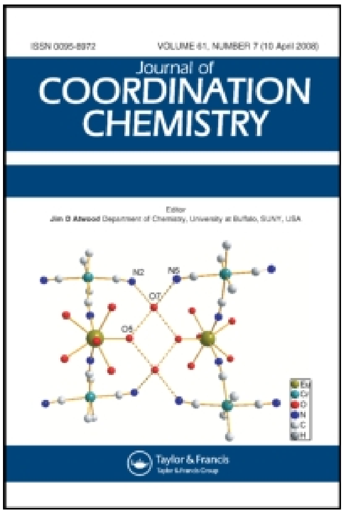

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Crystal structures of two Ca(II) complexes with imidazole-4,5-dicarboxylate and water ligands

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The structure of compound **I**: *poly*-diaqua(μ-imidazole-4,5-dicarboxylato-N,O; -O′; -O″, -O‴) calcium(II) monohydrate $[Ca(C_5H_2N_2O_4)(H_2O)_2 \cdot H_2O]$ is built of molecular sheets in which imidazole-4,5-dicarboxylate ligands bridge the metal ions using both carboxylate groups, each bidentate. Ca(II) is coordinated by six oxygen atoms and one hetero-ring nitrogen atom distributed at the apices of a capped tetragonal bipyramid. The basal plane of the pyramid is formed by two carboxylate oxygen atoms [d(Ca–O2 = 2.374(1) Å, d(Ca–O4) = 2.412(1) Å] and two water oxygen atoms [d(Ca–O5) = 2.384(1) Å, d(Ca–O6) = 2.455(1) Å], the capped position is occupied by the carboxylate oxygen atom O3 [d(Ca–O3) = 2.325(1) Å], the hetero-ring nitrogen atom [d(Ca–N2) = 2.523(1) Å] and the carboxylate oxygen atom O4 [d(Ca–O2) = 2.412(1) Å] form the apices of the prism. The solvation water molecule plays a significant role in a framework of hydrogen bonds responsible for the stability of the crystal. The structure of compound **II**: *trans*-tetraquadi(H-imidazole-4,5-dicarboxylato-N,O) calcium(II) monohydrate, $[Ca(C_5H_3N_2O_4)_2(H_2O)_4 \cdot H_2O]$ consists of monomers in which the Ca(II) ion is located on a centre of symmetry. The coordination around the Ca(II) is a strongly deformed pentagonal bipyramidal with the imidazole-4,5-dicarboxylate (4,5-IDA) ligands in the *trans* arrangement forming a dihedral angle of 68.3°. An imidazole-ring nitrogen atom [d(Ca–N) = 2.632(2) Å] and one carboxylate O atom [d(Ca–O) = 2.531(2) Å] from each ligand coordinate to the metal ion. The coordination is completed by four water oxygen atoms [d(Ca–O) = 2.393(2) Å] and [d(Ca–O) = 2.367(2) Å]. The coordinated water molecules act as hydrogen bond donors and acceptors to the unbonded carboxylate oxygen atoms in adjacent monomers giving rise to a three-dimensional molecular network.

1. Introduction

Crystal chemistry of calcium coordination compounds with carboxylate ligands attracts considerable interest due to the role calcium plays in biological systems. Calcium(II) shows great flexibility when bonding to carboxylate ligands resulting in a variety of coordination geometries and molecular patterns observed in the crystal structures

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of its complexes [1, 2]. These features are well-illustrated by the structures of Ca(II) complexes with carboxylate ligands containing five-membered heterocyclic rings, as for example, furan and pyrazole. The three-dimensional structure of a complex with furan-2-carboxylate contains four symmetry independent Ca(II) ions located in general positions with coordination numbers 7, 10, 8 and 7; two Ca(II) ions situated on the twofold axes, both with coordination number 8, while two other Ca(II) ions occupying the inversion centers are also eight-coordinate [3]. On the other hand, Ca(II) is eight-coordinate in the structure of a complex with furan-3-carboxylate and water ligands which is composed of catenated $[\mathrm{Ca(furan\text{-}3\text{-}carboxylate)(H_2O)_3}]^+$ polycations and $(\mathrm{furan\text{-}3\text{-}carboxylate})^-$ anions [4]. Different coordination geometries and molecular patterns have also been reported in the structures of three Ca(II) complexes with pyrazole-3,5-dicarboxylate and water ligands. It has been found that their formation is directly affected by the acidity of reaction solutions [5].

