metal-organic compounds

New coordination modes in potassium edta salts: K$_2$[H$_2$edta]·2H$_2$O, K$_3$[Hedta]·2H$_2$O and K$_4$[edta]·3.92H$_2$O

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Three potassium edta (edta is ethylenediaminetetraacetic acid, H$_4Y$) salts which have different degrees of ionization of the edta anion, namely dipotassium 2-({2-[bis(carboxylatomethyl)azaniumyl]ethyl}(carboxylatomethyl)azaniumyl)-acetate dihydrate, 2K$^+$·C$_{10}$H$_{14}$N$_2$O$_8^{2-}$·2H$_2$O, (I), tripotassium 2,2′-({2-[bis(carboxylatomethyl)amino]ethyl}ammonio)diacetate dihydrate, 3K$^+$·C$_{10}$H$_{13}$N$_2$O$_8^{3-}$·2H$_2$O, (II), and tetrapotassium 2,2′,2″,2‴-(ethane-1,2-diyldinitrilo)tetraacetate 3.92-hydrate, 4K$^+$·C$_{10}$H$_{12}$N$_2$O$_8^{4-}$·3.92H$_2$O, (III), were obtained in crystalline form from water solutions after mixing edta with potassium hydroxide in different molar ratios. In (II), a new mode of coordination of the edta anion to the metal is observed. The HY^{3-} anion contains one deprotonated N atom coordinated to K$^+$ and the second N atom is involved in intramolecular bifurcated N—H···O and N—H···N hydrogen bonds. The overall conformation of the HY^{3-} anions is very similar to that of the Y^{4-} anions in (III), although a slightly different spatial arrangement of the –CH$_2$COO$^-$ groups in relation to (III) is observed, whereas the H$_2Y^{2-}$ anions in (I) adopt a distinctly different geometry. The preferred synclinal conformation of the –NCH$_2$CH$_2$N– moiety was found for all edta anions. In all three crystals, the anions and water molecules are arranged in three-dimensional networks linked via O—H···O and C—H···O [and N—H···O in (I) and (II)] hydrogen bonds. K···O interactions also contribute to the three-dimensional polymeric architecture of the salts.

Comment

In the crystallographic literature, the most common form of edta [edta is ethylenediaminetetraacetic acid (H$_4Y$) or 2,2′,2″,2‴-(ethane-1,2-diyldinitrilo)tetraacetic acid] is the tetraanion, viz. Y^{4-}. Another anionic form of edta is H$_2Y^{2-}$ reported in salts of Na, K and Rb (Font-Bardia et al., 1993; Cotrait, 1969, 1970). Therefore, it seemed an attractive idea to obtain and structurally characterize crystalline potassium edta

salts, especially the tripotassium edta salt, (II), which is an example of a new coordination mode of this edta anion to a metal centre, and tetrapotassium edta, (III), which is analogous to the Na$_4Y$·5H$_2$O salt (Font-Bardia et al., 1993). Potassium edta salts are used as anticoagulants for haematologic examinations of human and animal blood (Balakrishnan et al., 2006; Hekimsoy et al., 2004; Vatn et al., 2000; Olsen et al., 2001; Sanchez-Migallon Guzman et al., 2008). In addition, potassium edta salts have applications as chelating agents in cosmetics (Lanigan & Yamarik, 2002).

(I)

(II)

(III)
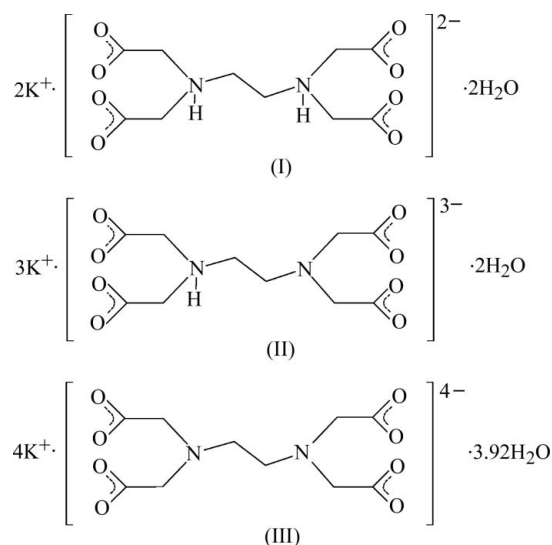
The strategies for preparing the potassium edta salts reported here, viz. (I), (II) and (III), result from the occurrence of acid–base equilibria in aqueous solution between edta anions in different ionization states. The acidity of the solutions plays a crucial role in controlling the particular forms of the edta anions, i.e. H$_3Y^-$, H$_2Y^{2-}$, HY^{3-} and Y^{4-} (Harris, 1999), as follows. The H$_3Y^-$ anion is dominant in aqueous solutions at pH values of around 2.5 and its conjugate acid, i.e. the H$_4Y$ zwitterion, is present at pH ∼ 1.8. In the pH range 2.7–6.1 (pK_a{H$_2Y^{2-}$} = 2.69; pK_a{HY^{3-}} = 6.13) the equilibrium shifts towards the H$_2Y^{2-}$ ion. The HY^{3-} ion dominates in aqueous solutions in the pH range 6.1–10.4 (pK_a{Y^{4-}} = 10.37), whereas the Y^{4-} anion dominates at pH above 10.4.

In contrast to the coordination modes in salts (I), (II), (III), in the majority of compounds that contain edta anions and potassium cations the usual coordination of edta to K$^+$ is via one carboxylate group in a monodentate or bidentate way. The literature provides many examples of such compounds, among which the most typical include: the acetate O atom acting as a linker between two metal atoms, e.g. between two K$^+$ cations, as in K$_4$[Co(H$_2$O)$_6$][Co(C$_{10}$H$_{12}$N$_2$O$_8$)]$_2$[Mo$_8$O$_{26}$]·6H$_2$O (Lee et al., 2002); or between one K$^+$ cation and another metal such as Fe, Sb or Mo (Solans et al., 1984; Ilyukhin & Petrosyants, 2001; Kneale & Geddes, 1975); or between one K$^+$ cation and a lanthanoid cation, as in K[Ho(C$_{10}$H$_{12}$N$_2$O$_8$)-(H$_2$O)$_3$]·2H$_2$O (Sakagami et al., 1999). Furthermore, the carboxylate O atom of edta can bridge three metal atoms, as in the following examples: three K$^+$ cations, as in K$_2$[Ga(C$_{10}$H$_{12}$-N$_2$O$_8$)(OH)]·6H$_2$O (Ilyukhin & Petrosyants, 2001); two K$^+$

cations and another cation such as a lanthanoid, as in K[Yb(C$_{10}$H$_{12}$N$_2$O$_8$)(H$_2$O)]·5H$_2$O (Sakagami *et al.*, 1997); or one K$^+$ cation and two transition metal centres, as in K[Mo$_2$(C$_{12}$H$_{15}$N$_2$O$_{10}$)(OH)$_2$] (Kneale & Geddes, 1975).

