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Stabilization of D_{5h} and C_{2v} valence tautomers of the croconate dianion†

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The non-benzenoid aromatic D_{5h} and enediolate C_{2v} form of $C_5O_5^{2-}$ have been stabilized by hydrogen bonding with urea and 1,3-dimethylurea, respectively, in the host lattices of two novel crystalline inclusion compounds.

Based on the premise that a monocyclic oxocarbon dianion $C_nO_n^{2-}$ (n = 3–6),[1] considered as a hub, could be stabilized by surrounding it with an optimized set of convergent NH donor sites, we have generated the relatively unstable rhodizonate ion $C_6O_6^{2-}$ *in situ* and incorporated it and its ring-contracted croconate product[2] $C_5O_5^{2-}$ into the host frameworks of the nearly isostructural inclusion compounds $[(n\text{-}C_4H_9)_4N^+]_2C_6O_6^{2-}\cdot 4(C_6H_5NHCONH_2)$ and $[(n\text{-}C_4H_9)_4N^+]_2C_5O_5^{2-}\cdot 4(C_6H_5NHCONH_2)$, respectively.[3] Further work then led to the selective entrapment of the non-benzenoid aromatic D_{6h} and enediolate C_{2v} valence tautomers of $C_6O_6^{2-}$ by *N*-(3-hydroxyphenyl)urea and 1,1′-ethylenediurea, respectively, in the corresponding inclusion compounds.[4] As previous theoretical[5] and experimental[6] studies on the $C_nO_n^{2-}$ system indicated that the extent of electron delocalization increases as ring size decreases,[7] we set about the presumably more challenging task of trapping analogous D_{5h} and C_{2v} valence tautomers of the lighter homolog $C_5O_5^{2-}$. We now describe our accomplishment of this objective through the synthesis and low-temperature (123 K) crystal structure analysis of two new inclusion compounds $[(n\text{-}C_3H_7)_4N^+]_2C_5O_5^{2-}\cdot 3(NH_2)_2CO\cdot 8H_2O$ (**1**) and $[(n\text{-}C_4H_9)_4N^+]_2C_5O_5^{2-}\cdot 3(CH_3NH)_2CO$ (**2**), respectively.‡

In the crystal structure of **1**, two of the three independent urea molecules constitute a hydrogen-bonded dimer, labeled motif **A** (Fig. 1). Adjacent pairs of urea dimer lying parallel to the [001] direction are twisted by 60° and bridged by pairs of water molecules derived from O1w and O2w *via* pairs of strong N_{syn}–H···O and O–H···O hydrogen bonds[8a] to form a twisted $[\text{urea dimer–}(H_2O)_2]_\infty$ ribbon with a new ring motif **B**. The third independent urea molecule is directly joined to the croconate anion *via* a pair of strong, charge-assisted N_{anti}–H···O⁻ hydrogen bonds with ring motif **C**. Neighboring croconate–urea building blocks rotated by about 60° along the *c*-axis are alternately bridged by pairs of two distinct types of water molecules derived from O4w and O3w *via* pairs of strong O–H···O⁻ hydrogen bonds to form another twisted ribbon $[\text{croconate–urea–}(H_2O)_4]_\infty$ characterized by two additional hydrogen-bonded rings **D** and **E**. The ribbon is further consolidated by independent water molecules O5w, O6w, O7w and O8w at four corners of the croconate–urea building block by forming pairs of strong negative-charge assisted O–H···O⁻, O–H···O and N–H···O hydrogen bonds to yield four new motifs **F**, **G**, **H**and **I**. These two types of twisted hydrogen-bonded ribbons are arranged alternately side by side parallel to the *c*-axis and constitute the [001] channel system (see Fig. 4 in ESI†). They are further cross-linked together by pairs of strong N–H_{anti}···O⁻ (ring motif **J**), O–H···O and N–H···O hydrogen bonds to produce a wide platform containing new ring patterns **K**, **L**, **M** and **N** for the construction of a side-wall of the [110] channel system. Two large voids characterized by ring motifs **O** and **P** define the cross-section of the channel with dimensions of about 10.8 Å × 7.4 Å, and a similar channel is directed along $[1\bar{1}0]$ [see Fig. 5 in ESI†]. The host lattice contains three systems of intersecting channels [see Fig. 6 in ESI†]. The two independent, well-ordered tetra-*n*-propylammonium cations, which occupies general and $\bar{1}$ positions, are accommodated in a single column along the [001] channel and in a double column along each of the other two channels.

