Synthesis and Characterization of a Tetrahedral and Octahedral Cobalt(II) Alternate Chain Complex

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Reaction between Co(II) ion and 4-phenoxybenzoate (L) under hydrothermal conditions gives a one-dimensional coordination polymer, $[Co_2L_4]$. $[Co_2L_4]$ consists of dinuclear motifs of pseudo octahedral $\{CoO_6\}$ and tetrahedral $\{CoO_4\}$ linked through μ-carboxylate ligands. The temperature dependence of magnetic susceptibility revealed the presence of ferromagnetic interaction between the adjacent tetrahedral Co(II) and octahedral Co(II) ions.

Synthesis and characterization of metal-organic hybrid materials using the concept of supramolecular engineering represents one of the most active research areas in the chemistry and material science.[1–3] One of the current challenges is to prepare metal clusters or low-dimensional materials which exhibit unique magnetic and/or optical properties.[4–12] Co(II) ion is one of the candidates to provide above-mentioned feature because of (a) variable coordination geometries (i.e., octahedral and tetrahedral), (b) significant stability in the air, (c) two spin states ($s = 3/2$ and $1/2$) depending on the ligand field, (d) different electronic structures and color, and (e) large orbital moment through a spin-orbit coupling in octahedral geometry. One of our objectives is to construct new type of framework using Co(II) and carboxylate ligands and investigate its magnetic properties. We have adopted the hydrothermal technique for the preparation of metal-organic framework polymers of various polycarboxylate ligands.[13–17] Here we report the synthesis, crystal structure and the preliminary magnetic behavior of a one-dimensional Co(II) chain compound, $[Co_2L_4]$, constructed by alternate array of tetrahedral Co(II) and octahedral Co(II) units.

$[Co_2L_4]$ was obtained by the hydrothermal reaction of $Co(NO_3)_2 \cdot 6H_2O$, NaOH, and 4-phenoxybenzoic acid in a Teflon lined autoclave at 120 °C for 3 d. The resulting violet crystals were washed with water and acetone and dried in the air (yield 60%).

The X-ray structure analysis of $[Co_2L_4]$ revealed the formation of one-dimensional chain structure constructed from dinuclear complex motifs.[18] The asymmetric unit consists of two types of cobalt ions and two types of 4-phenoxybenzoate ligands. The crystallographically independent Co(1) and Co(2) constitute the dinuclear motif (Figure 1). Co(1) exhibits a slightly distorted tetrahedral geometry comprising of four oxygen atoms of 4-phenoxybenzoate ligands. The O–Co–O bond angles in the distorted $\{CoO_4\}$ tetrahedral site range from 100.7(1)° to 116.85(9)° (av 108.8°) and bond distances range from 1.944(2) to 2.011(2) Å (av 1.98 Å). On the other hand, Co(2) shows an axially elongated octahedral geometry comprising of six oxygen atoms of 4-phenoxybenzoate ligands. The Co(2)–O(4) bond distance is the longest (2.206(2) Å) in the $\{CoO_6\}$ octahedral site since O(4) bridges Co(1) and Co(2) in a μ^2-mode. Furthermore, Co(1) and Co(2) are connected by two other 4-phenoxybenzoate ligands in a *syn*, *syn* mode affording the dinuclear motif. The Co(1)···Co(2) intermetallic separation is 3.1763(3) Å. In the crystal lattice, $[Co_2L_4]$ forms a zigzag chain structure by the alternate array of the tetrahedral Co(II) and octahedral Co(II) units along *a* axis (Figure 2). The shortest Co···Co distance is

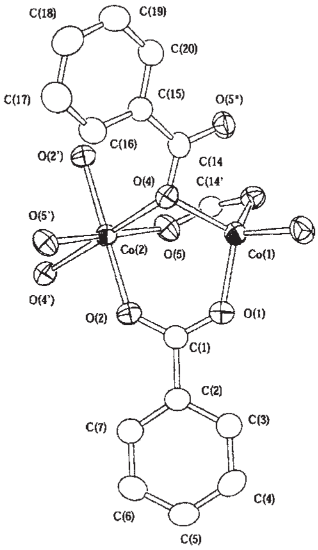

Figure 1. ORTEP drawing of dinuclear motif of $[Co_2L_4]$ with atomic numbering scheme. Hydrogen atoms and phenoxy groups are omitted for clarity.

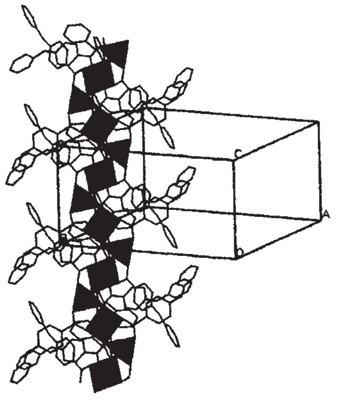

Figure 2. Zigzag chain structure of $[Co_2L_4]$.