The present paper reports the structures of three potassium edta salts, K$_2$[H$_2$Y]·2H$_2$O, (I), K$_3$[HY]·2H$_2$O, (II), and K$_4$[Y]·3.92H$_2$O, (III) (Fig. 1), and we discuss (II) first because of the fact that it is a unique example of a crystalline salt containing the HY^{3-} ion. The geometries of the anions in (I)–(III) are described and compared with those in the dirubidium, disodium and tetrasodium edta salts. In addition, the coordination modes of the edta anions to K$^+$ ions and the arrangements in the crystal lattices are discussed.

Compound (II) contains one HY^{3-} anion, three K$^+$ ions and two water molecules of hydration, where the anion is composed of four acetate arms linked to an NCH$_2$CH$_2$NH$^+$ fragment which adopts a *gauche* conformation; a novel coordination mode is observed. The HY^{3-} ion coordinates to the cation (K1) *via* one deprotonated N atom (N1) and three acetate O atoms (O11, O21 and O32), while the second N atom (N2) is involved in the intramolecular bifurcated N—H···O and N—H···N hydrogen bonds (Figs. 1b and 2a, and Tables 2 and 5). Furthermore, in the seven-coordination polyhedron of K1, two symmetry-related anions are bonded in a bidentate mode (*via* O32^{vi} and O42^{vi}) (all symmetry codes are as given in Table 5), forming an eight-membered ring, and
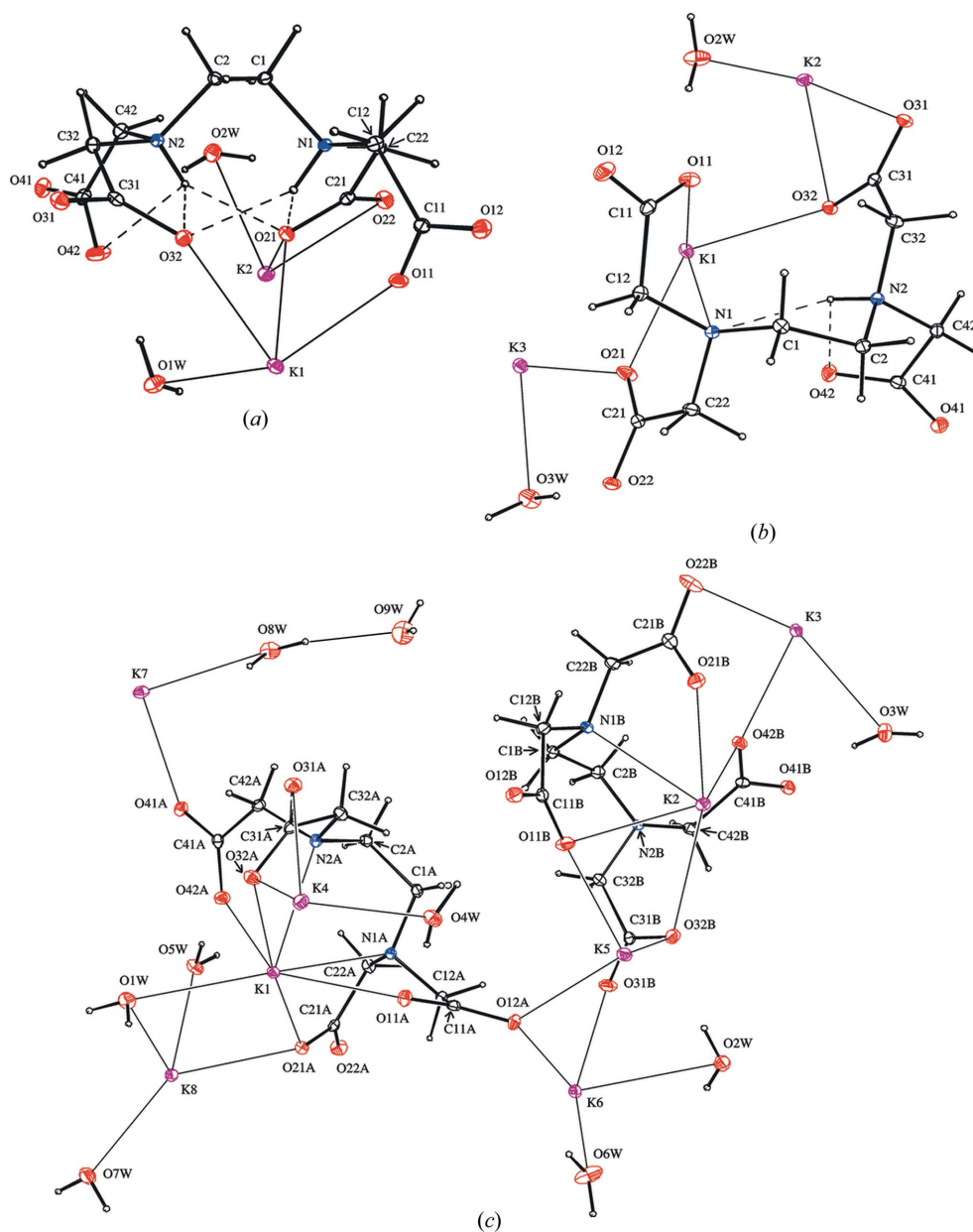
Figure 1
The asymmetric unit of (*a*) (I), (*b*) (II) and (*c*) (III). For (I) and (II), the N—H···O and for (II) the N—H···N intramolecular hydrogen bonds are shown by thin lines. Displacement ellipsoids are drawn at the 30% probability level. The disordered atoms (O31*C*, O32*C*, O71*W* and K71) in (III) have been omitted for clarity.

in a monodentate (*via* O41[vii]) mode (Fig. 2*b* and Table 5). The (OOCCH$_2$)$_2$NCH$_2$CH$_2$NH$^+$(CH$_2$COO)$_2$ unit observed here can also be distinguished in the structure of a fully esterified form of edta with the proton added to one of the N atoms, *viz.* (C$_{14}$H$_{25}$N$_2$O$_8$)$_2$[W$_6$Cl$_{14}$] (Adams *et al.*, 1993), where intra-molecular N—H···N and N—H···O hydrogen bonds occur, but coordination to the metal atom is not observed. In the case of K2, the six-coordination sphere is formed by three HY^{3-} anions and one water molecule, O2W (Fig. 2*c* and Table 5). The anion coordinates to K2 in a bidentate manner *via* O31 and O32, and is involved in coordination to K2[viii] in a monodentate way *via* O22, as well as interacting with K2[vi] *via* O21 and O42 (making an 11-membered chelate ring) (Fig. 2*d* and Table 5). The seven-coordinated K3 atom is surrounded by five edta anions coordinating *via* O atoms in a monodentate manner and by two water molecules.

