配合物$(BenzMeIm)_2[PtCl_4]$的合成与表征

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摘要：通过离子液体氯化 1-苄基-3-甲基咪唑(BenzMeIm-Cl)与 $PtCl_2$ 的反应，合成了配合物$(BenzMeIm)_2[PtCl_4]$，并用元素分析、红外光谱、紫外-可见光谱、^1H NMR、^{13}C NMR 和单晶 X 射线衍射对其进行了表征。单晶 X 射线分析表明，配合物结构属于 $P2_1/c$ 空间群，晶胞参数和结构解析参数为：a=0.981 80(5) nm，b=0.861 47(3) nm，c=0.144 332(7) nm，β=92.480(2)°，V=121.96(1) nm^3，R_1=0.014 4，wR_2=0.038 8。

关键词：氯化 1-苄基-3-甲基咪唑；铂；配合物；晶体结构
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Synthesis and Characterization of Complex $(BenzMeIm)_2[PtCl_4]$

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Abstract: A complex of $(BenzMeIm)_2[PtCl_4]$ was prepared by the reaction of 1-benzyl-3-methylimidazolium chloride (BenzMeIm-Cl) with $PtCl_2$. The structure of the complex was characterized by single crystal X-ray analysis, and it crystallizes in the monoclinic $P2_1/c$ space group, with a=0.981 80(5) nm, b=0.861 47(3) nm, c=0.144 332(7) nm, β=92.480(2)°, V=121.96(1) nm^3, R_1=0.014 4, wR_2=0.038 8. CCDC: 1532135.

Keywords: 1-benzyl-3-methylimidazolium chloride; Pt(Ⅱ); complex; crystal structure

0 Introduction

Ionic liquid salts have received an increasing interest due to their applications in many fields such as medicine, organic and inorganic synthesis, electrochemistry, separation processes and as novel materials[1]. For example, 2-methylsulfanyl-1*H*-pyrimidin-3-ium iodide is a potential antitumor agent[2-4]. The complexes containing the platinum group metals have also attracted great interest, mainly because of their application as catalysts[5], and several reports have described spectrochemical and electrochemical studies in ionic liquid media[6-8]. New complexes of palladium (Ⅱ) and platinum(Ⅱ) containing the carbazolium, indolium and pyrrolium benzyl derivatives have been synthesized and characterized and the results exhibit the square planar geometry for both of Pd(Ⅱ) and Pt(Ⅱ) complexes[9].

In this account we report the synthesis, characterization, and X-ray crystal structure of the complex $(BenzMeIm)_2[PtCl_4]$ from the reaction of 1-benzyl-3-methylimidazolium chloride (BenzMeIm-Cl) with $PtCl_2$ (Scheme 1).

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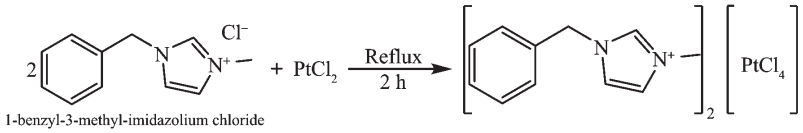

Scheme 1　Synthesis of the complex (BenzMeIm)$_2$[PtCl$_4$]

1　Experimental

1.1　Materials and instrument

1-Benzyl-3-methylimidazolium chloride (BenzMeIm-Cl) is commercially available (Shanghai Biochemical, China), and $PtCl_2$ was obtained from Yuri Chemicals, China.

The ^{1}H and ^{13}C NMR spectra were recorded at 300 K using a Bruker Ultra-Shield 300 MHz spectrometer. Deuterated dimethyl sulfoxide was used as the solvent and the peak positions were obtained relative to $SiMe_4$. Infrared spectra were recorded on a Shimadzu FTIR spectrometer using KBr discs in the 4 000~400 cm^{-1} range, and a Pye-Unicam 300 spectrometer using CsI discs in the range 4 000~200 cm^{-1}. UV-Vis spectra were obtained using an AE-UV 1690 (UK) 330 spectrophotometer with the samples in DMSO solution (1 mmol·L^{-1}). Melting points were determined with a MPD-100 melting point Pixel technology. The elemental analyses for carbon, hydrogen and nitrogen were performed by a Vario Elementary EL Ⅲ Microcube CHNS elemental analyzer. The molar conductivity measurements were carried out with 1 mmol·L^{-1} solutions at 298 K with a Jenway 4200 (0.93 cell constant) conductometer.

