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3,3-Bis(2-imidazolyl)propionic Acid Hemihydrate

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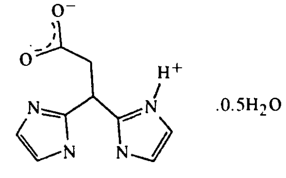
Abstract

Slow evaporation of an aqueous solution of 3,3-bis(2-imidazolyl)propionic acid monohydrate, $C_9H_{10}N_4O_2$.-H_2O, yields crystals of the hemihydrate, $C_9H_{10}N_4O_2$.-$0.5H_2O$. In both hydrates the molecules of 3,3-bis(2-imidazolyl)propionic acid are in a zwitterionic form containing $-COO^-$ and $-(imidazole)H^+$ residues, *i.e.* 3-(2-imidazolyl)-3-(2-imidazolio)propionate. The crystal structure of the hemihydrate contains two crystallographically independent zwitterions and one water molecule linked by hydrogen bonds. In the two molecules of the hemihydrate, as well as in the monohydrate, the dihedral angles between the planes of the imidazole rings and the carboxylate group show remarkable differences, indicating that 3,3-bis(2-imidazolyl)propionic acid can be used as a flexible ligand.

Comment

This paper is part of a general study of the structural properties of transition metal complexes which contain carboxylate and imidazole groups. Such compounds are commonly used for modelling the active centre of various metalloproteins, since these groups are the most important and versatile binding sites for metals in many biological systems (Creighton, 1984). The interest in 3,3-bis(2-imidazolyl)propionic acid (HBIP) as a ligand is mainly due to the flexibility of the molecule which allows it to accomodate the preferred geometries of most transition metal ions. This ligand was first obtained in the solid state as a monohydrate, $C_9H_{10}N_4O_2.H_2O$ (HBIP.H_2O, hereafter referred to as HBIP-1), the crystal structure of which has been reported (Gimeno, Soto, Sancho, Dahan & Legros, 1992). In the course of our experiments, routine X-ray powder analysis of the starting materials showed that another crystalline phase can be obtained depending on the conditions of crystallization. Thermogravimetric analysis indicated that this new phase (hereafter referred to as HBIP-2) is a hemihydrate, $C_9H_{10}N_4O_2.0.5H_2O$. The crystal structure of HBIP-2 was determined in order to compare the molecular conformation and the hydrogen-bonding network in the two crystalline hydrates.



HBIP-2

HBIP-1 is triclinic, while HBIP-2 is monoclinic. In both hydrates the HBIP molecules are in a zwitterionic form, containing $-COO^-$ and $-(imidazole)H^+$ residues. The asymmetric unit (Fig. 1) of the crystal structure of HBIP-2 consists of two crystallographically independent HBIP zwitterions and one molecule of water of crystallization linked by hydrogen bonding. The imidazole rings are planar with bond distances and angles (Table 2) similar to those reported for other compounds containing imidazole (Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1989; Martinez, Legros, Soto & Sancho, 1991). The flexibility of the HBIP molecule is well reflected in the difference between the conformations of the zwitterions in HBIP-2 and HBIP-1, as indicated by the dihedral angles between the imidazole groups and the carboxylate group of each molecule (Table 3).

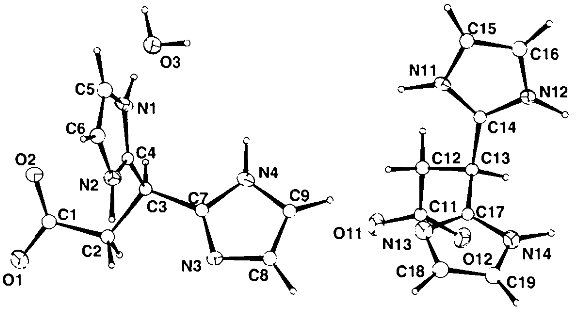


Fig. 1. View of the asymmetric unit of HBIP-2 showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level. H atoms are drawn as small circles of arbitrary radii.

The crystal structures of both hydrates are characterized by strong intermolecular hydrogen bonds between the carboxylate group, the imidazole rings and the water molecules. The details of the hydrogen-bonding contacts in HBIP-2 are given in Table 4 and represented in Fig. 2.

