 10.95$ (2), $c = 7.80$ (2) Å, $V = 809.94$ Å³, $Z = 9$, and $D_x = 3.597$ Mg m⁻³, $\lambda = 1.249$ Å, $\mu = 0.0576$ mm⁻¹. The single-crystal neutron diffraction intensity data were moderately affected by extinction. Inclusion of an isotropic extinction correction was found adequate to allow for this and when combined with anisotropic temperature factors in the least-squares refinement of 859 (non-equivalent-averaged) reflections gave a converged conventional *R* factor of 0.066. The structure has the Cs atoms forming a pseudocubic sublattice with nine

pseudocubes per unit cell. The NO₃-groups' configurations within the unit cell are derived from an asymmetric unit of three NO₃ groups. Average N—O distances and O—N—O angles are 1.24 (4) Å and 120 (4)° respectively. Each NO₃ group is essentially parallel to one of the faces of its surrounding Cs-atom pseudocube and one of the N—O bonds is almost parallel to a pseudocube cell edge. The relationship between the crystal structure and previously reported pyroelectricity is discussed. The thermal ellipsoids of the O atoms were found to be markedly anisotropic and are illustrated.

Introduction. At atmospheric pressure, CsNO_3 undergoes the thermal polymorphic phase transition (Plyushev, Markina & Shklover, 1956; Owen & Kennard, 1971):



The $\text{CsNO}_3(\text{II})$ crystal structure has been investigated previously by X-ray (Ferroni, Sabatini & Orioli, 1957) and neutron (DeLacy & Kennard, 1971) single-crystal diffraction methods. Ferroni *et al.* (1957) reported the crystal data as trigonal, $a = 10.87$, $c = 7.76 \text{ \AA}$, $Z = 9$, Laue group $\bar{3}m$, space group $P31m$. However, DeLacy & Kennard (1971) suggested the Laue group is $\bar{3}$ and space group $P3_1$ (or its enantiomorph $P3_2$). Hence, the correct space group was uncertain and no complete crystal structure had been reported.

Raman and infrared spectroscopic investigations (Brooker, 1973) suggested that $\text{CsNO}_3(\text{II})$ and $\text{RbNO}_3(\text{IV})$ have isomorphous crystal structures and supported the assignment of the space group $P3_1$ (or its enantiomorph $P3_2$). Recently, the crystal structure of $\text{RbNO}_3(\text{IV})$ has been determined by single-crystal neutron diffraction methods (Shamsuzzoha & Lucas, 1982) and this result was used as the basis for the present $\text{CsNO}_3(\text{II})$ crystal structure determination.

Experimental. Single crystals of $\text{CsNO}_3(\text{II})$ grown by slow evaporation of an aqueous solution at room temperature (CsNO_3 powder of stated purity 99.8% from Koch-Light Laboratories, England, was used). Hexagonally-shaped prism, approximately $2.1 \times 4.0 \times 5.5 \text{ mm}$, mounted with c almost parallel to the ϕ axis of a computer-controlled four-circle neutron diffractometer belonging to the Australian Institute of Nuclear Science and Engineering (AINSE), installed at the Australian Atomic Energy Commission (AAEC) research reactor HIFAR, at Lucas Heights; wavelength $1.249 (1) \text{ \AA}$ (graphite monochromator), obtained by previous calibration using a spherically-shaped single-crystal standard; ω - 2θ scans, 2θ step size of 0.01° and width of 2.2° , background-peak-background measurements made for each Bragg reflection, standard reflection ($\bar{4}\bar{4}\bar{4}$) monitored after every 25 reflections, equivalent sets of Bragg intensities (for half of the reciprocal-space sphere, $-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $0 \leq l \leq 8$) collected out to a limit of $\sin\theta/\lambda \leq 0.566 \text{ \AA}^{-1}$; cell dimensions obtained from the single-crystal neutron diffraction data collected (71 reflections, $0.138 < \sin\theta/\lambda < 0.491 \text{ \AA}^{-1}$).

