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Diaqua(nitrato- κ^2O,O')bis(L-valine- κO)lead(II) nitrate at 296 K

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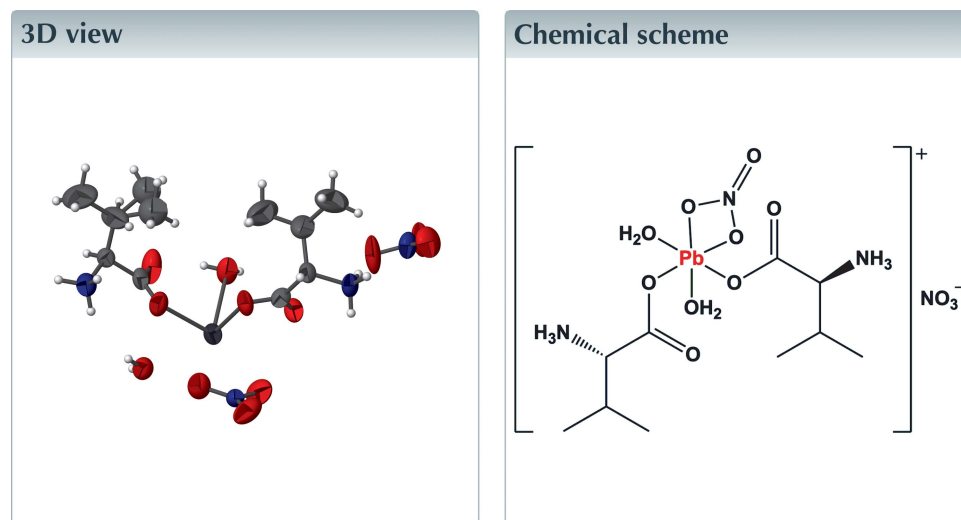
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Structural data: full structural data are available from iucrdata.iucr.org

The structure of the title complex, $[\text{Pb}(\text{NO}_3)(\text{C}_5\text{H}_{11}\text{NO}_2)_2(\text{H}_2\text{O})_2]\text{NO}_3$, had been determined previously at 173 and 193 K, and is now reported at 296 K, in the same space group. The main difference with the low-temperature structures is that a methyl group of one valine ligand is clearly disordered over two positions, for which the occupancies converged to 0.56 (3) and 0.44 (3). Bond-length variations within the coordination sphere of Pb^{II} as a function of T are difficult to assess because uncertainties on these parameters are high. On the other hand, $\text{Pb}\cdots\text{O}$ distances above 2.9 Å cannot be assigned unambiguously to formal $\text{Pb}-\text{O}$ bonds. As a consequence, the polymeric nature of the complex previously described at 173 K is uncertain, as well as the actual coordination number of Pb^{II} , and it is thus not possible to determine if the metal environment is holo- or hemidirected.



Structure description

The complex $[\text{Pb}(\text{H}_2\text{O})_2(\text{L-valine})_2(\text{NO}_3)]^+\text{NO}_3^-$ has been synthesized by many groups, in a context related to lead–aminoacids and lead–enzymes interactions studies. The X-ray structure has been published twice, using data collected at $T = 173$ K (Burford *et al.*, 2004) and $T = 193$ K (Saunders *et al.*, 2011). However, these structures appear with different names and connectivity diagrams in the CSD: the former, ESAPET, is considered as a polymeric compound with the coordinated nitrate ion bridging metal centers in the crystal, while the latter, ESAPET01, is deposited as a monomeric species. These representations are indeed consistent with the structure descriptions given in both articles.

We have now determined the structure of the same compound at room temperature (Fig. 1). One L-valine ligand has a different conformation at room temperature, with one methyl group disordered over two positions, C14A and C14B, a feature not present at low

