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Syntheses of Mixed-Ligand Tetranuclear Gold(I)–Nitrogen Clusters by Ligand Exchange Reactions with the Dinuclear Gold(I) Formamidinate Complex $Au_2(2,6\text{-}Me_2Ph\text{-}form)_2$

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The reaction of the sterically crowded dinuclear gold(I) amidinate complex $Au_2(2,6\text{-}Me_2Ph\text{-}form)_2$, **1**, with the less bulky bidentate nitrogen ligands results in the formation of tetranuclear gold(I) complexes. When the less bulky amidinate, K(4-MePh-form), **A**, was reacted with **1** in a 1:1 stoichiometric ratio, crystals containing equal amounts of the tetranuclear and dinuclear gold(I) aryl formamidinates, $Au_4(4\text{-}MePh\text{-}form)_4$ and $Au_2(2,6\text{-}Me_2Ph\text{-}form)_2$, where $2,6\text{-}Me_2Ph\text{-}form = \mathbf{B}$, were found in the same unit cell, **2**·2THF: space group $P\bar{1}$, $a = 10.794(11)$ Å, $b = 14.392(15)$ Å, $c = 25.75(3)$ Å, $\alpha = 82.564(17)°$, $\beta = 85.443(18)°$, $\gamma = 82.614(19)°$. The reaction of K(4-MePh-form), **A**, and **1** in a 1:2 ratio (excess) produced the tetranuclear complex only, **3**. The potassium salt of the exchanged bulky ligand, $K(2,6\text{-}Me_2Ph\text{-}form)$, formed as a byproduct. The reaction of the dinuclear gold(I) complex $Au_2(2,6\text{-}Me_2Ph\text{-}form)_2$ with the 3,5-diphenylpyrazolate salt, $K(3,5\text{-}Ph_2pz)$, resulted in the formation of two tetranuclear mixed-ligand complexes, $Au_4(3,5\text{-}Ph_2pz)_2(2,6\text{-}Me_2Ph\text{-}form)_2$·2THF, **4**·2THF (space group $P2_1/c$, $a = 11.5747(19)$ Å, $b = 25.497(4)$ Å, $c = 21.221(3)$ Å, $\beta = 96.979(3)°$) and $Au_4(3,5\text{-}Ph_2pz)_3(2,6\text{-}Me_2Ph\text{-}form)$·THF, **5**·THF (space group $P2_1/c$, $a = 23.058(5)$ Å, $b = 14.314(3)$ Å, $c = 18.528(4)$ Å, $\beta = 90.94(3)°$. The block crystals from the tetranuclear complex, **4**·2THF, contain mixed ligands with each pyrazolate ring facing an amidinate ring. The tetranuclear mixed ligand complex, **5**·THF, was isolated as needles with ligands alternating above and below the Au_4 plane. The two tetranuclear mixed-ligand complexes emit at 490 and 530 nm, respectively, under UV excitation.

Introduction

It is often assumed that the "soft" metal ion gold(I) will not effectively coordinate to the "hard" element nitrogen.[1] The dearth of compounds of gold(I) coordinated to nitrogen seems to bear this out.[2] Nitrogen coordination to gold(I) has produced interesting chemistry with pyrazolates, carbeniates, benzylimidazolates,[3] and recently, amidinates and related ligands.[4−8] Gold(I) compounds with amidinates and related ligands had not been formed until recently. Furthermore, the short ligand N···N bite distance suggested that the formation of dinuclear gold complexes would require very short gold−gold distances. Indeed this proved to be true, and as communicated,[4−6] dinuclear gold products have been obtained with Au(I)···Au(I) distances of about 2.7 Å and Au(II)−Au(II) distances of about 2.5 Å. The first compounds obtained were new tetranuclear species,[8] and later the trinuclear and the dinuclear gold(I) complexes were obtained.[4] With sterically bulky groups in the ortho positions of the aryl groups in ArNH(CH)NAr, such as Ar = 2,6-$(CH_3)_2$-C_6H_3 (2,6-Me_2Ph) and 2,6-$(C_3H_7)_2$-C_6H_3 (2,6-

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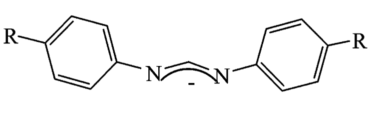
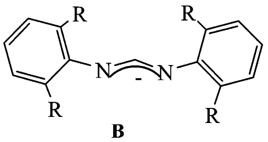
(^{i}Pr)$_2$Ph), the formation of the tetranuclear species is blocked and isolation of di- and trinuclear gold(I) amidinates is achieved.[4]

This new class of gold complexes show several features such as reversible electrochemical oxidation, variable nuclearities,[4,8] high catalytic activity as precursors for CO oxidation,[9] 2-D supramolecular formation with Hg(CN)$_2$,[7] susceptibility to oxidative addition,[4,5] luminescence at room temperature, and formation of mixed gold-silver metal complexes.[8,10] A combination of electronic and steric factors are probably involved in each of these properties.[11] The versatility of the system in that substituents on the phenyl rings can be varied, which allows easy adjustment of the electronic and steric properties of the complexes.



