DALTON
FULL PAPER

The structural chemistry of lithium, sodium and potassium anthranilate hydrates†

Frank Wiesbrock and Hubert Schmidbaur*

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

Received 10th September 2002, Accepted 24th October 2002
First published as an Advance Article on the web 13th November 2002

Lithium, sodium and potassium anthranilates (2-aminobenzoates) have been prepared by neutralization of anthranilic acid with the corresponding alkali hydroxides in aqueous solution. Li(Anth) and Na(Anth) crystallize as hemihydrates, K(Anth) as the monohydrate. A single crystal structure determination has shown that Li(Anth)(H_2O)$_{0.5}$ forms a chain structure composed of unique polyhedral compartments with ten-membered ring rims sharing two opposite rectangular faces. The strings are connected *via* hydrogen bonds involving the amino groups which are not part of the inner coordination sphere of the penta-coordinated lithium atoms. By contrast, Na(Anth)(H_2O)$_{0.5}$ has a layer structure with the hexa- and hepta-coordinated sodium atoms O,N-chelated by anthranilate anions and interconnected *via* bridging carboxylate groups and water molecules. Hydrogen bonding contributes to the connectivity within a given sheet with its corrugated double-layer of sodium atoms, but not beyond the layers which are shielded by the arene rings. K(Anth)(H_2O) also forms a sheet structure with a single corrugated layer of seven-coordinated potassium cations O,O-chelated and bridged by the anthranilate anions and by the water molecules. The amino groups have no contact with the metal centres and are involved solely in hydrogen bonding. The hydrocarbon rings extending above and below the sheets show no π–π-stacking and are not indented.

Introduction

Anthranilic acid is an almost ubiquitous constituent of biological systems and a metabolic precursor of important amino acids such as tryptophane.[1] It is also a component of humic acids and serves as a useful model for the coordination chemistry of this complex biopolymer.[2] With the amino group in the 2-position at the aromatic ring, anthranilic acid belongs to the class of β-amino acids that are rare in nature.[3] For this reason the coordination chemistry of β-amino acids is poorly developed and it is only recently that interest in the ligand properties of representative substrates like β-glutamic acid became the subject of thorough analytical, spectroscopic and structural investigations.[4,5]

A first series of investigations focused on the anthranilate complexes of the earth alkaline metals magnesium,[6] calcium, strontium and barium.[7] Of these four elements, magnesium and calcium are among the bulk metals in biological systems and are known to have an extremely complex coordination chemistry with bioligands including in particular amino acids and proteins.[8] By contrast, information of the coordination chemistry of anthranilic acid and the alkali metals is still very limited.[9,10]

Crystalline samples of sodium- or potassium-activated proteins for structure analysis are generally difficult to obtain, and there is no straightforward technique available to directly probe the environment of the two metal nuclei, *e.g.* by [Na^+] and [K^+] NMR or NQR spectroscopy, in solution or in the solid state.[11] The [Na^+]–ATP complex is one of the few examples of alkali metal protein coordination for which the structure has been established.[12] The sodium cation was found to be hexa-coordinated to one nitrogen and five oxygen atoms in a distorted octahedral environment.

For most systems, information on the coordination of alkali metals to amino acids and proteins relies on suitable model systems. Previous studies focused on the α-glutamates and -aspartates[13–18] which are considered the prime binding sites for metals in proteins.

Investigations in the anthranilate series showed that the magnesium bis(anthranilate) crystallized from aqueous solution is in fact a hexaaquo complex with the anthranilate anions excluded from the first coordination sphere of the metal di-cation.[6] It is only for the larger cations of the group (Ca, Sr, Ba) that anthranilate anions are accepted as ligands in an environment with expanded coordination numbers (7 or 8). Nitrogen coordination is observed solely in the barium anthranilate while oxygen coordination prevails in all other examples.[7]

The present account of a systematic study of lithium, sodium and potassium anthranilate complexes gives a first set of fundamental data on the ligand properties of the anthranilate anion towards the biologically most relevant alkali metals.

Experimental

General

All experiments were carried out in bidistilled water and under a nitrogen atmosphere to exclude carbon dioxide. Anthranilic acid (2-aminobenzoic acid) (Acros Organics) and all other reagents are commercially available. Standard equipment was used throughout.

Lithium anthranilate hemihydrate (lithium 2-aminobenzoate hemihydrate)

A suspension of anthranilic acid (2.74 g, 20 mmol) in 20 mL of water is treated with lithium hydroxide (0.48 g, 20 mmol) for 30 min at room temperature. The reaction mixture is then heated to reflux temperature for 15 min and subsequently cooled to 20 °C. For the growth of single crystals, the vessel is

---

† Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagrams in CHIME format. See http://www.rsc.org/suppdata/dt/b2/b208836n/

DOI: 10.1039/b208836n

set aside for four weeks at 20 °C. 1.24 g (41% yield) lithium anthranilate crystallize as the hemihydrate from the mother liquor. Elemental analysis calcd. for $Li(Anth)(H_2O)_{0.5}$ ($C_7H_7LiNO_{2.5}$): C 55.26, H 4.63, N 9.21, Li 4.56; found: C 58.74, H 4.28, N 9.79, Li 4.50%. IR (KBr, cm^{-1}): 3382, s, ν_{asym}(N–H); 3268, s, ν_{sym}(N–H); 1612, s, ν_{asym}(C–O), δ(N–H); 1565, s, ν(C=C); 1522, s, ν(C=C); 1448, s, ν(C=C); 1400, s, ν_{sym}(C–O); 1318, m, ν(C–N); 1237, m, δ(=C–H); 1165, m, δ(=C–H); 1033, w, δ(=C–H); 851, m, γ(=C–H); 795, m, γ(=C–H); 746, s, γ(=C–H); 668, m, γ(N–H); 536, m, $r(CO_2)$.

