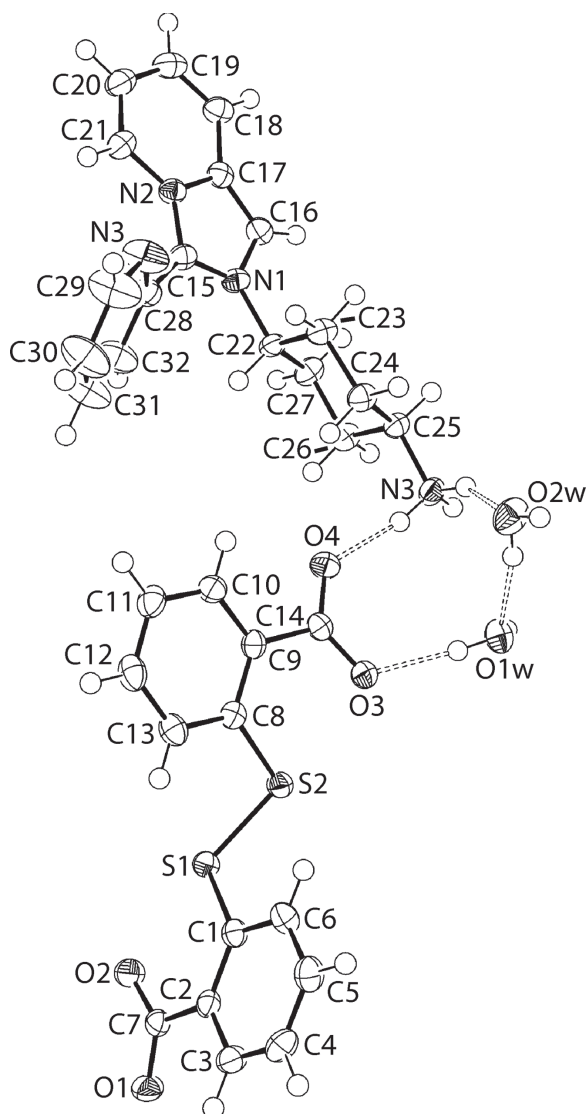


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Crystal structure of 2-(4-ammoniocyclohexyl)-3-(pyridin-2-yl)imidazo [1,5-*a*]pyridin-2-ium 2-[(2-carboxylatophenyl)disulfanyl]benzoate dihydrate, $[C_{18}H_{22}N_4][C_{14}H_8O_4S_2] \cdot 2H_2O$

**Abstract**

$[C_{18}H_{22}N_4][C_{14}H_8O_4S_2] \cdot 2H_2O$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 9.7616(1)$ Å, $b = 16.7411(2)$ Å, $c = 18.6843(2)$ Å, $V = 3053.39(6)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0265$, $wR_{ref}(F^2) = 0.0679$, $T = 100(2)$ K.

CCDC no.: 1902630

The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Prism, Yellow
Size:	0.08 × 0.06 × 0.05 mm
Wavelength:	Cu K α radiation (1.54178 Å)
μ :	2.01 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω -scans
θ_{max} , completeness:	76.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	21914, 5964, 0.036
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 5732
$N(param)_{refined}$:	418
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX and ORTEP [4]

Source of material

The title salt dihydrate was prepared through solvent drop assisted grinding of 2-mercaptobenzoic acid (2-MBA; Merck) and an authenticated sample of N1,N4-bis((pyridine-2-yl)methylene)-cyclohexane-1,4-diamine (2-PMCD) [5] (*M. pt* (Hanon MP-450): 439.6–441.1 K; lit.: 440–441 K) in a 1:1 molar ratio (0.001 mol, 0.154 g for 2-MBA and 0.001 mol, 0.292 g for 2-PMCD). The mixture was ground for 15 min in the presence of a few drops of methanol that led to a yellowish slurry, which was subsequently dissolved in DMF (2 mL) and carefully layered with the same volume of ethanol. Yellow crystals were obtained approximately one week after the experiment. *M. pt*: 501.8–503.4 K. **IR** (Bruker Vertex 70v; cm⁻¹): 3355–3268(w) $\nu(N-H)$, 3053–2866(w) $\nu(C-H)$, 1694(*m*) $\nu(C=O)$, 1587–1450(s) $\nu(C=C)$, 1369(s) $\nu(C-N)$, 735(s) $\delta(C=C)$.

