

Poly[*diaquabis*(μ -4-carboxy-2-propyl-1*H*-imidazole-5-carboxylato- $\kappa^3 N^3, O^4: O^5$)-calcium(II)]

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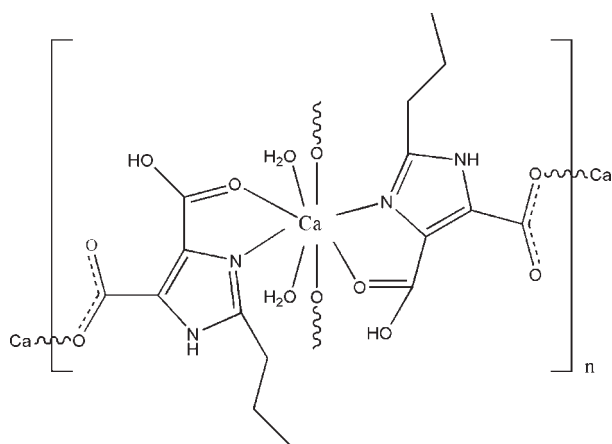
Received 3 December 2009; accepted 8 December 2009

Key indicators: single-crystal X-ray study; $T = 273$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.034; wR factor = 0.099; data-to-parameter ratio = 11.9.

In the title complex, $[\text{Ca}(\text{C}_8\text{H}_9\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_2]_n$, the Ca^{II} atom is eight-coordinated in a distorted square-antiprismatic environment. The water-coordinated Ca atom is *N,O*-chelated by the monocarboxylate anion; the carboxyl $-\text{CO}_2$ portion engaged in chelation bears an acid hydrogen. The free $-\text{CO}_2$ portion engages in bonding to adjacent Ca atoms. The Ca^{II} centres are connected through the ligand, forming a layer structure; the layers are linked by hydrogen bonds into a three-dimensional network.

Related literature

For the potential uses and diverse structural types of structures containing metals and *N*-heterocyclic carboxylic acids, see: Liang *et al.* (2002); Net *et al.* (1989); Nie *et al.* (2007).



Experimental

Crystal data

$[\text{Ca}(\text{C}_8\text{H}_9\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$
 $M_r = 470.46$
 Monoclinic, $C2/c$
 $a = 12.703$ (3) Å
 $b = 13.006$ (3) Å
 $c = 11.697$ (2) Å
 $\beta = 97.864$ (2)°

$V = 1914.3$ (7) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.40$ mm⁻¹
 $T = 273$ K
 $0.32 \times 0.24 \times 0.20$ mm

Data collection

Bruker APEXII area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2004)
 $T_{\text{min}} = 0.884$, $T_{\text{max}} = 0.925$

4830 measured reflections
 1718 independent reflections
 1504 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.099$
 $S = 1.02$
 1718 reflections
 144 parameters

3 restraints
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.29$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.23$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N2}-\text{H2}\cdots\text{O1}^{\text{i}}$	0.86	2.01	2.859 (2)	171
$\text{O1W}-\text{H2W}\cdots\text{O1}^{\text{ii}}$	0.83	2.31	3.088 (2)	156
$\text{O1W}-\text{H1W}\cdots\text{O3}^{\text{iii}}$	0.84	2.12	2.947 (2)	172

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

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); 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); software used to prepare material for publication: SHELXTL.

The authors acknowledge Guang Dong Ocean University for supporting this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2702).

References

- Bruker (2004). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
 Liang, Y. C., Cao, R. & Hong, M. C. (2002). *Inorg. Chem. Commun.* **5**, 366–368.
 Net, G., Bayon, J. C., Butler, W. M. & Rasmussen, P. (1989). *J. Chem. Soc. Chem. Commun.* pp. 1022–1023.
 Nie, X.-L., Wen, H.-L., Wu, Z.-S., Liu, D.-B. & Liu, C.-B. (2007). *Acta Cryst. E* **63**, m753–m755.
 Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.

supplementary materials

Acta Cryst. (2010). E66, m53 [doi:10.1107/S1600536809052799]

