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## Two-electron redox-active tricyano iron(II) complex with 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine as a building block for coordination polymers

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A new tricyano iron(II) building unit,  $[\{K(H_2O)_4\}Fe^{II}(CN)_3(L)] \cdot 3H_2O$  (**1**), was synthesized by the reaction of Moor's salts with 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (L) as a capping ligand. X-ray structural analysis reveals that the mononuclear iron(II) tricyano complex consists of one ligand and three cyanide groups, with  $K^+$  ions coordinated between neighboring units to form a one-dimensional chain network structure. **1** shows two reversible redox waves at +0.713 and -0.849 V vs. SCE, which are assigned as  $Fe(II)/Fe(III)$  and  $L/L^{•-}$  processes, respectively. One-dimensional 4,2-ribbon chain type coordination polymers,  $[M^{II}(H_2O)_2\{Fe^{II}(CN)_3(L)\}_2] \cdot 6H_2O$  ( $M = Fe$  (**2**) and  $Mn$  (**3**)), were synthesized by using **1** as a building unit. Cryomagnetic studies reveals that **2** and **3** show paramagnetic behaviour of  $S = 2$  and  $5/2$ , respectively. On the other hand, reaction of **1** and  $Gd(NO_3)_3 \cdot 6H_2O$  forms another one-dimensional chain,  $[Gd^{III}(NO_3)_2(H_2O)_3\{Fe^{II}(CN)_3(L)\}] \cdot 0.5H_2O \cdot 2CH_3OH$  (**4**), showing  $S = 7/2$  paramagnetic behaviour.

### Introduction

Cyanide ligands mediate significant electronic and magnetic interactions between metal ions, and their coordination polymers exhibit a wide variety of tuneable and switchable physical properties.<sup>1</sup> Hexacyanometallates can be considered the archetypal cyanide complexes and are the molecular building blocks of Prussian Blue and its analogues, however, polycyano complexes with auxiliary capping ligands such as tp (tris pyrazoryl borate), tach (1,3,5-triaminocyclohexane), tacn (1,4,7-triazacyclononane) and bpy (2,2'-bipyridine), have been extensively employed as building units in the synthesis of coordination compounds with a range of structure types, from 0-D molecules to 3-D networks.<sup>2–4</sup> For example, tetracyanometallate complexes with the general formula  $[M(CN)_4(L^{bi})]^{n-}$  ( $L^{bi}$  = bidentate ligand), are a prime example of complex ligands employed in the synthesis of clusters and network compounds, and such systems have recently been reviewed by Wang and Huang.<sup>3</sup> These building units have four available donor atoms located in axial and equatorial positions on the metal centre and can be employed to construct coordination compounds of different shapes and sizes with a degree of control. This approach has led, in particular, to the

controlled fabrication and isolation of desirable single-molecule magnets (SMMs), single-chain magnets (SCMs), and bulk ordered molecule-based magnets. On the other hand, tricyanometallates with the general formula  $[M(CN)_3(L^{tri})]^{n-}$  ( $L^{tri}$  = tridentate ligand) are also useful building blocks for low-dimensional magnetic materials.<sup>4</sup> The coordination modes of tridentate capping ligands can be categorized as *fac*- or *mer*-. Consequently, the coordination direction of tricyanometallates is restricted to *fac*- or *mer*- modes. Simple bridging modes lead to the formation of low-dimensional assemblies such as clusters and one-dimensional networks. Many SMMs and SCMs based on tricyanometallates have been reported, but few examples of bulk magnets. In the case of tricyanometallate systems, single-molecule electron-transfer-coupled spin transition (ETCST) phenomena<sup>5</sup> have been extensively investigated. The combination of predictable coordination chemistry and their propensity to stabilize switchable magnetic clusters makes tricyanometallates among the most promising candidate systems for applications in future molecular switch-based technologies. However, the range of auxiliary ligands utilized to date is limited.<sup>6</sup> In order to develop the next generation of functional molecular materials, polycyanide building blocks with a range of bridging modes and physical properties will be required. Recently we reported a new tetracyano iron compound,  $K_2[Fe^{III}(CN)_4(L^1)]$  ( $HL^1 = 3,5$ -di(pyrid-2-yl)-pyrazole) with the ditopic ligand  $HL^1$  as a capping group with two bidentate NN coordination sites. In addition, tetranuclear  $[Ni^{II}_2Fe^{III}_2]$  square complexes were synthesized by the combination of  $K_2[Fe^{III}(CN)_4(L^1)]$  with  $Ni^{2+}$  with the chiral ligands  $L^R$  or  $L^S$  ( $L^R$  or  $L^S = N$ -(2-pyridylmethylene)-(R or S)-1-phenylethylamine).<sup>7</sup> In the course of this research, we aim to develop new polycyano

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building units with planar polydentate ligands and construct functional cyanide bridged coordination assemblies.<sup>8</sup>

The use of the flexible bridging ligand, 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (L), which typically adopts a near planar conformation and three chelating  $\kappa^3-N,N',N''$ -tridentate sites, was recently reported by M. Murugesu et al.<sup>9</sup> L has unique coordination behaviour due to its nitrogen-rich structure, and has been used to stabilise polynuclear complexes and high dimensional networks. We aimed to explore the use of L as a capping ligand for polycyano compounds and studied the coordination chemistry of the resultant systems. In this paper, the syntheses, structures, and electrochemical properties of an iron(II) tricyano complex,  $[\{K(H_2O)_4\}\{Fe^{II}(CN)_3(L)\}]\cdot 3H_2O$  (**1**) are reported. Its one-dimensional double-chain network compounds,  $[M^{II}(H_2O)_2\{Fe^{II}(CN)_3(L)\}]\cdot 6H_2O$  (M = Fe (**2**) and Mn (**3**)) and its one-dimensional zig-zag chain compound  $[Gd^{III}(NO_3)_2(H_2O)_3\{Fe^{II}(CN)_3(L)\}]\cdot 0.5H_2O\cdot 2CH_3OH$  (**4**), obtained by the reaction of the tricyano building unit with iron, manganese, and gadolinium metal sources are investigated.

