

Croconic Acid and Alkali Metal Croconate Salts: Some New Insights into an Old Story

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Abstract: The solid-state structures of a series of alkali metal salts of the croconate dianion ($C_5O_5^{2-}$) and of croconic acid ($H_2C_5O_5$) have been determined. The alkali metal croconates were obtained by ring contraction of rhodizonic acid ($H_2C_6O_6$), upon treatment with alkali metal hydroxides and recrystallisation from water. The novel species $Na_2C_5O_5 \cdot 2H_2O$, $Rb_2C_5O_5$ and $Cs_2C_5O_5$, as well as the mixed hydrogencroconate/croconate salt $K_3(HC_5O_5)(C_5O_5) \cdot 2H_2O$

are described and compared with the Li^+ , K^+ and NH_4^+ salts. Single crystals of croconic acid were obtained by crystallisation of croconic acid in the presence of HCl. Crystal structure determinations showed that the $C_5O_5^{2-}$ ions tend to organize themselves in columns. The

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interplanar separations lie in the narrow range 3.12–3.42 Å and do not necessarily reflect the presence of π -stacking interactions. It is argued that the small interplanar separation is the result of a compromise between packing of flat croconate units and the spherical cations together with the water molecules that fill the coordination spheres of the alkali metal atoms.

Introduction

Crystal engineering, the bottom-up construction of crystalline solids with desired arrangements of the component molecules and ions,^[1] has fuelled new interest in some old issues of structural chemistry. Like supramolecular chemistry, defined as chemistry beyond the molecule,^[2] crystal engineering is concerned with the assembly of molecules^[3] and ions in aggregates of higher complexity, with collective properties that depend upon the plethora of intermolecular interactions that are responsible for crystal cohesion and stability.^[4] The complex relationship between molecular size and shape (and ionic charge in the case of ions) and the type and number of intermolecular interactions often favours the utilisation of (relatively) simple ions and molecules as building blocks. Simplicity will (hopefully) provide better insight into the factors that are truly important for crystal construction. However provocative it may sound, chemical novelty is not a necessary prerequisite for a crystal-engineering building block to be useful. Chemical and physical novelty arises from the

supramolecular aggregation of the building blocks rather than from their nature.

Indeed most of the successful crystal-engineering experiments have been conducted on simple systems, like guanidinium and sulfonate ions,^[5] organometallic acids,^[6] halometalate systems,^[7] copper halides,^[8] nanoporous systems^[9, 10] and coordination networks.^[11, 12] We have followed a similar type of approach in one of our lines of crystal-engineering research.^[13] We used polyprotic organic and inorganic acids to exploit the robustness and reproducibility of hydrogen-bonding interactions. A family of such acids that has proved to be particularly well suited are the oxocarbon acids, which include rhodizonic ($H_2C_6O_6$), croconic ($H_2C_5O_5$), squaric ($H_2C_4O_4$) and deltic ($H_2C_3O_3$) acids.^[14] We have used the monodeprotonation products of squaric acid to construct interdigitated coordination complexes and hybrid organic–organometallic materials for magnetic studies.^[15] We were attracted by the structural characteristics of these simple and elegant chemical systems.

Here we report the synthesis and structural characterization of a series of salts of the croconate dianion ($C_5O_5^{2-}$) and the structure of croconic acid ($H_2C_5O_5$). While the solid-state structures of deltic^[16] and squaric acids^[17] were established long ago, that of croconic acid was only recently communicated.^[18a] The croconate dianion belongs, together with the rhodizonate $C_6O_6^{2-}$, the squarate $C_4O_4^{2-}$ and the deltate $C_3O_3^{2-}$ ions, to the family of oxocarbon dianions. The prototype of these dianions is the rhodizonate dianion $C_6O_6^{2-}$,^[18b] which has attracted the interest of many research-

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ers in view of the structural analogy with benzene. Rhodizionate salts have found many applications, for example as markers for lead, in the analysis of radium in fresh waters, and also for their luminescence properties.^[19] Yellow croconic acid was discovered, together with orange potassium croconate dihydrate (see below), by L. Gmelin in 1825.^[20] Gmelin himself derived the name “croconic” from the Greek *τὸ χρῶλον* for saffron or egg yolk, because of the yellow and orange colours of croconic acid and of many of its compounds. Gmelin wrote: “Were it confirmed that it is a hydroxyacid, then it should be given the name hydrocroconic acid and its radical should be called crocon”.^[20]

We have utilised oxocarbon anions for evaluating some fundamental aspects of hydrogen-bonding interactions between ions.^[21] Structural investigation on rubidium and cesium hydrogencroconates afforded some insight into the relationship between anion–anion hydrogen-bonding interactions and the presence of a coulombic field generated by the ions. It has been argued that interactions between ions are often the result of a compromise between the need to achieve maximum packing density and that of preserving weaker intermolecular (or interionic) interactions, which, however feeble with respect to the strength of the coulombic field generated by small ions, are highly directional and contribute to packing cohesion. This reasoning applies not only to hydrogen bonding between ions but also to π stacking, as shown previously for short interplanar separations observed in crystals of squarate and hydrogensquarate salts.^[22] In these cases the weak noncovalent interactions are charge-com-

pressed by the strong surrounding coulombic field. This study provides further examples of charge-compressed stacking of anions.

Results and Discussion

Table 1 summarises the compounds that are described in this paper and provides references to those reported by others.^[23] Relevant intra- and interionic structural parameters are compared. While the structure of $\text{K}_2\text{C}_5\text{O}_5 \cdot 2\text{H}_2\text{O}$ was reported recently,^[23b] the structures of the sodium, rubidium and cesium salts are novel.

Croconic acid: Yellow transparent single crystals of croconic acid were obtained by crystallisation of croconic acid from an aqueous solution of HCl (1M; see Experimental Section). In fact the first characterisation of the croconic acid molecule was not performed on the pure molecular crystal, but on a serendipitous product obtained in the course of the reaction of the organometallic hydroxide $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]\text{OH}$ with rhodizonic acid, followed by acidification of the solution with HCl,^[18] which yielded the co-crystal $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}]\text{Cl} \cdot \text{H}_2\text{C}_5\text{O}_5$. Rhodizonic acid is known to undergo ring contraction upon treatment with bases, and this route yielded all the croconate compounds described here.

