

# Exploration on Au(S-4-py)PR<sub>3</sub> complexes as a viable building block for constructing hetero-nuclear supramolecules: synthesis and X-ray study on M(acac')<sub>2</sub>[Au(S-4-py)PR<sub>3</sub>]<sub>2</sub>(ClO<sub>4</sub>)<sub>x</sub> (M = Cr, Cu; acac' = acetylacetonate, hexafluoro-acetylacetonate; x = 0 or 1)

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## Abstract

Transition metal acetylacetonates, M(acac')<sub>2</sub>(ClO<sub>4</sub>)<sub>x</sub> (M = Cr, Cu; acac' = acetylacetonate, hexafluoro-acetylacetonate; x = 0 or 1) were reacted as a scaffolding for constructing a hetero metallic supra molecule with Au(S-4-py)L (L = PPh<sub>3</sub>, PPh<sub>2</sub>(2-py)) as a ligand. A trimetallic monomer, Au–Cr–Au, **5** was yielded from [Cr(acac)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>ClO<sub>4</sub>. However, [Cu(hfac)<sub>2</sub>] yielded a dimer **6** composed of a trimetallic monomer (Au–Cu–Au) moiety and an infinite chain polymer (··Au–Cu–Au··Au–Cu–Au··) **7** by virtue of aurophilicity in the solid state, the higher order structure of which depends on the co-existing ligand L. Basic structures of **6** and **7** are affected by L; **6** has a *cis* geometry, while **7** a *trans* geometry. Cooperative effect of the steric bulkiness of L and aurophilicity is presumed to determine the geometry.

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**Keywords:** Au–S-py complexes; Au–M hetero molecules; Aurophilicity; Acac derivatives; Au complex as a ligand

## 1. Introduction

The possible applications to nano-technologies have kindled interest in the design and the synthesis of supra molecules [1–4]. Self-assembling techniques have now gained great reputation as an elegant strategy for such syntheses; they cover a weak interaction such as a hydrogen bonding and  $\pi$ – $\pi$  stacking and a strong inter-

action such as a coordination bond. Aurophilicity has been attracting increasing interests for the past decade as a new technique for such self-assembling stratagem and rationally stipulated aurophilicity has led to many fruitful outcomes for constructing gold-based extended structures which should serve as such prospective fabricated nano-materials [5–7]. An S-containing ligand is an especially attractive scaffolding to build-up such nano-molecules [8,9], because theoretical calculations have proved that aurophilicity is augmented by substituting SR for X in LAuX [10]. We have, therefore, been inter-

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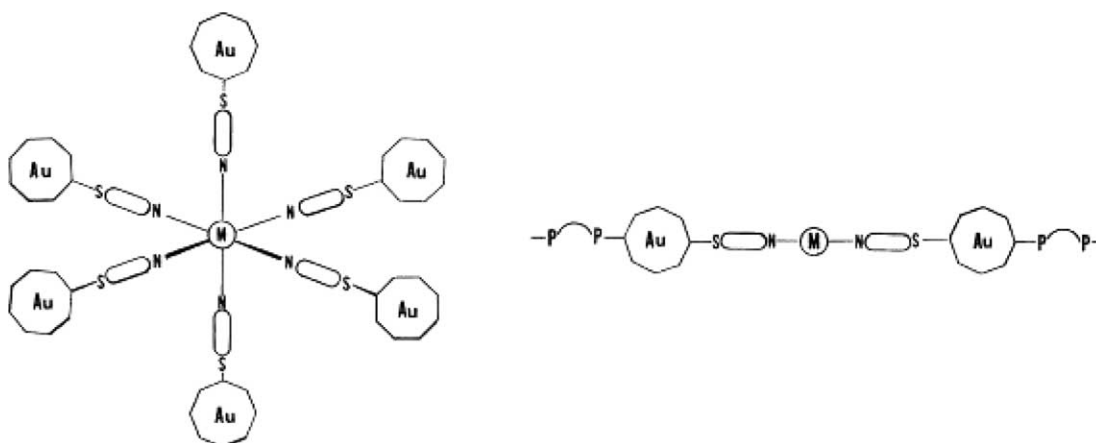
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ested in S–R–4-py, S–4-py, and S–2-py [11]. The reasons for selection of these ligands are twofold. First, these ligands have a potential coordinating ability to other transition metal(s) through the pyridine–N atom in order to construct new supra molecules such as “molecular-dots” and/or “molecular-wires” (Scheme 1) by virtue of the strong interaction [12,13]. Second, the S atom sometimes works as a multidendate coordinating site to yield sophisticated supra structures in addition to induce and/or strengthening aurophilicity [14–16]. Another interesting examples were reported previously by Che and Puddephat for  $(\text{LAu})_3(\text{S}_3\text{C}_3\text{N}_3)$ , which loses two ligand groups L in solution and dimerized to give a hexamer,  $\text{Au}_6\text{L}_4(\text{S}_3\text{C}_3\text{N}_3)$  [17,18]. Quite interesting issue is that the initially formed trimer exhibits no Au–Au interaction, while four Au among six Au atoms in the hexamer were involved in Au–Au interactions. As a logical extension of these findings and our strategy mentioned above, we have examined a number of reactions of  $\text{Ph}_3\text{P–Au–S–4–C}_6\text{H}_4\text{–N=CH–4'–py}$  and/or  $\text{Ph}_3\text{P–Au–S–4–C}_6\text{H}_4\text{–N=CH–2'–py}$  with various transition metal derivatives (Ru, Rh, Re, Pd). However, single crystals of these products have not been obtained and satisfactory characterization have not been attained [11]. We then undertook attempts to synthesize  $(\text{L}'\text{Au})_3(\text{S}_3\text{C}_3\text{N}_3)$ , where L' denotes commercially available  $\text{P}(\text{C}_6\text{H}_5)_2(2\text{-pyridine})$  and to tether the Au block to other transition metals. The former aim of the trimer synthesis was successful [19], but the latter attempts have not so far been accomplished for this phosphine ligand. We have therefore, simplified our system by employing smaller  $\text{Au}(\text{S–4–py})\text{L}$  and  $\text{Au}(\text{S–2–py})\text{L}$  analogues and to tether them to other transition metals. Purported results have been obtained by the use of Au–S–4-py derivatives and acetylacetonates of some transition metals. This paper describes our synthetic concept principally based on the above building block strategy and X-ray structure analyses on three new

