Coordination Networks

In Situ Observation of a Reversible Single-Crystal-to-Single-Crystal Apical-Ligand-Exchange Reaction in a Hydrogen-Bonded 2D Coordination Network

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Functionalization of coordination networks is a crucial step for their application.[1] One of the salient features of coordination networks is that they often contain substitution-active metal sites in their framework. Ligand exchange will considerably affect their d-orbital configuration and lead to the electronic and spin control of coordination networks. Cobalt is a classical example that shows chromism upon ligand exchange in the solid state, as commonly observed in

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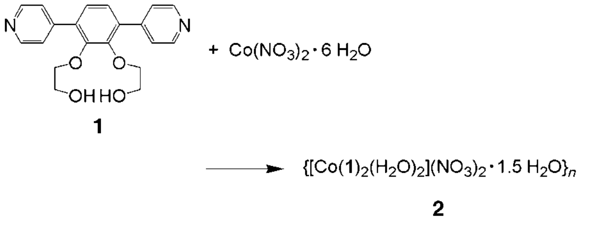
the hydration-induced color change of silica gel. Such a ligand-exchange process is, however, seldom observable by single-crystal X-ray diffraction studies because the drastic structural changes during the process readily cause loss of crystallinity. Here we report the crystallographic observation of reversible apical-ligand exchange at a cobalt center in situ. The metal center is incorporated in a square-grid coordination network that provides a relatively fluid cavity within the solid. We show that aqua and nitrate ligands can be reversibly coordinated to the cobalt center in a single-crystal-to-single-crystal fashion.[2–4]

We designed a 4-pyridyl-terminated, rodlike ligand containing ethylene glycol side chains (**1**).[5] Slow complexation of $Co(NO_3)_2{\cdot}6H_2O$ in MeOH over a solution of **1** in toluene produced orange-yellow single crystals of $\{[Co(\mathbf{1})_2(H_2O)_2](NO_3)_2{\cdot}1.5H_2O\}_n$ (**2**) in 76 % yield [Eq. (1)].



(1)

X-ray crystallographic analysis revealed the square-grid network structure of **2** (Figure 1 a). The grid sheet layers are stacked above each other in an offset fashion on both edges (Figure 1 b). The ethylene glycol chains play two important roles: they add considerable stabilization to the crystal due to hydrogen-bond formation and they also introduce moderate flexibility inside the cavity by allowing guest molecules to behave as in solution. As regards the stabilization effect, we assume that the crystal is stabilized by infinite 1D hydrogen-bond (O–H···O) arrays that interpenetrate the layers (Figure 1 c).[6] In fact, a similar square-grid coordination network that does not contain an ethylene glycol chain on the ligand is much less stable than **2**:[7] a crystal of the coordination network with no substituent gradually deteriorated above room temperature due to the loss of guest molecules.

The stability and flexibility of **2** enabled us to directly observe a reversible apical-ligand-exchange reaction at the hinge metals by X-ray crystallography. Two water molecules are coordinated to the cobalt(II) center at the apical positions (aqua form) with four pyridyl groups at the equatorial positions (Figure 2 a). Upon heating at 150 °C for 24 h the yellow crystal turned red, with no loss of crystallinity. The crystallographic analysis revealed that the apical water molecules had been substituted by two nitrate ions and extruded from the crystal to give the nitrate complex $[Co^{II}(\mathbf{1})_2(NO_3)_2]_n$ (**3**; Figure 2 b). Upon exposure of **3** to air at room temperature, it changed back to the initial aqua form. The color of the crystal returned to yellow within a few minutes and the crystallinity was again retained. Crystallographic and elemental analysis showed that the newly obtained aqua form $\{[Co(\mathbf{1})_2(H_2O)_2](NO_3)_2{\cdot}1.5H_2O\}_n$ (**2′**) is almost superimposable on the original structure of **2** (Figure 2 c).

