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Syntheses, structures and characterization of novel cobalt(II) mono- and bi-triazole complexes

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Abstract

Using the bi- and mono-triazole ligand, two novel cobalt(II) complexes $[Co(L_1)_2(NCS)_2(H_2O)_2]\cdot 2H_2O$ (**1**) and $[Co_3(L_2)_6(NCS)_4(H_2O)_2](NCS)_2\cdot H_2O$ (**2**) ($L_1 = $4-[3-(1,2,4-triazolyl)-1,2,4-triazole] and $L_2 = $4-aminotriazole) have been synthesized. The crystal structures of **1** and **2** have been determined by X-ray single-crystal diffraction. **1** has the mononuclear fundamental structure unit while **2** form the linear trinuclear structure unit. **1** and **2** were furthermore assembled into two-dimensional (2D) network and three-dimensional (3D) supramolecular complex via the intermolecular hydrogen-bonds, respectively. The complexes **1** and **2** also have been characterized by elemental analysis, FT-IR, UV/vis spectra.

Keywords: Bitriazole; Cobalt(II) complex; Crystal structure; Hydrogen bonds

1. Introduction

Material science is a rapidly growing area of interest. The study of structural design or modification of the coordination framework is especially rapidly expanding, due to the fact that the self assembly of the functional metal coordination compounds can be achieved by careful choice of organic ligands, inorganic metal species, metal coordination geometry preference, inorganic counterion, solvent system and metal salt-to-ligand ratio [1–10]. Among these factors, organic ligands play a very important role in dictating polymer framework topology.

1,2,4-Triazole and, in particular, its derivatives are very interesting ligands for their important properties [11]. Because of the position of the donor atoms in the five-membered ring, the triazoles appear to possess the possibility of linking metal ions together. The triazole ligands thereby constitute a bridge between the metal ions. This bridge can be of several different geometries, depending on the donor atoms of the ligand and the properties of the metal [12–14]. Furthermore, the triazole ligand strength is just in the region to give spin crossover compounds with iron(II) salts. Such systems are applicable for information storage and some other applications [15–20].

Despite this interest in triazole ligands in the development of new magnetic materials, relatively few cobalt(II) complexes have been reported [21]. In this work attention will be focused on the diversity of the geometries of the cobalt(II) complexes resulting from the change of triazole ligands. Herein 4-[3-(1,2,4-triazolyl)-1,2,4-triazole] (L_1) and 4-aminotriazole (L_2) were employed in syntheses of cobalt(II) complexes (see Scheme 1).

For L_1, it is interesting that although five nitrogen atoms are available for coordination, steric reasons hamper coordination only at N1, the complexes of bi-triazole ligands have not been extensively exploited except for some limited cases [22–26]. Using the mixture of $CoCl_2\cdot 6H_2O$ and KSCN, the following stoichiometries have been obtained: $[Co(L_1)_2(NCS)_2(H_2O)_2]\cdot 2H_2O$ (**1**).

For L_2, by blocking the N4 donor position through substitution, the bridging mode N1, N2 is the coordination mode usually found in many cases [27] (see Scheme 2). In this N1, N2 mode the two metal ions are brought close

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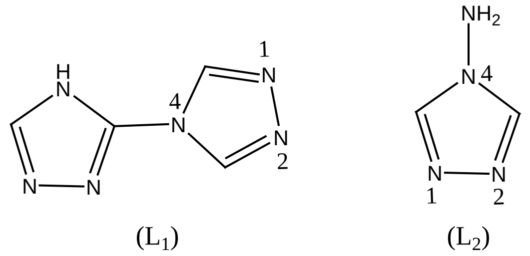
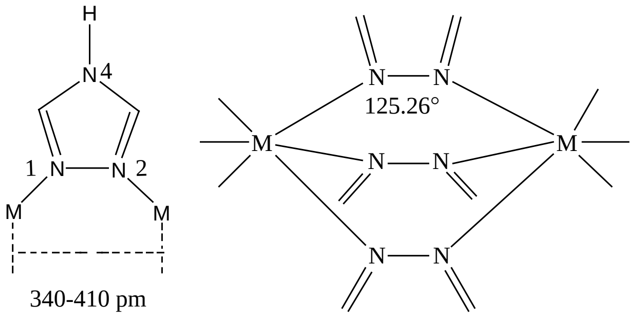


Scheme 1. The schematic diagram of the complex L_1(4-[3-(1,2,4-triazolyl)-1,2,4-triazole]) and L_2(4-aminotriazole).



