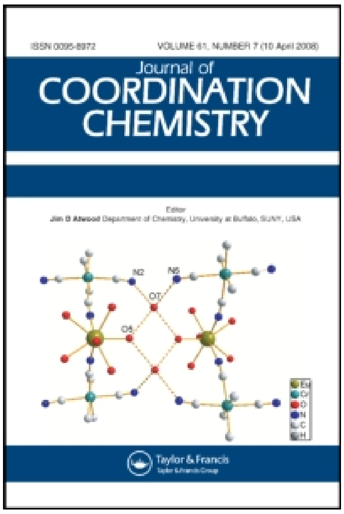

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, structure and magnetic properties of $Ni_2(NO_3)_4(APTY)_4$ (APTY=1,5-dimethyl-2-phenyl-4-{[(1<i>E</i>)-pyridine-4-ylmethylene]amino}-1,2-dihydro-3<i>H</i>-pyrazol-3-one)

Xian-Wen Wang[a]; Yue-Qing Zheng[a]
[a] Faculty of Materials Science and Chemical Engineering, The State Key Laboratory Base of Novel Functional Materials and Preparation Science, Ningbo University, Ningbo, P.R. China

To cite this Article Wang, Xian-Wen and Zheng, Yue-Qing(2007) 'Synthesis, structure and magnetic properties of $Ni_2(NO_3)_4(APTY)_4$ (APTY=1,5-dimethyl-2-phenyl-4-{[(1**<i>E</i>**)-pyridine-4-ylmethylene]amino}-1,2-dihydro-3**<i>H</i>**-pyrazol-3-one)', Journal of Coordination Chemistry, 60: 7, 763 — 769

To link to this Article: DOI: 10.1080/00958970600915355

URL: http://dx.doi.org/10.1080/00958970600915355

Journal of Coordination Chemistry
Vol. 60, No. 7, 10 May 2007, 763–769

Taylor & Francis
Taylor & Francis Group

Synthesis, structure and magnetic properties of $Ni_2(NO_3)_4(APTY)_4$ (APTY = 1,5-dimethyl-2-phenyl-4-{[(1*E*)-pyridine-4-ylmethylene]amino}-1,2-dihydro-3*H*-pyrazol-3-one)

XIAN-WEN WANG and YUE-QING ZHENG*

Faculty of Materials Science and Chemical Engineering, The State Key Laboratory
Base of Novel Functional Materials and Preparation Science, Ningbo University,
Ningbo, 315211, P.R. China

(*Received in final form 9 May 2006*)

A novel dinuclear nickel(II) complex $Ni_2(NO_3)_4(APTY)_4$ (**1**) (APTY = 1,5-dimethyl-2-phenyl-4-{[(1*E*)-pyridine-4-ylmethylene]amino}-1,2-dihydro-3*H*-pyrazol-3-one), was synthesized by solvothermal reaction of $Ni(NO_3)_2 \cdot 6H_2O$ with APTY in methanol at 353 K. The structure consists of centrosymmetric dimers resulting from octahedrally coordinated Ni atoms bridged by APTY ligands. Weak intermolecular interactions (C–H $\cdots$ N, C–H $\cdots$ O hydrogen bonding, C–H $\cdots \pi$ and π–π stacking interactions) are responsible for a supramolecular assembly of molecules in the lattice. Magnetic measurements over 1.8–300 K show weak antiferromagnetic coupling between Ni(II) ions with $J = 2.969\,cm^{-1}$, $g = 2.280$, $\theta = -5.903$.

Keywords: Schiff base; Ni(II) complex; Crystal structure; Supramolecular assembly; Magnetic properties

1. Introduction

Schiff-base ligands have played an integral role in the development of coordination chemistry since the late nineteenth century. Schiff base coordination complexes have attracted great attention over the last few decades due not only to their facile synthesis, their wide application and the accessibility of diverse structural modifications, but also because of their biological modelling applications, catalysis, design of molecular magnets and materials chemistry [1–9]. Schiff bases of 4-aminoantipyrine and their coordination complexes have been extensively investigated because of their biological, clinical, pharmacological, analytical and materials applications [10–19]. However, only a few structurally characterized metal complexes with 4-aminoantipyrine Schiff bases have been reported [17, 20–24]. Herein we describe the synthesis, crystal structure and magnetic properties of a new dinuclear nickel(II) complex, $Ni_2(APTY)_4(NO_3)_4$ (**1**) (APTY = 1,5-dimethyl-2-phenyl-4-{[(1*E*)-pyridine-4-ylmethylene]amino}-1,2-dihydro-3*H*-pyrazol-3-one), obtained by solvothermal reaction of $Ni(NO_3)_2 \cdot 6H_2O$ with APTY in methanol solution at 353 K.