13.4 Å. The 4-phenoxybenzoate groups are fanning out from the backbone like rungs of a ladder.

The infinite chain structure of [Co_2L_4] with the alternate array of {CoO_4} and {CoO_6} relates to a unique magnetic property of this compound. Isothermal magnetization measurements on the polycrystalline sample at 2 K exhibit a rapid increase in magnetization value suggesting a tendency of long range magnetic ordering. The magnetization is saturated in the field of $H > 2T$ and the value of ca $6\,\mu_B$ is in good agreement with ferromagnetically coupled two high-spin Co(II) centers. The magnetic susceptibility of a polycrystalline sample in an applied field of 100 Oe behaves as a Curie–Weiss paramagnet in the temperature range of $T > 50$ K, with a Curie constant of 5.25 cm^3 K/mol and a Weiss constant of 13.3 K. (Figure 3) The positive Weiss constant indicates ferromagnetic interaction between the nearest neighbors. The effective magnetic moments of [Co_2L_4] at 300 K is 6.59 μ_B, which are larger than the spin-only value of 5.48 μ_B for two Co(II) ions because of a large orbital contribution of Co(II) ion in a near octahedral surrounding. The $\chi_m T$ value gradually increases with decreasing temperature and then more rapidly below 5 K. This behavior is consistent with the positive Weiss constant. The ferromagnetic coupling between Co(1) and Co(2) may be interpreted by an orthogonarity between the magnetic orbitals of octahedral Co(II) and tetrahedral Co(II) through vertex sharing oxygen atoms. Another possibility is the antisymmetric interaction due to the low symmetry of the dinuclear subunit. This may result in a ferromagnetic zigzag chain.[7,19] In an applied field of 5 Oe the ZFCM-FCM dc data shows a rapid increase below 5 K. The FCM and ZFCM magnetic susceptibility data obtained for [Co_2L_4] overlie each other over the temperature range from 3.5 K to 30 K. AC susceptibility measurements show a rapid increase of χ' value; however, χ'' value remains constant down to 2 K. The sharp rise in magnetization, FCM and χ' value at low temperature region suggest a tendency of long range magnetic ordering below 2 K. These results are well agreement with one-dimensional structure of [Co_2L_4]. One-dimensional ferro- or ferrimagnets are considered as important target molecules of molecular magnetism due to their unique magnetic properties.[12] Further works are now in progress to prove the magnetic ordering and/or spin dynamics in [Co_2L_4].

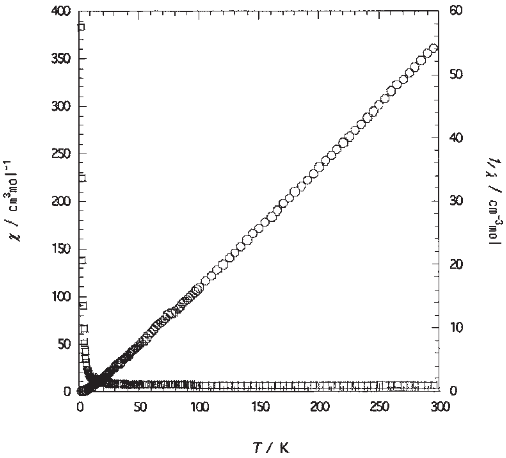

Figure 3. Temperature dependence of magnetic susceptibility of [Co_2L_4].

In conclusion, compound [Co_2L_4] is a unique example of a structurally characterized zigzag 1-D coordination polymer comprising of a tetrahedral Co(II) and an octahedral Co(II) ions. The arrangement of the polyhedron yields the ferromagnetic coupling between cobalt(II) centers. In our knowledge, one-dimensional coordination polymer consisting of alternate structure of tetrahedral Co(II) and octahedral Co(II) are still sparse example.

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18 Crystallographic Data for [Co_2L_4]; Empirical Formula, $Co_2O_{12}C_{52}H_{36}$, fw, 970.72, Crystal System, monoclinic, Space Group, $C2/c$, $a = 22.322(3)$ Å, $b = 19.329(2)$ Å, $c = 10.345(1)$ Å, $\beta = 93.573(2)^\circ$, $V = 4454.6(9)$ Å^3, $Z = 4$, $D_{calcd} = 1.447\ g\,cm^{-3}$, μ(Mo Kα) = 8.11 cm^{-1}, R (R_w) (all data), 0.126 (0.1517), R (I > 2σ(I)), 0.0630. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-000000.

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