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Synthesis and Structural Characterization of Luminescent Trinuclear Gold(I) Complexes with Dithiocarbamates

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We have synthesized a series of trinuclear gold(I) complexes, namely, $[Au_3(\mu\text{-dpmp})(S_2CNR_2)_nCl_{3-n}]$ ($n = 0-3$; R = Me, CH_2Ph), $[Au_3(\mu\text{-dpmp})(\mu\text{-}S_2CNR_2)Cl](CF_3SO_3)$ (R = Me, CH_2Ph), and $[Au_3(\mu\text{-dpmp})(\mu\text{-}S_2CNMe_2)(C_6F_5)]X$ (X = Cl, CF_3SO_3), containing the triphosphine dpmp [bis(diphenylphosphinomethyl)phenylphosphine] and varying amounts of dithiocarbamate. NMR experiments show fluxional behavior in solution for most of these derivatives because several arrangements of the ligands are possible. The crystal structure of $[(\mu\text{-dpmp})(AuCl)_3]$ has been determined by X-ray diffraction studies; the molecule displays mirror symmetry and involves an angular arrangement of the gold atoms [Au−Au−Au 119.603(14)°, Au−Au 3.3709(4) Å]. We have studied the optical properties of these derivatives in the solid state, finding a red shift as a function of the dithiocarbamate number and, for some derivatives, wavelength-dependent emission spectra at low temperature.

Introduction

The synthesis and photophysical properties of closed shell gold(I) complexes have attracted considerable attention during recent years because of the intriguing short gold−gold distances, which have been attributed to relativistic and correlation effects.[1,2] Photoluminescence studies have shown that most derivatives involving such weak gold−gold interactions display luminescence in the visible region; it has been suggested that this arises from metal-centered electronic excited states that are modified by metal−metal interaction.[3−6] The use of polyphosphines promotes both the gold−gold contacts and the luminescence.[7]

Furthermore, some mononuclear phosphine−thiolate−gold(I) and dinuclear diphosphine−thiolate−gold(I) derivatives have been described that are luminescent because of sulfur to gold charge transfer modified by the presence of gold−gold contacts.[8−10] The combination of both polyphosphines and S-donor ligands could thus be a promising method of enhancing this phenomenon.

In this paper we report the synthesis and spectroscopic characterization of a series of trinuclear gold(I) complexes $[Au_3(\mu\text{-dpmp})(S_2CNR_2)_nCl_{3-n}]$ ($n = 0-3$; R = Me, CH_2Ph), $[Au_3(\mu\text{-dpmp})(\mu\text{-}S_2CNR_2)Cl](CF_3SO_3)$ (R = Me, CH_2Ph), and $[Au_3(\mu\text{-dpmp})(\mu\text{-}S_2CNMe_2)(C_6F_5)]X$ (X = Cl, CF_3SO_3), where dpmp is the triphosphine bis(diphenylphosphinomethyl)phenylphosphine. We have studied the luminescence properties of these derivatives in the solid state at room temperature and at 77 K. The crystal structure of $[(\mu\text{-dpmp})(AuCl)_3]$ has been determined by X-ray diffraction studies, showing an angular arrangement of the gold atoms.

Experimental Section

General. All reactions were carried out under an argon atmosphere at room temperature. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer, over the range 4000−200 cm^{-1}, using Nujol mulls between polyethylene sheets. ^1H, $^1H\{^{31}P\}$, ^{19}F, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian UNITY 300, Bruker ARX·300, or GEMINI 2000 apparatus in $CDCl_3$ solutions (if no other solvent is stated); chemical shifts are quoted relative to $SiMe_4$ (external, ^1H), $CFCl_3$ (external, ^{19}F), and 85% H_3PO_4 (external, ^{31}P). C, H, N, and S

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analyses were performed with a Perkin-Elmer 2400 microanalyzer. Melting points were measured on a Büchi apparatus and are uncorrected. Conductivities were measured in acetone solution with a Philips PW 9509 apparatus. Mass spectra were recorded on a VG Autospec using LSIMS technique (with Cs gun) and 3-nitrobenzyl alcohol as matrix. UV−visible absorption spectra, either in solid or in dichloromethane solution, were recorded at 300 K on a HITACHI U-3400. Emission and excitation spectra were measured at room temperature and 77 K with a Perkin-Elmer LS-50B spectrofluorometer.

Preparation of Compounds. a. [Au$_3$(*μ*-dpmp)(*μ*-S$_2$CNR$_2$)Cl$_2$], R = Me (1), CH$_2$Ph (2). To a dichloromethane suspension (20 mL) of [(*μ*-dpmp)(AuCl)$_3$][11] (0.12 g, 0.1 mmol) was added NaS$_2$CNR$_2$ (0.1 mmol; R = Me, 14 mg; R = CH$_2$Ph, 30 mg). The solid dissolved rapidly, and the resulting yellow solution was stirred for about 2 h and then filtered through Celite and concentrated to ca. 2 mL. Addition of hexane (20 mL) afforded complexes **1** and **2** as yellow solids, which were washed with hexane (2 × 5 mL). Yield of **1**, 95%; mp, 195 °C (decomp). ^{1}H NMR: δ 8.2−7.0 (m, 25H, Ph), 4.70 ("q", 2H, N = 12.0 Hz, P−CH$_2$−P), 4.02 (brs, 2H, P−CH$_2$−P), 3.66 (s, 6H, Me). ^{1}H{^{31}P} NMR: δ 8.2−7.0 (m, 25H, Ph), 4.70 (d, 2H, ^2J(HH) = 14.8 Hz, P−CH$_2$−P), 4.02 (brs, 2H, P−CH$_2$−P), 3.65 (s, 6H, Me). ^{31}P{^{1}H} NMR: δ 35.7 (m), 32.9 (m) with ca. the same intensity. ^{1}H NMR (−55 °C): δ 8.2−6.8 (m, 25H, Ph), 5.2−5.0 (m, 3H, P−CH$_2$−P), 3.68 (s, 3H, Me), 3.51 (s, 3H, Me), 2.46 (br, 1H, P−CH$_2$−P). ^{31}P{^{1}H} NMR (−55 °C): δ 36.5, 33.5, 27.4. ABX spin system with ^2J(AB) = 67.8 Hz, ^2J(AX) = 65.2 Hz, and ^4J(BX) = 0 Hz. Anal. Calcd for $C_{35}H_{35}Au_3Cl_2NP_3S_2$: C, 32.65; H, 2.75; N, 1.1; S, 5.0. Found: C, 32.5; H, 2.65; N, 1.0; S, 4.7. Λ: 46 ohm^{-1} cm^2 mol^{-1}. Yield of **2**, 93%; mp, 175 °C (decomp). ^{1}H NMR: δ 8.2−7.0 (m, 35H, Ph), 5.27 (s, 4H, CH$_2$Ph), 4.73 ("q", 2H, N = 12.3 Hz, P−CH$_2$−P), 4.02 (brs, 2H, P−CH$_2$−P). ^{31}P{^{1}H} NMR: δ 36.2 (m), 32.6 (m) with ca. the same intensity. ^{1}H NMR (−55 °C): δ 8.2−7.0 (m, Ph), 5.8−2.5 (m, CH$_2$Ph and P−CH$_2$−P). ^{31}P{^{1}H} NMR (−55 °C): δ 37.6, 33.7, 28.0. ABX spin system with ^2J(AB) = 67.0 Hz, ^2J(AX) = 64.7 Hz, and ^4J(BX) = 0 Hz. Anal. Calcd for $C_{47}H_{43}Au_3Cl_2NP_3S_2$: C, 39.2; H, 3.0; N, 0.95; S, 4.45. Found: C, 38.8; H, 3.05; N, 0.9; S, 4.1. Λ: 24 ohm^{-1} cm^2 mol^{-1}.