Poly[diaquabis(μ -4-carboxy-2-propyl-1*H*-imidazole-5-carboxylato- $\kappa^3N^3,O^4:O^5$)calcium(II)]

W.-D. Song, J.-B. Yan, S.-J. Li, D.-L. Miao and X.-F. Li

Comment

Recently, structures containing metals and N-heterocyclic carboxylic acids has attracted much attention, they can function as a multidentate ligand, exhibiting diverse structural type and can be potentially used as functional materials (Nie *et al.*, 2007; Liang *et al.*, 2002; Net *et al.*, 1989). In this paper, we report the synthesis and structure of a new Ca(II) complex obtained from 2-Propyl-1*H*-imidazole-4,5-dicarboxy with metal salts under hydrothermal conditions.

As illustrated in figure 1, the title complex molecule is eight-coordinated by two chelating rings [Ca—N=2.5998 (15)Å and Ca—O=2.605 (5) Å] and two carboxylate O atoms from two different 2-Propyl-1*H*-imidazole-4,5-dicarboxylate ligands and two water molecules, exhibiting a distorted square antiprismatic structure, the title Complex displays an extended two-dimensional layer structure constructed of quasi-squares, with four Ca atoms at the corners and 2-Propyl-1*H*-imidazole-4,5-dicarboxylate anions at each edge as linkers connecting two Ca atoms. the edge lengths are equal, with a value of 9.0901 (16) Å. the angles of the rhombus are 88.650 (2)° and 91.350 (5)°(Fig. 2). Two dimensional layers are further linked by hydrogen bonds(Table 1), forming a three-dimensional network(Fig. 3)

Experimental

A mixture of Ca(II)chloride (0.5 mmol, 0.055 g) and 2-propyl-1*H*-imidazole-4,5-dicarboxylic acid(0.5 mmol, 0.99 g) in 10 ml of distilled water was sealed in an autoclave equipped with a Teflon liner (20 ml) and then heated at 433k for 3 days. Crystals of the title compound were obtained by slow evaporation of the solvent at room temperature.

Refinement

Carbon and nitrogen bound H atoms were placed at calculated positions and were treated as riding on the parent C or N atoms with C—H = 0.93 Å, N—H = 0.86 Å, and with $U_{iso}(H) = 1.2 U_{eq}(C, N)$. The water H-atoms were located in a difference map, and were refined with a distance restraint of O—H = 0.84 Å; their U_{iso} values were refined.

Figures

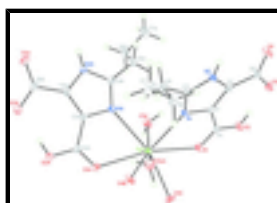


Fig. 1. The structure of the title compound, showing the atomic numbering scheme. Non-H atoms are shown with 30% probability displacement ellipsoids(H atoms are represented by arbitrary spheres). [Symmetry codes:[(A)1 - x,y,1.5 - z;(B)-1/2 + x,1/2 + y,z;(C)1.5 - x,1/2 + y,1.5 - z.]

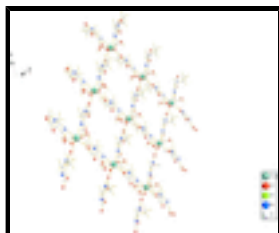


Fig. 2. A view of an extended two-dimensional layer structure of the title compound.

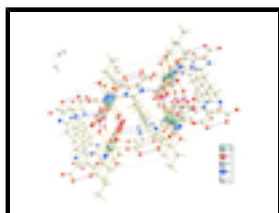


Fig. 3. View the three-dimensional network.