## Experimental

### Materials

Unless otherwise stated, all of the starting materials and solvents were reagent grade and were purchased from Wako or Tokyo Chemical Industry Co. Ltd. and used without further purification. Ligand 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (L) was synthesized according to a procedure described in reference 9. All solvents were used without degassing treatment and distillation.

**Synthesis of  $[\{K(H_2O)_4\}\{Fe^{II}(CN)_3(L)\}]\cdot 3H_2O$  (**1**).**  $Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$  (2.8 g, 7.18 mmol) was added as a solid to a suspension of L (650 mg, 2.1 mmol) in boiling water (100 mL). The colour of the reaction mixture changed to red-purple. After stirring for a few minutes with continuous heating, KCN (2.0 g, 30.7 mmol) was added. The resulting solution was filtered and the filtrate was allowed to stand at room temperature yielding dark reddish purple needles of  $[\{K(H_2O)_4\}\{Fe^{II}(CN)_3(L)\}]\cdot 3H_2O$  (**1**). The crystals were collected by suction and air-dried. Yield: 750 mg (58 %). Elemental analysis calcd. (%) for  $C_{18}H_{15}N_{12}O_3KFe$ : C 39.86, H 2.79, N 30.99; found: C 39.63, H 2.92, N 30.88. IR (KBr,  $cm^{-1}$ ): 2089.7 ( $\nu_{C\equiv N}$ ).

**Synthesis of  $[M^{II}(H_2O)_2\{Fe^{II}(CN)_3(L)\}]\cdot 6H_2O$  (M = Fe (**2**) and M = Mn (**3**)).** Complexes **2** and **3** were synthesized by similar synthetic methods, described as follows. A solution of **1** (30.0 mg, 0.05 mmol) in methanol (10 mL) was layered on a solution of  $FeCl_3\cdot 6H_2O$  (14 mg, 0.05 mmol), 2-pyridine carbaldehyde (12.0  $\mu$ L, 0.10 mmol) and (*R*)-phenylethylamine (11.6  $\mu$ L, 0.10 mmol) in methanol (10 mL). After a few weeks of diffusion, dark reddish purple needles of  $[Fe^{II}(H_2O)_2\{Fe^{II}(CN)_3(L)\}]\cdot 6H_2O$  (**2**) were obtained. The crystals were collected by suction and air-dried. The resulting polycrystalline sample,  $[Fe^{II}(H_2O)_2\{Fe^{II}(CN)_3(L)\}]\cdot 5.5H_2O$ , was used for the physical

measurements. Yield: 6.0 mg (21 %). Elemental analysis calcd. (%) for  $C_{36}H_{33}N_{24}O_{7.5}Fe_3$  ( $[Fe^{II}(H_2O)_2\{Fe^{II}(CN)_3(L)\}]\cdot 5.5H_2O$ ): C 39.69, H 3.05, N 30.86; found: C 39.96, H 3.02, N 30.74. IR (KBr,  $cm^{-1}$ ): 2125.4, 2092.6 ( $\nu_{C\equiv N}$ ). Complex **3**,  $[Mn^{II}(H_2O)_2\{Fe^{II}(CN)_3(L)\}]\cdot 6H_2O$ , was synthesized by a similar method, using  $MnCl_2\cdot 4H_2O$  (10.0 mg, 0.05 mmol) instead of  $FeCl_3\cdot 6H_2O$ . Yield: 6.0 mg (21 %). Elemental analysis calcd. (%) for  $C_{36}H_{34}N_{24}O_8Fe_2Mn$  ( $[Mn^{II}(H_2O)_2\{Fe^{II}(CN)_3(L)\}]\cdot 6H_2O$ ): C 39.40, H 3.12, N 30.63; found: C 39.60, H 2.91, N 30.42. IR (KBr,  $cm^{-1}$ ): 2121.6, 2090.7 ( $\nu_{C\equiv N}$ ).

**Synthesis of  $[Gd^{III}(NO_3)_2(H_2O)_3\{Fe^{II}(CN)_3(L)\}]\cdot 0.5H_2O\cdot 2MeOH$  (**4**).** To a methanolic solution (20 mL) of  $Gd(NO_3)_3\cdot 6H_2O$  (91.6 mg, 0.2 mmol) a bluish-green solution of **1** (112.4 mg, 0.2 mmol) in methanol (20 mL) was added. The colour of the mixture changed to blue. After stirring for a few minutes at room temperature, the resulting solution was filtered and left to stand for a few days, forming green needle crystals of  $[Gd^{III}(NO_3)_2(H_2O)_3\{Fe^{II}(CN)_3(L)\}]\cdot 0.5H_2O\cdot 2MeOH$  (**4**). The crystals were collected by suction and air-dried. The dried sample was used for physical measurements. Yield: 12.9 mg (7.8 %). Elemental analysis calcd. (%) for  $C_{18.5}H_{20}N_{14}O_{11}FeGd$  ( $[Gd^{III}(NO_3)_2(H_2O)_3\{Fe^{II}(CN)_3(L)\}]\cdot 1.5H_2O\cdot 0.5MeOH$ ): C 26.85, H 2.44, N 23.70; found: C 26.72, H 2.23, N 23.54. IR (KBr,  $cm^{-1}$ ): 2121.7, 2094.7 ( $\nu_{C\equiv N}$ ), 1390.7 ( $\nu_{NO_3}$ ).