The structure of croconic acid is shown in Figure 1 (top). Importantly, all hydrogen atom positions could be obtained from the diffraction data, and this allowed unambiguous

Table 1. Relevant intra- and intermolecular parameters [$\text{\AA}$] in the hydrogencroconate and croconate salts.

Salt	Interplanar distance	Distance between ring centroids	Shift between the centroids	C–O	C–C	Shortest O $\cdots$ M ⁺ interactions [$<r_{\text{vdW}}(\text{O}) + r_{\text{vdW}}(\text{M})$]	O _{croconate} $\cdots$ O _{water}
$\text{Li}_2\text{C}_5\text{O}_5 \cdot 2\text{H}_2\text{O}$ ^[23a]	3.30	3.46	1.04	1.268(3) 1.245(2) 1.235(2)	1.451(2) 1.469(2) 1.477(2)	1.917(3) 1.984(3) 1.990(4) ^[a] 1.994(3) ^[a]	2.747(2) 2.691(2)
$\text{Na}_2\text{C}_5\text{O}_5 \cdot 2\text{H}_2\text{O}$	3.12	4.36	3.0	1.248(2) 1.249(2) 1.242(2)	1.461(2) 1.470(2) 1.471(3)	2.318(1) 2.468(1) 2.507(1) 2.586(1) 2.320(1) ^[a] 2.400(1) ^[a]	2.827(2) 2.774(2)
$\text{K}_2\text{C}_5\text{O}_5 \cdot 2\text{H}_2\text{O}$ ^[23b]	3.30	3.43	1.10	1.248(3) 1.241(2) 1.252(2)	1.474(2) 1.474(2) 1.465(3)	2.784(1) 2.870(1) 2.789(1) 2.864(1) 2.910(3) 3.118(4) 3.352(5) 2.726(4) ^[a] 2.809(4) ^[a]	2.783(2) 2.877(2)
$\text{K}_3(\text{HC}_5\text{O}_5)(\text{C}_5\text{O}_5) \cdot 2\text{H}_2\text{O}$	3.19	4.23	2.78	1.234(4) 1.233(4) 1.289(4) 1.243(4) 1.231(4)	1.477(5) 1.450(5) 1.435(5) 1.476(5) 1.473(5)	2.661(3) 2.719(3) 2.738(3) 2.767(4) 2.820(3) 2.847(4) 2.892(5) 3.021(3) 2.851(5) 3.106(3) 3.029(5) 3.126(4) 3.048(6) 3.235(6)	2.444(5) ^[b] 2.972(6) 2.786(6)
$\text{Rb}_2\text{C}_5\text{O}_5$	3.30	3.82	1.92	1.24(1) 1.244(8) 1.240(8)	1.458(7) 1.463(9) 1.47(1)	2.838(5) 3.021(3) 2.851(5) 3.106(3) 3.077(7) 3.337(2) 3.117(7)	
$\text{Cs}_2\text{C}_5\text{O}_5$	3.42	4.02	2.11	1.231(9) 1.226(8) 1.261(9)	1.46(1) 1.448(7) 1.46(2)	3.029(5) 3.126(4) 3.048(6) 3.235(6)	
$(\text{NH}_4)_2\text{C}_5\text{O}_5$ ^[23c]	3.30	3.47	1.07	1.24(1) 1.27(1) 1.29(1)	1.46(1) 1.45(1) 1.45(2)	2.82(1) ^[c] 2.83(1) ^[c]	2.83(1) ^[c] 2.91(1) ^[c]

[a] O_{water} $\cdots$ M⁺. [b] O_{croconate} $\cdots$ O_{hydrogencroconate}. [c] O $\cdots$ N distance.

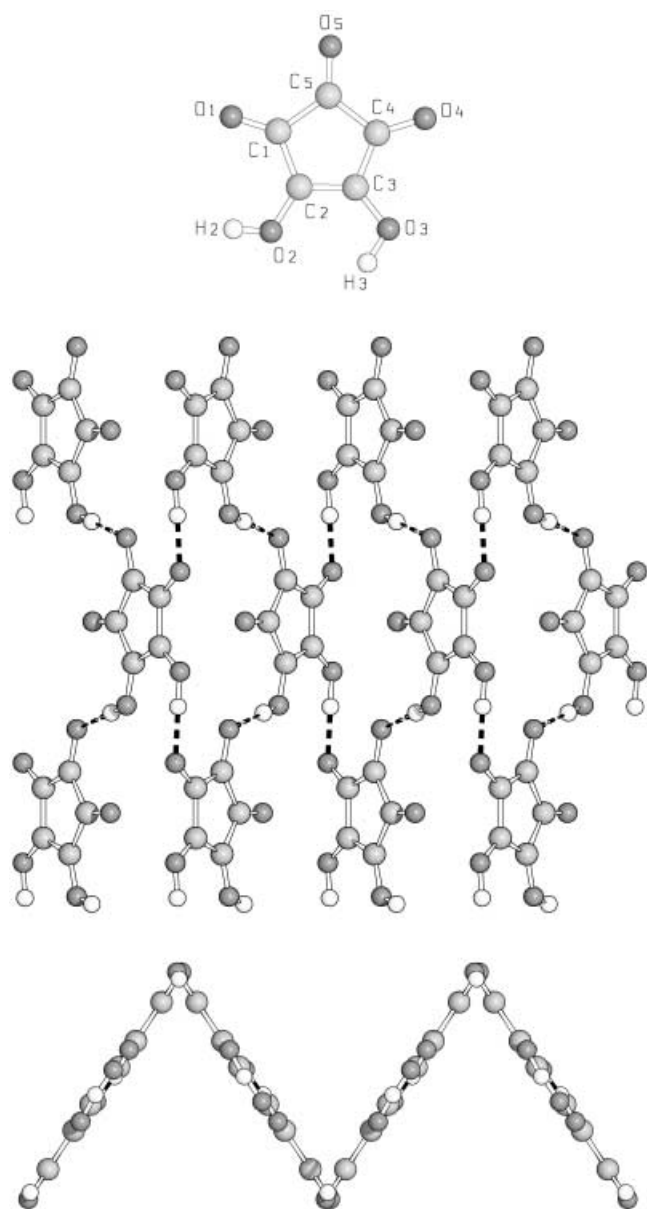


Figure 1. Top: The structure of croconic acid. Middle: A view of the crystal down the *a* axis, showing the large tetrameric rings formed by the croconic acid molecules. Bottom: The same molecular ensemble viewed down the *c* axis, showing the accordion-type superstructure formed by the tetramolecular rings.

