第 11 期
2007 年 11 月

无 机 化 学 学 报
CHINESE JOURNAL OF INORGANIC CHEMISTRY

Vol.23 No.11
Nov., 2007

研究简报

具有自旋涨落性质的单一手性三核镍(Ⅱ)配合物

王国喜[1] 李 波[1] 熊仁根*[,1] Tomoyuki Akutagawa*[,2]
(南京大学配位化学研究所，南京 210093)
([2]Research Institute for Electronic Science, Hokkaido University, Sapporo, 060-0812, Japan)

关键词：镍(Ⅱ)；同手性配合物；铁电性与铁磁性；自旋涨落
中图分类号：O614.81+3 文献标识码：A 文章编号：1001-4861(2007)11-1994-03

Homochiral Trinuclear Nickel(Ⅱ) Complex with a Spin Fluctuation

WANG Guo-Xi[1] LI Bo[1] XIONG Ren-Gen*[,1] Tomoyuki Akutagawa*[,2]
(*Coordination Chemistry Institute, Nanjing University, Nanjing* 210093)
([2]*Research Institute for Electronic Science, Hokkaido University, Sapporo*, 060-0812, *Japan*)

Abstract: $[Ni_3O(TBPLA)(H_2O)](ClO_4)_4(H_2O)_6$ [TBPLA=(*S*)-1,1′,1″-2,4,6-trimethylbenzene-1,3,5-triyl)-tris(methylene)-tris-(pyrrolidine-2-carboxylate)] was found to possibly display multiferroic property (the coexistence of ferroelectricity and ferromagnetism). The magnetic property of this compound was studied and no magnetic hysteresis loop was found probably due to an intrinsic fluctuation for the magnetic exchange energy.

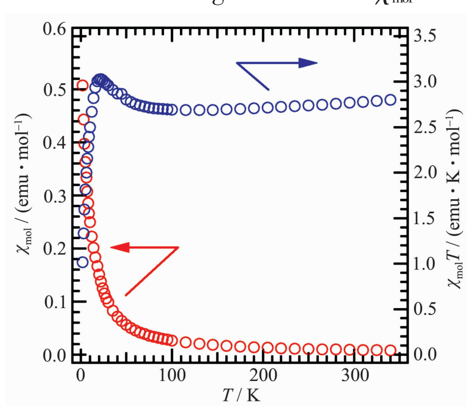
Key words: nickel(Ⅱ); homochiral coordination compound; ferroelectricity and ferromagnetism; spin fluctuation

A homochiral trinuclear nickel(Ⅱ) complex, $[Ni_3O(TBPLA)(H_2O)](ClO_4)_4(H_2O)_6$ (**1**) where TBPLA=(*S*)-1,1′1″-2,4,6-trimethyl-benzene-1,3,5-triyl-tris (methylene)-tris-(pyrrolidine-2-carboxylate) was synthesized, and its crystal structure, dielectric anisotropy as well as ferroelectricity were determined in our previous work[1].

As a continuation of the work, its possible multiferroic property was studied in this work, we report here magnetic property characterization in detail since the coexistence of ferroelectricity and ferromagnetism is current interest in material science[2].

1 Results and discussion

Fig.1 shows that a broad maximum peak is observed at T=18 K. The ferromagnetic coupling between three Ni(Ⅱ) sites (S=1) is observed in the temperatures from 70 to 20 K due to slight increase of $\chi_{mol}T$ values.



$\chi_{mol}T$ at 300 K=2.77 emu·K·mol^{-1}

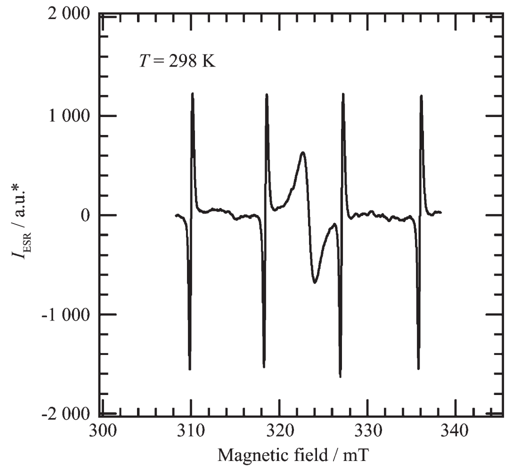
Fig.1 *M-T* behavior at a magnetic filed of 1 T

Interestingly, Fig.2 shows that four sharp signals

收稿日期：2007-09-02。收修改稿日期：2007-10-26。
国家自然科学基金(No.NSFC50673039，20471029，20490214)资助项目。
*通讯联系人。E-mail：xiongrg@nju.edu.cn；takuta@imd.es.hokudai.ac.jp
第一作者：王国喜，男，41 岁，博士研究生，副教授；研究方向：手性化合物的合成。

are the Mn marker, and a central broad signal corresponds to Ni(Ⅱ). The g value and line-width (ΔH) of the Ni(Ⅱ) signal are 2.003 31 and 1.326 mT, respectively. From the g value, the calculated $\chi_{mol}T$ value for one $S=1$ of Ni(Ⅱ) is 1 emu·K·mol^{-1}. Therefore, the $\chi_{mol}T$~2.7 emu·K·mol^{-1} in the temperatures from 70 to 350 K is almost consistent with three S=1 spins. Three S=1 spins in the Ni_3 triangle follow the Curie-Weiss law in high temperature range.

