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Synthesis and Magnetic Property of a New Dialkoxo-Bridged Bicobalt(II) Complex with Triethanolamine as Ligand

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Ethanolamines are a class of organic molecules containing amine and alcohol groups, and are also versatile ligands that readily form coordination compounds with almost all metal ions and behave as N and O-donor ligands. Their transition metal complexes have been synthesized and characterized [1–3]. In some cases, ethanolamines lose their ethanolic hydrogen being as ethanolaminate anions, which as multidentate ligands form homo- and heteropolymetallic ethanolaminate derivatives of a number of metal have been reported recently [4–6]. As an extension of that investigation, in this communication we report the synthesis, magnetism and spectral character of a new alkoxo-bridged dicobalt(II) complex, $Co_2(\mu\text{-tea})_2(NCS)_2$, where tea = triethanolaminate anion. For the magnetic analysis, the data reveal a good fitting between experimental and theoretical values, and the complex implied an antiferromagnetic coupling between the paramagnetic ions.

All chemicals were of analytical grade and were purchased from the Peking Chemical Company. $Co_2(\mu\text{-tea})_2(NCS)_2$ was synthesized as follows: To 485.9 mg (5 mmol) KSCN dissolved in 10 cm^3 of distilled water was added 10 cm^3 distilled water solution of 1189.7 mg (5 mmol) $CoCl_2{\cdot}6H_2O$. While stirring the mixture for several minutes, 746.0 mg tea (5 mmol) was dissolved in 10 cm^3 of distilled water and mixed with the previously prepared KSCN-$CoCl_2$ solution. Purple precipitates formed immediately. After stirring for 2 h at room temperature, the product was filtered and then collected by suction filtration, washed several times with absolute ethanol and ether, and dried *in vacuo*. Anal. Calcd. for $C_{14}H_{28}N_4O_6S_2Co_2$: C, 31.7; H, 5.3; N, 10.6. Found: C, 31.3; H, 4.9; N, 10.6.

Elemental analyses of carbon, hydrogen and nitrogen were carried out on a Perkin-Elmer analyzer, Model 240. The infrared spectrum was recorded with a Perkin-Elmer IR spectrophotometer Model 983G, using KBr pellets. UV-Vis spectrum was recorded on a Perkin-Elmer Hitachi-240 spectrophotometer. Variable temperature magnetic susceptibilities (4.9–300 K) were performed at the Institute of Physics, Chinese Academy of Science, using a Superconducting Quantum Interference Device

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(SQUID) magnetometer in an applied magnetic field of 10000G. The molar conductance was measured with a DDS-11A conductometer. The diamagnetic corrections were made with Pascal's constants for all the constituent atoms, and the magnetic moments were calculated using the equation $\mu_{eff} = 2.828\ (\chi_M T)^{1/2}$.

It is known from the crystal structure determination of $Cu_2(\mu\text{-dea})_2(NCS)_2$ [3] that the dea ligand is in the deprotonated form by loosing one ethanolic H and acts as a bidentate donor through its N and deprotonate O. The other ethanolic group is not involved in coordination geometry. Considering the structure resemblance, Co(II)–Co(II) binuclear complex, $Co_2(\mu\text{-tea})_2(NCS)_2$, is obtained by using Co(II) ion and tea instead of Cu(II) ion and dea, respectively. For the complex, analytical data indicate that the reaction of tea with $CoCl_2{\cdot}6H_2O$ and KSCN yielded the binuclear complex. The molar conductance value is 45 $\Omega^{-1}{\cdot}cm^2{\cdot}mol^{-1}$ in DMF, which falls in the expected range for non-electrolytes, indicating that both thiocyanate anions are located inside the metal coordination sphere [7]. The infrared spectrum of the complex presents strong absorption band at 2080 cm^{-1} for the $\nu(CN)$ vibration and medium band at 890 cm^{-1} for the $\nu(CS)$ vibration. The stretching vibrations of the CN and CS groups shift significantly to higher frequencies in the complex, as indicated by $\Delta\nu(CN) = 35\ cm^{-1}$, compared to free SCN group ($\nu(CN) = 2045\ cm^{-1}$ and $\nu(CS) = 751\ cm^{-1}$). This finding indicates the coordination of the SCN group through the nitrogen, resulting in the formation of isothiocyanate complexes [8], as supported by the single crystal X-ray studies reported elsewhere [9]. In addition, the metal complex of tea exhibits a broad band near 3400 cm^{-1}, which indicates that some of the OH groups are not coordinated with the iron in the complex of tea. But a broad absorption at 2550 cm^{-1} is found, which is assigned to the stretching vibration of the OH group, $\nu(OH)$. On the other hand, $\delta(OH)$ for the coordinated OH group is also present at 1160 cm^{-1} in the binuclear complex, which indicates that at least one OH group in the tea is involved in coordination geometry [3,10,11]. The result is consistent with the measured conductance data. Moreover, the splitting of the CH stretching absorption bands occurs at the 2976 cm^{-1} and 2920 cm^{-1}. The weak band at 430 cm^{-1} is due to Co–O stretching vibration, and Co–N absorption at 260 cm^{-1} is also found.

