

Sang Loon Tan and Edward R.T. Tiekink*

Crystal structure of the co-crystal *N,N'*-bis(3-pyridylmethyl)oxalamide acetic acid (1/2), $C_{14}H_{14}N_4O_2 \cdot 2C_2H_4O_2$

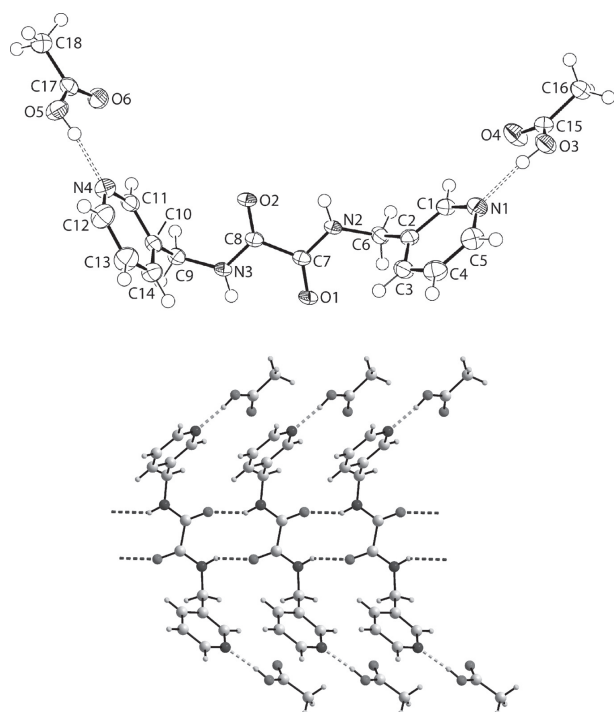


Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	$0.12 \times 0.06 \times 0.03$ mm
Wavelength:	Cu K α radiation (1.54184 Å)
μ :	0.88 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	76.4° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	23452, 3961, 0.046
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3434
$N(\text{param})_{\text{refined}}$:	267
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

the atoms including atomic coordinates and displacement parameters.

Source of material

N,N'-Bis(pyridin-3-ylmethyl)oxalamide, $^3\text{LH}_2$, was prepared according to the literature procedure [5] (melting point, m.pt: 474–475 K). The title co-crystal was prepared by dissolving $^3\text{LH}_2$ (0.154 g, 1 mmol) in an excess of glacial acetic acid (3 mL). Upon its dissolution, benzene (3 mL) was carefully layered on top of the solution. Colourless crystals formed approximately one week after the crystallisation and shown crystallographically to be $^3\text{LH}_2 \cdot 2\text{CH}_3\text{C}(=\text{O})\text{OH}$. **M.pt.**: 373–374 K. **IR** (ATR, cm^{-1}): 3323–3282(m) $\nu(\text{N-H})$, 3152–2934(w) $\nu(\text{C-H})$, 1697–1660(s) $\nu(\text{C=O})$, 1516(s) $\nu(\text{C=C})$, 1361(m) $\nu(\text{C-N})$, 802(s) $\delta(\text{C=C})$.

Experimental details

The C-bound H atoms were geometrically placed ($\text{C-H} = 0.95\text{--}0.99$ Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C})$. The O- and N-bound H-atoms were located in a difference Fourier map but were refined with distance restraints of $\text{O-H} = 0.84 \pm 0.01$ Å and $\text{N-H} = 0.88 \pm 0.01$ Å, respectively, and with $U_{\text{iso}}(\text{H})$ set to $1.5U_{\text{equiv}}(\text{O})$ and $1.2U_{\text{equiv}}(\text{N})$, respectively.

