

4-[Bis(4-hydroxy-3,5-dimethylphenyl)-methyl]pyridinium chloride and bromide

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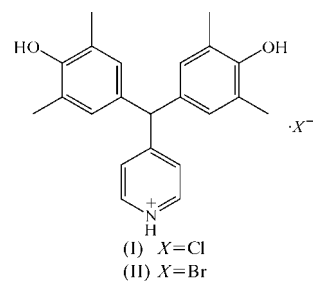
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The isostructural title salts, 4-[bis(4-hydroxy-3,5-dimethylphenyl)methyl]pyridinium chloride and bromide, $C_{22}H_{24}NO_2^+ \cdot Cl^-$ and $C_{22}H_{24}NO_2^+ \cdot Br^-$, exhibit extended hydrogen-bonded ribbons in the solid state. The halide ions form hydrogen bonds to the pyridinium NH^+ group and to the phenol OH groups of the cation. These bonds are coplanar to within 0.1 Å and form a T configuration at the anion.

Comment

The coordination chemistry of anions is a fast-growing area of supramolecular chemistry (see, for example, Bianchi *et al.*,

1997; Schmidtchen & Berger, 1997), both on account of the importance of anion binding, recognition and transport in many biochemical processes (Lehn, 1995; Beer, 1996; Pajewski *et al.*, 2004, and references therein) and because anions can be



used to direct the self-assembly of organic (and organo-metallic) molecules in desired ways (Gale, 2000, 2001; Sessler *et al.*, 2003). Thus, the Cl^- anion has been successfully used to assemble double-helical motifs of various molecules containing aromatic groups, with π -stacking within the helices (Hasenknopf *et al.*, 1996, 1997). Indeed, halide anions can be particularly useful for such applications because of the high flexibility of their coordination (Ilioudis *et al.*, 2000). In the present work, we have investigated the effects of Cl^- and Br^- ions on the assembly of 4-[bis(4-hydroxy-3,5-dimethylphenyl)methyl]pyridine, *L*, a molecule with a relatively rigid tripodal framework. To our knowledge, neither this molecule nor any other with one pyridyl and two 4-hydroxyphenyl groups linked through a single C atom has been structurally characterized to date. Meanwhile, related $ArCH(C_6H_4OH-p)_2$ (*e.g.* with $Ar = C_6H_4Br-p$) compounds have been used as ligands to obtain topologically chiral [2]catenane complexes of gold(I), whereby the unsymmetrical $ArCH$ 'hinge group' plays a crucial role in imposing chirality (McArdle *et al.*, 2002).