Trends in the values of the integrated intensity of the standard reflection, as measured at regular intervals during the data collection, were used for scaling the integrated intensities. The sums of differences between the mean of the standard intensities and the intensity of the standards in sequence, starting from the first

standard, were accumulated. The value of this sum, at each standard in the sequence, was plotted against the standard number. Changes in the intensity of the standard were considered indicated by a change in the slope of the cumulative sum plot (Moore, 1980).

The measured integrated intensities I (reflections greater than 1σ were considered as observed), and $\sigma(I)$ based on counting statistics alone, in the scaled neutron-data set were corrected for absorption by numerical integration. The crystal shape was divided into 125 volume elements, according to three-dimensional, five-point Gaussian integration intervals. An examination of the absorption-corrected data revealed that the intensities associated with the set of crystallographic planes (hki), for cyclic permutation of hki , had equal magnitudes within the (absorption-corrected) counting statistics. Similar equality within the set of (khi) for cyclic permutation of khi , was also apparent. Comparison of intensity magnitudes between these sets indicated their inequality and hence the Laue class could be assigned as $\bar{3}$.

In order to define the reliability of the data, statistical analysis was performed (F test at the 1% level) for the above-mentioned Laue group's symmetry-related reflections. This analysis led to rejection of only three reflections, *i.e.* 022, 300 and 131. Lorentz-factor corrections were applied to all statistically reliable reflections. Although inclusion of an isotropic extinction parameter in the subsequent least-squares refinement strictly precludes the possibility of averaging equivalent reflections, previous experience has shown that with the relatively small magnitude of μ , the fairly regular crystal specimen shape, and the accuracy of the specimen-dimensions' determination, the symmetry-related intensities could be combined without significant effect. (The negligible effect on the final structure was confirmed subsequently when individual reflections were maintained for the inclusion of anisotropic extinction correction in the least-squares refinement.) The number of independent reflections thus obtained was 859. $\sigma(I)$'s used were from Poisson statistics if greater than $\sigma(I)$'s from equivalent reflections.

The observed pyroelectricity (Bury & McLaren, 1969) and optical activity (Karpov & Shultin, 1970), in conjunction with the crystallographic data, require the point-group symmetry to be 3. The point group 3 has the possible space groups $P3$, $R3$, $P3_1$ (or its enantiomorph $P3_2$). The systematic absences, $00l$ for $l \neq 3n$, eliminated all except $P3_1$ (or its enantiomorph $P3_2$).

$\text{CsNO}_3(\text{II})$ has been suggested to have a crystal structure isomorphous with $\text{RbNO}_3(\text{IV})$ (Brooker, 1973). As the crystal structure of $\text{RbNO}_3(\text{IV})$ has recently been determined by a single-crystal neutron diffraction study (Shamsuzzoha & Lucas, 1982), this structure with the space group $P3_1$ was used as the initial model structure. The atomic positions were refined by full-matrix least-squares calculations, using

the complete neutron data set. The refinement was initially performed with isotropic temperature factors, but subsequently anisotropic temperature factors and an isotropic extinction factor were introduced; the function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$ and the weighting factor was $w(hkl) = \{\sigma^2[|F(hkl)|^2]\}^{-1}$. The coherent scattering lengths used were: Cs = 5.5, N = 9.4 (*International Tables for X-ray Crystallography*, 1974), and O = 5.83 fm (Schneider, 1976).

The refinement (136 variables) converged and although examination of $|F_o|^2$ and $|F_c|^2$ values for the stronger reflections indicated that the single-crystal data were affected by extinction this was in contrast to the severe extinction effects found for the recently published RbNO₃(IV) room-temperature data (Shamsuzoha & Lucas, 1982). Nevertheless, to allow complete comparison with the RbNO₃(IV) results anisotropic extinction corrections were introduced in further least-squares refinements. A total of 2766 statistically reliable reflections (equivalents not averaged) were employed in the refinements. It was apparent, however, that inclusion of anisotropic extinction correction did not significantly improve the refinement result. The positional parameters for the isotropic extinction model are listed in Table 1.* Final $R = 0.066$, $R_w = 0.10$, $(\Delta/\sigma)_{\max} = 1.04$. The final structure was confirmed by Fourier and difference Fourier syntheses. For the Fourier maps, all the atomic positions appeared as well resolved peaks at essentially the least-squares-refined positions, while with the difference Fourier synthesis no significant peaks occurred.

