Self assembling perovskite-type organic–inorganic hybrids have been the focus of a number of investigations in recent years. Combining the characteristics of the organic and inorganic components offers an opportunity to incorporate useful properties, and thus providing access to a vast area of complex, multifunctional materials.1 Fascination with these materials is generated by their interesting structural, magnetic, electrical, optical and chemical properties.

Compounds having the general formula \((\text{NH}_3(\text{CH}_2)_n\text{NH}_3)\text{MX}_4\) with \(X = \text{Br}, \text{Cl}, \text{I}\) and \(M = \text{metal}\) are known to crystallize in a layer structure.2 These hybrid materials can be classified into two groups, based on the nature of the interface between the organic and inorganic entities; in a first group organic and inorganic compounds are linked only by weak bonds (hydrogen or van der-Waals bonds), while in a second group the two entities are linked together through strong chemical (either covalent or ionic) bonds. It has been shown that the structure of the MX₄ units can vary considerably, ranging from isolated molecules (0D)³ to extended chains (1D)⁴ and up to two³ or three-dimensional⁶ networks.

In this article we report on a new 0-dimensional compound that contains alkyl-chain diammonium 1,8-diammoniumoctane (abbreviated DAO), \([\text{CoCl}_4]^-\) (abbreviated TCC) tetrahedral and uncoordinated chloride ions, connected by hydrogen bonds. The crystal structure was determined by X-ray diffraction (XRD).

A new organic–inorganic hybrid (abbreviated DAOTCC) with the formula \(\text{C}_{24}\text{H}_{66}\text{Cl}_{10}\text{Co}_2\text{N}_6\) was obtained by the reaction of 1,8-diaminooctane, \(\text{CoCl}_2\cdot6\text{H}_2\text{O}\) and hydrochloric acid at room temperature. One of the grown crystals was subjected to X-ray diffraction. The titled compound crystallizes in the monoclinic space group \(P2_1/c\) with the cell parameters: \(a = 12.7153(14)\AA; b = 17.5474(11)\AA; c = 10.3409(8)\AA; \beta = 91.582(7)^\circ; V = 2306.39(3)\AA^3; Z = 2; R_1 = 0.047; wR_2 = 0.1115\) for 3104 observed reflexions. The structure is a 0D hybrid; the organic cations are linked to the inorganic layers by N–H–Cl hydrogen bonds.

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Table 1 Crystal data and structure refinement parameters of DAOTCC

<table>
<thead>
<tr>
<th>Formula: (\text{C}<em>{24}\text{H}</em>{66}\text{Cl}_{10}\text{Co}_2\text{N}_6)</th>
<th>Formula weight: 911.19</th>
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<tr>
<td>(T = 293) K</td>
<td>Crystal system: monoclinic</td>
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<tr>
<td>space group: (P2_1/c)</td>
<td>(a = 12.7153(14)\AA; b = 17.5474(11)\AA; c = 10.3409(8)\AA; \beta = 91.582(7)^\circ; V = 2306.39(3)\AA^3; Z = 2; D_q = 1.312 g cm(^{-3})</td>
</tr>
<tr>
<td>Radiation: (\text{Mo } K_a (\lambda = 0.71073) Å)</td>
<td>(\mu(\text{Mo } K_a) = 1.321) mm(^{-1})</td>
</tr>
<tr>
<td>(\mu(\text{Mo } K_a) = 1.321) mm(^{-1})</td>
<td>(F(0 0 0) = 952)</td>
</tr>
<tr>
<td>Crystal size: (0.21 \times 0.22 \times 0.12) mm(^3)</td>
<td>(r_\text{max} = 0.0956, wR_2 = 0.1320)</td>
</tr>
<tr>
<td>(r_\text{max} = 0.0956, wR_2 = 0.1320)</td>
<td>((\Delta\sigma)_{\text{max}} &lt; 0.001)</td>
</tr>
<tr>
<td>((\Delta\rho)<em>{\text{max}} = 0.67, (\Delta\rho)</em>{\text{max}} = -0.31) e(^{-})Å(^{-3})</td>
<td>Measurements: Enraf-Nonius CAD4</td>
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<td>Programs system: SHELXL-97, SADABS</td>
<td>Structure determination: SHELXS-97</td>
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<td>CCDC deposition number: 777147</td>
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Fig. 1 Asymmetric unit of DAOTCC, with atom labels and 50% probability displacement ellipsoids for non-H atoms.

