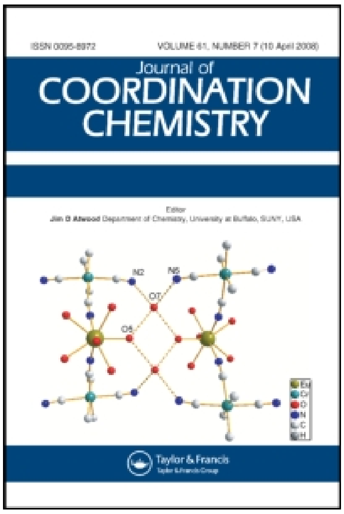

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Synthesis, crystal structure, and properties of a new zinc coordination polymer [Zn(PMP)$_2$Cl]_n

Rui-Bo Xu[ab]; Xing-You Xu[c]; Yu-He Yin[d]; Ming-Yan Wang[a]; Xu-Jie Yang[b]; Qian-Qian Xu[a]; Li-Ping Ma[a]
[a] Department of Chemical Engineering, Huaihai Institute of Technology, Lianyungang 222005, P.R. China [b] Laboratory of Soft Chemistry and Functional Materials, Nanjing University of Science and Technology (Ministry of Education), Nanjing 210094, P.R. China [c] Huaiyin Institute of Technology, Huaian 223003, P.R. China [d] School of Chemistry and Life Science, Changchun University of Technology, Changchun 130012, P.R. China

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Synthesis, crystal structure, and properties of a new zinc coordination polymer [Zn(PMP)$_2$Cl]$_n$

RUI-BO XU†‡, XING-YOU XU*§, YU-HE YIN¶, MING-YAN WANG†,
XU-JIE YANG‡, QIAN-QIAN XU† and LI-PING MA†

†Department of Chemical Engineering, Huaihai Institute of Technology,
Lianyungang 222005, P.R. China
‡Laboratory of Soft Chemistry and Functional Materials, Nanjing University of Science
and Technology (Ministry of Education), Nanjing 210094, P.R. China
§Huaiyin Institute of Technology, Huaian 223003, P.R. China
¶School of Chemistry and Life Science, Changchun University of Technology,
Changchun 130012, P.R. China

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A new coordination polymer [Zn(PMP)$_2$Cl]$_n$ (PMP = 1-phenyl-3-methyl-5-pyrazolone) has been prepared by the reaction of zinc chloride and PMP, and characterized by elemental analysis, IR, UV, and fluorescence spectra, TG/DTA, and electrochemical analysis. Single crystal X-ray diffraction revealed that the complex is monoclinic, space group $P\,2(1)/n$, with $a = 10.850(17)$, $b = 17.578(2)$, $c = 10.997(18)$ Å, $\beta = 104.999(3)°$, $V = 2025.8(5)$ Å^3, $Z = 4$, $D_c = 1.470\ \mathrm{mg\,m^{-3}}$, $F(000) = 920$, goodness-of-fit = 0.905, and $R_1 = 0.0441$. The complex is a 1-D coordination polymer, and the coordination geometry of Zn(II) is a distorted tetrahedron.

Keywords: PMP; Zinc coordination polymer; Crystal structure; Electrochemistry; Thermal analysis

1. Introduction

Self-assembly of molecules into well-defined supramolecules and applications in optical and magnetic devices, catalysis, adsorption, fluorescence, and molecular recognition have received attention, especially metal-organic framework structures based on transition metals and multifunctional bridging ligands [1–3]. Metal coordination polymers with 1-, 2-, and 3-D frameworks have been the subject of intensive research, most of which were constructed with ligands containing carboxylates [4–8], relatively less with other ligands.

Zinc is an essential transition metal element in all living systems, and plays important roles in metabolism, as a structural template in protein folding, etc. [9–13]. Pyrazolone compounds are of biological and chemical importance, widely used in many fields, especially in clinical (principally as hypnotic drugs and producing depressive effects on the central nervous system) and analytical applications [14–16].

