

A novel one-dimensional mixed ligands silver(I) coordination polymer containing two different chains

Fu-Jing Liu^{a,1}, Di Sun^{b,*}, Hong-Jun Hao^a, Rong-Bin Huang^{a,*}, Lan-Sun Zheng^a

^aState Key Laboratory for Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, Fujian 361005, China

^bSchool of Chemistry and Chemical Engineering, Shandong University, Jinan, Shandong 250100, China

ARTICLE INFO

Article history:

Received 4 January 2012

Received in revised form 31 January 2012

Accepted 31 January 2012

Available online 10 February 2012

Keywords:

Silver(I)

1,4-Bis(2-methylimidazol-1-ylmethyl)benzene

Naphthalene-1,4-dicarboxylic acid

Photoluminescence

ABSTRACT

A mixed-ligand coordination polymer (CP) of the formula $\{[Ag_3(bmimb)_2(ndca)_{1.5}] \cdot H_2O\}_n$ (**1**) (where *bmimb* = 1,4-bis(2-methylimidazol-1-ylmethyl)benzene and *H₂ndca* = naphthalene-1,4-dicarboxylic acid) was synthesized by reaction of *Ag₂O* and *bmimb* ligand with *H₂ndca* under the ammoniacal condition. It has been structurally characterized by element analysis, IR and X-ray single-crystal diffraction. The *bmimb* acts as bidentate μ_2-N,N' ligand, and the *ndca* ligand adopts two different coordination modes in **1**, which are $\mu_4-\eta^1:\eta^1:\eta^1:\eta^1$ and $\mu_2-\eta^1:\eta^0:\eta^1:\eta^0$, respectively. Coordination of *Ag(I)* ions with *bmimb* and *ndca* ligands produces two different 1D chains, which is attributed to the different coordination modes of the *ndca* ligand, indicating the *ndca* ligand plays an important role in the formation of the diverse 1D chains. The complex **1** exhibits photoluminescent emission in the solid state at room temperature.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The continuing interest in the crystal engineering of coordination polymers (CPs) not only originates from their potential applications in catalysis, storage, conduction, non-linear optics (NLOs), luminescence, ferroelectricity and magnetism, but also from their fascinating architectures and topologies [1–9]. As we know, construction of CPs is mainly dependent on the metal centers and organic ligands. The *Ag(I)* ion with *d¹⁰* closed-shell electronic configuration is famous for having pliant coordination geometries including linearity, triangle, tetrahedron and trigonal-pyramid with occasional instances of square and octahedron [10]. The coordination features of the organic ligand including the coordination mode and orientation of the donor groups also play an important role in controlling CPs' structures. In recent years, although heterocyclic *N*-donor ligands (such as pyridine, pyrazine, pyrimidine, and their derivatives) have been widely used in transition metal CPs as either bridging or chelating ligands [11–24], we are currently investigating the use of the flexible ligand 1,4-bis(2-methylimidazol-1-ylmethyl)benzene (*bmimb*) to construct novel architectures. The *bmimb* ligand is rarely used in *Ag(I)* CPs due to its two turning points and can act as bidentate μ_2-N,N' ligand. Herein, we utilized

mixed-ligand strategy to construct a new 1D coordination polymer which contains two different 1D chains, and the influence of the coordination mode of the *ndca* ligand on the resulting structure was discussed.

2. Experimental

2.1. Materials and physical measurements

All the reagents and solvents employed were commercially available and used as received without further purification. Infrared spectrum was recorded on a Nicolet AVATAT FT-IR330 spectrometer as KBr pellets in the frequency range 4000–400 cm^{-1} . The elemental analysis (C, H, N contents) was determined on a CE instruments EA 1110 analyzer. Photoluminescence measurement was performed on a Hitachi F-7000 fluorescence spectrophotometer with solid powder on a 1 cm quartz round plate.

