Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1295). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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N,N-Bis(2-hydroxybenzyl)-N-(2-pyridyl-methyl)amine, H2BBPA

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Abstract

In connection with our interest in the use of multidentate ligands for the preparation of iron complexes as models for the active site of the metalloenzyme transferrin, we have prepared the title compound [N-(2-pyridylmethyl)-2,2'-(iminodimethyl)diphenol, $C_{20}H_{20}N_2O_2$], which contains one amine and one pyridine N atom and two phenolate O atoms capable of forming a N_2O_2 donor set.

Comment

Multidentate ligands derived from amines containing phenolate-type and α-pyridyl groups as pendant arms are recognized as an important class of ligands, since they are able to mimic the amino acid residues tyrosine and histidine, respectively, in the active site of certain metalloenzymes such as transferrins (Pyrz, Roe, Stern & Que, 1985) and purple acid phosphatases (Que, 1990). In this work, we report the synthesis and crystal structure of a new tetradentate ligand, H2BBPA, which may act as a potent chelator for M^{3+} transition metals. This is part of our programme of preparation and characterization of iron and vanadium complexes with bioinorganic relevance (Neves, Brito et al., 1993; Neves, Vencato & Mascarenhas, 1994; Neves, Ceccato et al., 1993).
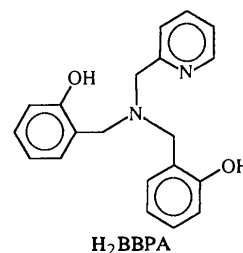
H2BBPA

The crystal structure reveals that H2BBPA exhibits adequate geometry of the N1, N2 and O2 donor atoms for facial coordination in octahedral complexes. The bond angles around the amine N atom range from 108.5 (7) to 110.6 (6)° and show that the N2 atom lies in a slightly distorted tetrahedral environment. The C—O(phenol) distances are very similar [C13—O1 = 1.411 (9) and C20—O2 = 1.39 (1) Å] and agree very well with the corresponding distances detected in related ligands (Campbell, Parsons & Pennington, 1993; Neves et al., 1995). The pyridine ring in the title compound is planar and forms dihedral angles of 81.2 (2) and 14.6 (9)° with the C8–C13 and C15–C20 phenol rings, respectively.
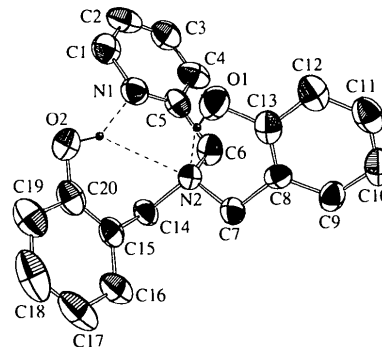

Fig. 1. The atomic numbering scheme and hydrogen bonds. Displacement ellipsoids are plotted at the 50% probability level. H atoms of the phenol O atoms have arbitrary size and other H atoms are omitted.

Finally, the relatively compact conformation adopted by the molecule is achieved through one intramolecular hydrogen bond involving a phenolic proton and the aliphatic N atom [O1$\cdots$N2 2.709 (8), H(O1)$\cdots$N2 1.70 Å, O1—H(O1)$\cdots$N2 158°] and an internal bifurcated hydrogen bond involving the other phenolic proton, the pyridine N atom and the aliphatic N atom [O2$\cdots$N1 = 2.746 (1), H(O2)$\cdots$N1 1.90 Å, O2—H(O2)$\cdots$N1 150°; O2$\cdots$N2 3.275 (10), H(O2)$\cdots$N2 2.50 Å, O2—H(O2)$\cdots$N2 133°; angle N1$\cdots$H(O2)$\cdots$N2 76°].

Experimental

To a solution of (2-hydroxybenzyl)(2-pyridylmethyl)amine (35 mmol) (Neves, Brito *et al.*, 1993) in tetrahydrofuran (100 ml) was added 2-bromomethylphenyl acetate (35 mmol) (Karlin, Cohen, Hayes, Farooq & Zubieta, 1987) under an argon atmosphere. After the addition of Et$_3$N (120 mmol) and stirring for 24 h a precipitate of Et$_3$NHBr (6.0 g) formed, which was removed by filtration. After removal of the solvent by rotatory evaporation, a yellow oil was obtained which was dissolved in methanol (100 ml) and KOH (53 mmol), refluxed for 40 min and then cooled to room temperature. A white precipitate of the desired ligand was filtered off, washed with cold methanol and ether, and dried under vacuum. Yield 5.7 g (51%), m.p. 445–446 K. ^{1}H NMR (CDCl$_3$); δ 3.6–3.8 (*m*, 6H, N-CH$_2$py; N-CH$_2$Ph), 6.6–7.7 (*m*, 11H, phenyl and pyridine), 8.7 (*d*, 1H, α-pyH). Single crystals were obtained by recrystallization from a methanolic solution of the title compound.