b. [Au$_3$(*μ*-dpmp)(*μ*-S$_2$CNR$_2$)Cl]CF$_3$SO$_3$, R = Me (3), CH$_2$Ph (4). To a dichloromethane solution (20 mL) of [Au$_3$(*μ*-dpmp)(*μ*-S$_2$CNR$_2$)Cl$_2$] (0.05 mmol; R = Me, 64 mg; R = CH$_2$Ph, 72 mg) was added AgCF$_3$SO$_3$ (13 mg, 0.05 mmol). The mixture was stirred for about 2 h protected from light, then filtered through Celite and concentrated to ca. 2 mL. Addition of diethyl ether (20 mL) afforded **3** and **4** as yellow solids, which were washed with diethyl ether (2 × 5 mL). Yield of **3**, 85%; mp, 195 °C (decomp). ^{1}H NMR: δ 7.8−6.9 (m, 25H, Ph), 4.24 ("q", 2H, N = 11.6 Hz, P−CH$_2$−P), 3.65 (s, 6H, Me), 3.40 (brs, 2H, P−CH$_2$−P). ^{31}P{^{1}H} NMR: δ 35.1 (m, 2P), 29.3 (m, 1P). ^{1}H NMR (−55 °C): δ 7.9−6.8 (m, 25H, Ph), 4.7−3.4 (m, 4H, P−CH$_2$−P), 3.68 (s, 3H, Me), 3.51 (s, 3H, Me). ^{31}P{^{1}H} NMR (−55 °C): δ 35.0, 33.3, 27.9. ABX spin system with ^2J(AB) = 67.5 Hz, ^2J(AX) = 67.1 Hz, and ^4J(BX) = 0 Hz. Anal. Calcd for $C_{36}H_{35}Au_3ClF_3NO_3P_3S_3$: C, 30.85; H, 2.5; N, 1.1; S, 6.85. Found: C, 30.5; H, 2.3; N, 1.15; S, 7.05. Λ: 100 ohm^{-1} cm^2 mol^{-1}. Yield of **4**, 80%; mp, 160 °C (decomp). ^{1}H NMR: δ 7.9−6.9 (m, 35H, Ph), 5.27 (m, 4H, CH$_2$Ph), 4.23 ("q", 1H, N = 13.6 Hz, P−CH$_2$−P), 4.19 ("q", 1H, N = 13.6 Hz, P−CH$_2$−P), 3.58 ("q", 1H, N = 12.4 Hz, P−CH$_2$−P), 3.23 ("q", 1H, N = 13.5 Hz, P−CH$_2$−P). ^{1}H{^{31}P} NMR: δ 7.9−6.9 (m, 35H, Ph), 5.25 (m, 4H, CH$_2$Ph), 4.23 (d, 1H, ^2J(HH) = 13.6 Hz, P−CH$_2$−P), 4.19 (d, 1H, ^2J(HH) = 12.5 Hz, P−CH$_2$−P), 3.58 (d, 1H, ^2J(HH) = 12.5 Hz, P−CH$_2$−P), 3.23 (d, 1H, ^2J(HH) = 13.6 Hz, P−CH$_2$−P). ^{31}P{^{1}H} NMR: δ 35.5, 34.6, 28.9. ABX spin system with ^2J(AB) = 67.0 Hz, ^2J(AX) = 62.0 Hz, and ^4J(BX) = 6.7 Hz. ^{1}H NMR (−55 °C): δ 7.8−6.9 (m, 35H, Ph), 5.55 (d, 1H, ^2J(HH) = 15.7 Hz, CH$_2$Ph), 5.37 (d, 1H, CH$_2$Ph), 4.94 (d, 1H, CH$_2$Ph), 4.92 (d, 1H, CH$_2$Ph), 4.27 ("q", 2H, N = 13.7 Hz, P−CH$_2$−P), 3.61 (m, 2H, P−CH$_2$−P). ^{31}P{^{1}H} NMR (−55 °C): δ 35.9, 33.1, 27.8. ABX spin system with ^2J(AB) = 70.0 Hz, ^2J(AX) = 67.3 Hz, and ^4J(BX) = 0 Hz. Anal. Calcd for $C_{48}H_{43}Au_3ClF_3NO_3P_3S_3$: C, 37.1; H, 2.8; N, 0.9; S, 6.2. Found: C, 36.7; H, 2.5; N, 0.85; S, 5.85. Λ: 102 ohm^{-1} cm^2 mol^{-1}.

