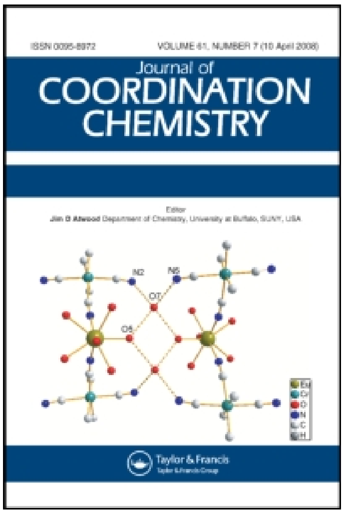

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Gao, Dong-Zhao , Sun, Ya-Qiu , Liao, Dai-Zheng , Jiang, Zong-Hui and Yan, Shi-Ping(2008) 'Synthesis and crystal structures of two metal-nitroxide complexes including a phenanthroline-substituted nitroxide radical', Journal of Coordination Chemistry, 61: 15, 2413 — 2421

To link to this Article: DOI: 10.1080/00958970801914082

URL: http://dx.doi.org/10.1080/00958970801914082

Journal of Coordination Chemistry
Vol. 61, No. 15, 10 August 2008, 2413–2421

Synthesis and crystal structures of two metal-nitroxide complexes including a phenanthroline-substituted nitroxide radical

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(*Received 1 July 2007; in final form 31 August 2007*)

Two metal-nitroxide complexes, $[Cu(IMPhenCOO)(CH_3OH)]_2 \cdot (NO_3)_2$ (**1**) and $[Co(NIT2Py)(H\text{-}2,5\text{-}PDA)_2] \cdot 0.5CH_3OH \cdot 2H_2O$ (**2**) (IMPhenCOOH = 2-carboxyl-9-(4,4,5,5-tetramethylimidazoline-1-oxyl-2-yl)-1,10-phenanthroline, NIT2Py = 2-(2′-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide and H_2-2,5-PDA = pyridine-2,5-dicarboxylic acid), have been synthesized and structurally characterized by X-ray diffraction. Complex **1** exists as discrete binuclear molecules and each copper(II) is five-coordinate with one tridentate radical ligand (IMPhenCOOH), the other radical ligand through one carboxyl oxygen and one methanol molecule. Complex **1** is the first structurally characterized complex containing the phenanthroline-substituted nitroxide radical. In **2**, the Co(II) is six-coordinate with one radical ligand (NIT2Py) and two bidentate pyridine-2,5-dicarboxylate anions.

Keywords: Copper(II) complex; Cobalt(II) complex; Crystal structure; Nitroxide radical; Phenanthroline

1. Introduction

During the last 20 years, nitroxide chemistry has developed for the "metal-radical approach" to design of molecular-based magnets [1, 2]. Free radicals capable of serving as bridging ligands for magnetic metal ions are of great interest in designing and constructing metal-radical hybrid spin systems that exhibit meta, ferri-, and ferromagnetism depending on the dimension of the extended structure and the mode of exchange interaction [3–5]. Oligopyridine biradicals (2,2′-bipyridine and 1,10-phenanthroline) [6, 7] have also been investigated, and in particular, α,α'-disubstituted 2,2′-bipyridine or 1,10-phenanthroline residues behave as a semirigid molecular tweezer that holds two radicals in a *cis* configuration when coordinated to a transition metal [8]. The use of oligopyridine nitroxide derivatives offers a strong

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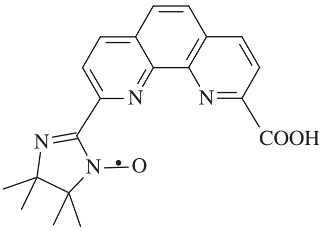
Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970801914082



Scheme 1. IMPhenCOOH.

coordination center, affording very stable metal complexes with a controlled geometry. However, no crystal structures including 1,10-phenanthroline-substituted nitroxide radicals have been reported. Herein we report two hetero-spin nitroxide complexes $[Cu(IMPhenCOO)(CH_3OH)]_2 \cdot (NO_3)_2$ (**1**) and $[Co(NIT2Py)(H\text{-}2,5\text{-}PDA)_2] \cdot 0.5CH_3OH \cdot 2H_2O$ (**2**), in which **1** is the first structurally characterized complex containing the 1,10-phenanthroline-substituted nitroxide radical (shown in scheme 1).