In the crystal structure of (II), O—H···O hydrogen bonds are present, where water molecules act as donors and carboxylate O atoms act as acceptors (Table 2). Weak

hydrogen bonds of the C—H···O type, where the acetate O atoms participate, also contribute to the structure. The HY^{3-} anions, water molecules and K$^+$ cations are arranged in layers parallel to (100) (Fig. 3*a*). The interaction between acetate O atoms, water molecules and K$^+$ cations results in a three-dimensional network.

The asymmetric unit of compound (III) comprises two Y^{4-} anions [denoted (III*a*) and (III*b*)], eight potassium cations and water molecules (Fig. 1*c*). Although the overall conformations of the (III*a*) and (III*b*) anions are similar (see *Experimental*), the spatial arrangements of their acetate arms are not quite the same (Fig. 4). The overall conformations of the anions in (III) are comparable with those of the corresponding Y^{4-} anion in Na$_4$[edta]·5H$_2$O (Font-Bardia *et al.*, 1993) and of the HY^{3-} ion in (II), although the analogous acetate arms are not arranged in exactly the same manner. Both edta anions in compound (III) chelate K$^+$ *via* six ligating atoms (two N and four carboxylate O atoms), which results in the formation of five-membered rings at both K1 and K2, similar to the
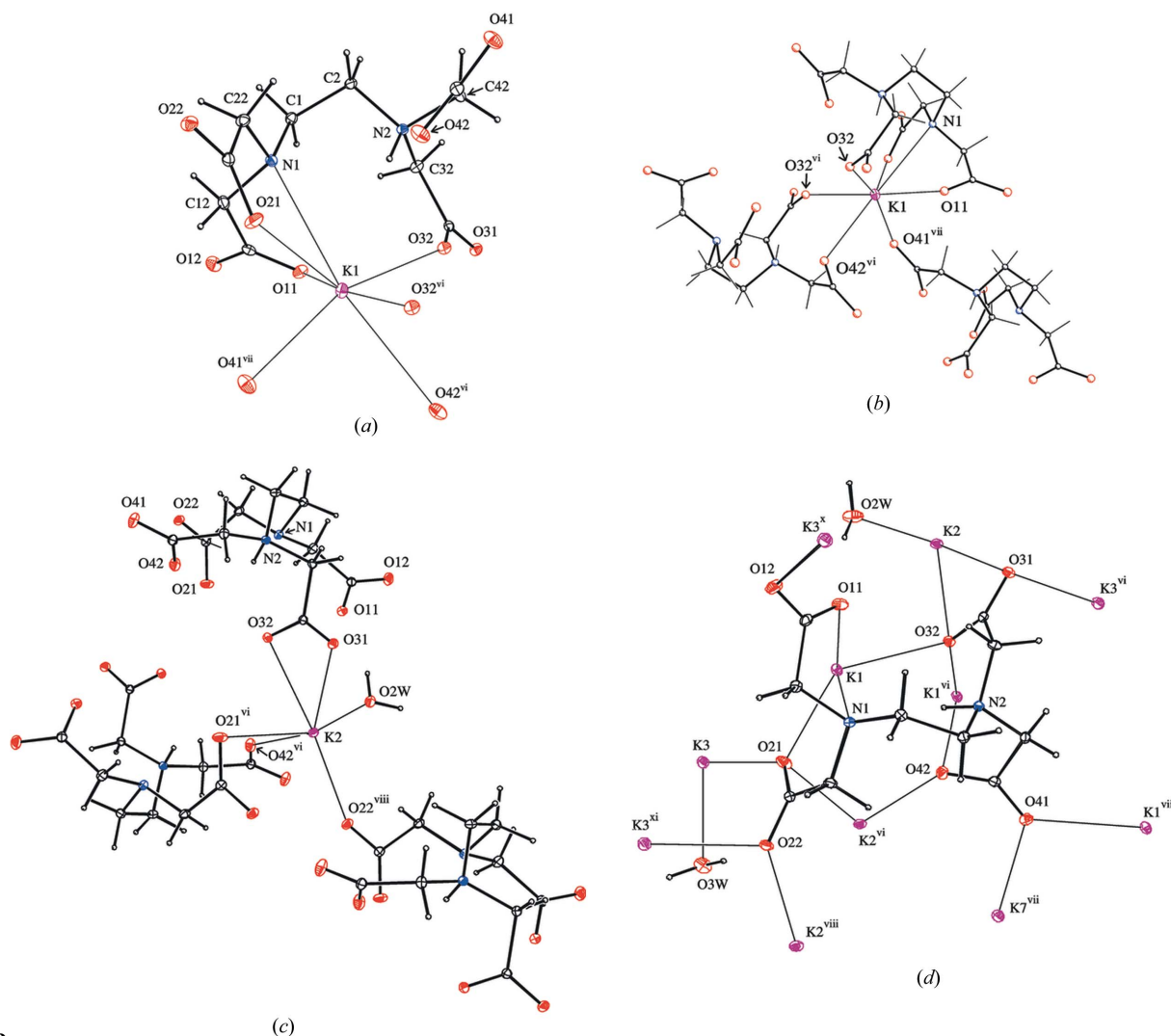
Figure 2
(*a*) The new coordination mode of the HY^{3-} anion to K$^+$ in (II); only ligating O atoms from symmetry-related anions in the coordination sphere of K1 are shown for clarity. (*b*) The coordination environment of K1 in (II). (*c*) The coordination sphere of the K2 cation in (II). (*d*) The environment of the HY^{3-} anion. [Symmetry codes: (vi) −*x* + 1, −*y* + 2, −*z* + 1; (vii) *x* − 1, *y*, *z*; (viii) *x*, *y*, *z* + 1; (x) *x*, *y* + 1, *z*; (xi) −*x*, −*y* + 2, −*z*.]

Figure 3
Packing diagrams: (a) for (II) showing layers parallel to the (010) plane; (b) for (III) showing ribbons built up from the anions, water molecules and K^{+} cations extending along the [001] direction. Water molecules in cavities (O9W and O91W) and disordered atoms (O31C, O32C, O7W and K71) in (III) have been omitted for clarity.

complexes of Y^{4-} ions with many metals; for example, $NH_4[Co(C_{10}H_{12}N_2O_8)]\cdot 2H_2O$ (Weakliem & Hoard, 1959), $\{[(H_2O)_4Mn(C_{10}H_{12}N_2O_8)Cu]\cdot 2H_2O\}_n$ (Solans et al., 1983) and $[Ti(C_{10}H_{12}N_2O_8)]\cdot 2H_2O$ (Fackler et al., 1985).