* Lists of structure factors, anisotropic thermal parameters, and some information about the extinction effects have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38782 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic positional parameters of CsNO₃(II) as determined by least-squares refinement at 298 K

Standard deviations are in parentheses and the parameter without standard deviation was fixed to define the origin. $B_{eq} = \frac{2}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{\AA}^2)$
Cs(1)	0.4530 (2)	0.5644 (3)	0.6336 (4)	1.83
Cs(2)	0.1179 (3)	0.2229 (2)	0.0000	2.03
Cs(3)	-0.2220 (2)	0.2197 (3)	0.6459 (6)	2.31
N(1)	0.4422 (2)	0.5737 (2)	0.1113 (5)	2.13
N(2)	0.1056 (2)	0.2035 (1)	-0.4698 (5)	1.89
N(3)	-0.2578 (2)	0.2069 (1)	0.1340 (5)	2.48
O(1)	0.3367 (3)	0.5581 (3)	0.0203 (6)	3.46
O(2)	0.4157 (5)	0.4942 (4)	0.2237 (7)	5.98
O(3)	0.5595 (3)	0.6616 (3)	0.0576 (7)	4.25
O(4)	0.0018 (2)	0.1128 (2)	-0.3849 (6)	2.94
O(5)	0.2251 (2)	0.2346 (3)	-0.4171 (7)	4.28
O(6)	0.0847 (6)	0.2561 (5)	-0.6029 (6)	6.24
O(7)	-0.3227 (4)	0.1187 (3)	0.2555 (6)	4.07
O(8)	-0.1312 (4)	0.2723 (5)	0.1217 (9)	7.00
O(9)	-0.3315 (3)	0.2241 (3)	0.0304 (6)	3.49

All calculations were carried out on the University's PDP-10 computer (using a suite of programs from various sources), except for the initial stages of the data reduction which were carried out on the IBM 370 computer at the AAEC.

Discussion. The crystal structure (with space group $P3_1$) is isomorphous with the structure of RbNO₃(IV), i.e. the Cs atoms form a pseudocubic sublattice with nine pseudocubes per unit cell. The NO₃-group configurations, within the unit cell, are derived from an asymmetric unit of three NO₃ groups (Fig. 1). The NO₃ groups are closely planar and each is enclosed by a pseudocube of Cs atoms. The plane of each NO₃ group

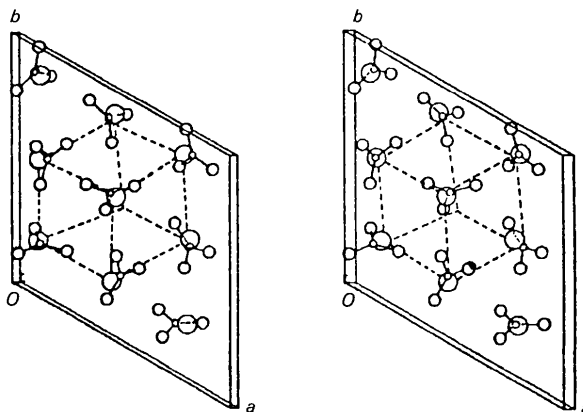


Fig. 1. A stereoview ([001] out of paper) of the unit-cell contents for CsNO₃(II) at 298 K. A typical Cs-atom pseudocube is outlined.

Table 2. Interatomic distances (Å) and angles (°) for CsNO₃(II) at 298 K

Standard deviations are in parentheses. Superscripts i, ii, iii represent the equivalent positions $x, y, z; \bar{y}, x - y, \frac{1}{3} + z; y - x, \bar{x}, \frac{2}{3} + z$ respectively.