2. Experimental

2.1. *General*

All reagents were AR grade and used without further purification. Carbon, hydrogen and nitrogen elemental analyses were carried out on a Model 240 Perkin-Elmer elemental analyzer.

2.2. *Preparation of $[Cu(IMPhenCOO)(CH_3OH)]_2 \cdot (NO_3)_2$ (1)*

The nitroxide radical ligand containing 1,10-phenanthroline was prepared by the method described in the literature [7, 9] and not separated. The crude ligand and $Cu(NO_3)_2 \cdot 6H_2O$ were dissolved in 10 mL methanol. Then, the mixture was stirred for 2 h and the filtrate was allowed to stand at room temperature for four weeks. Brown block crystals of **1** suitable for X-ray analysis were obtained by slow evaporation. Anal. Calcd (%) for $C_{42}H_{44}Cu_2N_{10}O_{14}$: C, 48.46; H, 4.23; N, 13.46. Found (%): C, 48.58; H, 4.55; N, 13.71.

2.3. *Preparation of $[Co(NIT2Py)(H\text{-}2,5\text{-}PDA)_2] \cdot 0.5CH_3OH \cdot 2H_2O$ (2)*

The NIT2Py was prepared by the method described in the literature [10]. 34 mg pyridine-2,5-dicarboxylic acid (0.2 mmol) was dissolved in 10 mL water by adding several drops of triethylamine. The solution was added to 10 mL methanol solution obtained by mixing $Co(NO_3)_2 \cdot 6H_2O$ (30 mg, 0.1 mmol) and NIT2Py (23 mg, 0.1 mmol). The mixture was stirred for 2 h and the filtrate was allowed to stand at room temperature for four weeks. Dark brown block crystals of **2** suitable for X-ray analysis were obtained by slow evaporation. Anal. Calcd (%) for $C_{26.5}H_{30}CoN_5O_{12}$: C, 47.77; H, 4.81; N, 10.35. Found (%): C, 47.54; H, 4.52; N, 10.46.

Table 1. Crystal data and structure refinement for **1** and **2**.

Empirical formula	$C_{42}H_{44}Cu_2N_{10}O_{14}$	$C_{26.5}H_{30}CoN_5O_{12}$
Formula weight	1039.95	669.48
Temperature (K)	293(2)	294(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	8.852(3)	9.814(12)
b	9.525(3)	14.08(3)
c	14.569(5)	14.730(18)
α	78.533(4)	110.89(2)
β	72.478(4)	109.302(16)
γ	69.727(4)	97.16(2)
Volume (Å^3)	1092.7(6)	1725(5)
Z	1	2
Calculated density (Mg m^3)	1.580	1.288
Absorption coefficient (mm^{-1})	1.054	0.559
$F(000)$	536	693
Crystal size (mm^3)	$0.25 \times 0.20 \times 0.10$	$0.12 \times 0.10 \times 0.08$
θ range for data collection (°)	2.29–25.03	1.73–25.00
Limiting indices	$-10 \le h \le 10$, $-11 \le k \le 10$, $-17 \le l \le 9$	$-9 \le h \le 11$, $-16 \le k \le 15$, $-17 \le l \le 17$
Reflections collected/unique	5883/3804 [$R_{\text{int}} = 0.0255$]	9005/5827 [$R_{\text{int}} = 0.0873$]
Completeness to $\theta = 25.03$	98.2%	96.0%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.000000 and 0.271755	1.000000 and 0.664585
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/Restraints/Parameters	3804/1/316	5827/50/452
Goodness-of-fit on F^2	1.049	1.059
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0447$, $wR_2 = 0.1160$	$R_1 = 0.1216$, $wR_2 = 0.3106$
R indices (all data)	$R_1 = 0.0636$, $wR_2 = 0.1249$	$R_1 = 0.2100$, $wR_2 = 0.3822$
Largest diff. peak and hole (e Å^{-3})	0.635 and −0.559	1.205 and −0.830

