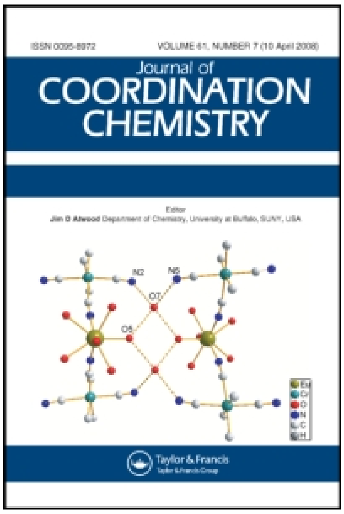

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A mercury(II)-radical complex with a 1D ladder structure

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To cite this Article Zhang, Jian-Ying , Liu, Cai-Ming , Zhang, De-Qing and Zhu, Dao-Ben(2008) 'A mercury(II)-radical complex with a 1D ladder structure', Journal of Coordination Chemistry, 61: 8, 1325 — 1332, First published on: 18 November 2007 (iFirst)

To link to this Article: DOI: 10.1080/00958970701598951

URL: http://dx.doi.org/10.1080/00958970701598951

Journal of Coordination Chemistry
Vol. 61, No. 8, 20 April 2008, 1325–1332

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A mercury(II)-radical complex with a 1D ladder structure

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(*Received 7 February 2007; accepted 24 May 2007*)

Interaction of HgI_2 with a new long rigid nitronyl nitroxide radical ligand, 2-[4-(2-pyridin-4-yl-vinyl)phenyl]-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (L), leads to the formation of the mercury-radical complex $[Hg_2I_4L_2]_n$ (**1**). The single crystal structure analysis reveals that **1** exhibits a one-dimensional (1D) ladder structure. Magnetic susceptibility data of **1** were simulated by a uniform chain model composed of the NIT–NIT dimers, indicating that there exist an antiferromagnetic exchange between the nitroxides within the dimer ($J_1 = -8.41\,\text{cm}^{-1}$) and a very weak interdimer antiferromagnetic interaction ($J_c = -0.39\,\text{cm}^{-1}$).

Keywords: Nitronyl nitroxide complex; Mercury complex; Ladder structure; Magnetic properties

1. Introduction

Nitronyl nitroxide radical has played an important role in the design and construction of molecular-based magnetic materials [1] because it possesses the following virtues: (1) it is a stable spin carrier; (2) it has delocalized unpaired spin distribution, which leads to various magnetic exchange interactions between the spin carriers. A series of metal-nitroxide complexes with 0-dimensional (0D), 1-dimensional (1D), 2-dimensional (2D) or 3-dimensional (3D) structures have been explored [2]. In order to coordinate metal ions, pyridyl-substituted nitronyl nitroxide radicals containing additional coordination sites have been utilized to construct various magnetic materials [3]. However, compared with extensive paramagnetic metal-radical complexes [4], only a few diamagnetic metal-radical complexes have been reported, including 0D, 1D and 2D structures [5]. Antiferro- and ferro-magnetic interactions can be mediated by diamagnetic metal centers such as Cu(I) [6], Ag(I) [7], Pb(II) [8], Zn(II) [9] and Cd(II) ions [10]. To the best of our knowledge, no 1D ladder radical complex has been reported though 1D ladder coordination polymers are not rare [11]. Herein, we report the synthesis, crystal structure and magnetic properties of the first 1D ladder

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970701598951

radical complex, $[Hg_2I_4L_2]_n$ (**1**) {L = 2-[4-(2-pyridin-4-yl-vinyl)phenyl]-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide}, which was prepared by reaction of a new long nitronyl nitroxide ligand L with HgI_2.

