Reversible solid-state interconversion of rhodizonic acid $H_2C_6O_6$ into $H_6C_6O_8$ and the solid-state structure of the rhodizonate dianion $C_6O_6^{2-}$ (aromatic or non-aromatic?)

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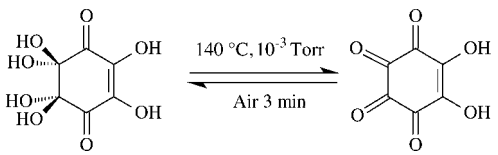
Anhydrous rhodizonic acid $H_2C_6O_6$ is obtained by (fully reversible) thermal dehydration of solid 2,3,5,5,6,6-hexahydroxycyclohex-2-ene-1,4-dione, $H_6C_6O_8$, commonly known as rhodizonic acid dihydrate. Treatment of $H_6C_6O_8$ with RbOH yields crystals of $Rb_2C_6O_6$; the oxocarbon dianion $C_6O_6^{2-}$ is shown to possess a flat, benzene-type structure, with C–C bonds shorter than expected for a (non-aromatic) ketonic-type structure.

One of the reasons for the continuing interest in the structure of oxocarbon acids and of their deprotonation products is the view that cyclic oxocarbon anions of the general formula $C_nO_n^{2-}$ might show aromaticity, stabilised by electron delocalisation of the π electrons around the ring.[1] The oxocarbon anion family comprises the rhodizonate, $C_6O_6^{2-}$, croconate, $C_5O_5^{2-}$, squarate, $C_4O_4^{2-}$ and deltate, $C_3O_3^{2-}$, dianions.[2] The prototype for all these is the rhodizonate dianion, $C_6O_6^{2-}$, because of the structural analogy with benzene, C_6H_6. Rhodizonate 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.[3] We have utilised oxocarbon acids, and the corresponding mono- and dianions, in the course of our crystal engineering studies[4] and in the evaluation of some fundamental aspects of hydrogen bonding interactions between ions.[5] While the solid state structure of croconic acid has been recently determined by us,[6a] that of rhodizonic acid has been assigned on the basis of solution studies.[6b,c] Analogously, there is no previous report on the solid state structure of the rhodizonate dianion, $C_6O_6^{2-}$.

In this preliminary communication, we report that when crystalline $H_8C_6O_8$ (2,3,5,5,6,6-hexahydroxycyclohex-2-ene-1,4-dione) **1** is subjected to a thermogravimetric experiment (TGA), the loss of two water molecules per formula unit is observed at 180 °C, and an orange powder is obtained.[7] The product was identified as rhodizonic acid $H_2C_6O_6$ **2** on the basis of mass spectrometric measurements.[7] The same powder material was subsequently obtained by thermal treatment of solid **1** at 140 °C under vacuum (10^{-3} Torr).[8] Although hydration of carbonyl groups is a well-known process, usually studied in solution, the controlled and reversible dehydration of a solid hexol has never been investigated before. The process is fully reversible and uptake of water vapour by **2** leads quantitatively back to **1** in 3 min, as demonstrated by powder X-ray diffraction. The process is summarised in Scheme 1.

The single crystal X-ray structure of **1** has been determined (see Fig. 1).[9] The crystal is constituted of layers of molecules linked by both intra-planar and inter-planar hydrogen bonds between the six –OH groups [six O···O distances in the range 2.72–3.01(1) Å]. It is interesting to note that the shortest O···O interactions formed by the two "axial" –OH groups in each molecule are intra-layer interactions. Although not yet proved, a reasonable "Occam's razor" hypothesis is that the dehydration process involves precisely these two –OH groups occupying the intra-layer space. After proton abstraction from adjacent –OH groups, the water molecules, once formed, would be able to leave the crystal structure easily by diffusing between the layers.

All attempts to grow single crystals of **2** have, thus far, been unsuccessful. Treatment of **1** with RbOH in ethanol yields a deep-red powder of $Rb_2C_6O_6$, which, upon recrystallisation from a small amount of water, affords dark-green crystals of anhydrous $Rb_2C_6O_6$, **3**.[9] The product can assume different colours depending on subtle changes in the preparation procedure, thus appearing deep-red, purple or dark-green in reflected light, but it is always red in transmitted light.[10] The



Scheme 1 The reversible dehydration process.

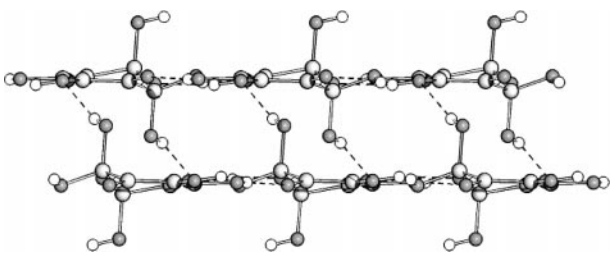


Fig. 1 A view of two layers of molecules in crystalline **1**; two –OH groups from each molecule protrude above and below the molecular layers and form intermolecular hydrogen bonds that link the layers together (only intermolecular hydrogen bonds are shown).

