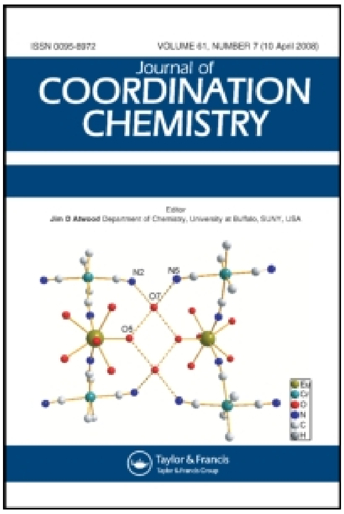

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Molecular sheets in the crystal structure of a Ba(II) complex with imidazole-4,5-dicarboxylate and water ligands

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The structure of *poly*-tetraaquabis(μ-*H*imidazole-4,5-dicarboxylato-N,O;-O′)barium(II) dihydrate, $Ba(C_5H_3N_2O_4)_2(H_2O)_4 \cdot 2H_2O$ is built of molecular sheets in which singly-deprotonated imidazole-4,5-dicarboxylate [H(4,5-IDA)] bridges metal ions using its N, O bonding moiety and one oxygen atom of its second carboxylate group. Each barium(II) is coordinated by N, O bonding moieties of two ligands, two carboxylate oxygen atoms of two other ligands and four waters. The coordination number of Ba(II) is ten, and the coordination polyhedron contains fourteen faces. A network of hydrogen bonds is responsible for the stability of the crystal.

Keywords: Barium(II) compounds; Imidazole-4,5-dicarboxylate ligand; Crystal structure

1. Introduction

Barium occurs as a trace element in a number of biological systems being an antagonist to magnesium and calcium in cell processes. As a heavy element, it acts as a poison. In structures of carboxylate complexes, barium(II) shows coordination numbers from six to twelve and a flexibility in bonding modes giving rise to polymeric molecular patterns. These properties are well illustrated by the structures of Ba(II) complexes with such five-membered heterocyclic carboxylate ligands as furan-2-carboxylate and furan-3-carboxylate [1]. The structure of the former is composed of three-dimensionally extended and cross-linked molecular chains in which symmetry independent Ba(II) ions show coordination numbers seven, ten and twelve. The structure of the latter complex is also polymeric with Ba(II) showing coordination number of six. Recently completed structural study of Ca(II) complexes with imidazole-4,5-dicarboxylate and water ligands has shown that the structure of one of them is composed of two-dimensional sheets with Ca(II) coordination number of seven, while the structure of the other consists of monomeric molecules in which Ca(II) ion coordinates two singly deprotonated ligand molecules and water oxygen atoms and shows coordination number of eight [2]. One may expect that the structures Ba(II) complexes and

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coordination modes will be similar to those observed in relevant Ca(II) compounds. Therefore, a Ba(II) complex with imidazole-4,5-dicarboxylate ligand has been obtained, single crystals grown and crystal structure determined. The results are reported in this article.

2. Experimental

The title compound was obtained by adding 50 mL of aqueous solution containing 0.01 mol of barium nitrate hydrate to 50 mL of hot aqueous solution contaning 0.02 mol of imidazole-4,5-dicarboxylic acid (ALDRICH). Two millilitres of 10% hydrazine hydrate were then added with constant stirring. The resulting clear solution was concentrated on a steam bath to one half of its volume and left to crystallize. Well formed colourless single crystals seperated from the mother solution after a couple of days. The dimensions of a sample crystal are listed in table 1.

Table 1. Crystal data and structure refinement details for Ba[H(4,5-IMC)]$_2$(H$_2$O)$_4\cdot$2H$_2$O.

Compound	Ba[H(4,5-IMC)]$_2$(H$_2$O)$_4\cdot$2H$_2$O
Color/shape	Colourless/rectangular block
Empirical formula	$C_{10}H_{18}N_4O_{14}Ba$
Formula weight	555.6
Temperature (K)	293(2)
Wavelength (Mo-Kα) (Å)	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions (Å, °)	
a	17.929(4)
b	6.757(1)
c	14.868(3)
β	95.18(3)
V (Å^3)	1793.79
Z	4
Calculated density (g cm^{-3})	2.057
μ (Mo-Kα) (mm^{-1})	2.30
F(000)	1096.0
Crystal size (mm^3)	0.20 × 0.21 × 0.40
$\theta_{\min}$, $\theta_{\max}$ (°).	2.52–30.06
Index range	$-25 \le h \le 25$, $0 \le k \le 9$, $-20 \le l \le 20$.
Total data	2628
Observed data [$I > 4\sigma(I)$]	2479
R_{int}	0.0254
Method of structure solution	Patterson
Method of structure refinement	Full-matrix least-squares on F^2
No. of parameters	169
Goodness-of-fit on F^2	1.172
Final R_1 [$I > 4\sigma(I)$]	0.0191
Final wR_2 index	0.0496
Completeness to $\theta = 30.06°$	0.994
Absorption correction	Analytical
Min. and max. transmission	0.24606, 0.32024
Extinction correction	None
Largest diff. peak and hole (e Å^{-3})	0.81 −0.42
SHELX-97 weight parameters (A, B)	0.0217, 1.23
Mean shift (esd)	0.000