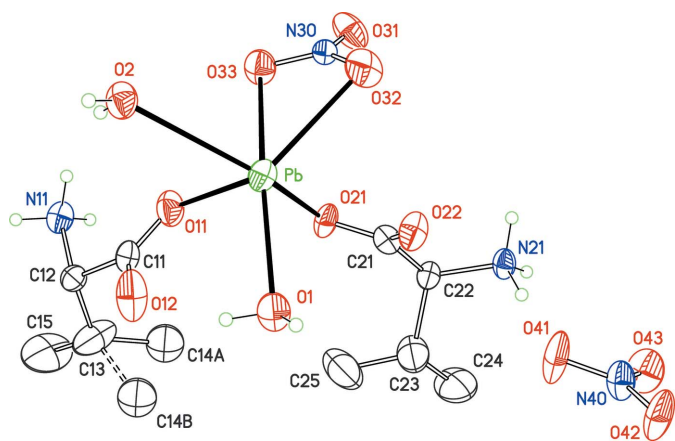


Figure 1
The asymmetric unit for the title complex, with displacement ellipsoids at the 30% probability level. The chosen asymmetric unit is identical to that used in Saunders *et al.* (2011), as well as the labeling scheme. H atoms bonded to C atoms are omitted for clarity. Atoms C14A and C14B are disordered sites for C14 and were refined isotropically.

temperature. The positions of the other ligands around Pb^{II} are unchanged at 296 K (see Fig. 2 for a fit between the three refinements).

A comparison of the Pb···O distances in the coordination sphere of the metal at $T = 173$, 193 and 296 K is given in Table 1. No clear trend can be extracted from these data, because uncertainties for the 173 and 296 K refinements are four to six times higher than those of the 193 K refinement. However, these distances are informative regarding the mode of coordination of the L-valine ligands. The first one is clearly monodentate, since the Pb···O12 distance is greater than 3.2 Å at any temperature. The situation for the other ligand is more ambiguous. Distance Pb···O22 increases as T increases, to reach 2.934 (10) Å at 296 K. Taking into account the upper limit of 2.9 Å for a Pb—O bond, retained by Saunders *et al.* (see Fig. 5 in Saunders *et al.*, 2011), we could consider that the

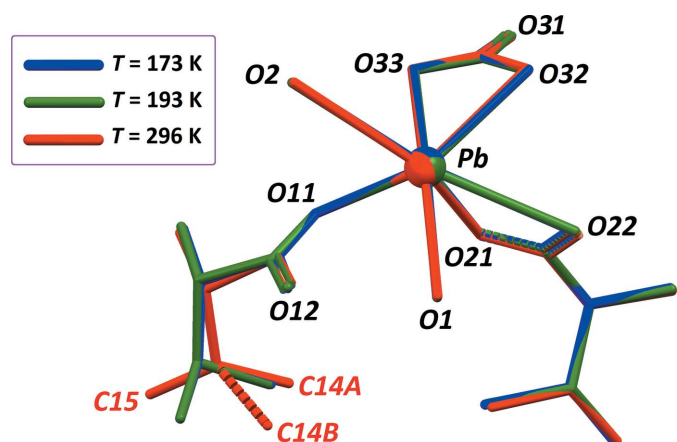


Figure 2
A fit between the refinements of the title compound at $T = 173$ (blue), 193 (green) and 296 K (red). The fit was carried out using Pb and O atoms of cation [Pb(H₂O)₂(L-valine)₂(NO₃)₂]⁺ (Macrae *et al.*, 2008). Labels are for the $T = 296$ K refinement. Sites C14A and C14B correspond to a single atom disordered over two positions.

Table 1
Comparison for distances in the coordination sphere (Å) at different temperatures.

Bond ^a	$T = 173$ K ^b	$T = 193$ K ^c	$T = 296$ K ^d
Pb···O1	2.510 (12)	2.512 (3)	2.504 (14)
Pb···O2	2.891	2.915 (2)	2.891 (13)
Pb···O11	2.442 (10)	2.459 (2)	2.462 (12)
Pb···O12	3.275	3.266 (3)	3.209 (19)
Pb···O21	2.362 (11)	2.356 (2)	2.363 (12)
Pb···O22	2.873	2.892 (2)	2.934 (10)
Pb···O32	2.853	2.847 (3)	2.878 (18)
Pb···O33	2.778	2.790 (3)	2.820 (13)
Pb···O31'	2.95 (1)	2.969 (3)	2.996 (16)

