

两个含有混磷配体的发光银(I)配合物的合成和表征

张彦茹¹ 王梦秦¹ 崔洋哲¹ 刘 敏² 李中峰¹ 金琼花^{*,1}

(¹ 首都师范大学化学系, 北京 100048)

(² 北京工业大学材料科学与工程学院, 北京 100124)

摘要: 合成了两个新的银(I)配合物, $[\text{Ag}_2\text{Br}_2(\text{DPEphos})_2(\text{dppe})](\mathbf{1})$ 和 $[\text{Ag}(\text{DPEphos})(\text{dppe})]\text{NO}_3(\mathbf{2})$ (DPEphos =双[(2-二苯膦基)苯基]醚; dppe =1,2-双(二苯膦)乙烷), 通过红外光谱、X-射线单晶衍射、核磁共振氢谱、磷谱和荧光光谱进行分析和表征。 $\mathbf{1}$ 是由 AgBr , DPEphos 和 dppe 以 2:2:1 的比例混合反应得到的双核化合物, dppe 通过 2 个 P 原子桥连 2 个 Ag 原子, 而 $\mathbf{2}$ 是由 AgNO_3 , DPEphos 和 dppe 以 1:1:1 的比例混合反应得到的简单的单核化合物, Ag 原子与 DPEphos 和 dppe 配体螯合。在配合物 $\mathbf{2}$ 的磷谱中, 存在 4 个分裂峰(双峰或者三重峰)。荧光光谱表明所有的发射峰均源于配体中的 $\pi-\pi^*$ 跃迁。

关键词: 双[(2-二苯膦基)苯基]醚; 1,2-双(二苯膦)乙烷; 银; 荧光

中图分类号: O614.122

文献标识码: A

文章编号: 1001-4861(2015)10-2089-06

DOI: 10.11862/CJIC.2015.274

Syntheses and Characterization of Two Luminescent Silver(I) Complexes Based on Mixed Phosphine Ligands

ZHANG Yan-Ru¹ WANG Meng-Qin¹ CUI Yang-Zhe¹ LIU Min² LI Zhong-Feng¹ JIN Qiong-Hua^{*,1}

(¹ Department of Chemistry, Capital Normal University, Beijing 100048, China)

(² College of Materials Science and Engineering, Beijing University of Technology, Beijing 100124, China)

Abstract: Two novel silver(I) complexes $[\text{Ag}_2\text{Br}_2(\text{DPEphos})_2(\text{dppe})](\mathbf{1})$ and $[\text{Ag}(\text{DPEphos})(\text{dppe})]\text{NO}_3(\mathbf{2})$ (DPEphos =bis [2-(diphenylphosphino)phenyl]ether, dppe =bis (diphenylphosphino)ethane) have been synthesized and characterized by IR, single-crystal X-ray diffraction, ^1H NMR, ^{31}P NMR spectroscopy and fluorescence spectra. $\mathbf{1}$ is comprised of AgBr , DPEphos and dppe in 2:2:1 molar ratio generating a binuclear complex. The dppe ligand bridges two Ag atoms through two P atoms in $\mathbf{1}$. While, $\mathbf{2}$ is obtained by the reactions of AgNO_3 , DPEphos and dppe in 1:1:1 molar ratio generating a sample mono-nuclear complex. The Ag(I) atom is chelated by DPEphos and dppe ligand. In the ^{31}P NMR spectra of $\mathbf{2}$, there are four splitting signals (doublets or triplets). The luminescent spectra show that the origin of these emissions all involves emissive state derived from ligand centered $\pi-\pi^*$ transition. CCDC: 1043375, $\mathbf{1}$; 1043376, $\mathbf{2}$.

