Hydrogen-bonded extended structure of the 1 : 3 adduct of a C_3 symmetric cobalt(III) complex with a tripod-ligand involving three imidazolate groups and hydroquinone or resorcinol

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The assembly reaction arising from hydrogen bonding between a chiral C_3 symmetric cobalt(III) complex and a tripod-ligand involving three imidazolate groups [tris[2-(((2-methylimidazolato-4-yl)methylidene)amino)ethyl]amine]cobalt(III) and either hydroquinone or resorcinol gave the 1 : 3 adducts, with 3D extended structures showing the template effect of the complex.

The field of supramolecular chemistry and crystal engineering has advanced to a stage at which it is possible to select building blocks that will self-assemble into structures with specific network topologies.[1] Hydrogen bonding is the intermolecular force in self-assembling systems by virtue of its directionality, specificity, and biological relevance.[2] We have previously reported a self-assembly process from achiral components to chiral metal complex molecule, homochiral 2D layer, and finally conglomerate, in which a cobalt(III) complex with a tripod-ligand $[Co(H_3L^1)]^{3+}$ $(H_3L^1 = tris[2-(((imidazol-4-yl)methylidene)amino)ethyl]amine]$ induces the chirality of clockwise (C) and anticlockwise (A) enantiomers because of the screw coordination arrangement. The deprotonation of the complex generates equal numbers of completely protonated and completely deprotonated molecules, $[Co(H_3L^1)]^{3+}$ and $[Co(L^1)]$, to form an extended 2D homochiral assembly structure because of the intermolecular imidazole–imidazole hydrogen bonds.[3]

As an alternative method of constructing a hydrogen-bonded assembly network structure instead of the self-assembly process of a single self-complementary molecule, in this study the multi-component assembly reaction between the fully deprotonated complex $[Co(L^2)]$ $(H_3L^2 = tris[2-(((2-methylimidazol-4-yl)methylidene)amino)ethyl]amine)$ and either hydroquinone (HQ) or resorcinol (RC) has been used, in which $[Co(L^2)]$ and hydroquinone or resorcinol can be expected to behave as acceptor and donor building components, respectively (Scheme 1). We report here the unique hydrogen-bonded network structures of the 1 : 3 adducts of $[Co(L^2)]$ having a chiral C_3 symmetry and either hydroquinone or resorcinol, $[Co(L^2)]\cdot3HQ$ **1** and $[Co(L^2)]\cdot3RC$ **2**.

The 1 : 3 adducts, $[Co(L^2)]\cdot3HQ$ **1** and $[Co(L^2)]\cdot3RC$ **2**, were obtained as red crystals from the reaction mixture of the electrically neutral fully-deprotonated complex $[Co(L^2)]\cdot3.5H_2O$ and hydroquinone or resorcinol in methanol.† Even if $[Co(L^2)]\cdot3.5H_2O$ and HQ or RC were mixed in 1 : 1 molar ratio, the 1 : 3 adduct was obtained as well-grown crystals. The elemental analyses agreed with the 1 : 3 chemical formulas. The IR spectrum showed an intense single band attributable to the C=N stretching vibration at 1607 and 1606 cm⁻¹ for **1** and **2**, respectively. The band's wavenumber is lower than the 1634 cm⁻¹ of the protonated species $[Co(H_3L^2)](ClO_4)_3\cdot0.5H_2O$ by about 25 cm⁻¹ and much closer to the 1596 cm⁻¹ of the fully deprotonated complex $[Co(L^2)]\cdot3.5H_2O$.