Since the ferromagnetic coupling was observed at the $\chi_{mol}T$ vs T plots in the temperatures from 70 to 20 K, we measured the M vs H plots at 2, 10, 20, 100, and 200 K in order to understand the low temperature magnetic state (Fig.3). Although the linear M vs H plots observed at 10, 20, 100, and 200 K, the nonlinear behavior was confirmed at 2 K. The hysteresis measurements at 2 K did not correspond to the ferromagnetic ordering due to a lack of hysteresis loop typically observed in the ferromagnetic state. Therefore, the low temperature magnetic state of Ni_3 triangle complex did not show the ferromagnetic ordering, which is consistent with the structural properties.



*a.u.=atomic unit

Fig.2　ESR measurement at 298 K (powder sample)

Thus, we could not explain the difference of magnetic behavior between the filed cooling and zero-field cooling temperature dependence (Fig.4) at present.

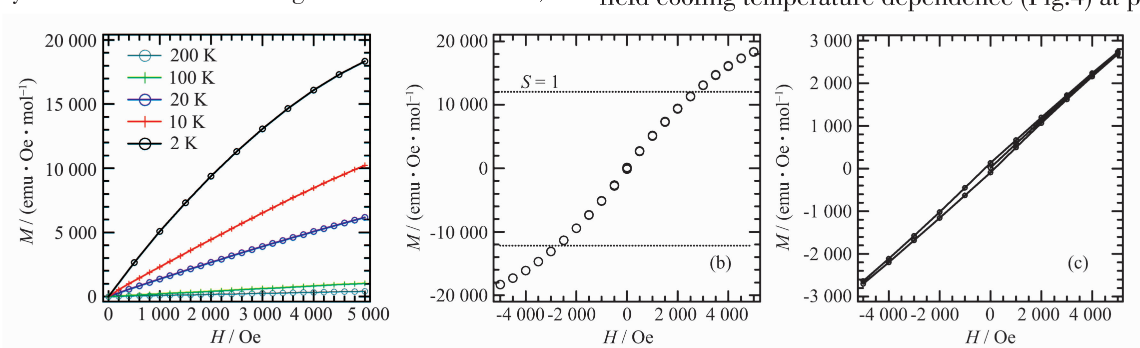


Fig.3　M-H curves (a) M_s value of one S=1 spin was saturated to ca 12 000 emu·Oe·mol^{-1}. Since the M vs H plots at 2 K shows an inflection point at around 12 000 emu·Oe·mol^{-1}, one S=1 spin is active at 2 K; (b) Other two S=1 spins form a antiferromagnetic coupling (singlet) state; (c) Magnitude of $\chi_{mol}T$ value in temperatures from 18 to 2 K show a saturation behavior from three S=1 ($\chi_{mol}T$=2.7 emu·K·mol^{-1}) to one S=1 ($\chi_{mol}T$=1.0 emu·K·mol^{-1})

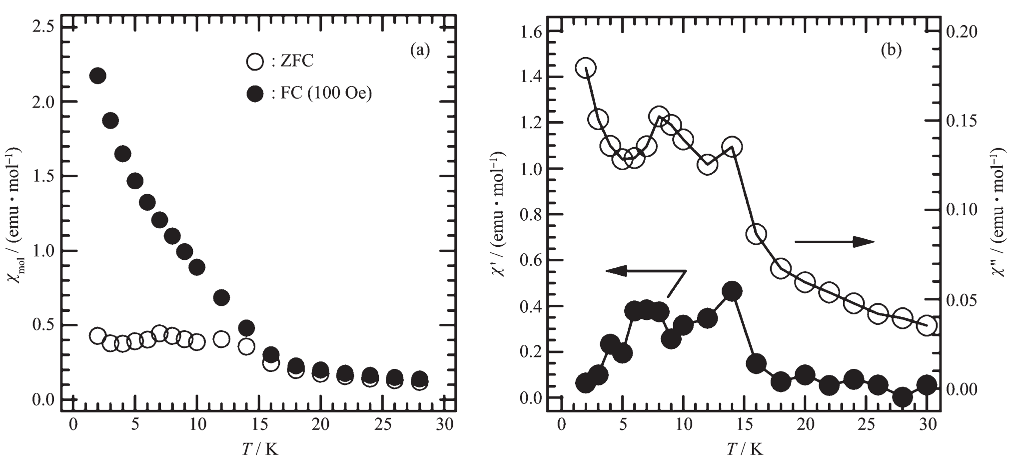
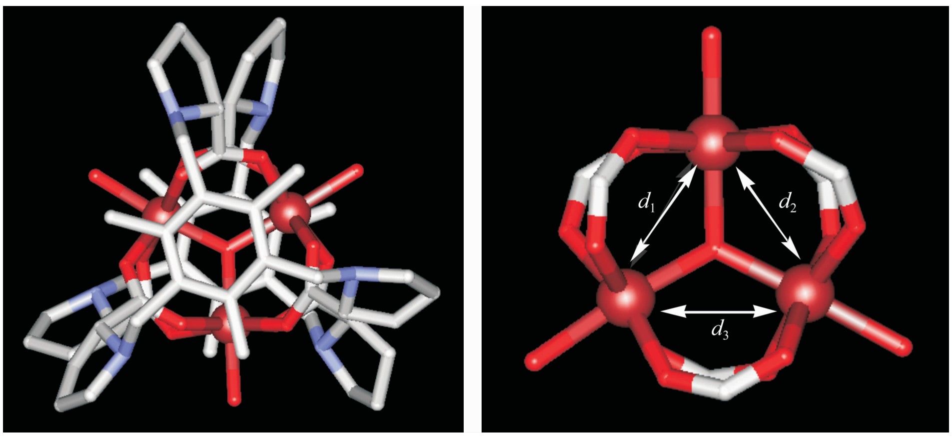