Notes: (a) In the last entry, Pb···O31' is the shortest intermolecular Pb···O_{nitrate} distance. (b) Burford *et al.* (2004) [distances not found in the deposited CIF were estimated using Mercury (Macrae *et al.*, 2008)]; (c) Saunders *et al.* (2011); (d) this work.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H11···O12	0.85 (3)	1.99 (10)	2.724 (19)	144 (17)
O1—H12···O21 ⁱ	0.85 (3)	1.92 (5)	2.756 (16)	171 (20)
O2—H21···O32 ⁱⁱ	0.85 (3)	2.50 (10)	3.26 (2)	150 (16)
O2—H22···O22 ⁱⁱⁱ	0.85 (3)	2.10 (6)	2.919 (17)	162 (19)
N11—H11A···O32 ⁱⁱ	0.93	2.24	2.85 (2)	123
N11—H11B···O42 ^{iv}	0.93	1.90	2.817 (16)	169
N11—H11C···O12 ^v	0.93	1.93	2.80 (2)	156
N21—H21A···O2 ^{vi}	0.93	2.24	2.947 (19)	132
N21—H21B···O42 ^v	0.93	2.03	2.924 (18)	160
N21—H21C···O41	0.93	1.86	2.785 (18)	177

Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $x + 1, y - 1, z$; (v) $x + 1, y, z$; (vi) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$.

carbonyl group C21=O22 is not engaged in coordination. As a consequence, both zwitterionic valine ligands in our refinement should be considered as monodentate (Fig. 1), in contrast with the low-temperature refinements, described with κO and $\kappa^2 O, O'$ coordination modes.

Using the same criterion, the complex at $T = 296$ K is not a polymeric compound, since the shortest intermolecular Pb···O_{nitrate} distance is Pb···O31ⁱ = 2.996 (16) Å [symmetry code: (i) $-1 + x, y, z$]. This distance was 2.95 (1) Å at 173 K and 2.969 (3) Å at 193 K. As commented by Saunders *et al.*, these distances close to the 2.9 Å threshold mean that ‘the assignment of the environment of lead in these compounds as hemi- or holodirected is arbitrary’.

In the here reported structure, all H atoms bonded to heteroatoms are engaged in hydrogen bonds (Table 2) of variable strengths.

Synthesis and crystallization

2 mmol (0.67 g) of Pb(NO₃)₂ were dissolved in 20 ml of previously degassed distilled water. To this solution, 4 mmol (0.47 g) of solid valine were added in several portions and with constant stirring. The pH value was adjusted to 5.0 with NaOH 0.1 M, and the solution was left to rest. Two weeks later, suitable crystals were collected.

Table 3

Experimental details.

Crystal data	
Chemical formula	[Pb(NO ₃)(C ₅ H ₁₁ NO ₂) ₂ (H ₂ O) ₂]-NO ₃
<i>M_r</i>	601.54
Crystal system, space group	Orthorhombic, <i>P</i> 2 ₁ 2 ₁
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.4311 (5), 13.6861 (15), 27.340 (4)
<i>V</i> (Å ³)	2032.2 (4)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
<i>μ</i> (mm ⁻¹)	8.37
Crystal size (mm)	0.40 × 0.25 × 0.10
Data collection	
Diffractometer	Bruker P4
Absorption correction	<i>ψ</i> scan (<i>XSCANS</i> ; Bruker, 1997)
<i>T_{min}</i> , <i>T_{max}</i>	0.143, 0.437
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	5226, 3566, 2874
<i>R_{int}</i>	0.039
(sin <i>θ</i> /λ) _{max} (Å ⁻¹)	0.595
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.044, 0.116, 1.02
No. of reflections	3566
No. of parameters	256
No. of restraints	9
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δ <i>ρ</i> _{max} , Δ <i>ρ</i> _{min} (e Å ⁻³)	1.47, -1.82
Absolute structure	Flack <i>x</i> determined using 1007 quotients [(<i>I</i> ⁺) - (<i>I</i> ⁻)] / [(<i>I</i> ⁺) + (<i>I</i> ⁻)] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.001 (19)