Therefore, as an ongoing step in our crystal chemical studies on Ca(II) coordination compounds with carboxylate ligands containing five- and six-membered hetero-rings we have determined the crystal structures of two complexes with imidazole-4,5-dicarboxylate (4,5-IDA) and water ligands. The results are reported in this article.

2. Experimental

Fifty millilitres of aqueous solution containing 0.01 mmol of calcium nitrate tetrahydrate was added with constant stirring to 50 mL of hot aqueous solution containing 0.02 mmol of imidazole-4,5-dicarboxylic acid and 2 mL of 10% hydrazine hydrate. The resulting clear solution was concentrated on a water bath to one half of its volume, filtered and left for crystallization at room temperature. After several days, pale yellow crystals deposited in the mother liquid, collected, were washed with cold water, ethanol and ether, then dried in a desiccator. The yield was 93%. Examination under a microscope showes two kinds of crystals: columns and plates. They were identified as compounds **I** and **II**, respectively. The dimensions of single crystals selected for X-ray diffraction data collection are given in table 1.

X-ray diffraction data were measured at room temperature using a KUMA KM4 four circle diffractometer operating in ω–2θ mode. Two standard reflections were monitored every 200 reflections. Unit cell dimensions and standard deviations were obtained by least-squares fit to 25 reflections in the 2θ range from 15 to 30°. Reflections were processed using profile analysis and corrected for Lorentz and polarization effects. An analytical absorption correction [6] was applied. Non-hydrogen atoms were located by direct method using the SHELXLS program [7] and hydrogen atoms then found by successive Fourier syntheses. Final refinement on F^2 by full-matrix least squares (program SHELXL97 [8]) was performed on positional parameters of all atoms, anisotropic vibrational parameters of all non H-atoms and isotropic temperature factors of hydrogen atoms. A weighting scheme was used in the form: $w = 1/[\sigma^2(F_o^2) + (A * P)^2 + B * P]$, where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c{}^2]/3$. A, B are the parameters listed in table 1 with other crystal structure, data collection and refinement parameters. Selected bond lengths and angles are collected in tables 2 and 3.

Table 1. Crystal data and structure refinement details for $\mathrm{Ca(4,5\text{-}IDA)(H_2O)_4 \cdot H_2O}$ [compound **I**] and $\mathrm{Ca[H(4,5\text{-}IDA)]_2(H_2O)_4 \cdot H_2O}$ [compound **II**].

