

从配位聚合物到单分子化合物的转化: Demko-Sharpless 四唑 合成法制备两个新颖的 Co(II)配合物

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From Coordination Polymer to Monomeric Complex: Two Cobalt Complexes from a Single Demko-Sharpless' s Tetrazole Synthesis Reaction

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Abstract: The reaction of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with 4-cyanopyridine N-oxide in the presence of NaN_3 affords two novel complexes, $\{[(\text{POTZ})(\text{H}_2\text{O})_2\text{N}_3]\text{Co}(\text{H}_2\text{O})\}$ (**1**) and $\text{Co}(\text{POTZ})_2(\text{H}_2\text{O})_4$ (**2**) (POTZ=4-tetrazolyl pyridine N-oxide), which are two different phases yielded at different stages of a single Demko-Sharpless' s tetrazole synthesis reaction. Surprisingly the 1D chain coordination polymer **1** is almost completely converted into monomeric complex **2** in this reaction, and, in a separate test, **2** also can be converted into **1**. CCDC: 641222, **1**; 641223, **2**.

Key words: coordination polymer; tetrazole; crystal structure

The *in-situ* generation of bridging ligands through the employment of hydrothermal techniques has proven to be a successful approach for the synthesis of coordination polymers in the form of high quality single crystals^[1]. Tetrazole ligands have found wide applications in coordination chemistry, medicinal chemistry and material science^[2]. Recently, Demko and Sharpless have reported a safe, convenient and environmentally friendly procedure for the synthesis of 5-substituted 1H-tetrazoles in water with zinc salts as catalysts^[3]. This new, efficient approach offers exciting and fascinating prospects for the synthesis of a variety of new compounds. A solid precipitate/intermediate,

presumably $(\text{PhCN}_4)_2\text{Zn}$, was observed in the reactions, although the exact role of zinc and the mechanistic pathway (s) in this new synthesis of tetrazoles are not clear^[3]. Trapping and characterizing the “intermediate” in this new preparation of 5-substituted 1H-tetrazole in water may offer organic chemists an opportunity to optimize reaction conditions. We have been interested in the construction of novel supramolecular motifs through *in-situ* hydrothermal reactions^[4]. The structural characterization of such an intermediate may provide important clues to the mechanistic role of metal in this reaction that in turn may allow synthetic chemists to further optimize this reaction.

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Generally, 1H-tetrazoles were prepared by the addition of azide to nitriles in water using zinc salts (as Lewis acid) as catalysts, although the role of the Zn ion in this reaction is unclear. The uses of other metal salts (such as Co^{2+} , Cu^{2+} , Fe^{2+} et. al.) (as Lewis acid) as catalysts during Demko-Sharpless' tetrazole synthesis are hardly successful, because the cyano groups easily hydrolyze in acid solution^[5] in the presence of NaN_3 . Toward this end, we have performed the hydrothermal reaction of 4-cyanopyridine N-oxide with CoCl_2 in the presence of NaN_3 . The reaction afforded two novel complexes, $\{[(\text{POTZ})(\text{H}_2\text{O})_2\text{N}_3]\text{Co}(\text{H}_2\text{O})\}$ (**1**) and $\text{Co}(\text{POTZ})_2(\text{H}_2\text{O})_4$ (**2**), which are two different phases yielded at different stages of a single Demko-Sharpless' tetrazole synthesis reaction. To our surprise, the 1D chain coordination polymer **1** has been almost completely converted into monomeric complex **2** in this reaction, which are unprecedented in tetrazole-metal coordination chemistry, as far as we are aware^[6]. A separate test showed that **2** can also be converted into **1**. Here we report their synthesis, solid state structures, and thermal stability of **2**.

1 Experimental

Synthesis of 1: hydrothermal treatment of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.0475 g, 0.2 mmol) and 4-cyanopyridine oxide (0.0240 g, 0.2 mmol) with NaN_3 (0.0196 g, 0.3 mmol) and H_2O (5.0 mL) was frozen and sealed under vacuum and placed inside an oven at 110~120 °C. Dark purple block crystals were obtained after 3~5 h of heating which was only one phase. The yield of **1** was 98% based on the free ligand, IR (KBr, cm^{-1}) for **1**: 3263(br,s), 3127(w), 3060(w), 2080(s), 1654(m), 1627(w), 1531(m), 1457(m), 1439(m), 1370(m), 1297(m), 1213(s), 1191(s), 1126(w), 1066(w), 956(w), 861(m), 842(m), 762(m), 708(w), 685(w), 654(m), 605(w), 582(w), 527(w), 464(w), 437(w).

