metal-organic compounds

catena-Poly[[[4-bromo-2-(2-pyridyl-methyliminomethyl)phenolato]-zinc(II)]-μ-chloro]

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The title complex, $[Zn(C_{13}H_{10}BrN_2O)Cl]_n$, is a chloride-bridged polynuclear zinc(II) compound. Each Zn^{II} ion is five-coordinated in a square-pyramidal configuration, with one O and two N atoms of one Schiff base and one bridging Cl atom defining the basal plane, and another bridging Cl atom occupying the apical position. The novelty of the compound lies in the bridging by chlorine of two square-pyramidal Zn atoms, so that the bridging atom is apical for one Zn ion and basal for the other. This structural arrangement has not been observed before. The linked moieties form polymeric zigzag chains running along the a axis.

Comment

Metal–organic complexes containing bridging ligands are of current interest because of their interesting molecular topologies and crystal-packing motifs, as well as the fact that they may be designed with specific functionalities (Supriya *et al.*, 2005; Batten & Robson, 1998; Colacio *et al.*, 2005; Abourahma *et al.*, 2002; Konar *et al.*, 2002). In general, chloride anions only bridge two metals or reside at the terminal positions (Gladkikh *et al.*, 1997; Ülkü *et al.*, 2000; Tatar *et al.*, 2002). A similar pattern can be observed in the bromo-coordinated complexes (Hong *et al.*, 2005). Dance (1985) has reported an interesting zinc(II) complex, in which the chloride anion is located on a twofold axis and coordinated to four Zn atoms. There are a few other complexes with similar chain or bridged Zn^{II} structures (Niu *et al.*, 1999; Schneider *et al.*, 1999; Bottomley *et al.*, 1989; Martin *et al.*, 1998). There are also some complexes with N,O-bidentate ligands coordinating to Zn and 'capping' by a bridged $ZnCl_4$ group (Müller & Vahrenkamp, 1999; Tesmer *et al.*, 1997; Follner, 1972). However, a major obstacle to a more comprehensive study of such chloride-coordinated complexes is the lack of rational synthetic procedures, since with the present state of knowledge it is hardly possible to determine which coordination mode will be adopted by the chloride anion.
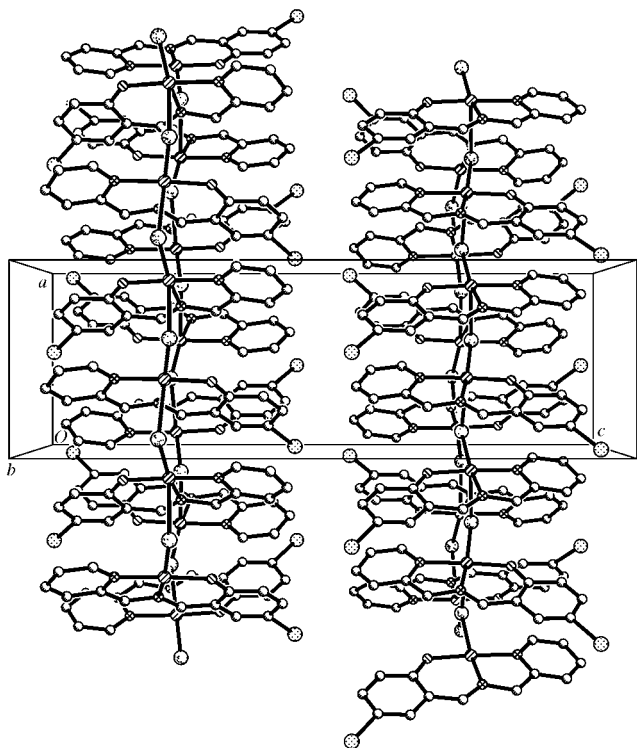
Our work is aimed at obtaining multidimensional polymetallic complexes. We have designed and synthesized a rigid tridentate ligand, namely 4-bromo-2-(2-pyridylmethyliminomethyl)phenol (BPMM). The reason we did not use a flexible ligand is that the rigid BPMM ligand should adopt an almost fixed coordination mode through the three donor atoms (You *et al.*, 2004; You & Zhu, 2004). The second ligand, *viz.* chloride, would then probably act as a bridging group. Zinc(II) is a good candidate for square-pyramidal coordination geometry (Erxleben, 2001). We report here a novel chloride-bridged polynuclear zinc(II) complex, (I), formed from the reaction of the BPMM ligand with zinc(II) chloride.