2.2. Synthesis of compound $\{[Ag_3(bmimb)_2(ndca)_{1.5}] \cdot H_2O\}_n$ (**1**)

A mixture of *Ag₂O* (23 mg, 0.1 mmol), *bmimb* (27 mg, 0.1 mmol) and *H₂ndca* (22 mg, 0.1 mmol) was stirred in methanol-DMF mixed solvent (5 mL, *v/v*: 3/2). Then aqueous *NH₃* solution (25%, 2 mL) was dropped into the mixture to give a clear solution under ultrasonic treatment. The resultant solution was allowed to evaporate slowly in darkness at room temperature for several days to give yellow crystals of **1** (yield: 67%, based on silver). Anal. Calcd (found) for

* Corresponding authors. Fax: +86 592 2183047.

E-mail addresses: dsun@sdu.edu.cn (D. Sun), rbhuang@xmu.edu.cn (R.-B. Huang).

¹ These authors contributed equally to this work.

Ag₃C₅₀H₄₅N₈O₇: C, 49.88 (50.32); H, 3.70 (3.80); N, 9.45 (9.39)%. IR (KBr): $\nu(\text{cm}^{-1}) = 3421$ (s), 1561 (s), 1518 (m), 1502 (s), 1470 (m), 1414 (s), 1365 (s), 1287 (m), 1270 (m), 1212 (w), 1156 (m), 1138 (m), 1076 (w), 989 (w), 865 (w), 797 (m), 738 (s), 665 (m), 630 (m), 566 (m), 478 (m).

3. X-ray crystallography

Single crystal of the complex **1** with appropriate dimensions was chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) before being mounted on a glass fiber for data collection. Data for **1** was collected on a Bruker-AXS CCD single-crystal diffractometer with graphite-monochromated Mo K α radiation source ($\lambda = 0.71073$ Å). A preliminary orientation matrix and unit cell parameters were determined from 3 runs of 20 frames each, each frame corresponds to a 0.3° scan in 5 s, followed by spot integration and least-squares refinement. Data were measured using ω scans of 0.3° per frame for 10 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART software and refined with SAINT on all observed reflections [25]. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS. [25] In all cases, the highest possible space group was chosen. The structure was solved by direct methods using SHELXS-97 [26] and refined on F^2 by full-matrix least-squares procedures with SHELXL-97 [27]. Atoms were located from iterative examination of difference F -maps following least squares refinements of the earlier models. Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2–1.5 times U_{eq} of the attached C or N atoms. The structure was examined using the Addsym subroutine of PLATON [28] to assure that no additional symmetry could be applied to the models. The crystallographic details of **1** are summarized in Table 1. Selected bond lengths and angles for **1** are collected in Table 2.

4. Results and discussion

4.1. Syntheses and IR

The synthesis of complex **1** was carried out in the darkness to avoid photodecomposition. The infrared spectrum and elemental

Table 1
Crystallographic data for complex **1**.

Complex	1
Formula	Ag ₃ C ₅₀ H ₄₅ N ₈ O ₇
M_r	1193.55
Crystal system	Orthorhombic
Space group	Cmca
a (Å)	21.901(5)
b (Å)	30.645(7)
c (Å)	14.201(3)
Z	8
V (Å ³)	9531(4)
D_c (g cm ⁻³)	1.664
μ (mm ⁻¹)	1.281
$F(000)$	4784
No. of unique reflns	4323
No. of obsd reflns [$I > 2\sigma(I)$]	3134
Parameters	301
GOF	1.047
Final R indices [$I > 2\sigma(I)$] ^{a,b}	$R_1 = 0.0805$ $wR_2 = 0.2032$
R indices (all data)	$R_1 = 0.1075$ $wR_2 = 0.2230$
Largest difference peak and hole (e Å ⁻³)	1.763 and -0.861

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR_2 = \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}^{0.5}$$

