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Letter

Synthesis and structure of a one-dimensional cobalt(II) coordination polymer with 1,3-bis(1,2,4-triazol-1-yl)propane

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A novel 1D-coordination polymeric Co(II) complex [Co(btp)$_2$(NCS)$_2$]$_n$ [1, btp = 1,3-bis(1,2,4-triazol-1-yl)propane] was synthesized and characterized. The coordination geometry of the cobalt ions is distorted octahedral, with the equatorial plane formed by the four nitrogen atoms of the four triazole groups and the axial sites occupied by two terminal *trans* thiocyanato ligands. The Co(II) ions are linked by the btp ligands, building up coordination polymers of infinite 1D-neutral chains.

Synthesis of new organic-inorganic hybrid polymeric compounds is a relatively new research area that has evolved rapidly in the last several years. The interest in these systems is justified by the numerous applications that they may have unusual properties that they may exhibit, such as new electronic, optical, magnetic and catalytic properties.[1–6] Amongst the synthetic strategies to achieve these polymeric compounds, one of the most fruitful choices consists in taking advantage of neutral organic groups containing *N*,*N*′-bidentate donors that can act as bridging ligands towards transition metal ions.[7–14] So far a number of one-, two- and three-dimensional infinite frameworks have already been generated with rigid or flexible ligands such as bipyridyl-based systems or derived imidazoles.[15–17] To date, a number of 2D and 3D frameworks of Co(II) with *N*,*N*′-bidentate spacers[8,17–19] have been produced. It is well-known that quasi-1D materials often exhibit unique physical properties. However, very few 1D chains of cobalt complexes with *N*,*N*′-bidentate ligands have been reported.[20]

Recently, a new class of flexible ligands, [bis(1,2,4-triazole-1-yl)-alkanes], have been found to be very effective in the formation of various interesting extended structures. Whereas a variety of new types of polymeric 2D and 3D frameworks with Fe(II) and Mn(II) have been documented, the cobalt complexes of these systems have never been isolated and structurally characterized. It is evident that the crystallization media such as solvent and template may influence the nucleation and architecture of coordination polymers.[21] We report herein the first successful isolation and characterization of a cobalt coordination polymer containing a flexible bis(1,2,4-triazole-1-yl)alkane ligand, obtained by changing reaction conditions.

The treatment of Co(ClO$_4$)$_2$·H$_2$O with btp and NH$_4$SCN in aqueous solution produces the title complex [Co(btp)$_2$(NCS)$_2$]$_n$, **1**, as pink crystals. The molecular structure of **1** was unequivocally confirmed by X-ray diffraction. The structure of **1** exhibits a one-dimensional chain.

Fig. 1 shows the local coordination about the cobalt center. In the molecular structure, the coordination polyhedra of the cobalt(II) ions are distorted octahedral, in which the equatorial plane is formed the four nitrogen atoms of the triazoles and the axial positions are occupied by two *trans* thiocyanato ligands. The Co–N$_{\mathrm{NCS}}$ distances [2.101(14) Å] are slightly shorter than the Co–N$_{\mathrm{btp}}$ distances [2.106(2) and 2.191(2) Å]. The N(7)#1–Co–N(7), N(1)–Co–N(1)#1 and N(6)#2–Co–N(6)#3 angles are 180.0°. The other N–Co–N angles around the Co centers range from 87.11(8)° to 92.89(8)°. The imidazole ring is canted to the equatorial plane at an angle of 64.03°, while the five atoms of the imidazole ring are almost coplanar (maximum deviation 0.0054 Å). The NCS group is almost linear with an N(7)–C(8)–S(1) angle of 176.9(3)°. The connection between Co atoms and NCS groups are bent with a C(8)–N(7)–Co(1) angle of 154.1(2)°.

Fig. 2 shows the extended structure of **1**. The Co(II) ions are linked by the btp ligands, building up coordination polymers into one-dimensional neutral looped chains (Fig. 3) instead of forming a two-dimensional Cu-btp polymer network. The NCS groups occupy terminal positions. Each ligand adopts a *trans-gauche* conformation. Each chain consists of sixteen-membered rings, in which two cobalt ions are joined to two btp molecules. The Co–Co separation across the bridging btp is 10.4472 Å.

