

Tetrakis(2,4,6-triamino-1,3,5-triazin-1-ium) tris(pyridine-2,6-dicarboxylato)-calcate(II) hexahydrate

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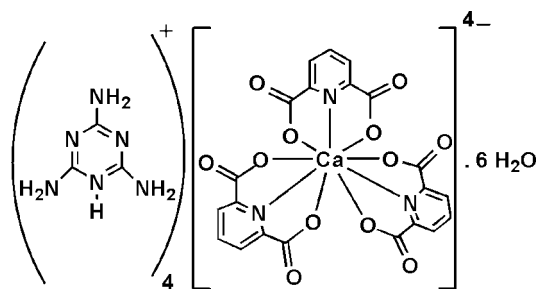
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.052; wR factor = 0.127; data-to-parameter ratio = 17.0.

The title compound, $(\text{C}_3\text{H}_7\text{N}_6)_4[\text{Ca}(\text{C}_7\text{H}_3\text{NO}_4)_3] \cdot 6\text{H}_2\text{O}$ or $(\text{tataH})_4[\text{Ca}(\text{pydc})_3] \cdot 6\text{H}_2\text{O}$ (where tata is 2,4,6-triamino-1,3,5-triazine and pydcH_2 is pyridine-2,6-dicarboxylic acid), was obtained by reaction of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ with the proton-transfer compound $(\text{tataH})_2(\text{pydc})$ in aqueous solution. The $[\text{Ca}(\text{pydc})_3]^{4-}$ anion has twofold crystallographic symmetry. It is a nine-coordinate Ca^{II} complex with a distorted tricapped trigonal-prismatic coordination geometry. The structure also contains four tataH^+ cations and six uncoordinated water molecules. There are extensive $\text{O}-\text{H} \cdots \text{O}$, $\text{O}-\text{H} \cdots \text{N}$, $\text{N}-\text{H} \cdots \text{O}$, $\text{N}-\text{H} \cdots \text{N}$ and $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds in the crystal structure.

Related literature

For related literature, see: Aghabozorg *et al.* (2006); Aghabozorg, Attar Gharamaleki *et al.* (2008); Aghabozorg, Manteghi & Sheshmani (2008); Aghajani *et al.* (2006); Sharif *et al.* (2007).



Experimental

Crystal data

$(\text{C}_3\text{H}_7\text{N}_6)_4[\text{Ca}(\text{C}_7\text{H}_3\text{NO}_4)_3] \cdot 6\text{H}_2\text{O}$
 $M_r = 1152.07$
 Monoclinic, $C2/c$
 $a = 17.9605$ (15) Å
 $b = 10.1672$ (9) Å
 $c = 25.922$ (2) Å
 $\beta = 94.467$ (2)°
 $V = 4719.1$ (7) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.24$ mm⁻¹
 $T = 100$ (2) K
 $0.30 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART APEXII diffractometer
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\text{min}} = 0.928$, $T_{\text{max}} = 0.954$
 16983 measured reflections
 6215 independent reflections
 4412 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.127$
 $S = 1.09$
 6215 reflections
 365 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.51$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.77$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1W—H1WB···O2 ⁱ	0.84	1.91	2.710 (3)	160
O1W—H1WA···O6 ⁱⁱ	0.84	1.92	2.751 (3)	170
O2W—H2WB···N4 ⁱⁱⁱ	0.84	2.26	3.022 (3)	151
N3—H3N···O2	0.88	1.79	2.667 (2)	176
O2W—H2WA···O5	0.84	2.05	2.888 (3)	175
O3W—H3WB···O2W ^{iv}	0.84	2.18	2.963 (3)	154
O3W—H3WA···N14 ^v	0.84	2.17	3.007 (3)	180
N6—H6NA···O1W ⁱ	0.88	2.45	3.294 (3)	162
N6—H6NB···O1W	0.88	1.90	2.740 (3)	160
N7—H7NA···N11 ^v	0.88	2.22	3.103 (3)	176
N7—H7NB···O2W ⁱⁱ	0.88	2.44	3.205 (3)	146
N7—H7NB···O4 ⁱⁱ	0.88	2.53	3.111 (2)	124
N8—H8NA···O1	0.88	2.07	2.948 (2)	172
N12—H11A···N10 ^{vi}	0.88	2.23	3.109 (2)	178
N12—H11B···O5	0.88	2.32	3.196 (2)	175
N8—H8NB···O3W	0.88	2.15	2.832 (4)	134
N9—H9NA···O3	0.88	1.89	2.754 (2)	165
N13—H13A···O4 ^{vii}	0.88	2.08	2.925 (2)	160
N13—H13B···O6 ^{vi}	0.88	1.96	2.790 (2)	157
N14—H14A···O3	0.88	2.39	3.143 (2)	144
N14—H14B···N5 ^{viii}	0.88	2.10	2.978 (3)	178
C4—H4A···O2 ^{ix}	0.95	2.55	3.370 (3)	145

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2249).

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Acta Cryst. (2008). E64, m1063-m1064 [doi:10.1107/S1600536808022873]

Tetrakis(2,4,6-triamino-1,3,5-triazin-1-ium) tris(pyridine-2,6-dicarboxylato)calcate(II) hexahydrate

H. Aghabozorg, S. Daneshvar and A. Nemati

Comment

Hydrogen bonding plays a key role in chemical, catalytic and biochemical processes, as well as in supramolecular chemistry and crystal engineering. Recently we have reported the reaction between the proton-transfer compound, (tataH)₂(pydc) with metal salts Co(NO₃)₂·6H₂O, Bi(NO₃)₃·5H₂O, Zn(NO₃)₂·4H₂O and Cd(NO₃)₂·2H₂O in a 2:1 molar ratio. These reactions lead to the formation of the (tataH)₂[Co(H₂O)₆][Co(pydc)₂]₂·4H₂O (Aghabozorg, Attar Gharamaleki *et al.*, 2008), (tataH)_n[Bi(pydc)₂(H₂O)]_n (Sharif *et al.*, 2007), (tataH)₂[Zn(pydc)₂]₂·10H₂O (Aghajani *et al.*, 2006) and (tataH)₂[Cd(pydc)₂] (Aghabozorg, Aghajani *et al.*, 2006) compounds respectively. For more details and related literature see our recent review article (Aghabozorg, Manteghi *et al.*, 2008).

