

Tetranuclear Gold(I) Clusters with Nitrogen Donor Ligands: Luminescence and X-Ray Structure of Gold(I) Naphthyl Amidinate Complex

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The syntheses and characterization of gold(I) naphthyl, pentafluorophenyl, and trifluoromethylphenyl amidinate complexes are reported. The tetranuclear clusters are obtained from the reaction of Au(tetrahydrothiophene)Cl with the potassium salt of the corresponding amidinate in a THF solvent. The crystal structures of the gold(I) naphthyl, **2**, and pentafluorophenyl, **3**, amidinates show a short Au...Au distance of ~ 3.0 Å typical of compounds having an aurophilic interaction. The gold atoms are arranged in a square (Au...Au...Au = 87° – 92°) in the pentafluorophenyl derivative and in a parallelogram (Au...Au...Au = 68° – 110°) in the naphthyl amidinate complexes. The naphthyl and trifluoromethylphenyl complexes are visibly luminescent in the solid state at liquid nitrogen temperature displaying asymmetric emission bands at 538 and 473 nm, respectively. The luminescent lifetimes of these species are in the millisecond range indicating phosphorescent processes.

KEY WORDS: Gold; amidinate; luminescence; tetranuclear.

INTRODUCTION

The quest for small gold clusters for catalyst preparation is increasing. Gold clusters have shown high catalytic activity for the room temperature

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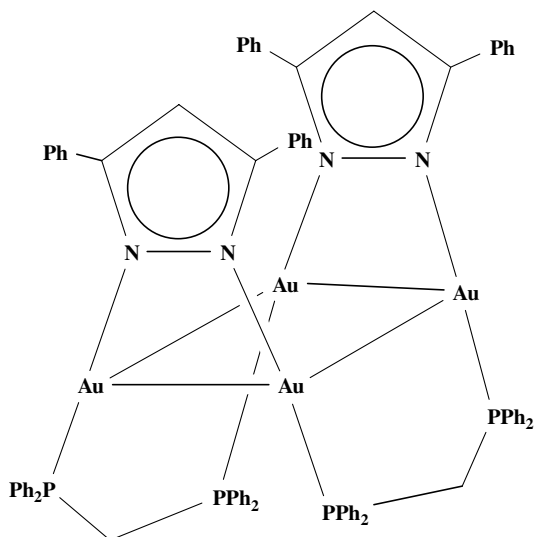
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*This manuscript is dedicated to the birthday anniversary and career of Dick Walton, an outstanding scientist and friend over many years. Even as a student whom I met in Southampton, England, his success could be predicted. Congratulations Dick!

oxidation of CO on a TiO₂ surface [1]. Phosphine and thiolate free gold clusters have advantages due to their low oxide residues after calcination. Recent catalytic studies suggest that gold amidinates and related gold–nitrogen complexes are the best catalyst precursors for CO oxidation reported to date (J. P. Fackler *et al.*, unpublished results).

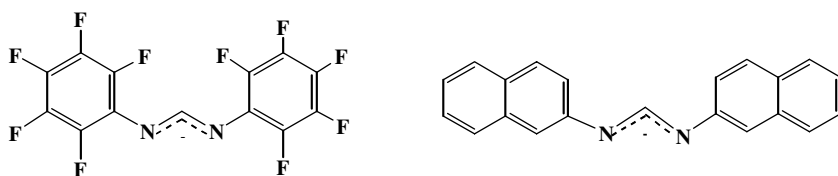
Amidinates are known to form metal complexes in different coordination modes including chelated, bridged, and pi-bonded [2]. Cotton has been able to exploit amidinates for the synthesis of a variety of complexes spanning the transition elements [3]. Recent results from his laboratory have demonstrated the synthesis and characterization of Mo₂(hpp)₄, hpp = 1, 3, 4, 6, 7, 8-hexahydro-pyrimido[1,2-*a*]pyrimidinate, a molecule with an ionization potential lower than that of cesium metal [4]. The use of these amidinate ligands in the coordination chemistry has produced complexes with extraordinarily short M–M distances. The origin of these short distances, which involve small ligand bite distances and delocalized electronic structure, is still under investigation [5]. The electron rich NCN linkage induces unique electrochemical and photo-physical properties in gold(I) amidinate complexes not seen before in group 11 pyrazolates [6].