gold-hetero metal complexes, one of which exhibits a quasi-one dimensional infinite chain structure woven by aurophilicity.

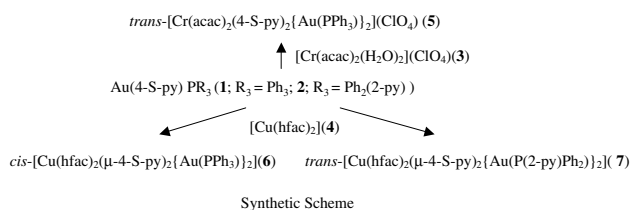
## 2. Preparative results

Our original exploration on the construction of the hetero metallic edifice containing Au(I)–S–R–4-py groups as “complexes as a ligand” (Scheme 1) was started several years ago [11]. A number of Ru, Rh, Pd and Pt coordination compounds have been employed as a target transition metal center to which aforementioned “Au ligands” would be introduced. However, these transition metal centers prefer S to pyridine N and the Au–S bond in the above ligand was easily cleaved (Au scavenge) upon reaction to yield insoluble solids in ordinary organic solvents; perhaps these solids are S- and N-containing polymers of these transition metal derivatives. Therefore, our effort seeking for appropriate other transition metal derivatives has been continued in addition to simplify the Au ligand. Requisites for these transition metal derivatives are that labile ligands should be coordinated to them for being replaced by pyridine N in  $\text{Au}(\text{S–4–py})\text{L}$  or they should be coordinatively unsaturated. Finally we have found that acetylacetonate derivatives of Cr(III) (**3**) and Cu(II) (**4**) just fit for this purpose; **3** corresponds to the former candidate and **4** to the latter. Selection of bis(acetylacetonato)chromium(III) **3** is not surprising. However, bis(hexafluoro acetylacetonato)(hfac)Cu(II) **4** was serendipitously chosen as one of transition metal hfac derivatives. Because of the strong affinity of Cu(II) ion to  $\text{S}^{2-}$ , it is surprising for us that the thiophilic Cu site in **4** scaffolding does not abstract the S-py from the Au(I) ligand, **1** and **2**, and desired hetero metallic tectonics **6** and **7** have been yielded; **6** takes a *cis* geometry, while **7** takes a *trans* geometry. Earlier studies on the reaction



Scheme 1.

of  $\text{Cu}(\text{hfac})_2$  with pyridine derivatives described the formation of 1:2 adducts,  $\text{Cu}(\text{hfac})_2\text{L}_2$  [20]. Synthesis of **6** and **7** as a bis-adduct and their stability are quite interesting in addition to the behavior of  $\text{Au}(\text{S-4-py})\text{L}$  as a pyridine-like ligand. The synthetic reactions are summarized in the Synthetic Scheme.



Another interesting finding is that thus obtained **5**, **6** and the infinite chain polymer **7** have a reasonable solubility in ordinary organic solvents. As is described Section 3, the  $[\text{Cu}(\text{hfac})_2\{\text{Au}(\text{S-4-py})\text{PPh}_2(2\text{-py})\}_2]$  units are connected by intermolecular aurophilicity to yield quasi one-dimensional infinite chains in the solid state of **7**, and yet the polymer has a reasonable solubility to laboratory organic solvents. Presumably neutral nature of **6** and **7** have some connection with this solubility, but the fact should not be overemphasized because of a reasonable solubility of the ionic **5** to organic solvents. The reason we emphasize the solubility comes from our previous study for constructing a “molecular-dot” by incorporating several 3-py- $\text{Co}_3(\text{CO})_9$  blocks into a Pd scaffolding; the purpose was hampered because of a quite low solubility of the product [12]. Thus, the solubility has a crucial importance to tessellate metallo-building blocks into 2- and/or 3-dimensional frameworks and yet to treat them as a molecule, not particles.