The structure of the title compound is shown in Fig.1. The anion has crystallographic 2-fold symmetry. The compound contains [Ca(pydc)₃]⁴⁻ anion, four (tataH)⁺ cations and six uncoordinated water molecules. In the [Ca(pydc)₃]⁴⁻ anions, Ca^{II} atom is nine-coordinated by three N atoms (N1, N1a and N2) and six O atoms (O1, O1a, O3, O3a, O5 and O5a) with the range of 2.5031 (14)–2.5472 (15) Å from the carboxylate groups of three (pydc)²⁻ groups that act as tridentate ligands. The coordination geometry around the Ca^{II} atom is distorted tricapped trigonal prism (Fig.2). Three N atoms (N1, N1a and N2) occupying three cap positions and make a flat triangle with N1—Ca1—N1a: 119.78 (8)°, N1—Ca1—N2: 120.11 (4)° and N1a—Ca1—N2: 120.11 (4)° that the sum of these angles is 360.00° and six O atoms (O1, O1a, O3, O3a, O5 and O5a) forming the trigonal prism positions.

There are various hydrogen bonds such as O—H···O, O—H···N, N—H···O and N—H···N [in the range 2.667 (2)–3.294 (3) Å] in this structure (Fig.3) and C—H···O hydrogen bonds [with D···A 3.370 (3) Å] are also present (Table 1). These extensive hydrogen bonds between [Ca(pydc)₃]⁴⁻ anions, (tataH)⁺ cations and uncoordinated water molecules play an important role in stabilization of the crystal packing.

Experimental

The proton-transfer compound, (tataH)₂(pydc), was prepared by the reaction of pyridine-2,6-dicarboxylic acid (pydcH₂) with 2,4,6-triamino-1,3,5-triazine (tata). The reaction between Ca(NO₃)₂·4H₂O (118 mg, 0.5 mmol) in water (20 ml) and (tataH)₂(pydc) (420 mg, 1.0 mmol) in water (20 ml), in 1:2 molar ratio gave a colorless compound after slow evaporation of the solvent at the room temperature.

Refinement

The hydrogen atoms of NH groups and also H atoms of water molecule were found in difference Fourier synthesis. The hydrogen atoms of the H(C) atom positions were calculated. All hydrogen atoms were refined in isotropic approximation

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in riding model with the $U_{\text{iso}}(\text{H})$ parameters equal to $1.2 U_{\text{eq}}(\text{Xi})$, where $U(\text{Xi})$ the equivalent thermal parameters of the carbon or nitrogen or oxygen atom to which corresponding H atom is bonded. Distances employed in the riding model are, N-H, 0.88 Å; O-H, 0.84 Å; C-H, 0.95 Å.

Figures

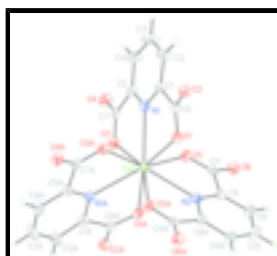


Fig. 1. The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. The anion is located on a 2-fold axis and thus, the asymmetric unit contains one half anion, two cations and three water molecules.

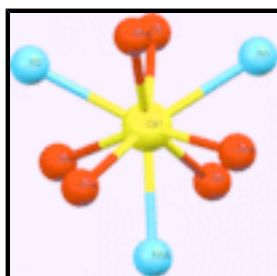


Fig. 2. A view of the distorted tricapped trigonal prism around the Ca^{II} atom.

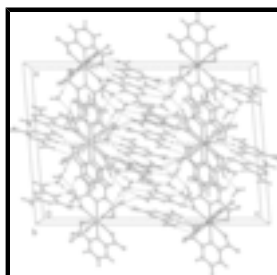


Fig. 3. Crystal packing with hydrogen bonds shown as dashed lines.

Tetrakis(2,4,6-triamino-1,3,5-triazin-1-ium) tris(pyridine-2,6-dicarboxylato)calcate(II) hexahydrate

Crystal data

$(\text{C}_3\text{H}_7\text{N}_6)_4[\text{Ca}(\text{C}_7\text{H}_3\text{N}_1\text{O}_4)_3] \cdot 6\text{H}_2\text{O}$

$M_r = 1152.07$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 17.9605 (15) \text{ \AA}$

$b = 10.1672 (9) \text{ \AA}$

$c = 25.922 (2) \text{ \AA}$

$\beta = 94.467 (2)^\circ$

$V = 4719.1 (7) \text{ \AA}^3$

$Z = 4$

$F_{000} = 2400$

$D_x = 1.622 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 935 reflections

$\theta = 3\text{--}29^\circ$

$\mu = 0.24 \text{ mm}^{-1}$

$T = 100 (2) \text{ K}$

Prism, colourless

$0.30 \times 0.20 \times 0.20 \text{ mm}$

Data collection

Bruker SMART APEXII diffractometer	6215 independent reflections
Radiation source: fine-focus sealed tube	4412 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.031$
$T = 100(2)$ K	$\theta_{\text{max}} = 29.0^\circ$
ω scans	$\theta_{\text{min}} = 1.6^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -19 \rightarrow 24$
$T_{\text{min}} = 0.928$, $T_{\text{max}} = 0.954$	$k = -13 \rightarrow 13$
16983 measured reflections	$l = -35 \rightarrow 35$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.051$	H-atom parameters constrained
$wR(F^2) = 0.127$	$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 1P]$
$S = 1.09$	where $P = (F_o^2 + 2F_c^2)/3$
6215 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
365 parameters	$\Delta\rho_{\text{max}} = 0.51 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.77 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ca1	0.0000	0.32225 (5)	0.2500	0.01468 (13)
C1	0.17008 (12)	0.2206 (2)	0.21823 (8)	0.0189 (4)
N1	0.12161 (10)	0.19798 (16)	0.25401 (6)	0.0167 (3)
O1	0.08882 (8)	0.38891 (14)	0.18496 (5)	0.0198 (3)
O1W	0.25538 (11)	0.3625 (2)	-0.08194 (7)	0.0511 (6)

