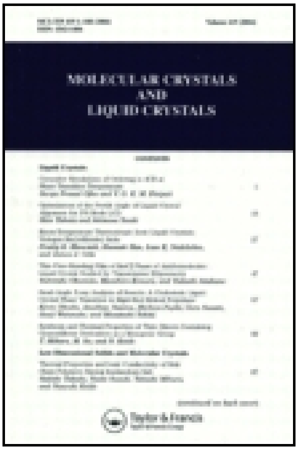


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Magnetic Phase Transition of Py_2N^-- and $NCNH^-$-Bridged Nickel(II) Complexes at about 25 K

Kenji Zusai [a], Tomoo Katayama [a], Takayuki Ishida [a] & Takashi Nogami [a]

[a] Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo, 182-8585, Japan

Version of record first published: 24 Sep 2006

To cite this article: Kenji Zusai, Tomoo Katayama, Takayuki Ishida & Takashi Nogami (2000): Magnetic Phase Transition of Py_2N^-- and $NCNH^-$-Bridged Nickel(II) Complexes at about 25 K, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 343:1, 121-126

To link to this article: http://dx.doi.org/10.1080/10587250008023513

Mol. Cryst. and Liq. Cryst., 2000, Vol. 343, pp. 121-126
Reprints available directly from the publisher
Photocopying permitted by license only

Magnetic Phase Transition of Py_2N^-- and $NCNH^-$-Bridged Nickel(II) Complexes at about 25 K

KENJI ZUSAI, TOMOO KATAYAMA, TAKAYUKI ISHIDA and TAKASHI NOGAMI

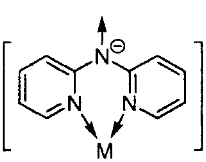
Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182–8585, Japan

Magnetic properties of nickel(II) complexes containing di(2-pyridyl)amine anion (dpa^-) or cyanamide anion (ca^-) are investigated. Ni/dpa complexes prepared from $NiCl_2$ and $Ni(NO_3)_2$ showed magnetic transition at 17 and 19 K, respectively. The Ni/ca complex prepared from $NiCl_2$ showed magnetic transition at 25 K.

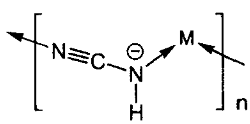
Keywords: dipyridylamine; cyanamide; magnetic susceptibility

INTRODUCTION

Magnetism of transition-metal complexes with a 3-dimensional network is of current interest for developing high T_C magnets. Various magnets have been reported containing polycyano-anion bridges such as tricyanomethanide [1] and dicyanamide anions [2]. We have developed new bridging organic ligands, paying attention to some structural requirements; π-conjugated, anionic, and compact ligands. We will report here magnetic phase transitions of Ni(II) complexes containing di(2-pyridyl)amine anion (dpa^-) or cyanamide anion (ca^-). These ligands possess an $N{=}C{-}N^-$ moiety as a bridging backbone.



M / dpa



M / ca

RESULTS AND DISCUSSION

Ni(II) / dpa

We synthesized Ni(II)/dpa complexes according to two methods. The chloride or nitrate ions of the starting material were exchanged with dpa⁻ anions which were formed in situ from dpaH with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) (Scheme 1). Another preparation is based on the literature method [3,4]. After a precursor, $Ni(dpaH)_2Cl_2$, was synthesized and isolated, the treatment of the precursor with NaO-t-Bu lead dehydrochlorination (Scheme 2). A possible structure of the target complex is illustrated as **1** [4].

