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Photophysical properties, electronic and crystal structures of luminescent diphosphine digold(I)-pyridine-2-thiolate complexes $\stackrel{\approx}{\sim}$

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Abstract

Treatment of diphosphine digold(I) complexes, PP(AuCl)₂ [PP = bis(diphenylphosphino)methane, dppm; 1,6-bis(diphenylphosphino)hexane, dpph], with two equivalents of pyridine-2-thiol (HNS) in the presence of NaOCH₃ affords two luminescent diphosphine digold(I)-pyridine-2-thiolate complexes, dppm(AuSN)₂ (1) and dpph(AuSN)₂ (2), respectively. Both crystal structures have been determined by crystallographic studies. The intramolecular aurophilic contact of 3.0478(3) Å is observed in the crystal structure of 1, whereas there is not any aurophilic interaction present in the crystal lattices of 2. At room temperature, 1 shows a low-energy emission at ca. 660 nm as well as a very weak high-energy emission at ca. 496 nm in the solid state, but 2 shows only a strong high-energy one at ca. 482 nm. Thus, the emission energy strongly dependent on the Au(I) ··· Au(I) interaction can be demonstrated in the diphosphine digold(I) thiolates studied herein.

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1. Introduction

Aurophilicity, the propensity for closed-shell d¹⁰ gold(I) centers to form weakly bonding interactions, leading to the fabrication of a large variety of supramolecular gold(I) compounds with novel structural and intriguing spectroscopic properties, has recently been an interesting and common phenomenon in gold(I) chemistry [1–10]. These interactions are typically identified by means of X-ray diffraction studies in all cases where gold(I) \cdots gold(I) distances are found to be in the same order as the energies of standard hydrogen bonds (ca. 6– 12 kcal/gold(I) \cdots gold(I) at gold(I) \cdots gold(I) distances of 2.8–3.2 Å) [11]. The presence of aurophilic interactions may be recognized not only from short $gold(I) \cdots gold(I)$ distances and novel structural features, but also from intriguing electronic absorption and luminescence properties. It is becoming clear that the $gold(I) \cdots gold(I)$ bonding interaction is responsible for the relevant transitions and luminescence has thus become an important diagnostic tool for aurophilicity [12]. Recently, a spectacular experiment carried out by Balch and coworkers [3a] has demonstrated that luminescence of gold(I) complexes can be triggered by the solvation of the donor-free solid substrate either from the vapor phase or by dissolving the material in a solvent. In the meantime, a remarkable example of the strong solvent dependence of the luminescence of a gold(I) compound in solution has been observed by Che and co-workers [10d]. Moreover, an unusual chromic luminescence behavior linked to a structural change in the solid state induced by exposure to the vapor phase of volatile organic compounds (VOCs) was also observed by Eisenberg and co-workers [13]. The "luminescent switch" for the detection of VOCs using gold(I) dimers following the pioneering work by Mann and co-workers [14] on

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absorption and emission spectra of vapochromic platinum(II) and palladium(II) compounds shows that phenomena of this kind of luminescent gold(I) compounds hold great potential for analytical applications.

Among a large number of gold(I) compounds, gold(I) thiolates are the most extensively used gold(I) complexes, with applications in medicine and in surface technology. Virtually all of the classical and modern drugs based on gold(I) ions for arthritis and rheumatism have been gold(I)-sulfur compounds [15-17]. As a first contribution to the topic of luminescent gold(I) thiolate compounds, Bruce and co-workers [18] have investigated a series of neutral and dinuclear gold(I) complexes containing phosphine and thiolate (aromatic and aliphatic) ligands, where the length of the bridging bis(phosphine) backbone was systematically increased from dppm to dpppn [1,5-bis(diphenylphosphino)pentane]. The number of methylene groups in the bis(phosphine) backbone increased from 1 to 5, forming an increasingly larger series of open-chain and dinuclear gold(I) complexes with absorption bands at 300-360 nm as well as luminescence at 485–515 nm, which are assigned to $S \rightarrow Au$ charge-transfer transitions. In the meantime, Fackler and co-workers [19] also studied a series of mononuclear gold(I) complexes containing phosphine and thiolate (aromatic) ligands, and all of the compounds only luminesce at 77 K (485-702 nm) in the solid state, and the excitation was also assigned to a $S \rightarrow Au$ charge-transfer transition. Although the presence of a $Au(I) \cdot \cdot \cdot Au(I)$ interaction in the solid state for Bruce's system does not significantly perturb the emission energy, Fackler and co-workers [19] did find the emission energy affected by $Au(I) \cdots Au(I)$ interactions. However, there are only a handful of examples demonstrating a close relationship between the emission energy and aurophilic interaction for gold(I) thiolates [10d,19]. Pyridine-2-thiolate (NS) has been extensively used because of its versatile coordination behavior, but only a few gold(I)-pyridine-2thiolate complexes are known so far [20]. Herein, we report the photophysical properties, electronic and crystal structures of two luminescent digold(I)-pyridine-2-thiolate complexes of dppm and dpph, wherein the relationship between the emission energy and aurophilic interaction is also clarified.

