Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information (ESI)

Creation and stabilisation of tuneable open metal sites in thiocyanato-bridged heterometallic coordination polymers to be used as heterogeneous catalysts

Hiroyasu Tabe,[ab] *Masaaki Matsushima,*[a] *Rika Tanaka,*[ac] *and Yusuke Yamada*[*a]

[a] *Graduate School of Engineering, Osaka City University, Sugimoto, Sumiyoshi, Osaka 558-8585, Japan.*

E-mail: ymd@a-chem.eng.osaka-cu.ac.jp

[b] *The OCU Advanced Research Institute for Natural Science and Technology (OCARINA), Osaka City University, Sugimoto, Sumiyoshi, Osaka 558-8585, Japan*

[c] *Analytical Centre of Osaka City University, Sugimoto, Sumiyoshi, Osaka 558-8585, Japan*

Experimental

Materials

All chemicals and solvents were of analytical grade and used without any further processing. Aqueous solutions were prepared with distilled water provided by a water purification system, Advantec RFD210TA (electronic conductance: 18.2 MΩ cm). Potassium thiocyanate, manganese(II) nitrate hexahydrate, iron(II) chloride tetrahydrate, iron(III) nitrate nonahydrate, cobalt(II) nitrate hexahydrate, nickel(II) nitrate hexahydrate, copper(II) nitrate trihydrate, dehydrated pyridine, methanol, sodium hydroxide, silver(I) sulphate, disodium hydrogenphosphate, sodium dihydrogenphosphate and sodium persulphate were obtained from FUJIFILM Wako Pure Chemical Corporation, Japan. Potassium hexachloroplatinate(IV), *p*-nitrophenyl phosphate disodium salt hexahydrate and 4-(2-hydroxyethyl)-1piperazineethanesulphonic acid (HEPES) were purchased from Sigma-Aldrich Co. LLC. Tris(2,2'-bipyridine)ruthenium(II) chloride ($Ru(bpy)_3Cl_2$) was purchased from Tokyo Chemical Industry Co., Ltd. Tris(2,2'-bipyridine)ruthenium(II) sulphate ($Ru(bpy)_3SO_4$) was synthesised by adding one equivalent of Ag_2SO_4 to an aqueous solution of $Ru(bpy)_3Cl_2$ (0.13 mol, 10 mL).

Synthesis of $K_2[Pt^{IV}(SCN)_6]$

$K_2[Pt^{IV}(SCN)_6]$ was synthesised by modification of a literature procedure.[S1] An aqueous solution of potassium thiocyanate (6.4 M, 5 mL) was heated and stirred at 95 °C on a steam bath, followed by slow addition of potassium hexachloroplatinate (IV) (10 mM, 500 mL). After stirring for 15 minutes, this solution was recrystallised. The precipitated red orange solid was filtered and dried *in vacuo*. IR (KBr): 2123 (ν_{CN}), 2116 (ν_{CN}), 694 (ν_{CS}), 428 (δ_{SCN}), 420 cm^{-1} (δ_{SCN}).

Synthesis of $\{M^{II}[Pt^{IV}(SCN)_6]\}_n$ ($M^{II} = Mn^{II}, Co^{II}, Ni^{II}$ or Cu^{II})

An aqueous solution of $K_2[Pt^{IV}(SCN)_6]$ (0.05 M, 10 mL) was added to an aqueous solution of manganese(II) nitrate, cobalt(II) nitrate, nickel(II) nitrate or copper(II) nitrate (0.5 M, 1 mL) with vigorous stirring for 20 hours. The precipitates were collected by centrifugation, washed with distilled water several times and dried *in vacuo* at room temperature for 12 h. $\{Mn^{II}[Pt^{IV}(SCN)_6]\}_n$: IR (KBr): 2154 ($\nu_{CN}$), 725 ($\nu_{CS}$), 428 ($\delta_{SCN}$), 419 cm^{-1} (δ_{SCN}); Molar ratio evidenced by X-ray fluorescence: Mn : Pt = 1.2 : 1. $\{Co^{II}[Pt^{IV}(SCN)_6]\}_n$: IR (KBr): 2164 ($\nu_{CN}$), 731 ($\nu_{CS}$), 430 ($\delta_{SCN}$), 420 cm^{-1} (δ_{SCN}). Molar ratio evidenced by X-ray fluorescence: Co : Pt = 1.2 : 1.$\{Ni^{II}[Pt^{IV}(SCN)_6]\}_n$: IR (KBr): 2174 ($\nu_{CN}$), 2125 ($\nu_{CN}$), 731($\nu_{CS}$), 430 ($\delta_{SCN}$), 420 cm^{-1} (δ_{SCN}); Molar ratio evidenced by X-ray fluorescence: Ni : Pt = 1.2 : 1. $\{Cu^{II}[Pt^{IV}(SCN)_6]\}_n$: IR (KBr): 2181 ($\nu_{CN}$), 2145 ($\nu_{CN}$), 744 ($\nu_{CS}$), 426 ($\delta_{SCN}$), 420 cm^{-1} (δ_{SCN}); Molar ratio evidenced by X-ray fluorescence: Cu : Pt = 1.4 : 1.

