研究简报

发光 Pt^{II}-Cu^{I}异核配合物 $[Pt_4Cu_2(edt)_4(PPh_3)_6](ClO_4)_2(4H_2O)$的合成及其表征

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Synthesis and Characterization of Luminescent Pt^{II}-Cu^{I} Heteronuclear Complex $[Pt_4Cu_2(edt)_4(PPh_3)_6](ClO_4)_2(4H_2O)$ (edt=1,2-Ethanedithiolate)

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Abstract: Self-assembly between Pt(phen)(edt) (phen=phenanthroline, edt=1,2-ethanedithiolate) and $[Cu(PPh_3)_2(MeCN)_2](ClO_4)$ (PPh_3=triphenylphosphine) gave rise to formation of heterohexanuclear complex $[Pt_4Cu_2(edt)_4(PPh_3)_6](ClO_4)_2(4H_2O)$ (**1**). The complex was characterized by elemental analyses, ES-MS, UV-Vis, IR, ^{31}P NMR spectroscopy and X-ray crystallography. The molecule consists of two $[Pt_2Cu(edt)_2(PPh_3)_3]$ units which has a centrosymmmetric inversion to give a cyclic heterohexanuclear skeleton. The Pt^{II} and Cu^{I} center adopt square-planar and trigonal coordination modes, respectively. The compound shows intense emission at 632 nm in the solid state and at 678 nm in frozen dichloromethane glass at 77 K.

Key words: 1,2-ethanedithiol; copper(I); heteronuclear; luminescent; platinum(II)

Luminescent square-planar platinum (II) diimine complexes are increasingly studied owing to their possibility as excellent candidates in the design of molecular-based system for light-driven energy conversion and luminescence-sensing reactions[1~3]. To probe further the electronic structure of emissive Pt complexes as well as to develop heterometallic assemblies based on PtL(dithiolate) (L=diphosphines and diimines) components for more efficient photoluminescence and molecular devices of light-to-chemical energy conversion and storage, we are interested in incorporation of PtL_2 (dithiolate) chromophores with another metal component possessing easily substituted solvate sites to achieve multicomponent luminescent molecular materials[4,5]. Herein, a heterohexanuclear complex $[Pt_4Cu_2(edt)_4(PPh_3)_6](ClO_4)_2(4H_2O)$ (**1**) is described by reaction of Pt(diimine)(dithiolate) with $[Cu(PPh_3)_2(MeCN)_2](ClO_4)$.

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1 Experimental

Reaction of Pt(phen)(edt) (46.7 mg, 0.1 mmol) with $[Cu(PPh_3)_2(MeCN)_2](ClO_4)$ (153.8 mg, 0.2 mmol) (Caution! Perchlorate salts are potentially explosive and should be handled with care and in small amounts.) in dichloromethane (30 mL) under dry argon at room temperature for one day afforded a bright yellow solution. After concentrated in vacuo, the solution was chromatographed on a silica gel column. Complex **1** was eluted with dichloromethane-acetone (*V*/*V*, 10:1) as the second band to give a yellow product (76 mg). Yield: 30%. Well shaped crystals suitable for X-ray analysis were obtained by layering diethyl ether onto the solution in a few days. Anal. (%) Calcd. for $C_{116}H_{114}Cl_2Cu_2O_{12}P_6Pt_4S_8$: C, 44.64; H, 3.68. Found: C, 45.06; H, 3.41. Selected FTIR data (cm^{-1}): 1 094 (s, ClO_4^-). ^{31}P NMR: δ 10.6 [s, $J_{Pt\text{-}P}$=1 503 Hz], 16.8 [s, $J_{Pt\text{-}P}$=1 578 Hz] and 20.7 ppm [s, $J_{Pt\text{-}P}$=1 643 Hz]. FAB-MS (*m*/*z*): 1 424 ($[M-(ClO_4)_2]^{2+}$), 1 162 ($[Pt_2Cu(edt)(PPh_3)_2]^+$), 1 100 ($[Pt_2(edt)_2(PPh_3)_2]$), 901 ($[Pt_4Cu_2(edt)_4(PPh_3)_2]^{2+}$).