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

Complex 1			
Ag1–O1	2.093(6)	Ag1–Ag2	3.3216(17)
Ag2–O2	2.658(6)	Ag3–N3	2.165(7)
Ag2–N1	2.116(7)	Ag3–O4	2.532(18)
O1 ⁱ –Ag1–O1	175.9(4)	O2–Ag2–Ag1	53.92(13)
N1 ⁱ –Ag2–O2	92.0(3)	N1–Ag2–N1	177.0(4)
N1–Ag2–O2	89.7(3)	N3–Ag3–N3 ⁱⁱ	146.6(4)
N1–Ag2–Ag1	91.5(2)	N3–Ag3–O4	106.7(2)

Symmetry codes: (i) $-x + 1/2, y, -z + 1/2$; (ii) $x, -y + 1, -z + 2$.

analysis of **1** are fully consistent with its formation. Its IR spectrum (Fig. S2) exhibits strong absorptions centered at ~ 3400 cm⁻¹ corresponding to the O–H stretching vibration of the lattice water molecule. Strong characteristic bands of carboxylic group are observed in the range of ~ 1560 – 1500 cm⁻¹ for asymmetric vibrations and ~ 1470 cm⁻¹ for symmetric vibrations, respectively.

4.2. Crystal structure of $\{[Ag_3(\text{bmimb})_2(\text{ndca})_{1.5}]\cdot\text{H}_2\text{O}\}_n$ (**1**)

X-ray single-crystal analysis reveals that **1** crystallizes in the orthorhombic space group Cmca whose asymmetric unit contains one and a half Ag(I) ions, one bmimb ligand, three fourths of ndca anion and a half of lattice water molecule. Analysis of the local symmetry of the metal atoms and ligands showed that all Ag(I) ions (Ag1, Ag2 and Ag3) and water molecule reside on the crystallographic 2-fold axis (site occupancy factor (SOF) = 1/2); the ndca ligand is bisected by a crystallographic mirror along the bc plane and disordered in two equal positions related to a 2-fold axis. As shown in Fig. 1a, Ag1 is coordinated by two oxygen atoms from two ndca anions to form a line geometry [Ag1–O1 = 2.093(6) Å]. Ag2 is located in a distorted tetrahedral coordination geometry by coordinating with two nitrogen atoms from two different bmimb ligands and two oxygen atoms from two different ndca anions [Ag2–N1 = 2.116(7), Ag2–O2 = 2.658(6) Å] without consideration of Ag...Ag interaction. While Ag3 is coordinated by two nitrogen atoms from two different bmimb ligands and one oxygen atom from ndca anion to form a T-shape geometry [Ag3–N3 = 2.165(7), Ag3–O4 = 2.532(18) Å]. The distortion of the tetrahedron can be indicated by the calculated value of the τ_4 parameter introduced by Houser [29] to describe the geometry of a four-coordinate metal system, which is 0.53 for Ag2 (for perfect tetrahedral geometry, $\tau_4 = 1$).

It is noteworthy that a pair of oppositely arranged μ_2 -bmimb ligands bind two Ag3 atoms to form a $[Ag_2(\text{bmimb})_2]$ ring subunit. These subunits are linked by ndca anions to form a 1D chain [chain (I), Fig. 1b]. Except for this kind of 1D chain, another kind of 1D chain also coexists in **1**. A pair of Ag1 and Ag2 atoms are ligated by two ndca anions to form a $[Ag_2(\text{ndca})_2]$ eight-membered ring subunit and these subunits link each other by sharing the two carboxyl groups of the ndca anion to form a 1D chain. The intra-subunit shortest Ag...Ag contact is 3.3216(17) Å, which is slightly shorter than the twice the van der Waals radius of Ag(I) [30] and indicates so-called argentophilic interaction [31–35]. Then the 1D chain is stabilized by the bmimb ligands, which act as bridges of the adjacent Ag2 atoms with a μ_2 - η^1 : η^1 coordination mode, thus, chain (II) is formed (Fig. 1c).