Computer programs: *XSCANS* (Bruker, 1997), *SHELXS97* and *SHELXTL* (Sheldrick, 2008) and *SHELXL2014* (Sheldrick, 2015).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The structure refinement was started using coordinates deposited for ESAPET01, since the first structure, ESAPET, was collected with permuted cell axis

for the orthorhombic cell. Atom C14 is disordered over two sites, C14A and C14B, for which occupancies converged to 0.56 (3) and 0.44 (3). Both atoms C14A and C14B were refined isotropically with a common displacement parameter, which was fixed in the last cycles, in order to avoid correlation with the refined occupancy. Bond lengths C13–C15 and C13–C14(A,B) in this *iso*-propyl group were restrained to 1.54 (2) Å. It was also necessary to refine nitrate atom N30 isotropically, otherwise a non-positive definite ellipsoid is obtained for this atom. C- and N- bonded H atoms were placed in calculated positions, with fixed bond lengths C–H = 0.96 Å (methyl), 0.98 Å (methine) and N–H = 0.93 Å (ammonium, with free rotation about the C–N bonds). Water H atoms were found in a difference map and refined with restrained distances: 0.85 (2) Å for O–H bonds and 1.40 (3) Å for H···H separation in each water molecule. Displacement parameters for H atoms were calculated as $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{carrier atom})$, with $x = 1.5$ (methyl, ammonium, water) or $x = 1.2$ (methine).

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x160539 [doi:10.1107/S2414314616005393]

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Sylvain Bernès and Laura Gasque

Diaqua(nitrato- κ^2O,O')bis(L-valine- κO)lead(II) nitrate

Crystal data

[Pb(NO₃)(C₃H₁₁NO₂)₂(H₂O)₂]₂NO₃

$M_r = 601.54$

Orthorhombic, $P2_12_12_1$

$a = 5.4311$ (5) Å

$b = 13.6861$ (15) Å

$c = 27.340$ (4) Å

$V = 2032.2$ (4) Å³

$Z = 4$

$F(000) = 1168$

$D_x = 1.966$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 75 reflections

$\theta = 4.7$ – 12.5°

$\mu = 8.37$ mm⁻¹

$T = 296$ K

Prism, colorless

$0.40 \times 0.25 \times 0.10$ mm

Data collection

Bruker P4

diffractometer

Radiation source: fine-focus sealed tube, FN4

Graphite monochromator

$2\theta/\omega$ scans

Absorption correction: ψ scan

(*XSCANS*; Bruker, 1997)

$T_{\min} = 0.143$, $T_{\max} = 0.437$

5226 measured reflections

3566 independent reflections

2874 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$

$\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 1.7^\circ$

$h = -6 \rightarrow 6$

$k = -16 \rightarrow 16$

$l = -32 \rightarrow 32$

3 standard reflections every 97 reflections

intensity decay: 1.5%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.116$

$S = 1.02$

3566 reflections

256 parameters

9 restraints

0 constraints

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2 + 11.4316P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 1.47$ e Å⁻³

$\Delta\rho_{\min} = -1.82$ e Å⁻³

Absolute structure: Flack x determined using 1007 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)

Absolute structure parameter: 0.001 (19)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Pb	0.24568 (16)	0.10974 (4)	0.28034 (2)	0.0475 (2)	

