Journal of Organometallic Chemistry 732 (2013) 102–108

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Communication

Synthesis and characterization of a new dinuclear platinum(II) alkynyl complex with a ferrocene bridge and its interaction with silver ion

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ARTICLE INFO

Article history:
Received 24 September 2012
Received in revised form
30 January 2013
Accepted 12 February 2013

Keywords:
Alkynyl platinum(II) complex
Luminescent sensor
Silver ion
Chemosensing

ABSTRACT

A new dinuclear alkynyl platinum(II) complex with a ferrocene (Fc) bridge (Pt(II)–Fc–Pt(II)), referred as **Sensor 1**(**1**), was synthesized and characterized. The photophysical, luminescent and cation-binding properties were studied by UV–Vis spectrophotometric, fluorometric, ^{1}H NMR titration methods, and the ESI-MS. **Sensor 1** showed a significant luminescent quenching in the presence of silver ions (Ag^+).

1. Introduction

The spectroscopic and photophysical behavior of square-planar platinum(II) alkynyl complexes has been extensively studied, due to their intriguing spectroscopic and luminescence properties [1–14]. A series of luminescent platinum(II) terpyridyl complexes and their spectroscopic and luminescence properties, as well as their aggregation [1,15–17], biological properties [2] and utilization in cation sensing have been reported by Prof. V. W.-W. Yam and Dr. K. M.-C. Wong [18]. However, the utilization of the rich π-electron of alkynyl in such systems in heavy metal ion sensing, such as Ag^+, is very rare in literature. Despite the widespread applications and the broad prospects of silver in the electronic industry and photographic and imaging industry, more attention had suddenly been paid to its negative environmental impacts, especially to organisms [19–21]. This is due to technological and research advancement, with new improved analytical tools, gradually able to exploit more chemical behaviors of ions/elements. Many traditional detection method approaches, such as atomic absorption spectroscopy, ICP atomic emission spectroscopy, inductively coupled plasma-mass spectroscopy and anodic stripping voltammetric methods have been employed to measure trace amounts of silver ions [22], but most of them are expensive and time-consuming in practice. Therefore, more simple and affordable methods such as luminescent techniques are highly desired, especially by downstream users [23–30]. In addition, luminescent probes are suitable for in vivo or in vitro cellular imaging [31]

Accordingly, silver and its compounds are widely used in electronic and photographic film production industry as mentioned. Moreover, silver compounds have been used as clean water disinfectants, even though they are more applied in medicinal tools such as in biofilms, bandages and dental treatments, due to its ionic form's antimicrobial activity. Thus, most of the previous silver related studies were primarily focused on its positive rather than its negative impacts. However, with the advances in technologies especially in analytical methods and tools, recent studies have demonstrated that, in its ionic form silver is the second most toxic metal of the heavy metals in biosystems, behind mercury only, as it is consumed through bioaccumulations and natural streams. Notably, silver contents of environmental samples have been increasing on daily basis with the increasing use of silver compounds in industry, medicine and technology. The current detection methods at a trace quantity levels are comparatively unfavorable due to their high costs and time-consuming. Therefore, designs of chemosensors targeting Ag(I) ions with excellent sensitivity and selectivity, simple instrumental implementation and easy operation remain the highest in the priority list [32–38]

Considering the good spectroscopic and luminescence properties of platinum(II) complexes, in this communication, a new dinuclear platinum(II) alkynyl complex with a ferrocene bridge was designed and synthesized as shown in Scheme 1. With the