Key words: bis[2-(diphenylphosphino)phenyl]ether; bis(diphenylphosphino)ethane; silver(I); fluorescence

0 Introduction

More and more interests are focused on the group

11 metal complexes owing to their rapid developments in their structural diversity^[1-2] and intriguing optical properties^[3-4]. In recent years, many efforts have been

收稿日期: 2015-06-28。收修改稿日期: 2015-07-12。

国家自然科学基金(No.21171119), 863 国家高技术研究发展计划(No. 2012AA063201), 北京教育委员会基金(No. KM201210028020), 北京市优秀人才项目(No.2010D005016000002), 北京市自然科学基金(No.7122015)资助项目。

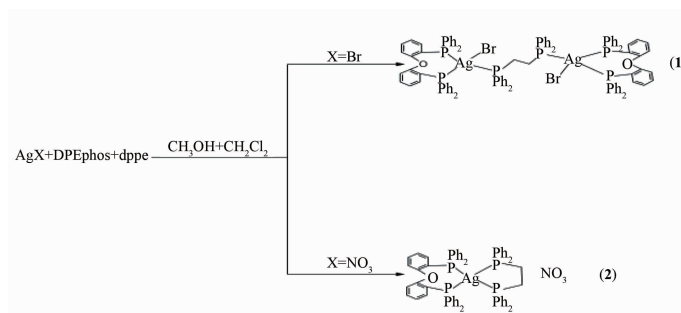
*通讯联系人。E-mail: jinqh@cnu.edu.cn ; 会员登记号: S06N3669M1105。

done to get a deeper research on their potential applications of the closed-shell d^{10} metals complexes, such as luminescent-based chemical sensors^[5], organic light emitting diodes^[6], catalysis^[7-8] and sensitizers in solar-energy conversion^[9]. The Ag(I) atom commonly adopts four-coordinated mode indicating a distorted tetrahedron.

The Ag(I) compounds containing P-donor ligands attract much attention due to their low cost, nontoxicity and luminescence. Among a number of P-donor ligands, the type $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ligand is used to form extensive and varied coordination compounds^[10]. The coordination behavior (chelating or bridging mode) primarily depends on the length of the methylene chain between the two P donors^[11-12]. In addition, the transition metal chemistry and catalytic utility of the bis [2-(diphenylphosphino)phenyl]-ether (DPEphos) have been extensively studied by van

Leeuwen and co-workers^[13] and others^[14-15]. Recently, considerable attention has been paid on the coordination architectures of metal-DPEphos complexes, such as ruthenium(II)^[16], gold(I)^[17] and silver(I) complexes^[18].

Last year, our group reported a series of Ag(I) complexes based on mixed phosphine ligands and splitting phenomenon of ^{31}P NMR signals^[19]. After that, we synthesized two novel silver (I) complexes (Scheme 1), $\text{Ag}_2\text{Br}_2(\text{DPEphos})_2(\text{dppe})$ (**1**) and $[\text{Ag}(\text{DPEphos})(\text{dppe})]\text{NO}_3$ (**2**), (DPEphos = bis [2-(diphenylphosphino) phenyl] ether, dppe = bis (diphenylphosphino) ethane). They have been characterized by IR, single-crystal X-ray diffraction, $^1\text{H}/^{31}\text{P}$ NMR spectroscopy and fluorescence spectrum. We also discussed the role of the impact of anion and the proportion of different diphosphine ligands in the synthesis. Furthermore, a similar splitting phenomenon in ^{31}P NMR was found.



Scheme 1 Routine of synthesis for complexes **1** and **2**

1 Experimental

1.1 Materials and measurements

All chemical reagents are commercially available and used without furthermore treatment. FTIR spectra (KBr pellets) were measured on a Perkin-Elmer Infrared spectrometer. C, H and N elemental analysis were carried out on an Elementar Vario MICRO CUBE (Germany) elemental analyzer. Room-temperature fluorescence spectra were measured on F-4500 FL Spectrophotometer. ^1H NMR and ^{31}P NMR was recorded at room temperature with a Varian VNMRs 600MHz spectrometer and ^{31}P NMR was recorded at room temperature with a Varian VNMRs 243MHz spectrometer.