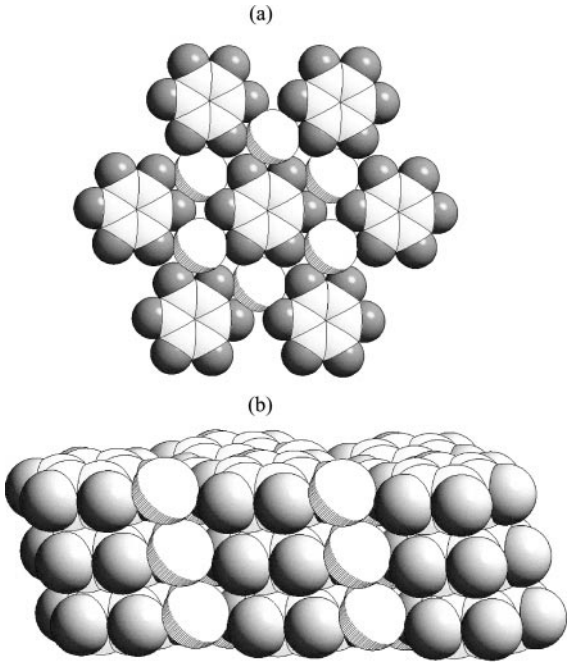


Fig. 2 (a) The distribution of $C_6O_6^{2-}$ dianions and Rb^+ cations in the layers of crystalline $Rb_2C_6O_6$. (b) The layer stacking, note how the $C_6O_6^{2-}$ dianions (interplanar distance 3.30 Å) are shifted while the Rb^+ cations are in close contact, forming a cationic pile. Rb···O distances in the range 2.904(6)–3.369(7) Å.

structure of **3** is shown in Fig. 2. Both the dianion and its crystal possess some remarkable features: (i) the crystal is formed of layers of rhodizonate dianions, $C_6O_6^{2-}$, organised with pseudo-sixfold symmetry within the layer [see Fig. 2(a)]; the $C_6O_6^{2-}$ units lie flat on each other at an interplanar distance of 3.30 Å; (ii) the Rb cations form cationic rows in between the rhodizonate units [see Fig. 2(b)]. Similar stacking has been recently observed in crystalline potassium croconate dihydrate.[11]

Within the dianion there are two independent C–O distances [1.252(9) and 1.248(6) Å] and two independent C–C distances [1.468(6) and 1.469(6) Å]. These latter values are intermediate between those of aromatic systems[12a] and those expected for a cyclic –C(=O)–C(=O)– system [1.508(6), 1.518(6) Å in croconic acid,[6a] 1.537_2 Å from a CSD[12b] search of diketonic six-membered ring systems]. The value of 1.468(5) Å is also slightly shorter than predicted theoretically in a recent computational study of isolated oxocarbon dianions.[13] Whether this difference is due to a significant aromatic contribution to the C–C bonds, or to the fact that, in the solid state, the rhodizonate anion interacts with the cations, needs further investigation.

In this context, it is worth noting that the interplanar distance between the dianions along the stack is even shorter than in graphite and in many other systems where π–π stacking is observed.[14] We believe that this short separation is due to the Rb cations, which pinch together dianions along the stacking sequence, this being a manifestation of the "charge compression" effect previously discussed in the cases of the stacking of flat squarate and hydrogen squarate ions.[15]

Since hydration of rhodizonic acid can be achieved in a reversible solid-state process, we are currently exploring the possibility of using the uptake of nucleophilic molecules *via* a heterogeneous process, to prepare other adducts.

Note added in proof. While this paper was being processed, we have become aware of the report by Lam and Mak of the structure of the rhodizonate dianion in the salt $[Bu^n{}_4N^+]_2C_6O_6^{2-}\cdot 4PhNHCONH_2$: C.-K. Lam and T. C. W. Mak, *Chem. Commun.*, 2001, 1568.

Crystallography

Single crystal X-ray diffraction data for **1** were collected on a Bruker AXS SMART diffractometer: $C_6H_6O_8$, $T = 223(2)$ K, $M = 206.11$, monoclinic, $C2/c$, $a = 11.216(1)$, $b = 9.612(1)$, $c = 12.786(2)$ Å, $\beta = 91.796(6)^\circ$, $V = 1377.8(3)$ Å^3, $Z = 8$, $F(000) = 848$, $\mu = 0.193$ mm^{-1}, θ range 2–34°, 9624 reflections, 2589 independent, refinement on F^2 for 152 parameters, wR (F^2, all refl.) = 0.1462, R_1 [$I > 2\sigma(I)$] = 0.0592. The powder X-ray diffraction pattern measured on the commercial powder corresponds precisely to that calculated on the basis of the single-crystal structure. Crystal data for **3** were collected on a Nonius CAD4 diffractometer equipped with an Oxford Cryostream liquid-N_2 device: $Rb_2C_6O_6$, $T = 223(2)$ K, $M = 339.00$, Monoclinic, $C2/m$, $a = 12.522(4)$, $b = 8.354(4)$, $c = 3.761(3)$ Å, $\beta = 96.93(5)^\circ$, $V = 390.6(4)$ Å^3, $Z = 2$, $F(000) = 316$, $\mu = 12.528$ mm^{-1}, θ range 3–28°, 1001 reflections, 501 independent, refinement on F^2 for 36 parameters, wR (F^2, all refl.) = 0.1061, R_1 [$I > 2\sigma(I)$] = 0.0374. Both diffractometers equipped with a graphite monochromator (Mo-Kα radiation, $\lambda = 0.710\,73$ Å). SHELXS-97[9a] and SHELXL-97[9a] were used for structure solution and refinement based on F^2. SCHAKAL99[9b] was used for the graphical representation of the results.

CCDC reference numbers 163618 and 163619. See http://www.rsc.org/suppdata/nj/b1/b107317f/ for crystallographic data in CIF or other electronic format.

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