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# The enigma of a (±)-tartaric acid–urea cocrystal

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**By repeated synthesis and X-ray diffraction study it was cleared up that a (±)-tartaric acid–urea cocrystal is a true racemate, which crystallizes in noncentrosymmetric space group $P2_1$ due to a chiral packing of the molecules in the crystal.**

The communication by Lü *et al.*[1] is of interest as an example of non-linear optical (NLO) properties of a (±)-tartaric acid–urea cocrystal **1** but it seems enigmatic to us. Indeed, one can expect that **1** (space group $P2_1$) would form a conglomerate. However, it is not in agreement with the data for a (+)-tartaric acid–urea cocrystal (**2**), which was reported to crystallize in space group $P2_12_12_1$ ($Z = 4$, $Z' = 1$).[2] Note that neither the values of $Z$ nor atomic coordinates were reported[1] for **1**. That is why we have reiterated the synthesis† and X-ray diffraction (XRD) study‡ of **1**.

According to XRD analysis, the crystal of **1** is composed of the opposite enantiomers of tartaric acid, which are interconnected by O–H···O bonds into double chains. The latter are formed by two homochiral strands with the O–H···O–H bonding [O···O 2.735(2)–2.769(2) Å], which are cross-linked through the centrosymmetric eight-membered H-rings [O···O 2.628(2)–2.678(2) Å] typical of carboxylic acids (Figure 1).

The heterochiral chains, in turn, are assembled into a 3D framework *via* N–H···O [N···O 2.902(2)–3.341(2) Å] and O–H···O [2.537(2)–2.759(2) Å] bonds (Figure 2). There is no direct bonding between the independent urea molecules; therefore, significant enhancement of NLO properties can be regarded as a consequence of urea polarization upon the formation of H-bonds with acids.

Thus, the enigma of **1** was resolved unambiguously. It is a new rare case of the crystallization of racemate in noncentrosymmetric space group. A similar example is *erythro*-phenylglyceric acid,[3,4] its (±)-form crystallizes in space group $P2_1$, whereas (+)-form in $P2_12_12_1$. The racemates of *ortho*-tyrosine, α-methylsuccinic acid and camphoroxime are known to crystallize in space group $P2_1$.[3,4] Five examples of racemate crystallization in space group $P2_12_12_1$ and one in space group $P4_1$ were reported.[4]

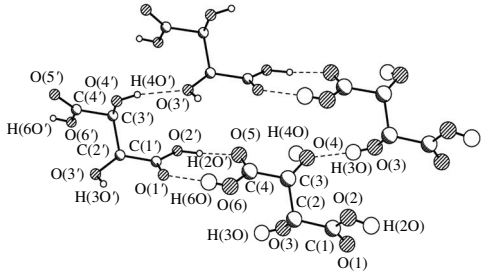


**Figure 1** Heterochiral double chains in **1**. The opposite enantiomers are symbolized by bigger and smaller circles, respectively.

Attempts to perform a cocrystallization of (±)-tartaric acid with another ureas, thiourea, and oxamide under the same conditions have failed. So, in the cases of 1-methyl, 1-ethyl, 1,3-dimethyl-ureas, thiourea, and oxamide the crystals of (±)-tartaric acid were isolated whereas upon cocrystallization of (±)- or (+)-1-*sec*-butyl-3-methylurea with (+)- or (±)-tartaric acid the crystals of the corresponding initial ureas were obtained.

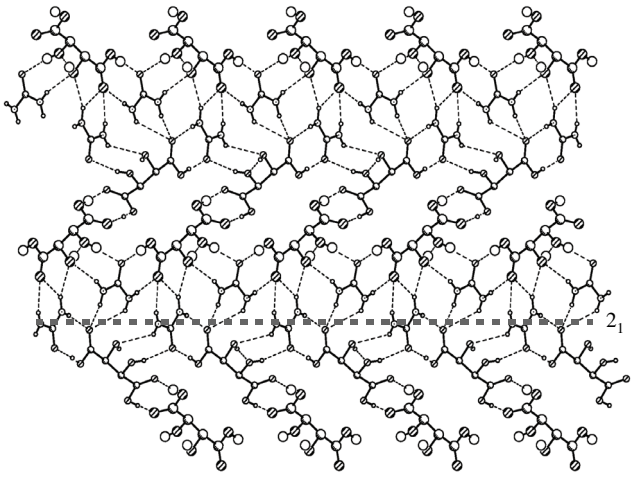


**Figure 2** Fragment of crystal packing illustrating the 3D H-bonded framework. The opposite enantiomers are shown by bigger and smaller circles, respectively.

† Cocrystal **1** was prepared as described earlier[1] in a sealed capillary, mp 155–159 °C (with sublimation and decomposition). A colourless transparent single crystal of (±)-**1** was grown from distilled water.

‡ *Crystals of* **1**, $C_5H_{10}N_2O_7$, $M = 210.14$, are monoclinic, space group $P2_1$, at 100 K: $a = 4.8116(4)$, $b = 23.0797(19)$ and $c = 7.6462(6)$ Å, $\beta = 101.0770(18)°$, $V = 833.29(12)$ Å$^3$, $Z = 4$, $d_{calc} = 1.675$ g cm$^{-3}$, $\mu$(MoKα) = 1.59 cm$^{-1}$, $F(000) = 440$. Intensities of 10253 reflections were measured with a Bruker SMART APEX2 CCD diffractometer [$\lambda$(MoKα) = 0.71072 Å, $\omega$-scans, $2\theta < 58°$] and 12963 independent reflections ($R_{int} = 0.0463$) were used in a further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against $F^2$ in the anisotropic–isotropic approximation. Hydrogen atoms were located from the Fourier synthesis of the electron density and refined in the isotropic approximation. For **1** the refinement converged to $wR_2 = 0.0816$ and GOF = 1.049 for all independent reflections [$R_1 = 0.03340$ was calculated against $F$ for 2079 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0. The X-ray diffraction investigation was carried out by I. V. Glukhov (X-Ray Diffraction Center, INEOS RAS).

CCDC 713420 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2009.

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## References

1 M. K. Lü, F. Q. Meng, Z. H. Yang, W. T. Y and H. Zeng, *Cryst. Res. Technol*., 1996. **31**, 833.
2 M. K. Lü, F. Q. Meng, H. Zeng and W. T. Yu, *Chin. Sci. Bull*., 1996, **41**, 1392.
3 J. Jacques, A. Collet and S. H. Wilen, *Enantiomers, Racemates and Resolutions*, Krieger Publishing Company, Malabar, FL, 1994, pp. 15, 23.
4 C. P. Brock, W. B. Schweizer and J. D. Dunitz, *J Am. Chem. Soc*., 1991, **113**, 9811.

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