The structures of **1** and **2** were determined by single-crystal X-ray diffraction analyses.‡ The 1 : 3 adducts **1** and **2** crystal-

lized in a trigonal non-centrosymmetric space group $R3c$ (no. 161) with similar cell dimensions, so that the two crystal structures are essentially similar. Fig. 1 shows the crystal structure of **1**. The crystal structure consists of one third of $[Co(L^2)]$ and one hydroquinone or one resorcinol as the unique atoms. The cobalt(III) ion and the central amine nitrogen atom of the tripod-ligand lie on a crystallographic C_3 axis, and the complex $[Co(L^2)]$ becomes a chiral C_3 symmetric molecule because of the screw coordination arrangement of the tripod-ligand around the Co(III) ion. The Co(III) ion assumes an octahedral coordination environment with the N_6 donor atoms of three Co–N (imidazolate) bonds and three Co–N (imine) bonds. The Co–N (imidazolate) and Co–N (imine) bond distances are 1.939(3) and 1.956(3) Å for **1** and 1.922(6) and 1.955(6) Å for **2**, respectively; these values are in the range reported for Co(III) complexes with similar nitrogen ligands.

A hydrogen bond is formed between the imidazolate nitrogen atom $N(4)$ of $[Co(L^2)]$ and $O(1)$ of hydroquinone, with a distance of $N(4)\cdots H(14)–O(1) = 2.612(4)$ Å. Another hydrogen bond is formed between $O(1)$ and $O(2)$ of the adjacent hydroquinone molecule with a distance of $O(2)–H(15)\cdots O(1) = 2.715(4)$ Å. These two hydrogen bonds play roles of connector between $[Co(L^2)]$ and hydroquinone and between two adjacent
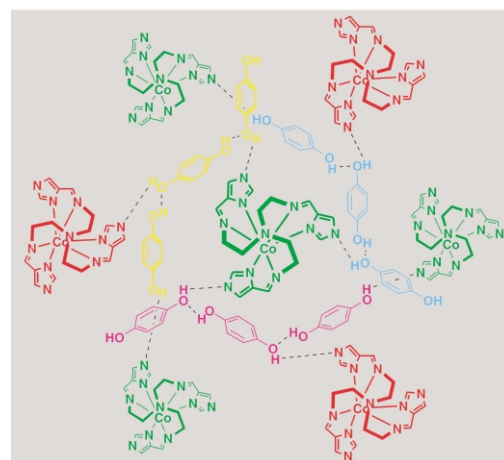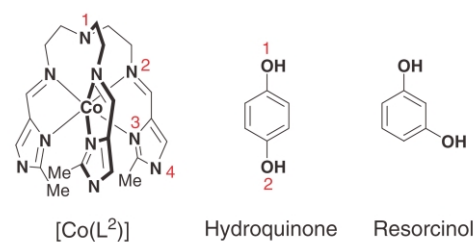
Scheme 1 Molecular structures of a chiral C_3 symmetric molecule $[Co(L^2)]$, hydroquinone, and resorcinol. Hydrogen-bonded extended structure.
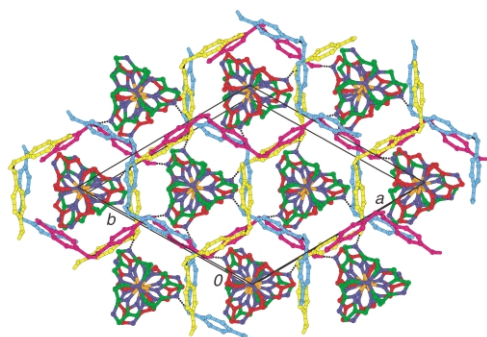
Fig. 1 X-Ray crystal structure of [Co(L²)]·3HQ **1** projected on the *ab*-plane. The hydrogen bonds are represented by dotted lines.

Fig. 3 X-Ray crystal structure of [Co(L²)]·3RC **2** projected on the *ab*-plane showing a similar hydrogen-bonded network structure to **1**.

hydroquinones, to form a 3D assembly structure as shown in Fig. 1. It should be noted that one hydroxy group O(1) of the hydroquinone functions as both donor and acceptor building components for the formation of the hydrogen bonds, while another hydroxy group O(2) functions only as a donor building block.

