

# Synthesis, crystal structure and metamagnetic properties of a two-dimensional honeycomb network based on ferricyanide and (3,10-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane)nickel(II) building blocks †

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The 2-D bimetallic complex  $[\text{NiL}]_3[\text{Fe}(\text{CN})_6]_2 \cdot 9\text{H}_2\text{O}$  (L represents 3,10-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane) has been prepared and its structure and magnetic properties studied. The structure consists of cyano-bridged neutral  $\text{Ni}_3\text{Fe}_2$  units. Each hexacyanoferrate(III) ion connects three nickel(II) ions using three *cis*  $\text{CN}^-$  groups and the remaining  $\text{CN}^-$  groups are terminal. The bridging cyanide ligands co-ordinate to the nickel ion in a *trans* fashion forming *trans*- $\text{NiL}(\text{N}\equiv\text{C})_2$  moieties. The nine water molecules are situated between the 2-D layer and hydrogen bonded to the terminal  $\text{CN}^-$  ligands. Magnetic studies show that the complex displays a metamagnetic behaviour originating from intralayer ferromagnetic coupling and interlayer antiferromagnetic interaction. A long-range magnetic ordering over the lattice at  $T_c = 5$  K is also observed.

## Introduction

Cyanide-bridged bimetallic assemblies of Prussian Blue type, derived from  $[\text{M}(\text{CN})_6]^{n-}$  ( $\text{M} = \text{Cr}^{\text{III}}, \text{Mn}^{\text{III}}, \text{Fe}^{\text{III}}$  or  $\text{V}^{\text{II}}$ ) and simple transition metal ions, have attracted much attention in the area of molecular-based magnets.<sup>1–12</sup> In order to clarify the magneto-structural correlation of cyano-bridged bimetallic systems, a wide variety of hybrid Prussian Blue complexes have been studied structurally and magnetically.<sup>13–27</sup> These complexes are based on the building blocks, *e.g.*  $\text{M}(\text{CN})_6^{3-}$  ( $\text{M} = \text{Fe}, \text{Cr}$  or  $\text{Mn}$ ) and co-ordinatively unsaturated transition metal complexes. For instance, as variations of  $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2 \cdot x\text{H}_2\text{O}$ , pentanuclear cluster  $[\text{Ni}(\text{bpm})_2]_3[\text{Fe}(\text{CN})_6]_2 \cdot 7\text{H}_2\text{O}$  (bpm = bis(1-pyrazolyl)methane),<sup>13</sup> 1-D chain complexes  $[\text{Ni}(\text{en})_2]_3[\text{Fe}(\text{CN})_6]_2 \cdot 2\text{H}_2\text{O}$ <sup>14</sup> and  $[\text{PPh}_4][\text{Ni}(\text{pn})][\text{Fe}(\text{CN})_6]$  (pn = 1,2-propanediamine),<sup>15</sup> 2-D layer complexes  $[\text{Ni}(\text{diamine})_2]_2[\text{Fe}(\text{CN})_6]_2\text{X}$  (diamine = 1,1-dimethylethylenediamine or pn,  $\text{X} = \text{ClO}_4^-, \text{NO}_3^-, \text{PhCH}_2\text{O}_2^-$  or  $\text{N}_3^-$ ; diamine = en or 1,3-propanediamine,  $\text{X} = \text{NO}_3^-$ )<sup>16,17</sup> and 3-D  $[\text{Ni}(\text{tren})]_3[\text{Fe}(\text{CN})_6]_2 \cdot 6\text{H}_2\text{O}$  (tren = tris(2-aminoethyl)amine)<sup>18</sup> have been synthesized by the reaction of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  with  $\text{NiN}_4^{2+}$  complexes that possess two available co-ordination sites. Magnetic investigations on these complexes show that they exhibit ferri-, ferro- or meta-magnetic behaviours dependent on the difference in the network structures.

