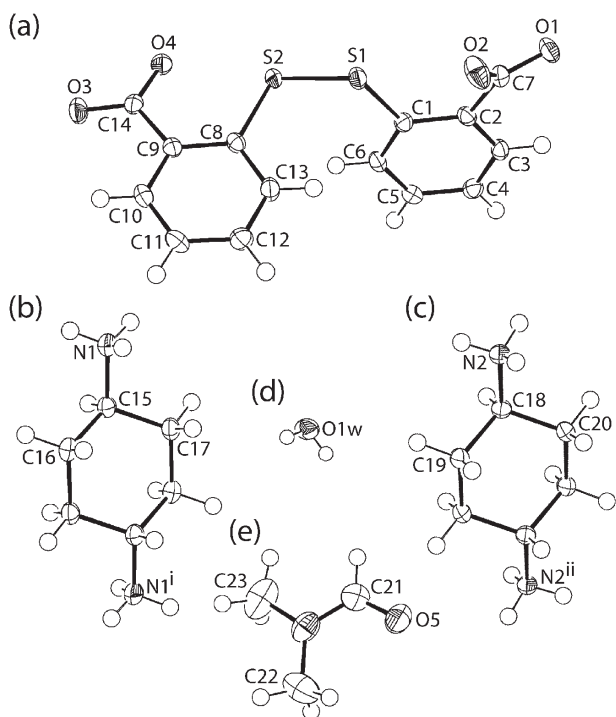


Sang Loon Tan and Edward R.T. Tiekink*

Crystal structure of cyclohexane-1,4-diammonium 2-[(2-carboxylatophenyl)disulfanyl]benzoate – dimethylformamide – monohydrate (1/1/1), [C₆H₁₆N₂][C₁₄H₈O₄S₂] · C₃H₇NO · H₂O

**Table 1:** Data collection and handling.

| | |
|--|--|
| Crystal: | Yellow prism |
| Size: | 0.10 × 0.07 × 0.02 mm |
| Wavelength: | Cu K α radiation (1.54184 Å) |
| μ : | 2.39 mm ⁻¹ |
| Diffractometer, scan mode: | XtaLAB Synergy, ω |
| θ_{\max} , completeness: | 76.6°, >99% |
| $N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} : | 30359, 5016, 0.034 |
| Criterion for I_{obs} , $N(hkl)_{\text{gt}}$: | $I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4635 |
| $N(\text{param})_{\text{refined}}$: | 333 |
| Programs: | CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4] |

The asymmetric unit of the title crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title co-crystal salt was prepared through the solvent drop-assisted grinding of 2-mercaptobenzoic acid (2-MBA; Merck) and *N,N*-bis((pyridine-4-yl)methylene)-cyclohexane-1,4-diamine (4-PMCD) in a 1:1 molar ratio (0.001 mol, 0.154 g for 2-MBA and 0.001 mol, 0.292 g 4-PMCD). The former was used as received without purification, while the latter was prepared according to the literature procedure [5], M. pt. (Hanon MP-450); 480.7–481.4 K; lit. [5]: 481–482 K. The mixture was ground for 15 min in the presence of a few drops of methanol that lead to a yellow slurry. This was dissolved in dimethylformamide (2 mL) and carefully layered with the same volume of benzene. Yellow crystals were obtained approximately 1 week after the experiment. M. pt.: 441.5–443.9 K. IR (Bruker Vertex 70v; cm⁻¹): 3357–3275(w) ν (NH), 3048–2866(w) ν (CH), 1692(m) ν (C=O), 1584–1447(s) ν (C=C), 1367(s) ν (C–N), 735(s) ν (C=C).