---

*Corresponding author. Email: zhengcm@nbu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970600915355

2. Experimental

2.1. *Physical measurements*

All chemicals of reagent grade were commercially available and used without further purification. Elemental analysis was performed using a Perkin Elmer 2400II CHNS/O system. IR spectra (KBr pellets) were recorded using a Shimadzu FT-IR 8900 spectrophotometer in the range 4000–400 cm^{-1}. Combined TG/DTA measurements were carried out in range 25–900°C using powdered samples in a nitrogen stream an a Seiko Exstar 6000 TG/DTA6300 system with a heating rate of 10°C min^{-1}. Magnetic measurements were performed using crystalline samples on a Quantum Design MPMS-7 SQUID magnetometer with an applied field of 2000G in the temperature range $1.8 \leq T(\mathrm{K}) \leq 300$.

2.2. *Synthesis*

The Schiff base APTY was synthesized by condensation of 4-aminoantipyrine with pyridine-3-carboxaldehyde in a 1 : 1 molar ratio in ethanol at 353 K for 2 h. $Ni_2(NO_3)_4(APTY)_4$ was synthesized as follows. A 25 cm^3 Teflon-lined stainless steel autoclave was charged with 0.290 g (1 mmol) of $Ni(NO_3)_2 \cdot 6H_2O$, 0.260 g (1 mmol) of APTY and 18 cm^3 of CH_3OH, and heated at 353 K for 168 h, then cooled to room temperature. Green crystals were obtained in 90% yield based on initial $Ni(NO_3)_2 \cdot 6H_2O$. Anal. Calcd for $C_{68}H_{64}Ni_2N_{20}O_{16}$ (%): C, 53.17; H, 4.17; N, 18.24. Found: C, 53.25; H, 4.40; N, 18.00. IR (cm^{-1}): 2927w, 1639vs, 1589m, 1566vs, 1544m, 1488s, 1456m, 1419m, 1384vs, 1298vs, 1188w, 1155w, 1137w, 1049w, 1026m, 981w, 950w, 889w, 812m, 765m, 702s, 640w, 569w, 505w. Two absorption bands centered at 1639 and 1598 cm^{-1} are attributed to $\nu_{C=O}$ and $\nu_{-C=N}$, respectively. The ν_{N-O} stretching vibrations of nitrate groups result in absorptions at 1384 and 1298 cm^{-1}, and the strong absorptions at 1589, 1566, 1488 and 1456 cm^{-1}, may be due to C–C stretching vibrations of the phenyl groups [15]. According to combined TG-DTA measurements, the compound is stable below ca 250°C and weight loss reached 18.8% at 287°C. Upon further heating, the sample lost weight gradually and the total weight loss was 67.4% at 900°C.

2.3. *X-Ray crystallography*

A crystal of $Ni_2(APTY)_4(NO_3)_4$ was selected under a polarizing microscope and mounted on a Bruker P4 diffractomerter with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) for cell determination and subsequent data collection. Lattice parameters were refined from the 2θ values (10–25°) of 25 carefully centred reflections. Reflection intensities with $2\theta_{\max} = 55°$ were collected at 293 K using the θ–2θ scan technique. No detectable decay was observed during data collection. Data were corrected for Lp and absorption effects. SHELXS-97 and SHELXL-97 [25, 26] were used for structure solution and refinement. The structure was solved using direct methods. Subsequent difference Fourier syntheses enabled all non-hydrogen atoms to be located. After several cycles of refinement, all hydrogen atoms of APTY were geometrically generated. Finally, all non-hydrogen atoms were refined with anisotropic

Table 1. Summary of crystal data, data collection, structure solution and refinement details for $Ni_2(NO_3)_4(APTY)_4$.