Sodium anthranilate hemihydrate

Anthranilic acid (2.74 g, 20 mmol) is dissolved in an aqueous solution (20 mL) of sodium hydroxide (0.80 g, 20 mmol) at room temperature. The solution is stirred for 30 min and then set aside for crystallization. After four weeks, pale yellow crystals of the hemihydrate are collected, 1.21 g (36% yield). Elemental analysis calcd. for $Na(Anth)(H_2O)_{0.5}$ ($C_7H_7NNaO_{2.50}$): C 50.01, H 4.20, N 8.33, Na 13.68; found: C 50.06, H 4.23, N 8.37, Na 13.50%. IR (KBr, cm^{-1}): 3500–3300, s, ν_{asym}(N–H), ν_{sym}(N–H); 1610, s, ν_{asym}(C–O), δ(N–H); 1576, s, ν(C=C); 1534, s, ν(C=C); 1446, s, ν(C=C); 1392, s, ν_{sym}(C–O); 1322, s, ν(C–N); 1246, s, δ(=C–H); 1152, s, δ(=C–H); 1030, m, δ(=C–H); 863, m, γ(=C–H); 824, s, γ(=C–H); 752, s, γ(=C–H); 664, m, γ(N–H); 537, m, $r(CO_2)$.

Potassium anthranilate monohydrate

A suspension of potassium hydroxide (1.12 g, 20 mmol) and anthranilic acid (2.74 g, 20 mmol) in 20 mL of bidistilled water is stirred at room temperature for 15 min. The solution obtained is set aside for four weeks. 0.76 g (20% yield) of single crystals are obtained. Elemental analysis calcd. for $K(Anth)(H_2O)$ ($C_7H_8KNO_3$): C 43.51, H 4.17, N 7.25, K 20.23; found: C 48.24, H 4.15, N 8.04, K 18.90%. IR (KBr, cm^{-1}): 3430, s, ν_{asym}(N–H); 3326, s, ν_{sym}(N–H); 1612, s, ν_{asym}(C–O), δ(N–H); 1565, s, ν(C=C); 1524, s, ν(C=C); 1447, s, ν(C=C); 1391, s, ν_{sym}(C–O); 1315, s, ν(C–N); 1251, s, δ(=C–H); 1150, s, δ(=C–H); 1028, w, δ(=C–H); 860, m, γ(=C–H); 807, m, γ(=C–H); 757, s, γ(=C–H); 676, s, γ(N–H); 517, s, $r(CO_2)$.

Single crystal X-ray diffraction analysis

The crystalline samples were placed in an inert oil, mounted on a glass pin and transferred to the cold gas stream of the diffractometer. Crystal data were collected and integrated with an Enraf-Nonius DIP-2020 image plate system (Silicon Graphics O2-workstation) with monochromated Mo-K_α (λ = 0.71073 Å) radiation at −130 °C. The structures were solved by direct methods using SHELXS-97[19a] and refined by full-matrix least-squares calculations on F^2 with SHELXL-97.[19b] Non-H-atoms were refined with anisotropic thermal parameters. H-Atoms were located and refined with isotropic contributions; for lithium anthranilate, O–H-distances of the water molecule were restrained to the values found before refinement. An extinction correction was applied for the sodium compound only, extinction coefficient 0.067(8). A summary of the crystal data, experimental details and refinement results is listed in Table 1. For atomic numbering and selected bond lengths and angles, see Figs. 1, 2, 5, 6 and 9.

CCDC reference numbers 193293–193295.

See http://www.rsc.org/suppdata/dt/b2/b208836n/ for crystallographic data in CIF or other electronic format.

Results

The alkali anthranilates can be prepared by neutralization of the alkali hydroxides (MOH) with anthranilic acid (AnthH) in dilute aqueous solution (c = 1.0 mol L^{-1}) at reflux temperature. The products [M(Anth)] crystallize from the reaction mixture on slow cooling to room temperature. After a few weeks the products are obtained as pale yellow single crystals in moderate yield. Complete evaporation of the mother liquor affords additional material of poor crystallinity. Elemental analyses have shown that air-dried samples of lithium and sodium anthranilate are hemihydrates $M(Anth)(H_2O)_{0.5}$ (M = Li, Na) while the potassium salt is a monohydrate $K(Anth)(H_2O)$. This composition was confirmed in the determination of the crystal structures.