2. Experimental

2.1. General information

All reactions were performed under a nitrogen atmosphere and solvents for syntheses (analytical grade) were used without further purification. NMR: Bruker DPX 400 MHz NMR; deuterated solvents with the usual standards. MS : Positive ion FAB mass spectra were recorded on a Finnigan MAT95 mass spectrometer. $Dppm(AuCl)_2$ and $dpph(AuCl)_2$ were prepared by literature methods [21].

2.2. Synthesis

[dppm(AuSN)₂] (1). The reaction of NaNS (133 mg, 1 mmol), prepared by adding NaOMe (65 mg, 1.2 mmol) to HNS (111 mg, 1 mmol) in CH₂Cl₂/CH₃OH (1:1, 25 ml), with dppm(AuCl)₂ (425 mg, 0.5 mmol) in CH₂Cl₂/MeOH (1:1, 50 ml) at room temperature for 4 h gave a pale-yellow precipitate. The precipitate was filtered off in a vacuum and pale-yellow solids of [dppm(AuSN)₂] were obtained in a 75% yield. Single crystals were grown by ether diffusion to a DMF solution. MS (FAB): [dppm(AuSN)Au (M-SN)], m/e = 887, 100%. ³¹P–{¹H} NMR (DMSO-*d*₆, 25 °C): δ 32.78 [s]. *Anal.* Calc. for C₃₅H₃₀Au₂N₂P₂S₂: C, 42.09; H, 3.03; N, 2.81. Found: C, 41.96; H, 2.95; N, 2.61%.

[dpph(AuSN)₂] (2). **2** was prepared in a similar way with an 86% yield except that dpph(AuCl)₂ was used instead of dppm(AuCl)₂. Single crystals were grown by ether diffusion to a DMF solution. MS (FAB): [dpph(AuSN)Au (M-SN)], m/e = 957, 100%. ³¹P–{¹H} NMR (DMSO- d_6 , 25 °C): δ 35.89 [s]. *Anal.* Calc. for C₄₀H₄₀Au₂N₂P₂S₂: C, 44.95; H, 3.77; N, 2.62. Found: C, 44.66; H, 3.95; N, 2.51%.

2.3. Physical measurements and instrumentation

UV–Vis spectra were recorded on a Perkin–Elmer Lambda 19 spectrophotometer and steady state emission spectra on a SPEX Fluorolog-2 spectrophotometer. Emission lifetime measurements were performed with a Quanta Ray DCR-3 Nd-YAG laser (pulse output 355 nm, 8 ns). The decay signal was recorded by a R928 PMT (Hamamatsu), which was connected to a Tektronix 2430 digital oscilloscope. Solutions for photophysical experiments were degassed by at least four freeze–pump–thaw cycles.

