Asian Journal of Chemistry Vol. 21, No. 3 (2009), 2020-2026

Synthesis and Crystal Structure of Cobalt(II) Complex of 4,4′-Diamino-1-[(cyclohexa-2,4-dienyl)methyl]benzene

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The crystal structure of cobalt(II) complex of 4,4′-diamino-1-[(cyclohexa-2,4-dienyl)methyl]benzene has been determined by single crystal X-ray diffraction method. The crystal belongs to orthorhombic system, space group P_1 with unit cell constants a = 9.2500(8), b = 11.6619(10), c = 11.9660(11) Å, V = 1273.36(19) $Å^3$, Z = 1, Dc = 1.363 g/cm^3, μ = 0.406 mm^{-1}, F(000) = 550, R and wR are 0.0499 and 0.1498, respectively for 5981 unique reflections with 5095 observed reflections ($I > 2\sigma(I)$). In the crystal structure, molecules are linked into chains along the a axis by N–H···O intermolecular hydrogen bonds along the a axis.

Key Words: Synthesis, Crystal structure, Cobalt(II) complex, 4,4′-Diamino-1-[(cyclohexa-2,4-dienyl)methyl]benzene.

INTRODUCTION

The investigation of transition metal complexes become a very important field in the development of DNA molecule probes and chemotherapeutics[1-6]. Among these complexes, metals or ligands can be varied in an easily controlled way to facilitate the individual applications[7-10]. Trace element cobalt is an important element of life. The cobalt complexes as metal ions in biological/enzyme/substrate interaction simulation study has been very active. Cobalt complexes are good indicators for the hybridization detection of DNA in electrochemical biosensors[11]. In search for new indicators, a new complex of cobalt(II) with 4,4′-diamino-1-[(cyclohexa-2,4-dienyl)methyl]benzene was synthesized and its structure is elucidated.

EXPERIMENTAL

All chemicals were of analytical reagent grade and used directly without further purification. 5 mL of aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.5 mmol, 0.1456 g) was added dropwise to 30 mL of ethanol solution of 4,4'-diaminobiphenyl methane (2 mmol, 0.3968 g) with constant stirring. The mixture was filtered after refluxed for 2 h. The filtrate was left to stand undisturbed and slow evaporation at room temperature for 2 weeks. Crystal suitable for X-ray diffraction analysis were obtained. Anal. data for the title compound: C, 59.76; H, 5.88; N, 13.40 ; Found: C, 59.11; H, 6.01; N, 13.76.

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Crystal data and structure determination: A colourless single crystal with approximate dimension of 0.21 mm × 0.19 mm × 0.16 mm was mounted on glass fibre in a random orientation. The data were collected by Bruker Smart 1000 CCD diffractometer with graphite minochromated MoKα radiation (λ = 0.71073 Å) using ω scan mode in the range of $2.27 \leq \theta \leq 25.56^{o}$ at temperature 293(2) K. A total of 7113 reflections were collected with 5981 unique ones (Rint = 0.012), of which 5095 reflections with $I > 2\sigma(I)$ were considered to be observed and used in the succeeding refinements. Intensity data were corrected for Lp factors and empirical absorption. The structure was solved by direct methods[12] and expanded by using Fourier differential techniques with SHELXL-9712. All non-hydrogen atoms were located with successive difference Fourier syntheses. The structure was refined by full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added according to the theoretical models. Full matrix least-squares refinement gave the final R = 0.0449 and wR = 0.1498, $w = 1/[\sigma^2(Fo)^2 + (0.1000P)^2]$ where $P = (Fo^2 + 2F_c^2)/3$.

RESULTS AND DISCUSSION

The asymmetric unit of the title compound is composed of 3 parts, *viz.*, one crystallographically independent $[Co(H_2O)_2L_4]^{2+}$ cations ($L = C_{13}H_{14}N_2$), two water molecules and two nitrate anions. Fig. 1 shows a perspective view of the monomeric unit with the atomic numbering scheme of the title compound. Fig. 2 shows a perpective view of the crystal packing in the unit cell for the complex. Atomic coordinates and equivalent isotropic displacement paraments are presented in Table-1. Selected bond lengths and angles are presented in Tables 2 and 3.