Our work with gold–nitrogen chemistry first resulted in the synthesis and characterization of [Au₂(hpp)₂Cl₂], which was obtained from spontaneous oxidative–addition by halogenated solvents such as CH₂Cl₂ [7]. This gold(II) complex shows a Au···Au distance of 2.47 Å, the shortest Au···Au distance structurally reported. Ongoing research with gold amidinates has resulted in tetranuclear, trinuclear, and dinuclear products (H.E. Abdou *et al.*, unpublished). The dinuclear product [Au₂(2,6-Me₂-form)₂] undergoes oxidative–addition of halogens, CH₃I, and benzoyl peroxide, similar to what has been observed with the ylide compounds [8]. Moreover, the dinuclear species has been found to form 2-D chains with Hg(CN)₂. This substance traps two tetrahydrofuran solvent molecules in the grid (H.E. Abdou *et al.*, unpublished). The nitrogen ligand chemistry with pyrazolate ligands has produced mainly trinuclear complexes of group 11 and in low yield a hexanuclear [Au₆(μ-3,5-Ph₂pz)₆] [9]. The isolobal analogy between the tetranuclear [μ-3,5-HPh₂pz]₄ and [(dppm)₂Au₄(μ-3,5-Ph₂pz)₂]²⁺ has been discussed in a recent paper (Scheme 1) [10]. The arrangement of the gold atoms and the hydrogen atoms about a mean plane is the same in both species. The mononuclear and dinuclear base-stabilized gold(I) pyrazolate complexes, (PPh₃)Au(μ-3,5-Ph₂pz), (TPA)Au(μ-3,5-Ph₂pz), TPA = 1,3,5-triaza-7-phosphaadamantane, [(PPh₃)₂Au(μ-3,5-Ph₂pz)]NO₃, and [(dppp)Au(μ-3,5-Ph₂pz)]NO₃, dppp = bis(diphenylphosphine)propane, have been synthesized and structurally characterized [11].



Scheme 1.

In this paper, we describe the synthesis and photoluminescence properties of three tetranuclear gold(I) amidinate complexes. The naphthyl amidinate complex is structurally characterized (Scheme 2). Electrochemical and photophysical studies of gold(I) amidinates suggest that the electronic properties of the ligands play an important role in their chemistry.



Scheme 2.

EXPERIMENTAL

Synthesis of naphthyl amidine, 1

Triethyl orthoformate (orthoester) (5.92 mL, 0.04 mol) and the naphthyl amine (11.45 g, 0.08 mol) were mixed and the reaction mixture was heated to 140–160°C in a reflux vessel for 1–2 h. The reaction mixture

was distilled at the same temperature to remove ethanol and left at room temperature to solidify. The solid was extracted with warm toluene and left overnight at room temperature or in the refrigerator to give white blocks in yields of 70–85%. The ligand is characterized by X-ray crystallography.

Synthesis of pentafluoroamidine

Triethyl orthoformamate (orthoether) (3 mL, 0.02 mol) and pentafluoroaniline (7.32 g, 0.04 mol) were mixed in a round bottom flask and acetic acid (1 mL) was added. The reaction mixture was heated to 140–160°C for 30–40 min until the mixture became viscous. It was left at room temp to solidify. The dark solid was extracted with warm toluene and layered with petroleum ether and left overnight at room temperature or in the refrigerator to give a white crystalline product.

Synthesis of gold(I) naphthyl amidinate, 2

Naphthyl amidine (301 mg, 1 mmol) was stirred with (56 mg, 1 mmol) of KOH powder in THF for 1 h. The colorless solution turned yellow. Au(THT)Cl (320 mg, 1 mmol) was added and stirring was continued for additional 4 h. The solution was filtered over a Celite 545 bed after treatment with Darco. The volume was decreased under reduced pressure to 5 mL and hexanes was added to form an off-white precipitate. The product was filtered and recrystallized from THF/hexanes (3 × 10 mL) to give the tetragold cluster product. The product is air stable in the solid state. Elemental analysis: Calcd: C, 50.79, H, 3.85; Found: C, 50.72; H, 4.11. Yield: 31%. ¹H NMR 8.3 ppm. UV–Vis: λ_{nm} ($C_{\text{M/L}}$, $\epsilon_{\text{L/M-cm}}$): 333 (2×10^{-5} , 64.9×10^3).