Empirical formula	$C_{68}H_{64}N_{20}Ni_2O_{16}$
Formula weight	1534.81
Description	Green
Crystal size (mm^3)	0.289 × 0.267 × 0.133
Temperature (K)	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions (Å, °)	
a	10.556(2)
b	12.063(2)
c	15.220(3)
α	74.73(3)
β	81.46(3)
γ	70.58(3)
Volume ($Å^3$)	1759.4(6)
D_{Calcd} ($g\,cm^{-3}$)	1.449
$F(000)$	796
μ (mm^{-1})	0.618
Absorption correction	Empirical psi scan
Refinement method	Full-matrix least-squares on F^2
θ range (°)	1.39–27.49
Reflections collected	9353
Unique reflections (R_{int})	8035 (0.0655)
Data, restraints, parameters	5374, 0, 480
Goodness of fit on F^2	1.021
R_1, wR_2 $[I \geq 2\sigma(I)]^a$	0.0568, 0.1442
R_1, wR_2 (all data)^a	0.0963, 0.1666
Extinction coefficients	0.006(4)
A, B values in w^b	0.0964, 0.0000
Res. ρ_{max}, ρ_{min} ($e\,Å^{-3}$)	0.839, –0.559

$^a wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $^b w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$.

displacement parameters by full-matrix least-squares techniques and hydrogen atoms with isotropic displacement parameters. Details concerning crystal data and structure determination are summarized in table 1. Selected interatomic distances and bond angles are given in table 2.

3. Results and discussion

3.1. *Crystal structure of $Ni_2(NO_3)_4(APTY)_4$*

The asymmetric unit of the complex contains a Ni^{2+} ion, two nitrate ions, and two APTY molecules. The two crystallographically distinct nitrate anions function as chelating and monodentate ligands, respectively, and crystallographically different APTY molecules as monodentate ligand and bidentate bridging ligands, respectively, with normal bonding values comparable with the free molecule [27]. The Ni atoms are each coordinated by two N atoms of two APTY ligands and four O atoms of two nitrato ligands and one APTY ligand to form a distorted octahedral NiN_2O_4 chromophore with d(Ni–O) = 2.037–2.156 Å and d(Ni–N) = 2.095, 2.124 Å (figure 1, table 2). Bonding in the NiN_2O_4 chromophore is similar to that in other reported cases

Table 2. Selected interatomic distances (Å) and bond angles (°) for $Ni_2(NO_3)_4(APTY)_4$.

Ni–O(2)	2.156(3)	O(2)/Ni/O(3)	60.13(9)	O(3)/Ni/O(5)	172.16(9)
Ni–O(3)	2.138(2)	O(2)/Ni/O(5)	112.18(10)	O(3)/Ni/O(8)	99.45(9)
Ni–O(5)	2.048(2)	O(2)/Ni/O(8)	159.38(9)	O(8)/Ni/N(4)	91.59(10)
Ni–O(8)	2.037(2)	O(3)/Ni/N(10)$^{\#1}$	87.31(9)	O(8)/Ni/N(10)$^{\#1}$	92.26(10)
Ni–N(4)	2.124(3)	O(2)/Ni/N(10)$^{\#1}$	89.71(10)	O(5)/Ni/N(4)	91.10(10)
Ni–N(10)$^{\#1}$	2.095(2)	O(2)/Ni/N(4)	84.82(10)	N(10)$^{\#1}$/Ni/N(4)	173.41(10)
Hydrogen bonds					
D–H	d(D–H)	d(H···A)	∠(D–H···A)	d(D–H···A)	A
C(17)–H(17)	0.93	2.61	173	3.538(6)	N(3)$^{\#2}$
C(24)–H(24)	0.93	2.58	133	3.287(5)	O(4)$^{\#3}$
C(31)–H(31)	0.93	2.54	130	3.213(6)	O(2)$^{\#4}$
C(31)–H(31)	0.93	2.47	146	3.288(6)	O(7)$^{\#4}$

Symmetry codes: #1: $-x+1, -y+1, -z+1$; #2: $-x+2, -y+2, -z+2$; #3: $x, y-1, z$; #4: $x+1, y, z$.