1.2 Synthesis of $[\text{Ag}_2\text{Br}_2(\text{DPEphos})_2(\text{dppe})]$ (**1**)

Complex **1** was prepared by the reaction of AgBr (0.037 7 g, 0.2 mmol) with DPEphos (0.107 3 g, 0.2 mmol) and dppe (0.039 9 g, 0.1 mmol) in the mixed solvents of 5 mL CH_2Cl_2 and 5 mL CH_3OH . The mixture was stirred for 6 hours and filtered. Colorless crystals were obtained from the filtrate after standing at room temperature for several days. Yield: 49%. Element analysis Calcd.(%) for $\text{C}_{98}\text{H}_{80}\text{Ag}_2\text{Br}_2\text{O}_2\text{P}_6$: C, 63.53; H, 4.32; Found(%): C, 62.13; H, 4.60. IR data (cm^{-1} , KBr pellets): 3 427m, 3 048w, 1 621w, 1 562w, 1 480w, 1 458w, 1 433s, 1 257w, 1 218m, 1 094w, 1 025w, 741s, 693s, 510m, 497m, 469w. ^1H NMR (600 MHz, CDCl_3 , 298 K): δ 7.3~7.1 (m, $\text{CH}_{\text{benzene}}$), 1.6(s, CH_2). ^{31}P NMR (243 MHz, CDCl_3 , 298 K): δ -4.0(br), -11.0(br, d).

1.3 Synthesis of [Ag(DPEphos)(dppe)]NO₃(2)

The preparation of complex **2** was similar to **1** except that the salt was changed to AgNO₃ (0.034 1 g, 0.2 mmol). Colorless crystals were obtained with a yield of 57%. Element analysis Calcd.(%) for C₆₂H₅₂AgNO₄P₄: C, 67.22; H, 4.70; N, 1.26; Found(%): C, 66.67; H, 4.72; N, 1.31. IR data (cm⁻¹, KBr pellets): 3 435w, 3 052w, 1 633w, 1 586w, 1 564w, 1 480w, 1 460w, 1 434s, 1 384s, 1 341m, 1 258w, 1 215m, 1 095w, 744s, 495s, 512m, 477w. ¹H NMR (600 MHz, CDCl₃, 298 K): δ 7.4~6.8 (m, CH_{benzene}), 1.7(s, CH₂). ³¹P NMR (243 MHz, CDCl₃, 298K): δ 3.2(dd), -2.7(dt), -7.2(dt), -8.8(dd)

1.4 Structure determination

Single crystals of the title complexes were mounted on a Bruker Smart 1000 CCD diffractometer equipped with a graphite-monochromated Mo Kα (λ=0.071 073 nm) radiation at 298 K. Semi-empirical absorption

corrections were applied using SABABS program. All the structures were solved by direct methods using SHELXS program of the SHELXTL-97 package and refined with SHELXL-97^[19]. Metal atom centers were located from the *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinements were performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on *F*². The hydrogen atoms were generated geometrically and refined with displacement parameters riding on the concerned atoms.

Crystallographic data and experimental details for structural analysis are summarized in Table 1, and selected bond lengths and angles of complexes **1**~**2** are summarized in Table 2.

CCDC: 1043375, **1**; 1043376, **2**.