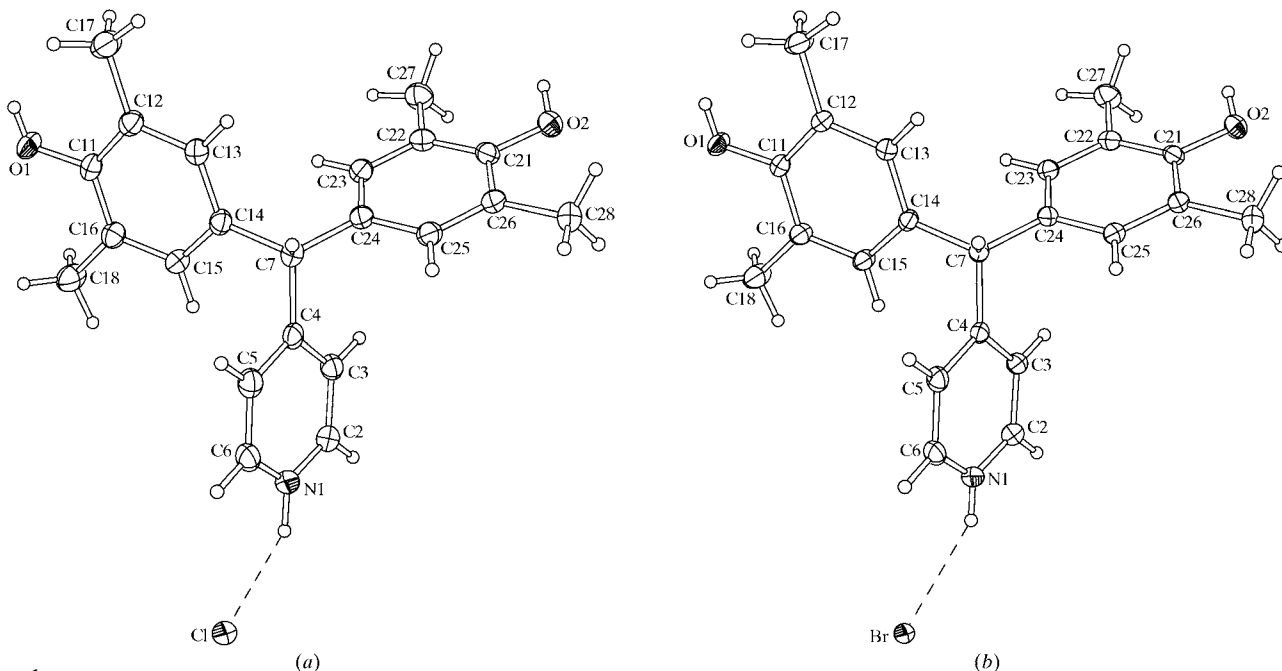


Figure 1

The cations and anions in the structures of (a) (I) and (b) (II), showing the atomic numbering schemes. Displacement ellipsoids are drawn at the 50% probability level.

Originally, we intended to prepare a copper(II) complex of *L* to serve as a building block for the construction of a supermolecule. However, crystallization from an aqueous solution containing equivalent quantities of HCl, *L* and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ unexpectedly yielded $\text{LH}^+ \cdot \text{Cl}^-$, (I). This compound and its analogue $\text{LH}^+ \cdot \text{Br}^-$, (II), were also formed from an acidic solution of *L* and HCl (or HBr) in the presence of catalytic quantities of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, but in the complete absence of the latter we could not obtain any crystals of the salts.

The crystals of (I) and (II) are isomorphous. The asymmetric unit comprises one halide anion and one LH^+ cation (with N1 protonated), which adopts practically the same propeller-like conformation in both crystals; the pyridine ring and benzene rings bearing atoms O1 and O2 (Fig. 1) are inclined to the $C_4/C_{14}/C_{24}$ plane in the same sense by 53.9 (1), 42.6 (1) and 41.5 (1)°, respectively, in (I) and by 55.0 (1), 39.7 (1) and 41.4 (1)°, respectively, in (II).

The asymmetric unit contains three H atoms (two hydroxyl and one pyridinium) capable of forming strong hydrogen bonds, and three potential acceptors, *viz.* two O atoms and the halide anion. In fact, only the anion acts as the acceptor of all three such bonds (Table 5), probably because the competitiveness of the O atoms as acceptors is severely diminished by the masking effect of the adjacent methyl groups. The anion and the three bonded H atoms are coplanar to within 0.1 Å. The configuration can be described as T-shaped rather than trigonal (Fig. 2), which is relatively rare but not unknown (Ilioudis *et al.*, 2000). Indeed, halide anions are known to behave as 'spherical' acceptors without any clearly favoured coordination geometry, although some preference towards quasi-tetrahedral and trigonal configurations can be discerned (Ilioudis *et al.*, 2000).

These three strong hydrogen bonds link the cations into ribbons running parallel to the crystallographic *b* axis (Fig. 2). Besides these, the anion participates in three weak interactions (Table 5) with aromatic and methyl H atoms, with each of the six contacts involving a different cation. It is noteworthy that strong bonds in (II) are longer than those in (I), roughly in line with the increase of the ionic radius of Br^- (1.96 Å; Shannon & Prewitt, 1969) compared with Cl^- (1.81 Å), but the weak bonds lengthen much less or even contract on going