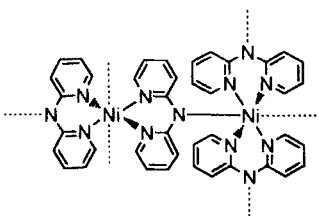
Scheme 1

$NiCl_2$ [or $Ni(NO_3)_2$] + 2 dpaH + 2 DBU $\xrightarrow{EtOH}$ $Ni(dpa)_2$; $- 2$ DBU•HCl [or $- 2$ DBU•HNO_3]

Scheme 2

$NiCl_2$ + 2 dpaH $\xrightarrow{PhH,\ MeOH}$ $N(dpaH)_2Cl_2$

$N(dpaH)_2Cl_2$ + 2 NaO-t-Bu $\xrightarrow{BuOH}$ $Ni(dpa)_2$; $- 2$ NaCl, $- 2$ t-BuOH



1

Brown polycrystalline samples (**2a** and **2b**) were obtained from $NiCl_2$ and $Ni(NO_3)_2$, respectively, by the preparation of Scheme 1. The temperature dependence of the magnetic susceptibility measured at 0.5 T indicates the presence of ferromagnetic interaction; the Weiss temperatures were 7.3 and 9.0 K for **2a** and **2b**, respectively.

As Figure 1 shows, we measured the field-cooled magnetization (FCM), remnant magnetization (RM), and zero-field cooled magnetization (ZFCM). Both **2a** and **2b** showed an upsurge of the FCM curves at about 20 K on cooling, and, after removal of the applied field at 10 K, the RMs were present and completely disappeared at about 18 K on heating. The ac magnetic susceptibility measurements showed a sharp peak at 17 and 19 K, which we define as transition temperatures, for **2a** and **2b**, respectively.

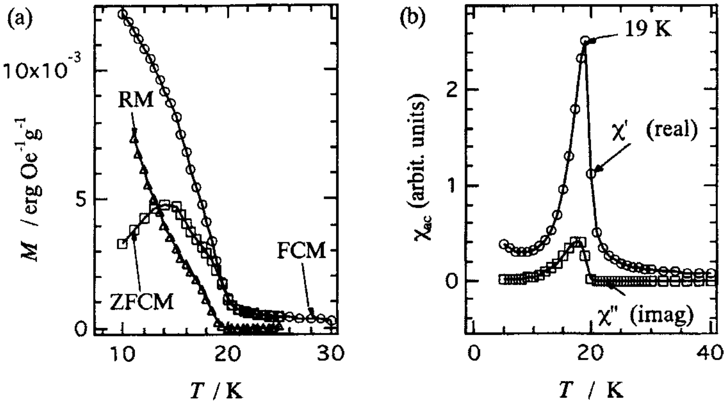


FIGURE 1 Magnetic phase transition of **2b** (Ni(II)/dpa) shown by (a) FCM (3 Oe), RM, and ZFCM (3 Oe) and (b) ac magnetic susceptibility measurements (10 Oe, 10^4 Hz).

Their *M-H* curves were measured at 10 K (below the transition temperature). The S-shape curves were found in a low field region, but the spontaneous magnetizations at 10 K were very small; 2.7 and 1.8 % of the theoretical values for **2a** and **2b**, respectively. Furthermore, the paramagnetic crystals were found as impurities in the solid specimens. The X-ray crystallographic analysis revealed that mononuclear complexes Ni(dpa)-(dpaH)$_2$Cl•0.5dpaH (**3a**) [5] and Ni(dpa)(dpaH)$_2$NO$_3$•CH$_3$OH (**3b**) [6] were included in specimens **2a** and **2b**, respectively. Figure 2a shows the structure of the Ni(dpa)(dpaH)$_2^+$ ion in **3a**. A four-membered ring N-C-N-Ni is found. The structure of Ni(dpa)(dpaH)$_2^+$ ion in **3b** was almost identical to that in **3a**. Although the presence of dpa$^-$ is confirmed, no bridging structure could been found in **3a** or **3b**. Figure 2b shows the crystal structure of **3a**.

Thus, the specimens of **2a** and **2b** are concluded to be of poor quality, judging from the small spontaneous magnetizations and paramagnetic impurities. We are now trying purification of a fraction showing ferromagnetic transition behavior.