Synthesis of gold(I) pentafluorophenyl amidinate, 3

Elemental analysis: Calcd: C, 27.27, N, 4.89; Found: C, 27.75; N, 4.64. ¹⁹F NMR: 30 (triplet, F3); 34 (triplet, F2 and F4); 43 (doublet, F1 and F5). Yield 77%. ¹H NMR 8.3 ppm. UV–Vis: λ_{nm} ($C_{\text{M/L}}$, $\epsilon_{\text{L/M-cm}}$): 260 (2×10^{-5} , 102.8×10^3), 285 (2×10^{-5} , 76.9×10^3), 300 (2×10^{-5} , 46.7×10^3).

Synthesis of gold(I) 3-trifluoromethanephenyl amidinate, 4

Elemental analysis: Calcd: C, 34.08; H, 1.71; N, 5.30; Found: C, 34.29; H, 2.06; N, 5.28. ¹⁹F NMR: 129 (singlet, 2 CF₃). Yield: 42% ¹H

NMR: 8.3 ppm. UV-Vis: $\lambda_{\text{nm}}(\text{C}_{\text{M/L}}, \varepsilon_{\text{L/M-cm}})$: 266 (2×10^{-5} , 68×10^3), 306 (2×10^{-5} , 45×10^3), 330 (2×10^{-5} , 31×10^3).

Crystallography

Data for **1–2** were collected using a Siemens (Bruker) SMART CCD (charge coupled device) based diffractometer equipped with a LT-2 low-temperature apparatus operating at 110 K. A suitable crystal was chosen and mounted on a glass fiber using cryogenic grease. Data were measured using omega scans of 0.3° per frame for 60 s, such that a hemisphere was collected. The first 50 frames were recollected at the end of data collection as a monitor for decay. No decay was detected. Cell parameters were retrieved using SMART software and refined using SAINT on all observed reflections [12]. Data reductions were performed using SAINT software [13]. The structures were solved by direct methods using SHELXS-97 and refined by least squares on F_2 , with SHELXL-97 incorporated in SHELXTL-PC V 5.03 [14, 15]. The structures were determined in the space groups $P\bar{1}$ and $P2_1/n$ by analysis of systematic absences. Hydrogen atom positions were calculated by geometrical methods and refined as a riding model. The crystallographic details for **1** and **2** are given in Table I. Selected bond distances and angles are presented in

Table I. Details of Data Collection and Structure Refinement for Compounds **1–2**

	1	2
Empirical formula	$\text{C}_{21}\text{H}_{16}\text{N}_2$	$\text{C}_{84}\text{H}_{60}\text{Au}_4\text{N}_8$
Formula weight	296.36	1969.28
Temperature	110(2)	110(2)
Wavelength	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
Unit cell dimensions	7.8205(16), 73.929(4) 8.0828(16), 78.189(4) 13.853(3), 65.493(4)	15.081(5) 20.823(8), 90.669(7) 20.736(7)
Volume, Z	761.6(3), 2	6511(4), 4
Density (calculated)	1.292	2.009
Absorption coefficient	0.076	9.041
Goodness-of-fit on F^2	0.969	1.128
Final R indices [$I > 2\sigma(I)$] ^{a,b}	0.0884, 0.0908	0.0472, 0.0920

^a Reported here.

^b Synthesis reported, but these structures, even at 77 K, are not sufficiently well resolved because of fluorine atom disorder and perhaps other factors to report the data here.

Table II. Bond Distances (Å) and Angles (°) of Naphthyl Amidine, **1**

Bond distances (Å)			
N(1)–C(1)	1.285(3)	N(2)–C(1)	1.341(3)
N(1)–C(2)	1.421(3)	N(2)–C(12)	1.407(3)
Bond angles (°)			
N(1)–C(1)–N(2)	123.3(2)	C(1)–N(1)–C(2)	116.0(2)
C(1)–N(2)–C(12)	123.4(2)		

Table III. Bond Distances (Å) and Angles (°) of Tetranuclear Gold(I) Amidinate (R = naphthyl), **2**