2. Experimental

2.1. *Materials and methods*

All commercial chemicals were used as received without further purification. 4-(2-Pyridin-4-yl-vinyl)benzaldehyde was synthesized using the reported method [12]. The solvents were purified by standard methods. *IR* spectra were recorded using a Perkin-Elmer 2000 spectrophotometer with KBr pellets in the range 4000–400 cm^{-1}. Elemental analyses were carried out on a Carlo-Erba-1106 elemental analyzer. Mass spectra were recorded using an HP-5989A spectrometer. Melting point was measured using an XT_4-100x apparatus and uncorrected. The magnetic susceptibility measurement was carried out on a polycrystalline sample (23.2 mg) using a Quantum Design MPMS-XL5 SQUID magnetometer in the temperature range 2–300 K and at applied field of 0.1T. Diamagnetic correction was estimated from Pascal's constants for all constituent atoms. Absorption spectra were measured with a Hitachi (model U-3010) UV-Vis spectrophotometer.

2.2. *Synthesis of L*

2,3-*bis*(Hydroxylamina)-2,3-dimethylbutane (148 mg, 1 mmol) and 4-(2-pyridin-4-yl-vinyl)benzaldehyde (183 mg, 1 mmol) were dissolved in the minimum amount of methanol. The solution was stirred overnight at ambient temperature to give white precipitate. The solvent was removed under reduced pressure. The residue was suspended in 40 ml CH_2Cl_2 and cooled to 0 °C before adding an aqueous solution of $NaIO_4$ (2 mmol). The resulting mixture was stirred vigorously for 10 min and filtered. The dark green organic layer was collected, washed with water and dried over Na_2SO_4. The green product was purified by chromatography on silica gel with ethyl acetate-petroleum ether (v/v: 2/1) as eluent. Yield: 68%. Anal. Calcd for $C_{20}H_{22}N_3O_2$ (%): C, 71.43; N, 12.50; H, 5.95. Found: C, 71.24; N, 12.27; H, 6.10. IR (cm^{-1}): 2983(w), 1596(s), 1390(m), 1363(s), 1132(w), 829(w). *M*/*z*: 336(M^+). UV-Vis {CH_3OH, λ_{max} [ε ($M^{-1}\,cm^{-1}$)]}: 331 nm (4.6×10^4), 385 nm (6.9×10^3).

2.3. *Synthesis of (1)*

To a 10 ml methanol solution of HgI_2 (46 mg, 0.1 mmol), L (35 mg, 0.1 mmol) dissolved in 4 ml methanol was added. The mixture was stirred for 2 h. After filtration, the filtrate was evaporated at room temperature for 6 days and X-ray-quality dark-blue crystals of **1** were obtained. Yield: 61%. Mp: 241–242°C. Anal. Calcd for $C_{20}H_{22}HgI_2N_3O_2$ (%): C, 30.34; N, 5.31; H, 2.78. Found: C, 30.12; N, 5.44; H, 2.61. IR (cm^{-1}): 2986(w), 1603(s), 1386(m), 1358(s), 1132(w), 829(w). UV-Vis {CH_3OH, λ_{max} [ε ($M^{-1}\,cm^{-1}$)]}: 325 nm (1.4×10^4), 388 nm (2.3×10^3), 599 nm (2.3×10^2).

2.4. *Crystal structure determination*

The diffraction data were collected at 293 K with Mo-Kα radiation ($\lambda = 0.071073$ nm) using a Bruker SMART APEX-CCD diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares on F^2_{obs} by using SHELXL 97 [13]. Empirical absorption corrections from Ψ scan were applied. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were allowed for as riding atoms. Crystal data, data collections and refinement parameters for **1** are given in table 1, selected bond lengths and angles for **1** are listed in table 2.

