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Studies on Gold(II) Complexes with Hard and Soft Donor Ligands. 3.[1] Complexes with *N*-(2-Pyridylmethyl)-2-mercaptoaniline

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Received April 15, 1991

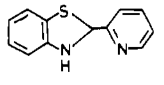
The synthesis and characterization of gold(II) complexes with *N*-(2-pyridylmethyl)-2-mercaptoaniline (Hpma) are reported. Both mononuclear and dinuclear complexes are isolated by using different synthetic procedures. The solution EPR spectra of the mononuclear complexes Au(pma)X (X = Cl, Br) (**1a,b**) are identical and consist of four hyperfine lines of equal intensity due to the interaction of the unpaired electron with one ^{197}Au nucleus ($I = {}^3/_2$). The solution EPR spectra of the dinuclear complexes $Au_2(pma)X_4$ (**1c,d**) exhibiting unsymmetrical seven-line pattern with varying intensities show that the unpaired electron is interacting with two inequivalent ^{197}Au nuclei. A spontaneous dissociation of these mixed-valent Au(II)/Au(III) compounds occurs in nitrobenzene solution, and ultimately a four-line EPR pattern is obtained. The Au(4f) ESCA spectrum of **1c** clearly shows the presence of the Au(II) and Au(III) centers. Another dimeric compound $[Au(pma)Cl]_2$ (**1e**) exhibits only a broad EPR signal in solution. Though the stoichiometries of compounds **1a** and **1e** are found to be identical, their structural differences are clearly reflected in their solution EPR spectra and cyclic voltammetric results. The electronic spectra of compounds **1a–e** exhibit low-energy ligand field transitions in the red and near-infrared (near-IR) regions followed by intense LMCT bands in the visible region. The very small hyperfine coupling originating from the gold in these complexes is strongly indicative of the low metal character of the highest occupied molecular orbital. The large delocalization of the unpaired electron largely accounts for the experimentally observed *g* values.

Introduction

Authentic Au(II) complexes are rare, and the synthesis of paramagnetic Au(II) complex is a challenging synthetic problem. Monomeric gold(II) complexes with the unsaturated sulfur-donor ligands *N,N*-dialkyldithiocarbamate (dtc)[3] and maleonitriledithiolate (mnt)[4] are found to be stabilized by delocalization of the unpaired electron over the unsaturated ligand.[5] In the diamagnetic dimeric complexes,[1] gold(II) is stabilized through a Au–Au bond. However, it has been possible to isolate[6] an isomeric pair of paramagnetic gold(II) dimeric complexes $[Au(abt)_2]_2$ (Habt = *o*-aminobenzenethiol) (**2a,b**) which exhibit a well-resolved seven-line EPR multiplet originating from two ^{197}Au nuclei ($I = {}^3/_2$). Also a monomeric Au(II) complex, $Au(abt)_2(DMF)_2$ (**2c**), has been obtained from a refluxing DMF solution of either **2a** or **2b**. Recently we have reported[1] the preparation of an isomeric pair of monomeric gold(II) complexes $[Au(mta)_2Cl]Cl$ (Hmta = *o*-methylthioaniline) (**3a,b**), which exhibit a four-line EPR multiplet in dichloromethane solution. This isomeric pair undergoes dimerization in DMF, leading to the formation of $[Au(mta)_2Cl]_2Cl_2$ (**3c**), which is characterized by a seven-line solution EPR spectrum. The corresponding dimeric bromo (**3d**) and thiocyanato (**3e**) complexes display similar EPR profiles. The ligand 1,2-bis((*o*-aminophenyl)thio)ethane (dae) forms monomeric gold (II) complexes [Au(dae)X]X (X = Cl, Br) (**4a,b**).

Presently we have studied the reactions of $NaAuCl_4{\cdot}2H_2O$ and $KAuBr_4{\cdot}2H_2O$ with 2-(2-pyridyl)benzothiazole (A) in a methanol/ethanol medium in an attempt to prepare the complexes of the corresponding Schiff base[7] *N*-(2-mercaptophenyl)-2′-pyridylmethylenimine (B) in the monoanionic tridentate form. Quite unexpectedly all the isolated complexes are found to contain the reduced form[8] *N*-(2-pyridylmethyl)-2-mercaptoaniline (C) of the Schiff base B acting as a monoanionic tridentate ligand with the metal ion in the +2 formal oxidation state. The reductive chelation of the ligand has been confirmed by elemental analysis and IR and NMR spectral studies.

