



Short communication

Structural and photophysical characterization of gold(I) complexes bearing naphthyl chromophores

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ABSTRACT

We prepared two chlorido-gold(I) complexes of the type L–Au–Cl bearing a naphthyl moiety: Complex **1** with L = tris-1-naphthyl-phosphine shows standard linear coordination without further aggregation in the solid state. Complex **2** with L = 2-naphthyl-isonitrile is engaged in a complex network of aurophilic and π – π interactions. The two complexes show similar luminescence behaviour in solution at room temperature with both intraligand fluorescence and phosphorescence. At 77 K the emission spectra are dominated by intraligand phosphorescence, which is typical of gold complexes with extended π -chromophores.

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Gold(I) compounds feature a rich structural chemistry [1] and often exhibit interesting photophysical properties [2,3,4]. In general, luminescence of gold(I) complexes is based on four different mechanisms: i) In the solid state, gold(I) complexes often aggregate via aurophilic interactions, and these Au···Au contacts also determine their luminescence properties. Their luminescence can be explained by an excimer/exciple model known from organic aromatics: In the ground state, only strong dispersion (= aurophilic) interactions are operative, whereas in the excited state formal Au–Au bonds are formed [5,6,7,8]. This leads to a strong distortion in the excited state and a huge Stokes shift of the emission band. Due to high spin–orbit coupling (SOC), the excited state is a triplet, and the emission is classified as phosphorescence. No simple relationship between the Au–Au distance and the wavelength of the emission band has so far been identified. Since these emissions occur only as long as aurophilic interactions are present, no luminescence is observed for unsupported Au···Au contacts in solution at low concentration. For high concentrations, luminescence is sometimes detected at 77 K also for unsupported Au···Au contacts [9]. However, for gold complexes bearing bridging ligands, emissions are usually found both in the solid state and in solution. (ii) Trigonal-planar gold complexes such as [(Ph₃P)₃Au]⁺ or (Ph₃P)₂AuX feature metal-centred p \leftrightarrow d transitions, which are in most cases emissive only in the solid state at low

temperature [10,11]. (iii) Gold(I) complexes containing easy to oxidize ligands, such as phosphine gold(I) thiolate complexes [12], have low-lying ligand-to-metal charge transfer (LMCT) excited states which are sometimes emissive. (iv) Gold(I) complexes bearing an extended π -chromophore are emissive due to π – π^* intraligand (IL) transitions [13]. The shape of the emission band is often very similar to that of the corresponding non-aurophilic chromophores. If the gold atom is close to the chromophoric moiety, SOC allows intersystem crossing, which results in phosphorescence in addition to fluorescence. In several cases, only the phosphorescence band is present. However, the emission lifetime is very long (in the μ s to ms range), which indicates that the gold atom induces only moderate SOC comparable to external heavy atom effects.

Recently, we have reported on several gold complexes bearing an extended π -system attached *directly* to the gold atom [14,15,16,17,18]. For example, we presented the phenanthroline homologue carbene ligand (L), which forms homo- and heteroleptic gold complexes of the form [L₂Au]PF₆ and LAuBr. At room temperature, these complexes feature dual emission assignable to both fluorescence and phosphorescence. At 77 K, the spectra are dominated by the phosphorescence band. In this work, we examined a configuration where the π -chromophore is *not directly* bonded to the gold atom, but separated by a phosphor atom of a phosphine ligand. For this purpose, we synthesized R₃P–Au–Cl (**1**, R = 1-naphthyl). In addition, R–N \equiv C–Au–Cl (**2**, R = 2-naphthyl) was investigated in order to determine the efficiency

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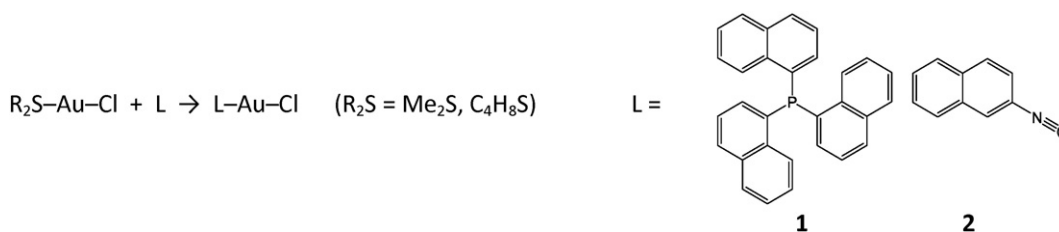
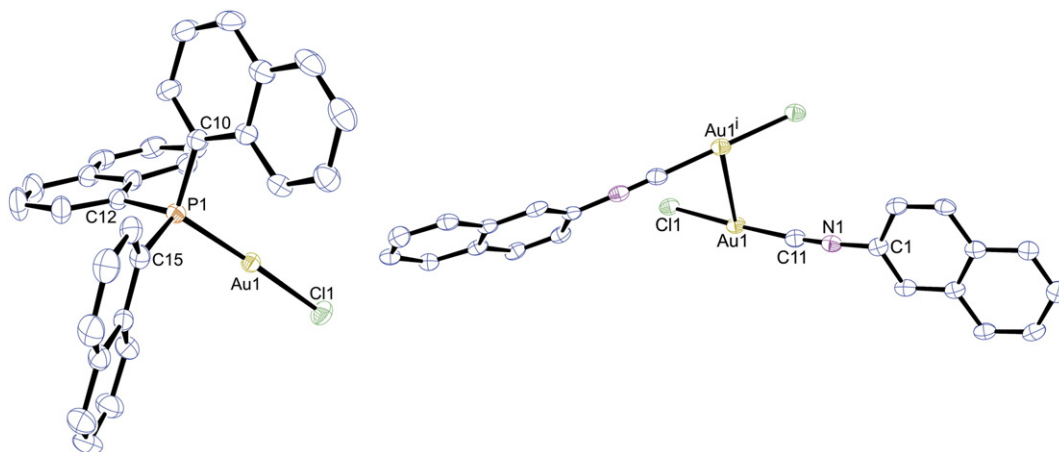
Scheme 1. Preparation of **1** and **2**.