O1	-0.032 (2)	0.1354 (9)	0.3523 (6)	0.067 (4)	
H11	-0.04 (3)	0.075 (4)	0.359 (9)	0.101*	
H12	-0.170 (16)	0.162 (11)	0.347 (8)	0.101*	
O2	0.185 (2)	-0.0767 (9)	0.2321 (5)	0.061 (3)	
H21	0.29 (2)	-0.106 (12)	0.249 (7)	0.092*	
H22	0.06 (2)	-0.114 (11)	0.226 (8)	0.092*	
O11	0.485 (3)	-0.0106 (8)	0.3275 (5)	0.065 (3)	
O12	0.140 (3)	-0.0502 (11)	0.3636 (8)	0.085 (6)	
O21	0.506 (2)	0.2061 (7)	0.3299 (5)	0.053 (3)	
O22	0.226 (3)	0.3153 (7)	0.3106 (4)	0.060 (3)	
N30	0.722 (3)	0.1876 (8)	0.2209 (4)	0.039 (3)*	
O31	0.914 (3)	0.2259 (12)	0.2149 (7)	0.080 (5)	
O32	0.531 (3)	0.2376 (12)	0.2190 (7)	0.078 (5)	
O33	0.711 (2)	0.0993 (8)	0.2349 (5)	0.067 (3)	
N11	0.723 (3)	-0.1705 (9)	0.3596 (5)	0.052 (3)	
H11A	0.7041	-0.1627	0.3260	0.079*	
H11B	0.7564	-0.2357	0.3665	0.079*	
H11C	0.8533	-0.1319	0.3704	0.079*	
N21	0.486 (2)	0.4622 (8)	0.3514 (5)	0.044 (3)	
H21A	0.5030	0.4649	0.3176	0.066*	
H21B	0.5980	0.5048	0.3659	0.066*	
H21C	0.3269	0.4802	0.3600	0.066*	
C11	0.360 (4)	-0.0632 (14)	0.3549 (9)	0.048 (5)	
C12	0.487 (3)	-0.1396 (11)	0.3855 (6)	0.044 (4)	
H12A	0.3792	-0.1968	0.3874	0.053*	
C13	0.547 (6)	-0.1088 (17)	0.4366 (8)	0.109 (10)	
H13A	0.3853	-0.1090	0.4526	0.131*	0.56 (3)
H13B	0.6821	-0.0638	0.4292	0.131*	0.44 (3)
C14A	0.638 (9)	-0.008 (3)	0.4464 (17)	0.099*	0.56 (3)
H14A	0.5374	0.0383	0.4294	0.149*	0.56 (3)
H14B	0.8055	-0.0025	0.4353	0.149*	0.56 (3)
H14C	0.6316	0.0047	0.4809	0.149*	0.56 (3)
C14B	0.390 (10)	-0.040 (4)	0.466 (2)	0.099*	0.44 (3)
H14D	0.2737	-0.0085	0.4447	0.149*	0.44 (3)
H14E	0.4921	0.0079	0.4813	0.149*	0.44 (3)
H14F	0.3024	-0.0764	0.4906	0.149*	0.44 (3)
C15	0.689 (7)	-0.182 (2)	0.4660 (9)	0.143 (15)	
H15A	0.6268	-0.2464	0.4595	0.215*	
H15B	0.6720	-0.1676	0.5001	0.215*	
H15C	0.8599	-0.1790	0.4570	0.215*	
C21	0.414 (3)	0.2902 (12)	0.3333 (6)	0.044 (4)	
C22	0.535 (3)	0.3606 (10)	0.3686 (6)	0.045 (4)	
H22A	0.7134	0.3491	0.3685	0.054*	
C23	0.435 (5)	0.3465 (16)	0.4217 (8)	0.089 (8)	
H23A	0.2585	0.3610	0.4206	0.106*	
C24	0.552 (6)	0.421 (2)	0.4562 (9)	0.123 (11)	
H24A	0.5494	0.4846	0.4411	0.184*	
H24B	0.7185	0.4028	0.4630	0.184*	