In recent publications a diamagnetic tetraazamacrocyclic nickel(II) complex,  $[\text{Ni}(\text{cyclam})][\text{ClO}_4]_2$ , has been used to construct cyanide-bridged bimetallic compounds,  $[\text{Ni}(\text{cyclam})]_3[\text{Cr}(\text{CN})_6]_2 \cdot 20\text{H}_2\text{O}$ <sup>19</sup> and  $[\text{Ni}(\text{cyclam})]_3[\text{Fe}(\text{CN})_6]_2 \cdot 6\text{H}_2\text{O}$ .<sup>28</sup> We have adopted another diamagnetic macrocyclic nickel(II)

complex as a precursor to prepare a new  $\text{CN}^-$ -bridged nickel(II)-iron(III) compound,  $[\text{NiL}]_3[\text{Fe}(\text{CN})_6]_2 \cdot 9\text{H}_2\text{O}$  (**1** (L = 3,10-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane). Here, we report the synthesis, crystal structure and magnetic studies of the new 2-D cyano-bridged assembly with waved layers.

## Experimental

### Physical measurements

The elemental analyses of carbon, hydrogen and nitrogen were carried out with a model 240 Perkin-Elmer analyzer. The infrared spectroscopy on KBr pellets was performed on a Nicolet 5DX FT-IR spectrophotometer in the 4000–400  $\text{cm}^{-1}$  region. The ac magnetic susceptibility, magnetic susceptibilities, and field dependence of magnetization up to 7 T at 1.93 K were obtained using a Model MagLab System 2000 magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's Tables). Effective magnetic moments were calculated using the equation  $\mu_{\text{eff}} = (8\chi_m T)^{1/2}$ , where  $\chi_m$  is the molar magnetic susceptibility.

### Preparations

The precursor  $[\text{NiL}][\text{ClO}_4]_2$  was prepared by the literature method;<sup>29</sup>  $\text{K}_3[\text{Fe}(\text{CN})_6]$  was an analytical reagent used without purification.

**[NiL]<sub>3</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub>·9H<sub>2</sub>O 1.** To an aqueous solution of  $\text{NiL}(\text{ClO}_4)_2$  (0.3 mmol, 146.4 mg) in 20  $\text{cm}^3$  of water was added  $\text{K}_3\text{Fe}(\text{CN})_6$  (0.5 mmol, 165 mg) in water (10  $\text{cm}^3$ ) at room temperature. Brown microcrystals precipitated from the resulting brown solution in 10 min. They were collected by suction

† Non-SI unit employed:  $\mu_B \approx 9.27 \times 10^{-24}$  J T<sup>-1</sup>.

filtration, thoroughly washed with water and dried *in vacuo* over  $P_2O_5$ . Yield 130.8 mg, 90% (Found: C, 34.87; H, 6.48; N, 28.95.  $C_{42}H_{96}Fe_2N_{30}Ni_3O_9$  requires C, 34.71; H, 6.66; N, 28.92%). IR:  $\nu_{max}/cm^{-1}$  2150, 2130 and 2110 ( $C\equiv N$ ).

Well shaped dark brown crystals suitable for structure analysis were grown at room temperature by slow diffusion of an orange acetonitrile solution of  $[NiL][ClO_4]_2$  and a yellow aqueous solution of  $K_3[Fe(CN)_6]$  in an H tube.

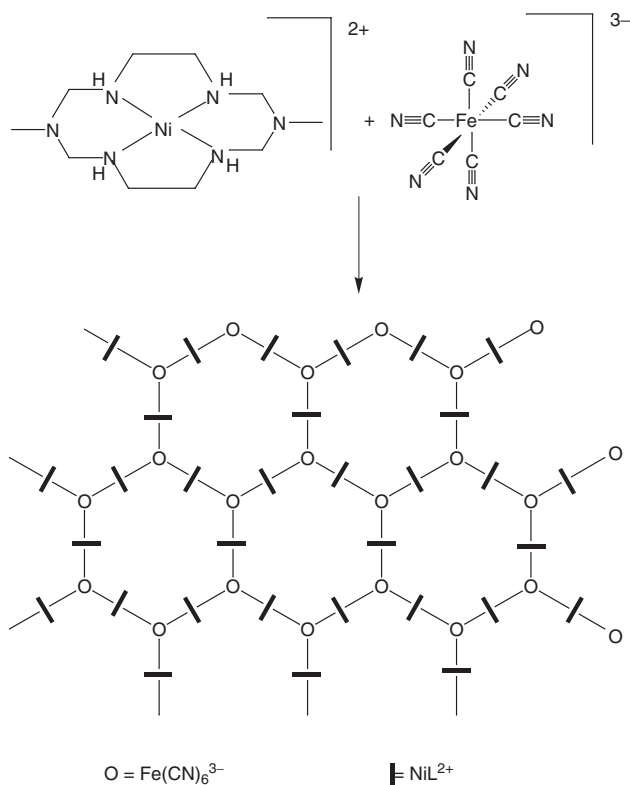
### Crystal structure determination of complex 1