	Compound **I**	Compound **II**
Empirical formula	$\mathrm{C_5H_8N_2O_7Ca}$	$\mathrm{C_{10}H_{16}N_4O_{13}Ca}$
Formula weight	248.21	440.35
Temperature	293K	
Wavelength ($\mathrm{MoK_\alpha}$) (Å)	0.71073	
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
Unit cell dimensions	$a = 6.561(1)$ Å	$a = 8.165(1)$ Å
	$b = 17.728(3)$ Å	$b = 11.933(2)$ Å
	$c = 7.850(2)$ Å	$c = 17.572(4)$ Å
	$\beta = 97.93(3)^\circ$	$\beta = 103.41(3)^\circ$
	$V = 904.33$ Å^3	$V = 1665.4(6)$ Å^3
Z	4	4
Calculated density ($\mathrm{g\,cm^{-3}}$)	1.823	1.757
μ ($\mathrm{MoK_\alpha}$) ($\mathrm{mm^{-1}}$)	0.72	0.46
$F(000)$	512.0	912.0
Crystal size (mm)	$0.18 \times 0.10 \times 0.25$	$0.12 \times 0.15 \times 0.20$
θ_{min}, θ_{max} (deg.)	2.52–30.06	2.52–30.06
Index range	$0 \leq h \leq 9$	$-9 \leq h \leq 11$
	$0 \leq k \leq 24$	$-9 \leq k \leq 16$
	$-11 \leq l \leq 10$	$-5 \leq l \leq 24$
Total data	2643	2064
Observed data [$I > 4\sigma(I)$]	2030	1593
R_{int}	0.0157	0.0336
No. of parameters	168	157
Goodness-of-fit on F^2	1.056	1.126
Final $R1$ [$I > 4\sigma(I)$]	0.0272	0.0400
Final $wR2$ index	0.0850	0.1205
Min. and max. transmission	0.87736, 0.95944	0.72852, 0.82896
Extinction correction	None	None
Largest diff. peak and hole (e Å^3)	0.49, −0.36	0.55, −0.42
SHELX-97 weight parameters (A, B)	0.05501, 0.23	0.0743, 1.36
Mean shift/esd	0.000	0.000

3. Results and discussion

The structure of compound **I** is built of molecular sheets stacked along the a axis. In a sheet, adjacent Ca(II) ions are bridged by a doubly deprotonated imidazole-4,5-dicarboxylate ligand molecule which uses both carboxylate groups, each bidentate. The N,O bonding moiety composed of the hetero-ring nitrogen atom and the nearest carboxylate oxygen atom is chelated to a Ca(II) ion while the second oxygen of this carboxylate group is bonded to an adjacent ion. The latter is also coordinated by an oxygen atom donated by the second carboxylate group of the ligand molecule. Figure 1 shows a fragment of the sheet with atom labelling scheme. The coordination polyhedron around the metal can be visualized as a capped tetragonal bipyramid. This is shown in figure 2. The capped position is occupied by O3 atom from a bridging carboxylate group. The base of the tetragonal bipyramid is comprised from four oxygen atoms: two of coordinated water molecules O5 and O6 and two of coordinated carboxylate oxygen atoms O1 and O2. Two apices on the other side of the basal plane are occupied by the hetero-ring nitrogen atom N2 and the carboxylate oxygen atom O4. The base of the pyramid is almost planar with r.m.s. of 0.0563 Å. The Ca(II) ion is situated 0.3258 Å below the mean plane in the direction inside the prism. The relevant bond

Table 2. Selected bond distances and bond angles (Å, °) for $Ca(4,5\text{-}IDA)(H_2O)_4 \cdot H_2O$.

Ca(II) coordination polyhedron

Ca–O1	2.413(1)	O2–Ca–O6	93.23(4)
Ca–O2	2.374(1)	O6–Ca–O5	76.59(5)
Ca–O3	2.325(1)	O5–Ca–O1	102.07(5)
Ca–O4	2.412(1)	O1–Ca–O2	83.97(4)
Ca–N2	2.523(1)	O6–Ca–O3	83.29(4)
Ca–O5	2.384(1)	O1–Ca–O3	78.62(4)
Ca–O6	2.455(1)	O2–Ca–O3	81.28(5)
		O5–Ca–O3	86.00(5)
		O4–Ca–N2	76.89(4)

Hydrogen bond parameters

D–H···A	D–A	D–H	H···A	D–H–A
O5–H52···O10	2.839(2)	0.83(3)	2.04(3)	162(3)
O6–H62···O10[c]	2.784(2)	0.82(3)	1.97(3)	175(2)
O10–H12···O4[d]	2.817(2)	0.75(3)	2.10(3)	163(3)
O10–H11···O2[e]	2.759(2)	0.77(3)	1.99(3)	176(3)
O6–H61···O4[b]	2.880(2)	0.93(3)	2.03(3)	158(3)
N1–H1···O1[f]	2.756(2)	0.87(3)	1.89(3)	174(3)

Symmetry code: [b] $-x+1, -y, -z$; [c] $-x, -y, -z+1$; [d] $-x+1, -y, -z+1$; [e] $x, y, z+1$; [f] $x+1, -y+1/2, z+1/2$.