c. [Au$_3$(*μ*-dpmp)(S$_2$CNR$_2$)$_2$Cl], R = Me (5), CH$_2$Ph (6). To a dichloromethane suspension (20 mL) of [(*μ*-dpmp)(AuCl)$_3$] (0.12 g, 0.1 mmol) was added NaS$_2$CNR$_2$ (0.2 mmol; R = Me, 29 mg; R = CH$_2$Ph, 59 mg). The solid dissolved rapidly, and the resulting yellow solution was stirred for about 2 h, then filtered through Celite and concentrated to ca. 2 mL. Addition of hexane (20 mL) afforded complexes **5** and **6** as yellow solids, which were washed with hexane (2 × 5 mL). Yield of **5**, 95%; mp, 160 °C (decomp). ^{1}H NMR: δ 8.1−6.9 (m, 25H, Ph), 4.68 (m, 2H, P−CH$_2$−P), 3.95 (m, 2H, P−CH$_2$−P), 3.58 (s, 12H, Me). ^{1}H{^{31}P} NMR: δ 8.1−6.9 (m, 25H, Ph), 4.68 (d, 2H, ^2J(HH) = 14.7 Hz, P−CH$_2$−P), 3.95 (d, 2H, P−CH$_2$−P), 3.58 (s, 12H, Me). ^{31}P{^{1}H} NMR: δ 33.6 (br). ^{1}H NMR (−55 °C): δ 8.2−6.9 (m, 25H, Ph), 4.64 (m, 2H, P−CH$_2$−P), 3.89 (m, 2H, P−CH$_2$−P), 3.62 (s, 12H, Me). ^{31}P{^{1}H} NMR (−55 °C): δ 34.5, 32.0. AB$_2$ spin system with ^2J(AB) = 72.8 Hz. Anal. Calcd for $C_{38}H_{41}Au_3ClN_2P_3S_4$: C, 33.25; H, 3.0; N, 2.05; S, 9.35. Found: C, 33.1; H, 2.85; N, 2.0; S, 9.35. Λ: 47 ohm^{-1} cm^2 mol^{-1}. Yield of **6**: 84%, mp 130 °C (decomp). ^{1}H NMR: δ 8.2−6.9 (m, 45H, Ph), 5.04 (s, 8H, CH$_2$Ph), 4.73 ("q", 2H, N = 12.1 Hz, P−CH$_2$−P), 4.0 ("q", 2H, N = 9.2 Hz, P−CH$_2$−P). ^{1}H{^{31}P} NMR: δ 8.1−7.0 (m, 45H, Ph), 5.02 (s, 8H, CH$_2$Ph), 4.66 (d, 2H, ^2J(HH) = 14.7 Hz, P−CH$_2$−P), 3.92 (d, 2H, P−CH$_2$−P). ^{31}P{^{1}H} NMR: δ 35.2, 33.3. AB$_2$ spin system with ^2J(AB) = 68.6 Hz. ^{1}H NMR (−55 °C): δ 8.2−6.9 (m, 45H, Ph), 4.81 (s, 8H, CH$_2$Ph), 4.70 (br, 2H, P−CH$_2$−P), 3.80 (br, 2H, P−CH$_2$−P). ^{31}P{^{1}H} NMR (−55 °C): δ 35.9, 32.4. AB$_2$ spin system with ^2J(AB) = 76.4 Hz. Anal. Calcd for $C_{62}H_{57}Au_3ClN_2P_3S_4$: C, 44.4; H, 3.4; N, 1.65; S, 7.65. Found: C, 44.0; H, 3.4; N, 1.55; S, 7.4. Λ: 45 ohm^{-1} cm^2 mol^{-1}.

d. [Au$_3$(*μ*-dpmp)(*μ*-S$_2$CNMe$_2$)(C$_6$F$_5$)Cl] (7). To a dichloromethane solution (20 mL) of [Au$_3$(*μ*-dpmp)(*μ*-S$_2$CNMe$_2$)$_2$Cl] (0.137 g, 0.1 mmol) was added [Au(C$_6$F$_5$)(tht)][12] (0.045 g, 0.1 mmol). The mixture was stirred for about 2 h. A yellow solid ([Au$_2$(*μ*-S$_2$CNMe$_2$)$_2$] by infrared spectrum) was filtered off, and the clear solution was concentrated to ca. 2 mL. Addition of hexane (20 mL) afforded **7** as a yellow solid, which was washed with hexane (2 × 5 mL). Yield, 92%; mp, 160 °C (decomp). ^{1}H NMR: δ 8.1−6.9 (m, 25H, Ph), 5.15 ("q", 1H, N = 14.0 Hz, P−CH$_2$−P), 4.55 (m, 2H, P−CH$_2$−P), 3.47 (m, 7H, Me + P−CH$_2$−P). ^{1}H{^{31}P} NMR: δ 8.1−6.9 (m, 25H, Ph), 5.15 (d, 1H, ^2J(HH) = 15.0 Hz, P−CH$_2$−P), 4.55 (s, 2H, P−CH$_2$−P), 3.46 (m, 7H, Me + P−CH$_2$−P). ^{19}F NMR: δ −115.6 (m, 2F, F$_o$), −160.1 (t, 1F, F$_p$), −163.6 (m, 2F, F$_m$). ^{31}P{^{1}H} NMR: δ 35.0, 33.8, 32.6. ABC spin system with calculated ^2J(AB) = 67.9 Hz, ^4J(AC) = 4.8 Hz, ^2J(BC) = 70.7 Hz. ^{1}H NMR (−55 °C): δ 8.1−6.9 (m, 25H, Ph), 5.41 (br, 1H, P−CH$_2$−P), 4.72 (br, 1H, P−CH$_2$−P), 3.93 (br, 1H, P−CH$_2$−P), 3.41 (s, 3H, Me), 3.32 (s, 3H, Me), 2.74 (br, 1H, P−CH$_2$−P). ^{31}P{^{1}H} NMR (−55 °C): δ 34.1, 33.7, 30.8. ABC spin system with calculated ^2J(AB) = 69.5 Hz, ^4J(AC) = 1.3 Hz, ^2J(BC) = 68.8 Hz. Anal. Calcd for $C_{41}H_{35}Au_3ClF_5NP_3S_2$: C, 34.7; H, 2.5; N, 1.0; S, 4.5. Found: C, 34.4; H, 2.45; N, 1.15; S, 4.8. Λ: 49 ohm^{-1} cm^2 mol^{-1}.

e. [Au$_3$(*μ*-dpmp)(*μ*-S$_2$CNMe$_2$)(C$_6$F$_5$)]CF$_3$SO$_3$ (8). To a dichloromethane solution (20 mL) of [Au$_3$(*μ*-dpmp)(*μ*-S$_2$CNMe$_2$)(C$_6$F$_5$)Cl] (71 mg, 0.05 mmol) was added AgCF$_3$SO$_3$ (13 mg, 0.05 mmol). The mixture was stirred for about 2 h, protected from light. The solid AgCl was filtered off, and the clear solution was concentrated to ca. 2 mL. Addition of diethyl ether (20 mL) afforded **8** as a yellow solid, which was washed with diethyl ether (2 × 5 mL). Yield: 90%, mp 155 °C (decomp). ^{1}H NMR: δ 8.0−7.0 (m, 25H, Ph), 4.54 ("q", 1H, N = 13.5 Hz, P−CH$_2$−P), 4.18 ("q", 1H, N = 12.5 Hz, P−CH$_2$−P), 3.75 ("q", 1H, N = 12.6 Hz, P−CH$_2$−P), 3.57 (s, 3H, Me), 3.42 (s, 3H, Me), 3.06 ("q", 1H, N = 12.6 Hz, P−CH$_2$−P). ^{1}H{^{31}P} NMR: δ 7.9−7.0 (m, 25H, Ph), 4.48 (d, 1H, ^2J(HH) = 14.7 Hz, P−CH$_2$−P), 4.16 (d, 1H,^2J(HH) = 14.5 Hz, P−CH$_2$−P), 3.72 (d, 1H, ^2J(HH) = 14.7 Hz, P−CH$_2$−P), 3.55 (s, 3H, Me), 3.39 (s, 3H, Me), 3.08 (d, 1H, ^2J(HH) = 14.5 Hz, P−CH$_2$−P). ^{19}F NMR: δ −78.9 (s, 3F, CF$_3$), −115.6 (m, 2F, F$_o$), −159.8 (t, 1F, F$_p$), −163.4 (m, 2F, F$_m$). ^{31}P{^{1}H} NMR: δ 34.4, 33.2, 32.4. ABC spin system with calculated ^2J(AB) = 68.1 Hz, ^4J(AC) = 2.2 Hz, and ^2J(BC) = 72.4 Hz. ^{1}H NMR (−55 °C): δ 8.0−