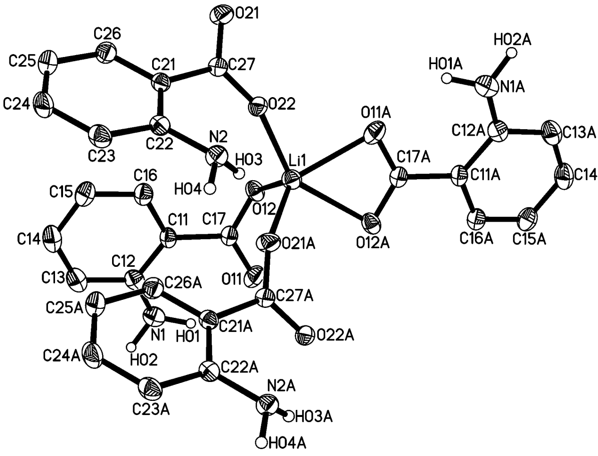

Fig. 1 Coordination sphere of Li1 in $Li(Anth)(H_2O)_{0.5}$ with atomic numbering (ORTEP[19c] drawing with 50% probability ellipsoids). Selected bond lengths [Å], angles [°], and symmetry transformations: Li1–O12 1.976(3), Li1–O22 1.966(3), Li1–O11A^1 2.207(3), Li1–O12A^1 2.266(3), Li1–O21A^2 1.900(3); O11A^1–Li1–O12A^1 58.86(7), O22–Li1–O12 107.10(12), O21A^2–Li1–O22 105.23(12), O21A^2–Li1–O12 108.65(12), O22–Li1–C17 116.35(11); 1 $-x+1, -y+2, -z+1$; 2 $x+1, y, z$.

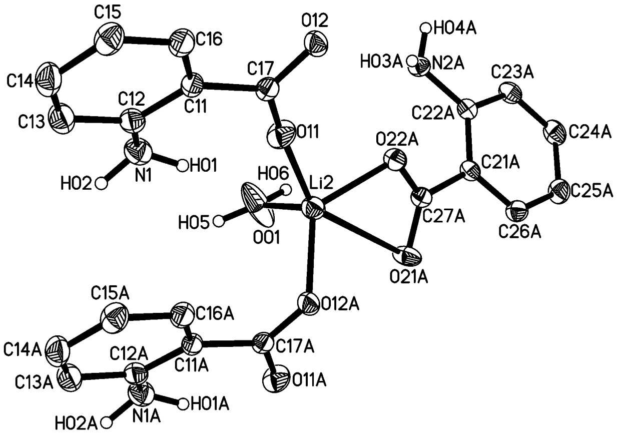

Fig. 2 Coordination sphere of Li2 in $Li(Anth)(H_2O)_{0.5}$ with atomic numbering (ORTEP[19c] drawing with 50% probability ellipsoids). Selected bond lengths [Å], angles [°], and symmetry transformations: Li2–O01 1.924(3), Li2–O11 1.936(3), Li2–O12A^1 1.954(3), Li2–O21A^2 2.673(3), Li2–O22A^2 1.994(3); O22A^2–Li2–O21A^2 54.34(7), O01–Li2–O11 106.51(14), O01–Li2–O12A^1 104.95(13), O11–Li2–O12A^1 118.62(13), O01–Li2–C27A^2 94.16(11); 1 $x+1, y, z$; 2 $-x+1, -y+2, -z+1$.

$$\mathrm{MOH + AnthH} \xrightarrow[\mathrm{H_2O}]{} \mathrm{M(Anth)(H_2O)}_n$$

$$M = \mathrm{Li},\ n = 0.5$$

$$M = \mathrm{Na},\ n = 0.5$$

$$M = \mathrm{K},\ n = 1$$

When air-dried extensively, the crystals of the potassium salt slowly loose water; for the lithium and sodium salts the weight is constant. The compounds are thus not hygroscopic, but redissolve readily in water.

Table 1 Summary of crystal data for lithium anthranilate hemihydrate, sodium anthranilate hemihydrate and potassium anthranilate hydrate

Empirical formula	$C_7H_7LiNO_{2.5}$	$C_7H_7NNaO_{2.5}$	$C_7H_8KNO_3$
Formula weight	152.08	168.13	193.24
T/°C	−130	−130	−130
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	Pc	$P2_1/c$
a/Å	5.2250(1)	15.4990(3)	14.7016(3)
b/Å	9.1650(2)	5.7220(1)	7.6112(1)
c/Å	15.2200(5)	8.1530(1)	7.4325(1)
α/°	75.638(1)	90	90
β/°	87.278(1)	104.340(1)	96.897(1)
γ/°	84.999(2)	90	90
U/Å^3	703.12(3)	700.52(2)	825.65(2)
Z	4	4	4
D_c/Mg m^{-3}	1.437	1.594	1.555
No. of refl. collected	19977	17617	36873
No. of refl. unique	2913	2866	2822
No. of parameters	232	266	141
R_{int}	0.028	0.031	0.033
μ(Mo-K$_\alpha$)/mm^{-1}	0.107	0.172	0.607
$R1$, $wR2$ (all data)	0.0473, 0.1144	0.0313, 0.0815	0.0459, 0.1221
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0434, 0.1112	0.0313, 0.0814	0.0447, 0.1202
ρ/e Å^{-3}	0.391/−0.289	0.286/−0.273	0.314/−0.729

The three title compounds have very different structures not only owing to very different ionic radii of the metal atoms, but also due to different affinities of the carboxylate and amino functions of the ligand.