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*Corresponding author. Email: xuxy@hhit.edu.cn

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The 1-phenyl-3-methyl-5-pyrazolone (PMP), produces marked attenuation of brain damage caused by ischemia-reperfusion, and its pharmacological actions were attributed to antioxidant activity, as a potent hydroxyl radical scavenger [17]. Synthesis of rare earth complex, fluorescent properties, and some applications of PMP derivatives have been reported [15–19], but no reports on the PMP complex is found. Because PMP possesses carbonyl group and imino group, it can display several different coordination modes. Here, as a multidentate ligand, PMP was employed in self-assembly to construct complex with zinc(II) and a new coordination polymer $[Zn(PMP)_2Cl]_n$ was obtained. To the best of our knowledge, it is the first single crystal of a PMP complex. Synthesis, crystal structure, fluorescence, thermal stability, and electrochemical properties of the title complex were reported.

2. Experimental

2.1. *Synthesis of* $[Zn(PMP)_2Cl]_n$

A solution of $ZnCl_2$ (272 mg, 2 mmol in 5 mL anhydrous methanol) was added dropwise into the solution of PMP (871 mg, 5 mmol in 20 mL anhydrous methanol) at room temperature with constant stirring, then 8 mL chloroform was added. The resulting mixture was stirred and refluxed at 60°C for 3 h; after cooling, no precipitate was found. On slow evaporation of the solution for several days, pink block crystals suitable for X-ray analysis were collected and washed with a small amount of methanol and dried in vacuum. m.p.: 291–293°C (dec.). Anal. Calcd for $C_{20}H_{19}ClN_4O_2Zn$ (%): C, 53.60; H, 4.27; N, 12.50. Found (%) : C, 53.22; H, 4.56; N, 12.77. The molar conductance of the complex in anhydrate methanol was $20.9\ \Omega^{-1}\,cm^2\,mol^{-1}$, much lower than expected for a 1 : 1 electrolyte, indicating that the complex is a non-electrolyte [20].

2.2. *X-ray crystallography*

Diffraction data for a crystal of dimensions $0.21 \times 0.16 \times 0.13\ mm^3$ were collected on a Bruker Smart CCD diffractometer with graphite monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation by using the ω-2θ scan technique ($2.24° \le \theta \le 25.00°$) at 293(2) K. The crystal structure was solved by direct methods and Fourier synthesis (SHELXS-97) [21] and refined by full-matrix least-squares on F^2 with SHELXL-97 [21]. The non-hydrogen atoms were refined anisotropically and hydrogens were added according to theoretical models. A summary of crystallographic data and refinement parameters is given in table 1.

2.3. *Reagents and instrumentation*

PMP and zinc chloride were purchased from commercial sources, of reagent grade, and used as received. IR spectrum was recorded on a Spectrum One BFT-IR spectrophotometer using KBr pellet from 4000 to 450 cm^{-1}. The ^1H NMR spectrum was recorded on a Bruker DRX300 MHz spectrometer. The electronic spectrum was recorded on a UV-2550 spectrophotometer. Fluorescence emission spectra were

Table 1. Crystal data and structure refinement details for $[Zn(PMP)_2Cl]_n$.

Empirical Formula	$C_{20}H_{19}ClN_4O_2Zn$
Formula weight	448.21
Color	Pink
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Radiation	Mo Kα
Crystal system	Monoclinic
Space group	$P\ 2(1)/a$
Unit cell dimensions (Å, °)	
a	10.850(17)
b	17.578(2)
c	10.997(18)
β	104.999(3)
Volume ($Å^3$), Z	2025.8(5), 4
Calculated density ($mg\ m^{-3}$)	1.470
Absorption coefficient (mm^{-1})	1.367
$F(000)$	920
θ range for data collection (°)	2.24–25.00
Reflections collected	10,317
Independent reflection	3526 [$R_{int} = 0.0700$]
Completeness to $2\theta = 25.00$ (%)	99.0
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3526/18/253
Goodness-of-fit on F^2	0.905
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0441$, $wR_2 = 0.0492$
R indices (all data)	$R_1 = 0.0989$, $wR_2 = 0.0561$
Largest difference peak and hole ($e\ Å^{-3}$)	0.465 and −0.483