H24C	0.4597	0.4235	0.4862	0.184*
C25	0.458 (7)	0.2498 (19)	0.4397 (10)	0.136 (13)
H25A	0.4333	0.2496	0.4744	0.204*
H25B	0.6199	0.2255	0.4324	0.204*
H25C	0.3372	0.2089	0.4244	0.204*
N40	-0.025 (2)	0.5992 (10)	0.3857 (6)	0.058 (4)
O41	0.002 (2)	0.5112 (9)	0.3745 (8)	0.095 (6)
O42	-0.239 (3)	0.6316 (7)	0.3869 (6)	0.088 (4)
O43	0.150 (3)	0.6499 (10)	0.3947 (6)	0.086 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb	0.0392 (3)	0.0462 (3)	0.0572 (3)	0.0063 (4)	-0.0086 (5)	-0.0039 (2)
O1	0.038 (6)	0.060 (8)	0.104 (11)	0.003 (5)	0.015 (7)	0.007 (8)
O2	0.067 (10)	0.054 (6)	0.063 (8)	-0.010 (6)	-0.017 (6)	0.000 (5)
O11	0.079 (9)	0.046 (7)	0.071 (9)	0.007 (7)	-0.011 (8)	0.008 (6)
O12	0.043 (8)	0.054 (9)	0.157 (19)	0.001 (7)	-0.021 (10)	0.011 (10)
O21	0.045 (6)	0.035 (6)	0.080 (9)	0.010 (5)	0.002 (6)	-0.008 (6)
O22	0.067 (8)	0.050 (6)	0.063 (7)	0.015 (8)	-0.038 (9)	-0.007 (5)
O31	0.082 (10)	0.087 (11)	0.072 (11)	-0.022 (9)	-0.026 (9)	0.029 (10)
O32	0.059 (8)	0.093 (11)	0.083 (12)	0.034 (7)	-0.011 (9)	0.024 (10)
O33	0.054 (8)	0.062 (7)	0.086 (8)	-0.003 (7)	0.010 (7)	0.003 (6)
N11	0.049 (8)	0.049 (6)	0.060 (7)	0.002 (8)	-0.016 (9)	-0.004 (6)
N21	0.034 (6)	0.032 (6)	0.067 (9)	-0.005 (5)	0.001 (7)	0.001 (6)
C11	0.050 (11)	0.034 (9)	0.060 (12)	-0.003 (8)	-0.005 (9)	-0.006 (9)
C12	0.042 (8)	0.043 (8)	0.048 (10)	0.006 (6)	0.002 (8)	-0.001 (7)
C13	0.16 (3)	0.113 (19)	0.051 (12)	0.086 (19)	-0.022 (15)	-0.007 (13)
C15	0.19 (4)	0.17 (3)	0.064 (14)	0.08 (3)	-0.03 (2)	0.028 (16)
C21	0.036 (8)	0.049 (9)	0.047 (10)	-0.003 (7)	-0.008 (7)	0.007 (8)
C22	0.049 (9)	0.036 (8)	0.050 (10)	0.003 (7)	-0.003 (8)	-0.003 (7)
C23	0.14 (2)	0.066 (13)	0.058 (13)	-0.005 (14)	-0.021 (14)	-0.004 (10)
C24	0.19 (3)	0.12 (2)	0.066 (16)	-0.04 (2)	0.007 (19)	-0.026 (15)
C25	0.23 (4)	0.10 (2)	0.077 (18)	-0.06 (2)	0.00 (2)	0.015 (17)
N40	0.041 (7)	0.042 (8)	0.092 (12)	-0.009 (7)	-0.008 (8)	0.003 (8)
O41	0.052 (8)	0.033 (7)	0.199 (19)	0.005 (6)	0.015 (10)	-0.009 (9)
O42	0.052 (7)	0.050 (6)	0.161 (14)	0.017 (8)	-0.001 (13)	-0.014 (7)
O43	0.070 (9)	0.071 (8)	0.117 (13)	-0.026 (7)	-0.014 (8)	-0.017 (9)

Geometric parameters (Å, °)

Pb—O21	2.363 (12)	C12—H12A	0.9800
Pb—O11	2.462 (12)	C13—C14A	1.49 (2)
Pb—O1	2.504 (14)	C13—C15	1.50 (2)
Pb—O33	2.820 (13)	C13—C14B	1.50 (3)
Pb—O32	2.878 (18)	C13—H13A	0.9800
Pb—O2	2.891 (13)	C13—H13B	0.9800
Pb—O22	2.934 (10)	C14A—H14A	0.9600