The structure of lithium anthranilate hemihydrate

Crystals of Li(Anth)$(H_2O)_{0.5}$ are triclinic, space group $P\bar{1}$, with $Z = 4$ formula units and two water molecules in the unit cell. The asymmetric unit contains two crystallographically independent Li(Anth) components and one water molecule. The two lithium atoms feature very different ligand environments. The nitrogen atoms of the amino groups are not involved in coordinative bonding and the lithium atoms are therefore coordinated solely to oxygen atoms (Figs. 1 and 2).

Li1 is penta-coordinated with one carboxylate group chelating the metal [Li1–O11A 2.207(3), Li1–O12A 2.266(3) Å] and the remaining ones attached through only one of their oxygen atoms [Li1–O12 1.976(3), Li1–O21A 1.900(3), Li1–O22 1.966(3) Å]. Li2 is only tetracoordinated by carboxylate, but accommodates the water molecule in its coordination sphere [Li2–O01 1.924(3) Å]. One carboxylate group is chelating in a very unsymmetrical way [Li2–O21A 2.673(3), Li2–O22A 1.994(3) Å] while the other two are monodentate [Li2–O11 1.936(3), Li2–O12A 1.954(3) Å]. The Li–O contacts thus vary within the wide range from 1.900(3) to 2.673(3) Å, with the upper limit represented by very asymmetric chelation (O21A).

All oxygen atoms of the carboxylate groups are in bridging positions between the lithium atoms and give rise to a bulk structure of strings of multihedral compartments sharing rectangular faces [$(Li1)_2(O12)_2$] on opposite sides (Fig. 3). A set of ten quadrilateral faces forms the outer walls of each compartment around a centre of inversion with ten-membered rings representing the top and bottom rims.

The 2-aminophenyl groups and the water molecules are oriented towards the periphery of the strings of compartments and form connections through a set of hydrogen bonds (Fig. 4 and Table 2). Together with O01 of the water molecule the carboxylate oxygen atom O21 and the nitrogen atoms N1 and N2 are also involved. An inspection of the packing shows that there is no discernible π–π-stacking of the phenyl rings.

In summary the crystal structure of Li(Anth)$(H_2O)_{0.5}$ shows a distinct preference of the lithium cation for oxygen over nitrogen coordination. Note that the anthranilate anion would be ideally suited for lithium O,N-chelation in strain-free six-membered rings, but this opportunity is not exploited. It is also interesting to find that the lithium cations readily become penta-coordinated in very irregular geometries (Figs. 1 and 2).

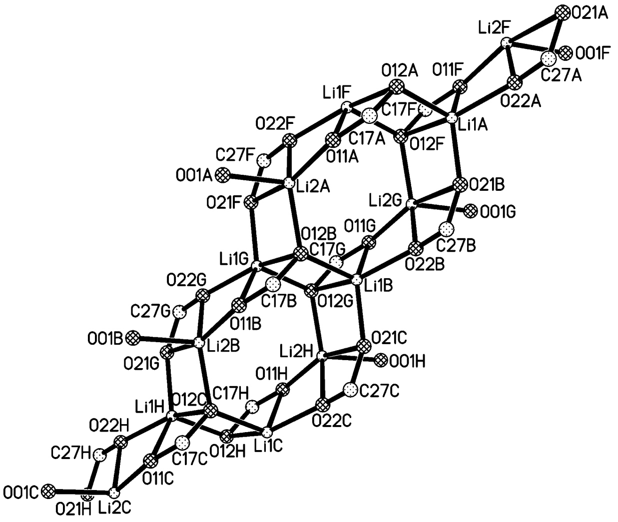

Fig. 3 Formation of compartments in Li(Anth)$(H_2O)_{0.5}$. Phenyl rings and amino groups are omitted for clarity.

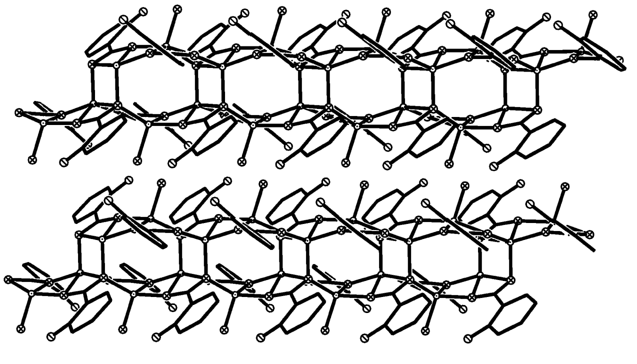

Fig. 4 Arrangement of one chain relative to the other in the crystalline phase of Li(Anth)$(H_2O)_{0.5}$ rendering the formation of hydrogen bonds.

Both observations suggest that the ligand-to-metal bonding in this structure is dictated largely by electrostatic forces. This concept is corroborated by the ease of degradation of the crystal frame-work by solvation as the compound is redissolved in water.