A
R = CH_3, OCH_3



B
R = CH_3, $CH(CH_3)_2$

In this paper, we describe new work which changes the nuclearity of the sterically crowded dinuclear gold(I) amidinate complex [Au$_2$(2,6-Me$_2$Ph-form)$_2$], **1**, by ligand exchange with the anionic ligand 3,5-diphenylpyrazole and other less bulky substituted amidinates, **A**, to form tetranuclear species. Density functional theory calculations show that the tetrameric structure is more stable than the dimeric structure for these gold(I) amidinates at both Gaussian 98 and ADF levels, by about 20 kcal/mol. The reaction of less bulky anionic ligands with the dinuclear gold(I) amidinate complex, **1**, causes rearrangement to form more stable tetranuclear gold(I) complexes. Previous studies in gold(I) chemistry, wherein ligand exchange results in an increase in metal nuclearity from two to four, have not been reported. Preliminary results of the luminescence studies of these materials also are presented.

Experimental Section

General Procedures. All glassware were oven-dried prior to use. Triethyl orthoformate (orthoester), *p*-toluidine, 2,6-dimethylaniline, *o*-anisidine (4-methoxyaniline), 3,5-diphenylpyrazole, KOH, and NaOH were purchased from Aldrich. Tetrahydrothiophene was purchased from TCI, Tokyo. The solvents, THF, CH_2Cl_2, hexanes, toluene, ethanol, and ethyl ether, were purchased from Aldrich and used as received. The dinuclear gold(I) amidinate complex, Au$_2$(2,6-Me$_2$Ph-form)$_2$, was prepared as described previously.[4] Trinuclear silver(I) pyrazolate, [Ag(μ-3,5-Ph$_2$Pz)]$_3$, was prepared following a literature procedure.[12] Elemental analyses were performed by Guelph Chemical laboratories Ltd. and Chemisar Laboratories Inc., Guelph, Ontario, Canada. UV−vis spectra were recorded on a Shimadzu UV-2501 PC spectrometer. ^{1}H spectra were recorded on a Unity Plus 300 NMR spectrometer using the $CHCl_3$ in the solvent peak to reference the chemical shifts (δ). Emission and excitation spectra were recorded on a SLM AMINCO Model 8100 spectrofluorometer equipped with a xenon lamp. Spectra were corrected for instrumental response. Solid-state low-temperature measurements were made using a cryogenic sample holder of local design. Powder samples were attached to the holder with a mixture of copper powder, Cryogen oil (used for mounting crystals for X-ray structures), and collodion (an ether- and alcohol-soluble transparent nitrocellulose). The glue was scanned for a baseline subtraction. Liquid nitrogen was used to obtain the 77 K measurements using a cell of local design. Mass spectrometry data (electrospray ionization) were recorded at the Laboratory for Biological Mass Spectrometry at Texas A&M University, using an MDS Series Qstar Pulsar with a spray voltage of 5 keV.

The yields of products obtained in the syntheses below are not reported but are generally between 15 and 60%, based on recovery of isolated, crystallographically characterized material. No attempt was made to optimize the yields, which requires separation of the partially soluble salts formed in the reaction from any residual starting materials.

Synthesis of [Au$_2$(2,6-Me$_2$Ph-form)$_2$][Au$_4$(4-MePh-form)$_4$], 2. N,*N*′-di(4-Me)phenylformamidine (56 mg, 0.25 mmol) was stirred with (14 mg, 0.25 mmol) of KOH in 15−20 mL of THF for 24 h. Gradually, the colorless solution turned yellow. [Au$_2$(2,6-Me$_2$Ph-form)$_2$] (220 mg, 0.25 mmol) was added, and the mixture was stirred for an additional 12 h. The solvent was removed under vacuum, and the crude product was collected. The exchanged salt of the ligand was extracted with water−ethanol after dissolution of the crude product in CH_2Cl_2. The product **2**·2THF was recrystallized from THF/hexanes.