Synthesis of $\{Fe^{II}[Pt^{IV}(SCN)_6]\}_n$

An aqueous solution of $K_2[Pt^{IV}(SCN)_6]$ (0.05 M, 10 mL) was added to an aqueous solution of iron(II) chloride (0.5 M, 1 mL) with vigorous stirring for 20 hours under argon atmosphere. The formed black precipitates were collected by centrifugation, washed with distilled water several times and dried *in vacuo* at room temperature. IR (ATR): 2151 (ν_{CN}), 729 (ν_{CS}), 429 (δ_{SCN}), 419 cm^{-1} (δ_{SCN}). Molar ratio evidenced by X-ray fluorescence: Fe : Pt = 1.3 : 1.

Synthesis of $\{Mn^{II}[Pt^{IV}(SCN)_6]\}_n$ in methanol

A methanol solution of $K_2[Pt^{IV}(SCN)_6]$ (20 mM, 0.5 mL) was added to a methanol solution of manganese(II) nitrate (40 mM, 0.5 mL) with vigorous stirring for 20 hours. The precipitates were collected by centrifugation, washed with absolute methanol several times and dried *in vacuo* at room temperature for 12 h. Single crystals of

$\{Mn^{II}[Pt^{IV}(SCN)_6]\}_n$ were grown by slow evaporation of a methanol solution (1 mL) containing $K_2[Pt^{IV}(SCN)_6]$ (20 mM) and manganese(II) nitrate (20 mM). The crystal have the identical structure to $\{Mn^{II}[Pt^{IV}(SCN)_6]\}_n$ synthesised in water as evidenced by the powder X-ray diffraction (XRD) measurement and the single-crystal X-ray structure analysis.

Synthesis of $\{[M^{II}(CH_3OH)_2][Pt^{IV}(SCN)_6]\}_n$ (M^{II} = Co^{II}, Ni^{II} or Cu^{II})

A methanol solution of $K_2[Pt^{IV}(SCN)_6]$ (20 mM, 0.5 mL) was added to a methanol solution of cobalt(II) nitrate, nickel(II) nitrate or copper(II) nitrate (40 mM, 0.5 mL) with vigorous stirring for 20 hours. The precipitates were collected by centrifugation, washed with absolute methanol several times and dried *in vacuo* at room temperature for 12 h. Single crystals of $\{[Co^{II}(CH_3OH)_2][Pt^{IV}(SCN)_6]\}_n$ in red were grown by slow diffusion of an methanol solution (1 mL) of $K_2[Pt^{IV}(SCN)_6]$ (10 mM) and cobalt(II) nitrate (10 mM). IR (ATR): 2158 (ν_{CN}), 728 (ν_{CS}), 421 cm^{-1} (δ_{SCN}). Molar ratio evidenced by X-ray fluorescence: Co : Pt = 1.3 : 1.

