Full Paper

Molecular Assemblies and Spin-Crossover Behaviour of Cobalt(II) Complexes with Terpyridine Incorporating Different Nitrogen Positions in Pyridine Rings

Risa Nakahara,^A Manabu Nakaya,^A Jong Won Shin,^B Ryo Ohtani,^A Masaaki Nakamura,^A and Shinya Hayami^{A,C,D}

^ADepartment of Chemistry, Graduate School of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Kumamoto, 860-8555, Japan.

^BDaegu-Gyeongbuk Branch, Korea Institute of Science and Technology Information,

90 Yutongdanji-ro, Buk-gu, Daegu 41515, South Korea.

^CInstitute of Pulsed Power Science (IPPS), Kumamoto University, 2-39-1 Kurokami,

Chuo-ku, Kumamoto, 860-8555, Japan.

^DCorresponding author. Email: hayami@sci.kumamoto-u.ac.jp

Cobalt(II) complexes with terpyridine-type ligands, $[Co(n-pyterpy)_2](ClO_4)_2$ (n=3 (1), 4 (2)), were prepared and characterised. Different positions of the nitrogen atom in the terpyridine ligands influenced their assembly properties in the crystal structures. Complex 1 showed a 2D network structure consisting of 1D chains connected by intermolecular N···HC interactions. On the other hand, complex 2 consisted of two different cobalt ion sites (Co1 and Co2) with slightly different coordination environments. Complex 2 showed 1D chains with no interchain interactions. Such differences are discussed with the cooperativities estimated by their spin crossover behaviours.

Manuscript received: 4 October 2016. Manuscript accepted: 12 November 2016. Published online: 14 December 2016.

Introduction

Spin crossover (SCO) compounds show bistability in their magnetic, optical, and structural properties, which have potential applications in switching and sensing devices.^[1] Bistability is a necessary property in these compounds, which must be stable in two distinct electronic states. Numerous d^n (n = 4-7) transition metal compounds exhibiting SCO have been reported and their spin state changes can be induced by the variation of temperature, pressure, or light illumination.^[2] SCO phenomena are often observed in cobalt(II), iron(II), and iron(III) compounds. SCO behaviours of numerous cobalt(II) complexes between low spin (LS) (S = 1/2) and high spin (HS) (S = 3/2) states have been observed, which, accompanied by entropy changes, gives the following equation, $\Delta S_{spin} = R[\ln(2S + 1) HS - \ln(2S + 1)LS] = 5.8 J K^{-1} mol^{-1}$.^[3] This entropy change is smaller than SCO compounds of iron(II) (13.4 J K^{-1} mol^{-1}).^[4]

The gradual or abrupt spin transitions are generally observed in the solid state and depend on cooperativity from intermolecular interactions.^[5] Cooperativities in the compounds play an important role to control the magnetic behaviour. Molecules that are arranged by intermolecular interactions such as hydrogen bonds,^[6] π – π interactions,^[7] fastener effects,^[8] and so on lead to an increase of the cooperativities and produce unique magnetic behaviour. Thus, controlling the assembly of SCO compounds would be an important key to obtain cooperative behaviour in SCO compounds. Since metal complexes consisting of 2,2':6',2''-terpyridine (terpy) ligands (or their derivatives) show various physical properties such as redox activities^[9] and photoluminescence^[10] that depend on both metal ions and the nature of substituent groups, we focussed on complexes with these ligands. A large number of cobalt(II) SCO compounds consisting of terpy ligand derivatives have produced a suitable ligand-field for SCO phenomenon.^[11] Thus cobalt(II) compounds with terpy derivatives incorporating various organic substituents such as alkyl chain,^[8] ferrocene^[9] and so on^[12] have been previously reported. In addition, counter anions in metal complexes have played an important role in controlling the cooperativity and SCO behaviour.^[12,13]