performed on a FL3-TCSPC spectrophotometer at room temperature. Molar conductivity was measured at room temperature with a DDX-11A conductivity meter. Electrochemical experiments were carried out with a CHI 660A electrochemistry workstation (CHI USA) connected to a Pentium 200 MHz PC. Thermal analyses were performed on a METTLER TOLEDO TGA/SDTA 851^e.

3. Results and discussion

3.1. *Spectral analyses*

On comparison with the infrared spectrum of the ligand, the complex shows a new strong band at $1607\,cm^{-1}$ assigned to $\nu(C{=}O)$ of the pyrazolone-ring coordinated to Zn(II) [16, 17]. Furthermore, by comparing the ^1H NMR of ligand and complex, the characteristic chemical shift at 4.900 ppm of NH in the ligand is shifted to 5.335 ppm in the complex, indicating coordination of the imino group [22].

UV-Vis absorption spectra of PMP and the complex in methanol solution were determined. The UV-Vis spectrum of the complex exhibits an intense absorption at 243 nm (PMP at 242 nm) with almost the same spectral shape and absorption intensity, indicating that the absorption is not from charge transfer of metal to ligand, or ligand to metal, but by the ligand centered π–π^* transition [12, 23]. Emission and excitation spectra of the ligand and complex in solid state at room temperature were measured. As depicted in figure 1, the complex exhibits weak fluorescence with maximum emission

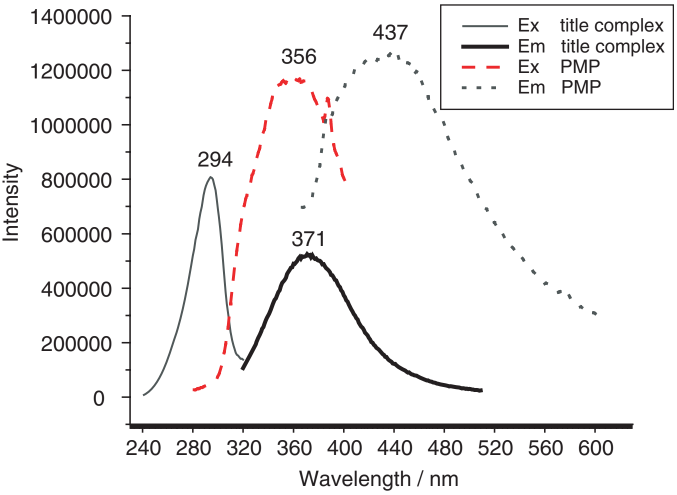

Figure 1. Emission and excitation spectra of ligand and complex in the solid state at room temperature.

at 371 nm when excited at 294 nm, while the ligand exhibits an intense emission maximum at 437 nm upon excitation at 356 nm. The emission spectrum shape of the zinc complex closely resembles that of the ligand, so the emission of the complex is assigned to fluorescence from the intraligand emission excited state [24–26], and the blue shift with respect to ligand may be ascribed to the structure change in the ligand during the formation of the complex. The emission intensity of the complex is much weaker than that of the ligand, because organic fluorescence can be quenched upon Zn(II) ion bonding though it is not complete [16, 26].