Analysis. ^{1}H NMR (298 K, CDCl$_3$): δ 2.23 (s, 24H (CH$_3$, tetranuclear)), 6.84 (d, 16H (CH, phenyl tetranuclear)), 7.05 (br, 16H (CH, phenyl tetranuclear)), 8.25 (s, 4H (CH, amidinate tetranuclear)), 2.47 (s, 24H (CH$_3$, dinuclear)), 6.93 (br, 12H (CH, phenyl dinuclear)), 7.43 (s, 2H (CH, amidinate dinuclear)).

Preparation of [Au$_4$(4-MePh-form)$_4$], 3. Although this compound was reported previously by our group,[8] the synthesis reported here starts with a different gold complex. *N*,*N*′-di(4-Me)phenylformamidine (226 mg, 1 mmol) was stirred with 56 mg (1 mmol) of KOH in 15−20 mL of THF for 24 h. The colorless solution turned yellow. [Au$_2$(2,6-Me$_2$Ph-form)$_2$] (450 mg, 0.5 mmol) was added, and the mixture was stirred for an additional 24 h. The solvent was removed under vacuum, and the crude product was collected. The exchanged salt of the ligand was extracted with water−ethanol, 1:1, after dissolution of the crude product in CH_2Cl_2. Product **3** was recrystallized from THF/hexanes.

Analysis. ^{1}H NMR (298 K, (CDCl$_3$): δ 6.86 (d, 16H (CH, phenyl tetranuclear)), 7.02 (br, 16H (CH, phenyl tetranuclear)), 8.25 (s, 4H (CH amidinate)), 2.23 (s, 24H (CH$_3$)). Complex **3** was prepared previously by the reaction of K(4-MePh-form), **A**, with Au(THT)Cl.[8]

Preparation of [Au$_4$(3,5-Ph$_2$pz)$_2$(2,6-Me$_2$Ph-form)$_2$], 4. 3,5-Diphenylpyrazole (110 mg, 0.5 mmol) was stirred with 20 mg (0.5 mmol) of KOH in 15−20 mL of THF for 24 h. Au$_2$(2,6-Me$_2$Ph-form)$_2$ (450 mg, 0.5 mmol) was added, and the mixture was stirred for an additional 12 h. The solvent was removed under vacuum, and the crude product was collected. The exchanged salt of the ligand was extracted with water−ethanol after dissolution of the crude product in CH_2Cl_2. The product was recrystallized from THF−hexanes to give a mixture of complex **4**·2THF, Au$_4$(Ph$_2$pz)$_2$(2,6-Me$_2$Ph-form)$_2$·2THF, and **5**·THF, Au$_4$(3,5-Ph$_2$pz)$_3$(2,6-Me$_2$Ph-

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form), in ∼25:75% ratio. The block crystals from **4**·2THF, which give a pink emission at room temperature (RT) when irradiated with UV light, were separated with a spatula from the needle crystals, **5**·THF.

Anal. Calcd for **4**·2THF ($C_{72}H_{76}N_8Au_4O_2$): C, 46.15; H, 4.05. Found: C, 48.13; H, 3.84. ^{1}H NMR (298 K, $CDCl_3$): δ 8.11 (br, 8H (Ph rings pyrazolate)), 7.84 (t, 12H (Ph ring pyrazolate)), 6.69 (s, 2H (CH pyrazolate)), 2.50 (s, 24H (CH_3 amidinate)), 6.94−7.02 (br, 12H (CH, phenyl dinuclear)), 7.45 (br, 2H (CH amidinate)).

Preparation of [Au_4(3,5-Ph_2pz)$_3$(2,6-Me_2Ph-form)], 5. 3,5-Diphenylpyrazole (80 mg, 0.38 mmol) was stirred with 22 mg (0.38 mmol) of KOH in 15−20 mL of THF for 24 h. Au_2(2,6-Me_2Ph-form)$_2$ (220 mg, 0.25 mmol) was added, and the mixture was stirred for an additional 12 h. The solvent was removed under vacuum, and the crude product was collected. The exchanged salt of the ligand was extracted with water−ethanol after dissolution of the crude product in CH_2Cl_2. The product **5**·THF, which emits light blue/green, was recrystallized from THF−hexanes.

