Spin transition triggered by desorption of crystal solvents for a two-dimensional cobalt(II) complex with hydrogen bonding†

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[Co(StpybNOH)2][BPh4]2 (1; StpybNOH = 5,5″-bis(2,2″-terpyridine) has a two-dimensional (2D) structure through a hydrogen bond between the NOH sites, as revealed by X-ray crystallography. The crystal solvents were desorbed above 300 K as shown by thermal analyses and powder X-ray crystallography. The removal of the crystal solvents allowed irreversible structural changes and a spin transition of the Co centre from \( S = 1/2 \) to \( 3/2 \).

Introduction

The spin crossover (SCO) phenomenon is a reversible spin transition based on the difference in the spin configuration of a metal centre caused by external stimuli. The SCO-active materials have been applied to the development of switches, sensors and memory devices. To obtain a beneficial magnetic–switching material, it is necessary to enhance the cooperativity between the SCO units. Molecular design with intermolecular hydrogen bonding is an effective approach to obtain high cooperativity because of its high directivity and strong intermolecular interaction compared to other non-covalent contacts such as π–π interactions.

A cobalt(II) complex can exhibit SCO behaviour between the high-spin (HS; \( S = 3/2 \)) and low-spin (LS; \( S = 1/2 \)) states with a small difference in entropy. The compound 2,2″-terpyridine (terpy, Fig. 1a) has been utilised as a ligand and has contributed to the SCO behaviour in the Co2+ ion. In addition, a variety of functional groups (R = hydroxy, alkoxyl, pyridyl and others) may be easily introduced at the 4″-position of the terpy ligand. This chemical modification allows the Co-terpy complexes to control the molecular and crystal structures. However, in previous studies of the Co-terpy complexes, there have been no reports on the terpy ligand being chemically modified at positions other than the 4″-position.

In this study, we focused on the introduction of substituents at the 5,5″-positions of the terpy molecule and prepared a terpy analogue, 5,5″-bis(2,2″-terpyridine) (StpybNOH, Fig. 1b). The chemical modification at the 5,5″-positions allows the formation of a 2D network along two terpy ligands because the [Co(terpy)]2+ unit has a cross-like structure. In addition, the insertion of the hydroxylamine (NOH) is expected to provide an intermolecular hydrogen bond through the NOH sites. A novel cobalt(II) complex [Co(StpybNOH)2][BPh4]2 (1; BPh4 = tetraphenyl borate) was synthesised and it showed intermolecular contact through the NOH sites. Crystallisation solvents (acetone and water molecules) were present in the void spaces. The solvents can be easily desorbed above 300 K, and simultaneously, the desorption can result in a structural change and spin transition.

Experimental

Materials and methods

Tetrahydrofuran (THF) was used after distillation from sodium/benzophenone under N2 gas. Other solvents were purchased and used without further purification. 1H and 13C NMR experiments (400 and 100 MHz, respectively) were performed in DMSO-d6 on an ECZ400S spectrometer (JEOL). The chemical shifts (given in ppm) were measured versus the central peak of DMSO (\( 1^H \) NMR: 2.50 ppm and \( 13^C \) NMR: 39.52 ppm) as a reference. The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet), dd (doublet...
of doublets) and m (multiplet). Infrared (IR) spectra were obtained on an FT/IR-4600 (Jasco) spectrometer using a diamond attenuated total reflectance (ATR) method. The spectral data are obtained as major peaks in wavenumbers (cm⁻¹) and recorded in a spectral window of 4000–400 cm⁻¹. Elementanalyses were carried out with a PerkinElmer Series II CHNS/O 2400 analyser. High resolution mass spectra (HRMS) were recorded in an electrospray ionization (ESI) mode using an AccuTOF-JMS-T100LP (JEOL) spectrometer. The specimen was dissolved in methanol. Powder X-ray diffraction (PXRD) spectra were recorded using a Rigaku MiniFlex600 diffractometer (Cu Kα radiation: λ = 1.54184 Å) in the range of 30°–430 K. Thermogravimetry (TG) and differential thermal analysis (DTA) of 1 were carried out on a Bruker AXS TG2000SA instrument. The temperature scan rate was 2 K min⁻¹ in the range of 296–481 K. Differential scanning calorimetry (DSC) was performed on a Bruker DSC3200A apparatus. The temperature scan rate was 5 K min⁻¹.

