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Hydrogen-bonded cubanes in the crystal structure of 2,6-di(Pr^i)aniline hydrochloride and their inorganic analogues $[M^{2+}(2,6\text{-di}(Pr^i)C_6H_5N^{2-})]_4$ (M = Sn, Pb)†

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The crystal structure of 2,6-di(Pr^i)aniline hydrochloride contains hydrogen-bonded cubanes analogous to those in the complexes $[M^{2+}(2,6\text{-di}(Pr^i)C_6H_5N^{2-})]_4$, M = Sn, Pb.

The cubane structural motif is ubiquitous in solid-state inorganic chemistry. Examples of discrete $[M(\mu_3\text{–}X)]_4$ units are observed for elements in all areas of the periodic table, including the alkali metals, *e.g.* $[K(\mu_3\text{-}OBu^t)]_4$ and $[((Me_2N)_3P\text{=}O)Li(\mu_3\text{-}Cl)]_4$,[1,2] transition elements, *e.g.* $[(Ph_3P)Cu(\mu_3\text{-}Cl)]_4$ and $[((Me_3Si)_3C)Cd(\mu_3\text{-}Cl)]_4$,[3,4] and main-group elements, *e.g.* $[Sn(\mu_3\text{-}N\text{-}2,5\text{-}MeOC_6H_3)]_4$ and $[Bu^tGa(\mu_3\text{-}Se)]_4$.[5,6] We report here the observation of discrete hydrogen-bonded cubanes in the hydrochloride of 2,6-di(Pr^i)aniline, **1**, which are analogous to those found in the complexes of Sn^{2+} and Pb^{2+} with the dianion derived from the same organic moiety.[7] Compound **1** is not the first example of a hydrogen-bonded cubane: the cubane motif is also adopted by the hydrochlorides of the primary amines 2-ethylcyclohexylamine[8], methylenedioxyamphetamine,[9] and 2-(1-ammonio-2-methylcyclohexyl)benzothiopene.[10] The significance of **1** lies in the existence of directly comparable cubane units in a hydrogen-bonded organic molecule and two complexes of the same organic moiety with main-group elements. Compound **1** provides the closest link observed to date between the archetypal cubane motif observed in inorganic chemistry and a hydrogen-bonded system in the organic solid state.

Compound **1** was initially obtained fortuitously as a by-product of the reaction of PCl_3 with 2,6-di(Pr^i)aniline in THF. Single crystals of **1** were isolated from the reaction mixture,‡ which also contained the expected dimeric product $[ClP(\mu\text{-}N\text{-}2,6\text{-}Pr^i\text{-}C_6H_3)]_2$. Compound **1** may be obtained more directly by the reaction of HCl/dioxane with 2,6-di(Pr^i)aniline in THF (for synthesis details, see ESI†). In the crystal, a complete cubane moiety comprises the asymmetric unit in space group $P\bar{1}$ (Fig. 1), and there is no hydrogen bonding between these units. A disordered THF molecule (one per two cubanes) is also present in the crystal lattice, which does not participate in any hydrogen-bond interactions. The $H\cdots Cl^-$ and associated $N^+\cdots Cl^-$ distances within the cubane core lie in relatively broad ranges: $H\cdots Cl^-$ 2.03–2.34 Å and $N^+\cdots Cl^-$ 3.058(2)–3.245(2) Å (Table 1). In general, the $N^+\text{—}H\cdots Cl^-$ angles are inversely correlated with the $H\cdots Cl^-$ distances, typical of strong hydrogen bonds. The 2,6-di(Pr^i)aniline moieties adopt two distinct orientations with respect to the cubane core. Newman-type projections along the $N^+\text{—}C$ bonds (Fig. 2) reveal that in two of the moieties (N1A and N1B) the aromatic ring plane adopts an eclipsed alignment with respect to the $N^+\text{—}H$ bonds, so that it lies directly along one cube edge and bisects the angle between the two adjacent edges in projection (orientation **A**). In the other two moieties (N1C and N1D) the aromatic ring plane adopts a staggered alignment with respect to the $N^+\text{—}H$ bonds so that it lies perpendicular to one cube edge and makes an angle of *ca.* 30° to the two adjacent edges in projection (orientation **B**). The pattern of the hydrogen-bond geometry in the cubane core is correlated with the adoption of these two orientations:

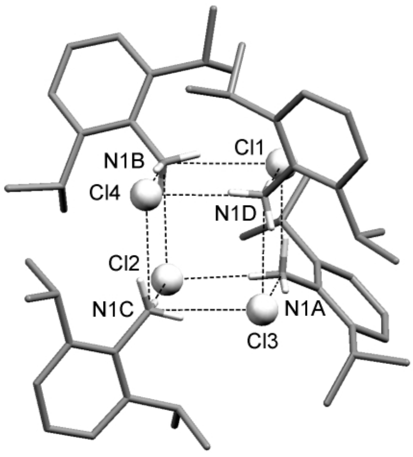

Fig. 1 Hydrogen-bonded cubane unit in the crystal structure of **1**. H atoms not involved in hydrogen bonding are omitted.