Pb—O31 ⁱ	2.996 (16)	C14A—H14B	0.9600
Pb—O12	3.209 (19)	C14A—H14C	0.9600
O1—H11	0.85 (3)	C14B—H14D	0.9600
O1—H12	0.85 (3)	C14B—H14E	0.9600
O2—H21	0.85 (3)	C14B—H14F	0.9600
O2—H22	0.85 (3)	C15—H15A	0.9600
O11—C11	1.24 (2)	C15—H15B	0.9600
O12—C11	1.23 (2)	C15—H15C	0.9600
O21—C21	1.260 (19)	C21—C22	1.52 (2)
O22—C21	1.24 (2)	C22—C23	1.56 (3)
N30—O31	1.18 (2)	C22—H22A	0.9800
N30—O32	1.241 (19)	C23—C25	1.42 (3)
N30—O33	1.269 (16)	C23—C24	1.53 (3)
N11—C12	1.52 (2)	C23—H23A	0.9800
N11—H11A	0.9301	C24—H24A	0.9600
N11—H11B	0.9301	C24—H24B	0.9600
N11—H11C	0.9301	C24—H24C	0.9600
N21—C22	1.492 (19)	C25—H25A	0.9600
N21—H21A	0.9301	C25—H25B	0.9600
N21—H21B	0.9301	C25—H25C	0.9600
N21—H21C	0.9301	N40—O43	1.201 (17)
C11—C12	1.51 (3)	N40—O42	1.25 (2)
C12—C13	1.49 (3)	N40—O41	1.251 (18)
O21—Pb—O11	75.9 (4)	C13—C12—C11	115.0 (14)
O21—Pb—O1	80.3 (4)	C13—C12—N11	109.4 (16)
O11—Pb—O1	90.0 (5)	C11—C12—N11	108.6 (14)
O21—Pb—O33	75.2 (4)	C13—C12—H12A	107.9
O11—Pb—O33	74.0 (4)	C11—C12—H12A	107.9
O1—Pb—O33	153.3 (4)	N11—C12—H12A	107.9
O21—Pb—O32	70.9 (5)	C14A—C13—C12	120 (3)
O11—Pb—O32	115.3 (4)	C14A—C13—C15	110 (3)
O1—Pb—O32	134.2 (4)	C12—C13—C15	115.0 (18)
O33—Pb—O32	44.8 (4)	C12—C13—C14B	124 (3)
O21—Pb—O2	145.4 (3)	C15—C13—C14B	115 (3)
O11—Pb—O2	73.1 (4)	C14A—C13—H13A	102.8
O1—Pb—O2	114.4 (4)	C12—C13—H13A	102.8
O33—Pb—O2	81.7 (4)	C15—C13—H13A	102.8
O32—Pb—O2	109.4 (5)	C12—C13—H13B	98.3
O21—Pb—O22	47.6 (4)	C15—C13—H13B	98.3
O11—Pb—O22	120.9 (4)	C14B—C13—H13B	98.3
O1—Pb—O22	67.8 (4)	C13—C14A—H14A	109.5
O33—Pb—O22	101.9 (4)	C13—C14A—H14B	109.5
O32—Pb—O22	66.5 (5)	H14A—C14A—H14B	109.5
O2—Pb—O22	166.0 (3)	C13—C14A—H14C	109.5
O21—Pb—O31 ⁱ	114.0 (4)	H14A—C14A—H14C	109.5
O11—Pb—O31 ⁱ	170.1 (4)	H14B—C14A—H14C	109.5
O1—Pb—O31 ⁱ	91.9 (5)	C13—C14B—H14D	109.5

O33—Pb—O31 ⁱ	107.6 (5)	C13—C14B—H14E	109.5
O32—Pb—O31 ⁱ	69.7 (4)	H14D—C14B—H14E	109.5
O2—Pb—O31 ⁱ	97.3 (4)	C13—C14B—H14F	109.5
O22—Pb—O31 ⁱ	68.7 (4)	H14D—C14B—H14F	109.5
O21—Pb—O12	94.6 (4)	H14E—C14B—H14F	109.5
O11—Pb—O12	42.9 (4)	C13—C15—H15A	109.5
O1—Pb—O12	55.3 (4)	C13—C15—H15B	109.5
O33—Pb—O12	116.0 (4)	H15A—C15—H15B	109.5
O32—Pb—O12	157.6 (4)	C13—C15—H15C	109.5
O2—Pb—O12	72.6 (4)	H15A—C15—H15C	109.5
O22—Pb—O12	116.6 (4)	H15B—C15—H15C	109.5
O31 ⁱ —Pb—O12	132.7 (4)	O22—C21—O21	122.9 (16)
Pb—O1—H11	94 (10)	O22—C21—C22	120.1 (14)
Pb—O1—H12	118 (10)	O21—C21—C22	117.0 (14)
H11—O1—H12	112 (6)	N21—C22—C21	108.3 (13)
Pb—O2—H21	96 (10)	N21—C22—C23	110.3 (14)
Pb—O2—H22	135 (10)	C21—C22—C23	111.2 (15)
H21—O2—H22	111 (6)	N21—C22—H22A	109.0
C11—O11—Pb	114.5 (13)	C21—C22—H22A	109.0
C11—O12—Pb	77.8 (16)	C23—C22—H22A	109.0
C21—O21—Pb	108.2 (10)	C25—C23—C24	112 (2)
C21—O22—Pb	81.1 (9)	C25—C23—C22	114 (2)
O31—N30—O32	119.1 (13)	C24—C23—C22	110 (2)
O31—N30—O33	120.4 (14)	C25—C23—H23A	106.7
O32—N30—O33	119.9 (15)	C24—C23—H23A	106.7
N30—O32—Pb	95.1 (10)	C22—C23—H23A	106.7
N30—O33—Pb	97.2 (9)	C23—C24—H24A	109.5
C12—N11—H11A	109.5	C23—C24—H24B	109.5
C12—N11—H11B	109.5	H24A—C24—H24B	109.5
H11A—N11—H11B	109.5	C23—C24—H24C	109.5
C12—N11—H11C	109.5	H24A—C24—H24C	109.5
H11A—N11—H11C	109.5	H24B—C24—H24C	109.5
H11B—N11—H11C	109.5	C23—C25—H25A	109.5
C22—N21—H21A	109.5	C23—C25—H25B	109.5
C22—N21—H21B	109.5	H25A—C25—H25B	109.5
H21A—N21—H21B	109.5	C23—C25—H25C	109.5
C22—N21—H21C	109.5	H25A—C25—H25C	109.5
H21A—N21—H21C	109.5	H25B—C25—H25C	109.5
H21B—N21—H21C	109.5	O43—N40—O42	121.9 (15)
O12—C11—O11	124 (2)	O43—N40—O41	120.9 (15)
O12—C11—C12	116 (2)	O42—N40—O41	117.3 (14)
O11—C11—C12	119.1 (17)		
O31—N30—O32—Pb	−154.4 (14)	N11—C12—C13—C15	−53 (3)
O33—N30—O32—Pb	17.3 (15)	C11—C12—C13—C14B	33 (4)
O31—N30—O33—Pb	153.9 (15)	N11—C12—C13—C14B	156 (4)
O32—N30—O33—Pb	−17.7 (16)	Pb—O22—C21—O21	3.5 (16)
Pb—O12—C11—O11	7 (2)	Pb—O22—C21—C22	−173.8 (15)