Bond distances (Å)			
Au(2)–N(2)	2.024(7)	Au(2)···Au(1)	3.0139(11)
N(1)–C(1)	1.306(12)	Au(2)···Au(3)	2.9920(9)
Au(4)···Au(3)	2.9721(11)	Au(4)···Au(1)	2.9944(10)
Au(1)–N(1)	2.022(7)	Au(3)–N(4)	2.033(7)
Bond angles (°)			
N(3)–Au(2)–N(2)	171.0(3)	N(3)–Au(2)···Au(1)	97.3(2)
N(2)–Au(2)···Au(1)	85.16(18)	N(3)–Au(2)···Au(3)	81.3(2)
Au(1)···Au(2)···Au(3)	68.59(2)	N(2)–Au(2)···Au(3)	107.58(19)
N(1)–Au(1)–N(8)	165.9(3)	N(6)–Au(4)–N(7)	172.1(3)
N(1)–C(1)–N(2)	126.2(8)	N(6)–Au(4)···Au(1)	105.7(2)
C(1)–N(1)–Au(1)	132.4(6)	Au(1)···Au(4)···Au(3)	69.11(2)
N(3)–C(22)–N(4)	126.1(8)	N(5)–Au(3)···Au(2)	105.5(2)
Au(2)···Au(1)···Au(4)	110.07(2)	Au(2)···Au(3)···Au(4)	111.29(2)

Tables II and III. The structure of complex **3** was solved but with high R_1 and wR_2 (0.1281, 0.2132). Crystals from gold(I) trifluoromethylphenyl amidinate **4** decomposed during data collection. The structure was solved with $R_{\text{int}} = 0.4$ and with high R_1 and wR_2 (>0.1 – 0.2). The Au···Au distances for complexes **3** and **4** will be used for comparison purposes, and are sufficiently good for this purpose, but the crystallographic data and structure parameters are not included in this manuscript.

Luminescence measurements

Corrected excitation and emission spectra of the complexes diluted with KBr were recorded in the solid state using quartz cells on a Jobin-Yvon Horiba Fluorolog 3-22 Tau-3 spectrofluorimeter. Phosphorescence lifetimes were recorded in a Perkin-Elmer LS-50B spectrofluorimeter at liquid nitrogen temperature using the commercially available Perkin-Elmer's sample

holder. Phosphorescence lifetime is calculated (assuming exponential decay) from the following equation: $\log I_t = -0.434t/\tau + \log I_0$, where I_t is the luminescence intensity at time t , t is the delay time, τ is the lifetime, and I_0 is the luminescence intensity at time zero.

RESULTS AND DISCUSSION

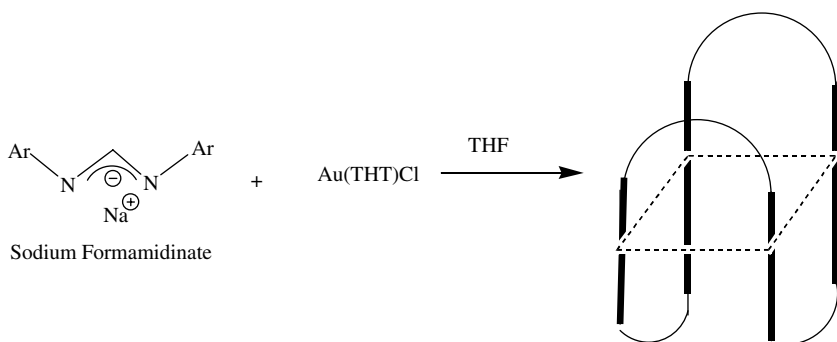
Synthesis

Tetranuclear gold(I) amidinate complexes are synthesized by the reaction between Au(THT)Cl and the potassium salt of the amidinate in THF. The reaction is stirred for few hours before filtration of the KCl. Crystallization is from hexanes. A pale yellow product is isolated in a good yield. The yields vary for the synthesis of different gold(I) amidinates. For example, in the synthesis of the naphthyl derivative the yield is 31 versus 77% for the pentafluorophenyl complex.

We have observed a violet or pink color for the hexane solutions which give a pale yellow product. The reaction forming product happens rapidly after adding the gold precursor. Drying a drop of the reaction mixture on a filter paper produces a spot with a strong green luminescence under a hand-held UV lamp. Similar observations were noticed during the synthesis of other gold amidinates. The clusters are stable at room temperature for weeks and show gray coloration after standing for months in the light and open air.