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H1WB	0.2800	0.3196	-0.1025	0.061*
H1WA	0.2150	0.3792	-0.0992	0.061*
O2W	0.20543 (11)	0.3177 (2)	0.38198 (7)	0.0464 (5)
H2WB	0.2093	0.3575	0.4105	0.056*
H2WA	0.1704	0.3502	0.3627	0.056*
O2	0.18167 (9)	0.32683 (15)	0.13789 (6)	0.0225 (3)
N2	0.0000	0.5723 (2)	0.2500	0.0160 (5)
C2	0.23993 (13)	0.1634 (3)	0.21999 (9)	0.0291 (5)
H2A	0.2733	0.1824	0.1943	0.035*
O3W	0.16530 (16)	0.8783 (3)	0.17830 (10)	0.0743 (8)
H3WB	0.2094	0.8677	0.1704	0.089*
H3WA	0.1367	0.9132	0.1550	0.089*
N3	0.16153 (10)	0.53273 (18)	0.07458 (7)	0.0222 (4)
H3N	0.1666	0.4663	0.0963	0.027*
O3	0.02261 (8)	0.15716 (14)	0.32346 (5)	0.0203 (3)
C3	0.26030 (14)	0.0777 (3)	0.26017 (9)	0.0345 (6)
H3A	0.3079	0.0366	0.2624	0.041*
O4	0.10324 (9)	0.02965 (15)	0.37134 (6)	0.0252 (3)
C4	0.21035 (14)	0.0525 (2)	0.29714 (9)	0.0292 (5)
H4A	0.2230	-0.0063	0.3249	0.035*
N4	0.18475 (10)	0.62366 (18)	-0.00573 (7)	0.0217 (4)
O5	0.08073 (9)	0.43271 (14)	0.32086 (6)	0.0220 (3)
C5	0.14127 (12)	0.1153 (2)	0.29278 (8)	0.0183 (4)
N5	0.12433 (10)	0.75024 (17)	0.05810 (7)	0.0207 (4)
N6	0.22996 (11)	0.41835 (19)	0.01860 (8)	0.0275 (4)
H6NA	0.2338	0.3554	0.0419	0.033*
H6NB	0.2477	0.4118	-0.0120	0.033*
O6	0.11801 (9)	0.61386 (15)	0.36402 (6)	0.0236 (3)
C6	0.14421 (12)	0.3194 (2)	0.17714 (7)	0.0174 (4)
N7	0.13887 (10)	0.83102 (18)	-0.02277 (7)	0.0224 (4)
H7NA	0.1188	0.9049	-0.0129	0.027*
H7NB	0.1526	0.8246	-0.0545	0.027*
C7	0.08494 (12)	0.09839 (19)	0.33279 (8)	0.0171 (4)
N8	0.09931 (11)	0.64715 (19)	0.13431 (7)	0.0257 (4)
H8NA	0.0972	0.5743	0.1525	0.031*
H8NB	0.0923	0.7219	0.1503	0.031*
C8	0.04098 (11)	0.6393 (2)	0.28661 (8)	0.0175 (4)
N9	-0.02526 (10)	0.21627 (17)	0.41916 (6)	0.0189 (4)
H9NA	-0.0085	0.2124	0.3882	0.023*
C9	0.04259 (14)	0.7762 (2)	0.28768 (9)	0.0250 (5)
H9A	0.0724	0.8215	0.3138	0.030*
C10	0.0000	0.8452 (3)	0.2500	0.0301 (8)
H10A	0.0000	0.9386	0.2500	0.036*
N10	-0.03939 (10)	0.32331 (17)	0.49808 (6)	0.0179 (4)
C11	0.08390 (11)	0.5555 (2)	0.32701 (8)	0.0170 (4)
N11	-0.07504 (10)	0.09514 (17)	0.48552 (7)	0.0187 (4)
N12	0.01468 (10)	0.42995 (18)	0.43181 (7)	0.0219 (4)
H11A	0.0226	0.4986	0.4522	0.041 (8)*
H11B	0.0304	0.4273	0.4005	0.033 (7)*