Table 1 Crystallographic data for complexes **1**~**2**

	1	2
Formula	C ₉₈ H ₈₀ Ag ₂ Br ₂ O ₂ P ₆	C ₆₂ H ₅₂ AgNO ₄ P ₄
Formula weight	1 851.00	1 006.80
<i>T</i> / K	293(2)	293(2)
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
Crystal size / mm	0.43×0.40×0.27	0.38×0.30×0.23
<i>a</i> / nm	1.230 23(10)	1.477 45(13)
<i>b</i> / nm	1.242 10(9)	1.280 48(11)
<i>c</i> / nm	1.706 81(14)	3.586 6(3)
α / (°)	98.161 0(10)	90.00
β / (°)	100.546 0(10)	112.650(3)
γ / (°)	113.365(2)	90.00
<i>V</i> / nm ³	2.286 3(3)	6.262 0(9)
Reflections collected/unique	19 649 / 13 416	28 061 / 10 723
Data/restraints/parameters	13 416 / 0 / 901	10 723 / 0 / 649
<i>Z</i>	1	4
μ / mm ³	1.453	0.466
<i>F</i> (000)	938	2 280
Goodness-of-fit on <i>F</i> ²	1.046	1.054
<i>R</i> _{int}	0.061 3	0.117 6
<i>R</i> ₁ [<i>I</i> >2σ(<i>I</i>)] ^a	0.063 1	0.078 9
<i>wR</i> ₂ [<i>I</i> >2σ(<i>I</i>)] ^b	0.084 1	0.136 6
<i>R</i> ₁ (all data) ^a	0.126 3	0.179 3
<i>wR</i> ₂ (all data) ^b	0.096 7	0.163 4

^a $R = \sum (|F_o| - |F_c|) / \sum |F_o|$; ^b $wR = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(F_o^2)]^{1/2}$

Table 2 Selected bond distances(nm) and bond angles(°) for complexes 1~2

Complex 1					
Ag(1)-P(1)	0.247 12(18)	Ag(1)-P(3)	0.251 29(18)	Ag(1)-P(2)	0.253 53(16)
Ag(1)-Br(1)	0.277 90(9)				
P(1)-Ag(1)-P(3)	122.91(5)	P(1)-Ag(1)-Br(1)	93.94(4)	P(1)-Ag(1)-P(2)	118.78(6)
P(3)-Ag(1)-Br(1)	102.24(5)	P(3)-Ag(1)-P(2)	106.30(6)	P(2)-Ag(1)-Br(1)	109.83(4)
Complex 2					
Ag(1)-P(4)	0.247 9(2)	Ag(1)-P(2)	0.253 6(3)	Ag(1)-P(3)	0.252 8(2)
Ag(1)-P(1)	0.253 7(2)				
P(4)-Ag(1)-P(3)	104.47(8)	P(4)-Ag(1)-P(2)	124.61(8)	P(3)-Ag(1)-P(2)	114.48(8)
P(4)-Ag(1)-P(1)	123.74(8)	P(3)-Ag(1)-P(1)	105.96(8)	P(2)-Ag(1)-P(1)	81.92(8)

Symmetry code: $^11-x, 1-y, 1-z$

2 Results and discussion

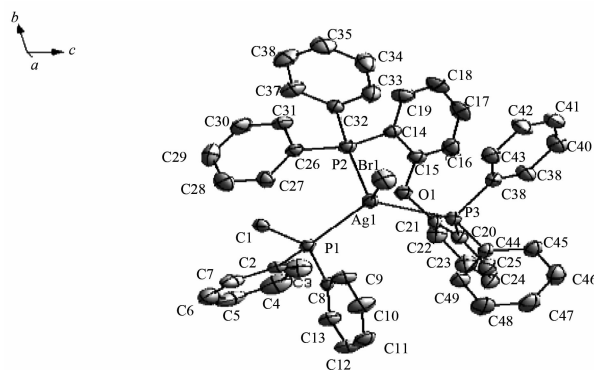
2.1 Syntheses of the single crystals

As we all know, different solvents can also affect the structures of the products. Last year, our group synthesized two complexes $[\text{Ag}_2\text{Cl}_2(\text{DPEphos})_2(\text{dppe})] \cdot 2\text{CH}_3\text{OH} \cdot \text{DMF}$ and $[\text{Ag}_2\text{Br}_2(\text{DPEphos})_2] \cdot 2\text{DMF}$ in different solvents^[20]. It should be mentioned that different complexes are synthesized in the same molar ratio and solvent, when the anion is different halogen atom. It isn't found that Ag(I) atom is connected to dppe ligand in any mode. Now, the complex **1** is prepared in the mixed solution environment (5 mL CH_3OH and 5 mL CH_2Cl_2). The crystal structure is similar with $[\text{Ag}_2\text{Cl}_2(\text{DPEphos})_2(\text{dppe})] \cdot 2\text{CH}_3\text{OH} \cdot \text{DMF}$. It is proved that solvents are important to the formation of the coordination compounds.

