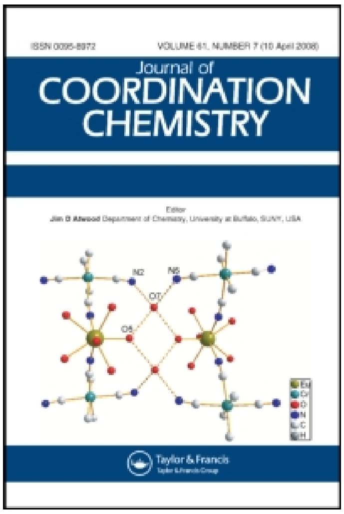

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, crystal structure and magnetic properties of $Co(NIT4Py)(H_2PDA)(H_2O)_3$

Chen-Xi Zhang[a]; Yuying Zhang[b]
[a] College of Science, Tianjin University of Science and Technology, Tianjin 300222, People's Republic of China [b] Department of Chemistry, NanKai University, Tianjin 300071, People's Republic of China

To cite this Article Zhang, Chen-Xi and Zhang, Yuying(2008) 'Synthesis, crystal structure and magnetic properties of $Co(NIT4Py)(H_2PDA)(H_2O)_3$', Journal of Coordination Chemistry, 61: 11, 1797 — 1803
To link to this Article: DOI: 10.1080/00958970701624302
URL: http://dx.doi.org/10.1080/00958970701624302

Journal of Coordination Chemistry
Vol. 61, No. 11, 10 June 2008, 1797–1803

Synthesis, crystal structure and magnetic properties of $Co(NIT4Py)(H_2PDA)(H_2O)_3$

CHEN-XI ZHANG*† and YUYING ZHANG‡

†College of Science, Tianjin University of Science and Technology,
Tianjin 300222, People's Republic of China
‡Department of Chemistry, NanKai University, Tianjin 300071,
People's Republic of China

(*Received 12 April 2007; in final form 12 July 2007*)

A Co(II)-pyridyl substituted nitronyl nitroxide complex $Co(NIT4Py)(H_2PDA)(H_2O)_3$ has been synthesized and structurally characterized (NIT4Py: 2-(4′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide and H_2PDA: 2,5-pyridine dicarboxylic acid). The compound is in the monoclinic space group $P2(1)/c$, $a = 16.892(5)$ Å, $b = 7.371(2)$ Å, $c = 18.856(5)$ Å, $\beta = 108.770(5)^\circ$, $V = 2223.0(11)$ Å^3, $Z = 4$ and $F(000) = 1064$. The cobalt is in a distorted octahedral environment with one nitrogen from NIT4Py, one oxygen atom from H_2PDA, two oxygens from two water molecules in the basal plane and one nitrogen from H_2PDA and one water in the axial positions. The molecules are connected as a layered structure by intermolecular hydrogen bond interactions. Variable temperature magnetic susceptibility measurements reveal the occurrence of weak antiferromagnetic interactions in the compound.

Keywords: Crystal structure; Nitronyl nitroxide radical; Co(II) complex; antiferromagnetic interaction

1. Introduction

Nitronyl nitroxide radicals, as one of the best characterized free radicals, have been widely employed as molecular units in the design and synthesis of molecular magnetic materials [1–4]. In the 'metal-organic' strategy, nitronyl nitroxide radicals have been used in conjunction with paramagnetic transition metal ions to form polymeric species. The chelating H_2PDA has good binding ability for formation of polymeric structures [5, 6]. Combining the abilities of both nitronyl nitroxide radicals and H_2PDA to coordinate transition metals, we have synthesized the metal-radical complex $Co(NIT4Py)(H_2PDA)(H_2O)_3$ (NIT4Py = 2-(4′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide). Here we report the synthesis, crystal structure and magnetic properties of the title complex.

---

*Corresponding author. Email: zcx@tust.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970701624302

2. Experimental

2.1. *Physical measurements*

Elemental analyses for carbon, hydrogen, and nitrogen were carried out on a Model 240 Perkin-Elmer elemental analyzer. The infrared spectrum was taken on a Shimadzu IR spectrophotometer model 408 in the 4000–600 cm^{-1} region, using KBr pellets. Temperature dependence of magnetic susceptibilities was measured on a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.

