Synthesis and crystal structure of polymer cobalt(II) complex, 1,2,4,5-benzenetetracarboxylate hexaimidazole tetraaqua cobalt(II) tetrahydrate

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The crystal structure of the title complex $\{[Co(TCB)_{2/2}(IMI)_2(H_2O)_2][Co(IMI)_4(H_2O)_2]\}(H_2O)_4$ (where TCB = 1,2,4,5-benzenetetracarboxylic anion; IMI = imidazole) has been determined by X-ray diffraction method. Crystal data for $\{[Co(TCB)_{2/2}(IMI)_2(H_2O)_2][Co(IMI)_4(H_2O)_2]\}(H_2O)_4$: triclinic, space group $P\bar{1}$, $a = 1.0647(2)$ nm, $b = 1.1165(1)$ nm, $c = 1.00361(1)$ nm, $\alpha = 91.56(1)°$, $\beta = 111.34(1)°$, $\gamma = 115.642(10)°$, $V = 0.9772(3)$ nm^3, $Z = 1$. The polymer cobalt(II) complex has a novel three-dimension network structure. Co(1) atom and Co(2) atom both are coordinated in an octahedral arrangement and located in the center of the coordination anion and the center of the coordination cation, respectively. Moreover four carboxyl groups of TCB are divided into two types, two *para*-carboxyl groups bridge Co(1) atom in monodentate fashion and other two *para*-carboxyl groups are in free.

Keywords Polymer cobalt(II) complex, crystal structure, octahedron geometry, 1,2,4,5-benzenetetracarboxylic anion bridged

Introduction

Because the polymer complexes consisting of aromatic multi-carboxylic acids and transition metal have a variety of possible applications ranging from fine retardants to catalysts and potentially valuable properties reminiscent of zeolites,[1,2] the study of these polymer complexes has been an active field of coordination chemistry in recent years. Multi-dentate complexing agents like anion of pyrometallic acid (TCB) are capable of forming one-, two-, or three-dimensionally infinite connections between cations and anions.[3,4] Furthermore, carboxyl ligand has shown a good capable of bridging and providing exchange pathways when paramagnetic metals are involved.[5,6] As a part of a continuing investigation into these complexes, we report here a novel three-dimensional network structure of polynuclear cobalt(II) complex. To our knowledge, this is the first report about $\{[Co(TCB)_{2/2}(IMI)_2(H_2O)_2][Co(IMI)_4(H_2O)_2]\}(H_2O)_4$.

Experimental

Synthesis

1,2,4,5-Tetracarboxylbenzene acid (2.5 mmol) was added into the aqueous solution containing 0.40 g NaOH with stirring at room temperature. Imidazole (15 mmol) was added to 10 mL of water, and $CoSO_4 \cdot 6H_2O$ (1.25 mmol) was also dissolved in 10 mL of water. Two solutions of $CoSO_4$ and imidazole were mixed and a pink solution was formed, then the aqueous solution containing 1,2,4,5-benzenetetracarboxylate was added into the pink solution. The reaction mixture was filtered, and then the filtrate was stood for three days until the well formed, and the light red single crystals were obtained.

Elemental analysis

C, H and N were analyzed using a Carlo-Erba 1106 Elemental Analyzer and Co was analyzed by complexo-

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metric titration with EDTA. Anal. $Co_2C_{28}H_{42}N_{12}O_{16}$. Found: C, 36.24; H, 4.78; N, 18.13; Co, 12.54. Calcd: C, 36.53; H, 4.60; N, 18.26; Co, 12.80.

Infrared spectrum

Infrared spectrum of the title complex was recorded with a Shimadzu IR-470 spectrophotometer (4000—400 cm^{-1}) using a powdered sample spread on a KBr plate.

Crystal structure determination

A light red single crystal of the title complex with approximate dimensions of 0.22 mm × 0.20 mm × 0.32 mm was mounted on a Rigaku AFC7R diffractometer. X-ray diffraction intensity data were collected up to 2θ value of 50.00° with graphit monochromatized Mo $K\alpha$ radiation ($\lambda = 0.071069$ nm) by the ω-2θ scan technique. A total of 3313 independent reflections were collected, of which 2817 reflections with [$I > 3\sigma(I)$] were considered as observed and used for the structure refinement. Usual Lp and empirical absorption corrections were applied. The structure was solved by the Patterson method and followed by Fourier synthesis. Structure refinement was carried out by full-matrix least-squares procedures using the TEXSAN program package.[7] H atoms were located in a difference Fourier map, and coordinates and thermal parameters were fixed during structure refinement. Anisotropic refinement including all the non-H atoms converged at agreement factors $R = 0.028$ and $R_w = 0.038$, where $\omega = 1/(2\sigma F)$. Atomic scattering factors were taken from International Tables for X-ray Crystallography.[8]