3.2. *Crystal structure*

Crystallographic analysis indicates that $[Zn(PMP)_2Cl]_n$ has an infinite 1-D coordination polymeric structure. The molecular structure is shown in figure 2 with the atom-labeling scheme; selected bond lengths, and angles are given in table 2. Each zinc is tetrahedrally coordinated by two oxygens and one nitrogen from pyrazole rings of three PMP ligands and one chloride. Bond angles around zinc range from 96.25(11)° to 115.96(9)° deviating from ideal 109.28° values, indicating that zinc adopts a slightly distorted tetrahedral geometry. The N(2A)–Zn(1) distance is 2.017(3) Å, shorter than other zinc complexes [27–31], and the Zn(1)–O bond length in the bridging PMP (1.986(2) Å) is slightly longer than that in monodentate PMP (1.957(2) Å), both comparable to the reported values [27–30]. The Cl–Zn distance is 2.210(4) Å, shorter than reported values [30]. The ligands have two different coordination modes, one is neutral monodentate that provided O(2) (called L_1), on one side of the polymeric chain, and the other is bidentate bridging bearing one negative charge, which provides O(1) and in deprotonated N(2) (called L_2). The charge of zinc(II) is satisfied by Cl^- and PMP^- due to the deprotonedated N of the imino in the pyrazole ring of L_2.

For L_2 the dihedral angle between pyrazole and phenyl is 70.6°, while the dihedral angle between the pyrazole rings, and that between the phenyl rings for two neighboring

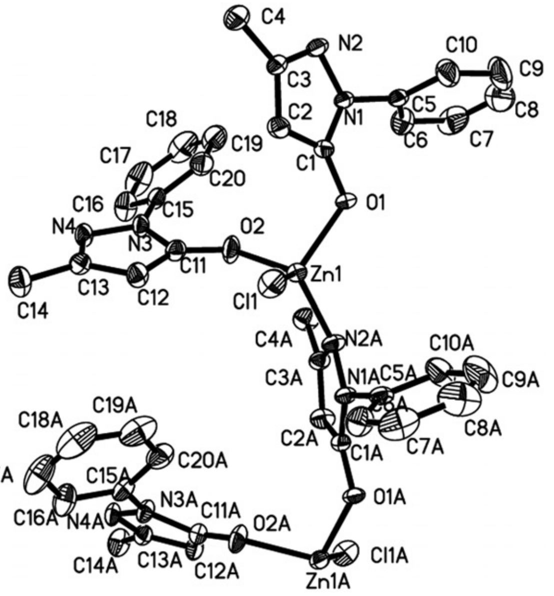

Figure 2. ORTEP view of the complex with full-labeling scheme. The ellipsoids enclose 50% of the electronic density. Symmetry operators for equivalent position: A = $-1/2+x$, $3/2-y$, $1/2+z$.

Table 2. Selected bond lengths (Å) and angles (°) for [Zn(PMP)$_2$Cl]$_n$.

Zn(1)–O(2)	1.957(2)	O(2)–Zn(1)–O(1)	96.25(11)
Zn(1)–O(1)	1.986(2)	O(2)-Zn(1)–N(2)#1	106.38(12)
Zn(1)–N(2)#1	2.017(3)	O(1)-Zn(1)–N(2)#1	109.82(11)
Zn(1)–Cl(1)	2.210(11)	O(2)–Zn(1)–Cl(1)	114.08(8)
N(2)–Zn(1)#2	2.017(3)	O(1)–Zn(1)–Cl(1)	112.48(8)
N(1)–C(1)	1.368(4)	N(2)#1–Zn(1)–Cl(1)	115.96(9)
N(1)–N(2)	1.389(4)	C(3)–N(2)–Zn(1)#2	125.10(2)
N(2)–C(3)	1.336(4)	N(1)–N(2)–Zn(1)#2	119.40(2)
N(3)–N(4)	1.370(3)	C(1)–O(1)–Zn(1)	117.80(2)
N(3)–C(11)	1.377(4)	C(11)–O(2)–Zn(1)	130.30(3)
N(4)–C(13)	1.338(4)	O(1)–C(1)–N(1)	121.20(3)
O(1)–C(1)	1.291(4)	O(1)–C(1)–C(2)	133.30(4)
O(2)–C(11)	1.276(4)	O(2)–C(11)–N(3)	120.00(4)

Symmetry transformations used to generate equivalent atoms: #1: $x+1/2$, $-y+3/2$, $z+1/2$; #2: $x-1/2$, $-y+3/2$, $z-1/2$.