The lattice water molecule (donor) is hydrogen bonded to oxygen atoms of the carboxyl groups of two different ndca anions with the $O_{\text{water}} \cdots O_{\text{carboxyl}}$ distances of 2.74(2) Å (Table 3). This kind of hydrogen bond extends the chain (I) into a 2D network (Fig. 1d). The $\pi \cdots \pi$ interactions (as shown in Table 4, Fig. S1, Supporting Information) bond the 2D network and chain (II) into a 3D supramolecule.

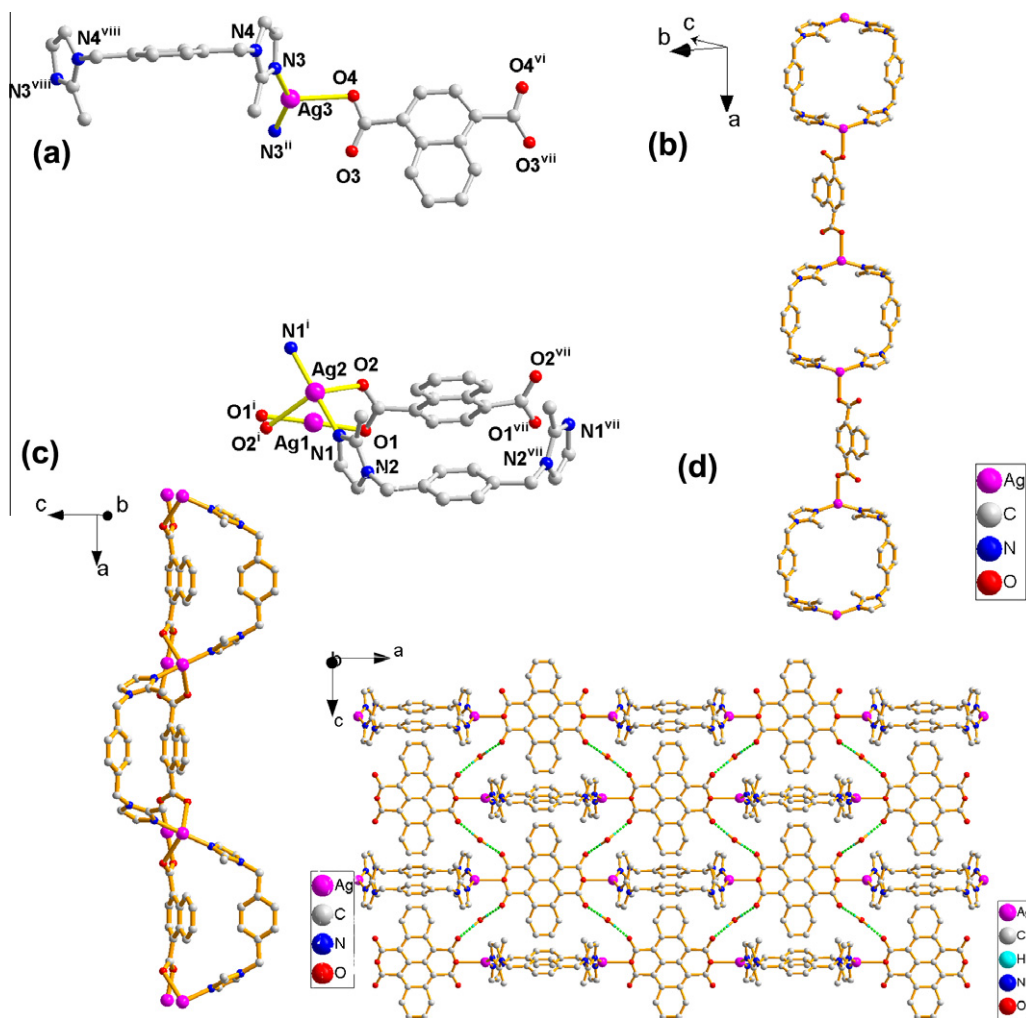


Fig. 1. (a) The coordination environment of the Ag(I) ions and the linkage modes of ligands in **1** with 50% thermal ellipsoid probability. Water molecule and hydrogen atoms are omitted for clarity. (b) Chain (I). (c) Chain (II). (d) The 2D network arranged from chain (I) and hydrogen bonds of adjacent chains. (Symmetry codes: (i) $-x + 1/2, y, -z + 1/2$; (ii) $x, -y + 1, -z + 2$; (vi) $-x, -y + 1, -z + 2$; (vii) $-x, y, z$; (viii) $-x + 1, y, z$.)

Table 3
The hydrogen bond geometry for **1**.

Complex 1	D–H	H...A	D...A	D–H...A
O1W–H1WA...O3	0.85	1.89	2.74(2)	180

Table 4
 $\pi \cdots \pi$ Interactions in **1**.

Ring (i) → ring (j)	Cg...Cg (Å)	Dihedral angle (i,j) (°)	Cg(i) → ring (j) (Å)	Cg(j) → ring (i) (Å)	β (°)
Cg1...Cg4 ⁱⁱⁱ	3.863(6)	10.3(6)	3.623(4)	−3.648(4)	19.20
Cg3...Cg7 ^{iv}	3.971(5)	27.0(4)	3.960(4)	−3.661(3)	22.81
Cg4...Cg1 ⁱⁱⁱ	3.863(6)	10.3(6)	−3.648(4)	3.624(4)	20.28