assignment of the hydrogen-bonding motifs. In the crystal each molecule of croconic acid is linked to four other molecules by two (crystallographically) independent types of hydrogen bonds ($\text{O} \cdots \text{O}$ 2.628(5), 2.617(5) Å) to give sheets of large tetrameric rings (Figure 1, middle). The sheets, however, are not flat but pleated in an “accordion” pattern, as can be seen in the side-on view in Figure 1 (bottom). The angle between the croconic acid planes is 68°, and the hinges are formed by one row of $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds. Squaric acid $\text{H}_2\text{C}_4\text{O}_4$ ^[17] also forms large tetramolecular rings in the solid state (Figure 2), but in this case the sheets are flat. The hydrogen bonds in squaric acid ($\text{O}(\text{H}) \cdots \text{O}$ 2.532(4), 2.544(4) Å) are slightly shorter than in croconic acid ($\text{O}(\text{H}) \cdots \text{O}$ 2.628(5), 2.617(5) Å). Whether this reflects strain

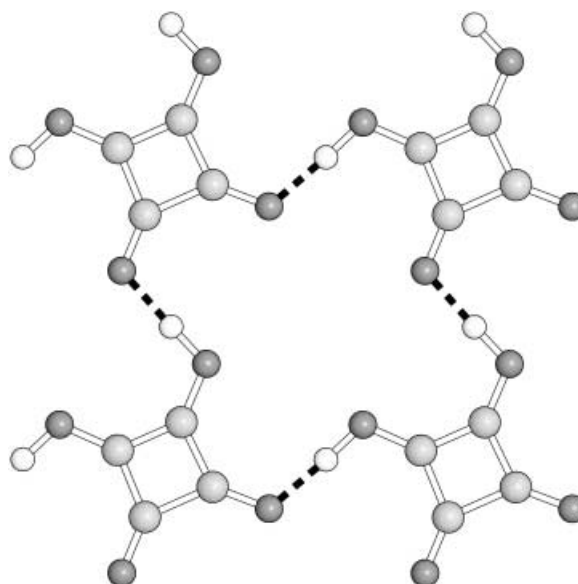
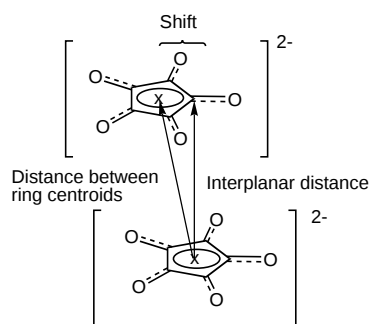


Figure 2. The flat tetramolecular rings formed by squaric acid can be compared with the rings formed by croconic acid (see Figure 1, middle).

in the structure of croconic acid with respect to the more relaxed molecular distribution in crystalline squaric acid or some other electronic effect^[24] is difficult to say on the basis of the structural comparison alone.

We can now move to the alkali and ammonium salts compared in Table 1. Some common structural features are noteworthy:

- 1) The lithium, sodium and potassium croconates are all known as dihydrate salts, whereas the ammonium, rubidium and caesium salts crystallise in the anhydrous form. The water molecules act as “coordination fillers” in crystallisation with the lighter alkali cations.
- 2) All the crystals show some degree of dianion stacking. The distance between planes varies in a rather narrow range (3.12–3.42 Å), but these data should not be taken as indicative of significant overlap between the rings. It has been pointed out by us^[22] and others^[25, 26] that examination of the interplanar separation alone can be extremely misleading when discussing small ions or molecules in crystals. In the case of flat, discoidal fragments such as the croconate ions, a complete topological analysis of the relationship between the planes would require knowledge of not less than four parameters, namely, the distance between ring centroids, the shift between ring centroids, the distance between the ring centroid and the underlying plane, and the angle between the normals to the ring planes. Because in all the examined cases this last quantity is invariably zero or close to zero, only the first three parameters have been calculated and reported in Table 1.^[26] On the basis of this information it is clear that the short interplanar separation in the Na^+ salt (3.12 Å) does not correspond to “super-tight” π stacking, because the shift distance between the rings is large (3.0 Å) and indicates that even if the planes containing the molecules are very close, the two molecular units are not. In contrast, the Li^+ , K^+ and NH_4^+ salts show the best combination of



interplanar separation (3.30, 3.24 and 3.30 Å) and “shift” parameters (1.04, 1.10 and 1.07 Å; see also below).

- 3) The Rb^+ and Cs^+ salts, which are anhydrous, show ring stacking. Both interplanar separations (3.30 and 3.42 Å)

and shifts (1.92, 2.11 Å) correlate with the increase in the cation size on from Rb^+ to Cs^+ . This is also reflected by the increase in the $\text{O} \cdots \text{M}^+$ distances (see Table 1).

Lithium croconate: The structure of lithium croconate was determined by Gonçalves et al. in 1996^[23a] Since we are interested in comparing the arrangements of the croconate dianions in this family of salts, we summarise here the main structural features. Coordinates were retrieved from the CSD. Figure 3 (top) shows how the Li^+ ion is linked to two croconate dianions and two water molecules, and thus achieves a tetrahedral coordination geometry. The water molecules form hydrogen bonds to the oxygen atoms of the dianions. The $\text{O}_{\text{croconate}} \cdots \text{O}_{\text{water}}$ separations are 2.691(2) and 2.747(2) Å. The water molecules knit together the dianions to give the sheet shown in Figure 3 (middle). The dianion layer in the Li^+ salt is related to that in croconic acid (see Figure 1,