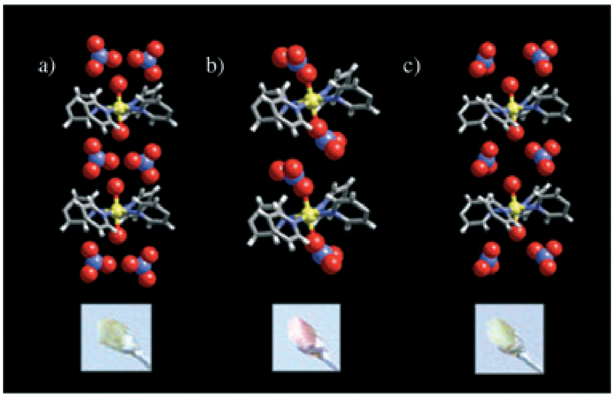


Figure 2. Photographs and crystal views around the cobalt ion: a) original crystal **2**, b) the crystal after heating at 150 °C for 24 h (**3**), and c) the crystal after exposure of **3** to air (**2′**). Two other disordered nitrate ions have been omitted for clarity.

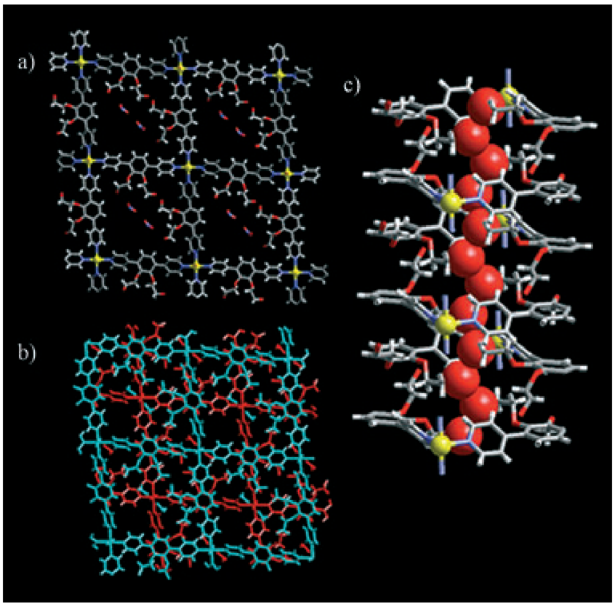


Figure 1. a) The square-grid network of **2**. Guest molecules (H_2O) have been omitted for clarity. b) The two-layer stack of **2**. c) The infinite 1D hydrogen bond (O–H···O) array in **2**. The oxygen atoms of the OH groups are represented by a space-filling model.

The chromism of the crystal is principally ascribed to the energy-level change of the d orbitals of cobalt induced by apical-ligand exchange. The nitrate anion, which has a weaker crystal-field-splitting ability than water, decreases the HOMO–LUMO energy gap in the complex, which causes a red shift of the absorption bands. The energy-level change also influences the geometrical parameters of the cobalt center.[8]

The void present after removal of the water molecules is mainly offset by framework distortion. The grid framework is slightly compressed, which causes a decrease of cell volume from 4263.9(7) to 4036.0(16) Å^3. Interestingly, the void is also offset by dynamic disordering of the flexible ethylene glycol chains. The mobility of the carbon and oxygen atoms in the side chains significantly increases in the absence of guest molecules, as shown by the ORTEP drawing of the square-grid cavity in Figure 3.