Synthesis of $\{[Fe^{II}(CH_3OH)_2][Pt^{IV}(SCN)_6]\}_n$

A methanol solution of $K_2[Pt^{IV}(SCN)_6]$ (20 mM, 0.5 mL) was added to a methanol solution of iron(II) chloride (20 mM, 0.5 mL) with vigorous stirring for 20 hours under argon atmosphere. The orange precipitates were collected by centrifugation, washed with absolute methanol several times and dried *in vacuo* at room temperature for 12 h. Single crystals of $\{[Fe^{II}(CH_3OH)_2][Pt^{IV}(SCN)_6]\}_n$ in black were grown by slow diffusion of a methanol solution (0.5 mL) containing $K_2[Pt^{IV}(SCN)_6]$ (24 mM) and iron(III) nitrate (18 mM) at 4 °C. Fe^{III} were converted to Fe^{II} ion via autoreduction process, which is often observed in preparing of iron-thiocyanato complexes.[S2] IR (ATR): 2146 (ν_{CN}), 727 (ν_{CS}), 426 cm^{-1} (δ_{SCN}). Molar ratio evidenced by X-ray fluorescence: Fe : Pt = 1.1 : 1.

Synthesis of $\{[Co^{II}(py)_2][Pt^{IV}(SCN)_6]\}_n$ (py = pyridine)

A methanol solution of pyridine (160 mM, 0.25 mL) was added to a methanol solution of cobalt(II) nitrate (80 mM, 0.25 mL) followed by the addition of a methanol solution of $K_2[Pt^{IV}(SCN)_6]$ (40 mM, 0.5 mL). The red precipitates were collected by centrifugation, washed with absolute methanol several times and dried *in vacuo* at room temperature for 12 h. IR (KBr): 2156 (ν_{CN}), 2143(ν_{CN}), 2120 (ν_{CN}), 1604 (ν_{CC}), 1444 (ν_{CC}), 1217 (ν_{CN}), 1154 (ν_{CN}), 1065 (py), 1041 (py), 756 (ν_{CS}), 695 (ν_{MC}), 634 (ν_{MC}), 424 (δ_{SCN}), 418 cm^{-1} (δ_{SCN}); Molar ratio evidenced by X-ray fluorescence: Co : Pt = 1.3 : 1.

Synthesis of $\{[Co^{II}(py)(CH_3OH)][Pt^{IV}(SCN)_6]\}_n$

A methanol solution of pyridine (80 mM, 0.25 mL) was added to a methanol solution of cobalt(II) nitrate (80 mM, 0.25 mL) followed by the addition of a methanol solution of $K_2[Pt^{IV}(SCN)_6]$ (40 mM, 0.5 mL). The red precipitates were collected by centrifugation, washed with absolute methanol several times and dried *in vacuo* at room temperature for 12 h. IR (KBr): 2156 (ν_{CN}), 2143(ν_{CN}), 2120 (ν_{CN}), 1604 (ν_{CC}), 1444 (ν_{CC}), 1217 (ν_{CN}), 1154 (ν_{CN}), 1065 (py), 1041 (py), 756 (ν_{CS}), 695 (ν_{MC}), 634 (ν_{MC}), 424 (δ_{SCN}), 418 cm^{-1} (δ_{SCN}); Molar ratio evidenced by X-ray fluorescence: Co : Pt = 1.3 : 1.

Physical measurements

UV-vis absorption spectra were obtained using a V−770 spectrometer (JASCO, Japan). IR spectra were recorded on a JASCO FT/IR−6200 spectrometer coupled with an attenuated total reflectance (ATR) accessory for the samples pelletised with potassium bromide (KBr). The molar ratio of the atoms in each coordination polymer was determined using a Shimadzu EDX−730 X-ray fluorescence spectrometer. Powder X-ray diffraction patterns at room temperature were measured using a Shimadzu XD−3A. Incident X-ray radiation was produced by a Fe X-ray tube operating at 40 kV and 15 mA with Fe *K*α radiation (λ = 1.94 Å). The scan rate was 1° min^{-1} from 2θ = 10−50°. Thermogravimetric and differential thermal analyses (TG/DTA) were carried out using a Thermo plus EVO2 (Rigaku). A weighed sample in an aluminium pan was heated from room temperature to 500 °C in an air flow (50 mL/min) with a ramp rate of 10 °C.

Single-crystal X-ray structure analysis

Single-crystal X-ray crystallographic analyses were carried out using a Rigaku AFC/Mercury CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) monochromated by graphite. The crystal structures were solved by a direct method using SIR92 and refined by the full-matrix least-squares method on F^2 with anisotropic displacement parameters for non-hydrogen atoms using SHELXL-97.

