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Crystal structure of sodium isosaccharate, $NaC_6H_{11}O_6 \cdot H_2O$

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Abstract—Sodium isosaccharate, $NaC_6H_{11}O_6 \cdot H_2O$ (Na-ISA), has been synthesized, and its crystal structure solved by single-crystal X-ray diffraction methods. Na-ISA crystallizes in the monoclinic space group $P2_1$ (#4) with cell parameters $a = 9.2267(11)$ Å, $b = 5.0765(6)$ Å, $c = 9.7435(11)$ Å, $\beta = 103.304(2)°$, $V = 444.13(9)$ Å^3, $Z = 2$. The structure was refined by full-matrix least-squares on F^2 yielding final R-values (all data) $R1 = 0.0361$ and $R_w2 = 0.0935$.

The structure of Na-ISA consists of $(C_6H_{11}O_6)^-$ anions arranged in layers parallel to the *bc* plane. An extended network of O–H···O hydrogen bonds links the $(ISA)^-$ anions and the crystal water molecules. Each sodium atom is coordinated by four oxygen atoms belonging to four different $(ISA)^-$ anions and by one water molecule. The resulting NaO_5 polyhedra are linked by sharing common corners in zig-zag chains running parallel to the *b*-axis.

Keywords: Crystal structure; Single crystal; Sodium isosaccharate; Isosaccharinic acid

1. Introduction

Isosaccharinic acid, $C_6H_{12}O_6$ (ISA), and its derivative salts are one of the main products of cellulose degradation.[1] Although these compounds have been isolated and known for more than a century, very limited information exists about their crystal structures, physical properties, and chemical reactivities.[2–5] Recently there has been increased interest in the synthesis and characterization of ISA derivatives based on the potential for practical application of these materials in the area of nuclear waste treatment and disposal sites management. It has been demonstrated that the presence of ISA and/or its derivatives strongly affects the migration of radionuclides. Several recent studies have centered on determining the effect of ISA complexation on radionuclide solubility and sorptive properties, particularly focusing on actinides in the (+4) oxidation state. As a result, Na-ISA has been proposed as a component of decontamination formulations for actinide-contaminated surfaces.[6] It has also been shown that ISA enhances Np(IV) and Th(IV) solubility in water by several orders of magnitude by way of forming Np(IV) hydroxyl isosaccharinate complexes $M(OH)_3$ ISA and $M(OH)_2$ISA (M = Np, Th).[7,8] A significant ISA effect on the reduction and sorption of Th and Pu by concrete surfaces have been recently reported.[9] These studies clearly indicate the necessity of further and deeper study of the ISA derivatives.

To date the crystal structures of only two isosaccharates, Ca-ISA and Sr-ISA, have been determined by X-ray diffraction (XRD) methods.[4,5] The two compounds are isostructural and crystallize in the non-centrosymmetric orthorhombic space group $P2_12_12$ with closely related cell parameters ($a = 20.040$ Å, $b = 6.909$ Å, and $c = 5.738$ Å for Sr-ISA).[5] In both compounds, the divalent Ca^{2+} and Sr^{2+} cations are coordinated in distorted Archimedean antiprisms by eight oxygen atoms belonging to four different ISA molecules. In turn this fact illustrates the potential of ISA to act as a bidentate ligand in complexation processes with different metal species.

In this paper, we report the crystal structure of Na-ISA. The main crystallographic features of Na-ISA are discussed and compared to those of Ca-ISA and Sr-ISA.

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2. Experimental

2.1. Materials

All chemicals used were of analytical grade (Fisher Chemical Co.). All solutions were prepared using deionized water from a Barnstead Nanopure Water Purification System.

2.2. Preparation of Na-ISA

Ca-ISA was prepared using the method developed by Whistler and BeMiller[10] through the hydrolysis of α-lactose by $Ca(OH)_2$. The Ca-ISA was purified by dissolutions in 1 M HCl followed by pH adjustment to 6.0 using NaOH and precipitation of Ca-ISA with $CaCl_2$. Na-ISA was prepared by converting purified Ca-ISA using Na → Ca ion exchange in a procedure similar to that reported by Glaus et al.[11] In a typical reaction 10 g Ca-ISA were mixed with 100 g of the sodium form of Chelex ion-exchange resin. The mixture was stirred overnight using a rotary shaker and filtered through 0.5-μm filter paper. XRD-pure crystalline Na-ISA was isolated by slow evaporation of the remaining solution in a vacuum oven set at 40 °C for 48 h. Large Na-ISA crystals suitable for single-crystal X-ray analysis were grown by slow evaporation of concentrated Na-ISA water solution at 60 °C in air.