Then the query comes out what induces an essential geometrical difference in **6** and **7**? As was suggested in the previous paper [11,19],  $\text{PPh}_2(2\text{-py})$  ligand lacks an *ortho*-proton in an aromatic ring and the cone angle of this ligand is smaller than that of  $\text{PPh}_3$ . The compactness of this ligand afford a delicate effect on the advent of aurophilicity; the use of compact ligand is sometimes advantageous to the induction of intermolecular aurophilicity, but some cases, it does not [11,19]. It has been considered that the event depends on the crystal packing force as a whole [19,21]. However, it is apparent that the *trans* geometry is preferred in **7** for more compact  $\text{PPh}_2(2\text{-py})$ , which makes strong intermolecular aurophilicity possible, whereas the *cis* geometry is preferred in **6** for  $\text{PPh}_3$ , which ends in dimerization by weak aurophilicity (see Section 3). The following is a reasonable imagination that there occurs a *cis trans* isomerization in solutions at first and the *cis*-geometry is predominant for **6**, while the *trans*-geometry prevails for **7** in the process of yielding single crystals. However, UV-Vis measurements for **6** and **7** showed a single main peak in

$\text{CH}_2\text{Cl}_2$  (see Section 4), which indicates that such a *cis-trans* equilibrium is unlikely in solutions. Therefore, we suggest that the cooperative effect of aurophilicity plays crucial role for determining the geometry and the dimensionality. Aurophilicity as a “soft binding force”, therefore, should be quite important for the tailored synthesis of such a nano-molecule as **7**.

Vicente et al. [22] have recently reported similar hetero di-, tri-, and tetra-nuclear Au-M systems ( $\text{M} = \text{Pd}, \text{Pt}, \text{Ni}, \text{Cd}, \text{Hg}$ ) by reacting  $[\text{Au}(\text{PPh}_3)(\text{OCMe}_2)]\text{ClO}_4$  with these transition metal derivatives of  $\text{S}_2\text{C}=\text{C}\{\text{C}(\text{O})\text{Me}\}$ . However, aurophilicity was not invoked in these systems. In this view, our choice of S-4-py and  $\text{PPh}_2(2\text{-py})$  ligands opens a new vista for Au-hetero metallic supra molecules.

### 3. Molecular and crystal structures

Fig. 1 shows the structure of the cationic molecular part of **5**. The chromium ion is located on the inversion center. Thus the core structure around the chromium ion has a *trans*-geometry. As two  $\text{H}_2\text{O}$  ligands occupy the *trans* position in the parental chromium derivative **3**, the reaction of **3** with  $\text{Au}(\text{S-4-py})\text{PPh}_3$  retains its original geometry. Although each composite molecule of **5** is not tethered by aurophilicity, the crystal packing diagram (Fig. 2; viewed along the *c*-axis) has shown that the partial  $\pi$ - $\pi$  stacking between phenyl rings each of which comes from another  $\text{PPh}_3$  ligands forms quasi one-dimensional structures (two phenyl rings are almost parallel and the closest C-C distance is 3.44 Å).

The core structure around the copper ion, however, has a *cis*-geometry for **6** in which  $\text{PPh}_3$  is coordinated to each Au(I) site (Fig. 3). Quite interesting finding is that the *cis*-geometry is changed to a *trans*-geometry when the  $\text{PPh}_2(2\text{-py})$  is substituted for  $\text{PPh}_3$  in **7** (Fig. 4). In addition, strong aurophilicity ( $r(\text{Au}\cdots\text{Au}) = 3.0120(5)$  and  $3.0951(4)$  Å) is induced for **7** to give quasi-one dimensional infinite chain structures (Fig. 5). To the best of our knowledge, **7** is the first example of a soluble polymer which is composed of a self-assembled composite of three hetero metal atoms building blocks, which are linked with aurophilicity.

The main geometric parameters abstracted from Table 2 for these new supra molecules are described below. The M-N distances are 2.09(1) Å for **5**, 1.99(1) and 1.98(1) Å for **6**, and 1.992(6), 1.991(7), 1.989(6) and 1.992(6) Å for **7**, respectively. The Au-S distances for **5-7** are not altered significantly compared with those of **1** and **2** (Table 2). The M-O (acac or hfac) distances are 1.94(1) and 1.986(9) Å for **5**, 1.95(1), 1.99(1), 2.27(1), 2.33(2) Å for **6**, 2.169(7), 2.098(7), 2.175(8), 2.081(7), 2.269(6), 2.011(6), 2.330(6) and 1.980(6) Å for **7**, respectively. The N-M-N bond angles are 180° for **5**, 92.4(5)°