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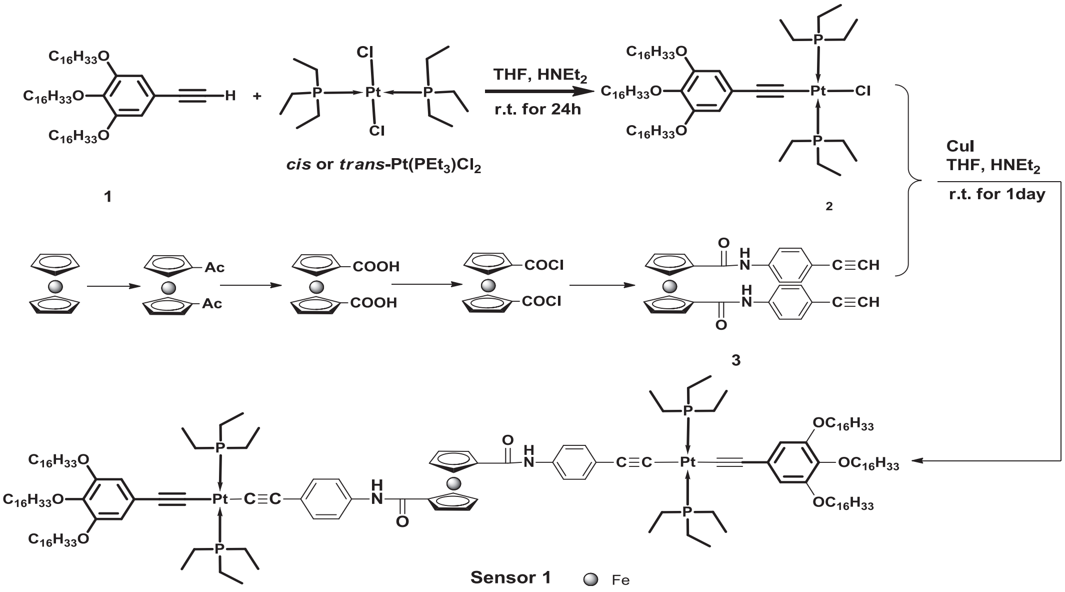
http://dx.doi.org/10.1016/j.jorganchem.2013.02.009



Scheme 1. The synthesis route of the **Sensor 1**.

exception of being a magnificent building block, ferrocene-bearing systems have been useful for incorporating redox functions into supramolecular complexes to bind and allow electrochemical sensing of ions and neutral molecules by change in the oxidation potential of Fe(III)/Fe(II) redox couples [39–41]. Additionally, such assembly is well-known for providing interesting electronic and optical properties [42–49]. The photophysical properties and ion-binding properties of **Sensor 1** with metal ions such as Na^+, K^+, Ca^{2+}, Ni^{2+}, Mg^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^+ and Hg^{2+} ions were investigated.

2. Experimental

2.1. Materials and methods

5-Ethynyl-1,2,3-tris(hexadecyloxy)benzene (Compound **1**) was synthesized according to the literature procedure [50].

All other chemicals were of reagent grade quality obtained from commercial sources and used without further purification. Elemental analyses (C, H and N) were carried out on a Perkin–Elmer 240C analytical instrument. Electrospray mass spectra were carried out on an LCQ system (Finnigan MAT, USA) using methanol as mobile phase. Electronic absorption spectra were obtained at room temperature on a Shimadzu 3100 spectrophotometer in $CHCl_3$:MeOH (9:1) solution. Luminescent spectra were measured on an Edinburgh Instruments analyzer model FL920 in $CHCl_3$:MeOH (9:1) solution.

2.2. Synthesis of compound **2**

[$H{-}C{\equiv}C{-}(C_6H_2){-}(OC_{16}H_{33})_3$] (360 mg, 0.44 mmol) was added to a degassed solution of *cis*-$Pt(PEt_3)_2Cl_2$(250 mg, 0.47 mmol) in the mixed solvents including THF (5 mL), dichloromethane (5 mL) and diethyamine (5 mL). The reaction mixture was stirred at room temperature for 24 h under argon. After removing the solvent, the crude solid was purified by column chromatography on Silica gel/dichloromethane to give a white solid; 0.41 g, yield 72%. ^1H NMR (600 MHz, $CDCl_3$): δ 6.42 (s, 2H), 3.90 (q, 6H, $J = 6.4$ Hz), 1.95–2.07 (m, 12H), 1.68–1.78 (m, 6H), 1.38–1.45 (m, 6H), 1.10–1.35 (m, 90H), 0.86 (t, 9H, $J = 7.2$ Hz). Elemental analysis calcd. (%) for $C_{68}H_{131}ClO_3P_2Pt$: C 63.35, H 10.24; found: C 63.32, H 10.28.