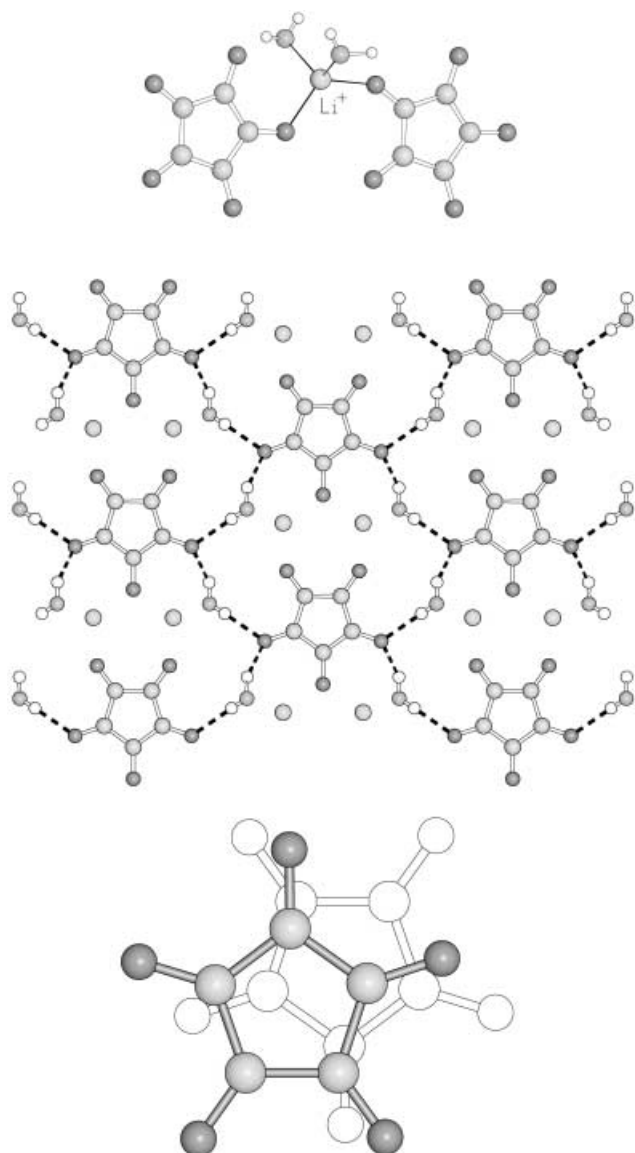


Figure 3. Top: The tetrahedral disposition of two water molecules and two croconate dianions around the Li^+ ion in $\text{Li}_2\text{C}_5\text{O}_5 \cdot 2\text{H}_2\text{O}$. Middle: The water molecules in $\text{Li}_2\text{C}_5\text{O}_5 \cdot 2\text{H}_2\text{O}$ bridge the oxygen atoms of the dianions by hydrogen bonding. Bottom: The relative arrangement of the croconate anions along the stacking.

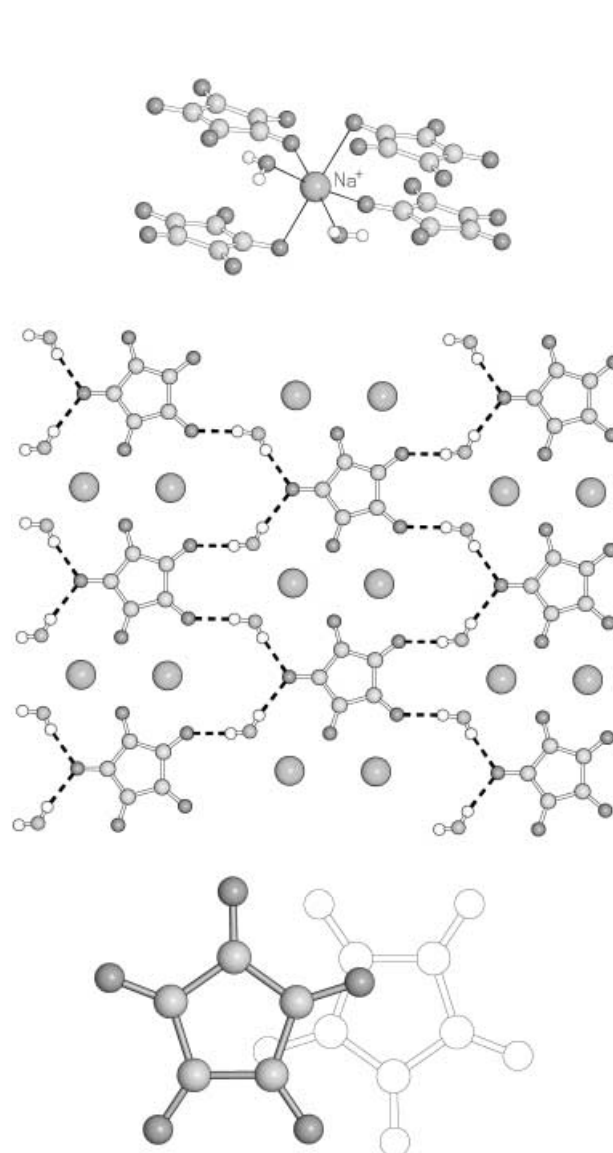


Figure 4. Top: Octahedral arrangement of four croconate dianions and two water molecules around the Na^+ ions in crystalline $\text{Na}_2\text{C}_5\text{O}_5 \cdot 2\text{H}_2\text{O}$. Middle: Two water molecules join the croconate anions to form a sheet similar to that observed in crystalline $\text{Li}_2\text{C}_5\text{O}_5 \cdot 2\text{H}_2\text{O}$ (cf. Figure 3 middle). Bottom: The superimposition of croconate dianions.

middle), whereby the water molecules expand the network, and the Li^+ ions link together the dianions, which can thus adopt a flat arrangement. The croconate layers in the Li salt are superimposed (see Figure 3, bottom) such that the croconate dianions stack on each other at an interplanar distance of 3.30 Å.

Sodium croconate: The coordination number of the sodium cations in the salt $\text{Na}_2\text{C}_5\text{O}_5 \cdot 2\text{H}_2\text{O}$ is six, and the oxygen atoms of four croconate dianions and two water molecules occupy the vertices of an octahedron ($\text{Na}^+ \cdots \text{O}$ 2.318(1)–2.586(1) Å; Figure 4, top). Despite the different geometry around the cation, the solid-state structure is closely related to that of $\text{Li}_2\text{C}_5\text{O}_5 \cdot 2\text{H}_2\text{O}$: two water molecules join the croconate anions in large tetrameric units (Figure 4, middle). The relative orientation of the dianions is different from that in $\text{Li}_2\text{C}_5\text{O}_5 \cdot 2\text{H}_2\text{O}$, but the supramolecular organisation still has niches in which the Na^+ ions are encapsulated. Figure 4 (bottom) shows how the croconate dianions are superimposed in crystalline $\text{Na}_2\text{C}_5\text{O}_5 \cdot 2\text{H}_2\text{O}$. In contrast to the Li^+ salt, an oxygen atom of one dianion is located almost over the centre of the underlying croconate dianion. The shortest $\text{C} \cdots \text{C}$ separation between the two almost overlapping C atoms is

3.232(2) Å, considerably shorter than sum of the van der Waals radii (3.40 Å). The close, and supposedly repulsive, contact is a consequence of the charge–compression effect (see below).