Comment

A recent review [6] has summarised the structural chemistry of co-crystals, salts and metal complexes

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Abstract

$C_{18}H_{22}N_4O_6$, triclinic, $P\bar{1}$ (no. 2), $a = 5.03050(10)$ Å, $b = 12.4151(4)$ Å, $c = 15.5353(5)$ Å, $\alpha = 96.186(3)^\circ$, $\beta = 98.961(2)^\circ$, $\gamma = 96.669(2)^\circ$, $V = 944.05(5)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0421$, $wR_{\text{ref}}(F^2) = 0.1213$, $T = 100$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of

*Corresponding author: Edward R.T. Tiekink, Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia, e-mail: edwardt@sunway.edu.my, Edward.Tiekink@gmail.com

Sang Loon Tan: Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} */U _{eq}
O1	0.46011(17)	0.26057(8)	0.44552(7)	0.0227(2)
O2	1.08150(17)	0.40313(8)	0.56093(7)	0.0217(2)
N1	1.1023(2)	−0.08529(10)	0.29420(8)	0.0229(3)
N2	0.8899(2)	0.25133(9)	0.41867(8)	0.0181(2)
H2N	1.060(2)	0.2728(14)	0.4409(12)	0.022*
N3	0.6514(2)	0.41745(9)	0.58355(8)	0.0182(2)
H3N	0.480(2)	0.3944(14)	0.5640(12)	0.022*
N4	1.2770(2)	0.52811(10)	0.85107(9)	0.0238(3)
C1	1.0502(3)	0.01818(11)	0.29399(10)	0.0201(3)
H1	1.137845	0.062813	0.257911	0.024*
C2	0.8744(2)	0.06351(11)	0.34394(9)	0.0190(3)
C3	0.7520(3)	−0.00171(12)	0.39765(10)	0.0225(3)
H3	0.632169	0.026598	0.433174	0.027*
C4	0.8059(3)	−0.10883(12)	0.39916(10)	0.0254(3)
H4	0.725276	−0.154651	0.435906	0.030*
C5	0.9802(3)	−0.14727(12)	0.34570(11)	0.0255(3)
H5	1.014323	−0.220945	0.345712	0.031*
C6	0.8186(3)	0.17915(11)	0.33567(9)	0.0198(3)
H6A	0.923027	0.208994	0.292541	0.024*
H6B	0.623258	0.178041	0.312681	0.024*
C7	0.7078(2)	0.28844(11)	0.46330(9)	0.0171(3)
C8	0.8337(2)	0.37563(10)	0.54145(9)	0.0172(3)
C9	0.7312(3)	0.50968(11)	0.65300(10)	0.0202(3)
H9A	0.565877	0.539501	0.666288	0.024*
H9B	0.844765	0.567872	0.631190	0.024*
C10	0.8865(3)	0.48131(11)	0.73672(9)	0.0192(3)
C11	1.1326(3)	0.54366(11)	0.77476(10)	0.0200(3)
H11	1.201970	0.600576	0.744778	0.024*
C12	1.1788(3)	0.44756(13)	0.89287(11)	0.0290(3)
H12	1.279306	0.436054	0.947378	0.035*
C13	0.9373(3)	0.38039(13)	0.86012(11)	0.0299(3)
H13	0.873975	0.323596	0.891284	0.036*
C14	0.7890(3)	0.39754(11)	0.78080(10)	0.0242(3)
H14	0.622540	0.352433	0.756879	0.029*
O3	1.4448(2)	−0.14942(8)	0.18767(8)	0.0256(2)
H3O	1.345(4)	−0.1252(17)	0.2224(12)	0.038*
O4	1.4014(2)	0.00897(9)	0.13449(8)	0.0319(3)
C15	1.4974(3)	−0.07653(11)	0.13447(10)	0.0217(3)
C16	1.6897(3)	−0.10963(13)	0.07447(10)	0.0259(3)
H16A	1.649220	−0.078589	0.019269	0.039*
H16B	1.668207	−0.189548	0.062228	0.039*
H16C	1.876909	−0.082296	0.102827	0.039*
O5	1.7283(2)	0.66193(9)	0.92028(7)	0.0262(2)
H5O	1.589(3)	0.6206(15)	0.8934(13)	0.039*
O6	1.7052(2)	0.72550(8)	0.79044(7)	0.0252(2)
C17	1.8173(3)	0.72694(11)	0.86564(10)	0.0205(3)
C18	2.0714(3)	0.80222(13)	0.90705(11)	0.0279(3)
H18A	2.191622	0.810727	0.863596	0.042*
H18B	2.164395	0.771237	0.956931	0.042*
H18C	2.023887	0.873772	0.927622	0.042*