Cg7...Cg3 ^v	3.971(5)	27.0(4)	−3.660(3)	3.961(4)	4.17

Cg1: N3/C15/C16/N4/C17; Cg3: C20/C21/C21^a/C20^a/C22^a/C22; Cg4: N1/C6/C5/N2/C7; Cg7: C12/C13/C14/C14^b/C13^b/C12^b.

Symmetry codes: (iii) $x, 1 - y, 1 - z$; (iv) $1/2 - x, 1 - y, 1/2 + z$; (v) $1/2 - x, 1 - y, -1/2 + z$. β = Angle Cg(i) → Cg(j) or Cg(i) → Me vector and normal to ring (i).

4.3. Photoluminescence properties

Emissive CPs are of great current interest because of their various applications in chemical sensors, photochemistry and

electroluminescent display [36,37]. Thus, the photoluminescence property of **1** as well as free ligands was examined in the solid state at room temperature (Fig. 2). The bmimb and ndca ligands display photoluminescent emissions at 493 and 477 nm respectively under

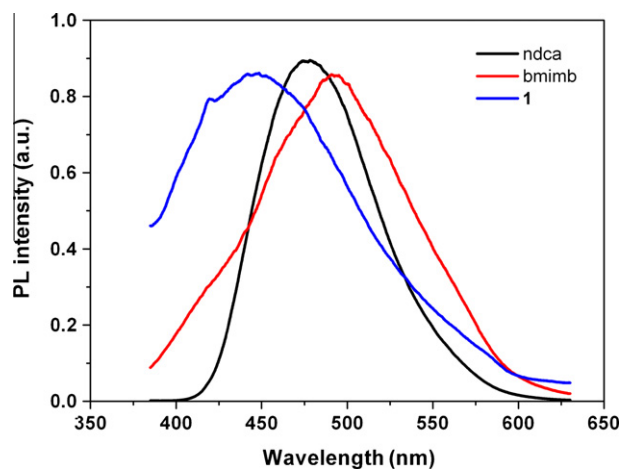


Fig. 2. Emission spectra of the ligands and complex **1**.

360 nm radiation which are probably attributed to the $\pi^* \rightarrow \pi$ transition [38–40]. Consideration of weak emissive essence of H_2ndca ligand [41], the photoluminescence of compound **1** should originate from the transitions between the energy levels of *N*-donor ligands [42]. The intense emission bands at 446 nm ($\lambda_{ex} = 360$ nm) for **1** is observed at room temperature which is blue-shifted by about 50 nm compared to that of the *bmimb* ligands.