1.2　Synthesis of (BenzMeIm)$_2$[PtCl$_4$]

A solution of $PtCl_2$ (2.66 g, 100 mmol) in 10 mL of ethanol was added to a solution of 1-benzyl-3-methylimidazolium chloride (BenzMeIm-Cl, 4.16 g, 200 mmol) in 20 mL of ethanol. The mixture was heated to reflux for 2 h, and then cooled to room temperature. A yellow precipitate was isolated by filtration. A small amount of the precipitate was dissolved in acetonitrile and left to evaporate slowly at room temperature. After one week yellow crystals were obtained. Yield: 68%. m.p. (dec) 163 ℃. Anal. Calcd. for $C_{22}H_{26}N_4Cl_4Pt$(%): C 38.63, H 3.80, N 8.19. Found(%): C 38.60, H 3.78, N 8.18. IR (cm^{-1}): ν(C-H aromatic) 3 025, ν(C-H aliphatic) 2 980, ν(C=N) 1 603, ν(C=C) 1 567, ν(C-N) 1 492, ν(Pt-Cl) 321. ^{1}H NMR: δ 9.28 (s, 1H, H(2)); 7.80 (d, 1H, H(4)); 7.72(d, 1H, H(3)); 7.40~7.64 (m, 5H, H(12)~H(16)); 5.43 (d, 2H, C(1)H$_2$); 3.86 (s, 3H, C(5)H$_3$). ^{13}C NMR: δ 136.61~136.67 for two N=CH-H (C(1), C(5)) totomerizems, 134.87 for C(7)~C(11), 128.71~128.90 for CH=CH aromatic ring, 51.79 for (CH$_2$C(5)) and 38.79 for (C(1)). UV-Vis (DMSO, λ_{max}/nm (ε/(dm^3·mol^{-1}·cm^{-1}))): 400 (2 500), 320 (8 000). A molar conductivity measurement of 1 mmol·L^{-1} DMSO solution of the compound (72 S·mol^{-1}·cm^2) indicates that it is a 1:2 electrolyte.

1.3　X-ray crystallography

Yellow crystals of (BenzMeIm)$_2$[PtCl$_4$] suitable for X-ray crystallographic measurements were obtained by the slow evaporation of its dichloromethane solutions. The crystal data of (BenzMeIm)$_2$ [PtCl$_4$] was collected at 200 K using a Bruker Kappa Apex Ⅱ diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.071 073 nm). APEX Ⅱ[10] was used for data collection and SAINT[10] for cell refinement and data reduction. The structure was solved and refined by least-squares procedures using SHELXL-2014[11] with SHELXLE[12] as a graphical interface. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were added in idealized geometrical positions in a riding model. Data were corrected for absorption effects using the numerical method implemented in SADABS[10]. Table 1 gives the crystallographic data and collection parameters. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in the models by calculating the positions (riding model) and refined with calculated isotropic displacement parameters. Selected bond distances and angles are summarized in Table 2.

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Table 1 Crystal data and structure refinement of the complex

Empirical formula	$C_{22}H_{26}N_4Cl_4Pt$	Z	2
Formula weight	683.35	D_c / (Mg·m^{-3})	1.861
Temperature / K	200	Absorption coefficient / mm^{-1}	6.209
Crystal system	Monoclinic	F(000)	664
Space group	$P2_1/c$	Crystal size / mm	0.06×0.24×0.49
a / nm	0.981 80(5)	θ range for data collection / (°)	2.5~28.4
b / nm	0.861 47(3)	Limiting indices h, k, l	−13~13, −11~11, −19~19
c / nm	1.443 32(7)	Reflection collected, unique	22 884, 3 040, (R_{int}=0.025)
β / (°)	92.480(2)	Observed data [I>2σ(I)]	2 570
Volume / nm^3	121.96(1)	R, wR_2, S	0.014 4, 0.038 7, 1.11