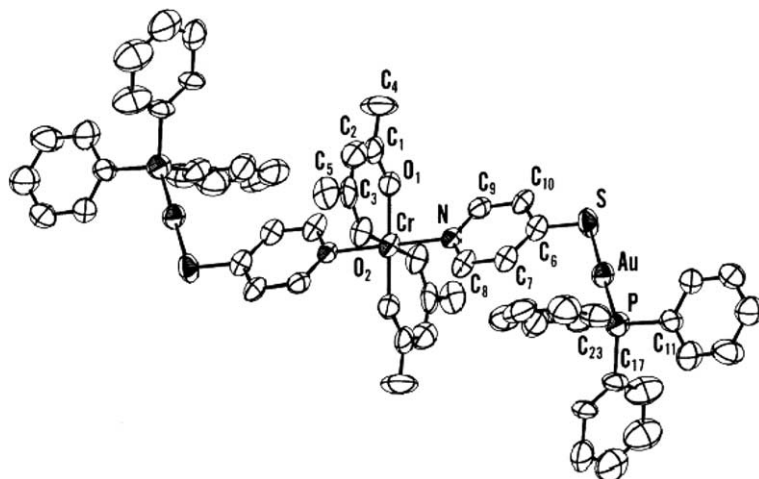


Fig. 1. An ORTEP drawing of the molecular part of *trans*-[Cr(acac)<sub>2</sub>{(S-4-py)AuPPh<sub>3</sub>}<sub>2</sub>](ClO<sub>4</sub>) (**5**).

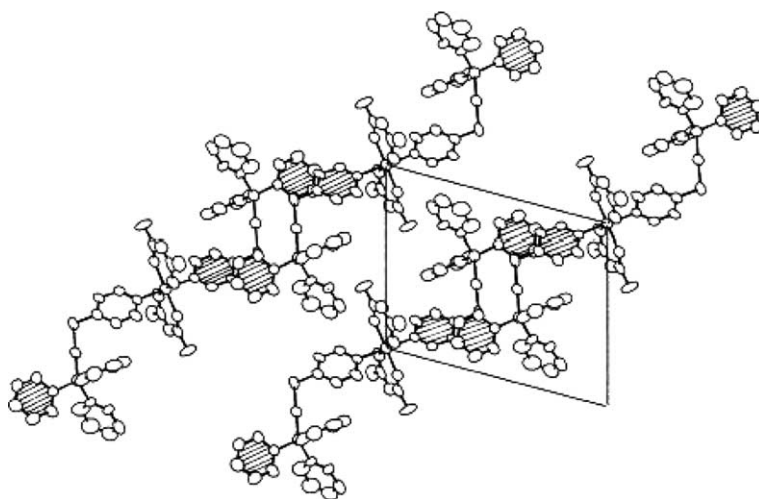


Fig. 2. The *c*-axis projection of **5** showing  $\pi$ - $\pi$  stacking.

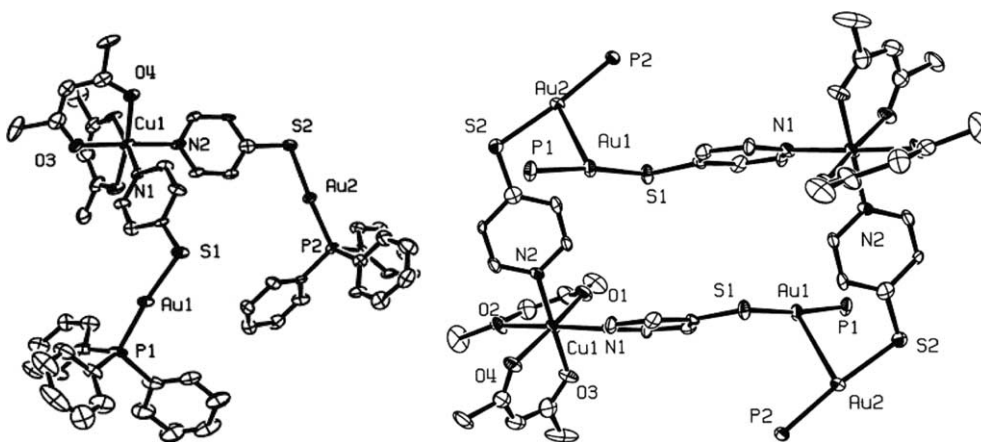


Fig. 3. An ORTEP drawing of *cis*-[Cu(hfac)<sub>2</sub>{(S-4-py)AuPPh<sub>3</sub>}<sub>2</sub>] (**6**) (left) and the dimer structure (right).

for **6**, and 179.2(3)° and 177.4(3)° for **7**, respectively. Among these parameters, significant differences in the Cu–O bond lengths for **6** and **7** are conspicuous; there

are two sets of Cu–O bonds for both of them, one is short and the other is long. At first glance, it was suspected that the *cis*-geometry for **6** is responsible for

