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2,6-Bis[bis(2-pyridiniomethyl)amino-methyl]-4-*tert*-butylphenol dichloride diperchlorate hydrate

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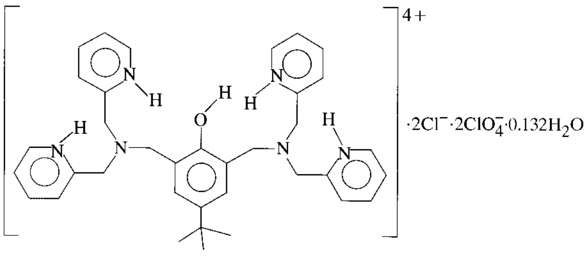
The title compound, $C_{36}H_{44}N_6O^{4+}\cdot2Cl^-\cdot2ClO_4^-\cdot0.132H_2O$, is shown to be protonated at all the pyridine N atoms; the two chloride ions are hydrogen bonded to three pyridine N atoms and to the phenolic O atom of the same cation [Cl···N = 3.045 (2)–3.131 (2) Å and Cl···O = 2.938 (2) Å], and the remaining pyridine N atom is hydrogen bonded to the phenolic O atom [N···O = 2.861 (2) Å]. The mean value of the C—N—C angle of the protonated pyridine rings is 123.4 (1)°, which is significantly larger than that found for unprotonated pyridine rings.

Comment

Compounds containing two transition metal ions have received considerable attention in the past two decades because of their potential reactivity in the activation of small molecules and catalysis of organic reactions, and as model systems for dimetallic enzymes (Reedijk, 1993; van den Beuken & Feringa, 1998). Several synthetic strategies for their preparation have been developed. These include self-asssembly methods, for example the spontaneous formation of dimetallic compounds with oxide and sulfide bridges, or the templated formation of suitable ditopic macrocyclic and acyclic ligands. The design of ligands containing two cavities suitable for metal binding is an important approach to a more controlled stepwise preparation of dimetallic compounds.

The title compound, $bpbpH_5^{4+}\cdot2Cl^-\cdot2ClO_4^-\cdot0.132H_2O$, (I), contains an example of such a preformed ditopic ligand. The compound bpbpH is an acyclic ditopic ligand precursor (it needs to be deprotonated in order to bind two metal ions); it has been used successfully by us for the preparation of dimetallic compounds. The ligand is normally septadentate, providing an amine and two pyridine donors to each metal ion in a dinuclear complex; the phenolate O atom 'bridges' the two metal ions. The remaining coordination sphere of the metal ions is usually filled by small 'exogenous' ligands, *e.g.* a typical formulation is $[M_2(bpbp)(CH_3CO_2)_2](ClO_4)_2$, where M is a transition metal ion.

Interestingly, $bpbp^-$ shows a remarkable ability to stabilize mixed-metal and mixed-valent compounds (Ghiladi, McKenzie *et al.*, 1997; Ghiladi, Jensen *et al.*, 1999). In the attempted preparation of one such compound from an acidic solution, we isolated a small amount of a colourless crystalline product, which has been shown, by X-ray diffraction, to be the double salt (I). The ligand is protonated at the pyridine N atoms and not at the tertiary N atoms as might be expected from their acidities (*cf.* pK_a = 5.17 for pyridine and pK_a = 11.72 for triethylamine). We have also observed this preference for protonation at the pyridine N atoms in salts of trispicolylamine (tpa), *i.e.* in $(H_3tpa)(SO_4)(NO_3)$ (Hazell *et al.*, 1999) and in $(H_3tpa)_2(HPO_4)(ClO_4)_4.2H_2O$ (Hazell & Toftlund, unpublished results).



(I)

The two Cl^- ions are both hydrogen bonded (Fig. 1) to three pyridine N atoms and to the phenolic O atom of the same cation [Cl···N = 3.045 (2)–3.131 (2) Å and Cl···O = 2.938 (2) Å]; the remaining pyridine N atom is hydrogen bonded to the phenolic O atom [N···O = 2.861 (2) Å].