Syntheses involving various substituted amidinates result in tetranuclear gold(I) clusters. The cause of the nuclearity of group 11 elements with nitrogen ligands still is not understood. In gold(I) pyrazolate chemistry, trinuclear and hexanuclear complexes were isolated with 3,5-diphenylpyrazolate [9]. Raptis also isolated supramolecular gold(I) pyrazolate complexes by using small substituents rings such as Me₂pz on the pyrazolate [16]. Tetranuclear gold(I) pyrazolates were isolated only with a 3,5-diisobutyl substituted pyrazolate [17]. In the amidinate chemistry we are pursuing, no change in the nuclearity is found by using substituents such as 4-Me-C₆H₄, 4-OMe-C₆H₄, 3,5-Cl-C₆H₃, C₁₀H₇, C₆F₅, 3-CF₃-C₆H₄. Only with 2,6-Me₂C₆H₃ do dinuclear products dominate Scheme 3.

In trials to investigate the effect of the solvent on the nuclearity of gold(I) amidinates, non-chlorinated solvents such as ethanol, pyridine, and tetrahydrofuran have been used. Only the reported tetranuclear clusters have been isolated. Our experience with chlorinated solvents shows that they oxidatively add chlorine to gold(I) guanidinate-like complexes as we reported for the orange product [Au₂(hpp)₂Cl₂] [7]. For the syntheses of gold amidinates here, CH₂Cl₂ and CHCl₃ were used without any



Scheme 3. Synthesis of tetranuclear gold(I) amidinates.

change in color. The reported clusters are the only products observed to date except for use of 2,6-Me₂C₆H₃ as the amidinate ligand.

Molecular structures

The X-ray structure of the naphthylamidine ligand, **1**, shows independent molecular units without hydrogen bonds, Fig. 1. Many amidine ligand structures report dimers linked through hydrogen bonding [18]. For the pyrazole ligand 3,5-Ph₂pzH exists a tetramer form [19]; however, trinuclear products also have been isolated. A X-ray structure for a tetranuclear cluster using the 3,5-diisobutylpyrazolate ligand has been reported

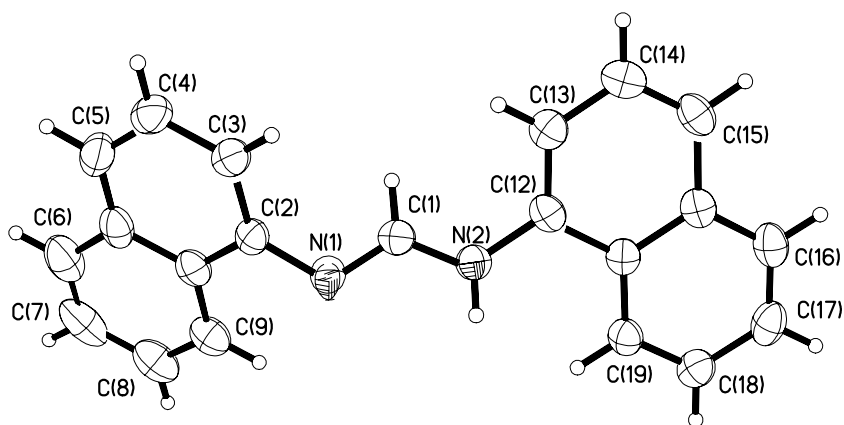


Fig. 1. View of **1** showing atomic numbering. Thermal ellipsoid drawing at the 50% level.

recently. The C–N amidine distances of 1.285(3) and 1.341(3) Å average to 1.306 (12) Å in **2**, which indicates delocalization occurs upon coordination with gold (Figs. 2 and 3). The naphthyl rings are in the plane of the ligand. The packing diagrams of the ligand **1** and its complex **2** show independent units.

The molecular structure of **2** is shown in Fig. 2. Each of the gold atoms is coordinated to two amidinate ligands in a nearly linear coordination. The average Au–N and Au···Au bond lengths are comparable with those observed in other gold–nitrogen complexes [20]. The bite distance in **2** is ~ 2.33 Å. The slant in the structure of **2** caused by crossed Au···Au interaction of 3.38 Å, which also induces the parallelogram arrangement.