2.3. Synthesis of compound **3**

A reaction mixture of 1,1′-dicarboxylferrocene (1.37 g, 5 mmol), oxalyl dichloride (2.2 mL, 25 mmol), and 2 drops of pyridine in 50 mL dry CH_2Cl_2 was stirred for 4 h at room temperature, then refluxed overnight under nitrogen. After removing the solvent and excessive oxalyl dichloride under vacuum, the resulting solid was redissolved in 50 mL dry CH_2Cl_2. To a solution of 4-ethynylbenzenamine (1.40g, 12 mmol) in 30 mL dry CH_2Cl_2 with 5 mL dry triethylamine, was added dropwise to the above solution at room temperature under nitrogen. After addition, the reaction mixture was stirred at room temperature for further 4 h, then washed with water and dried in $MgSO_4$. The product was purified by column chromatography (silica gel) in ethyl acetate mobile phase. Red crystal was obtained, 1.17 g, 50%. Elemental analysis calcd. (%) for $C_{28}H_{18}FeO_2N_2$: C 71.51, H 3.86, N 5.96; found: C 71.49, H 3.88, N 5.94. ^1H NMR (in $CDCl_3$): 8.66 (br, 2H, NH), 7.68 (d, 4H, $J = 8.0$ Hz, Ar–H), 7.37 (d, 4H, $J = 8.0$ Hz, Ar–H), 4.51 (t, 4H, $J = 1.6$ Hz, Cp–H), 4.36 (t, 4H, $J = 1.6$ Hz, Cp–H), 4.08 (s, 2H).

2.4. Synthesis of **Sensor 1**

A reaction mixture of compound **2** (25 mg, 0.05 mmol), compound **3** (119 mg, 0.1 mmol) with a small amount of CuI as a catalyst in 10 mL THF and 10 mL diethylamine was stirred at room temperature for 24 h. After evaporating most of the solvent, the resulting crude was extracted with dichloromethane, the organic phase was washed with brine and dried with Na_2SO_4. The product was purified by column chromatography (silica gel). The impurity co-product was removed with dichloromethane, the pure product obtained by dichloromethane with 5% triethylamine. Yellow solid, 75 mg, 50%. Elemental analysis calcd. (%) for $C_{166}H_{278}FeO_8N_2P_4Pt_2$: C 66.46, H 9.34, N 0.93; found: C 66.46, H 9.33, N 0.92. ^1H NMR (in $CDCl_3$): 8.69 (br, 2H, NH), 7.64 (d, 4H, $J = 8.0$ Hz, Ar–H), 7.27 (d, 4H, $J = 8.0$ Hz, Ar-H), 6.46 (s, 4H, Ar–H), 4.59 (t, 4H, $J = 1.6$ Hz, Cp-H), 4.43 (t, 4H, $J = 1.6$ Hz, Cp-H), 3.87–3.93 (m, 12H, OCH_2), 2.12–2.20 (m, 24H, PCH_2), 1.68–1.77 (m, 12H), 1.40–1.45 (m, 12H),1.17–1.34 (m, 180H), 0.86 (t, 18H, $J = 6.4$ Hz, CH_3).

3. Results and discussion

3.1. UV–vis absorption spectra

The UV–vis spectrum of **Sensor 1** in $CHCl_3$:MeOH (9:1) solution is characterized by intense high-energy absorption bands at wavelengths below 350 nm with extinction coefficients in the order of10^5 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$, and a moderate to low intense absorption bands at 367 and 430 nm respectively (Fig. 1). The high-energy intense absorption bands are assigned to an admixture of intraligand (IL) $\pi \rightarrow \pi^*$ transitions of the two alkynyl ligands (Ar–C≡C–), Ar = aromatic [1–14]. The moderate to low-energy absorption bands at approximately 367–430 nm are assigned as [$d\pi(Pt) \rightarrow \pi^*(-C\equiv C-Ar)$] metal-to-ligand charge transfer (MLCT) transitions mixed with predominant $\pi \rightarrow \pi^*$ intraligand charge transfer (ILCT) transitions [51–57]. In addition, it is well established that ferrocenyl moieties exhibit two charge transfer bands in the *UV–vis* region, with a lower energy band assigned to a donor-acceptor charge transfer transitions and the higher lying absorption as an intraligand $\pi \rightarrow \pi^*$ transition [49,54]. While the $\pi \rightarrow \pi^*$ transitions of ferrocenyl moiety has supposedly overlapped with the intraligand (IL) $\pi \rightarrow \pi^*$ transitions of aryl alkynyl, the low lying absorption band at 430 nm is believed to emanate from the donor-acceptor charge transfer of the ferrocene moiety with slight MLCT [$d\pi(Pt) \rightarrow \pi^*(-C\equiv C-Ar)$] characteristics, resulting in a slight blue shift [51].