We have previously reported 1D terpy cobalt(II) complexes, [Co(pyterpy)X₂]·solvent (pyterpy = 4'-(pyridin-4-yl)-2,2':6', 2'-terpyridine; X = Cl or Br; solvent = MeOH or 2H₂O), which have shown spin state change depending on the solvent molecules.^[14] The mononuclear cobalt(II) complex, [Co(pyterpy)₂] (PF₆)₂, also exhibited SCO behaviour with thermal hysteresis arising from a phase transition.^[15]

Herein, we focussed on the nitrogen position in the pyridine ring and investigated the assembly nature and the effect of cooperativities on the magnetic properties of two terpy cobalt(II) complexes. The cobalt(II) compounds, $[Co(n-pyterpy)_2]$ (ClO₄)₂ (n = 3 (1) or 4 (2)) were prepared and their single-crystal X-ray structure determined as a basic method of characterisation.

Results and Discussion

Both terpyridine ligands, 3-pyterpy (L1) and 4-pyterpy (L2) were prepared by literature methods (Fig. 1; see *Experimental*). The complexes, $[Co(3-pyterpy)_2](ClO_4)_2$ (1) and $[Co(4-pyterpy)_2]$ $(ClO_4)_2$ (2), formed crystals suitable for structure determination by slow diffusion by using a H-tube at room temperature. Brown block shaped crystals of 1.2MeOH and 2.MeOH were obtained following diffusion in MeOH and were fully characterised by elemental analyses and single crystal X-ray diffraction (XRD) determinations. Single crystal XRD measurements for 1.2MeOH and 2.MeOH were carried out at 100 K (Figs 2 and 3) and their crystallographic data are listed in the *Experimental*.

Compound 1·2MeOH was crystallised in the monoclinic space group $P2_1$ and its molecular structure is shown in Fig. 2a. The Co–N bond lengths are Co–N(1)=2.022(4), Co–N(2)= 1.877(3), Co–N(3)=2.019(4), Co–N(5)=2.113(4), Co–N(6)= 1.908(3), and Co–N(7)=2.118(4) Å. It was not possible to obtain a non-solvated single crystal of 1, since it was easily cracked at room temperature. In compound 1, intermolecular N…HC bonds between pyridine substituents (2.58 Å) were found (Fig. 2b). The N…HC bond networks were extended along the *c*-axis, in which 1 formed 1D network structures (Fig. 2c). Furthermore, the 1D chains were assembled by $\pi-\pi$ interactions at the terpyridine cores and hence they formed 2D assemblies consisting of 1D chains. The 2D assemblies were stacked along the *b*-axis through CH– π interactions (Fig. 2d).

 $2 \cdot$ MeOH was crystallised in the monoclinic space group *P*-1 and its molecular structure is shown in Fig. 3a. It consists of two



Fig. 1. Schematic structure of the ligands, L1 and L2.

cobalt(II) ion sites, of which Co1 and Co2 site are dimerised by CH– π interactions between pyridine rings in the terpyridine ligands (2.59 Å, PrH (in Co1 site)-Py (in Co2 site)). Co-N bond lengths in the Co1 site are Co(1)-N(1) = 2.147(2), Co(1)-N(2) =1.921(2), Co(1)-N(3) = 2.144(2), Co(1)-N(5) = 1.989(2), Co(1)-N(6) = 1.859(2), and Co(1)-N(7) = 1.993(2) Å, whereas those in the Co2 site are Co(2)-N(9) = 2.066(2), Co(2)-N(10) =1.891(2), Co(2)-N(11) = 2.074(2), Co(2)-N(13) = 2.070(2), Co(2) - N(14) = 1.889(2),and Co(2)-N(15) = 2.057(2)Å. Obtaining a non-solvated single crystal of 2 was also not successful for X-ray structure determination due to the same reason as for complex 1. The two cobalt ion sites in 2. MeOH had different assembling natures. At the Co1 site, intermolecular N…HC bonds between the pyridine substituent and the middle pyridine ring in the terpyridine ligand were observed (2.48 Å), while the side pyridine ring formed a N…HC bond with the pyridine substituent in the Co2 site (2.65 Å) (Fig. 3b). In the crystal packing of 2, the two molecules containing Co1 and Co2 sites produced independent 1D columns. Each 1D chain came into short contact by pyridine rings along the b-axis (Fig. 3c), and the 1D chains were arrayed along the a-axis, in which the 1D chains of Co1 and Co2 sites arranged along the a-axis consisting of layers. MeOH molecules existed between individual 1D chains and ClO_4^- counter anions existed between the layers (Fig. 3d).

