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一维化合物$(C_2H_8N)[Hg_2Cl_5]$的晶体结构与介电性质的研究

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摘要: 二甲基胺盐酸盐与氯化汞在水溶液中的反应,生产了一种有机无机杂化化合物$(C_2H_8N)[Hg_2Cl_5]$ (**1**)。单晶衍射分析证明化合物 **1** 的阴离子为沿 *b* 轴方向由氯桥构成的一维阴离子链,每 1 个汞都与 4 个氯离子配位。在处于 80~298 K 温度区间中,化合物 **1** 的介电没有出现介电异常的现象,这表明没有相变的发生。

关键词: 汞配合物; 二甲胺; 晶体结构; 介电性质
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Crystal Structure and Dielectric Property of a One-Dimentional Compound $(C_2H_8N)[Hg_2Cl_5]$

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Abstract: Reaction of dimethylammonium chloride with mercuric chloride in aqueous solution yielded one novel organic-inorganic hybrid compound $(C_2H_8N)[Hg_2Cl_5]$ (**1**). X-ray structure determination reveals that complex **1** shows a one-dimensional chloride-bridged $[Hg_2Cl_5]_n$ anionic chain structure along the *b* axis. Each Hg(Ⅱ) ion is coordinated with four chloride ions. Temperature-dependent dielectric constant of **1** shows no distinct anomalies, suggesting no phase transition occurred in the measured temperature range 80~298 K. CCDC: 880350.

Key words: Hg(Ⅱ) complex; dimethylamine; crystal structure; dielectric constant

0 Introduction

Much attention has been attracted by metal-organic framework (MOF) research due the advantage of structural tunability and multifunctionality to develop polarizable molecular materials with rich dielectric properties[1], and opened up new possibilities to realize hybrid materials with unique solid-state electric properties, such as ferroelectricity, piezoelectricity, and dielectricity[2-7].

Metal halide complex forming molecular-ionic salts arouse much research due to their interesting structural and physical properties. Crystals with composition A_2MX_4 (M^{2+}=Zn, Mn, Co, Fe, Cu, Cd) are one of the best known group in the solid state[8-9]. The structures of most of these compounds show successive phase transitions and quite often incommensurate phases[10]. The phase transitions are mainly due to order-disorder in the ammonium group. A point of further interest besides the study of phase transition in the mercury compounds, is the coordination of Hg(Ⅱ). A series of dimethylammonium mercury chlorides were prepared by A. Ben Salah et al. in early 1980s[11] and show interesting structure.

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In this contribution, one Hg(Ⅱ)coordination compound (C_2H_8N) [Hg_2Cl_5] (**1**) was prepared and dielectric property was also measured.

1 Experimental

1.1 Materials and measurements

A11 chemicals used were of analytical grade. Solvents were purified by conventional methods. Analyzer. IR spectrum was recorded on a IRPrestige-21 instrument with KBr pellets in the range of 4 000~400 cm^{-1}. Dielectric studies (capacitance and dielectric-loss measurements) were performed on powder samples which had been pressed into tablets, on the surfaces of which conducting carbon glue was deposited. An automatic impedance TongHui2828 Analyzer was used.

1.2 Synthesis of 1

A mixture of $HgCl_2$ (4.26 g, 25 mmol), hydrochloric acid (50 mmol, 36%, 8 mL), and dimethylamine (4.8 g, 50 mmol) in 30 ml water was stirred for 10 min at room temperature, slow evaporation of the resulting solution yielded colourless needle-like crystals after two weeks. IR data (ν, cm^{-1}): 3 581 (s); 3 527 (s); 3 170 (m); 1 612(s); 1 566(w); 1 392(w); 1 010(s); 812(s).

1.3 Single-crystal X-ray data structure determinations

Single-crystal X-ray diffraction data for **1** was collected on a Rigaku SCXmini diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71 073 nm). The structure was solved by SHELXL-97[12] and refined by full-matrix least-squares on F^2 [13]. All the nonhydrogen atoms were refined anisotropically. The hydrogen atoms on the carbon and nitrogen atoms were located in a Fourier map and refined as riding on their parent C or N atoms. The detailed crystallographic data and structure refinement parameters for the complexes are summarized in Table 1. Selected bond lengths and angles are listed in Table 2 and hydrogen-bonding geometry in Table 3.