3.2. Cation-binding study

The cation-binding studies of square-planar Pt(II) alkynyl complexes is limited in literature, except for alkali and alkaline-earth metals [58–61]. In this work, cation-binding properties of metal nitrate salts such as Na^+, K^+, Ca^{2+}, Ni^{2+}, Mg^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ag^+ and Hg^{2+} in $CHCl_3$:MeOH (9:1) and the luminescent studies for the binding metal were investigated. Fig. 1 shows the absorption spectra of **Sensor 1** upon the addition of Ag^+ (a–h) in molar ratio, where a slight red shift shoulder of 28 nm (367–395 nm) was observed. Previous studies on ferrocene-based complexes have indicated that their characteristic low-energy bands in the absorption spectra are perturbed by complexation [40].

In addition, both the size and chemical properties of Ag^+ toward **Sensor 1** have played a major role in its selectivity. Meanwhile, the addition of the other cations, such as Na^+, K^+, Ca^{2+}, Ni^{2+}, Mg^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} did not yield any substantial changes, except the slight response for Hg^{2+} (Fig. 2) which is perhaps due to closer chemical links to Ag^+.

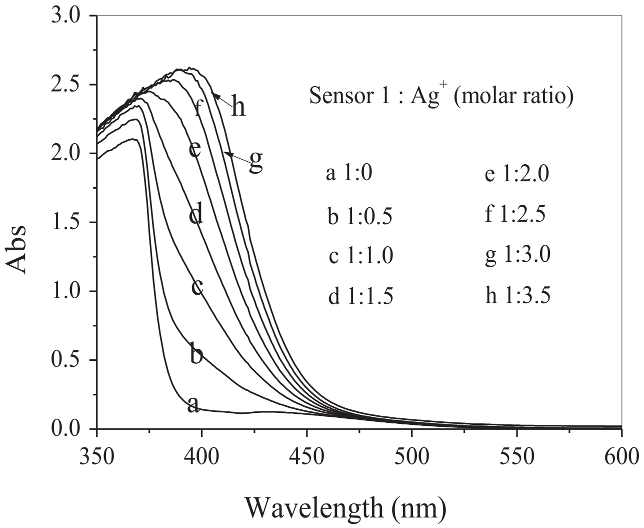


Fig. 1. UV–vis spectra of **Sensor 1** (1.0×10^{-5} M) in $CDCl_3$:MeOH (9:1) in the presence of different amounts of Ag^+.

3.3. Photoluminescent studies

Upon photoexcitation at 395 nm, **Sensor 1** displayed intense emission characterized by several emission peaks (412 nm, 437 nm and 463 nm) with maximum at 437 nm. Vibronic emission bands are signals of multiplets originating from different π-electron systems within the structure of **Sensor 1**. Fig. 3a shows luminescent quenching upon the addition of Ag^+. The luminescence intensities of **Sensor 1** at all four bands (412 nm, 437 nm and 463 nm) were linearly reduced (Fig. 3b) with the increasing concentration of Ag^+. The intensity was quenched more than 70% when the concentration of Ag^+ reached two equivalents. This may be due to the formation of a ground-state non-luminescent complex of Ag–**Sensor 1**, attributed to energy or electron transfer resulting in luminescence quenching [62].