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Crystal data

[Ca(C₈H₉N₂O₄)₂(H₂O)₂]

$M_r = 470.46$

Monoclinic, *C2/c*

Hall symbol: -C 2yc

$a = 12.703$ (3) Å

$b = 13.006$ (3) Å

$c = 11.697$ (2) Å

$\beta = 97.864$ (2)°

$V = 1914.3$ (7) Å³

$Z = 4$

$F(000) = 984$

$D_x = 1.632$ Mg m⁻³

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

Cell parameters from 3600 reflections

$\theta = 1.4$ – 28°

$\mu = 0.40$ mm⁻¹

$T = 273$ K

Block, white

$0.32 \times 0.24 \times 0.20$ mm

Data collection

Bruker APEXII area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

φ and ω scan

Absorption correction: multi-scan (*SADABS*; Bruker, 2004)

$T_{\min} = 0.884$, $T_{\max} = 0.925$

4830 measured reflections

1718 independent reflections

1504 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.040$

$\theta_{\max} = 25.2^\circ$, $\theta_{\min} = 2.3^\circ$

$h = -13 \rightarrow 15$

$k = -14 \rightarrow 15$

$l = -14 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$wR(F^2) = 0.099$	$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2 + 1.470P]$
$S = 1.02$	where $P = (F_o^2 + 2F_c^2)/3$
1718 reflections	$(\Delta/\sigma)_{\max} < 0.001$
144 parameters	$\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$
3 restraints	$\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: <i>SHELXL97</i> (Sheldrick, 2008), $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$ Extinction coefficient: 0.0076 (9)

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	0.5000	0.07420 (4)	0.2500	0.0189 (2)
O1	0.33875 (11)	0.05035 (10)	0.36313 (12)	0.0262 (3)
O1W	0.55495 (11)	0.10622 (11)	0.45862 (12)	0.0319 (4)
H1W	0.5121	0.1347	0.4970	0.048*
H2W	0.5769	0.0519	0.4904	0.048*
O2	0.20033 (11)	0.11430 (10)	0.43530 (13)	0.0296 (4)
H1	0.1663	0.1680	0.4316	0.044*
O3	0.09452 (11)	0.27478 (11)	0.42169 (12)	0.0308 (4)
O4	0.09469 (12)	0.42512 (10)	0.33195 (13)	0.0352 (4)
N1	0.36595 (12)	0.22589 (11)	0.23987 (13)	0.0201 (4)
N2	0.26433 (12)	0.36382 (11)	0.21921 (13)	0.0225 (4)
H2	0.2403	0.4229	0.1951	0.027*
C1	0.28670 (14)	0.21777 (14)	0.30920 (15)	0.0192 (4)
C2	0.22299 (14)	0.30376 (14)	0.29747 (16)	0.0209 (4)
C3	0.34950 (14)	0.31557 (14)	0.18572 (16)	0.0215 (4)
C4	0.27622 (14)	0.12212 (14)	0.37333 (16)	0.0204 (4)
C5	0.40949 (15)	0.36092 (15)	0.09774 (17)	0.0255 (4)
H5A	0.4753	0.3231	0.0974	0.031*
H5B	0.4277	0.4315	0.1189	0.031*
C6	0.34718 (17)	0.35929 (17)	-0.02384 (18)	0.0334 (5)
H6A	0.3399	0.2888	-0.0508	0.040*
H6B	0.2764	0.3865	-0.0212	0.040*
C7	0.40144 (19)	0.42208 (18)	-0.1082 (2)	0.0382 (6)