Table 3. Selected bond distances and bond angles (Å, °) for $Ca[H(4,5\text{-}IDA)]_2(H_2O)_4 \cdot H_2O$.

Ca(II) coordination polyhedron

Ca–N1	2.632(2)	N1–Ca–O3[a]	63.80(5)
Ca–O3	2.533(2)	O3[a]–Ca–O5	69.98(5)
Ca–O5	2.392(2)	O5–Ca–N1[a]	79.27(5)
Ca–O6	2.367(2)	N1[a]–Ca–O6	73.65(5)
	O6–Ca–N1	76.47(5)	
	O6–Ca–O6[a]	98.40(9)	
	O6[a]–Ca–O5[a]	152.52(5)	
	O5[a]–Ca–O3	69.98(5)	

Hydrogen-bond parameters

D–H···A	D–H	H···A	D···A	D–H–A
O4–H41···O2[a]	0.91(5)	1.62(5)	2.511(2)	163(4)
O5–H51···O1[b]	0.83(3)	1.94(3)	2.750(2)	167(4)
O5–H52···O2[c]	0.83(4)	2.16(4)	2.964(3)	164(3)
O6–H62···O1[d]	0.82(4)	1.95(4)	2.745(2)	165(3)
O6–H61···O7[e]	0.82(5)	2.06(3)	2.823(2)	155(4)
O7–H71···O2[f]	1.010(2)	2.006(2)	2.938(2)	152.37(4)

Symmetry code: [a] $-x, y, -z+1/2$; [b] $x-1/2, -y+3/2, z+1/2$; [c] $-x-1/2, -y+3/2, -z$; [d] $x, -y+2, z+1/2$; [e] $x+1/2, y+1+1/2, z$; [f] $x, -y+1, z+1/2$.

distances and bond angles within the coordination polyhedron are listed in table 2. The imidazole ring of the ligand molecule is planar (r.m.s. 0.0031 A). The planes of C6, O1, O2 and C7, O3, O4 carboxylate groups make dihedral angles of 13.0 and 16.3° respectively with the imidazole ring plane. An additional bridging path within a sheet is represented by hydrogen bonds O6–H61 ··· O4 of 2.880(2) Å in which the coordinated water molecules O6 act as donors and the carboxylate oxygen atoms O4 coordinated to adjacent Ca(II) ions act as donors. Solvation water molecules O10 located in the space between sheets play significant role in the system of hydrogen bonds responsible for keeping the sheets together. Two Ca(II) coordination polyhedra related by a centre

