Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.0857$
$S = 1.078$
1795 reflections
174 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0337P)^2 + 0.566P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.279$ e Å^{-3}
$\Delta\rho_{\min} = -0.234$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.0 (3)

Table 1. *Selected geometric parameters (Å, °)*

S—O2	1.426 (4)	C1—C5	1.572 (5)
S—O1	1.444 (3)	C5—C8	1.506 (6)
S—C9	1.769 (4)	C5—C6	1.551 (6)
S—C1	1.780 (4)	C6—C7	1.530 (6)
C1—C7	1.532 (5)		
O2—S—O1	118.6 (3)	C7—C1—S	118.0 (3)
O2—S—C9	106.5 (2)	C5—C1—S	119.9 (3)
O1—S—C9	108.9 (2)	C8—C5—C4	111.8 (4)
O2—S—C1	108.1 (2)	C8—C5—C6	113.7 (4)
O1—S—C1	107.1 (2)	C4—C5—C6	115.7 (4)
C9—S—C1	107.2 (2)	C8—C5—C1	120.8 (3)
C2—C1—C7	112.3 (3)	C4—C5—C1	105.9 (3)
C2—C1—C5	104.4 (3)	C6—C5—C1	86.8 (3)
C7—C1—C5	90.0 (3)	C7—C6—C5	90.9 (3)
C2—C1—S	110.4 (3)	C6—C7—C1	89.0 (3)

H atoms were refined using a riding model and with $U(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C})$ for methyl and $1.2U_{\mathrm{eq}}(\mathrm{C})$ for other groups.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1995). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1177). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 97–99

N,*N*′-Bis(1-methylimidazol-2-ylmethylidene)-1,3-diaminopropan-2-ol, HBIMPNOL

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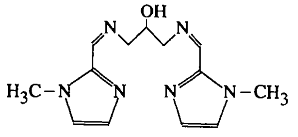
Abstract

The crystal structure of the title compound, $C_{13}H_{18}N_6O$, reveals that for such a species to act as a tetradentate ligand, significant rearrangement is required, as evidenced by the dihedral angle [67.5 (1)°] between the two imidazole rings which results in a large separation of 7.256 (4) Å between the N donor atoms of these rings.

Comment

In recent years, it has been recognized that pentadentate Schiff base ligands derived from 1,3-diaminopropan-2-ol containing adequate pendant donor groups such as phenolate, pyridine, pyrrole or imidazole play an important role in the synthesis of model complexes for copper-containing metalloproteins (Butcher *et al.*, 1986*a*,*b*; Borer & Sinn, 1988; Mazurek *et al.*, 1985; Nishida & Kida, 1986). Specifically, the title ligand, HBIMPNOL, has displayed the ability to function as both a tetradentate and a dinucleating ligand (Borer & Sinn, 1988; Doman, Richardson, Arar & Buchanan, 1989). However, no X-ray structures of uncoordinated pentadentate ligands of this type have been reported previously. Moreover, a Cambridge Structural Database (1996) search shows that the X-ray crystal structure of a mononuclear Cu$^{\mathrm{II}}$ complex with HBIMPNOL is the only structure in the literature which contains the title ligand (Doman *et al.*, 1989). We have, therefore, determined the crystal structure of HBIMPNOL so that subsequent changes upon coordination may be investigated.



HBIMPNOL

The molecular structure of HBIMPNOL, is shown in Fig. 1. The N7=C6 and N11=C12 distances of 1.257 (3) and 1.270 (3) Å, respectively, in the free ligand and are consistent with N=C double bonding and are similar to those detected in the corresponding copper complex. The bond angles of 117.7 (2) and 114.8 (2)° around these N atoms confirm their sp^2 character. Furthermore, the relatively compact conformation adopted by the molecule in the solid state is achieved through an O—H···N interaction: H18···N3^i 1.98 (3), O18···N3^i 2.849 (3) Å and O18—H18···N3^i 176 (2)°; symmetry code: (i) $-x+1$, $-y+2$, $-z+1$. As expected, this unique hydrogen contact strongly influences the conformational arrangement of the N1–C5 imidazole ring as well as the C10—C9—O18 [105.4 (2)°] and C8—C9—O18 [111.5 (2)°] angles which should be chemically equivalent. Consequently, the torsion angles about the N7—C8 and N11—C10 bonds are also different [C6—N7—C8—C9 −126.2 (2) and C12—N11—C10—C9 111.5 (2)°].

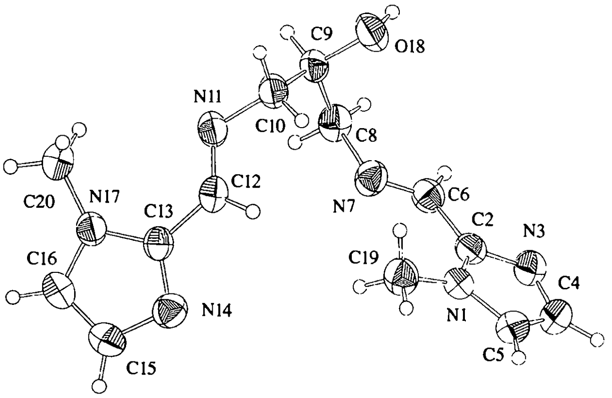


Fig. 1. The atomic arrangement in title molecule. Displacement ellipsoids are shown at the 50% probability level.

Finally, the conformation of the free ligand in the solid state is of interest for comparison with that in a metal complex. In the free ligand, the two imidazole rings are inclined at an angle of 67.5 (1)° with respect to one another. Clearly this conformation is not adequate for direct coordination to a metal ion in the usual manner of a tetradentate ligand. Therefore, significant rearrangement must occur as evidenced by the large N3···N14 donor-atom separation of 7.256 (4) Å, which should be compared with a value of 3.09 Å when the title ligand is coordinated to Cu^{II} in the [Cu(HBIMPNOL]$^{2+}$ ion complex (Doman *et al.*, 1989).