Fig.4　(a) M-T curves of zero- and field-cooling (100 Oe); (b) M-T of AC susceptibility

A distinct difference appears at ca 18 K, where three S=1 spins change to one S=1. One possible explanation is a spin fluctuation between three S=1 sites. The triangle spin structure has an intrinsic fluctuation for the magnetic exchange energy. This also has a possibility of the effect of spin fluctuation, but the detail is unclear at present.

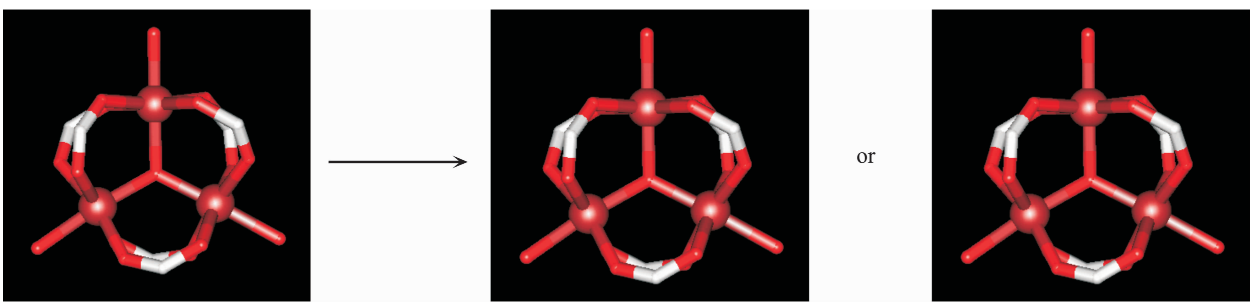
2 Conclusion

The magnetic behavior of Ni_3O triangle complex is discussed from the point view of the crystal structure. Within the complex, three Ni(Ⅱ) ions are interacted to each other due to the short Ni-Ni distances. However, nearest-neighboring Ni-Ni distance is far from the intra-molecular distances, which yields impossible magnetic interaction between the complexes. The inter-molecular magnetic interactions between the Ni_3O triangles are of negligible magnitude, suggesting that the magnetic properties of the salt are dominated by magnetic exchange energy in the Ni_3O triangle. The inter-molecular interactions between the Ni_3O tri-angle are necessary for the ferromagnetic ordering to appear in the crystal, which is inconsistent with the magnitude of inter-molecular interaction. The magnetic behavior of the salt should be explained by the Ni_3O triangle only (Fig.5 and 6).



d_1=0.342 83(15) nm, d_2=0.340 74(15) nm, d_3=0.345 56(12) nm

Fig.5 Intra-molecular interaction Ni-Ni distance in Ni_3O triangle



(a) High temperature curie of three S=1 spins (b)low temperature one S=1 (up spin) and singlet (up and down spins)

Fig.6 Spin status

References:

[1] (a)Ye Q, Song Y M, Wang G X, et al. *J. Am. Chem. Soc.*, **2006**, **128**(20):6554~6555

(b)Fu D W, Song Y M, Wang G X, et al. *J. Am. Chem. Soc.*, **2007**,**129**(17):5346~5347

(c)Cheetham A K, Rao C N R. *Science*, **2007**,**318**:58~59

[2] (a)Chen Z F, Xiong R G, Zhang J, et al. *J. Chem. Soc. Dalton*, **2000**:4010~4012

(b)Qu Z R, Zhao H, Wang X S, et al. *Inorg. Chem.*, **2003**,**42**(24):7710~7712

(c)Zhang J, Xie Y R, Ye Q, et al. *Eur. J. Inorg. Chem.*, **2003**: 2572~2577

(d)Zhang J, Xiong R G, Chen X T, et al. *Organometallics*, **2001**,**20**(19):4118~4121

(e)Huang S P D, Xiong R G, Han J D, et al. *Inorg. Chim. Acta*, **1999**,**294**(1):95~98

(f)Liu C M, Xiong R G, You X A, et al. *Polyhedron*, **1997**,**16**(1):119~123

(g)Eerenstein W, Mathur N D, Scott J F. *Nature*, **2006**,**442**(7104): 759~765