Pb—O12—C11—C12	177.6 (18)	Pb—O21—C21—O22	-5 (2)
Pb—O11—C11—O12	-9 (3)	Pb—O21—C21—C22	172.8 (11)
Pb—O11—C11—C12	180.0 (12)	O22—C21—C22—N21	-29 (2)
O12—C11—C12—C13	-76 (3)	O21—C21—C22—N21	153.5 (15)
O11—C11—C12—C13	96 (3)	O22—C21—C22—C23	92 (2)
O12—C11—C12—N11	161 (2)	O21—C21—C22—C23	-85 (2)
O11—C11—C12—N11	-27 (2)	N21—C22—C23—C25	176 (2)
C11—C12—C13—C14A	-40 (4)	C21—C22—C23—C25	56 (3)
N11—C12—C13—C14A	82 (3)	N21—C22—C23—C24	-57 (3)
C11—C12—C13—C15	-176 (2)	C21—C22—C23—C24	-177 (2)

Symmetry code: (i) $x-1, y, z$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H11 \cdots O12	0.85 (3)	1.99 (10)	2.724 (19)	144 (17)
O1—H12 \cdots O21 ⁱ	0.85 (3)	1.92 (5)	2.756 (16)	171 (20)
O2—H21 \cdots O32 ⁱⁱ	0.85 (3)	2.50 (10)	3.26 (2)	150 (16)
O2—H22 \cdots O22 ⁱⁱⁱ	0.85 (3)	2.10 (6)	2.919 (17)	162 (19)
N11—H11A \cdots O32 ⁱⁱ	0.93	2.24	2.85 (2)	123
N11—H11B \cdots O42 ^{iv}	0.93	1.90	2.817 (16)	169
N11—H11B \cdots N40 ^{iv}	0.93	2.61	3.510 (19)	164
N11—H11C \cdots O12 ^v	0.93	1.93	2.80 (2)	156
N21—H21A \cdots O2 ^{vi}	0.93	2.24	2.947 (19)	132
N21—H21A \cdots O33 ^{vi}	0.93	2.61	3.198 (18)	122
N21—H21B \cdots O41 ^v	0.93	2.21	2.951 (18)	136
N21—H21B \cdots O42 ^v	0.93	2.03	2.924 (18)	160
N21—H21B \cdots N40 ^v	0.93	2.48	3.384 (18)	163
N21—H21C \cdots O41	0.93	1.86	2.785 (18)	177
N21—H21C \cdots N40	0.93	2.61	3.477 (19)	156

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, y-1/2, -z+1/2$; (iii) $-x, y-1/2, -z+1/2$; (iv) $x+1, y-1, z$; (v) $x+1, y, z$; (vi) $-x+1, y+1/2, -z+1/2$.