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Synthesis, growth, spectral, optical and thermal properties of a novel metal–organic family single crystal: Bis (thiocyanato) cobalt(II) di thiourea

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ABSTRACT

Single crystals of bis(thiocyanato) cobalt(II) di thiourea $[Co(NCS)_2(N_2H_4CS)_2]$; BTCT were grown from an aqueous solution using slow evaporation technique for the first time. Interestingly, Co^{2+} ion present in the crystalline compound connects two N atoms of thiocyanate and four S atoms of thiourea ligands. The bridging thiourea ligands link Co ions into a one dimensional polymeric chain along [1 0 0] direction. Single crystal XRD shows that the BTCT crystal belongs to triclinic system with the space group $P\bar{1}$. BTCT single crystals were subjected to FT-IR, Laser Raman, UV–vis, CHNS, TG-DTA and DSC studies. The optical study shows that the UV cut-off wavelength of BTCT in ethanol–water mixed solvent is about 310 nm. The thermal analysis of BTCT reveals that the sample is thermally stable up to 196.01 °C. The VSM study shows that Co^{2+} in BTCT possesses higher coercivity (32.414 μCi) and retentivity (654.62E-6 emu/g) than Mn^{2+} of $[Hg(N_2H_4CS)_4Mn(SCN)_4]$; TMTM.

1. Introduction

Recently, scientists and researchers have turned their attention toward the metal–organic coordination compounds of transition metals with the incorporation of both thiourea and thiocyanate ligands as they have flexibility to tune the molecular architecture and topology of the resulting crystalline compound, often generating from one dimensional chain to even three dimensional networks. Such metal–organic coordination compounds will have a rapid change in their physicochemical properties including non-linear optical behavior [1–11]. It is a known fact that the thiocyanate $(SCN)^-$ is a highly versatile ambidentate ligand with two donor atoms that can coordinate to metals through either the nitrogen (N) or the sulfur (S) or both. In fact, there are many modes of coordination of the SCN ligand to metals that may be either terminal or bridging [12]. The modes of metal coordination of thiocyanate ligand could very well be inferred on the basis of Pearson's hard-soft acid-base concept. In addition, thiourea molecules have large dipole moment and have the ability to form extensive network of hydrogen bonds [13–15]. In this context, an effort was made to combine Co^{2+} metal ion with both thiourea and thiocyanate ligand so as to get a new crystalline compound with desired physico-chemical properties. As a result, a new class of metal–organic crystalline compound namely, Bis(thiocyanato) cobalt(II) di thiourea $[Co(NCS)_2(N_2H_4CS)_2$; BTCT] was synthesized and characterized for the first time. In BTCT, Co^{2+} being a hard acid preferentially coordinate to the hard base (N) of SCN and in turn thiocynate acts as a monodentate ligand. In addition, the incorporation of both thiocyanate and thiourea ligands with reference to the Co^{2+} metal centre forms a one dimensional polymeric chain along [1 0 0] direction. The crystal structure of BTCT was already solved and reported by our research group (IUCr Ref. TK5133) [16]. BTCT is isostructural with the previously reported crystal structure Bis(thiocyanato) cadmium (II) di thiourea $[Cd(NCS)_2(N_2H_4CS)_2]$ [17]. In the present work, the grown crystals of BTCT were subjected to Single crystal X-ray diffraction, FT-IR, Laser Raman, and CHNS analysis. The UV–vis, TG-DTA, DSC and VSM studies were also carried out on the samples to understand the optical, thermal and magnetic behavior of BTCT, respectively and the results are systematically reported.

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2. Experimental

2.1. Materials

All the raw materials ($CoCl_2{\cdot}6H_2O$, NH_4SCN and N_2H_4CS) used in the growth process were as purchased and of analytical reagent grade (MERCK).

2.2. Synthesis and growth of BTCT

The title compound (BTCT) was synthesized as per the following equation

$$CoCl_2{\cdot}6H_2O + 2NH_4SCN + 2N_2H_4CS \rightarrow Co(NCS)_2(N_2H_4CS)_2 + 2NH_4Cl$$

The calculated amounts of salts as shown above were dissolved in de-ionized water at ambient temperature and stirred for an hour in a magnetic stirrer in order to get homogenous solution. Then the colored solution was filtered and its pH was adjusted to an optimum value of 3.5 and finally kept in a glass beaker for slow evaporation. The dark brown single crystals of BTCT were obtained from mother solution after two weeks. The dark brown color of the crystal is due to the characteristic nature of cobalt (II) ions incorporated in the resulting crystalline compound. However, the color of the sample is a setback for optical applications. The as grown flat and axially grown crystals of BTCT are shown in Fig. 1a and b.