3. Results and discussion

3.1. *Crystal structure*

As shown in figures 1 and 2, **1** exhibits a 1D ladder structure constructed from the rectangle-like centrosymmetric dimer [$Hg_2I_4L_2$]. Two L ligands link to two Hg(II) ions in an anti-parallel mode, generating the rectangle-like dimer [$Hg_2I_4L_2$]. The dimers then connect with each other through the bridging role of the extra oxygen atom of the nitroxide unit to complete the ladder structure. The rigid nitronyl nitroxide radical acts as a 'T'-shape tridentate bridging ligand with a perpendicular coordination site from the nitrogen atom of the pyridine group and two coordination sites from the two oxygen atoms of the nitroxide unit. Each Hg(II) ion links to three L ligands and shows a distorted trigonal bipyramidal geometry, with a nitrogen atom from the pyridine group

Table 1. Crystal data and structural refinement parameters of **1**.

	Complex **1**
Formula	$C_{20}H_{22}HgI_2N_3O_2$
Fw	790.80
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	8.128(2)
b (Å)	9.862(2)
c (Å)	15.788(3)
α (°)	85.73(3)
β (°)	85.77(3)
γ (°)	67.31(3)
V (Å^3)	1163.0(4)
Z	2
T (K)	293(2)
λ(Mo-Kα) (Å)	0.71073
ρ_{Calcd} (Mg m^{-3})	2.258
μ(Mo-Kα) (mm^{-1})	9.291
Total data collected	6120
Unique data	3989
R(int)	0.0438
R_1^{a} [$I > 2\sigma(I)$]	0.0582
wR_2^{b} [$I > 2\sigma(I)$]	0.1491
Goodness-of-fit	1.042

[a] $R_1 = \|F_o| - |F_c\|/|F_o|$.
[b] $wR_2 = \{[w(F_o^2 - F_c^2)^2]/[wF_o^2]^2\}^{1/2}$.

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

Hg(1)–N(3)	2.451(8)	Hg(1)–I(2)	2.6312(12)
Hg(1)–I(1)	2.6374(13)	Hg–O(2)#1	2.690(7)
Hg–O(1)#2	2.980(7)	O(2)–Hg(1)#1	2.690(7)
O(1)–Hg(1)#2	2.980(7)		
N(3)–Hg(1)–I(2)	99.36(19)	I(2)–Hg(1)–I(1)	159.34(3)
N(3)–Hg(1)–I(1)	101.22(19)	O(2)#1–Hg(1)–O(1)#2	134.2(2)
I(2)–Hg(1)–O(2)#1	96.98(13)	I(1)–Hg(1)–O(2)#1	82.24(13)
N(3)–Hg(1)–O(2)#1	97.0(3)	N(3)–Hg(1)–O(1)#2	128.7(3)
I(2)–Hg(1)–O(1)#2	79.57(12)	I(1)–Hg(1)–O(1)#2	86.21(12)
N(1)–O(1)–Hg(1)#2	117.6(5)	N(2)–O(2)–Hg(1)#1	116.2(5)

Equivalent atoms at: #1 $-x-1, -y+1, -z$; #2 $-x-2, -y+1, -z$.

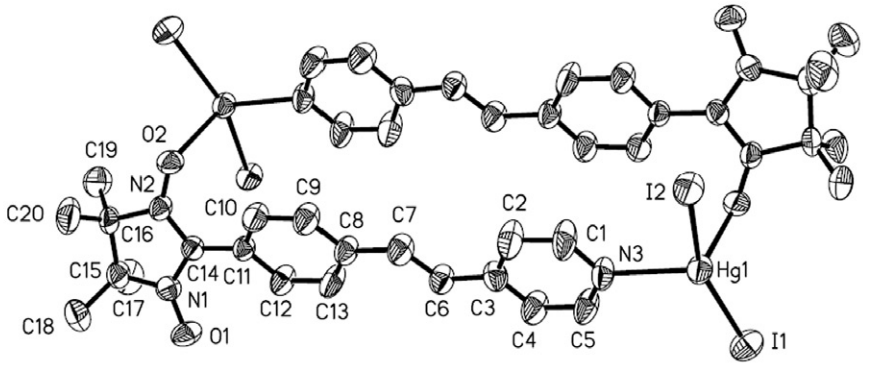


Figure 1. ORTEP diagram of one dimer unit of **1** with 50% probability displacement ellipsoids. All hydrogen atoms are omitted and some atoms are not labeled for ease of view.

