

## The lamellar architecture of 1,6-hexamethylenediammonium tetrachlorocobaltate(II)

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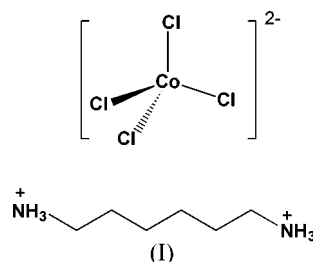
## Key indicators

Single-crystal X-ray study  
 $T = 183$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å  
 $R$  factor = 0.023  
 $wR$  factor = 0.061  
Data-to-parameter ratio = 22.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound,  $(\text{C}_6\text{H}_{18}\text{N}_2)[\text{CoCl}_4]$ , organic dications and inorganic dianions interact with each other through  $\text{N}-\text{H}\cdots\text{Cl}$  hydrogen bonds, forming infinite two-dimensional sheets of anions parallel to the  $ac$  plane. Alkyl chains act as spacers between these sheets. Only three Cl atoms are involved in hydrogen bonding with ammonium groups. The asymmetric unit consists of one anion together with half of each of two cations on inversion centres.

## Comment

A realistic goal in modern chemistry is the identification and application of reliable synthons which can control molecular aggregations and lead to crystal structures with particular patterns, creating new properties. For the construction of desirable materials, the nature and extent of weak (hydrogen bonding, van der Waals, or electrostatic) and strong (covalent or ionic) interactions between chemical components is an important issue. In the field of organic-inorganic hybrid materials, one of the most promising research areas in materials chemistry, these interactions occur within inorganic and organic components. The title compound, (I), belongs to a family of organic-inorganic hybrid solids with the general formula  $A_2MX_4$ , in which  $A$  (or  $A_2$ ) is an organic ammonium cation (or diammonium dication),  $M$  is a divalent metal ion, and  $X = \text{Cl}$  or  $\text{Br}$ . Physical and chemical properties of these materials have been widely investigated. Some of them show liquid-crystalline behavior (Bowles *et al.*, 1996; Kanazawa *et al.*, 2000; Neve *et al.*, 2001).  $\text{CoCl}_4^{2-}$  anions are capable of participating extensively in  $\text{N}-\text{H}\cdots\text{Cl}$  and  $\text{C}-\text{H}\cdots\text{Cl}$  hydrogen bonding with organic cations (Mahmoudkhani & Langer, 1999*a,b*; Mahmoudkhani *et al.*, 2001).

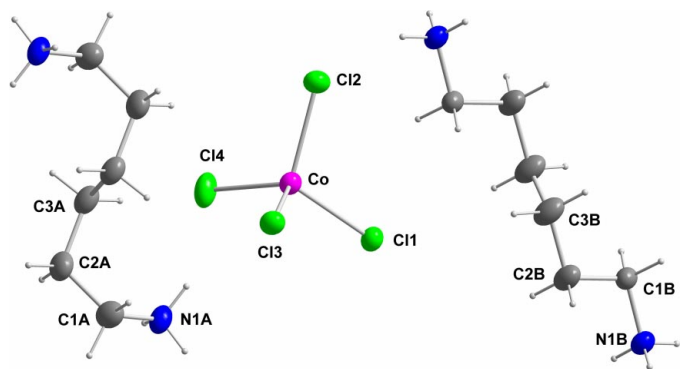


The hexamethylenediammonium cation in (I) is centrosymmetric and the asymmetric unit contains two halves of symmetry-independent organic dications and an inorganic dianion, as shown in Fig. 1. The coordination geometry of the  $\text{Co}^{\text{II}}$  ion is tetrahedral, with  $\text{Co}-\text{Cl}$  bond distances ranging from 2.2592 (4) to 2.2906 (4) Å. Only Cl1, Cl2 and Cl3 are involved in hydrogen bonds with the ammonium groups of surrounding organic cations, each acting as an acceptor of two

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**Figure 1**

The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level. Only the symmetry-independent atoms are labeled.