A yellow crystal with dimension of 0.52 mm × 0.50 mm × 0.18 mm was mounted on a Siemens Smart CCD diffractometer with Mo $K\alpha$ radiation (λ=0.071 073 nm) for the data collection at 293(2) K. A total of 15 811 reflections were collected, of which 8 565 (R_{int}=0.047 0) were independent in the range of $1.34° < \theta < 22.50°$, and 6 832 reflections were observed with $I > 2\sigma(I)$). The structure was solved by direct methods and the non-hydrogen atoms were determined by subsequent difference Fourier syntheses, while the hydrogen atoms were located in theoretical positions. The structure was refined by full-matrix least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms to converge at R=0.073 8 and wR=0.188 7 (w=1/$[\sigma^2(F_o)^2 + (0.089\,7P)^2 + 103.87P]$, where $P=(F_o^2 + 2F_c^2)/3$). S=1.257, $(\Delta/\sigma)_{max}$=0.001, $(\Delta\rho)_{max}$=1 554 e·nm^{-3} and $(\Delta\rho)_{min}$=−1 539 e·nm^{-3}. All of the calculations were performed by SHELXTL-97.

2 Results and discussion

Reaction of Pt(phen)(edt) with $[Cu(PPh_3)_2(MeCN)_2](ClO_4)$ gave the complex **1** instead of the target product by incorporating the two components. Formation of complex **1** is involved in dissociation of the components Pt(phen)(edt) and $[Cu(PPh_3)_2(MeCN)_2](ClO_4)$, and recombination between the metal ions and ligands. Reaction between Pt (phen) (tdt) (phen =phenanthroline, tdt = toluene-3,4-dithiolate) and $[Cu(PPh_3)_2(MeCN)_2](ClO_4)$, however, does not give the similar complex $[Pt_4Cu_2(tdt)_4(PPh_3)_6](ClO_4)_2$, but afforded products as $Pt(PPh_3)_2(tdt)$ and $[Cu(phen)_2](ClO_4)$, which are derived from the ligand exchange. Formation of **1** by self-assembly is likely due to the factors such as different affinity of Pt^{II} and Cu^{I} for the S, P and N donors, steric requirement and thermodynamic stability.

Fig.1 displays the structure of compound **1** with atomic numbering scheme. Selected bond lengths and angles are listed in Table 1. The molecule consists of two $[Pt_2Cu(edt)_2(PPh_3)_3]$ units which has a centrosymmmetric inversion to give a cyclic heterohexanuclear complex. The significant feature of this compound based on $Pt_2Cu_2S_4$ core is an eight-membered ring constructed by Pt(1)-S(1)-Cu(1)-S(2A)-Pt(1A)-S(1A)-Cu(1A)-S(2) forming a crown skeleton. Two six-membered rings, Pt(2)-S(3)-Pt(1)-S(1)-Cu(1)-S(4) and the centrosymmetry-related set of atoms adopt the skew-boat conformation, while the central eight-membered ring has the chair-like conformation. The platimum atom exhibits square-planar coordination geometry, built by two P atoms from triphenylphosphane ligands and two S atoms from 1,2-ethanedithiolate ligands. The copper center is located in an approximate trigonal environment with three S donors from 1,2-ethanedithiolate ligands, which are almost coplanar with the mean deviation of 0.005 07 nm. All the dithiolates exhibit a chelating and bridging coordination mode with two sulfur donors not only to chelate a Pt^{II} atom, but also to bridge two Pt^{II} or Pt^{II}-Cu^{I} atoms, inducing a formation of $Pt_4^{II}Cu_2^{I}$ heterohexanuclear assembly. The average Cu-S distance is 0.228 5(5) nm, close to the values reported in the literatures[6,7,9,10]. The average Pt-P and Pt-S lengths are 0.230 1(5) nm and 0.234 6(5) nm, respectively, comparable to those in $[Pt_2L_4(\mu\text{-}S)_2]$ (L =phosphine)[4,8]. The Cu-Pt distances (Cu1-Pt1 =0.350 nm, Cu1-Pt2 =0.336 nm) suggest the presence of weak metal-metal contacts.