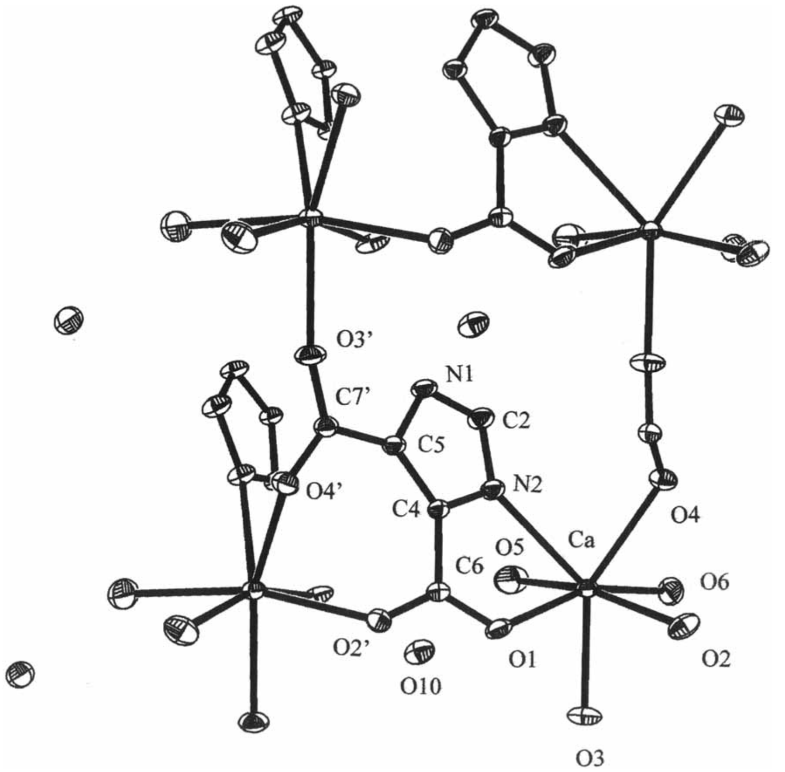

Figure 1. A fragment of the molecular sheet constituting the structure of $Ca(4,5\text{-IDA})(H_2O)_4 \cdot H_2O$ with atom labelling scheme. Non-hydrogen atoms are drawn at the 50% probability level. For clarity, hydrogen atoms are not shown.

of symmetry but belonging to adjacent sheets are bridged by hydrogen bonds provided by two O10 water molecules acting as acceptors, related also by the same centre of symmetry. Two bridging paths are thus observed: the first O5–H52 ··· O10 and O10 ··· H62–O6, the second O6–H62 ··· O10 and O10 ··· H52–O5. Simultenously, the O10 water molecules act as donors in hydrogen bonds linking the above, related by symmetry centre but belonging to adjacent sheets, Ca(II) polyhedra. This is the bond to carboxylic oxygen atom O4. However, the other bond is to carboxylic oxygen atom O2 coordinated to another Ca(II) polyhedron in the adjacent sheet. The hydrogen atom attached to the nitrogen atom N1 of the imidazole ring participates in a bond to the carboxylate oxygen atom O1 in the neighbouring sheet. Figure 3 shows schematically the network of the hydrogen bonds, their geometric parameters are listed in table 2.

The structure of **II** is composed of discrete neutral monomers with Ca(II) ions chelated by two, singly deprotonated molecules of the ligand acid molecules in *trans* arrangement, each of them contributing one hetero-ring nitrogen atom and one carboxylate oxygen atom. The proton remains attached to the second oxygen atom of the above group. Four water oxygen atoms complete the coordination number of the Ca(II) ion to 8. Figure 4 shows the molecule of **II** with atom numbering scheme. The coordinated atoms are distributed at the corners of a strongly distorted

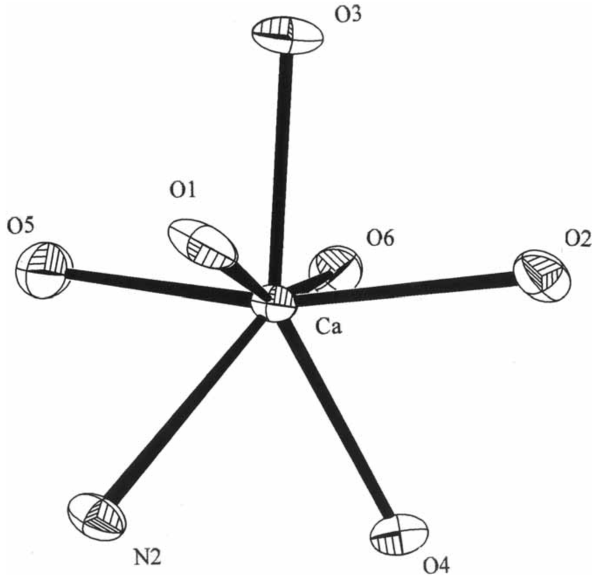

Figure 2. The coordination around the Ca(II) ion in the structure of Ca(4,5-IDA)$(H_2O)_4 \cdot H_2O$.

