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Crystal structure of ammonium isosaccharate and aqueous solubility of ammonium and sodium isosaccharates

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Abstract—Ammonium isosaccharate, $C_6H_{15}NO_6{\cdot}H_2O$ (NH_4-ISA), has been synthesized and its crystal structure solved by single-crystal X-ray diffraction methods. NH_4-ISA crystallizes in the monoclinic space group $P2_1$ (#4) with cell parameters $a = 8.6470(12)$ Å, $b = 5.0207(7)$ Å, $c = 9.8193(14)$ Å, $\beta = 91.643(3)°$, $V = 426.12(10)$ Å^3, $Z = 2$. The structure was refined by full-matrix least-squares on F^2 yielding final R-values (all data) $R1 = 0.0485$ and $R_w2 = 0.1104$. The structure consists of alternating $(NH_4)^+$ and $(C_6H_{11}O_6)^-$ layers parallel to the *ab* plane. An extended network of O–H···O intermolecular (ISA)···(ISA) hydrogen bonds links the $(ISA)^-$ anions within the *ab* plane, while the 3-D connectivity along the *c*-axis is provided only by $(ISA^-){\cdots}(NH_4^+){\cdots}(ISA^-)$ hydrogen bonds. The aqueous solubility (S_i, $[M\,L^{-1}]$) of NH_4- and Na-ISA has been shown to be pH independent at ambient conditions within the range $4.5 < pH < 10$ with $S_{NH_4\text{-ISA}} = 4.035$ and $S_{Na\text{-ISA}} = 1.731$, respectively, which values are about two orders of magnitude higher than that of the Ca-ISA analogue.

Keywords: Crystal structure; Single crystal; Isosaccharate; Isosaccharinic acid; Aqueous solubility

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1. Introduction

Isosaccharinic acid, $C_6H_{12}O_6$ (ISA), and some of its derivative salts (A-ISAs) have been isolated and known for more than a century as part of the main products of cellulose degradation.[1] Recently there has been an increased interest in these compounds since it has been demonstrated that the presence of ISA and/or its derivatives strongly affects the migration of radionuclides. For example, it has been shown that ISA enhances Np(IV) and Th(IV) solubility in water by several orders of magnitude and has a significant effect on the reduction and sorption of Th and Pu by concrete surfaces.[2–4] Consequently, Na-ISA has been proposed as a key component in formulations for actinides-sorbed surfaces decontamination.[5]

In spite the increased practical interest in ISA and its derivatives, the detailed knowledge of their crystal structures, physical properties and chemical reactivities is still relatively limited.[6–10] To date the crystal structures of only three isosaccharates, Ca-, Sr- and Na-ISA, have been accurately determined by X-ray diffraction (XRD) methods.[8,9,11]

This paper is a continuation of our ongoing program for studies of highly soluble biodegradable carbohydrate (sugar) derivatives with high complexating affinity towards actinides in high oxidation states. Here we report the crystal structure of a new member of the ISA-family, NH_4-ISA, together with the results of our experimental studies on the aqueous solubility of NH_4- and Na-ISA as a function of pH.

2. Experimental

2.1. Materials

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

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2.2. Synthesis

NH_4-ISA was prepared using a simple and fast method developed in our Lab. It is essentially based on the very low water solubility of calcium oxalate ($1.78 \times 10^{-9}\,\mathrm{M\,L^{-1}}$ at 18 °C)[12] compared to that of Ca-ISA ($1 \times 10^{-2}\,\mathrm{M\,L^{-1}}$)[6,7] and NH_4-ISA ($4.0\,\mathrm{M\,L^{-1}}$, see further in the text) and could be described by the following reaction:

$$[(NH_4)_2C_2O_4]_{sln} + [Ca(C_6H_{11}O_6)_2]_{sln} \rightarrow (CaC_2O_4) \cdot H_2O_{solid} + [2NH_4(C_6H_{11}O_6)]_{sln}$$