3.4. ^{1}H NMR and ESI-MS studies

The ^{1}H NMR experiment was performed to further understand and comprehend the spectroscopic analysis of **Sensor 1** interaction with Ag^+. **Sensor 1** was titrated with Ag^+ under ^{1}H NMR in molar ratio to verify the binding activity of Ag–**Sensor 1**, and their peaks in $CHCl_3$:MeOH (9:1) are displayed in Fig. 4. The respective proton peaks are clearly assigned as shown and their changes upon the addition of Ag^+ are displayed as well. Upon the addition of Ag^+, significant changes of ^{1}H NMR peaks are observed in the regions of 2.0–2.7 ppm, 4.6 ppm, 6.4 ppm, 7.0–7.8 ppm and 8.5–9.4 ppm, respectively. The peak in the region of 8.5–9.4 ppm is initially assigned to –NH proton of the amino moiety of **Sensor 1**. After the addition of little amounts (1–2 equiv.) of Ag^+, the –NH band of **Sensor 1** broadened and disappeared, which suggested that the first binding activities should happen between the Ag^+ and nitrogen atoms, resulting in Ag–**Sensor 1** complexation. At the same time, changes were simultaneously observed around 4.62 (Fc) and 7.29 (Ar) ppm, assigned to ferrocene and aromatic protons (Fig. 4), respectively, which broadened with the addition of Ag^+, the action ascribed to space effect for being too close in proximity to the bonding field.

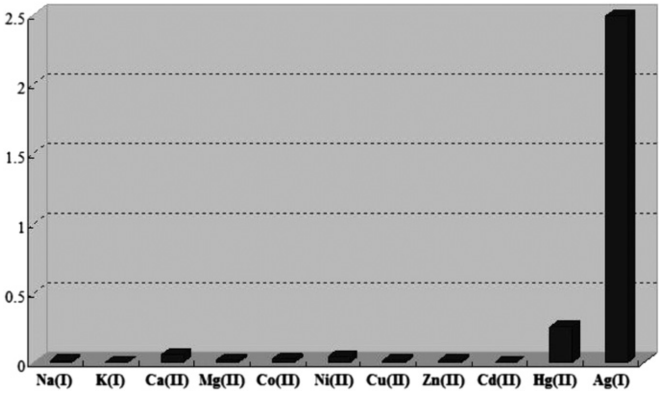
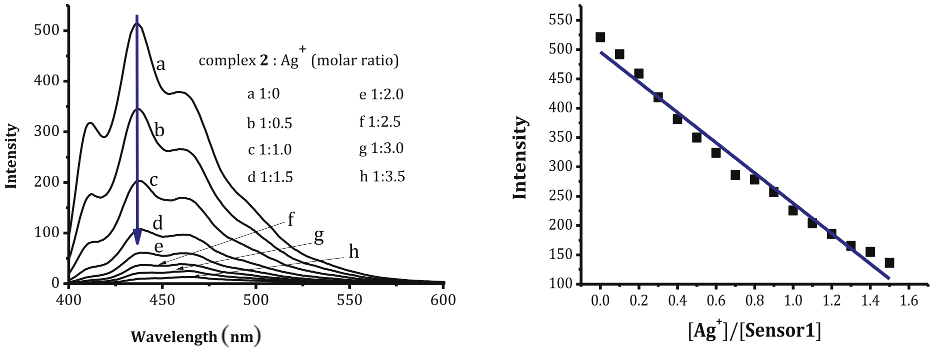


Fig. 2. Absorption changes at 395 nm of the **Sensor 1** (10 μM) in the presence of 10 equiv. of different metal ions.



(a) (b)

Fig. 3. (a) Luminescent response of **Sensor 1** (10^{-5} M) in $CHCl_3$:MeOH (9:1) upon addition of Ag^+ at $\lambda_{ex} = 395$ nm, and (b) Job's plot of **Sensor 1** and Ag^+in $CHCl_3$:MeOH (9:1, v/v).