Table 2. Selected bond distances and bond angles (Å, °) for $Ba[H(4,5\text{-IDA})]_2(H_2O)_4 \cdot 2H_2O$.

Ba(II) coordination			
Ba–O1(O1^{I})	2.858(2)	O1–Ba–N2	56.46(6)
Ba–N2(N2^{I})	2.960(2)	O1–Ba–N2^{I}	119.41(6)
Ba–O3(O3^{I})	2.875(1)	O3–Ba–O3^{I}	68.9(1)
Ba–O5(O5^{I})	2.901(2)	O5–Ba–O5^{I}	138.4(1)
Ba–O6(O6^{I})	2.847(2)	O6–Ba–O6^{I}	67.2(1)

D–H···A	d(D–H···A)	∠DHA
Hydrogen bonds		
N1–H1···O10	2.769(2)	177(2)
O2–H21···O4^{II}	2.459(2)	175(3)
O5–H51···O1^{V}	2.879(2)	164(4)
O5–H52···O4	2.763(2)	169(3)
O6–H61···O10^{IV}	3.102(3)	147(3)
O6–H62···O3^{VI}	2.971(2)	165(4)
O10–H101···O6^{VIII}	2.948(2)	153(4)
O10–H102···O5^{VII}	2.962(3)	162(4)

Symmetry code: $^{I}-x+1, y, -z+3/2$; $^{II}x-1/2, y+1/2, z$; $^{III}x+1/2, y-1/2, z$; $^{IV}x+1/2, y+1/2, z$; $^{V}x-1, -y, -z+2$; $^{VI}-x+1, y+1, -z+3/2$; $^{VII}-x+1/2, y+1/2, -z+3/2$; $^{VIII}-x+1/2, -y+1/2, -z+1$.

X-ray diffraction data were collected 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 [3] was applied. Non-hydrogen atoms were located by direct methods and hydrogen atoms then found by successive Fourier syntheses. Final refinement on F^2 by full-matrix least-squares was performed on positional parameters of all atoms, anisotropic vibrational parameters of all non H-atoms and isotropic temperature factors of hydrogen atoms [4]. A weighting scheme was used in the form: $w = 1/[\sigma^2(F_o^2) + (A * P)^2 + B * P]$, where $P = [\mathrm{Max}(F_o^2, 0) + 2F_o^2]/3$. A, B are the parameters listed in table 1 with other data collection and refinement parameters. Selected bond lengths and angles are collected in table 2.

3. Discussion

The structure of the title compound is composed of molecular layers in which Ba(II) ions are bridged by singly deprotonated imidazole-4,5-dicarboxylate ligand molecules. Figure 2 shows a fragment of the layer illustrating the bridging mode, figure 2 – a $Ba[H(4,5\text{-IDA})]_2(H_2O)_4$ structural unit with atom numbering scheme. Each ligand coordinates a Ba(II) ion using its N, O bonding moiety consisting of a hetero-ring nitrogen atom and one oxygen atom of the neighbouring carboxylate group. The second oxygen with a hydrogen attached does not participate in coordination. The other carboxylate group of the ligand coordinates one oxygen to an adjacent Ba(II). Such bridging results in molecular layers as illustrated in figure 2. However, each Ba(II), being situated on a twofold axis, exhibits a unique coordination mode: it is coordinated by the N, O bonding moieties donated by two ligand molecules.