The difference in the hydrogen-bonding scheme between crystals of HBIP-1 and HBIP-2 is reflected in the IR spectra and in the difference of the melting points of the two phases (HBIP-1 m.p. 530 K and HBIP-2 m.p. 513 K).

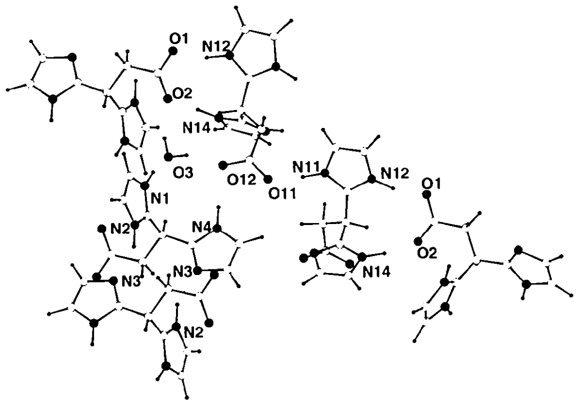


Fig. 2. The hydrogen-bonding scheme: hydrogen bonds involving H atoms of the asymmetric unit are drawn as dotted lines. N and O atoms are drawn as black circles.

Experimental

Synthesis of HBIP was carried out according to the method described by Joseph, Leigh & Swain (1977). The HBIP:H_2O ratio is affected by the crystallization method; the crystals of the hemihydrate HBIP-2 (HBIP:H_2O ratio 1:0.5) were grown by slow evaporation at room temperature of an aqueous solution of the monohydrate HBIP-1 (HBIP:H_2O ratio 1:1). The crystals obtained were colourless needles. The HBIP:H_2O ratio for each hydrate was checked by thermogravimetric analysis.

Crystal data

$2C_9H_{10}N_4O_2.H_2O$
M_r = 430.42
Monoclinic
$P2_1/n$
a = 9.484 (2) Å
b = 7.812 (2) Å
c = 26.171 (5) Å
β = 94.64 (3)°
V = 1932.6 (7) Å^3
Z = 4
D_x = 1.48 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 5.3–13.3°
μ = 0.112 mm^{-1}
T = 293 K
Needle
0.4 × 0.06 × 0.02 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1881 measured reflections
1881 independent reflections
1058 observed reflections
[$I > 3\sigma(I)$]

θ_{max} = 20°
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 7$
$l = -25 \rightarrow 25$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F
R = 0.040
wR = 0.043
S = 2.44
1058 reflections
196 parameters
$w = 1/[\sigma^2(F) + 0.00008F^2]$
$(\Delta/\sigma)_{max}$ = 0.0027

$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)*

U_{iso} for C atoms; $U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for O and N atoms.

	x	y	z	U_{eq}/U_{iso}
O1	0.8785 (5)	−0.1478 (5)	0.4461 (1)	0.0448
O2	0.8820 (4)	0.1361 (5)	0.4431 (1)	0.0359
O3	0.9421 (5)	0.5722 (5)	0.5503 (2)	0.0394
O11	0.8405 (4)	0.0758 (5)	0.8042 (1)	0.0391
O12	0.7224 (4)	0.1004 (5)	0.8723 (1)	0.0345
N1	0.7248 (5)	0.4549 (6)	0.4875 (2)	0.0286
N2	0.5711 (5)	0.2674 (6)	0.4594 (2)	0.0280
N3	0.5479 (5)	0.0377 (6)	0.5798 (2)	0.0282
N4	0.6520 (4)	0.2644 (6)	0.6170 (2)	0.0271
N11	0.5734 (5)	0.6656 (6)	0.7843 (2)	0.0254
N12	0.4827 (5)	0.6808 (6)	0.8574 (2)	0.0267
N13	0.4210 (5)	0.2336 (6)	0.7658 (2)	0.0348
N14	0.3305 (5)	0.2626 (6)	0.8401 (2)	0.0335
C1	0.8499 (6)	−0.0035 (9)	0.4625 (2)	0.033 (2)
C2	0.7659 (6)	−0.0053 (7)	0.5093 (2)	0.030 (2)
C3	0.7424 (6)	0.1720 (7)	0.5335 (2)	0.025 (1)
C4	0.6793 (6)	0.2945 (7)	0.4941 (2)	0.023 (1)
C5	0.6450 (6)	0.5281 (8)	0.4470 (2)	0.037 (2)
C6	0.5497 (6)	0.4128 (8)	0.4294 (2)	0.037 (2)
C7	0.6467 (6)	0.1548 (8)	0.5765 (2)	0.027 (2)
C8	0.4860 (6)	0.0762 (8)	0.6245 (2)	0.033 (2)
C9	0.5494 (6)	0.2133 (7)	0.6482 (2)	0.028 (2)
C11	0.7567 (6)	0.1530 (8)	0.8304 (2)	0.027 (2)
C12	0.7051 (6)	0.3294 (7)	0.8109 (2)	0.032 (2)
C13	0.5700 (6)	0.3893 (7)	0.8343 (2)	0.027 (2)
C14	0.5453 (6)	0.5771 (7)	0.8253 (2)	0.025 (2)
C15	0.5278 (6)	0.8318 (8)	0.7903 (2)	0.036 (2)
C16	0.4726 (6)	0.8408 (8)	0.8355 (2)	0.036 (2)
C17	0.4423 (6)	0.2912 (7)	0.8127 (2)	0.025 (2)
C18	0.2870 (7)	0.1621 (8)	0.7634 (2)	0.041 (2)
C19	0.2309 (7)	0.1772 (8)	0.8083 (2)	0.041 (2)