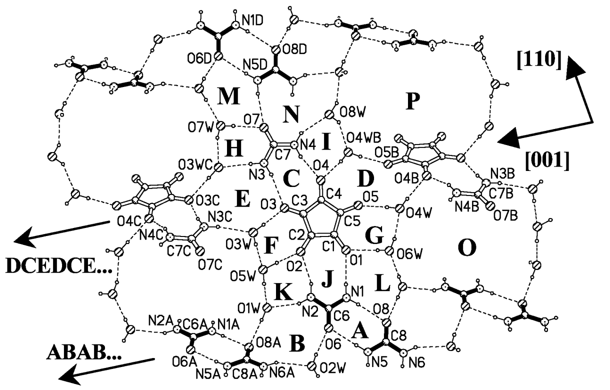

Fig. 1 Projection diagram on the $(1\bar{1}0)$ plane showing the hydrogen-bonding scheme for a portion of the host lattice in **1**. The slanted vertical $(\text{urea dimer–croconate–urea})_\infty$ chain constitutes a side wall of the [110] channel system. The parallel $[\text{urea dimer–}(H_2O)_2]_\infty$ **ABAB**··· and $[\text{croconate–urea–}(H_2O)_4]_\infty$ **DCEDCE**··· ribbons define the channel system in the *c*-direction. Symmetry transformations: A(x, $-y$, $-1/2 + z$), B($1-x$, y, $3/2 - z$), C($1-x$, y, $1/2 - z$) and D($1-x$, $1/2 + y$, z).

To create an asymmetric hydrogen-bond donor environment that stabilizes the C_{2v} valence tautomer of $C_5O_5^{2-}$, we replaced urea with its 1,3-dimethyl derivative to generate inclusion compound **2**. In the resultant host lattice, the croconate dianion resides on a 2-fold axis, being directly linked to three 1,3-dimethylurea molecules through pairs of N–H···O (ring motifs **A** and **B**) hydrogen bonds to form a semi-circular structural unit (Fig. 2). In particular, each type O1 oxygen atom forms two strong acceptor hydrogen bonds with the N–H donors from a pair of 1,3-dimethylurea molecules, while each type O2 oxygen atom forms only one N–H···O hydrogen bond. In contrast, the solitary type O3 oxygen atom is stabilized by two weak C–H···O hydrogen bonds[8b] with neighboring tetra-*n*-butylammonium cations (see Fig. 7 in ESI†).

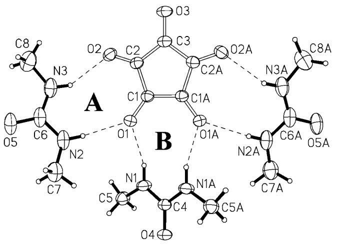

Fig. 2 Hydrogen-bonding environment of the croconate dianion in the crystal structure of $[(C_4H_9)_4N^+]_2C_5O_5^{2-}\cdot 3(CH_3NH)_2CO$ (**2**). Thermal ellipsoids are drawn at the 50% probability level. Symmetry transformation: A($1-x$, y, $1/2 - z$).

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† Electronic supplementary information (ESI) available: synthesis details for **1** and **2**, Figs. 4–8, and Tables 1–5. See http://www.rsc.org/suppdata/cc/b3/b312545a/

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Such a highly unsymmetrical environment engenders a sharp gradient of hydrogen-bonding donor strength around the croconate ion, which is conducive to stabilization of its C_{2v} valence tautomer with significantly different C–C and C–O bond lengths around the cyclic system. The $C_5O_5^{2-}\cdot 3(CH_3NH)_2CO$ aggregates are further connected together by weak C(sp^3)–H···O donor hydrogen bonds from the quaternary ammonium cations to form a highly puckered layer. Stacking of layers in the crystal structure of **2** is displayed in Fig. 8 in ESI†.

The croconate ion is a very stable species that can coordinate to a transition metal in the terminal bidentate mode,[9] in which case the C–C and C–O bond lengths involving atoms in the resulting five-membered chelate ring are in agreement with their formal bond orders of two and one, respectively, in the enediolate form of the ligand. When $C_5O_5^{2-}$ functions as a multidentate ligand that bridges two or more metals to form a dinuclear, polynuclear or polymeric coordination compound,[10] the bond-length variation exhibits a more complex pattern. The measured bond lengths and bond angles of $C_5O_5^{2-}$ in the crystal structure of **1** (Fig. 3a) are consistent with its expected charge-delocalized D_{5h} structure in the ground state. In contrast, the molecular dimensions of $C_5O_5^{2-}$ in **2** are indicative of a vicinal triketo-endiolate structure (Fig. 3b), which corresponds to the less stable, partially charge-localized C_{2v} valence tautomer, whose stabilization can be attributed to its highly unsymmetrical hydrogen-bonding environment within the host layer (Fig. 2).