CCDC: 880350.

2 Results and discussion

2.1 Crystal structure of complex 1

The title compound was prepared from dimethylammonium chloride and mercury(Ⅱ) chloride in hydrochloric acid solution. X-ray crystal structure of the title complex at 298 K shows that **1** crystallizes in the monoclinic system with space group $P2_1/c$. The packing structure shows novel centrosymmetric one-dimensional coordination chains along the b axis. The N–H⋯Cl hydrogen bonds between the dimethylammonium cations and the anion chain lead to a Two-dimensional network as shown in Fig.2(a).

A view of the complex is shown in Fig.1. Compound **1** consists of two Hg (Ⅱ) atoms, one dimethylamine anion, five chlorine atoms. The two Hg (Ⅱ) atoms in the crystal structure of $[(C_2H_8N)(Hg_2Cl_5)]_n$ are rather similar. Each Hg atom is involved in four Hg-Cl bonds. Two are short with Hg-Cl

Table 1 Crystal data and structure refinement for 1

Formula weight	624.52	Crystal size / mm	0.33×0.28×0.20
Temperature / K	293(2)	θ range for data collection / (°)	3.21~27.48
Crystal system	Monoclinic	Limiting indices	$-13 \leqslant h \leqslant 13, -9 \leqslant k \leqslant 9, -22 \leqslant l \leqslant 22$
Space group	$P2_1/c$	Reflections collected / unique	11 436 / 2 599 (R_{int}=0.106 3)
a / nm	1.041 3(2)	Completeness to θ=27.48°	99.90%
b / nm	0.694 06(14)	Max. and min. transmission	0.119 and 0.012
c / nm	1.708 8(6)	Data / restraints / parameters	2 599 / 0 / 93
β / (°)	112.53(2)	Goodness-of-fit on F^2	1.047
Volume / nm^3	1.140 7(5)	Final R indices ($I>2\sigma(I)$)	R_1=0.057 5, wR_2=0.132 5
Z	4	R indices (all data)	R_1=0.091 6, wR_2=0.144 4
D_c / (g·cm^{-3})	3.636	Largest diff. peak and hole / (e·nm^{-3})	1 438 and −5 037
Absorption coefficient / mm^{-1}	27.995		

Table 2　Bond lengths (nm) and angles (°) for 1

Hg(1)-Cl(2)	0.235 1(4)	Hg(2)-Cl(4)	0.232 3(4)	Cl(3)-Hg(1)^{iii}	0.279 2(4)
Hg(1)-Cl(1)	0.235 4(4)	Hg(2)-Cl(3)^{ii}	0.289 5(4)	Cl(3)-Hg(2)^{iv}	0.289 5(4)
Hg(1)-Cl(3)	0.276 6(4)	Hg(2)-Cl(1)	0.297 5(4)		
Hg(1)-Cl(3)^{i}	0.279 2(4)	Hg(2)-Cl(5)	0.233 5(4)		
Cl(2)-Hg(1)-Cl(1)	162.04(15)	Cl(1)-Hg(1)-Cl(3)^{i}	97.59(14)	Cl(5)-Hg(2)-Cl(3)^{ii}	93.44(13)
Cl(2)-Hg(1)-Cl(3)	96.05(14)	Cl(3)-Hg(1)-Cl(3)^{i}	95.15(8)	Cl(4)-Hg(2)-Cl(1)	97.51(14)
Cl(1)-Hg(1)-Cl(3)	95.10(13)	Cl(4)-Hg(2)-Cl(5)	171.54(14)	Cl(5)-Hg(2)-Cl(1)	88.60(12)
Cl(2)-Hg(1)-Cl(3)^{i}	95.38(13)	Cl(4)-Hg(2)-Cl(3)^{ii}	92.99(14)	Cl(3)-Hg(2)-Cl(1)^{ii}	84.22(11)

