

Bis(4-methylbenzylammonium) tetrachloridozincate: a new noncentrosymmetric structure characterized by ^{13}C CP–MAS NMR spectroscopy

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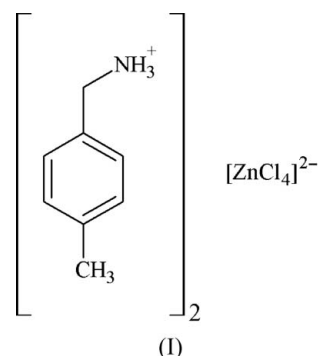
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A new noncentrosymmetric organic–inorganic hybrid material, $(\text{C}_8\text{H}_{12}\text{N})_2[\text{ZnCl}_4]$, has been synthesized as single crystals at room temperature and characterized by X-ray diffraction and solid-state NMR spectroscopy. Its novel structure consists of two 4-methylbenzylammonium cations and one $[\text{ZnCl}_4]^{2-}$ anion connected by $\text{N}-\text{H}\cdots\text{Cl}$ and $\text{C}-\text{H}\cdots\text{Cl}$ hydrogen bonds, two of which are three-centre interactions. The Zn^{II} metal centre has a slightly distorted tetrahedral coordination geometry. Results from ^{13}C CP–MAS NMR spectroscopy are in good agreement with the X-ray structure. Density functional theory calculations allow the assignment of the carbon peaks to the independent crystallographic sites.

Comment

Organic–inorganic hybrid materials having a noncentrosymmetric structure are interesting for their applications in various fields such as quadratic nonlinear optical materials research (Masse *et al.*, 1993). Structural investigation of the tetrahalometallate anions of the metals of the first transition series with different counter-cations is of interest because of their large structural variabilities (Smith, 1976). Hybrid d_{10} -metal halides have been found to exhibit important structural properties because of their wide range of stereochemical features, such as distorted tetrahedral (Bhattacharya *et al.*, 2002), square-pyramidal (Antolini *et al.*, 1980) and trigonal-bipyramidal (Raymond *et al.*, 1968) geometries. As a contribution to the investigation of the above materials, we report here the crystal structure of one such compound, bis(4-methylbenzylammonium) tetrachloridozincate, (I), formed from the reaction of 4-methylbenzylamine and zinc chloride.

The asymmetric unit of (I) comprises two 4-methylbenzylammonium cations and a $[\text{ZnCl}_4]^{2-}$ anion (Fig. 1). The crystal structure of this material consists of a network of the constituent cations and anions connected by $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds, two of which are three-centre interactions, *viz.* $\text{N15}-\text{H152}\cdots(\text{Cl2},\text{Cl5})$ and $\text{N15}-\text{H153}\cdots(\text{Cl2}^{\text{ii}},\text{Cl5}^{\text{i}})$ (details and symmetry codes in Table 1). Multiple hydrogen bonds connect the different entities of (I) to form layers, built up from the $[\text{ZnCl}_4]^{2-}$ anions and the ammonium groups, parallel to the *ac* plane (Fig. 2). Fig. 3 shows that two such layers cross the unit cell at $z = 0$ and $z = \frac{1}{2}$, and the bodies of the organic groups are located between these layers and connect them *via* weak $\text{C}-\text{H}\cdots\text{Cl}$ hydrogen bonds. The organic molecule exhibits a regular spatial configuration with normal $\text{C}-\text{C}$ and $\text{C}-\text{N}$ distances and $\text{C}-\text{C}-\text{C}$ and $\text{C}-\text{C}-\text{N}$ angles (El Glaoui *et al.*, 2010). No $\pi-\pi$ stacking interactions between the phenylene rings or $\text{C}-\text{H}\cdots\pi$ interactions towards them are observed.