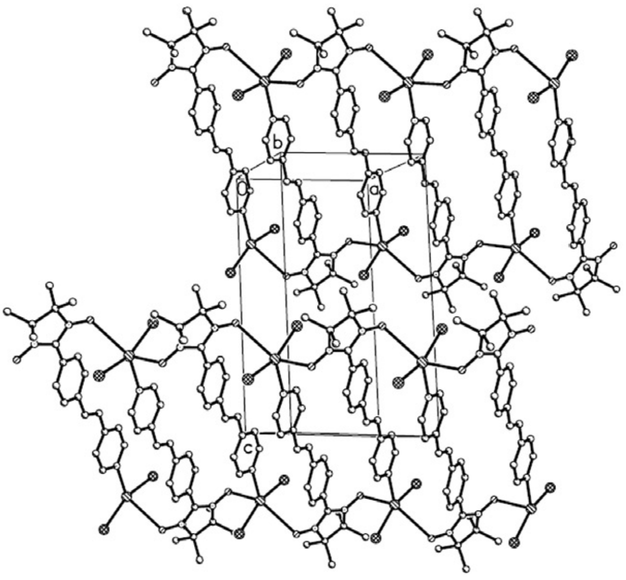


Figure 2. The ladder structure of **1**.

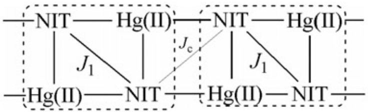
of one L ligand and two oxygen atoms of the other two L ligands in the plane, while two iodine atoms occupy axial positions. The pyridin-4-yl-vinylphenyl group of L is almost coplanar with the dihedral angle between the phenyl plane and the pyridine ring only 4.6°. The phenyl plane and the pyridine ring from two neighboring L ligands within the dimer are parallel to each other with the shortest interplane distances of about 3.681 and 3.736 Å, respectively, suggesting the existence of $\pi-\pi$ stacking interactions. The planes of ONCNO in the nitroxide units from every other L ligand are parallel to each other too, but deviate from the phenyl planes with a dihedral angle of 33.6°. The intradimer Hg–O(NIT) bond length [2.690(7) Å] is much smaller than the interdimer Hg–O(NIT) bond distance [2.980(7) Å], but both are obviously larger than that observed in [$HgBr_2$(2NITPy)] [2.521(9) Å] [14]. The bond length of Hg–N [2.451(8) Å] is smaller than that of [$HgBr_2$(2NITPy)] [2.666(11) Å] [14], but larger than that of [$HgBr_2$(4NITPy)] [2.292(8) Å] [14]. The I–Hg–I angle [159.34(3)°] is smaller than the Br–Hg–Br angle of [$HgBr_2$(2NITPy)] [162.05(7)°] [14], suggesting that the coordination environment of **1** deviates from the ideal trigonal bipyramid toward square pyramidal with the nitrogen atom in the axial position.

The intradimer and interdimer Hg–Hg distances separated by L are 12.471 and 13.871 Å, respectively, while the Hg–Hg distance linked by two oxygen atoms of the nitroxide unit is 8.128 Å. The $[Hg_2I_4L_2]_n$ ladders are arranged along the *a*-axis (figure 2). To the best of our knowledge, **1** is the first 1D ladder complex of nitronyl nitroxide. Because there is no close inter-ladder contact between the sites of significant spin density in **1**, the magnetic effects discussed in the following section are mainly attributed to intra-ladder exchanges.

3.2. *Magnetic properties*

Based on the above structural analysis, **1** is not a uniform 1D ladder complex, because the interdimer Hg–O(NIT) bond length is much larger than the intradimer Hg–O(NIT) bond distance. There are two main types of magnetic couplings between nitroxides in **1**: the intradimer one (J_1) and the interdimer one (J_2), as illustrated in scheme 1. Therefore, the magnetic susceptibility of **1** can be analyzed using an approximate model method [15], and **1** is treated as a uniform chain with the NIT-NIT dimer as a subunit.