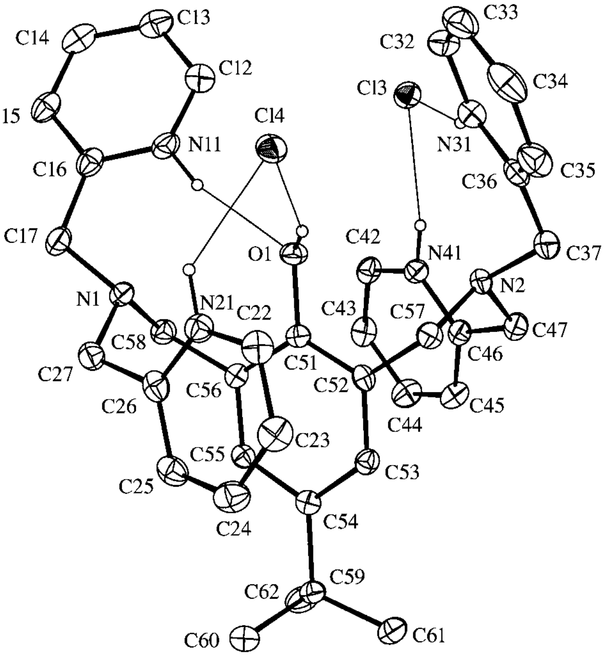


Figure 1
View of (I) showing the hydrogen bonding. Displacement ellipsoids are shown at the 50% probability level. H atoms involved in hydrogen bonds are drawn as small circles of arbitrary radii and the other H atoms have been omitted.

Bond distances and angles are generally similar to those in bpbp complexes, the exception being that the C—N_{py}—C angles are in the range 123.0 (2)–123.7 (2)°, whereas in both coordinated and non-coordinated pyridine groups this angle is less than 120°. Mean values from the Cambridge Structural Database (Allen & Kennard, 1993) are 117.8° for non-coordinated pyridine (5255 observations, mean standard uncertainty 0.03), 118.6° for pyridine coordinated to a metal atom (10000 observations, mean standard uncertainty 0.02) and 122.6° for pyridinium compounds (901 observations, mean standard uncertainty 0.07). The molecule is not as symmetric as might have been expected; C51—O1 is bent towards N1 and the torsion angle C51—C52—C57—N2 is 11.4° larger than C51—C56—C58—N1, distortions which may be caused by repulsion between N41 and O1 [O1···N41 = 2.982 (2) Å]. This result is interesting with respect to the apparent propensity of $bpbp^-$ to form unsymmetric dimetallic complexes, *i.e.* the incorporation of different metal ions in each cavity (Ghiladi *et al.*, 1997, 1999). A difference map showed a small peak which is interpreted as a partially occupied water site 2.62 (1) Å from one of the perchlorate O atoms.

Experimental

The title compound was isolated in an attempted preparation of a titanium complex of $bpbp^-$. $TiCl_4$ (0.05 ml, 0.45 mmol), bpbpH (Ghiladi *et al.*, 1997) (0.05 g, 0.09 mmol) and tetrabutylammonium perchlorate (0.1 g, 0.29 mmol) were mixed at room temperature in dry ethanol. A red precipitate (0.7 g) resulted. The precipitate was dissolved in CH_2Cl_2/CH_3CN (3:1), filtered, and pentane was diffused into the filtrate. Colourless crystals of the title double salt of bpbpH were deposited.