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slowly combined, and the solvent was allowed to evaporate at room temperature. After two weeks, blue crystals suitable for X-ray investigation were obtained.

A suitable crystal of the title compound was selected under an optical microscope. A block cut out of a crystal of approximate size (0.21 × 0.22 × 0.12) mm³ was used for diffraction data on an Enraf-Nonius CAD4 automated diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). A total of 7392 reflexions were measured in the range of 2.3 < 2θ < 27.0.

The block was a single crystal; the crystallographic data, the details concerning the refinements of the title compound are summarized in Table 1. The positions of the heavier atoms, including the Co and Cl atoms, were located by a direct method using the program SHELXS-97. The remaining N and C atoms were found in a series of alternating difference Fourier maps and least-squares refinements. All hydrogen atoms were geometrically fixed using the instructions of SHELXL-97 “HFIX 23” and “HFIX 137”, respectively, for the C–H and N–H geometrically fixed using the instructions of SHELXL-97.

The final cycles of full-matrix least-squares refinement included anisotropic temperature factors for all non hydrogen atoms, which led to satisfactory convergence with R1 = 0.047, wR2 = 0.1115 for 3104 observed reflections (I > 2σ(I) and 193 refined parameters).

An asymmetric unit of the title compound comprises one and half of DAO, one TCC and one Cl⁻ anions. A view of the asymmetric unit of the structure drawing with 50% probability thermal ellipsoids is depicted in Fig. 1. The crystal structure of DAOTCC is composed of altering organic–inorganic layers. The projection of the structure along the c axis is given in Fig. 2, which shows the 0D periodic arrangement of the inorganic layer formed by TCC tetrahedral and uncoordinated Cl⁻ ions sandwiched between organic layers.

The tetrahedral cobalt (TCC) structure has Co–Cl distances ranging from 2.262(11) to 2.294(10)Å and Cl-Co-Cl angles varying from 104.01(4) to 111.50(4)°. Those values show a slight distortion from a regular tetrahedral. These results are similar to data known for tetrachlorocobaltate anions in homologous compounds. The differences in the Co-Cl bond lengths correlate with the number of hydrogen bonds accepted by the Cl atoms (Table 2S). There are nine possible hydrogen bonds of ammonium to Cl atoms (Fig. 2); Co-C12 and Co-C13 bonds are the longest they have similar, intermediate lengths of 2.294(10)Å and 2.292(11)Å; C12 and C13 accept two hydrogen bonds, Co-C14 has lengths of 2.281(11)Å and makes one N–H–Cl hydrogen bond; C11, which also accepts only one N–H–Cl hydrogen bond, makes the shortest Co-C1 bond of 2.262(11)Å (Table 3S). To achieve electroneutrality, lattice chloride ions are incorporated into the structure via N–H–Cl hydrogen bonds with the diammmonium cations, and each lattice chloride ion Cl1 forms three N–H–Cl hydrogen bonds.

The C–C distance in DAO range from 1.453(6)Å to 1.523(9)Å and the C–N distance average bond length is 1.477 Å. These distances are similar in length to the same bonds in homologous compounds containing long linear chains. Each (CH₄N₂)⁺⁺ entity displays N–C–C–C and C–C–C–C distortion angles of close to 180°, except for the gauche conformation, N₁–C₁–C₂–C₃, which is equal to 72.2(6)°, near to the NH₂ polar heads (Table 2S). In the related title compound, as shown in Fig. 2, tetrahedral TCC, Cl⁻ anions and DAO cations are held together through weak and strong N–H–Cl hydrogen bonding interacts (d₁₂, c) <3.19 Å: strong bending and (d₁₂, c) >3.19 Å: weak bending). These hydrogen bonds ensure the stability of the structure.

Supplementary materials

CCDC 777147 contains supplementary crystallographic data for this paper. This data can be obtained free of charge via ftp://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data centre, 12 Union Rood, Cambridge CB2 1EZ, UK (Fax: (international) +44 1223/336 033; e-mail: deposit@ccdc.cam.ac.uk).

Table 2S (Main interatomic distances and angles) and 3S (Bond distances in the hydrogen-bonding) are available from the journal web site.

Acknowledgments

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References