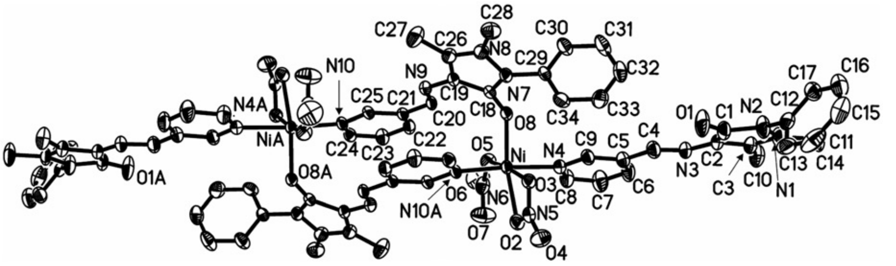

Figure 1. ORTEP view of the complex with atom labelling (displacement ellipsoids are drawn at the 30% probability level).

[15, 21–24, 28–31]. Ni atoms are bridged by APTY ligands to generate centrosymmetric (2*i*) $[Ni_2(NO_3)_4(APTY)_4]$ dimers with an 18-membered ring and a Ni–Ni separation of 8.504 Å. Along the [111] direction, the dimers are linked *via* intermolecular C–H···N hydrogen-bonds to form 1D chains, which are linked by intermolecular C–H···O hydrogen-bonds into two dimensional layers parallel to $(0\bar{1}1)$ as shown in figure 2(a). The layers are further assembled into a 3D supermolecular structure by π–π stacking between the terminal phenyl groups of the Schiff base ligands (mean interplanar distance 3.80 Å) (figure 2b). The structure is further stabilized by weak C–H···π interactions and interlayer C–H···O hydrogen bonds.

3.2. *Magnetic properties*

Figure 3 shows the temperature dependence of the magnetic behaviour of $Ni_2(APTY)_4(NO_3)_4$ in the form of χ_M and $\chi_M T$ *versus* T plots, χ_M being the magnetic susceptibility per Ni(II) and T being the temperature. The $\chi_M T$ product of $1.105\,cm^3\,K\,mol^{-1}$ at 300 K is close to the expected value for magnetically dilute, high-spin Ni(II) (spin-only value is $1.000\,cm^3\,K\,mol^{-1}$). The value of $\chi_M T$ increases gradually to a maximum of approximately $1.209\,cm^3\,K\,mol^{-1}$ at 35 K. The value then decreases sharply to a minimum value of approximately $0.440\,cm^3\,K\,mol^{-1}$ at 1.8 K.

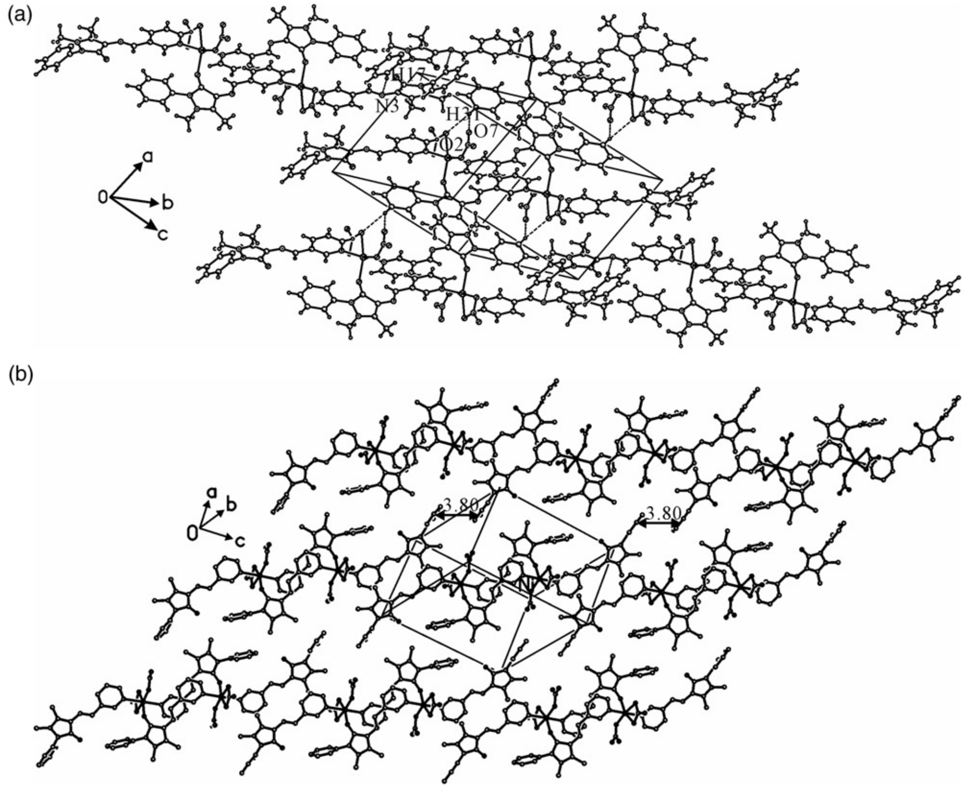

Figure 2. (a) Supramolecular assembly of the complex molecules into 2D layers by C–H ··· N and C–H ··· O hydrogen bonds; (b) 2D supramolecular layer extended by π–π stacking interactions and C–H ··· π interactions.

