A new water···Na^+ coordination motif in an unexpected diatrizoic acid disodium salt crystal form

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Electronic Supporting Information

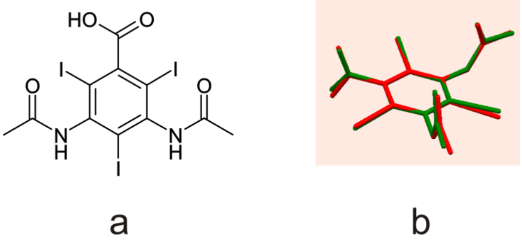

Fig. S1 (a) Molecular structure of diatrizoic acid and (b) molecular overlay of the two diatrizoic acid dianions in the asymmetric unit of **I**. Hydrogen atoms are omitted for clarity.

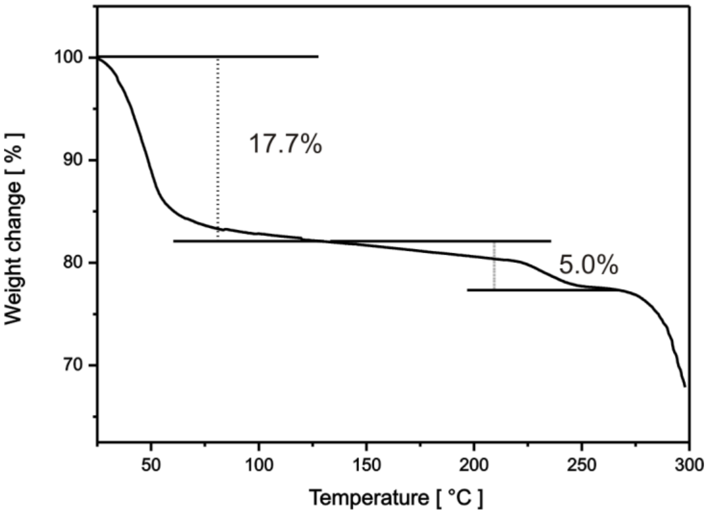

Fig. S2 Thermogravimetric analysis of **I**. In the first step up to 110 °C, a mass loss of 17.7% corresponds to the loss of ethanol and 5 water molecules. The second mass loss of a further 5% corresponds to a mass loss of the remaining 3.5 water molecules.

<u>Crystallisation and crystallographic data</u>

Crystals of **I** were grown from a solution of diatrizoic acid (0.1 g, 0.16 mmol) in ethanol (4 ml) neutralised by addition of aqueous NaOH solution (0.75 mmol) as prismatic colourless blocks. Crystal data: $C_{13}H_{30}I_3N_2Na_2O_{13.5}$, M =857.07, tetragonal, a = 30.2764(12) Å, c = 12.3234(5) Å, V = 11296.4(8) Å^3, T = 120(2), space group I-4 (no. 82), Z = 16, μ(MoKα) = 3.409, 42933 reflections measured, 16622 unique (R_{int} = 0.0626) which were used in all calculations. The final wR_2 was 0.0707 (all data) and R_1 was 0.0353 ($>2\sigma(I)$).

DFT calculations

In situations with long, ionic interactions it is possible that DFT calculations can unphysically distribute the electrons amongst the centres; we have therefore used the Coulomb-attenuated CAM-B3LYP functional to avoid such problems. All calculations were performed using the Gaussian 09 program with the large aug-cc-pVTZ basis set, which includes diffuse functions to minimise any artificial localisation of the electrons.

Calculations were performed at both the crystal structure geometry, and a CAM-B3LYP/aug-cc-pVTZ geometry obtained by holding fixed the Na and O nuclei at their crystal structure coordinates, but allowing the position of the two H nuclei to optimise. The two structures are qualitatively the same, so for simplicity we present results only for the crystal structure geometry. By computing the total energies of the two individual fragments consisting of (A) the three sodium ions, and (B) the water molecule, together with that of the interacting system, it is possible to compute the $3Na^+\ldots H_2O$ interaction energy as an indication of the effect due to the presence of the water molecule: it has a stabilising effect of around 35 kcal/mol.

Thermogravimetry

Thermogravimetric analysis was run on a Perkin Elmer Pyris 1 TGA purged with CP grade helium at a rate of 50 ml min^{-1}. The temperature was programmed to rise from room temperature (25 °C) to 350 °C at a heating rate of 10 °C min^{-1}.

Citations

Full citation for Ref 30:

Gaussian 09 Revision A.02, M. J. Frisch and G. W. Trucks and H. B. Schlegel and G. E. Scuseria and M. A. Robb and J. R. Cheeseman and G. Scalmani and V. Barone and B. Mennucci and G. A. Petersson and H. Nakatsuji and M. Caricato and X. Li and H. P. Hratchian and A. F. Izmaylov and J. Bloino and G. Zheng and J. L. Sonnenberg and M. Hada and M. Ehara and K. Toyota and R. Fukuda and J. Hasegawa and M. Ishida and T. Nakajima and Y. Honda and O. Kitao and H. Nakai and T. Vreven and Montgomery, {Jr.}, J. A. and J. E. Peralta and F. Ogliaro and M. Bearpark and J. J. Heyd and E. Brothers and K. N. Kudin and V. N. Staroverov and R. Kobayashi and J. Normand and K. Raghavachari and A. Rendell and J. C. Burant and S. S. Iyengar and J. Tomasi and M. Cossi and N. Rega and J. M. Millam and M. Klene and J. E. Knox and J. B. Cross and V. Bakken and C. Adamo and J. Jaramillo and R. Gomperts and R. E. Stratmann and O. Yazyev and A. J. Austin and R. Cammi and C. Pomelli and J. W. Ochterski and R. L. Martin and K. Morokuma and V. G. Zakrzewski and G. A. Voth and P. Salvador and J. J. Dannenberg and S. Dapprich and A. D. Daniels and Ö. Farkas and J. B. Foresman and J. V. Ortiz and J. Cioslowski and D. J. Fox, 2009.