The data of electronic absorption spectra of the complex in DMF exhibit a strong absorption at $37.4{\times}10^3\ cm^{-1}$ in the UV range and a weak absorption at $18.1{\times}10^3\ cm^{-1}$ in the visible range. The former may be attributed to the charge-transfer absorption band and the latter to the d-d transitions [12]. Based on the composition, IR and electronic spectrum, the complex is proposed to have dialkoxo-bridge structure and consist of the cobalt(II) ions in an octahedron environment, as shown in Fig. 1.

Meanwhile, variable-temperature (4.9–300 K) magnetic susceptibilities data were collected for a microcrystalline sample of $Co_2(\mu\text{-tea})_2(NCS)_2$. The χ_M *versus* T plots is shown in Fig. 2. The magnetic moments decrease with decreasing temperature, implying the existence of an antiferromagnetic coupling of dicobalt(II) complex. In order to understand quantitatively the magnitudes of spin-exchange interaction, variable-temperature magnetic susceptibility data were analyzed for the binuclear(II) complex, and the magnetic analysis was carried out with the susceptibility

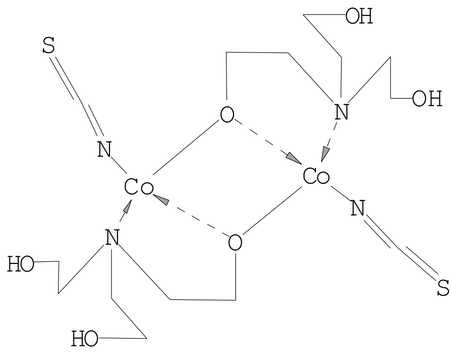

Figure 1. Tentative structure for the complex.

equation based on the Heisenberg spin-exchange operator $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$. The molar susceptibility of the Co(II)–Co(II) ($S_1 = S_2 = 3/2$) system is given by (1)

$$\chi_M = (2Ng^2\beta^2/kT)(A/B)(1-\rho) + 0.9375g^2\rho/T \tag{1}$$

$$A = 14 + 5\exp(-6J/kT) + \exp(-10J/kT)$$

$$B = 7 + 5\exp(-6J/kT) + 3\exp(-10J/kT) + \exp(-12J/kT),$$

where χ_M denotes the susceptibility per binuclear complex, ρ is the fraction of uncoupled cobalt(II) impurity and the remaining symbols have their usual meanings. As shown in Fig. 2, good fits to the experimental data are attained with (1). For the complex, $Co_2(\mu\text{-tea})_2(NCS)_2$, the magnetic parameters thus determined are $J = -0.50\ cm^{-1}$, $g = 2.16$, $\rho = 0$. The agreement factor F defined here as $[(\chi_M T)_{obs.} - (\chi_M T)_{calc.}]^2/(\chi_M T)_{obs.}$ is then equal to 7.68×10^{-5}. This result (negative, small J values) indicates that the complex undergoes a weak antiferromagnetic spin-exchange interaction between the metal ions.

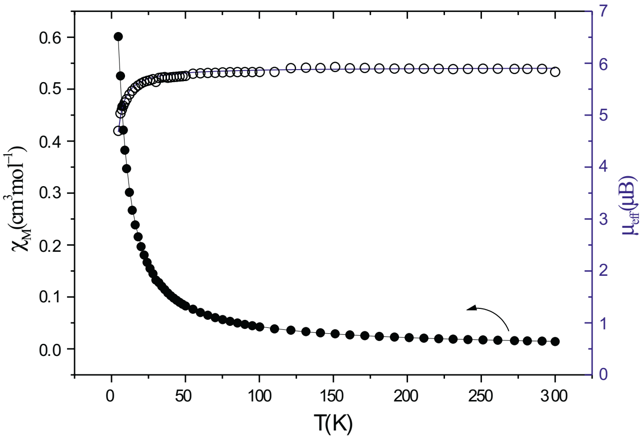

Figure 2. Temperature variation of the experimental and calculated magnetic susceptibility and magnetic moment of $Co_2(\mu\text{-tea})_2(NCS)_2$.

In conclusion, this communication presents several appealing aspects: (i) the self-assembling of the tea, Co(II) and SCN^- constituents; (ii) the tentative structure of the compound is corresponding to the analysis data in this paper and from others [11,13]; (iii) finally, antiferromagnetic nature of Co(II)–Co(II) interaction through alkoxo-bridge. We intend to develop the crystal and to explore further the physics of this compound.

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