formed by isomeric molecules with the general formula (n-C₅H₄N)CH₂N(H)C(=O)C(=O)N(H)CH₂(C₅H₄N-n), for n = 2, 3 and 4, hereafter abbreviated as ⁿLH₂. Hydrogen bonding

functionality is apparent in these molecules, namely in the central di-amide group as well as in the two terminal pyridyl residues. As a part of on-going studies in forming co-crystals and coordination polymers of ⁿLH₂ [7–9], the title 2:1 co-crystal, ³LH₂·2CH₃C(=O)OH, was formed and characterised crystallographically.

The molecular structures of the molecules comprising the asymmetric unit are shown in the figure (70% displacement ellipsoids). The ³LH₂ molecule features a planar, central C₂N₂O₂ residue with the r.m.s. deviation of the fitted atoms = 0.0204 Å; the maximum deviation from the plane is 0.0286(7) Å for the N2 atom. The planarity does not extend to the appended methylene-carbon atoms which lie 0.207(2) Å, for the C6 atom, and 0.189(2) Å, for C9, to one side of the plane through the central atoms. Indeed, the pyridyl rings lie to the same side of the molecule so that the conformation is syn-periplanar. The dihedral angles between the central plane and the N1- and N4-pyridyl rings are 71.34(4) and 77.78(4)°, respectively; the dihedral angle between the pyridyl rings is 85.83(4)°. The observed syn-periplanar conformation is found in one of the two polymorphs of ³LH₂, the other exhibiting an anti-periplanar conformation in each of the independent molecules [10]. DFT calculations showed the energy difference between the two observed conformations in the polymorphs was less than 1 kcal mol^{−1}, consistent with the conformational flexibility of these molecules [6]. Finally, two intramolecular amide-N···O(amide) hydrogen bonds are noted [N2–H2n···O2: H2n···O2 = 2.314(18) Å, N2···O2 = 2.7170(16) Å with angle at H2n = 108.4(11)° and N3–H3n···O1: H3n···O1 = 2.325(18) Å, N3···O1 = 2.7091(16) Å with angle at H3n = 106.9(12)°]; each of these gives rise to an S(5) loop using graph-set notation [11]. The acetic acid molecules are attached to ³LH₂ via hydroxy-O–H···N(pyridyl) hydrogen bonds, indicated by dashed bonds in the figure. The great disparity in the C–O bonds confirms the location of the acidic protons in the carboxylic acids [C15–O3, O4 = 1.3213(18) and 1.2163(18) Å; C17–O5, O6 = 1.3244(18) and 1.2129(18) Å].

As mentioned above, conventional hydroxy-O–H···N(pyridyl) hydrogen bonds link the components of the asymmetric unit into a three-molecular aggregate [O3–H3o···N1: H3o···N1 = 1.85(2) Å, O3···N1 = 2.6952(16) Å with angle at H3o = 174(2)° and O5–H5o···N4: H5o···N4 = 1.820(17) Å, O5···N4 = 2.6550(16) Å with angle at H5o = 172(2)°]. The di-amide residues self-associate to form a supramolecular tape along the a-axis direction and mediated by 10-membered {···HNC₂O}₂ syn-thons, as shown in the lower view of the figure [N2–H2n···O1ⁱ: H2n···O1ⁱ = 2.027(11) Å, N2···O1ⁱ = 2.8206(14) Å with angle at H2n = 151.2(16)° and N3–H3n···O2ⁱⁱ: H3n···O2ⁱⁱ = 2.014(11) Å, N3···O2ⁱⁱ = 2.8157(14) Å with angle

