Crystal Structure and Magnetic Property Studies of a Novel Hybrid Compound ($\text{C}_6\text{H}_{16}\text{N}_2$) CoCl_4

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Abstract 1-(2Aminoethyl) pyrrolidinium tetrachlorocobaltat ($\text{C}_6\text{H}_{16}\text{N}_2$) CoCl_4 has been prepared and analyzed by X-ray diffraction. The compound crystallizes in the orthorhombic system with space group $\text{P2}_1\text{2}_1\text{2}_1$. The unit cell dimensions are $a = 7.3279(13)$, $b = 13.051(2)$ and $c = 13.831(2)$ Å with $Z = 4$. The crystal structure of this salt was solved by Patterson methods and refined by full-matrix least squares on F^2 to the final values of $R = 0.0486$ and $wR = 0.1347$. The structure consists of diprotonated 1-(2aminoethyl) pyrrolidinium cations and monomeric CoCl_4^{2-} . These entities are interconnected by means of hydrogen bonding contacts forming a three-dimensional network. Magnetization was used to investigate the magnetic properties. This compound exhibits an antiferromagnetic (AFM) to paramagnetic (PM) phase transition at a temperature (T_N) lower than 2 K. The values of paramagnetic Curie–Weiss temperature (θ_{CW}) and the exchange parameter (J/K_B) emphasize the existence of an antiferromagnetic interaction between the neighboring cobalt ions.

Keywords Synthesis · Crystal structure · Antiferromagnetic

1 Introduction

The organic–inorganic hybrid materials based on metal halide units have been the subject of many recent investigations because of their interesting structural and magnetic properties [1–5]. The potential applications of these compounds have drawn the attention of numerous scientists due to their catalysis, bioinorganic, biomimetic and coordination chemistry [6]. They have also played a significant role in the development of the understanding of lowdimensional magnetic systems and, more recently, in semiconducting materials [7]. As known magnetic susceptibility is an important tool for the magnetic characterization of the material. One of the beststudied groups of halide transition-metal complexes, both in solution and the solid state, is the cobalt(II) halide complexes. An extensive study has been performed on magnetic compounds in which the 3-d magnetic ions are tetrahedrally coordinated by the ligand [$\text{C}_6\text{H}_{18}\text{N}_3$] [8].

An extensive study has been performed on magnetic compounds in which magnetic and thermal behavior of the series of isostructural *N*-methylmorpholinium compounds $(\text{nmH})_2[\text{MX}_4]$ where $\text{M} = \text{Mn}^{2+}$, Co^{2+} or Cu^{2+} and $\text{X} = \text{Cl}^-$ or Br^- [$\text{nmH} = N$ -methylmorpholinium]. The compounds are all isomorphous and exhibit weak onedimensional antiferromagnetic interaction, with a contribution from singleion anisotropy in the case of the cobalt complexes [9].

In this paper, we report the preparation, crystal structure and magnetic properties of the compound 1-(2aminoethyl) pyrrolidinium tetrachlorocobaltat.

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Table 1 Summary of intensity data collection and structure refinement

Empirical formula	[C ₆ H ₁₆ N ₂]CoCl ₄
Formula weight(g/mol)	316.94
Crystal size(mm ³)	0.24 × 0.15 × 0.1
Crystal system	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	7.3279(13)
<i>b</i> (Å)	13.051(2)
<i>c</i> (Å)	13.831(2)
<i>V</i> (Å ³)	1322.7(4)
<i>Z</i>	4
<i>D_x</i> (g/cm ³)	1.59
<i>F</i> (000)	644
Data collection	
Diffractometer	BRUKER APEX II CCD
Radiation, λ (Å)	0.71073
<i>T</i> (K)	293(2)
θ range(°)	2.2–25.4
Index range	−8 ≤ <i>h</i> ≤ 3 −15 ≤ <i>k</i> ≤ 15 −16 ≤ <i>l</i> ≤ 16
No. of reflections collected	8517
No. of independent reflections	2399
Goodness-of-fit on <i>F</i> ²	1.056
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.049 <i>wR</i> 2 = 0.13
<i>R</i> indices [all data]	<i>R</i> 1 = 0.053 <i>wR</i> 2 = 0.135
(Δρ) _{max} (e/Å ^{−3})	1.209
(Δρ) _{min} (e/Å ^{−3})	−0.571
Program system	SHELXL-97
Structure determination	SHELXS-97

2 Experimental

2.1 Crystal Chemistry

The (C₆H₁₆N₂) CoCl₄ crystals were obtained by dissolving in a concentrated HCl (36 %) solution a stoichiometric mixture of 1-(2-aminoethyl) pyrrolidine and a solution of CoCl₂·6H₂O in a minimum volume of water. The resulting aqueous solution was left to evaporate slowly at room temperature. After several weeks of evaporation, the product separates as crystals, which were isolated by filtration and dried in air. The new compounds show satisfactory elemental analyses.