TABLE-1
ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS ($Å^2$)

Atom	x	y	z	Ueq
Co1	0.68066(15)	0.94367(11)	0.83349(11)	0.0359(2)
O1W	0.6299(7)	0.7688(5)	0.8671(5)	0.0553(19)
O2W	0.7400(6)	1.1161(4)	0.8035(4)	0.0469(19)
N1	0.6627(11)	0.5022(6)	1.6504(7)	0.071(3)
N2	0.4669(7)	0.9856(6)	0.9093(5)	0.043(2)
N3	0.3181(11)	1.4269(8)	-0.0377(7)	0.071(3)
N4	0.5682(8)	0.9529(6)	0.6748(5)	0.046(2)
N5	1.0427(10)	0.4658(6)	1.7057(6)	0.056(3)
N6	0.7966(8)	0.9358(6)	0.9938(5)	0.041(2)
N7	0.6998(11)	1.3889(8)	0.0203(7)	0.081(4)
N8	0.8978(8)	0.8984(6)	0.7533(5)	0.045(2)
C1	0.5748(8)	0.7358(7)	1.4191(6)	0.045(2)
C2	0.6381(10)	0.6431(8)	1.4819(7)	0.050(3)
C3	0.5848(12)	0.5902(8)	1.5840(7)	0.052(3)
C4	0.4535(10)	0.6316(8)	1.6225(7)	0.054(3)

Atom	x	y	z	Ueq
C5	0.3839(11)	0.7174(10)	1.5612(7)	0.060(3)
C6	0.4397(9)	0.7788(7)	1.4560(6)	0.043(3)
C7	0.3559(10)	0.8836(9)	1.3952(6)	0.058(3)
C8	0.3904(10)	0.9121(9)	1.2667(7)	0.046(3)
C9	0.4582(11)	1.0141(7)	1.2167(8)	0.056(3)
C10	0.4814(10)	1.0380(8)	1.1024(7)	0.046(3)
C11	0.4396(8)	0.9629(7)	1.0303(6)	0.037(2)
C12	0.3703(9)	0.8574(7)	1.0833(7)	0.044(3)
C13	0.3470(10)	0.8336(8)	1.1969(7)	0.045(3)
C14	0.6163(10)	1.1300(8)	0.5441(6)	0.053(3)
C15	0.5190(9)	1.0611(7)	0.6151(6)	0.037(2)
C16	0.3786(8)	1.1002(7)	0.6318(5)	0.041(2)
C17	0.3339(10)	1.2064(8)	0.5761(7)	0.050(3)
C18	0.4272(9)	1.2799(8)	0.5020(7)	0.042(3)
C19	0.5692(10)	1.2384(9)	0.4910(7)	0.052(3)
C20	0.3837(10)	1.3933(7)	0.4418(6)	0.048(3)
C21	0.3735(8)	1.4003(7)	0.3138(6)	0.040(2)
C22	0.3271(11)	1.3081(8)	0.2674(7)	0.052(3)
C23	0.3049(10)	1.3138(8)	0.1508(7)	0.052(3)
C24	0.3340(9)	1.4128(8)	0.0785(7)	0.048(3)
C25	0.3902(12)	1.5067(8)	0.1232(7)	0.055(3)
C26	0.4073(9)	1.4995(7)	0.2403(6)	0.041(2)
C27	0.9541(11)	0.3878(8)	1.4277(7)	0.052(3)
C28	0.9706(10)	0.3765(7)	1.5416(7)	0.046(3)
C29	1.0214(9)	0.4670(7)	1.5875(6)	0.047(3)
C30	1.0560(10)	0.5728(7)	1.5119(7)	0.046(3)
C31	1.0437(9)	0.5815(6)	1.4005(7)	0.040(2)
C32	0.9915(9)	0.4885(7)	1.3518(7)	0.044(3)
C33	0.9822(11)	0.4898(7)	1.2273(7)	0.056(3)
C34	0.9299(9)	0.6085(7)	1.1615(6)	0.042(3)
C35	0.7915(10)	0.6454(9)	1.1789(7)	0.053(3)
C36	0.7485(10)	0.7505(8)	1.1228(7)	0.051(3)
C37	0.8431(9)	0.8238(7)	1.0521(6)	0.038(3)
C38	0.9799(10)	0.7882(8)	1.0381(7)	0.053(3)
C39	1.0236(9)	0.6769(8)	1.0916(7)	0.044(3)
C40	0.8793(11)	0.8501(8)	0.5653(8)	0.053(3)
C41	0.9277(9)	0.9269(7)	0.6325(6)	0.040(2)
C42	0.9946(9)	1.0243(8)	0.5884(6)	0.043(3)
C43	1.0183(10)	1.0528(8)	0.4707(7)	0.047(3)
C44	0.9715(10)	0.9803(8)	0.3973(7)	0.044(3)
C45	0.9038(9)	0.8810(8)	0.4466(6)	0.048(3)
C46	0.9978(11)	1.0071(9)	0.2703(6)	0.065(4)
C47	0.9226(9)	1.1078(9)	0.2080(7)	0.048(3)
C48	0.9787(10)	1.1626(8)	0.1063(7)	0.048(3)
C49	0.9034(12)	1.2578(9)	0.0453(7)	0.066(4)
C50	0.7750(11)	1.2959(9)	0.0853(7)	0.052(3)
C51	0.7147(10)	1.2405(9)	0.1885(7)	0.054(3)
C52	0.7985(11)	1.1475(9)	0.2491(6)	0.058(3)

