APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2006; **20**: 399–403
Published online 15 May 2006 in Wiley InterScience
(www.interscience.wiley.com) DOI:10.1002/aoc.1073

Synthesis, crystal structure and magnetic property of a two-dimensional herringbone-like network with praseodymium(III) nitrate and 1-bromo-3,5-bis(imidazol-1-ylmethyl)benzene (bib)

Wen-Li Meng[1], Zheng-Hua Zhang[1], Yang Lv[1], Hiroyuki Kawaguchi[2] and Wei-Yin Sun[1]*

[1]Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, People's Republic of China
[2]Coordination Chemistry Laboratories, Institute for Molecular Science, Okazaki, Aichi 444-8585, Japan

Received 22 January 2006; Revised 23 February 2006; Accepted 13 March 2006

A new complex $[Pr(bib)_2(NO_3)_3]$ (1) was synthesized by reaction of bidentate imidazole-containing ligand 1-bromo-3,5-bis(imidazol-1-ylmethyl)benzene (bib) with $Pr(NO_3)\cdot 6H_2O$ and characterized by X-ray crystallography. Complex 1 has a two-dimensional herringbone-like structure with the ligand bib serving as a bridging ligand using its two imidazolyl nitrogen atoms. Ligand bib adopts *cis* and *trans* two different conformations, and the Pr(III) atoms are bridged by bib in two different ways. Thermogravimetric analysis for complex 1 was carried out and the result shows that the complex is stable up to 180 °C. Variable-temperature magnetic susceptibility of complex 1 was measured between 1.8 and 300 K and the result shows that the $\chi_M T$ value decreases continuously over the whole temperature range. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: bidentate ligand; Pr(III) complex; herringbone; magnetic property

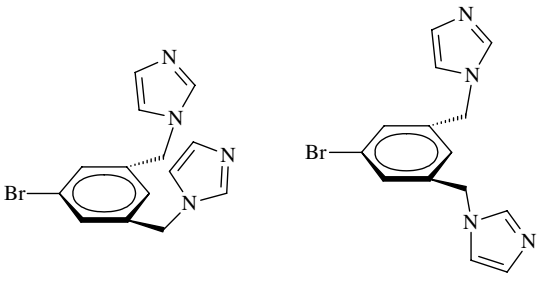
INTRODUCTION

In recent years, construction and characterization of metal-organic frameworks (MOFs) have attracted great interests from chemists.[1,2] Such interests can be considered to come from two broad fields. One is the design and control the structures of MOFs, and the another is the properties and potential applications of MOFs. Therefore, in recent years, a variety of MOFs with specific topologies such as cage,[3,4] honeycomb,[5] herringbone,[6,7] brick wall,[8] etc., have been obtained by assemblies of metal salts with organic ligands. Properties such as magnetism, molecular recognition and sorption, catalysis and so on have been reported.[9–12]

On the other hand, researches on lanthanide salts with organic bridging ligands have been widely carried out in recent years due to the unique nature of lanthanide ions, e.g. the large radius, high and variable coordination numbers and geometry and the presence of multi-non-pair electrons. Accordingly, various lanthanide MOFs with special luminescent and magnetic properties have been reported recently.[13–16] However, the reported MOFs are mainly constructed from bridging ligands with oxygen donor atoms alone[17] or both oxygen and nitrogen donors;[18] the use of bridging ligands with only the nitrogen donor atoms to construct lanthanide MOFs is rarely reported.[19]

In our previous studies, we synthesized a flexible imidazole-containing bidentate ligand 1-bromo-3,5-bis(imidazol-1-ylmethyl)benzene (bib) and obtained a series of MOFs built from bib and transition metal salts, such as Ag(I), Zn(II) and Mn(II) salts.[20] These MOFs possess different structures because of the different coordination geometries of the metal centers and the different conformations of bib ligand, namely *cis* and *trans* conformations, as illustrated in Scheme 1. In order to investigate the assembly reactions of

*Correspondence to: Wei-Yin Sun, Coordination and Chemistry Institute, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China.
E-mail: sunwy@nju.edu.cn
Contract/grant sponsor: National Natural Science Foundation of China; Contract/grant number: 20231020.
Contract/grant sponsor: National Science Fund for Distinguished Young Scholars; Contract/grant number: 20425101.