C12	0.15006 (12)	0.7326 (2)	0.01068 (8)	0.0199 (4)
N13	-0.08510 (11)	0.19908 (18)	0.56239 (7)	0.0230 (4)
H13A	-0.0983	0.1240	0.5759	0.039 (8)*
H13B	-0.0842	0.2683	0.5828	0.029 (7)*
C13	0.12875 (12)	0.6464 (2)	0.08866 (8)	0.0206 (4)
N14	-0.06375 (11)	0.00349 (19)	0.40544 (7)	0.0273 (4)
H14A	-0.0459	0.0126	0.3750	0.033 (7)*
H14B	-0.0830	-0.0706	0.4158	0.036 (8)*
C14	0.19208 (12)	0.5258 (2)	0.02825 (8)	0.0217 (4)
C15	-0.01687 (11)	0.3235 (2)	0.45053 (8)	0.0171 (4)
C16	-0.06599 (12)	0.2060 (2)	0.51433 (8)	0.0183 (4)
C17	-0.05485 (11)	0.1040 (2)	0.43758 (8)	0.0188 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca1	0.0160 (3)	0.0136 (3)	0.0145 (3)	0.000	0.0015 (2)	0.000
C1	0.0193 (11)	0.0216 (10)	0.0160 (9)	0.0004 (8)	0.0023 (8)	0.0019 (8)
N1	0.0178 (9)	0.0173 (8)	0.0150 (8)	-0.0001 (7)	0.0020 (6)	-0.0004 (6)
O1	0.0198 (8)	0.0186 (7)	0.0215 (7)	0.0008 (6)	0.0044 (6)	0.0036 (6)
O1W	0.0303 (10)	0.0852 (16)	0.0357 (10)	0.0236 (10)	-0.0111 (8)	-0.0261 (10)
O2W	0.0510 (12)	0.0472 (12)	0.0378 (10)	0.0222 (10)	-0.0160 (9)	-0.0154 (9)
O2	0.0240 (8)	0.0243 (8)	0.0200 (7)	0.0016 (6)	0.0077 (6)	0.0054 (6)
N2	0.0160 (12)	0.0156 (11)	0.0168 (11)	0.000	0.0044 (9)	0.000
C2	0.0240 (12)	0.0416 (14)	0.0227 (11)	0.0080 (11)	0.0074 (9)	0.0077 (10)
O3W	0.089 (2)	0.0615 (16)	0.0691 (17)	0.0005 (15)	-0.0175 (14)	-0.0047 (13)
N3	0.0229 (10)	0.0190 (9)	0.0250 (9)	0.0023 (7)	0.0041 (8)	0.0065 (7)
O3	0.0202 (8)	0.0223 (8)	0.0187 (7)	0.0012 (6)	0.0037 (6)	0.0027 (6)
C3	0.0242 (13)	0.0500 (16)	0.0300 (13)	0.0167 (11)	0.0075 (10)	0.0120 (11)
O4	0.0322 (9)	0.0242 (8)	0.0197 (7)	0.0030 (7)	0.0047 (6)	0.0077 (6)
C4	0.0303 (13)	0.0347 (13)	0.0227 (11)	0.0120 (11)	0.0038 (9)	0.0097 (10)
N4	0.0190 (9)	0.0227 (9)	0.0230 (9)	0.0009 (7)	0.0003 (7)	0.0035 (7)
O5	0.0249 (8)	0.0161 (7)	0.0238 (8)	-0.0007 (6)	-0.0048 (6)	-0.0004 (6)
C5	0.0209 (11)	0.0182 (10)	0.0160 (9)	0.0029 (8)	0.0022 (8)	0.0008 (7)
N5	0.0205 (9)	0.0192 (9)	0.0220 (9)	-0.0017 (7)	0.0004 (7)	0.0015 (7)
N6	0.0297 (11)	0.0248 (10)	0.0290 (10)	0.0063 (8)	0.0080 (8)	0.0063 (8)
O6	0.0250 (8)	0.0246 (8)	0.0205 (7)	-0.0011 (7)	-0.0031 (6)	-0.0052 (6)
C6	0.0188 (10)	0.0183 (10)	0.0149 (9)	-0.0030 (8)	0.0006 (8)	0.0002 (7)
N7	0.0233 (10)	0.0222 (9)	0.0217 (9)	0.0012 (8)	0.0006 (7)	0.0037 (7)
C7	0.0231 (11)	0.0117 (9)	0.0167 (9)	-0.0021 (8)	0.0029 (8)	-0.0013 (7)
N8	0.0339 (11)	0.0198 (9)	0.0241 (9)	0.0005 (8)	0.0065 (8)	0.0028 (7)
C8	0.0183 (10)	0.0171 (9)	0.0178 (9)	-0.0006 (8)	0.0055 (8)	-0.0011 (7)
N9	0.0219 (9)	0.0207 (9)	0.0147 (8)	0.0016 (7)	0.0050 (7)	0.0009 (7)
C9	0.0322 (13)	0.0194 (10)	0.0228 (11)	-0.0025 (9)	-0.0019 (9)	-0.0030 (8)
C10	0.044 (2)	0.0179 (15)	0.0273 (17)	0.000	-0.0032 (15)	0.000
N10	0.0215 (9)	0.0158 (8)	0.0167 (8)	0.0008 (7)	0.0032 (7)	0.0012 (6)
C11	0.0146 (10)	0.0199 (10)	0.0168 (9)	-0.0012 (8)	0.0034 (7)	-0.0010 (7)
N11	0.0197 (9)	0.0173 (8)	0.0193 (8)	-0.0011 (7)	0.0038 (7)	-0.0011 (7)

supplementary materials

N12	0.0249 (10)	0.0214 (9)	0.0200 (9)	-0.0006 (8)	0.0068 (7)	0.0025 (7)
C12	0.0144 (10)	0.0228 (10)	0.0217 (10)	-0.0031 (8)	-0.0035 (8)	0.0027 (8)
N13	0.0356 (11)	0.0160 (9)	0.0182 (8)	-0.0043 (8)	0.0071 (8)	-0.0012 (7)
C13	0.0185 (10)	0.0201 (10)	0.0227 (10)	-0.0027 (8)	-0.0004 (8)	0.0012 (8)
N14	0.0353 (11)	0.0258 (10)	0.0221 (9)	-0.0079 (9)	0.0106 (8)	-0.0068 (8)
C14	0.0152 (10)	0.0234 (11)	0.0265 (11)	-0.0008 (8)	0.0009 (8)	0.0033 (8)
C15	0.0150 (10)	0.0172 (9)	0.0189 (9)	0.0024 (8)	0.0004 (7)	0.0021 (8)
C16	0.0170 (10)	0.0183 (10)	0.0197 (10)	0.0016 (8)	0.0014 (8)	0.0009 (8)
C17	0.0155 (10)	0.0206 (10)	0.0204 (10)	0.0015 (8)	0.0020 (8)	-0.0013 (8)