Results and discussion

Crystallographic data and refinement details are summarized in Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters for non-H atoms are listed in Table 2, selected bond distances and angles in Table 3. The molecular structure of the title complex with the atom numbering scheme is illustrated in Fig. 1. The molecular packing in the unit cell is shown in Fig. 2. In the title complex, there are two independent parts in every unit cell. One is the anion and the other is cation of the complex. In the anion [$Co(TCB)_{2/2}(IMI)_2(H_2O)_2]^{2-}$, two oxygen atoms of *para*-carboxyl groups of TCB, two oxygen atoms from two water molecules and two nitrogen atoms from two imidazole molecules coordinate to the Co(1) atom to complete a six-coordinated octahedron coordination geometry around the Co(1) atom. The *para*-carboxyl groups of each TCB are coordinated two Co(II) ions through monodentate interactions, the other *para*-carboxyl groups of each TCB are in free, which forms a coordinated anion chain $[Co(TCB)_{2/2}(IMI)_2(H_2O)_2]_n^{2n-}$ along the C axis. In the cation $[Co(IMI)_4(H_2O)_2]^{2+}$, a Co(2) atom has octahedral geometry, of which the equatorial plane consists of N(3), N(5), N(3)* and N(5)* from four imidazole molecules and apical positions are occupied by two oxygen atoms O(6) and O(6)* from the two water molecules. But the anion and cation structures exhibit ideal C_i symmetry. The bond angles between neighboring coordination atoms in the basal plane near by 90°, which implies that the atomic orbits of the donors in the basal plane overlap well with the d orbit of the Co atom, the coordination bond distances in the basal plane are normal.

Table 1 Crystallographic data for $Co_2C_{28}H_{42}N_{12}O_{16}$

Formula	$Co_2C_{28}H_{42}N_{12}O_{16}$
crystal system	Triclinic
space group	$P\bar{1}$
a (nm)	1.0647(2)
b (nm)	1.1165(1)
c (nm)	1.0036(1)
α (°)	91.56(1)
β (°)	111.34(1)
γ (°)	115.642(10)
V (nm^3)	0.9772(3)
D_c ($g \cdot cm^{-3}$)	1.56
Z	1
θ range(°)	1 to 25
T (K)	293
Unique reflections	3313
Reflections with $I > 3\sigma(I)$	2817
No. of paraments refined	$R = 0.028$, $R_w = 0.038$
Largest Δ/σ	0.00
Goodness-of-fit	1.51
Residual extrema in final difference map ($e \times 10^3$ nm^{-3})	0.36 to −0.29

A carboxyl anion can coordinate to a metal atom in

a number of ways.[9] Up to date, five coordination types of carboxyl group have been found.[10] The stretching vibration of the carboxyl group was observed at 1578 cm^{-1} [ν(C = O)] and 1370 cm^{-1} [ν(C - O)] in the title complex, which are in agreement with the values reported previously.[11] The Δν value [ν(C = O) - ν(C - O)] of 208 cm^{-1} suggests the unidentate coordination of the carboxyl group.[12] It is also in agreement with the crystal structure as mentioned above.

Table 2 Fractional atomic coordinates and equivalent isotropic thermal parameters for $Co_2C_{28}H_{42}N_{12}O_{16}$