In a typical preparation 8 g of purified Ca-ISA (synthesized as previously described)[11,13] were dissolved in 2 L of DI water upon heating at 60 °C. A solution of 2.85 g of $(NH_4)_2C_2O_4$ in 100 mL of DI water was slowly added with stirring, resulting in the immediate precipitation of CaC_2O_4 precipitate. The flask was left overnight in a refrigerator to ensure the highest degree of precipitation of CaC_2O_4. After filtering the CaC_2O_4 residue, the filtrate was evaporated at diminished pressure and temperature in a freeze-dry unit until a well-crystallized, off-white powder formed at the bottom of the flask. Powder XRD analysis of the product did not show any traces of the starting Ca-ISA or any other impurity phases. Single crystals of NH_4-ISA large enough for single-crystal X-ray analysis were grown by slow evaporation of concentrated Na-ISA water solution at room temperature and pressure.

The same procedure was also successfully applied for the synthesis of Na-ISA used for the solubility measurements.

2.3. Physical measurements

The purity of the Ca-, Na- and NH_4-ISA was routinely monitored by powder X-ray diffraction (XRD) using a Bruker D8 Advance instrument with monochromatized Cu Kα radiation. All lines in the powder XRD pattern of the new NH_4-ISA derivative were indexed using the structural model and cell parameters described below, and no impurity phases have been detected. A typical powder XRD pattern is shown in Figure 1.

Infrared spectra were recorded on a Perkin–Elmer Spectrum One spectrometer within the range of 400–4000 $\mathrm{cm^{-1}}$ using the KBr pellet method. The FTIR spectrum of NH_4-ISA exhibiting the typical C–O, C–C, C–H and O–H vibrations in ISA, together with the characteristic NH_4-band at ca. 1400 $\mathrm{cm^{-1}}$, is shown in Figure 2.[11,14] As expected, considering the related crystal structures and overall symmetry of Na- and NH_4-ISA, their spectra (except for the strong NH_4-band in the latter) are virtually identical.[11] The lack of significant shifts of any of the characteristic bands confirms the lack of major distortions and change of coordination and conformation of the $(ISA)^-$ fragments.

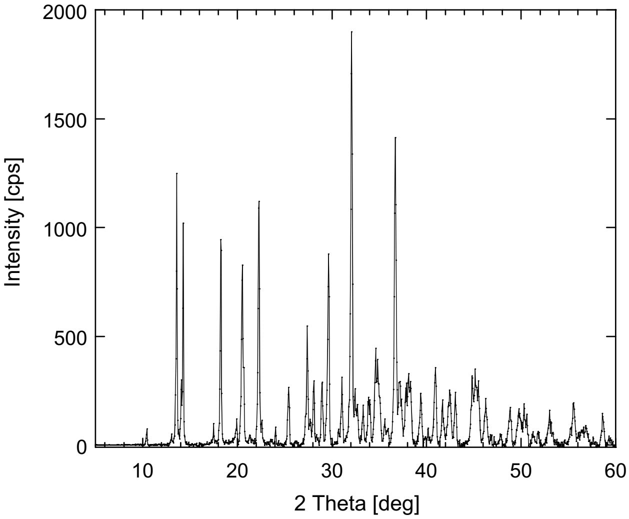

Figure 1. Powder XRD pattern of NH_4-ISA.

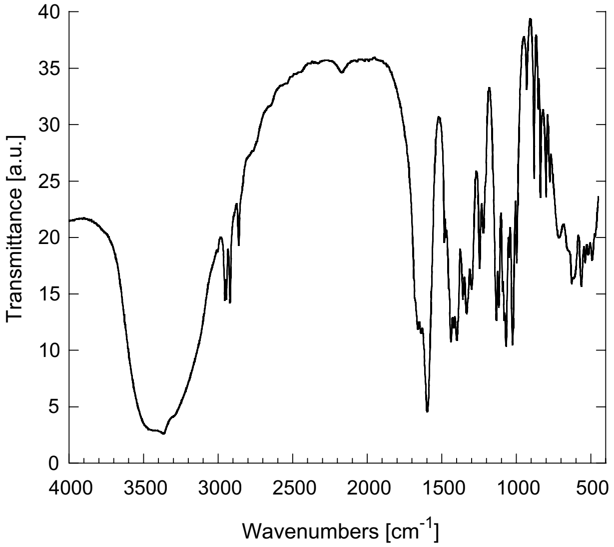

Figure 2. FTIR spectrum of NH_4-ISA.