The structure of sodium anthranilate hemihydrate

Crystals of Na(Anth)$(H_2O)_{0.5}$ are monoclinic, space group Pc, with $Z = 4$ formula units and two water molecules in the unit

Table 2 Hydrogen bond lengths [Å] and angles [°]. For atomic numbering, see Figs. 1, 2, 5, 6 and 9

D–H ··· A	d(D–H)	d(H ··· A)	d(D ··· A)	∠(DHA)
Li(Anth)(H_2O)$_{0.5}$				
N(2)–H(03)–O(21)^1	0.92(2)	2.13(2)	2.989(2)	156(2)
N(2)–H(04)–N(1)^2	0.90(2)	2.34(2)	3.198(2)	160(2)
O(01)–H(05)–N(2)^3	0.92(1)	1.85(1)	2.763(2)	173(3)
O(01)–H(06)–O(01)^4	0.92(1)	2.05(6)	2.846(3)	144(9)
Na(Anth)(H_2O)$_{0.5}$				
O(01)–H(01)–O(21)^5	0.82(3)	1.98(3)	2.792(2)	169(3)
O(01)–H(02)–O(11)^6	0.81(4)	1.98(4)	2.783(2)	171(3)
N(1)–H(04)–O(01)^2	0.92(2)	2.44(2)	3.178(2)	138(2)
N(2)–H(06)–O(21)^5	0.90(3)	2.44(3)	3.192(2)	141(2)
K(Anth)(H_2O)				
O(01)–H(01)–O(2)^2	0.92(3)	1.83(3)	2.727(2)	163(2)
O(01)–H(02)–N(1)	0.96(3)	2.13(3)	3.002(2)	150(2)

Symmetry transformations used to generate equivalent atoms: 1 $x + 1, y, z$; 2 $x, y - 1, z$; 3 $x + 1, y + 1, z$; 4 $-x + 2, -y + 3, -z + 1$; 5 $x, y + 1, z$; 6 $x, -y, z + 1/2$.

cell. The asymmetric unit contains two crystallographically independent components Na(Anth) and one water molecule. The two sodium atoms Na1 and Na2 have coordination numbers 6 and 7, respectively, with rather irregular coordination geometries (Figs. 5 and 6). Contrary to the situation with the lithium analogue (above), the nitrogen atoms of the ligands are involved in sodium coordination, and each sodium atom is N,O-chelated by an anthranilate anion. The water molecule (with its oxygen atom O01) is in a bridging position between the two metal cations.

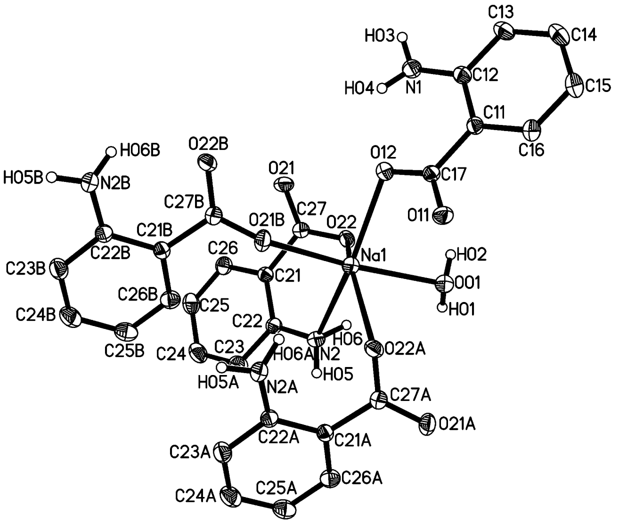

Fig. 5 Coordination sphere of Na1 in Na(Anth)(H_2O)$_{0.5}$ with atomic numbering (ORTEP[19c] drawing with 50% probability ellipsoids). Selected bond lengths [Å], angles [°], and symmetry transformations: Na1–O01 2.417(1), Na1–O12 2.401(1), Na1–O22 2.466(1), Na1–N2 2.666(1), Na1–O21B^1 2.346(1), Na1–O22A^2 2.489(1); O22–Na1–N2 63.69(4), O21B^1–Na1–O22A^2 96.82(4), O(12)–Na1–O01 84.65(4); 1 $x, -y - 1, z - 1/2$; 2 $x, -y, z - 1/2$.

In addition to the N2,O22-chelating anthranilate ligand and the bridging water molecule (O01), six-coordinated Na1 entertains contacts with carboxylate oxygen atoms of three other anions (O12, O22A and O21B). These anions are also in bridging positions between metal cations as shown in Fig. 7 for a one-dimensional series of metal atoms. The Na–O distances (including those of Na2) cover the range from 2.401(1) to 2.895(1) Å, and the two Na–N distances fall in the same region: 2.666(1) and 2.782(1) Å.