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Table 1. Crystal Data and Structure Refinement (Additional Values Can Be Found in the Text)

empirical formula	$C_{32}H_{29}Au_3Cl_3P_3$
fw	1203.71
temp (K)	173
cryst syst	monoclinic
space group	$P2_1/m$
a (Å)	$a = 7.2032(10)$
b (Å)	$b = 20.7396(10)$
c (Å)	$c = 11.6983(10)$
α (deg)	90
β (deg)	106.672(10)
γ (deg)	90
vol (Å^3)	1674.2(3)
Z	2
density (calcd) (Mg/m^3)	2.388
abs coeff (mm^{-1})	13.52
F(000)	1108
θ range for data collection (deg)	1.82−28.21
index range	$-8 \leq h \leq 9$, $-21 \leq k \leq 27$, $-15 \leq l \leq 14$
refinement method	full-matrix least-squares on F^2
data/restraint/parameter	4212/17/141
goodness-of-fit on F^2	0.982
final R indices [$I > 2\sigma(I)$]	R1 $^a = 0.0381$, wR2 $^b = 0.0839$
R indices (all data)	R1 $^a = 0.0518$, wR2 $^b = 0.0885$
largest diffraction peak and hole (e Å^{-3})	2.409 and −2.836

[a] $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2) = [\sum\{w(F_o^2 - F_c^2)2\}/\sum\sum\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program.

6.9 (m, 25H, Ph), 4.57 (br, 1H, P−CH$_2$−P), 3.77 (br, 2H, P−CH$_2$−P), 3.51 (s, 3H, Me), 3.44 (s, 3H, Me), 2.64 (br, 1H, P−CH$_2$−P). ^{19}F NMR (−55 °C): δ −78.7 (s, 3F, CF$_3$), −115.0 (m, 2F, F$_o$), −158.1 (t, 1F, F$_p$), −161.9 (m, 2F, F$_m$). ^{31}P{^{1}H} NMR (−55 °C): δ 33.1, 32.8, 30.8. ABC spin system with calculated ^2J(AB) = 71 Hz, ^2J(BC) = 68 Hz, and ^4J(AC) = 1 Hz. Anal. Calcd for $C_{42}H_{35}Au_3F_8NO_3P_3S_3$: C, 32.9; H, 2.3; N, 0.9; S, 6.25. Found: C, 32.65; H, 2.1; N, 0.9; S, 6.25. Λ: 101 ohm^{-1} cm^2 mol^{-1}.

f. [Au$_3$(μ-dpmp)(S$_2$CNR$_2$)$_3$], R = Me (9), CH$_2$Ph (10). To a dichloromethane suspension (20 mL) of [(μ-dpmp)(AuCl)$_3$] (0.12 g, 0.1 mmol) was added NaS$_2$CNR$_2$ (0.3 mmol; R = Me, 43 mg; R = CH$_2$Ph, 89 mg). The solid dissolved rapidly, and the resulting yellow solution was stirred for about 2 h, then filtered through Celite and concentrated to ca. 2 mL. Addition of diethyl ether (20 mL) afforded complexes **9** and **10** as yellow solids, which were washed with diethyl ether (2 × 5 mL). A second fraction was obtained by concentration and precipitation with hexane. Yield of **9**, 95%; mp, 125 °C (decomp). ^{1}H NMR: δ 7.9−6.9 (m, 25H, Ph), 3.98 (br, 2H, P−CH$_2$−P), 3.52 (br, 2H, P−CH$_2$−P), 3.50 (s, 18H, Me). ^{31}P{^{1}H} NMR: δ 26.5 (m, 2P), 23.2 (m, 1P). ^{1}H NMR (−55 °C): δ 7.8−6.8 (m, 25H, Ph), 3.8−3.2 (m, 4H, P−CH$_2$−P), 3.52 (s, 18H, Me). ^{31}P{^{1}H} NMR (−55 °C): δ 25.7 (2P), 20.7 (1P). Anal. Calcd for $C_{41}H_{47}Au_3N_3P_3S_6$: C, 33.75; H, 3.25; N, 2.9; S, 13.2. Found: C, 33.5; H, 3.6; N: 2.9; S: 13.05. Λ: 19 ohm^{-1} cm^2 mol^{-1}. Yield of **10**, 88%; mp, 110 °C (decomp). ^{1}H NMR: δ 7.9−6.9 (m, 55H, Ph), 5.09 (s, 12H, CH$_2$Ph), 3.84 (br, 2H, P−CH$_2$−P), 3.53 (br, 2H, P−CH$_2$−P). ^{31}P{^{1}H} NMR: δ 26.1 (m, 2P), 22.6 (m, 1P). ^{1}H NMR (−55 °C): δ 7.9−6.6 (m, 55H, Ph), 5.02 (s, 12H, CH$_2$Ph), 4.92 (s, P−CH$_2$−P), 3.50 (s, P−CH$_2$−P), 2.90 (s, P−CH$_2$−P). ^{31}P{^{1}H} NMR (−55 °C): δ 25.9 (2P), 21.0 (1P). A$_2$B spin system with ^2J(AB) = 63.3 Hz. Anal. Calcd for $C_{77}H_{71}Au_3N_3P_3S_6$: C, 48.3; H, 3.75; N, 2.2; S, 10.05. Found: C, 48.1; H, 3.6; N, 2.25; S, 9.85. Λ: 18 ohm^{-1} cm^2 mol^{-1}.

Crystal Structure Determination of [(μ-dpmp)(AuCl)$_3$]. Crystal data and details of data collection and structure refinement of [(μ-dpmp)(AuCl)$_3$] are given in Table 1. Crystals of [(μ-dpmp)(AuCl)$_3$] were grown from dimethyl sulfoxide. A colorless plate ca. 0.70 mm × 0.26 mm × 0.04 mm was mounted in an inert oil on a glass fiber. A total of 11 050 intensities were registered using monochromated Mo Kα radiation (λ = 0.710 73 Å) on a Siemens Smart diffractometer; 4212 unique reflections (R_{int} = 0.0519) were used for all calculations. Absorption corrections were based on multiple scans (program SADABS); transmission factors are 0.509−0.999. The structure was refined on F^2 using the program SHELXL-97.[13] H atoms were included using a riding model. *Special feature of refinement*: The phenyl rings C21−26 and C31−36 are disordered over two positions; the disorder components were refined with idealized geometry. The structure could also be refined without disorder in $P2_1$, but the temperature factors of the corresponding rings were unsatisfactory. It is unlikely that the alternative models could be distinguished on the basis of X-ray measurements alone.