Fig. 1. Molecular structure of **1** (left) and dimer of **2** (right). Selected bond distances [Å] and angles [°] for **1**: Au1–P1 2.2430(5); Au1–Cl1 2.2914(5); P1–Au1–Cl1 177.82(3); C10–P1–Au1 113.51(8); C12–P1–Au1 111.84(8); C15–P1–Au1 111.70(7); for **2**: Au1–Cl1 1.939(7); Au1–Cl1 2.280(2); Au1–Au1ⁱ 3.224(1); C11–Au1–Cl1 177.2(2); Cl1–Au1–Au1ⁱ–Cl1ⁱ 94.07.

of the SOC of the gold atom via the $-N\equiv C$ group. Both complexes have previously been prepared, but have not been characterized structurally or photophysically [19,20].

Reactions of the respective ligands with $R_2S-Au-Cl$ ($R_2S = Me_2S, C_4H_8S$) in dichloromethane (dcm) under ambient conditions yielded almost quantitatively both compounds as colourless solids with high purity (Scheme 1) [21]. For **1**, the ^{31}P NMR resonance shifts from -32.6 ppm [19] for the free ligand to 6.1 ppm. In the mass spectrum of **1**, intensive signals are found for $[Nap_3PAu]^+$ and $[(Nap_3P)_2Au]^+$ at 609.41 and 1021.75 , respectively. The latter results from a ligand-scrambling reaction which is frequently found for gold complexes [22]. A very weak signal is found for the chloronium ion $[(Nap_3P)_2AuCl]^+$ at 1253.87 . For **2**, the most intensive signal is found for $[(NapNC)_2Au]^+$ at 503.33 . Additional signals indicate $[(NapNC)Au(OH_2)]^+$ at 368.20 and the chloronium ion $[(NapNCAu)_2Cl]^+$ at 503.33 . The detection of halonium ions $[(LAu)_2X]^+$ ($X = Cl, Br$) is common for phosphine gold(I) complexes, but is relatively seldom reported for other ligands [13,23,24,25]. In the IR spectrum, the band associated with $-N\equiv C$ bond stretching of the free ligand is found at 2221 cm^{-1} . The value for the corresponding band in **2** is 2260 cm^{-1} .

Single crystals suitable for X-ray diffraction were obtained from slow gas-phase diffusion of diethylether into dcm solutions of the complexes

(see [26] for crystallographic details). In both complexes, the gold atoms are linearly coordinated with P–Au–Cl and C–Au–Cl angles of $177.82(3)^\circ$ and $177.2(2)^\circ$, respectively. In **1**, the naphthyl-groups adopt propeller geometry, although the complex does not possess crystallographic C_3 -symmetry. Due to the high steric bulkiness of the naphthyl groups, the phosphine complex exists as a monomer that does not aggregate via auriphilic interactions (Fig. 1, left). In contrast, the isonitrile complex is aggregated both by auriphilic interactions and by π – π stacking. In the crystals, three different Au–Au distances are present: Two isonitrile complexes dimerize with short Au–Au contacts of 3.224 Å in a crossed-sword arrangement (Fig. 1, right). These dimers are further connected by relatively long Au–Au contacts of 3.565 Å (Fig. 2, left). Perpendicular to this chain of dimers, the naphthalene moieties are engaged in π – π stacking interactions with distances of $\sim 3.9\text{ Å}$ between the naphthyl moieties, which obviously determine the Au–Au distance of 3.943 Å (Fig. 2, right).

Like other gold complexes that bear ligands with extended π -systems, **1** and **2** also exhibit highly temperature-dependent luminescence behaviour. For comparison, the absorption and emission spectra of the isonitrile ligand were measured. The phosphine ligand was not further investigated because of its more complex electronic structure due to potential sp-transitions. As was to be expected, the absorption

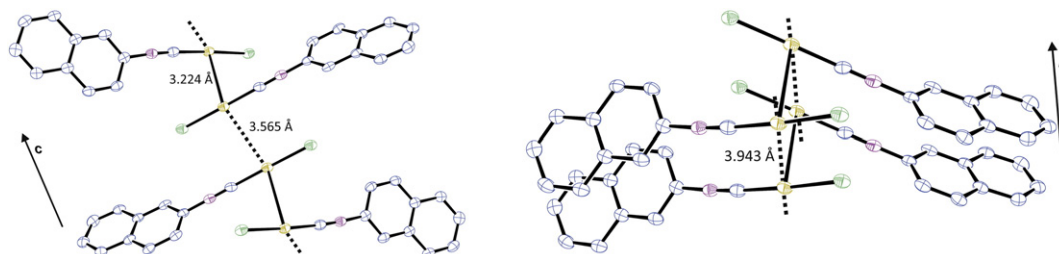


Fig. 2. Aggregation of molecules of **2** into chains along the c -axis (left) and π – π stacking along the b -axis (right).

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