Atoms	*X*	*Y*	*Z*	$B_{eq} \times 10^2$ (nm)
Co(1)	0.0000	0.5000	0.5000	1.540(9)
Co(2)	0.0000	0.0000	0.0000	1.958(9)
O(1)	0.1747(2)	0.5072(2)	0.7035(2)	1.93(3)
O(2)	0.2832(2)	0.4204(2)	0.6054(2)	2.46(3)
O(3)	0.2493(2)	0.1739(2)	0.7311(2)	2.54(3)
O(4)	0.4793(2)	0.2556(2)	0.7297(2)	2.65(4)
O(5)	-0.1057(2)	0.5389(2)	0.6258(2)	2.17(3)
O(6)	-0.0603(2)	-0.1412(2)	0.1333(2)	2.88(4)
O(7)	0.0501(2)	0.3864(2)	0.8996(2)	3.11(4)
O(8)	0.2116(2)	0.5807(2)	0.1743(2)	3.30(4)
N(1)	0.1315(2)	0.7128(2)	0.5299(2)	2.13(4)
N(2)	0.2160(2)	0.9323(2)	0.5990(2)	2.75(4)
N(3)	0.1917(2)	0.1413(2)	0.1906(2)	2.52(4)
N(4)	0.3490(3)	0.2303(3)	0.4212(2)	3.98(5)
N(5)	-0.1340(2)	0.0860(2)	0.0320(2)	2.47(4)
N(6)	-0.1941(3)	0.2300(2)	0.1129(2)	3.04(5)
C(1)	0.2716(2)	0.4669(2)	0.7118(2)	1.65(4)
C(2)	0.3853(2)	0.4792(2)	0.8626(2)	1.55(4)
C(3)	0.4448(2)	0.3886(2)	0.8877(2)	1.57(4)
C(4)	0.4403(2)	0.5886(2)	0.9751(2)	1.67(4)
C(5)	0.3862(2)	0.2642(2)	0.7729(2)	1.77(4)
C(6)	0.2876(3)	0.7822(3)	0.5731(3)	3.36(6)
C(7)	0.3399(3)	0.9165(3)	0.6163(3)	3.68(6)
C(8)	0.0939(3)	0.8079(2)	0.5471(3)	2.45(5)
C(9)	0.2288(3)	0.1198(3)	0.3240(3)	3.32(6)
C(10)	0.3916(3)	0.3290(3)	0.3478(3)	3.85(6)
C(11)	0.2953(3)	0.2737(3)	0.2059(3)	3.23(6)
C(12)	-0.0829(3)	0.1999(3)	0.1228(3)	2.87(5)
C(13)	-0.3253(3)	0.1284(3)	0.0092(4)	4.77(8)
C(14)	-0.2877(3)	0.0412(3)	-0.0387(4)	4.51(7)

$$B_{eq} = \frac{8}{3}\Pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha.$$

The crystal consists of the complexes and crystalline water molecules. The H-bonding exists between the carboxyl groups and water as verified by the O(7) - O(1) distance of 0.2820(2) nm and the H-bonding also exists between the coordinated water and crystalline water as verified by the O(5) - O(8)[-*x*, -*y* + 1, -*z* + 1] distance of 0.2752(2) nm and O(6) - O(7)[-*x*, -*y*, -*z* + 1] distance of 0.2801(2) nm, especially the H-bonding also exists between the coordinated anion chain $[Co(TCB)_{2/2}(IMI)_2(H_2O)_2]_n^{2n-}$ and coordinated cation $[Co(IMI)_4(H_2O)_2]^{2+}$ as verified by the O(3) - O(6)[-*x*, -*y*, -*z* + 1] distance of 0.2724(2) nm and O(4)-N(4) distance of 0.2842(3) nm, so that the complex molecules form the three-dimensional network

through the H-bondings.

Table 3 Selected interatomic distances (nm) and interbond angles (°) for $Co_2C_{28}H_{42}N_{12}O_{16}$

Co(1) – O(1)	0.2175(1)	Co(1) – O(5)	0.2115(2)
Co(1) – N(1)	0.2115(2)	Co(2) – O(6)	0.2134(2)
Co(2) – N(3)	0.2126(2)	Co(2) – N(5)	0.2136(2)
O(1) – C(1)	0.1271(3)	O(2) – C(1)	0.1243(3)
O(3) – C(5)	0.1256(3)	O(4) – C(5)	0.1254(3)
O(7) – O(1)	0.2820(2)	O(5) – O(8)	0.2752(2)
O(6) – O(7)	0.2801(2)	O(3) – O(6)	0.2724(2)
O(4) – N(4)	0.2842(3)		
O(1)-Co(1)-O(1)	180.00	O(1)-Co(1)-O(5)	87.95(6)
O(1)-Co(1)-O(5)	92.05(6)	O(1)-Co(1)-N(1)	89.12(7)
O(1)-Co(1)-N(1)	90.88(7)	O(5)-Co(1)-O(5)	180.00
O(5)-Co(1)-N(1)	88.41(7)	O(5)-Co(1)-N(1)	91.59(7)
N(1)-Co(1)-N(1)	180.0000	O(6)-Co(2)-O(6)	180.0000
O(6)-Co(2)-N(5)	88.40(7)	O(6)-Co(2)-N(5)	91.60(7)
O(6)-Co(2)-N(3)	90.88(7)	O(6)-Co(2)-N(3)	89.12(7)
N(3)-Co(2)-N(3)	180.00	N(3)-Co(2)-N(5)	89.56(8)
N(3)-Co(2)-N(5)	90.44(8)	N(5)-Co(2)-N(5)	180.00
O(1)-C(1)-O(2)	125.3(2)	O(1)-C(1)-C(2)	118.0(2)
O(2)-C(1)-C(2)	116.7(2)	O(3)-C(5)-O(4)	124.2(2)
O(3)-C(5)-C(3)	118.0(2)	O(4)-C(5)-C(3)	117.7(2)