The extended structure constructed by the inter-hydroquinone hydrogen bonds is shown in Fig. 2(a) and (b), in which [Co(L²)] is omitted to show the crystal structure. Because the two hydrogen atoms of the hydroxy groups of a hydroquinone assume a *syn*-form, and the O(2) and O(1) atoms of the hydroxy groups act as donor and acceptor atoms for the inter-hydroquinone hydrogen bond of O(2)–H(15)···O(1), respectively, hydroquinone molecules are connected linearly by the hydrogen bond to form a 1D zigzag chain. As the crystal structure exhibits C_3 symmetry, there are three 1D zigzag chains around a [Co(L²)] molecule. These three 1D chains are represented by yellow, red, and blue colors in Fig. 2. The 3D framework constructed by the array of three 1D chains gives hexagonal voids. In each void, a chiral C_3 symmetric Co(III) complex is trapped by three N(4)···H(14)–O(1) hydrogen bonds so that the cavity is filled. The crystal structure consists of two

enantiomers of [Co(L²)], and the *C* and *A* enantiomers are arrayed alternately along the *c*-axis.

Fig. 3 shows the hydrogen-bonded network structure of **2**. The network structure is essentially similar to that of **1**, although the 3D framework constructed by inter-resorcinol hydrogen bonds is more distorted from a regular hexagon than that of **1**.

The present extended network structure is constructed using the two components [Co(L²)] and hydroquinone or resorcinol, in which [Co(L²)] acts as a hydrogen-bonding acceptor and shows a template effect on the final network structure, while hydroquinone or resorcinol act as both hydrogen-bonding acceptor and donor.
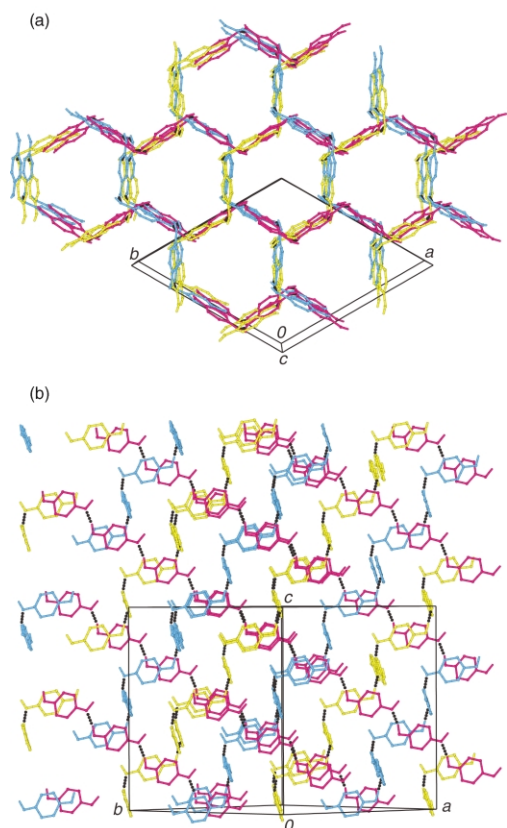
Notes and references

Fig. 2 Extended structure constructed by inter-hydroquinone hydrogen bonds. Each 1D chain is represented by a single color. (a) Top view projected on the *ab*-plane. (b) Side view projected along the *ab*-plane.
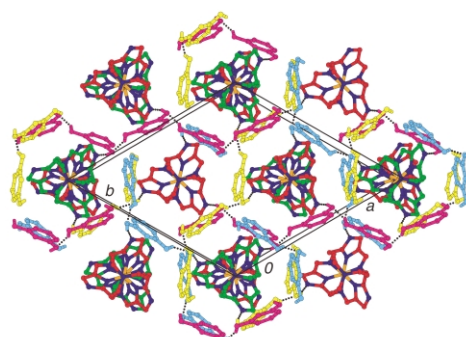
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