### Physical measurements

Infrared (IR) spectra were recorded (400-4000  $cm^{-1}$  region) on a SHIMADZU IRAffinity-1 spectrometer using KBr pellets. Direct current magnetic susceptibility measurements of polycrystalline samples were measured in the temperature range of 1.8 – 300 K with a Quantum Design MPMS-5XL SQUID magnetometer under an applied magnetic field of 500 Oe or 1 T. Data were corrected for the diamagnetic contribution calculated from Pascal's constants including the contribution of the quartz glass sample holder. Cyclic voltammetry measurements were carried out in a standard one-compartment cell under  $N_2$  at 20 °C equipped with a platinum-wire counter electrode, an SCE reference electrode, and a glassy carbon (GC) working electrode, using a BAS 620A electrochemical analyser. The measurements were performed in MeCN with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (*n*-Bu<sub>4</sub>NPF<sub>6</sub>) as the supporting electrolyte.

## Results and discussion

### Synthesis and characterization

The mononuclear tricyano iron(II) complex,  $[\{K(H_2O)_4\}\{Fe^{II}(CN)_3(L)\}]\cdot 3H_2O$  (**1**), was synthesized by the reaction of Moor's salt with TPT in hot water. This synthetic method is commonly used for  $[Fe(bpy)_2(CN)_2]$ -type complexes.<sup>10</sup> We recently synthesised the tetracyano iron(II) mononuclear complex  $K_2[Fe^{II}(CN)_4(L^1)]$  described in reference 7 using a similar synthetic method. The previously reported compound includes a trivalent iron ion, where the iron ion has

been oxidised by air, while the present complex has a divalent iron ion. Under mild conditions, the oxidation of an iron ion in L is disfavoured due to the weak donor character of the neutral ligand. In the case of syntheses of **2** and **3**, 2-pyridinecarbaldehyde and (*R*)-phenylethylamine were used, but the expected Schiff-base (*N*-(2-pyridylmethylene)-(*R*)-1-phenylethylamine) was absent from the product. Self-assembly reactions without these reagents were attempted, but the one-dimensional complexes were not obtained in those cases. These facts suggest that an intermediate species involving these reagents or auxiliary ligands performs an important role in the formation of the one-dimensional network compounds.

### Crystal structure of **1**

X-ray structural analysis of **1** reveals that a mononuclear iron(II) tricyanide complex was formed (Figure 1). In this structure, one of the tridentate chelating  $\kappa_3$ -*N,N',N''*- moieties of L coordinates to the iron(II) ion. A second tridentate chelating  $\kappa_3$ -*N,N',N''*- site interacted with a  $K^+$  ion. The iron(II) ion has six coordinate geometry with  $N_3C_3$  donor atoms from one ligand and the carbon atoms of three cyanide groups. The potassium ion can be assumed to exhibit nona-coordinate geometry, coordinated by the  $\kappa_3$ -*N,N',N''*- site of L, four water molecules and a neighbouring cyanide group. The terminal cyanide group interacts with the potassium ion, forming a one-dimensional chain structure.

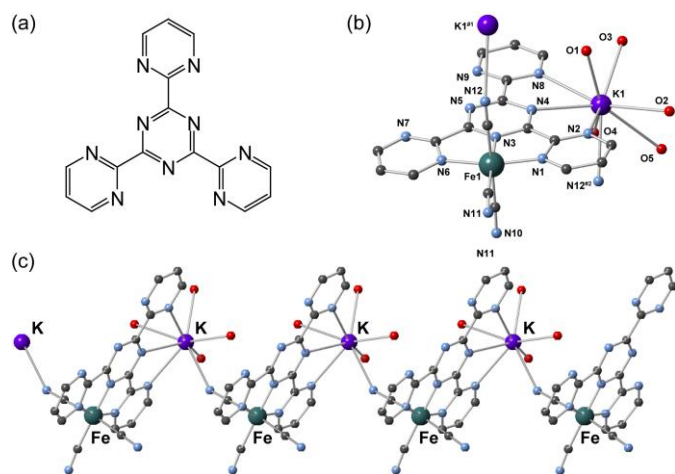


Fig. 1. (a) Structural diagram of L. (b) Molecular structure of  $[K(H_2O)_4][Fe(CN)_3(L)] \cdot 3H_2O$  (**1**). (c) One-dimensional structure of **1**. Lattice solvents have been omitted for clarity. Colour code: C, gray; N, light blue; Fe(II), turquoise. Symmetry code: #1:  $1+x, +y, +z$ ; #2:  $-1+x, +y, +z$ .

The one-dimensional network structure was formed through K-NC-Fe linkages and stabilised by inter chain  $\pi$ - $\pi$  stacking interactions between the pyrimidine rings of neighbouring tricyanide units (Figure S1).