2.2 Crystal Structure

Intensity data were collected using an Enraf–Nonius Kappa CCD diffractometer with graphite-monochromator (MoK α ,

$\lambda = 0.71073\text{Å}$). The positional parameters for the heavy atoms were obtained from a three-dimensional Patterson map, while the non-H atoms were found from successive difference Fourier maps. The structure was refined by full-matrix least squares using anisotropic temperature factors for all non-hydrogen atoms and the hydrogen atoms were localized and optimized to restraint positions. Calculations were performed with the programs SHELXS and SHELXL [10], using the scattering factors enclosed therein. The crystal data, collected reflections and parameters of the final refinement are reported in Table 1. The final reliability factor converged to *R* = 0.0486 and *wR* = 0.1347.

2.3 Magnetic Measurements

Magnetic measurements were obtained in the temperature range 2–15 K, with an external magnetic field varying from 0.05 to 5 T.

3 Results and Discussion

3.1 Structure Description

The final atomic coordinates with *U*_{eq} of non-hydrogen atoms are given in Table 2. Interatomic distances, bond angles, and the hydrogen bond scheme are listed in Table 3.

The structure of the title compound consists of isolated monomeric [CoCl₄]^{2−} and diprotonated 1-(2-aminoethyl) pyrrolidinium as shown in Fig. 1.

An examination of the structure shows that the atomic arrangement can be described by an alternation of organic and inorganic species. The anionic groups are built up of isolated tetrahedral of [CoCl₄]^{2−} arranged in sandwich between two organic species (Fig. 2).

The anion exhibits tetrahedral geometry, with the Co(II) ion surrounded by four chlorine atoms, with Cl–Co–Cl angles ranging from 102.78(1)° to 117.36(8)°. The mean Co–Cl bond length, 2.28 Å, is close to those observed in similar complex [11, 12].

Generally, the Co–Cl bond lengths and Cl–Co–Cl bond angles in the [CoCl₄]^{2−} anion are not equal to one another, but vary with the environment around the Cl atoms. In the title compound, the Co–Cl₁ and Co–Cl₄ are obviously longer than Co–Cl₂ and Co–Cl₃. The Co–Cl₄ bond length 230(18) Å is the longest one and the Co–Cl₂ bond 226(18) Å the shortest. Owing to the obvious differences in the Co–Cl bond lengths and the Cl–Co–Cl angles, the coordination geometry of the Co atom can be regarded as being a distorted tetrahedron.

A projection of the structure in the plane (*bc*) shows that the organic and inorganic groups alternate, whichever direction is chosen (Fig. 2). In the title compound, the mean plan

Table 2 Atomic coordinates and U_{eq} or U_{iso} for $(C_6H_{16}N_2) CoCl_4$

Atoms	X/a	Y/b	Z/c	U_{eq}^a
Co ₁	0.61928(11)	0.41283(6)	0.17372(5)	0.0433(2)
Cl ₁	0.7812(3)	0.33698(15)	0.29411(11)	0.0628(5)
Cl ₂	0.6397(3)	0.58532(13)	0.18775(15)	0.0737(5)
Cl ₃	0.7304(3)	0.34080(15)	0.03641(12)	0.0640(5)
Cl ₄	0.3092(2)	0.38388(12)	0.18607(12)	0.0563(4)
C ₁	0.4400(12)	0.4897(1)	0.4448(1)	0.081(2)
C ₂	0.4781(15)	0.4054(11)	0.5067(9)	0.117(4)
C ₃	0.325(3)	0.3343(10)	0.4909(11)	0.169(1)
C ₄	0.1670(15)	0.3973(11)	0.4559(1)	0.122(5)
C ₅	0.2155(1)	0.5871(4)	0.3878(4)	0.100(3)
C ₆	0.0722(18)	0.5982(8)	0.3215(6)	0.121(5)
N ₁	0.2654(9)	0.4784(5)	0.3987(4)	0.0696(18)
N ₂	0.6893(4)	0.3229(4)	0.0561(13)	

$$^a U_{eq} = 1/3 \sum \sum U_{ij} a_i a_j a_i * a_j$$

Table 3 Selected bond (Å) lengths and angles (°) and the hydrogen bonding scheme of $(C_6H_{16}N_2) CoCl_4$