Potassium croconate: As recalled by Dunitz et al.,^[23b] potassium croconate was first isolated by Gmelin more than 175 years ago and reported together with croconic acid. In the course of this study we also prepared $\text{K}_2\text{C}_5\text{O}_5 \cdot 2\text{H}_2\text{O}$. We do not report our data here, but rather use those obtained by Dunitz et al. The coordination around the potassium cation is quite irregular (see Figure 5, top left), with six $\text{K}^+ \cdots \text{O}_{\text{croconate}}$ and two $\text{K}^+ \cdots \text{O}_{\text{water}}$ contacts in the range 2.649(1)–3.064(1) Å (see Table 1). Contrary to the Li^+ and Na^+ salts, the water molecules do not link the dianions in layers. The larger cations can presumably no longer be accommodated between contiguous anions within the same plane, and the structure “evolves” into the arrangement shown in Figure 5 (top, right). The croconate dianions form columns that extend parallel to the *c* axis and are completely surrounded by cations and water molecules, with these latter acting as “pincers” towards the dianions (see Figure 5, bottom left). The short interplanar separation (3.30 Å) is thus the result of external

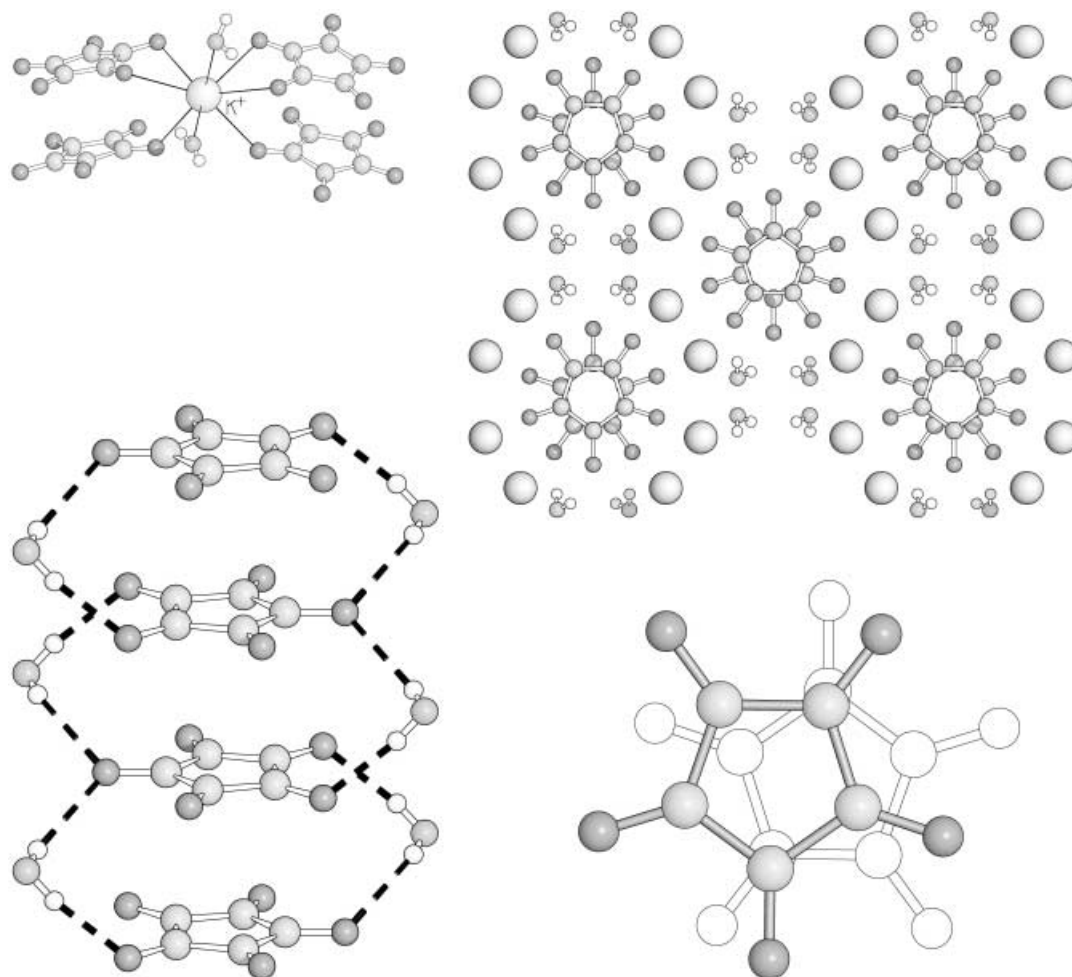


Figure 5. Top left: The coordination of two water molecules and four croconate dianions around the K^+ ion in crystalline $\text{K}_2\text{C}_5\text{O}_5 \cdot 2\text{H}_2\text{O}$. Top right: A view of the crystalline salt in the *bc* plane, showing how the dianions are stacked in columns surrounded by the cations and water molecules. $\text{O}_{\text{croconate}} \cdots \text{O}_{\text{water}}$ interactions omitted for clarity. Bottom right: A projection in the ring plane along the column, showing how the dianions are staggered, and the centroids only slightly shifted. Bottom left: A front view of the stacking of the anion, showing the interactions with the water molecules.

interactions that “compress” the anions together. Figure 5 (bottom right) shows how two consecutive croconate dianions along a column are staggered and slightly shifted (1.1 Å).

Ammonium croconate: In spite of the difference in chemical composition and in the type of noncovalent interactions that can be exploited, the ionic arrangement in ammonium croconate^[23c] is reminiscent of that discussed above for potassium croconate. The structure of ammonium croconate was determined by Baenziger et al. in 1964, and we summarise here the main structural features. Figure 6 (top) shows how the ammonium cations take the place of the potassium cations between croconate layers and act as bridges between the anions by forming charge-assisted $\text{N-H}^+\cdots\text{O}^-$ hydrogen bonds^[27] (four interactions with $\text{N}\cdots\text{O}$ separations in the range 2.82(1)–2.91(1) Å). The anion stacking (Figure 6, bottom) is comparable to that in the K^+ salt, both in terms of interplanar distance and shift (3.30 and 1.07 versus 3.30 and 1.10 Å for the NH_4^+ and K^+ salts, respectively).