2.4. *Crystal structure determinations*

All measurements were made on an APEX II CCD area detector equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). For **1**, a brown block crystal ($0.25 \times 0.20 \times 0.10$ mm^3) was selected and mounted on a glass fiber and a total of 5883 reflections were collected by an Φ–ω scan technique in the $2.29 \le \theta \le 25.03°$ range at room temperature with index ranges $-10 \le h \le 10$, $-11 \le k \le 10$, $-17 \le l \le 9$ including 3804 independent reflections ($R_{\text{int}} = 0.0255$). For **2**, a dark brown block crystal ($0.12 \times 0.10 \times 0.08$ mm^3) was selected and mounted on a glass fiber and a total of 9005 reflections collected by an Φ–ω scan technique in the $1.73 \le \theta \le 25°$ range at room temperature with index ranges $-9 \le h \le 11$, $-16 \le k \le 15$, $-17 \le l \le 17$ including 5827 independent reflections ($R_{\text{int}} = 0.0873$). Empirical absorption corrections by SADABS were carried out. The structure was solved by direct methods using SHELXS-97 [11] and refined with SHELXL-97 [12] using full-matrix least-squares techniques on F^2. All non-hydrogen atoms were refined anisotropically, while H atoms were located geometrically and refined isotropically. Crystallographic data of both complexes are given in table 1 and selected bond lengths and angles are listed in tables 2 and 3, respectively. Because of small crystal size and disorder of the solvent molecule, the R indices of **2** are a little high.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Cu(1)–O(7A)	1.915(2)	Cu(1)–N(1)	2.059(3)
Cu(1)–O(2)	1.924(3)	Cu(1)–O(1)	2.289(3)
Cu(1)–N(2)	1.995(3)	O(2)–N(3)	1.341(4)
O(7A)–Cu(1)–O(2)	89.57(10)	N(2)–Cu(1)–N(1)	81.91(10)
O(7A)–Cu(1)–N(2)	178.06(11)	O(7A)–Cu(1)–O(1)	95.69(11)
O(2)–Cu(1)–N(2)	88.95(11)	O(2)–Cu(1)–O(1)	107.23(12)
O(7A)–Cu(1)–N(1)	99.04(10)	N(2)–Cu(1)–O(1)	85.96(12)
O(2)–Cu(1)–N(1)	157.99(11)	N(1)–Cu(1)–O(1)	92.13(12)

Symmetry transformations used to generate equivalent atoms (A): $-x+1$, $-y+2$, $-z+2$.

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Co(1)–O(1)	1.884(7)	Co(1)–O(7)	1.889(6)
Co(1)–O(3)	1.904(6)	Co(1)–N(5)	1.923(10)
Co(1)–N(4)	1.953(8)	Co(1)–N(3)	1.971(9)
N(1)–O(1)	1.349(10)	N(2)–O(2)	1.428(17)
O(1)–Co(1)–O(7)	88.4(3)	O(1)–Co(1)–O(3)	93.3(3)
O(7)–Co(1)–O(3)	178.2(3)	O(1)–Co(1)–N(5)	85.5(3)
O(7)–Co(1)–N(5)	85.9(3)	O(3)–Co(1)–N(5)	93.5(3)
O(1)–Co(1)–N(4)	176.2(3)	O(7)–Co(1)–N(4)	94.1(3)
O(3)–Co(1)–N(4)	84.2(3)	N(5)–Co(1)–N(4)	91.7(3)
O(1)–Co(1)–N(3)	88.1(3)	O(7)–Co(1)–N(3)	88.8(3)
O(3)–Co(1)–N(3)	91.9(3)	N(5)–Co(1)–N(3)	171.8(3)
N(4)–Co(1)–N(3)	94.9(3)		

3. Results and discussion

3.1. *Synthesis of 1*

To synthesize the α,α'-disubstituted 1,10-phenanthroline nitroxide radical ligand and its complex, the radical ligand was prepared by the method described in the literature [7, 9]. The crude product includes *bis*(nitronyl nitroxide) and some side-products such as *bis*(imino nitroxide), mono(nitronyl nitroxide) and mono(imino nitroxide). The crude compounds were inconvenient to separate and were used to synthesize the complex directly. We did not obtain the desired complex but **1**, where IMPhenCOOH is an imino nitroxide radical containing 1,10-phenanthroline and the carboxyl group, a strong coordinating ligand and also a bridging ligand. Complex **1** is the first structurally characterized complex containing the 1,10-phenanthroline-substituted nitroxide radical.