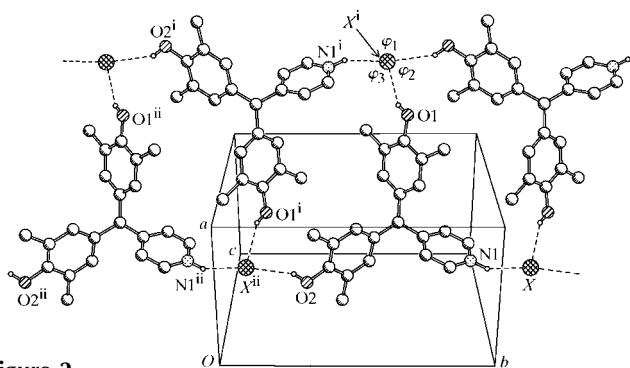


Figure 2

The system of strong hydrogen bonds in structures (I) ($X = \text{Cl}$) and (II) ($X = \text{Br}$). The $\text{H} \cdots \text{X} \cdots \text{H}$ angles are $\varphi_1 = 170^\circ$, $\varphi_2 = 84^\circ$ and $\varphi_3 = 104^\circ$ in (I), and $\varphi_1 = 73^\circ$, $\varphi_2 = 82^\circ$ and $\varphi_3 = 105^\circ$ in (II); s.u. values are $\sim 1^\circ$. The symmetry codes are as given in the tables.

from (I) to (II). The difference can be explained by the higher polarizability of the Br^- anion and hence higher (C)H \cdots X dispersion interactions in (II), while this difference is less relevant for the strong hydrogen bonds, which have larger contributions of (time-independent) ion–dipole interactions. The weak hydrogen bonds are roughly normal to the T-plane of the strong hydrogen bonds, while the wide angle φ_1 is occupied by pyridine atom C2 of another cation, generated by inversion at $(1 - x, 2 - y, -z)$. The corresponding distances [$\text{Cl} \cdots \text{C2} = 3.382$ (2) Å and $\text{Br} \cdots \text{C2} = 3.458$ (1) Å] are both shorter than the sums of the van der Waals radii (3.53 and 3.65 Å, respectively; Rowland & Taylor, 1996).

Thus, through this system of hydrogen bonds, the halide anions are decisive in directing the packing of the LH^+ cations. However, the resulting structure is ribbon-like rather than helical. Substitution of a Br^- anion for Cl^- affects different types of hydrogen bonds selectively. Also noteworthy is the ability of copper(II) chloride to facilitate the crystallization of (I) and (II) without itself being incorporated into the structure. This effect may be useful as a method for controlling molecular self-assembly. Therefore, we intend a further study of its mechanism and possible applications.

Experimental

Compound *L* was synthesized by condensation of 2,6-dimethylphenol with pyridine-4-carbaldehyde. Specifically, pyridine-4-carbaldehyde (0.534 g, 5.0 mmol) and 2,6-dimethylphenol (1.221 g, 10 mmol) were dissolved in 1 *M* sulfuric acid (1.4 ml) mixed with methanol (10 ml). Trifluoroacetic acid (1 ml) was then added. The mixture was heated at 353 K for 8 h, after which the solvents were removed under vacuum. The residue was dissolved in water (15 ml), extracted with ethyl acetate (15 ml) and dried over anhydrous Na_2SO_4 . Removal of the solvents and subsequent column chromatography (silica gel 60–120 mesh; hexanes/ethyl acetate, 4:1) gave *L* as a white solid (yield: 1.43 g, 86%; m.p. 478 K). IR (KBr, ν , cm^{-1}): 3385 (s), 3083 (s), 2914 (w), 2079 (w), 1634 (s), 1485 (s), 1147 (s), 1004 (s); ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 2.18 (s, 12H), 3.70 (s, 2H), 5.43 (s, 1H), 6.60 (s, 4H), 7.6 (d, 2H, $J = 6.4$ Hz), 6.7 (d, 2H, $J = 6.4$ Hz); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 17.4, 55.68, 125.18, 127.78, 129.25, 131.46, 141.63, 152.81, 166.53. Slow evaporation of a solution of *L* (0.332 g, 1 mmol) and HCl (0.3 ml, 11.5 *M*) in methanol in the presence of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.085 g, 5 mol%) gave (I) as a pale-yellow precipitate, which was recrystallized from methanol (m.p. 487 K). IR (KBr, ν , cm^{-1}): 3375 (s), 2786 (s), 2034 (s), 1629 (s), 1481 (s), 1317 (s), 1194 (s), 1024 (w). Slow evaporation of a solution of *L* (0.333 g, 1 mmol) in methanol containing HBr (0.5 ml, 60%) and cupric bromide (0.012 g, 5 mol%) gave (II) as pale-orange crystals (m.p. 492 K). IR (KBr, ν , cm^{-1}): 3334 (s), 3228 (w), 2930 (s), 2022 (s), 1775 (s), 1629 (s), 1492 (s), 1190 (s), 1134 (w).