Table 2. *Selected geometric parameters (Å, °)*

O1—C1	1.244 (7)	N13—C17	1.307 (6)
O2—C1	1.251 (7)	N13—C18	1.385 (7)
O11—C11	1.246 (6)	N14—C17	1.347 (6)
O12—C11	1.240 (6)	N14—C19	1.379 (7)
N1—C4	1.341 (6)	C1—C2	1.514 (7)
N1—C5	1.376 (7)	C2—C3	1.546 (7)
N2—C4	1.331 (6)	C3—C4	1.495 (7)
N2—C6	1.386 (7)	C3—C7	1.509 (7)
N3—C7	1.317 (6)	C5—C6	1.331 (7)
N3—C8	1.383 (6)	C8—C9	1.354 (7)
N4—C7	1.360 (6)	C11—C12	1.535 (7)
N4—C9	1.378 (6)	C12—C13	1.537 (7)
N11—C14	1.322 (6)	C13—C14	1.501 (7)
N11—C15	1.382 (7)	C13—C17	1.505 (7)
N12—C14	1.340 (6)	C15—C16	1.334 (8)
N12—C16	1.376 (7)	C18—C19	1.333 (7)
C4—N1—C5	109.0 (5)	N3—C7—C3	125.8 (5)
C4—N2—C6	109.0 (5)	N4—C7—C3	122.6 (5)
C7—N3—C8	104.9 (5)	N3—C8—C9	110.8 (5)
C7—N4—C9	107.2 (5)	N4—C9—C8	105.5 (5)
C14—N11—C15	108.3 (5)	O11—C11—O12	123.4 (6)
C14—N12—C16	107.9 (5)	O11—C11—C12	116.9 (5)
C17—N13—C18	104.6 (5)	O12—C11—C12	119.5 (5)
C17—N14—C19	106.8 (5)	C11—C12—C13	113.3 (5)
O1—C1—O2	125.6 (5)	C12—C13—C14	111.1 (5)
O1—C1—C2	114.5 (6)	C12—C13—C17	111.5 (4)
O2—C1—C2	119.9 (6)	C14—C13—C17	109.1 (5)
C1—C2—C3	115.2 (5)	N11—C14—N12	108.8 (5)
C2—C3—C4	110.7 (4)	N11—C14—C13	126.8 (5)
C2—C3—C7	109.9 (5)	N12—C14—C13	124.3 (5)

C4—C3—C7	109.8 (4)	N11—C15—C16	107.4 (5)
N1—C4—N2	107.4 (5)	N12—C16—C15	107.6 (6)
N1—C4—C3	124.9 (5)	N13—C17—N14	112.0 (5)
N2—C4—C3	127.7 (5)	N13—C17—C13	126.0 (5)
N1—C5—C6	107.5 (6)	N14—C17—C13	121.9 (5)
N2—C6—C5	107.1 (6)	N13—C18—C19	110.8 (6)
N3—C7—N4	111.6 (5)	N14—C19—C18	105.8 (5)

Table 3. *Dihedral angles (°) in the HBIP zwitterions in HBIP-2 and HBIP-1*

The planes of the imidazole rings are denoted (1) and (3) whether they contain atoms N1 (or N11) or N3 (or N13); the planes of the carboxylate groups are denoted (2).