Figure 3 shows the plots of $\chi_M T$ and χ_M *versus* T for **1**. The $\chi_M T$ at 300 K is 0.73 emu K mol^{-1}, a little smaller than the value expected for two independent spin $S = 1/2$ (0.75 emu K mol^{-1}), assuming $g = 2.0$. In the temperature range of 70–300 K, the value of $\chi_M T$ slightly decreases from 0.73 to 0.70 emu K mol^{-1}, then drops rapidly below 70 K. Above 20 K, the plot of $1/\chi_M$ *versus* T follows the Curie–Weiss law, and the corresponding Weiss constant is calculated to be −8.93 K, indicating the antiferromagnetic interaction.



Scheme 1. Illustration of the magnetic exchange interactions in the ladder chain, J_1 and J_c reflect the intradimer and interdimer magnetic exchanges, respectively.

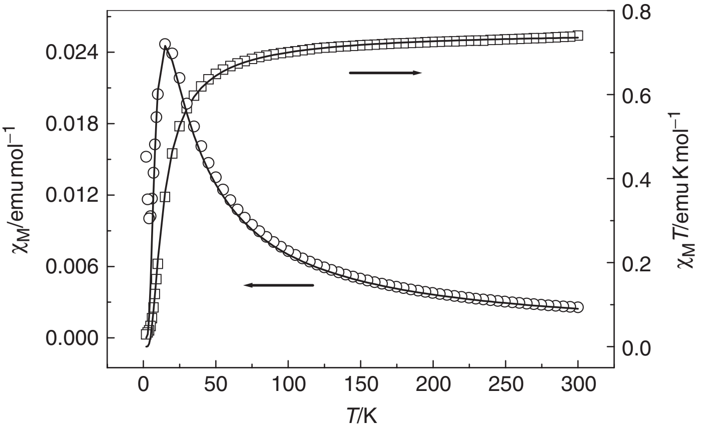


Figure 3. Plots of $\chi_M T$ and χ_M *vs.* T of **1**. The solid lines represent the best theoretical fitting.

To fit the magnetic susceptibility data, equations (1) [16] and (2) were utilized, which are derived from the Hamiltonians $\hat{H} = -2J_1\hat{S}_{\mathrm{NIT1}}\hat{S}_{\mathrm{NIT2}}$ {for the dimer} and $\hat{H} = -2J_c\sum\hat{S}_{\mathrm{T,i}}\hat{S}_{\mathrm{T,i+1}}$ {$\hat{S}_{\mathrm{T}}$ for dimer as a classical system}, respectively, assuming $g_{\mathrm{Cu}} = g_{\mathrm{NIT}} = g$. The parameters J_1 and J_c reflect the intradimer and the interdimer magnetic exchanges, respectively. The other constants, N, k and β, have their usual meanings.

$$\chi_d = \frac{2N}{kT}\frac{g^2\beta^2}{[3+\exp(-2J1/kT)]} \tag{1}$$

$$\chi_T = \frac{N}{3kT}g^2\beta^2 S_{\mathrm{T}}(S_{\mathrm{T}}+1) \tag{2}$$

$$\chi_{\mathrm{Chain}} = \frac{N}{3kT}\frac{g^2\beta^2 S_{\mathrm{T}}(S_{\mathrm{T}}+1)(1+u)}{(1-u)} \tag{3}$$

Here $u = \coth(J_c\ S_{\mathrm{T}}\,(S_{\mathrm{T}}+1)/kT) - kT/J_c S_{\mathrm{T}}\,(S_{\mathrm{T}}+1)$

