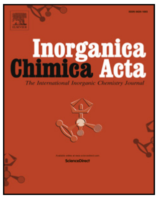
Inorganica Chimica Acta 482 (2018) 785–790

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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



Research paper

Au(I) and Ag(I) formamidinate tetranuclear complexes and coordination polymers: Synthesis, structures and luminescent properties

Wayne Hsu[a], Xiang-Kai Yang[a], Pradhumna Mahat Chhetri[a], Shi-Jie Lin[a], Yu-Sian Li[a], Tsun-Ren Chen[b,*], Jhy-Der Chen[a,*]

[a] Department of Chemistry, Chung Yuan Christian University, Chung-Li, Taiwan, ROC
[b] Department of Applied Chemistry, National Pingtung University, Pingtung, Taiwan, ROC

A R T I C L E I N F O

Keywords:
Formamidine
Tetranuclear complex
Coordination polymer
Luminescence

A B S T R A C T

Reactions of $AuClS(CH_3)_2$ and Ag(I) salts (AgSCN, AgOAc and $AgSbF_6$) with the lithiated formamidines afforded the tetranuclear complexes $[Au_4(4\text{-pyf})_4]\cdot 4CH_3OH$ [4-Hpyf = N,N'-bis(pyridine-4-yl)formamidine], **1**, $[Au_4(pmf)_4]$ [Hpmf = N,N'-bis(pyrimidine-2-yl)formamidine], **2**, and $[Ag_4(pmf)_4]$, **3**, and the coordination polymers $[Ag_2(OAc)(4\text{-pyf})]_n$, **4**, and $\{[Ag_2(4\text{-pyf})_2]\cdot THF\}_n$, **5**, which have been structurally characterized by X-ray crystallography. The intramolecular Au···Au separations in **1** and **2** are in the range 2.8832(2)–3.3338(10) Å and the Ag···Ag separations in **3**–**5** are 2.7927(3)–2.9819(19) Å, indicating the existence of aurophilicity and argentophilicity, respectively. Complex **3** is a unique tetranuclear complex of the type $Ag_4(form)_4$ in which "form" represents the formamidinate ligands. The short lifetimes of 1.06–49.15 ns for **1**–**5** indicate that the emissions belong to fluorescence. Moreover, complex **4** emits white luminescence in the solid-state and the CIE coordinate appears at (0.30, 0.38), which represents the first single-emitting component white phosphor in the class of formamidinate coordination polymers.

1. Introduction

The metal-metal interactions (metallophilicity) of group 11 metal ions that are associated with their structures have been the subject of extensive studies during recent years [1–7], because complexes of this type exhibit rich luminescent properties [8–11]. In this regard, several cyclic tetranuclear Au(I) formamidinate complexes, which exhibit interesting luminescence that are subject to the changes in the substituents on the phenyl rings have been reported [11–14]. However, to the best of our knowledge, a cyclic tetranuclear Ag(I) complex containing formamidinate ligands has not been reported, and the exact prediction and control of final products is still one of the major challenges.

The formamidine compound bis(pyrimidine-2-yl)formamidine (Hpmf) has been prepared to construct linear metallic chains [15–18]. The four nitrogen atoms of the pmf^- ligands in $K[Cu_4(pmf)_3(SCN)_2]$ and $[(n\text{-}Bu)_4N][Cu_4(pmf)_3(SCN)_2]$ [16] form a linear array and those in $[Cu_3(pmf)_4][PF_6]_2$ [17] feature chelation and bridge, while in the cyclic tetranuclear complex $Cu_4(pmf)_4$ [16], the pmf^- ligands coordinate to the metal ions through only two amine nitrogen atoms. Moreover, in the dinuclear d^{10}-metal complexes of the types $[Zn_2(pmf)_3](I_3)$, $[Zn_2(pmf)_3](NO_3)$, $[Zn_2(pmf)_3](ClO_4)$, $[Cd_2(pmf)_3](NO_3)$, $[Cd_2(pmf)_3](ClO_4)$ and $Hg_2(pmf)_2X_2$ (X = Cl, Br or I), the pmf^- ligands coordinate to the metal ions through three and four nitrogen atoms [18].

The formamidine compound *N,N'*-bis(pyridine-4-yl)formamidine (4-Hpyf) has been prepared to construct coordination polymers (CPs) [19–21]. While the dimolybdenum paddlewheel complex $[Mo_2(4\text{-pyf})_4]$ reacted with Hg(II) salts to afford 2D and 3D heteronuclear networks [19], by one-pot solvothermal reactions of 4-aminopyridine and triethylorthoformate with divalent copper salts, several 2D layers that showed crystal-to-crystal transformations with photoluminescence changes can be prepared [20]. Recently, the 2D layer $\{[Hg(4\text{-pyf})_2]\cdot THF\}_n$ and 1D helical chains $\{[HgX_2(4\text{-Hpyf})]\cdot MeCN\}_n$ (X = Br and I) that demonstrate the effect of the halide anions on the folding and unfolding the Hg(II) CPs have also been reported [21]. Similar to the pmf^- ligands, the 4-pyf^- ligand shows various bonding modes and coordinates to the metal ions through two, three or four nitrogen atoms.