Furthermore, careful observation and analysis suggested that a two successive step-action was experienced by the sensor as the amount of Ag^+ increased. Gradually, as the addition of Ag^+ increased to certain amounts (3–5 equiv.), more changes were experienced at 2.18 (P–CH_2), 4.62 (Fc), 7.29 (Ar) and 7.65 (Ar) ppm, where peaks accordingly shifted to 2.56 (P–CH_2, downfield), 5.19 (Fc, downfield), 6.94 (Ar, upfield) and 7.53 (Ar, upfield) ppm, respectively. And the initially disappeared amino moiety (–NH) protons were observed again. All of these changes are suggestive to different binding modes after the addition of more than 2 equiv. Ag^+ [63,64]. Considering the rich π-electron in **Sensor 1** and the coordination between the Ag^+ and alkynyl group, the second changes of proton shifts may be reasonable. This can also explain why (at first) peaks at 8.657 (NH), 4.622 (Fc) and 7.289 (Ar) ppm experienced intensity decrease (only) upon gradual addition of minimum amount Ag^+, presumably attributed to being closer to the coordination (N and O donor atoms) area, while in addition to protons shifts at 2.176 (P–CH_2) and 7.647 (Ar) ppm, the same protons experienced secondary changes (upfield or downfield shifts) which are completely different in nature to the initial effects, the action attributable to the second mode of interaction. More evidence to the secondary activities can be pronounced through the late upfield shift of the protons at 2.176 (P–CH_2), which in practice are distant from the coordination area, thereby resulting in a slightly tilted structure. The late shifts of the PR_3 protons are strongly evident to π → π stacking bonding, as they lay in the midst of the rich π-electron alkynyl units. However, the stabilities of **Sensor 1** and **Sensor 1**–Ag^+ have to be determined.

In order to further understand **Sensor 1** and its interaction with Ag^+, mass spectrometry technology (ESI-MS) was used to provide more information as shown in Figs. 5 and 6, respectively. The ESI-MS results of **Sensor 1** indicates that the structure is slightly unstable due to the mesh of fragments obtained as shown (Fig. 5), this can be ascribed to its large molecular area and structure. Even

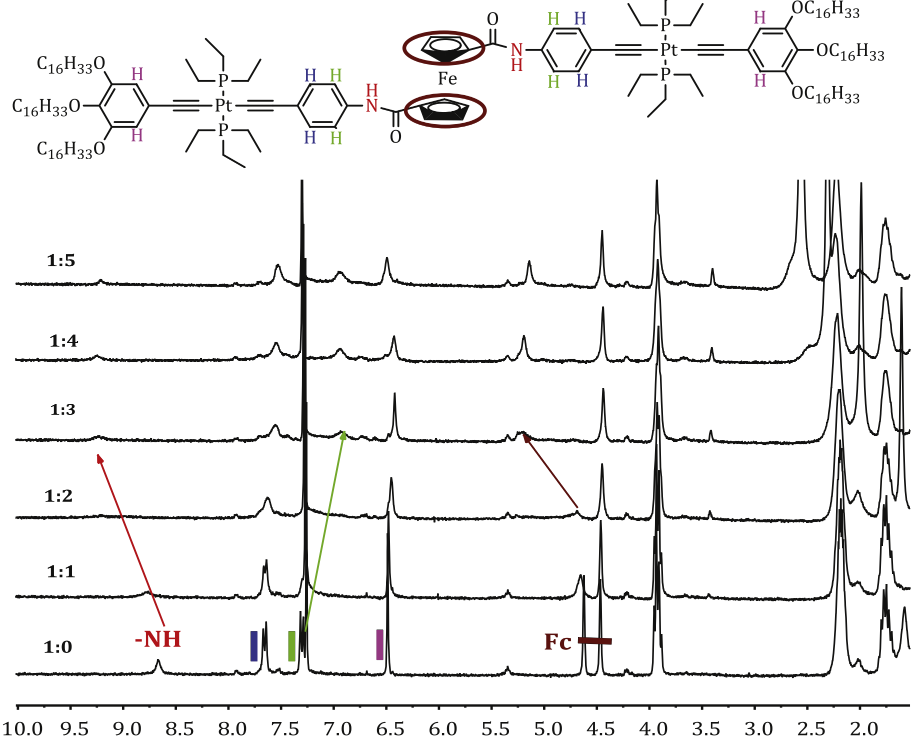


Fig. 4. ^1H NMR spectra of **Sensor 1** upon addition of Ag^+ (0–5 equiv.) in $CDCl_3$:CD_3OD (9:1).