### Crystal structure of **2** and **3**

Complexes **2** and **3** are isostructural. Both consist of two mononuclear  $[Fe^II(CN)_3(L)]^-$  units linked by one  $[M^II(H_2O)_2]^{2+}$  unit, forming a one-dimensional 4,2-ribbon chain structure (Figures 2a and 3). This structural motif has been previously reported.<sup>11</sup> The ribbon structure was formed by joining

vertices of squares based on  $\{Fe^II_2M^II_2(CN)_4\}$  units, which are built up from two Fe(II) and two M(II) atoms linked by bridging cyanide groups. Two of the three cyanide groups of the tricyanide building units were used to bridge to neighbouring metal centres. The transition metal ion of the  $[M^II(H_2O)_2]^{2+}$  unit has a  $N_4O_2$  coordination environment of four equatorial cyanide nitrogen atoms and two water molecules in the apical positions. The double Fe-M cyanide ribbons interacted with neighbouring chains through  $\pi$ - $\pi$  stacking interactions (Figure S2).

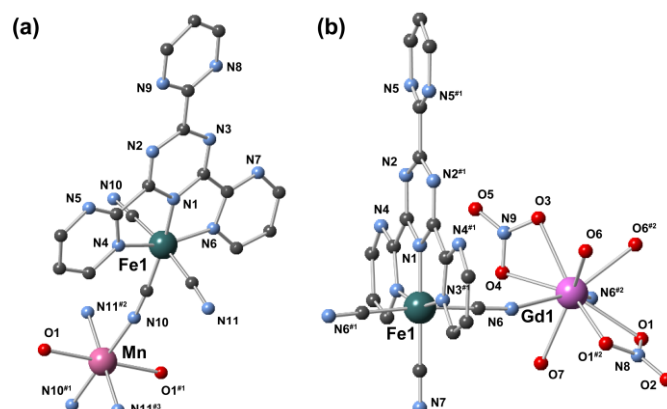


Fig. 2. Asymmetric unit of (a)  $[Mn(H_2O)_2][Fe(CN)_3(L)]_2 \cdot 6H_2O$  (**3**). (b)  $[Gd(NO_3)_2(H_2O)_3][Fe(CN)_3(L)] \cdot 0.5H_2O \cdot 2CH_3OH$  (**4**). Lattice solvents have been omitted for clarity. Colour code: C, gray; N, light blue; Fe(II) for tricyano unit, turquoise; Mn(II) and Gd(III), pink. Symmetry code for (a); #1:  $-x, -y, -z$ ; #2:  $-1+x, +y, +z$ ; #3:  $1-x, -y, -z$ ; for (b); #1:  $+x, 3/2-y, 1-z$ ; #2:  $+x, +y, 1/2-z$ .

In complex **2**, the coordination bond lengths of the Fe2 ion ranged from 2.127(2) Å to 2.1715(18) Å. BVS calculations suggested that the Fe2 ion was in the divalent state.<sup>12</sup> The coordination bond lengths of the Mn ion in complex **3** are 2.189(4) – 2.243(3) Å without Jahn-Teller distortions, suggesting that Mn is in its divalent state. BVS calculations were consistent with a divalent Mn ion.<sup>13</sup>

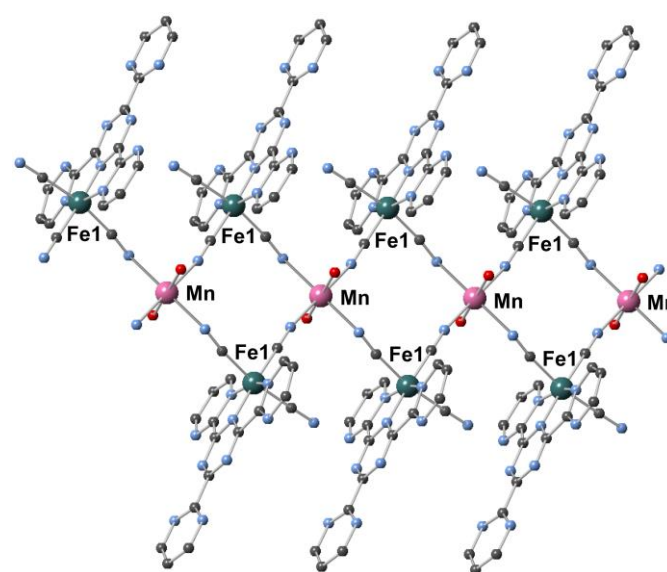


Fig. 3. Network structure of  $[\text{Mn}^{\text{II}}(\text{H}_2\text{O})_2\{\text{Fe}^{\text{II}}(\text{CN})_3(\text{L})\}]_2 \cdot 6\text{H}_2\text{O}$  (**3**). Lattice solvents have been omitted for clarity. Colour code: C, gray; N, light blue; Mn(II), pink; Fe(II) for tricyano unit, turquoise.

### Crystal structure of **4**

$[\text{Gd}^{\text{III}}(\text{NO}_3)_2(\text{H}_2\text{O})_3\{\text{Fe}^{\text{II}}(\text{CN})_3(\text{L})\}] \cdot 0.5\text{H}_2\text{O} \cdot 2\text{MeOH}$ , has a different one-dimensional structure, with a Gd-NC-Fe zig-zag chain (Figures 2b and 4). The asymmetric unit consists of half of one  $[\text{Fe}(\text{CN})_3(\text{L})]^-$  unit and half of one  $[\text{Gd}(\text{NO}_3)_2(\text{H}_2\text{O})_3]$ . The Gd ion, one nitrate anion, and the nitrogen and oxygen atoms of one nitrate anion are located on a mirror plane. A crystallographic two-fold axis runs along the Fe ion and the central nitrogen atom. The Gd ion has nona-coordinate geometry with a  $\text{N}_2\text{O}_7$  coordination environment, where the two nitrogen atoms are from cyanide groups of the tricyano unit, three oxygen atoms are coordinated water molecules and four oxygen atoms are from two bidentate nitrate ions.  $[\text{Fe}^{\text{II}}(\text{CN})_3(\text{L})]^-$  units bridge the Gd ions via two *trans* cyanide groups. One polycyanide unit bridges two Gd(III) ions, with a N-Gd-N angle of  $141.18^\circ$ , forming zig-zag chain structure. The chains also interact with neighbouring chains through  $\pi$ - $\pi$  stacking (Figure S3).