<https://doi.org/10.1515/ncrs-2019-0120>

Received February 17, 2019; accepted March 12, 2019; available online May 8, 2019

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
S1	0.10619(5)	0.44611(3)	0.41057(3)	0.01673(11)
S2	0.18558(5)	0.38997(3)	0.32128(3)	0.01731(11)
O1	−0.20388(17)	0.59298(10)	0.51663(9)	0.0233(3)
O2	0.00968(16)	0.54687(10)	0.50663(9)	0.0228(3)
O3	0.33001(16)	0.33437(9)	0.21125(8)	0.0189(3)
O4	0.53431(16)	0.27471(10)	0.22333(9)	0.0221(3)
C1	−0.0755(2)	0.42959(12)	0.40504(11)	0.0167(4)
C2	−0.1653(2)	0.47779(12)	0.44501(11)	0.0164(4)
C3	−0.3067(2)	0.46336(13)	0.44000(12)	0.0208(4)
H3	−0.368221	0.494930	0.467435	0.023*
C4	−0.3584(2)	0.40405(14)	0.39588(13)	0.0231(5)
H4	−0.454364	0.395060	0.393352	0.028*
C5	−0.2696(2)	0.35796(15)	0.35552(13)	0.0233(5)
H5	−0.304774	0.317837	0.324608	0.028*
C6	−0.1289(2)	0.37035(13)	0.36017(12)	0.0208(4)
H6	−0.068517	0.338230	0.332589	0.025*
C7	−0.1158(2)	0.54426(13)	0.49310(11)	0.0172(4)
C8	0.2680(2)	0.30304(12)	0.35755(12)	0.0158(4)
C9	0.3792(2)	0.26903(12)	0.32043(11)	0.0165(4)
C10	0.4516(2)	0.20681(13)	0.35238(12)	0.0194(4)
H10	0.528169	0.184669	0.328091	0.023*
C11	0.4148(3)	0.17624(13)	0.41882(12)	0.0226(5)
H11	0.466185	0.134238	0.440001	0.027*
C12	0.3017(3)	0.20814(14)	0.45376(12)	0.0234(5)
H12	0.273512	0.186593	0.498437	0.028*
C13	0.2292(2)	0.27154(13)	0.42366(12)	0.0206(4)
H13	0.152838	0.293461	0.448324	0.025*
C14	0.4180(2)	0.29523(12)	0.24571(11)	0.0164(4)
N1	1.11919(18)	0.14807(11)	0.23636(10)	0.0180(4)
N2	1.25499(18)	0.06081(11)	0.28509(10)	0.0175(4)
N3	0.64899(19)	0.26872(12)	0.09157(10)	0.0195(4)
H1N	0.601(3)	0.2366(15)	0.0632(13)	0.029*
H2N	0.657(3)	0.3137(11)	0.0659(14)	0.029*
H3N	0.607(3)	0.2799(17)	0.1325(10)	0.029*
N4	0.9948(2)	−0.00595(13)	0.34435(13)	0.0329(5)
C15	1.1306(2)	0.09599(13)	0.29119(12)	0.0180(4)
C16	1.2343(2)	0.14566(13)	0.19461(12)	0.0188(4)
H16	1.250442	0.175926	0.152434	0.023*
C17	1.3219(2)	0.09152(13)	0.22494(11)	0.0178(4)
C18	1.4560(2)	0.06437(14)	0.20862(13)	0.0209(5)
H18	1.503083	0.083826	0.167677	0.025*
C19	1.5157(2)	0.01005(14)	0.25263(14)	0.0246(5)
H19	1.605555	−0.008558	0.242476	0.029*
C20	1.4449(2)	−0.01932(14)	0.31389(14)	0.0237(5)
H20	1.488793	−0.057058	0.344146	0.028*
C21	1.3165(2)	0.00532(13)	0.32997(13)	0.0213(4)
H21	1.269856	−0.014780	0.370792	0.026*
C22	0.9876(2)	0.18617(13)	0.21515(12)	0.0175(4)
H22	0.935171	0.199667	0.259524	0.021*
C23	0.9069(2)	0.12430(13)	0.17309(13)	0.0200(4)
H23A	0.892756	0.076232	0.203055	0.024*
H23B	0.959663	0.108271	0.130189	0.024*
C24	0.7683(2)	0.15765(13)	0.15013(13)	0.0196(4)
H24A	0.720792	0.118251	0.119390	0.023*
H24B	0.710812	0.167202	0.192935	0.023*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C25	0.7867(2)	0.23528(13)	0.10934(12)	0.0185(4)
H25	0.836779	0.223873	0.063771	0.022*
C26	0.8679(2)	0.29648(13)	0.15222(13)	0.0206(4)
H26A	0.816931	0.310526	0.196265	0.025*
H26B	0.879747	0.345699	0.123510	0.025*
C27	1.0091(2)	0.26240(13)	0.17226(13)	0.0205(4)
H27A	1.062288	0.250693	0.128399	0.025*
H27B	1.060737	0.301798	0.201115	0.025*
C28	1.0231(2)	0.07296(13)	0.34253(12)	0.0203(5)
C29	0.8933(3)	−0.02962(16)	0.38778(18)	0.0407(7)
H29	0.872335	−0.084987	0.389933	0.049*
C30	0.8179(3)	0.02193(18)	0.42935(17)	0.0402(7)
H30	0.744488	0.002943	0.458049	0.048*
C31	0.8516(3)	0.10171(19)	0.42832(17)	0.0422(7)
H31	0.803059	0.138438	0.457644	0.051*
C32	0.9565(3)	0.12836(15)	0.38435(15)	0.0303(6)
H32	0.981611	0.183168	0.383143	0.036*
O1W	0.34070(18)	0.32707(10)	0.06603(9)	0.0236(3)
H1W	0.392(3)	0.3613(15)	0.0475(16)	0.035*
H2W	0.337(3)	0.3339(19)	0.1107(7)	0.035*
O2W	0.42462(18)	0.17183(11)	0.04604(10)	0.0294(4)
H3W	0.368(3)	0.1403(16)	0.0266(18)	0.044*
H4W	0.388(3)	0.2176(11)	0.048(2)	0.044*

