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4-[Bis(1,5-dimethyl-1*H*-pyrazol-3-ylmethyl)amino]phenol monohydrate

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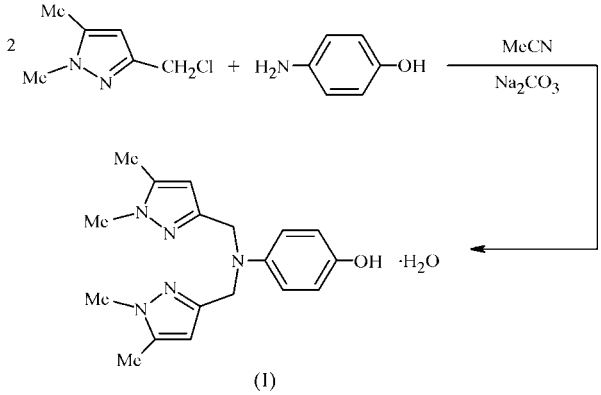
The crystal structure of the title compound, $C_{18}H_{23}N_5O\cdot H_2O$, shows molecules containing a phenol group linked perpendicularly to a roughly planar fragment comprising two pyrazole rings. Molecules are stacked perpendicular to the [101] direction, with their phenol groups disposed alternately. The molecular packing in the crystal is stabilized by hydrogen bonding involving water molecules.

Comment

There is considerable interest in the synthesis of multidentate organic ligands for a variety of purposes. These ligands are involved in the building of organic complexes that are used as potential bioinorganic model systems, as well as in immobilization on the surface of a solid material, such as an organic resin or a silica gel. Copper phenolate coordination occurs in a



(I)

number of native and metal-substituted proteins (Klinman, 1996). A biologically important example of phenoxy coordination to Cu^{II} concerns the metalloproteases astacin and serralysin, where Cu^{II} substitution for the native Zn gives a hyper-reactive enzyme (Park & Ming, 1998, 2002; Locher *et al.*, 1987).

In this paper, we report the synthesis and crystal structure of the monohydrate, (I), of a new pyrazolyl ligand, namely 4-[bis(1,5-dimethyl-1*H*-pyrazol-3-ylmethyl)amino]phenol. Compound (I) was prepared using a method developed in our laboratory (Radi *et al.*, 2000, 2004; Malek *et al.*, 2002, 2004) by the condensation of 3-chloromethyl-1,5-dimethylpyrazole with *p*-aminophenol in a 2:1 ratio in acetonitrile using sodium carbonate as base.

The product was characterized by IR and NMR spectroscopy and by mass spectrometry. Molecules of the organic ligand have been found to crystallize in a 1:1 ratio with water molecules.

The title molecule may be viewed as resulting from substitution of the two amine H atoms of an aminophenol system by pyrazolyl methyl groups that are bonded to the benzene ring by C—C—N junctions (Fig. 1), instead of the N—C—N junctions that are found in bis[(3,5-dimethylpyrazol-1-yl)-methyl]aniline (pabd; Driessen, 1982; Blonk *et al.*, 1985). The dihedral angles of 81.5 (2) and 80.4 (2)° between the planes of the pyrazole rings and the plane of the benzene ring are slightly different from those observed in *N*,*N*,*N*′,*N*′-tetrakis-[(1,5-dimethylpyrazol-3-yl)methyl]-1,4-phenylenediamine, (II) (84.7 and 79.8°; Bouabdallah *et al.*, 2005), in which the pyrazole rings are also linked to the benzene ring by C—C—N junctions. These values differ strongly from the dihedral angles of 50.4 (2) and 72.1 (2)° found in the isomeric compound *N*,*N*,*N*′,*N*′-tetrakis[(3,5-dimethylpyrazol-1-yl)-methyl]-1,4-phenylenediamine, (III), where the junctions are of the N—C—N type (Daoudi *et al.*, 2003). The value of 20.2 (4)° for the dihedral angle between the planes of the two pyrazole rings, which indicates the deviation from flatness, can be compared with the values of 7.7 and 87.9 (1)° in the related compounds (II) and (III), respectively.

The C10—C11 and C16—C17 bond lengths (Table 1) are very close to the distance of 1.49 Å observed in 4-acetyl-3(5)-amino-5(3)-methylpyrazole (Hergold-Brundic *et al.*, 1991).

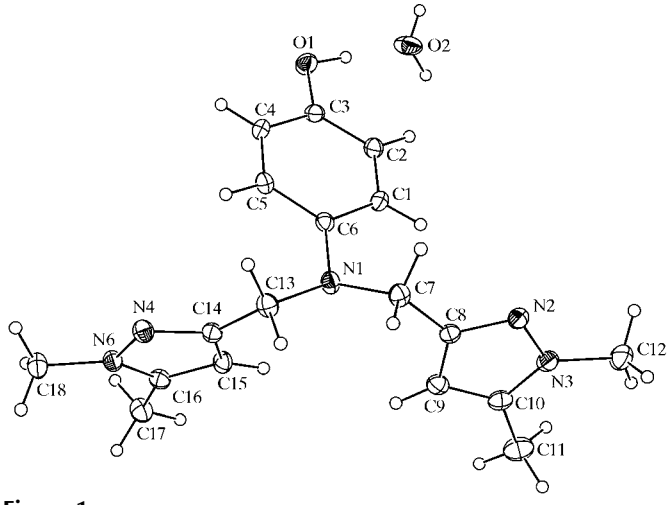


Figure 1
A view of (I), with displacement ellipsoids drawn at the 30% probability level.