Previous studies [see, for example, Guo *et al.* (2007)] have showed that, in the $[\text{ZnCl}_4]^{2-}$ anion, the $\text{Zn}-\text{Cl}$ bond lengths and $\text{Cl}-\text{Zn}-\text{Cl}$ bond angles are not equal, but vary with the environment around the Cl atom. In complex (I), the $\text{Zn}-\text{Cl}$ bond lengths vary between 2.2564 (17) and 2.2841 (14) Å, and the $\text{Cl}-\text{Zn}-\text{Cl}$ angles range from 104.28 (6) to 115.70 (6)°. Owing to these differences in the geometric parameters, the $[\text{ZnCl}_4]^{2-}$ anion has a slightly distorted tetrahedral stereochemistry (as in Guo *et al.*, 2007). In (I), since atom Cl4 is involved in a strong $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bond ($\text{H}\cdots\text{Cl} =$

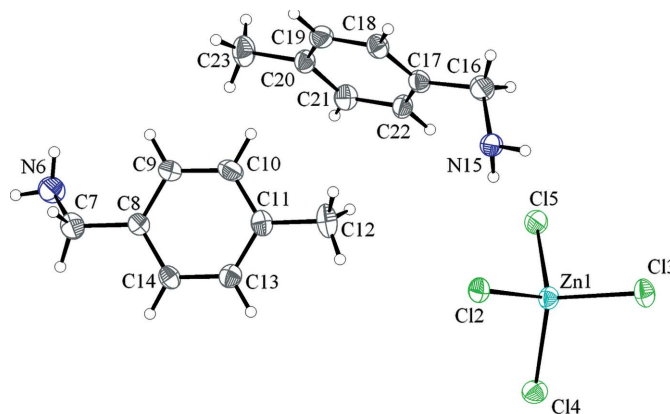


Figure 1

A view of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at 50% probability level.

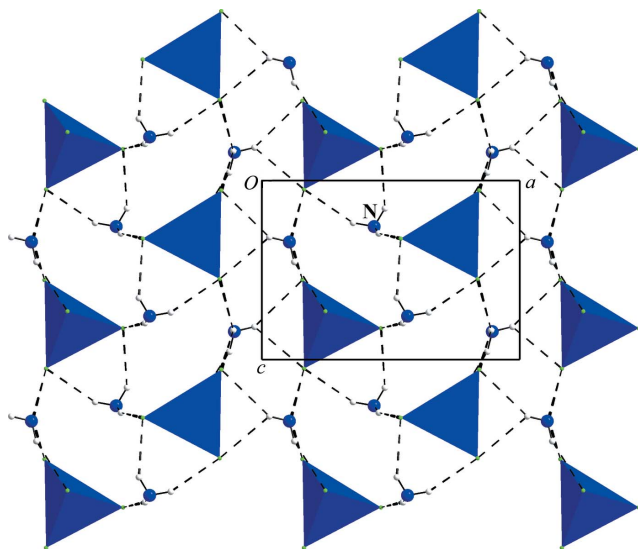


Figure 2

A projection, along the *b* axis, of a layer in the structure of (I), showing the N—H...Cl hydrogen-bonding interactions (dashed lines). Only the ammonium and tetrachloridozincate (tetrahedra) sections are shown, for clarity.

2.30 Å), the Zn1—Cl4 bond is obviously longer than the other Zn—Cl bonds (Table 1).

Refining the structure in the noncentrosymmetric space group gives a value of 0.00 (2) for the Flack parameter (Flack & Bernardinelli, 1999), confirming that the direction of the polar axis has been correctly determined.

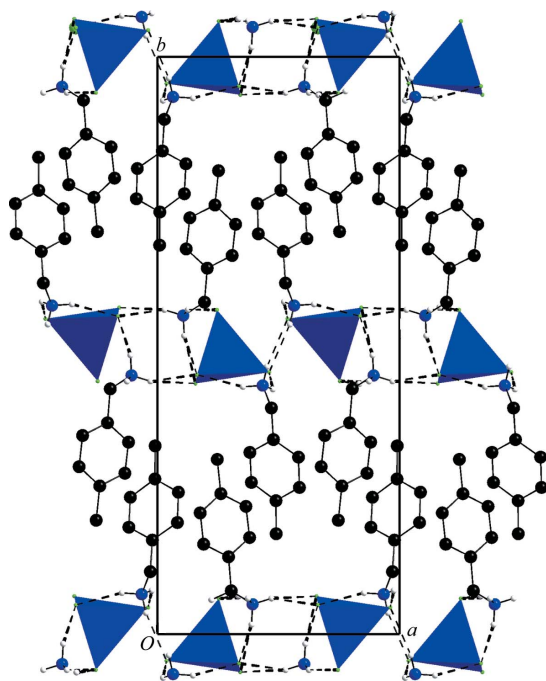


Figure 3

A projection of the structure of (I) along the *c* axis. Hydrogen bonds are denoted as dashed lines.