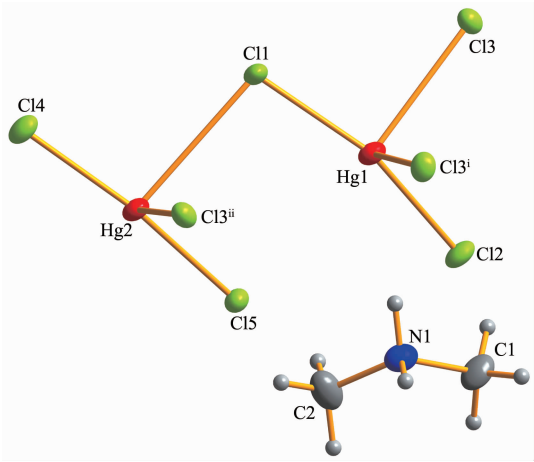
Symmetry transformations used to generate equivalent atoms: ^{i} $-x+1, y+1/2, -z+3/2$; ^{ii} $x, y+1, z$; ^{iii} $-x+1, y-1/2, -z+3/2$; ^{iv} $x, y-1, z$.

Table 3　Hydrogen-bonding geometry

D–H···A	d(D-H) / nm	d(H···A) / nm	d(D···A) / nm	∠DHA / (°)
N1–H1D···Cl4^{i}	0.090	0.249	0.327 3(11)	145.6
N1–H1E···Cl3^{ii}	0.090	0.233	0.320 2(11)	163.7

Symmetry transformations used to hydrogen-bonding: ^{i} $x+1, y, z$; ^{ii} $-x+1, y+1/2, -z+3/2$.

distances of 0.233~0.235 nm and involve terminal Cl atoms. The Hg(Ⅱ) atoms are connected by four Cl atoms among which the Cl1 atoms act as bridges between Hg(1) and Hg(2) centers, and the Cl(3) atom is a node to connect two Hg(1) and one Hg(2) together. It seems that the chain of anion was formed by infinite rings: a 6-number Hg1-Cl2-Hg2-Cl3A-Hg1A-Cl3B ring Fig.2(b). The distance between the Hg1(Hg2) and Hg1(Hg2) ions is 0.6941 nm. The bond length of the terminal Hg1-Cl2 is 0.235 1(4) nm, shorter than the values of Hg-Cl (μ) (0.235 4(4) nm) and Hg-Cl(μ_3) (0.279 2(4) nm). Fifth and sixth Hg-Cl contacts are found for some of the atoms, but these distances are in the order of 0.310 1~0.332 4 nm and are no longer considered to contribute to the bonding as Fig.2 (b). The adjacent chains formed two-dimensional net work by this weak interaction, and the dimethylamine anions were filled between the layers as the bridge connect the chain of anion by N–H···Cl hydrogen bonds.



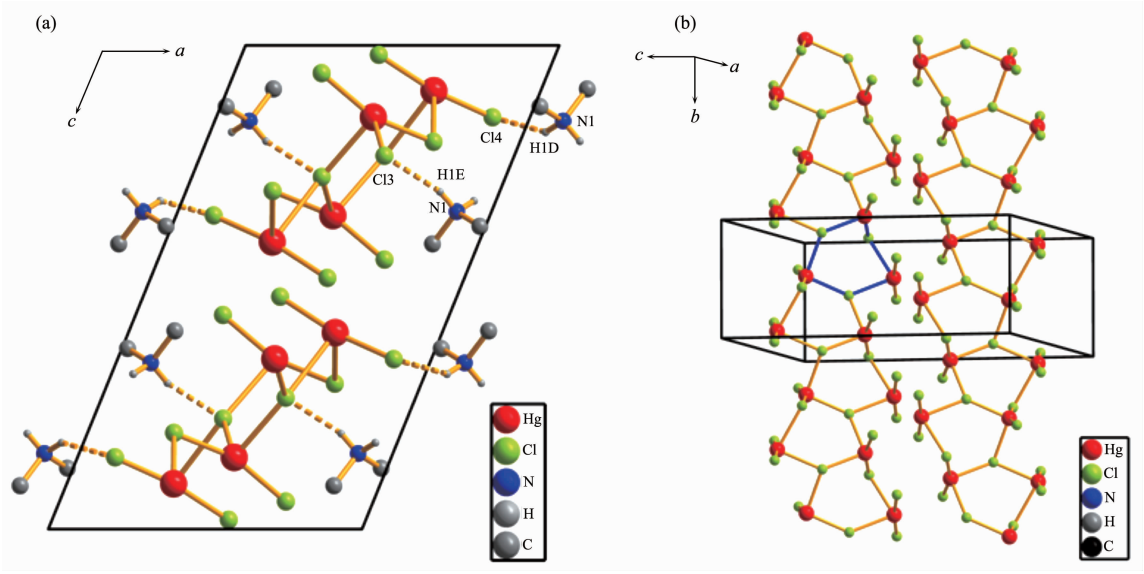
Symmetry code: ^{i} $1-x, 0.5+y, 1.5-z$; ^{ii} $x, 1+y, z$