2.4. Structure determination

A colourless polyhedral NH_4-ISA crystal was mounted on a SIEMENS SMART X-ray diffractometer with a 1 K CCD area detector. Data were collected at room temperature using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). A hemisphere of data (1271 frames at 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 data were integrated using the Siemens SAINT program.[15] The program SADABS was used for the absorption correction.[16] The structure was solved by direct methods and refined by full-matrix least-squares techniques with the SHELX97 software package.[17] The main crystallographic details are summarized in Table 1.

Table 1. Crystal data and structure refinement for NH_4-ISA

Empirical formula	$C_6H_{15}NO_6$
Formula weight	197.19
Temperature	293(2) K
Wavelength	0.71073
Crystal system, space group	Monoclinic, S.G. $P2_1$ (#4)
Unit cell dimensions	$a = 8.6470(12)$ Å $\alpha = 90°$ $b = 5.0207(7)$ Å $\beta = 91.643(3)°$ $c = 9.8193(14)$ Å $\gamma = 90°$
Volume, Z	426.12(10) Å^3, 2
Calculated density	1.537 g cm^{-3}
Absorption coefficient	0.138 mm^{-1}
$F(000)$	212
Crystal size	0.33 × 0.22 × 0.19 mm
θ Range for data collection	2.07°–29.95°
Limiting indices	$-12 \leqslant h \leqslant 12$, $-7 \leqslant k \leqslant 7$, $-13 \leqslant l \leqslant 13$
Reflections collected/unique	4832/2414 [R(int) = 0.0448]
Refinement method	Full-matrix least-squares on F^2
Data/parameters	2414/179
Goodness-of-fit on F^2	0.981
Final R indices [$I > 2\sigma(I)$]	$^aR1 = 0.0465$, $^bR_w2 = 0.1090$
R indices (all data)	$R1 = 0.0485$, $R_w2 = 0.1104$
Largest diff. peak and hole	0.457 and −0.233 e Å^{-3}

[a] $R1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$ (based on reflections with $I > 2\sigma(I)$).

[b] $R_w = [\Sigma w(|F_0| - |F_0|)^2/\Sigma w|F_0|2]^{1/2}$; $w = 1/[\sigma^2(F_0^2) + (0.0640P)^2]$.

$P = [\mathrm{Max}(F_0^2, 0) + 2F_c^2]/3$ (all data).

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). Since the structure of Na-ISA was refined successfully using the low-symmetry model, our refinement was attempted in the same space group, $P2_1$ (#4). Initially all non-hydrogen atoms were located and assigned, and their thermal parameters were refined anisotropically. Next, all hydrogen atoms were located directly from 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.[18] All atomic coordinates and isotropic thermal parameters are listed in Table 2.

2.5. Water solubility

Solubility measurements were carried out within the range $4.5 < \mathrm{pH} < 10$. The samples were prepared as follows: 5 g of each NH_4- and Na-ISA were mixed with 3 mL DI water in capped test tubes. The pH was adjusted by adding NH_4OH, NaOH and/or HCl, and the samples were left to equilibrate for two weeks at room temperature. After filtration of the liquid, 1.00 mL of each saturated solution was transferred to a small aluminium tray, weighed and let to dry at 30 °C for another week. The dried products were weighed again, and the molar solubility was calculated based on the weight difference between the saturated solutions and the dried products. Powder XRD and FTIR analyses confirmed that all dried samples correspond to well-crystallized NH_4- and Na-ISA. Two control samples of both the NH_4- and Na- series at pH 7 were processed in the same way after equilibrating for four weeks. The results matched perfectly the linear fits of the water solubilities of the two-week equilibrated series.