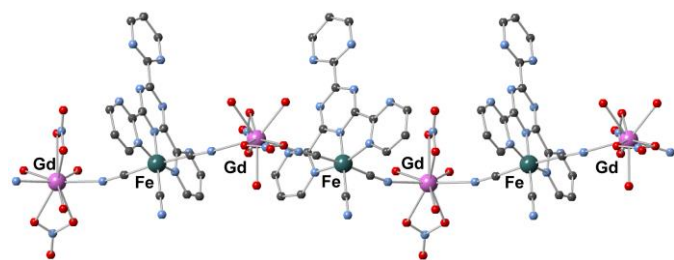


Fig. 4. One-dimensional network structure of  $[\text{Gd}^{\text{III}}(\text{NO}_3)_2(\text{H}_2\text{O})_3\{\text{Fe}(\text{CN})_3(\text{L})\}] \cdot 3\text{H}_2\text{O}$  (**4**). Lattice solvents have been omitted for clarity. Colour code: C, gray; N, light blue; Gd(III) pink; Fe(II) for tricyano unit, turquoise.

### Electrochemical property of **1**

Electrochemical properties of **1** were investigated. Stabilities of **1** in acetonitrile solution were confirmed by ESI-MS spectra, shown in Figure S4. A cyclic voltammogram of **1** is shown in Figure 5, and exhibits quasi-reversible redox waves at  $+0.713$  and  $-0.849$  V versus SCE. Considering the electrochemical properties of similar complexes and organic molecules,<sup>14</sup> the oxidation wave at  $+0.713$  V was assigned to a  $\text{Fe}(\text{II})/\text{Fe}(\text{III})$  redox process. Tricyanide complex,  $\text{Na}[\text{Fe}(\text{CN})_3(\text{tpd})]$  (tpd = tetrakis(2-pyridyl)-1,4-diazine), with similar terpyridine-type tridentate ligand shows  $+0.54$  V (versus SCE) in DMF, which is close to the redox potential of **1**. It is therefore considered that the redox behavior of **1** is reasonable. On the other hand, the reduction wave at  $-0.849$  V can be assigned to a  $\text{L}/\text{L}^-$  reduction process. As a comparison, a ruthenium complex with the triazine-based analogue tptz (2,4,6-tris(2-pyridyl)-1,3,5-triazine) exhibits a redox process centred at  $-1.27$  V, which is assigned as a ligand-centred process.<sup>15</sup> In accordance with these examples, the reduction wave at  $-0.849$  V was primarily assigned to a ligand-based process. The electrochemical properties of this building unit may be useful due to the dual redox processes shown by the iron and ligand

moieties, rendering the molecule an excellent candidate for the construction of redox-active coordination polymers.

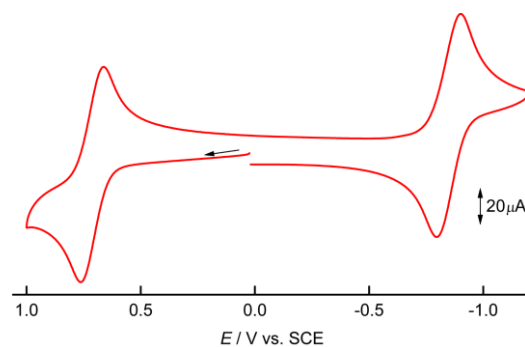


Fig. 5. Electrochemical property of  $\text{K}[\text{Fe}^{\text{II}}(\text{CN})_3(\text{L})(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$  (**1**) in acetonitrile. Conditions: Scan rate,  $0.1 \text{ V sec}^{-1}$ .

### Magnetic properties

The magnetic properties of **2**, **3** and **4** were investigated by SQUID magnetometry. Sample purities were confirmed by powder X-ray diffraction measurements, and the data of complex **2** is shown in Figure S5. The building unit **1** consists of a diamagnetic low spin Fe(II) ion ( $S = 0$ ), which was confirmed by magnetic measurement. This spin state was also supported by the stretching bands of the cyanide groups, which appeared at  $2089.7 \text{ cm}^{-1}$ , a value indicative of low spin Fe(II)-CN. In addition, similar tricyano complexes have been shown to exist in the low-spin state due to the strong ligand field.<sup>4</sup> The  $\chi_m T$  vs.  $T$  plots for complexes **2-4** are shown in Figure 6. All compounds include diamagnetic low-spin Fe(II) tricyanide units, therefore paramagnetic behaviour based on the linked metal ions were observed in the measured temperature range. The  $\chi_m T$  values for **2**, **3** and **4** at room temperature are  $3.68$ ,  $4.81$  and  $8.25 \text{ emu mol}^{-1} \text{ K}$ , values consistent with the usual magnetic behaviour of magnetically isolated ions with spin states of  $S = 2$ ,  $5/2$  and  $7/2$ , respectively. In **2**, there are two kinds of iron ion with different spin states. Fe1 of the building unit retains a divalent low spin state. On the other hand, the connected iron ion Fe2 has a divalent high spin state with  $S = 2$  due to the weak ligand field comprised of four cyanide N donor groups and two water molecules. Complex **3** has a high spin Mn(II) ion with  $S = 5/2$ , which is in an  $\text{N}_4\text{O}_2$  coordination site similar to complex **2**. These spin states are reasonable considering similar ribbon-type network compounds.<sup>4</sup> For complex **4**, a paramagnetic Gd(III) ion was included as a connector. In general, Gd(III) ion has an  $S = 7/2$  state regardless of the strength of the ligand field.