**Crystal data.**  $C_{42}H_{96}Fe_2N_{30}Ni_3O_9$ ,  $M = 1453.32$ , trigonal,  $a = b = 14.809(2)$ ,  $c = 18.390(3)$  Å,  $\alpha = \beta = 90$ ,  $\gamma = 120^\circ$ ,  $U = 3492.7(9)$  Å<sup>3</sup>,  $T = 293(2)$  K, space group  $P3c1$ ,  $Z = 2$ ,  $\mu(Mo-K\alpha) = 1.266$  mm<sup>-1</sup>, 6176 reflections measured ( $1.59 \leq \theta \leq 27.51^\circ$ ) and 2688 considered unique ( $R_{int} = 0.0466$ ). The final  $R_w$  was 0.109, with conventional  $R_F$  0.0485 for 133 parameters. CCDC reference number 186/1489.

See <http://www.rsc.org/suppdata/dt/1999/2477/> for crystallographic files in .cif format.

### Results and discussion

The low-spin four-co-ordinate nickel(II) macrocyclic  $NiL^{2+}$  can accept two donor atoms giving rise to high-spin six-co-ordinate  $NiLX_2$  species. The reaction of  $[NiL][ClO_4]_2$  with  $K_3[Fe(CN)_6]$  in aqueous solution yields a cyanide-bridged 2-D honeycomb-like complex **1**, as shown in Scheme 1.



Scheme 1

The IR spectrum of the complex shows three sharp bands at 2150, 2130 and 2110  $cm^{-1}$ , which are attributed to  $C\equiv N$  stretching modes. The shift of  $\nu(C\equiv N)$  to higher wavenumber compared with that of  $K_3[Fe(CN)_6]$  (2119  $cm^{-1}$ ) suggests a lowered symmetry about the  $Fe(CN)_6^{3-}$  entity and the formation of  $CN^-$  bridges, as observed for other cyano-bridged systems.

Complex **1** is stable in air and insoluble in most inorganic and organic solvents.

Table 1 Selected bond lengths (Å) and angles ( $^\circ$ ) for complex 1

Fe–C(1)	1.916(10)	Fe–C(2)	1.930(10)
C(1)–N(1)	1.152(12)	C(2)–N(2)	1.132(12)
Ni–N(1)	2.088(9)	Ni–N(3)	2.094(9)
Ni–N(4)	2.065(9)		
N(1)–C(1)–Fe	177.2(9)	N(2)–C(2)–Fe	175.1(8)
Ni–N(1)–C(1)	164.6(8)		

Table 2 Intermolecular contacts (Å) involving H atoms

OW(1)⋯N(2 <sup>i</sup> )	2.993	OW(2)⋯N(2)	3.099
OW(1)⋯OW(1 <sup>ii</sup> )	2.942	OW(2)⋯N(2 <sup>iii</sup> )	3.099
OW(1)⋯OW(1 <sup>iv</sup> )	2.959	OW(2)⋯N(4 <sup>v</sup> )	3.180
OW(1)⋯N(4 <sup>vi</sup> )	3.180		

Symmetry transformations: i  $-x + y, +y, 0.5 + z$ ; ii  $y, x, 0.5 - z$ ; iii  $y, +x, -0.5 - z$ ; iv  $-x, -x + y, 0.5 - z$ ; v  $1 - y, x - y + 1, +z$ ; vi  $x - y + 1, x + 1, -0.5 - z$ .