Table 2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for NH_4-ISA

Atom	x	y	z	U(eq)
C(1)	1660(2)	19(3)	2800(2)	10(1)
C(2)	3216(2)	768(3)	2174(2)	9(1)
C(3)	4523(2)	−540(3)	3024(2)	12(1)
C(4)	3325(2)	−258(4)	710(2)	10(1)
C(5)	2301(2)	1199(3)	−334(2)	10(1)
C(6)	2448(2)	−111(4)	−1718(2)	13(1)
O(1)	939(2)	1861(2)	3371(1)	14(1)
O(2)	1272(1)	−2389(2)	2732(1)	12(1)
O(3)	3473(2)	3564(2)	2228(1)	13(1)
O(4)	4424(2)	−65(3)	4464(1)	16(1)
O(5)	725(1)	1081(3)	76(1)	13(1)
O(6)	1778(1)	1399(3)	−2813(1)	16(1)
H(1)	770(30)	1620(50)	−2670(30)	28(6)
H(2)	4380(20)	−100(50)	470(20)	25(5)
H(3)	2620(20)	3040(40)	−400(20)	23(5)
H(4)	4580(30)	1540(50)	4630(20)	23(6)
H(5)	4490(20)	−2280(40)	2947(19)	20(4)
H(6)	5520(20)	150(50)	2690(20)	27(5)
H(7)	3510(20)	−320(40)	−1920(20)	25(5)
H(8)	2000(20)	−2060(50)	−1700(20)	23(5)
H(9)	3040(20)	−2120(50)	700(20)	29(5)
H(10)	2610(30)	4300(50)	2410(20)	28(6)
H(11)	280(40)	2300(90)	10(40)	22(9)
N(1)	8215(2)	810(4)	4544(2)	16(1)
H(12)	7600(30)	2100(80)	4580(30)	24(8)
H(13)	7790(30)	−480(70)	4020(30)	26(8)
H(14)	−800(30)	1260(60)	4190(30)	22(7)
H(15)	8390(40)	160(80)	5470(30)	29(9)

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

3. Results and discussion

3.1. Description of the structure

The structure of NH_4-ISA consists of aligned $(C_6H_{11}O_6)^-$ anions, $(ISA)^-$, which are arranged in slabs parallel to the ab plane. The charge balance is provided by NH_4^+ cations, which are located in layers between the ISA^- slabs (Fig. 3b). The main C–C and C–O distances and angles, listed in Table 3, are virtually identical to those previously reported for Na-ISA.[11]

A complex network of O–H···O hydrogen bonds links the $(ISA)^-$ and NH_4^+ units and provides the 3-D connectivity (Fig. 4, Table 4; only intermolecular O···H bonds with $d \leqslant 2.1$ Å have been considered). Three of the hydrogen atoms of each NH_4^+ (H13, H14, H15) form four N–H···O bonds with four of the oxygen atoms of the ISA^- species (2O1, O2, O6)