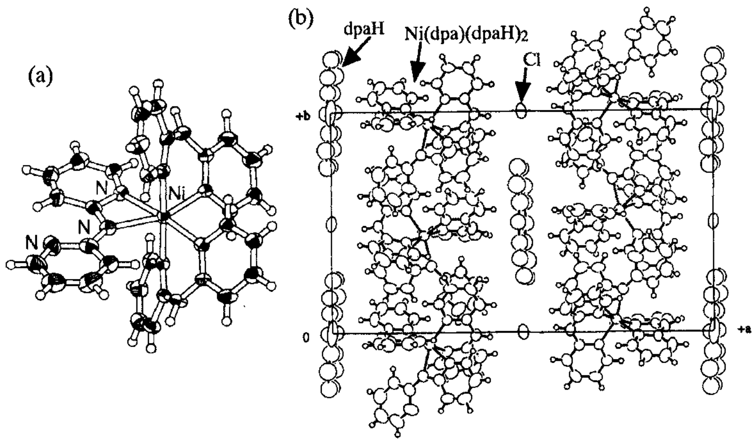


FIGURE 2 (a) Ortep drawing of $Ni(dpa)(dpaH)_2^+$ ion in **3a**.
(b) Molecular arrangement in the crystal of **3a**. $Ni(dpa)(dpaH)_2^+$ ions are isolated.

Dark greenish brown powder sample (**4**) was obtained from Scheme 2. The temperature dependence of the magnetic susceptibility of **4** showed a positive Weiss temperature of about 30 K. Although elemental analysis of **4** indicated the small content of nitrogen (ca. 4 %), the *M-H* curve measured at 2.0 K exhibited an upsurge within a weak applied field, being typical of a ferromagnet (Figure 3). The ac susceptibility measurement of **4** indicated T_C = 16 K.

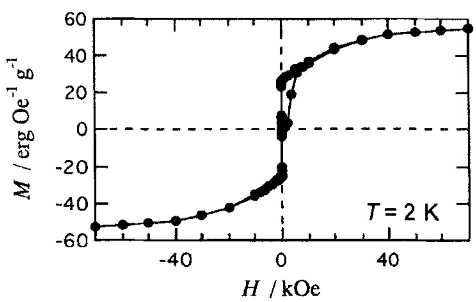
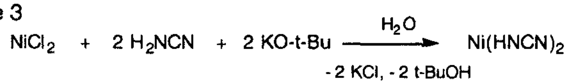


FIGURE 3 *M-H* curve of **4** (Ni(II) / dpa) complex measured at 2 K.

Ni(II) / ca

Ni(II)/ca complex was prepared by mixing $NiCl_2$ and $NCNH_2$ in H_2O in the presence of KO-t-Bu (Scheme 3). After standing for a few days, resultant dark precipitates (**5**) were collected on a filter. The elemental analysis indicated somewhat low nitrogen and carbon contents, suggesting that chloride ions are remained in the solid of **5**.

Scheme 3



The temperature dependence of the magnetic susceptibility of **5** measured at 0.5 T indicated a positive Weiss temperature of ca. 30 K. The FCM (3 Oe) showed an upsurge at 29 K on cooling, and the RM completely disappeared at 27 K on heating (Figure 4a). The ZFCM (3 Oe) increased with increasing temperature, exhibited a peak at 24 K. The ac magnetic susceptibility measurements showed a peak at 25 K (Figure 4b). The *M-H* curve measured at 15 K revealed a ferromagnetic behavior with a small hysteresis (Figure 5).