We have carried out *ab initio* and DFT calculations at various correlation levels[11] employing basis sets of increasing complexity [see Tables 1 and 2 in ESI†] to study the geometry and charge distribution of the croconate dianion in isolated and hydrogen-bonded situations. For a starting model consisting of an isolated charge-localized $C_5O_5^{2-}$ system with imposed C_{2v} symmetry, the calculated bond lengths converge to the values that correspond to idealized D_{5h} molecular structure, showing that the latter geometry adequately represents the ground state of the dianion. In other words, the C_{2v} form of the croconate dianion cannot exist as a single entity. For the charge-delocalized D_{5h} form of $C_5O_5^{2-}$, the computed bond lengths at either the rather primitive HF/3-21G(d) level (C–C = 1.462 Å and C–O = 1.249 Å) or the much more sophisticated CASSCF(6,4)/3-21G(d) level (1.460, 1.252 Å) agree reasonably well with the measured metrics of **1** and previously reported values (1.451–1.465, 1.241–1.254 Å).[3] Our calculated results compare favorably with those (1.488, 1.247 Å) optimized at the B3LYP/6-311+G(d) level in a recent theoretical study.[5f] In model calculations on a 1:1 hydrogen-bonded aggregate of urea with $C_5O_5^{2-}$ constrained to C_s, C_2 or C_{2v} symmetry (which converged to the same results), the $C_5O_5^{2-}$ moiety exhibits the enediolate characteristics similar to those observed in **2**. Notably the best agreement with the measured bond lengths (Fig. 3b) is obtained at the HF/3-21G(d) level (C1–C2 = 1.433, C2–C3 = 1.457, C3–C4 = 1.477, C1–O1 = 1.267, C3–O3 = 1.238, C4–O4 = 1.232), as higher-level computations invariably yield significantly longer C–C bond distances [see Tables 3, 4 and 5 in ESI†]. Natural bond orbital (NBO) analysis[12] lends credence to non-benzenoid aromaticity in the isolated $C_5O_5^{2-}$ system, with equal negative charge (−0.716) on each O atom and equal positive charge (+0.316) on each C atom. On the other hand, in the 1:1 adduct of $C_5O_5^{2-}$ with urea, the pair of O atoms in the hydrogen-bonded ring carry a higher negative charge of −0.759, whereas those on the remaining three O atoms of $C_5O_5^{2-}$ range from −0.644 to −0.671; when urea is replaced by 1,3-dimethylurea, the corresponding charges are changed to −0.790 and −0.618 to −0.691, respectively.

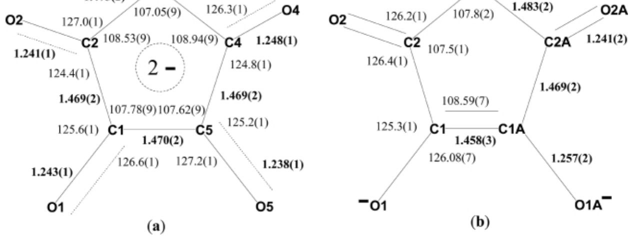

Fig. 3 Bond lengths (Å) and angles (°) of the D_{5h} (a) and C_{2v} (b) valence tautomers of the croconate dianion as observed in **1** and **2**, respectively, with standard deviations enclosed in parentheses.

This work clearly shows that crystal engineering provides a viable route to breaking the degeneracy of cannonical forms of a molecular species (Fig. 2 and 3b).

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Notes and references

‡ Crystal data for **1**: $[(n\text{-}C_3H_7)_4N^+]_2C_5O_5^{2-}\cdot 3(NH_2)_2CO\cdot 8H_2O$, monoclinic, space group $C2/c$ (no. 15), a = 33.399(2), b = 16.2615(8), c = 17.7104(9) Å, β = 104.210(1)°, Z = 8, 11221 unique MoKα reflections (R_{int} = 0.0184), final R_1 = 0.0439, wR_2 = 0.1261, 9545 observed reflections [$I > 2\sigma(I)$]. Crystal data for **2**: $[(n\text{-}C_4H_9)_4N^+]_2C_5O_5^{2-}\cdot 3(CH_3NH)_2CO$, M = 889.31, monoclinic, space group $C2/c$ (no. 15), a = 25.211(4), b = 13.570(2), c = 15.775(2) Å, β = 93.20(2)°, Z = 4, 5304 unique MoKα reflections (R_{int} = 0.0222), final R_1 = 0.0466, wR_2 = 0.1337, 4687 observed reflections [$I > 2\sigma(I)$]. CCDC reference numbers 210097 and 216681. See http://www.rsc.org/suppdata/cc/b3/b312545a/ for crystallographic data in .cif or other electronic format.

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