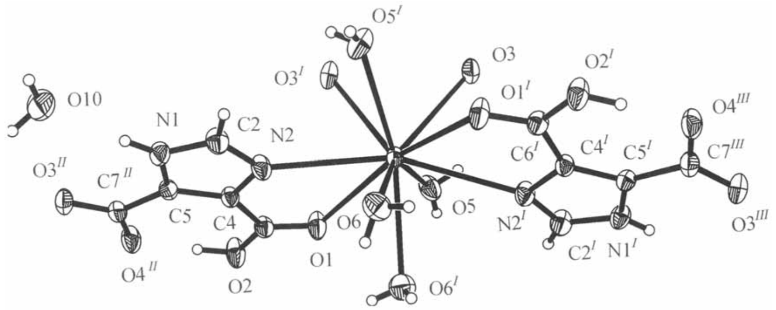

Figure 1. A molecular layer in the structure of $Ba[H(4,5\text{-}IDA)]_2(H_2O)_4 \cdot 2H_2O$. For clarity, hydrogen atoms are not shown.

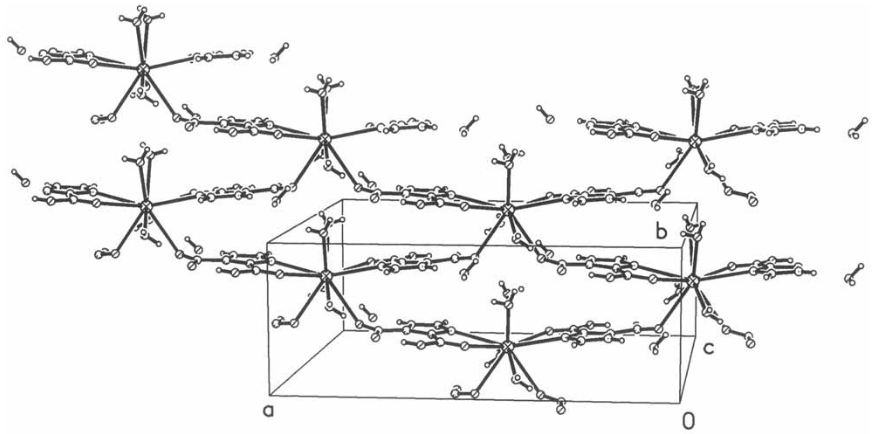

Figure 2. The molecular unit of the $Ba[H(4,5\text{-}IDA)]_2(H_2O)_4 \cdot 2H_2O$ structure with atom labelling scheme. Non-hydrogen atoms are drawn at the 50% probability level. For symmetry code, see table 2.

Therefore, taking into account four coordinated water molecules, a monomeric unit $Ba[H(4,5\text{-}IDA)]_2(H_2O)_4$ can be distinguished. Two bridging carboxylate oxygen atoms contributed by two different ligands complete the coordination at ten. Cross-linked molecular chains forming the layer can be visualized (see figure 2).

The coordination number of Ba(II) is ten. Decacoordination is commonly represented by a bicapped square antiprism. However, in the case of the title compound it is a complicated geometrical figure. Both coordinated N, O bonding moieties (atoms O1^I, N2^I, O1, N2) form a tetragonal plane (r.m.s 0.1069 Å) with the Ba(II) ion shifted from it by 0.519(1) Å. Taking this plane as an equatorial reference plane, water oxygen atoms O6 and O6^I form a double apex resulting in a tetragonal prism with two triangular faces and two tetragonal faces. Coordinated carboxylate oxygen atoms O3 and O3^I form a double apex on the other side of the equatorial plane. The planes Ba, O6, O6^I and Ba, O3, O3^I make an angle of 90° with the equatorial plane and are tilted by 93.8° to each other. Water oxygen atoms O5 and O5^I are also situated on the same side of the equatorial plane with the O5–Ba–O5^I angle almost twice as large as the O3–Ba–O3^I angle (see table 2). The plane Ba, O5, O5^I is normal to the equatorial