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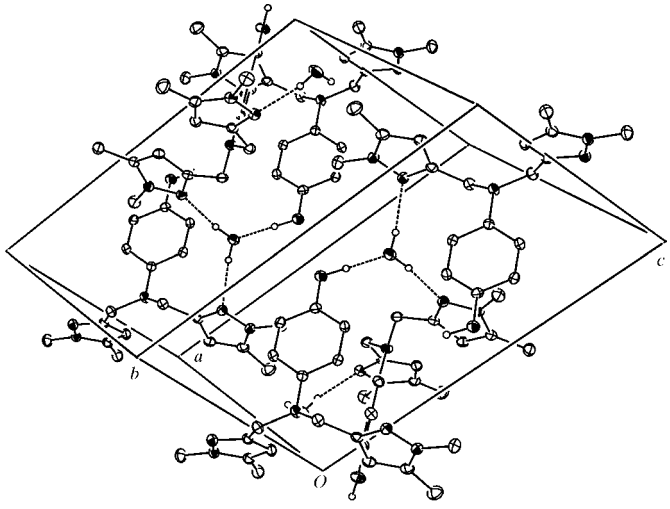

Figure 2
The packing of (I), showing the hydrogen bonds involving the hydroxy groups and water molecules. For clarity, H atoms not involved in hydrogen bonding have been omitted.

The low steric strain between the methyl groups may be explained by the torsion angles of −1.0 (4)° for C12—N3—C10—C11 and 2.5 (4)° for C18—N6—C16—C17.

The C—N—C angles around aniline atom N1 obviously deviate from the ideal tetrahedral value, but they are very close to those found for (II). The C6—N1 distance in (I) is slightly longer than the corresponding distance in (II). This difference can be explained by some involvement, through electron donation, of the aniline N atom in the multicenter bonding of the benzene ring.

The most interesting feature of this structure is the arrangement of the molecules in the crystal. The almost planar part of the molecule, comprising the two roughly coplanar pyrazole rings, is aligned parallel to the (101) diagonal plane. Molecules are stacked nearly along the [101] direction with their phenol groups alternately disposed. The molecular packing is stabilized by hydrogen bonding of phenol groups and pyrazole rings with water molecules.

An extended three-dimensional network is built in this way (Fig. 2). Atom O2 of the water molecule is involved in three hydrogen bonds with three neighbouring phenol molecules, one to a hydroxy group (O1···O2^{i}) and two to pyrazole N atoms [O2···N4^{ii} and O2···N2^{iii}; symmetry codes: (i) $x+1$, y, z; (ii) $-x+1$, $y-\frac{1}{2}$, $-z+\frac{1}{2}$; (iii) $-x+1$, $-y+1$, $-z+1$; Table 2].

Experimental

A solution of *p*-aminophenol (1.13 g, 1.04×10^{-2} mol) in acetonitrile (50 ml) was added dropwise to a mixture of 3-chloromethyl-1,5-dimethylpyrazole (2.03 g, 5×10^{-2} mol) and sodium carbonate (8.8 g, 1.6×10^{-2} mol) in acetonitrile (200 ml). The mixture was refluxed for four days. The organic layer was filtered and concentrated at reduced pressure to form (I) (yield 95%), which was recrystallized from dimethyl sulfoxide as light-yellow crystals suitable for X-ray analysis [m.p. 433–434 K (DMSO)].

Crystal data

$C_{18}H_{23}N_5O\cdot H_2O$
$M_r = 343.43$
Monoclinic, $P2_1/c$
$a = 13.922$ (1) Å
$b = 9.4366$ (6) Å
$c = 16.799$ (1) Å
$\beta = 126.08$ (1)°
$V = 1783.7$ (3) Å^3
$Z = 4$
$D_x = 1.279$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 14369 reflections
$\theta = 3.6$–25.0°
$\mu = 0.09$ mm^{-1}
$T = 173$ (2) K
Platelet, light yellow
0.34 × 0.32 × 0.22 mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer
ω scans
14369 measured reflections
3128 independent reflections
2500 reflections with $I > 2\sigma(I)$
$R_{int} = 0.061$
$\theta_{max} = 25.0°$
$h = -16 \rightarrow 15$
$k = -11 \rightarrow 11$
$l = -17 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.124$
$S = 1.12$
3128 reflections
243 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0589P)^2 + 0.3372P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.19$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0072 (13)

Table 1
Selected geometric parameters (Å, °).

O1—C3	1.375 (2)	N3—C12	1.447 (3)
N1—C6	1.417 (2)	N4—C14	1.332 (2)
N1—C13	1.456 (2)	N4—N6	1.364 (2)
N1—C7	1.461 (2)	N6—C16	1.349 (2)
N2—C8	1.333 (2)	N6—C18	1.453 (2)
N2—N3	1.366 (2)	C10—C11	1.494 (3)
N3—C10	1.350 (3)	C16—C17	1.486 (3)
C6—N1—C13	118.21 (15)	C5—C6—N1	122.11 (17)
C6—N1—C7	116.55 (15)	C1—C6—N1	120.75 (17)
C13—N1—C7	115.80 (15)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H1O···N4^{ii}	0.89 (3)	1.93 (3)	2.816 (2)	172 (3)
O2—H2O···N2^{iii}	0.82 (3)	2.06 (3)	2.840 (2)	169 (3)
O1—H3O···O2^{i}	0.96 (3)	1.69 (3)	2.619 (2)	174 (3)

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

All C-bound H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with U_{iso}(H) values of $1.5U_{eq}$(C) for methyl groups and $1.2U_{eq}$(C) for the other H atoms. H atoms attached to O atoms were first placed in ideal positions, and then their positions and displacement parameters were refined.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2004); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1231). Services for accessing these data are described at the back of the journal.

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