3.2. *Crystal structure of 1*

$[Cu(IMPhenCOO)(CH_3OH)]_2 \cdot (NO_3)_2$ (**1**) is composed of a $[Cu(IMPhenCOO)(CH_3OH)]_2^{2+}$ cation and two NO_3^- anions. An ORTEP drawing of the cation is shown in figure 1; the cation is centro-symmetric as a four-spin system. Each Cu(II) ion is distorted five-coordinate square pyramidal (CuN_2O_3) with two radical ligands (IMPhenCOOH) and one methanol. The basal plane of Cu(II) is formed by two phenanthroline nitrogen atoms (N(1) and N(2)) and one nitroxide oxygen atom (O(2))

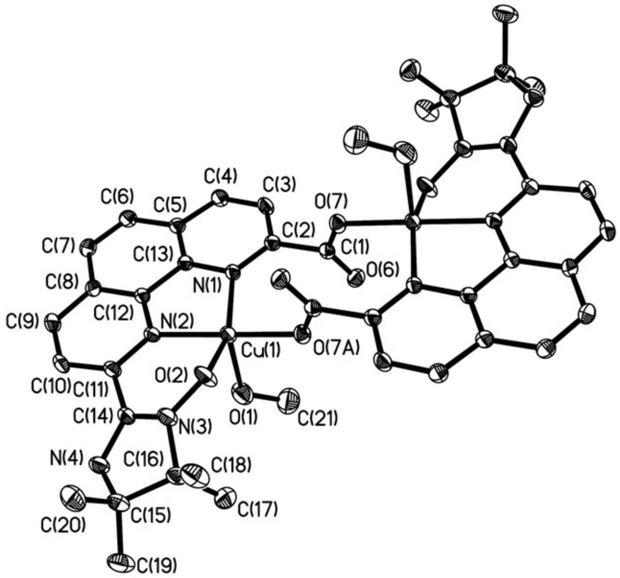


Figure 1. ORTEP drawing of $[\mathrm{Cu(IMPhenCOO)(CH_3OH)}]_2{}^{2+}$ in **1** showing the atom labelling scheme with 30% thermal ellipsoids and H atoms omitted for clarity.

of one tridentate IMPhenCOOH, while the fourth site is occupied by one carboxyl oxygen atom (O(7A), symmetry code A: $(-x+1, -y+2, -z+2)$ of the other radical ligand. In the basal plane, the Cu–N(1), Cu–N(2), Cu–O(2) and Cu–O(7A) bond lengths are 2.059(3), 1.995(3), 1.924(3) and 1.915(2) Å, respectively. The phenanthroline plane makes an angle of 8.7° with the basal plane of the Cu(II). The apical site is occupied by one oxygen atom (O(1)) from methanol with Cu–O(1) bond length of 2.289(3) Å, longer than the basal plane ones. In **1**, the nitroxide O(2)–N(3)–C(14)–N(4) moiety is almost coplanar indicating easy delocalization of the free electron within this moiety, however, the nitroxide moiety forms a dihedral angle of 24.1° with the phenanthroline plane. The IMPhenCOOH ligand coordinates to Cu(II) through the phenanthroline nitrogen (N(2)) and imino nitroxide oxygen (O(2)) forming a six-membered $\kappa^2 N$,O-chelate rarely found in the literature [13, 14], in contrast to the five-membered $\kappa^2 N,N$-chelate usually found for imino nitroxide complexes [2, 15–17]. The N(3)–O(2) bond length is 1.341(4) Å, a little longer than uncoordinated ones. Furthermore, two carboxyl groups of two radicals coordinate to two Cu(II) ions leading to a binuclear structure with Cu–Cu distance of 5.335(2) Å.