It has been possible to isolate both mononuclear and dinuclear compounds of gold(II) with pma by using different preparative conditions. Here we report the synthesis, characterization, and properties of these complexes.



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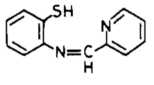

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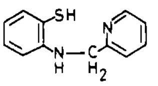

C

Experimental Section

Chemicals. *o*-Aminobenzenethiol was obtained from E. Merck and pyridine-2-carboxaldehyde was obtained from Fluka; both were used without further purification. The compound $HAuCl_4{\cdot}3H_2O$ was obtained from Johnson Matthey; $NaAuCl_4{\cdot}2H_2O$ and $KAuBr_4{\cdot}2H_2O$ were prepared using standard procedures.[9] All other chemicals were of reagent grade and were used as such. All solvents were dried and distilled using standard procedures. Tetraethylammonium perchlorate (TEAP) was prepared from tetraethylammonium bromide (Fluka AG) following a method described in literature.[10]

Preparation of 2-(2-Pyridyl)benzothiazoline (A). A 3.2-g (0.03-mol) sample of pyridine-2-carboxaldehyde was slowly added to 3.75 g (0.03 mol) of *o*-aminobenzenethiol in dry dinitrogen atmosphere with constant stirring at room temperature. The reaction mixture became warm and a cream-colored solid began to appear. Stirring was continued for half an hour during which the mass solidified. To this was added 30 mL of dehydrated ethanol, and the solid mass was finely ground, stirred for 2 h, and filtered. The compound was washed with ethanol and dried in vacuo. It was recrystallized from ethanol at room temperature as colorless crystals: yield 60%; mp 94 °C. Anal. Calcd for $C_{12}H_{10}N_2S$: C, 67.29; H, 4.67; N, 13.08. Found: C, 67.31; H, 4.67; N, 13.10.

Preparation of the Complexes. All operations were carried out under dinitrogen atmosphere using deaerated dry solvents.

Au(pma)Cl (1a). A 0.43-g (0.002-mol) sample of 2-(2-pyridyl)benzothiazoline in 15 mL of methanol was rapidly added to a solution of 0.80 g (0.002 mol) of $NaAuCl_4{\cdot}2H_2O$ in 20 mL of methanol with constant stirring at room temperature. Stirring was continued for 30 min while the solution turned purple and a deep purple, almost black, compound separated out from the solution. This was filtered, washed with methanol, and air-dried. The compound was then thoroughly washed with water until free from sodium chloride and any acid and finally washed with methanol; it was then dried in vacuo and recrystallized from dichloromethane: yield ~40%. Anal. Calcd for $C_{12}H_{11}N_2SClAu$: C, 32.18; H, 2.46; N, 6.25; Cl, 7.93; Au, 44.02. Found: C, 32.36; H, 2.51; N, 6.35; Cl, 8.21; Au, 43.17.

Au(pma)Br (1b). To a solution of 0.59 g (0.001 mol) of $KAuBr_4{\cdot}2H_2O$ in 25 mL of methanol was rapidly added 0.215 g (0.001 mol) of 2-(2-pyridyl)benzothiazoline in 10 mL of methanol with stirring at room temperature. Stirring was continued for about 2 h while the reaction mixture turned purple and a black solid separated out. This was filtered,

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washed with methanol, and air-dried. The compound was then washed with water to remove KBr and finally washed with methanol and dried in vacuo. It was recrystallized from dichloromethane: yield 25%. Anal. Calcd for $C_{12}H_{11}N_2SBrAu$: C, 29.27; H, 2.23; N, 5.69; Au, 40.04. Found: C, 29.48; H, 2.15; N, 5.83; Au, 39.06.