Since complexes 1 and 2 show different molecular assemblies which affects the cooperativity influencing their SCO behaviour, their magnetic susceptibility measurement was performed using a superconducting quantum interference device (SQUID) and the cooperative factors, C, also estimated. The $\chi_{\rm m}T$ versus T curves ($\chi_{\rm m}$, molar magnetic susceptibility; T, temperature) for 1.2MeOH and 2.MeOH are shown in Fig. 4. Both compounds showed gradual SCO behaviour. In compound 1.2MeOH, stepwise SCO behaviour was observed around 320 K upon heating. The solvent molecules in the crystal were removed during the cooling process but the stepwise SCO behaviour was still observed. In compound 2. MeOH, stepwise SCO behaviour was also observed around 350 K upon heating although it was incomplete and gradual. On cooling, however, 2 showed gradual SCO behaviour. This stepwise behaviour of 2. MeOH seems to be observed due to the removal of solvent



Fig. 2. (a) Molecular structures of 1-2MeOH. Hydrogen atoms, ClO_4^- counter anions, and solvent molecules are omitted for clarity. Colour code: Co, magenta; N, blue; C, grey. (b) N…HC bonds between neighbouring pyridine substituents. (c) 2D structure of 1 at the *ac* plane. (d) Stacking structures of 2D assemblies of 1. Blue coloured molecules are MeOH and pink ClO_4^- , respectively.



Fig. 3. (a) Molecular structure of 2·MeOH. Hydrogen atoms, ClO_4^- counter anions and solvent molecules are omitted for clarity. Colour code: Co, magenta; N, blue; C, grey. (b) Dimerisation of molecule **2**. (c, d) Molecular packing structure of **2**. Red coloured molecules show Co1 sites and green coloured molecules Co2 sites. Blue coloured molecules are MeOH and pink ClO_4^- , respectively.



Fig. 4. $\chi_m T$ versus *T* plots for the compound 1-2MeOH (a) and compound 2-MeOH (b). Red and blue circles show heating and cooling modes, respectively. Black solid lines indicate the fit by the regular solution models.

molecules from the crystals, while the solvent molecules in 1.2MeOH did not influence the SCO behaviour.

To estimate the cooperativity of SCO behaviour, the experimental $\chi_m T$ versus *T* curves were simulated by applying the regular solution model (see *Experimental*). The simulated parameters for the compounds before and after removal of solvent molecules are shown in Table 1. The cooperative factors in 1·2MeOH and 1 were almost the same. 2D networks consisting of 1D chains of 1 were stacked through CH– π interactions, which revealed that the removal of MeOH solvent did not influence the cooperativity of 1. Since molecules of 2 experienced intermolecular interactions through MeOH, it seems they could not interact with each other after removal of MeOH.

Table 1.	$\Delta H, \Delta S, T_{1/2}$, and C values obtained from the regular solution			
model				

Compound	$\Delta H [\mathrm{J} \mathrm{mol}^{-1}]$	$\Delta S [J K^{-1}]$	$T_{1/2}$ [K]	С
1.2MeOH	3261.5	9.79	333	0.78
1	1904.8	5.54	344	0.75
2 ·MeOH	5390	15.6	345	0.62
2	12962.6	43.2	300	0.15

The ClO_4^- counter anions also prevent interactions between the Co1 and Co2 sites. Therefore, the cooperative factor seems to significantly decrease after removal of solvents.