Anal. Calcd. for **5**·THF ($C_{66}H_{60}N_8Au_4O$): C, 44.79; H, 3.39. Found: C, 44.61; H, 2.67. ^{1}H NMR for **5** (298 K, $CDCl_3$): δ 8.12−8.15 (d, 12H (ph ring pyrazolate)), 7.82−7.87 (t, 18H (ph ring pyrazolate)), 6.75 (s, 3H (CH pyrazolate)), 6.87−6.93 (br, 6H (CH, phenyl dinuclear)), 7.47 (s, 1H (CH amidinate)), 2.50 (s, 12H (CH_3 amidinate)).

Structure Determinations. Suitable crystals for X-ray diffraction of **2**, **4**, and **5** were obtained by slow diffusion of *n*-hexane into a concentrated THF solution of the complexes. X-ray data were collected using a Siemens (Bruker) SMART CCD-based (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 ω 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.[13] Data reductions were performed using SAINT software.[14] The structures were solved by direct methods using SHELXS-97 and refined by least-squares on F^2, with SHELXL-97 incorporated into SHELXTL-PC, version 5.03.[15,16] Hydrogen atom positions were calculated by geometrical methods and refined as a riding model. Cell parameters and refinement results of **2**·2THF, **4**·2THF, and **5**·THF are summarized in Table 1. Unfortunately, the refinement is not optimal for any of the complexes because of the phenyl ring disorder and THF solvent loss. The metal atoms and coordinated atoms are well positioned, but a few H atoms on the THF molecules could not be refined and a two-position disorder for the phenyl rings is observed in **5**. Selected bond lengths and angles are presented in Table 2. The crystal structures are shown in Figures 1−3.

Table 1. Details of X-ray Data Collection and Structure Refinement for Complexes **2**·2THF, **4**·2THF, and **5**·THF

	2·2THF	**4**·2THF	**5**·THF
empirical formula	$C_{102}H_{114}Au_6N_{12}O_2$	$C_{72}H_{76}Au_4N_8O_2$	$C_{66}H_{60}Au_4N_8O$
fw	2721.65	1872	1768
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a (Å)	10.794(11)	11.5747(19)	23.058(5)
b (Å)	14.392(15)	25.497(4)	14.314(3)
c (Å)	25.75(3)	21.221(3)	18.528(4)
α (deg)	82.564(17)	90.00	90.00
β (deg)	85.443(18)	96.979(3)	90.94(3)
γ (deg)	82.614(19)	90.00	90.00
V (Å^3)	3926(7)	6216.3(18)	6114(2)
Z	2	4	4
d_{calcd} (g/cm^{-3})	1.922	1.950	1.922
μ (mm^{-1})	9.363	9.462	9.616
R1,	0.0924,	0.0566,	0.0589,
wR2	0.1595	0.1227	0.1374
GOF^c	0.985	0.770	1.178

Table 2. Selected Bond Distances (Å) and Angles (deg) for **2**·2THF, **4**·2THF, and **5**·THF

complex **2**			
Au(1)···Au(2)	3.057(2)	Au(1)···Au(2)···Au(3)	63.47(4)
Au(2)···Au(3)	2.926(3)	Au(4)···Au(1)···Au(2)	114.30(5)
Au(3)···Au(4)	3.007(2)	Au(2)···Au(3)···Au(4)	118.27(4)
Au(1)···Au(4)	3.006(3)	N(10)−Au(5)−N(9)	169.0(5)
Au(5)···Au(5A)	2.701(2)	N(3)−Au(2)−N(2)	172.9(5)
Au(1)−N(1)	2.044(13)	N(4)−Au(3)−N(5)	174.4(6)
complex **4**			
Au(1)···Au(2)	3.1149(9)	Au(2)···Au(1)···Au(4)	84.62(2)
Au(3)···Au(4)	3.1153(9)	Au(3)···Au(2)···Au(1)	94.93(2)
Au(1)···Au(4)	3.1482(9)	N(8)−Au(4)−N(6)	174.2(5)
Au(2)···Au(3)	3.1020(9)	Au(3) Au(4) Au(1)	94.00(2)
N(8)−Au(1)−N(6)	174.2(5)		
complex **5**			
Au(1)−N(1)	2.023(11)	Au(2)···Au(3)···Au(4)	93.05(3)
Au(1)···Au(4)	3.0277(9)	Au(4)···Au(1)···Au(2)	93.14(3)
Au(1)···Au(2)	3.2075(10)	Au(3)···Au(2)···Au(1)	86.13(3)
Au(2)···Au(3)	3.0541(9)	N(2)−Au(2)−N(3)	176.3(5)
Au(3)···Au(4)	3.1870(10)	N(1)−Au(1)−N(8)	174.6(5)
Au(2)···Au(3)···Au(4)	93.05(3)	N(7)−Au(4)−N(6)	171.8(5)
N(4)−Au(3)−N(5)	174.5(5)		