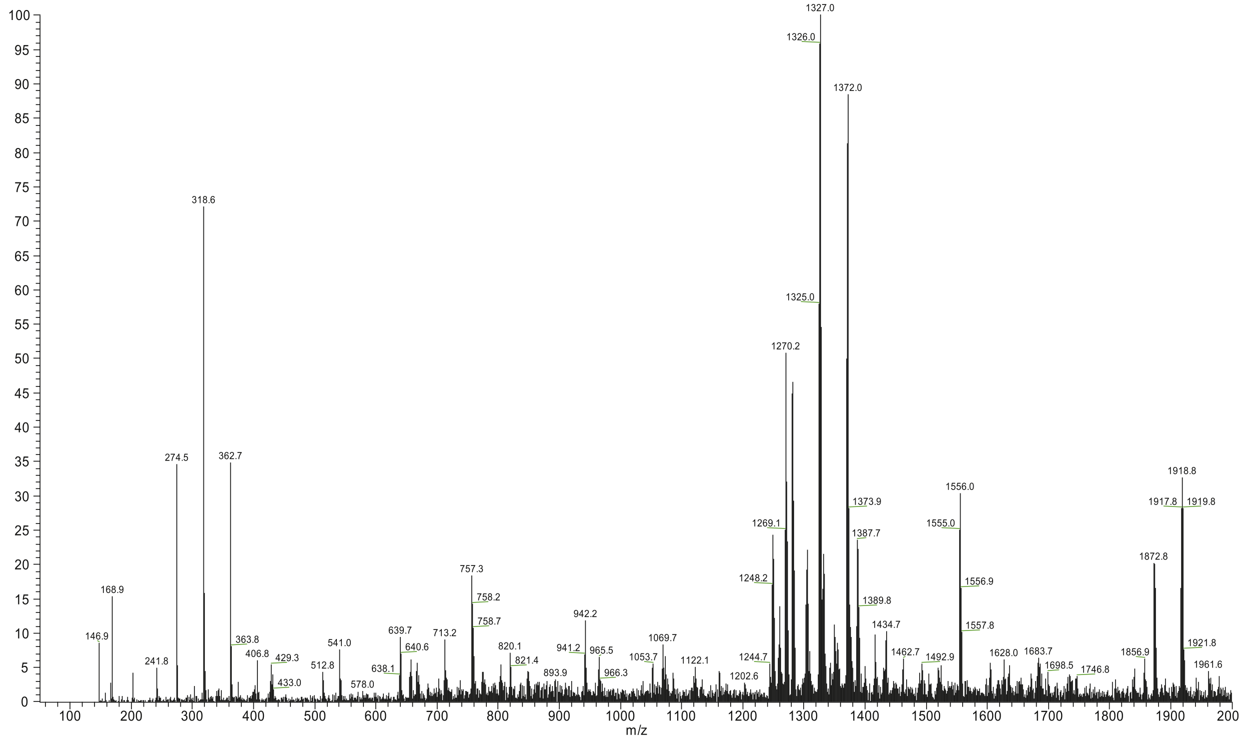


Fig. 5. ESI-MS spectra of **Sensor 1** upon addition of Ag^+ (5 equiv.) in CH_3Cl:CH_3OH (9:1).

