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Molecular and Crystal Structures of bis{1,4-bis(1,2,4-triazol-1-yl)butane}dichlorocobalt(II)[1]

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Abstract—The structure of $[Co(Btb)_2Cl_2]$ (Btb = 1,4-bis(1,2,4-triazol–1-yl)butane) demonstrates a two-dimensional (4,4) network through the Btb bridge in which the Co(II) atom is in a distorted octahedral environment formed by four nitrogen atoms of the triazoles and two *trans*-Cl^- ions. The crystals are monoclinic, space group $P2_1/c$ with a = 7.3143(3), b = 18.5703(7), c = 8.8713(4) Å, β= 117.0633(10)°.

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INTRODUCTION

Recently a new class of flexible ligands, [bis(1,2,4-triazol-1-yl)-alkanes], have been found to be very efficient in the formation of various interesting extended structures [1–5]. As bridging ligands, these 1,2,4-triazole derivatives show a great coordination diversity. Among these ligands, 1,4-bis(1,2,4-triazol-1-yl)butane (**Btb**), which is more flexible than 1,2-bis(1,2,4-triazol-1-yl)ethane (**Bte**) and 1,3-bis(1,2,4-triazol-1-yl)propane (**Btp**), is expected to play an important role in the construction of coordination polymers. Few reports on the crystal structures of the cadmium(II), manganese(II), and iron(II) complexes with bridging Btb ligand were reported [6–9]. Lately we also synthesized and reported two complexes of zinc(II) and cadmium(II) with Btb, which exhibited a one-dimensional zigzag chain and a two-dimensional network [10]. As a part of our further investigations of the coordination mode of this ligand in metal complexes incorporating 1,2,4-triazole derivatives, here we report the synthesis and crystal structure of a new polymeric Co(II) complex with Btb bridges (**I**).

EXPERIMENTAL

1,4-Bis(1,2,4-triazol-1-yl)was prepared according to literature [11] and confirmed by the means of melting point measurements and IR.

Synthesis of complex I. A 20 ml of an aqueous solution of Btb (2 mmol) was added to a 10 ml of methanol with $CoCl_2 \cdot 6H_2O$ (1 mmol). The precipitate was filtered after stirring for an hour, and the mother liquid was left to stand at room temperature. Five days later, red crystals suitable for single-crystal X-ray determination were formed.

For $C_{16}H_{24}N_{12}Cl_2Co$

anal. calcd, %:	C, 37.33;	H, 4.67;	N, 32.67.
Found, %:	C, 37.36;	H, 4.59;	N, 32.71.

X-ray structure determination. A single crystal with dimensions $0.33 \times 0.28 \times 0.21$ mm was mounted on a glass fiber and used for structure determination. Diffraction intensity data were collected at 296(1) K on a Rigaku RAXIS-RAPID diffractometer up to $2\theta_{max}$ of 55.0° with graphite-monochromatized MoK_α radiation (λ = 0.71075 Å) using the ω scan technique. A total of 2465 independent reflections were collected, among which 2108 reflections were considered as observed ($I > 2\sigma(I)$) and used for structure refinement. Usual Lp and empirical absorption corrections were applied.

The structure **I** was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELX97 [12]. All non-hydrogen atoms were anisotropically refined. The hydrogen atoms were treated as riding atoms. Anisotropic refinement including all non-H atoms converged to agreement factors R = 0.0254 and R_w = 0.0794, where $w = 1/[0.0007(F_o^2) + 1.0000\sigma \times (F_o^2)]/(4F_o^2)]$.]. The highest peak in the final difference Fourier map was 0.28 e Å^{-3}. Atomic scattering factors used were taken from Cromer and Waber [13]. The crystallographic data are summarized in the table.

Crystallographic data for complex **I** was deposited with the Cambridge Crystallographic Data Center (no. 714200; deposit@ccdc.cam.ac.uk).

[1] The article is published in the original.

