There has been great interest in the preparation of molecule-based magnet in recent years [1–6]. Hexacyanometalate ions, acting as good building units, have been successfully utilized to obtain a large number of one-, two-, and three-dimensional cyanide-bridged assemblies with high magnetic ordering temperature and interesting architectures [7–11]. A few high-temperature molecular magnets based on cyanide building blocks were reported by Girolami and Verdaguer [12–15] et al. with $T_c$ at 230, 190, 240 and 376 K. These works show that transition metal cyanides are good candidates for the synthesis of molecule-based magnetic materials, but there are extreme difficulties in growing crystals of these cyanide-containing complexes. On the other hand, a more creative strategy for design of cyano-bridged magnetic coordination polymers is utilizing metal complexes containing complementary macrocycle ligands instead of simple metal ions [16–20]. The macrocycle ligands not only play an important role in stabilizing structures but also impose a specific topology through their coordination binding modes and geometries. However, to our knowledge, there are still a few complex-based magnets containing macrocycle ligands being explored to date. It is important and interesting to know whether metal complexes with macrocycle ligands can be utilized to construct complex-based magnets. We have now utilized that a copper(II) complex containing a macrocycle ligand, $[\text{CuLCl}]\text{ClO}_4$ as one of starting materials, and obtained a new dimetallic cyano-bridged assembly $[\text{CuL(H}_2\text{O})_2][[\text{CuL}][\text{Fe(CN)}_6]\cdot 2\text{H}_2\text{O}]$ (1) showing the one-dimensional chain structure.

**EXPERIMENTAL**

**Materials and methods.** All reagents are of analytical grade and are used without further purification. Distilled water was used for all procedures. Elemental analyses for C, H, and N are carried out on a Perkin–Elmer elemental analyzer (model 240). The infrared spectrum is obtained on a Perkin–Elmer 983G infrared spectroscopy in the 4000–400 cm$^{-1}$ regions, using KBr pellets. Variable temperature magnetic susceptibilities were measured on a SQUID magnetometer from 2.0 K to 300 K in a magnetic field of 1000 Oe, and the diamagnetic corrections were applied by using Pascal’s constants.

**Preparation of** $[\text{CuL(H}_2\text{O})_2][[\text{CuL}][\text{Fe(CN)}_6]\cdot 2\text{H}_2\text{O}]$ (1). The procedure for the synthesis of the $[\text{Cu(L)}\text{Cl}]\text{ClO}_4$ has been reported previously [21]. The violet block microcrystals of the complex 1 can be obtained by the same procedure as described previously in the literature [22], but using $[\text{Cu(L)}\text{Cl}]\text{ClO}_4$ (2 mmol, 906.0 mg) instead of $[\text{Cu(teta)}][\text{ClO}_4]_2$ (teta = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane). We were tried widely, but single crystals suitable for X-ray determination were not obtained in studied period. $C_{30}H_{60}N_{18}O_{10}Cu_2Fe$ (983.9): Anal. Calcd.: C, 36.6; H, 6.1; N, 25.6%. Found: C, 36.8; H, 5.4; N, 25.6%. $IR$ (KBr, cm$^{-1}$): 2140; 2100 v(C≡N).
[Cu(L)Cl]$^+$ cation, which is a weak ligand as Lewis base for coordinating the copper(II) ion, was permuted by nitrogen atom of the [Fe(CN)$_6$]$^{3-}$ anion during this self-assembly process. The loss of Cl$^-$ anion from precursor complexes is quite unusual [23]. The IR spectrum of the complex I exhibits two typical C≡N bands at 2140, 2100 cm$^{-1}$; the shift of ν(C≡N) to higher wavenumber compared with that of K$_3$[Fe(CN)$_6$] (2122 cm$^{-1}$) is in agreement with the formation of two types of νC≡N bridges [24]. A broad, intense stretching vibration of the ClO$_4^-$ anion at 1100 cm$^{-1}$ is observed in the IR spectra of the complex I, which is typical for a non-coordinated perchlorate ion [25]. A broad peak at 3430 cm$^{-1}$ owing to ν(O−H) vibration indicates that the complex contains crystal water molecules, and a band at 2910 cm$^{-1}$ can attributed to ν(N−H) vibration of Cu$^{2+}$ macrocycle ligand. In addition, elemental analyses have indicated that the reaction of Cu$^{2+}$ macrocycle ligand with [Fe(CN)$_6$]$^{3-}$ anion yielded the cyano-bridged Cu$^{II}$− Fe$^{III}$ bimetallic complex. A similar complex, [Cu(teta)(H$_2$O)$_2$][Cu(teta)Fe(CN)$_6$]ClO$_4$·2H$_2$O (teta = 5, 7, 7, 12, 14, 14-hexamethyl-1, 4, 8, 11-tetraazacyclotetradecane) has also been synthesized as described previously in the literature [22] and structural characterized as well [22].