Table 1 Hydrogen-bond parameters in **1**[a]

	H-bond donor	H-bond acceptor	$N^+\cdots Cl^-$/Å	$H\cdots Cl^-$/Å	$N^+\text{–}H\cdots Cl^-$/°	
(A)	N1A	Cl3	3.078(2)	2.06	171	*(s)*
		Cl1	3.141(2)	2.13	166	*(s)*
		Cl2 (*)	3.210(2)	2.27	152	*(l)*
(A)	N1B	Cl2	3.091(2)	2.11	158	*(s)*
		Cl1	3.121(2)	2.09	175	*(s)*
		Cl4 (*)	3.176(2)	2.22	153	*(l)*
(B)	N1C	Cl3 (*)	3.104(2)	2.08	174	*(s)*
		Cl2	3.183(2)	2.25	150	*(l)*
		Cl4	3.245(2)	2.34	147	*(l)*
(B)	N1D	Cl4 (*)	3.058(2)	2.03	172	*(s)*
		Cl3	3.227(2)	2.29	151	*(l)*
		Cl1	3.252(2)	2.29	154	*(l)*

[a] H atom positions normalised (ref. 11). Asterisks denote the cube edges that lie parallel to the aromatic ring planes in the **A** orientation, and perpendicular to the ring planes in the **B** orientation.

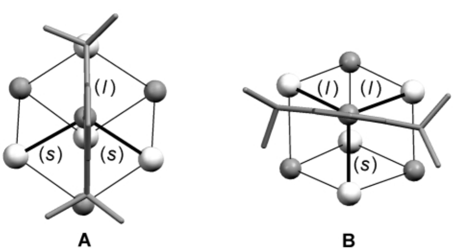

Fig. 2 Projections along the $N^+\text{—}C$ bonds of the 2,6-di(Pr^i)aniline moieties in **1** showing the different orientations (**A** and **B**) of the aromatic ring plane with respect to the cubane core.

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† Electronic supplementary information (ESI) available: details of the synthesis and spectroscopic characterization of **1** and details of the cubane geometries of **2** and **3**. See http://www.rsc.org/suppdata/cc/b3/b307400e/.

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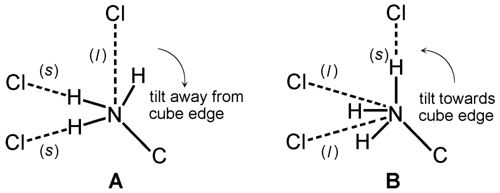
both organic moieties in orientation **A** display a short, short, long (*s*,*s*,*l*) pattern of $N^+\cdots Cl^-$ distances, while both moieties in orientation **B** display a short, long, long (*s*,*l*,*l*) pattern. In orientation **A**, the aromatic ring plane is aligned exactly along the cube edge that contains the long $N^+\cdots Cl^-$ contact of the *s*,*s*,*l* pattern. In orientation **B**, the short $N^+\cdots Cl^-$ contact of the *s*,*l*,*l* pattern lies in the cube edge perpendicular to the aromatic ring plane.

The cubane motif in **1** is directly comparable to those observed in the isomorphous Sn^{2+} (**2**) and Pb^{2+} (**3**) complexes of the dianion derived from 2,6-di(Pr^i)aniline, $[M^{2+}(2,6\text{-di-}(Pr^i)C_6H_5N^{2-})]_4$ (Fig. 3).[7] In both **2** and **3**, two crystallographically-independent cubanes are present, which display different geometries: the first cubane contains two organic moieties with orientation **A** and two with orientation **B**, while the second contains three **A** and one **B**. In each case, the **A** moieties display an *s*,*s*,*l* pattern of M—N contacts and the **B** moieties display an *s*,*l*,*l* pattern, comparable to those in **1**. The bonding in **2** and **3** has been reported previously to be largely ionic,[7] so that the bonding requirements of the M^{2+} cations are comparable to those of the Cl^- anions in **1**, *i.e.* both M^{2+} and Cl^- form electrostatic contacts that are isotropic with respect to M^{2+} or Cl^-. In addition, the directional bonding requirements of the amine moieties in **2** and **3** are comparable to those in **1**: in **2** and **3**, the *sp*^{3} hybrid orbitals of the N atom (having predominantly lone-pair character) are directed at 109.5° to each other and form the strongest, shortest bonds to M when the M—N—M angles are close to 109.5°. Similarly, the N^+—H groups in **1** are oriented at 109.5° to each other and form the strongest, shortest bonds to Cl^- when the $N^+—H\cdots Cl^-$ angles are close to linear. Thus, the cationic ammonium moieties in **1** and the dianionic amine moieties in **2** and **3** may be considered to be essentially "isolobal". The geometrical difference between the cubane cores is simply that the H-mediated $N^+\cdots Cl^-$ distances in **1** are longer than the M—N distances in **2** and **3**.