L$_2$ are 60.7° and 31.9°, respectively. The corresponding dihedral angles between the above-mentioned planes for L$_1$ are 36.7°, 56.2°, and 55.3°, respectively. The pyrazole rings or the phenyl rings between neighboring L$_1$ (or L$_2$) are not parallel to each other. Torsion angles of neighboring Cl(1)–Zn(1)–Zn(1A)–Cl(1A) is 176.618(48)°, close to 180°, indicating that Cl, Zn, and PMP are in staggered arrangement along the 1-D polymeric chain.

There is only one kind of hydrogen bonding in the complex; N(4) of L$_1$ in the side chain from one polymeric strand is hydrogen-bonded to O(1) of L$_2$ from the adjacent strand, forming an intermolecular hydrogen bond. The H(4)$\cdots$O(1) bond length is 1.899 Å, the N(4)$\cdots$O(1) is 2.758 Å and the N(4)–H(4)$\cdots$O(1) angle is 176.23°, very close to 180°, so it can be considered as a strong intermolecular hydrogen bond [32, 33],

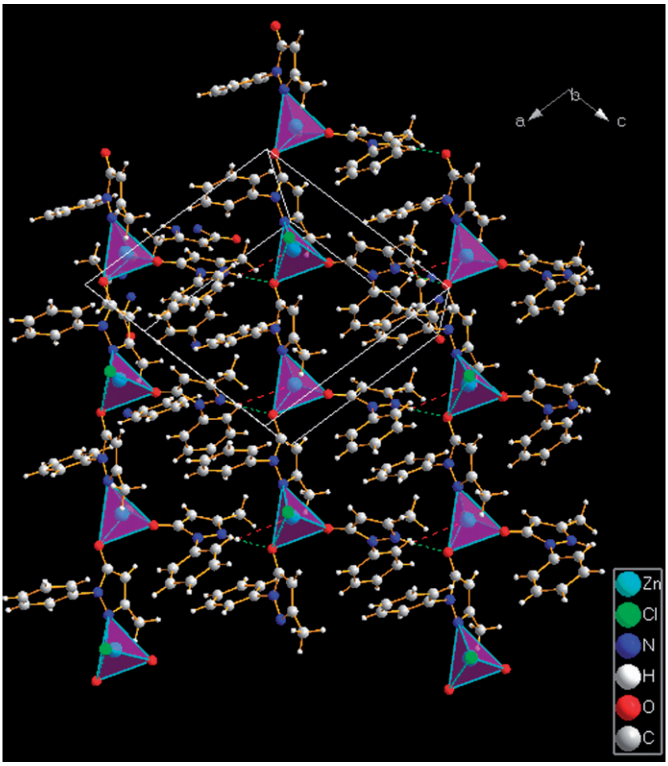

Figure 3. Intermolecular hydrogen bonding interaction among adjacent strands of the complex.

through which a 2-D sheet structure is formed as displayed in figure 3. There is a weak intermolecular interaction between zinc and H(4)–N(4) among adjacent strands, namely N–H···Zn (N···Zn 3.923 Å, H···Zn 3.215 Å, and N–H···Zn 141.23°), a type of intermolecular interaction specific to organometallic systems [34].

As shown in figure S4 (Supplementary material), the title complex is stable upto 230°C, and the DTA curve of the complex reveals one endothermic peak at 282°C and one intense exothermic peak at 636°C during decomposition; the thermogravimetric (TG) curve shows two weight loss steps correspondingly. The first is a continuous weight loss process in the range 230–515°C, 40.48% attributed to the loss of L_1 (Calcd 38.87%). Upon further heating, loss of 43.32% is observed between 515°C and 690°C, consistent with loss of L_2 absence of oxygen in the hetero-ring and coordinated chloride (Calcd 42.98%). A total weight loss of 83.8% is observed in the range 18–997°C. The residue is zinc oxide, whose weight percentage of 16.2% is consistent with the calculated value 18.15%.