Each of the four chelate rings formed by the acetate arms with K1 adopt the δ conformation ($\delta\delta\delta\delta$) (Corey & Bailar, 1959; Beattie, 1971; Lee, 1972). In the case of coordination at K2 (coordination number = 8) (Fig. 5b and Table 5), the {K2, O11B, C11B, C12B, N1B} ring adopts the λ conformation, the {K2, O21B, C21B, C22B, N1B} and {K2, O32B, C31B, C32B, N2B} rings are in the δ conformation, whereas the {K2, O42B, C41B, C42B, N2B} ring adopts a near-envelope conformation; four atoms (O42B, C41B, C42B and N2B) are nearly in the same plane (Table 4).

The eight-coordination polyhedron of K1 is made up of two type-(IIIa) anions and one water molecule (Fig. 5a and Table 5). The (IIIa) anion chelates K1 forming a cage structure and coordinates to K1[xii] in a monodentate way via O11A. The seven-coordinate sphere of K3 is built up from three Y^{4-} anions and two water molecules (Fig. 5c and Table 5). The (IIIa) anion is bonded to K3[xvi] through a bidentate acetate group and coordinates to K3[xv] in a monodentate manner via O41A. The (IIIb) anion coordinates to K3 in a bidentate manner through O22B and O42B atoms of acetate groups bonded to two different N atoms which results in the formation of an 11-membered ring, as in (II) and in Rb_2[H_2edta]·2H_2O (Cotrait, 1970). Such an 11-membered ring can be distinguished at K5 as well (Table 5). The environment of K4 is made up of three Y^{4-} ions and two water molecules (Table 5). The coordination spheres of the K6–K8 cations are built by anions linked to K^{+} ions through monodentate carboxylate groups and water molecules.

The shortest K···K distances are in the range 3.6949 (9)–4.4803 (15) Å, where adjacent K^{+} cations are bridged by edta anions via O atoms, giving a three-dimensional polymeric structure. Compound (III) also contains numerous O—H···O hydrogen bonds in which the O atoms of anions and water molecules are involved (Table 3). Adjacent anions and water molecules form layers, while K^{+} cations act as linkers between such layers. The Y^{4-} anions, K^{+} cations and water molecules are arranged in ribbons extending along the [001] direction (Fig. 3b). Weak C—H···O hydrogen bonds are also observed between neighbouring anions, and between anions and water molecules.

Figure 4
The molecular structure of two crystallographically independent Y^{4-} anions in (III) (left). A comparison of the geometry of respective anions (right). The common reference points are N1, C1, C2 and N2. Disordered atoms O31C and O32C have been omitted for clarity.
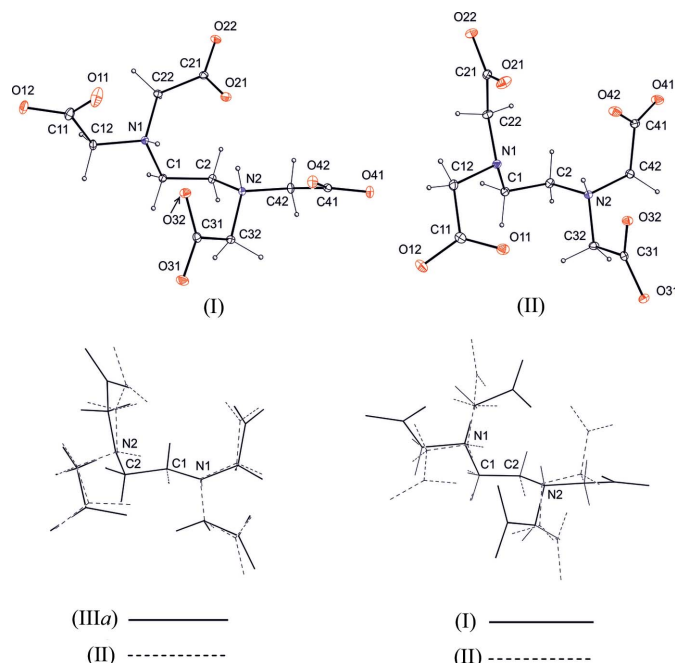
Figure 5
The coordination environment of (*a*) the K1, (*b*) the K2 and (*c*) the K3 cation in (III). Disordered atoms O31*C* and O32*C* in (III) have been omitted for clarity. [Symmetry codes: (xii) $x + \frac{1}{2}$, $-y + \frac{1}{2}$, $-z + 1$; (xiii) $-x + \frac{1}{2}$, $y + \frac{1}{2}$, $-z + \frac{3}{2}$; (xv) $-x + 1$, y, $-z + \frac{3}{2}$; (xvi) x, $-y + 1$, $z + \frac{1}{2}$.]
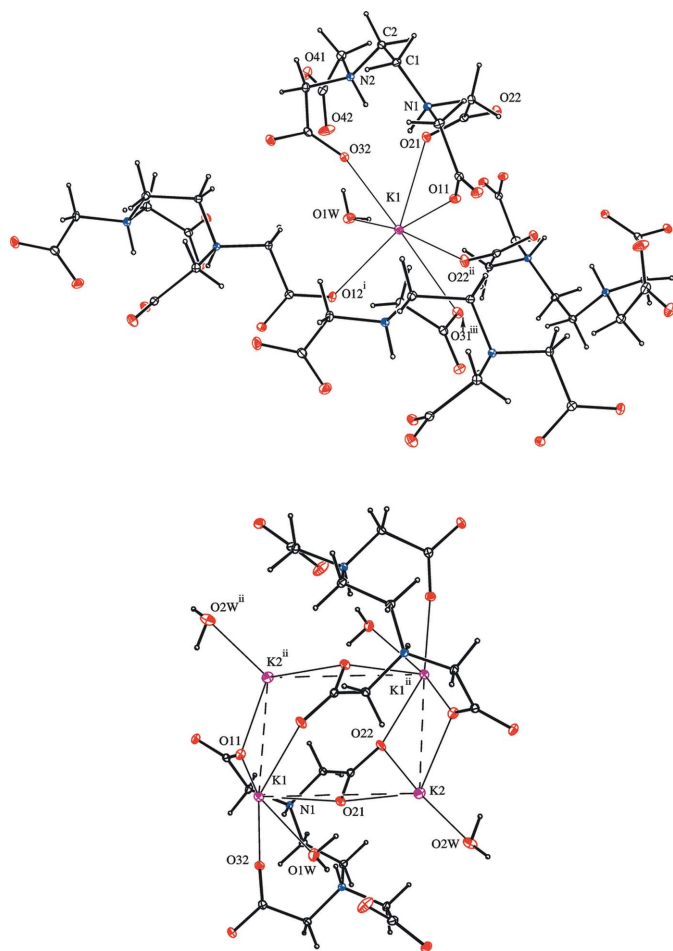
Figure 6
The coordination sphere of K1 in (I) (top). The tetrameric structure built by four adjacent K^+ cations in (I) (bottom). [Symmetry codes: (i) $x + \frac{1}{2}$, $-y + \frac{3}{2}$, $z + \frac{1}{2}$; (ii) $-x + 1$, $-y + 1$, $-z + 1$; (iii) $x + \frac{1}{2}$, $-y + \frac{3}{2}$, $z - \frac{1}{2}$.]