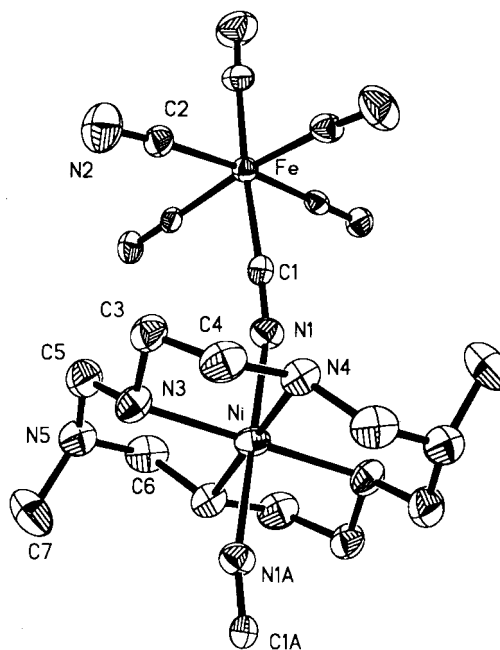
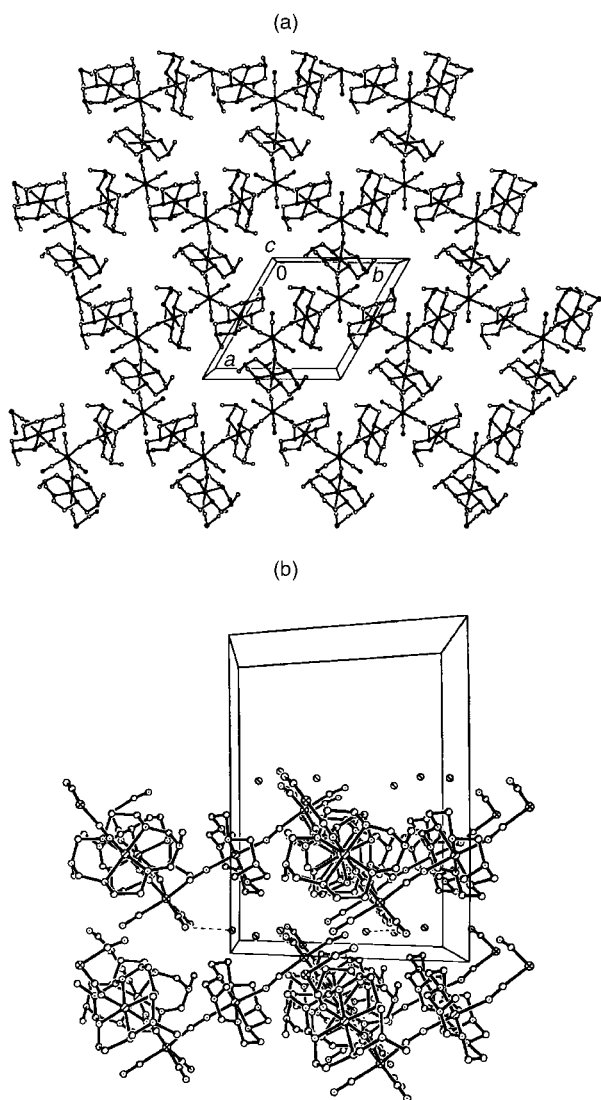


Fig. 1 An ORTEP<sup>30</sup> drawing of complex 1 showing the unique atoms.

### Crystal structure of complex 1

The asymmetric unit is shown in Fig. 1. The projections of the molecular entity in the lattice along and perpendicular to the  $c$  axis are presented in Fig. 2(a) and (b). Selected bond distances and angles are listed in Table 1 and intermolecular contacts involving H atoms in Table 2.

The structure consists of a neutral stair-shaped layer network with the stoichiometry  $[NiL]_3[Fe(CN)_6]_2$  and a hexagonal pattern. Each  $Fe(CN)_6^{3-}$  unit uses three  $C_3$  rotational symmetry related *cis*  $C\equiv N$  groups to connect with three  $[NiL]^{2+}$  giving rise to  $Fe-C\equiv N-Ni$  linkages, whereas the three remaining symmetry related *cis*  $CN^-$  groups are monodentate. The adjacent  $Fe\cdots Ni$  distance is 5.102 Å. Each  $NiL$  unit is linked to two hexacyanoferrate(III) ions in *trans* positions. Four secondary amine nitrogen atoms of the macrocycle co-ordinate to the nickel center with an average  $Ni-N$  distance of 2.080(9) Å. Both six-membered chelate rings adopt a chair conformation and the methyl groups on N5 are axial. The five-membered rings adopt a *gauche* conformation. Two nitrogen atoms of the bridging  $C\equiv N$  ligands axially co-ordinate to the  $Ni^{II}$  with  $Ni-N$  contacts of 2.088(9) Å. The  $Ni-N\equiv C$  bond angle is 164.6(8) $^\circ$ . The average  $Fe-C$  and  $C\equiv N$  distances are 1.923(10) and 1.142(12) Å, and the  $Fe-C\equiv N$  bonds do not deviate significantly from linearity [177.2(9) and 175.1(8) $^\circ$ ].