Synthesis of 2: the same procedure of **1**. Orange prism crystals were obtained after 24 h of heating which was only one phase. The yield of **1** was 80% based on the free ligand. IR (KBr, cm^{-1}) for **1**: 3262(br,s), 3119(w), 3058(w), 1532(m), 1462(m), 1439(m), 1215(s), 1194(m), 1176(w), 1051(w), 857(m), 845(m),

762(m), 708(w), 655(m), 582(w), 527(m).

Conversion of 1 into 2: Treatment of powdered or crystals **1** (0.1 mmol) in H_2O (3 mL) was frozen and sealed under vacuum and placed inside an oven at 110~120 °C. After 24 h, the pale purple crystals of **2** appeared (approximately 0.1 mmol, 100% yield).

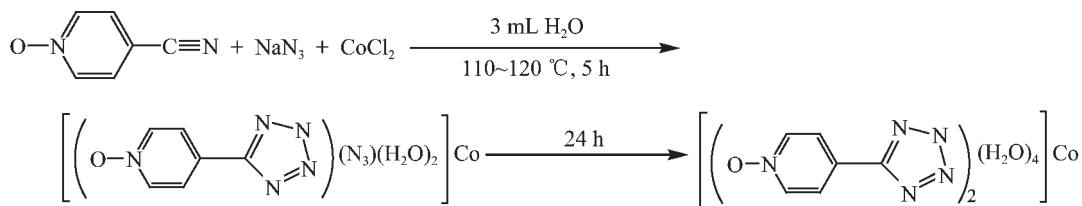
Conversion of 2 into 1: Treatment of powdered or crystals **2** (0.1 mmol) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol) with NaN_3 (0.15 mmol) in H_2O (2 mL) was frozen and sealed under vacuum and placed inside an oven at 110~120 °C. After 24 h, the dark purple crystals of **1** appeared (approximately 0.1 mmol, 100% yield).

Crystal data for 1: $\text{C}_6\text{H}_{10}\text{N}_8\text{O}_4\text{Co}$, Monoclinic, space group $P2_1/c$, $M_r=317.15$, $a=0.72726$ (8) nm, $b=2.1649$ (2) nm, $c=0.7293$ (1) nm, $\beta=93.930$ (2)°, $V=1.1456$ (2) nm³, $Z=4$, $D_c=1.839$ Mg·m⁻³, $\mu=1.527$ mm⁻¹, $S=0.828$, $R_1=0.443$, $wR_2=0.1182$, $T=293$ K. **Crystal data for 2:** $\text{C}_6\text{H}_8\text{N}_5\text{O}_3\text{Co}_{0.5}$, Monoclinic, space group $C2/c$, $M_r=227.64$, $a=2.15744$ (1) nm, $b=0.69784$ (4) nm, $c=1.11751$ (6) nm, $\beta=95.747$ (1)°, $V=1.66921$ (2) nm³, $Z=8$, $D_c=1.812$ Mg·m⁻³, $\mu=1.090$ mm⁻¹, $S=0.724$, $R_1=0.0284$, $wR_2=0.0859$, $T=293$ K.

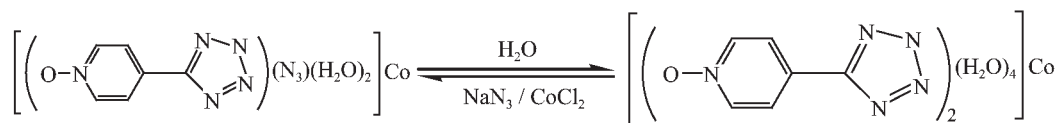
CCDC: 641222, **1**; 641223, **2**.

2 Results and discussion

The reaction of 4-cyanopyridine N-oxide with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was conducted in the presence of NaN_3 in water at 110~120 °C under hydrothermal conditions. After five hours, dark purple crystals of the complex **1** appeared. When the reaction continued at 110~120 °C, the colour of the crystals of **1** slowly disappeared in 24 h, yielding pale purple crystals of **2** (Scheme 1). The powder or crystals of **1** were treated in H_2O at 110~120 °C under hydrothermal conditions. After 24 h, the pale purple crystals of **2** appeared. Powders or crystals of **2** reacted with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in the present of NaN_3 in water at 110~120 °C under hydrothermal conditions afforded the dark purple crystals of **1** in 24 h (Scheme 2). The IR spectra of **1** and **2** show the absence of a cyano peak in the 2200 cm^{-1} region, supporting the proposed reaction between the nitrile and the azide. The emergence of a peak at ca. 1400 cm^{-1} revealed the formation of a tetrazole group. A



Scheme 1



Scheme 2

peak at $3\,400\sim 3\,500\text{ cm}^{-1}$ is that of water, as **1** and **2** contain coordinated water and perhaps uncoordinated water as well. **1** also shows one strong peak of the N_3^- at $2\,080\text{ cm}^{-1}$.