The gold atoms are arranged in a square (Au···Au···Au = 87–92°) in the pentafluorophenyl derivative (but see Table IV, footnote b), **3**, in a parallelogram (Au···Au···Au = 68–110°) in the naphthyl derivative **2**, and a distorted square (Au···Au···Au = 84–95°) in the trifluoromethylphenyl derivative (see Table IV, footnote b), **4**, with the amidinate ligands bridged above and below the near plane of the four Au(I) atoms.

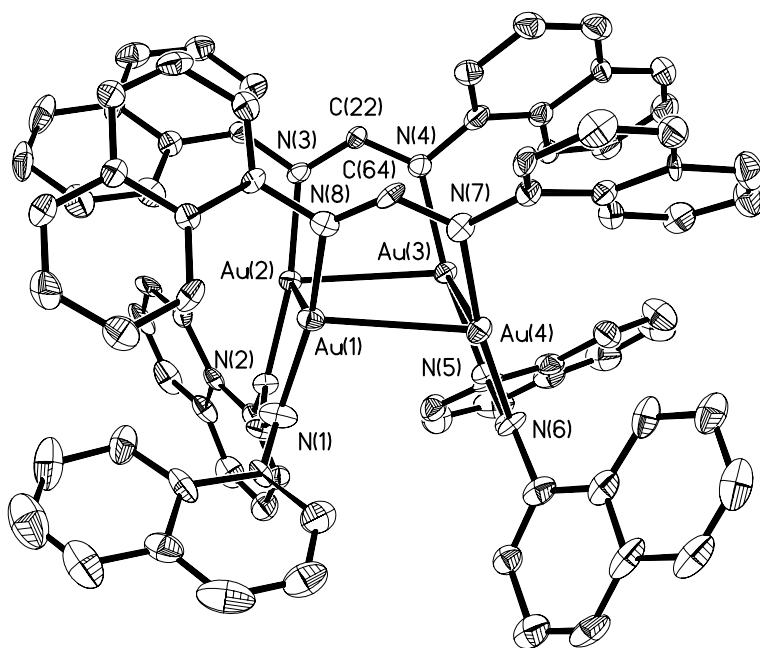


Fig. 2. View of **2** showing atomic numbering. Thermal ellipsoid drawing at the 50% level.

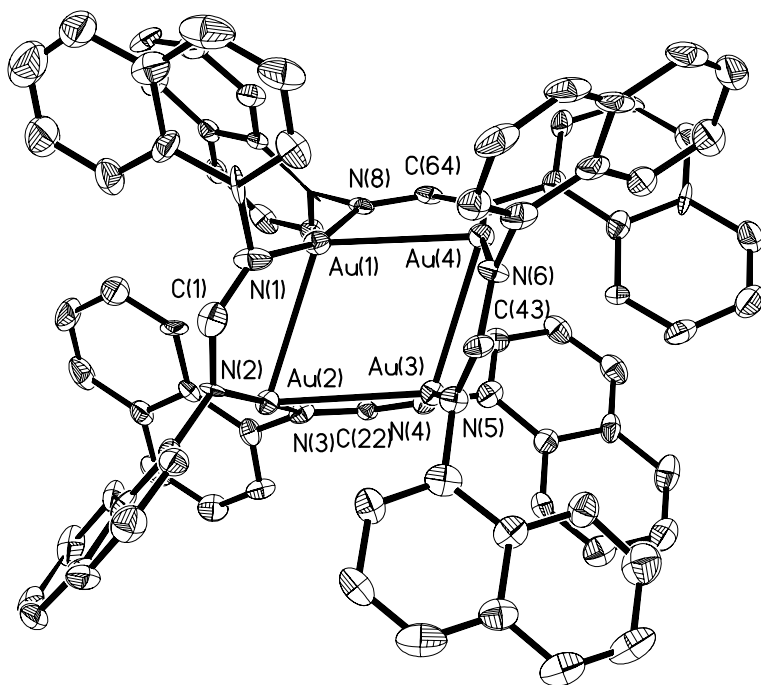


Fig. 3. Top view of **2** showing the parallelogram arrangement of the gold atoms and the vertical arrangement of the naphthyl rings.