Results and Discussion

Synthesis. Reacting the potassium salt of the arylamidinate, K(4-MePh-form), **A** (Me), with the dinuclear gold(I) complex Au_2(2,6-Me_2Ph-form)$_2$, **1**, in a 1:1 stoichiometry ratio in THF forms the mixed crystal of the dinuclear and tetranuclear complexes, [Au_2(2,6-Me_2Ph-form)$_2$][Au_4(4-MePh-form)$_4$]·2THF, **2**·2THF. Each unit cell contains one tetranuclear and one dinuclear molecule, Figure 1. The potassium salt of the exchanged, bulky ligand, K(2,6-Me_2-Ph-form), forms as a byproduct. The ^{1}H NMR spectrum of the crude product shows a spectrum consistent with a mixture of the two complexes. The addition of excess potassium salt, **A** (Me), to an NMR tube charged with complex **2** in $CDCl_3$ results in further exchange of the bulky anionic ligand [2,6-Me_2Ph-form]$^-$ in **2** with the formation of complex **3**, as was confirmed by the disappearance of the methine peak in the ^{1}H NMR for **1** at 7.43 ppm. The reaction of **A** (Me) with **1** in a 1:2 ratio (excess) forms only **3**, Chart 1. Similar results were also obtained from the reaction of the salt K(4-OMePh-form), **A** (OMe), with the dinuclear complex, **1**.

The reaction of the 3,5-diphenylpyrazolate salt, K(3,5-Ph_2-pz), with the dinuclear gold(I) complex **1** in a 1:1 stoichiometric ratio results in the formation of two tetranuclear

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(14) *SAINT*, version 4.035; Bruker Analytical X-Ray Systems: Madison, WI, 1995.

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(16) *SHELXTL, Program Library for Structure Solution and Molecular Graphics*, version 5.03 (PC version); Bruker Analytical X-ray Systems: Madison, WI, 1995.

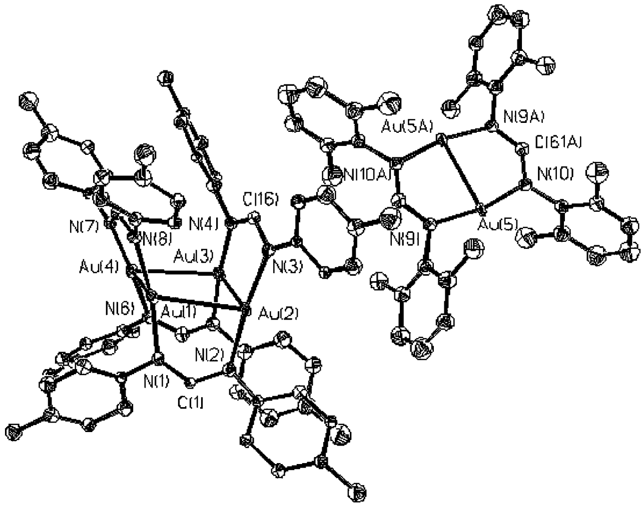


Figure 1. X-ray structure of **2**·2THF, [Au$_2$(2,6-Me$_2$Ph-form)$_2$][Au$_4$(4-MePh-form)$_4$], with the THF removed.

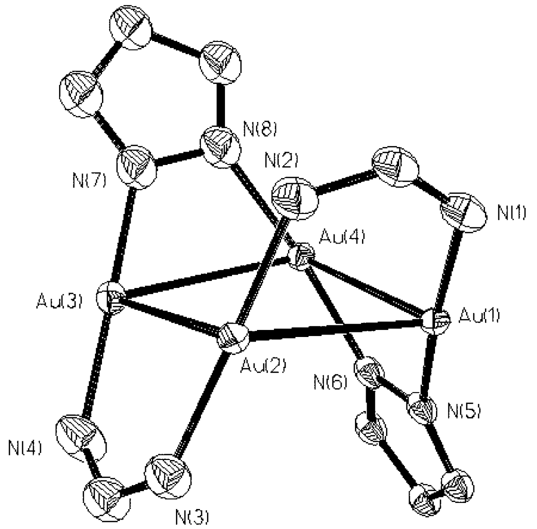


Figure 2. Structure of the metal cluster of **4**·2THF, Au$_4$(3,5-Ph$_2$pz)$_2$(2,6-Me$_2$Ph-form)$_2$. All phenyl rings and protons of the pyrazolate and formamidinate ligands are omitted for clarity.