Fig.1　Coordination environment of the Hg(Ⅱ) ions in **1**, with the displacement ellipsoids drawn at the 30% probability level

In the case of transition metal chloride complexes, the M-Cl moieties can act as good hydrogen-bond acceptors[14-16]. In the title compound, the anions and caions are assembled into a layer structure via N–H···Cl hydrogen bonds between the dimethylamine ligands and Cl atoms as shown in Table 2. Three of the five chlorides in [Hg_2Cl_5] are not engaged in the hydrogen-bonds.

2.2　Dielectric constant

It is known that thermally activated molecular disorder can arouse striking dielectric responses. In order to examine possible structure phase transitions of the title compound, we measured its temperature-dependent dielectric constant. Large dielectric anomalies usually indicate structural changes such as paraelectric-to-ferroelectric phase transitions. However, the temperature-dependent dielectric constant of I at 1 MHz shows no anomalies only with a smooth increases from 10.7 to 11.7 in the measured



6-number ring are shown in blue lines; N1–H1D···Cl4^{i}, N1–H1E···Cl3^{ii}, Symmetry code: ^{i} x+1, y, z; ^{ii} $-x$+1, y+1/2, $-z$+3/2

Fig.2 (a) Packing diagram of $[(C_2H_8N)\text{-}(Hg_2Cl_5)]_n$, viewed down the b axis; (b) 1D structure of $[(C_2H_8N)\text{-}(Hg_2Cl_5)]$

temperature range 130~295 K (Fig.3), together with the dielectric loss tangent ($\varepsilon''/\varepsilon'$) (from 0.006 to 0.003), suggesting no distinct phase transitions occurred[6-7]. This is probably because of the freezing of the molecular disorder in the measured temperature range which is similar to that found in[17-18]. For I, the freezing of the molecular disorder would be activated at a relatively high temperature range. Further studies on these features are in progress.

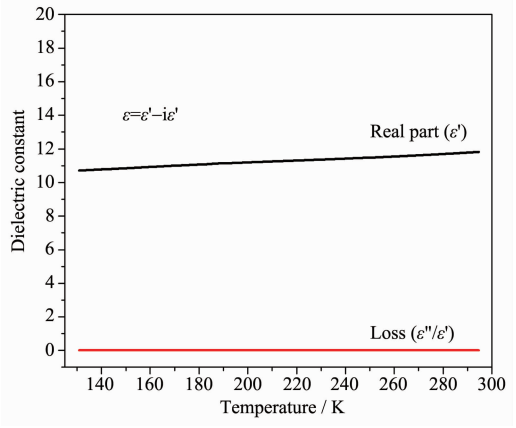


Fig.3 Temperature-dependent dielectric constant of **1** at 1 MHz

3 Conclusions

Compound **1** show a 1D structure which was formed by infinite 6-number rings. Dimethylammonium cations as the bridge connect the 1D chain of anions by N–H···H hydrogen bonds defined a 2D network. There is no notable dielectric anomaly observed between 130 and 295 K, probably because the molecular disorder is frozen in the measured temperature range.

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