In **1**, there exist the intermolecular hydrogen bond interactions between the $[\mathrm{Cu(IMPhenCOO)\ (CH_3OH)}]_2^{2+}$ cations and the $\mathrm{NO_3^-}$ anions forming a 1D structure. The packing arrangement in a unit cell is shown in figure 2 and the 1D structure is shown in figure 3.

3.3. *Crystal structure of 2*

$[\mathrm{Co(NIT2Py)(H\text{-}2,5\text{-}PDA)_2}]\cdot 0.5\mathrm{CH_3OH}\cdot 2\mathrm{H_2O}$ (**2**) is composed of [Co(NIT2Py) $(\mathrm{H\text{-}2,5\text{-}PDA})_2$] units and uncoordinated methanol and water. An ORTEP drawing

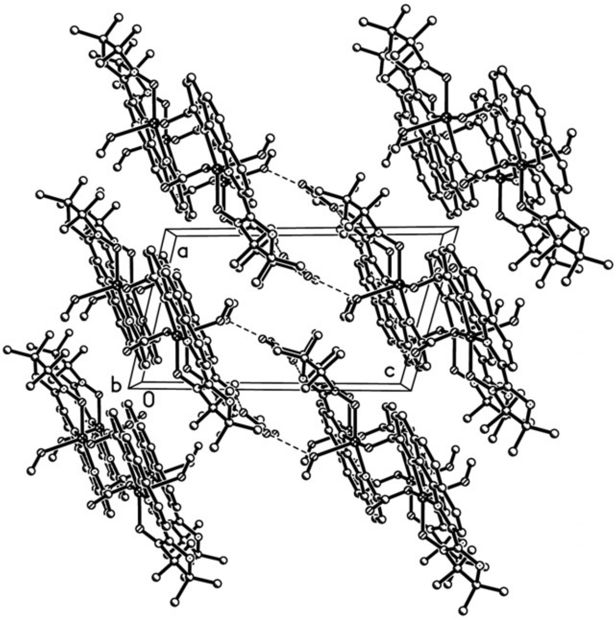


Figure 2. The packing arrangement in a unit cell of **1**.

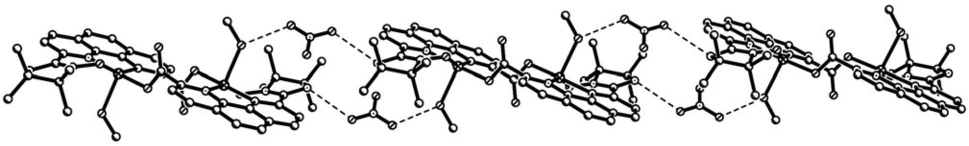


Figure 3. The 1D linear structure formed by hydrogen-bonding interactions of **1**.

of [Co(NIT2Py)(H-2,5-PDA)$_2$] is shown in figure 4. Each Co(II) is distorted octahedral (CoN_3O_3) with one radical ligand (NIT2Py) and two 2,5-PDA anions. The NIT2Py and two 2,5-PDA anions are bidentate chelating with Co–N and Co–O bond lengths of 1.884(7) to 1.971(9) Å. The uncoordinated carboxyl makes the 2,5-PDA anion bidentate, not bridging. The O(2) of the nitroxide group is disordered with occupancy equal to 0.5 indicating that half of the radical ligands have been reduced. The nitroxide O(1)–N(1)–C(1)–N(2)–O(2) is almost coplanar indicating delocalization of the free electron within this moiety; the nitronyl nitroxide moiety forms a dihedral angle of 27.7° with the pyridyl ring plane. In the intermolecular arrangement, the uncoordinated N–O groups are isolated and the shortest contact between the uncoordinated N–O groups of two radicals is 4.973 Å. The packing arrangement in a unit cell of **2** is shown in figure 5.