products which crystallize as blocks, [Au$_4$(3,5-Ph$_2$pz)$_2$(2,6-Me$_2$Ph-form)$_2$]·2THF, **4**·2THF, and as needles, [Au$_4$(3,5-Ph$_2$pz)$_3$(2,6-Me$_2$Ph-form)]·THF, **5**·THF (Figures 2 and 3). The block crystals from **4**·2THF, which give a red emission at RT when irradiated with UV light, were separated with a spatula from the needle crystals, **5**·THF. Attempts to isolate the tetranuclear complex **4** only by carrying out the reaction in 1:0.5 of **1**/K(3,5-Ph$_2$pz) still produced a mixture of complexes **4** and **5**. Adjusting the reaction ratio to 1:1.5 (excess) of the K(3,5-Ph$_2$pz) resulted in the isolation of only the tetranuclear mixed ligand complex **5**·THF.

The exchange processes of **1** with bidentate nitrogen ligand salts have been followed by ^{1}H NMR in a CDCl$_3$ solvent. In the case of the exchange with K(4-MePh-form), new peaks appear at 8.6 and 8.07 ppm, while K(3,5-Ph$_2$pz) gives a new resonance at 7.56 ppm (see Supporting Information). These new peaks relate to the formation of an intermediate in the exchange reaction and largely disappear when the reaction is complete. Similar peaks are seen during the synthesis of the tetranuclear complexes Au$_4$(4-MePh-form)$_4$ and Au$_4$(4-OMePh-form)$_4$ when the potassium amidinate salts react with Au(THT)Cl.[8] These intermediates have not been conclusively identified (see Supporting Information) but may relate to the formation of species of lower nuclearity.[4]

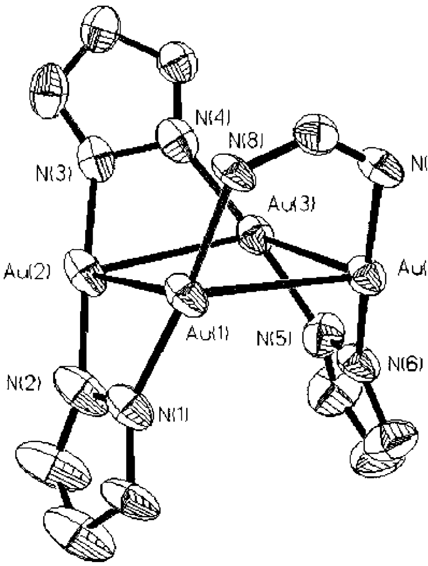
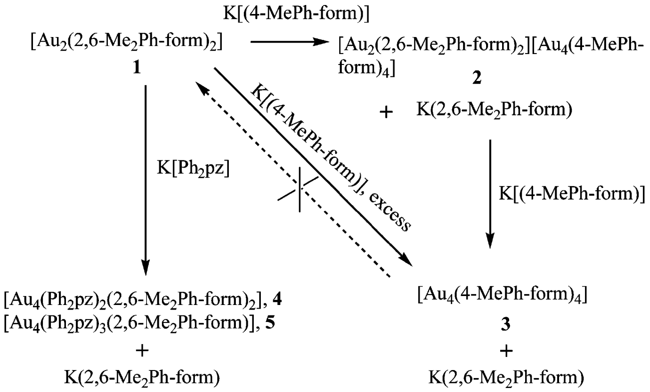


Figure 3. Structure of the metal cluster of **5**·THF, [Au$_4$(3,5-Ph$_2$pz)$_3$(2,6-Me$_2$Ph-form)]. All phenyl rings and protons of the pyrazolate and formamidinate ligands are omitted for clarity.

Chart 1



Mass spectra (ESI positive field) of the tetranuclear complex Au$_4$(4-OMePh-form)$_4$ in CH$_3$CN showed peaks from [Au$_2$L$_2$]$^+$ ($m/z = 904$), [[Au$_2$L$_2$]-OMe]$^+$ ($m/z = 879$), and [[Au$_2$L$_2$]CH$_3$CN]$^+$ ($m/z = 950$), in addition to [[Au$_3$L$_2$]-OMe] $^+$ ($m/z = 1064$). The mass spectra of the dinuclear complex Au$_2$(2,6-Me$_2$Ph-form)$_2$ and the tetranuclear complex Au$_4$(4-MePh-form)$_4$, **3**, produced two similar peaks, although in low intensity, at $m/z = 701$ and 676, respectively, which probably are related to structures such as [AuL$_2$]$^+$: fw = 701 for L = (2,6-Me$_2$Ph-form) and fw = 680 for L = (4-MePh-form).