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–1.00 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2–1.5U_{\text{eq}}(\text{C})$. 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, respectively, and with $U_{\text{iso}}(\text{H})$ set to

<https://doi.org/10.1515/ncrs-2019-0131>

Received February 20, 2019; accepted March 19, 2019; available online May 22, 2019

Abstract

[C₆H₁₆N₂][C₁₄H₈O₄S₂] · C₃H₇NO · H₂O, triclinic, $P\bar{1}$ (no. 2), $a = 7.86120(10)$ Å, $b = 12.2464(2)$ Å, $c = 14.1615(2)$ Å, $\alpha = 111.293(1)^\circ$, $\beta = 105.767(2)^\circ$, $\gamma = 93.690(1)^\circ$, $V = 1202.11(3)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0373$, $wR_{\text{ref}}(F^2) = 0.1054$, $T = 100(2)$ K.

CCDC no.: 1904095

*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. <https://orcid.org/0000-0003-1401-1520>

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 | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|-------------|--------------|-------------|----------------------------------|
| S1 | 0.47247(5) | -0.09550(3) | 0.75674(3) | 0.01450(11) |
| S2 | 0.46421(5) | 0.06994(3) | 0.75039(3) | 0.01334(11) |
| O1 | 0.73605(16) | -0.39304(11) | 0.72755(10) | 0.0184(3) |
| O2 | 0.50258(19) | -0.31583(12) | 0.76985(11) | 0.0249(3) |
| O3 | 0.19676(17) | 0.37981(11) | 0.76832(10) | 0.0200(3) |
| O4 | 0.44096(15) | 0.29557(10) | 0.78509(9) | 0.0160(2) |
| C1 | 0.5042(2) | -0.18708(14) | 0.63395(13) | 0.0126(3) |
| C2 | 0.5723(2) | -0.29253(14) | 0.62601(13) | 0.0130(3) |
| C3 | 0.5971(2) | -0.36196(14) | 0.52982(13) | 0.0137(3) |
| H3 | 0.646027 | -0.432120 | 0.524340 | 0.016* |
| C4 | 0.5526(2) | -0.33193(14) | 0.44177(13) | 0.0146(3) |
| H4 | 0.568503 | -0.381703 | 0.376614 | 0.018* |
| C5 | 0.4844(2) | -0.22786(15) | 0.45021(13) | 0.0144(3) |
| H5 | 0.453322 | -0.206110 | 0.390617 | 0.017* |
| C6 | 0.4618(2) | -0.15587(14) | 0.54600(13) | 0.0133(3) |
| H6 | 0.416767 | -0.084383 | 0.551651 | 0.016* |
| C7 | 0.6073(2) | -0.33633(14) | 0.71590(13) | 0.0151(3) |
| C8 | 0.2286(2) | 0.06397(14) | 0.69131(13) | 0.0122(3) |
| C9 | 0.1568(2) | 0.16901(14) | 0.70518(12) | 0.0122(3) |
| C10 | -0.0295(2) | 0.15931(15) | 0.66802(13) | 0.0150(3) |
| H10 | -0.079408 | 0.229846 | 0.679465 | 0.018* |
| C11 | -0.1436(2) | 0.04968(16) | 0.61496(14) | 0.0168(3) |
| H11 | -0.270184 | 0.045257 | 0.592797 | 0.020* |
| C12 | -0.0713(2) | -0.05358(15) | 0.59448(14) | 0.0170(3) |
| H12 | -0.147843 | -0.129176 | 0.554436 | 0.020* |
| C13 | 0.1133(2) | -0.04625(14) | 0.63262(14) | 0.0157(3) |
| H13 | 0.161982 | -0.117333 | 0.618601 | 0.019* |
| C14 | 0.2723(2) | 0.29144(14) | 0.75705(12) | 0.0128(3) |
| N1 | 0.0944(2) | 0.56987(13) | 0.72609(12) | 0.0195(3) |
| H1N | -0.0130(18) | 0.584(2) | 0.7277(18) | 0.023* |
| H2N | 0.128(3) | 0.5145(16) | 0.7493(18) | 0.023* |
| H3N | 0.178(2) | 0.6346(14) | 0.7635(16) | 0.023* |
| C15 | 0.0930(2) | 0.52648(14) | 0.61238(13) | 0.0141(3) |
| H15 | 0.212534 | 0.504818 | 0.609576 | 0.017* |
| C16 | -0.0516(2) | 0.41505(14) | 0.54447(13) | 0.0150(3) |
| H16A | -0.168926 | 0.432639 | 0.553102 | 0.018* |
| H16B | -0.021943 | 0.350674 | 0.569311 | 0.018* |
| C17 | 0.0654(2) | 0.62665(14) | 0.57342(13) | 0.0145(3) |
| H17A | 0.167321 | 0.694092 | 0.616591 | 0.017* |
| H17B | -0.045980 | 0.655262 | 0.583449 | 0.017* |
| N2 | 0.65562(18) | 0.52327(12) | 0.88085(11) | 0.0141(3) |
| H4N | 0.578(2) | 0.4563(12) | 0.8439(15) | 0.017* |
| H5N | 0.597(3) | 0.5768(15) | 0.9131(16) | 0.017* |
| H6N | 0.691(3) | 0.5457(18) | 0.8353(14) | 0.017* |
| C18 | 0.8100(2) | 0.50552(14) | 0.95961(13) | 0.0129(3) |
| H18 | 0.764259 | 0.486933 | 1.012422 | 0.015* |
| C19 | 0.8883(2) | 0.40004(14) | 0.90183(13) | 0.0144(3) |
| H19A | 0.927510 | 0.414866 | 0.846082 | 0.017* |
| H19B | 0.794557 | 0.327198 | 0.866282 | 0.017* |
| C20 | 0.9514(2) | 0.61912(14) | 1.01969(13) | 0.0144(3) |
| H20A | 0.898118 | 0.684828 | 1.059189 | 0.017* |
| H20B | 0.992685 | 0.641863 | 0.968148 | 0.017* |
| O5 | 0.2162(2) | 0.78571(13) | 0.91767(12) | 0.0323(3) |
| N3 | 0.1420(2) | 0.96296(15) | 0.91935(14) | 0.0275(4) |
| C21 | 0.2513(3) | 0.89438(19) | 0.95340(17) | 0.0290(4) |