Seven-coordinated Na2 has N1,O12- and O21,O22-chelating ligands, the bridging water molecule and two further contacts with carboxylate oxygen atoms (O12A, O11B) of two other anthranilate anions which form bridges to neighbouring units. The mode of connectivity leads to corrugated double-layers of

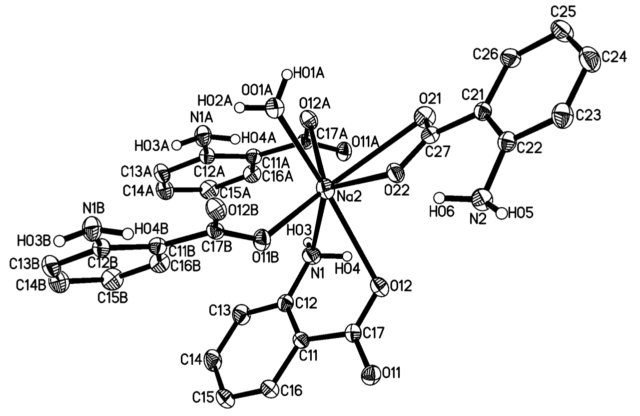

Fig. 6 Coordination sphere of Na2 in Na(Anth)(H_2O)$_{0.5}$ with atomic numbering (ORTEP[19c] drawing with 50% probability ellipsoids). Selected bond lengths [Å], angles [°], and symmetry transformations: Na2–O01A^1 2.511(1), Na2–N1 2.782(1), Na2–O12 2.686(1), Na2–O21 2.895(1), Na2–O22 2.382(1), Na2–O12A^2 2.468(1), Na2–O11B^1 2.284(1); N1–Na2–O12 58.63(4), O21–Na2–O22 48.75(3), O11B^1–Na2–O01A^1 78.30(4), O12A^2–Na2–O01A^1 75.76(4), O11B^1–Na2–O12A^2 130.49(4); 1 $x, -y, z + 1/2$; 2 $x, -y - 1, z + 1/2$.

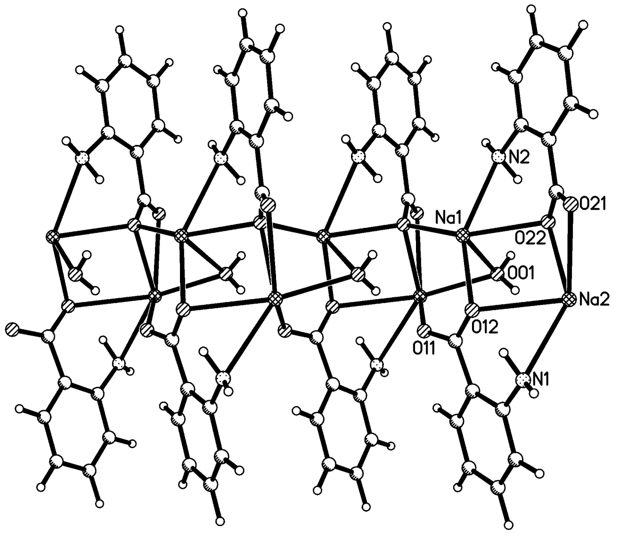

Fig. 7 Section through a layer in crystalline Na(Anth)(H_2O)$_{0.5}$.

sodium atoms bridged by the anthranilate units and water molecules. The inner region of the double layers has corner- and edge-sharing four-membered rings complemented by the six-membered rings arising from the N,O-chelation of each metal cation (Fig. 8).

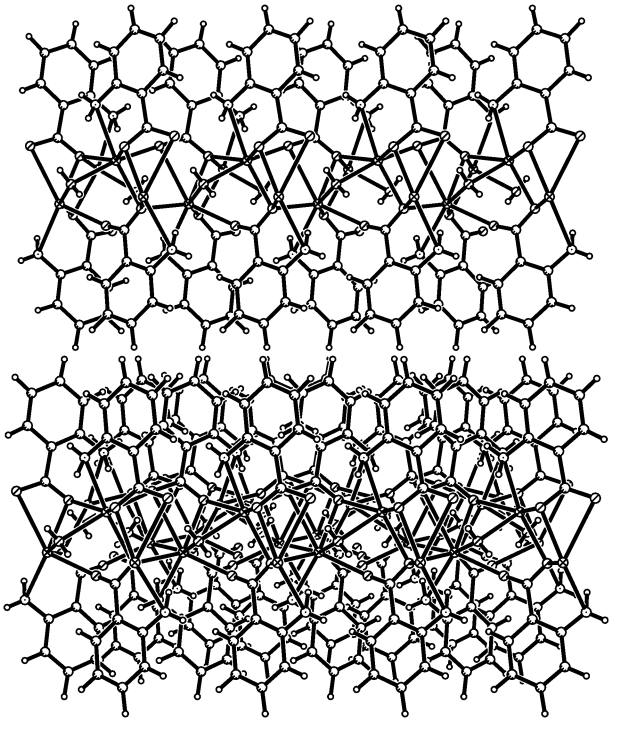

Fig. 8 Cell plot of Na(Anth)$(H_2O)_{0.5}$ showing the formation of hydrophobic layers separating the hydrophilic layers.

Above and below these sheets the anthranilate rings reach out to form a surface consisting solely of hydrocarbon units as a cover for the polar core system. Therefore there are no hydrogen-bonding contacts between the layers. Note that the two sides of a given double-layer are crystallographically non-equivalent.

Hydrogen bonds involving the amino groups, the water molecules and a selection of carboxylate oxygen atoms are contributing to the framework of the double layers (Table 2). These hydrogen bonds are not shown in the figures for clarity. Above and below the layers neighbouring phenyl rings are far apart and strongly tilted against each other which rules out any significant contributions from π–π-stacking. Neighbouring layers are not indented.