3.4. *The structure speciality of two complexes*

According to the literature results, α,α'-disubstituted 2,2′-bipyridine and 1,10-phenanthroline nitroxide biradicals both act as quadridentate ligands leading to

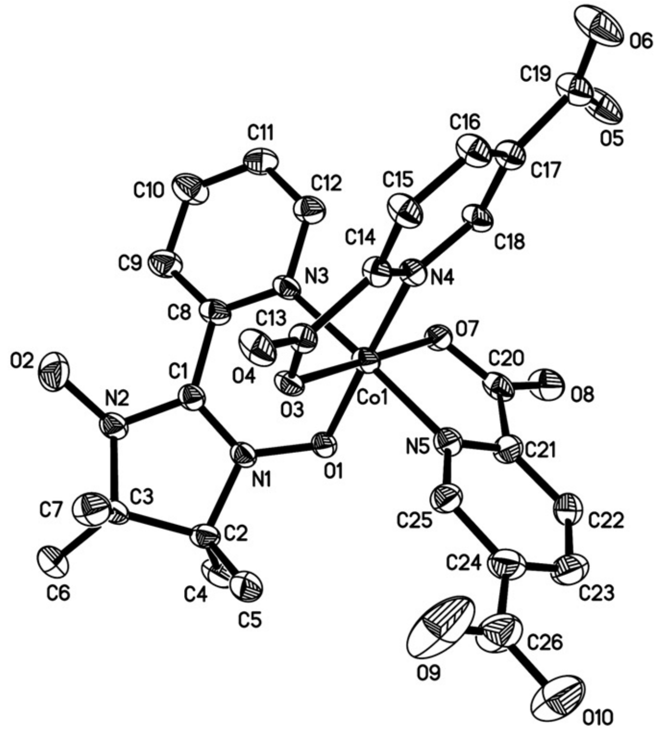


Figure 4. ORTEP drawing of $[Co(NIT2Py)(H\text{-}2,5\text{-}PDA)_2]$ in **2** showing the atom labelling scheme with 30% thermal ellipsoids and H atoms omitted for clarity.

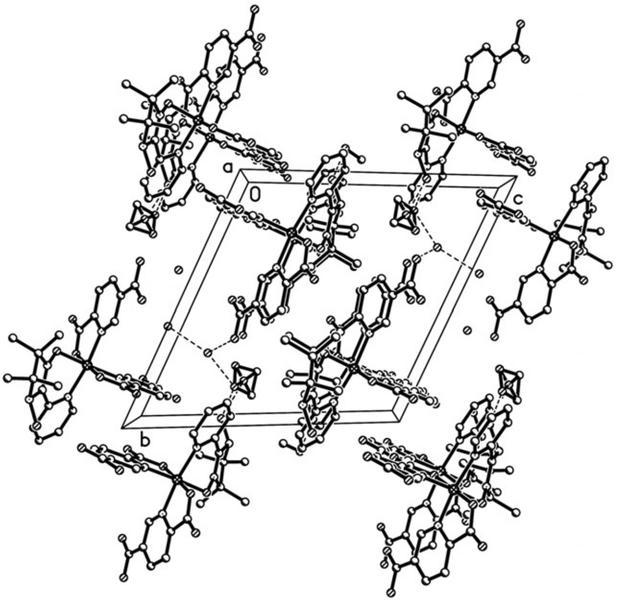


Figure 5. The packing arrangement in a unit cell of **2**.

mononuclear complexes [6, 9]. This limits development of both structure and magnetism to multi-dimensions. In **1**, however, the monoradical IMPhenCOOH is a tridentate ligand with the carboxyl group not coordinated to the same ion for tensile force. It is rather useful that the carboxyl group links metal ions into multi-nuclear or multi-dimensional structures.

In previous work, we reported several radical-metal complexes including NIT4Py or IM4Py radicals and 2,5-PDA or 2,4-PDA bridging ligands [18–20]. In those complexes, NIT4Py or IM4Py radicals coordinated to metal ions at the axial sites and 2,5-PDA or 2,4-PDA ligands either bridged the metal ions leading to a 1-D chain structure or linked each other through hydrogen bond interactions leading to a 2-D structure in the basal plane of the metal ion. Unfortunately, when the radical is NIT2Py in **2**, 2,5-PDA is bidentate, not bridging.

Supplementary material

CCDC 631978 and 635596 contain the supplementary crystallographic data for two complexes. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk).

Acknowledgements

This project was supported by the National Natural Science Foundation of China (Nos. 20331010 and 20571045) and Tianjin Normal University (No. 5RL053).

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