5. Conclusions

In summary, we demonstrate the synthesis and characterization of a photoluminescent 1D chain Ag(I) CP under the ammoniacal condition. As the change of the coordination mode of the *ndca* ligand, two different kinds of chains [chain (I) and chain (II)] are formed. These results provide a way of understanding the influence of the coordination modes of the *ndca* ligand on the resultant structures. Moreover, photoluminescent property of this CP is also discussed.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (Nos. 21021061 and 21071118), 973 Project (Grant 2007CB815301) from MSTC, Independent Innovation Foundation of Shandong University (2011GN030), and the Special Fund for Postdoctoral Innovation Program of Shandong Province (201101007).

Appendix A. Supplementary material

CCDC 853976 contains the supplementary crystallographic data for **1** in this paper. 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 CB 21EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.molstruc.2012.01.052](https://doi.org/10.1016/j.molstruc.2012.01.052).

References

- [1] S.R. Batten, R. Robson, *Angew. Chem., Int. Ed.* 37 (1998) 1460.
- [2] M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T. Reineke, M. O'Keeffe, O.M. Yaghi, *Acc. Chem. Res.* 34 (2001) 319.
- [3] G. Férey, *Chem. Soc. Rev.* 37 (2008) 191.
- [4] S.L. James, *Chem. Soc. Rev.* 32 (2003) 276.
- [5] B. Moulton, M.J. Zaworotko, *Chem. Rev.* 101 (2001) 1629.
- [6] J.J. Vittal, *Coord. Chem. Rev.* 251 (2007) 1781.
- [7] S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem., Int. Ed.* 43 (2004) 2334.
- [8] J.P. Zhang, X.C. Huang, X.M. Chen, *Chem. Soc. Rev.* 38 (2009) 2385.
- [9] J.P. Zhang, X.M. Chen, *J. Am. Chem. Soc.* 130 (2008) 6010.
- [10] D. Venkataraman, Y. Du, S.R. Wilson, P. Zhang, K. Hirsch, J.S. Moore, *J. Chem. Ed.* 74 (1997) 915.
- [11] D. Sun, G.G. Luo, R.B. Huang, N. Zhang, L.S. Zheng, *Acta Cryst. C65* (2009) m305.
- [12] D. Sun, G.G. Luo, N. Zhang, J.H. Chen, R.B. Huang, L.R. Lin, L.S. Zheng, *Polyhedron* 28 (2009) 2983.
- [13] D. Sun, G.G. Luo, N. Zhang, R.B. Huang, L.S. Zheng, *Acta Cryst. C65* (2009) m418.
- [14] D. Sun, G.G. Luo, N. Zhang, R.B. Huang, L.S. Zheng, *Acta Cryst. C65* (2009) m440.
- [15] D. Sun, G.G. Luo, N. Zhang, Q.J. Xu, C.F. Yang, Z.H. Wei, Y.C. Jin, L.R. Lin, R.B. Huang, L.S. Zheng, *Inorg. Chem. Commun.* 13 (2010) 290.
- [16] D. Sun, N. Zhang, R.-B. Huang, L.-S. Zheng, *Cryst. Growth Des.* 10 (2010) 3699.
- [17] D. Sun, G.G. Luo, N. Zhang, Z.H. Wei, C.F. Yang, Q.J. Xu, R.B. Huang, L.S. Zheng, *J. Mol. Struct.* 967 (2010) 147.