Bond lengths (Å)		Angles (°)		
Co – Cl ₁	2,271 (2)	Cl ₂ – Co – Cl ₁	109,63(8)	
Co – Cl ₂	2,264 (2)	Cl ₂ – Co – Cl ₃	117,36(8)	
Co – Cl ₃	2,270 (2)	Cl ₁ – Co – Cl ₃	104,20(8)	
Co – Cl ₄	2,309 (2)	Cl ₂ – Co – Cl ₄	102,78(7)	
		Cl ₁ – Co – Cl ₄	112,85(7)	
		Cl ₃ – Co – Cl ₄	110,31(7)	
C ₁ – C ₂	1,421(2)	C ₁ – N ₁ – C ₅	99,6(6)	
C ₁ – N ₁	1,437(1)	C ₁ – N ₁ – C ₄	105,4(7)	
C ₂ – C ₃	1,474(2)	C ₅ – N ₁ – C ₄	127,7(8)	
C ₂ – N ₂	1,496(8)	N ₁ – C ₄ – C ₃	100,7(9)	
C ₃ – C ₄	1,50(2)	C ₂ – C ₁ – N ₁	111,3(8)	
C ₄ – N ₁	1,505(1)	C ₁ – C ₂ – C ₃	104,4(9)	
C ₅ – N ₁	1,474(8)	C ₅ – C ₆ – N ₂	121,9(8)	
C ₅ – C ₆	1,402(1)	C ₂ – C ₃ – C ₄	106,8(9)	
		C ₆ – C ₅ – N ₁	110,6(6)	
$D - H \dots A$	$d(D - H)$	$d(H \dots A)$	$\angle DHA$	$d(D \dots A)$
N ₁ –H ₁ ...Cl ₄	0,910	2,297	174,89	3,205
N ₂ –H ₂ C...Cl ₂ ^a	0,890	2,406	154,66	3,233
N ₂ –H ₂ D...Cl ₁ ^b	0,890	2,403	149,74	3,203
N ₂ –H ₂ E...Cl ₃ ^c	0,890	2,391	163,64	3,254

^aCode of symmetry: $x-1, y, z$

^bCode of symmetry: $-x+1, y+1/2, -z+1/2$

^cCode of symmetry: $-x+1/2, -y+1, z+1/2$

Fig. 1 Atom numbering scheme for the title compound $(C_6H_{16}N_2)CoCl_4$

through the pyrrolidine ring built up by the atoms (N_1 , C_1 , C_2 , C_3 , C_4) is less planar (r.m.s. deviation = $0.144(1) \text{ \AA}^\circ$). In fact, the conformation of the ethylamine side chain with respect to pyrrolidine ring is usually described by torsion angles $C_1-N_1-C_5-C_6$ (τ_1) and $N_1-C_5-C_6-N_2$ (τ_2). Cation has an extended conformation with $\tau_1 = 164.19(1)$ and $\tau_2 = 156.51(1)$. The C–C bond lengths vary from $1.4(11)$ to $1.5(2) \text{ \AA}$. The C–N bond lengths vary from $1.43(11)$ to $1.50(12) \text{ \AA}$. Table 3 reports the main geometrical features of $(C_6H_{16}N_2)^{2+}$.

In $(C_6H_{16}N_2)CoCl_4$, the organic species interact with the inorganic chains via N–H...Cl hydrogen bonds, forming a three-dimensional network (Fig. 2). All the hydrogen

Fig. 2 Projection in the plane (bc) of the atomic arrangement of $(C_6H_{16}N_2)CoCl_4$

Fig. 3 Variation of the magnetization as a function of temperature for different magnetic fields

bonded to the nitrogen atoms participate in the formation of (N–H...Cl) hydrogen bonding with distances 2.297 to $2.406 \text{ \AA}$. Details of the hydrogen bonding scheme are reported in Table 3.