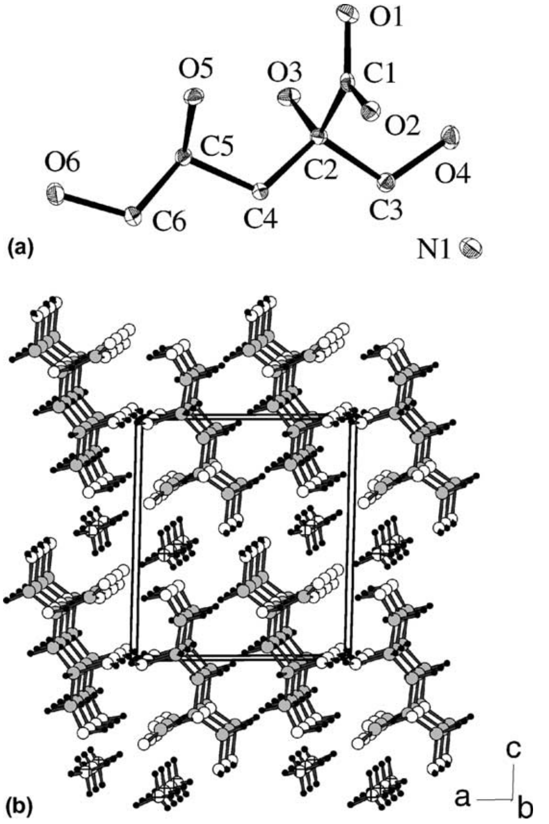

Figure 3. Asymmetric unit, 50% thermal ellipsoids (a) and unit cell and 3-D packing (b) in NH_4-ISA. The atoms in the structure are drawn as the following circles: nitrogen (cross-hatched), carbon (filled), oxygen (white) and hydrogen (black).

Table 3. Selected bond lengths (Å) and angles (deg) for NH_4-ISA

C(1)–O(1)	1.256(2)	C(3)–C(2)–C(1)	108.47(13)
C(1)–O(2)	1.256(2)	C(3)–C(2)–C(4)	107.60(13)
C(2)–O(3)	1.422(2)	C(1)–C(2)–C(4)	111.70(13)
C(3)–O(4)	1.438(2)	C(2)–C(4)–C(5)	114.81(14)
C(5)–O(5)	1.433(2)	C(2)–C(3)–O(4)	113.59(14)
C(6)–O(6)	1.425(2)	O(1)–C(1)–O(2)	126.65(16)
C(1)–C(2)	1.541(2)	O(3)–C(2)–C(1)	111.31(13)
C(2)–C(3)	1.534(2)	O(3)–C(2)–C(4)	110.65(13)
C(2)–C(4)	1.532(2)	O(5)–C(5)–C(6)	109.77(13)
C(4)–C(5)	1.523(2)	O(5)–C(5)–C(4)	109.32(13)
C(5)–C(6)	1.519(2)	O(6)–C(6)–C(5)	113.74(15)
N1–H(12)	0.84(4)	N1–H(14)	0.98(3)
N1–H(13)	0.90(3)	N1–H(15)	0.97(3)
H–N–H vary between 107.3(3)° and 110.1(3)°			

Symmetry transformation used to generate equivalent atoms: $-x$, $y^{+1/2}$, $-z$.

(Fig. 4a, Table 4). The last one, H12, is too far away from the closest oxygen atom and thus does not contribute to the H-bonding network. In each ISA^- anion four of the oxygen atoms (O2, O3, O5, O6) participate in intermolecular (ISA)···(ISA) hydrogen bonds (Fig. 4b, Table 4). Thus, all oxygen atoms of the ISA species except for the terminal O4 (Fig. 3a) contribute to the H-bonding network.