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–1.00 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The O- and N-bound H-atoms were located in difference Fourier maps but were refined with distance restraints of O–H = 0.84+–0.01 Å and N–H = 0.88+–0.01 Å, and with $U_{\text{iso}}(\text{H})$ set to $1.5U_{\text{equiv}}(\text{O}, \text{N})$. The absolute structure was determined based on differences in Friedel pairs included in the data set.

Discussion

Recently, a product from the co-crystallization experiment between 3-mercaptopbenzoic acid and *N,N'*-bis((pyridine-2-yl)methylene)-cyclohexane-1,4-diamine [5] was described which led to the crystallographic characterization of an unexpected salt formulated as [cyclohexane-1,4-diammonium][pyridine-2-carboxylate]₂ [6], whereby the original Schiff base had been converted to a di-cation. Unexpected outcomes of co-crystallization experiments involving *n*-mercaptopbenzoic acids, such as desulfurization [7] and oxidation [8], are well documented. In the present study, the results of another co-crystallization experiment are described where X-ray crystallography shows the original 2-mercaptopbenzoic acid has been oxidized and doubly deprotonated to 2-[(2-carboxylatophenyl)disulfanyl]benzoate [8] and the original (2-py)–CH=N–C₆H₁₀–N=CH–(2-py) Schiff

base converted to the 2-(4-ammoniocyclohexyl)-3-(pyridin-2-yl)imidazo[1,5-*a*]pyridin-2-ium di-cation. A closely related precedent for the latter species has been reported in a study in which (1*R*,2*R*)-*N,N'*-bis(2-pyridylmethylene)cyclohexane-1,2-diamine was reacted with two equivalents of $TeBr_4$ leading to the isolation of the isomeric 2-(2-ammoniocyclohexyl)-3-(pyridin-2-yl)imidazo[1,5-*a*]pyridin-2-ium di-cation with the charge-balance provided by $[TeBr_6]^{2-}$, crystallized as a di-acetonitrile solvate [9].