Cs(1) ⁱ ...		Cs(2) ⁱⁱ ...		Cs(3) ⁱⁱⁱ ...	
O(1 ⁱⁱ)	3.25 (1)	O(1 ⁱ)	3.23 (1)	O(2 ⁱⁱⁱ)	3.21 (1)
O(1 ⁱⁱⁱ)	3.25 (1)	O(2 ⁱ)	3.58 (1)	O(3 ⁱⁱⁱ)	3.20 (1)
O(1 ⁱ)	3.26 (1)	O(3 ⁱⁱⁱ)	3.28 (1)	O(4 ⁱ)	3.21 (1)
O(2 ⁱ)	3.27 (1)	O(4 ⁱⁱ)	3.27 (1)	O(5 ⁱⁱ)	3.23 (1)
O(2 ⁱⁱ)	3.71 (1)	O(4 ⁱⁱⁱ)	3.27 (1)	O(6 ⁱ)	3.72 (1)
O(3 ⁱⁱⁱ)	3.45 (1)	O(4 ⁱ)	3.25 (1)	O(7 ⁱ)	3.24 (1)
O(3 ⁱ)	3.49 (1)	O(5 ⁱⁱ)	3.46 (1)	O(7 ⁱⁱ)	3.33 (1)
O(5 ⁱ)	3.23 (1)	O(5 ⁱ)	3.44 (1)	O(8 ⁱⁱⁱ)	3.88 (1)
O(6 ⁱⁱ)	3.14 (1)	O(6 ⁱⁱⁱ)	3.73 (1)	O(8 ⁱ)	3.81 (1)
O(7 ⁱⁱⁱ)	3.43 (1)	O(6 ⁱ)	3.16 (1)	O(9 ⁱⁱ)	3.31 (1)
O(8 ⁱⁱ)	3.17 (1)	O(7 ⁱⁱⁱ)	3.20 (1)	O(9 ⁱⁱⁱ)	3.25 (1)
O(9 ⁱⁱⁱ)	3.30 (1)	O(8 ⁱ)	3.18 (1)	O(9 ⁱ)	3.24 (1)
N(1) ⁱ -		N(2) ⁱⁱ -		N(3) ⁱⁱⁱ -	
O(1 ⁱ)	1.29 (1)	O(4 ⁱⁱ)	1.26 (1)	O(7 ⁱ)	1.28 (1)
O(2 ⁱ)	1.16 (1)	O(5 ⁱⁱ)	1.25 (1)	O(8 ⁱⁱ)	1.21 (1)
O(3 ⁱ)	1.23 (1)	O(6 ⁱⁱ)	1.26 (1)	O(9 ⁱⁱ)	1.22 (1)
O(1 ⁱ)-N(1 ⁱ)-O(2 ⁱ)		116.2 (3)	O(4 ⁱⁱ)-N(2 ⁱⁱ)-O(5 ⁱⁱ)		116.9 (4)
O(1 ⁱⁱ)-N(1 ⁱⁱ)-O(3 ⁱⁱ)		115.5 (4)	O(4 ⁱⁱⁱ)-N(2 ⁱⁱⁱ)-O(6 ⁱⁱⁱ)		119.6 (3)
O(2 ⁱⁱ)-N(1 ⁱⁱ)-O(3 ⁱⁱ)		127.8 (4)	O(5 ⁱ)-N(2 ⁱ)-O(6 ⁱ)		123.6 (4)
O(7 ⁱⁱⁱ)-N(3 ⁱⁱⁱ)-O(8 ⁱⁱⁱ)		123.1 (5)			
O(7 ⁱ)-N(3 ⁱ)-O(9 ⁱ)		116.4 (3)			
O(8 ⁱⁱ)-N(3 ⁱⁱ)-O(9 ⁱⁱ)		120.6 (4)			

is almost parallel to one of the faces of its enclosing pseudocube. The interatomic distances and interbond angles below 4 Å are shown in Table 2. The average N—O bond lengths and O—N—O bond angles are 1.24 (4) Å and 120 (4)°. The magnitudes of the extinction parameters are considerably smaller than those for RbNO₃(IV) at room temperature. This suggests that the crystal of the CsNO₃(II) sample was closer to being 'ideally imperfect' than the RbNO₃(IV) sample at the same temperature.

The temperature factors of the nitrate atoms are markedly anisotropic. The thermal ellipsoids for each NO₃ group in the asymmetric unit are illustrated in Fig. 2. One O atom in each group [O(2ⁱ), O(6ⁱ), and O(8ⁱ), respectively] has significantly larger thermal ellipsoids than the other O atoms within its group. This could explain the apparent foreshortening of the N(1ⁱ)—O(2ⁱ) distance to 1.16 Å, the N(3ⁱ)—O(8ⁱ) distance to 1.21 Å, and the apparent distortion of the nitrate groups generally, when compared to the configurations found for NO₃ groups in other nitrate compounds (*e.g.* Lucas, Ahtee & Hewat, 1979).