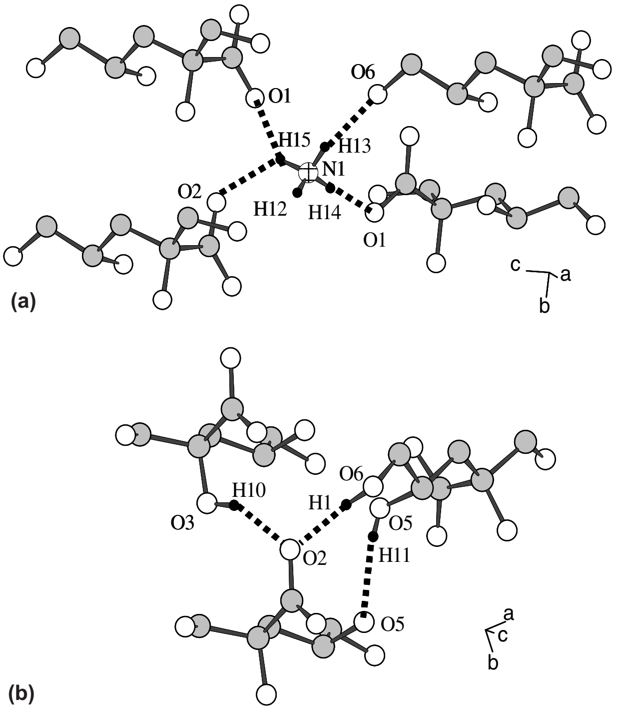

Figure 4. Hydrogen bonds in NH_4-ISA: N–H···O_{ISA} (a) and O_{ISA}–H···O_{ISA} (b). The atoms in the structure are drawn as the following circles: nitrogen (cross-hatched), carbon (filled), oxygen(white) and hydrogen (black). Hydrogen bonds are shown as dotted lines.

Table 4. Hydrogen bonds (Å) in NH_4-ISA

D–H···A	d(D–H)	d(H···A)
N1–H(13)···O(6)	0.90(3)	2.00(3)
N1–H(14)···O(1)	0.98(3)	1.73(3)
N1–H(15)···O(1)	0.97(3)	2.09(3)
N1–H(15)···O(2)	0.97(3)	2.17(3)
O(3)–H(10)···O(2)	0.84(3)	2.07(3)
O(6)–H(1)···O(2)	0.89(3)	1.84(3)
O(5)–H(11)···O(5)	0.72(3)	2.09(3)

In order to better understand the solubility properties of NH_4- and Na-ISA, it is worthwhile to compare their main structural features (Table 1, Ref. 11). Although seemingly very close (same symmetry, space group and similar cell parameters), there are some significant differences in their crystal structures. The first one concerns the asymmetric units and chemical composition. Although NH_4^+ and Na^+ are of the same charge (+1) and fairly close in size, Na-ISA crystallizes with one water molecule per formula unit, while there is no water of crystallization in NH_4-ISA. A comparison of the cell volumes of both unit cells (444.13(9) for Na- and 426.12(10) for NH_4^+-ISA, respectively), shows a difference of 18 Å^3. This volume corresponds very well to a difference of two water molecules per two formula units ($V_{H_2O} \sim 10$ Å^3, $Z = 2$ for both structures) and thus confirms the results of both structure refinements.

The second main difference concerns the overall packing in NH_4- and Na-ISA (Fig. 3, Ref. 11). In Na-ISA there are layers of aligned $(ISA)^-$ species separated by layers of (Na^+/H_2O), both being oriented parallel to the *bc* plane. In NH_4-ISA there is a similar arrangement-$(ISA)^-$ layers separated by (NH_4^+) ones. In this case, however, both layers are parallel to the *ab* plane. Hence, considering the closely related cell parameters, the structure of NH_4-ISA could be formally described as derived from that of Na-ISA by rotating at 90° around the *b*-axis, taking out the water molecules and substituting Na^+ by NH_4^+.

The next structural difference between NH_4- and Na-ISA concerns the direction and dimensionality of the hydrogen bonds. In Na-ISA there are $(ISA)\cdots(H_2O)$ and $(ISA)\cdots(ISA)$ hydrogen bonds resulting only in $[(ISA)^-/H_2O]$ layers parallel to the *ac* plane, the connectivity in the third direction provided by O_{ISA}–Na–O_{ISA} bonding.[11] In NH_4-ISA there is a similar 2-D connectivity provided only by $(ISA)\cdots(ISA)$ hydrogen bonds and resulting in $(ISA)^-$ layers (Figs. 3 and 4b). The connectivity along the third direction is provided by $(ISA^-)\cdots(NH_4^+)\cdots(ISA^-)$ hydrogen bonds (Fig. 4a).