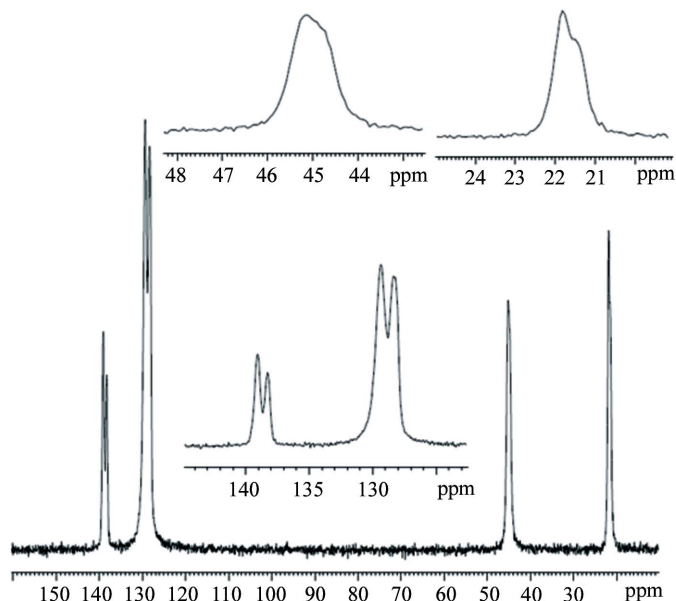


Figure 4

^{13}C CP-MAS NMR spectrum of $(\text{C}_8\text{H}_{11}\text{N}_2)_2[\text{ZnCl}_4]$.

The ^{13}C CP-MAS NMR spectrum of crystalline (I) is shown in Fig. 4. In the aliphatic resonance domain, the spectrum displays four resonances corresponding to two methyl and two methylene C atoms. This result is consistent with the presence of two organic moieties in the asymmetric unit of the compound, in agreement with the X-ray diffraction data. Density functional theory (DFT) calculations were undertaken in order to assign the NMR resonances to the different crystallographically non-equivalent C atoms of the unit cell. These calculations were made at the B3LYP/6-31+G* level using the GAUSSIAN98 program (Frisch *et al.*, 1998). Three different calculations were made on the two non-equivalent organic cations in the unit cell and in all cases the theoretical chemical shifts were subtracted from those of the reference (tetramethylsilane) calculated at the same level of theory. Firstly, calculation of the NMR chemical shifts [with the Gauge-Independent Atomic Orbital (GIAO) method] by taking the geometry obtained from X-ray diffraction. Secondly, optimization of the positions of the H atoms in the molecule and calculation of the NMR chemical shifts in this semi-optimized geometry. (X-ray diffraction always leads to underestimated X—H bond lengths, due to the fact that it is sensitive to the electron cloud and does not see the nuclei.) Thirdly, full optimization of all atoms and calculation of NMR chemical shifts. This calculation, compared with that above, will give indications of the steric hindrance around the organic cation and the positions where it is the strongest. The results are listed in Table 2. Clearly, there is a very good agreement between the experimental and theoretical values calculated after optimization of the H-atom positions, allowing the unambiguous assignment of the different NMR signals to the various C atoms of the structure.

In conclusion, compound (I) was prepared as single crystals at room temperature and characterized by two physicochemical methods. On the structural level, the atomic arrangement

of this material consists of a network of 4-methylbenzylammonium cations and tetrachloridozincate anions connected by N—H...Cl and C—H...Cl hydrogen bonds. The number of ¹³C CP-MAS NMR components is in full agreement with those of the crystallographically independent sites.

Experimental

A mixture of 2-amino-5-chloropyridine (3 mmol, 0.385 g), zinc chloride (1.5 mmol, 0.297 g) and HCl (10 ml, 0.3 M) in water (10 ml) was placed in a Petri dish and allowed to evaporate slowly at room temperature. Colourless single crystals of the title compound, (I), were isolated after several days (yield 54%). The ¹³C CP-MAS NMR spectrum was recorded on a solid-state high-resolution Bruker DSX300 spectrometer operating at 75.49 MHz for ¹³C, with a classical 4 mm probe head allowing spinning rates up to 10 kHz. The chemical shifts are given relative to tetramethylsilane (external reference, precision 0.5 p.p.m.). The spectrum was recorded by use of cross-polarization (CP) from protons (contact time 5 ms) and MAS. It was checked that there was a sufficient delay between scans to allow full relaxation of the nuclei.