Scheme 1. Schematic drawing for ligand bib with *cis* and *trans* conformations.

the bib ligand with lanthanide salts, in this paper we report the synthesis, structure and magnetic property of a Pr(III) complex $[Pr(bib)_2(NO_3)_3]$ (**1**).

EXPERIMENTAL

Materials and methods

All commercially available chemicals are of reagent grade and used as received without further purification. Ligand bib was prepared using a previously reported method.[20] C, H and N analyses were carried out on a Perkin-Elmer 240C elemental analyzer at the analysis center of Nanjing University. Thermogravimetric analysis was performed on a simultaneous SDT 2960 thermal analyzer. Powder sample of complex **1** was heated from room temperature to 800 °C under flowing N_2 at a heating rate of 10 °C/min.

Synthesis of complex 1

A mixture of $Pr(NO_3)_3 \cdot 6H_2O$ (21.7 mg, 0.050 mmol), ligand bib (18.0 mg, 0.050 mmol), dried methanol (6.0 ml) and triethyl orthoformate (1.0 ml) was stirred and refluxed for about 2 h. The resulting solution was filtrated and the filtrate was allowed to stand in a desiccator at room temperature for two weeks. Colorless crystals were obtained in ca. 60% yield. Anal. calcd for $C_{28}H_{26}Br_2N_{11}O_9Pr$: C, 34.99; H, 2.73; N, 16.03. Found: C, 35.01; H, 2.73, N, 15.97.

X-ray crystallography

The data collection was carried out on a Rigaku Saturn CCD area detector at 173 K for the complex **1**, using graphite-monochromated Mo–Kα radiation ($\lambda = 0.7107$ Å). The structure was solved by direct method with SIR97,[21] and expanded using Fourier techniques.[22] All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method on F^2. The hydrogen atoms were generated geometrically. All calculations were carried out using the CrystalStructure crystallographic software package.[23] Details of the crystal parameters, data collection and refinement for complexes **1** are summarized in Table 1. Selected bond lengths and angles for complex **1** are listed in Table 2.

Table 1. Crystallographic data for complexes **1**

	1
Empirical formula	$C_{28}H_{26}Br_2N_{11}O_9Pr$
Formula weight	667.36
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	8.881(3)
b (Å)	23.043(7)
c (Å)	17.245(5)
β (deg)	106.862(4)
V (Å^3)	3377.1(18)
Z	4
D_{calc} (g/cm^3)	1.891
μ (mm^{-1})	3.881
T (K)	173.1
F(000)	1888
Reflections collected	53 810
Unique reflections	7916
R_{int}	0.035
Goodness-of-fit on F^2	1.005
R^a/wR^b	0.0320/0.0630

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. $P = (F_o^2 + 2F_c^2)/3$.

Crystallographic data (excluding structure factors) for the structure of complex **1** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-295607. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (+44)1223 336-033; e-mail: deposit@ccdc.cam.ac.uk].

Magnetic measurements

Variable-temperature magnetic susceptibility measurements were performed on a SQUID MPMS-XL7 at an applied field of 2000 G using crystalline samples of **1** in the range 300–1.8 K. The magnetic susceptibilities of the complex were corrected by Pascal's constant and the diamagnetism of holder.

RESULTS AND DISCUSSION

Crystal structure of complex 1

The X-ray crystallographic structure analysis of **1** reveals that it crystallizes in a monoclinic with space group $P2_1/c$. As shown in Fig. 1, the asymmetric unit of **1** contains one unique Pr(III) atom, two bib ligands and three nitrate anions. The Pr(III) atom is 10-coordinated with four nitrogen atoms from four imidazolyl groups of four different bib ligands with N–Pr–N bond angles varying from 71.0 to 144.13(8)° and Pr–N bond lengths in the range 2.636–2.650(3) Å, six oxygen atoms from three bidentate-chelating nitrate anions with O–Pr–O bond angles varying from 47.64(8) to 164.28(7)° and