The best fit to the magnetic data of **1** gives $g = 2.0$, $J_1 = -8.41\,\mathrm{cm}^{-1}$ and $J_c = -0.39\,\mathrm{cm}^{-1}$ with $R = 7\times10^{-5}$ ($R = \sum[(\chi_M)_{\mathrm{obs}} - (\chi_M)_{\mathrm{Calcd}}]^2/\sum[(\chi_M)_{\mathrm{obs}}]^2$). The result indicates that both types of magnetic exchanges are antiferromagnetic. In the absence of effective charge transfer through the Hg(II) ion as indicated by UV-vis spectra of **1**, McConnell's I mechanism is a useful tool to explain the exchange of organic radicals [17]. It is well known that the unpaired spin distribution is delocalized on the NO groups with the same spin densities on each atom. Because the pyridin-4-yl-vinylphenyl group of L ligand is almost coplanar in **1**, there are alternating negative and positive spin densities on the carbon backbone of the phenyl and pyridine rings due to the spin polarization. The adjacent atoms of the neighboring nitroxides carry equal spin densities, so the interactions between the *para*-stacking nitroxides are antiferromagnetic [14, 18]. In addition, the main spin density of the pyridine-substituted nitronyl nitroxide remains in the five-member ring of the nitroxide unit. As a result, the antiferromagnetic interactions are weak. Furthermore, the intradimer magnetic exchange is relatively stronger than the interdimer one. This can be explained by the structural factor: as mentioned above, the π–π stacking interaction makes the distance between two L ligands within the dimer to be shorter than the interdimer L–L distance, inducing the intradimer magnetic interaction between nitroxides easier with respect to the interdimer magnetic interaction.

In summary, the first 1D ladder radical complex $[Hg_2I_4L_2]_n$ (**1**) constructed from a new long rigid radical ligand 2-[4-(2-pyridin-4-yl-vinyl)phenyl]-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide and HgI_2 was synthesized and characterized. It exhibits two types of intrachain antiferromagnetic interactions.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center with the CCDC reference number 636042. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 20473096 and 20671093), Major State Basic Research Development Program of P. R. China (2001CB610507), Center for Molecular Science (CMS-CX200405), Institute of Chemistry and Chinese Academy of Sciences.

References

[1] (a) A. Caneschi, D. Gatteschi, R. Sessoli, P. Rey. *Acc. Chem. Res.*, **22**, 392 (1989); (b) D. Gatteschi, P. Rey. In *Magnetic Properties of Organic Materials*, P.M. Lahti (Ed.), Marcel Dekker: New York, (1999); (c) H. Iwamura, K. Inoue, T. Hayamizu. *Pure Appl. Chem.*, **68**, 243 (1996); (d) A. Caneschi, D. Gatteschi, J.P. Renard, P. Rey, R. Sessoli. *Inorg. Chem.*, **28**, 3314 (1989); (e) C. Stroh, E. Belorizky, P. Turek, H. Bolvin, R. Ziessel. *Inorg. Chem.*, **42**, 2938 (2003); (f) D. Luneau, C. Stroh, J. Cano, R. Ziessel. *Inorg. Chem.*, **44**, 633 (2005); (g) M. Sorai, M. Nakano, Y. Miyazaki. *Chem. Rev.*, **106**, 976 (2006); (h) S. Kaizaki. *Coord. Chem. Rev.*, **250**, 1804 (2006).

[2] For examples: (a) A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M.G. Pini, M.A. Novak. *Angew. Chem. Int. Ed.*, **40**, 1760 (2001); (b) D. Luneau, G. Resoan, P. Rey, A. Grand, A. Caneschi, D. Gatteschi, J. Laugier. *Inorg. Chem.*, **32**, 5616 (1993); (c) Z.-L. Liu, Z.-L. Lu, D.-Q. Zhang, Z.-H. Jiang, L.-C. Li, C.-M. Liu, D.-B. Zhu. *Inorg. Chem.*, **43**, 6620 (2004); (d) H.-M. Wang, Z.-L. Liu, C.-M. Liu, D.-Q. Zhang, Z.-L. Lu, H. Geng, Z.-G. Shuai, D.-B. Zhu. *Inorg. Chem.*, **43**, 4091 (2004); (e) Z.-L. Liu, L.-C. Li, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan. *Cryst. Growth Des.*, **5**, 783 (2005); (f) K.E. Vostrikova, D. Luneau, W. Wernsdorfer, P. Rey, M. Verdaguer. *J. Am. Chem. Soc.*, **122**, 718 (2000); (g) A. Caneschi, D. Gatteschi, N. Lalioti, R. Sessoli, L. Sorace, V. Tangoulis, A. Vindigni. *Chem. Eur. J.*, **8**, 286 (2002); (h) D. Luneau, P. Rey. *Coord. Chem. Rev.*, **249**, 2591 (2005).