hydrogen bonds (Table 2). Atom Cl4 is involved in a weak C—H···Cl hydrogen bond with Cl1B. This may explain a shortening of the Co—Cl4 bond compared to the other Co—Cl bonds. The N—H···Cl hydrogen bonds link organic dications and inorganic dianions together, to give layers of anions parallel to the *ac* plane (Fig. 2). In each layer, CoCl<sub>4</sub> tetrahedra adopt alternating up and down orientations relative to the *c* axis. Adjacent layers are pillared by the alkyl chains of the organic cations, to form a three-dimensional network. In this respect, compound (I) differs from the previously known homologues [H<sub>3</sub>N—(CH<sub>2</sub>)<sub>3</sub>—NH<sub>3</sub>][ClO<sub>4</sub>] (Guo *et al.*, 1992) and [H<sub>3</sub>N—(CH<sub>2</sub>)<sub>5</sub>—NH<sub>3</sub>][ClO<sub>4</sub>] (Criado *et al.*, 1999). In these compounds, the organic moieties do not act as spacers between layers.

## Experimental

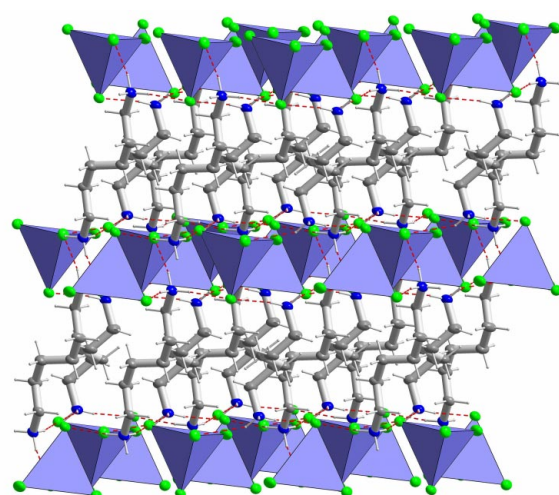
In a 25 ml round-bottomed flask, 100 mmol of 1,6-hexamethylenediamine was dissolved in concentrated aqueous HCl solution (10 ml). CoCl<sub>2</sub>·6H<sub>2</sub>O (100 mmol dissolved in 10 ml ethanol) was added. The mixture was warmed to about 333 K and stirred for about 2 h. Slow evaporation of the solvent gave blue crystals of the product suitable for X-ray diffraction study.

### Crystal data

(C <sub>6</sub> H <sub>18</sub> N <sub>2</sub> )[CoCl <sub>4</sub> ]	<i>Z</i> = 2
<i>M<sub>r</sub></i> = 318.95	<i>D<sub>x</sub></i> = 1.518 Mg m <sup>-3</sup>
Triclinic, <i>P</i> 1	Mo <i>K</i> α radiation
<i>a</i> = 7.2803 (1) Å	Cell parameters from 8192 reflections
<i>b</i> = 9.9479 (1) Å	<i>θ</i> = 1–28°
<i>c</i> = 9.9572 (1) Å	<i>μ</i> = 1.96 mm <sup>-1</sup>
<i>α</i> = 75.682 (1)°	<i>T</i> = 183 (2) K
<i>β</i> = 87.494 (1)°	Parallelpiped, blue
<i>γ</i> = 88.790 (1)°	0.40 × 0.20 × 0.15 mm
<i>V</i> = 698.029 (14) Å <sup>3</sup>	

### Data collection

Siemens SMART CCD diffractometer	3458 independent reflections
<i>ω</i> scans	3135 reflections with <i>I</i> > 2σ( <i>I</i> )
Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	<i>R</i> <sub>int</sub> = 0.024
<i>T</i> <sub>min</sub> = 0.508, <i>T</i> <sub>max</sub> = 0.758	<i>θ</i> <sub>max</sub> = 28.3°
9980 measured reflections	<i>h</i> = -9 → 9
	<i>k</i> = -13 → 13
	<i>l</i> = -13 → 13



**Figure 2**

The lamellar structure of (I). The hydrogen-bonded layers are arranged parallel to the *ac* plane.

