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Crystal Structure and Magnetic Property of Cobalt(II) Assembled Compound, $\{[Co(CA)(bipym)](H_2O)_2\}_n$ (H_2CA = chloranilic acid, bipym = 2,2′-bipyrimidine)

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Cobalt(II) assembled complex compound, $\{[Co(CA)(bipym)](H_2O)_2\}_n$($H_2CA$ = chloranilic acid, bipym = 2,2′-bipyrimidine) (**1**) has been synthesized and structurally characterized by single-crystal X-ray diffraction. Compound **1** crystalizes in the monoclinic, space group *C2/c*(#15), with $a = 16.652(4)$ Å, $b = 11.163(3)$ Å, $c = 10.081(3)$ Å, $\beta = 116.12(2)°$, $V = 1682.4(7)$ Å^3, $Z = 4$. The bipym ligands bridge the cobalt centers in bis-bidentate fashion and make zigzag chains. The chains form layer structures by stacking interaction and hydrogen bonding interaction with the help of interstitial water molecules. The temperature dependence of the magnetic susceptibility of **1** shows intramolecular antiferromagnetic interaction with $\theta = -39.7$ K.

Keywords: chloranilic acid; metal assembled complexes; 2,2'-bipyrimidine

INTRODUCTION

The crystal engineering of metal assembled complex structures with novel electronic, optical, magnetic and catalytic properties is a new challenge to chemical synthesis[1-3]. Self-assembly technique is an effective way to utilize the weak interactions between molecules to create a more complex superstructure or supramolecular system[3,4]. The predictable self-

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organization of molecules into multi dimensional networks is of the utmost importance in crystal engineering. The Strategy for designing of desired crystal architectures relies on the use of suitable ligands. Especially, bridging ligands have advantages to prepare polymeric structures having magnetic properties. Chloranilic acid (H_2O), is one of the polyoxo carbon compounds, affording one dimensional chains of various metal ions[5] and 2,2'-bipyrimidine is wel-known linking ligand, has a remarkable ability to mediate strong antiferrimagnetic interactions[2]. Transition metal-bipym assembled compounds show variable magnetic properties depending on the coordination nature of bipym. Extending the scope of using of these mixed ligands novel layered compound of cobalt is synthesized with the help of hydrogen bonding and stacking interactions. To our knowledge, this is the first bipym-bridged 1-D base assembled structure of Co(II). In this report crystal structure and magnetic property of the compound is described.

EXPERIMENTAL

Synthesis of $\{[Co(CA)(bipym)](H_2O)_2\}_n$ (1)

An aqueous solution of cobalt sulfate heptahydrate ($1x10^{-3}$ M) was transferred to a glass tube, then an ethanol-water mixture of 2,2'-bipyrimidine ($1x10^{-3}$ M) and chloranilic acid ($1x10^{-3}$ M) was poured into the tube without mixing the two solution. Red-purple plate crystals began to form at ambient temperature in a week.

Crystallographic Data Collection and Refinement of the Structure 1

A violet crystal having approximate dimensions of 0.20 x 0.10 x 0.10 mm was chosen and mounted on glass fiber with epoxy resin. Data collection of compound **1** was carried out on a Rigaku AFC7R four-circle diffractometer with graphite monochromated Mo-Kα radiation. The structure was solved by direct methods (Rigaku TEXSAN crystallographic software package of Molecular Structure Corporation).

Full-matrix least-squares refinements were carried out with anisotropic thermal parameters for all non-hydrogen atoms. The final cycle of full-matrix least-squares refinement was based on No and n variable parameters and converged with unweighted agreement factors of $R = \sum||F_o|-|Fc|| / \sum|F_o|$, $Rw = |\sum(|F_o|-|F_c|)^2 / \sum w |F_o|^2|^{1/2}$ where $w = 1/\sigma^2(F_o) = |\sigma_c^2(F_o) + p^2/4\ F_o^2|^{-1}$ and $p = 0.02$. Crystal Data of **1**. $Co N_4Cl_2C_{14}O_6H_{10}$, fw = 460.045, monoclinic, space group $C2/c$ (#15), with a = 16.652(4) Å, b = 11.163(3) Å, c = 10.081(3) Å, β = 116.12(2)°, V = 1682.4(7) Å^3, Z = 4, T = 23°C, μ(Mo Kα) = 13.80 cm^{-1}, λ(Mo Kα) = 0.71069 Å, n = 123; N, No ($I > 3\sigma(I)$) = 2035, 1373; R, Rw = 0.040, 0.041, GOF = 1.43.

Magnetic susceptibility measurement

Magnetic susceptibility data were recorded over the temperature range from 2 to 300 K at 1 T with a SQUID susceptometer (Quantum Design, San Diego, CA). All data were corrected for diamagnetism which were calculated from Pascal's table.