at $H3n = 152.5(16)^\circ$ for symmetry operations (i) $1 + x, y, z$ and (ii) $-1 + x, y, z$. The tapes are connected into a layer in the *ac*-plane by methylene-C—H \cdots O (carbonyl) [C6—H6a \cdots O6ⁱⁱⁱ: H6a \cdots O6ⁱⁱⁱ = 2.54 Å, C6 \cdots O6ⁱⁱⁱ = 3.5045(18) Å with angle at H6a = 165° for (iii) $3 - x, 1 - y, 1 - z$] and pyridyl-C—H \cdots O (hydroxy) [C12—H12 \cdots O5^{iv}: H12 \cdots O5^{iv} = 2.50 Å, C12 \cdots O5^{iv} = 3.327(2) Å with angle at H12 = 145° for (iv) $3 - x, 1 - y, 2 - z$]. The connections between layers along the *b*-axis direction are also of the type C—H \cdots O but at longer separations that is, pyridyl-C—H \cdots O (amide) [C4—H4 \cdots O1^v: H4 \cdots O1^v = 2.60 Å, C4 \cdots O1^v = 3.544(2) Å with angle at H4 = 172° for (v) $1 - x, -y, 1 - z$] and methyl-C—H \cdots O (amide) [C16—H16a \cdots O1^{vi}: H16a \cdots O1^{vi} = 2.61 Å, C16 \cdots O1^{vi} = 3.585(2) Å with angle at H16a = 172° for (vi) $3 - x, -y, -z$] interactions.

In order to understand more about the supramolecular interactions important in the molecular packing, Crystal Explorer 17 [12] was used for the calculation of the Hirshfeld surfaces as well as of the full and delineated two-dimensional fingerprint plots for the entire three-molecule aggregate using established procedures [13]. Important contributions to the calculated Hirshfeld surface come from H \cdots H [44.1%] and O \cdots H/H \cdots O [30.0%] contacts, the latter reflecting the significant H \cdots O contacts identified above. Other important surface contacts come from C \cdots H/H \cdots C [14.4%] as well as N \cdots H/H \cdots N [4.7%] and O \cdots C/C \cdots O [3.2%] contacts but, generally at distances greater than the sum of the respective van der Waals radii. The same calculations were also performed on each of the crystallographically independent components of the asymmetric unit. As anticipated, several differences in percentage contributions to the surface are apparent. For ${}^3\text{LH}_2$, the contributions from H \cdots H [40.6%] and O \cdots H/H \cdots O [25.3%] contacts have decreased significantly while those from N \cdots H/H \cdots N [11.0%] and C \cdots H/H \cdots C [16.9%] have increased compared with the overall three-molecule aggregate. A recent study [14] highlighted how the analysis of calculated Hirshfeld surfaces could be employed to distinguish between different molecules in the asymmetric unit. This is also true in the present case of the O3- and O5-carboxylic acids. Hence, differences in the percentage contributions to the overall surfaces for each molecule are apparent in the H \cdots H [41.4% compared with 43.7% for the O3- and O5-carboxylic acids, respectively], O \cdots H/H \cdots O [38.1 and 37.8%] and C \cdots H/H \cdots C [6.1 and 4.4%]; the contributions from N \cdots H/H \cdots N contacts remain the same [8.1 and 8.2%].

Similar overall percentage contributions calculated for the three-molecule aggregate in the title co-crystal were noted in a very closely related structure, that is, ${}^4\text{LH}_2 \cdot 2\text{CH}_3\text{C}(=\text{O})\text{OH}$, isolated as a dihydrate [15]; the calculations were performed on the overall five-molecule aggregate.

Here, despite the presence of water molecules of crystallisation that participate in significant hydrogen bonding interactions, the most important contribution to the Hirshfeld surface still comes from H \cdots H contacts [43.4%] with O \cdots H/H \cdots O [32.5%] contacts being a little more important than in the title structure. Contacts of the type H \cdots C/C \cdots H [14.4%] also make a significant contribution to the surface but, again at relatively long separations.

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