Dihedral angle	HBIP-2 Molecule (I)	HBIP-2 Molecule (II)	HBIP-1
(1)-(2)	79.2 (3)	166.3 (3)	102.8
(1)-(3)	108.3 (3)	76.0 (3)	66.7
(2)-(3)	37.3 (3)	88.2 (3)	10.5

Table 4. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots$$A$	H$\cdots$$A$	$D$$\cdots$$A$	D—H$\cdots$$A$
N1—H1$\cdots$O3	1.654 (7)	2.691 (7)	168.3 (6)
O3—H31$\cdots$O2^{i}	1.96 (5)	2.822 (6)	162 (4)
O3—H32$\cdots$O12^{ii}	1.82 (5)	2.664 (6)	160 (5)
N2—H2$\cdots$N3^{iii}	1.825 (5)	2.796 (6)	152.2 (5)
N4—H4$\cdots$O12^{ii}	1.892 (6)	2.887 (6)	156.8 (5)
N11—H11$\cdots$O11^{ii}	1.591 (6)	2.613 (6)	163.4 (6)
N12—H12$\cdots$O1^{iv}	1.584 (6)	2.608 (6)	163.5 (6)
N14—H14$\cdots$O2^{iv}	1.819 (6)	2.814 (6)	156.8 (6)

Symmetry codes: (i) $2 - x, 1 - y, 1 - z$; (ii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (iii) $1 - x, -y, 1 - z$; (iv) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$.

As a result of the small number of observed reflections available, only N and O atoms were refined anisotropically; C atoms were assigned isotropic displacement parameters. All H atoms were clearly located on difference Fourier maps and were assigned an arbitrary isotropic displacement parameter, $U = 0.07$ Å^2; the positions of the H atoms of the water molecule were refined using constrained geometry (O—H = 0.9 Å, H—O—H = 100°); the contributions of the other H atoms were computed assuming idealized geometry (C—H, N—H = 1.05 Å).

Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989). Data reduction: *CRYSTALS* (Watkin, Carruthers & Betteridge, 1988). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *CRYSTALS*. Molecular graphics: *CRYSTALS*. Software used to prepare material for publication: *CRYSTALS*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1214). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4-Methoxyphenyl 2-Nitrophenyl Sulfide

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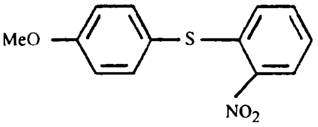
Abstract

An intramolecular S$\cdots$O interaction is present in the title compound, $(2\text{-}O_2NC_6H_4)S(C_6H_4OMe\text{-}4)$, with S$\cdots$O = 2.641 (2) Å and C—S$\cdots$O = 177.69 (8)°.

Comment

The literature contains various examples of compounds having non-bonded S$\cdots$O contacts shorter than the sum of the van der Waals radii (3.25 Å) (Kucsman & Kapovits, 1985). A typical group of such compounds is those containing the 2-nitroarylthio unit, 2-O_2N-*R*-C_6H_3S, as illustrated by the title compound, (I). The intramolecular S$\cdots$O1 distance in (I) is 2.641 (2) Å, with a C7—S$\cdots$O1 angle of 177.69 (8)°; the value of C1—S$\cdots$O1 is 75.16 (8)°. The nitro group is almost coplanar with the benzene ring (C1–C6) to which it is attached, the angle between the planes of the nitro and aryl units being 5.5 (5)°. In effect, the nitro group is rotated about the N—C2 bond such that O1 and O2 lie on either side of the C1–C6 plane, at a distance of *ca* 0.1 Å in each case. There are no intermolecular contacts involving the S atom, other than the S$\cdots$O separations, which are at distances less than the sum of the appropriate van der Waals radii.



(I)

The intramolecular S$\cdots$O separations in solid 2-nitroaryl sulfides are generally between 2.62 and 2.72 Å (Kucsman & Kapovits, 1985). A shorter separation of 2.590 Å was reported for the polycyclic derivative 9-