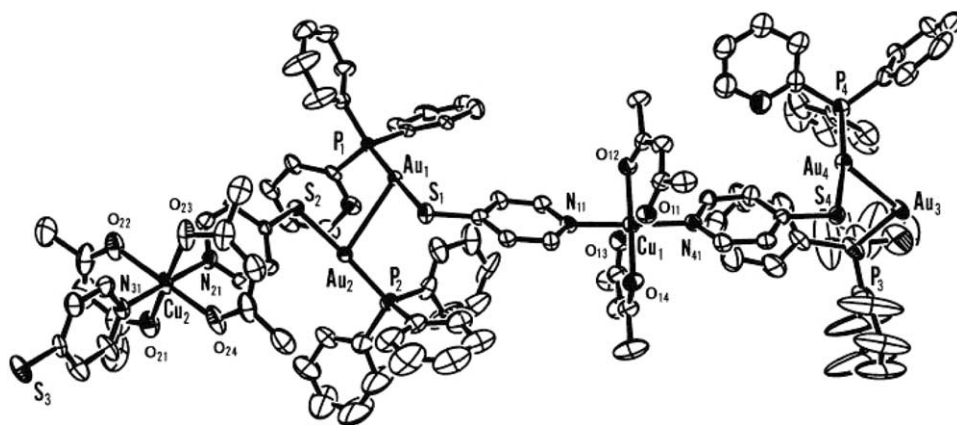


Fig. 4. An ORTEP drawing of *trans*-[Cu(hfac)<sub>2</sub>{(S-4-py)AuPPh<sub>2</sub>(2-py)}<sub>2</sub>] (7).

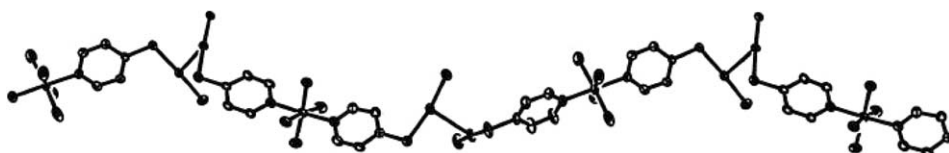


Fig. 5. An extended quasi-one-dimensional structure of complex 7.

steric crowding around the Cu(II) ion and would cause these distortions. However, the similar distortions were revealed for the *trans*-analogue 7. More detailed inspections of the data have shown that the elongated O atoms are coordinated to Cu(II) ion in a *trans* disposition for 6 and 7. The longer pair has the Cu–O distances of 2.267(14) and 2.329(16) Å and the shorter pair 1.949(11) and 1.993(12) Å for 6; the differences are larger than 0.3 Å. The longer pairs in 7 have the distances of 2.169(7) and 2.175(8) Å for molecule 1 and 2.330(6) and 2.269(6) Å for molecule 2, respectively, while the shorter pairs have the distances of 2.081(7) and 2.098(7) Å for molecule 1 and 1.980(6) and 2.011(6) Å for molecule 2, respectively; the differences are as large as 0.25 Å. Such a discordance was not described in the molecular data on Cu(acac)<sub>2</sub> [23] and Cu(hfac)<sub>2</sub> [24]. Cu(I)-hfac derivatives with alkynes, in which the copper ion takes the d<sup>10</sup> electron configuration, showed only narrow range of Cu–O distances [25]. Liao and coworkers [26] have prepared one-dimensional [Mn(hfac)<sub>2</sub>(4,4'-bipy)] and determined its structure. They have reported a significant distortion from the octahedral coordination around the central manganese ion and attributed the deviation to the large steric hindrance between hfac and 4,4'-bipy; the differences in Mn–O bonds is approximately 0.05 Å. Thus, the startling differences in 6 and 7 are highlighted. The distortion should be attributed to the Jahn–Teller effect for Cu(II) complexes with the d<sup>9</sup> electron configuration. The steric bulkiness of the “py–S–AuPR<sub>3</sub> ligands” works synergistically with the Jahn–Teller effect to give rise to such a large distortion.

#### 4. Spectral results

In Section 3, a large distortion around the Cu(II) center for 6 and 7 was described. We wondered if the distortion is reflected on the electronic state and/or on spectral characteristics. IR spectra were inspected. The IR spectrum of 5 displays three strong peaks at 1595, 1568 and 1522 cm<sup>-1</sup> in ν(CO) region and lacks peaks in ν(OH) region due to H<sub>2</sub>O groups detected in 3. These peaks become stronger and more distinct in 5 compared with those in 3. IR spectra of 6 and 7 are similar for each other in the ν(CO) region as is described in Section 6.2. However, the intensities and the numbers of peaks are significantly different for 6 and 7 from those of 5. Strong distortions around the Cu(II) ions in 6 and 7 should be reflected on the IR spectra of this region.