The constituents of the asymmetric unit are shown in the figure (70% probability displacement ellipsoids). The nine non-hydrogen atoms comprising the imidazo-pyridin-2-ium fused ring system are planar, exhibiting a r.m.s. deviation = 0.0142 Å, with the maximum deviation from the least-squares plane being 0.0247(16) Å for the N1 atom. The dihedral angle between this plane and that through the appended 2-pyridyl ring is 55.29(9)°, indicating an inclined disposition. A similar relationship is found between the fused-ring system and the cyclohexyl ring whereby the dihedral angle is 65.07(7)°. The cyclohexyl ring has a chair conformation and the two appended nitrogen atoms occupy equatorial positions. Within the five-membered ring, the N1–C15 [1.350(3) Å], N1–C16 [1.369(3) Å], N2–C15 [1.355(3) Å] and N2–C17 [1.398(3) Å] bond lengths span a relatively narrow range suggesting considerable delocalization of π -electron density over the ring; the C16–C17 bond length is 1.369(3) Å.

Confirmation that the 2-[(2-carboxylatophenyl)disulfanyl]benzoate is doubly deprotonated is readily evidenced by the experimental equivalence of the C7–O1, O2 [1.264(3), 1.251(3) Å] and C14–O3, O4 [1.257(3), 1.258(3) Å] bond lengths. As anticipated [10], there is a significant twist in the di-anion as seen in the C1–S1–S2–C2 torsion angle of –107.32(10)°. The dihedral angle between the phenyl rings is 86.84(6)°, indicating an orthogonal relationship. Finally, the carboxylate residues are twisted out of the planes through the phenyl rings to which they are connected as seen in the $C_6/(C7,O1,O2)$ [12.5(4)°] and $C_6/(C14,O3,O4)$ [18.0(3)°] dihedral angles.

As expected from the composition, in the crystal there are a considerable number of conventional hydrogen bonding interactions which assemble the constituents of the crystal into a three-dimensional architecture. The carboxylate-oxygen atoms participate in charge-assisted hydrogen bonds with ammonium-N–H atoms being donors for the O1 and O4 atoms, and water-O–H donors for the O1, O2 and O3 atoms, indicating the carboxylate-O1 atom accepts two hydrogen bonds [N3–H2n···O1ⁱ: H2n···O1ⁱ = 1.87(2) Å, N3···O1ⁱ = 2.758(3) Å with angle at H2n = 171(3)°; N3–H3n···O4: H3n···O4 = 1.84(2) Å, N3···O4 = 2.706(2) Å, angle at

H3n = 164(3)°; O1w–H1w···O2ⁱ: H1w···O2ⁱ = 1.97(3) Å, O1w···O2ⁱ = 2.796(2) Å, angle at H1w = 171(3)°; O1w–H2w···O3: H2w···O3 = 1.880(13) Å, O1w···O3 = 2.718(2) Å, angle at H2w = 172(3)°; O2w–H3w···O1ⁱⁱ: H3w···O1ⁱⁱ = 1.96(3) Å, O2w···O1ⁱⁱ = 2.785(2) Å, angle at H3w = 164(3)° for symmetry operations i: $1/2 - x, 1 - y, -1/2 + z$ and ii: $-x, -1/2 + y, 1/2 - z$. The third ammonium-N3–H1n atom forms a donor interaction to a water molecule [N3–H1n···O2w: H1n···O2w = 2.06(3) Å, N3···O2w = 2.855(3) Å with angle at H1n = 148(2)°] and the remaining water-O2w–H4w atom donates to the other water molecule [O2w–H4w···O1w: H4w···O1w = 1.92(2) Å, O2w···O1w = 2.750(2) Å with angle at H4w = 167(3)°] so that each water molecule participates in one acceptor and two donor interactions.

Acknowledgements: Sunway University is thanked for support of crystal engineering studies (Grant No. INT-FST-RCCM-2016–01).

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