Rubidium and caesium croconates: In spite of the difference in cation size, reflected in the different $\text{O}\cdots\text{M}^+$ separations (see Table 1), the Rb^+ and Cs^+ croconates are isomorphous and crystallise as anhydrous salts. The coordination around the cations is complex (see Figure 7, top) with at least seven close $\text{O}\cdots\text{M}^+$ interactions in the ranges 2.838(5)–3.135(5) and 3.029(5)–3.337(2) Å for the Rb^+ and Cs^+ salts, respectively. The middle structure in Figure 7 depicts a projection in the crystallographic ab plane; the stacks of flat croconate dianions are surrounded by piles of large cations. The interplanar separations in $\text{Rb}_2\text{C}_5\text{O}_5$ (3.30 Å) and in $\text{Cs}_2\text{C}_5\text{O}_5$ (3.42 Å) are comparable to that in $\text{K}_2\text{C}_5\text{O}_5\cdot 2\text{H}_2\text{O}$ (3.30 Å), but the shifts between the ring centroids are larger (1.92 and 2.11 Å in the Rb^+ and Cs^+ salts, respectively, versus 1.10 Å in

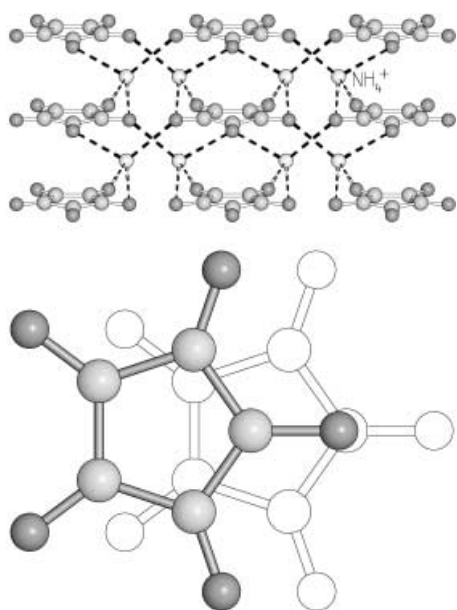


Figure 6. Top: The ammonium cations bridge the croconate anions through charge-assisted $\text{N-H}^+\cdots\text{O}^-$ hydrogen bonds. Bottom: The relationship between two consecutive rings along the anionic stacking.

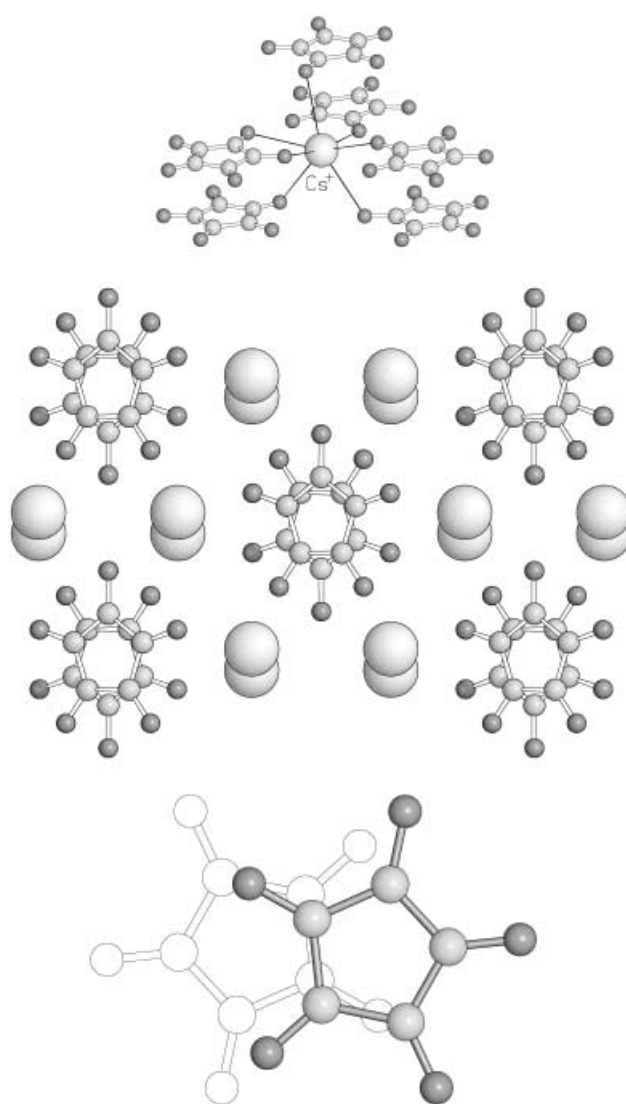


Figure 7. Top: The coordination around the Cs^+ ion in crystalline $\text{Cs}_2\text{C}_5\text{O}_5$ (the Rb^+ salt is isomorphous). Middle: A projection along the crystallographic c axis of the unit cell, showing how the anionic columns are surrounded by the Cs^+ ions along the columns. Bottom: The relationship between two consecutive rings along the anionic stacking in the Cs^+ salt.

the K^+ salt), so that the extent of overlap is smaller, as can be seen in Figure 7 (bottom).