The electrochemical behaviors of PMP and the complex have been examined by cyclic voltammograms (CV). A conventional three-electrode electrochemical system was used for all electrochemical experiments, consisting of a working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode (SCE). A glassy carbon disc electrode of formal surface area 0.071 cm^2 was used as the working electrode. All potentials reported are *versus* SCE. Cyclic voltammograms for

1×10^{-4} mol L^{-1} solution of PMP and the complex in DMF containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte were recorded by scanning from −0.2 to 0.7 V at scan rate of 50 mV s^{-1}.

Free PMP shows no electronic activity in the potential range from −0.2 to 0.7 V. In the same potential range for the complex, there are two strong oxidation peaks (E_{pa1} and E_{pa2} from oxidation of Zn and Zn$^+$, respectively) in the cathodic region and two weak reduction peaks (E_{pc3} and E_{pc4} assigned to the reduction of Zn^{2+} and Zn$^+$, respectively) in the anodic region, indicating a two-electron process (Supplementary material). The potentials for the cathodic peaks E_{pa1} is 0.185 V and E_{pa2} 0.513 V, while for the anodic peaks E_{pc3} is 0.421 V and E_{pc4} 0.078 V. Furthermore, the peak current ratios I_{pa2}/I_{pc3} are −1.59, and I_{pa1}/I_{pc4} is −8.125. On comparison with the anodic peaks, the cathodic peaks are weak, so the electrochemical behavior may be described as an irreversible redox process [35, 36]. These two redox peaks may be attributed to different coordination of Zn with the ligand.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Center, CCDC reference number 641773. Copies of these information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] X.B. Wang, J.D. Ranford, J.J. Vittal. *J. Mol. Struct.*, **796**, 28 (2006).
[2] W.M. Teles, R.A. Farani, M.I. Yoshida, A.J. Bortoluzi, M. Hörner, L.F.C. Oliveira, F.C. Machado. *Polyhedron*, **26**, 1469 (2007).
[3] J.G. Lin, L.L. Wen, S.Q. Zhang, Y. Su, Z.D. Lu, H.Z. Zhu, Q.J. Meng. *Inorg. Chem. Commun.*, **10**, 74 (2007).
[4] X.D. Wang, M. Liang, L.C. Li, Z.H. Jiang, D.Z. Liao, S.P. Yan, P. Cheng. *Struct. Chem.*, **18**, 5 (2007).
[5] Z.P. Yu, S.S. Xiong, G.P. Yong, Z.Y. Wang. *J. Coord. Chem.*, **62**, 242 (2009).
[6] Y.B. Zhang, X. Li, Y.Q. Li. *J. Coord. Chem.*, **62**, 583 (2009).
[7] L.L. Wen, D.E. Wang, Y.J. Chen, X.G. Meng, D.F. Li, S.M. Lan. *J. Coord. Chem.*, **62**, 789 (2009).
[8] A.A. Rexit. *J. Coord. Chem.*, **62**, 1373 (2009).
[9] A. Majumder, G.M. Rosair, A. Mallick, N. Chattopadhyay, S. Mitra. *Polyhedron*, **25**, 1753 (2006).
[10] H. Sakurai, Y. Kojima, Y. Yoshikawa, K. Kawabe, H. Yasui. *Coord. Chem. Rev.*, **226**, 187 (2002).
[11] Y.N. Zhou, Y.H. Fan, C.F. Bi, D.M. Zhang, Y.Y. Li. *Chin. J. Struct. Chem.*, **25**, 261 (2006).
[12] X.X. Sun, C.M. Qi, S.L. Ma, H.B. Huang, W.X. Zhu, Y.C. Liu. *Inorg. Chem. Commun.*, **9**, 911 (2006).
[13] L.F. Ma, X.K. Huo, L.Y. Wang, Y.T. Fan, S.Y. Zhang. *Chin. J. Struct. Chem.*, **26**, 352 (2007).