The silver(I) amidinate structures are parallel with those of gold(I) complexes. The silver structures are dinuclear, trimuclear, and tetranuclear with silver–silver interactions [21], although the dinuclear silver(I) amidinate is the most common product. Trinuclear and tetranuclear species were isolated by using a C-alkyl functionalized amidinate [21a]. The silver(I) centers in the tetranuclear clusters have a planar rhombic arrangement with bridging amidinate ligands above and below the Ag_4 plane, typical of $[\text{Ag}_4(\text{hpp})_4]$ [7].

Table IV gives $\text{Au}\cdots\text{Au}$ distances with $\text{Au}\cdots\text{Au}\cdots\text{Au}$ and ligand $\text{N}-\text{Au}-\text{N}$ angles for several homobridged tetranuclear Au(I) complexes and tetranuclear gold amidinate complexes characterized in our laboratory. Similar structural arrangements have been found in the tetrameric 1,3-diphenyltriazenidogold(I) complex, $[\text{Au}(\text{PhNNNPh})_4]$ ($\text{Au}\cdots\text{Au} = 2.85 \text{ \AA}$) [22], $[\text{Au}_4(\text{CH}_3\text{CS}_2)_4]$ ($\text{Au}\cdots\text{Au} = 3.01 \text{ \AA}$) [23] and the tetranuclear gold pyrazolate complex $[\text{Au}(\mu\text{-}4\text{-}^t\text{Bu-pz})_4]$ ($\text{Au}\cdots\text{Au} = 3.11 \text{ \AA}$) [17]. The Au(I) atoms bridged by the more flexible amidinate ligands show shorter $\text{Au}\cdots\text{Au}$

Table IV. Average Au···Au Distances (Å) and Au···Au···Au Angles (°) of tetranuclear gold(I) amidinate Clusters [Au₄(ArNC(H)NAr)₄] and Related Clusters

Complex	Au···Au	Au(1)···Au(2)···Au(3)	N–Au–N	Ref.
[Au(PhNNNPh)] ₄	2.85	89.92	176	22
[Au ₄ (CH ₃ CS ₂) ₄]	3.01	89.95	167	23
[Au(μ-4- ^t Bu-pz)] ₄	3.11		175	17
Amidinate clusters [Au ₄ (ArNC(H)NAr) ₄], Ar =				
C ₆ H ₄ -4-OMe	2.94	70.87, 109.12	174	6
C ₆ H ₃ -3,5-Cl	2.91	88.30, 91.53	177	6
C ₆ H ₄ -4-Me	3.03	63.59, 116.4	172	6
C ₁₀ H ₇ , 2	2.98	68.52, 110.88	170	^a
C ₆ F ₅ , 3	2.96	92.3, 87.5	169	^b
C ₆ H ₄ -2-CF ₃ , 4	2.92	84.6, 95.3	176	^b

^a Reported here.

^b Synthesis reported, but these structures, even at 77 K, are not sufficiently well resolved because of fluorine atom disorder and perhaps other factors to report the data here.

distances than those bridged by the rigid pyrazolate ligands (i.e., 2.9 Å versus 3.1 Å).

Photophysical Properties

The naphthyl and trifluoromethylphenyl amidinate derivatives are strongly luminescent at 77 K and, in addition, the trifluoromethyl complex displays also luminescence at room temperature. Interestingly, and in spite of similar structures for the three complexes, the pentafluorophenyl amidinate, **3**, does not show any photoluminescence in the solid state nor in the solution. For complex **2** (naphthyl amidinate), excitation at 375 nm gives rise to a very broad emission with maximum at 538 nm (Fig. 4). For complex **4** (trifluoromethyl amidinate), excitation at 365 nm leads to a room temperature emission at 468 nm, which is shifted to 473 nm at 77 K (Fig. 5). This asymmetry in the emission bands in **2** and **4** suggests a major contribution from the ligands to the emission process.