Table 2 (continued)

| Atom | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|-------------|-------------|-------------|----------------------------------|
| H21 | 0.362129 | 0.933309 | 1.008523 | 0.035* |
| C22 | -0.0258(3) | 0.9061(2) | 0.83582(19) | 0.0397(5) |
| H22A | -0.012743 | 0.900479 | 0.767406 | 0.060* |
| H22B | -0.118710 | 0.953060 | 0.850992 | 0.060* |
| H22C | -0.060425 | 0.825929 | 0.832038 | 0.060* |
| C23 | 0.2029(4) | 1.0896(2) | 0.9614(2) | 0.0422(6) |
| H23A | 0.314406 | 1.112284 | 1.021475 | 0.063* |
| H23B | 0.110759 | 1.130991 | 0.986101 | 0.063* |
| H23C | 0.225122 | 1.111792 | 0.905374 | 0.063* |
| O1W | 0.48304(19) | 0.68124(12) | 0.00114(11) | 0.0255(3) |
| H1W | 0.404(3) | 0.716(2) | -0.022(2) | 0.038* |
| H2W | 0.490(4) | 0.699(2) | 0.0654(10) | 0.038* |

1.5 $U_{\text{eq}}(\text{O})$ and 1.2 $U_{\text{eq}}(\text{N})$. The maximum and minimum residual electron density peaks of 1.16 and 0.45 eÅ⁻³, respectively, were located 1.07 and 0.62 Å from the H22b and C23 atoms, respectively.