2.3. Structure of BTCT

The structural aspects BTCT gains importance as it possesses both thiourea and thiocyanate ligands with the transition Co^{2+} metal ion. The Co^{2+} is located at the inversion centre and is octahedrally coordinated by two N atoms from two thiocynate and four S atoms from four thiourea molecules (Fig. 2). The bridging thiourea ligands link Co^{2+} ions into a one dimensional polymeric chain along [1 0 0] direction. The Co ... Co distance along the chain is 3.855 (3) Å. The octahedral coordination sphere of the cobalt (II) cation is slightly distorted with the distances in the range 2.016 (1) Å to 2.623 (1) Å. The thiocyanate ligand is almost linear with the bond angles N1-C1-S1 (179.2°), N1-Co-N1" (180°) and S2"-Co-S2 (180°). As per Hard Soft Acid Base (HSAB) rule, it is clearly observed that the Co ion being a hard acid is always coordinated with the hard base (N) of thiocynate ligand. The Co—N (NCS) bonds (2.0158 (10) Å) observed in BTCT is consistent with the corresponding bond lengths observed in $Co(NCS)_2(PPz)_2(CH_3OH)_2$; (Co—N (NCS) = 2.104 (4) Å) [18] and $[CoHg(SCN)_4(HCONHCH_3)_2]$; (Co—N (NCS) = 2.113 (19) Å) [19]. The selected geometric parameters of BTCT are listed in Table 1. The linear polymeric chain is extended along [1 0 0] direction with reference to Co^{2+} as shown in Fig. 3.

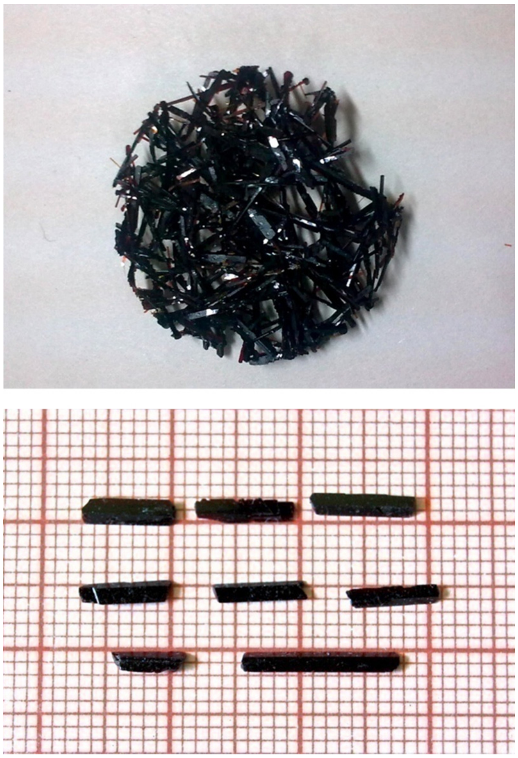

Fig. 1. (a) and (b) As grown single crystals of BTCT.

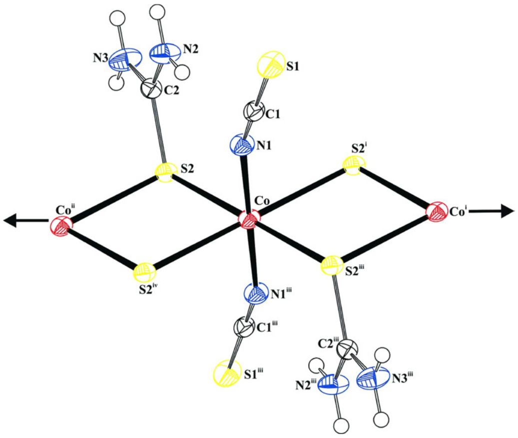

Fig. 2. Molecular structure of BTCT.

3. Results and discussion

3.1. Single crystal XRD

Single crystal X-ray diffraction analysis was carried out on BTCT using Bruker Kappa APEX II CCD diffractometer with graphite monochromated Mo-$K\alpha$ radiation (0.71073 Å). BTCT crystallizes in a centrosymmetric triclinic crystal system with the space group $P\bar{1}$ [16]. The unit cell parameters of BTCT are presented in Table 2.

3.2. CHNS test

The powdered sample (6.464 mg) of BTCT was subjected to elemental analysis using Vario EL III Elemental Analyzer, GERMANY so as to estimate the influence of each element (N, S, C, H) in the resulting compound. The experimental weight % values are comparable with the theoretically calculated values as listed in Table 3.

3.3. FT-IR studies

The functional groups of BTCT were confirmed from the transmission spectral profile (Fig. 4) recorded in the range 4000–400 cm^{-1} using Thermo Nicolet 6700 Model Spectrometer. The incorporation of both thiourea and thiocyanate ligand in BTCT were well identified as listed in Table 4. It is a well-known fact that the reliable data on bonding modes of thiocyanate ligand can be obtained mostly from Infrared spectroscopy. The S- or N- coordinated thiocyanate lignad gives significantly different shifts of absorption bands not only in relation to each other, but in comparison with the non-coordinated thiocyanate anion as well. Even, the positions of the frequencies can also be influenced by changes