The exchange reaction of the bulky amidinate anionic ligand, [2,6-Me$_2$Ph-form]$^-$, **B**, by the less bulky anionic amidinate ligand **A**, R = Me, OMe is irreversible. Furthermore, the tetranuclear clusters **4** and **5** do not react with sodium pyrazolate to form the well-known trinuclear gold(I) pyrazolate complex, [(3,5-Ph$_2$pz)Au]$_3$, Chart 1.[12]

Although details of the density functional studies carried out on these molecules are not reported here, both Gaussian

98 and ADF level calculations done in collaboration with Dr. Lisa Perez, suggest that the tetramer (sixteen-membered ring) is more stable by about 20 kcal/mol than the dimer for these gold(I) amidinates. Since the Au(I)···Au(I) distance is restricted to a shorter value in the dimer (eight-membered ring) than the tetramer, the results of the calculations are not surprising. Furthermore, by introduction of a Si atom in place of the amidinate C atom, thereby increasing the bite distance of the ligand, the energy differences between the dimeric and tetrameric structures reduce to negligible values.

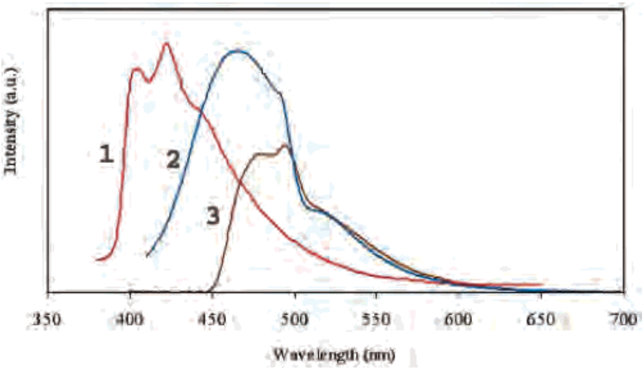


Figure 4. Emission spectra of **1** (excitation at 343 nm), **2**·2THF (excitation at 390 nm), and **3**·2THF (excitation at 350 nm) in the solid state at 77 K.

Crystallographic Results. The mixed crystal dinuclear/tetranuclear complex [Au_2(2,6-Me_2Ph-form)$_2$][Au_4(4-MePh-form)$_4$]·2THF, **2**·2THF, crystallizes with both the dinuclear complex and the tetranuclear complex in the same unit cell, Figure 1. The needle-like crystals of **2**·2THF are crystallized in the triclinic space group, $P\bar{1}$, Table 1. The dinuclear complex itself crystallizes in $P\bar{1}$. The tetranuclear complex crystallizes in the $C2/c$ space group (Table 1).[8] The bond distances and angles, Au···Au = ~2.7 Å in the dinuclear and ~3.0 Å in the tetranuclear, are similar to those of the parent complexes whose structures have been reported previously (Table 2).[4,8] The tetranuclear mixed-ligand gold(I) complexes, [Au_4(Ph_2pz)$_2$(2,6-Me_2Ph-form)$_2$]·2THF, **4**·2THF, and [Au_4(Ph_2pz)$_3$(2,6-Me_2Ph-form)]·THF, **5**·THF, crystallize in the space group $P2_1/c$ (Table 1). The **4**·2THF, which crystallizes in blocks, contains pyrazolate rings facing amidinate rings. This anti arrangement avoids steric crowding, Figure 2. The Au···Au distances are ~3.1 Å, slightly longer than those found in the gold(I) amidinates [Au_4(ArNC(H)NAr)$_4$], 2.8−3.0 Å,[8] Table 2. The tetranuclear mixed-ligand complex **5**·THF was isolated as needles with ligands alternating above and below the Au_4 plane, Figure 3. In the tetranuclear gold(I) pyrazolate complex, Au_4[(3,5-*t*-Bu-pz)$_4$], reported by Raptis, the Au···Au distances range from 3.11 to 3.18 Å,[17] while in complexes **4** and **5**, the Au···Au distances range from 3.10 to 3.15 Å, and from 3.03 to 3.21 Å, respectively. In these clusters, the Au···Au distances for atoms linked by the pyrazolate ligands are slightly longer, as expected from the geometry of the ligand, than those linked by the amidinate ligands.