RESULT AND DISCUSSIONS

Crystal structure

The structure of complex **1** is made up of CA^{2-} and bipym coordinated neutral [Co(CA)(bpm)] unit and two interstitial water molecules. The crystal structure of **1** with atom numbering scheme is shown in Figure 1. The geometry around the cobalt ion is a distorted octahedron, where each cobalt ion is bound to four nitrogen atoms belonging to bipym and two oxygen atoms from a CA^{2-} anion. Cobalt to nitrogen and oxygen bond distances are: Co-N(1), 2.162(3) Å; Co-N(2), 2.136(3) Å and Co-O(1), 2.065(3) Å. The bipym coordinate *cis* position each other and serves as a bridging ligand between cobalt centers, which lead to infinite chains exhibiting a zigzag pattern along the c axis. The Co-N(bipym) bonds of **1** are shorter than Mn-N(bipym) bonds[6] and longer than Cu-N(bipym) bonds[7]. These results are expected from the metal ion radii (Cu^{2+},

0.870; Co^{2+}, 0.885; and Mn^{2+}, 0.970 Å). The pyrimidal rings of bipym are planar as is the ligand as a whole. Å@The zigzag chains of $[Co(bipym)(CA)]_n$ are interlinked by two types of hydrogen bonds between the interstitial water molecules and the oxygen atoms of CA^{2-} on the adjacent chain, forming a two dimensional sheet, spreading

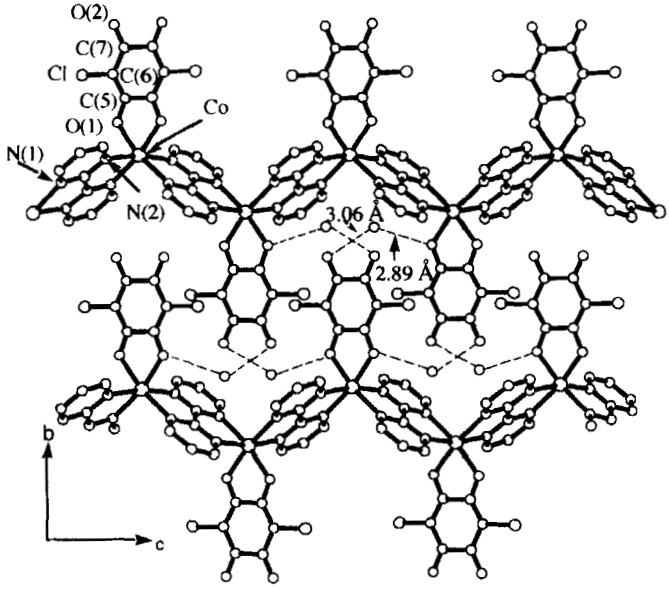

Figure 1. Crystal structure of **1** with the atom numbering scheme. Selected Bond Distances (Å) and Angles (°); Co-O(1), 2.065(3); Co-N(1) , 2.162(3); Co-O(3), 2.136(3); O(1)-Co-N(1), 169.1(1); O(1)-Co-N(2), 90.9(1); N(1)-Co-N(2), 94.1(1).

along the *bc* plane. The first type of hydrogen bonding occurs between the interstitial water molecules and the coordinated oxygen atoms on the CA^{2-} anion with a distance of 2.89 Å. The second type of the hydrogen bonding involves the interstitial water molecules and the free oxygen atom on CA^{2-} dianion (3.06 Å). Stacking interaction (3.6 Å) between the chloranilate rings also help the chains to make layer structure. 2,2'-

bipyrimidine-linked dinuclear compounds[8] and honeycomb sheet like structures[9] of Co(II) are reported. In the later case, the 2-D sheets are formed with alternating double end-on azide and bipym bridging groups. In **1** the layer structure is made of purely bipym-linked 1-D chains.

Magnetic properties

The magnetic susceptibility (χ) of **1** was measured over temperatures of 2-300 K. The magnetic property of the complex in the form of χ_m and $1/\chi_m$ versus T are depicted in figure 2. The χ_m versus T curve show maxima at 15.0 K and $1/\chi_m$ versus T plot intersects at the negative

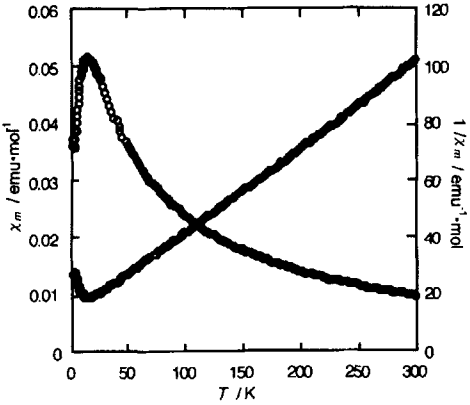

Figure 2. Plots of observed $\chi_m T$ and $1/\chi_m$ vs T

value (θ = - 39.7 K). The occurrence of maxima in susceptibility curve and negative value of Weiss constant is indicative of bpiym mediated intramolecular antiferromagnetic interaction between the paramagnetic cobalt centers. Similar antiferromagnetic interaction is observed in some bipym-bridged dinuclear compounds of Co(II)[8].

CONCLUSION

The bipym-bridged 1-D chains of **1** make novel layered structure by hydrogen
bonding and stacking interactions. One of the striking features is that the stacking direction of CA^{2-} is alternative and parallel to the direction of coordination-bonded chains. Hydrogen bonding and stacking interactions can be used to provide dynamic properties concerning electron or charge transfer through hydrogen bonds and stacking plane. By proper reduction of the compound, electrical conductivity maybe induced with the existing magnetism in the same structure. Therefore, this step will afford a strategy to synthesize advanced materials with multifunctional properties.

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