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Key indicators

Single-crystal X-ray study
 $T = 180\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.051
 wR factor = 0.138
Data-to-parameter ratio = 13.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.2,6-Bis[bis(pyridin-2-ylmethyl)aminomethyl]-
4-*tert*-butylphenol

The title compound (Hbpbp), $\text{C}_{36}\text{H}_{40}\text{N}_6\text{O}$, is a phenol with one intramolecular bifurcated hydrogen bond. This result furnishes an explanation as to why the otherwise symmetric deprotonated ligand shows a propensity for forming asymmetric, *e.g.* heterovalent and heterometallic, coordination compounds.

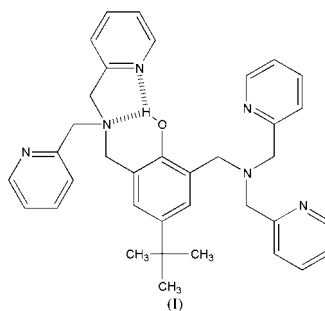
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Comment

We have used the phenolate-hinged dinucleating ligand bpbp^- for the synthesis of dimetallic coordination compounds and have succeeded in crystallizing the parent phenol, Hbpbp, (I). This, together with the dichloride diperchlorate double salt of tetraprotonated $\text{H}_5\text{bpbp}^{4+}$ (Gomes *et al.*, 2000), has given us further insight into the mechanism of the ligand coordination.



The conformation of (I) (Fig. 1) is dominated by an intramolecular bifurcated hydrogen bond from the phenol $\text{O1}-\text{H1}$ group to N2 [2.11 (2) Å] of one arm and N221 [2.43 (2) Å] of one pyridine of that same arm. The angles around H1 sum to $255 (3)^\circ$. This hydrogen bond gives a $\text{C1}-\text{C2}-\text{C20}-\text{N2}$ torsion angle of $-47.7 (3)^\circ$ (*syn*). The $\text{C1}-\text{C6}-\text{C60}-\text{N6}$ torsion angle, on the other hand, is $174.48 (17)^\circ$ (*anti*). This can be explained by a 2.53 Å hydrogen bond from $\text{C5}-\text{H5}$ of the phenol ring to N6 of the other ligand arm. In addition, atoms H613 and H623 of the attached pyridine rings form similar hydrogen bonds to N6 (2.53 and 2.55 Å, respectively). In the previously investigated $\text{H}_5\text{bpbp}^{4+}$ cation, these $\text{C}-\text{H}$ donors are replaced by $\text{N}-\text{H}$ donors from the protonated pyridines. As a result, both amines are oriented *syn* with respect to the $\text{O}-\text{H}$ group.

The molecular packing is dominated by $\text{C}-\text{H}\cdots\text{N}$ [shortest contacts 2.61 Å for $\text{H8a}\cdots\text{N621}^{\text{i}}$ and $\text{H626}\cdots\text{N611}^{\text{ii}}$; symmetry codes: (i) $1+x, y, 1+z$; (ii) $x, y, -1+z$] and $\text{C}-\text{H}\cdots\pi$ bonding interactions [shortest contacts are to the central phenol ring (centroid = PC): $\text{H216}\cdots\text{PC}^{\text{iii}} = 2.85\text{ \AA}$ and $\text{H224}\cdots\text{PC}^{\text{iv}}$; symmetry codes: (iii) $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$].

We propose that the asymmetry between the bis(pyridin-2-ylmethyl)aminomethyl arms, one hydrogen-bonded, one dangling, can account for the observed asymmetric coordination chemistry of the bpbp^- ligand (Ghiladi *et al.*, 1997, 1999). A stepwise insertion of two metal ions seems likely, because the dangling arm is more available for coordination.

Experimental

Compound (I) was synthesized according to a published procedure (Ghiladi *et al.*, 1997). The raw product was subjected to column chromatography with acetone as eluent. Prismatic crystals suitable for diffraction were formed by subsequent recrystallization from acetone.

Crystal data

$\text{C}_{36}\text{H}_{40}\text{N}_6\text{O}$	$D_x = 1.199 \text{ Mg m}^{-3}$
$M_r = 572.74$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 16 912 reflections
$a = 9.892 (5) \text{ \AA}$	$\theta = 3.7\text{--}24.7^\circ$
$b = 31.185 (5) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$c = 10.524 (5) \text{ \AA}$	$T = 180 (2) \text{ K}$
$\beta = 102.188 (5)^\circ$	Prism, colourless
$V = 3173 (2) \text{ \AA}^3$	$0.48 \times 0.35 \times 0.15 \text{ mm}$
$Z = 4$	

Data collection

Bruker SMART CCD diffractometer	5388 independent reflections
Narrow-frame φ and ω scans	3501 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.052$
$T_{\text{min}} = 0.753$, $T_{\text{max}} = 0.989$	$\theta_{\text{max}} = 24.7^\circ$
16 542 measured reflections	$h = -11 \rightarrow 11$
	$k = -36 \rightarrow 27$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0705P)^2 + 0.1173P]$
$R[F^2 > 2\sigma(F^2)] = 0.051$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.138$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
5388 reflections	$\Delta\rho_{\text{min}} = -0.18 \text{ e \AA}^{-3}$
392 parameters	Extinction correction: SHELXL97
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.0053 (9)

Table 1

Selected geometric parameters ($^\circ$).

O1—C1—C2	122.73 (17)	C222—N221—C226	116.7 (2)
O1—C1—C6	116.91 (17)	C616—N611—C612	117.20 (19)
C212—N211—C216	116.0 (3)	C626—N621—C622	117.15 (19)
C1—C2—C20—N2	−47.7 (3)	C1—C6—C60—N6	174.48 (17)

All H atoms were located in a Fourier difference map. The phenol H atom was refined isotropically in the riding mode, with $U_{\text{iso}}(\text{H1}) = 1.2U_{\text{eq}}(\text{O1})$ and the bond length O1—H1 restrained to 0.90 (5) Å.

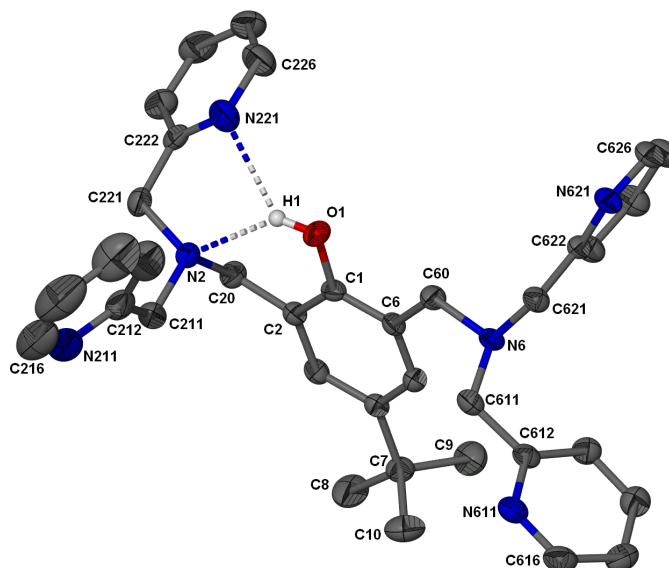


Figure 1

View of (I) (50% probability displacement ellipsoids). Only the phenolic H atom is included. The omitted atom numbers are consecutive to those shown.

The remaining ligand H atoms were constrained to ideal positions with $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{parent atom})$.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: X-Seed (Barbour, 2001); software used to prepare material for publication: WinGX (Farrugia, 1999).

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