Catalysis evaluation for hydrolysis of organophosphates

A typical procedure for catalysis measurements is as follows: A coordination polymer (2.5 mg, [substrate]/[M^{N}] = 4.5) was added to a HEPES buffer solution (100 mM, pH 8.2, 750 μL) containing *p*-nitrophenyl phosphate disodium salt (*p*-NPP, 25 mM). The resulting mixture was shaken at 900 rpm at 60 °C for 24 hours. Periodic monitoring via UV−vis spectroscopy was carried out by removing a 10 μL aliquot from the reaction mixture and diluting with the HEPES buffer solution (100 mM, pH 8.2, 2,490 μL). The conversion of *p*-NPP as a function of reaction time was obtained by monitoring the increase of absorbance of the *p*-nitrophenolate ion (*p*-NP) at 400 nm ($\varepsilon = 1.57 \times 10^4\ \text{M}^{-1}$ cm). Reaction rates were calculated based on the yield of *p*-NP in 24 h.

Catalysis evaluation for photocatalytic water oxidation

A typical procedure for catalysis measurements is as follows: A phosphate buffer solution (50 mM, pH 8.0, 2.0 mL) containing the coordination polymer (1.0 mg), tris(2,2'-bipyridine)ruthenium sulphate ($[\text{Ru(bpy)}_3]\text{SO}_4$, 1.0 mM) and sodium persulphate ($\text{Na}_2\text{S}_2\text{O}_8$, 5.0 mM) was flushed with argon gas for 20 min. The suspension was irradiated with an LED lamp (Iris−s450, λ > 400 nm) at room temperature for 10 min. Oxygen evolved in a headspace was quantified by a gas chromatograph (Shimadzu GC−2014).