Geometric parameters (Å, °)

Ca1—O1	2.5031 (14)	O5—C11	1.259 (2)
Ca1—O1 ⁱ	2.5032 (14)	C5—C7	1.514 (3)
Ca1—O5 ⁱ	2.5145 (15)	N5—C13	1.319 (3)
Ca1—O5	2.5145 (15)	N5—C12	1.358 (3)
Ca1—N1 ⁱ	2.5184 (18)	N6—C14	1.321 (3)
Ca1—N1	2.5184 (18)	N6—H6NA	0.8800
Ca1—N2	2.542 (2)	N6—H6NB	0.8798
Ca1—O3 ⁱ	2.5472 (15)	O6—C11	1.248 (2)
Ca1—O3	2.5472 (15)	N7—C12	1.329 (3)
C1—N1	1.340 (3)	N7—H7NA	0.8800
C1—C2	1.380 (3)	N7—H7NB	0.8800
C1—C6	1.511 (3)	N8—C13	1.333 (3)
N1—C5	1.337 (3)	N8—H8NA	0.8800
O1—C6	1.250 (2)	N8—H8NB	0.8800
O1W—H1WB	0.8400	C8—C9	1.393 (3)
O1W—H1WA	0.8400	C8—C11	1.514 (3)
O2W—H2WB	0.8400	N9—C15	1.362 (3)
O2W—H2WA	0.8400	N9—C17	1.361 (3)
O2—C6	1.265 (2)	N9—H9NA	0.8800
N2—C8 ⁱ	1.340 (2)	C9—C10	1.384 (3)
N2—C8	1.340 (2)	C9—H9A	0.9500
C2—C3	1.385 (3)	C10—C9 ⁱ	1.384 (3)
C2—H2A	0.9500	C10—H10A	0.9500
O3W—H3WB	0.8400	N10—C15	1.327 (3)
O3W—H3WA	0.8401	N10—C16	1.363 (3)
N3—C13	1.360 (3)	N11—C17	1.324 (3)
N3—C14	1.360 (3)	N11—C16	1.355 (3)
N3—H3N	0.8800	N12—C15	1.330 (3)
O3—C7	1.275 (3)	N12—H11A	0.8801
C3—C4	1.386 (3)	N12—H11B	0.8799
C3—H3A	0.9500	N13—C16	1.319 (3)
O4—C7	1.243 (2)	N13—H13A	0.8800
C4—C5	1.392 (3)	N13—H13B	0.8799
C4—H4A	0.9500	N14—C17	1.320 (3)
N4—C14	1.329 (3)	N14—H14A	0.8800
N4—C12	1.356 (3)	N14—H14B	0.8800

O1—Ca1—O1 ⁱ	148.58 (7)	N1—C5—C4	122.08 (19)
O1—Ca1—O5 ⁱ	75.43 (5)	N1—C5—C7	115.77 (18)
O1 ⁱ —Ca1—O5 ⁱ	90.55 (5)	C4—C5—C7	122.11 (19)
O1—Ca1—O5	90.55 (5)	C13—N5—C12	115.43 (19)
O1 ⁱ —Ca1—O5	75.43 (5)	C14—N6—H6NA	119.0
O5 ⁱ —Ca1—O5	126.94 (7)	C14—N6—H6NB	117.5
O1—Ca1—N1 ⁱ	134.76 (5)	H6NA—N6—H6NB	123.4
O1 ⁱ —Ca1—N1 ⁱ	64.37 (5)	O1—C6—O2	125.19 (19)
O5 ⁱ —Ca1—N1 ⁱ	75.23 (5)	O1—C6—C1	117.84 (17)
O5—Ca1—N1 ⁱ	134.68 (5)	O2—C6—C1	116.96 (18)
O1—Ca1—N1	64.37 (5)	C12—N7—H7NA	119.8
O1 ⁱ —Ca1—N1	134.76 (5)	C12—N7—H7NB	121.1
O5 ⁱ —Ca1—N1	134.68 (5)	H7NA—N7—H7NB	119.1
O5—Ca1—N1	75.23 (5)	O4—C7—O3	126.11 (19)
N1 ⁱ —Ca1—N1	119.78 (8)	O4—C7—C5	117.75 (19)
O1—Ca1—N2	74.29 (4)	O3—C7—C5	116.14 (17)
O1 ⁱ —Ca1—N2	74.29 (4)	C13—N8—H8NA	120.4
O5 ⁱ —Ca1—N2	63.47 (4)	C13—N8—H8NB	120.4
O5—Ca1—N2	63.47 (4)	H8NA—N8—H8NB	117.4
N1 ⁱ —Ca1—N2	120.11 (4)	N2—C8—C9	122.1 (2)
N1—Ca1—N2	120.11 (4)	N2—C8—C11	115.19 (18)
O1—Ca1—O3 ⁱ	75.39 (5)	C9—C8—C11	122.70 (19)
O1 ⁱ —Ca1—O3 ⁱ	127.53 (5)	C15—N9—C17	119.35 (17)
O5 ⁱ —Ca1—O3 ⁱ	72.48 (5)	C15—N9—H9NA	123.4
O5—Ca1—O3 ⁱ	152.84 (5)	C17—N9—H9NA	117.0
N1 ⁱ —Ca1—O3 ⁱ	63.34 (5)	C10—C9—C8	118.9 (2)
N1—Ca1—O3 ⁱ	77.73 (5)	C10—C9—H9A	120.6
N2—Ca1—O3 ⁱ	131.22 (3)	C8—C9—H9A	120.6
O1—Ca1—O3	127.53 (5)	C9 ⁱ —C10—C9	119.1 (3)
O1 ⁱ —Ca1—O3	75.39 (5)	C9 ⁱ —C10—H10A	120.5
O5 ⁱ —Ca1—O3	152.84 (5)	C9—C10—H10A	120.5
O5—Ca1—O3	72.48 (5)	C15—N10—C16	115.35 (18)
N1 ⁱ —Ca1—O3	77.73 (5)	O6—C11—O5	125.73 (19)
N1—Ca1—O3	63.34 (5)	O6—C11—C8	117.19 (18)
N2—Ca1—O3	131.22 (3)	O5—C11—C8	117.06 (18)
O3 ⁱ —Ca1—O3	97.56 (7)	C17—N11—C16	115.51 (18)
N1—C1—C2	122.86 (19)	C15—N12—H11A	118.7
N1—C1—C6	114.91 (18)	C15—N12—H11B	119.2
C2—C1—C6	122.16 (19)	H11A—N12—H11B	121.9
C5—N1—C1	118.70 (18)	N7—C12—N4	117.41 (19)
C5—N1—Ca1	121.61 (13)	N7—C12—N5	116.5 (2)
C1—N1—Ca1	119.56 (13)	N4—C12—N5	126.05 (19)
C6—O1—Ca1	120.86 (12)	C16—N13—H13A	121.4