Comment

Recent co-crystallization studies involving isomeric Schiff bases appended with pyridyl donors, *i.e.* *N,N'*-bis((pyridine-*n*-yl)methylene)cyclohexane-1,4-diamines, for *n* = 2, 3 and 4, as cofomers have resulted in the isolation of crystals whereby the original *n* = 2 species has been converted into a cyclohexane-1,4-diammonium di-cation, as in its salt with pyridine-2-carboxylate [6]. In another experiment, the *n* = 2 species was converted to a 2-(4-ammoniocyclohexyl)-3-(pyridin-2-yl)imidazo[1,5-*a*]pyridin-2-ylum dication in a salt with 2-[(2-carboxylatophenyl)disulfanyl]benzoate [7]. These experiments are doubly complicated as the isomeric *n*-mercaptobenzoic acids employed are also known to be susceptible to side reactions in co-crystallization experiments [8, 9]. In another example of an unexpected outcome of a co-crystallization experiment with these molecules, the title salt solvate hydrate was isolated from the 1:1 co-crystallization of (4-py)-CH=NC₆H₁₀N=CH-(4-py) and 2-mercaptobenzoic acid.

X-ray crystallography shows the product to comprise two independent cyclohexane-1,4-diammonium dications, each located about a centre of inversion, a 2-[(2-carboxylatophenyl)disulfanyl]benzoate di-anion, and a molecule each of dimethylformamide (DMF) and water (figure, 70% probability displacement ellipsoids with unlabelled atoms related by the symmetry operations i: -*x*, 1 - *y*, 1 - *z* and ii: 2 - *x*, 1 - *y*, 2 - *z*). The cation/anion assignments are readily confirmed based on the pattern of hydrogen bonding in the crystal (see below) and in the near equivalence of the C7—O1, O2 [1.271(2), 1.247(2) Å] and C14—O3, O4 [1.248(2), 1.269(2) Å] bond lengths. Each

dication adopts a crystallographically imposed chair conformation so that the 1,4-ammonium groups are anti, typical for this cation [10]. The dianion is twisted as seen in the C1–S1–S2–C2 torsion angle of $91.42(8)^\circ$, and in the dihedral angle of $79.32(8)^\circ$ formed between the two phenyl rings. The O1-carboxylate group is twisted significantly out of the plane of the phenyl ring to which it is bound as seen in C1–C2–C7–O1 torsion angle of $-148.22(16)^\circ$ and dihedral angle of $35.77(9)^\circ$ between these residues. A significantly more coplanar relationship is evident for the O3-carboxylate with the C8–C9–C14–O3 torsion angle being $-178.31(15)^\circ$ and the dihedral angle being $4.84(13)^\circ$.

Significant hydrogen bonding occurs in the crystal, most being charge-assisted, which results in the stabilization of a three-dimensional architecture. The N1-dication forms donor interactions to carboxylate-O1 and O3 atoms as well as to the DMF-O5 atom [N1–H1n \cdots O1ⁱⁱⁱ: H1n \cdots O1ⁱⁱⁱ = $2.010(16)$ Å, N1 \cdots O1ⁱⁱⁱ = $2.887(2)$ Å with angle at H1n = $177(3)^\circ$; N1–H2n \cdots O3: H2n \cdots O3 = $1.86(2)$ Å, N1 \cdots O3 = $2.723(2)$ Å and angle = $168(2)^\circ$; N1–H3n \cdots O5: H3n \cdots O5 = $2.22(2)$ Å, N1n \cdots O5 = $2.884(2)$ Å and angle = $132.0(15)^\circ$ for symmetry operation iii: $-1+x, 1+y, z$]. A similar pattern occurs for the N2-dication but, the third hydrogen bond is oriented to the water molecule [N2–H4n \cdots O4: H4n \cdots O4 = $1.944(17)$ Å, N2 \cdots O4 = $2.805(2)$ Å with angle at H4n = $166.9(16)^\circ$; N2–H5n \cdots O1w^{iv}: H5n \cdots O1w^{iv} = $1.90(2)$ Å, N2 \cdots O1w^{iv} = $2.772(2)$ Å with angle = $170.0(19)^\circ$; N2–H6n \cdots O1^v: H6n \cdots O1^v = $2.03(2)$ Å, N2 \cdots O1^v = $2.906(2)$ Å with angle = $171(2)^\circ$; for symmetry operations iv: $x, y, 1+z$ and v: $x, 1+y, z$]. The water molecule forms donor interactions to carboxylate-O4 and DMF-O5 atoms [O1w–H1w \cdots O5^{vi}: H1w \cdots O5^{vi} = $1.91(3)$ Å, O1w \cdots O5^{vi} = $2.744(2)$ Å with angle at H1w = $176(3)^\circ$; O1w–H2w \cdots O4^{vii}: H2w \cdots O4^{vii} = $2.013(15)$ Å, O1w \cdots O4^{vii} = $2.8237(18)$ Å with angle = $162(3)^\circ$ for symmetry operations vi: $x, y, -1+z$ and vii: $1-x, 1-y, 1-z$]. In this scheme, there is no role for the carboxylate-O2 atom. However, it is noted that this atom accepts two weak hydrogen bonds from ammonium-N1