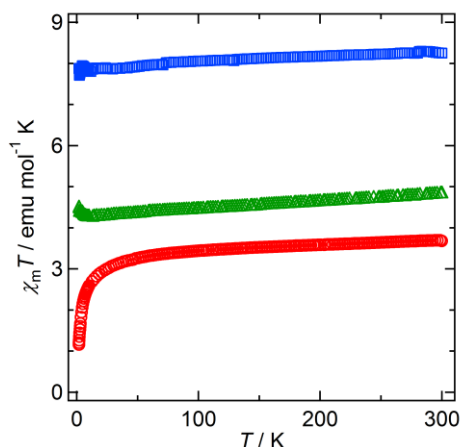


Fig. 6. Magnetic properties of **2** (○), **3** (△), and **4** (□).

## Conclusions

A new tricyano iron(II) building unit,  $[\{K(H_2O)_4\}Fe^{II}(CN)_3(L)] \cdot 3H_2O$  (**1**), with a planar multidentate ligand 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (L) was synthesized. **1** shows two reversible redox waves at +0.713 and -0.849 V versus SCE, which are assigned as Fe(II)/Fe(III) and L/L<sup>-</sup> processes, respectively. One-dimensional 4,2-ribbon chain coordination polymers,  $[M^{II}(H_2O)_2\{Fe^{II}(CN)_3(L)\}_2] \cdot 6H_2O$  (M = Fe (**2**) and Mn (**3**)), were synthesized using **1** as a building unit. In contrast, the reaction of **1** with a gadolinium source afforded another one-dimensional zig-zag chain structure,  $[Gd^{III}(NO_3)_2(H_2O)_3\{Fe^{II}(CN)_3(L)\}] \cdot 0.5H_2O \cdot 2CH_3OH$  (**4**). Cryomagnetic studies reveals that **2**, **3** and **4** show paramagnetic behaviour of  $S = 2$ ,  $5/2$  and  $7/2$ , respectively. The present research into the molecular design of new polycyano building blocks can be employed as a first step toward the rational development of functional cyanide-bridged coordination polymers as electrode materials in rechargeable batteries<sup>16</sup>, ion/proton conducting coordination compounds<sup>17</sup> and external field stimuli responsive materials.<sup>18</sup>

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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## Notes and references

- 1 Reviews of Cyanide coordination polymers: M. Shatruk, C. Avendano and K. R. Dunbar, *Prog. Inorg. Chem.*, 2009, **56**, 155; P. Przychoździn, T. Korzeniak, R. Podgajny and B.