Scheme 2. Geometry of bridging modes of 1,2,4-triazole.

together at distances of about 400 pm by the first bridging ligand. And the coordination angles N–M–N around the metal ions are all 90°, the M–N–N angles are ideally 125.26° [11].

However, to the best of our knowledge, the complexes of bi-triazole ligands have been exploited so limit. In this work, the bitraizole L_1 and mono-triazole L_2 ligands have been prepared and two novel cobalt(II) complexes **1** and **2** have been synthesized and further characterised by single-crystal X-ray single-crystal diffraction, elemental analysis, FT-IR and UV/vis spectrum.

2. Experimental

2.1. General

All reagents were purchased commercially and used without further purification. X-ray diffraction data were collected on a BRUKER SMART 1000 CCD detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The ligands L_1 [28] and L_2 [29] were synthesized using the literature method. Elemental analyses of carbon, hydrogen and nitrogen were carried out with a Perkin-Elmer analyzer model 240. The infrared spectra on KBr pellets were obtained on a Bruker Vector 22 FT-IR instrument in the range 400–4000 cm^{-1} region. The electronic spectra were performed with a Shimadzu UV-2101PC spectrophotometer in the range of 200–2000 nm at room temperature.

2.2. Syntheses of **1** and **2**

L_1 (0.5 mmol, 0.06806 g) in boiling aqueous (15 ml) was added to the water solution (5 ml) of $CoCl_2 \cdot 6H_2O$ (0.5 mmol, 0.1190 g) with stirring for 30 min. Then the mixture was added into an aqueous solution containing KSCN (1 mmol, 0.0972 g) with stirring for 1 h. The resulting solution was filtered and the filtrates were allowed to stand in air at room temperature for several days, yielding the red crystals of **1** (Yield: 35%). Anal. Found: C, 23.10; H, 3.11; N, 37.76%. Calcd for $C_{10}H_{16}CoN_{14}O_4S_2$(%): C, 23.12%; H, 3.10%; N, 37.75%.

Compound **2** was produced by dissolving a mixture of $CoCl_2 \cdot 6H_2O$ (0.5 mmol, 0.1190 g) and KSCN (1 mmol, 0.0972 g) in 10 ml water with stirring for 0.5 h, then an ethanol solution (10 ml) of L_2 (0.5 mmol, 0.0420 g) was slowly added. The resulting solution was heated and stirred for 2 h, and then filtered to remove any undissolved material. The filtrate was allowed to stand in air at room temperature for several days, giving orange crystals of two suitable for X-ray diffraction (Yield: 40%). Anal. Found: C, 19.93; H, 2.83; N, 38.80%. Calcd for $C_{18}H_{30}Co_3N_{30}O_3S_{6:}$ C, 19.95; H, 2.79; N, 38.77%.

Table 1
Crystal data and structure refinement for **1** and **2**

	1	2
Empirical formula	$C_{10}H_{16}CoN_{14}O_4S_2$	$C_{18}H_{30}Co_3N_{30}O_3S_6$
Formula mass (g/mol^{-1})	519.40	1083.87
Temperature (K)	293(2)	293(2)
λ (Mo Kα) (Å)	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic
Space group	$P-1$	$P2(1)2(1)2(1)$
a (Å)	7.1325(15)	10.922(3)
b (Å)	7.5380(16)	11.781(3)
c (Å)	10.518(2)	32.055(8)
α (°)	75.290(3)	90
β (°)	88.428(4)	90
γ (°)	72.097(3)	90
V (Å^3)	519.7(2)	4124.9(19)
Z	1	4
Crystal size (mm)	0.30×0.20×0.16	0.14×0.10×0.06
D_{calcd} (mg/m^3)	1.653	1.745
Abs. coeff. (mm^{-1})	1.078	1.564
F (000)	267	2196
2θ range (°)	2.00–25.00	1.27–26.41
Reflections collected	2743	21399
R(int)	0.0166	0.0666
Completeness to θ (%)	99.6	99.7
Goodness-of-fit on F^2	1.106	1.014
Max./min. transmission	1.000000, 0.778314	1.000000, 0.837669
Data/restraints/parameters	1832/0/142	8453/0/542
R_1 ($I > 2\sigma(I)$)	0.0329	0.0525
wR_2 (all data)	0.0935	0.1021
Largest diff. Peak hole (e Å^{-3})	0.410, −0.446	0.355, −0.470