The hydrogen bonding within the cubane core of **1** may be described as "frustrated" in that it is not possible to accommodate optimal linear geometries for all $N^+—H\cdots Cl^-$ interactions within the cubane, on account of the *ca*. 109.5° angle between the N^+—H bonds at the NH_3^+ centre. Orientations **A** and **B** represent two different compromise arrangements within this frustrated framework. In orientation **A**, two of the N^+—H groups lie within one cube face, but the third N^+—H bond vector must then adopt a significant angle to the perpendicular cube edge (Scheme 1(a)). Since the $H\cdots Cl^-$ distance is inversely correlated with the $N^+—H\cdots Cl^-$ angle, the latter N^+—H group forms a longer contact, giving rise to the *s*,*s*,*l* pattern of $N^+\cdots Cl^-$ distances. In orientation **B**, one N^+—H group forms an $N^+—H\cdots Cl^-$ contact that is close to linear along one cube edge and the remaining two must then adopt angles to the perpendicular cube face (Scheme 1(b)). This results in the *s*,*l*,*l* pattern of $N^+\cdots Cl^-$ distances. An analogous argument may be applied to the *sp*^{3} hybrid orbitals on N to rationalize the cubane geometry in **2** and **3**. The relationship between the *s*,*s*,*l* and *s*,*l*,*l* patterns and the orientation of the aromatic ring planes is attributable to steric effects: in orientation **A**, where the ring plane lies parallel to one cube edge, the ring and the N^+—C bond of the ligand tilt away from that cube edge (Scheme 1(a)). In orientation **B**, where the ring plane lies perpendicular to one cube edge, the ring and the N^+—C bond of the ligand tilt towards that cube edge (Scheme 1(b)). The observation of two different cubane geometries in the structures of **2** and **3** suggests that the cubane geometry can also be influenced by *inter*-cubane interactions in the solid state.



Scheme 1 Hydrogen-bond arrangements in **1** illustrating the origin of the short/long variation of $N^+—H\cdots Cl^-$ distances.

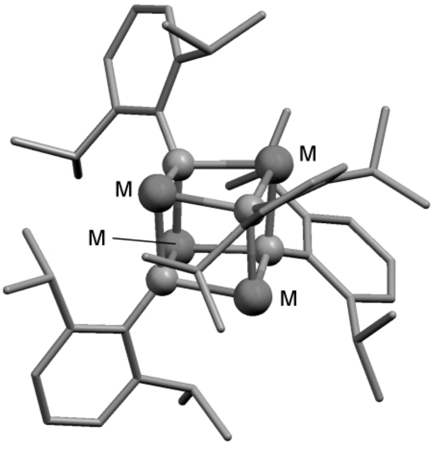


Fig. 3 Cubane unit in the crystal structure of **2** (M = Sn). H atoms are omitted for clarity. A comparable arrangement is observed in **3** (M = Pb).

A comprehensive analysis of the hydrogen-bond motifs in organic ammonium halides suggests that the similarity with the structural motifs observed in inorganic chemistry is in fact much more general. A full report of this study is in preparation.

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Notes and references

‡ *Crystal data for* **1**: $[C_{12}H_{20}ClN]_4\cdot\frac{1}{2}C_4H_8O$, M = 891.01, triclinic, space group $P\bar{1}$, Z = 2, a = 11.5989(4), b = 14.6215(5), c = 17.3570(6) Å, U = 2697.0(2) Å^3, μ(Mo-Kα) = 1.097 mm^{-1}, T = 180(2) K. Data were collected on a Nonius Kappa CCD diffractometer. Of a total of 28837 reflections collected, 12290 were independent (R_{int} = 0.039). The structure was solved by direct methods and refined by full-matrix least squares on F^2. Final $R1$ = 0.0505 [$I > 2\sigma(I)$] and $wR2$ = 0.1359 (all data). H atoms bonded to N were located in difference Fourier maps and refined with isotropic displacement parameters, with all N–H distances restrained to be equal with a standard uncertainty of 0.01 Å (*i.e.* one common N–H distance refined). For discussion of the hydrogen-bond geometry, H atom positions are normalised to neutron-derived distances (1.03 Å; see ref. 11) along the N–H bond vectors derived from the X-ray analysis. CCDC 213937. See http://www.rsc.org/suppdata/cc/b3/b307400e/ for crystallographic data in .cif or other electronic format.

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