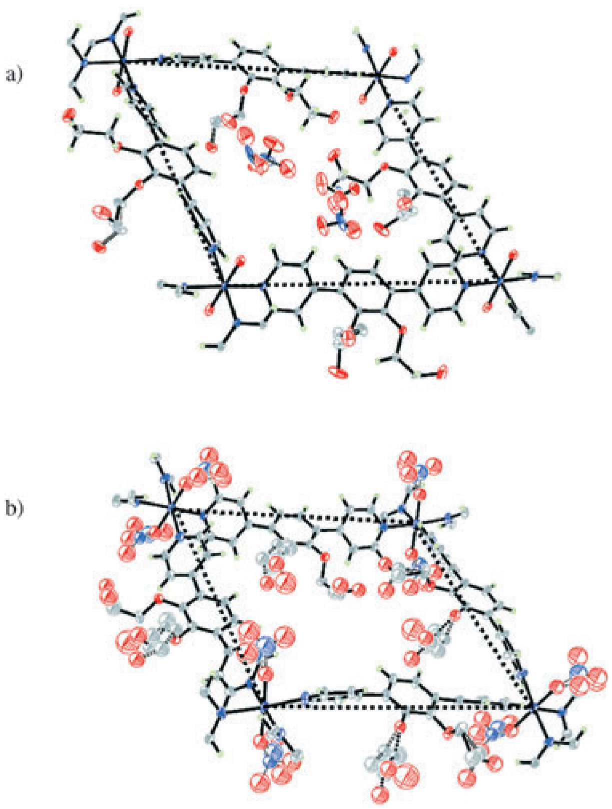


Figure 3. ORTEP drawing (30% probability) of a square-grid unit of **2** (a) and **3** (b). The bridging ligand of **3** shows considerable distortion compared to that of **2**. The disordered guest water molecules in (a) have been omitted for clarity.

Thermogravimetric analysis of the crystal of **2** showed loss of all water molecules in the range 25–90 °C. The number of water molecules removed (weight loss of 6.47%) agrees well with that determined by X-ray analysis (6.6%). DSC analysis of a crystal of **2** showed two endothermic peaks at 93.8 °C and 77.4 °C, which are attributed to the release of coordinated water from the cobalt ion and noncoordinated water from the cavity, respectively.

In summary, we have succeeded in the crystallographic observation of an apical-ligand-exchange reaction at a cobalt ion within a square-grid coordination network. Since ligand exchange at a metal is a bimolecular reaction, the process can only rarely be observed by X-ray crystallography. We have realized the in situ crystallographic observation of this dynamic process, which involves drastic structural changes around the reaction center, by utilizing functionalized bridging ligands. The in situ observation of various chemical processes in the fluid cavity is our next challenge, and the results will be reported in due course.

Experimental Section

Single crystals of **2** were grown by layering a methanol solution of $Co(NO_3)_2 \cdot 6H_2O$ (5.8 mg in 1 mL) onto a toluene solution of **1** (15.0 mg in 2 mL). After allowing the solution to stand for 4 d, the crystals were isolated in 76% yield by filtration. Elemental analysis (%) calculated: C 50.53, H 4.98, N 8.84; found: C 50.34, H 4.86, N 8.72. Crystal data for **2**: orthorhombic, *Pbcn*, $a = 20.580(6)$, $b = 23.717(7)$, $c = 8.820(3)$ Å, $V = 4263.9(7)$ Å^3, $Z = 4$, $T = 80$ K, $\rho_{calcd} = 1.434$ g cm^{-3}, $\mu = 0.483$ mm^{-1}, final R_1 ($I > 2\sigma(I)$) = 0.0762, wR_2 (all data) = 0.2062, GOF = 1.044.

Crystal data for **3**: orthorhombic, *Pbcn*, $a = 20.572(5)$, $b = 23.092(5)$, $c = 8.496(2)$ Å, $V = 4036.0(16)$ Å^3, $Z = 4$, $T = 423$ K, $\rho_{calcd} = 1.441$ g cm^{-3}, $\mu = 0.506$ mm^{-1}, final R_1 ($I > 2\sigma(I)$) = 0.1039, wR_2 (all data) = 0.2384, GOF = 1.039.

2′: Elemental analysis (%) calculated: C 50.53, H 4.98, N 8.84; found: C 50.60, H 4.89, N 8.73. Crystal data for **2′**: orthorhombic, *Pbcn*, $a = 20.576(2)$, $b = 23.677(3)$, $c = 8.7155(9)$ Å, $V = 4246.0(8)$ Å^3, $Z = 4$, $T = 80$ K, $\rho_{calcd} = 1.304$ g cm^{-3}, $\mu = 0.466$ mm^{-1}, final R_1 ($I > 2\sigma(I)$) = 0.0948, wR_2 (all data) = 0.2206, GOF = 1.025.

All the diffraction data were measured on a Siemens SMART/CCD diffractometer ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). Non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at calculated positions and refined using a riding model. CCDC-250540 (**2**), -250541 (**3**), and -250542 (**2′**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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