Atom	x	y	z	Ueq
O1	1.2239(8)	1.2022(6)	0.8701(6)	0.067(3)
O2	1.0174(8)	1.2022(6)	0.7898(5)	0.060(3)
O3	1.1026(8)	1.0436(5)	0.8815(5)	0.064(3)
N9	1.1172(7)	1.1483(6)	0.8483(5)	0.042(2)
O4	0.2615(8)	0.8429(6)	0.7861(6)	0.066(3)
O5	0.3462(8)	0.6827(6)	0.8744(5)	0.058(3)
O6	0.1407(8)	0.6844(7)	0.7950(6)	0.065(3)
N10	0.2479(9)	0.7372(7)	0.8185(6)	0.054(3)
O3W	0.8150(10)	0.5982(7)	0.8291(8)	0.100(4)
O4W	0.5542(10)	0.2862(7)	1.8446(8)	0.092(3)

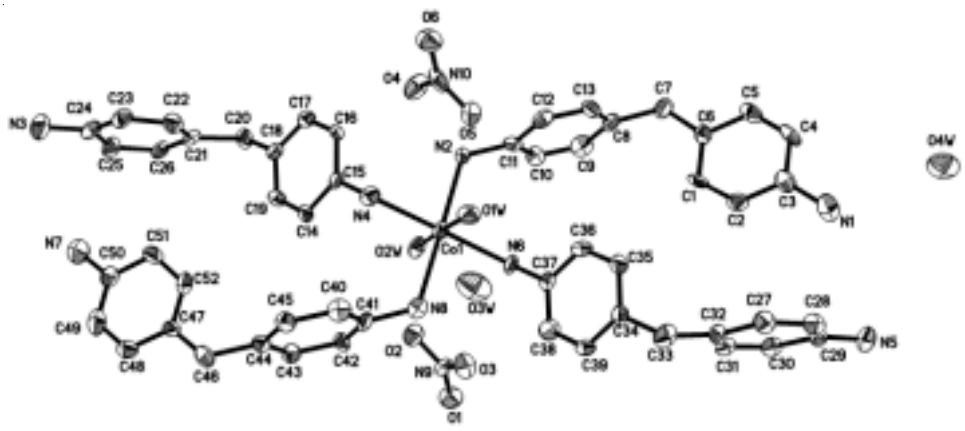

Fig. 1. The molecular structure of the title compound with the atomic numbering scheme

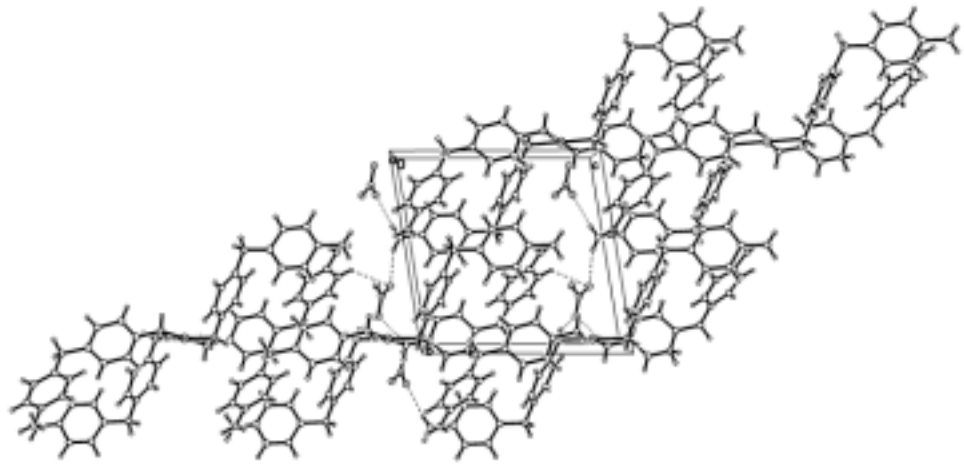

Fig. 2. A view of the crystal packing for the title compound

TABLE-2
SELECTED BOND LENGTHS (Å)