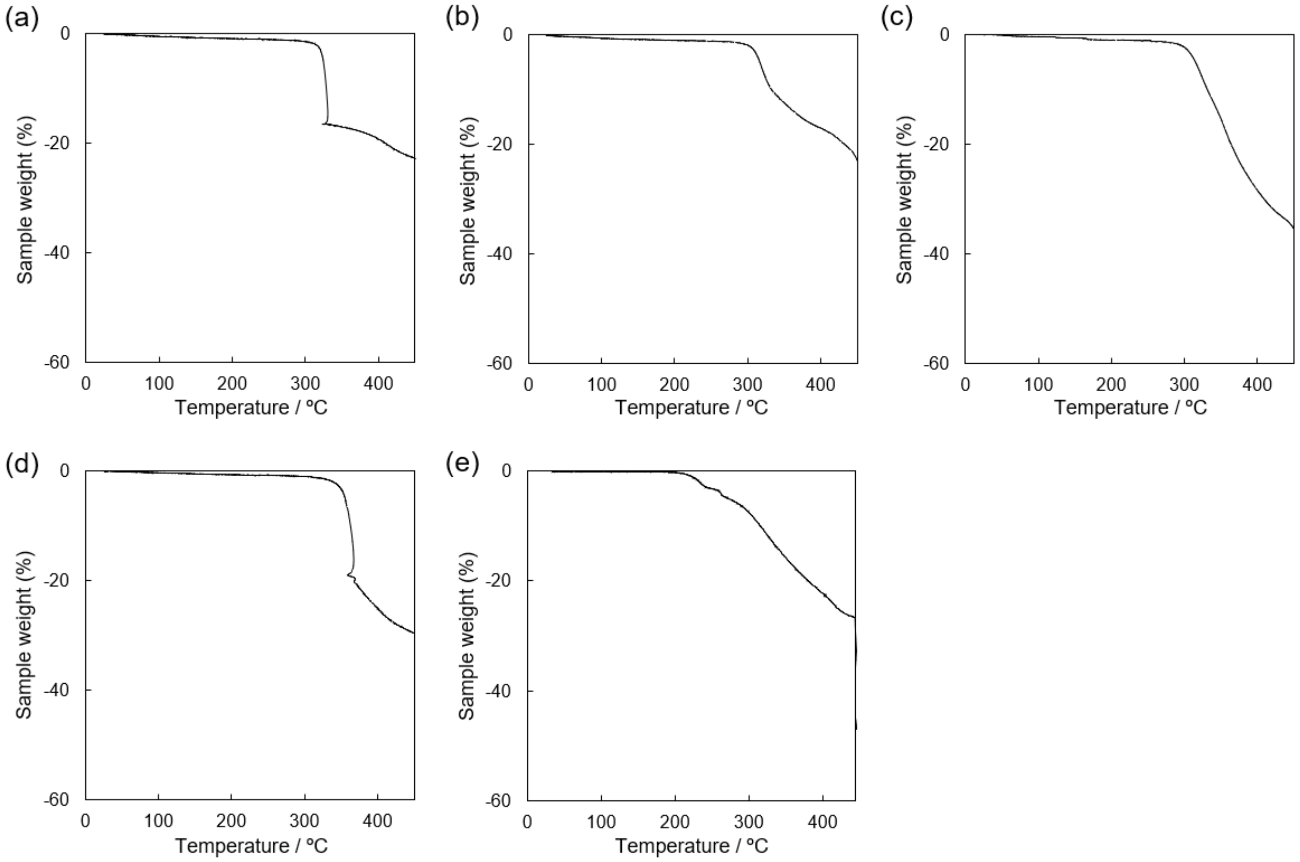

Fig. S1 Thermogravimetric analyses (TGA) of $\{M^{II}[Pt^{IV}(SCN)_6]\}_n$s in an air flow. [(a) $\{Mn^{II}[Pt^{IV}(SCN)_6]\}_n$, (b) $\{Fe^{II}[Pt^{IV}(SCN)_6]\}_n$, (c) $\{Co^{II}[Pt^{IV}(SCN)_6]\}_n$, (d) $\{Ni^{II}[Pt^{IV}(SCN)_6]\}_n$ and (e) $\{Cu^{II}[Pt^{IV}(SCN)_6]\}_n$]