- Sieklucka, *Coord. Chem. Rev.*, 2006, **250**, 2234; L. M. C. Beltran and J. R. Long, *Acc. Chem. Res.*, 2005, **38**, 325; R. Lescouezec, L.M. Toma, J. Vaissermann, M. Verdager, F.S. Delgado, C. Ruiz-Pérez, F. Lloret, M. Julve, *Coord. Chem. Rev.*, 2005, **249**, 2691; M. Ohba and H. Ōkawa, *Coord. Chem. Rev.*, 2002, **198**, 313; A.A. Karyakin, *Electroanalysis*, 2001, **13**, 813; M. Verdager, A. Bleuzen, V. Marvaud, J. Vaissermann, M. Seuleiman, C. Desplanches, A. Scullier, C. Train, R. Garde, G. Gelly, C. Lomenech, I. Rosenman, P. Veillet, C. Cartier dit Moulin and F. Villain, *Coord. Chem. Rev.*, 1999, **192**, 1023.
- 2 Reviews about cyanide bridged units with analogue of tp (tris(pyrazolyl)borate), tach (1,3,5-triaminocyclohexane), tacn (1,4,7-triazacyclononane) and bpy: Y.-H. Li, W.-R. He, X.-H. Ding, S. Wang, L.-F. Cui and W. Huang, *Coord. Chem. Rev.*, 2012, **256**, 2795; S. Wang, X.-H. Ding, J.-L. Zuo, X.-Z. You, W. Huang, *Coord. Chem. Rev.*, 2011, **255**, 1713; J.L. Heinrich, P.A. Berseth and J.R. Long, *Chem. Commun.*, 1998, 1231; F. Galsbol, C.H. Petersen and K. Simonsen, *Acta Chem. Scand.*, 1996, **50**, 567; J.Y. Yang, M.P. Shores, J.J. Sokol and J.R. Long, *Inorg. Chem.*, 2003, **42**, 1403; J.J. Sokol, M.P. Shores and J.R. Long, *Inorg. Chem.*, 2002, **41**, 3052.
- 3 Y.-H. Li, W.-R. He, X.-H. Ding, S. Wang, L.-F. Cui, W. Huang, *Coord. Chem. Rev.*, 2012, **256**, 2795.
- 4 S. Wang, X.-H. Ding, J.-L. Zuo, X.-Z. You, W. Huang, *Coord. Chem. Rev.*, 2012, **256**, 2795.
- 5 G.N. Newton, M. Nihei, H. Oshio, *Eur. J. Inorg. Chem.*, 2011, **20**, 3031; D. Aguilà, Y. Prado, E.S. Koumoussi, C. Mathonière, R. Clérac, *Chem. Soc. Rev.*, 2016, **45**, 203.
- 6 Recent examples of polycyano complexes with different auxiliary ligands: I.-R. Jeon, S. Calancea, A. Panja, D.M. Piñero Cruz, E.S. Koumoussi, P. Dechambenoit, C. Coulon, A. Wattiaux, P. Rosa, C. Mathonière and R. Clérac, *Chem. Sci.*, 2013, **4**, 2463; A. Panja, P. Guionneau, I.-R. Jeon, S. M. Holmes, R. Clérac and C. Mathonière, *Inorg. Chem.*, 2012, **51**, 12350; M. Ray, R. Mukherjee, J.F. Richardson and R.M. Buchanan, *J. Chem. Soc., Dalton Trans.*, 1993, 2451; S.K. Dutta, U. Beckmann, E. Bill, T. Weyhermuller and K. Wieghardt, *Inorg. Chem.*, 2000, **39**, 3355; R. Lescouezec, J. Vaissermann, L.M. Toma, R. Carrasco, F. Lloret and M. Julve, *Inorg. Chem.*, 2004, **43**, 2234; Z.-H. Ni, H.-Z. Kou, L.-F. Zhang, W.-W. Ni, Y.-B. Jiang, A.-L. Cui, J. Ribas and O. Sato, *Inorg. Chem.*, 2005, **44**, 9631; Z.-H. Ni, H.-Z. Kou, Y.-H. Zhao, L. Zheng, R.-J. Wang, A.-L. Cui and O. Sato, *Inorg. Chem.*, 2005, **44**, 2050; L. Toma, R. Lescouezec, J. Vaissermann, P. Herson, V. Marvaud, F. Lloreta and M. Julve, *New J. Chem.*, 2005, **29**, 210.
- 7 C. Krüger, H. Sato, T. Matsumoto, T. Shiga, G.N. Newton, F. Renz and H. Oshio, *Dalton Trans.*, 2012, **41**, 11270.
- 8 Y. Sekine, M. Nihei, H. Oshio, *Chem. Eur. J.*, 2017, **23**, 5193; K. Mitsumoto, J.M. Cameron, R.J. Wei, H. Nishikawa, T. Shiga, M. Nihei, G.N. Newton, H. Oshio, *Chem. Eur. J.*, 2017, **23**, 1502; M. Nihei, Y. Yanai, I.-J. Hsu, Y. Sekine, H. Oshio, *Angew. Chem. Int. Ed.*, 2017, **56**, 591; R.J. Wei, T. Shiga, G.N. Newton, D. Robinson, S. Takeda, H. Oshio, *Inorg. Chem.*, 2016, **55**, 12114; R.J. Wei, R. Nakahara, J.M. Cameron, G.N. Newton, T. Shiga, H. Sagayama, R. Kumai, Y. Murakami, H. Oshio, *Dalton Trans.*, 2016, **45**, 17104; Y. Sekine, M. Nihei, R. Kumai, H. Nakao, Y. Murakami, H. Oshio, *Inorg. Chem. Front.*, 2014, **1**, 540; T. Shiga, T. Tetsuka, K. Sakai, Y. Sekine, M. Nihei, G.N. Newton, H. Oshio, *Inorg. Chem.*, 2014, **53**, 5899; Y. Sekine, M. Nihei, H. Oshio, *Chem. Lett.*, 2014, **43**, 1029; G.N. Newton, K. Mitsumoto, R.J. Wei, F. Iijima, T. Shiga, H. Nishikawa, H. Oshio, *Angew. Chem. Int. Ed.*, 2014, **53**, 2941; Y. Sekine, M. Nihei, R. Kumai, H. Nakao, Y. Murakami, H. Oshio, *Chem. Commun.*, 2014, **50**, 4050; T. Shiga, M. Takeo, F. Iijima, G.N. Newton, H. Oshio, *New J. Chem.*, 2014, **38**, 1946; M.L. Baker, Y. Kitagawa, T. Nakamura, K. Tazoe, Y. Narumi, Y. Kotani, F. Iijima, G.N.