This behaviour is consistent with dominant antiferromagnetic interactions. The magnetic data have been interpreted using the expression for the molar magnetic susceptibility for $S = 1$ dimers [32], $\chi_M = Ng^2\beta^2/\kappa(T - \theta)\ [(5 + e^{4x})/(5 + 3e^{4x} + e^{6x})]$ (1), where $x = -J/\kappa T$ and J is the energy gap defined by the spin Hamiltonian with quantum spin operators S_{Ni} and $S_{\text{Ni}}^{\#1}$, $\text{H} = -2J[S_{\text{Ni}}S_{\text{Ni}}^{\#1}]$ (2). In equation (1), N, g, β, θ J, κ and T have their usual meanings. The best fit from a least-squares analysis of the experimental data gave $J = 2.969\,\text{cm}^{-1}$, $g = 2.280$, $\theta = -5.903$, and the agreement factor defined by $R = \Sigma[(\chi i_{\text{obs}} - \chi i_{\text{calcd}})^2/\Sigma(\chi i_{\text{obs}})^2]$ is equal to 7.1738×10^{-6}. The relatively weak antiferromagnetic coupling with the small J value is due to the rather long distance between paramagnetic metal centers (8.504 Å).

Supplementary data

Crystallographic data (excluding structure factors) have been deposited with Cambridge Crystallographic Data Centre as supplementary publication CCDC 293261. Copies of the data can be obtained, free of charge, on application to

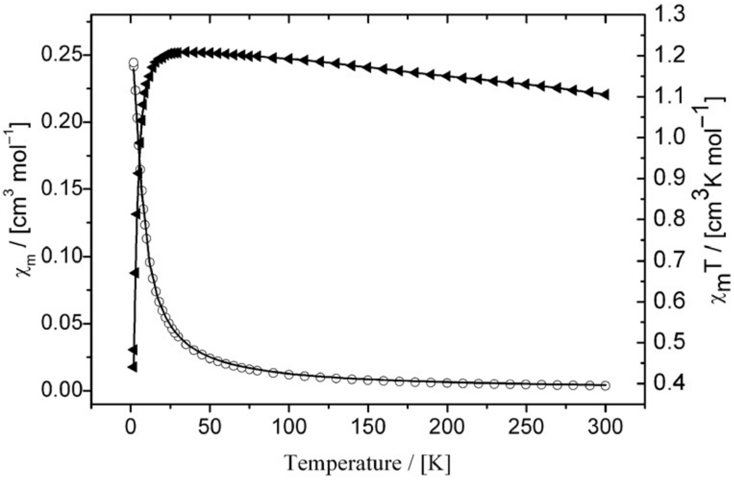

Figure 3. Temperature variation of magnetic susceptibility *vs*. temperature for [$Ni_2(NO_3)_4(APTY)_4$].

CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033 or E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

The project was supported by grants from the Ministry of Science and Technology of China (2003CCA00800), the Zhejiang Provincial Natural Science Foundation (Z203067), the Ningbo Municipal Natural Science Foundation (2003A62026) and the Scientific Research Fund of Ningbo University (XK200459, SS2004033).