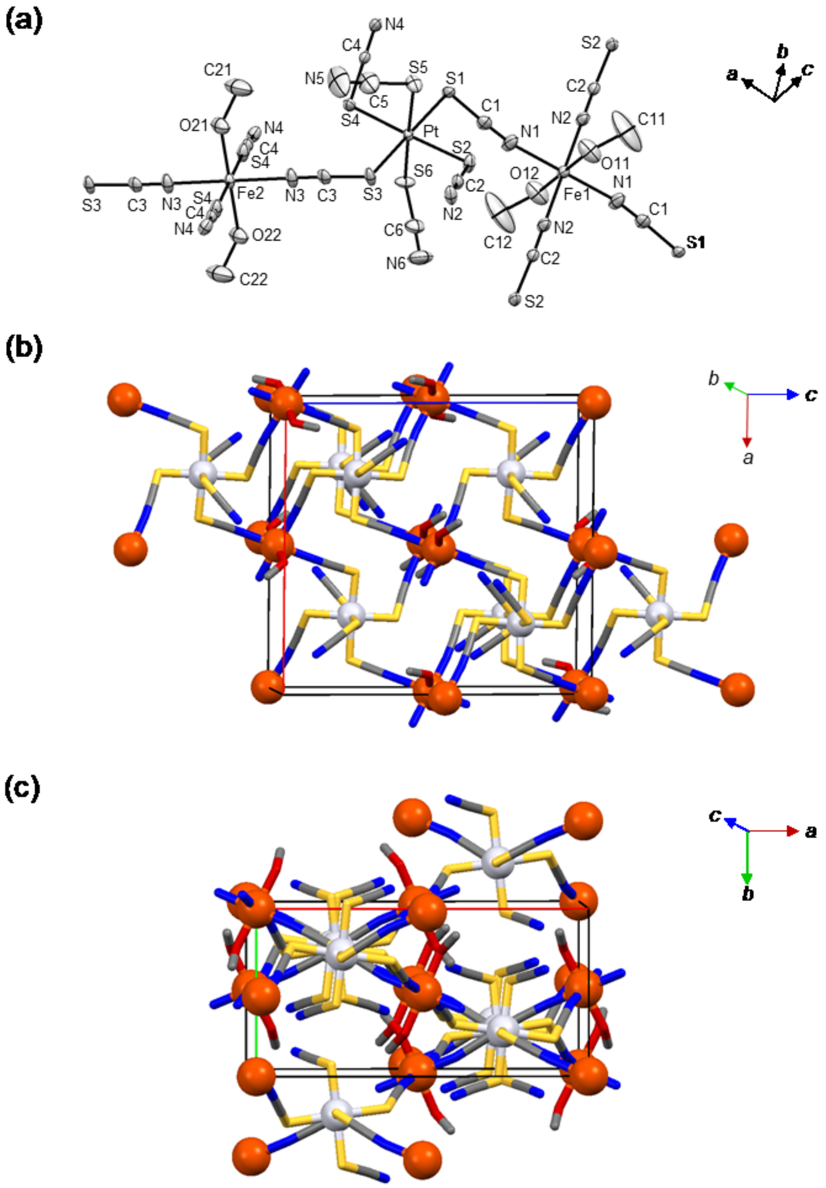

Fig. S2 Crystal structures of $\{[Fe^{II}(CH_3OH)_2][Pt^{IV}(SCN)_6]\}_n$ (CCDC ID: 1949925). (a) The Oak Ridge thermal ellipsoid plot (ORTEP) of the asymmetric unit. Ellipsoids are drawn at the 50% probability level. (b, c) Three-dimensional network structure seen from the *b* and *c* axis for (b) and (c), respectively. Atoms are coloured as follows: Fe, orange; Pt, white; C, grey; N, blue; O, red; S, yellow. A unit cell is represented by a parallelepiped. Hydrogen atoms are omitted for clarity.

Comments: The observed bond lengths of Pt−S (2.366(8)−2.397(9) Å) and the bond angle of Pt−S−C (101.23(12)−104.62(11)°) are comparable to those of $K_2[Pt^{IV}(SCN)_6]$.[S3] Each Fe ion has similar octahedral geometry composed of four equatorial N atoms from thiocyanate ligands and two axial O atoms from a pair of coordinating methanol molecules. Four N atoms of $[Pt^{IV}(SCN)_6]^{2-}$ described as N1−N4 coordinate to neighbouring Fe ions, where the Fe−N bond lengths are within 2.100(3) and 2.139(3) Å. While two N atoms described as N5 and N6 do not coordinated to Fe^{II} ions but form N···H−O hydrogen bonds with coordinated methanol molecules (N···O, 2.747 and 2.758 Å). Note that the structure of the coordination polymers composed of Fe^{II} and Pt^{IV} synthesised in methanol in the presence of pyridine was not clarified due to the low crystallinity.