supplementary materials

H7A	0.4067	0.4924	-0.0832	0.057*
H7B	0.3606	0.4184	-0.1835	0.057*
H7C	0.4714	0.3952	-0.1113	0.057*
C8	0.13058 (15)	0.33836 (15)	0.35251 (16)	0.0240 (4)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca1	0.0189 (3)	0.0157 (3)	0.0229 (3)	0.000	0.0052 (2)	0.000
O1	0.0267 (7)	0.0187 (7)	0.0336 (8)	0.0026 (6)	0.0051 (6)	0.0014 (6)
O1W	0.0345 (8)	0.0327 (8)	0.0299 (8)	0.0035 (6)	0.0095 (6)	0.0011 (6)
O2	0.0303 (8)	0.0228 (7)	0.0384 (8)	0.0041 (6)	0.0140 (7)	0.0073 (6)
O3	0.0295 (8)	0.0300 (8)	0.0360 (8)	0.0045 (6)	0.0155 (6)	0.0036 (6)
O4	0.0385 (9)	0.0295 (8)	0.0394 (9)	0.0182 (6)	0.0119 (7)	0.0052 (6)
N1	0.0188 (8)	0.0190 (8)	0.0231 (8)	0.0000 (6)	0.0049 (6)	0.0001 (6)
N2	0.0250 (8)	0.0157 (8)	0.0275 (9)	0.0045 (6)	0.0059 (7)	0.0042 (6)
C1	0.0185 (9)	0.0192 (9)	0.0198 (9)	-0.0003 (7)	0.0023 (7)	-0.0013 (7)
C2	0.0219 (9)	0.0200 (9)	0.0212 (9)	0.0015 (7)	0.0046 (8)	-0.0011 (7)
C3	0.0207 (9)	0.0201 (9)	0.0236 (10)	-0.0007 (7)	0.0027 (8)	-0.0004 (7)
C4	0.0203 (9)	0.0191 (9)	0.0215 (10)	-0.0007 (7)	0.0020 (7)	-0.0016 (7)
C5	0.0230 (10)	0.0255 (10)	0.0288 (11)	-0.0018 (8)	0.0062 (8)	0.0047 (8)
C6	0.0311 (11)	0.0350 (12)	0.0332 (12)	-0.0093 (9)	0.0012 (9)	0.0059 (9)
C7	0.0419 (13)	0.0429 (13)	0.0294 (12)	-0.0077 (10)	0.0037 (10)	0.0069 (9)
C8	0.0235 (10)	0.0266 (10)	0.0219 (10)	0.0022 (8)	0.0035 (8)	-0.0017 (8)

Geometric parameters (\AA , $^\circ$)

Ca1—O4 ⁱ	2.4104 (14)	N1—C1	1.380 (2)
Ca1—O4 ⁱⁱ	2.4104 (14)	N2—C3	1.354 (2)
Ca1—O1W	2.4798 (15)	N2—C2	1.362 (2)
Ca1—O1W ⁱⁱⁱ	2.4799 (15)	N2—H2	0.8600
Ca1—N1 ⁱⁱⁱ	2.5982 (15)	C1—C2	1.376 (3)
Ca1—N1	2.5982 (15)	C1—C4	1.468 (3)
Ca1—O1	2.6048 (14)	C2—C8	1.484 (3)
Ca1—O1 ⁱⁱⁱ	2.6049 (14)	C3—C5	1.484 (3)
O1—C4	1.242 (2)	C5—C6	1.530 (3)
O1W—H1W	0.8378	C5—H5A	0.9700
O1W—H2W	0.8287	C5—H5B	0.9700
O2—C4	1.287 (2)	C6—C7	1.517 (3)
O2—H1	0.8200	C6—H6A	0.9700
O3—C8	1.284 (2)	C6—H6B	0.9700
O4—C8	1.228 (2)	C7—H7A	0.9600
O4—Ca1 ^{iv}	2.4102 (14)	C7—H7B	0.9600
N1—C3	1.330 (2)	C7—H7C	0.9600
O4 ⁱ —Ca1—O4 ⁱⁱ	72.89 (8)	C3—N2—C2	108.98 (15)
O4 ⁱ —Ca1—O1W	125.76 (5)	C3—N2—H2	125.5
O4 ⁱⁱ —Ca1—O1W	71.69 (5)	C2—N2—H2	125.5