Synthesis

Synthesis of 5,5”-bis(N-tert-butyl hydroxylamino)-2,2’:6’,2”-terpyridine (5tpybNOH). An n-hexane solution of n-BuLi (1.57 mol L⁻¹, 4.0 mL, 6.3 mmol) was added dropwise to a THF solution (30 mL) of 5,5”-dibromo-2,2’:6’,2”-terpyridine (1.13 g, 2.89 mmol) under a nitrogen atmosphere with a syringe below 0°C. After the mixture was stirred for 0.5 h and a THF solution (20 mL) of 2-methyl-2-nitropropanoic acid (0.85 g, 14.3 mmol) was added using a dropping funnel. The mixture was stirred for 1 h and spontaneously warmed up to room temperature for 1 h. After the reaction was quenched with a saturated NH₄Cl aqueous solution, the mixture was neutralized with a saturated NaHCO₃ aqueous solution. The organic layer was extracted with CHCl₃ and the reaction mixture was dried. The filtrate was concentrated under reduced pressure, and the crude product was purified by recrystallization with CH₂Cl₂ affording a colourless powder of 375.2 mg (2.89 mmol, 31%). Mp. 205 °C (decomp.).

1H NMR (400 MHz, DMSO-d₆): δ 8.64 (s, 2H), 8.53–8.51 (m, 4H), 8.34 (d, J = 7.8 Hz, 2H), 8.03 (t, J = 7.8 Hz, 1H), 7.82 (dd, J = 8.2 Hz, J’ = 2.7 Hz, 2H) and 7.15 (s, 18H). 13C NMR (100 MHz, DMSO-d₆): δ 154.7, 150.7, 147.4, 144.8, 138.2, 131.9, 119.8, 119.7, 60.15 and 25.91. IR (ATR): 1447, 1361, 1197, 818, 756, 653, 617, 573, 553 and 412 cm⁻¹. HRMS (ESI+): m/z calcd for C₂₂H₃₀N₄O₂ [M + H⁺]: 408.23995, found: 408.24279.

Synthesis of [Co(5tpybNOH)₂][BPh₄]₂(C₆H₅O)₂.5(H₂O)₃.3 (1·(C₆H₆O)₂.5(H₂O)₃). CoCl₂·6H₂O (23.8 mg, 0.100 mmol) and 5tpybNOH (82.9 mg, 0.203 mmol) were dissolved in MeOH (15 mL). The mixture was stirred for 5 minutes. After NaBPh₄ as a powder (68.5 mg, 0.200 mmol) was added to the solution, a brown powder was collected and dried over air. The product was purified by recrystallization via a vapor diffusion approach with acetone and n-hexane, affording black crystals of 46.0 mg (0.0268 mmol, 26%). Anal. calcd for C₁₀₁.5H₁₁₉.6B₂CoN₁₀O₉: C, 71.00; H, 7.02; N, 8.16%. Found: C, 71.18; H, 6.70; N, 7.98%. IR (ATR): 3447, 2974, 1559, 1447, 1183, 1030, 813, 731, 703 and 611 cm⁻¹.

Single crystal X-ray diffraction (SXRD)

The X-ray diffraction data of 1·C₆H₅O₂ were collected on a Rigaku XtaLAB Synergy-S diffractometer (Cu Kα radiation: λ = 1.54184 Å). X-ray data analyses were carried out using the SHELXT²⁶ and SHELXL²⁷ programs operated with the Olex2 interface.²⁸ A numerical absorption correction was applied. All the hydrogen atoms were refined as “riding”. The thermal displacement parameters of the non-hydrogen atoms were refined anisotropically. The contribution of the disordered solvent was removed using the SQUEEZE option from PLATON operated with the Olex2 interface.²⁸ The CCDC number is 2087500.

Magnetic measurements

The direct current (dc) magnetic susceptibility of 1 was measured on a Quantum Design MPMS-XL7 SQUID magnetometer equipped with a 7 T coil in the temperature range of 2–400 K. The magnetic data were corrected using diamagnetic blank data of the sample holder measured separately. The diamagnetic contribution of the sample itself was estimated from Pascal’s constant.²⁹

Results and discussion

Synthesis and characterization

The terpyridine-based bishydroxylamine ligand 5tpybNOH was prepared using 5,5”-dibromo-2,2’:6’,2”-terpyridine via the conventional organolithium method. After complexation between CoCl₂·6H₂O, 5tpybNOH and NaBPh₄ in methanol, the product was purified by recrystallisation via the vapour diffusion approach with acetone and n-hexane, affording black crystals of 1. For elemental analysis, the experimental values agreed with the calculated values, including 2.5 acetone and 3.3 water molecules (1·(C₆H₅O)₂.5(H₂O)₃) after collection and immediate measurement. The presence of solvents was also confirmed by thermal and X-ray crystallographic analyses (for details, see below).