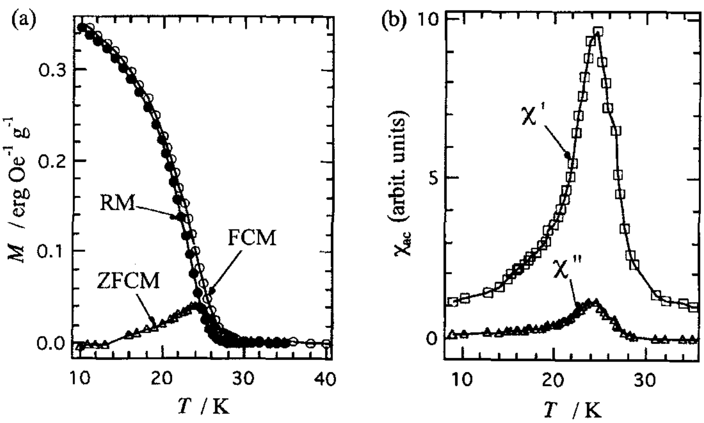


FIGURE 4 Magnetic phase transition of **5** (Ni(II)/ca) shown by (a) FCM (3 Oe), RM, and ZFCM (3 Oe) and (b) ac magnetic susceptibility measurements (10 Oe, 10^4 Hz).

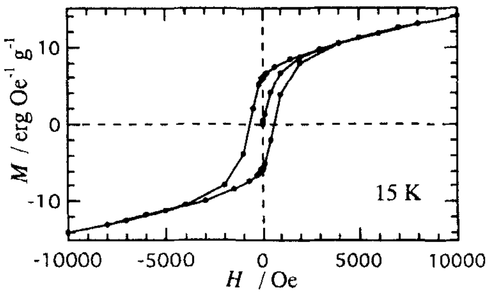


Figure 5 Hysteresis curve of **5** (Ni(II)/ca) measured at 15 K.

Acknowledgments

This work was supported by Grants-in-Aid for Scientific Research on Priority Areas of "Metal-assembled Complexes" (no. 11136212) and "Molecular Conductors and Magnets" (no. 11224204) from the Ministry of Education, Science, Sports and Culture, Japan. We thank Dr. Mikio Yamasaki (Rigaku) for the X-ray crystal structure determination of **3a**.

References

[1] S. R. Batten, B. F. Hoskins, B. Moubaraki, K. S. Murray, and R. Robson, *J. Chem. Soc., Dalton Trans.*, **1999,** 2977; H. Hoshino, K. Iida, T. Kawamoto, and T. Mori, *Inorg. Chem.*, **38,** 4229 (1999); J. L. Manson, C. Campana, and J. S. Miller, *Chem. Commun.*, **1998,** 251 (1998).

[2] S. R. Batten, P. Jensen, B. Moubaraki, K. S. Murray, and R. Robson, *Chem. Commun.*, **1998,** 439; M. Kurmoo and C. J. Kepert, *New J. Chem.*, **22,** 1515 (1998); J. L. Manson, C. R. Kmety, Q. Z. Huang, J. W. Lynn, G. M. Bendele, S. Pagola, P. W. Stephens, L. M. LiableSands, A. L. Rheingold, A. J. Epstein, and J. S. Miller, *Chem. Mater.*, **10,** 2552 (1998); J. L. Manson, C. R. Kmety, A. J. Epstein, and J. S. Miller, *Inorg. Chem.*, **38,** 2552 (1999).

[3] C. D. Burbridge, D. M. L. Goodgame, *J. Chem. Soc. A*, **1968,** 237.

[4] T. J. Hurley and M. A. Robinson, *Inorg. Chem.*, **7,** 33 (1968).

[5] Data of **3a:** monoclinic, $P2_1/n$, $a = 25.581(1)$, $b = 14.9982(9)$, $c = 9.5775(5)$ Å, $\beta = 97.656(1)°$, $V = 3641.8(3)$ Å^3, $Z = 4$, $d_{calc} = 1.263$ g/cm^3, μ(MoKα) = 21.60 cm^{-1}, $R = 0.064$ for 3349 observed reflections.

[6] D. Hashizume, F. Iwasaki, K. Zusai, T. Ishida, and T. Nogami, unpublished results for the X-ray structure determination of **3b**.