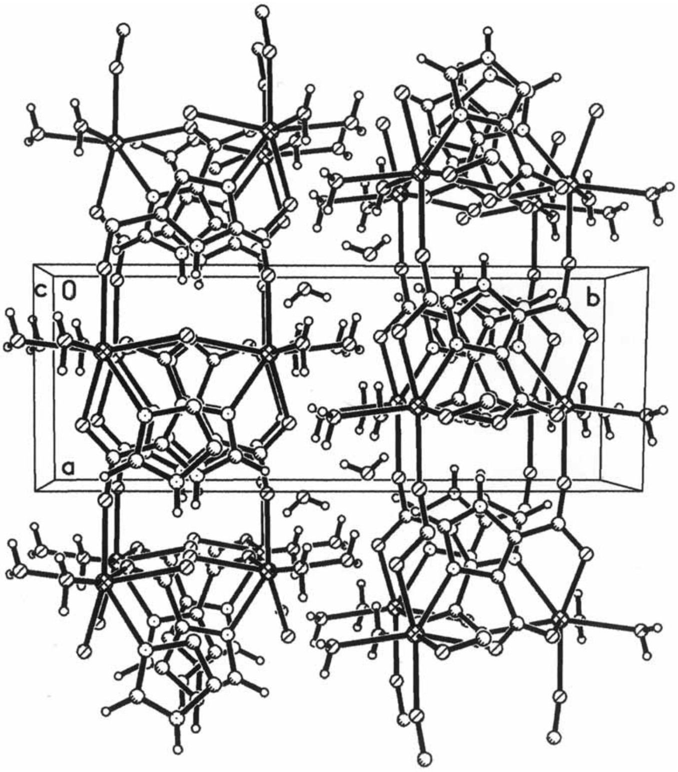

Figure 3. The packing diagram of Ca(4,5-IDA)$(H_2O)_4 \cdot H_2O$ showing the alignment of the molecular layers along the *c* axis.

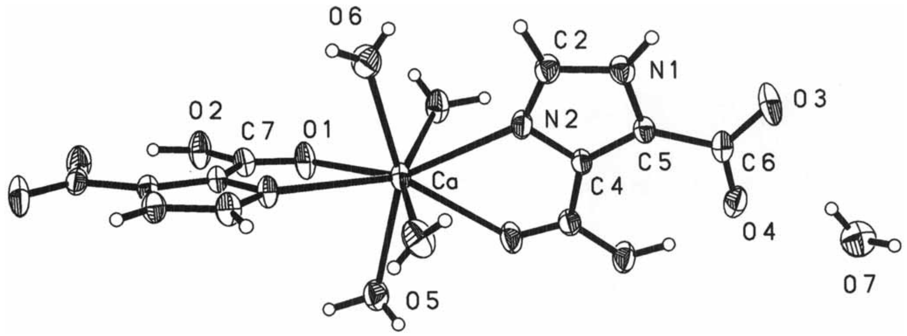

Figure 4. A molecule of Ca[H(4,5-IDA)]$_2$(H$_2$O)$_4$ with numbering of atoms. Non-hydrogen atoms are drawn at the 50% probability level.

pentagonal bipyramid – a polyhedron very common among Ca(II) complexes with carboxylate ligands. Its equatorial plane is formed by Ca, N2, O1A, O5, N2A and O6 atoms with the maximum shifts from the mean plane +0.443 Å (O6) and –0.530 Å (N2). O6A is located at the single apex, O1 and O5A form two apices on the other side of the equatorial plane. The relevant Ca–N and Ca–O bond lengths and bond angles are listed in table 3. The imidazole ring is planar with r.m.s. equal to 0.001 Å. The carboxylate groups make an angle of 2.5° with the imidazole ring. The planes of the imidazole-4,5-dicarboxylate ligands form an angle of 68.2° to each other. The carboxylate oxygen atom O2 and the attached hydrogen atom H21 act as donors in an intramolecular, fairly short hydrogen bond of 2.509(3) Å to the carboxylate oxygen atom O4A. Coordinated water molecules O5 and O6 participate as donors in hydrogen bonds to the unbonded carboxylate oxygen atoms in adjacent monomers bridging them into a three-dimensional molecular network (figure 5). In addition, solvation water molecule O7, acts as a donor and as an acceptor to the carboxylate oxygen atom O4 and to the coordinated water molecule O6, respectively. Table 3 lists the relevant geometric parameters. The same molecular pattern, consisting of monomeric molecules in which the metal ion is chelated by two singly deprotonated imidazole-4,5-dicarboxylate ligands has been reported in the structure of the Mn(II) complex exhibiting octahedral coordination characteristic for this ion [9].