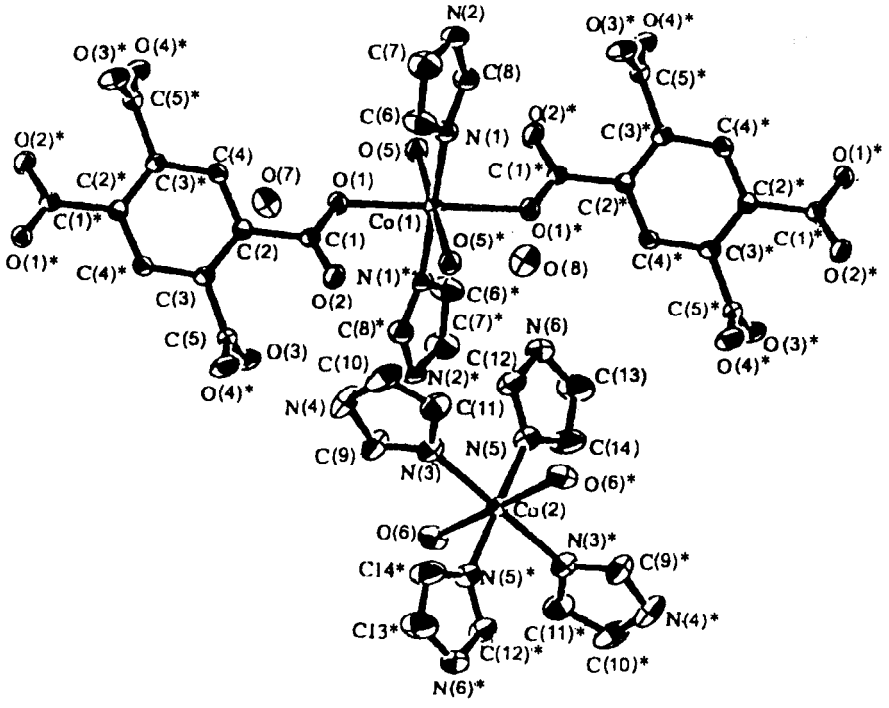

Fig. 1 Molecular structure of the title complex.

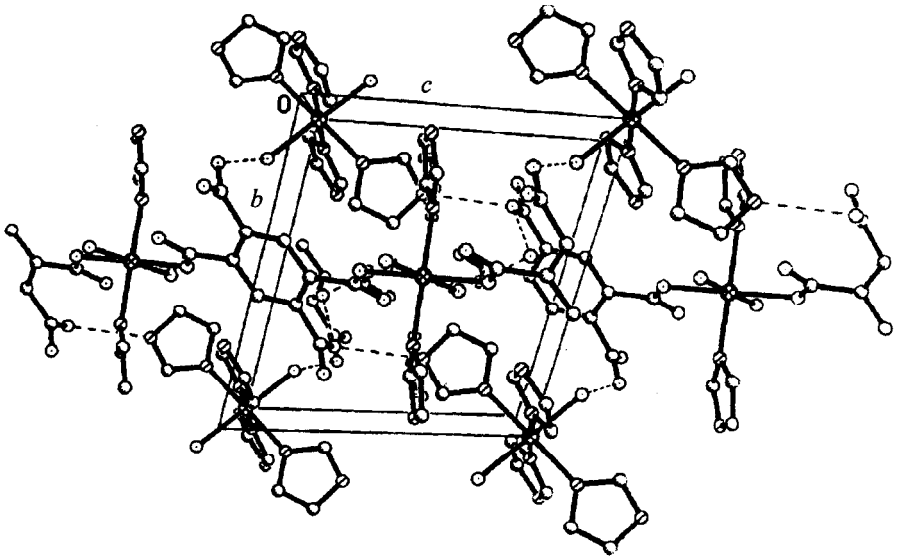

Fig. 2 Crystal packing diagram of title complex (H atom omitted for clarity).

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