Literatures report strong absorptions at 330 and 384 nm longer than 300 nm for 3 in aqueous solution due to the *cis*–*trans* isomerization [27]. The supra molecule 5 exhibits a peak at 329 nm (340, sh) in dichloromethane. The hfac derivative of 4 shows two strong absorptions at 310 (main) and 333 (sh) nm in CHCl<sub>3</sub> [28]. Fackler et al. have assigned these absorptions to π<sub>3</sub>–π<sub>4</sub><sup>\*</sup> transition. 6 and 7 exhibits a single absorption at 316 nm with a shoulder at 339 and 340 nm, respectively, in dichloromethane [28]. As Au(I) ligands, 1 and 2 have an absorption at 295 nm, these strong absorptions at 329, 316 and 316 nm for 5, 6 and 7, respectively, should be mainly originated from the Cr(acac)<sub>2</sub> and/or Cu(hfac)<sub>2</sub> moieties. Observation of one main peak in this region for 5–7 suggests that only a single main component exists in solutions for respective derivatives.



These molecules are expected to exhibit excitation and emission spectra, because our previous reports on Au–Ru and Au–Re derivatives revealed interesting emission behaviors upon the excitation of the Au sites in this energy region [29]. However, no emission has been detected so far. Perhaps strong absorptions in 310–330 nm region due to diketone ligands monopoly the irradiating energy and disturb excitation from the “Au(I) ligands”. We are extending our research on photophysical properties of these molecules by use of a more sophisticated measurement.

## 5. Conclusion

Our strategy to employ “Au(S-4-py)L” as a coordinating ligand has gained decent results by the successful synthesis of hetero metallic supra molecules **5–7**. Especially construction of the infinite chain of **7**, which consists of tessellated “Au(S-4-py)L ligand”, should not be overemphasized from the view point as a synthon and a self-assembling scaffolding. Thus reactions of “Au(S-4-py)L” with other transition metal acetylacetonates including V, Mn, Co and Ni acac and hfac derivatives, Re derivatives, and Pd derivatives have been attempted. Although some spectroscopic evidences for the synthesis of the targeted supra molecule have been obtained for V, Mn and Ni systems, single crystals of these derivatives have not been obtained and full characterization for these hetero metallic supra molecules are left for future exploration at this moment.

## 6. Experimental

### 6.1. General

Reactions were carried out under an argon atmosphere by standard Schlenk techniques. The reaction vessel was covered with a piece of black cloth. The PPh<sub>2</sub>(2-pyridyl) ligand was purchased from Aldrich. HS-4-py was purchased from Aldrich. Au(S-4-py)PPh<sub>3</sub> (**1**) and Au(S-4-py)PPh<sub>2</sub>(2-py) (**2**) were prepared as reported previously [21]. *trans*-[Cr(acac)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>) (**3**) was also prepared according to the literature methods [27]. [Cu(hfac)<sub>2</sub>](**4**) (hfac = hexafluoro acetylacetonate) was obtained from TCI.

IR spectra were measured by use of a JASCO Herschel 460+ for KBr samples. UV spectra were measured by use of a JASCO Ubest V-570 DS spectrometer.

### 6.2. Synthesis

#### 6.2.1. *trans*-[Cr(acac)<sub>2</sub>{(S-4-py)AuPPh<sub>3</sub>}<sub>2</sub>](ClO<sub>4</sub>) (**5**)

60 mg (0.1 mmol) of **1** was dissolved in 5 ml of benzene. To this was added a methanol solution (5 ml) of **3** (20 mg,

0.05 mmol) for 2 h with stirring. Solvents were rotary-evaporated and the resulting pale pink solid was washed with small amount of toluene and the residue was extracted with methanol. The product was recrystallized from acetone:hexane to afford pale-yellow single crystals of **5**. Yield 40 mg (54%). IR ( $\nu(\text{CO})$  region)/cm<sup>-1</sup>/(KBr-disk); 1594vs, 1553vs, 1524vs. Other strong main peaks of **5** are as follows (not assigned)  $\nu_{\text{max}}$  (cm<sup>-1</sup>): 1478m, 1464m, 1435s, 1369s, 1281s, 1215s, 1098vs, 1056s, 1026s, 934s, 825s, 742s, 732s, 723s, 709s, 692vs, 622s, 535vs, 508vs, 479s. Found: C, 44.34; H, 3.56; N, 1.92%. C<sub>56</sub>H<sub>54</sub>Au<sub>2</sub>Cr<sub>1</sub>Cl<sub>1</sub>N<sub>2</sub>O<sub>8</sub>P<sub>2</sub>S<sub>2</sub> requires C, 45.12; H, 3.65; N, 1.88%. UV–Vis absorptions.  $\lambda_{\text{max}}$ /nm (CH<sub>2</sub>Cl<sub>2</sub>) 329 ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  51200), 340 (sh).