Conclusion

Cobalt(II) compounds with a different nitrogen position in the pyridine ring, $[Co(3-pyterpy)_2](ClO_4)_2(1)$ and $[Co(4-pyterpy)_2](ClO_4)_2(2)$, showed different molecular assemblies depending on the pyridine ring. Complex 1 showed a 2D assembly consisting of 1D chains, while 2 was formed as individual 1D chain assemblies with each Co1 and Co2 site separated by ClO_4^- anions. The cooperativities estimated by their magnetic behaviours reflected the assembly natures, in which the nitrogen position in the pyridine substituent has an important role controlling the molecular assemblies. The slight differences, such as nitrogen position in a molecule, seem to play an important role in the construction of supramolecules.

Experimental

The preparation of ligands L1 and L2 and compounds 1 and 2 were essentially carried out according to the literature with slight modifications.^[14] All reagents were commercially available and used without further purification.

Synthesis

3-Pyterpy (L1)

2-Acetylpyridine (4.8 g, 40 mmol) was added to a solution of pyridine-3-carbaldehyde (2.2 g, 20 mmol) in EtOH (10 mL). NaOH (2.0 g, 50 mmol in 10 mL H₂O) and ammonium acetate (2.3 g, 30 mmol in 10 mL H₂O) were slowly added to the mixture and stirred overnight at ambient temperature. The off-white solid was collected by filtration and washed with H₂O (3×15 mL) and EtOH (3×15 mL). $\delta_{\rm H}$ (500 MHz, CDCl₃) 9.03 (d, 1H), 8.62–8.55 (m, 7H), 8.09 (d, 1H), 7.79 (t, 2H), 7.34 (t, 1H), 7.25 (t, 2H).

4-Pyterpy (L2)

L2 was prepared by a similar method as described for L1, except for using of pyridine-4-carbaldehyde instead of pyridine-3-carbaldehyde. $\delta_{\rm H}$ (500 MHz, CDCl₃) 8.71 (d, 4H), 8.68 (d, 2H), 8.62 (d, 2H), 7.86 (t, 2H), 7.57 (d, 2H), 7.30 (t, 2H).

$[Co(3-pyterpy)_2](ClO_4)_2$ (1)

L1 (20 mg, 6.5×10^{-5} mol) was placed into one sidearm of an H-tube. Co(NO₃)₂·6H₂O (7.2 mg, 3.3×10^{-5} mol) and NaClO₄ (7.9 mg, 6.5×10^{-5} mol) were placed into the other side, and MeOH was gently layered over both sides to fill the H-tube and the system left at ambient temperature to produce brown crystals suitable for X-ray structure determination. Anal. Calc. for [Co(3-pyterpy)₂](ClO₄)₂·2MeOH (C₄₂H₃₆CoN₈Cl₂O₁₀): C 53.52, H 3.85, N 11.89. Found: C 53.30, H 3.74, N 11.52 %.

$[Co(4-pyterpy)_2](ClO_4)_2 \cdot (2)$

Compound **2** was prepared by the same method as **1** except using **L2** instead of **L1**. Anal. Calc. for $[Co(4-pyterpy)_2]$ $(ClO_4)_2$ ·MeOH $(C_{41}H_{32}CoN_8Cl_2O_9)$: C 54.08, H 3.54, N 12.31. Found: C 54.24, H 3.35, N 12.49 %.

Single Crystal Structural Analysis

A crystal of 1-2MeOH was coated with paratone-*N* oil and the diffraction data measured at 100(2) K with synchrotron radiation (λ 0.63000 Å) on an ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Korea. The *PAL BL2D-SMDC* program^[16] was used for data collection (detector

distance was 63 mm, omega scan; $\Delta \omega = 1^{\circ}$, exposure time was 1 s per frame) and *HKL3000sm* (ver. 703r)^[17] was used for cell refinement, reduction, and absorption correction. XRD data for single crystals of **2**·MeOH were collected with a Rigaku R-AXIS RAPID 191R diffractometer. Crystal evaluation and data collection were performed using Cu K α radiation (λ 1.54187 Å) with a detector-to-crystal distance of 1.91 cm. The crystal structures were solved by direct methods,^[18] and refined by fullmatrix least-squares refinement using the *SHELXL-2014* computer program.^[19] The positions of all non-hydrogen atoms were refined with anisotropic displacement factors. All hydrogen atoms were placed using a riding model, and their positions were constrained relative to their parent atoms using the appropriate HFIX command in *SHELXL-2014*.