DOI: 10.1002/aoc

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

	1		
Pr1–O1	2.652(2)	Pr1–O2	2.635(2)
Pr1–O4	2.606(2)	Pr1–O5	2.536(2)
Pr1–O7	2.571(2)	Pr1–O8	2.578(3)
Pr1–N1	2.650(3)	Pr1–N5	2.649(3)
Pr1–N4[a]	2.650	Pr1–N8[b]	2.636
O1–Pr1–O2	47.64(8)	O1–Pr1–O4	99.38(8)
O1–Pr1–O5	122.19(8)	O1–Pr1–O7	65.05(8)
O1–Pr1–O8	90.05(8)	O1–Pr1–N1	67.32(7)
O1–Pr1–N5	134.45(7)	O1–Pr1–N4[a]	145.6
O1–Pr1–N8[b]	77.5	O2–Pr1–O4	61.02(6)
O2–Pr1–O5	75.42(7)	O2–Pr1–O7	106.08(7)
O2–Pr1–O8	136.52(7)	O2–Pr1–N1	79.50(8)
O2–Pr1–N5	136.25(7)	O2–Pr1–N4[a]	129.5
O2–Pr1–N8[b]	68.0	O4–Pr1–O5	49.62(7)
O4–Pr1–O7	164.28(7)	O4–Pr1–O8	132.75(7)
O4–Pr1–N1	67.89(8)	O4–Pr1–N5	121.15(7)
O4–Pr1–N4[a]	68.7	O4–Pr1–N8[b]	108.4
O5–Pr1–O7	139.68(7)	O5–Pr1–O8	147.73(7)
O5–Pr1–N1	117.31(8)	O5–Pr1–N5	78.04(8)
O5–Pr1–N4[a]	75.5	O5–Pr1–N8[b]	72.0
O7–Pr1–O8	49.51(6)	O7–Pr1–N1	102.21(8)
O7–Pr1–N5	74.15(7)	O7–Pr1–N4[a]	122.7
O7–Pr1–N8[b]	72.0	O8–Pr1–N1	73.77(9)
O8–Pr1–N5	77.76(8)	O8–Pr1–N4[a]	77.6
O8–Pr1–N8[b]	118.8	N1–Pr1–N5	144.13(8)
N1–Pr1–N4[a]	78.4	N1–Pr1–N8[b]	142.9
N5–Pr1–N4[a]	74.5	N5–Pr1–N8[b]	71.0
N4[a]–Pr1–N8[b]	136.5		

Symmetry transformation used to generate equivalent atoms: [a] $-x, -1/2+y, 1/2-z$; [b] $2-x, -y, 1-z$.

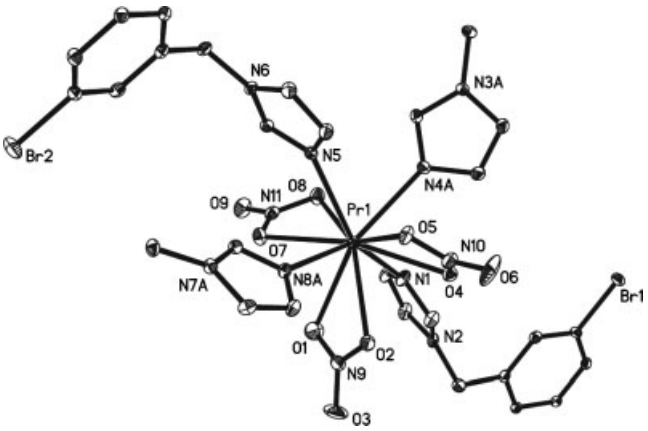


Figure 1. ORTEP plot of **1** showing local coordination environment of Pr(III) with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity. Symmetry operations: $-x, -0.5+y, 0.5-z$ for N3A and N4A; $2-x, -y, 1-z$ for N7A and N8A.

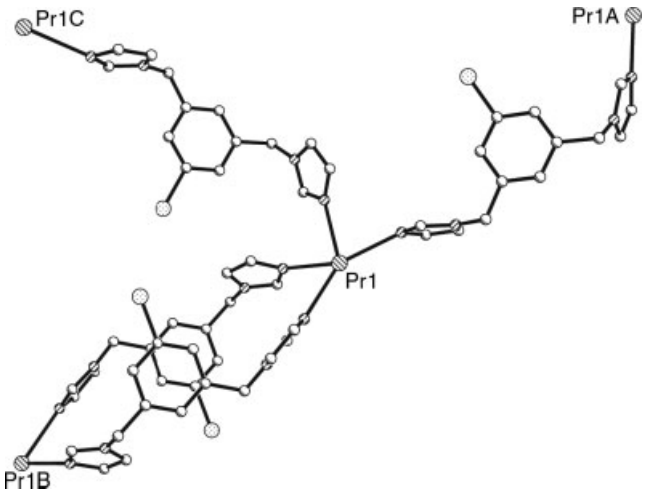


Figure 2. Bridging models of bib in which the Pr1 atom is connected to three adjacent Pr(III) atoms; the nitrate anions are omitted for clarity.