[3] (a) M.G.F. Vaz, L.M.M. Pinheiro, H.O. Stumpf, A.F.C. Alcântara, S. Golhen, L. Ouahab, O. Cador, C. Mathonière, O. Kahn. *Chem. Eur. J.*, **5**, 1486 (1999); (b) H.-H. Lin, S. Mohanta, C.-J. Lee, H.-H. Wei. *Inorg. Chem.*, **42**, 1584 (2003); (c) T. Tsukuda, T. Suzuki, S. Kaizaki. *J. Chem. Soc., Dalton Trans.*, 1721 (2002); (d) H. Oshio, M. Yamamoto, T. Ito. *Inorg. Chem.*, **41**, 5817 (2002); (e) L.-Y. Wang, B. Zhao, C.-X. Zhang, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan. *Inorg. Chem.*, **42**, 5804 (2003).

[4] (a) K. Fegy, D. Luneau, T. Ohm, C. Paulsen, P. Rey. *Angew. Chem. Int. Ed.*, **37**, 1270 (1998); (b) M. Baskett, P.M. Lahti, A. Paduan-Filho, N.F. Oliveira, Jr. *Inorg. Chem.*, **44**, 6725 (2005); (c) L.M. Field, P.M. Lahti. *Inorg. Chem.*, **42**, 7447 (2003); (d) T. Ise, T. Ishida, D. Hashizume, F. Iwasaki, T. Nogami, *Inorg. Chem.*, **42**, 6106 (2003); (e) F. Lanfranc de Panthou, E. Belorizky, R. Calemczuk, D. Luneau, C. Marcenat, E. Ressouche, P. Turek, P. Rey. *J. Am. Chem. Soc.*, **117**, 11247 (1995).

[5] (a) L.-Y. Wang, C.-X. Zhang, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan. *J. Mol. Struct.*, **657**, 1 (2003); (b) C.-J. Lee, H.-H. Wei. *Inorg. Chem. Acta*, **310**, 89 (2000); (c) M. Fettouhi, B.E. Ali, A.M. El-Ghanam, S. Golhen, L. Ouahab, N. Daro, J.-P. Sutter. *Inorg. Chem.*, **41**, 3705 (2002); (d) G. Frances, F.M. Romero, A. Neels, H. Stoeckli-Evans, S. Decurtins. *Inorg. Chem.*, **39**, 2087 (2000); (e) S.-P. Wang, D.-J. Li, Y. Song, D.-Z. Gao, J. Chen, Z.-Q. Liu, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan. *Z. Anorg. Allg. Chem.*, **631**, 1702 (2005); (f) H. Oshio, M. Yamamoto, T. Ito. *J. Chem. Soc., Dalton Trans.*, 2641 (1999); (g) C. Stroh, P. Turek, P. Rabu, R. Ziessel. *Inorg. Chem.*, **40**, 5334 (2001).

[6] H. Oshio, T. Watanabe, A. Ohto, T. Ito, U. Nagashima. *Angew.Chem. Int. Ed. Engl.*, **33**, 670 (1994).

[7] (a) D.-Q. Zhang, L. Ding, W. Xu, H.-M. Hu, D.-B. Zhu, Y.-Y. Huang, D.-C. Fang. *Chem. Commun.*, 44 (2002); (b) H.-H. Lin, H.-H. Wei. *Inorg. Chem. Commun.*, **7**, 27 (2004).