Table 2 Selected bond distances (nm) and angles (°) of the complex

Pt1-Cl2^i	0.230 95(6)	N1-C1	0.147 2(3)	C11-C16	0.138 8(3)
Pt1-Cl1^i	0.230 74(6)	N2-C2	0.132 6(3)	C11-C12	0.138 8(4)
Pt1-Cl1	0.230 74(6)	N2-C3	0.137 8(3)	C12-C13	0.138 8(3)
Pt1-Cl2	0.230 95(6)	N2-C5	0.146 7(3)	C13-C14	0.136 9(4)
N1-C2	0.132 6(3)	C1-C11	0.150 8(3)		
N1-C4	0.137 5(3)	C3-C4	0.134 9(4)		
Cl1-Pt1-Cl1^i	180.00	Cl1^i-Pt1-Cl2^i	89.91(2)	N1-C1-C11	112.83(17)
Cl1-Pt1-Cl2^i	90.09(2)	Cl1-Pt1-Cl2	89.91(2)	N1-C2-N2	108.63(17)
C1-N1-C2	125.36(17)	C2-N1-C4	108.98(17)	C11-C12-C13	120.0(2)
C1-N1-C4	125.50(17)	C3-N2-C5	125.6(2)	C12-C13-C14	120.7(3)
Cl1^i-Pt1-Cl2	90.09(2)	C2-N2-C5	125.90(19)		
Cl2-Pt1-Cl2^i	180.00	C2-N2-C3	108.39(19)		

Symmetry codes: ^{i} 1−x, 1−y, 1−z

2 Results and discussion

2.1 IR and UV-Vis spectrum analysis

The IR spectrum of the compound (Fig.S1) is characterized by absorption bands at 3 025 and 2 980 cm^{-1}, which are assigned to ν(C-H aromatic) and ν(C-H aliphatic) respectively, at 1 603 cm^{-1} for ν(C=N), 1 560 cm^{-1} for ν(C=C), 1 456 cm^{-1} for ν(C-N) and at 321 cm^{-1} for ν(Pt-Cl)[13].

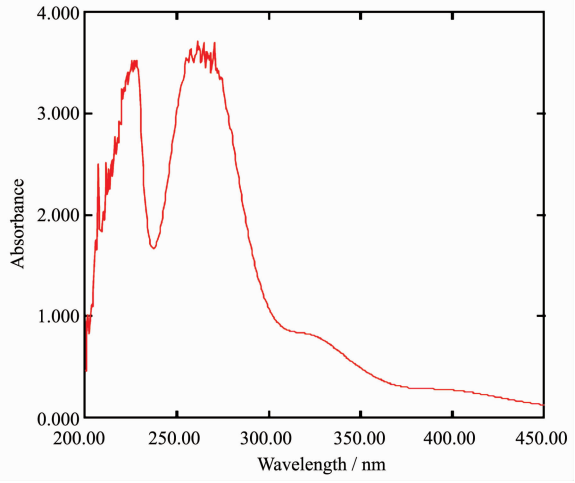


Fig.1 Electronic spectra of (BenzMeim)$_2$[PtCl$_4$]

The UV-Vis spectrum of the salt in DMSO (Fig. 1) shows three absorption bands at 400 nm (25 000 cm^{-1}), 320 nm (31 250 cm^{-1}) and 270 nm (37 037 cm^{-1}) which are assigned to the transitions $^1A_{1g}\rightarrow{}^1B_{1g}$, $^1A_{1g}\rightarrow{}^1E_g$ and $Cl^-\rightarrow Pt^{2+}$ (charge transfer), typical of a square planar geometry[14].

2.2 NMR spectra

^{1}H NMR spectrum of the complex is shown in Fig.2. The ^{1}H NMR spectrum shows the singlet band for N-CH=N at 9.27, doublets in the range of 7.82~7.73 for the CH=CH protons, and triplets in the range of 4.22~4.19 for (CH$_2$Et), and at 3.87~3.82 for (-N-CH$_3$), triplets at 1.44~1.38 for 3H (CH$_3$Et) groups.