2.2. *Preparation of $Co(NIT4Py)(H_2PDA)(H_2O)_3$*

2-(4′-Pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide was prepared by the literature method [7]. The complex Co(NIT4Py)(H_2PDA)(H_2O)$_3$ was synthesized by addition of aqueous (5 mL) H_2PDA (0.046 g, 0.3 mmol) to a MeOH mixture solution of $Co(ClO_4)_2 \cdot 6H_2O$ (0.110 g, 0.3 mmol) and NIT4Py (0.072 g, 0.3 mmol) at room temperature. The mixture was stirred for 40 min, and then filtered; the blue filtrate was allowed to stand at room temperature for one week to obtain blue crystals. Anal Found: (Calcd for $C_{19}H_{25}N_4O_9Co$): C, 44.86(44.54); H, 4.88(4.92); N, 11.08(10.94)%. The IR spectrum displays a strong broad bands at 1655, 1572 and 1354 cm^{-1}, attributed to the $\nu_{C=O}$ and $\nu_{C–O}$ stretching vibrations indicating the presence of H_2PDA. The weak band observed at 1372 cm^{-1} is assigned to the N–O absorption of NIT4Py.

2.3. *Crystal structure determination and refinement*

A blue single crystal ($0.24 \times 0.16 \times 0.10\ \mathrm{mm}^3$) of the title complex was selected and mounted on a Bruker Smart 1000 diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Data were collected at room temperature by φ–ω scan technique in the range $1.27° \le \theta \le 26.40°$. The collected data were reduced using the program SAINT [8] and empirical absorption correction was done by using the SADABS program [9]. The structure was solved with direct methods using SHELXS-97 [10]. The H atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 [11]. All non-hydrogen atoms were readily located and refined with anisotropic vibrational thermal parameters; $R_1 = \sum(\|F_o| - |F_c\|)/\Sigma|F_o|$ and $wR_2 = (\Sigma(|F_o|^2 - |F_c|^2)^2/(\Sigma w|F_o|^2)^2$, respectively, with the weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0602P)^2 + 0.3603P]$ where $P = (F_o^2 + 2F_c^2)/3$. A summary of the crystallographic data is given in table 1. Selected bond distances and angles are given in table 2.

3. Results and discussion

3.1. *Description of the crystal structure*

An ORTEP drawing of the title complex is shown in figure 1. The Co is six-coordinate in a distorted octahedral N_2O_4 environment. The equatorial plane is formed by N(1)

Table 1. Crystallographic data and processing parameters for Co(NIT4Py)(H_2PDA)(H_2O)$_3$.

Empirical formula	$C_{19}H_{25}CoN_4O_9$
Formula weight	512.36
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cell dimensions (Å, °)	
a	16.892(5)
b	7.371(2)
c	18.856(5)
β	108.770(5)
Volume, Z (Å^3)	2223.0(11), 4
Calculated density (g cm^{-3})	1.531
Absorption coefficient (mm^{-1})	0.830
F(000)	1064
Crystal size (mm^3)	$0.24 \times 0.16 \times 0.10$
θ Range for data collection (°)	1.27–26.40
Limiting indices	$-21 \le h \le 17$, $-8 \le k \le 9$, $-17 \le l \le 23$
Reflections collected	12381
Independent reflection	4541 [R(int) = 0.0334]
Completeness to $\theta = 25.02$	99.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000000 and 0.858951
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4541/0/302
Goodness-of-fit on F^2	1.090
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0368$, $wR_2 = 0.0953$
R indices (all data)	$R_1 = 0.0559$, $wR_2 = 0.1109$
Largest diff. peak and hole (e Å^{-3})	0.472 and −0.653

Table 2. Selected bond lengths (Å) and angles (°) for Co(NIT4Py)(H_2PDA)(H_2O)$_3$.

Co(1)–O(9)	2.0487(19)	O(1)–N(3)	1.278(3)
Co(1)–O(3)	2.0554(18)	Co(1)–N(1)	2.164(2)
Co(1)–O(8)	2.0641(18)	Co(1)–N(4)	2.167(2)
Co(1)–O(7)	2.1541(18)		
O(9)–Co(1)–O(3)	91.88(8)	O(3)–Co(1)–O(8)	178.96(7)
O(9)–Co(1)–O(8)	88.93(8)	O(9)–Co(1)–O(7)	88.50(7)
O(3)–Co(1)–O(7)	88.92(6)	O(8)–Co(1)–O(7)	91.75(7)
O(9)–Co(1)–N(1)	175.38(8)	O(3)–Co(1)–N(1)	86.66(8)
O(8)–Co(1)–N(1)	92.58(8)	O(9)–Co(1)–N(4)	88.08(7)