The ability of the Ca(II) to form a number of compounds with the same ligand, each showing different stoichiometry and crystal structure has also been reported in the case of Ca(II) complexes with a ligand exhibiting very similar geometry – pyrazole-3,5-dicarboxylate. The structures of three compounds have been determined. Two of them show catenated molecular patterns, however, each with a different bridging mode, Ca(II) coordination number (7 and 8) and the shape of coordination polyhedron – a capped trigonal prism and a trigonal dodecahedron. The structure of the third complex shows a three-dimensional pattern composed of molecular layers in which two separate bridging pathways are observed. The coordination number of the Ca(II) ion is eight and the coordination polyhedron – a fairly regular pentagonal bipyramid [5]. The results of the present study indicate that the ability to form complexes with different molecular patterns and coordination geometries appears also in the case of the imidazole-4,5-dicarboxylate ligand. In the case of the Ca(II) complexes with pyrazole-3,4-dicarboxylate and water this feature has been correlated with the acidity (pH) of solutions used in the course of chemical preparation [5].

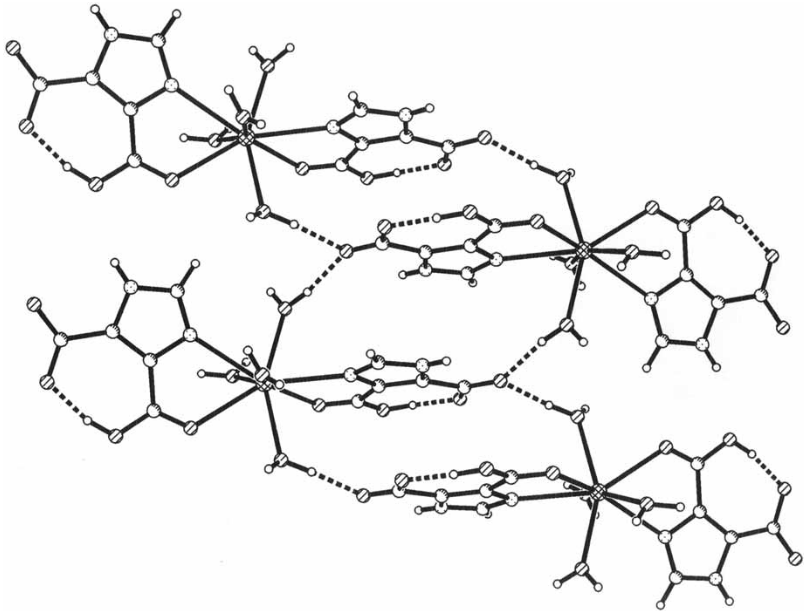

Figure 5. A fragment of the molecular pattern in the structure of $Ca[H(4,5\text{-}IDA)]_2(H_2O)_4 \cdot H_2O$. Hydrogen bonds are shown as dashed lines.

A simultenous appearence of two kinds of crystals with different structures in the mother liquid suggests that the sensitivity to pH is smaller in Ca(II) complexes with the imidazole-4,5-dicarboxylate ligand and water ligands.

Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC 270334 and CCDC 270335. Copies of the available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: teched@chemcrys.cam.ac.uk).

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