2.3. Physical measurements

The purity of Ca- and Na-ISA was monitored mainly by powder XRD using a Bruker D8 Advance instrument with monochromatized Cu K_α radiation. The observed low-speed scan XRD patterns of the starting Ca-ISA perfectly matched those reported by Rai and co-workers,[2] and no impurity phases including CaO, $Ca(OH)_2$, and/or $CaCO_3$ were detected within the methods limitations (2–3%). All lines in the powder XRD pattern of the Na-ISA product were indexed using the structural model and cell parameters described below, and no impurity phases have been detected. The powder XRD patterns of the starting Ca-ISA and the Na-ISA product are compared in Figure 1.

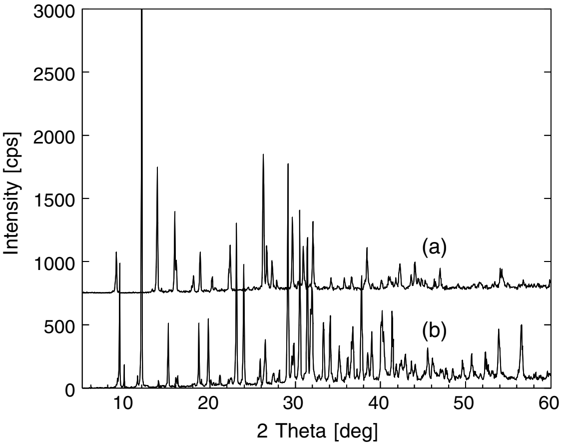

Figure 1. Powder XRD patterns of Ca-ISA (a) and the Na-ISA product (b).

For the structure determination, a colorless polyhedral Na-ISA crystal of approximate dimensions $0.17 \times 0.12 \times 0.09\ mm^3$ was mounted on a SIEMENS SMART X-ray diffractometer with a 1K CCD area detector. Data were collected at room temperature using graphite-monochromatized Mo K_α radiation ($\lambda = 0.71073$ Å). A hemisphere of data (1271 frames at a 5-cm detector distance) was collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 30 s/frame. The first 50 frames were measured again at the end of the data collection to monitor instrument and crystal stability. The data were integrated using the Siemens SAINT program.[12] The program SADABS was used for the absorption correction.[13] The structure was solved by direct methods and refined by full-matrix least-squares techniques with the SHELX97 software package.[14] A total of 3739 reflections ($R_{int} = 0.016$) of which 2342 independent were collected within the range $2.15° < \theta < 30.00°$ ($-9 \leqslant h \leqslant 12$; $-7 \leqslant k \leqslant 7$; $-13 \leqslant l \leqslant 12$). The final cycle of refinement performed on F_o^2 converged at $R_w = 0.093$ and $R = 0.036$ based on $F_o^2 > 2\sigma(F_o^2)$. The main crystallographic details are summarized in Table 1.

Infrared spectra were recorded on a Perkin–Elmer Spectrum One spectrometer within the range 400–4000 cm^{-1} using the KBr pellet method. The FTIR spectra of Na- and Ca-ISA are compared in Figure 2. The spectra are virtually identical and show the characteristic C–O, C–C, C–H, and O–H vibrations in ISA. The lack of measurable shifts of any of these bands confirms the lack of significant distortions and change of interatomic distances in Na-ISA compared to Ca-ISA.

Upon heating in air Na-ISA begins to lose water at temperatures slightly above ambient and melts incongruently at 85 °C. Upon further heating the melt loses more water, turns solid, and completely decomposes forming carbon and Na_2CO_3, the products identified by powder XRD.