(I)
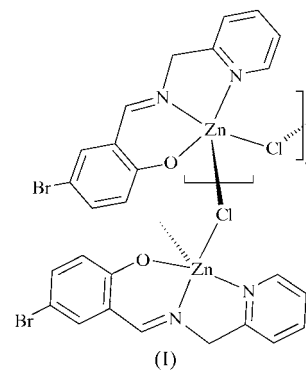
Complex (I) (Fig. 1 and Table 1) contains Zn(BPMM) units connected to one another by a single bridging chloride anion. Each Zn^{II} ion is five-coordinated in a square-pyramidal configuration, with one O and two N atoms of one Schiff base and one bridging Cl atom defining the basal plane, and a symmetry-related Cl atom occupying the apical position, that is, atom Cl1 acts as a basal donor of the Zn1 moiety, while for the Zn1^i moiety, it acts as the apical donor atom [symmetry code: (i) $x + \frac{1}{2}, y, -z + \frac{1}{2}$]. Thus, the Zn1—Cl1^i bond is longer by 0.548 (3) Å than the Zn1—Cl1 bond (Table 1). The basal least-square planes of two adjacent Zn^{II} centres are nearly parallel, with a dihedral angle of 4.6 (4)°. The deviation of atom Zn1 from the best fit square plane towards Cl1^i is 0.138 (4) Å. Each
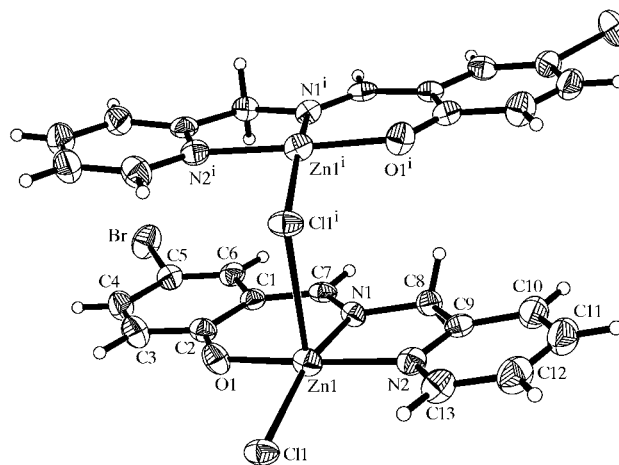
Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms unlabelled or labelled with the superscript i are at the symmetry position ($\frac{1}{2} + x, y, \frac{1}{2} - z$).

Figure 2
The crystal packing of (I), viewed down the *b* axis. H atoms have been omitted.

was stirred for another 10 min at room temperature. Colourless block-shaped crystals were formed after keeping the filtrate in air for 13 d.

Crystal data

[Zn(C$_{13}$H$_{10}$BrN$_2$O)Cl]	Mo *K*α radiation
$M_r = 390.96$	Cell parameters from 2244
Orthorhombic, *Pbca*	reflections
$a = 7.924$ (1) Å	$\theta = 2.3–22.2°$
$b = 13.578$ (2) Å	$\mu = 4.99$ mm^{-1}
$c = 25.003$ (3) Å	$T = 298$ (2) K
$V = 2689.9$ (6) Å^3	Block, colourless
$Z = 8$	$0.31 \times 0.13 \times 0.12$ mm
$D_x = 1.931$ Mg m^{-3}	

Data collection

Bruker SMART CCD area-detector diffractometer	1792 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.113$
Absorption correction: multi-scan	$\theta_{max} = 27.5°$
(*SADABS*; Sheldrick, 1996)	$h = -10 \rightarrow 10$
$T_{min} = 0.288$, $T_{max} = 0.550$	$k = -17 \rightarrow 17$
28481 measured reflections	$l = -32 \rightarrow 32$
3091 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0498P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.056$	$+ 1.3612P]$
$wR(F^2) = 0.128$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
3091 reflections	$\Delta\rho_{max} = 0.64$ e Å^{-3}
172 parameters	$\Delta\rho_{min} = -0.64$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Zn1—O1	1.896 (4)	Zn1—Cl1^i	2.822 (2)
Zn1—N1	1.959 (4)	N1—C7	1.276 (6)
Zn1—N2	2.006 (5)	N1—C8	1.456 (6)
Zn1—Cl1	2.274 (3)		
O1—Zn1—N1	92.67 (17)	O1—Zn1—Cl1	89.86 (12)
O1—Zn1—N2	175.83 (18)	N1—Zn1—Cl1	164.67 (13)
N1—Zn1—N2	83.21 (19)	N2—Zn1—Cl1	94.28 (14)

Symmetry code: (i) $x + \frac{1}{2}, y, -z + \frac{1}{2}$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C13—H13$\cdots$Cl1	0.93	2.71	3.270 (8)	120

All H atoms were placed in geometrically idealized positions and allowed to ride on their parent atoms, with C—H distances of 0.93–0.97 Å and with U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

zinc(II) moiety of the complex is nearly coplanar, with a mean deviation from the Br1/C1–C6/C7/N1/C8/C9–C13/N2/O1 plane of 0.091 (1) Å. This planar configuration can decrease the steric repulsion of the two near planar zinc(II) moieties, and also promote a square-pyramidal geometry rather than trigonal–bipyramidal geometry for the Zn^{II} atom.

The C7=N1 bond length conforms to the value for a double bond, while the C8—N1 bond length conforms to the value for a single bond (You, 2005*a,b*). As expected, the bond involving pyridine atom N2 is longer than that involving imine atom N1 (Mondal *et al.*, 2001).

The distance between atom H8*A* and the planar ring Zn1/O1/C2/C1/C7/N1 is 2.616 (2) Å, with a C8—H8*A*···(centre-of-ring) angle of 112.5 (4)°, indicating that there may be a somewhat fortuitous weak intramolecular C8—H8*A*···π interaction. There is also another intramolecular interaction, C13—H13···Cl1 (Table 2). In the crystal structure, the [4-bromo-2-(2-pyridylmethylaminomethyl)phenolato]zinc(II) moieties are linked by the bridging chloride anions, forming polymeric zigzag chains running along the *a* axis (Fig. 2).

Experimental

5-Bromosalicylaldehyde (0.1 mmol, 20.1 mg) and 2-(aminomethyl)-pyridine (0.1 mmol, 10.8 mg) were dissolved in MeOH (10 ml). The mixture was stirred at room temperature for 10 min to give a yellow solution. To this solution was added an MeOH solution (5 ml) of ZnCl$_2$·6H$_2$O (0.1 mmol, 24.4 mg), with stirring. The resulting mixture

metal-organic compounds

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