from NIT4Py, O(7) and O(9) from two water molecules and O(3) from the carboxyl group of H_2PDA. The Co–O bond lengths in the basal plane are 2.0641(18), 2.0487(19) and 2.0554(18) Å, for Co–O$_{\text{water}}$ and Co–O$_{\text{H}_2\text{PDA}}$, respectively. The Co–N bond length in the basal plane is 2.164(2) Å, for Co–N$_{\text{NIT4Py}}$. The axial positions are occupied by one nitrogen from the H_2PDA and one oxygen atom from water. The Co–N bond length and the Co–O bond length are 2.167(2) and 2.1541(18) Å, respectively. The torsion angle between the pyridyl rings for the NIT4Py ligand and the O–N–C–N–O moieties (O1, N3, C6, N2 and O2) is 31.4°.

A sketch of the intermolecular hydrogen bonds of the complex is shown in figure 2. The intermolecular hydrogen bonds occur between one oxygen atom from one carboxyl

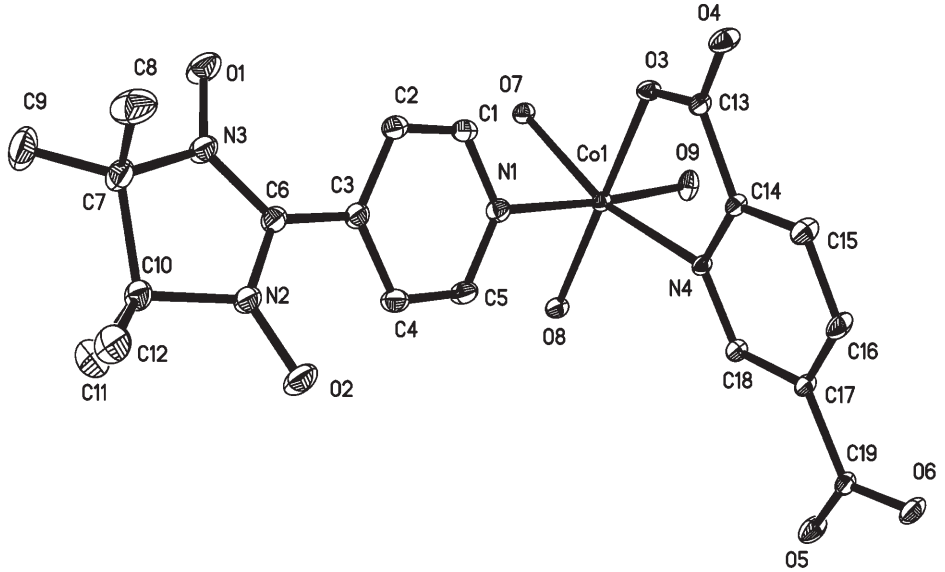

Figure 1. ORTEP view of Co(NIT4Py)(H_2PDA)(H_2O)$_3$. Thermal ellipsoids are scaled to enclose 15% probability.

group and one coordinated water molecule (2.716 Å for O(5)–O(7)) and between another oxygen from the carboxyl group and one coordinated water molecule (2.704 Å for O(6)–O(8). Intermolecular hydrogen bonds also occur between two oxygen atoms, one of which is carboxyl and the other coordinated water (2.800 Å for O(4)–O(8A), A: $-x$, $-y+2$, $-z+1$). Thus the complex possesses a layered topology in which two layers are parallel to the ac plane of H_2PDA-Co-H_2PDA groups, and the radicals lie in the interlayer regions of the two layers along the *b*-axis.

3.2. *Magnetic properties*

The magnetic susceptibilities, χ_M, of the complex were measured in the range 2–300 K at 10,000 G; plots of χ_M and $\chi_M T$ *versus* T are shown in figure 3. The $\chi_M T$ value per molecule at room temperature is 2.79 $cm^3\,K\,mol^{-1}$, higher than the spin-only value expected for one $S = 1/2$ and one $S = 3/2$ in an uncoupled spin system (2.25 $cm^3\,K\,mol^{-1}$). When further cooling, the $\chi_M T$ value decreases which indicate that weak antiferromagnetic interactions take place.

