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Magneto-structural studies of the bis (1,4-bis (3-aminopropylamine) piperazinium) chloride pentachlorocuprate (II) trihydrate

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ABSTRACT

Bis (1,4-bis (3-aminopropylamine) piperazinium) chloride pentachlorocuprate (II) trihydrate $(C_{10}H_{26}N_4)_2Cl\ CuCl_5.3H_2O$ has been prepared and characterized by various physicochemical techniques including Raman spectroscopy and magnetic properties. A preliminary single crystal X-ray diffraction structural analysis reveals that the title compound belongs to the orthorhombic system with space group Pnma. The unit cell dimensions are: $a = 8.216(9)$, $b = 13.006(8)$, $c = 21.376(20)$ Å, with $Z = 4$. Its crystal structure was determined and refined down to $R = 0.028$. The structure of this compound consists of diprotonated (1,4 bis (3-aminopropyl) piperazinium) cations, polynuclear anions and water molecules. These entities are interconnected by means of hydrogen bonding contacts [N–H…O(Cl), O(W)–H…Cl and O(W)–H…O] forming a three-dimensional network.

Differential scanning calorimetry study was carried out. The Raman of polycristalline samples, have been recorded at different temperatures between 263 and 300 K. A low temperature phase transition at 283 K of order–disorder type was found.

The temperature dependence of the magnetic susceptibility was measured in the temperature range of 2–120 K at different magnetic field intensities. The experimental effective magnetic moment coincides with theoretical one. The results indicate that the complex exhibit weak antiferromagnetic coupling between the copper (II) centers. The ferromagnetic ordering is further confirmed by the presence of hysteresis loops with rapid saturation in the $(C_{10}H_{26}N_4)_2Cl\ CuCl_5.3H_2O$ compounds.

1. Introduction

Halide transition-metal complexes represent a growing class of compounds whose chemistry is currently a topic of intense research.These types of materials are used in microwave devices [1,2] due to their high resistivity, high permittivity and low losses. The hybrid organoammonium halometallate (II) have played a significant role in the development of the understanding of low dimensional magnetic systems and, more recently, of semiconducting materials [3]. With $M = Mn^{2+}$, the systems behave as classical two dimensional antiferromagnets [4], while with $M = Cr^{2+}$ and Cu^{2+}, the spins in the layers order ferromagnetically [5]. The magnetic susceptibility is an important tool for the magnetic characterization of the materials.

One of the best studied groups, both in solution and the solid state, are the halocuprate complexes [6,7]. The large structural variability of Cu (II) due to the presence of an active Jahn–Teller effect in the d^9 electronic system and the relative flatness of the potential surfaces make the thermochromism in chlorocuprates of continual interest. These compounds and their properties are of interest not only in inorganic chemistry but also in fields ranging from solid-state physics to bioinorganic chemistry. Among solid-state physicists and chemists, there is a great interest in the copper (II) halides owing to the plasticity of the metal coordination sphere which leads to a great variety of crystalline architectures with different coordination numbers, geometries and nuclearties, and makes copper systems excellent candidates for analysing correlations between structural parameters and magnetic properties [8,9].

In this paper, we report the preparation, crystal structure and solid-state properties of the compound bis (1,4-bis (3-aminopropylamine) piperazinium) chloride pentachlorocuprate (II) trihydrate. The choice of 1,4-bis (3-aminopropylamine) piperazine base was determined by the presence of two amino groups capable of etablishing strong hydrogen bonds, which involve the chlorine and water oxygen atoms as acceptors and stabilize the

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Table 1
Crystal and experimental data.