Results and Discussion

Synthesis and Spectroscopic Characterization. The starting material, which allows us to introduce the S-donor ligands, is the trinuclear gold(I) derivative recently described by us,[11] namely, [(μ-dpmp)(AuCl)$_3$] (dpmp = bis(diphenylphosphinomethyl)phenylphosphine), and whose X-ray crystal structure and optical properties will be described later in this paper. The reaction of this insoluble complex with sodium dithiocarbamate salts in the appropriate molar ratio proceeds with dissolution of the starting material to give a yellow solution from which the corresponding product containing one, two, or three dithiocarbamate ligands can be isolated (see Scheme 1). Chloride anion can be replaced by triflate, a noncoordinating counterion for gold, in complexes **1** and **2** by reaction with silver(I) triflate. Complex **5** reacts with AuXtht (tht = tetrahydrothiophene; X = Cl, C$_6$F$_5$) to afford not the expected tetranuclear derivatives but the trinuclear derivatives, by exchanging a dithiocarbamate for X (Cl (**1**) or C$_6$F$_5$ (**7**)) and the insoluble polymeric gold(I) derivative [AuS$_2$CNMe$_2$]$_n$. Again, chloride can be substituted by triflate to give complex **8** (see Scheme 1).

These derivatives are air- and moisture-stable yellow solids at room temperature. Their IR spectra show absorptions due to ν(Au−Cl)[14] at 334 and 326 (**1**), 331 (**2**), 322 (**3**), 335, and 324 (**4**) cm^{-1}, at 1257, 1223, and 638 cm^{-1} from triflate anions[15] (**3**, **4**, **8**), and at 955 and 791 cm^{-1} from the pentafluorophenyl groups[16] (**7**, **8**). Acetone solutions behave as 1:1 electrolytes for complexes **3**, **4**, and **8** and as nonconducting for the others, although showing some conductivity if chloride is the counterion; this implies some equilibrium between neutral species, arising from chloride coordination to gold(I), and 1:1 electrolytes, as will be described for the NMR experiments.

Fluxional behavior is observed in most of the ^{31}P{^{1}H} NMR spectra at room temperature but can be stopped at low temperature. This behavior could be produced in some cases for the equilibria shown in Scheme 2; the dithiocarbamate can bridge two gold centers associated with P^1 and P^2 phosphorus (type I), the mirror image of type I (type II), or the dithiocarbamate bridging the terminal phosphine phosphorus P^1 and P^3 (type III), although the last one is less probable because the phosphorus atoms could be far away. Another fact to consider is the presence of chloride anion, which can coordinate to the gold(I) centers. In Table 2 are summarized the chemical shifts at room temperature and −55 °C, the numbering scheme P^1, P^2, and P^3 being as shown in Scheme 2. The phosphorus spectra of **1**−**4** at low temperature show an ABX spin system as expected for a type I (or type II) structure. For complexes **1**

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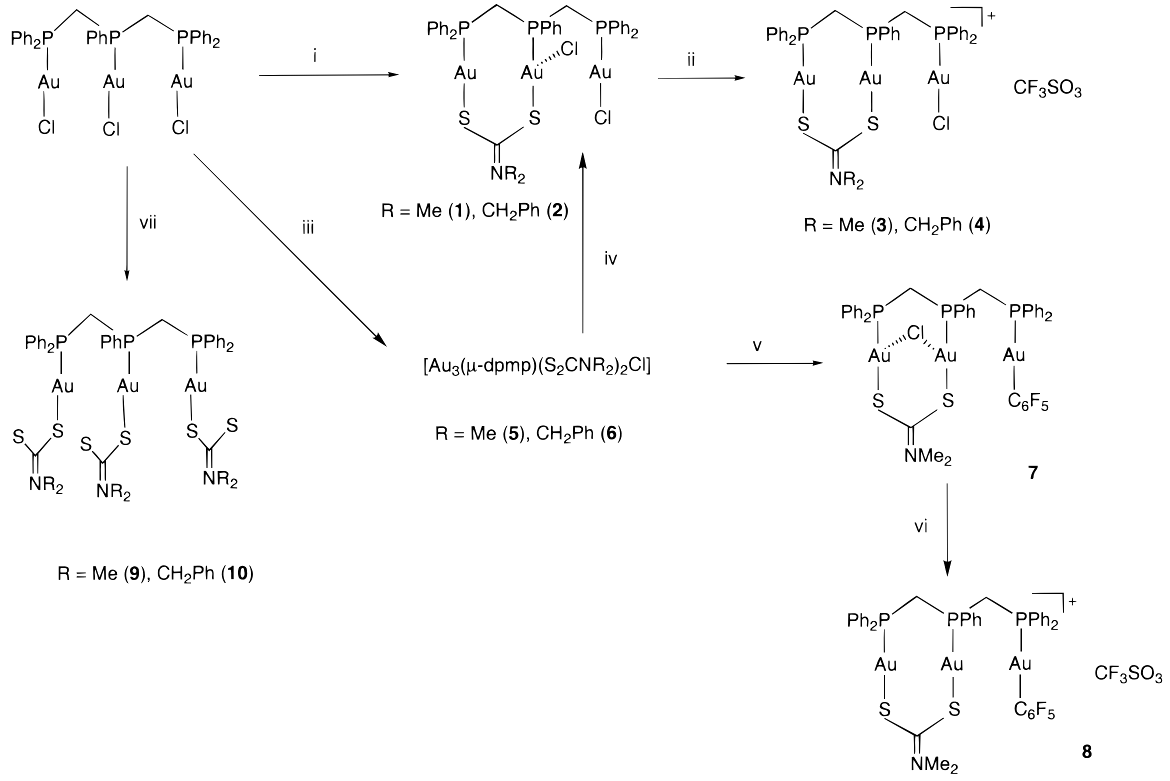
Scheme 1[a]



[a] (i) +NaS_2CNMe_2 − NaCl; (ii) +$AgCF_3SO_3$ − AgCl; (iii) +2NaS_2CNMe_2 − 2NaCl; (iv) +AuCltht − ($^1/_n$)$[AuS_2CNMe_2]_n$; (v) +$Au(C_6F_5)$tht − ($^1/_n$)$[AuS_2CNMe_2]_n$; (vi) +$AgCF_3SO_3$ − AgCl; (vii) +3NaS_2CNMe_2 − 3NaCl.

