

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O12—H12...N31	0.84	1.85	2.685 (3)	171
O13—H13...N51	0.84	1.89	2.720 (3)	172
O15—H15...N71	0.84	1.98	2.814 (3)	176
O22—H22...N41 ¹	0.84	1.88	2.721 (3)	177
O23—H23...N61	0.84	1.92	2.750 (3)	170
O25—H25...N81	0.84	1.92	2.756 (3)	178

Symmetry code: (i) 3 + x, 1 + y, z.

The DENZO-SMN program uses a scaling algorithm (Fox & Holmes, 1966) which effectively corrects for absorption effects. Compound (I) crystallized in the triclinic system and space group *P*1̄ was assumed. Examination of the structure using PLATON (Spek, 1999) confirmed the absence of any symmetry beyond that required by space group *P*1̄. H atoms were treated as riding, with C—H 0.95 and O—H 0.84 Å.

Data collection: Kappa-CCD Server Software (Nonius, 1997). Cell refinement: DENZO-SMN (Otwinowski & Minor, 1997). Data reduction: DENZO-SMN. Program(s) used to solve structure: SHELXS97 (Sheldrick, 1997b). Program(s) used to refine structure: NRCVAX96 (Gabe *et al.*, 1989) and SHELXL97 (Sheldrick, 1997a). Molecular graphics: NRCVAX96, ORTEPII (Johnson, 1976) and PLATON. Software used to prepare material for publication: NRCVAX96, SHELXL97 and PRPKAPPA (Ferguson, 1999).

The X-ray data were collected at the University of Toronto using a Nonius KappaCCD diffractometer purchased with funds from NSERC, Canada.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1293). Services for accessing these data are described at the back of the journal.

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2,2'-Bi-2-imidazoline

CONOR J. BRENNAN AND VICKIE MCKEE

School of Chemistry, Queen's University, Belfast BT9 5AG, Northern Ireland. E-mail: v.mckee@qub.ac.uk

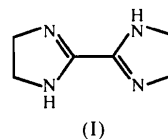
(Received 20 April 1999; accepted 10 May 1999)

Abstract

The title compound, C₆H₁₀N₄, forms hydrogen-bonded ribbons which are packed in a herring-bone pattern controlled by CH...N(imine) interactions.

Comment

2,2'-Bi-2-imidazoline is a versatile ligand for transition metals; it has the potential to act as a bidentate α-diimine, a diamine or, if deprotonated, as a dianionic bridge between two metal ions. The infrared spectrum of the compound shows some unusual features; the imine stretching frequency ($\nu_{C=N}$, 1571 cm⁻¹) is very low, much closer to that expected for a complex with a metal ion bound to the imine than for the free imine. In comparison, the equivalent band in the infrared spectrum of the closely related 2,2'-bi-2-oxazoline appears at 1625 cm⁻¹ (Burnett *et al.*, 1981). Wang & Bauman (1965) have noted the low frequency of the ν_{NH} stretch, at 3179 cm⁻¹ and observed that this band shifted to 3450 cm⁻¹ in chloroform solution, suggesting that this might indicate intermolecular association in the solid state. A structure determination of 2,2'-bi-2-imidazoline, (I), was undertaken to investigate the origin of these effects and to provide a basis for the interpretation of spectral data for metal complexes of this ligand.



The 2,2'-bi-2-imidazoline molecule sits on a centre of symmetry, so that the asymmetric unit consists of one five-membered ring. The non-H atoms of the molecule are close to planar (r.m.s. deviation 0.008 Å) and the α-diimine is in the *trans* configuration. The amine-H atom, located from difference maps, lies within 0.01 (2) Å of the mean plane of the imidazole ring. This observation, together with the slightly elongated C1—N(imine) and shortened C1—N(amine) distances of 1.285 (2) and 1.344 (2) Å, respectively, suggests a partial delocalization of the π system over the section comprising of N1, C1 and N2 of both rings.