supplementary materials

H1WB—O1W—H1WA	104.1	C16—N13—H13B	122.1
H2WB—O2W—H2WA	109.9	H13A—N13—H13B	116.5
C8 ⁱ —N2—C8	118.9 (2)	N5—C13—N8	121.3 (2)
C8 ⁱ —N2—Ca1	120.53 (12)	N5—C13—N3	121.8 (2)
C8—N2—Ca1	120.53 (12)	N8—C13—N3	116.96 (19)
C3—C2—C1	118.4 (2)	C17—N14—H14A	116.7
C3—C2—H2A	120.8	C17—N14—H14B	120.1
C1—C2—H2A	120.8	H14A—N14—H14B	123.0
H3WB—O3W—H3WA	114.4	N6—C14—N4	121.3 (2)
C13—N3—C14	119.60 (18)	N6—C14—N3	117.3 (2)
C13—N3—H3N	120.4	N4—C14—N3	121.4 (2)
C14—N3—H3N	119.8	N10—C15—N12	120.64 (19)
C7—O3—Ca1	122.48 (12)	N10—C15—N9	121.73 (18)
C2—C3—C4	119.2 (2)	N12—C15—N9	117.63 (18)
C2—C3—H3A	120.4	N13—C16—N11	116.54 (19)
C4—C3—H3A	120.4	N13—C16—N10	117.51 (19)
C3—C4—C5	118.7 (2)	N11—C16—N10	125.96 (18)
C3—C4—H4A	120.7	N14—C17—N11	120.7 (2)
C5—C4—H4A	120.7	N14—C17—N9	117.33 (19)
C14—N4—C12	115.36 (18)	N11—C17—N9	121.95 (19)
C11—O5—Ca1	123.58 (13)		
C2—C1—N1—C5	-0.8 (3)	N1—Ca1—O5—C11	138.44 (17)
C6—C1—N1—C5	-177.72 (18)	N2—Ca1—O5—C11	3.08 (14)
C2—C1—N1—Ca1	175.25 (18)	O3 ⁱ —Ca1—O5—C11	132.90 (16)
C6—C1—N1—Ca1	-1.6 (2)	O3—Ca1—O5—C11	-155.35 (17)
O1—Ca1—N1—C5	171.11 (17)	C1—N1—C5—C4	0.2 (3)
O1 ⁱ —Ca1—N1—C5	22.09 (19)	Ca1—N1—C5—C4	-175.81 (17)
O5 ⁱ —Ca1—N1—C5	-158.97 (14)	C1—N1—C5—C7	177.82 (18)
O5—Ca1—N1—C5	73.20 (15)	Ca1—N1—C5—C7	1.8 (2)
N1 ⁱ —Ca1—N1—C5	-60.19 (14)	C3—C4—C5—N1	0.4 (4)
N2—Ca1—N1—C5	119.81 (14)	C3—C4—C5—C7	-177.1 (2)
O3 ⁱ —Ca1—N1—C5	-109.38 (16)	Ca1—O1—C6—O2	162.52 (16)
O3—Ca1—N1—C5	-4.32 (14)	Ca1—O1—C6—C1	-19.1 (2)
O1—Ca1—N1—C1	-4.88 (14)	N1—C1—C6—O1	13.5 (3)
O1 ⁱ —Ca1—N1—C1	-153.89 (14)	C2—C1—C6—O1	-163.4 (2)
O5 ⁱ —Ca1—N1—C1	25.05 (18)	N1—C1—C6—O2	-167.97 (18)
O5—Ca1—N1—C1	-102.78 (15)	C2—C1—C6—O2	15.1 (3)
N1 ⁱ —Ca1—N1—C1	123.83 (16)	Ca1—O3—C7—O4	170.52 (16)
N2—Ca1—N1—C1	-56.17 (16)	Ca1—O3—C7—C5	-9.4 (2)
O3 ⁱ —Ca1—N1—C1	74.64 (15)	N1—C5—C7—O4	-175.02 (18)
O3—Ca1—N1—C1	179.70 (17)	C4—C5—C7—O4	2.6 (3)
O1 ⁱ —Ca1—O1—C6	148.51 (15)	N1—C5—C7—O3	4.9 (3)
O5 ⁱ —Ca1—O1—C6	-145.46 (15)	C4—C5—C7—O3	-177.5 (2)
O5—Ca1—O1—C6	86.33 (15)	C8 ⁱ —N2—C8—C9	-0.29 (15)
N1 ⁱ —Ca1—O1—C6	-94.42 (16)	Ca1—N2—C8—C9	179.71 (15)