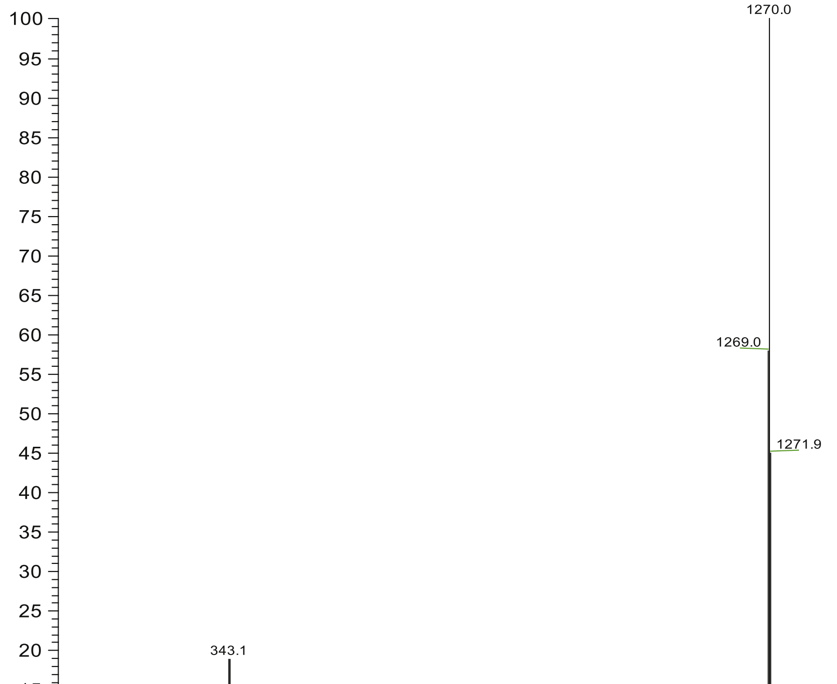


Fig. 6. ESI-MS spectra of **Sensor 1** with Ag^+ (5 equiv.) in CH_3Cl:CH_3OH (9:1).

though, it has not been possible to identify all the peaks, it is obvious most of the detected fragments could very well originate from **Sensor 1**. For example, a number of peaks could be identified, m/z 1270.0 belongs to a platinum(II) fragment (Ar−C≡C−Pt−H_2O), m/z 821.0 could possibly come from the cycloxybenzyl fragment, while most of the peaks in the range of m/z 1280−1450 results from the charged ion of **Sensor 1**([**Sensor 1**], 1488.95 **1**$^{2+}$, 992.63**1**$^{3+}$, 744.47, **1**$^{4+}$ etc.) and fragments of [Ar−C≡C−Pt−Fc−Ar−C≡C−R_1, $R_1 = CH_3$]. There is also strong evidence that the $PR_3(R = C_6H_{15})$ ligands coordinated to Pt(II) might have been removed (in some cases) in the process, resulting in several possible fragments such as m/z (**1**$^+$) 1430.42, 1388.5, 1370.87,1251.78, etc. In addition, after losing the cycloxybenzyl fragment (m/z 820), the remaining fragments at m/z 1369.13, 1332.10, 1298.71, 1161.95, 1052.16,968.06 (etc.), as a result of [RPt−Fc−PtR, R ranges from PR_3, CH_3OH, CH_3Cl, H_2O or combination, $n = 1 \rightarrow 4$], were observed. The principal peak at m/z 1326.9 is strongly associated to the R−Pt−Fc−Pt−R fragments. Additional information on ESI-MS can be found on the electronic supplementary information (ESI) addendum.

Interestingly, the addition of Ag^+ [**Sensor 1**−Ag^+] resulted in fewer peaks (Fig. 6) than **Sensor 1** (Fig. 5) over the same range. The majority of peaks subsequently disappeared in the presence of Ag^+, especially those in the range of m/z 1000−1500, which are associated with RPt−Fc−PtR, except the peak at m/z 1270 (Ar−C≡C−Pt−H_2O), which was still visible and suggestive that the chemical bonds between Pt and −Fc−Ar−C≡C− were broken. Accordingly, m/z at 343.1 was assigned to the [Ag−C≡C−Ar−Fc−Ar−C≡C−Ag]$^{2+}$. The difference between the ESI-MS results of **Sensor 1** and it is the complex (**Sensor 1**−Ag^+) provides another piece of evidence that the presence of Ag^+ has a significant effect to the **Sensor 1**. The existing ESI-MS results and the ^{1}H NMR data are all in good agreement. Therefore it can be concluded that the **Sensor 1** can form an adduct with Ag^+ in the presence of a small amount of silver ions. However, in the presence of excessive amount of silver ions, **Sensor 1** may display different behaviors.

4. Conclusion

The new dinuclear alkynyl platinum(II) complex was successfully synthesized and characterized. Like all other alkynyl platinum(II) complexes, it showed excellent photophysical and luminescent properties. In addition, **Sensor 1** has a unique property of discriminating Ag^+ through luminescent quenching among other cations. Only a handful of platinum(II) based alkynyl complexes have been reported so far capable of cation sensing, which are all based on alkali and alkaline-earth metal ions. **Sensor 1** can be a good contribution to opening a new dimension toward soft heavy metal ion sensing.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 21101121), the Natural Science Fund (2010CDB01301) of Hubei Province and Dalian University of Technology State Key Laboratory of Fine Chemicals Fund (KF0912).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.02.009.

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