Potassium hydrogencroconate croconate dihydrate: In an attempt to prepare potassium croconate we also obtained the “mixed” salt $\text{K}_3(\text{HC}_5\text{O}_5)(\text{C}_5\text{O}_5)\cdot 2\text{H}_2\text{O}$, which formally contains both the hydrogencroconate monoanion (HC_5O_5^-) and the croconate dianion ($\text{C}_5\text{O}_5^{2-}$). To the best of our knowledge, this is the first example of such a derivative of croconic acid; thus far only hydrogencroconate or croconate salts have been isolated and structurally characterised. The interest in this compound stems from the presence of a hydrogen-bonding interaction that joins the two anions. Figure 8 (top) shows that the crystal contains discrete $\text{HC}_5\text{O}_5^-\cdots\text{C}_5\text{O}_5^{2-}$ units, which would be more appropriately described as $[\text{C}_5\text{O}_5\cdots\text{H}\cdots\text{C}_5\text{O}_5]^{3-}$ dimeric units. These could be regarded as superanions, and indeed the distinction between hydrogencroconate and croconate ions is only semantic: the hydrogen atom of

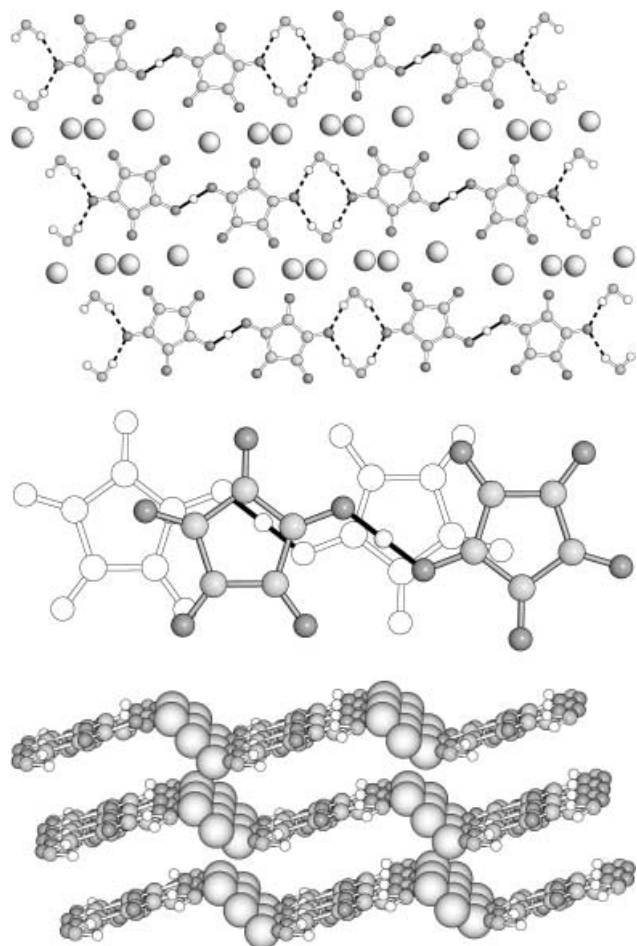


Figure 8. Top: The chains of water-bridged $[\text{C}_5\text{O}_5 \cdots \text{H} \cdots \text{C}_5\text{O}_5]^{3-}$ units. The K^+ ions are located between the chains. Bottom: The $[\text{C}_5\text{O}_5 \cdots \text{H} \cdots \text{C}_5\text{O}_5]^{3-}$ units are superimposed along the stacking, parallel to the b axis. Bottom: A side view showing the alternation of stacked anion/water chains and cationic layers.

the bridge resides on a centre of inversion and is therefore exactly midway between the two oxygen atoms, the $\text{O} \cdots \text{O}$ separation being as short as 2.444(5) Å. The $[\text{C}_5\text{O}_5 \cdots \text{H} \cdots \text{C}_5\text{O}_5]^{3-}$ units are bridged by two hydrogen-bonded water molecules ($\text{O}_{\text{anion}} \cdots \text{O}_{\text{water}}$ 2.786(6) and 2.972(6) Å; see Figure 8, top). The resulting chains are organized in stacks along the b axis: The middle structure in Figure 8 depicts how the dimeric units are superimposed along the stacking. The packing in crystalline $\text{K}_3(\text{HC}_5\text{O}_5)(\text{C}_5\text{O}_5) \cdot 2\text{H}_2\text{O}$ can thus be described as consisting of layers of anion/water chains that are intercalated with layers of cations, as shown in Figure 8 (bottom). The interanion $\text{O} \cdots \text{O}$ separation within the dimer is comparable to the values observed in other classes of hydrogen-bridged anions, such as hydrogenoxalates and hydrogensquarates^[21–22] (range 2.417–2.503 Å), as well as to the $\text{O} \cdots \text{O}$ separations in chains of hydrogencroconates in RbHC_5O_5 (2.443(8) Å). The interplanar separation of 3.19 Å is one of the shortest in this study, but, as evidenced by the shift value of 2.78 Å, it does not correspond to a π -stacking interaction.

The relatively large sample of croconate compounds now available allows an evaluation of the bonding parameters. The C–C distances within the $\text{C}_5\text{O}_5^{2-}$ ion lie within a narrow range

(1.45–1.48 Å). These values are clearly intermediate between that of aromatic systems and the average^[28] value expected for a cyclic $-\text{C}(=\text{O})-\text{C}(=\text{O})-$ system (1.537(2) Å from a CSD^[28] search of diketonic cyclic systems). In croconic acid (Figure 1, top), the two $-\text{C}(=\text{O})-\text{C}(=\text{O})-$ distances are C3–C4 1.508(6) and C4–C5 1.518(6) Å, which are considerably longer than in the croconate dianions and only slightly shorter than the average value of 1.537(2) Å. However, the C1–C2 distance of 1.382(5) Å is appreciably shorter and in agreement with the presence of a double bond. This comparison suggests that there is some degree of aromaticity in the C_5 ring. The average C–C bond lengths (1.460(1), 1.467(5), 1.472(4), 1.462(5), 1.455(7), 1.454(5) Å, for $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}$ and Cs , respectively) are, in fact, in reasonable agreement with that calculated for the isolated oxocarbon dianion (1.488 Å).^[29] In agreement with the observation by Dunitz et al.^[23b] the geometry of all croconate dianions discussed herein deviate only slightly from fivefold symmetry.