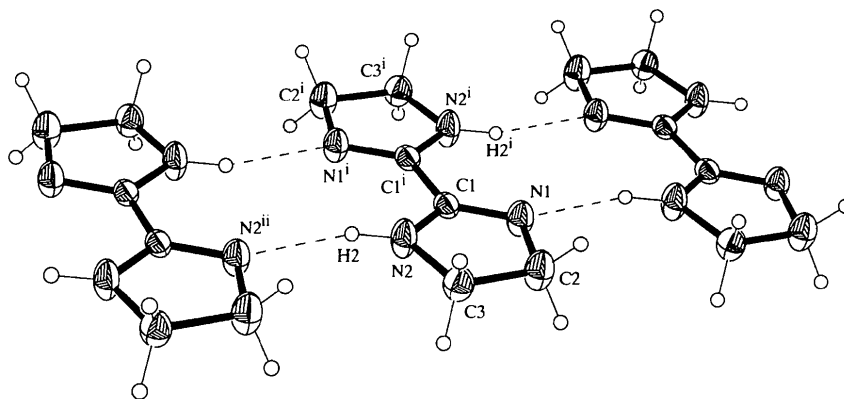


Fig. 1. Perspective view showing 50% probability displacement ellipsoids and hydrogen bonding [symmetry codes: (i) $1-x, 1-y, 2-z$; (ii) $1+x, y, z$].

As shown in Fig. 1, each molecule is linked by two equivalent hydrogen bonds to each of two neighbouring molecules [$\text{NH}\cdots\text{N}$ 2.09 (2) Å], forming a hydrogen-bonded ribbon running parallel to the a axis. This interaction accounts for the unusual features in the infrared spectrum noted above; the $\text{NH}\cdots\text{N}$ bonds form the predicted intermolecular links while the delocalization of the π system over both the N atoms and C1 is consistent with the low frequency of the $\nu_{\text{C}=\text{N}}$ vibration. Both N1 and N2 are bonded to hydrogen, the distinction being that N2 is the hydrogen-bond donor and N1 the acceptor; in the limit where the two N—H distances are equal, the distinction between imine and amine would disappear and the structure could be described as a chain of dianions linked by pairs of H^+ cations.

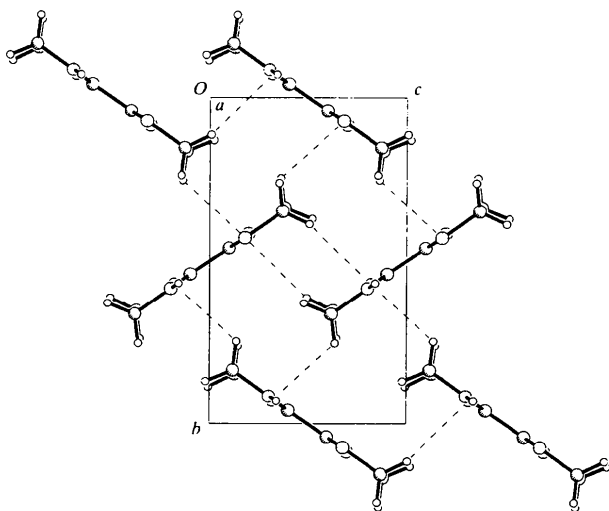


Fig. 2. Packing diagram perpendicular to the a axis. Dashed lines represent $\text{CH}\cdots\text{N}$ interactions (2.91 and 2.97 Å for those between parallel and 'perpendicular' pairs of molecules, respectively).

Fig. 2 shows that the ribbons are packed together in a manner reminiscent of the α -type herring-bone pattern defined by Desiraju & Gavezzotti (1989). Detailed examination suggests that the packing is controlled by weak hydrogen-bonding interactions between H atoms on the saturated C atoms C2 and C3 and the imine-N atoms of adjacent molecules. The imine-N atom N1 interacts both with $\text{H2B}(-x, 1-y, 1-z)$ at 2.91 Å and with $\text{H3B}(x-\frac{1}{2}, \frac{3}{2}-y, \frac{1}{2}+z)$ at 2.97 Å. These H atoms are more than 3.5 Å from C1, indicating that the interaction is with the N atom, not the π system.

Experimental

The compound was prepared by literature methods (Wang & Bauman, 1965; Burnett *et al.*, 1981). Dithiooxamide (20 g, 0.166 mol) suspended in ethanol (100 ml) was treated with ethyl bromide (30 ml, 0.4 mol) and stirred at 333 K for 4 h. After cooling to room temperature, 1,2-diaminoethane (75 ml, 1.1 mol) was added slowly over 1 h, maintaining a steady evolution of ethanethiol. The mixture was heated briefly to 353 K and then stirred for an hour at 273 K. The resulting product was filtered off and recrystallized from boiling ethanol (yield 75%). The white crystalline product consisted of fibrous needles; a sample of adequate quality for crystallographic study was grown from ethanol by slow evaporation.