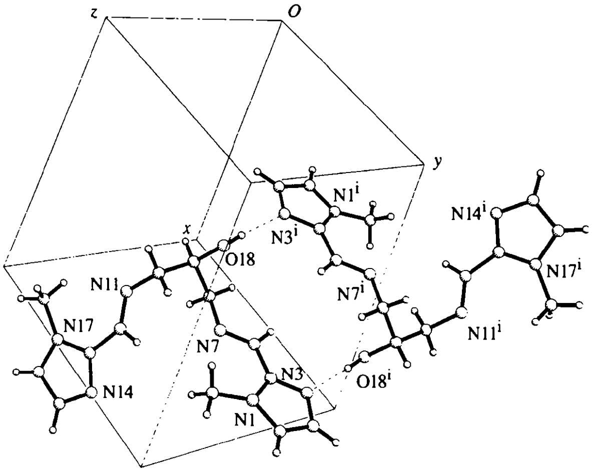


Fig. 2. The unit cell illustrating the hydrogen-bonding scheme.

Experimental

The title compound was prepared in high yield by slight modifications of the method described in the literature (Doman *et al.*, 1989). To a solution of 1,3-diaminopropan-2-ol (2.25 g; 24.96 mmol) in dry diisopropyl ether (200 ml) was added 1-methylimidazole-2-carboxyaldehyde (5.49 g; 49.92 mmol) (Oberhausen, Richardson, Buchanan & Pierce, 1989) under an argon atmosphere. The mixture was stirred for 24 h and, after removal of the solvent by rotatory evaporation, a precipitate of the desired ligand was obtained. Yield 6.0 g (96%), m.p. 412–414 K. Analysis calculated for $C_{13}H_{18}N_6O$: C 56.92, H 6.61, N 30.64%; found: C 56.71, H 6.47, N 30.57%. Single crystals were obtained by slow evaporation of a diisopropyl ether solution of the title compound.

Crystal data

$C_{13}H_{18}N_6O$
$M_r = 274.33$
Triclinic
$P\overline{1}$
$a = 9.538\ (2)$ Å
$b = 9.603\ (2)$ Å
$c = 9.769\ (2)$ Å
$\alpha = 82.46\ (3)°$
$\beta = 64.00\ (3)°$
$\gamma = 61.59\ (3)°$
$V = 704.0\ (4)$ Å^3
$Z = 2$
$D_x = 1.294$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.74$–$13.66°$
$\mu = 0.088$ mm^{-1}
$T = 293\ (2)$ K
Block
0.40 × 0.33 × 0.30 mm
Colourless

Data collection

Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2594 measured reflections
2437 independent reflections
1958 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.012$
$\theta_{\rm max} = 25.0°$
$h = -11 \rightarrow 0$
$k = -11 \rightarrow 10$
$l = -11 \rightarrow 10$
3 standard reflections
frequency: 60 min
intensity decay: −4.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.121$
$S = 1.093$
2334 reflections
185 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0514P)^2 + 0.3355P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.014$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}
Extinction correction: *SHELXL93*
Extinction coefficient: 0.101 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C6—N7	1.257 (3)	C9—C10	1.520 (3)
N7—C8	1.462 (3)	C10—N11	1.464 (3)
C8—C9	1.520 (3)	N11—C12	1.270 (3)
C9—O18	1.422 (3)		
O18—C9—C8	111.5 (2)	C8—C9—C10	112.9 (2)
O18—C9—C10	105.4 (2)		

Refinement was on F^2 for all reflections except for 103 with very negative F^2 or flagged by the user for potential systematic errors. The H18 atom was located from a $\Delta\rho$ map and refined positionally with fixed $U = 0.05$ Å^2. All other H atoms were placed in calculated positions using a riding model [C—H = 0.93 Å, $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for C_{sp^2}; C—H = 0.96 Å, $U(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for C_{sp^3}]. All calculations were performed on a DEC 3000 AXP and PC/486 computer.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *SET*4 in *CAD*-4 *EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1996). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1056). Services for accessing these data are described at the back of the journal.

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2,2,6,6-Tetramethyl-4-oxopiperidinium Bis(pentafluorophenyl)phosphinate

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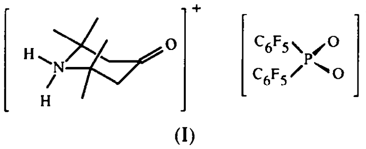
Abstract

The structure consists of centrosymmetric $\{(\text{C}_9\text{H}_{18}\text{NO})^+\text{-}[(\text{C}_6\text{F}_5)_2\text{PO}_2]^-\}_2$ units linked by N—H···O hydrogen bonds to form 12-membered [H—N—H···O—P—O···H—N—H···O—P—O···] rings.

Comment

As part of a general study of metal phosphinate compounds (Du, Rettig, Thompson & Trotter, 1991), we attempted the preparation of a formamide complex of cobalt(II) bis(pentafluorophenyl)phosphinate (see *Experimental*). Instead of the target complex, crystals of the title complex, (I), were isolated. The reaction to produce this salt likely involves the acid-catalyzed condensation of acetone with formamide.



(I)

The asymmetric unit consists of two independent sets of cations and anions. The structure of the piperidonium cation is as expected and does not differ significantly from those reported previously (Rees & Weiss, 1971; Simpson, 1992; Conary *et al.*, 1993), although the structural parameters resulting from this study are considerably more precise. Metrical data for one of the two independent cations are given in Table 1.