3. Results and discussion

The observed Laue symmetry and reflection conditions ($0k0$; $k = 2n$) were indicative of the monoclinic space groups $P2_1$ (#4) and $P2_1/m$ (#11). No solution was found using a trial model based on the higher symmetry space group $P2_1/m$. On the other hand, the direct methods yielded an initial solution with $R \sim 15\%$ based on $P2_1$, and the refinement was further carried on using this space group model. All nonhydrogen atoms were

Table 1. Crystal data and structure refinement for Na-ISA

Empirical formula	$C_6H_{13}NaO_7$
Formula weight	220.15
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, S.G. $P2_1$ (#4)
Unit cell dimensions	$a = 9.2267(11)$ Å $\alpha = 90°$ $b = 5.0765(6)$ Å $\beta = 103.304(2)°$ $c = 9.7435(11)$ Å $\gamma = 90°$
Volume, Z	444.13(9) Å^3, 2
Calculated density	1.646 g cm^{-3}
Absorption coefficient	0.189 mm^{-1}
$F(000)$	232
Crystal size	0.17×0.12×0.09 mm
θ range for data collection	2.15–30.00°
Limiting indices	$-9 \leqslant h \leqslant 12$, $-7 \leqslant k \leqslant 7$, $-13 \leqslant l \leqslant 12$
Reflections collected/unique	3739/2342 [$R_{(\text{int})} = 0.0161$]
Refinement method	Full-matrix least-squares on F^2
Data/parameters	2342/179
Goodness-of-fit on F^2	1.081
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0359$[a], $R_w2 = 0.0932$[b]
R indices (all data)	$R1 = 0.0361$, $R_w2 = 0.0935$
Largest diff. peak and hole	0.340 and −0.214 e Å^{-3}

[a] $R1 = \sum |F_o| - |F_c| / \sum |F_o|$ (based on reflections with $I > 2\sigma(I)$).

[b] $R_w = \left[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|2\right]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0573P)^2 + 0.09P]$; $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$ (all data).

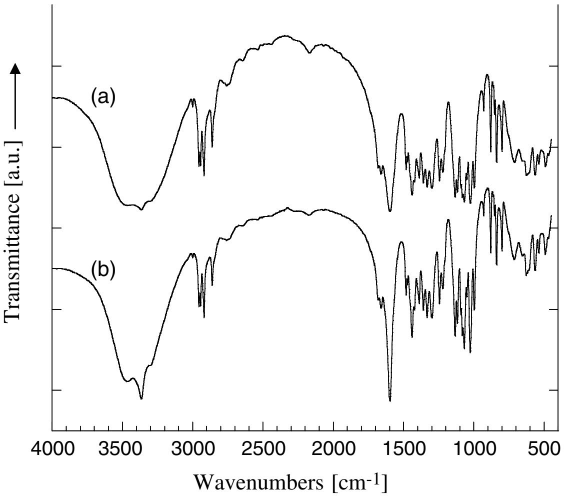

Figure 2. FTIR spectra of Na-ISA (a) and Ca-ISA (b).

located and assigned, and their thermal parameters were refined anisotropically. Hydrogen atoms were located using the difference Fourier map and refined with isotropic thermal parameters. After the refinement converged, a close examination of the solution, as well as a test using the PLATON program, confirmed the lack of possible higher symmetry.[15] Atomic coordinates are listed in Table 2. All the C–C, C–O, and Na–O distances and angles, listed in Table 3, are within the typical ranges for such organic species and are close to those reported for Ca- and Sr-ISA.[4,5]

Table 2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for Na-ISA

Atom	x	y	z	U(eq)[a]
Na	9844(1)	213(1)	6153(1)	12(1)
O_w	161(1)	823(3)	8607(1)	14(1)
O(1)	8012(1)	7982(2)	3575(1)	12(1)
O(2)	1655(1)	7235(2)	5856(1)	11(1)
O(3)	6466(1)	3930(2)	1838(1)	11(1)
O(4)	8488(1)	801(3)	684(1)	13(1)
O(5)	4908(1)	1048(3)	4432(1)	13(1)
O(6)	8251(1)	6715(3)	6396(1)	18(1)
C(1)	7728(2)	389(3)	3371(2)	9(1)
C(2)	6538(2)	1147(3)	2023(2)	9(1)
C(3)	7001(2)	20(3)	733(2)	10(1)
C(4)	4995(2)	15(3)	2031(2)	9(1)
C(5)	4162(2)	1460(3)	2983(2)	9(1)
C(6)	7420(2)	5408(4)	7250(2)	14(1)
H(1)	330(30)	2490(70)	8650(30)	28(7)
H(2)	9540(30)	620(60)	9080(30)	15(6)
H(3)	3020(30)	9600(60)	7470(30)	25(7)
H(4)	8600(30)	2350(70)	870(30)	24(7)
H(5)	4990(40)	2340(70)	4760(40)	33(9)
H(6)	2110(30)	1330(70)	4420(30)	30(7)
H(7)	7020(20)	8200(40)	830(20)	1(4)
H(8)	6330(20)	630(50)	9940(20)	9(5)
H(9)	5130(30)	8100(50)	2310(20)	13(6)
H(10)	4370(30)	10(50)	1090(20)	13(5)
H(11)	4140(20)	3300(40)	2800(20)	3(5)
H(12)	7320(30)	3540(60)	7080(20)	14(6)
H(13)	7940(30)	5700(50)	8220(20)	11(5)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected bond lengths [Å] and angles [deg] for Na-ISA[a]