In summary, the crystal structure of Na(Anth)$(H_2O)_{0.5}$ differs significantly from the structure of its lithium analogue by the accommodation of the amino group in the inner coordination sphere of the metal. Anthranilate anions are found to chelate sodium cations, but not lithium cations. The preference for oxygen over nitrogen is not very pronounced as shown by comparable distances Na–O/Na–N. The larger radius of sodium leads to an increase in coordination number and thus also to a two-directional connectivity to give corrugated double-layers instead of strings of compact units. Owing to the orientation of the amino groups towards the sodium atoms the layers of the sodium compound are covered by the non-polar ends of the ligand which leave no functionality for inter-layer hydrogen bonding, while hydrogen-bonding has been shown to be a significant principle of connectivity between the strings of the lithium compound.

The crystal structure of potassium anthranilate hydrate

Crystals of K(Anth)(H_2O) are monoclinic, space group $P2_1/c$, with $Z = 4$ formula units and four water molecules in the unit cell. The asymmetric unit comprises one potassium cation, one anthranilate anion and one water molecule. Each potassium cation is seven-coordinated with one O,O-chelating and three O-monodentate anthranilate anions and two water molecules (Fig. 9). Like the anthranilate anions, these water molecules are in bridging positions between potassium cations. The connectivity pattern leads to a layer structure in which a corrugated sheet of potassium cations is connected solely *via* the oxygen atoms (Fig. 10). The K–O distances are in the range from 2.698(1) to 2.904(1) Å.

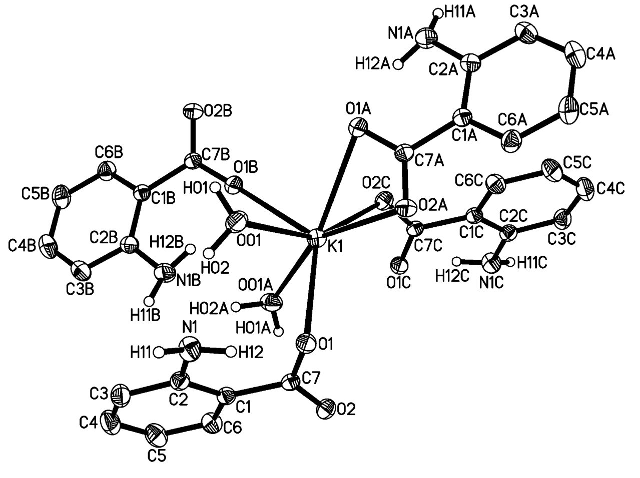

Fig. 9 Coordination sphere of K1 in K(Anth)$(H_2O)_{0.5}$ with atomic numbering (ORTEP[19c] drawing with 50% probability ellipsoids). Selected bond lengths [Å], angles [°], and symmetry transformations: K1–O01 2.755(1), K1–O1 2.896(1), K1–O1A^1 2.904(1), K1–O2A^1 2.755(1), K1–O01A^2 2.876(1), K1–O1B^2 2.713(1), K1–O2C^3 2.689(1); O1A^1–K1–O2A^1 46.28(3), O01–K1–O01A^2 112.28(4), O01–K1–O1 67.16(3), O01A^2–K1–O1B^2 68.01(3); 1 $-x + 1, y - 1/2, -z + 1/2$; 2 $x, -y + 3, z + 1/2$; 3 $-x + 1, -y + 2, -z + 1$.

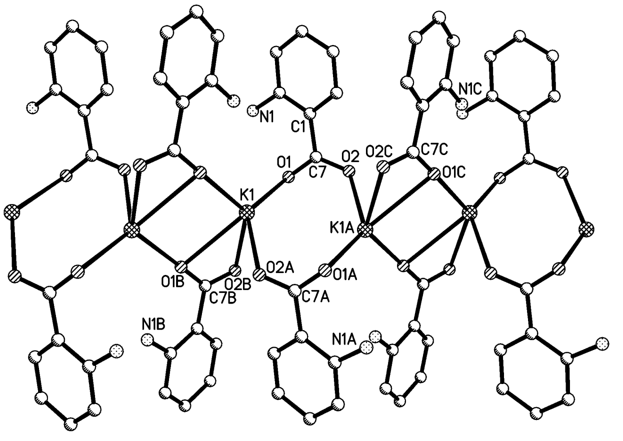

Fig. 10 Section through a layer in crystalline K(Anth)(H_2O).

In the potassium compound the nitrogen atoms are not part of the inner coordination sphere of the metal cations. Instead, the anthranilate anions are rotated into conformations which allow the formation of hydrogen bonding between the amino groups, the water molecule and the carboxylate oxygen atoms. The water molecule is a difunctional donor (for N1 and O2) (Fig. 11 and Table 2).

Coverage of the inner corrugated sheet of potassium cations with anthranilate anions leads to a surface made up of the aromatic hydrocarbon part of the ligands above and below. The phenyl rings show no π–π-stacking and the layers are not indented.