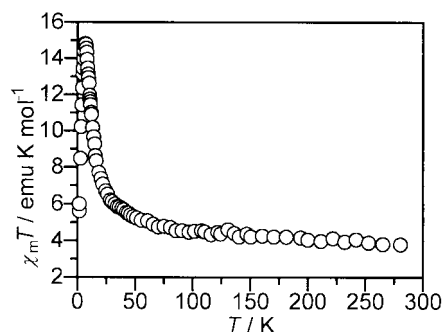


**Fig. 2** (a) Projection along the  $c$  axis, showing the polymeric layer including  $\text{Fe}_6\text{Ni}_6$  hexagons. (b) Projection perpendicular to the  $c$  axis, showing stacking of the waved layers.

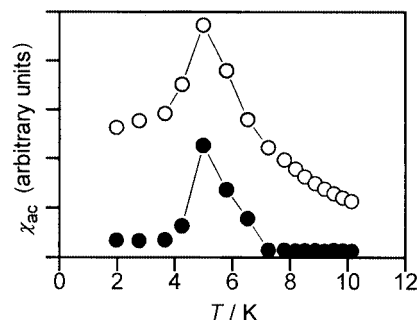
The particular local molecular disposition leads to a honeycomb-like structure (Fig. 2a). The repeating hexagonal-like units adopt a chair conformation giving rise to an infinite waved layer (Fig. 2b), which is similar to that of  $[\text{Ni}(\text{cyclam})]_3[\text{Cr}(\text{CN})_6]_2 \cdot 20\text{H}_2\text{O}$ .<sup>19</sup> In the crystal the layers align along the  $c$  axis with a separation of *ca.* 9.19 Å, and the nearest interlayer metal–metal distance is 7.706 Å for  $\text{Ni} \cdots \text{Fe}$ . The water molecules are positioned between the sheets and linked to the terminal CN ligands of  $\text{Fe}(\text{CN})_6^{3-}$  via hydrogen bonding (Table 2).

### Magnetic properties

The magnetic susceptibilities of complex **1** have been measured in the temperature range 1.7–280 K. A plot of  $\chi_m T$  vs.  $T$  is shown in Fig. 3, where  $\chi_m$  is the magnetic susceptibility per  $\text{Ni}_3\text{Fe}_2$  unit. The  $\chi_m T$  value at room temperature is *ca.* 3.8 emu K mol<sup>-1</sup> ( $5.5 \mu_B$ ) which increases smoothly down to *ca.* 28.6 K and then sharply reaches a maximum value of 14.8 emu K mol<sup>-1</sup> ( $10.9 \mu_B$ ) at 6.85 K, which is much larger than the spin-only value of 10.0 emu K mol<sup>-1</sup> ( $8.9 \mu_B$ ) for  $S_T = 4$  resulting from the ferromagnetic coupling of three nickel(II) ions ( $S = 1$ ,  $g = 2.0$ ) and two low-spin iron(III) ions ( $S = 1/2$ ,  $g = 2.0$ ), strongly suggestive of the occurrence of magnetic ordering. Below 6.85 K  $\chi_m T$  decreases rapidly, which indicates the presence of interlayer antiferromagnetic interaction. The magnetic susceptibility above 6 K obeys the Curie–Weiss law with a



**Fig. 3** Temperature dependence of  $\chi_m T$  for complex **1**.



**Fig. 4** Real,  $\chi'$  (○), and imaginary,  $\chi''$  (●), ac magnetic susceptibility as a function of temperature taken at 133 Hz for complex **1**.