N1—Ca1—O1—C6	13.04 (14)	C8 ⁱ —N2—C8—C11	178.57 (19)
N2—Ca1—O1—C6	148.51 (15)	Ca1—N2—C8—C11	-1.43 (19)
O3 ⁱ —Ca1—O1—C6	-70.16 (15)	N2—C8—C9—C10	0.6 (3)
O3—Ca1—O1—C6	18.19 (17)	C11—C8—C9—C10	-178.21 (17)
O1—Ca1—N2—C8 ⁱ	80.76 (10)	C8—C9—C10—C9 ⁱ	-0.27 (14)
O1 ⁱ —Ca1—N2—C8 ⁱ	-99.24 (10)	Ca1—O5—C11—O6	173.48 (15)
O5 ⁱ —Ca1—N2—C8 ⁱ	-0.53 (11)	Ca1—O5—C11—C8	-5.0 (2)
O5—Ca1—N2—C8 ⁱ	179.47 (11)	N2—C8—C11—O6	-174.49 (16)
N1 ⁱ —Ca1—N2—C8 ⁱ	-52.29 (11)	C9—C8—C11—O6	4.4 (3)
N1—Ca1—N2—C8 ⁱ	127.71 (11)	N2—C8—C11—O5	4.1 (3)
O3 ⁱ —Ca1—N2—C8 ⁱ	27.26 (11)	C9—C8—C11—O5	-177.1 (2)
O3—Ca1—N2—C8 ⁱ	-152.74 (11)	C14—N4—C12—N7	-177.40 (19)
O1—Ca1—N2—C8	-99.24 (10)	C14—N4—C12—N5	1.4 (3)
O1 ⁱ —Ca1—N2—C8	80.76 (10)	C13—N5—C12—N7	172.95 (19)
O5 ⁱ —Ca1—N2—C8	179.47 (11)	C13—N5—C12—N4	-5.9 (3)
O5—Ca1—N2—C8	-0.53 (11)	C12—N5—C13—N8	-173.9 (2)
N1 ⁱ —Ca1—N2—C8	127.71 (11)	C12—N5—C13—N3	4.3 (3)
N1—Ca1—N2—C8	-52.29 (11)	C14—N3—C13—N5	1.3 (3)
O3 ⁱ —Ca1—N2—C8	-152.74 (11)	C14—N3—C13—N8	179.6 (2)
O3—Ca1—N2—C8	27.26 (11)	C12—N4—C14—N6	-174.6 (2)
N1—C1—C2—C3	0.8 (4)	C12—N4—C14—N3	4.7 (3)
C6—C1—C2—C3	177.5 (2)	C13—N3—C14—N6	173.2 (2)
O1—Ca1—O3—C7	2.23 (17)	C13—N3—C14—N4	-6.2 (3)
O1 ⁱ —Ca1—O3—C7	-153.52 (15)	C16—N10—C15—N12	-175.54 (19)
O5 ⁱ —Ca1—O3—C7	145.59 (14)	C16—N10—C15—N9	4.7 (3)
O5—Ca1—O3—C7	-74.48 (15)	C17—N9—C15—N10	-2.6 (3)
N1 ⁱ —Ca1—O3—C7	140.11 (15)	C17—N9—C15—N12	177.67 (18)
N1—Ca1—O3—C7	7.43 (14)	C17—N11—C16—N13	-179.39 (19)
N2—Ca1—O3—C7	-100.42 (14)	C17—N11—C16—N10	0.9 (3)
O3 ⁱ —Ca1—O3—C7	79.58 (14)	C15—N10—C16—N13	176.27 (19)
C1—C2—C3—C4	-0.2 (4)	C15—N10—C16—N11	-4.0 (3)
C2—C3—C4—C5	-0.4 (4)	C16—N11—C17—N14	-177.5 (2)
O1—Ca1—O5—C11	75.17 (16)	C16—N11—C17—N9	1.6 (3)
O1 ⁱ —Ca1—O5—C11	-76.38 (16)	C15—N9—C17—N14	178.31 (19)
O5 ⁱ —Ca1—O5—C11	3.08 (14)	C15—N9—C17—N11	-0.8 (3)
N1 ⁱ —Ca1—O5—C11	-104.08 (16)		

Symmetry codes: (i) $-x, y, -z+1/2$.

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

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1W—H1WB \cdots O2 ⁱⁱ	0.84	1.91	2.710 (3)	160
O1W—H1WA \cdots O6 ⁱⁱⁱ	0.84	1.92	2.751 (3)	170
O2W—H2WB \cdots N4 ^{iv}	0.84	2.26	3.022 (3)	151

supplementary materials

N3—H3N…O2	0.88	1.79	2.667 (2)	176
O2W—H2WA…O5	0.84	2.05	2.888 (3)	175
O3W—H3WB…O2W ^v	0.84	2.18	2.963 (3)	154
O3W—H3WA…N14 ^{vi}	0.84	2.17	3.007 (3)	180
N6—H6NA…O1W ⁱⁱ	0.88	2.45	3.294 (3)	162
N6—H6NB…O1W	0.88	1.90	2.740 (3)	160
N7—H7NA…N11 ^{vi}	0.88	2.22	3.103 (3)	176
N7—H7NB…O2W ⁱⁱⁱ	0.88	2.44	3.205 (3)	146
N7—H7NB…O4 ⁱⁱⁱ	0.88	2.53	3.111 (2)	124
N8—H8NA…O1	0.88	2.07	2.948 (2)	172
N12—H11A…N10 ^{vii}	0.88	2.23	3.109 (2)	178
N12—H11B…O5	0.88	2.32	3.196 (2)	175
N8—H8NB…O3W	0.88	2.15	2.832 (4)	134
N9—H9NA…O3	0.88	1.89	2.754 (2)	165
N13—H13A…O4 ^{viii}	0.88	2.08	2.925 (2)	160
N13—H13B…O6 ^{vii}	0.88	1.96	2.790 (2)	157
N14—H14A…O3	0.88	2.39	3.143 (2)	144
N14—H14B…N5 ^{ix}	0.88	2.10	2.978 (3)	178
C4—H4A…O2 ^x	0.95	2.55	3.370 (3)	145