Scheme 2

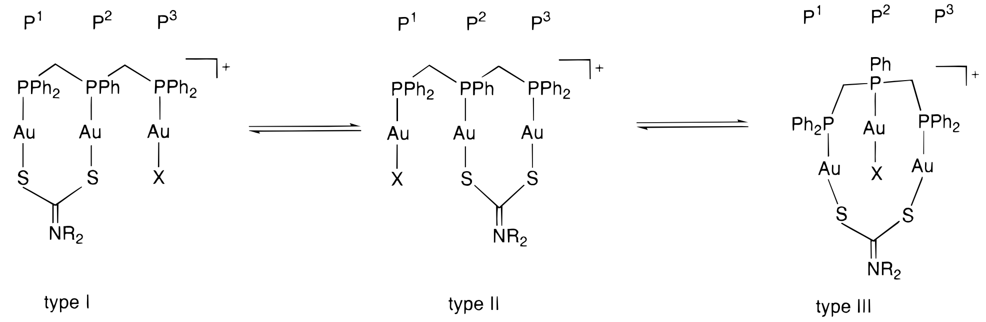


Table 2. $^{31}P\{^1H\}$ NMR Data in $CDCl_3$ Solution[a]

complex	δ (18°C) P^1, P^2, P^3	δ (−55°C) P^1, P^2, P^3
1	35.7, 32.9[b]	33.5, 36.5, 27.4
2	36.2, 32.6[b]	33.7, 37.6, 28.0
3	35.1, 29.3[b]	33.3, 35.0, 27.9
4	35.5, 34.6, 28.9	33.1, 35.9, 27.8
5	33.6[b]	32.0, 34.5, 32.0
6	33.3, 35.2, 33.3	32.4, 35.9, 32.4
7	35.0, 33.8, 32.6	33.7, 34.1, 30.8
8	34.4, 33.2, 32.4	33.1, 32.8, 30.8
9	26.5, 23.2, 26.5	25.7, 20.7, 25.7
10	26.1, 22.6, 26.1	25.9, 21.0, 25.9

[a] P^1, P^2, P^3 assigned as in Scheme 2. Coupling constants and spin system are described in Experimental Section. [b] There are only broad signals, so the corresponding values are given, but it is not possible to assign to P^1, P^2, P^3.

and **2** a structure with a monodentate dithiocarbamate bound to P^1 and two P−Au−Cl units could be produced. However, for this triphosphine, δ for the P−Au−Cl unit should occur near 23 ppm[11] and the ^{31}P NMR spectra would be considerably different from those of **3** and **4**. Consequently, such a structure is unlikely. P^2 becomes chiral, and therefore, these complexes should be racemic mixtures. It is also clear that chloride is not an innocent counterion because P^2 is shifted by ca. 1.6 ppm (in **1** and **2** compared to **3** and **4**) even at −55 °C. This chloride coordination to gold is observed in the crystal structure of the related derivative $[Au_3(\mu\text{-dpmp})_2Cl_2]Cl$.[17] At room temperature two broad signals are observed for **1** and **2**, while for **3** two broad signals 3.5 ppm farther apart are found, and for **4** an ABX spin system is already observed, showing the effect of changing the counterion, chloride versus triflate, on the equilibria. In the $^{31}P\{^1H\}$ NMR spectrum of **5** only a broad signal is observed whereas at low temperature an AB_2 spin system is found; for **6** the AB_2 spin system is already observed at room temperature, which indicates (by comparison of **3** vs **4**) that the greater steric requirements of benzyl (CH_2Ph) versus methyl can, at least partially, hinder the fluxionality. These spectra and the non-

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conducting behavior in acetone solution do not permit the assignment of a unique reasonable structure, and we have been unable to grow single crystals. The $^{31}P\{^1H\}$ NMR spectra of **7** and **8** show ABC spin systems at room temperature and at low temperature, which can be explained with a type I arrangement (as for complexes **1** and **2** a structure with a monodentate dithiocarbamate and two gold-chloride units can be discarded), and indicate again the importance of the steric requirements around the gold center. As observed previously, chloride shifts P^2 1.3 ppm at low temperature and 0.6 ppm at room temperature (**8** versus **7**) while P^1 is shifted 0.6 ppm at both temperatures. Again, these complexes should be racemic mixtures after P^2 becomes chiral. Finally the $^{31}P\{^1H\}$ NMR spectra of **9** and **10** show two broad signals with an integration area ratio of 2:1; only for **10** at low temperature can the typical A_2B spin system characteristic of $[(\mu\text{-dpmp})(AuL)_3]$ complexes be observed.[11]

The ^{19}F NMR spectra of **7** and **8** show the presence of one pentafluorophenyl group as expected. The ^1H NMR spectra at room temperature usually involve two multiplets or two broad signals due to the four diastereotopic methylene protons of the triphosphine (see Experimental Section). For complexes **4** and **8** four signals are observed, which are pseudoquartets by coupling with the two neighboring phosphorus and the vicinal proton. Therefore, in a $^1H\{^{31}P\}$ NMR experiment for these complexes, pseudoquartets became doublets by coupling with the vicinal proton. For complex **7**, three signals (integral 1:2:1) are observed and a $^1H\{^{31}P\}$ NMR experiment confirms that two methylene protons have the same chemical shift as already observed in $[Au_4(\mu\text{-dpmp})_2Cl_2](CF_3SO_3)_2$ (here, the four protons have the same chemical shift at room temperature).[11] In the ^1H NMR spectra the number of signals for the dithiocarbamate substituents is also important. Complexes **1**−**3**, **5**−**7**, and **9** and **10** show only one resonance at room temperature, while **4** shows a multiplet (for CH_2Ph) and **8** two resonances (for Me), as expected because their $^{31}P\{^1H\}$ NMR spectra show asymmetric environments for these. At low temperature, the ^1H NMR spectra of complexes **1**, **3**, **7**, and **8** show two resonances for Me and the spectra of **2** and **4** multiplets for CH_2Ph while for **5**, **6** and **9**, **10** only singlets are observed, which cannot always be interpreted as three coordination of gold(I), as has been shown in other cases.[18]

The LSIMS mass spectra show the peak corresponding to $[M-X]^+$ at *m/z* (complex, % abundance, X): 1252 (**1**, 100, Cl; **3**, 100, CF_3SO_3), 1404 (**2**, 40, Cl; **4**, 100, CF_3SO_3), 1337 (**5**, 25, Cl; **9**, 20, S_2CNMe_2), 1641 (**6**, 100, Cl; **10**, 100, $S_2CN(CH_2Ph)_2$), and 1384 (**7**, 25, Cl; **8**, 100, CF_3SO_3).