2.4. X-ray crystallography

Suitable crystals were mounted on a glass capillary. Data collection was carried out on a Bruker SMART CCD diffractometer with Mo radiation at 293 K for 1 and 150 K for 2. A preliminary orientation matrix and unit cell parameters were determined from 3 runs of 15 frames each, each frame corresponding to 0.3° scan in 15 s, followed by spot integration and least-square refinement. Data were measured using an ω scan of 0.3° per frame for 20 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART [22] software and refined with SAINT [23] on all observed reflections. Data reduction was performed with the

Table 1 Crystallographic data for **1** and **2**

	1	2		
Empirical formula	$C_{35}H_{30}Au_2N_2P_2S_2$	$C_{40}H_{40}Au_2N_2P_2S_2$		
Formula weight	998.10	1068.73		
Crystal system	triclinic	monoclinic		
Space group	Pbca	$P2_1/c$		
a (Å)	11.2947(5)	11.9211(11)		
b (Å)	21.7831(10)	19.6518(18)		
<i>c</i> (Å)	27.3307(13)	8.2989(8)		
α (°)	90	90		
β (°)	90	101.143(2)		
γ (°)	90	90		
V (Å ³)	6724.3(5)	1907.5(3)		
$\rho_{\rm calc}~({\rm g~cm^{-3}})$	1.973	1.861		
Ζ	8	2		
μ (Mo K α) (cm ⁻¹)	89.64	79.06		
F(000)	472	1028		
T (K)	273(2)	150(1)		
Observed reflections	5667	4378		
$(F_{\rm o} \ge 2\sigma F_{\rm o})$				
Refined parameters	389	218		
R^{a}	0.0297	0.0235		
$R_{\rm w}^{\rm b}$	0.0587	0.0511		
${}^{a}R = \sum F_{0} - F_{c} / \sum F_{0} .$				

$${}^{h} wR_{2} = \{ [\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum [w(F_{o}^{2})^{2}] \}^{1/2} .$$

SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS [24]. The structure was solved by direct methods with the SHELX93 [25] program and refined by full-matrix least-squares methods on F^2 with SHEXLTL-PC V 5.03 [25]. All non-hydrogen atomic positions were located in difference Fourier maps and refined anisotropically. The hydrogen atoms were placed in their geometrically generated positions. Detailed data collection and refinement of the complexes are summarized in Table 1.

3. Results and discussion

3.1. Description of crystal structure

Perspective views of **1** and **2** are shown in Figs. 1 and 2, respectively. The Au(I) centers are all two-coordinate and adopt an almost linear geometry with P–Au–S angles ranging from 169.93(3) to 175.48(4)°. Au–P [2.2468(9)–2.2705(13) Å] and Au–S [2.2948(14)–2.3062(9) Å] distances all fall in a normal range [12a,12b,18,26].

As shown in Fig. 1, the crystal structure of 1 features a dinuclear unit with an intramolecular aurophilic interaction at a distance of 3.0478(3) Å, which is close to the values of 3.0353(3) Å in $[Au_2(dppm)(dtp)_2]$ $[dtp = S_2P(p-C_6H_4-OCH_3)(Oc-C_5H_9)^-]$ [26e] and 3.0987(10) Å in $[dppm(Au(SSNH_2))_2]$, [26c] but slightly shorter than the value of 3.351(2) Å in $[dppm(AuCl)_2]$ [21a]. Due to the steric effect of dppm bearing four



Fig. 1. Molecular structure of **1**. ORTEP diagram shows 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Au(1)–S(1) 2.3044(13), Au(2)–S(2) 2.2948(14), Au(1)–P(1) 2.2613(12), Au(2)–P(2) 2.2705(13), Au(1)···Au(2) 3.0478(3); P(1)–Au(1)–S(1) 175.48(4), P(2)–Au(2)–S(2) 171.93(5).



Fig. 2. Molecular structure of **2**. ORTEP diagram shows 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Au(1)-S(1) 2.3062(9), Au(1)-P(1) 2.2468(9); P(1)-Au(1)-S(1) 169.93(3).

phenyl groups, the intermolecular aurophilic interaction is normally prevented in the solid state. However, there is an additional intramolecular $\pi \cdots \pi$ interaction with a shortest distance of 3.49 Å between the C atoms of the roughly parallel phenyl rings of the neighboring diphenylphosphino moieties in **1**. The distance of an intramolecular Au···S contact is 3.62 Å suggestive of a weak interaction and the dihedral angle defined by Au(1)– P(1)···Au(2)–P(2) is 27.5°. Fig. 2 shows that there is a twofold axis passing through the mid-point of the C(8)– C(8A) bond for **2**. The dpph adopts an *anti* conformation, so that the Au–SN moieties are well separated. A close intermolecular gold(I)···gold(I) contact is absent