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

Fig. 1

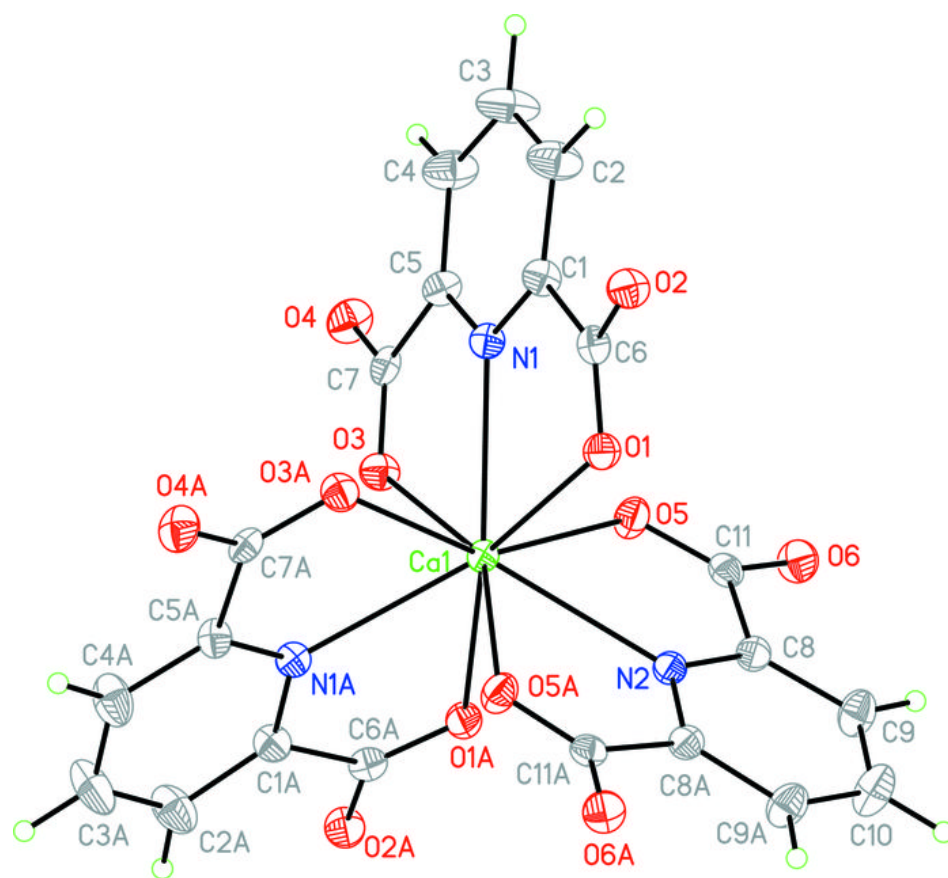


Fig. 2

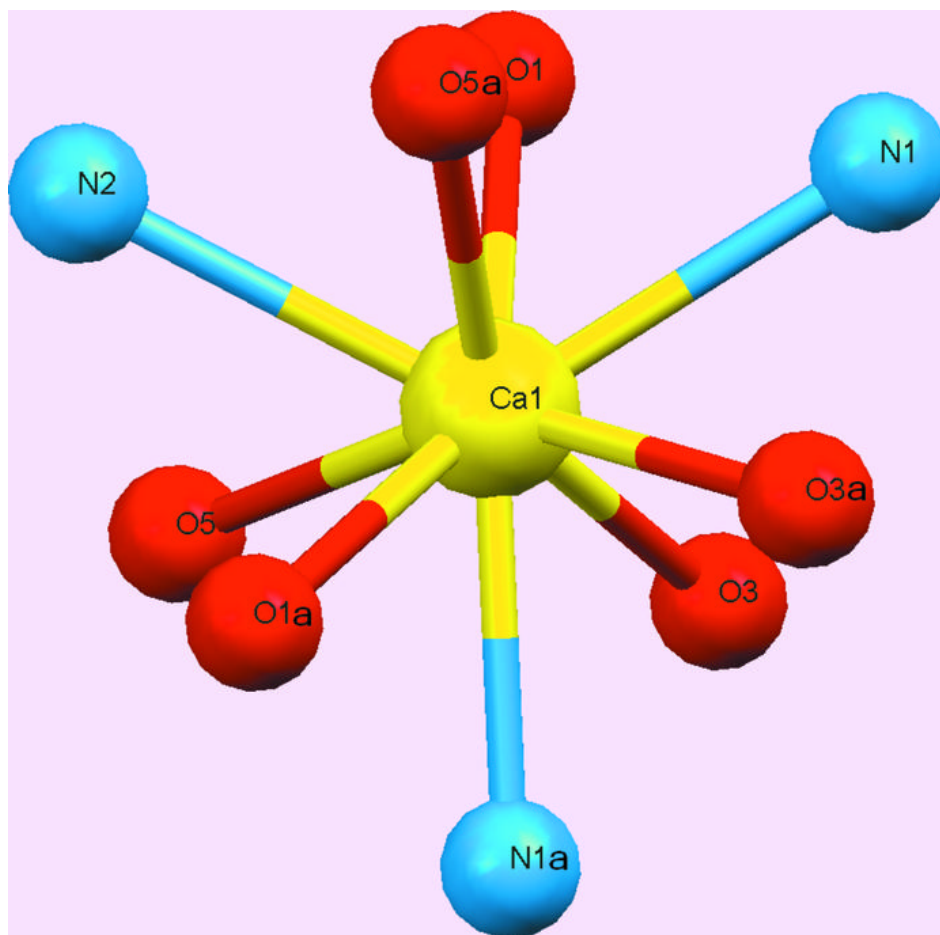


Fig. 3

