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Synthesis, Crystal Structure and Magnetic Behavior of a One-Dimensional Chain Complex: $\{[Cu(N\text{-}m\text{-}en)_2Fe(CN)_5(NO)]\cdot H_2O\}_n$

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For a long time much research interest has been focused on the magnetic interaction of multinuclear complexes, for it may benefit the understanding of the life mechanism and the preparation of molecular-based magnets. Although the theory of Kahn's magnetic interaction enable us to forecast the magnetic behaviors for most complexes [1], there are still many problems to explore in this area. Prussian blue analogues are very useful bridging ligands and many complexes that contain such ligand exhibit special magnetic behaviors [2–9]. The complexes with nitroferricyanide anion as bridging ligand generally show the property of antiferromagnetic interaction [10–12], whereas the title complex exhibits the ferromagnetic interaction at 20~300 K range. Obviously, the magnetic behavior of the title complex is not explained by Kahn's theory. Here we report the synthesis, crystal structure and its magnetic behavior.

The one-dimensional complex $\{[Cu(N\text{-}m\text{-}en)_2Fe(CN)_5(NO)]\cdot H_2O\}_n$ was prepared in the following way: N-methylethylenediamine (0.0842 g, 1.14×10^{-3} mol) and $CuCl_2\cdot2H_2O$ (0.0968 g, 5.68×10^{-4} mol) were dissolved in H_2O (5 cm^3), and then 5 cm^3 H_2O solution of $Na_2Fe(CN)_5(NO)\cdot2H_2O$ (0.1692 g, 5.68×10^{-4} mol) was added into the previous solution and was stirred for a few minutes. The purple single crystals were obtained after the solution was kept at room temperature for a week. Elemental analysis confirmed the composition. The strong IR absorption peaks of CN group and NO group for the complex appear at 2140 cm^{-1} and 1938 cm^{-1}, respectively, and the peaks at 1619 cm^{-1}, 1589 cm^{-1}, 3439 cm^{-1}, 3323 cm^{-1} and 3242 cm^{-1} may be assigned to the vibrations of NH and NH_2 groups. Determination of the crystal structure at 293(2) K was carried out on an X-ray diffractometer, Model Bruker Smart-1000 CCD using graphite-monochromatic MoKα radiation ($\lambda = 0.71073$ Å) with ω scan mode. A total of 5191 reflections were collected in the range $2.67 \le \theta \le 26.42°$, of which 3615 reflections were independent (R(int) = 0.021) and 3051 reflections with $I > 2\sigma(I)$ were considered to be observed and used in the succeeding refinement. The programs of

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structure solution and refinement are SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997), respectively. The semi-empirical absorption correction was used on equivalent reflections. The selected bond lengths and angles are listed in Table 1. The variable-temperature magnetic susceptibility measurements were performed using a single crystal sample in the 4–300 K range with a SQUID magnetometer.

Table 1. Selected bond lengths (Å) and the associated angles (°).

Fe(1)–N(5)	1.659(3)	Fe(1)–C(3)	1.933(3)	Fe(1)–C(1)	1.939(3)
Fe(1)–C(5)	1.939(3)	Fe(1)–C(2)	1.941(3)	Fe(1)–C(4)	1.948(3)
Cu(1)–N(7)	2.029(3)	Cu(1)–N(8)	2.047(3)	Cu(1)–N(6)	2.483
Cu(2)–N(9)	2.007(3)	Cu(2)–N(10)	2.046(3)	Cu(2)–N(2)	2.601

N(5)–Fe(1)–C(3)	91.87(13)	N(5)–Fe(1)–C(1)	95.95(12)
C(3)–Fe(1)–C(1)	90.91(13)	N(5)–Fe(1)–C(5)	97.41(12)
C(3)–Fe(1)–C(5)	170.43(13)	C(1)–Fe(1)–C(5)	90.44(12)
N(5)–Fe(1)–C(2)	175.34(12)	C(3)–Fe(1)–C(2)	83.49(13)
C(1)–Fe(1)–C(2)	84.59(13)	C(5)–Fe(1)–C(2)	87.21(13)
N(5)–Fe(1)–C(4)	94.51(12)	C(3)–Fe(1)–C(4)	90.13(13)
C(1)–Fe(1)–C(4)	169.45(12)	C(5)–Fe(1)–C(4)	86.84(12)
C(2)–Fe(1)–C(4)	85.10(13)	N(7)–Cu(1)–N(7A)	180.0
N(7)–Cu(1)–N(8)	84.05(11)	N(7)–Cu(1)–N(8A)	95.95(11)
N(8)–Cu(1)–N(8A)	180.0	N(6A)–Cu(1)–N(6)	180.0
N(6)–Cu(1)–N(7)	90.67	N(6)–Cu(1)–N(8)	91.53
Cu(1)–N(6)–C(5)	140.76	N(9A)–Cu(2)–N(9)	180.0
N(9A)–Cu(2)–N(10)	84.47(12)	N(9)–Cu(2)–N(10)	95.53(12)
N(10)–Cu(2)–N(10A)	180.0	N(2A)–Cu(2)–N(2)	180.0
N(2)–Cu(2)–N(9)	90.25	N(2)–Cu(2)–N(10)	91.05
N(2)–Cu(2)–N(9)	88.95	Cu(2)–N(2)–C(2)	127.39