Compounds	λ_{abs} (nm) (ϵ , dm ³ mol ⁻¹ cm ⁻¹) in CH ₂ Cl ₂	$\lambda_{\rm em}$ (nm)/ τ (µs) in CH ₂ Cl ₂	$\lambda_{\rm em}$ (nm)/ τ (µs) solid state (RT) (77 K)	
1	268 (31 150) 324 (13 180)	400/1.1 ^a	496/40.8 660/7.8	482/123.9 685/21.2
2	274 (23 230) 312 (11 940)	450/1.7	482/142.1	473 507/406.3 544

 Table 2

 Spectroscopic and photophysical properties of 1 and 2

^a Possibly an artifact.

in the solid state, and this was not originally expected because of the flexible nature of dpph. Since the NS moiety is not bulky and there is no other competing force present in the crystal lattice (i.e., hydrogen bonding), the absence of aurophilic interactions for **2** seems to be only ascribed to crystal packing.

3.2. UV-Vis absorption spectra

Spectroscopic and photophysical data of 1 and 2 are shown in Table 2. As shown in Fig. 3, the absorption spectra of 1 and 2 measured in dichloromethane are very similar and exhibit poorly vibronic-structured absorption bands at ca. 268 and 274 nm as well as broad absorption bands at ca. 324 and 312 nm, respectively. The ca. 268 and 274 nm bands due to an intraligand transition of the diphosphine ligands are suggested based on the work reported by Bruce and co-workers [18]. The ca. 324 and 312 nm absorption bands are tentatively assigned to an intraligand transition of the NS moieties in character, since the free ligand shows the absorption bands in a similar spectral region. However, a $S \rightarrow Au$ charge-transfer transition sitting under the intraligand transition of NS is still possible. Notably, the absorption

 $\frac{4 \times 10^{4}}{3 \times 10^{4}} = \frac{4 \times 10^{4}}{1 \times 10^{4}} = \frac{1}{1 \times 10^$

Fig. 3. The absorption spectra of 1 (solid line) and 2 (dash line) measured in dichloromethane.

bands at ca. 320 nm of $[8-QNS(AuPPh_3)_2] \cdot BF_4$ (8-QNS = quinoline-8-thiolate) [10d] and ca. 326 nm of $[Au_3(dpmp)_2]^{3+}$ [27] are suggested to be related to the ¹MC [metal-centered, $5d(d\sigma^*) \rightarrow 6p(p\sigma)$] transition (aurophilicity), and thus the red-shift from 312 nm for **2** to 324 nm for **1** may be rationalized by the aurophilicity present in **1**.

3.3. Emission spectra

The emission spectra of 1 and 2 measured in the solid state at room temperature are shown in Fig. 4. At room temperature, 1 displays a strong low-energy emission at ca. 660 nm and a weak high-energy emission at ca. 496 nm upon photoexcitation at 355 nm, whereas 2 shows only a strong high-energy emission at ca. 482 nm. Upon cooling these samples to 77 K, 1 shows an energy conversion process, where the high-energy emission (ca. 476 nm) increases in intensity while the low-energy one (ca. 685 nm) decreases. Similar emission properties have been reported on the [(TPA)AuX] (X = Cl, Br, I; TPA = 1,3,5-triaza-7-phosphaadamantane) [28] and [N4P4(AuX)₄] (X = Cl, Br, I; N4P4 = 1,4,8,11-tetra(diphenylphosphinomethyl)-1,4,8,11-tetraazacyclote-



Fig. 4. The solid-state emission spectra of 1 (solid line) and 2 (dash line) measured at room temperature with an excitation wavelength at 355 nm.