#### 6.2.2. *cis*-Cu(hfac)<sub>2</sub>[(S-4-py)AuPPh<sub>3</sub>]<sub>2</sub> (**6**)

60 mg (0.1 mmol) of **1** was dissolved in 5 ml of benzene. To this was added a methanol solution (5 ml) of **4** (25 mg, 0.05 mmol) for 15 min with stirring and the mixture was stirred overnight at room temperature. Solvents were rotary-evaporated and the resulting pale blue-green solid was recrystallized from benzene:hexane to afford pale-blue green single crystals of **6**. Yield 66 mg (81%). IR ( $\nu(\text{CO})$ )/cm<sup>-1</sup>/(KBr-disk); 1657s, 1652s, 1595vs, 1547m, 1530m. Other strong main peaks of **6** are as follows (not assigned);  $\nu_{\text{max}}$ /cm<sup>-1</sup>; 1500m, 1480m, 1437m, 1427m, 1256vs, 1200vs, 1147vs, 1112m, 1102m, 1085m, 1063m, 1029m, 998m, 816m, 791m, 745m, 729s, 710m, 692s, 667s, 584m, 537s, 500s. Found: C, 41.98; H, 2.54; N, 1.77%. C<sub>56</sub>H<sub>42</sub>Au<sub>2</sub>Cu<sub>1</sub>F<sub>12</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>S<sub>2</sub>C<sub>6</sub>H<sub>6</sub> requires C, 41.56; H, 2.62; N, 1.73%. UV–Vis absorptions.  $\lambda_{\text{max}}$ /nm (CH<sub>2</sub>Cl<sub>2</sub>) 316 ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  54300), 339 (sh).

#### 6.2.3. *trans*-[Cu(hfac)<sub>2</sub>{(S-4-py)AuPPh<sub>2</sub>(2-py)}<sub>2</sub>] (**7**)

60 mg (0.1 mmol) of **2** was dissolved in 10 ml of methanol. To this was added a methanol solution (10 ml) of **4** (25 mg, 0.05 mmol) with stirring and the mixture was stirred for 30 min at room temperature. After the solution turned to pale green, solvent was rotary-evaporated and the resulting pale blue-green solid was recrystallized from methanol:hexane to afford pale green single crystals of **7**. Yield 60 mg (73%) in a form of single crystals. IR ((CO))/cm<sup>-1</sup>/(KBr-disk); 1667s, sh, 1652vs, 1595 vs, 1571m, 1547m, 1528s. Other strong main peaks of **7** are as follows (not assigned);  $\nu_{\text{max}}$ /cm<sup>-1</sup>; 1499m, 1480m, 1437s, 1425m, 1256vs, 1200vs, 1146vs, 1112m, 1102m, 1085m, 1063m, 1027m, 988m, 816m, 791m, 741m, 728s, 691s, 667s, 584m, 538s, 510s. Found: C, 40.15; H, 2.34; N, 3.41%. C<sub>54</sub>H<sub>40</sub>Au<sub>2</sub>Cu<sub>1</sub>F<sub>12</sub>N<sub>4</sub>O<sub>4</sub>P<sub>2</sub>S<sub>2</sub> · C<sub>6</sub>H<sub>6</sub> requires C, 40.02; H, 2.49; N, 3.46%. UV–Vis absorptions.  $\lambda_{\text{max}}$ /nm (CH<sub>2</sub>Cl<sub>2</sub>) 316 ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  52800), 340 (sh).

### 6.3. X-ray crystallography

Selected crystals of **5** and **6** were glued to the top of a fine glass rod for room temperature measurements and a

selected crystal of **7** was attached on a nylon loop for low temperature measurements. The reflection data for **5** were collected by use of a MAC MXC3 diffractometer and those for **6** were collected on a Bruker SMART-APEX CCD diffractometer with graphite-monochro-

ated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at room temperature. A MAC Science DIP-LABO imaging plate diffractometer installed in the BL04B2 beamline of the SPring-8 synchrotron radiation facility ( $\lambda = 0.3282 \text{ \AA}$ ) was used for the data collection of **7** at 120 K because