Bond	Dist.	Bond	Dist.
Co1-O1W	2.069(6)	C17-C18	1.405(12)
Co1-O2W	2.061(5)	C18-C19	1.405(13)
Co1-N2	2.226(7)	C18-C20	1.463(12)
Co1-N4	2.189(6)	C20-C21	1.527(10)
Co1-N6	2.224(6)	C21-C22	1.366(12)
Co1-N8	2.285(7)	C21-C26	1.367(11)
O1-N9	1.233(10)	C22-C23	1.409(12)
O2-N9	1.280(9)	C23-C24	1.350(13)
O3-N9	1.229(9)	C24-C25	1.405(13)
O4-N10	1.238(11)	C25-C26	1.406(11)
O5-N10	1.258(11)	C27-C28	1.363(12)
O6-N10	1.237(11)	C27-C32	1.402(12)
N1-C3	1.406(13)	C28-C29	1.360(12)
N2-C11	1.442(9)	C29-C30	1.439(11)
N3-C24	1.388(12)	C30-C31	1.330(12)
N4-C15	1.428(11)	C31-C32	1.408(11)
N5-C29	1.434(10)	C32-C33	1.493(12)
N6-C37	1.450(11)	C33-C34	1.563(12)
N7-C50	1.424(14)	C34-C35	1.366(13)
N8-C41	1.447(9)	C34-C39	1.352(12)
C1-C2	1.357(12)	C35-C36	1.365(14)
C1-C6	1.423(11)	C36-C37	1.391(12)
C2-C3	1.354(12)	C37-C38	1.341(12)
C3-C4	1.392(14)	C38-C39	1.416(13)
C4-C5	1.322(14)	C40-C45	1.418(12)
C5-C6	1.425(12)	C40-C41	1.383(12)
C6-C7	1.540(12)	C41-C42	1.322(12)
C7-C8	1.542(11)	C42-C43	1.403(11)
C8-C9	1.386(13)	C43-C44	1.395(13)
C8-C13	1.405(13)	C44-C46	1.512(11)
C9-C10	1.360(13)	C44-C45	1.359(13)
C10-C11	1.390(12)	C46-C47	1.473(14)
C11-C12	1.435(11)	C47-C48	1.366(12)
C12-C13	1.352(12)	C47-C52	1.339(13)
C14-C15	1.382(12)	C48-C49	1.422(14)
C14-C19	1.396(13)	C49-C50	1.360(15)
C14-C19	1.396(13)	C50-C51	1.397(12)
C15-C16	1.390(11)	C51-C52	1.444(14)
C16-C17	1.378(12)		

TABLE-3
SELECTED BOND ANGLES (°)

Angle	(°)	Angle	(°)
O1W-Co1-O2W	177.4(2)	C14-C19-C18	123.9(8)
O1W-Co1-N2	89.8(3)	C18-C20-C21	115.0(7)
O1W-Co1-N6	92.6(3)	C20-C21-C22	121.4(7)
O1W-Co1-N8	89.5(3)	C22-C21-C26	116.7(7)
O2W-Co1-N2	91.8(2)	C20-C21-C26	121.9(7)