To explore the effect of the polydentate 4-pyf^- and pmf^- ligands on the structures and luminescent properties of the Au(I) and Ag(I) complexes, we have synthesized and characterized $[Au_4(4\text{-pyf})_4]\cdot 4CH_3OH$, **1**, $[Au_4(pmf)_4]$, **2**, $[Ag_4(pmf)_4]$, **3**, $[Ag_2(OAc)(4\text{-pyf})]_n$, **4**, and $\{[Ag_2(4\text{-pyf})_2]\cdot THF\}_n$, **5**. The syntheses, structures and luminescence properties of these complexes form the subject of this report.

---

* Corresponding authors.
E-mail addresses: trchen@mail.nptu.edu.tw (T.-R. Chen), jdchen@cycu.edu.tw (J.-D. Chen).

https://doi.org/10.1016/j.ica.2018.07.024
Received 18 May 2018; Received in revised form 12 July 2018; Accepted 16 July 2018

2. Experimental sections

2.1. General procedures

Elemental analyses were obtained from a HERAEUS VarioEL analyzer. IR spectra (KBr disk) were recorded on a Jasco FT/IR-460 plus spectrometer. Thermal gravimetric analyses (TGA) measurements were performed on a TG/DTA 6200 analyzer and the samples were heated up in N_2 with a heating rate of 10 °C min^{-1}. Emission spectra were obtained from a Hitachi F-4500 spectrometer and UV-vis spectra from a Shimadzu UV-2450 spectrometer. Powder X-ray diffraction measurements were carried out on a PANalytical PW3040/60 X'Pert Pro diffractometer or on a Bruker D2 PHASER X-ray Diffractometer. ^{1}H NMR spectra were measured on a Bruker Avance 400 MHz spectrometer.

2.2. Materials

The reagents 4-aminopyridine and pyrimidine were purchased from Alfa Aesar and chloro(dimethylsulfide)gold(I), silver(I) hexafluoroantimonate, silver(I) acetate and silver(I) thiocyanate were from Sigma-Aldrich Co. The ligand precursors 4-Hpyf [*N,N'*-bis(pyridine-4-yl)formamidine] [19] and Hpmf [bis(pyrimidine-2-yl)formamidine] [16] were prepared according to reported procedures.

2.3. Preparation

2.3.1. $[Au_4(4\text{-pyf})_4]\cdot 4CH_3OH$, (1)

A fresh suspension of Li(4-pyf), which was prepared by the reaction of 4-Hpyf (0.40 g, 2.02 mmol) with 0.8 mL of 2.5 M ^{n}BuLi in 20 mL THF, was added dropwise to a solution of $AuClS(CH_3)_2$ (0.59 g, 2.00 mmol) in 10 mL THF at −78 °C. The mixture was then stirred at 5 °C for 12 h to yield a colorless solution. The volume of the solvent was reduced and diethylether added to induce a precipitate. A precipitate was collected through filtration and extracted with CH_3OH (3 × 10 mL). Diffusion of diethyl ether into the combined extracts yielded colorless crystals. The crystals were collected, washed with diethyl ether and dried under vacuum. Yield: 0.70 g (82%). Anal. Calcd. for $C_{48}H_{52}N_{16}O_4Au_4$ (MW = 1704.92): C, 33.82; H, 3.07; N, 13.14. Found: C, 33.65; H, 2.81; N, 13.24. ^{1}H NMR (400 MHz, δ, ppm in d^4-methanol): 8.53 (s, 1H, C–*H*), 7.93 (d, 4H, py), 6.55 (d, 4H, py). IR (cm^{-1}, KBr disk): 3408 (s, broad), 1557(s), 1620(s), 1429(m), 1389(m), 1212.04(m), 1171(w), 1006(w), 822(m), 673(w), 522(w).

2.3.2. $[Au_4(pmf)_4]$, (2)

A fresh suspension of Li(pmf), which was prepared by the reaction of Hpmf (0.40 g, 2.02 mmol) with 0.8 mL of 2.5 M ^{n}BuLi in 20 mL THF, was added dropwise to a solution of $AuClS(CH_3)_2$ (0.59 g, 2.0 mmol) in 10 mL THF at −78 °C. The mixture was then stirred at room temperature for 3 h to yield a colorless solution. The volume of the solvent was reduced and diethylether added to induce precipitate. The precipitate was filtered, washed with diethylether and then dried under vacuum. Yield: 0.43 g (53%). Anal. Calcd. for $C_{36}H_{28}N_{24}Au_4$ (MW = 1584.69): C, 27.29; H, 1.78; N, 21.21. Found: C, 27.66; H, 2.03; N, 20.15. ^{1}H NMR (400 MHz, δ, ppm in d^4-methanol): 9.96 (s, 1H, C–*H*), 8.48 (d, 4H, py), 6.94 (t, 2H, py). IR (cm^{-1}, KBr disk): 3391(w), 1581(m), 1548(s), 1390(s), 1298(s), 988(w), 846(m), 806(m), 708(w), 645(w), 558(w).

