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Synthesis, Crystal Structure and Magnetic Behavior of a Two-dimensional Cobalt(II) Complex with Benzene-1,4-dinitro-2,3,5,6-tetracarboxylate Tetravalent Anion as Bridging Ligand

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Much research interest has been focused on the crystal engineering of coordination compounds that may provide new materials with useful properties such as catalytic, microporosity, electrical conductivity, non-linear optical activity and co-operative magnetic behavior. Benzene polycarboxylate anions such as terephthalate [1–7], phthalate [8–11], benzene-1,3,5-tricarboxylate [12–15], benzene-1,2,4,5-tetracarboxylate [16–19] and mellitic anion [20–23] belong to versatile bridging ligands and many multi-nuclear complexes have been synthesized and some of them display interesting characteristics as regards magnetic properties [5,8,10] and structural feature [6,13]. In this polycarboxylate ligands area, no complexes with benzene-1,4-dinitro-2,3,5,6-tetracarboxylate tetravalent anion (BDT) as bridging ligand have been described and in view of the interest in its novel coordinate function we prepared the title complex and here we report its synthesis, crystal structure and magnetic behavior.

The two-dimensional complex $\{[Co_2(BDT)(DMF)_4(H_2O)_2]\}_n$ (DMF = N,N-dimethylformamide) was prepared in the following way: a dilute NaOH solution was added in drops into a mixture of benzene-1,4-dinitro-2,3,5,6-tetracarboxylic acid (0.1258 g, 0.35 mmole) and 5 cm^3 H_2O until the pH value was about 4, then hydrated cobalt perchlorate (0.2723 g, 0.75 mmole) and 10 cm^3 DMF were added into the mixture and a clear solution appeared. The pinkish crystals were obtained after the clear solution rested at room temperature for a few days. Elemental analysis confirmed the composition. The IR spectra show that the characteristic peak of carboxylic group for benzene-1,4-dinitro-2,3,5,6-tetracarboxylic acid at 1725 cm^{-1} has shifted to 1645 cm^{-1} in the complex, which indicate that the carboxylates take part in the coordination. In addition, a strong and broad band for the coordinated H_2O molecules appears at *ca.* 3422 cm^{-1}. The determination of the crystal structure at 298(2) K was carried out on an X-ray diffractometer, Model Bruker Smart-1000 CCD using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$Å) with ω scan mode. A total of

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4617 reflections were collected in the range $2.15 \le \theta \le 26.37°$, of which 3092 reflections were independent ($R_{int} = 0.1407$) and 824 reflections with $I > 2\sigma(I)$ were considered to be observed and used in the succeeding refinement. The programs of structure solution and refinement are SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997), respectively. The semi-empirical absorption correction was used on equivalent reflections. The selected bond lengths and angles are listed in Table 1. The variable-temperature magnetic susceptibility measurements were performed using a single crystal sample in the 5–291 K range with a SQUID magnetometer.

Table 1. Selected bond lengths (Å) and angles (°) for the complex.

Bond lengths			
Co(1)–O(1)	2.010(7)	Co(1)–O(7)	2.128(7)
Co(1)–O(3)	2.127(8)	Co(2)–O(8)	2.077(9)
Co(2)–O(4)	2.088(7)	Co(2)–O(9)	2.106(8)
Bond angles			
O(1)–Co(1)–O(7)	91.4(3)	O(1A)–Co(1)–O(7)	88.6(3)
O(1)–Co(1)–O(3A)	89.9(3)	O(1)–Co(1)–O(3)	90.1(3)
O(7)–Co(1)–O(3A)	87.4(3)	O(7)–Co(1)–O(3)	92.6(3)
O(8)–Co(2)–O(4)	86.7(3)	O(8B)–Co(2)–O(4)	93.3(3)
O(8)–Co(2)–O(9)	92.2(4)	O(8)–Co(2)–O(9B)	87.8(4)
O(4)–Co(2)–O(9B)	93.1(3)	O(4)–Co(2)–O(9)	86.9(3)
C(5)–O(4)–Co(2)	129.7(8)	C(5)–O(3)–Co(1)	120.9(7)