Compound (I)

Crystal data

$\text{C}_{22}\text{H}_{24}\text{NO}_2^+ \cdot \text{Cl}^-$
 $M_r = 369.87$
 Monoclinic, $P2_1/n$
 $a = 8.6590$ (2) Å
 $b = 14.3920$ (17) Å
 $c = 15.7057$ (12) Å
 $\beta = 102.519$ (14)°
 $V = 1910.7$ (3) Å³
 $Z = 4$

$D_x = 1.286$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4680 reflections
 $\theta = 2.4$ – 29.7°
 $\mu = 0.22$ mm⁻¹
 $T = 120$ (2) K
 Tetragonal prism, yellow
 $0.26 \times 0.15 \times 0.09$ mm

Data collection

Bruker SMART 6000 CCD area-detector diffractometer
 ω scans
 Absorption correction: integration (XPREP in SHELXTL; Bruker, 2001)
 $T_{\min} = 0.953$, $T_{\max} = 0.984$
 21 158 measured reflections

4383 independent reflections
 3330 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.058$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -11 \rightarrow 11$
 $k = -18 \rightarrow 18$
 $l = -20 \rightarrow 20$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.142$
 $S = 1.05$
 4383 reflections
 255 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0817P)^2 + 0.4133P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.014$
 $\Delta\rho_{\text{max}} = 0.65 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.24 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °) for (I).

O1—C11	1.377 (2)	C4—C7	1.514 (2)
O2—C21	1.374 (2)	C7—C24	1.529 (2)
N1—C2	1.338 (2)	C7—C14	1.533 (2)
N1—C6	1.340 (3)		
C2—N1—C6	122.11 (17)	C4—C7—C14	109.72 (14)
C4—C7—C24	112.16 (14)	C24—C7—C14	115.71 (14)

Table 2

Hydrogen-bond geometry (Å, °) for (I).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1 \cdots Cl	0.94 (3)	2.19 (3)	3.0371 (17)	150 (2)
O1—HO1 \cdots Cl ⁱ	0.81 (2)	2.36 (3)	3.0732 (15)	147 (2)
O2—HO2 \cdots Cl ⁱⁱ	0.84 (3)	2.45 (3)	3.1990 (15)	148 (2)
C7—H7 \cdots Cl ^{iv}	1.00	2.99	3.9568 (19)	162
C17—H17 ^v \cdots Cl ^v	0.98	3.02	3.956 (2)	160
C18—H18 ^{vi} \cdots Cl ^{vi}	0.98	3.11	3.802 (2)	129

Symmetry codes: (i) $-x + \frac{5}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x, y - 1, z$; (iii) $-x + 1, -y + 2, -z$; (iv) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (v) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (vi) $-x + 2, -y + 2, -z$.

Compound (II)

Crystal data

$C_{22}H_{24}NO_2^+ \cdot Br^-$
 $M_r = 414.33$
 Monoclinic, $P2_1/n$
 $a = 8.7217 (4) \text{ Å}$
 $b = 14.7461 (6) \text{ Å}$
 $c = 15.4836 (6) \text{ Å}$
 $\beta = 101.59 (1)^\circ$
 $V = 1950.73 (14) \text{ Å}^3$
 $Z = 4$

$D_x = 1.411 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 5710 reflections
 $\theta = 2.8\text{--}30.5^\circ$
 $\mu = 2.12 \text{ mm}^{-1}$
 $T = 120 (2) \text{ K}$
 Tetragonal prism, pale orange
 $0.32 \times 0.22 \times 0.12 \text{ mm}$

Data collection

Bruker APEX CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2003)
 $T_{\min} = 0.803$, $T_{\max} = 1.000$
 21 226 measured reflections

5943 independent reflections
 5263 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.017$
 $\theta_{\text{max}} = 30.5^\circ$
 $h = -12 \rightarrow 12$
 $k = -20 \rightarrow 21$
 $l = -21 \rightarrow 22$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.070$
 $S = 1.05$
 5942 reflections
 256 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 0.4161P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.90 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.23 \text{ e } \text{Å}^{-3}$

Table 3

Selected geometric parameters (Å, °) for (II).