In addition, three simple mono-nuclear complexes are prepared in the same proportion and solvent. The complex **2** is prepared by AgNO_3 , dppe, and DPEphos in 1:1:1 molar ratio generating a mono-nuclear complex. While, the complex $[\text{Ag}_2(\text{NO}_3)_2(\text{DPEphos})_2(\text{dppe})]$ is synthesized by AgNO_3 , dppe, and DPEphos in 2:1:2 molar ratio generating a binuclear complex^[20]. By comparing to complex **2**, we find dppe ligand can act as bridging or chelating ligand depending on the proportion.

2.2 Description of the Crystal Structure

Complex **1** is crystallized in the triclinic crystal system and contains a crystallographic center of symmetry (Fig.1). Each asymmetric unit is composed of half of a dppe ligand, a bromine atom and a DPEphos ligand chelating a Ag(I) atom. In complex **1**, two silver atoms are linked by bridging dppe ligand to

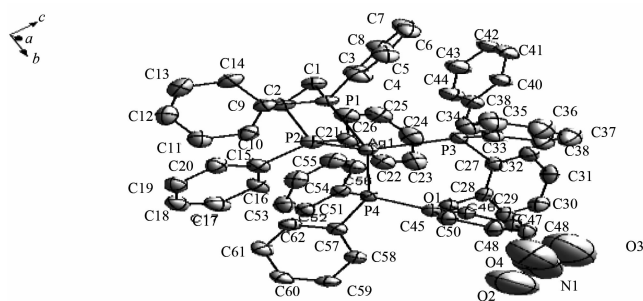


All hydrogen atoms are omitted for clarity; Thermal ellipsoids drawn at the 30% probability level

Fig.1 Asymmetric unit of complex **1**

form a binuclear structure. The Ag(I) metal adopts four-coordinated mode establishing a distorted tetrahedral geometry. The geometry around metal center is distorted tetrahedral because of the angles in the range of $93.94(4)^\circ \sim 122.91(5)^\circ$. The Ag-P(dppe) bond distance is 0.247 12(18) nm in accord with that of $[\text{Ag}_2\text{Cl}_2(\text{DPEphos})_2(\text{dppe})] \cdot 2\text{CH}_3\text{OH} \cdot \text{DMF}$ ^[20], indicating that free solvent molecular and halogen atom are influented. The Ag-P (DPEphos) bond distances (0.251 29(18) nm and 0.253 53(16) nm) are similar compared with those of complexes in previous literature^[19]. The bite angles of the DPEphos ligand is $106.30(6)^\circ$, which is 11.10° and 11.80° less than the same angle in the complex $[\text{Ag}_2(\kappa^2\text{-P,P-DPEphos})_2(\mu\text{-OTf})_2]$ ^[21] and $\text{Ag}_2\text{I}_2(\text{DPEphos})_2$ ^[22].

Complex **2** is simple mono-nuclear complex formed with distinctly soft Ag(I), dppe ligand, DPEphos ligand and anion (Fig.2). Each Ag(I) atom is four-coordinated, attached to two P atoms from a chelating dppe ligand and two P atoms from a chelating DPEphos ligand. In Complex **2**, the angles around Ag(I) atom ranging from $81.92(8)^\circ$ to $124.61(8)^\circ$ indicate that the geometry around Ag atom is distortedly tetrahedral. The bite angles of the DPEphos ligand is $104.47(8)^\circ$, which is smaller than the same angle in the complexes $[\text{Ag}(\text{POP})_2]^+$ ^[23] and $[\text{Ag}(\text{DPEphos})(\text{PY}_2\text{SH})_2]\text{NO}_3$ ^[24]. The Ag-P(DPEphos or dppe) bond distance is similar with that in $[\text{Ag}(\text{DPEphos})(\text{dppe})]\text{BF}_4$ ^[19].