- Newton, M. Okumura, H. Oshio, H. Nojiri, *Inorg. Chem.*, 2013, **52**, 13956; T. Shiga, F. Iijima, T. Tetsuka, G.N. Newton, H. Oshio, *Macromol. Symp.*, 2012, **317-318**, 286; K. Mitsumoto, H. Nishikawa, G.N. Newton, H. Oshio, *Dalton Trans.*, 2012, **41**, 13601; M. Nihei, Y. Okamoto, Y. Sekine, N. Hoshino, T. Shiga, I.P.C. Liu, H. Oshio, *Angew. Chem. Int. Ed.*, 2012, **51**, 6361; N. Hoshino, F. Iijima, G.N. Newton, N. Yoshida, T. Shiga, H. Nojiri, A. Nakao, R. Kumai, Y. Murakami, H. Oshio, *Nat. Chem.*, 2012, **4**, 921; K. Mitsumoto, H. Nishikawa, H. Oshio, *Polyhedron*, 2011, **30**, 3245; K. Mitsumoto, E. Oshiro, H. Nishikawa, T. Shiga, Y. Yamamura, K. Saito, H. Oshio, *Chem. -A Eur. J.*, 2011, **17**, 9612; M. Nihei, Y. Sekine, N. Suganami, K. Nakazawa, A. Nakao, H. Nakao, Y. Murakami, H. Oshio, *J. Am. Chem. Soc.*, 2011, **133**, 3592; T. Shiga, G.N. Newton, J.S. Mathieson, T. Tetsuka, M. Nihei, L. Cronin, H. Oshio, *Dalton Trans.*, 2010, **39**, 4730; N. Hoshino, Y. Sekine, M. Nihei, H. Oshio, *Chem. Commun.*, 2010, **46**, 6117; K. Mitsumoto, M. Ui, M. Nihei, H. Nishikawa, H. Oshio, *CrystEngComm*, 2010, **12**, 2697; M. Nihei, Y. Sekine, N. Suganami, H. Oshio, *Chem. Lett.*, 2010, **39**, 978; M. Nihei, M. Ui, H. Oshio, *Polyhedron*, 2009, **28**, 1718; M. Nihei, M. Ui, N. Hoshino, H. Oshio, *Inorg. Chem.*, 2008, **47**, 6106; M. Nihei, M. Ui, M. Yokota, L.-Q. Han, A. Maeda, H. Kishida, H. Okamoto, H. Oshio, *Angew. Chem. Int. Ed.*, 2005, **44**, 6484; H. Oshio, M. Yamamoto, T. Ito, *Inorg. Chem.*, 2002, **41**, 5817; H. Oshio, H. Onodera, O. Tamada, H. Mizutani, T. Hikichi, T. Ito, *Chem. - Eur. J.*, 2000, **6**, 2523.
- 9 D.A. Safin, J.M. Frost and M. Murugesu, *Dalton Trans.*, 2015, **44**, 20287 and references herein.
- 10 A.A. Schilt, *J. Am. Chem. Soc.*, 1960, **82**, 3000.
- 11 J. Černák, M. Orendáč, I. Potočník, J. Chomič, A. Orendáčová, J. Skoršepa and A. Feher, *Coord. Chem. Rev.*, 2002, **224**, 51; L. Toma, R. Lescouëzec, J. Vaissermann, F.S. Delgado, C. Ruiz-Pérez, R. Carrasco, J. Cano, F. Lloret, M. Julve, *Chem. Eur. J.*, 2004, **10**, 6130; L. Toma, R. Lescouëzec, J. Vaissermann, P. Herson, V. Marvaud, F. Lloret, M. Julve, *New J. Chem.*, 2005, **29**, 210.
- 12 BVS calculation: for Fe(II), 2.036; for Fe(III), 2.292.
- 13 BVS calculation: for Mn(II), 2.174; for Mn(III), 2.005; for Mn(IV), 1.967.
- 14 R.R. Ruminski and J.L. Kiplinger, *Inorg. Chem.*, 1990, **29**, 4581; K.J. Brewer, W.R. Murphy and J.D. Petersen, *Inorg. Chem.*, 1987, **26**, 3376.
- 15 S. Ghumaan, S. Kar, S.M. Mobin, B. Harish, V.G. Puranik and G.K. Lahiri, *Inorg. Chem.*, 2006, **45**, 2413.
- 16 Electrode materials in rechargeable batteries: Y. Mizuno, M. Okubo, K. Kagesawa, D. Asakura, T. Kudo, H. Zhou, K. Oh-ishi, A. Okazawa and N. Kojima, *Inorg. Chem.*, 2012, **51**, 10311; D. Asakura, M. Okubo, Y. Mizuno, T. Kudo, H. Zhou, K. Ikeda, T. Mizokawa, A. Okazawa and N. Kojima, *J. Phys. Chem. C*, 2012, **116**, 8364;
- 17 Ion/proton conducting coordination materials: K. Ono, M. Ishizaki, K. Kanaizuka, T. Togashi, T. Yamada, H. Kitagawa and M. Kurihara, *Angew. Chem. Int. Ed.*, 2017, **56**, 5531; P. Higel, F. Villain, M. Verdaguer, E. Rivière and A. Bleuzen, *J. Am. Chem. Soc.*, 2014, **136**, 6231; K. Imoto, K. Nakagawa, H. Miyahara and S. Ohkoshi, *Cryst. Growth Des.*, 2013, **13**, 4673; S. Ohkoshi, K. Nakagawa, K. Tomono, K. Imoto, Y. Tsunobuchi and H. Tokoro, *J. Am. Chem. Soc.*, 2010, **132**, 6620.
- 18 Extra-field stimuli responsive materials: D. Aguilá, Y. Prado, E.S. Koumoussi, C. Mathonière and R. Clérac, *Chem. Soc. Rev.*, 2016, **45**, 203; H. Ohmagari, R. Ohtani, M. Nakaya, M. Ohba, M. Nakamura, L.F. Lindoy, O. Sato and S. Hayami, *Dalton Trans.*, 2016, **45**, 16784; H. Tokoro, K. Nakagawa, K. Imoto, F. Hakoe and S. Ohkoshi, *Chem. Mater.*, 2012, **24**, 1324; J.-D. Cafun, G. Champion, M.-A. Arrio, C. Cartier dit Moulin and A. Bleuzen, *J. Am. Chem. Soc.*, 2010, **132**, 11552; R. Gheorghie, M. Kalisz, R. Clérac, C. Mathonière, R. Herson, Y. Li, M. Seuleiman, R. Lescouëzec, F. Lliet and M. Julve, *Inorg. Chem.*, 2010, **49**, 11045; M. Ohba, W. Kaneko, S. Kitagawa, T. Maeda and M. Mito, *J. Am. Chem. Soc.*, 2008, **130**, 4475; C.-F. Chow, M.H.W. Lam and W.-Y. Wong, *Inorg. Chem.*, 2004, **43**, 8387.