Single-crystal X-ray crystallography

The crystal structure of 1 was determined by SXRD measurement at 100 K, as shown in Fig. 2 and Table 1. There are a [Co(5tpybNOH)₂] dication, two BPh₄ anions and an acetone molecule as a crystallographically independent molecule in a unit cell. In addition, disordered solvent molecules, which were accounted for in the SQUEEZE program operated using the Olex2 interface, are present.²⁸ The Co²⁺ centre was 6-coordinated with two 5tpybNOH ligands, giving the N₆ coordination environment. The Co1-N2 and –N7 bond lengths of 1.892(9) and 1.912(9) Å, respectively, are smaller than the other Co–N bond lengths of 2.053(8)–2.070(9) Å. These findings suggest that the N2 and N7 atoms are located at the axial positions around the Co²⁺ ion, and the coordination polyhedra have a suppressed octahedral geometry along the N2, Co1 and N7 atoms. The mean of the Co–N bond lengths (dmean) and the octahedral distortion parameter (Σ²) allowed the prediction of the spin state of the cobalt(u) centre. Fig. 3 shows a plot of the
Table 1 Selected crystallographic data for 1-C$_2$H$_6$O$_3$

| Complex          | Formula          | T/K    | a/Å  | b/Å  | c/Å  | β (°) | V/Å$^3$ | Z     | d$_{calc}$/g cm$^{-3}$ | ρ(Mo Kα)/mg mm$^{-1}$ | R(F)$^a$ (I > 2σ(I)) | R$_{w}$(F$^2$)$^a$ (all data) | Goodness of fit | No. of unique refin | Value of 99.62°. The data are superimposed in Fig. 3 (black diamond), indicating that the Co centre in 1 is of the LS state. The N–O bond length can provide information on the electronic structure of the NOH site. Three NOH sites, N4–O1, N5–O2 and N9–O3, have N–O bond lengths of 1.432(9), 1.482(2) and 1.447(10) Å, respectively, which are close to those established in previous works (1.451–1.497 Å). On the other hand, the N10–O4 bond length of 1.396(15) Å is close to that of a polar-
ized form \( (>\text{N}^+\text{O}^-) \) of 1.4170(15) Å. The polarization at the N10–O4 site could be related to the intermolecular contact. The interatomic O1⋯O3 and O2⋯O4 distances as shown in Fig. 4a and b are 3.336 and 2.641 Å, respectively, in which the latter is smaller than the sum of the van der Waals radii (O/O: 3.04 Å). These findings suggest that the O2⋯O4 contact is strong H-bonding, while the O1⋯O3 contact is weak. With these intermolecular contacts, 1 formed a 2D structure on the bc plane (Fig. 4c). The 2D structure was stacked along the a-axis, and a BPh4 anion was present between these layers. In addition, one acetone molecule as a crystal solvent was located in the void space, and there was a strong intermolecular contact between the acetone and NOH sites (O3⋯O7: 2.863 Å).

**Thermal analyses**

To determine the presence of crystal solvents observed in the elemental and X-ray crystallographic analyses, 1 was analyzed by thermogravimetry (TG) and differential thermal analysis (DTA), as shown in Fig. 5a. The TG spectrum showed a gradual decrease from 296 to 370 K. Upon further heating, the TG spectrum showed a sharp drop from 370 to 375 K. Above 375 K, the TG spectrum plateaued at 460 K, and then decreased sharply, indicating decomposition. Here, the decrease upon heating from 296 to 375 K suggests the desorption of all crystallisation solvents of 1, giving the formula of 1 with no solvents (Fw: 1512.44) in the range of 375–460 K. From this finding, it can be inferred that the change in the weight in the 370–375 K range of approximately 3.3% corresponds to one acetone molecule (Fw: 58.08). Furthermore, the change in the weight at 296–370 K of approximately 8.4% corresponds to 1.5 acetone and 3.3 water molecules (Fw: 146.57). These findings support the formula 1·(C3H6O)2.5(H2O)3.3 obtained from the results of elemental analysis. On the other hand, the DTA spectrum showed endothermic and unexpected exothermic peaks at 370–375 K. To understand the details, we performed differential scanning calorimetry (DSC), as shown in Fig. 5b. The red and blue lines represent the heating and cooling processes, respectively. During the heating process, there are two endothermic peaks and one exothermic peak at 330, 385 and 390 K, respectively. The two endothermic peaks suggest the desorption of the solvents (acetone and water molecules) from 1. On the other hand, the exothermic peak suggests that the irreversible structural change was triggered by the removal of the solvents because there was no peak observed during the cooling process.