X-ray crystallographic data for 1·2MeOH at 100 K ($C_{42}H_{36}O_{10}N_8Cl_2Co$): FW 942.62; brown block crystals, monoclinic, space group *P*2₁, *a* 8.5800(17), *b* 12.097(2), *c* 19.706(4) Å, β 99.22(3)°, *V*2018.9 Å³, *Z*2, D_{calc} 1.551 g cm⁻³, μ 0.453 mm⁻¹, R_1 0.0528 for $I > 2\sigma(I)$, R_1 0.0627, and wR_1 0.1375 for all data.

X-ray crystallographic data for **2**·MeOH at 100 K (C₄₁H₃₂O₉N₈Cl₂Co): FW 910.59; brown block crystals, triclinic, space group $P\bar{1}$, a 10.6786(8), b 17.909(2), c 21.752(1) Å, α 102.569(4)°, β 90.237(3)°, γ 107.244(3)°, V 3867.2 Å³, D_{calc} 1.564 g cm⁻³, μ 0.652 mm⁻¹, R_1 0.0399 for $I > 2\sigma(I)$, R 0.0747, and wR 0.1062 for all data.

Elemental Analysis

Elemental analyses were carried out with a J-SCIENCE LAB-ORATORY JM10 analyser at the Instrumental Analysis Centre of Kumamoto University.

Magnetic Susceptibility Measurements

Temperature-dependent magnetic susceptibilities for 1.2MeOH and 2.MeOH were measured on a SQUID magnetometer at field strengths of 1 T with a sweep mode in the temperature range 5 to 400 K. Crystalline samples were put into a gelatine capsule, mounted inside the straw, and then fixed to the end of the sample transport rod.

Regular Solution Model

Cooperativity was estimated from the measured $\chi_m T$ versus T curves (χ_m ; molar magnetic susceptibility, T; temperature) by applying the regular solution model (Eqn 1),^[20] where ΔH , ΔS , and Γ are the enthalpy and the entropy variations, and the parameter accounting for cooperativity based on SCO, respectively. The HS molar fraction, γ_{HS} , is shown as a function of the magnetic susceptibility through Eqn 2, where ($\chi_m T$)_m is the $\chi_m T$ value at any temperature, ($\chi_m T$)_{HS} and ($\chi_m T$)_{LS} are the pure LS and HS states, respectively. R is the gas constant, 8.314 J K⁻¹ mol⁻¹. The cooperativity value, C, is given by Eqn 3.

$$\ln[(1 - \gamma_{\rm HS})/(\gamma_{\rm HS})] = [\{\Delta H + \Gamma(1 - 2\gamma_{\rm HS})\}/RT] - \Delta S/R \quad (1)$$

$$\gamma_{\rm HS} = \left[(\chi_{\rm m} T)_m - (\chi_{\rm m} T)_{\rm LS} \right] / \left[(\chi_{\rm m} T)_{\rm HS} - (\chi_{\rm m} T)_{\rm LS} \right]$$
(2)

$$C = \Gamma/(2RT_{1/2}), T_{1/2} = \Delta H/\Delta S \tag{3}$$

Acknowledgements

This work was supported by a JSPS Grant-in-Aid for Young Scientists (B) 15K17833 and a JSPS Grant-in-Aid for Scientific Research on Innovative Areas (Dynamical Ordering & Integrated Functions) 16H00777. This work

was also supported by a KAKENHI Grant-in-Aid for Scientific Research (B) 26288026. This work was partially supported by the Cooperative Research Program of 'Network Joint Research Centre for Materials and Devices'. M.N. is grateful to JSPS Research Fellowships for Young Scientists (No. 15J11333).