Crystal Structure of $[(\mu\text{-dpmp})(AuCl)_3]$. The geometry of this trinuclear derivative was confirmed by an X-ray diffraction study, although the phenyl rings C21−26 and C31−36 are disordered. The molecular structure is shown in Figure 1, with selected bonds and angles in Table 3. The molecule possesses mirror symmetry, with Au1, Cl1, P1, and the ring C11−16 lying in the mirror plane. The gold atoms display aurophilic contacts with a gold−gold distance Au1⋯Au2 of 3.3709(4) Å and an angular geometry (Au2⋯Au1⋯Au2′ 119.603(14)°) This distance is longer than in the related tetranuclear derivative $[Au_4(\mu\text{-dpmp})_2Cl_2](CF_3SO_3)_2$ (3.1025(11), 3.1059 (14) Å)[11] or in the trinuclear derivatives $[Au_3(\mu\text{-dpmp})_2Cl_2]Cl$ (2.946(3), 2.963(3) Å)[17] $[Au_3(\mu\text{-dpmp})_2][SCN]_3$ (3.0137(8), 3.0049(8) Å),[19] $[(\mu\text{-dpma})(AuCl)_3]$ (dpma = bis[(diphenylphosphino)methyl]phenylarsine (3.131(1), 3.138(1) Å),[20] and $[(\mu\text{-TP})(AuCl)_3]$ (TP = bis[2-(diphenylphosphino)phenylene]phenylphosphine (2.9671(4), 2.9250(4) Å)),[21] but it is of the same order as in $[(\mu\text{-dppm})(AuCl)_2]$ (dppm = bis(diphenylphosphino)methane (3.351(2) Å)).[22] The intergold angle is greater than in the tetranuclear $[Au_4(\mu\text{-dpmp})_2Cl_2](CF_3SO_3)_2$ (112.25 (3)°) or in $[(\mu\text{-dpma})(AuCl)_3]$ (110.9°) but smaller than in $[(\mu\text{-TP})(AuCl)_3]$ (126.88(2)°), in $[Au_3(\mu\text{-dpmp})_2Cl_2]Cl$ (149.56(9)°(1)), or in $[Au_3(\mu\text{-dpmp})_2][SCN]_3$ (167.21(2)°).

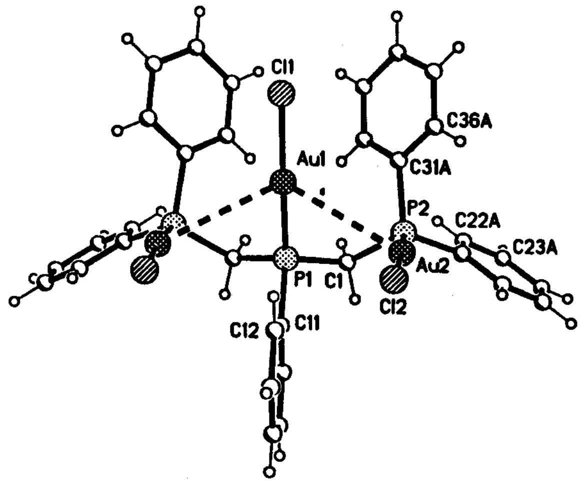

Figure 1. Molecular structure of complex $[(\mu\text{-dpmp})(AuCl)_3]$. Atom radii are arbitrary.

Table 3. Selected Bond Lengths [Å] and Angles [deg][a]

Au(1)−P(1)	2.248(2)	Au(2)−P(2)	2.2411(17)
Au(1)−Cl(1)	2.308(2)	Au(2)−Cl(2)	2.3036(18)
Au(1)−Au(2)	3.3709(4)		
P(1)−Au(1)−Cl(1)	173.78(8)	Au(2)−Au(1)−Au(2)#1	119.603(14)
P(1)−Au(1)−Au(2)	73.88(3)	P(2)−Au(2)−Cl(2)	176.20(7)
Cl(1)−Au(1)−Au(2)	108.75(3)	P(2)−Au(2)−Au(1)	73.62(4)
P(1)−Au(1)−Au(2)#1	73.88(3)	Cl(2)−Au(2)−Au(1)	104.67(5)
Cl(1)−Au(1)−Au(2)#1	108.75(3)		

[a] Symmetry transformation used to generate equivalent atoms: (#1) $x, -y + {}^1/_2, z$.

The P−Au−Cl units are almost linear (173.78(8)° and 176.20(7)°, respectively). Au−Cl bond distances (2.308(2) and 2.3036(18) Å) are as expected and compare well with those found in the related polynuclear complexes mentioned above.[11,20−22] Au−P bond lengths (2.248(2) and 2.2411(17) Å) are similar to those found in $[(\mu\text{-dpma})(AuCl)_3]$ (2.234(4), 2.227(4) Å), in $[(\mu\text{-TP})(AuCl)_3]$ (2.228(2)−2.243(2) Å), and or in $[(\mu\text{-dppm})(AuCl)_2]$ (2.238(5) Å) but shorter than that found in $[Au_4(\mu\text{-dpmp})_2Cl_2](CF_3SO_3)_2$ (2.326(4) Å trans to P; 2.264(4) Å trans to Cl), in $[Au_3(\mu\text{-dpmp})_2Cl_2]Cl$ (2.32(1)−2.35(1) Å), and in $[Au_3(\mu\text{-dpmp})_2][SCN]_3$ (2.295(3)−2.312(3) Å) probably as a consequence of the lesser trans influence of Cl.

Photophysical Characterization. The optical absorption spectra in dichloromethane were measured for all the complexes. The spectra of complexes **1**, **3**, **5**, and **8** are plotted in Figure 2. The main features are the following: (a) an intense absorption at 230 nm due to phenyl phosphine rings;[23] (b) an absorption at 270 nm (for methyl dithiocarbamate derivatives **1**, **3**, **5**, **7**−**9**)

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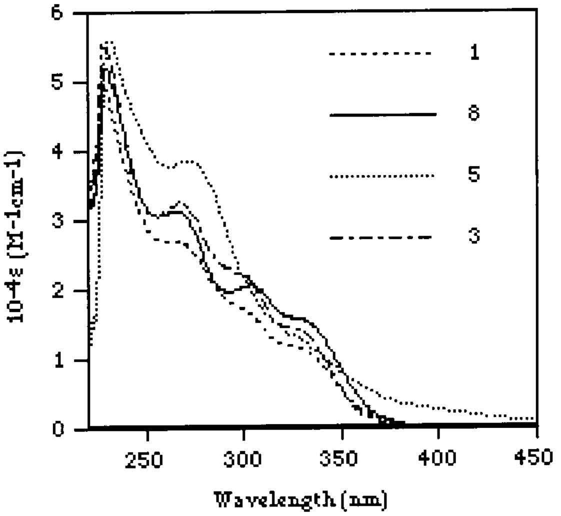

Figure 2. Absorption spectra in dichloromethane solution of complexes **1**, **3**, **5**, and **8**.