Angle	(°)	Angle	(°)
O2W-Co1-N4	94.2(2)	C21-C22-C23	123.2(8)
O2W-Co1-N6	85.3(2)	C22-C23-C24	120.1(9)
O2W-Co1-N8	88.9(2)	N3-C24-C25	117.5(8)
N2-Co1-N4	85.7(2)	C23-C24-C25	117.8(8)
N2-Co1-N6	94.6(2)	N3-C24-C23	124.6(9)
N2-Co1-N8	178.8(2)	C24-C25-C26	120.8(8)
N4-Co1-N6	179.4(2)	C21-C26-C25	121.3(8)
N4-Co1-N8	93.3(2)	C28-C27-C32	123.4(8)
N6-Co1-N8	86.4(2)	C27-C28-C29	120.1(8)
Co1-N2-C11	120.7(5)	C28-C29-C30	117.7(7)
Co1-N4-C15	121.3(5)	N5-C29-C30	117.1(7)
Co1-N6-C37	119.0(5)	N5-C29-C28	125.2(7)
Co1-N8-C41	121.2(5)	C29-C30-C31	121.7(7)
Co1-N8-C41	121.2(5)	C30-C31-C32	121.3(7)
O1-N9-O2	119.6(7)	C31-C32-C33	124.2(7)
O1-N9-O3	122.1(7)	C27-C32-C33	119.9(7)
O5-N10-O6	119.7(8)	C27-C32-C31	115.9(8)
O4-N10-O5	119.2(8)	C32-C33-C34	113.6(7)
O4-N10-O6	121.0(8)	C33-C34-C35	119.9(8)
C2-C1-C6	120.2(7)	C35-C34-C39	120.1(8)
C1-C2-C3	124.0(9)	C33-C34-C39	119.9(8)
N1-C3-C4	121.8(8)	C34-C35-C36	119.2(8)
N1-C3-C2	121.4(9)	C35-C36-C37	122.0(8)
C2-C3-C4	116.7(9)	C36-C37-C38	118.3(8)
C3-C4-C5	121.3(8)	N6-C37-C36	121.6(8)
C4-C5-C6	123.6(9)	N6-C37-C38	120.1(7)
C1-C6-C5	114.0(8)	C37-C38-C39	120.0(8)
C1-C6-C7	126.2(7)	C34-C39-C38	120.2(8)
C5-C6-C7	119.7(8)	C41-C40-C45	117.0(8)
C6-C7-C8	114.4(7)	N8-C41-C40	117.3(7)
C7-C8-C13	118.8(8)	C40-C41-C42	121.7(7)
C7-C8-C9	122.6(9)	N8-C41-C42	121.0(7)
C9-C8-C13	118.6(8)	C41-C42-C43	120.4(8)
C8-C9-C10	120.7(8)	C42-C43-C44	121.3(8)
C9-C10-C11	122.5(8)	C43-C44-C46	122.7(8)
N2-C11-C10	123.1(7)	C45-C44-C46	121.1(8)
C10-C11-C12	116.2(7)	C43-C44-C45	116.1(8)
N2-C11-C12	120.7(7)	C40-C45-C44	123.5(8)
C11-C12-C13	121.4(8)	C44-C46-C47	118.0(8)
C8-C13-C12	120.6(8)	C46-C47-C52	121.1(8)
C15-C14-C19	118.1(8)	C46-C47-C48	120.3(8)
C14-C15-C16	120.0(8)	C48-C47-C52	118.6(9)
N4-C15-C16	121.3(7)	C47-C48-C49	119.9(9)
N4-C15-C14	118.6(8)	C48-C49-C50	121.6(8)
C15-C16-C17	120.6(7)	N7-C50-C49	120.2(8)
C16-C17-C18	122.0(8)	C49-C50-C51	119.6(9)
C19-C18-C20	121.2(8)	N7-C50-C51	120.1(9)
C17-C18-C20	123.5(8)	C50-C51-C52	116.5(8)
C17-C18-C19	115.2(8)	C47-C52-C51	123.7(8)

In the molecule of the title compound (Fig. 1), the bond lengths and angles are within normal ranges[13]. The Co atom is hexa-coordinated by four N atoms from the 4,4'-diaminodiphenylmethane ligand and two O atoms from two water molecules. This CoO_2N_4 coordination forms a distorted octahedral geometry (Fig. 1). The four N atoms and Co atom are coplanar, while the line through the two O atoms is almost perpendicular to the plane, with O1W-Co1-O2W bond angle of 177.4(3)º. Two nitrate anions is outside the coordination sphere, balancing the charge. In the crystal structure, molecules are linked into chains along the a axis by N–H···O intermolecular hydrogen bonds along the a axis (Table-4).

TABLE 4
HYDROGEN BOND DISTANCES (nm) AND
ANGLE (º) OF THE TITLE COMPOUND

D	H	A	Symm	D-H	H···A	D···A	D-H···A
N2	O4	H2C	x, y, z	0.90	2.207	3.101(10)	171.39
N3	H3A	O1	-1+x, y, -1+z	0.86	2.290	3.142(12)	171.74
N3	H3B	O5	x, 1+y, -1-z	0.86	2.201	3.026(12)	156.81
N4	H4C	O4	x, y, z	0.90	2.434	3.250(11)	154.23
C4	H4B	O5	x, y, 1+z	0.93	2.579	3.278(10)	132.32

ACKNOWLEDGEMENT

The authors thank the Natural Science Foundation of Shandong Province (grant Nos. Z2006B01 and Y2006B07).

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(*Received*: 14 March 2008; *Accepted*: 12 November 2008) AJC-7022