The crystal is triclinic, space group P$\bar{1}$ with $a = 7.6429(10)$ Å, $b = 9.4444(12)$ Å, $c = 13.9990(18)$ Å, $\alpha = 85.602(2)°$, $\beta = 81.544(2)°$, $\gamma = 71.681(2)°$, $F(000) = 458$, $\mu(\mathrm{Mo}K\alpha) = 1.913\ \mathrm{mm}^{-1}$, $R1 = 0.0352$ and $wR2 = 0.0862$ for 3051 observed reflections ($I > 2\sigma(I)$). The completeness to $\theta = 26.42°$ is 92.5% and the goodness of fit on F^2 is 0.979. The maximum peak in the final difference Fourier map is 0.920 and the minimum one –0.607 e · Å^{-3}.

Fig. 1 shows the coordination diagram of the complex with its atom numbering scheme. It indicates that Cu(1) atom is coordinated by six nitrogen atoms, which come from two N-methylethylenediamine molecules and two cyanides of two nitroferricyanide anions. The data of bond lengths and the associated angles in Table 1 indicate that Cu(1) atom is located in a typical Jahn-Teller distortion octahedral environment. Except the minor difference in the bond lengths and the associate angles the coordination condition of Cu(2) is almost as that of Cu(1) atom. Through the coordination of two nitrogen atoms of each nitroferricyanide anion to two copper(II) ions, the one-dimensional chain is formed, which is shown in Fig. 2. Compared with the complex $\{[Cu(en)_2Fe(CN)_5(NO)]\cdot H_2O\}_n$ the two complexes are almost identical in the coordination mode and the crystal structures, except the cell of the present complex is larger than that of complex $\{[Cu(en)_2Fe(CN)_5(NO)]\cdot H_2O\}_n$ [12] for the volume of N-methylethylenediamine is larger than that of ethylenediamine. The CCDC deposition number of this crystal is 161869. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336-033; or deposit@ccdc.cam.ac.uk).

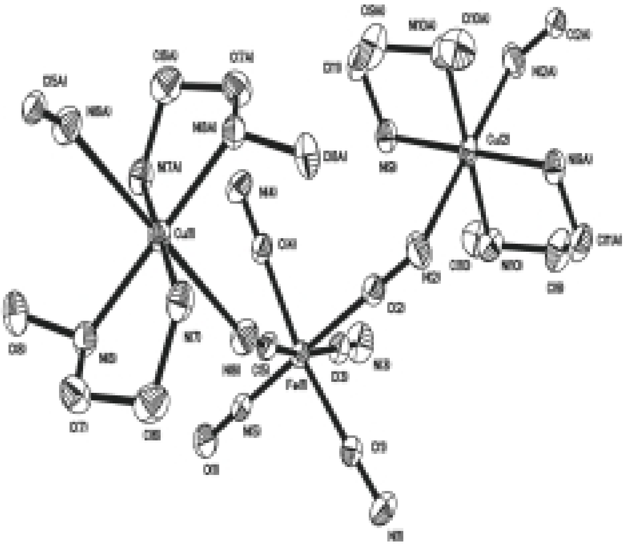

Figure 1. A diagram of the title complex coordination with atom numbering scheme.

