The First Mixed-Valence $Co^{II}Co^{III}$ One-dimensional Chain Coordination Polymer: Synthesis and Structure of $[Co^{II}_2Co^{III}(nta)_2(azpy)_4(H_2O)_6]\cdot[Co^{II}Co^{III}(nta)_2(azpy)_2(H_2O)_2]\cdot 4H_2O$ (nta=Nitrilotriacetate and azpy= 4,4'-Azobispyridine)

Baolong Li, Huibiao Liu, Yan Xu, Gui Yin, Jiutong Chen,[†] and Zheng Xu*
Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China
[†]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, the Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China

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A novel mixed-valence $Co^{II}Co^{III}$ complex $[Co^{II}_2Co^{III}(nta)_2(azpy)_4(H_2O)_6]\cdot[Co^{II}Co^{III}(nta)_2(azpy)_2(H_2O)_2]\cdot 4H_2O$ was synthesized and characterized. Its structure is composed of new motifs, called "the rod with open sidearms" anion and H-like trinuclear cation, which interlock each other. The stack of one-dimensional chains of $[Co^{II}Co^{III}(nta)_2(azpy)_2(H_2O)_2]$ forms two-dimensional rhombus pores through π–π stacking interaction of pyridyl rings from azpy.

The development of inorganic supramolecular architectures is a rapidly developing area of research that has implications for the rational design of functional materials.[1] A particularly promising class of ligands is represented by molecules containing two 4-pyridyl donor units interconnected by chains or groups of different types, such as pyrazine, 4,4'-bipyridine and 4,4'-azobispyridine and a number of extended structure with diverse topologies have been synthesized.[2–6]

To extend the scope of this work to a system containing two different organic ligands is so far less well explored,[7–10] and it is generally not yet possible to predict either the composition or structure of the product of a reaction consisting of a metal center and two different organic ligands. In order for some rationalization and predictive power to be achieved, a much large database of this type of structure needs to be obtained. In the present work, by using a flexible ligand nitrilotriacetate (nta) and a rigid ligand 4,4'-azobispyridine (azpy) as a mixed ligand system, we have synthesized the first mixed-valence cobalt one-dimensional chain coordination polymer, $[Co^{II}_2Co^{III}(nta)_2(azpy)_4(H_2O)_6]\cdot[Co^{II}Co^{III}(nta)_2(azpy)_2(H_2O)_2]\cdot 4H_2O$ **1**.[11]

$CoCO_3\cdot H_2O$ (0.411 g, 3 mmol) and nta (0.094 g, 0.5 mmol) were dissolved in 20 mL boiling water with strong stirring for 1.0 h and filtered, then a 1:1 $EtOH/H_2O$ 20 mL solution of azpy (0.092 g, 0.5 mmol) was slowly added. After two weeks, single crystals suitable for X-ray analysis were obtained. Yield: 0.163 g (55.1%). IR spectrum[12,13] and elemental analysis confirmed the organic content (observed: C, 42.23; H, 4.22; N, 16.32%. Calcd for $C_{84}H_{96}Co_5N_{28}O_{36}$: C, 42.60; H, 4.09; N, 16.56%.)

This complex is composed of a trinuclear H-like cation, $[Co^{II}_2Co^{III}(nta)_2(azpy)_4(H_2O)_6]^+$, and an anion $[Co^{II}Co^{III}(nta)_2(azpy)_2(H_2O)_2]^-$ (Figure 1). Simple[5] and interpenetrated ladders[6] already have been reported and examples of ladders bearing additional ligand as sidearms[14] have also been characterized; however, the title coordination supramolecular compound represents new motif and we call it "the rod with open sidearms" (Figure 2). In the rod with open sidearms, Co(3)

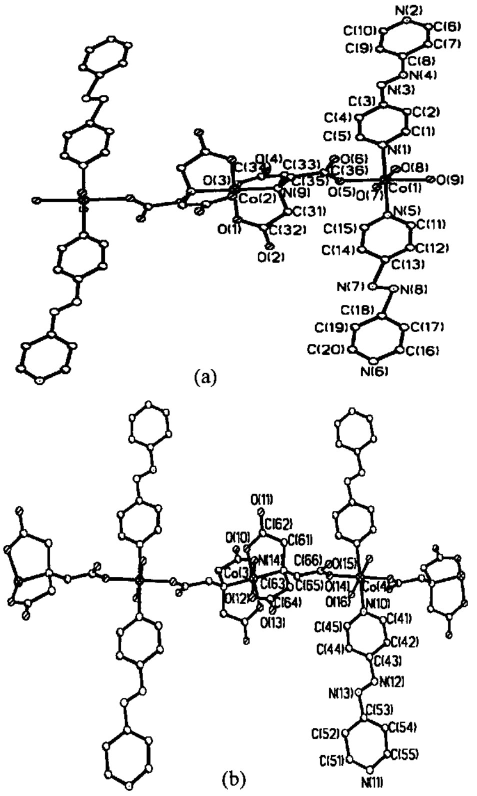

Figure 1. (a) The local coordination of cobalt cation and (b) cobalt anion in **1**.