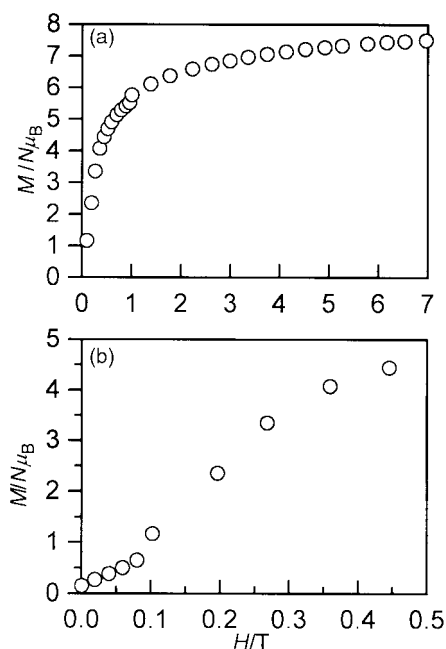
positive Weiss constant  $\theta = +9.0$  K, which also indicates the presence of ferromagnetic coupling within the  $\text{Ni}_3\text{Fe}_2$  sheet of **1**. The ferromagnetic interaction between the iron(III) and nickel(II) ions is due to the strict orthogonality of the magnetic orbitals of low-spin  $\text{Fe}^{\text{III}}$  ( $t_{2g}^5$ ) and  $\text{Ni}^{\text{II}}$  ( $e_g^2$ ).<sup>31</sup>

The onset of a long-range magnetic phase transition is further confirmed by the temperature dependence of the ac molar magnetic susceptibility displayed in Fig. 4. The real part of the zero field ac magnetic susceptibility,  $\chi'(T)$ , has a maximum at *ca.* 5 K for a frequency of 133 Hz, suggesting that  $T_c$  of complex **1** is about 5 K.<sup>32</sup>

The field dependence of the magnetization (0–7 T) measured at 1.93 K is shown in Fig. 5(a) in the form of  $M/N\mu_B$  (per  $\text{Ni}_3\text{Fe}_2$  unit) vs.  $H$ , where  $M$ ,  $N$ ,  $\mu_B$  and  $H$  are the magnetization, Avogadro's number, the electron Bohr magneton and applied magnetic field, respectively. The magnetization reaches a value of  $7.5 N\mu_B$  at 7 T which is close to the expected  $S = 4$  value of  $8 N\mu_B$  for the  $\text{Ni}_3\text{Fe}_2$  system, indicating the presence of ferromagnetic interaction between the adjacent  $\text{Fe}^{\text{III}}$  and  $\text{Ni}^{\text{II}}$ .

The magnetization was elaborately measured as a function of the external magnetic field (0–0.5 T) at 1.93 K (Fig. 5b). A noticeable sigmoidal behaviour is observed which suggests a metamagnet: the magnetization first increases slowly with the increased field and then sharply showing a spin-flipping from antiferromagnetic to ferromagnetic arrangement between the layers. In addition, the extremely small zero-field susceptibility value also suggests a metamagnet. Considering the small interlayer separation (9.19 Å), interlayer antiferromagnetic interaction could operate, which could be regarded as the origin of the metamagnetic behaviour.<sup>24–27</sup> This result agrees well with the conclusion drawn by Ohba *et al.*,<sup>16</sup> *i.e.* a small interlayer separation (<10 Å) provides metamagnets owing to interlayer antiferromagnetic interaction. The critical field (the lowest field which is used to reverse the interlayer antiferromagnetic interaction) is *ca.* 0.1 T at 1.93 K.

In conclusion, the present example is a new demonstration of the versatility of organic ligands in building molecular-based magnets. The magnetic measurements show that the present complex exhibits an intralayer ferromagnetic interaction and a long-range magnetic ordering over the lattice at *ca.* 5 K. The intralayer ferromagnetic interaction and the interlayer anti-



**Fig. 5** Magnetization at 1.93 K as a function of the applied magnetic field (a) up to 7 T and (b) at 0–0.5 T.

ferromagnetic interaction give rise to a metamagnetic behaviour. The synthesis of similar complexes for comparison is in progress in our laboratory.

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