Pr–O bond distances in the range 2.536(2)–2.652(2) Å, as listed in Table 2. The Pr–N and Pr–O bond distances are similar to those observed in the reported Pr(III) complexes with nitrogen donors[24] and oxygen donors.[14] The coordination geometry of each Pr(III) atom is distorted bicapped square antiprism, which is a common coordination geometry for the 10-coordinated lanthanide ions.[25,26]

It is clear that in the title complex, each bib acts as a bidentate-bridging ligand to connect two Pr(III) atoms using its two flexible arms, as shown in Fig. 2. It is interesting that there are two different bridging modes. Between Pr1 and Pr1A atoms, and Pr1 and Pr1C atoms, there is only one bridging bib ligand, and each bib adopts a *trans* conformation with the dihedral angles of 71.5 and 85.8° between the central phenyl and each imidazolyl group, and the Pr···Pr distances are both 14.73 Å. However, between Pr1 and Pr1B atoms, two bib ligands with *cis* conformation bridge the two Pr(III) atoms to form a 24-membered M_2L_2 macrocyclic ring. The dihedral angles between the phenyl and imidazolyl groups are 78.7° and 85.9°, and the distance between Pr1 and Pr1B atoms is 15.27 Å. In our previous studies, we have obtained a series of transition metal complexes with bib ligand,[14] complex **1** is the first example with two different conformations and two kinds of bridging modes of the bib ligand. Compared with the transition metal ions, the lanthanide ions have higher coordination number and the coordination geometry is more complex, thus the bib ligands in complex **1** adopt different conformations to satisfy the coordination requirement of the Pr(III) atoms.

The polymeric structure of **1** is a two-dimensional herringbone-like network as illustrated in Fig. 3. Six Pr(III) atoms and eight bib ligands compose an approximate parallelogram of 96-membered M_6L_6 macrocyclic ring. The

DOI: 10.1002/aoc

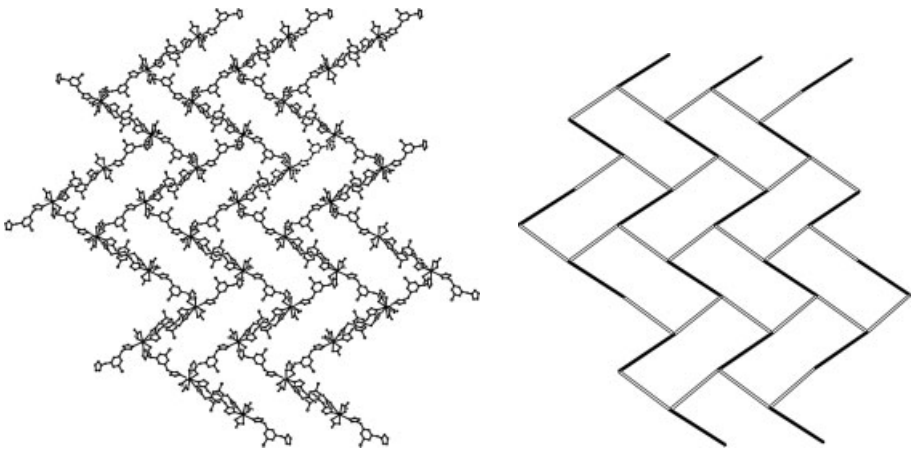


Figure 3. (a) Two-dimensional herringbone-like network of complex **1**. (b) Schematic drawing of a herringbone-like network of complex **1**; the hollow line represents the single-ligand-bridging model between the Pr(III) atoms, and the solid line represents the double-ligand-bridging model between Pr(III) atoms.