References

[1] (a) O. Kahn, C. J. Martinez, *Science* 1998, *279*, 44. doi:10.1126/SCI ENCE.279.5347.44
 (b) J. A. Real, E. Andres, M. C. Muñoz, M. Julve, T. Granier,

A. Bousseksou, F. Varret, *Science* **1995**, *268*, 265. doi:10.1126/SCI ENCE.268.5208.265

[2] (a) Spin Crossover in Transition Metal Compounds III, Topics in Current Chemistry, Vol. 235 (Eds P. Gütlich, H. A. Goodwin) 2004 (Springer-Verlag: Berlin).
(b) P. Gütlich, Y. Garcia, T. Woike, Coord. Chem. Rev. 2001,

(b) F. Guinen, T. Garcia, T. Worke, *Coord. Chem. Rev.* 2001 219–221, 839.

(c) P. Gütlich, Y. Garcia, H. A. Goodwin, *Chem. Soc. Rev.* **2000**, *29*, 419. doi:10.1039/B003504L

(d) P. Gütlich, A. Hauser, H. Spiering, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2024. doi:10.1002/ANIE.199420241

(e) H. A. Goodwin, *Coord. Chem. Rev.* **1976**, *18*, 293. doi:10.1016/ S0010-8545(00)80430-0

[3] (a) J. Zarembowitch, R. Claude, O. Kahn, *Inorg. Chem.* 1985, 24, 1576. doi:10.1021/IC00204A033
 (b) A. B. Gaspar, M. C. Munoz, V. Niel, J. A. Real, *Inorg. Chem.* 2001,

40, 9. doi:10.1021/IC000788M

- [4] Spin Crossover in Transition Metal Compounds I, Topics in Current Chemistry, Vol. 233 (Eds P. Gütlich, H. A. Goodwin) 2004 (Springer-Verlag: Berlin).
- [5] (a) A. J. Conti, C. L. Xie, D. N. Hendrickson, J. Am. Chem. Soc. 1989, 111, 1171. doi:10.1021/JA00186A002
 (b) J. A. Real, E. Andrés, M. C. Muñoz, M. Julve, T. Granier, A. Bousseksou, F. Varret, Science 1995, 268, 265. doi:10.1126/SCI ENCE.268.5208.265
 (c) J.-F. Létard, P. Guionneau, E. Codjovi, O. Lavastre, G. Bravic, D. Cherrer, J. Mar. Chem. Soc. 1997, 100 (1921)

D. Chasseau, O. Kahn, *J. Am. Chem. Soc.* **1997**, *119*, 10861. doi:10.1021/ JA972441X

- [6] Y. Sunatsuki, Y. Ikuta, N. Matsumoto, H. Ohta, M. Kojima, S. Iijima, S. Hayami, Y. Maeda, S. Kaizaki, F. Dahan, J. P. Tuchagues, *Angew. Chem. Int. Ed.* 2003, *42*, 1614. doi:10.1002/ANIE.200250399
- [7] (a) S. Hayami, Z. Z. Gu, M. Shiro, Y. Einaga, A. Fujishima, O. Sato, J. Am. Chem. Soc. 2000, 122, 7126. doi:10.1021/JA001406E
 (b) S. Hayami, Z. Z. Gu, H. Yoshiki, A. Fujishima, O. Sato, J. Am. Chem. Soc. 2001, 123, 11644. doi:10.1021/JA0017920
- [8] (a) S. Hayami, Y. Shigeyoshi, M. Akita, K. Inoue, K. Kato, K. Osaka, M. Takata, R. Kawajiri, T. Mitani, Y. Maeda, *Angew. Chem. Int. Ed.* 2005, 44, 4899. doi:10.1002/ANIE.200500316

(b) S. Hayami, R. Moriyama, A. Shuto, Y. Maeda, K. Ohta, K. Inoue, *Inorg. Chem.* **2007**, *46*, 7692. doi:10.1021/IC700754S

(c) Y. Komatsu, K. Kato, Y. Yamamoto, H. Kamihata, Y. H. Lee, A. Fuyuhiro, S. Kawata, S. Hayami, *Eur. J. Inorg. Chem.* **2012**, 2769. doi:10.1002/EJIC.201101040