The magnetic data from 2 K to 300 K were fitted to equation (1) reduced from the spin Hamiltonian operator $\hat{H} = -2J\hat{S}_{\mathrm{NITR}}\hat{S}_{\mathrm{M}}$, where J is the interaction parameter between Co(II) ion and NIT4Py. An additional coupling parameter, zJ', was added in equation (2), a mean field correction, to take into account the magnetic behavior between Co(NIT4Py) units [12–14]. The theoretical expression of the molar magnetic susceptibility is

$$\chi_{bi} = \frac{Ng^2\beta^2}{KT}\left[\frac{10 + 2\exp(-4J/KT)}{5 + 3\exp(-4J/KT)}\right]^{-1} \qquad (1)$$

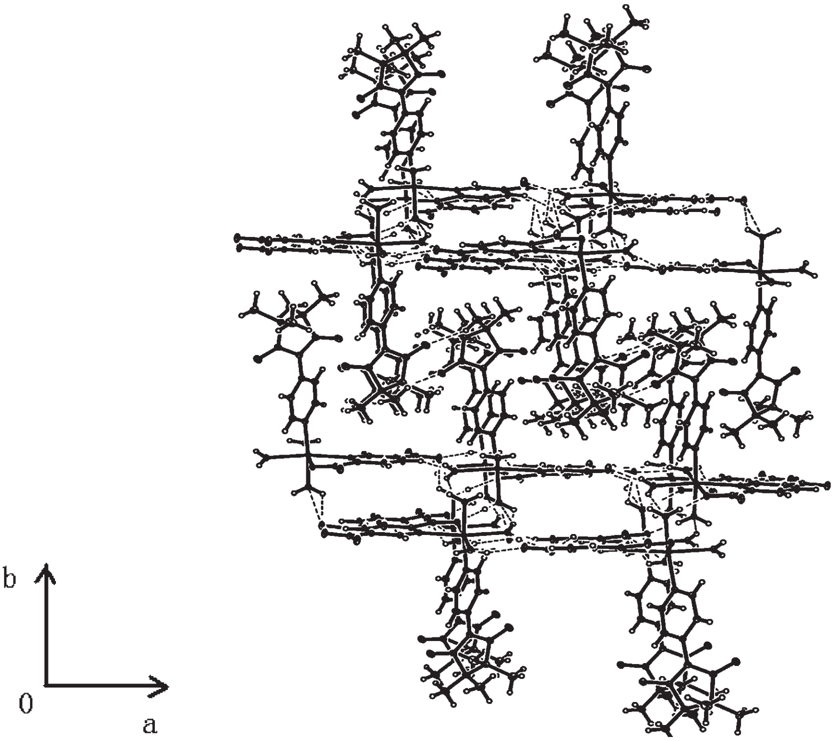

Figure 2. A three-dimensional representation of Co(NIT4Py)(H_2PDA)(H_2O)$_3$. Thermal ellipsoids are scaled to enclose 15% probability.

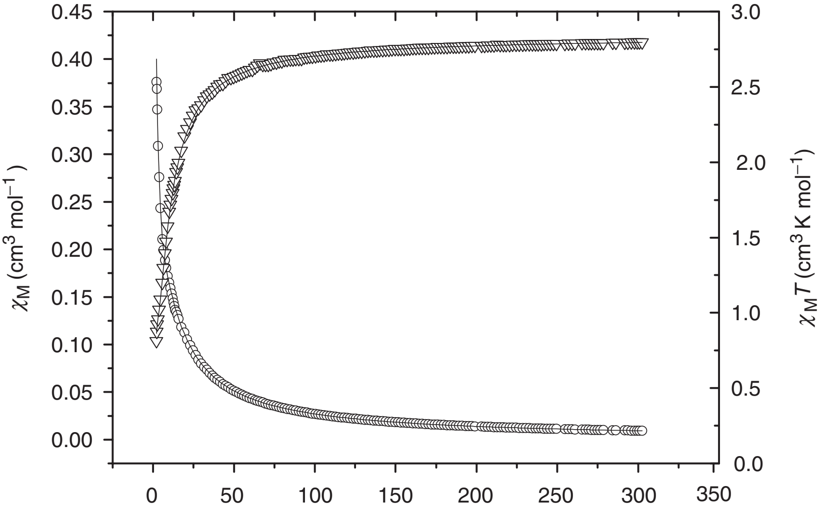

Figure 3. Temperature dependence of $\chi_M T$ (Δ) and χ_M (○) for Co(NIT4Py)(H_2PDA)(H_2O)$_3$ and their corresponding theoretical curves (solid lines).

$$\chi_{\mathrm{M}} = \frac{\chi_{bi}}{1 - (2zJ'/N\beta^2 g^2)\chi_{bi}}. \tag{2}$$