Table 3. Hydrogen bonding data for complex **1**

D–H···A	Distance (Å) (D···A)	D–H–A	Angle (deg) (D–H–A)
	1		
C1–H1···O4	2.956(4)	C1–H1–O4	115
C2–H2···O8	3.114(4)	C2–H2–O8	116
C3–H3···O3[a]	3.441(4)	C3–H3–O3[a]	160
C6–H6···O1[a]	3.047(4)	C6–H6–O1[a]	124
C11–H10···O2[b]	3.227(4)	C11–H10–O2[b]	163
C11–H10···O4[b]	3.212(4)	C11–H10–O4[b]	123
C14–H13···O4[c]	2.868(4)	C14–H13–O4[c]	111
C16–H15···O5	3.122(4)	C16–H15–O5	122
C24–H21···O6[d]	3.261(4)	C24–H21–O6[d]	151
C26–H24···O6[e]	3.142(4)	C26–H24–O6[e]	144
C27–H25···O9[f]	3.320(5)	C27–H25–O9[f]	140

Symmetry transformation used to generate equivalent atoms: [a] $-1-x, 1-y, -1-z$; [b] $-x, 1-y, -1-z$; [c] $-x, 1/2+y, -1/2-z$; [d] $-1+x, y, z$; [e] $-1-x, -y, -1-z$; [f] $-2-x, -1/2+y, -1/2-z$; [g] $-2-x, -y, -1-z$. D: donor; A: acceptor.

Pr(III) atoms serve as the nodes of the parallelogram while the bib ligands serve as rods. Among the six rods within one M_6L_6 macrocyclic ring, four are single-ligand-bridging model and the other two rods are double-ligand-bridging model. Furthermore, there are C–H···O hydrogen bonds between the O atoms of nitrate anions and benzene ring C–H, methylene C–H as well as the imidazole ring C–H, as listed in Table 3. The C···O distances of the hydrogen bonds are in the range from 2.868(4) to 3.441(4) Å, which are comparable to those of previously reported hydrogen bonds.[27] Such hydrogen bonds link the two-dimensional networks into a three-dimensional framework.

Thermogravimetric analysis of complex 1

Complex **1** is air stable. TGA for complex **1** was carried out to examine its thermal stability by heating the sample up to 800 °C. The TGA data of **1** showed that the complex is stable up to 180 °C where it starts to decompose.

Magnetic property of complex 1

The measurements of variable-temperature magnetic susceptibility were carried out for the crystalline sample of **1** in the temperature range 1.8–300 K. The plots of $\chi_M T$ vs T and χ_M vs T are shown in Fig. 4. The χ_M value is 0.00521 emu/mol at 300 K, and the values increase continuously with the decrease of the temperature in the range 1.8–300 K. At the temperature of 1.8 K, the χ_M reaches a value of 0.07513 emu/mol. On the other hand, the $\chi_M T$ value is

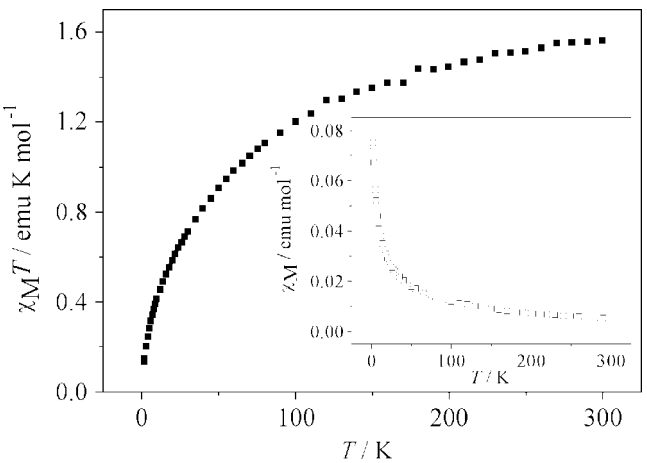


Figure 4. Temperature dependence of the $\chi_M T$ values for complex **1**. Inset: temperature dependence of the χ_M values for **1**.

DOI: 10.1002/aoc

1.56 emu K/mol at room temperature, which is lower than the spin-only value of 1.6 emu K/mol for Pr(III) unit ($^3H_4$, $g = 0.8$, $S = 1$), and it decreases gradually with cooling of the sample. It reaches 0.1354 emu K/mol at 1.8 K. Similar behavior of the variable-temperature magnetic susceptibility has been reported for the Pr(III)–PDA (PDA = pyridine-2,6-dicarboxylate) complexes.[28]

Acknowledgments

This work was supported by the National Natural Science Foundation of China (grant no. 20231020) and the National Science Fund for Distinguished Young Scholars (grant no. 20425101).