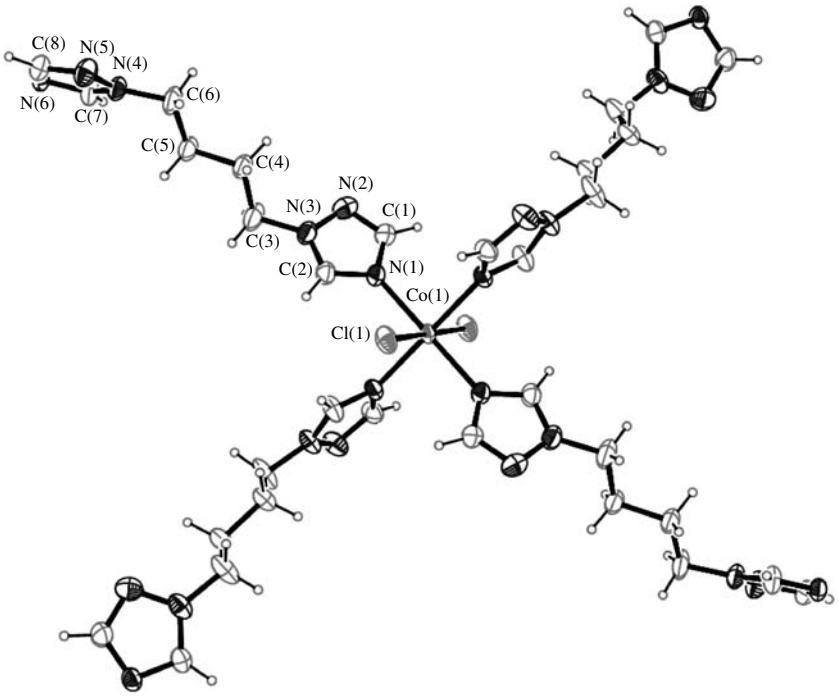

Fig. 1. Molecular structure of $C_{16}H_{24}Cl_2CoN_{12}$, showing 50% probability displacement ellipsoids. Selected bond lengths (Å) and angles (deg): Co(1)–N(1) 2.1280(14), Co(1)–N(6) 2.1738(16), N(1)–C(1) 1.350(2), N(1)–C(2) 1.323(2), N(2)–N(3) 1.362(2), N(6)–C(7) 1.324(2), N(6)–C(8) 1.3502(2), N(4)–N(5) 1.3530(19); N(1)Co(1)N(6) 88.81(5), Cl(1)Co(1)N(1) 90.79(3), Cl(1)Co(1)N(6) 89.93(3).

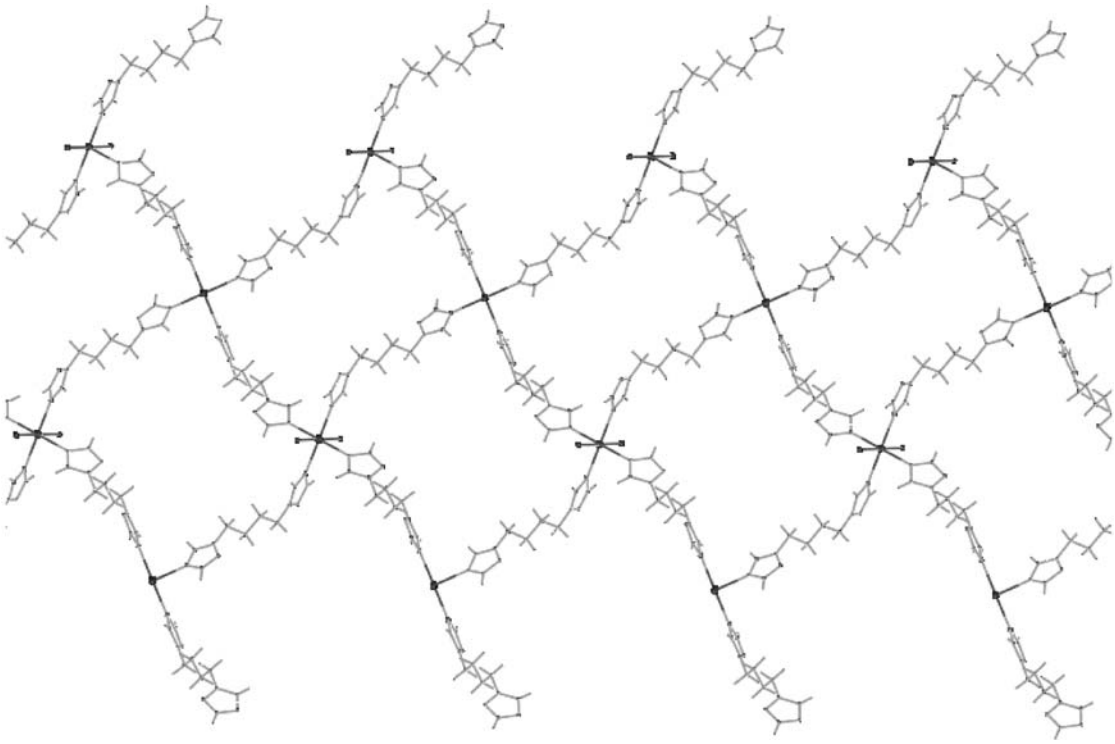

Fig. 2. Planar two-dimensional (4,4) network of the title complex.