[8] H. Oshio, A. Ohto, T. Ito. *Chem. Commun.*, 1541 (1996).

[9] (a) H. Oshio, M. Yamamoto, N. Hoshino, T. Ito. *Polyhedron*, **20**, 1621 (2001); (b) C.-X. Zhang, J. Sheng. *Trans. Met. Chem.*, **31**, 93 (2006); (c) L.-Y. Wang, L.-F. Ma, Y.-F. Wang, B. Zhao, Z.-H. Jiang, D.-Z. Liao, S.-P. Yan. *Inorg. Chem. Commun.*, **10**, 212 (2007).

[10] (a) C.J. Lee, H.H. Wei, G.H. Lee, Y. Wang. *Inorg. Chem. Commun.*, **3**, 690 (2000); (b) S.-P. Wang, D.-Z. Gao, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan. *Trans. Met. Chem.*, **31**, 214 (2006).

[11] For examples: (a) Y. Chen, B.-Q. Ma, Q.-D. Liu, J.-R. Li, S. Gao. *Inorg. Chem. Commun.*, **3**, 319 (2000); (b) Z.-L. Liu, D.-Q. Zhang, C.-M. Liu, D.-B. Zhu. *Chem. Lett.*, **33**, 180 (2004); (c) B. Sui, W. Zhao, G.-H. Ma, T. Okamura, J. Fan, Y.-Z. Li, S.-H. Tang, W.-Y. Sun, N. Ueyama. *J. Mater. Chem.*, **14**, 1631 (2004); (d) P. Losier, M.J. Zaworotko. *Angew. Chem., Int. Ed. Engl.*, **35**, 2779 (1996); (e) P. Gamez, P. deHoog, O. Roubeau, M. Lutz, W.L. Driessen, A.L. Spek, J. Reedijk. *Chem. Commun.*, 1488 (2002).

[12] H. Masaki, M. Yashunari, K. Satoshi, S. Kazuhiko. *Chem. Lett.*, 907 (1987).

[13] G.M. Sheldrick. *SHELX 97, PC Version*, University of Göttingen (1997).

[14] C.-J. Lee, C.-H. Huang, H.-H. Wei, Y.-H. Liu, G.-H. Lee, Y. Wang. *J. Chem. Soc., Dalton Trans.*, 171 (1998).

[15] (a) H.Z. Kou, B.C. Zhou, S. Gao, D.-Z. Liao, R.-J. Wang. *Inorg. Chem.*, **42**, 5604 (2003); (b) G. Wrzeszcz, L. Dobrzanska, A. Wojczak, A. Grodzicki. *J. Chem. Soc., Dalton Trans.*, 2862 (2002); (c) S.G. Kang, K. Ryu, S.-K. Jung, J. Kim. *Inorg. Chim. Acta*, **293**, 140 (1999); (d) A. Caneschi, D. Gatteschi, M.C. Melandri, P. Rey, R. Sessoli. *Inorg. Chem.*, **29**, 4228 (1990).

[16] (a) X.-J. Lin, Z. Shen, Y. Song, H.-J. Xu, Y.-Z. Li, X.-Z. You. *Inorg. Chim. Acta*, **385**, 1963 (2005); (b) B. Bleaney, K.D. Bowers. *Proc. R. Soc. London, Ser. A*, **214**, 451 (1952).

[17] (a) H.M. McConnell. *J. Chem. Phys.*, **39**, 1910 (1963); (b) C. Kollmar, O. Kahn. *Acc. Chem. Res.*, **26**, 259 (1993).

[18] F.M. Romero, R. Ziessel, M. Bonnet, Y. Pontillon, E. Ressouche, J. Schweizer, B. Delley, A. Grand, C. Paulsen. *J. Am. Chem. Soc.*, **122**, 1298 (2000).