All hydrogen atoms are omitted for clarity; Thermal ellipsoids drawn at the 30% probability level

Fig.2 Molecular structure of complex **2**

2.3 Infrared spectroscopy

The infrared spectra of complexes **1~2** show the absorptions around $1\,434\text{ cm}^{-1}$ are due to C-C stretch vibration of the phenyl rings and the middle absorptions around $3\,052\text{ cm}^{-1}$ are caused by C-H vibration of the phenyl rings. The absorptions of the C-O-C stretch vibration are around $1\,215\text{ cm}^{-1}$. The absorptions in $1\,384\text{ cm}^{-1}$ and $1\,341\text{ cm}^{-1}$ are derived from nitrate(NO_3^-) in complex **2**.

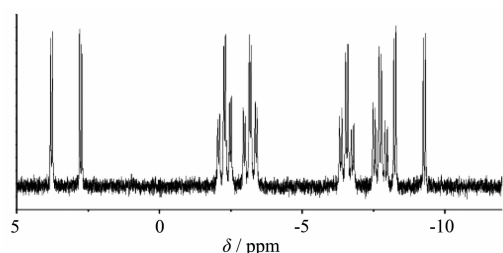
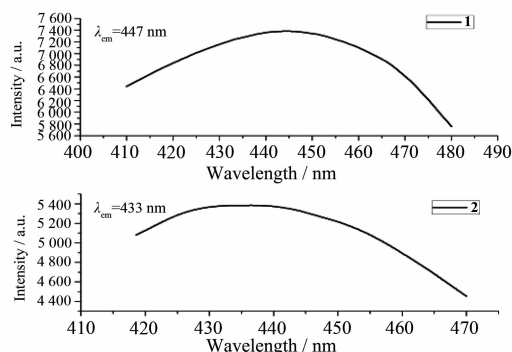
2.4 ^{31}P NMR spectroscopy

The ^{31}P NMR spectra of complexes **1~2** and two kinds of phosphine (DPEphos and dppe) ligands have been measured at room temperature in CDCl_3 . In ^{31}P NMR spectra of two kinds of phosphine ligands, the ^{31}P NMR spectra show a singlet resonance peak. The P signals of free DPEphos and free dppe exist at -16.9 and -12.6 , respectively.

Interestingly, the ^{31}P NMR spectrum of **2** consists of two pairs of well resolved doublets centered at 3.2 and -8.8 . Furthermore, ^{31}P NMR spectrum of **2** consists of two pairs of triplets centered at -2.7 and -7.2 . Every peak of the triplets changes into doublet(Fig.3).

2.5 Fluorescence Spectrum

The luminescent emission spectra of complexes **1~2** in the solid state at room temperature are obtained (Fig.3). In the fluorescence emission spectra of solid dppe and DPEphos, the emission peaks are found at 435 nm ($\lambda_{\text{ex}}=357\text{ nm}$ for dppe) and 453 nm ($\lambda_{\text{ex}}=317\text{ nm}$ for DPEphos), respectively^[19]. In the fluorescence emission spectra of **1~2**, the emission peaks are found at 447 nm ($\lambda_{\text{ex}}=372\text{ nm}$ for **1**) and 433nm ($\lambda_{\text{ex}}=362\text{ nm}$ for **2**). The emissions of complex **1** exhibits a red-shift distinctly, compared to that of the corresponding free ligand dppe. The emission

Fig.3 ^{31}P NMR spectrum of **2** in CDCl_3 Fig.4 Solid-state emission spectra of **1-2** at 298 K

peak is similar to that of dppe, which indicates that the origin of the emission involves emissive state derived from ligand-centered $\pi-\pi^*$ transition.

