



NOTE

Synthesis of a Bridged Tetraaza Macrocycle Cu(II) Complex and Its Molecular Magnetic Properties

JIAN-HONG BI^{1,*}, WEN-TAO BI² and NAI-LIANG HU³

¹Department of Chemistry and Chemical Engineering, Hefei Normal University, Hefei, P.R. China

²Hefei Training and Analysis Center, Institute of Petroleum Exploration and Development, SINOPEC, Hefei 230022, P.R. China

³School of Chemistry and Chemical Engineering, Anhui University, Hefei 230039, P.R. China

*Corresponding author: E-mail: bi010101@126.com

(Received: 31 May 2011;

Accepted: 24 October 2011)

AJC-10568

A novel self-assembled tetraaza macrocycle Cu(II) complex: $[(\text{CuL})_2\text{Fe}(\text{SCN})_4](\text{ClO}_4)_2$ ($\text{L} = 5,5,7,12,12,14$ -hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) has been synthesized and characterized by IR spectra and elemental analysis. Its molecular magnetic properties investigation shows that weak antiferromagnetic interactions are mediated between the tetraaza macrocycle Cu(II) ions through the $[\text{Fe}(\text{SCN})_4]^{2-}$ bridged in the complex.

Key Words: Copper(II) complex, Tetraaza macrocycle, Self-assemble, Magnetic property.

The molecular-based magnetic materials as a new material, because of its small size, low power consumption and other advantages, can be developed rapidly in recent years¹⁻³. Molecular-based magnetic materials can be used as the magnetic quantum device memory or building blocks. Multinuclear assembly of metal ions has attracted special attention. This study link up directly strategic of designing the new system with excellent physical and chemical properties^{4,6}. Here a novel self-assembled tetraaza macrocycle Cu(II) complex: $[(\text{CuL})_2\text{Fe}(\text{SCN})_4](\text{ClO}_4)_2$ ($\text{L} = 5,5,7,12,12,14$ -hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) has been synthesized and characterized and its molecular magnetic properties are investigated.

All the reagents were of AR grade and used without further purification. $\text{CuL}(\text{ClO}_4)_2$ ($\text{L} = 5,5,7,12,12,14$ -hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) was synthesized according to the literature⁷. IR spectra were recorded on a Nexus-870 spectrophotometer. Elemental analysis were performed on a Elementar Vario ELZ(III) analyzer. Variable temperature magnetic data (5-300 K) were collected with Quantum Design MPMS XL5 Squid magnetometer.

Synthesis of the $[(\text{CuL})_2\text{Fe}(\text{SCN})_4](\text{ClO}_4)_2$: The mixture of 25 mL H_2O solution of 40 mmol KSCN and 10 mmol FeSO_4 was added to 25 mL CH_3CN solution of 20 mmol $\text{CuL}(\text{ClO}_4)_2$, then refluxed for 1 h and standing at room temperature. The blue-black powder solids was obtained separately. Yield 43 %. IR spectrum (KBr, ν_{max} , cm^{-1}): 3422, 3220, 2927, 2260, 1662, 1090, 622. Elemental analysis (%): calcd. (found); C,

46.19 (46.33), H, 5.17 (5.08); N, 13.46(13.65). The magnetic susceptibility data on the complex were collected over the temperature range 5~300 K at 0.1 T.

Magnetic properties: Fig. 1 shows the plots of χ_m versus T and χ_m^{-1} versus T for $[(\text{CuL})_2\text{Fe}(\text{SCN})_4](\text{ClO}_4)_2$. When the temperature was decreased from 300 to 5 K, the χ_m values increased gradually from 0.014 to 0.68 cm^3/mol . This indicates that the χ_m of $[(\text{CuL})_2\text{Fe}(\text{SCN})_4](\text{ClO}_4)_2$ is accord with the Curie-Weiss law in wide temperature range. With the temperature decreasing, the χ_m values increased continuously and got biggest value at 10 K. This shows that there are intramolecular antiferromagnetic coupling. From 5.0 to 300 K, the magnetic data can be fitted to the Curie-Weiss law with C =

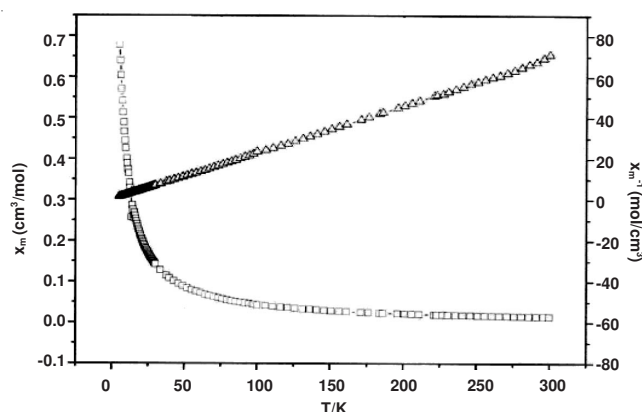


Fig. 1. χ_m -T and $1/\chi_m$ -T curves of $[(\text{CuL})_2\text{Fe}(\text{SCN})_4](\text{ClO}_4)_2$

4.420 emu k/mol and $\theta = -0.86$ K, The small negative value of Weiss temperature also indicates that there is a weak antiferromagnetic exchange coupling between the tetraaza macrocycle Cu(II) ions through the bridged $[\text{Fe}(\text{SCN})_4]^{2-}$ in the complex⁸.

In summary, a tetraaza macrocycle Cu(II) complex: $[(\text{CuL})_2\text{Fe}(\text{SCN})_4](\text{ClO}_4)_2$ was obtained and characterized by IR spectra and elemental analysis. The molecular magnetic measurement reveals that there is a weak antiferromagnetic interactions between the tetraaza macrocycle Cu(II) ions through the bridged $[\text{Fe}(\text{SCN})_4]^{2-}$ in the synthesized complex.

ACKNOWLEDGEMENTS

This work is financially supported by Natural Science Foundation of China (20871039). Follow-up support from the Nature Science Foundation of Anhui Universities (KJ2011Z299) and Key Disciplines Foundation of Hefei Normal University.

REFERENCES

1. L.K. Thompson, *Coord. Chem. Rev.*, **193**, 233 (2002).
2. J.H. Bi, R.J. Ding, Z.X. Huang, Y. Chen and N.-L. Hu, *Asian J. Chem.*, **20**, 4963 (2008).
3. P. Chaudhuri, V. Kataev, B. Buchner, H.-H. Klaus, B. Kersting and F. Meyer, *Coord. Chem. Rev.*, **253**, 2261 (2009).
4. J.M. Lehn, *Angew. Chem. Int. Ed.*, **43**, 3644 (2004).
5. A.Y. Robin and K.M. Fromm, *Coord. Chem. Rev.*, **250**, 2127 (2006).
6. J.H. Bi, H.F. Wang, Z.X. Huang, W.T. Bi and N.-L. Hu, *Asian J. Chem.*, **20**, 4966 (2008).
7. J.H. Bi, *Acta Crystallogr E.*, **65**, m1561 (2009).
8. J.S. Miller and A. Epstein, *Chem. Rev.*, **88**, 201 (1988).