Chemical formula: $[C_{10}H_{26}N_4]_2Cl\ CuCl_5.3H_2O$	
Formula weight = 734.98PL	
$T = 274(2)$ K	
Crystal system: monoclinic	Space group: *Pnma*
$a = 8.216(9)$ Å	$\alpha = 90°$
$b = 13.006(8)$ Å	$\beta = 90°$
$c = 21.376(20)$ Å	$\gamma = 90°$
$V = 2284.18(4)$ Å^3	$Z = 4$
$D_x = 1.601$ g/cm^3	
Radiation: ($\lambda = 0.71073$ Å)	
μ (Mo K_α) = 1.68 mm^{-1}	$F(000) = 1140$
Crystal size = 0.75 × 0.08 × 0.02 mm^3	
No. of reflections collected = 13 274	
No. of independent reflections = 1528	
θ range for data collection: 18.48°–26.37°	
Data/restraints/parameters = 1528/0/145	
Goodness-of-fit on F^2 = 1.145	
R indices	
$[I > 2\sigma(I)]$: $R1 = 0.028$, $wR2 = 0.047$	
R indices [all data]: $R1 = 0.037$, $wR2 = 0.051$	
$(\Delta/\sigma)_{\max} = 0.001$	
$(\Delta\rho)_{\max} = 0.445$ e/Å^{-3}	$(\Delta\rho)_{\min} = -0.295$ e/Å^{-3}
Measurement: Bruker SMART CCD	
Program system: SHELXL-97	
Structure determination: SHELXS-97	
CCDC deposit number: CCDC 777203	

crystal structure of the compound. This work is a part of our studies of hybrid organic–inorganic materials based on organoammonium salts of copper (II) halides, in which we are attempting to analyse the influence of the organic cation features (size, shape, nature and position of the substituent) on the packing interactions that govern the crystal organisation and, as a consequence, the properties of this kind of complex [7,8].

2. Experimental

The compound, $[C_{10}H_{26}N_4]_2Cl\ CuCl_5.3H_2O$ was synthesized by dissolving a stoichiometric mixture of 1.4-bis (3-aminopropyl) pyperazine in a concentrated HCl (36%) solution and $CuCl_2$. $2H_2O$ in acetone. The resulting aqueous solution was then kept at room temperature. After several weeks of evaporation, parallelepiped-shaped monocrystals appeared in the solution, which were isolated by filtration and dried in air.

The X-ray single crystal structure for this compound was determined with a Bruker SMART CCD area-detector diffractometer. Experimental conditions used for the single crystal data collection are reported in Table 1. The positional parameters for the copper atoms were obtained from the three-dimensional Patterson map, while the remaining atoms were found from successive difference Fourier map. After introducing thermal displacement parameters for the non hydrogen atoms, the hydrogen atoms were localized and optimized to restraint positions. Their thermal displacement contributions were isotropically introduced into the calculation and fixed. The final anisotropic full-matrix least squares resulted in a convergence of the R factor at 0.028, $Rw = 0.051$ incorporating the weighting scheme $w = 1/[\sigma^2(F_0^2) + (0.0044P)^2 + 17.56P]$ where $P = [\mathrm{Max}(F_0^2, 0) + 2F_c^2]/3$.

DSC measurements were performed on heating samples from 250 to 300 K on a NETZSCH apparatus (Model 204 Phoenix) at a heating rate of 5 K min^{-1}. The FT Raman spectrum of compound was collected on Horiba Jobin Yvon HR 800 accessory spectrometer. The sample was excited with 633 nm line of He–Ne laser. The applied resolution was 0.3 cm^{-1}. The magnetic susceptibility for the prepared samples was measured using a Foner magnetometer equipped with a super-conducting coil in different magnetic field. The temperature dependence of the magnetic susceptibility was measured in the temperature range of 2–120 K at different magnetic field intensities.

Table 2
Atomic coordinates and U_{eq} for $(C_{10}H_{26}N_4)_2Cl\ CuCl_5.3H_2O$.