Table 4. Emision and Excitation Maxima (in nm) Measured for Complexes **1**−**10** and [(μ-dpmp)(AuCl)$_3$] at 298 and 77K

complex	excitation 289 K	emission 298 K	excitation 77 K	emission 77 K
[(μ-dpmp)(AuCl)$_3$]			350	465, 520 (sh)
1	455	540, 545	405 (sh), 415	535
2	455	545	405 (sh), 415	535
3	440 (sh), 455	530	405 (sh), 415	520
4	440 (sh), 455	530	405 (sh), 415	520
5	455	540, 555	440, 455	565
6	470	560	460	565
7	455	545	415, 425	540
8	430	490 (sh), 525	405 (sh), 415	480 (sh), 530
10			455	580

or 277 nm (for benzyl dithiocarbamate derivatives **2**, **4**, **6**, **10**), which becomes more intense when the proportion of dithiocarbamate grows and has previously been assigned to these ligands;[10] (c) shoulders around 300−305 and 330 nm for derivatives **1**−**4**, **7** (in which the absorption at 330 nm is relatively more intense), and **8** (in which the absorption at 300 nm is relatively more intense), while for complexes **5**−**6** and **9**−**10** these absorptions are not clearly seen probably because they are weak and eclipsed by the more intense 270 or 277 nm peak; there is absorption up to around 400 nm for all the complexes. These shoulders can be assigned to LMCT (S → Au) and/or to MC transitions as reported for other mononuclear or dinuclear phosphine−thiolate−gold(I) derivatives[10,24] and for trinuclear tris(phosphine)gold(I) derivatives.[11,17,19] Solid samples in KBr pellets show similar, but very broad and ill-defined, absorption bands.

The solid-state emission and excitation spectra at 298 and 77 K have been determined, and the results are summarized in Table 4. Optimal excitation was observed at the low-energy side of the absorption bands, due presumably to autoabsorption of the emitting light. Complexes **1**−**8** luminesce at room temperature, the maxima being located in the range 525−560 nm. Complexes **3** and **4** are strongly luminescent, whereas **5** and **6** are less intense, and finally, **9** and **10** do not emit. Excitation maxima are observed from 430 to 470 nm.

At low temperature all the complexes except **9** are luminescent and in all cases luminesce much more intensely than at room temperature, as expected because of the decrease of nonradiative thermal activated processes. Even complex [(μ-dpmp)(AuCl)$_3$], which was reported by us as nonemitting at room temperature, becomes strongly luminescent at 77 K, the excitation and emission frequencies (350 and 465 nm, respectively) being very different from those of the other complexes, probably because of the different nature of the electronic transition involved. In this case, ligand base transitions could be involved as described in [$\{AuXPPhMe_2\}_n$] (X = Cl, Br, I; n = 2, 3)[25] or in AuX(ER$_3$) (X = Cl, Br; E = P, As) complexes.[26] The emissions have the maximum in the range 520−580 nm, the frequency growing gradually with the number of dithiocarbamate ligands: 520−540 nm for derivatives containing one (slightly blue-shifted versus room temperature except **8**), 565 nm for derivatives with two (slightly red-shifted versus room temperature), and 580 nm with three of these ligands. Maxima in the excitation spectra are also different, depending on the number of dithiocarbamate: 415−425 nm for derivatives with one dithiocarbamate (**1**−**4**, **7**−**8**), 440−460 nm with two (**5** and **6**), and 455 nm with three (**10**); all of them are blue-shifted versus room temperature. The intensity follows the same order as at room temperature; the most intense are **3**, **4**, then **1**, **2**, **5**, **7**, **8**, and [(μ-dpmp)(AuCl)$_3$], followed by **6** and finally **10** (**9** does not emit).

The effect of exchanging the coordinating chloride for the noncoordinating triflate at room and low temperature (**1**, **2**, **7** versus **3**, **4**, **8**, respectively) is a blue shift of the emission maxima (10−20 nm), while the effect of replacing chloride by pentafluorophenyl (**1**, **3** versus **7**, **8**) is a shift from −5 to 10 nm.

It is also important to note that sodium dithiocarbamate salts and the tris(phosphine) dpmp do not emit in the visible range. In luminescent mononuclear or dinuclear phosphine−thiolate−gold(I) complexes, these emissions have been assigned to LMCT transitions that in some cases can be shifted by the gold−gold interactions, the emission maxima being between 480 and 702 nm.[8−10] On the other hand, the nature of luminescence in most gold(I) complexes with a tris(phosphine) or a bis(phosphine) has been described as related to metal−metal interactions, being therefore MC transitions.[17,19,27] In our case both kinds of transitions are plausible; the emission is found to be wavelength-dependent for derivatives **3**, **4**, **7**, **8**, and [(μ-dpmp)(AuCl)$_3$] at low temperature, with higher energy emission seen for higher energy excitation (excitation spectra is also wavelength-dependent for these derivatives). In Figure 3 we can observe the emission spectrum of **4** where the emission maxima go from 500 to 540 nm with excitation frequency from 380 to 460 nm, the maximum of intensity being at 520 nm. A wavelength-dependent emission spectrum was recently described for the dinuclear gold(I) derivative [Au(S$_2$(CN(C$_5$H$_{11}$)$_2$]$_2$ and tentatively explained by a distribution of aggregates in the glass (it was measured at 77 K) with gold(I) chains of different length absorbing and emitting at different wavelengths.[6] We can also propose a nonhomogeneous system arising from a multiple

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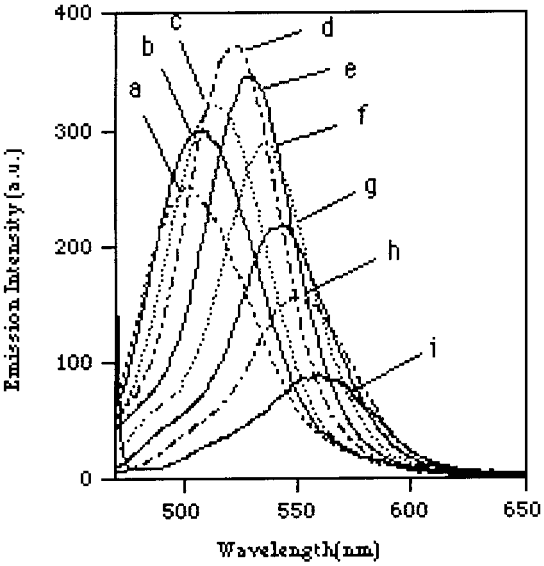

Figure 3. 77 K solid-state emission spectra of complex **4** with excitation frequency going from 380 nm (a) to 460 nm (i) in 10 nm increments.

excitation state due to the influence of gold(I) interactions on ligand to metal charge-transfer excited states, complicated by the fact that the tris(phosphine) is a flexible ligand and that different interactions may be possible with several geometries for the gold atoms.

The red shift at low temperature, related to the number of dithiocarbamate ligands, can be explained in a similar way as the reported red shift in mononuclear phosphine−thiolate−gold(I) derivatives, arising from gold(I)−gold(I) interactions that perturb the orbital energies involved in the LMCT transition,[8] mainly stabilizing the empty gold orbital and destabilizing the filled sulfur orbital. In our case, raising the number of dithiocarbamate ligands that can interact with the gold(I) centers to give tricoordinated gold(I) leads to a splitting of orbitals and consequently to a red shift of the emission maxima.

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Supporting Information Available: X-ray crystallographic files in CIF format for complex [(μ-dpmp)(AuCl)$_3$]. This material is available free of charge via the Internet at http://pubs.acs.org.

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