Crystal data

(C ₈ H ₁₂ N) ₂ [ZnCl ₄]	$V = 2008.2 (3) \text{ \AA}^3$
$M_r = 451.57$	$Z = 4$
Orthorhombic, $Pna2_1$	Mo $K\alpha$ radiation
$a = 10.6623 (8) \text{ \AA}$	$\mu = 1.76 \text{ mm}^{-1}$
$b = 25.395 (2) \text{ \AA}$	$T = 110 \text{ K}$
$c = 7.4167 (5) \text{ \AA}$	$0.26 \times 0.17 \times 0.09 \text{ mm}$

Data collection

Agilent Gemini CCD area-detector diffractometer	Clark & Reid (1995)
Absorption correction: analytical [CrysAlis PRO (Agilent Technologies, 2010), based on expressions derived by	$T_{\min} = 0.692, T_{\max} = 0.866$
	26378 measured reflections
	5120 independent reflections
	4699 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.061$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.066$	$\Delta\rho_{\max} = 1.10 \text{ e \AA}^{-3}$
$wR(F^2) = 0.143$	$\Delta\rho_{\min} = -1.36 \text{ e \AA}^{-3}$
$S = 0.92$	Absolute structure: Flack & Bernardinelli (1999), with 2877 Friedel pairs
5120 reflections	Flack parameter: 0.00 (2)
210 parameters	
1 restraint	
H-atom parameters constrained	

Table 1

Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N15—H153...Cl5 ⁱ	0.89	2.69	3.417 (5)	138
N15—H153...Cl2 ⁱⁱ	0.89	2.78	3.445 (5)	132
N15—H152...Cl2	0.89	2.69	3.262 (5)	122
N15—H152...Cl5	0.89	2.77	3.552 (5)	146
N15—H151...Cl3 ⁱ	0.89	2.40	3.242 (5)	155
N6—H61...Cl4 ⁱⁱⁱ	0.88	2.57	3.274 (6)	136
N6—H62...Cl2 ⁱⁱⁱ	0.89	2.50	3.315 (6)	151
N6—H63...Cl4 ^{iv}	0.89	2.30	3.171 (5)	163
C7—H72...Cl3 ^{iv}	0.96	2.81	3.459 (7)	125
C7—H71...Cl5 ^v	0.97	2.92	3.711 (6)	139
C16—H161...Cl4 ^{vi}	0.97	2.88	3.824 (8)	162
C16—H162...Cl3 ⁱⁱ	0.97	2.82	3.636 (8)	142

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

Table 2

Calculated and experimental carbon-13 chemical shifts in (C₈H₁₁N)₂[ZnCl₄].

Atom	No optimization	Optimization of all atoms	Optimization of protons	Experimental
C12	1.6	23.1	23.4	21.85
C7	28.2	56.1	45.2	45.23
C11	143.4	147.2	142.2	139.1
C13	120	129.1	125.3	129.38
C14	118.3	124.2	123.7	129.38
C8	114.1	116.1	113.9	128.32
C9	113.2	124.2	119.7	128.32
C10	121.7	129.1	126.6	129.38
C23	0.9	23.1	23.0	21.41
C16	28.1	56.1	44.1	44.72
C20	143	147.2	141.2	138.3
C21	121.4	129.1	126.2	129.38
C22	108.9	124.2	112.9	128.32
C17	112.3	116.1	112.3	128.32
C18	114.1	124.2	121.9	129.38
C19	120.8	129.1	126.1	129.38

All H atoms were located in a difference map. They were initially refined with soft restraints on the bond lengths and angles to regularize their geometry, with C—H = 0.93–0.98 \AA and N—H = 0.86–0.89 \AA , and with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{parent atom})$, after which the positions were refined with riding constraints. Software and methods used for extinction correction and weighting scheme: Larson (1970); Prince (1982); Watkin (1994).

Data collection: *CrysAlis PRO* (Agilent Technologies, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: WQ3001). Services for accessing these data are described at the back of the journal.

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