Crystallographic data and details of the experiment and refinement of structure **I**

Parameter	Value
Formula weight	514.29
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions:	
a, Å	7.3143(3)
b, Å	18.5703(7)
c, Å	8.8713(4)
β, deg	117.0633(10)
Z; ρ_{calcd}, mg/m^3	2; 1.592
μ, mm^{-1}	1.081
F (000)	530.00
Crystal size, mm	0.33 × 0.28 × 0.21
θ range for data collection, deg	3.0 to 27.5
Index ranges	$-8 \le h \le 9$ $-24 \le k \le 24$ $-11 \le l \le 11$
Reflections collected/unique	10417/2465 (R_{int} = 0.021)
Completeness to θ, %	99.9
Absorption correct	Multiscan
Max and min transmission	0.797 and 0.696
Parameters	155
Goodness-of-fit on F^2	1.000
Final R indices ($I > 2\sigma(I)$)	R_1 = 0.0254, wR_2 = 0.0794
Largest diff. peak and hole, e Å^{-3}	0.28 and –0.21

RESULTS AND DISCUSSION

The ORTEP view of the molecule structure of the complex, together with the atom numbering scheme is presented in Fig. 1. The Co(II) atom in inversion center is a distorted octahedral arrangement with four triazole nitrogen atoms from four Btb ligands in a basal plane. The apical position is occupied by two chloride ions with a Co(1)–Cl(1) distance of 2.5027(3) Å. The Co(1)–N bond distances of triazole (2.1280(14) and 2.1738(16) Å) are close to the values observed in $[Co_2(Bte)_3(NCS)_4(H_2O)_2]_n$ [14] and $[Co(Btp)_2(SCN)_2]_n$ [15]. The angles around the Co centers range from 88.81(5)° to 91.19(5)° (close to 90°).

As shown in Fig. 2, each bridging Btb ligand links Co(II) and each Co(II) atom bonds four Btb ligands to form a two-dimensional (4,4) network containing square $Co_4(Btb)_4$ units. Figure 3 shows that the 2D sheets are stacked in parallel along the z axis. Each Btb ligand exhibits the completely *anti* conformation, which is different from *anti-anti-gauche* conformation observed in $\{[Mn(Btb)_2(H_2O)_2)](NO_3)_2(H_2O)\}_n$ [7]. The dihedral angle between two triazole ring planes is 64.55°. The torsion angles C(3)–C(4)–C(5)–C(6), N(3)–C(3)–C(4)–C(5), and C(4)–C(5)–C(6)–N(4) are 174.77(16)°, 174.42(14)°, and 171.38(14)°, respectively. The Co–Co separation across the bridging Btb is 13.744(12) Å. This separation is apparently longer than the corresponding Co–Co separation in $[Co_2(Bte)_3(NCS)_4(H_2O)_2]_n$ [14] and $[Co(Btp)_2(SCN)_2]_n$ [15], two compounds that have different alkane chains as a spacer, in which the Co–Co distances are 12.315

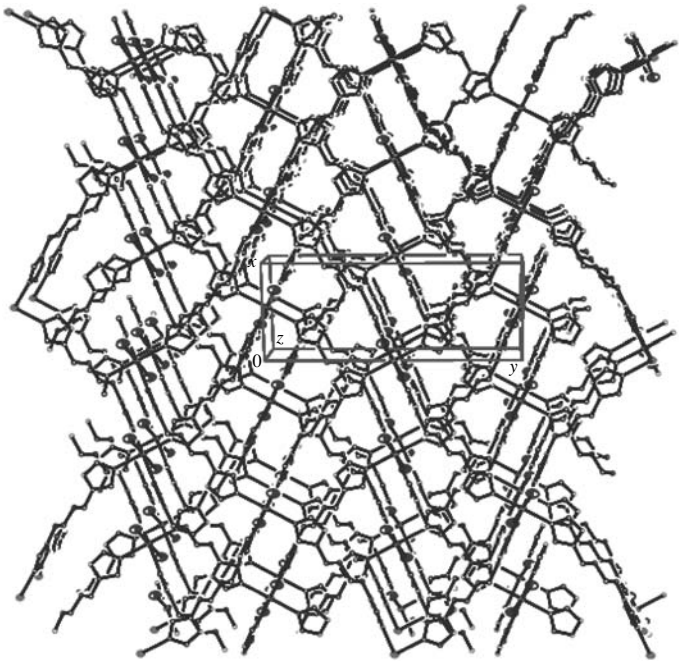

Fig. 3. View of the stacked sheets along the z axis of title complex.

and 10.4472 Å, respectively. In fact, this confirms the importance of this family of ligands in adjusting the metal–metal distance.

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