Crystal data

$C_{36}H_{44}N_6O^{4+}\cdot 2Cl^-\cdot 2ClO_4^-\cdot 0.132H_2O$
$M_r = 848.97$
Monoclinic, $P2_1/c$
$a = 20.376$ (1) Å
$b = 13.0504$ (8) Å
$c = 15.8870$ (9) Å
$\beta = 110.491$ (1)°
$V = 3957.4$ (4) Å^3
$Z = 4$
$D_x = 1.425$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5631 reflections
$\theta = 1.9$–29.8°
$\mu = 0.360$ mm^{-1}
$T = 120$ K
Prism, colourless
0.40 × 0.24 × 0.10 mm

Data collection

Siemens SMART CCD diffractometer
ω rotation scans with narrow frames
Absorption correction: integration using crystal faces (*XPREP*; Siemens, 1995)
$T_{min} = 0.885$, $T_{max} = 0.975$
39 525 measured reflections
10 979 independent reflections
6374 reflections with $I > 3\sigma(I)$
$R_{int} = 0.055$
$\theta_{max} = 29.8°$
$h = -26\rightarrow 25$
$k = -17\rightarrow 18$
$l = -22\rightarrow 21$

Table 1
Selected geometric parameters (°).

C12—N11—C16	123.7 (2)	C42—N41—C46	123.4 (2)
C22—N21—C26	123.6 (2)	O1—C51—C52	122.2 (2)
C32—N31—C36	123.0 (2)	O1—C51—C56	116.9 (2)
C51—C52—C57—N2	−70.3 (2)	C51—C56—C58—N1	−58.9 (2)

Refinement

Refinement on F
$R = 0.033$
$wR = 0.037$
$S = 1.078$
6374 reflections
506 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/\{[\sigma_{cs}(F^2) + 1.03F^2]^{1/2} - F\}^2$
$(\Delta/\sigma)_{max} = 0.0018$
$\Delta\rho_{max} = 0.40$ (5) e Å^{-3}
$\Delta\rho_{min} = -0.46$ (5) e Å^{-3}
Extinction correction: type 1 Lorentzian isotropic (Becker & Coppens, 1974)
Extinction coefficient: 150 (17)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—HN11···O1	0.95	1.98	2.861 (2)	153
N21—HN21···Cl4	0.95	2.32	3.062 (2)	135
N31—HN31···Cl3	0.95	2.16	3.045 (2)	154
N41—HN41···Cl3	0.95	2.26	3.131 (2)	152
O1—HO1···Cl4	0.81 (2)	2.18 (3)	2.938 (2)	155 (2)

H atoms were located from a difference map. The phenolic H atom was refined isotropically and H atoms of the ligand were kept fixed at calculated positions (C—H = 0.95 Å) with $U_{iso} = 1.2U_{eq}$ of the atom to which each is attached. H atoms of the water molecule were not included in the calculations.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SIR*97 (Cascarano *et al.*, 1996), *KRYSTAL* (Hazell, 1995). Program(s) used to refine structure: modified *ORFLS* (Busing *et al.*, 1962), *KRYSTAL*. Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996), *KRYSTAL*. Software used to prepare material for publication: *KRYSTAL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1067). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
Becker, P. J. & Coppens, P. (1974). *Acta Cryst.* A**30**, 129–153.
Beuken, E. K. van den & Feringa, B. L. (1998). *Tetrahedron*, **54**, 12985–13011.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.
Cascarano, G., Altomare, A., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Siliqi, D., Burla, M. C., Polidori, G. & Camalli, M. (1996). *Acta Cryst.* A**52**, C-50.
Ghiladi, M., Jensen, K. H., Jiang, J., McKenzie, C. J., Mørup, S., Søtofte, I. & Ulstrup, J. (1999). *J. Chem. Soc. Dalton Trans.* pp. 2675–2681.
Ghiladi, M., McKenzie, C. J., Meier, A., Powell, A. K., Ulstrup, J. & Wocadlo, S. (1997). *J. Chem. Soc. Dalton Trans.* pp. 4011–4018.
Hazell, A. (1995). *KRYSTAL*. Aarhus University, Denmark.
Hazell, A., McGinley, J. & Toftlund, H. (1999). *J. Chem. Soc. Dalton Trans.* pp. 1271–1276.
Reedijk, J. (1993). Editor. *Bioinorganic Catalysis*. New York: Dekker.
Siemens (1995). *SAINT*, *SMART* and *XPREP*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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