The dipotassium edta salt, (I), was initially studied by Cotrait (1969) who used photographic methods at room temperature. This salt contains an H_2Y^{2-} anion, two K^+ cations and two water molecules. In the H_2Y^{2-} anion, the $NH^+CH_2CH_2NH^+$ fragment adopts a *gauche* conformation. Atoms N1 and N2 are both involved in intramolecular bi- and trifurcated hydrogen bonds, respectively (Table 1 and Fig. 1*a*). This anion is also found in $Rb_2[H_2edta]\cdot 2H_2O$ (Cotrait, 1970) and $Na_2[H_2edta]\cdot 2H_2O$ (Font-Bardia *et al.*, 1993). The H_2Y^{2-} ion in (I) has a different overall conformation in relation to the relevant anions in the dirubidium and disodium edta salts (Cotrait, 1970; Font-Bardia *et al.*, 1993), in which NCH_2CH_2N units adopt an antiperiplanar conformation and the acetate arms have a different geometry. However, the anion in (I) has similar overall geometry to the Y^{4-} ligand in complexes such as $Li[FeY]\cdot 3H_2O$, $NH_4[CoY]\cdot 2H_2O$, $[MgY(H_2O)][Mg-(H_2O)_6]\cdot 2H_2O$, $[Ca_2Y(H_2O)_3]\cdot 4H_2O$ (Lind *et al.*, 1964; Weakliem & Hoard, 1959; Pozhidaev *et al.*, 1973; Barnett & Uchtman, 1979). Such similarity may result from the occurrence of intramolecular hydrogen bonds of the N—H···O type in (I) mentioned above.

In the coordination polyhedron of K1 in (I), the edta anion acts as a tridentate ligand (Fig. 6). The coordination sphere of K1 involves four different edta anions and one water molecule, O1*W*. The coordination is *via* two O atoms (O11 and O21) derived from two different acetate groups joined to the N1 atom and *via* O32. The symmetry-related anions which occupy positions in the coordination sphere of the K1 cation are bonded to K1 in a monodentate fashion *via* atoms O12^{i}, O22^{ii} and O31^{iii} (Table 5 and Fig. 6). Similarly, the coordination sphere of the K2 cation involves four H_2Y^{2-} anions and one water molecule (O2*W*). However, two anions chelate K2 through bidentate carboxylate groups (O21/O22 and O41^{v}/O42^{v}), while the other two are

Figure 7
The molecular structures for the H_2Y^{2-} anion in (I) and the HY^{3-} anion in (II) (top). A comparison of the geometry of respective anions (bottom). The common reference points are N1, C1, C2 and N2.

bonded in a monodentate manner through O11[ii] and O31[iv] (Table 5).

As with compounds (II) and (III), compound (I) has a three-dimensional polymeric structure in which potassium cations are bridged by acetate O atoms. Additionally, K···O interactions result in tetrameric centrosymmetric motifs where the shortest K···K distances are in the range 3.6987 (10)–4.6515 (11) Å (Fig. 6 and Table 5).

The crystal structure of (I) features a three-dimensional network of intermolecular hydrogen bonds of the O—H···O and C—H···O types (Table 1). As in (II) and (III), a layered architecture built of anions, water molecules and K+ cations is observed.

Consideration of the geometries of the anions in (I)–(III) leads to the following conclusions. The preferred conformation of the NCH₂CH₂N unit of anions in (I)–(III) is synclinal. The overall geometry of the edta anions in potassium salts can be classified into two basic types. The first is formed by anions in (II) and (III), the overall conformations of which are very similar, with small differences in the spatial arrangement of the corresponding acetate groups (Fig. 7), whereas a distinctly different conformation is adopted by the anion in (I) (Fig. 7). The overall conformation of H_2Y^{2-} in (I) is similar to that in the complexes noted above, in which the acetate arms of Y^{4-} are involved in five-membered rings with a metal atom. The values of C—N$_{protonated}$ bond lengths in (I) are similar to values in (II), and the relevant values of C—N$_{unprotonated}$ bond lengths in (II) and (III) are also similar (Table 4).

Experimental

The three title salts were obtained by reactions of edta with potassium hydroxide and they were crystallized from aqueous solutions under a gentle stream of nitrogen. All operations were performed at room temperature. All compounds used for syntheses were obtained commercially and not further purified. Contrary to our procedures of preparation, both the corresponding disodium and tetrasodium edta salts were obtained in the reactions between edta and disodium carbonate in aqueous solutions at controlled pH (Font-Bardia et al., 1993).

For the synthesis of (I), edta (0.16 g, 0.55 mmol) and potassium hydroxide (0.064 g, 1.1 mmol) were mixed in a 1:2 molar ratio. A small amount of distilled water (about 5 ml) was added, and the mixture was stirred for about 15 min. The solution (pH value ca 4–4.5) was filtered to remove insoluble crystals of edta and crystals were grown by evaporation. Crystals have the same unit-cell dimensions as those reported by Cotrait (1969).
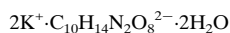
Compound (I) was also obtained as a result of mixing edta with potassium hydroxide in a 1:3 molar ratio. KOH (2.318 g, 41.39 mmol) was dissolved in distilled water (about 7 ml) and edta (4.031 g, 13.79 mmol) added to this solution. This mixture was stirred at room temperature until a clear solution was obtained. Crystallization was carried out by evaporation as in the case of the previous procedure. Crystals in the form of long plates were obtained from a solution with a pH of about 6.5–7.

For the synthesis of (II), potassium hydroxide (0.3832 g, 6.843 mmol) was dissolved in a minimal amount of distilled water. Edta (0.5003 g, 1.712 mmol) was added to give a molar ratio of 4:1. Continuous stirring gave a clear solution with a pH of about 10.5. Evaporation from the solution over the course of 1 d gave colourless crystals in the form of plates.

The crystalline salt (III) was obtained as a result of the reaction of edta with potassium hydroxide mixed in a 1:5 molar ratio. Preparative procedures were performed as in the case of salt (II). KOH (1.85 g, 33.4 mmol) was dissolved in a minimal amount of distilled water. Edta (1.928 g, 6.597 mmol) was added (the pH was about 13). Evaporation from the solution under a nitrogen stream yielded block-like crystals.