The ^{13}C NMR spectral data (Fig.3) show peaks at 136.24 for N =CH-N, 123.51 ~121.93 for CH =CH,

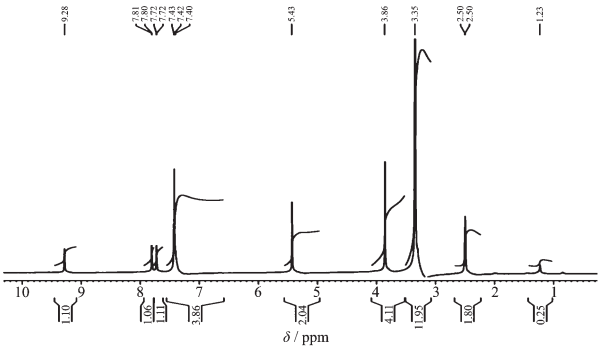


Fig.2　^{1}H NMR for [BenzMeim]$_2$[PtCl$_4$]

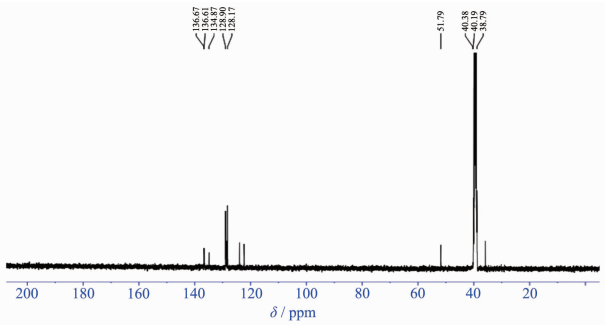
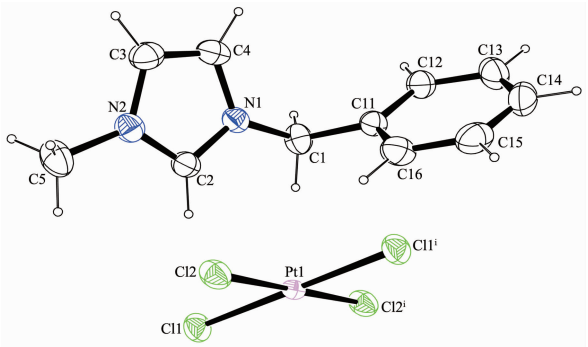


Fig.3　^{13}C NMR for [BenzMeim]$_2$[PtCl$_4$]

44.08~40.11 for H_2Et, 35.69 for CH_3-N, the band at 15.11 for CH_3Et. The ^{13}C-DEPT -135 spectrum shows one upward singlet at 136.87 for N=CH-N, two upward singlets at 124.14~122.55 for CH=CH, an downward singlet at −44.71 for CH_2Et, another upward singlet at 36.33 for N-CH_3 and an upward singlet at 15.76 for CH_3Et[15-16].

2.4　Crystal structure of the complex

The molecular structure of the complex is shown in Fig.4. The structure is centrosymmetrical with the Pt(Ⅱ) on the inversion point. The two BenzMeIm$^+$ cations are identical and symmetrical, and only one is shown in Fig.1. The [PtCl$_4$]$^{2-}$ anion assumes the distorted square planar geometry D_{4h}, and the metal is coordinated to four chlorides. Both *trans*-angles in the anion are ideal at 180.00° and the *cis*-angles Cl(1)-Pt(1)-Cl(2)^i and Cl(1)^i-Pt(1)-Cl(2) are both 90.09(2)°, with Cl(1)-Pt(1)-Cl(2) and Cl(1)^i-Pt(1)-Cl(2)^i equal to 89.91(2)°. The lengths of the Pt(1)-Cl(1) and Pt(1)-Cl(2) bonds are 0.230 74(6) and 0.230 95(6) nm, respectively.



Thermal ellipsoids drawn at 50% probability level; Symmetry codes: ^{i} 1−x, 1−y, 1−z

Fig.4　Crystal structure of (BenzMeIm)$_2$[PtCl$_4$]

The bond lengths in the imidazolium ring of the (BenzMeIm)$^+$ cations show the delocalization of the double bond over N(2)-C(2)-N(1), with both the C(2)-N bond lengths equal to 0.132 6(3) nm. Both the C(3)-N(2) (0.137 8(3) nm) and C(4)-N(1) (0.137 5(3) nm) bonds are single, with the C(3)-C(4) bond double at 0.134 9(4) nm. The N(1)-C(1)-C(11) bond angle is 112.8(2)°, typical of a sp^3-hybridized carbon atom.

3　Conclusions

The Pt(Ⅱ) complex (BenzMeIm)$_2$[PtCl$_4$] has been synthesized from the reaction of PtCl$_2$ with 1-benzyl-3-methylimidazolium chloride. The characterization of the structure of the compound shows a square planar geometry around the metal.

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Supporting information is available at http://www.wjhxxb.cn

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