The last structural feature is the (ISA) configuration. Due to the monodentate character of the A-(ISA) bonding (A = NH_4, Na) in both structures, the configuration of the ISA fragments as well as all C–C and C–O distances and O–C–O and O–C–C angles are virtually identical (Table 3, Fig. 3a, Ref. 11). In contrast, when ISA acts as a bidentate ligand coordinating divalent metal cations (Ca^{2+}, Sr^{2+}), the ISA changes its configuration resulting in a rotation of the O5 oxygen atom around the C4–C6 axis and significant shortening of the M–O5 distance.[8,9,11]

3.2. Thermal stability and water solubility

NH_4-ISA is stable and preserves well its crystallinity at ambient conditions. Upon heating in air it melts incongruently at 109–113 °C. Upon further heating the melt rapidly turns into a brown solid and completely decomposes to NH_3, CO_2 and an unidentified mixture of residual organics.

The aqueous solubility of both NH_4- and Na-ISA were determined to be independent of pH over the range of pH 4.5–10. This is illustrated in Figure 5. Linear fits of the solubility (S, $[\mathrm{M\,L^{-1}}]$) of both sets of experimental data yielded the following equations:

$$S_{NH_4\text{-ISA}} = 4.035 - 0.004(\mathrm{pH}); R = 0.99$$

$$S_{Na\text{-ISA}} = 1.731 + 0.012(\mathrm{pH}); R = 0.98$$

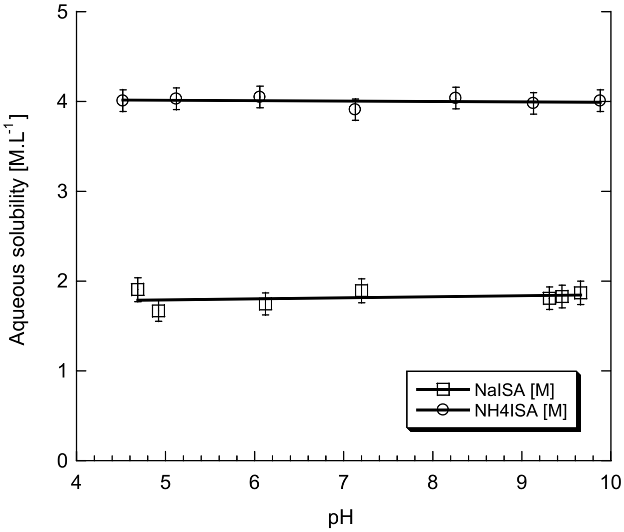

Figure 5. Aqueous solubility of NH_4-ISA and Na-ISA as a function of pH at 20 °C.

The higher water solubility of NH_4-ISA compared to that of Na-ISA can be explained by examining the structural differences between these compounds. The most important difference is the fact that the linkage in the direction perpendicular to the plane of the ISA layers in Na-ISA is provided by O_{ISA}–Na–O_{ISA} coordination bonds, which although relatively weak, are still stronger than the corresponding $O_{ISA}\cdots H$–N–$H\cdots O_{ISA}$ hydrogen bonds in NH_4-ISA. The second difference is the existence of additional $O_{ISA}\cdots H$–O–$H\cdots O_{ISA}$ bonds in Na-ISA besides the O_{ISA}–$H\cdots O_{ISA}$ bonds existing in both structures. These differences result in a lower aqueous solubility of Na-ISA compared to that of NH_4-ISA. Interestingly, the third main structural difference—the presence of water molecules in the structure of Na-ISA—is a factor that generally leads to an increased solubility. Clearly, the observed solubilities of Na- and NH_4-ISA appear as a sum of the above contradictory factors.

Although differing by a factor of 2, both Na- and NH_4-ISA show relatively high water solubility of order of 2 and $4\,\mathrm{M\,L^{-1}}$, respectively. In comparison with the other known ISA derivatives, Ca- and Sr-ISA, Na- and NH_4-ISA are about two orders of magnitude more soluble (e.g., $S_{Ca\text{-ISA}} \sim 1\times10^{-2}\,\mathrm{M\,L^{-1}}$]).[6,7] In turn this shows an excellent potential for the latter compounds to be used as highly soluble sources of complexating agents for radionuclide treatment and containment.

Acknowledgements

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Supplementary data

Full crystallographic details have been deposited in CIF format with the Cambridge Crystallographic Data Centre, CCDC No 245962. 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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