References

[1] S.J. Coles, M.B. Hursthouse, D.G. Kelly, A.J. Toner, N.M. Walker. *J. Chem. Soc., Dalton Trans.*, 3489 (1998).
[2] S. Gourbatsis, S.P. Perlepes, I.S. Butler, N. Hadjiliadis. *Polyhedron*, **18**, 2369 (1999).
[3] C.O. Rodriguez de Barbarin, N.A. Bailey, D.E. Fenton, Q.-Y. He. *J. Chem. Soc., Dalton Trans.*, 161 (1997).
[4] E.J. Larson, V.L. Pecoraro. *J. Am. Chem. Soc.*, **113**, 3810 (1991).
[5] M.M. Taqui Khan, D. Srinivas, R.I. Kureshi, N.H. Khan. *Inorg. Chem.*, **29**, 2320 (1990).
[6] H. Miyasaka, H. Ieda, N. Matsumoto, R. Crescenzi, C. Floriani. *Inorg. Chem.*, **37**, 255 (1998).
[7] I. Ramade, O. Kahn, Y. Jeannin, F. Robert. *Inorg. Chem.*, **36**, 930 (1997).
[8] D. Wohrle. *Adv. Polym. Sci.*, **50**, 45 (1983).
[9] M. Calligaris, L. Randaccio. In *Comprehensive Coordination Chemistry*, G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds), Vol. 2, p. 727, Pergamon Press, Oxford (1987).
[10] D.G. Craciunescu. *An. R. Acad. Farm.*, **43**, 256 (1977).
[11] J. Hosler, C. Tschanz, C.E. Hignite, D.L. Azarnoff. *J. Invest. Dermatol.*, **74**, 51 (1980).
[12] P.J. Meffin, R. Williams, T.F. Blaschke, M. Rowland. *J. Pharm. Sci.*, **66**, 135 (1977).
[13] N.L. Olenovich, L.I. Koval Chuk. *Anal. Khim.*, **28**, 2162 (1975).
[14] D.R. Williams. *Chem. Rev.*, **72**, 203 (1977).

[15] Z.I. Kamal, E.-D. Ali, Z.S. Aziza. *Polyhedron*, **16**, 2909 (1997).

[16] J.R. Chopra, U.S. Arora. *Asian J. Chem.*, **11**, 225 (1999).

[17] N. Raman, A. Kulandaisamy, A. Shunmugasundaram, K. Jeyasubramanian. *Trans. Met. Chem.*, **26**, 131 (2001).

[18] N. Raman, A. Kulandaisamy, A. Shunmugasundaram, K. Jeyasubramanian. *Synth. React. Inorg. Met.-Org. Chem.*, **31**, 1249 (2001).

[19] Y.-X. Zheng, J. Lin, Y.-J. Liang, Q. Lin, Y.-N. Yu, C. Guo, S.-B. Wang, H.-J. Zhang. *Mater. Lett.*, **54**, 424 (2002).

[20] R.K. Agarwal, K. Arora, M. Priyanka, I. Chakravorti. *Pol. J. Chem.*, **67**, 1913 (1993).

[21] G. Rajendran, G.S. Screeletha. *Asian J. Chem.*, **13**, 1142 (2001).

[22] H. Liang, Q. Yu, R.-X. Hu, Z.-Y. Zhou, X.-G. Zhou. *Trans. Met. Chem.*, **27**, 454 (2002).

[23] H. Liang, X.-W. Wang, Z.-F. Chen, L. Huang, H.-L. Zou, J. Zhou, K.-B. Yu. *Acta Cryst.*, **E60**, m294 (2004).

[24] X.-W. Wang. Assembly, Characterization and Properties Study of Metal Coordination Polymers Bridged by Schiff-Base Derived from Pyridime-3(4)-Carboxal-dehyde 4-Itminoantipyrime by Drug Chiniofon Ligand, MSc thesis, Ningbo University (2004).

[25] G.M. Sheldrick. *SHELXSI-97, Programm zur Lösung von Kristallstrukturen*, University of Göttingen, Germany (1997).

[26] G.M. Sheldrick. *SHELXL-97, Programm zur Verfeinerung von Kristallstrukturen*, University of Göttingen, Germany (1997).

[27] R. Montalvo-Gonzalez, A. Ariza-Castolo. *J. Mol. Struct.*, **655**, 375 (2003).

[28] K. Biradha, M. Fujita. *J. Chem. Soc., Chem. Comm.*, 15 (2001).

[29] B. Kumar, V.D. Konstantin, M. Brian, S. Corey, J.Z. Michael. *J. Chem. Soc., Chem. Comm.*, 1327 (1999).

[30] L. Carlucci, G. Ciani, D.M. Proserpio. *New J. Chem.*, **12**, 1319 (1998).

[31] S.C.-F. Cristian, R.G.-M. José, W.S. Bradley, R.D. Kim. *Eur. J. Inorg. Chem.*, **5**, 988 (2003).

[32] O. Kahn. *Molecular Magnetism*, VCH, New York (1993).