REFERENCES

1. James SL. *Chem. Soc. Rev.* 2003; **32**: 276.
2. Kitagawa S, Kitaura R, Noro S. *Angew. Chem. Int. Ed.* 2004; **43**: 2334.
3. Takeda N, Umemoto K, Yamaguchi K, Fujita M. *Nature* 1999; **398**: 794.
4. Sun WY, Fan J, Okamura T-A, Xie J, Yu KB, Ueyama N. *Chem. Eur. J.* 2001; **7**: 2557.
5. Hayashi M, Miyamoto Y, Inoue T, Oguni N. *J. Chem. Soc., Chem. Commun.* 1991; 1752.
6. Withersby MA, Blake AJ, Champness NR, Cooke PA, Hubberstey P, Schröder M. *New J. Chem.* 1999; **23**: 573.
7. Holmes KE, Kelly PF, Elsegood MRJ. *Dalton Trans.* 2004; 3488.
8. Gable RW, Hoskins BF, Robson R. *J. Chem. Soc., Chem. Commun.* 1990; 1677.
9. Kahn O. *Acc. Chem. Res.* 2000; **33**: 674.
10. Oshio H, Nagashima U. *Inorg. Chem.* 1992; **31**: 3295.
11. Yaghi OM, Li H, Davis C, Richardson D, Groy TL. *Acc. Chem. Res.* 1998; **31**: 474.
12. Seo JS, Whang D, Lee H, Jun SI, Oh J, Jeon YJ, Kim K. *Nature* 2000; **404**: 982.
13. Montalti M, Prodi L, Zaccheroni N, Charbonniere L, Douce L, Ziessel R. *J. Am. Chem. Soc.* 2001; **123**: 12 694.
14. Zhang ZH, Okamura T-A, Hasegawa Y, Kawaguchi H, Kong LY, Sun WY, Ueyama N. *Inorg. Chem.* 2005; **44**: 6219.
15. Panagiotopoulos A, Zafiropoulos TF, Perlepes SP, Bakalbassis E, Masson-Ramade I, Kahn O, Terzis A, Raptopoulou CP. *Inorg. Chem.* 1995; **34**: 4918.
16. Costes JP, Clemente-Juan JM, Dahan F, Nicodème F, Verelst M. *Angew. Chem., Int. Ed.* 2002; **41**: 323.
17. Zhang ZH, Sheng ZL, Okamura T-A, Zhu HF, Sun WY, Ueyama N. *Cryst. Growth Des.* 2005; **5**: 1191.
18. Sun YQ, Zhang J, Chen XM, Yang GY. *Angew. Chem., Int. Ed.* 2005; **44**: 5814.
19. Su CY, Kang BS, Yang QC, Mak TCW. *Supramol. Chem.* 2001; **12**: 411.
20. Fan J, Sun WY, Okamura T-A, Zheng YQ, Sui B, Tang WX, Ueyama N. *Cryst. Growth Des.* 2004; **4**: 579.
21. SIR97: Altomare A, Burla M, Camalli M, Cascarano G, Giacovazzo C, Guagliardi A, Moliterni A, Polidori G, Spagna R. *J. Appl. Crystallogr.* 1999; **32**: 115.
22. DIRDIF99: Beurskens PT, Admiraal G, Beurskens G, Bosman WP, de Gelder R, Israel R, Smits JMM, 1999.; The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.
23. CrystalStructure 3.5.1: Crystal Structure Analysis Package, Rigaku and Rigaku/MSC (2000–2003), Texas, USA.
24. Wang J, Zhang XD, Zhang Y, Jia WG, Liu ZR. *J. Struct. Chem.* 2004; **45**: 114.
25. Lescop C, Belorizky E, Luneau D, Rey PJ. *Inorg. Chem.* 2002; **41**: 3375.
26. Zhu YJ, Chen JX, Zhang WH, Ren ZG, Zhang Y, Lang JP, Ng SW. *J. Organomet. Chem.* 2005; **690**: 3479.
27. Desiraju GR. *Acc. Chem. Res.* 1996; **29**: 441.
28. Zhao B, Yi L, Dai Y, Chen XY, Cheng P, Liao DZ, Yan SP, Jiang ZH. *Inorg. Chem.* 2005; **44**: 911.