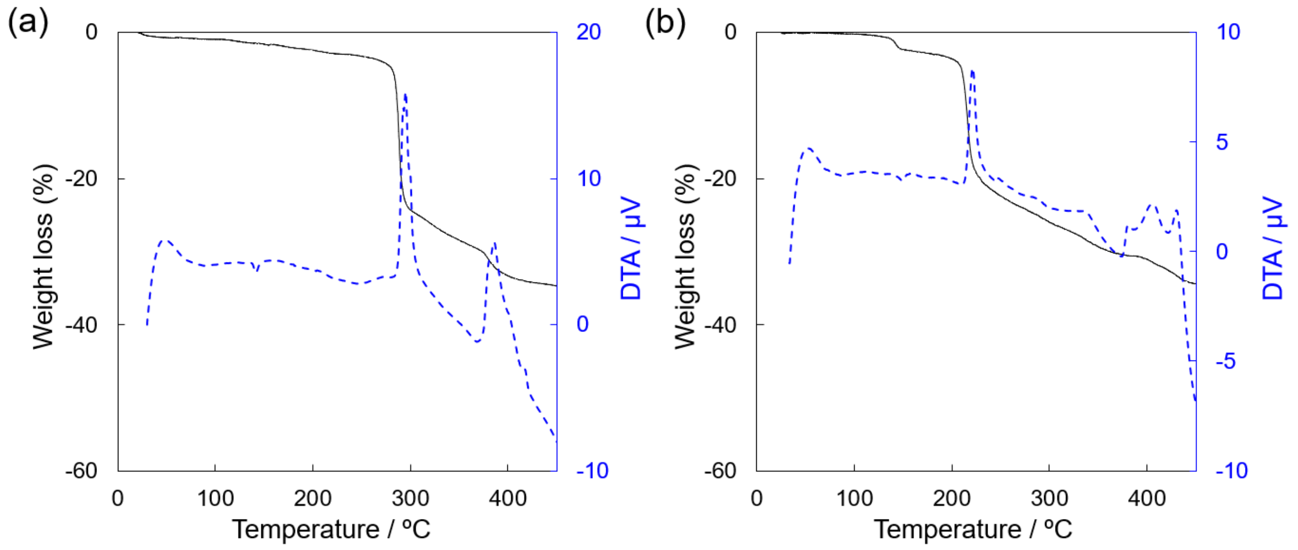

Fig. S3 Thermogravimetric analyses (TGA, solid lines) and differential thermal analyses (DTA, dotted lines) of the precipitates obtained from the reactions of $K_2[Pt^{IV}(SCN)_6]$ with (a) nickel(II) nitrate or (b) copper(II) nitrate in methanol.

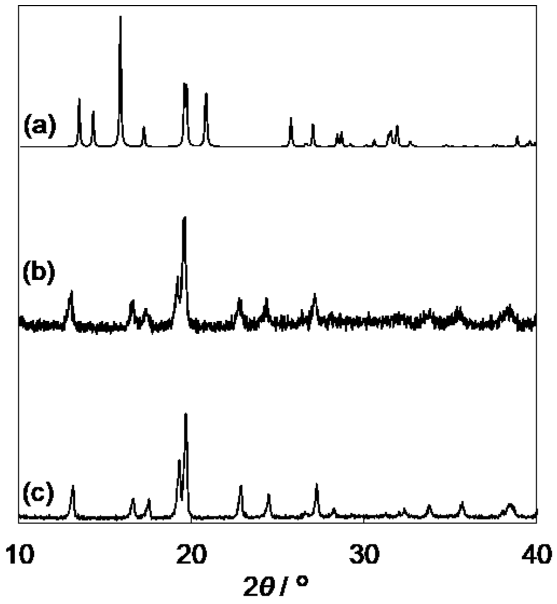

Fig. S4 Powder X-ray diffraction (XRD) patterns of (a) $\{[Fe^{II}(CH_3OH)_2][Pt^{IV}(SCN)_6]\}_n$, (b) $\{[Fe^{II}(CH_3OH)_2][Pt^{IV}(SCN)_6]\}_n$ soaked in distilled water and (c) $\{Fe^{II}[Pt^{IV}(SCN)_6]\}_n$.

Table S1 Crystal data for thiocyanato-bridged heterometallic coordination polymers

	$\{Mn^{II}[Pt^{IV}(SCN)_6]\}_n$	$\{[Co^{II}(CH_3OH)_2][Pt^{IV}(SCN)_6]\}_n$	$\{[Fe^{II}(CH_3OH)_2][Pt^{IV}(SCN)_6]\}_n$
Empirical formula	$C_6N_6S_6MnPt$	$H_8C_8N_6O_2S_6CoPt$	$H_8C_8N_6O_2S_6FePt$
Formula weight	598.51	666.58	663.50
Temperature / K	150(2)	200(2)	200(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P-1$	$C2/c$	$P2_1/c$
Z	1	8	4
a / Å	6.9591(5)	36.5312(16)	36.568(13)
b / Å	7.2934(6)	8.5217(2)	7.8934(2)
c / Å	9.0676(9)	13.7907(5)	16.5987(5)
α / °	76.040(12)	90	90
β / °	72.399(11)	109.9727(15)	90.3863(19)
γ / °	66.785(10)	90	90
V / Å^3	399.23(7)	4034.9(3)	2051.26(10)
Density calculated / g cm^{-3}	2.489	2.195	2.148
Goodness-on-fit F^2	1.077	1.089	1.069
R_1 [$I > 2\sigma(I)$]	0.0431	0.0327	0.0262
wR_2 for all data	0.0693	0.0694	0.0604
CCDC No.	1949922	1949923	1949925

References

S1. G. B. Buckton, *Lieb. Ann. Chem.,* 1854, **92**, 280−290.

S2. O. Barbosafilho and A. J. Monhemius, *Trans. Inst. Min. Metall., Sect. C*, 1994, **103**, C111−C116.

S3. J. Arpalahti, J. Hölsä and R. Sillanpää, *Acta Chem. Scand.*, 1993, **47**, 1078–1082.