- [9] K. Takami, R. Ohtani, M. Nakamura, T. Kurogi, M. Sugimoto, L. F. Lindoy, S. Hayami, *Dalton Trans.* 2015, 44, 18354. doi:10.1039/ C5DT02592C
- [10] (a) C. Y. Chung, S. P. Li, K. K. Lo, V. W. Yam, *Inorg. Chem.* 2016, *55*, 4650. doi:10.1021/ACS.INORGCHEM.6B00513
 (b) N. S. Kumar, M. Z. Shafikov, A. C. Whitwood, B. Donnio, P. B. Karadakov, V. N. Kozhevnikov, D. W. Bruce, *Chem. Eur. J.* 2016, *22*, 8215. doi:10.1002/CHEM.201505072
- [11] (a) C. A. Kilner, M. A. Halcrow, *Dalton Trans.* 2010, *39*, 9008. doi:10.1039/C0DT00295J
 (b) S. Hayami, M. Nakaya, H. Ohmagari, S. A. Amolegbe, M. Nakamura, R. Ohtani, R. Yamaguchi, T. Kuroda-Sowa, J. K. Clegg,
- Dalton Trans. 2015, 44, 9345. doi:10.1039/C4DT03743J
 [12] (a) A. B. Gaspar, M. C. Munoz, V. Niel, J. A. Real, *Inorg. Chem.* 2001, 40, 9. doi:10.1021/IC000788M
 (b) X. Zhang, Z.-X. Wang, H. Xie, M.-X. Li, T. J. Woods, K. R. Dunbar, *Chem. Sci.* 2016, 7, 1569. doi:10.1039/C5SC03547C
- [13] (a) S. Hayami, R. Moriyama, Y. Shigeyoshi, R. Kawajiri, T. Mitani, M. Akita, K. Inoue, Y. Maeda, *Inorg. Chem.* 2005, 44, 7295. doi:10.1021/ IC051059F
 (b) Y. The M. K. D. H. C. Prizz, Z. Y. W. K. D. D. J.

(b) X. Zhang, H. Xie, M. Ballesteros-Rivas, Z.-X. Wang, K. R. Dunbar, *J. Mater. Chem. C* **2015**, *3*, 9292. doi:10.1039/C5TC01851J

- [14] (a) S. Hayami, K. Hashiguchi, G. Juhasz, M. Ohba, H. Okawa, Y. Maeda, K. Kato, K. Osaka, M. Takata, K. Inoue, *Inorg. Chem.* 2004, 43, 4124. doi:10.1021/IC049509B
 (b) R. Ohtani, K. Shimayama, A. Mishima, M. Ohba, R. Ishikawa, S. Kawata, M. Nakamura, L. F. Lindoy, S. Hayami, *J. Mater. Chem. C* 2015, *3*, 7865. doi:10.1039/C5TC00864F
- [15] S. Hayami, K. Hashiguchi, G. Juhasz, M. Ohba, H. Okawa, Y. Maeda, K. Kato, K. Osaka, M. Takata, K. Inoue, *Inorg. Chem.* 2004, 43, 4124. doi:10.1021/IC049509B
- [16] J. W. Shin, K. Eom, D. Moon, J. Synchrotron Radiat. 2016, 23, 369. doi:10.1107/S1600577515021633
- [17] Z. Otwinowski, W. Minor, in *Methods in Enzymology* (Eds C. W. Carter, Jr, R. M. Sweet) **1997**, Vol. 276, pp. 307–326 (Academic Press: New York, NY).
- [18] G. M. Sheldrick, Acta Crystallogr. Sect. A: Found. Adv. 1990, 46, 467. doi:10.1107/S0108767390000277
- [19] G. M. Sheldrick, Acta Crystallogr. Sect. C: Struct. Chem. 2015, 71, 3. doi:10.1107/S2053229614024218
- [20] C. P. Slichter, H. G. Drickamer, J. Chem. Phys. 1972, 56, 2142. doi:10.1063/1.1677511