Conclusion

We have investigated the ion organisation in the family of crystalline salts $\text{M}_2\text{C}_5\text{O}_5$ ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$), $(\text{NH}_4)_2\text{C}_5\text{O}_5$ and the mixed hydrogencroconate/croconate salt $\text{K}_3(\text{HC}_5\text{O}_5)(\text{C}_5\text{O}_5) \cdot 2\text{H}_2\text{O}$. As pointed out in the introduction, the croconate dianion $\text{C}_5\text{O}_5^{2-}$ and the corresponding acid $\text{H}_2\text{C}_5\text{O}_5$, were first reported by Gmelin in 1825. His findings were contemporary with the isolation by Faraday of benzene, the prototype of aromatic molecules. Beside discussing the geometry of the croconate dianions in terms of average C–C distances, we sought the reason for the presence of short $\text{C}_5\text{O}_5^{2-} \cdots \text{C}_5\text{O}_5^{2-}$ inter-ring separations in the crystals. The inter-ring distances are, in fact, shorter than in graphite and in many other systems in which $\pi-\pi$ stacking is invoked.^[30] It has been pointed out previously, and supported by theoretical calculations,^[22] that, in many cases, short interplanar separations between ring systems (often called π -stacking interactions) are the result of a complex compromise between the need to occupy space efficiently and the need to optimise the ensemble of intermolecular interactions between building blocks.^[31] When the packing problem is that of accommodating spherical objects (the alkali metal cations) and flat discoidal units (the croconate dianions, but also the squarates, the hydrogencroconates, etc.), the best compromise is often attained by placing the disks “flat-on-flat” in a stack and by placing the spherical cations around the stack. If this is not sufficient to complete the coordination sphere of the smaller alkali metal cations, water molecules are incorporated in the crystal to take the place of the large dianions as coordination (and space) fillers. The fact that the discoidal dianions do not show a preferential relative orientation and can slide over each other indicates that the electronic gain from this type of weak noncovalent interaction is either zero or too small to be of any relevance in the presence of the much stronger electrostatic interactions.

Hence, it appears that the short interatomic/interplanar separations in the croconate salts are the result of the “electrostatic compression” arising from the attractive

$M^+ \cdots C_5O_5^{2-}$ interactions (or $N-H^+ \cdots O^-$ interactions when the cation is NH_4^+) that largely overcompensate for the repulsive $M^+ \cdots M^+$ and $C_5O_5^{2-} \cdots C_5O_5^{2-}$ interactions. Similar reasoning has been applied to arene–arene interactions in crystals of arene complexes containing large transition metal clusters, in which the compromise is between packing of the arene fragments and packing of the tubular CO ligands,^[32] and in crystals of salts containing the large PPh_4^+ ions, which tend to establish so-called phenyl embraces.^[33] These classes of different chemical systems all show preferential stacking or herringbone arrangements of ring systems, even though the dominant interactions are different. The relative role of attraction and repulsion in molecular crystals of fused aromatic hydrocarbons has also been discussed.^[34] All these investigations point to the fact that a packing analysis or a study of molecular/ionic recognition focused only on pairwise interactions can be misleading, as one may forget that it is the overall balance of intermolecular interactions, some acting at short range only, and others very long range, that accounts for molecular organisation and ultimately for crystal cohesion.

Experimental Section

Syntheses: Croconic acid (Aldrich) was dissolved in HCl (1M). Yellow crystals suitable for X-ray diffraction were obtained by slow evaporation of the solution. All croconate salts described here prepared by ring contraction of rhodizonic acid (Aldrich). In a typical procedure, rhodizonic acid (0.4 mg) was dissolved in an aqueous solution of the metal hydroxide (5 mL, 0.1M); crystals were obtained by slow evaporation of the solution. $K_3(HC_5O_5)(C_5O_5) \cdot 2H_2O$ was obtained by dropwise addition of HCl (3M) to a yellow solution of potassium croconate; the solution was then allowed to slowly evaporate.

Crystal structure determination: X-ray diffraction data of croconic acid and $Na_2C_5O_5 \cdot 2H_2O$ were collected on a Bruker AXS SMART diffractometer. X-ray diffraction data for the potassium, rubidium and caesium salts were collected on a Nonius CAD-4 diffractometer equipped with an Oxford Cryostream liquid- N_2 device. Crystal data and details of measurements are

reported in Table 2. Both diffractometers were equipped with a graphite monochromator (MoK_{α} radiation, $\lambda = 0.71073 \text{ \AA}$). SHELXS97^[35a] and SHELXL97^[35b] were used for structure solution and refinement based on F^2 . SCHAKAL99^[35b] was used for the graphical depiction of the results. CCDC 167861–167864 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

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Table 2. Crystal data and details of measurements for $H_2C_5O_5$, $Na_2C_5O_5 \cdot 2H_2O$, $Rb_2C_5O_5$, $Cs_2C_5O_5$ and $K_3(HC_5O_5)(C_5O_5) \cdot 2H_2O$.

	$H_2C_5O_5$	$Na_2C_5O_5 \cdot 2H_2O$	$Rb_2C_5O_5$	$Cs_2C_5O_5$	$K_3(HC_5O_5)(C_5O_5) \cdot 2H_2O$
formula	$C_2H_2O_5$	$C_5H_4Na_2O_7$	$C_5O_5Rb_2$	$C_5O_5Cs_2$	$C_{10}H_5K_3O_{12}$
M_r	142.07	222.06	310.99	405.87	434.44
T [K]	273(2)	293(2)	293(2)	293(2)	223(2)
system	orthorhombic	monoclinic	monoclinic	monoclinic	triclinic
space group	$Pca2_1$	$C2/c$	$C2/c$	$C2/c$	$P\bar{1}$
a [Å]	8.7108(8)	7.7442(8)	13.284(5)	13.679(6)	4.234(6)
b [Å]	5.1683(5)	17.363(2)	7.826(2)	8.0350(10)	8.005(4)
c [Å]	10.9562(9)	6.4024(7)	7.633(5)	8.023(2)	11.260(7)
α [°]	90	90	90	90	74.10(4)
β [°]	90	111.799(3)	114.22(5)	113.51(2)	83.94(8)
γ [°]	90	90	90	90	87.69(7)
V [Å ³]	493.25(8)	799.32(15)	723.7(6)	808.6(4)	365.0(6)
Z	4	4	4	4	1
$F(000)$	288	448	576	720	218
θ range [°]	4–34	2–34	3–27	3–30	3–25
$\mu(MoK_{\alpha})$ [mm ^{−1}]	0.179	0.260	2.854	8.993	1.002
measured reflns	6525	5721	843	1339	1342
unique reflns	1838	1513	782	1180	1270
refined parameters	91	74	57	56	115
GOF on F^2	0.864	0.812	1.012	0.930	1.054
$R1$ [on F , $I > 2\sigma(I)$]	0.0549	0.0406	0.0407	0.0314	0.0464
$wR2$ (F^2 , all data)	0.1240	0.0948	0.1096	0.0783	0.1368

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