**Powder X-ray crystallography**

We performed the variable-temperature powder X-ray diffraction (VT-PXRD) measurements from 300 K to 430 K, as shown in Fig. 6. The PXRD spectrum at 300 K showed two main peaks at 6.8° and 7.4° (p1 and p2, respectively). The p2 peak remained until 410 K, although p1 decreased upon heating and vanished at 360 K. The findings and the above thermal analyses suggest that the p1 peak corresponds to the simulation from the above SXRD study (black line in Fig. 6), while p2 can be assigned to the desolvated form of 1. Here, the position of p1 (6.8°) is shifted to lower than that of the strongest peak in the simulation pattern (7.0°) because of the thermal expansion from the difference between temperatures of 100 K for SXRD and 300 K for PXRD measurements. On further heating from 410 K, p2 was broadened, indicating the decomposition of 1.
**Magnetic properties**

The magnetic susceptibility of a polycrystalline specimen of 1-(C\(_5\)H\(_6\)O\(_2\))\(_2\)\(_{1.5}\)(H\(_2\)O)\(_3\)\(_{3.3}\) was measured in the temperature range of 2–400 K, as shown in Fig. 7. During the heating process (red filled circles), the \(\chi_m T\) value at 2 K was 0.412 cm\(^3\) K mol\(^{-1}\), which is close to the theoretical value of the LS state for the Co\(^{2+}\) ion (\(S = 1/2\) and \(g = 2.1; \chi_m T = 0.413\) cm\(^3\) K mol\(^{-1}\)). Upon heating, the \(\chi_m T\) value gradually increased from 200 to 310 K owing to the desorption of the disordered acetone and water molecules described in the above SXRD study. On further heating, the \(\chi_m T\) value increased sharply and reached 1.88 cm\(^3\) K mol\(^{-1}\) at 380 K, which is almost identical to the theoretical value of the HS state for the Co\(^{2+}\) ion (\(S = 3/2\) and \(g = 2.0; \chi_m T = 1.88\) cm\(^3\) K mol\(^{-1}\)). This spin transition could be triggered by the structural change caused by the desorption of the strongly bound acetone molecule. Upon cooling from 400 to 2 K (blue open squares), the magnetic behaviour showed a difference from that observed during the heating process and the SCO of the Co centre with \(T_{1/2} = 136\) K. In addition, the 2nd heating process from 2 K to 400 K (green filled triangles) showed a similar trend to that of the cooling process. These findings suggest that the desorption of crystal solvents in the 1st heating process caused irreversible structural changes and spin transitions. This was confirmed by the results obtained from the elemental, X-ray crystallographic and thermal analyses.

**Conclusions**

In this study, the novel 5,5”-substituted terpyridine ligand 5tpybNOH was utilised for the synthesis of 1. Compound 1 had a 2D structure through the H-bond between the NOH sites, and there were acetone and water molecules in the void spaces. This was revealed by elemental, X-ray structural and thermal analyses. The DSC and VT-PXRD results suggest that the desorption of acetone caused irreversible structural changes and spin transitions. In addition, 1, in the absence of crystal solvents, showed SCO behaviour with \(T_{1/2} = 136\) K during the cooling process. This study confirms the valuable role of the hydroxylamine group and the substitution at the 5,5”-positions of the terpy ligand in the Co-SCO compounds.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

This study was financially supported by KAKENHI (JSPS/21K14604). We acknowledge Mr Hiroyasu Sato and Mr Akihito Yamano (Rigaku Co.) for refinement of the SXRD data of 1.

**Notes and references**

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