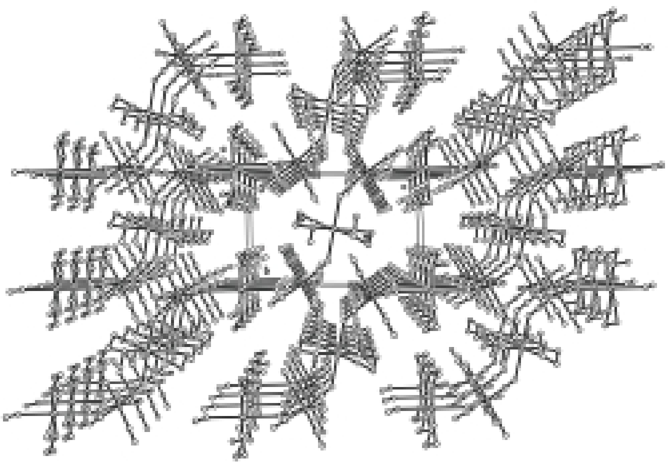

Figure 2. Packing plot of the complex viewed along the a-direction of the unit cell.

Fig. 3 shows the plot of $\chi_M T$ *vs*. *T* for the complex, where χ_M is the molar magnetic susceptibility of $[Cu(N\text{-}m\text{-}en)_2Fe(CN)_5(NO)] \cdot H_2O$ per CuFe unit. The values of $\chi_M T$ gradually increase from 0.3277 $cm^3 \cdot K \cdot mol^{-1}$ at 300.0 K to 0.4031 $cm^3 \cdot K \cdot mol^{-1}$ at 20.0 K and then decrease from 0.4030 $cm^3 \cdot K \cdot mol^{-1}$ at 18.0 K to 0.3804 $cm^3 \cdot K \cdot mol^{-1}$ at 4.9 K. The Weiss constants based on the equation $\chi_M = C/(T - \theta)$ are positive ($\theta = 8.8522$ K) and negative ($\theta = -0.3435$ K) in the ranges of 20 K to 300 K and 4.9 K to 18 K, respectively. The values indicate that there exists the ferromagnetic interaction above 18 K and the antiferromagnetic interaction below 20 K between the Cu(II) ions, which are bridged by the diamagnetic $Fe(CN)_5(NO)^-$ anion, and the magnetic interaction is very weak. The magnetic behavior of this complex is similar to that of 2-D complex $[Ni(tu)_2]_2[Co(CN)_6]NO_3 \cdot 2H_2O$ [13], which suggests that the origin of the ferromagnetic interaction arises from a σ-superexchange. The magnetic interactions of the complexes $[Ni(en)_2]_4[Fe(CN)_5(NO)] \cdot 3H_2O$, $[Mn(3\text{-}MeOsalen)(H_2O)]_2[Fe(CN)_5(NO)]$, $[Mn(5\text{-}Brsalen)]_2[Fe(CN)_5(NO)]$ [10] and $[Cu(oxpn)Fe(CN)_5(NO)]$ [11] are antiferromagnetic, whereas the present complex exhibits the ferromagnetic interaction. In these complexes the bridging ligand is identical, namely, the diamagnetic $Fe(CN)_5(NO)^-$ anion, and especially the composition and the structure of the complex $\{Cu(en)_2Fe(CN)_5(NO)\}_n$ [12] are close to the present complex, but the magnetic interaction is different. Obviously, in some cases the minor change in structure may affect the mechanism of magnetic interaction. Not much is known in this area at present.

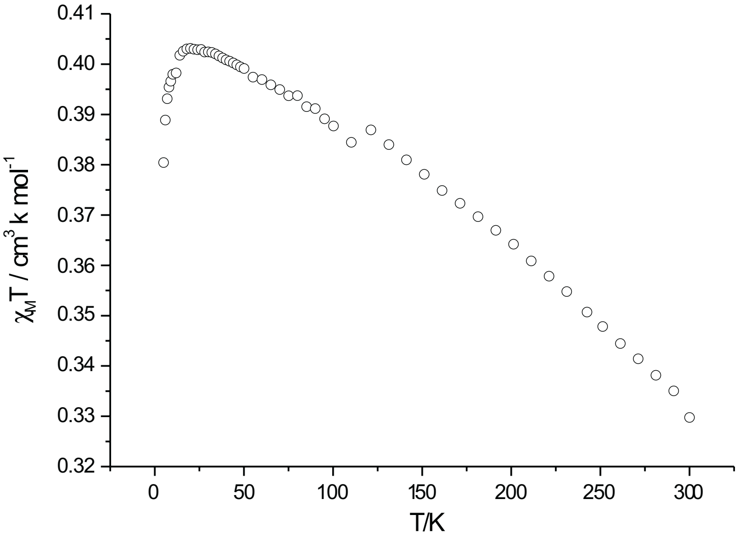

Figure 3. The relationship of $\chi_M T$ *versus T*.

Acknowledgments

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