The best-fit parameters are $J = -2.86\,\mathrm{cm}^{-1}$, $zJ' = -0.36\,\mathrm{cm}^{-1}$, $g = 2.25$ with $R = 3.20 \times 10^{-4}$, where R is defined as $R = \sum[(\chi_{\mathrm{M}})_{\mathrm{obs}} - (\chi_{\mathrm{M}})_{\mathrm{calc}}]^2 / \sum(\chi_M)^2_{\mathrm{obs}}$. The negative J value implies a weak antiferromagnetic interaction between Co(II) ion and NIT4Py. The zJ' value of $-0.36\,\mathrm{cm}^{-1}$ indicates weak intermolecular antiferromagnetic exchange interaction. Weak antiferromagnetic interactions between Co(II) and NIT4Py were reported [15–17]. The overlap of one of the magnetic orbitals (d_{xy}, d_{yz}, d_{xz}) in Co(II) and the π^* orbital of the NIT4Py leads to weak antiferromagnetic interaction between Co(II) and NIT4Py. The weak intermolecular antiferromagnetic exchange interactions can be explained by the arrangement of the stacked shortest distance (O–O distances: 4.207 Å) among the N–O groups of neighboring NIT4Py.

4. Conclusion

A complex formulated as $\mathrm{Co(NIT4Py)(H_2PDA)(H_2O)_3}$ was obtained and characterized structurally and magnetically. The Co(II) ion presents a distorted octahedral geometry. The magnetic analysis revealed that there are weak intramolecular and intermolecular antiferromagnetic interactions in the compound.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 648609. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the Science Foundation of Tianjin university of science and technology of China (Nos. 20060442 and 0218264).

References

[1] O. Kahn. *Molecular Magnetism*, VCH, Weinheim (1993).
[2] P.M. Lahti. *Magnetic Properties of Organic Materials*, Marcel Dekker, New York (1999).
[3] C. Benelli, D. Gatteschi. *Chem. Rev.*, **102**(6), 2369 (2002).
[4] S. Hiraoka, T. Okamoto, M. Kozaki, D. Shiomi, K. Sato, T. Takui, K.A. Okada. *J. Am. Chem. Soc.*, **126**(1), 58 (2004).

[5] H.-L. Gao, L. Yi, B. Zhao, X.-Q. Zhao, P. Chen, D.-Z. Liao, S.-P. Yan. *Inorg. Chem.*, **45**(15), 5980 (2006).

[6] B. Zhao, X.-Y. Chen, P. Chen, D.-Z. Liao, S.-P. Yan, Z.-H. Jiang. *J. Am. Chem. Soc.*, **126**(47), 15394 (2004).

[7] E.F. Ullman, J.H. Osiecki, D.G. Boocock, B.R. Darcy. *J. Am. Chem. Soc.*, **94**(20), 7049 (1972).

[8] Siemens, SMART and SAINT, *Area Detector Control and Integration Software*, Siemens analytical X-ray System, Inc, Madison, WI (1996).

[9] G.M. Sheldrick. *SADABS, Program for Empirical Absorption Correction of Area Dectector Data*, University of Göttingen, Germany (1996).

[10] G.M. Sheldrick. *SHELXS 97, Program for the Solution of Crystal Structure*, University of Göttingen, Germany (1997).

[11] G.M. Sheldrick. *SHELXL 97, Program for the Crystal Structure Refinement*, University of Göttingen, Germany (1997).

[12] Y. Ma, D.-Z. Gao, W. Zhang, K. Yoshimura, D.-Z. Liao, Z.-H. Jiang, S.-P. Yang. *Inorg. Chim. Acta*, **359**, 14 (2006).

[13] K. Hayakawa, D. Shiomi, T. Ise, K. Sato, T. Takui. *J. Mater. Chem.*, **16**, 4146 (2006).

[14] J. Tao, Y.-Z. Zhang, Y.-L. Bai, O. Sato. *Inorg. Chem.*, **45**(13), 4877 (2006).

[15] L. Zhang, L.-C. Li, D.-Z. Liao, Z.-H. Jiang, S.-P. Yang, P.-W. Shen. *Inorg. Chim. Acta*, **320**, 141 (2001).

[16] H.-B. Zhou, S.-P. Wang, Z.-Q. Liu, D.-Z. Liao, Z.-H. Jiang, S.-P. Yang, P. Cheng. *Inorg. Chim. Acta*, **359**, 533 (2006).

[17] H.-B. Zhou, S.-P. Wang, W. Dong, Z.-Q. Liu, D.-Z. Liao, Z.-H. Jiang, S.-P. Yang, P. Cheng. *Inorg. Chem.*, **43**(15), 4552 (2004).