2.3.3. $[Ag_4(pmf)_4]$, (3)

Compound **3** was prepared by following the procedure described for **2**, except that a fresh suspension of Li(pmf) was added dropwise to a solution of AgSCN (0.23 g, 2.0 mmol). Yield: 0.47 g (77%). Anal. Calcd. for $C_{36}H_{28}N_{24}Ag_4$ (MW = 1228.30): C, 35.20; H, 2.30; N, 27.37. Found: C, 35.73; H, 2.54; N, 27.19. ^{1}H NMR (400 MHz, δ, ppm in d^4-methanol): 8.84 (s, 1H, C–*H*), 8.33 (d, 4H, py), 6.74 (t, 2H, py). IR (cm^{-1}, KBr disk): 3440(s), 2924(m), 2857(m), 2364(w), 1644(m), 1566(m), 1409(w), 1298(w), 804.171(w), 618(m), 474(w).

2.3.4. $[Ag_2(OAc)(4\text{-pyf})]_n$, (4)

Compound **4** was prepared by following the procedure described for **1**, except that a fresh suspension of Li(4-pyf) was added dropwise to a solution of AgOAc (0.67 g, 4.0 mmol). The mixture was then stirred at room temperature for 24 h to yield a colorless solution with precipitate. The solvent was reduced and diethylether added to collect precipitate which was filtered and then washed with THF (3 × 10 mL). Yield: 0.30 g (64%). Anal. Calcd. for $C_{13}H_{12}N_4Ag_2O_2$ (MW = 472.01): C, 33.08; H, 2.56; N, 11.87. Found: C, 32.89; H, 2.79; N, 11.88. IR (cm^{-1}, KBr disk): 3421(s, broad), 2360(w), 2342(w), 1654(m), 1570(s), 1418(m), 1351(m), 1316(m), 1255(w), 1212(m), 1005(w), 826(m), 657(m), 535(m).

2.3.5. $\{[Ag_2(4\text{-pyf})_2]\cdot THF\}_n$, (5)

Compound **5** was prepared by following the procedure described for **4**, except that a fresh suspension of Li(4-pyf) was added dropwise to a solution of $AgSbF_6$ (0.69 g, 2.0 mmol). Yield: 0.42 g (61%). Anal. Calcd. for $C_{26}H_{26}N_8Ag_2O$ (MW = 682.29): C, 45.77; H, 3.84; N, 16.42. Found: C, 45.62; H, 3.74; N, 16.90. IR (cm^{-1}, KBr disk): 3421(s, broad), 2360(w), 2342(w), 1654(m), 1570(s), 1418(m), 1351(m), 1316(m), 1255(w), 1212(m), 1005(w), 826(m), 657(m), 535(m).

2.4. X-ray crystallography

The diffraction data of the complexes were collected using a Bruker AXS or a SMART APEX II diffractometer equipped with a graphite-monochromated MoK_α (λ_α = 0.71073 Å) radiation [22]. Data reduction was performed through standard methods with the use of well-established computational procedures. The structure factors were obtained after Lorentz and polarization correction. An empirical absorption correction based on "multi-scan" method was applied to the data. The positions of several of the heavier atoms including the Au and Ag atoms were located using the direct method. The remaining atoms were observed in a series of alternating difference Fourier maps and least-square refinements [23]. All hydrogen atoms were added using the HADD command in SHELXTL 5.10 and refined as riding atoms. Basic information pertaining to crystal parameters and structure refinement for **1**–**5** is summarized in Table 1.

3. Results and discussion

3.1. Structures of 1 and 2

The structures of the tetranuclear complexes **1** and **2** were solved in the space groups $P2_1/c$ and $C2/c$, and Figs. 1 and 2 depict the molecular structures of **1** and **2**, respectively. The four Au(I) are located at the corners of the distorted rhombus with the formamidinate ligands bridging above and below the plane of the four Au(I) ions. The angles at Au⋯Au⋯Au are acute [67.118(6) and 67.269(6)° for **1**; 68.34(3)° for **2**] and obtuse [113.165(7) and 112.364(7)° for **1**; 111.40(2)° for **2**]. The *N*-Au-N angles of 173.93(14)–178.25(15) for **1** and 179.0(3)–179.6(5) for **2** show small deviations from linearity. The Au⋯Au distances are 2.8832(2)–3.2194(2) Å for **1** and 2.9447(9)–3.3338(10) Å for **2**, respectively, which could be indicative of aurophilicity [1]. The Au(I) metal center that is coordinated by two amine nitrogen atoms from two 4-pyf$^-$ or pmf$^-$ ligands adopts the distorted linear geometry with Au-N distances of 2.029(3)–2.046(3) Å for **1** and 2.035(12)–2.073(13) Å for **2**, respectively. The 4-pyf$^-$ and pmf$^-$ ligands are coordinated to the Au (I) ions in bidentate fashions through the two central nitrogen atoms, leaving the pyridyl and pyrimidyl nitrogen atoms uncoordinated, respectively.

3.2. Structure of 3

Colorless crystals of **3** conform to the space group $C2/c$ with four molecules in a unit cell. Fig. 3 shows the molecular structure of **3**. The