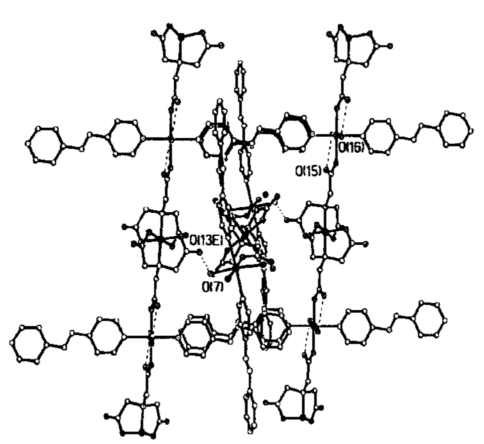

Figure 2. The two-dimensional rhombus network connected through weak interations in 1 view from the b direction.

atom has an elongated octahedral symmetry with four O atoms located at equatorial positions (Co(3)–O(10), 1.878(4), Co(3)–O(12), 1.857(4) Å) and two N atoms of two nta occupied at apical position (Co(3)–N(14), 1.956(5) Å). In contrast to Co(3), Co(4) atom has a suppress octahedral geometry with two O atoms from two water and two N atoms from two azpy located at equatorial positions (Co(4)–O(16), 2.216(4); Co(4)–N(10), 2.179(6) Å) and two O atoms from two nta occupied at apical position (Co(4)–O(14), 2.025(4) Å). The bridging nta links Co(3) and Co(4), which results in forming a infinitive rod with open-sidearms. The sidearms (azpy) stack each other with the neighbours via π–π interactions of the pyridyl rings of the azpy to result in formation of the two-dimensional rhombus network ca. 14.3 Å × 13.9 Å. The pyridyl rings of azpy sidearms from two different rods anions stack with a face-to-face separation of ca. 3.5–3.7 Å, indicating a significant π–π interaction. The two-dimensional networks stack in parallel with the sheet distance 14.706 Å. In the trinuclear cation, Co(1) is coordinated by four O atoms from three water and one nta at equatorial positions (Co(1)–O(7), 2.092(4); Co(1)–O(5), 2.099(4); Co(1)–O(9), 2.122(4); Co(1)–O(8), 2.131(4) Å) and two N atoms of two azpy ligand at apical position (Co(1)–N(5), 2.183(5); Co(1)–N(1), 2.202(5) Å). Co(2) is octahedral either which coordinated by four O atoms at equatorial positions (Co(2)–O(1), 1.871(5); Co(2)–O(3), 1.886(5) Å) and two N atoms at apical position (Co(2)–N(9), 1.974(5) Å). The trinuclear H-like cations interlock with the 2D network, namely, one side of the “H” locates above the sheet, while another side lays underneath the sheet, and the Co(2) complex subunit occupies at the center of the rhombus to connect two sides of the “H”. The coordinated water molecules from the trinuclear cation form strong hydrogen bonds with the oxygen atoms of the carboxylate of nta from “the rod with open-sidearms” anions (O(7)–O(13), 2.164 Å). Also, there are hydrogen bonds in intra-anions and intra-cations and between un-coordinated water and nta.

One remarkable feature of the structure is that the Co ions adopt different valence number, i.e. 2+ for Co(1) and Co(4) and 3+ for Co(2) and Co(3) based on the bond lengths and bond-valence sum calculations.[15] According to a literature search, none of mixed-valence cobalt 4-pyridine mixed ligand complex or one-dimensional chain mixed-valence cobalt complex has been previously reported.

The magnetic moment of the complex is 8.05 BM at 300 K. The value is greater than the spin-only value 6.71 BM for three local $S = 3/2$ and two diamagnetic $S = 0$ spins, suggesting an orbital contribution of the high spin $\mathrm{Co^{II}}$ to the magnetic moment. The magnetic moment exhibits continuous decrease upon cooling to 7.29 BM at 76 K.

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11 Crystal data for complex **1** $C_{84}H_{96}Co_5N_{28}O_{36}$: monoclinic, space group $P2_1/c$; $a = 14.2670(4)$, $b = 25.9132(6)$, $c = 13.9140(4)$ Å, $\beta = 96.3380(10)°$, $U = 512.6(2)$ Å^3, $Z = 2$, $M_r = 2368.54$, $D_c = 1.536$ g·cm^{-1}, $\lambda = 0.71073$ Å. A crystal of dimensional 0.50 × 0.32 × 0.20 mm was selected for indexing and intensity data collected at 293(2) K. Total number of measured and observed independent reflections ($I_{obs}>2\sigma(I)$) are 20668 and 9014. Final R_1=0.0686, wR_2=0.1500.

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13 Infrared spectrum of **1** exhibits three absorptions [1637, 1602 and 1591 cm^{-1}] due to ν(COOM) stretching bands which conform the presence of different coordination environment of monodentate carboxylate and no absorption band around 1700 cm^{-1} confirmed that there is no protonated nta.

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