- [18] D. Sun, H.-R. Xu, C.-F. Yang, Z.-H. Wei, N. Zhang, R.-B. Huang, L.-S. Zheng, *Cryst. Growth Des.* 10 (2010) 4642.
- [19] C.-Y. Lin, Z.-K. Chan, C.-W. Yeh, C.-J. Wu, J.-D. Chen, J.-C. Wang, *CrystEngComm* 8 (2006) 841.
- [20] Y.-H. Wang, K.-L. Chu, H.-C. Chen, C.-W. Yeh, Z.-K. Chan, M.-C. Suen, J.-D. Chen, *CrystEngComm* 8 (2006) 84.
- [21] D. Sun, D.-F. Wang, X.-G. Han, N. Zhang, R.-B. Huang, L.-S. Zheng, *Chem. Commun.* 47 (2010) 746.
- [22] D. Sun, C.-F. Yang, H.-R. Xu, H.-X. Zhao, Z.-H. Wei, N. Zhang, L.-J. Yu, R.-B. Huang, L.-S. Zheng, *Chem. Commun.* 46 (2010) 8168.
- [23] D. Sun, Q.-J. Xu, C.-Y. Ma, N. Zhang, R.-B. Huang, L.-S. Zheng, *CrystEngComm* 12 (2010) 4161.
- [24] D. Sun, G.G. Luo, N. Zhang, Z.H. Wei, C.F. Yang, Q.J. Xu, R.B. Huang, L.S. Zheng, *Chem. Commun.* 47 (2011) 1461.
- [25] Bruker. SMART, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA, 1998.
- [26] G.M. Sheldrick, SHELXS-97, Program for X-ray Crystal Structure Determination, University of Göttingen, Germany, 1997.
- [27] G. M. Sheldrick, SHELXL-97, Program for X-ray Crystal Structure Refinement, University of Göttingen, Germany, 1997.
- [28] A.L. Spek, Implemented as the PLATON Procedure, a Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 1998.
- [29] L. Yang, D.R. Powell, R.P. Houser, *Dalton Trans.* (2007) 955.
- [30] A. Bondi, *J. Phys. Chem.* 68 (1964) 441.
- [31] L. Dobrzanska, H.G. Raubenheimer, L.J. Barbour, *Chem. Commun.* (2005) 5050.
- [32] L. Pan, E.B. Woodlock, X. Wang, K.-C. Lam, A.L. Rheingold, *Chem. Commun.* (2001) 1762.
- [33] J.-P. Zhang, Y.-B. Wang, X.-C. Huang, Y.-Y. Lin, X.-M. Chen, *Chem.-Eur. J.* 11 (2005) 552.
- [34] C.-M. Che, M.-C. Tse, M.C.W. Chan, K.-K. Cheung, D.L. Phillips, K.-H. Leung, *J. Am. Chem. Soc.* 122 (2000) 2464.
- [35] E. Guney, V.T. Yilmaz, O. Buyukgungor, *Inorg. Chem. Commun.* 13 (2010) 563.
- [36] Y.R. Liu, L. Li, T. Yang, X.W. Yu, C.Y. Su, *CrystEngComm* 11 (2009) 2712.
- [37] G.D. Santis, L. Fabbrizzi, M. Licchelli, A. Poggi, A. Taglietti, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 202.
- [38] A. Thirumurugan, S. Natarajan, *Dalton Trans.* (2004) 2923.
- [39] S.Q. Liu, T. KurodaSowa, H. Konaka, Y. Suenaga, M. Maekawa, T. Mizutani, G.L. Ning, M. Munakata, *Inorg. Chem.* 44 (2005) 1031.
- [40] D. Sun, N. Zhang, Q.J. Xu, G.G. Luo, R.B. Huang, L.S. Zheng, *J. Mol. Struct.* 970 (2010) 134.
- [41] W.J. Chen, Y. Wang, C. Chen, Q. Yue, H.M. Yuan, J.S. Chen, S.N. Wang, *Inorg. Chem.* 42 (2003) 944.
- [42] F.-F. Li, J.-F. Ma, J. Yang, H.-Q. Jia, N.-H. Hu, *J. Mol. Struct.* 787 (2006) 106.