O4 ⁱ —Ca1—O1W ⁱⁱⁱ	71.69 (5)	C2—C1—N1	110.21 (16)
O4 ⁱⁱ —Ca1—O1W ⁱⁱⁱ	125.76 (5)	C2—C1—C4	130.27 (17)
O1W—Ca1—O1W ⁱⁱⁱ	160.66 (7)	N1—C1—C4	119.30 (15)
O4 ⁱ —Ca1—N1 ⁱⁱⁱ	156.52 (5)	N2—C2—C1	104.93 (16)
O4 ⁱⁱ —Ca1—N1 ⁱⁱⁱ	107.72 (5)	N2—C2—C8	121.21 (16)
O1W—Ca1—N1 ⁱⁱⁱ	74.52 (5)	C1—C2—C8	133.83 (17)
O1W ⁱⁱⁱ —Ca1—N1 ⁱⁱⁱ	90.68 (5)	N1—C3—N2	110.39 (16)
O4 ⁱ —Ca1—N1	107.72 (5)	N1—C3—C5	128.07 (17)
O4 ⁱⁱ —Ca1—N1	156.53 (5)	N2—C3—C5	121.51 (17)
O1W—Ca1—N1	90.68 (5)	O1—C4—O2	122.20 (17)
O1W ⁱⁱⁱ —Ca1—N1	74.52 (5)	O1—C4—C1	118.94 (16)
N1 ⁱⁱⁱ —Ca1—N1	81.19 (7)	O2—C4—C1	118.82 (16)
O4 ⁱ —Ca1—O1	73.86 (5)	C3—C5—C6	112.93 (16)
O4 ⁱⁱ —Ca1—O1	94.96 (5)	C3—C5—H5A	109.0
O1W—Ca1—O1	69.83 (5)	C6—C5—H5A	109.0
O1W ⁱⁱⁱ —Ca1—O1	112.64 (5)	C3—C5—H5B	109.0
N1 ⁱⁱⁱ —Ca1—O1	128.56 (5)	C6—C5—H5B	109.0
N1—Ca1—O1	63.74 (4)	H5A—C5—H5B	107.8
O4 ⁱ —Ca1—O1 ⁱⁱⁱ	94.96 (5)	C7—C6—C5	111.95 (17)
O4 ⁱⁱ —Ca1—O1 ⁱⁱⁱ	73.85 (5)	C7—C6—H6A	109.2
O1W—Ca1—O1 ⁱⁱⁱ	112.64 (5)	C5—C6—H6A	109.2
O1W ⁱⁱⁱ —Ca1—O1 ⁱⁱⁱ	69.82 (5)	C7—C6—H6B	109.2
N1 ⁱⁱⁱ —Ca1—O1 ⁱⁱⁱ	63.74 (4)	C5—C6—H6B	109.2
N1—Ca1—O1 ⁱⁱⁱ	128.56 (5)	H6A—C6—H6B	107.9
O1—Ca1—O1 ⁱⁱⁱ	166.32 (6)	C6—C7—H7A	109.5
C4—O1—Ca1	121.13 (12)	C6—C7—H7B	109.5
Ca1—O1W—H1W	119.1	H7A—C7—H7B	109.5
Ca1—O1W—H2W	109.3	C6—C7—H7C	109.5
H1W—O1W—H2W	109.8	H7A—C7—H7C	109.5
C4—O2—H1	109.5	H7B—C7—H7C	109.5
C8—O4—Ca1 ^{iv}	165.57 (15)	O4—C8—O3	124.05 (18)
C3—N1—C1	105.49 (14)	O4—C8—C2	119.22 (17)
C3—N1—Ca1	138.32 (12)	O3—C8—C2	116.72 (17)
C1—N1—Ca1	116.18 (11)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2 \cdots O1 ^v	0.86	2.01	2.859 (2)	171.
O1W—H2W \cdots O1 ^{vi}	0.83	2.31	3.088 (2)	156.
O1W—H1W \cdots O3 ^{vii}	0.84	2.12	2.947 (2)	172.