Compound (I)

Crystal data

$2K^+ \cdot C_{10}H_{14}N_2O_8^{2-} \cdot 2H_2O$	$V = 1585.3\ (8)$ Å³
$M_r = 404.46$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 8.869\ (3)$ Å	$\mu = 0.65$ mm⁻¹
$b = 18.653\ (5)$ Å	$T = 110$ K
$c = 9.613\ (3)$ Å	$0.31 \times 0.12 \times 0.08$ mm
$\beta = 94.56\ (3)°$	

Data collection

Oxford Diffraction Xcalibur PX KM-4-CCD diffractometer	30091 measured reflections
	8782 independent reflections
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2008)	6388 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.034$
$T_{min} = 0.879$, $T_{max} = 0.959$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$	217 parameters
$wR(F^2) = 0.072$	H-atom parameters constrained
$S = 1.02$	$\Delta\rho_{max} = 0.55$ e Å⁻³
8782 reflections	$\Delta\rho_{min} = -0.43$ e Å⁻³

Table 1
Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1···O32	0.93	2.01	2.8029 (12)	142
N1—H1···O21	0.93	2.19	2.6869 (11)	112
N2—H2···O21	0.93	2.04	2.8617 (12)	147
N2—H2···O32	0.93	2.32	2.7425 (11)	107
N2—H2···O42	0.93	2.38	2.7004 (13)	100
O1W—H12W···O42	0.86	1.90	2.7384 (13)	166
O1W—H11W···O41^i	0.86	1.88	2.7226 (12)	167
O2W—H21W···O1W^i	0.86	2.06	2.8588 (14)	154
O2W—H22W···O31^{ii}	0.86	1.90	2.7350 (11)	164
C1—H1A···O31^{iii}	0.99	2.35	3.2480 (15)	150
C2—H2A···O1W^{iv}	0.99	2.60	3.5644 (16)	165
C1—H1B···O12^v	0.99	2.50	3.0316 (12)	114
C22—H22A···O41^{vi}	0.99	2.28	3.2205 (14)	159
C32—H32A···O12^{vii}	0.99	2.33	3.2703 (14)	158
C32—H32B···O11^v	0.99	2.48	3.3647 (12)	148
C42—H42A···O2W	0.99	2.39	3.2365 (14)	143
C42—H42B···O2W^{viii}	0.99	2.36	3.3349 (15)	166

Symmetry codes: (i) $-x+1, -y+1, -z+2$; (ii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (iv) $x-1, y, z$; (v) $x-\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (vi) $x, y, z-1$; (vii) $x, y, z+1$; (viii) $-x, -y+1, -z+2$.

Compound (II)

Crystal data

$3K^+\cdot C_{10}H_{13}N_2O_8{}^{3-}\cdot 2H_2O$	$\gamma = 96.85\ (3)°$
$M_r = 442.56$	$V = 840.2\ (5)$ Å^3
Triclinic, $P\bar{1}$	$Z = 2$
$a = 8.074\ (3)$ Å	Mo $K\alpha$ radiation
$b = 9.987\ (3)$ Å	$\mu = 0.87$ mm^{-1}
$c = 11.045\ (3)$ Å	$T = 110$ K
$\alpha = 101.68\ (3)°$	$0.27 \times 0.19 \times 0.19$ mm
$\beta = 102.19\ (3)°$	

Data collection

Oxford Diffraction Xcalibur PX KM-4-CCD diffractometer	24301 measured reflections
	9029 independent reflections
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2008)	7083 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.022$
$T_{min} = 0.808, T_{max} = 0.886$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	226 parameters
$wR(F^2) = 0.065$	H-atom parameters constrained
$S = 1.01$	$\Delta\rho_{max} = 0.44$ e Å^{-3}
9029 reflections	$\Delta\rho_{min} = -0.34$ e Å^{-3}

Compound (III)

Crystal data

$4K^+\cdot C_{10}H_{12}N_2O_8{}^{4-}\cdot 3.92H_2O$	$V = 8369\ (5)$ Å^3
$M_r = 515.21$	$Z = 16$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 30.033\ (9)$ Å	$\mu = 0.91$ mm^{-1}
$b = 9.700\ (3)$ Å	$T = 90$ K
$c = 31.513\ (9)$ Å	$0.21 \times 0.15 \times 0.10$ mm
$\beta = 114.27\ (3)°$	

Data collection

Oxford Diffraction Xcalibur PX KM-4-CCD diffractometer	64671 measured reflections
	18115 independent reflections
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2008)	13121 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.035$
$T_{min} = 0.831, T_{max} = 0.931$	

Table 2
Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2···O42	0.93	2.12	2.6364 (11)	114
N2—H1···N1	0.93	2.50	2.9505 (15)	110
O2W—H21W···O12^i	0.85	1.86	2.6690 (15)	157
O2W—H22W···O11	0.86	1.96	2.7933 (12)	162
O3W—H31W···O22	0.86	1.92	2.7786 (12)	175
O3W—H32W···O41^{ii}	0.86	2.51	3.2101 (16)	139
O3W—H32W···O21^{iii}	0.86	2.55	3.2417 (17)	138
C1—H1B···O31^{iv}	0.99	2.34	3.3040 (13)	164
C2—H2A···O12^v	0.99	2.58	3.4313 (15)	144
C32—H32B···O31^{iv}	0.99	2.44	3.3870 (18)	161
C42—H42A···O11^v	0.99	2.53	3.4338 (15)	152

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x+1, -y+2, -z$; (iii) $-x, -y+2, -z$; (iv) $-x+1, -y+1, -z+1$; (v) $x+1, y, z$.