Na–O(1)	2.3914(14)	Na–O(6)	2.3516(15)
Na–O(2)	2.3203(14)	Na–O_w	2.3614(15)
Na–O(2)	2.3565(13)		
C(1)–O(1)	1.256(2)	C(3)–C(2)–C(1)	108.98(13)
C(1)–O(2)	1.254(2)	C(3)–C(2)–C(4)	107.40(12)
C(2)–O(3)	1.424(2)	C(1)–C(2)–C(4)	112.24(13)
C(3)–O(4)	1.439(2)	C(2)–C(4)–C(5)	114.89(13)
C(5)–O(5)	1.437(2)	C(2)–C(3)–O(4)	111.92(13)
C(6)–O(6)	1.419(2)	O(1)–C(1)–O(2)	125.65(15)
C(1)–C(2)	1.554(2)	O(3)–C(2)–C(1)	110.83(13)
C(2)–C(3)	1.529(2)	O(3)–C(2)–C(4)	110.85(13)
C(2)–C(4)	1.536(2)	O(5)–C(5)–C(6)	108.76(13)
C(4)–C(5)	1.522(2)	O(5)–C(5)–C(4)	109.51(13)
C(5)–C(6)	1.522(2)	O(6)–C(6)–C(5)	112.17(14)

[a] Symmetry transformation used to generate equivalent atoms: $-x, y + \frac{1}{2}, -z$.

The structure of Na-ISA consists of $(C_6H_{11}O_6)^-$, $(ISA)^-$ anions, which are arranged in layers parallel to the *bc* plane. The charge balance is provided by the Na^+ cations, which, together with the water molecules, are located in the space between the organic layers (Fig. 3). A complex bonding provides the 3-D connectivity. An extended network of O–H···O hydrogen bonds links the $(ISA)^-$ anions and the crystal water molecules (Fig. 4a, Table 4; only O···H bonds with $d \leqslant 2.1$ Å have been considered). This hydrogen bonding, however, takes

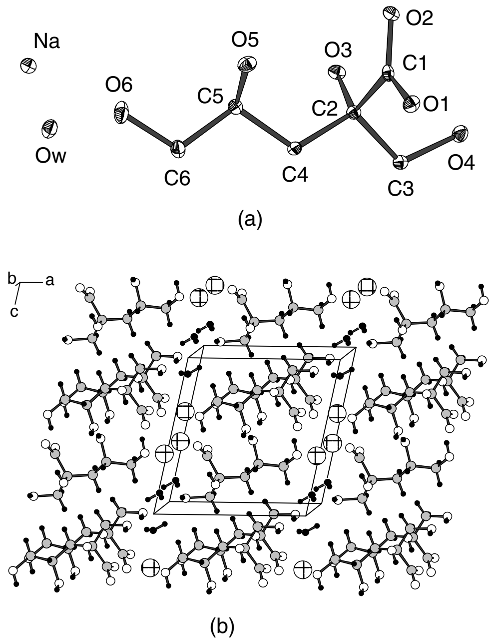

Figure 3. Asymmetric unit, 50% thermal ellipsoids (a) and unit cell and 3-D packing (b) in Na-ISA. The atoms in the structure are drawn as the following circles: sodium (cross-hatched), carbon (filled), oxygen (white), O_{water} (dark hatched), and hydrogen (black).

place only in two dimensions resulting in ISA/H_2O layers parallel to the *ac* plane, Figure 4b.

Each sodium atom is coordinated by four oxygen atoms belonging to four different $(ISA)^-$ anions and by one water molecule with Na–O distances ranging within 2.32–2.39 Å (Table 3, Fig. 5a). The resulting NaO_5 polyhedra are linked by sharing common corners (O(1) oxygen atoms) in zig-zag chains running parallel to the *b*-axis (Fig. 5b). The linkage between the ISA/H_2O layers in a 3-D structure is provided only by $O(1)_{ISA(i)}$–Na–$O(1)_{ISA(ii)}$ bonding.