Atoms	X/a	Y/b	Z/c	U_{eq}
Cu1	0.05411(4)	0.7500	0.841878(16)	0.0232(2)
Cl2	0.04699(6)	0.92780(3)	0.83635(2)	0.0274(2)
Cl1	0.21138(8)	0.7500	0.75302(3)	0.0235(2)
C13	−0.14377(8)	0.7500	0.91673(3)	0.0295(2)
Cl4	0.17483(10)	0.2500	0.42667(4)	0.0370(2)
Cl5	0.99374(15)	0.2500	0.81695(6)	0.0524(3)
N1	0.4600(2)	0.91455(16)	0.81977(9)	0.0299(4)
H1	0.4799	0.8849	0.7830	0.045
H2	0.3873	0.9646	0.8148	0.045
H3	0.4211	0.8679	0.8463	0.045
N2	0.8708(2)	1.01709(15)	0.95359(8)	0.0261(4)
C1	0.6135(2)	0.95836(18)	0.84519(11)	0.0293(4)
H1A	0.6566	1.0088	0.8161	0.035
H1B	0.6936	0.9041	0.8499	0.035
C2	0.5832(2)	1.0089(2)	0.90805(11)	0.0325(5)
H2A	0.5636	0.9560	0.9391	0.039
H2B	0.4859	1.0510	0.9053	0.039
C3	0.7252(3)	1.0761(2)	0.92968(12)	0.0353(5)
H3A	0.7596	1.1189	0.8950	0.042
H3B	0.6869	1.1213	0.9626	0.042
C4	0.8387(2)	0.96265(19)	1.01402(10)	0.0305(5)
H4A	0.7524	0.9127	1.0081	0.037
H4B	0.8028	1.0119	1.0452	0.037
C5	1.0097(3)	1.09130(18)	0.96288(11)	0.0321(5)
H5A	0.9778	1.1434	0.9929	0.039
H5B	1.0333	1.1254	0.9236	0.039
O1	0.3196(5)	0.1050(3)	0.7854(3)	0.0813(17)
H11	0.329(9)	0.133(6)	0.820(5)	0.054(15)
H12	0.376(13)	0.128(7)	0.763(5)	0.062(15)
O2	0.6022(8)	0.7500	0.0398(4)	0.0832(14)
H21	0.597(10)	0.830(7)	0.080(4)	0.067(16)
O3	0.5880(14)	0.2500	0.8428(4)	0.0938(19)
H31	0.497(13)	0.274(5)	0.838(4)	0.059(17)

3. Results and discussions

3.1. Crystallography study

The final atomic coordinates with U_{eq} or U_{iso} are given in Table 2. Interatomic distances, bond angles, and the hydrogen bonds schema are listed in Table 3.

The atomic arrangement of bis (1,4-bis (3-aminopropylamine) piperazinium) chloride pentachlorocuprate (II) trihydrate $(C_{10}H_{26}N_4)_2Cl\ CuCl_5.3H_2O$ is depicted in Fig. 1. The crystal structure shows a layer arrangement perpendicular to the c axis: planes of $CuCl_6$ octahedra alternate with planes of 1,4-bis (3-aminopropyl) piperazinium cations.

As shown on Fig. 1, the anionic sublattice of this crystal is built up of the one-dimensional polyanionic chains composed of distorted octahedra connected with others by corners and extended along the a-axis. The octahedra share the Cl_1 apex forming chains of $[CuCl_5]^{3-}$ in the [100] direction. The mid-planes of $[CuCl_5]^{3-}$ chains are located at $z = 1/4, z = 3/4$.

The $CuCl_5^{3-}$ anion assumes a distorted hexagonal geometry, consistent with the anticipated distortions predicted by the Jahn–Teller effect. These distortions are typically measured by the value of the trans Cl–Cu–Cl angle, which is vary from 88.395(14)° to 176.20(2)° [10]. Each Cu atom is surrounded by (5+1) Cl atoms, five with Cu–Cl distances in the range 2.281(8)–2.3163(5) Å, and the sixth, with a Cu–Cl_1^e distance of 3.470 Å. The Cu–Cl terminal bonds have distances of 2.3163(5), 2.2810(8) and 2.8710(1) Å, the Cu–Cl bridging bonds are Cu–Cl_1 = 2.2973(7) Å and Cu–Cl_1^e = 3.470 Å (5) Å. These values are comparable with those reported by other researchers [11,12].

The interatomic distance between the two nearest copper atoms is 5.684 Å. The nearest non-bonded distances between the copper and halogen atom is 5.769 Å, too far to allow the formation