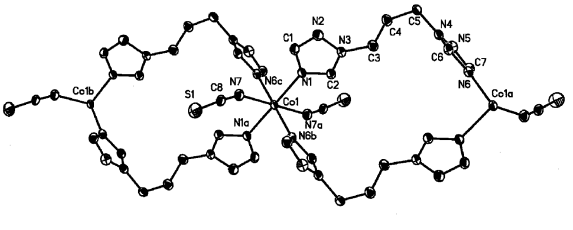

Fig. 1 The coordination environment of the Co atom in [Co(btp)$_2$(NCS)$_2$]$_n$ with atom labeling scheme. Selected bond lengths (Å) and angles (deg): Co(1)–N(7)#1, 2.101(2); Co(1)–N(7), 2.101(2); Co(1)–N(1), 2.160(2); Co(1)–N(1)#1, 2.160(2); Co(1)–N(6)#2, 2.191(2); Co(1)–N(6)#3, 2.191(2); N(6)–Co(1)#4, 2.191(2); N(7)#1–Co(1)–N(7), 180.0; N(1)–Co(1)–N(1)#1, 180.0; N(6)#2–Co(1)–N(6)#3,180.0; N(7)#1–Co(1)–N(1), 89.27(8); N(7)–Co(1)–N(1), 90.73(8); N(7)#1–Co(1)–N(1)#1, 90.73(8); N(7)–Co(1)–N(1)#1, 89.27(8); N(7)#1–Co(1)–N(6)#2, 89.30(9); N(7)–Co(1)–N(6)#2, 90.70(9); N(1)–Co(1)–N(6)#2, 87.11(8); N(1)#1–Co(1)–N(6)#2, 92.89(8); N(7)#1–Co(1)–N(6)#3, 90.70(9); N(7)–Co(1)–N(6)#3, 89.30(9); N(1)–Co(1)–N(6)#3,92.89(8); N(1)#1–Co(1)–N(6)#3, 87.11(8).

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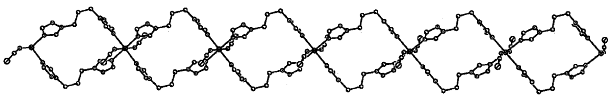

Fig. 2 The extended structure of $[Co(btp)_2(NCS)_2]_n$.

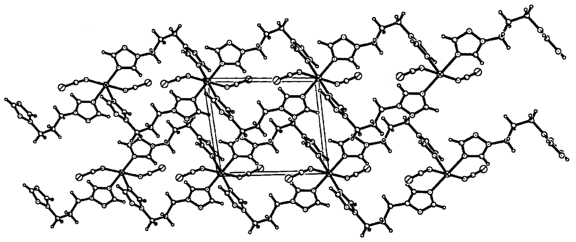

Fig. 3 Packing of $[Co(btp)_2(NCS)_2]_n$, along the c axis of the unit cell.

The infrared spectra of complex **1** exhibits characteristic bands for btp ligand and thiocyanate group. The C=N stretching vibration of the thiocyanate group appears as a single and strong peak at 2079 cm^{-1}, which is consistent with the occurrence of thiocyanate-N coordination.[22,23] The group of weak peaks at 3200–2870 cm^{-1} are attributed to the C–H vibration. The strong peak at 1519 cm^{-1} belongs to the vibration of the conjugated C–N–N in the imidazole ring.

Experimental

Synthesis

Btp was prepared as described in Ref. 23. Compound **1** was produced by dissolving a mixture of $Co(ClO_4)_2 \cdot 6H_2O$ (0.5 mmol, 183.0 mg) and NH_4SCN (1 mmol, 76.1 mg) in 20 ml water with stirring for 0.5 h, then an aqueous solution (5 ml) of btp (0.5 mmol, 90 mg) was slowly added. The resulting solution was stirred for 24 h and filtered to remove any undissolved material. The filtrate was allowed to stand in air at room temperature for several days, giving pink crystals suitable for X-ray diffraction (yield: 35%). The crystals of **1** have a good stability after being removed from the mother liquor. Anal. calcd for $C_8H_{10}Co_{0.50}N_7S$: C, 36.16; H, 3.79; N, 36.89%. found: C, 35.87; H, 3.53; N, 36.21%.

X-Ray crystallography

Determination of the unit cell and data collection was performed on a Rigaku RAXIS RAPID IP detector operating with graphite-monochromated Mo–Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. Structure was solved by direct methods and refined by least-squares method on F^2 (SHELXL-97).

Crystal data: compound **1** $[Co(btp)_2(NCS)_2]$, triclinic, space group P-1, $a = 8.6002(4)$, $b = 9.6688(3)$, $c = 7.8745(5)$ Å, $\alpha = 107.718(4)°$, $\beta = 112.927(2)°$, $\gamma = 77.416(2)°$, $U = 570.77(5)$ Å^3, $Z = 2$, $D_c = 1.546$ Mg m^{-3}, $\mu = 0.972$ mm^{-1}, final R value 0.0407 for 2456 unique reflections $[I > 2\sigma(I)]$, $wR_2 = 0.0929$ (all data).

CCDC reference number 188646. See: http://www.rsc.org/suppdata/nj/b2/b206315h/ for crystallographic files in CIF or other electronic format.

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