Based on the composition of this complex, IR spectrum, elemental analyses, and the crystal structure of the type complex reported in the previously [22], the complex I is proposed to possess the one-dimensional chain structure, as shown in Fig. 1.

**Magnetic Properties.** The temperature dependence of the magnetic susceptibility of the complex I was measured in the 2 to 300 K range. The magnetic behavior is shown in Fig. 2 in the forms of plots of χ$\text{M}$ and χ$\text{M}T$ versus $T$. As shown in Fig. 2, the χ$\text{M}T$ value was 0.494 cm$^3$ mol$^{-1}$ K at room temperature, which was much higher than the expected spin-only value (0.375 cm$^3$ mol$^{-1}$ K per Cu$^{II}$ ion) for the Cu(II) ($S_{\text{Cu}}$ = 1/2) chain system ($g$ = 2.0). On lowering the temperature, the χ$\text{M}T$ values decrease faintly until 10 K, and then decreases sharply below 10 K, reaching a minimum value of 0.339 cm$^3$ mol$^{-1}$ K at 2.0 K, implying the existence of an antiferromagnetic interaction between the paramagnetic ions. The decrease of χ$\text{M}T$ below 10 K probably results from a saturation of the χ$\text{M}$ value. A plot of 1/χ$\text{M}$ versus $T$ in the temperature range 300 to 30 K obeys the Curie-Weiss law with $\theta$ = −6.14 K and $C$ = 0.51 cm$^3$ K mol$^{-1}$ (see Fig. 3). The negative Weiss constant further confirms the presence of an antiferromagnetic exchange interaction between adjacent Cu(II) and Fe(III) ions.

In order to understand quantitatively the magnitudes of spin-exchange interaction, if the spin-orbital couple of the iron(III) ion is ignored, the susceptibility data can be analyzed by a linear chain exchange model [27], $\hat{H} = -2J\sum_{i=1}^{n-1} \hat{S}_i \cdot \hat{S}_{i+1}$. Expression of the magnetic susceptibility for a chain Cu(II) ($S = 1/2$) system was:

$$\chi_{\text{chain}} = \frac{Ng^2\beta^2}{kT} \left[ \frac{A + BX + CX^2}{1 + DX + EX^2 + FX^2} \right] + N_{\alpha},$$

where $X = 2J/kT$, $A = 0.25$, $B = 0.14995$, $C = 0.30094$, $D = 1.9862$, $E = 0.68854$ and $F = 6.0626$. $N$ is the Avogadro constant, $g$ is the $g$ factor, $k$ is the Boltzmann constant, $J$ is the exchange coupling constant and $N_{\alpha}$ is the temperature independent paramagnetism (60 × 10$^{-6}$ cm$^3$ mol$^{-1}$). The magnetic parameters obtained by the simulation of the experimental data using the above expression were $J = -0.239$ cm$^{-1}$, $g = 2.26$ and $R = 7.53 \times 10^{-4}$ [R = Σ($\chi_{\text{obs}} - \chi_{\text{calc}})^2/\Sigma(\chi_{\text{obs}}^2)$]. The results indicate a very weak antiferromagnetic interaction in the system.