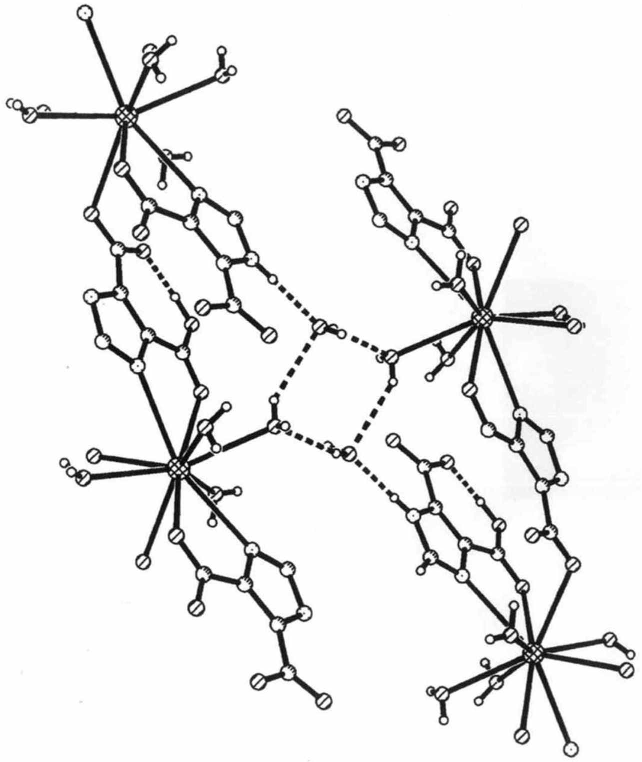

Figure 3. Hydrogen bonds formed by solvation water molecules in the structure of Ba[H(4,5-IDA)]$_2$(H$_2$O)$_4$ · 2H$_2$O. These bonds are represented by dashed lines. For clarity, only fragments of two adjacent molecular sheets are shown.

plane and almost parallel to the Ba, O6, O6^I plane: the relevant angle is 7.1°. Since the angle formed by the Ba, O5, O5^I and Ba, O3, O3^I planes is 100.9°, the O5 oxygen atom forms an apex above the O1, N2^I, O3, O3^I plane (the O5^I atom above the O1^{I}N2, O3, O3^I plane) so that, a tetragonal pyramid can be imagined with four triangular faces. Adding two faces (O1, N2, O3^I and O1^I, N2^I, O3), the coordination polyhedron around the Ba(II) ion has fourteen faces. The relevant bond lengths and bond angles are listed in table 2.

The imidazole ring of the ligand molecule is planar (r.m.s 0.0016 Å), the planes of the imidazole rings make an angle of 24.7° to each other. The planes of the C6, O1, O2 and C7, O3, O4 carboxylate groups make dihedral angles with the plane of the imidazole ring of 3.0° and 4.4°, respectively. The bond lengths and bond angles within the imidazole ring fall in the same range as those observed in other complexes with imidazole-4,5-dicarboxylate [2].

A network of hydrogen bonds *via* solvation water molecules O10 keeps the molecular sheets together. This is illustrated in figure 3. Solvation water molecules act as donors in the bonds to the coordinated water molecules in adjacent sheets O5^{VII} and O6^{VIII}. On the other hand, the coordinated water molecule O6 acts as a donor to form a bond to the carboxylate oxygen atom O3^{VI}. The hydrogen atom H1 attached to the imidazole ring nitrogen atom N1 is also bonded to the solvation water molecule O10. A short hydrogen bond of 2.459(2) Å is between the carboxylate oxygen atom O2 which acts as a donor to the carboxylate oxygen atom $O4^{II}$. The coordinated water molecule O5, acting as a donor, is linked to the carboxylate oxygen atom $O1^{V}$; it also forms an intramolecular hydrogen bond to the carboxylate oxygen atom O4. The geometrical data of the hydrogen bond system are listed in detail in table 2.

Monomeric molecules, similar to those forming the two-dimensional structure of the title compound have been observed in the structure of one Ca(II) complex with imidazole-4,5-dicarboxylate and water ligands $Ca[H(4,5\text{-}IDA)]_2(H_2O)_4$ [2]. However, the structure of the latter compound is composed of seperate monomeric molecules interacting *via* hydrogen bonds. The ligand molecules are singly deprotonated, their planes make a dihedral angle 68.3°. Four water oxygen atoms coordinate around a Ca(II) ion to eight atoms with a strongly deformed pentagonal bipyramid as the coordination polyhedron. These features indicate the preference of Ca(II) and Ba(II) ions to form similiar complexes with carboxylate ligands. Molecular layers formed by Ca(II) ions bridged by imidazole-4,5-dicarboxylate molecules have been also detected in the structure of another complex with this ligand: $Ca(4,5\text{-}IDA)(H_2O)_2 \cdot H_2O$ [2]. In this case only one fully deprotonated ligand molecule is coordinated to the metal ion *via* its N, O bonding moiety. Both carboxylate groups acting in a bidentate mode are bonded to adjacent Ca(II) ions giving rise to a two dimensional molecular pattern. Only two water oxygen atoms are coordinated to the Ca(II) ion, in contrast to four bonded to the Ba(II) ion in the structure of the title compound, indicating the tendency of Ba(II) ions in aqueous to form environment complexes with enhanced numbers of coordinated water molecules.

Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 285832. 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 Email: teched@chemcrys.cam.ac.uk).

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