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

Fig. 1

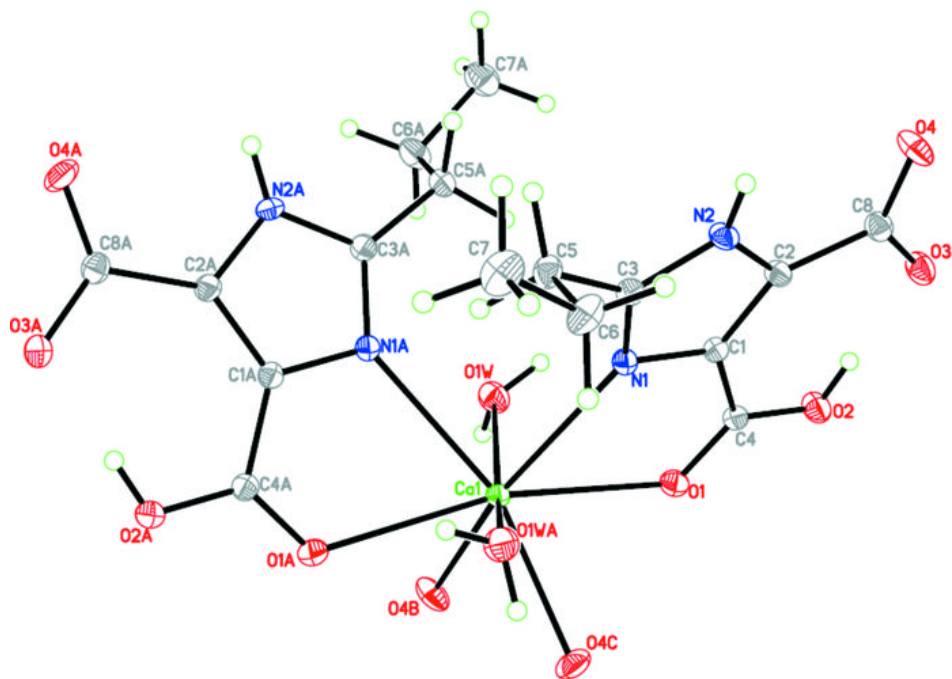


Fig. 2

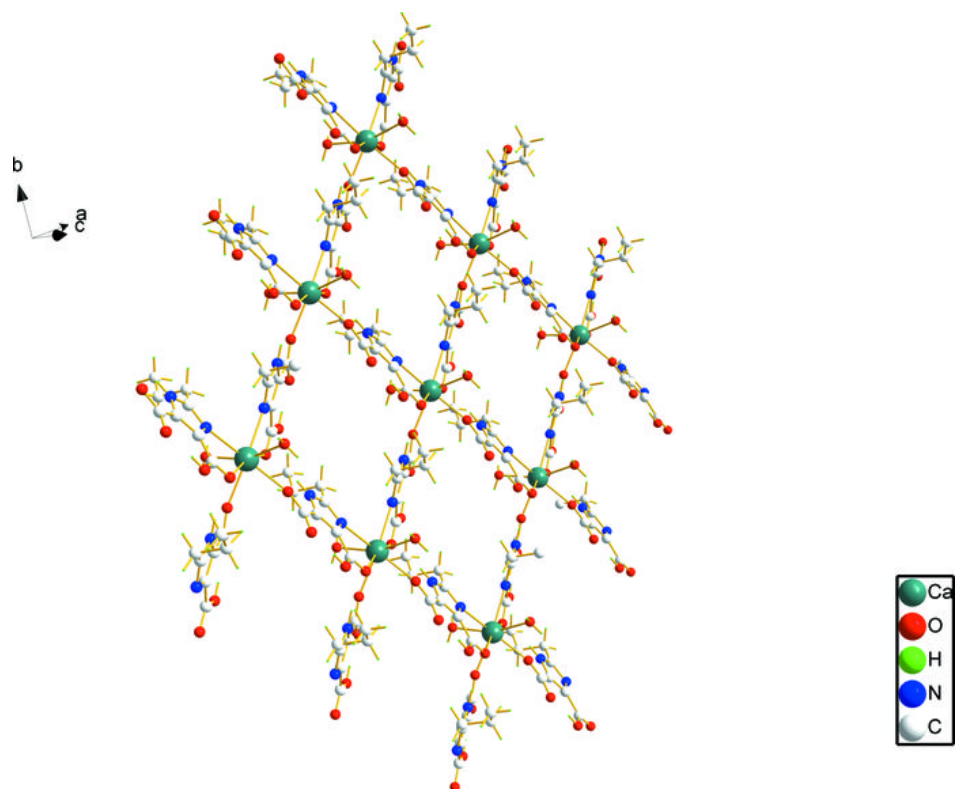


Fig. 3