Luminescence Studies. Solution studies of **2** using ^{1}H NMR and UV−vis techniques show the spectra expected for the presence of the independent dinuclear and tetranuclear complexes. These results are as follows: ^{1}H NMR ($CDCl_3$), methane 8.25 ppm, tetranuclear; 7.43 ppm, dinuclear. The UV−vis spectrum (CH_2Cl_2) of **2** shows bands at 265, 310, and 360 nm for the tetranuclear complex and 255 nm for the dinuclear species. Complex **2** as a solid shows a blue-green luminescence under UV radiation at RT and 77 K, Figure 4. The dinuclear complex, **1**, emits at ~430 nm at 77 K in the solid state but shows no emission at ambient temperature. The tetranuclear gold(I) complex **3** shows a bright blue-green luminescence as a solid under UV light, with a strong emission at ~490 nm and a weak emission at ~530 nm at RT and 77 K.[8] The emission of solid **2** at RT and 77 K shows two components: a broad, strong emission at 465 nm and a weak emission at 530 nm. The luminescence of **2**·2THF in the solid state is dominated by the emission from the tetranuclear species. The ligands themselves do not show any visible emission under these experimental conditions. Luminescence spectra, reported previously, of several tetranuclear gold(I) amidinate complexes show them to emit a bright blue-green light under UV excitation, with a strong emission at ~490 nm and a weak emission at ~530 nm in the solid state, at RT and 77 K. Lifetime measurements for the emission of the tetranuclear gold(I) amidinates at 77 K suggest that considerable metal contribution exists in the lower energy, MMCT emission.[8] Preliminary studies based on the small Stokes shift and the symmetric band profiles between the excitation and emission spectra suggest that the high-energy emission at ~490 nm is a fluorescence.

The emissions observed from various coinage metal−pyrazolate complexes are usually structured, typical of ligand-based processes.[18] For the gold(I) mixed-ligand complexes we have studied, there is a vibronic structure in the emission spectrum corresponding to the (C=N) or the (N=N) stretching vibrational modes of the pyrazolate ligand. On the basis of these observations, the emissions appear to involve ligand-to-metal charge transfer, LMCT, from a π-electronic ground state of the ligand. This is particularly true of **1**. The tetranuclear gold pyrazolates Au_4[(3,5-*t*-Bu-pz)$_4$] emit at 541 nm in the solid state at ambient temperature. The gold pyrazolates **4**·2THF and **5**·THF emit at 490 nm with a weak emission at 530 nm. The emission at 550 nm is more apparent in complex **5**·THF than it is in **4**·2THF (Figure 5). While the dinuclear gold(I) amidinate complex **1** shows a vibronic emission at 77 K at high energy (430 nm), complexes **4**·2THF and **5**·THF give broad emissions at lower energies. This suggests that the emissions from **4**·2THF and **5**·THF may have an increased gold contribution to the transition but further study is needed.

Conclusions

This work describes the syntheses of mixed-ligand tetranuclear gold(I) complexes. These complexes result from the

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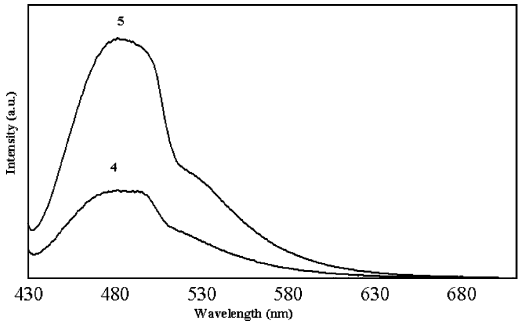

Figure 5. Emission spectra with excitation at 425 nm of **4**·2THF and **5**·THF in the solid state at 77 K, although crystal separation is incomplete.

reaction of less bulky amidinates and pyrazolates with the bulky ligand dinuclear $Au_2(2,6\text{-}Me_2Ph\text{-}form)_2$, **1**. The steric effect of the bulky ligands can block the formation of the tetranuclear species, allowing for isolation of the dinuclear and trinuclear complexes. The DFT calculations suggest that the tetranuclear complexes are energetically more stable than the dinuclear complexes since the latter requires the presence of a short Au(I)···Au(I) distance. Ligand exchange with less sterically bulky ligands provides a facile procedure for the synthesis of tetranuclear mixed-ligand complexes. Recent results from our laboratory have demonstrated the utilization of this approach for the synthesis of tetranuclear mixed-metal mixed-ligand gold−silver complexes containing pyrazolates and amidinates.[10]

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Supporting Information Available: X-ray crystallographic files in CIF format for complexes **3**·2THF, **4**·2THF, and **5**·THF and the NMR spectra related to the formation of intermediates in the exchange. This material is available free of charge via the Internet at http://pubs.acs.org.

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