[14] M.S. Masoud, A.E. Ali, R.H. Mohamed, M.A.Z. Mostafa. *Spectrochim. Acta A*, **62**, 1114 (2005).

[15] J. Li, L. Zhang, L. Liu, G.F. Liu, J.X. Guo, D.Z. Jia. *Inorg. Chim. Acta*, **360**, 3504 (2007).

[16] Y. Yang, L. Zhang, L. Liu, G.F. Liu, J.X. Guo, D.Z. Jia. *Inorg. Chim. Acta*, **360**, 2638 (2007).

[17] G. Cerchiaro, A.M. Da C. Ferreira, A.B. Teixeira, H.M. Magalhães, A.C. Cunha, V.F. Ferreira, L.S. Santos, M.N. Eerlin, J.M.S. Skakle, S.M.S.V. Wardell, J.L. Wardell. *Polyhedron*, **25**, 2055 (2006).

[18] J.H. Wang, L. Liu, G.F. Liu, L. Zhang, D.Z. Jia. *Struct. Chem.*, **18**, 59 (2007).

[19] Y.H. Jiang, R.D. Yang, L. Yan, X.L. Hu, W.B. Yuan. *J. Chin. Rare Earth Soc.*, **20**, 474 (2002).

[20] R. Allmann, M. Krestl, C. Bolos, G. Manoussakis, G.S. Nikolov. *Inorg. Chim. Acta*, **175**, 255 (1990).

[21] G.M. Sheldrick. *SHELXS-97 and SHELXL-97, Program for X-ray Crystal Structure Solution and Refinement*, University of Göttingen, Germany (1997).

[22] B.H. Peng, G.F. Liu, L. Liu, D.Z. Jia. *Tetrahedron*, **61**, 5926 (2005).

[23] M. Ghosh, P. Biswas, U. Flörke. *Polyhedron*, **26**, 3750 (2007).

[24] T.Z. Yu, K. Zhang, Y.L. Zhao, C.H. Yang, H. Zhang, D.W. Fan, W.K. Dong. *Inorg. Chem. Commun.*, **10**, 401 (2007).

[25] F. Li, Y.L. Wang, G.S. Li, Y.G. Sun, X.F. Gu, E.J. Gao. *Inorg. Chem. Commun.*, **10**, 76 (2007).

[26] Y.Q. Yang, C.H. Li, W. Li, D.P. Li, Y.F. Kuang. *Chem. J. Chin. Univ.*, **29**, 449 (2008).

[27] B. Lian, C.M. Thomas, O.L. Casagrande Jr, C.W. Lehmann, T. Rosnel, J.F. Carpentier. *Inorg. Chem.*, **46**, 328 (2007).

[28] J. Tao, J.X. Shi, M.L. Tong, X.X. Zhang, X.M. Chen. *Inorg. Chem.*, **40**, 6328 (2001).

[29] V. Zeleňák, I. Císarovák, P. Llewellyn. *Inorg. Chem. Commun.*, **10**, 27 (2007).

[30] G.F. Chen, C.Z. Cao. *Chin. J. Inorg. Chem.*, **24**, 649 (2008).

[31] T. Kawamoto, M. Nishiwaki, Y. Tsunekawa, K. Nozaki, T. Konno. *Inorg. Chem.*, **47**, 3095 (2008).

[32] S.S. Massoud, F.A. Mautner. *Inorg. Chem. Commun.*, **7**, 559 (2004).

[33] Y. Tang, K.Z. Tang, J. Zhang, C.Y. Su, W.S. Liu, M.Y. Tan. *Inorg. Chem. Commun.*, **8**, 1018 (2005).

[34] D. Braga, F. Grepioni, E. Tedesco, K. Biradha, G. Desiraju. *Organometallics*, **16**, 1846 (1997).

[35] E. Erasmus, J. Conradie, A. Muller, J.C. Swarts. *Inorg. Chim. Acta*, **360**, 2277 (2007).

[36] I. Yilmaz, A. Gürek, V. Ahsen. *Polyhedron*, **24**, 791 (2005).