3 Conclusions

Two new Ag(I) complexes of phosphine-containing ligands (DPEphos and dppe) have been synthesized and characterized by elemental analysis, IR, X-ray diffraction, fluorescence, ^1H NMR, ^{31}P NMR spectroscopy. Structure analyses show that two silver atoms are linked by bridging dppe ligand and chelated two DPEphos ligands to form a binuclear structure in complex **1**. While, complex **2** is a simple mononuclear structure. Each silver atom is chelated a dppe ligand and a DPEphos ligand. In the ^{31}P NMR spectra of **2**, there are four splitting signals (doublets or triplets). The luminescent spectra show that the origin of these emissions all involves emissive state derived from ligand centered $\pi-\pi^*$ transition. We hope our results could offer new strategy for the characterization and design of metalorganic compounds.

References:

- [1] Kim E, Lee H, Noh T H, et al. *Cryst. Growth Des.*, **2014**,**14**: 1888-1894
- [2] Yue C Y, Yan C F, Feng R, et al. *Inorg. Chem.*, **2009**,**48**: 2873-2879
- [3] Rajput G, Yadav M K, Drew M G, et al. *Inorg. Chem.*, **2015**, **54**:2572-2579
- [4] Nitsch J, Kleeberg C H, Fröhlich R, et al. *Dalton Trans.*, **2015**,**44**:6944-6960
- [5] Demas J N, Graff B A. *Coord. Chem. Rev.*, **2001**,**211**:317-351
- [6] Minaev B, Jansson E, Ågren H. *J. Chem. Phys.*, **2006**,**125**: 234704/1-18
- [7] Tsubomura T, Sakai K. *Coord. Chem. Rev.*, **1998**,**171**:107-113
- [8] Wang X X, Liu Y G, Hecke K V, et al. *Z. Anorg. Allg. Chem.*, **2015**,**641**:903-910
- [9] Felder D, Nierengarten J F, Barigelletti F, et al. *J. Am. Chem. Soc.*, **2001**,**123**:6291-6299
- [10] Effendy, Nicola C, Pettinari C, et al. *Inorg. Chim. Acta*, **2006**,**359**:64-80
- [11] Qiu Q M, Huang X, Zhao Y H, et al. *Polyhedron*, **2014**,**83**: 16-23
- [12] Cui L N, Li Z F, Jin Q H, et al. *Inorg. Chem. Commun.*, **2012**,**20**:126-130
- [13] Kranenburg M, Burgt Y, Kamer P, et al. *Organometallics*, **1995**,**14**:3081-3089
- [14] Kuang S, Cuttall D G, McMillin D R, et al. *Inorg. Chem.*, **2002**,**41**:3313-3322
- [15] Kuang S M, Fanwick P E, Walton R A. *Inorg. Chem.*, **2002**,**41**:405-411
- [16] Venkateswaran R, Mague J T, Balakrishna M S. *Inorg. Chem.*, **2007**,**46**:809-817
- [17] Partyka D V, Updegraff III J B, Zeller M, et al. *Dalton Trans.*, **2010**,**39**:5388-5397
- [18] Balakrishna M S, Venkateswaran R, Mobin S M. *Inorg. Chim. Acta*, **2009**,**362**:271-276
- [19] Sheldrick G M. *SHELXS-97* and *SHELXL-97*, University of Göttingen, Göttingen, Germany, **1997**.
- [20] Gao S, Li Z F, Liu M, et al. *Polyhedron*, **2014**,**83**:10-15
- [21] Balakrishna M S, Venkateswaran R, Mobin S M. *Polyhedron*, **2008**,**27**:899-904
- [22] Freudenmann D, Feldmann C. *Inorg. Chim. Acta*, **2011**, **375**:311-313
- [23] Adrien K, Omar M, Gianluca A, et al. *Eur. J. Inorg. Chem.*, **2014**,**2014**:1345-1355
- [24] George C, Philip J C, Paraskevas A. *Polyhedron*, **2012**,**31**: 502-505