The one-dimensional polymeric structure of **1** was studied by an X-ray single-crystal diffraction (Fig.1). The local coordination environment around Co atom in **1** can be best described as a distorted octahedron with four N atoms in the equatorial plane and two O atoms in water in the axial positions. Two N atoms from tetrazolyl and two other N atoms from different N_3^- ions as bridges link other Co atoms. Overall each POTZ ligand acts as a bidentate bridge to link two Co atoms using tetrazolyl group, resulting in the formation of a 1D zig-zag chain (Fig.2). To the best of our knowledge, this is the first example of 5-substituted 1H-tetrazole prepared from the conversion of a nitrile ligand using cobalt salts (as Lewis acid) as catalysts during the Demko-Sharpless' tetrazole synthesis. The results here well support Sharpless' proposed structures of the intermediate precipitates.

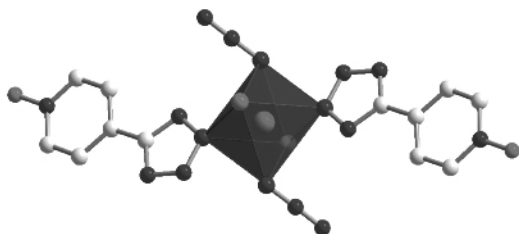


Fig.1 Polyhedral representation of **1** shows the local coordination geometry around Co centers has a slightly distorted octahedron

As indicated earlier the composition of **1** is quite different from that in **2**, although **2** was transformed

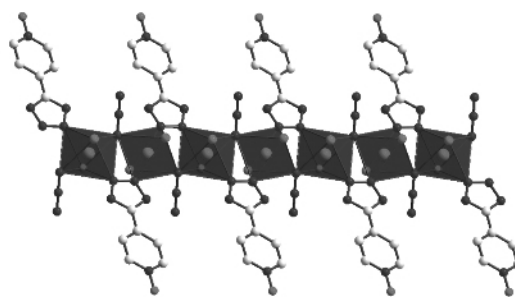


Fig.2 1D framework of **1** highlighting the Co tetrahedron

from coordination polymer **1**. **2** displayed a monomeric structure, and the local coordination environment around Co^{2+} ions in **2** is also a distorted octahedron with four O atoms from water in the equatorial plane and two N atoms from two POTZ in the axial positions (Fig.3). It is notable that hydrogen bonding of neighboring ligands plays an important role in linking the molecules to form a three-dimensional network as shown in Fig.4. Similarly, the results here also support well Sharpless' s proposed structures of the intermediate precipitates.

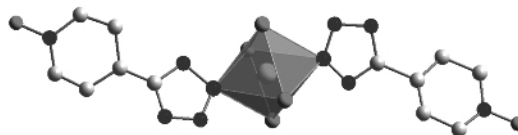


Fig.3 Polyhedral representation of **2** shows the local coordination geometry around Co centers has a slightly distorted octahedron

The thermal stability of compound **2** was studied. Thermogravimetric analysis (TGA) of the polycrystalline sample showed that one discrete weight loss (14.82%) occurred at $45\sim 208\text{ }^\circ\text{C}$, corresponding to the removal of 4 water molecules per formula unit (15.81%

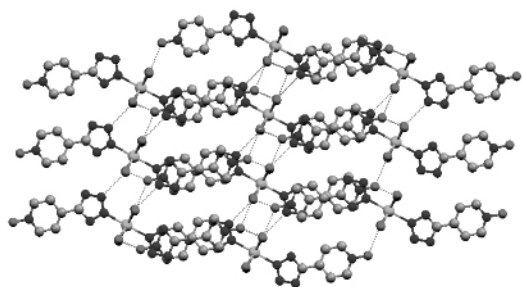


Fig.4 3D network representation of **2** through H-bonds

calculated). Above 250 °C, the decomposition of the network apparently occurred. However, the thermal stability of compound **1** cannot be studied, as it explodes during heating.

In conclusion, the current study provides a new insight into Sharpless' reaction of 5-substituted 1H-tetrazole, suggesting that the water is not only a solvent but also as a reactant. The results presented here demonstrate the value of hydrothermal approaches in the generation of novel coordination polymers.

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