The crystal is triclinic, space group $P\bar{1}$ with $a = 8.895(7)$ Å, $b = 9.195(8)$ Å, $c = 9.823(8)$ Å, $\alpha = 85.386(16)°$, $\beta = 74.799(16)°$, $\gamma = 86.577(14)°$, $F(000) = 404$, $\mu(\mathrm{MoK}\alpha) = 1.165\ \mathrm{mm}^{-1}$, $R1 = 0.0940$, and $wR2 = 0.1827$ for 824 observed reflections ($I>2\sigma(I)$). The completeness to $\theta = 26.37°$ is 97.9 % and the goodness of fit on F^2 is 0.756. The maximum peak in the final difference Fourier map is 0.641 and the minimum one $-0.740\ \mathrm{e{\cdot}Å^{-3}}$.

Fig. 1 shows the coordination diagram of the complex with the atom numbering scheme. It indicates that the coordination environments of Co(1) and Co(2) are different. Co(1) atom is coordinated by O(1), O(1A), O(3), O(3A), O(7) and O(7A) atoms and in which O(7) and O(7A) atoms come from two DMF molecules, O(1) and O(3) atoms from two carboxylate groups of a BDT ligand, and O(1A) and O(3A) from two carboxylate groups of another BDT ligand. Co(2) atom is coordinated by O(4), O(4D), O(8), O(8B), O(9) and O(9B) atoms in which O(9) and O(9B) atoms come from two H_2O molecules, O(8) and O(8B) from two DMF molecules and O(4) and O(4D) from carboxylate groups of two BDT ligands. The data of the bond lengths and associated bond angles dealing with Co(1) and Co(2) atoms in Table 1 indicate that both Co(1) and Co(2) atoms are located in a distorted octahedral environment. Fig. 1 also displays approximately that the six substituted groups are so crowded each other that the each plane of the carboxylate group deviates seriously from the plane of benzene ring. Fig. 2 displays the two-dimensional sheet structure, and it indicates

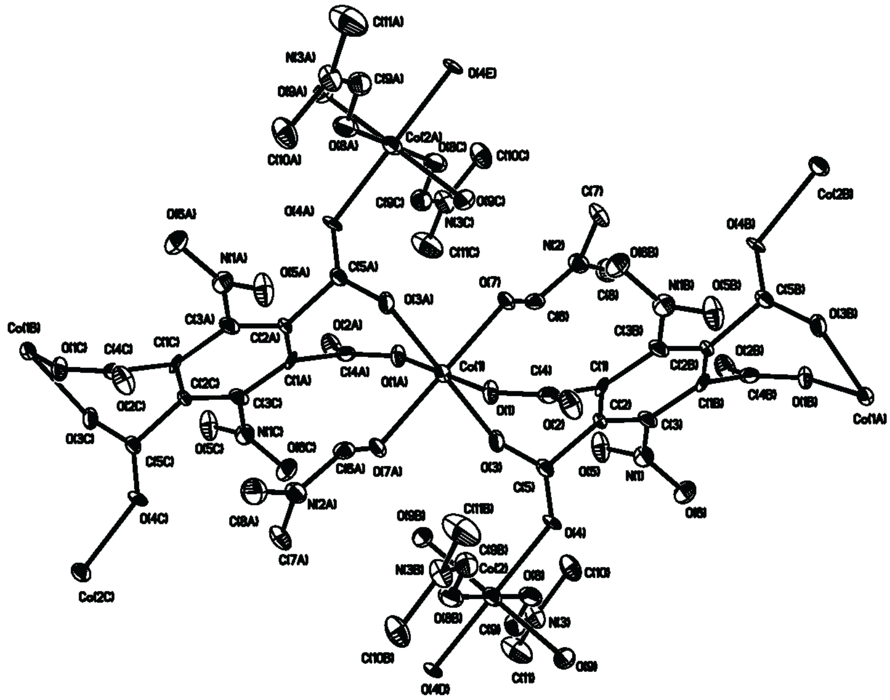

Figure 1. A diagram of the title complex coordination with atom numbering scheme.