In summary, the crystal structure of K(Anth)(H_2O) is different from the structures of both of its two analogues with

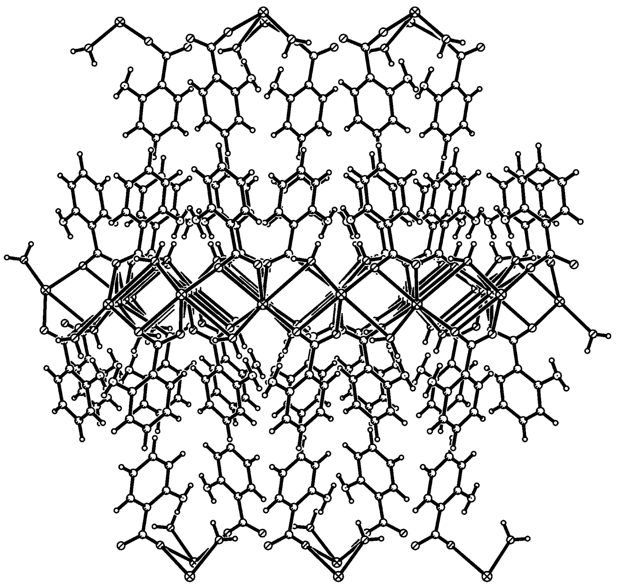

Fig. 11 Cell plot of K(Anth)(H_2O) showing the formation of hydrophobic layers separating the hydrophilic layers.

lithium or sodium. With the larger potassium cation the metals are in a uniform state of seven-coordination solely with oxygen donor atoms. The amino group of the anion is not part of this coordination sphere and – together with the water molecule – has become integrated in a network of hydrogen bonds. The oxygen coordination to the cations and the hydrogen bonds form the compact polar core region from which the arene rings are extending symmetrically above and below.

Although the core connectivities are very different, the layer motif of Na(Anth)$(H_2O)_{0.5}$ and K(Anth)(H_2O) is very similar: Sheets are formed in which the polar components and functions are gathering to form intimate aggregates covered by the non-polar aromatic hydrocarbon units. Efficient aggregation of polar groups is favoured by sizable cations which can accommodate a large number of ligand atoms and thus allow for multidimensional connectivity. For Li(Anth)$(H_2O)_{0.5}$ this connectivity is restricted by the smaller coordination number of the cation and no two-dimensional aggregation is possible. Compact cluster-type units are formed instead. With polar groups still unengaged, hydrogen bonding can be entertained beyond the cluster compartments. It appears that in all three compounds there is a delicate balance between several contributing factors which makes structural predictions exceedingly difficult. Even the difference in hydration (hemi- or mono-hydrate) may cause entirely different structural motifs.

References

1 J. Eder and M. Kutacek, *Biol. Plant.*, 1972, **14**, 390.
2 M. Maeda, Y. Murata and K. Ito, *J. Chem. Soc., Dalton Trans.*, 1987, 1853.
3 D. E. Robertson, S. Lesage and M. F. Roberts, *Biochim. Biophys. Acta*, 1989, **992**, 320.
4 F. Wiesbrock, S. Nogai, A. Schier and H. Schmidbaur, *Helv. Chim. Acta*, 2002, **85**, 1151.
5 F. Wiesbrock and H. Schmidbaur, *J. Chem. Soc., Dalton Trans.*, 2002, 3201.
6 F. Wiesbrock, A. Schier and H. Schmidbaur, *Z. Naturforsch., Teil B*, 2002, **57**, 251.
7 R. Murugavel, V. V. Karambelkar, G. Anantharaman and M. G. Walawalkar, *Inorg. Chem.*, 2000, **39**, 1381.
8 M. Abdulla, A. Behbedani and H. Dashti, in *Magnesium in Health and Disease*, Y. Itokawa and J. Purlach, eds., John Libbey Co. Ltd., London, 1989, p. 111.
9 A. K. Banerjee, D. Prakash and S. K. Roy, *J. Indian Chem. Soc.*, 1976, **53**, 465.
10 M. Olczak-Kolba, *J. Therm. Anal.*, 1992, **38**, 1487.
11 J. A. Cowan, *Inorganic Biochemistry: An Introduction*, Wiley, VCH, New York, 2nd edn., 1997.
12 W. Saenger (Editor), *Landolt-Börnstein: Nukleinsäuren; Teilband b; Kristallographische und strukturelle Daten II*, Springer Verlag, Berlin, 1989, 171 ff.
13 H. Schmidbaur, P. Mikulcik and G. Müller, *Chem. Ber.*, 1990, **123**, 1001.
14 C. Sano, N. Nagashima, T. Kawatika and Y. Iitaka, *Anal. Sci.*, 1985, **5**, 121.
15 H. Schmidbaur, I. Bach, D. L. Wilkinson and G. Müller, *Chem. Ber.*, 1989, **122**, 1427.
16 H. Schmidbaur, I. Bach, D. L. Wilkinson and G. Müller, *Chem. Ber.*, 1989, **122**, 1433.
17 H. Schmidbaur, I. Bach, D. L. Wilkinson and G. Müller, *Chem. Ber.*, 1989, **122**, 1445.
18 H. Schmidbaur, G. Müller, J. Riede, G. Manninger and J. Helbig, *Angew. Chem., Int. Ed. Engl.*, 1986, **98**, 1014.
19 (*a*) G. M. Sheldrick, SHELXS-97, Program for structure solution, University of Göttingen, 1997; (*b*) G. M. Sheldrick, SHELXL-97, Program for crystal structure analysis, University of Göttingen, 1997; (*c*) C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.