tradecane) [10b] systems reported by Fackler and coworkers and Che and co-workers, respectively. The emission spectrum of 2 displays vibronic structures with peak maximum at ca. 473, 507 and 544 nm upon cooling to 77 K, and this progression with a spacing at 1300-1400 cm⁻¹ is mostly due to the C=C or C=N stretching mode of the NS ligand. The slight red-shift from 660 (RT) to 685 nm (77 K) may be explained by a temperature effect, since cooling the crystals will cause a concomitant contraction in crystal lattices as well as a strengthening in aurophilic interactions. In degassed CH_2Cl_2 , 2 shows a slight blue-shift with an emission maximum at ca. 450 nm, whereas 1 displays only a weak emission at ca. 400 nm. The ca. 450 nm emission for 2 with a similar energy compared to the related value of ca. 482 nm in the solid state seems to have a similar emission origin, assigned to a $S \rightarrow Au$ charge-transfer transition. It is noted that the ca. 400 nm emission for 1 is dramatically different from the ca. 496 and 660 nm emissions in the solid state, and thus it is most likely ascribed to a scattering effect or an artifact. Although the non-emissive nature for 1 in solution, which is possibly due to solvent-induced quenching, prevents the comparison between the solid state and solution behavior, the direct comparison between the emission energy and aurophilic interaction for 1 and 2 in the solid state has been clearly made.

In a previous study [10d], 8-QNS(AuPPh₃) shows a very weak emission at ca. 477 nm in solution, whereas excitation of a dichloromethane solution of [8-QNS(AuPPh₃)₂] · BF₄ gives a very weak emission at 460nm and a strong and low-energy one with a long lifetime of 26 µs at ca. 640 nm. The low-energy emission is absent in 8-QNS(AuPPh₃) and the $gold(I) \cdots gold(I)$ interaction is most probably responsible for the ca. 640 nm emission. The excited state for the ca. 640 nm emission is tentatively assigned to mostly come from the metal-centered $5d(d\sigma^*) \rightarrow 6p(p\sigma)$ excitation. When compared to the 8-QNS system, 1 and 2 seem to have similar excited state properties. Thus, the low-energy emission at 660 nm is also suggested to mostly come from the metal-centered $5d(d\sigma^*) \rightarrow 6p(p\sigma)$ excitation. These high-energy emissions in 1 and 2 most likely come from the $S \rightarrow Au$ excitation, with reference to previous studies by Bruce and co-workers [18] on [Au(dppe)(pdt)Au] (515 nm; dppe = 1,2-bis(diphenylphosphino)ethane, pdt =1,3-propanedithiolate) and [Au(dppb) (pdt)Au] (510 nm; dppb = 1,4-bis(diphenylphosphino)butane).

The relationship between the emission energy and aurophilic interaction for gold(I) thiolates is so far still unconclusive. In an earlier communication, Che and co-workers [10e] reported a novel luminescent gold(I) supermolecule with trithiocyanuric acid, [(LAu)(Au-PPhMe_2)_2]_2 (H_3L = trithiocyanuric acid), which has a novel two-dimensional framework via intermolecular gold(I) \cdots gold(I) interactions as well as intramolecular

gold(I)...gold(I) ones. Despite the intramolecular and intermolecular gold(I)...gold(I) interactions for $[(LAu)(AuPPhMe_2)_2]_2$, its solid-state emission at 520–530 nm is comparable to that for $[L(AuPPh_3)_3]$, without any aurophilic interactions [10e]. Thus, 1 and 2 may provide valuable examples to examine a close relationship between the emission energy and aurophilic interaction.

4. Conclusion

Although it is becoming clear that the gold $(I) \cdots gold(I)$ bonding interaction is responsible for the rich luminescence properties of gold(I) compounds, there are only a handful of examples demonstrating a close relationship between the emission energy and aurophilic interaction for gold(I) thiolates [10d.19]. The crystal structures of 1 and 2 have been determined by crystallographic studies, and both feature a dinuclear gold(I) thiolate. In the crystal structure of 1, the intramolecular aurophilic interaction at a distance of 3.0478(3) A is observed, whereas there is not any aurophilic interaction present in the crystal lattices of 2. The ca. 324 and 312 nm absorption bands for 1 and 2, respectively, are tentatively assigned to an intraligand transition of the NS moieties in character, but the slight red-shift for the above absorption bands from 2 to 1 is suggested to be contributed in part from the aurophilic interaction. At room temperature 1 shows a low-energy emission at ca. 660 nm as well as a very weak high-energy emission at ca. 496 nm in the solid state, whereas 2 shows only a strong high-energy one at ca. 482 nm. Thus, the emission energy strongly dependent on the $Au(I) \cdots Au(I)$ interaction can be demonstrated in the diphosphine digold(I) thiolates studied herein.

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