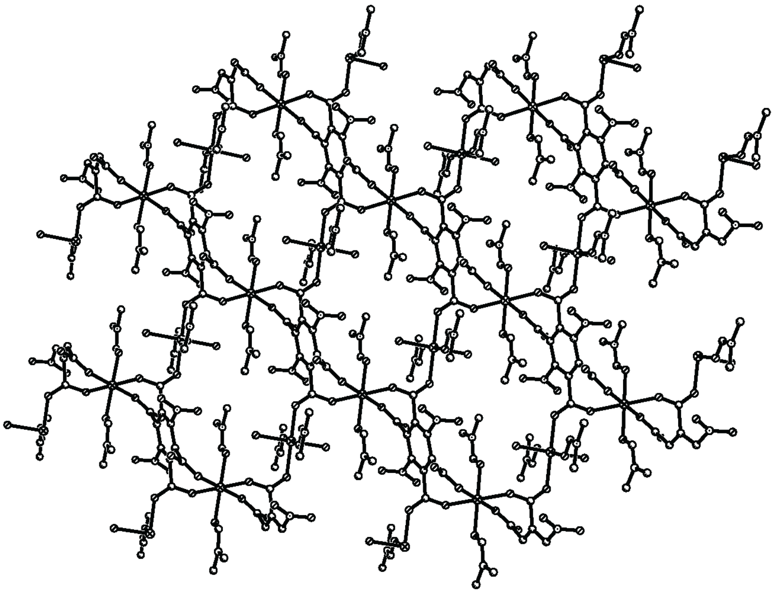

Figure 2. Structure of the two-dimensional sheet.

that each BDT bridging ligand provides six carboxylate oxygen atoms to coordinate four cobalt(II) ions and in this way the two-dimensional sheet structure was formed. Fig. 3 shows the unit cell and the arrangement of the sheets in the crystal. Obviously, the two-dimensional sheets extend along *bc* plane and then the sheets pile up along *a* axis to form a three-dimensional crystal structure. In addition, the symmetric element of the crystal, the inversion centre is located in cobalt(II) ions. The CCDC deposition number of this crystal is 201855. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Fig. 4 shows the relationship of $\chi_M T$ *versus* T, where χ_M is the molar magnetic susceptibility per Co(II) unit. At room temperature, the value of $\chi_M T$ is 1.736 cm^3·K·mol^{-1}, which is close to that expected for isolated S = 3/2 spins (1.876 for $g_{Co} = 2$). The $\chi_M T$ values decrease gradually with the decreasing temperature, from 1.736 cm^3·K·mol^{-1} at 291 K to 1.136 cm^3·K·mol^{-1} at 5 K. Viewed from the crystal structure, the major magnetic interaction of the present complex deals with Co(1) ion and Co(2) ion, and Co(1) ion and Co(1A) ion, and Co(2) and Co(2B). Up to now there is no appropriate theoretic model to be used for that system, therefore we use the Curie-Weiss law to analyze the magnetic data tentatively. The values of magnetic susceptibility obey the Curie-Weiss law with a negative Weiss constant $\theta = -11.823$ K.