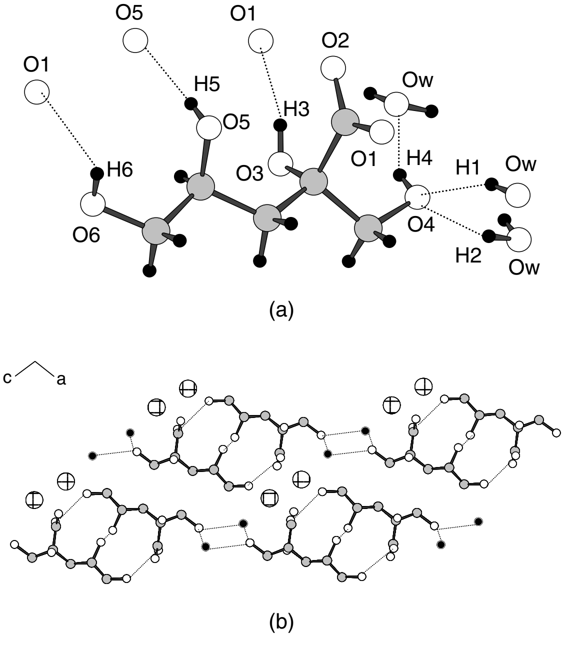

Figure 4. Hydrogen bonds scheme (a) and the resulting ISA/H_2O layers (b) in Na-ISA. The atoms in the structure are drawn as the following circles: sodium (cross-hatched), carbon (filled), oxygen (white), O_{water} (dark hatched), and hydrogen (black). Hydrogen bonds are shown as dotted lines.

Table 4. Hydrogen bonds [Å] in Na-ISA

D–H···A	*d*(D–H)	*d*(H···A)
O_w–H(1)···O(4)	0.86(3)	2.03(3)
O_w–H(2)···O(4)	0.82(3)	2.03(3)
O(3)–H(3)···O(1)	0.81(3)	2.10(3)
O(4)–H(4)···O_w	0.81(3)	2.10(3)
O(5)–H(5)···O(5)	0.72(3)	2.04(3)
O(6)–H(6)···O(1)	0.81(3)	2.06(3)

A careful examination reveals several significant differences between the chemical composition, metal coordination, and overall crystal structures of Ca(Sr)- and Na-ISA. The first difference concerns the chemical composition. Due to the difference in the charge of the cations involved, $Ca(Sr)^{2+}$ versus Na^+, obviously the M^{n+}:$(ISA)^-$ ratio changes from 1:2 in Ca(Sr)-ISA to 1:1 in Na-ISA. Also, there is no water of crystallization in Ca(Sr)-ISA. The second difference concerns the hydrogen bonds and the 3-D connectivity. In Na-ISA O–H···O hydrogen bonds result only in $(ISA)^-$/H_2O layers, the connectivity in the third direction provided by O_{ISA}–Na–O_{ISA} bonding. In Ca(Sr)-ISA there is an O–H···O network expanding in all three directions together with a set of O_{ISA}–Ca/Sr–O_{ISA} bonds. The next main difference concerns the metal coordination. In Na-ISA each sodium atom is coordinated by five oxygen atoms ($4O_{ISA}+1O_w$), while each metal atom in Ca(Sr)-ISA is coordinated by eight oxygen atoms ($8O_{ISA}$). In both Na- and Ca(Sr)-ISA the metal atoms are coordinated by four $(ISA)^-$ species. In Na-ISA, however, each of the four $(ISA)^-$s acts as a monodentate ligand, providing a single Na–O bond (Figs. 5a and 6a), while in Ca(Sr)-ISA each $(ISA)^-$ acts as a bidentate ligand forming two Ca(Sr)–O bonds (Fig. 6b). This change in the M-ISA coordination also affects the ISA configuration. The bidentate mode of Ca(Sr)-ISA coordination is achieved by a rotation of the O(5) oxygen atom from ISA approximately along the C(4)–C(6) axis thus changing the O(5)–C(6)–O(6) angle from 93.01° in Na-ISA to 85.15° in Ca-ISA (Fig. 6). In this way the O(5) oxygen atom moves closer to the Ca-center and provides two similar Ca–O distances of 2.40 (Ca–O(6)) and 2.51 Å (Ca–O(5)), respectively. For comparison, the corresponding Na–O(6) and Na–O(5) distances in Na-ISA (without rotation) are 2.35 and 4.78 Å, respectively (Fig. 6). Finally, all the changes in M-coordination and ISA-configuration inevitably lead to differences in the overall symmetry—the latter decreases from orthorhombic, S.G. $P2_12_12$ in Ca(Sr)-ISA[4,5] to monoclinic, S.G. $P2_1$ in Na-ISA.