Crystal data

$\text{C}_6\text{H}_{10}\text{N}_4$
 $M_r = 138.18$
 Monoclinic
 $P2_1/n$
 $a = 5.1520(5)$ Å
 $b = 10.4720(11)$ Å
 $c = 6.3709(7)$ Å
 $\beta = 105.659(2)^\circ$
 $V = 330.96(6)$ Å³
 $Z = 2$
 $D_x = 1.387$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from >50 reflections
 $\theta = 2-25^\circ$
 $\mu = 0.093$ mm⁻¹
 $T = 163(2)$ K
 Fibrous needle
 $0.70 \times 0.15 \times 0.01$ mm
 Colourless

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: none
 2031 measured reflections
 578 independent reflections

539 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.054$
 $\theta_{\text{max}} = 25^\circ$
 $h = -5 \rightarrow 6$
 $k = -12 \rightarrow 12$
 $l = -7 \rightarrow 7$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.098$
 $S = 1.082$
 578 reflections
 49 parameters
 H atoms: see text
 $w = 1/[\sigma^2(F_o^2) + (0.0414P)^2 + 0.134P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.003$
 $\Delta\rho_{\text{max}} = 0.16 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.15 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

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1,4,7,10,13,16,21,24-Octaazabicyclo-[8.8.8]hexacos-4,6,13,15,21,23-hexaene pentahydrate

VICKIE MCKEE AND JANE NELSON

School of Chemistry, Queen's University, Belfast BT9 5AG, Northern Ireland. E-mail: v.mckee@qub.ac.uk

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Abstract

The title compound, C₁₈H₃₀N₈·5H₂O, is a hexamine cryptand which crystallizes with pseudo-threefold symmetry, each strand having the *anti* conformation. Water molecules are hydrogen bonded to five of the six imine N atoms.

Comment

The title compound, hereinafter imBT·5H₂O, is a small azacryptand which acts as an efficient host for single main group (Apperley *et al.*, 1999), transition (Hunter *et al.*, 1990) or lanthanide (Bligh *et al.*, 1998) ions in redox states I–III, despite the presence of six imino functions which might normally be expected to be subject to metal-assisted hydrolysis in the presence of strong Lewis acids. While attempting to discover the effective limiting size of the cavity for group 13 cations, we treated the ligand with a number of cations in redox state +III, isolating products of acceptable purity for $M = \text{In}$ and Tl , though not for $M = \text{Ga}$. We also attempted synthesis of the Tl^{I} cryptate to discover whether the cryptand cavity could accommodate this cation, which is 0.2–0.3 Å larger than Hg^{II} or Sr^{II} but 0.1–0.2 Å smaller than Cs^{I} ; all three of these cations have previously been coordinated by this host. However, the expected Tl complex was not obtained and, as described in the *Experimental* section, the isolated product was imBT·5H₂O. Smith *et al.* (1993) have described the structure of imBT, but the pentahydrate has not previously been reported.

Table 1. Selected geometric parameters and hydrogen-bonding geometry (Å, °)

N1—C1	1.2847 (19)	N2—C3	1.450 (2)
N1—C2	1.4820 (19)	C1—C1'	1.479 (3)
N2—C1	1.3436 (19)	C3—C2	1.536 (2)
C1—N1—C2	105.66 (12)	N2—C1—C1'	120.31 (15)
C1—N2—C3	109.04 (13)	N2—C3—C2	101.51 (12)
N1—C1—N2	117.32 (14)	N1—C2—C3	106.44 (12)
N1—C1—C1'	122.37 (15)		

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H2...N1 ⁱⁱ	0.87 (2)	2.09 (2)	2.919 (2)	157 (2)
C2—H2B...N1 ⁱⁱⁱ	0.99	2.91	3.866 (2)	162
C3—H3B...N1 ^{iv}	0.99	2.97	3.684 (2)	130

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

The amine-H atom was located from difference maps and refined (with the atomic displacement parameter fixed at 0.05 Å²).

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINTE* (Siemens, 1995). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997b). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL97*.

We are grateful to Professor Ward T. Robinson, University of Canterbury, Christchurch, New Zealand, for access to the diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1338). Services for accessing these data are described at the back of the journal.

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