3.2 Magnetic Properties

In Fig. 3, we have plotted the temperature (T) dependence of magnetization (M) for $(C_6H_{16}N_2)CoCl_4$ compound for different applied fields. The increase of magnetization is due to the orientation of spins in the same direction as the applied magnetic field. Note that the thermal evolution of the magnetization has no maximum that shows that the transition ferromagnetic–paramagnetic took place at the Neel

Fig. 4 Temperature dependence of the inverse susceptibility of $(\text{C}_6\text{H}_{16}\text{N}_2)\text{CoCl}_4$ as a function of the temperature

temperature (T_N) lower than 2 K. The magnetic properties are also shown in Fig. 4, in the form of $\frac{1}{\chi}$ versus T plots. The low temperature magnetic susceptibility data was fit to the Curie–Weiss law, given by $\chi = \frac{C}{(T - \theta_{\text{cw}})}$. The experimental effective paramagnetic moments $\mu_{\text{eff}}^{\text{exp}}$ were calculated from $C = \left(\frac{N_A}{3K_B}\right) \mu_{\text{eff}}^2$, where C , θ_{cw} , N_A , K_B , and μ_B have their usual meanings. The values of C , θ_{cw} , and $\mu_{\text{eff}}^{\text{exp}}$ for the applied magnetic fields are deduced from Fig. 4 and are tabulated in Table 4. On the other hand, the theoretical effective moment can be calculated as follows [13]:

$$\mu_{\text{eff}}^{\text{the}} = g\mu_B \sqrt{J(J+1)};$$

In our case, according to our sample which contains one unpaired electron $\text{Co(II)} (3d^7, S = 5/2)$, we found that the value of the effective moment ($\mu_{\text{eff}}^{\text{the}}$) is the order of $5.91 \mu_B$. Such a difference between the experimental effective moment and the theoretical one can be explained by the existence of shortrange antiferromagnetic correlations in the paramagnetic state [14, 15]. The negative temperatures intercept together with the decrease of the effective magnetic moment and are in agreement with the existence of an antiferromagnetic exchange.

Table 4 shows the variation of experimental effective moment as a function of magnetic field. The observed decrease in effective magnetic moment is due to the spin–orbit coupling [2]. The similar behavior is observed by Issaoui et al. [4]. To investigate other magnetic effects, the

Fig. 5 Hysteresis loops obtained at 2 K temperature

variation of M vs $\mu_0 H$ were carried out and the results indicate that the compound possesses a hysteretic behavior (Fig. 5). This hysteresis is consistent with the observed deviation of the Curie–Weiss law (Fig. 4) since a weak ferromagnetic ordering at low temperatures takes place.

Table 5 summarizes the obtained results from the calculation of the exchange parameter (J/k_B) in order to estimate the order of the exchange interaction between the neighboring cobalt ions using the following equation: $\theta_{\text{cw}} = 2Z(S(S+1))/3(J/K_B)$.

Table 4 Values of the Curie constant, C , the Weiss temperature θ_{cw} , and the experimental magnetic moment $\mu_{\text{eff}}^{\text{exp}}$ ($\text{C}_6\text{H}_{16}\text{N}_2$) CoCl_4

μH	0.05	0.1	0.2	0.3	0.4	0.5	1
C	3.03	2.93	2.92	2.9	2.89	2.88	2.82
θ_{cw}	−3.36	−3.32	−3.3	−3.05	−3.01	−2.95	−2.91
μ_{eff}	4.92	4.89	4.85	4.84	4.81	4.80	4.74

Table 5 Variation of the exchange parameter in $(\text{C}_6\text{H}_{16}\text{N}_2)\text{CoCl}_4$ with applied magnetic field

μH	0.05	0.1	0.2	0.3	0.4	0.5	1
J/k_{B}	−446	−4.51	−4.54	−4.91	−4.98	−5.08	−5.15

The large values of J/k_{B} are suggestive of an antiferromagnetically coupled system with an $S = 3/2$ ground state between the neighboring cobalt ions as expected from the $1/\chi$ versus T plots as well as from the structural data.

4 Conclusion

Treatment of 1-(2-aminoethyl) pyrrolidine ($\text{C}_6\text{H}_{14}\text{N}_2$) with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in aqueous solution gives the organic–inorganic hybrid ionic compound $(\text{C}_6\text{H}_{16}\text{N}_2)\text{CoCl}_4$. The asymmetric unit of $(\text{C}_6\text{H}_{16}\text{N}_2)\text{CoCl}_4$ is constituted by isolated monomeric tetrachloro cobalt(II) and independent 1-(2-aminoethyl) pyrrolidinium cations linked via $\text{N} \cdots \text{Cl}$ hydrogen bonds. The compound crystallizes at room temperature in the orthorhombic space group $\text{P}2_12_12_1$.

Magnetic measurements revealed that the thermal variation of the magnetic susceptibility exhibited an antiferromagnetic interaction between the Co(II) centers which has been confirmed by the values of the exchange parameter. The isothermal magnetization curves with the absence of magnetic hysteresis loops proved the perfect magnetic reversibility of $(\text{C}_6\text{H}_{16}\text{N}_2)\text{CoCl}_4$ compound.

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