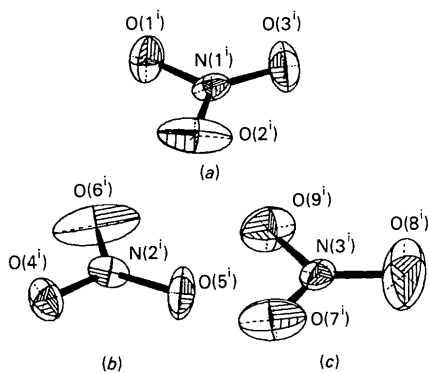


Fig. 2. The anisotropic thermal ellipsoids, drawn to include 50% probability, of the three nitrate groups in the asymmetric unit. (Their orientations, but not relative positions, are as in Fig. 1.)

The crystal structure of CsNO₃(II) determined is consistent with the observed properties of optical activity and pyroelectricity. The presence of a unique polar axis in its point group for pyroelectric behaviour is confirmed. The centroid of the Cs-cation pseudocubic lattice (surrounding the NO₃ anion) and that of the enclosed anion are displaced relative to each other along the *c* direction which is consistent with the observed presence of an electric moment.

The author thanks Dr J. K. Nimmo for some assistance during the data collection and the initial stages of data reduction. The use of the facilities of the Australian Institute of Nuclear Science and Engineering (AINSE) and the Australian Atomic Energy Commission (AAEC) is gratefully acknowledged. This work was supported by an AINSE Research Grant.

References

- BROOKER, M. H. (1973). *J. Chem. Phys.* **59**, 5828–5829.
 BURY, P. C. & McLAREN, A. C. (1969). *Phys. Status Solidi*, **31**(2), 799–806.
 DELACY, T. P. & KENNARD, C. H. L. (1971). *Aust. J. Chem.* **24**, 165–167.
 FERRONI, E., SABATINI, A. & ORIOLI, P. (1957). *Gazz. Chim. Ital.* **87**, 630–637.
International Tables for X-ray Crystallography (1974). Vol. IV, p. 323. Birmingham: Kynoch Press.
 KARPOV, S. V. & SHULTIN, A. A. (1970). *Phys. Status Solidi*, **39**, 33–38.
 LUCAS, B. W., AHTEE, M. & HEWAT, A. W. (1979). *Acta Cryst.* **B35**, 1038–1041.
 MOORE, F. H. (1980). Private communication, AINSE, Lucas Heights, NSW.
 OWEN, W. R. & KENNARD, C. H. L. (1971). *Aust. J. Chem.* **24**, 1295–1296.
 PLYUSCHEV, V. E., MARKINA, I. B. & SHKLOVER, L. P. (1956). *Dokl. Akad. Nauk SSSR*, **108**, 645–647.
 SCHNEIDER, C. S. (1976). *Acta Cryst.* **A32**, 375–379.
 SHAMSUZZOHA, M. & LUCAS, B. W. (1982). *Acta Cryst.* **B38**, 2353–2357.

Acta Cryst. (1983). **C39**, 1594–1597

Structure de l'Oxypentasulfure de Gallium et de Trilanthane, GaLa₃OS₅

PAR S. JAULMES, A. MAZURIER ET M. GUITTARD

Laboratoire de Physique et Laboratoire de Chimie Minérale Structurale (associé au CNRS n° 200), Faculté des Sciences Pharmaceutiques et Biologiques de Paris-Luxembourg, 4 avenue de l'Observatoire, 75270 Paris CEDEX 06, France

(Reçu le 17 mars 1983, accepté le 1 août 1983)

Abstract. $M_r = 662.74$, orthorhombic, $Pnma$, $a = 5.08$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 19.0$ mm⁻¹, 10.78 (1), $b = 4.03$ (1), $c = 19.95$ (1) Å, $V = F(000) = 1160$, 293 K, $R = 0.027$ for 1432 unique reflexions. The La atoms are in eight- and ninefold