### Refinement

Refinement on *F*<sup>2</sup>  
*R*(*F*) = 0.023  
*wR*(*F*<sup>2</sup>) = 0.061  
*S* = 1.02  
 3458 reflections  
 154 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0298P)^2 + 0.2211P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.48 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.51 \text{ e } \text{Å}^{-3}$$

**Table 1**

Selected geometric parameters (Å, °).

Co—Cl4	2.2592 (4)	Co—Cl1	2.2906 (4)
Co—Cl3	2.2859 (4)	N1B—Cl1B	1.494 (2)
Co—Cl2	2.2733 (4)	N1A—Cl1A	1.499 (2)
Cl4—Co—Cl1	110.86 (2)	Cl2—Co—Cl1	111.63 (2)
Cl4—Co—Cl2	110.58 (2)	Cl2—Co—Cl3	104.87 (2)
Cl4—Co—Cl3	112.21 (2)	Cl3—Co—Cl1	106.50 (2)

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1A—H11B···Cl1	0.87 (2)	2.35 (2)	3.2024 (16)	167 (2)
N1B—H11A···Cl1 <sup>i</sup>	0.88 (2)	2.38 (2)	3.2384 (15)	165 (2)
N1A—H12B···Cl2 <sup>ii</sup>	0.88 (3)	2.51 (3)	3.2267 (16)	139 (2)
N1B—H13A···Cl2	0.91 (2)	2.43 (2)	3.2795 (15)	155 (2)
N1A—H13B···Cl3 <sup>iii</sup>	0.90 (2)	2.43 (3)	3.2791 (16)	158 (2)
N1B—H12A···Cl3 <sup>iv</sup>	0.85 (3)	2.56 (3)	3.3656 (16)	157 (2)
Cl1B—H1B1···Cl4 <sup>ii</sup>	0.99	2.81	3.6627 (15)	145

Symmetry codes: (i) 1 + *x*, *y*, *z*; (ii) 1 - *x*, 1 - *y*, -*z*; (iii) -*x*, 1 - *y*, -*z*; (iv) 1 - *x*, 1 - *y*, 1 - *z*.

The H atoms of the ammonium groups were located in a difference Fourier map and refined isotropically, whereas the C-bonded H atoms were constrained to idealized geometries using an appropriate riding model.

Data collection: SMART (Siemens, 1995); cell refinement: SAINT (Siemens, 1995); data reduction: SAINT and SADABS (Sheldrick, 2001); program(s) used to solve structure: SHELXTL (Bruker, 2001);

program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXTL*.

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### References

- Bowlas, C. J., Bruce, D. W. & Seddon, K. R. (1996). *J. Chem. Soc. Chem. Commun.* pp. 1625–1626.
- Brandenburg, K. (2000). *DIAMOND*. Version 2.1d. Crystal Impact GbR, Bonn Germany.
- Bruker (2001). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Criado, J. J., Jimenez-Sanchez, A., Cano, F. H., Saez-Puche, R. & Rodriguez-Fernandez, E. (1999). *Acta Cryst.* **B55**, 947–952.
- Guo, N., Lin, Y.-H., Zeng, G.-F. & Xi, S.-X. (1992). *Acta Cryst.* **C48**, 542–543.
- Kanazawa, A., Ikeda, T. & Nagase, Y. (2000). *Chem. Mater.* **12**, 3776–3782.
- Mahmoudkhani, A. H. & Langer, V. (1999a). *Acta Cryst.* **B55**, 752–757.
- Mahmoudkhani, A. H. & Langer, V. (1999b). *Acta Cryst.* **C55**, 1631–1634.
- Mahmoudkhani, A. H., Langer, V. & Casari, B. M. (2001). *Acta Cryst.* **E57**, m392–m395.
- Neve, F., Francescangeli, O., Cruspini, A. & Charmant, J. (2001). *Chem. Mater.* **13**, 2032–2041.
- Sheldrick, G. M. (2001). *SADABS*. Version 2.03. University of Göttingen, Germany.
- Siemens (1995). *SMART* and *SAINTE*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.