Table 1　Selected bond lengths (nm) and bond angles (°) for 1

Pt(1)-P(1)	0.229 0(5)	Pt(1)-S(3)	0.235 7(5)	Cu(1)-S(1)	0.222 7(5)
Pt(1)-S(2)	0.231 5(5)	Pt(2)-S(3)	0.234 8(5)	Cu(1)-S(2A)	0.226 4(6)
Pt(1)-S(1)	0.235 4(5)	Pt(2)-S(4)	0.235 8(5)	Cu(1)-S(4)	0.236 2(5)
Pt(2)-P(3)	0.229 9(5)	Pt(2)-P(2)	0.231 3(5)		
P(1)-Pt(1)-S(2)	89.47(19)	S(1)-Pt(1)-S(3)	90.13(16)	P(2)-Pt(2)-S(4)	168.22(19)
P(1)-Pt(1)-S(1)	170.80(17)	P(3)-Pt(2)-P(2)	98.8(2)	S(3)-Pt(2)-S(4)	86.17(17)
S(2)-Pt(1)-S(1)	87.43(17)	P(3)-Pt(2)-S(3)	173.74(19)	S(1)-Cu(1)-S(2A)	136.8(2)
P(1)-Pt(1)-S(3)	92.79(18)	P(2)-Pt(2)-S(3)	87.42(19)	S(1)-Cu(1)-S(4)	110.7(2)
S(2)-Pt(1)-S(3)	177.37(17)	P(3)-Pt(2)-S(4)	87.62(18)	S(2A)-Cu(1)-S(4)	111.4(2)

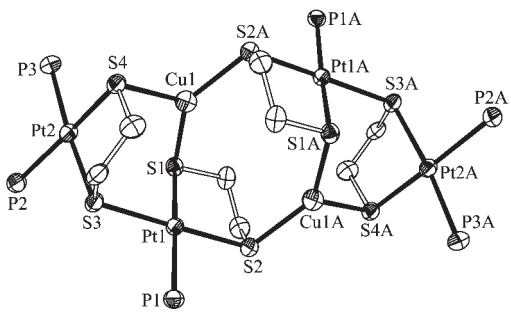
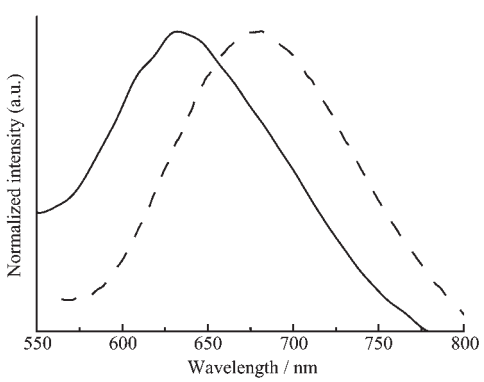


Fig.1　A perspective view of the complex cation of **1** with hydrogen atoms and phenyl rings omitted for clarity

UV-Vis spectra of complex **1** in dichloromethane solution show a broad intense absorption between 250~300 nm (ε>27 000) which is likely attributed to the ligand-centered transitions. A low-energy shoulder peak at 352 nm (ε=16 000) is likely assigned to the d(Pt/Cu) → π^*(edt) metal-to-ligand charge transfer (MLCT) transition. Complex **1** exhibits photoluminescence (λ_{ex}=350 nm) in both the solid state at 298 K and frozen CH_2Cl_2 solution at 77 K with emission maximum at 632 (lifetime τ=55 ns) and 678 nm, respectively (Fig.2), which is tentatively assigned to originate from the triplet excited state of the metal-to-dithiolate [d(Pt/Cu) → π^*(edt)] charge transfer (MLCT) transition.



—: Solid state emission spectra at 298 K, --: CH_2Cl_2 at 77 K

Fig.2　Emission spectra of complex **1**

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