Crystal data

$C_{20}H_{20}N_2O_2$	Mo $K\alpha$ radiation
$M_r = 320.39$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1$	reflections
$a = 11.494\,(1)$ Å	$\theta = 10.51$–$20.62°$
$b = 6.263\,(1)$ Å	$\mu = 0.083$ mm^{-1}
$c = 12.479\,(1)$ Å	$T = 298$ K
$\beta = 111.01\,(1)°$	Prismatic
$V = 838.6\,(2)$ Å^3	$0.35 \times 0.30 \times 0.15$ mm
$Z = 2$	Pink
$D_x = 1.269$ Mg m^{-3}	

Data collection

Nonius CAD-4 diffractom-eter	$R_{int} = 0.038$
	$\theta_{max} = 24.97°$
$\omega/2\theta$ scans	$h = -13 \rightarrow 0$
Absorption correction: none	$k = -7 \rightarrow 0$
	$l = -13 \rightarrow 14$
1702 measured reflections	3 standard reflections
1619 independent reflections	frequency: 25 min
1093 observed reflections	intensity decay: 4.9%
[$F > 6\sigma(F)$]	

Refinement

Refinement on F	Unit weights applied
$R = 0.0730$	$(\Delta/\sigma)_{max} = 0.090$
$wR = 0.0740$	$\Delta\rho_{max} = 0.33$ e Å^{-3}
$S = 0.99$	$\Delta\rho_{min} = -0.35$ e Å^{-3}
1093 reflections	Extinction correction: none
216 parameters	Atomic scattering factors
H-atoms displacement parameters not refined	from *MolEN* (Fair, 1990)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\AA^2$)*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O1	0.0470 (5)	0.7879	0.2200 (5)	5.3 (2)
O2	0.3980 (5)	0.857 (1)	0.4080 (5)	5.1 (2)
N1	0.2353 (6)	0.695 (1)	0.5034 (5)	4.1 (2)
N2	0.2045 (5)	0.459 (1)	0.3100 (5)	3.4 (2)
C1	0.2512 (8)	0.831 (2)	0.5937 (7)	5.1 (3)
C2	0.1977 (8)	0.774 (2)	0.6779 (7)	5.5 (3)
C3	0.1352 (8)	0.584 (2)	0.6686 (8)	5.1 (2)
C4	0.1179 (8)	0.449 (2)	0.5751 (7)	4.9 (2)
C5	0.1703 (7)	0.514 (2)	0.4930 (7)	4.0 (2)
C6	0.1500 (7)	0.370 (2)	0.3900 (6)	4.2 (2)
C7	0.1453 (7)	0.362 (2)	0.1938 (6)	3.9 (2)
C8	0.0099 (6)	0.427 (1)	0.1381 (6)	3.2 (2)
C9	−0.0740 (7)	0.278 (2)	0.0670 (6)	4.1 (2)
C10	−0.1996 (8)	0.340 (2)	0.0065 (7)	5.1 (2)
C11	−0.2381 (8)	0.549 (2)	0.0196 (7)	4.9 (2)
C12	−0.1572 (8)	0.696 (2)	0.0911 (7)	4.5 (2)
C13	−0.0311 (7)	0.629 (2)	0.1500 (6)	3.9 (2)
C14	0.3416 (7)	0.410 (2)	0.3527 (7)	3.7 (2)
C15	0.4073 (7)	0.548 (2)	0.2934 (7)	4.0 (2)
C16	0.4467 (7)	0.458 (2)	0.2071 (7)	5.0 (2)
C17	0.5173 (8)	0.584 (3)	0.1598 (8)	6.8 (3)
C18	0.5497 (9)	0.800 (2)	0.1964 (9)	7.4 (3)
C19	0.5105 (8)	0.882 (2)	0.2835 (8)	5.5 (3)
C20	0.4367 (7)	0.761 (2)	0.3266 (7)	4.6 (2)

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

O1—C13	1.411 (9)	N2—C6	1.46 (1)
O2—C20	1.39 (1)	N2—C7	1.49 (1)
N1—C1	1.37 (1)	N2—C14	1.502 (9)
N1—C5	1.34 (1)		
C1—N1—C5	120.7 (8)	C6—N2—C14	109.4 (6)
C6—N2—C7	110.6 (6)	C7—N2—C14	108.5 (7)

All H-atom positions were obtained from difference syntheses. They were assigned isotropic displacement parameters equal to 1.3B_{eq} of the attached atom. Calculations were performed on a DEC 3000 AXP computer.