Table 1  
Crystal data

Compound	<b>5</b>	<b>6</b>	<b>7</b>
Empirical formula	C <sub>56</sub> H <sub>52</sub> Au <sub>2</sub> Cr <sub>1</sub> Cl <sub>1</sub> N <sub>2</sub> O <sub>8</sub> P <sub>2</sub> S <sub>2</sub>	C <sub>57</sub> H <sub>45</sub> Au <sub>2</sub> Cu <sub>1</sub> F <sub>12</sub> N <sub>8</sub> O <sub>4</sub> P <sub>2</sub> S <sub>2</sub>	C <sub>60</sub> H <sub>44</sub> Au <sub>2</sub> Cu <sub>1</sub> F <sub>12</sub> N <sub>4</sub> O <sub>4</sub> P <sub>2</sub> S <sub>2</sub>
Formula weight	1456.5	1633.5	1696.6
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	11.881(6)	15.59(2)	9.0870(7)
<i>b</i> (Å)	15.348(7)	15.60(2)	20.550(2)
<i>c</i> (Å)	8.557(3)	16.15(2)	31.458(2)
$\alpha$ (°)	104.06(3)	66.30(2)	93.254(4)
$\beta$ (°)	95.14(3)	77.08(2)	96.502(4)
$\gamma$ (°)	74.07(4)	81.71(2)	88.954(3)
<i>Z</i>	1	2	4
<i>D</i> <sub>calc.</sub> (g cm <sup>-3</sup> )	1.70	1.53	1.85
Crystal dimensions (mm <sup>3</sup> )	0.7 × 0.7 × 0.45	0.3 × 0.2 × 0.2	0.1 × 0.07 × 0.02
<i>V</i> (Å <sup>3</sup> )	1455(1)	3500(7)	5826.8(7)
Diffractometer	MAC MXC3	SMART APEX	MAC DIP
$\lambda$ (Å)	0.71073	0.71073	0.3282
$\mu$ (mm <sup>-1</sup> )	5.67	4.66	0.76
$2\theta_{\max}$ (°)	50.0	56.0	27.1
Temperature (K)	298	293	120
Unique reflections	5338	15,082	31,978
Reflections with $ F_o  > 3\sigma( F_o )$	3799		
$I_0 > 2\sigma(I_0)$		12,819	22,231
No. of parameters refined	340	838	649
<i>R</i>	0.08	0.113	0.119
<i>wR</i> <sub>2</sub>	0.093 <sup>a</sup>	0.242	0.268

Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) or synchrotron radiation ( $\lambda = 0.3282 \text{ \AA}$ );  $R = \sum F_o - |F_c| / |F_o|$ .

$$^a R_w = [\sum (|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}, \text{ where } w = 1/\sigma^2(F), wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}, \text{ where } w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP].$$

Table 2  
Selected bond lengths (Å) and bond angles (°)

	<b>5</b>	<b>6</b>	<b>7</b>
Au...Au		3.503(3)	3.0951(4), 3.0120(5)
M–N	2.09(1)	1.99(1), 1.98(1)	1.992(6), 1.991(7), 1.989(6), 1.992(6)
M–O	1.94(1), 1.986(9)	2.33(1), 1.99(1), 1.95(1), 2.27(1)	2.169(7), 2.098(7), 2.175(8), 2.081(7), 2.269(6), 2.011(6), 2.330(6), 1.980(6)
Au–S	2.292(4)	2.292(4), 2.296(5)	2.302(2), 2.316(2), 2.318(2)
Au–P	2.246(5)	2.248(5), 2.266(5)	2.260(2), 2.257(2), 2.252(3), 2.271(2)
S–Au–Au		75.2(2), 76.5(2)	81.38(5), 74.59(5), 89.18(5)
P–Au–Au		109.3(2), 106.9(2)	99.68(5), 108.75(5), 100.10(6)
O–M–O	91.5(4)	84.9(5), 87.4(5), 86.9(5), 87.2(5), 88.5(5), 170.0(5)	86.7(3), 171.8(3), 90.7(3), 175.2(3), 86.5(2), 86.6(3), 96.5(3), 174.0(2), 86.7(2), 88.5(2), 98.3(2), 174.7(2)
O–M–N	89.9(4), 89.6(4)	93.1(5), 89.4(5), 89.3(5), 90.8(5), 95.8(5), 94.7(5), 176.2(5), 176.3(6)	85.4(3), 94.0(3), 93.0(3), 87.5(3), 93.7(3), 87.0(3), 88.7(3), 90.9(2), 93.0(2), 88.0(2), 87.9(2), 89.8(3), 90.7(2), 88.5(3), 90.7(3), 91.8(3)
N–M–N			179.12(3), 177.4(3)
S–Au–P	179.0(2)	173.1(2), 175.0(2)	177.96(7), 176.56(7), 170.46(8)
Au–S–C	110.3(6)	106.3(5), 106.6(6)	
S–Au–Au–S (torsional)		126.4(2), 128.1(2)	114.21(7), 108.56(8)
P–Au–Au–P (torsional)		128.1(2)	113.26(7), 104.98(9)
P–Au–Au–S (torsional)			67.56(7), 64.97(8), 72.78(9), 73.58(9)

only a limited size of crystals was available for this compound [30]. The structures of these crystals were solved by a direct method using Sir-92 in a CRYSTAN-GM program package provided by MAC Science (5) and SIR 97 in a WINGX program package (6,7) and refined with anisotropic thermal parameters by full-matrix least-squares programs on the CRYSTAN-GM program package for 5 and on SHELXS 97 in a WINGX program package for 6 and 7 [31]. The refinements were made on  $F$  for 5 and  $F^2$  for 6 and 7 and the final  $R$  and  $wR$  and/or  $wR_2$  values are given in Table 1. Tables for atomic coordinates, thermal parameters, and bond-lengths and angles are available as supplementary materials. Selected bond lengths and angles are given in Table 2. The supplementary crystallographic data are contained in CCDC-239643(5), -239644(6) and -239645(7).

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