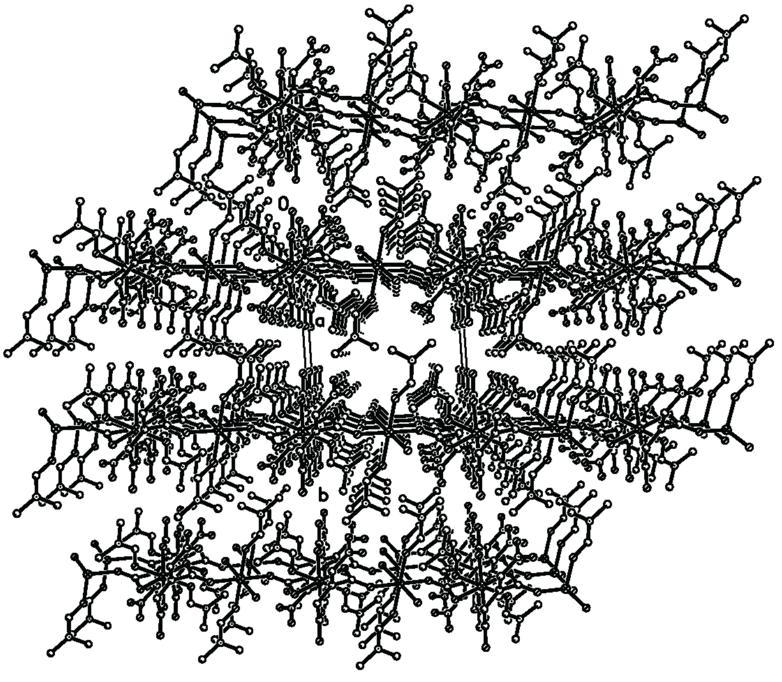

Figure 3. Packing plot of the complex viewed along *c* axis of the unit cell.

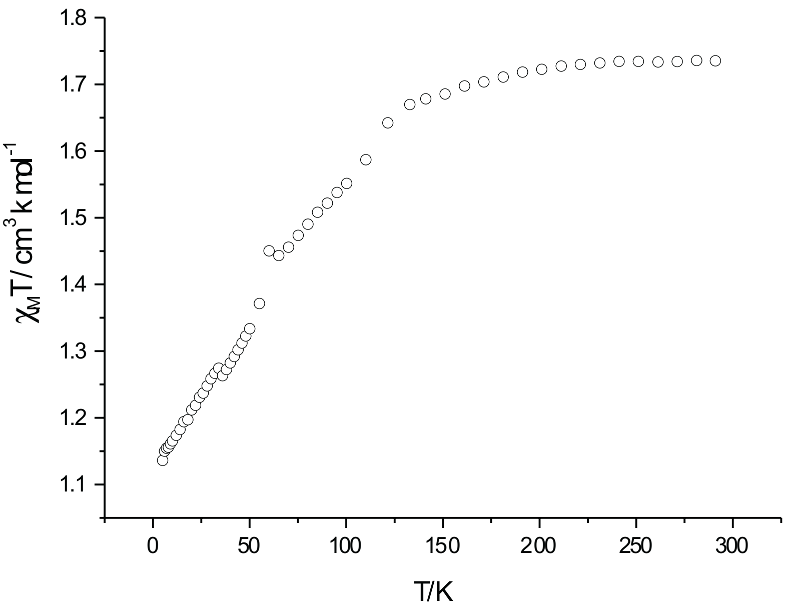

Figure 4. The relationship of $\chi_M T$ *versus T*.

The θ value suggests that there exists a weak antiferromagnetic coupling between the Co(II) ions. Generally, one of main factors that affects the magnetic exchange interaction is a delocalized π orbital between the bridging parametallic ions [24–25]. In the present complex there exist no bridging planes between Co(1) and Co(1A) atoms and between Co(2) and Co(2B) atoms, for the planes of carboxylate groups are not coplanar with benzene ring as mentioned above, which means that there exist no delocalized π orbitals between Co(1) ion and Co(1A) ion, or between Co(2) and Co(2B) atoms. The angles of Co(1)–O(3)–C(5) and Co(2)–O(4)–C(5) are 120.9(7) and 129.7(8)°, respectively, and Co(1), O(3), C(5), O(4) and Co(2) atoms are not located in a plane, which indicate that between Co(1) and Co(2) atoms there is no a delocalized π orbital to bridge them effectively. It may constitutes one of the factors that limits the magnetic exchange interaction effectively and leads to the weak coupling between the cobalt(II) ions.

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