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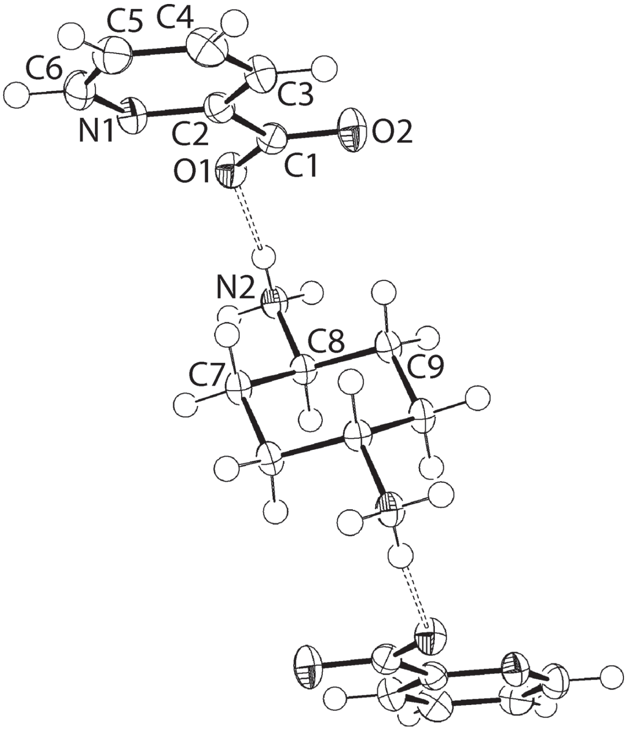
Crystal structure of hemikis(cyclohexane-1,4-diammonium) (pyridine-2-carboxylate), $[C_6H_{16}N_2]_{0.5}[C_6H_4NO_2]$



https://doi.org/10.1515/ncrs-2019-0091
Received January 28, 2019; accepted February 15, 2019; available online April 22, 2019

Abstract

$[C_6H_{16}N_2]_{0.5}[C_6H_4NO_2]$, triclinic, $P\bar{1}$ (no. 2), $a = 6.7956(2)$ Å, $b = 7.2840(3)$ Å, $c = 10.2615(4)$ Å, $\alpha = 70.483(3)°$, $\beta = 80.902(3)°$, $\gamma = 66.404(3)°$, $V = 438.55(3)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0359$, $wR_{ref}(F^2) = 0.0988$, $T = 100(2)$ K.

CCDC no.: 1897356

Table 1: Data collection and handling.

Crystal:	Prism, yellow
Size:	$0.17 \times 0.09 \times 0.09$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
μ:	0.81 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω-scans
θ_{max}, completeness:	76.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	11063, 1832, 0.031
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1702
$N(param)_{refined}$:	127
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX and ORTEP [4]

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.

Source of material

The title salt was prepared through solvent-drop assisted grinding of 3-mercaptobenzoic acid (3-MBA; Aldrich) and *N,N′*-bis((pyridine-2-yl)methylene)-cyclohexane-1,4-diamine (abbreviated as 2-PMCD) in a 1:1 molar ratio (0.001 mol, 0.154 g for 3-MBA and 0.001 mol, 0.292 g 2-PMCD). 3-MBA was used as received without further purification, while 2-PMCD was prepared according to the literature [5]; M. pt. (Hanon MP-450): 449.3–451.6 K; lit. [5]: 450–451 K. The mixture was ground for 15 min in the presence of few drops of methanol that lead to a yellowish slurry, some of which was subsequently dissolved in DMSO (2 mL) and carefully layered with the same volume of benzene. Yellow granular crystals were obtained approximately one week after the experiment. *M*. pt: 453.7–455.9 K. **IR** (Bruker Vertex 70v; cm^{-1}): 3375–3277 (w) ν(N—H), 3063–2860 (w) ν(C—H), 1630 (w) ν(COO), 1574–1551(*s*) ν(C=C), 1384(*s*) ν(C—N), 749 (*s*) δ(C=C).

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–0.99 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. The N-bound H-atoms were located in difference Fourier maps

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

Atom	x	y	z	U_{iso}*/U_{eq}
O1	0.35060(14)	0.51918(15)	0.84804(9)	0.0181(2)
O2	0.05542(15)	0.65042(16)	0.72322(10)	0.0213(2)
N2	0.20282(17)	0.55312(17)	1.10960(11)	0.0150(2)
H1N	0.3185(19)	0.502(2)	1.1604(15)	0.018*
H2N	0.115(2)	0.487(2)	1.1547(15)	0.018*
H3N	0.245(3)	0.530(3)	1.0281(11)	0.018*
N1	0.58332(17)	0.63984(17)	0.62398(11)	0.0172(2)
C1	0.2495(2)	0.61162(19)	0.73708(13)	0.0153(3)
C2	0.3748(2)	0.68728(19)	0.60768(13)	0.0148(3)
C3	0.2745(2)	0.8035(2)	0.48191(14)	0.0182(3)
H3	0.126710	0.833058	0.473916	0.022*
C4	0.3938(2)	0.8755(2)	0.36830(14)	0.0213(3)
H4	0.328803	0.957439	0.281505	0.026*
C5	0.6094(2)	0.8256(2)	0.38407(14)	0.0204(3)
H5	0.695873	0.870981	0.307963	0.025*
C6	0.6969(2)	0.7080(2)	0.51312(14)	0.0199(3)
H6	0.845021	0.674204	0.523258	0.024*
C7	0.2360(2)	0.8998(2)	1.00980(13)	0.0156(3)
H7A	0.280609	0.870294	0.919950	0.019*
H7B	0.366892	0.849663	1.062801	0.019*
C8	0.0902(2)	0.78292(19)	1.08993(13)	0.0143(3)
H8	0.054931	0.806113	1.182942	0.017*
C9	−0.1189(2)	0.8636(2)	1.01514(13)	0.0157(3)
H9A	−0.212803	0.789777	1.071309	0.019*
H9B	−0.087061	0.833039	0.925388	0.019*

but were refined with a distance restraint of N—H = 0.88 ± 0.01 Å, and with $U_{\mathrm{iso}}(\mathrm{H})$ set to $1.2U_{\mathrm{equiv}}(\mathrm{N})$. Owing to poor agreement, two reflections, i.e. (1 1 4) and (2 2 5), were omitted from the final cycles of refinement.