In the case of the trifluoromethylphenyl complex **4**, the energies of the excitation and emission bands are not very different from the other gold amidinates [Au₄(ArNC(H)NAr)₄] (Ar = C₆H₄-4-OMe, C₆H₃-3,5-Cl₂, C₆H₄-4-Me), previously reported [6]. For these complexes, two emitting states were proposed: a fluorescence process originating from a mixed π-π* intraligand/MLCT excited state, similar to that found in the silver amidinate [Ag₂(form)₂], and a lower energy band associated with a triplet excited state [24]. In spite of the relatively small Stokes shift (6000 cm⁻¹)

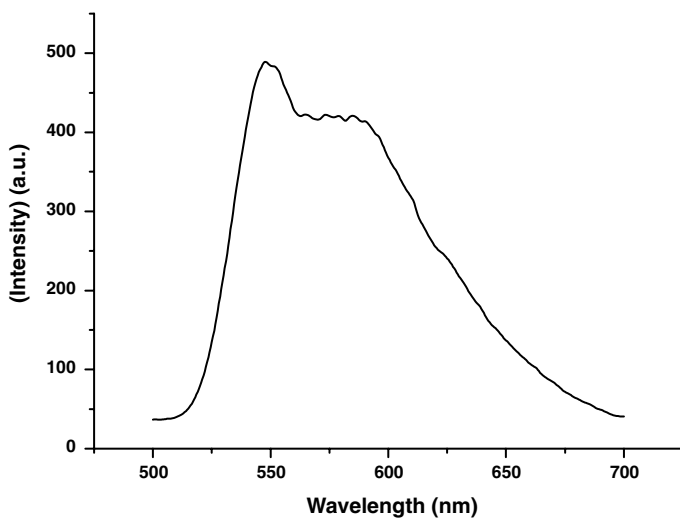


Fig. 4. Emission spectrum of **2** at 77 K.

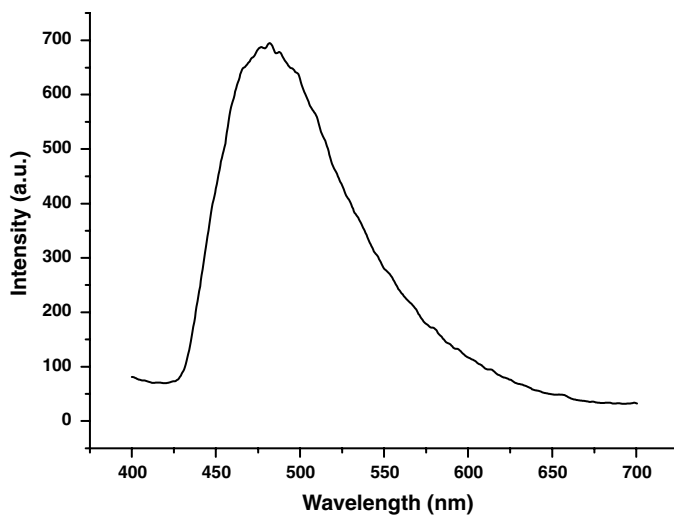


Fig. 5. Emission spectrum of **4** at 77 K.

found in **4**, the very long lifetime (within the milliseconds range 0.21 ms, $R = 0.98$), seems to suggest phosphorescence from a triplet state. The structure less profile, even at cryogenic temperatures, for the emission

bands does not allow us to establish the atoms or groups involved in the emission process.

The different luminescence behavior found here with respect to the previously reported amidinates is likely to be related to the substituents on the electron rich NCN linkage. The effect of the substituents on the optical behavior is even more pronounced in the naphthyl amidinate complex, **2**. In this case the lifetime is longer (1.17 ms, $R = 0.99$) and the emission band is broader and shifted to lower energy than in **4**. The shift and the spectral width perhaps is related to a higher contribution from the orbitals of the gold centers to the emissive excited state, since gold centered phosphorescence is reported at similar energies [25]. Another possibility is that the different electron donor abilities of these groups produce different photoluminescence behavior of the amidinate ligands and this electronic structural change is responsible for the shift in the emission energies from the MLCT excited state in both complexes, and even the absence of luminescence properties in the pentafluorophenyl derivative, a worst case electron donor. The origin of the luminescence of tetranuclear gold complexes remains an open area for further study.

SUPPLEMENTARY MATERIALS AVAILABLE

Crystallographic data for the structural analysis of **1** and **2** has been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 232542–232543. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, by quoting the publication citation and the deposition number (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk, URL: <http://www.ccdc.cam.ac.uk>).

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