Table 3
Hydrogen-bond geometry (Å, °) for (III).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H11W···O12A^i	0.84	1.85	2.6855 (14)	170
O1W—H12W···O21B^{ii}	0.84	2.07	2.8854 (13)	163
O1W—H12W···O22B^{ii}	0.84	2.38	3.0465 (14)	137
O2W—H21W···O12B^{iii}	0.84	1.97	2.8061 (12)	173
O2W—H22W···O32B	0.84	2.06	2.889 (2)	167
O2W—H22W···O31C	0.84	2.11	2.803 (10)	140
O2W—H22W···O32C	0.84	2.28	3.073 (7)	158
O2W—H22W···O31B	0.84	2.59	3.253 (4)	136
O3W—H31W···O41B	0.84	1.99	2.8261 (12)	171
O3W—H31W···O42B	0.84	2.47	2.9975 (13)	121
O3W—H32W···O22A^{iv}	0.84	1.84	2.6769 (13)	170
O4W—H41W···O11A	0.84	1.93	2.7673 (11)	175
O4W—H42W···O12B	0.84	2.10	2.9237 (14)	169
O5W—H51W···O42A	0.84	1.86	2.7045 (11)	175
O5W—H52W···O41B^v	0.84	2.05	2.8905 (15)	176
O6W—H61W···O1W^i	0.84	2.13	2.9645 (14)	172
O6W—H62W···O3W^{vi}	0.84	1.92	2.7506 (15)	170
O7W—H71W···O12B^i	0.83	2.13	2.8991 (15)	153.7
O7W—H72W···O32C^{vii}	0.84	1.83	2.647 (7)	165.9
O7W—H72W···O32B^{vii}	0.84	2.00	2.825 (3)	170.1
O71W—H71W···O12B^i	0.87	2.13	2.984 (9)	164.6
O71W—H72W···O32C^{vii}	0.85	1.83	2.496 (11)	134.6
O71W—H72W···O32B^{vii}	0.85	2.00	2.733 (9)	144.6
O8W—H82W···O9W	0.85	2.01	2.824 (11)	162
O8W—H81W···O22A^{viii}	0.84	2.27	3.033 (3)	152
O9W—H91W···O31B^{viii}	0.84	2.11	2.944 (7)	172
O9W—H92W···O9W^v	0.84	2.06	2.686 (16)	131
O9W—H92W···O91W^v	0.84	2.24	2.996 (15)	150
O91W—H94W···O31B^{viii}	0.84	2.18	2.936 (7)	149
O91W—H93W···O9W^v	0.84	2.46	2.996 (15)	123
C12A—H12B···O31A^{iii}	0.99	2.54	3.3905 (15)	144
C22A—H22A···O8W^{iii}	0.99	2.56	3.410 (3)	144
C42A—H42A···O8W	0.99	2.49	3.321 (3)	141
C42A—H42B···O22A^{viii}	0.99	2.58	3.3954 (15)	139
C2B—H2B2···O42B	0.99	2.49	3.0675 (15)	117

Symmetry codes: (i) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (ii) $x, -y+1, z-\frac{1}{2}$; (iii) $x, y-1, z$; (iv) $x, -y, z+\frac{1}{2}$; (v) $-x+1, y, -z+\frac{3}{2}$; (vi) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (vii) $x, -y, z-\frac{1}{2}$; (viii) $x, y+1, z$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	3 restraints
$wR(F^2) = 0.054$	H-atom parameters constrained
$S = 1.02$	$\Delta\rho_{max} = 0.50$ e Å^{-3}
18115 reflections	$\Delta\rho_{min} = -0.33$ e Å^{-3}
549 parameters	

In the case of the H_2Y^{2-} and HY^{3-} anions in (I) and (II), respectively, the H atoms of the N—H groups were located in the

Table 4
Selected interatomic distances (Å), valence and torsion angles (°) for the three title potassium edta salts.

The values of geometric parameters are shown only for atoms with high-occupancy positions.

	(I)	(II)	(IIIa)	(IIIb)
C1—C2	1.5163 (11)	1.5131 (12)	1.5225 (13)	1.5295 (14)
C11—C12	1.5326 (12)	1.5354 (11)	1.5313 (13)	1.5333 (14)
C21—C22	1.5316 (12)	1.5350 (11)	1.5339 (14)	1.5386 (14)
C31—C32	1.5252 (12)	1.5270 (11)	1.5353 (15)	1.498 (2)
C41—C42	1.5256 (13)	1.5333 (11)	1.5285 (14)	1.5324 (14)
C1—N1	1.5038 (11)	1.4741 (11)	1.4707 (13)	1.4714 (12)
C2—N2	1.5035 (11)	1.4987 (11)	1.4668 (13)	1.4773 (12)
C12—N1	1.4959 (10)	1.4696 (11)	1.4662 (12)	1.4688 (13)
C22—N1	1.5010 (11)	1.4694 (10)	1.4688 (12)	1.4634 (13)
C32—N2	1.4978 (11)	1.4894 (10)	1.4625 (12)	1.4642 (13)
C42—N2	1.5001 (10)	1.4937 (11)	1.4637 (12)	1.4658 (13)
C11—O11	1.2560 (10)	1.2508 (11)	1.2566 (12)	1.2413 (12)
C11—O12	1.2505 (10)	1.2585 (11)	1.2752 (11)	1.2874 (12)
C21—O21	1.2652 (10)	1.2471 (10)	1.2516 (12)	1.2615 (12)
C21—O22	1.2498 (10)	1.2636 (9)	1.2689 (12)	1.2607 (13)
C31—O31	1.2580 (10)	1.2496 (9)	1.2660 (12)	1.251 (2)
C31—O32	1.2579 (10)	1.2579 (9)	1.2548 (12)	1.278 (2)
C41—O41	1.2588 (11)	1.2499 (10)	1.2665 (11)	1.2784 (12)
C41—O42	1.2457 (12)	1.2512 (10)	1.2579 (12)	1.2507 (12)
N1—C1—C2	114.78 (7)	112.98 (7)	114.04 (8)	113.38 (8)
N2—C2—C1	115.54 (7)	111.15 (7)	113.78 (8)	113.61 (8)
C12—N1—C1	109.65 (6)	107.16 (6)	108.77 (7)	111.42 (8)
C22—N1—C1	113.01 (6)	110.20 (6)	111.41 (8)	112.37 (8)
C12—N1—C22	112.17 (6)	109.34 (6)	110.12 (8)	110.24 (8)
C32—N2—C2	112.83 (6)	114.23 (6)	112.36 (8)	110.38 (8)
C42—N2—C2	108.90 (6)	110.77 (6)	109.37 (8)	110.67 (8)
C32—N2—C42	110.61 (6)	112.28 (6)	110.29 (8)	110.58 (8)
N1—C12—C11	111.52 (7)	114.75 (6)	113.96 (8)	114.30 (8)
N1—C22—C21	112.00 (6)	116.01 (6)	113.48 (8)	114.30 (8)
N2—C32—C31	113.24 (7)	109.49 (6)	112.87 (8)	117.63 (14)
N2—C42—C41	111.53 (7)	109.40 (6)	114.24 (8)	114.69 (8)
N1—C1—C2—N2	66.78 (9)	58.12 (8)	61.45 (11)	65.79 (11)
O11—C11—C12—N1	−11.14 (10)	31.84 (10)	30.89 (12)	−14.70 (13)
O12—C11—C12—N1	170.42 (7)	−152.21 (7)	−151.88 (8)	165.53 (8)
O21—C21—C22—N1	−2.74 (10)	13.17 (10)	30.00 (12)	7.18 (13)
O22—C21—C22—N1	177.84 (7)	−169.15 (6)	−151.11 (8)	−176.39 (9)
O31—C31—C32—N2	174.33 (7)	−160.49 (6)	−154.80 (8)	−154.94 (13)
O32—C31—C32—N2	−6.78 (10)	20.36 (9)	27.39 (12)	28.7 (2)
O41—C41—C42—N2	165.31 (7)	−157.85 (7)	−163.13 (8)	176.88 (8)
O42—C41—C42—N2	−16.05 (11)	23.95 (9)	20.68 (12)	−1.98 (13)

Table 5
Coordination spheres of potassium cations in salts (I)–(III), with K—O, K—N and the shortest K···K distances (Å) given.