Discussion

The isomeric Schiff bases appended with pyridyl donors, *N,N′*-bis((pyridine-n-yl)methylene)cyclohexane-1,4-diamines for n = 2, 3 and 4, that is, of general formula (n-py)—CH=N—C_6H_{10}–N=CH–(n-py) for n = 2–4, were prepared and characterized sometime ago [5, 6]. Since the original syntheses [5], investigations have focused upon their utility in forming coordination polymers of cadmium [6], cobalt [7] and silver [8, 9] salts. To the best of our knowledge, no reports on co-crystals of these Schiff base molecules exist. Recent studies of co-crystals designed to incorporate n-mercaptobenzoic acid as a conformer [10, 11] resulted in unexpected outcomes, *e.g.* oxidation of the thiol, a well known phenomenon for n-mercaptobenzoic acids [12], and desulfurization [13], again observed previously [14]. As a follow up to these studies, a co-crystallization experiment between an authenticated [5] sample of (2-py)—CH=N—C_6H_{10}–N=CH—(2-py) and 3-mercaptobenzoic acid was undertaken which lead to the isolation of the title 1:2 salt, that is, $[H_3NC_6H_{10}NH_3]$: $2[C_6H_4NO_2]$.

X-ray crystallography showed the composition of the product isolated from the co-crystallization experiment to comprise a cyclohexane-1,4-diammonium di-cation, located about a center of inversion, and a pyridine-2-carboxylate anion in a general position (Figure, 70% probability displacement ellipsoids with unlabelled atoms related by the symmetry operation $-x$, $2-y$, $2-z$). The confirmation of the presence of ammonium and carboxylate groups is seen in the pattern of supramolecular aggregation (see below). In addition, the carboxylate-C1—O1, O2 bond lengths are essentially equivalent, being 1.2595(16) and 1.2546(16) Å, respectively. The cation has a chair conformation indicating the 1,4-ammonium groups are anti. The pyridine-2-carboxylate anion is planar as seen in the magnitude of the O1—C1—C2—N1 torsion angle of 2.71(17)°.

In the crystal, significant charge-assisted hydrogen bonding is apparent. Thus, ammonium-N—H⋯O(carboxylate), N(pyridyl) hydrogen bonds cooperate to assemble ions into a supramolecular layer parallel to [0 0 1]. The hydrogen bond donated by ammonium-N—H1n atoms is bifurcated, effectively bridging O(carboxylate) and N(pyridyl) atoms of the same anion forming a five-membered {H⋯OC$_2$N⋯} synthon [N2—H1n⋯O1$^{\mathrm{i}}$: H1n⋯O1$^{\mathrm{i}}$ = 2.181(14) Å, N2⋯O1$^{\mathrm{i}}$ = 2.9429(17) Å with angle at H1n = 143.1(12)°; N2—H1n⋯N1$^{\mathrm{i}}$: H1n⋯N1$^{\mathrm{i}}$ = 2.190(15) Å, N2⋯N1$^{\mathrm{i}}$ = 2.9352(16) Å with angle at H1n = 140.8(12)°; symmetry operation (i) $1-x$, $1-y$, $2-z$]. The H1n⋯O1 edge of this synthon, edge “1”, is connected to another edge “1” *via* a second ammonium-N1—H3n⋯O1 hydrogen bond to form an eight-membered {⋯HNH⋯O}$_2$ synthon [N2—H3n⋯O1: H3n⋯O1 = 1.889(13) Å, N2⋯O1 = 2.7687(14) Å with angle at H3n = 170.2(18)°], indicating the carboxylate-O1 atom participates in two hydrogen bonds. The remaining hydrogen bond involves the carboxylate-O2 atom and involves edge “2” of the aforementioned synthon, where two of these are linked into a 12-membered {⋯HNH⋯OCO}$_2$ synthon [N2—H2n⋯O2$^{\mathrm{ii}}$: H2n⋯O2$^{\mathrm{ii}}$ = 1.883(15) Å, N2⋯O2$^{\mathrm{ii}}$ = 2.7663(16) Å with angle at H2n = 170.4(13)°; symmetry operation (ii) $-x$, $1-y$, $2-z$]. In this way, supramolecular tapes comprising alternating eight- and 12-membered synthons along the *a*-axis are formed. The layers interdigitate along the *c*-axis enabling the formation of π⋯π stacking interactions between centrosymmetrically related pyridyl rings [inter-centroid separation = 3.6569(8) Å for symmetry operation (iii) $-x$, $-y$, $-z$] thereby stabilizing the three-dimensional packing.

The most closely related structure in the literature is that of the 2-isomeric structure, *i.e.* hemikis(cyclohexane-1,4-diammonium) (pyridine-2-carboxylate) [15]. It is interesting to note that supramolecular layers constructed by hydrogen bonds and connected by $\pi\cdots\pi$ stacking interactions are also apparent in this crystal.

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

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