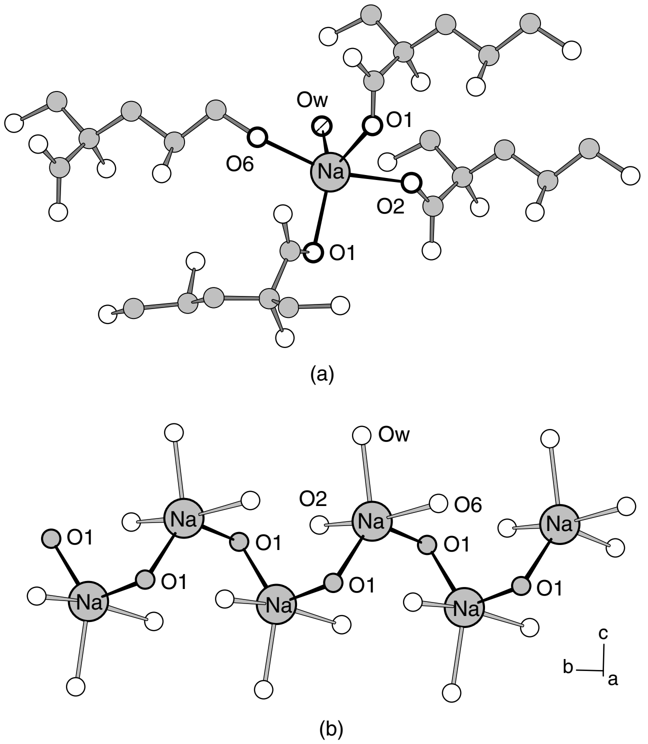

Figure 5. Sodium coordination (a) and the resulting zig-zag [–Na–O(1)–Na–]$_\infty$ chains running along the (0 1 0) direction (b) in Na-ISA.

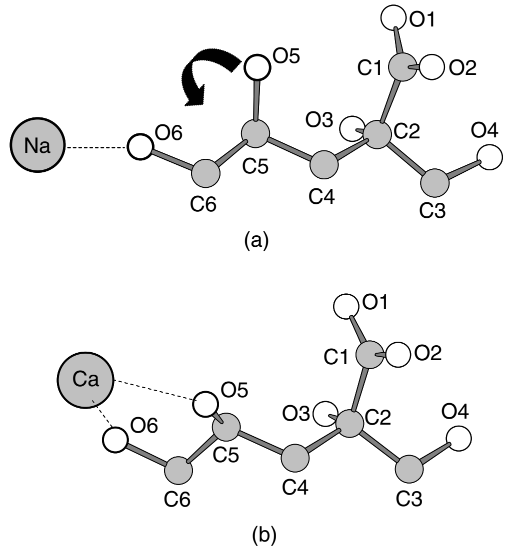

Figure 6. Differences in the M-(ISA) coordination and ISA configuration between Na-ISA (a) and Ca(Sr)-ISA (b).

Virtually all of the above structural differences between Na- and Ca(Sr)-ISA affect the solubility properties. The presence of water of crystallization in Na-ISA, the fact that the water molecules are arranged together with the Na$^+$ cations in separate layers, the weaker coordination of Na compared to Ca and Sr and the presence of a 2-D hydrogen bond network in Na-ISA compared to the 3-D one in Ca(Sr)-ISA are all factors, which should increase the solubility of Na-ISA. Indeed, our studies confirmed this assumption. The solubility experiments are described and discussed in another paper.[16]

4. Supplementary information

Full crystallographic details have been deposited in *cif*-format with the Cambridge Crystallographic Data Centre, CCDC No. 220723. Copies of this information could be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK, Fax: +44-1223-336-033, e-mail: deposit@ccdc.cam.ac.uk, Web: http://www.ccdc.cam.ac.uk/conts/retrieving/html.

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