(I)

K1—O11	2.6746 (11)	K1—O1W	2.7350 (11)	K2—O41^{v}	2.8218 (12)
K1—O21	2.9255 (9)	K2—O21	2.7836 (9)	K2—O42^{v}	2.8675 (12)
K1—O32	2.8129 (10)	K2—O22	2.9641 (12)	K2—O2W	2.8502 (12)
K1—O12^{i}	2.7447 (9)	K2—O11^{ii}	2.7138 (9)	K1···K2	4.6515 (11)
K1—O22^{ii}	2.7650 (9)	K2—O31^{iv}	2.9309 (9)	K1···K2^{ii}	3.6987 (10)
K1—O31^{iii}	3.1269 (12)				

(II)

K1—O11	2.7077 (11)	K2—O32	2.8625 (10)	K3—O31^{vi}	2.7363 (14)
K1—O21	2.6637 (9)	K2—O21^{vi}	2.9180 (14)	K3—O41^{vii}	2.7781 (10)
K1—O32	2.6962 (11)	K2—O22^{viii}	2.6767 (10)	K3—O3W	2.8185 (10)
K1—N1	3.1769 (13)	K2—O42^{vi}	2.6156 (9)	K3—O2W^{ix}	3.0512 (12)
K1—O32^{vi}	2.6767 (11)	K2—O2W	2.7386 (15)	K1···K1^{vi}	3.6881 (18)
K1—O41^{vii}	2.7351 (9)	K3—O21	3.0836 (12)	K1···K2^{vi}	4.0729 (13)
K1—O42^{vi}	3.0873 (12)	K3—O12^{x}	2.8447 (11)	K2···K3^{vi}	4.1238 (16)
K2—O31	2.7182 (11)	K3—O22^{xi}	2.7814 (14)	K2···K3^{ix}	4.0096 (15)

(III)

K1—O11A	2.8597 (10)	K3—O22B	2.9769 (11)	K5—O11B	2.6290 (10)
K1—O21A	2.7664 (10)	K3—O42B	2.7194 (9)	K5—O32B	2.883 (2)
K1—O32A	2.6942 (10)	K3—O41A^{xv}	2.6766 (10)	K5—O32C	2.757 (7)
K1—O42A	2.8555 (11)	K3—O41A^{xvi}	2.8124 (13)	K5—O21B^{iv}	2.7210 (11)
K1—N1A	2.8748 (12)	K3—O42A^{xvi}	2.9286 (10)	K5—O2W^{xiii}	2.8014 (10)
K1—N2A	2.9515 (13)	K3—O3W	2.9332 (11)	K5—O7W^{xii}	3.053 (4)
K1—O11A^{xii}	3.0339 (15)	K3—O1W^{xvi}	3.0778 (12)	K1···K8	4.0693 (9)
K2—O11B	2.9625 (12)	K4—O31A	2.8269 (13)	K3···K71^{xv}	3.886 (15)
K2—O21B	2.7452 (11)	K4—O32A	2.9176 (11)	K3···K3^{v}	3.9455 (18)
K2—O32B	3.076 (4)	K4—O21A^{xii}	2.7465 (10)	K3···K7^{xv}	4.012 (12)
K2—O32C	2.709 (9)	K4—O31A^{xvii}	2.8655 (11)	K4···K4^{xvii}	3.6949 (19)
K2—O42B	2.7474 (14)	K4—O32A^{xvii}	2.7610 (10)	K4···K6^{x}	4.0013 (14)
K2—N1B	2.8616 (10)	K4—O4W	2.7353 (10)	K5···K6	4.2267 (10)
K2—N2B	2.8092 (10)	K4—O6W^{x}	3.1637 (12)	K5···K2^{iv}	4.4600 (11)
K2—O2W^{xiii}	2.7098 (13)	K5—O12A	2.7412 (12)	K5···K8^{xii}	4.4563 (17)
K2—O6W^{xiii}	3.3299 (13)				

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $x + \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (iv) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (v) $-x + 1, -y + 1, -z + 2$; (vi) $-x + 1, -y + 2, -z + 1$; (vii) $x - 1, y, z$; (viii) $x, y, z + 1$; (ix) $-x, -y + 2, -z + 1$; (x) $x, y + 1, z$; (xi) $-x, -y + 2, -z$; (xii) $-x + \frac{1}{2}, -y + \frac{1}{2}, z + 1$; (xiii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (xiv) $x, -y, z + \frac{1}{2}$; (xv) $-x + 1, y, -z + \frac{3}{2}$; (xvi) $x, -y + 1, z + \frac{1}{2}$; (xvii) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$.

difference Fourier maps but were introduced in positions calculated from geometry, with N—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(N)$. The methylene H atoms in (I)–(III) were treated as riding atoms in geometrically idealized positions, with C—H = 0.99 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

In (III), partial disorder is present in the case of one acetate group (O31B, O32B and C31B), certain water molecules (O7W, O8W and O9W) and the K7 cation. Disorder of the carboxylate O atoms was identified from the difference Fourier map peaks close to O31B and O32B at distances of approximately 0.52 and 0.42 Å, respectively. Because both O atoms and C31B belong to the same carboxylate group, the disorder was modelled for each of them over two positions, with occupancies of 0.793 (11) and 0.207 (11); the minor-occupancy components were refined isotropically.

Additionally, two peaks in the difference Fourier map were interpreted as disorder of the O atoms of water. These peaks were at distances of 0.61 and 0.74 Å from O7W and O9W, respectively, and were introduced as O71W and O91W. O7W was modelled as disordered over two positions with occupancies of 0.892 (10) and

0.108 (10). The sum of the occupancies of O9W and O91W was smaller than unity. Therefore the disorder was modelled with occupancies of 0.282 (14) and 0.298 (14) for O9W and O91W, respectively. The K7 cation was also disordered over two positions, with occupancies of 0.947 (8) and 0.053 (8). O8W was located in a difference Fourier map and refined with an occupancy of 0.267 (2).

The H atoms of water molecules O7W, O8W and O9W were located in a difference Fourier map and introduced with distance restraints for the O—H and H···H distances of 0.84 (2) and 1.41 (2) Å, respectively. In the last stages of refinement, these H atoms were permitted to ride at the positions previously established, with $U_{iso}(H) = 1.5U_{eq}(O)$, giving O—H distances in the range 0.83–0.87 Å.

For all three salts, data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* and *publCIF* (Westrip, 2010).

metal-organic compounds

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