Data collection: *CAD-4-Express* (Nonius, 1993). Cell refinement: *MolEN* (Fair, 1990). Data reduction: *MolEN*. Program(s) used to solve structure: *SIR*92 (direct methods) (Burla *et al.*, 1992). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *PLATON* (Spek, 1990).

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Triclinic Form of Dipyrrolidinylthiuram Disulfide

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Abstract

A new polymorphic form of the title compound, di-1,4-butanediylthiuram disulfide [1,1'-dithiodicarbonothiolylbis(pyrrolidine)], $C_{10}H_{16}N_2S_4$, has been determined in the triclinic system. There are two simultaneous reports on structure determinations of this compound in the monoclinic system [Ymen (1983). *Acta Chem. Scand. Ser. B*, **37**, 707–713; Williams, Statham & White (1983). *Aust. J. Chem.* **36**, 1371–1377]. The two forms show differences in the conformation of one of the two pyrrolidine rings of the molecule.

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Comment

It is known that several metal dithiocarbamates are being used as pesticides, vulcanizing agents, antioxidants and lubricants, and therefore studies on these compounds has attracted interest since as early as 1908 (Thorn & Ludwig, 1962). However, the instability of some metal dithiocarbamates in several solvents leads to decomposition of the complex instead of recrystallization. As an example, crystals of the title compound, dipyrrolidinylthiuram disulfide (DPTD), were obtained by slow evaporation of tetrakis(pyrrolidine-1-carbodithioato)thorium(IV) from dimethyl sulfoxide (Williams, Statham & White, 1983). DPTD crystals were also obtained by bubbling air through an aqueous ethanol solution of $NaS_2CN(CH_3)_2.2H_2O$ (Ymen, 1983). The DPTD crystals thus obtained belonged to the monoclinic space group $C2/c$, the molecule having C_2 symmetry. In our studies on the reactivity of some metal dithiocarbamates, recrystallization of $[Fe\{S_2CN(CH_2)_4\}_3]$ from methanol gave some single crystals suitable for X-ray diffraction studies. Surprisingly, the crystals were found to be those of DPTD but belonging to the triclinic space group $P\bar{1}$ instead. In the triclinic form, the molecule occupies a general equivalent position and does not have any symmetry. DPTD has been reported as a potent inhibitor of the cytoplasmic aldehyde dehydrogenases of sheep liver (Kitson, 1976), hence the present report may be useful in assessing which form is more active in this regard.
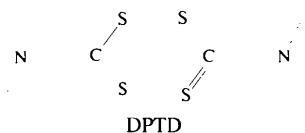
DPTD

A displacement ellipsoid plot of the DPTD molecule with the numbering scheme is shown in Fig. 1. The two pyrrolidine rings adopt two different conformations; ring 1 (N1, C2, C3, C4, C5) is a half-chair and ring 2 (N1A, C2A, C3A, C4A, C5A) adopts an envelope conformation. The deviations of atoms C3 and C4 from the plane of the other ring 1 atoms (N1, C2, C5) are −0.321 (6) and 0.226 (6) Å, respectively. In ring 2, C3A is the pivot atom of the envelope and deviates by 0.360 (7) Å from the plane formed by the remainder of the atoms (N1A, C2A, C5A, C4A). The asymmetry parameters according to Nardelli (1983a) are $D_2(N1) = 0.011$ (2) for ring 1 and $D_s(C3A) = 0.006$ (3) for ring 2. In the monoclinic form, the pyrrolidine rings both have half-chair conformations, and the bond lengths and angles show some deviations from those of ring 1 in the present triclinic form. The two S_2CN groups in the triclinic form (S1, S2, C1, N1 and S1A, S2A, C1A, N1A) are individually planar and make a dihedral angle of 91.13 (5)° with respect to one another, which is close to the angle of 86.01 (3)° found in the monoclinic form. The two terminal S atoms, S1 and S1A, tend to be further apart in the triclinic form (4.175 Å) than in the monoclinic form (4.048 Å).