and N3 groups [N1–H3n \cdots O2^v: H3n \cdots O2^v = $2.554(17)$ Å, N1 \cdots O2^v = $3.217(2)$ Å with angle at H3n = $132.5(15)^\circ$; N2–H6n \cdots O2^v: H6n \cdots O2^v = $2.58(2)$ Å, N2 \cdots O2^v = $3.054(2)$ Å with angle = $114.5(18)^\circ$].

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

References

1. Agilent Technologies: CrysAlis^{PRO}. Agilent Technologies, Santa Clara, CA, USA (2017).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr. C* **71** (2015) 3–8.
4. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* **45** (2012) 849–854.
5. Lai, C. S.; Mohr, F.; Tiekink, E. R. T.: The importance of C–H \cdots N, C–H \cdots π and $\pi\cdots\pi$ interactions in the crystal packing of the isomeric *N*¹,*N*⁴-bis((pyridine-*n*-yl)methylene)cyclohexane-1,4-diamines, *n* = 2, 3 and 4. *CrystEngComm* **8** (2006) 909–915.
6. Tan, S. L.; Tiekink, E. R. T.: Crystal structure of hemikis (cyclohexane-1,4-diammonium) (pyridine-2-carboxylate), $[C_6H_{16}N_2]_{0.5}[C_6H_4NO_2]$. *Z. Kristallogr. NCS* **234** (2019) 749–751.
7. Tan, S. L.; Tiekink, E. R. T.: Crystal structure of 2-(4-ammoniocyclohexyl)-3-(pyridin-2-yl)imidazo[1,5-*a*]pyridin-2-ylidium 2-[(2-carboxylatophenyl)disulfanyl]benzoate dihydrate, $[C_{18}H_{22}N_4][C_{14}H_8O_4S_2] \cdot 2 H_2O$. *Z. Kristallogr. NCS* **234** (2019) 797–799.
8. Broker, G. A.; Tiekink, E. R. T.: Co-crystal formation between 2,2'-dithiodibenzoic acid and each of 4,4'-bipyridine, trans-1,2-bis(4-pyridyl)ethene and 1,2-bis(4-pyridyl)ethane. *CrystEngComm* **9** (2007) 1096–1109.
9. Tan, S. L.; Tiekink, E. R. T.: A 1:2 co-crystal of 2,2'-thiodibenzoic acid and triphenylphosphane oxide: crystal structure, Hirshfeld surface analysis and computational study. *Acta Crystallogr. E* **74** (2018) 1764–1771.
10. Reiss, G. J.; Bajorat, S.: Redetermination of *trans*-cyclohexane-1,4-diammonium dichloride. *Acta Crystallogr. B* **64** (2008) o223.