O1—C11	1.3718 (14)	C4—C7	1.5139 (17)
O2—C21	1.3746 (15)	C7—C24	1.5270 (17)
N1—C2	1.3377 (18)	C7—C14	1.5293 (16)
N1—C6	1.340 (2)		
C2—N1—C6	122.65 (12)	C4—C7—C14	109.97 (10)
C4—C7—C24	111.83 (10)	C24—C7—C14	116.38 (10)

Table 4

Hydrogen-bond geometry (Å, °) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1 \cdots Br	0.84 (3)	2.46 (3)	3.2090 (11)	150 (2)
O1—HO1 \cdots Br ⁱ	0.83 (2)	2.47 (2)	3.1984 (10)	148 (2)
O2—HO2 \cdots Br ⁱⁱ	0.80 (2)	2.70 (2)	3.3745 (10)	143 (2)
C7—H7 \cdots Br ^{iv}	1.00	2.92	3.8791 (12)	161
C17—H17 ^v \cdots Br ^v	0.98	3.05	3.9690 (15)	157
C18—H18 ^{vi} \cdots Br ^{vi}	0.98	3.13	3.8243 (15)	129

Symmetry codes: (i) $-x + \frac{5}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x, y - 1, z$; (iii) $-x + 1, -y + 2, -z$; (iv) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (v) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (vi) $-x + 2, -y + 2, -z$.

Table 5

Corrected hydrogen-bond distances (Å) and angles (°) in (I) and (II).

Calculated for idealized bond lengths N—H = 1.01 Å, O—H = 0.97 Å and C—H = 1.08 Å, as determined by neutron diffraction (Allen *et al.*, 1987). X = Cl in (I) and Br in (II).

$D-H \cdots X$	$D \cdots Cl$	$H \cdots Cl$	$D-H \cdots Cl$	$D \cdots Br$	$H \cdots Br$	$D-H \cdots Br$
N1—H1 \cdots X	3.037 (2)	2.13 (3)	149 (2)	3.209 (1)	2.33 (3)	145 (2)
O1—HO1 \cdots X ⁱ	3.073 (2)	2.23 (3)	145 (2)	3.198 (1)	2.35 (2)	146 (2)
O2—HO2 \cdots X ⁱⁱ	3.199 (2)	2.35 (3)	147 (2)	3.375 (1)	2.61 (2)	136 (2)
C7—H7 \cdots X ^{iv}	3.957 (2)	2.92	162	3.879 (1)	2.84	161 (2)
C17—H17 \cdots X ^v	3.956 (2)	2.93	159	3.969 (1)	2.97	155 (2)
C18—H18 \cdots X ^{vi}	3.802 (2)	3.05	127	3.824 (1)	3.05	130 (2)

Symmetry codes: (i) $-x + \frac{5}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x, y - 1, z$; (iv) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (v) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (vi) $-x + 2, -y + 2, -z$.

All H atoms were located in a difference Fourier synthesis. Methyl groups were treated as rigid bodies rotating around the C—C bonds, with fixed C—H distances of 0.98 Å and a common (refined) $U_{\text{iso}}(\text{H})$ value for each group. H atoms bonded to O and N atoms were refined in the isotropic approximation. The remaining H atoms were treated as riding on their parent C atoms, with $C_{\text{sp}^2}\text{—H} = 0.95 \text{ Å}$ and $C7\text{—H} = 1.00 \text{ Å}$, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

For both compounds, data collection: SMART (Bruker, 2001). Cell refinement: SMART for (I); SAINT (Bruker, 2003) for (II). Data reduction: SAINT (Bruker, 2001) for (I); SAINT (Bruker, 2003) for (II). For both compounds, program(s) used to solve structure: SHELXTL (Bruker, 2001); program(s) used to refine structure:

SHELXTL; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1604). Services for accessing these data are described at the back of the journal.

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