Au_2(pma)Cl_4 (1c). A solution of 0.32 g (0.0015 mol) of 2-(2-pyridyl)benzothiazoline in 15 mL of absolute ethanol was added very slowly to a solution of 1.2 g (0.003 mol) of $NaAuCl_4 \cdot 2H_2O$ in 30 mL of absolute ethanol during 140 min with stirring at room temperature. A black compound precipitated out from the purple solution. This was filtered, washed with ethanol, and air-dried. The compound was then washed with water followed by ethanol and dried in vacuo: yield 65%. It was recrystallized from dichloromethane. Anal. Calcd for $C_{12}H_{11}N_2SCl_4Au_2$: C, 19.17; H, 1.46; N, 3.72; Cl, 18.90; Au, 52.46. Found: C, 20.06; H, 1.47; N, 3.83; Cl, 18.01; Au, 51.37.

Au_2(pma)Br_4 (1d). To a solution of 1.19 g (0.002 mol) of $KAuBr_4 \cdot 2H_2O$ in 35 mL of absolute ethanol was added very slowly a solution of 0.215 g (0.001 mol) of 2-(2-pyridyl)benzothiazoline in 10 mL of absolute ethanol during 2 h with stirring at room temperature. A black compound separated out from the solution. This was filtered, washed with ethanol, and air-dried. The compound was then washed with water followed by ethanol and dried in vacuo: yield 50%. The compound was recrystallized from dichloromethane. Anal. Calcd for $C_{12}H_{11}N_2SBr_4Au_2$: C, 15.50; H, 1.18; N, 3.01; Br, 34.41; Au, 42.43. Found: C, 16.26; H, 1.24; N, 3.21; Br, 33.12; Au, 41.33.

[Au(pma)Cl]$_2$ (1e). A 0.43-g (0.002-mol) sample of 2-(2-pyridyl)-benzothiazoline in 15 mL of methanol was slowly added to a solution of 0.8 g (0.002 mol) of $NaAuCl_4 \cdot 2H_2O$ in 20 mL of methanol during 2 h with stirring at room temperature. Stirring was continued for 3 h and the black compound which separated out from the red-violet solution was filtered, washed with methanol, and air-dried. It was then washed with water until free from sodium chloride and finally washed with methanol and dried in vacuo. This crude product was found to contain about 74% metal. The compound was purified from dichloromethane: yield ~15%. Anal. Calcd for $C_{24}H_{22}N_4S_2Cl_2Au_2$: C, 32.18; H, 2.46; N, 6.25; Cl, 7.93; Au, 44.02. Found: C, 31.88; H, 2.55; N, 5.97; Cl, 7.71; Au, 43.64.

Compound **1e** could be obtained in high yield by stirring a solution of **1a** dissolved in a minimum volume of DMF for 1 h at room temperature and finally by removing the solvent in vacuo. The compound was then washed with water followed by methanol and dried in vacuo: yield 80%.

Physical Measurements. Microanalyses (C, H, N) were performed in a Perkin-Elmer 240C elemental analyzer. Electronic absorption spectra were recorded on a CARY 2300 UV-vis-near-IR spectrophotometer. Infrared spectra were measured with a Perkin-Elmer Model 783 spectrophotometer using a KBr pellet. Far-infrared spectra were recorded with a polytech FIR-30 FT-far-IR spectrometer using a polyethylene pellet. Static susceptibility measurements were made with a PAR 155 vibrating-sample magnetometer. Conductances were determined with a Philips PR 9500 bridge, using a cell calibrated with 0.02 M KCl solution. Proton NMR spectra were recorded on a Varian XL 100 FT-NMR spectrometer. Electron paramagnetic resonance spectra were recorded on a Varian E-112 X/Q-band EPR spectrometer; diphenylpicrylhydrazyl (DPPH) was used as an internal field marker. The simulations were performed on a Varian 620L computer and an IBM compatible personnel computer. Electrochemical measurements were done with the help of a PAR Model 370-4 electrochemistry system incorporating the following: Model 174A polarographic analyzer; Model 175 universal programmer; Model RE 0074 X-Y recorder. All experiments were carried out under a dry dinitrogen atmosphere. A planar Beckman Model 39273 platinum-inlay working electrode, a platinum-wire auxiliary electrode, and an aqueous saturated calomel reference electrode (SCE) were used in the three-electrode configurations. All cyclic voltammetric data were collected at 298 ± 1 K and are uncorrected for junction contribution. XPS spectra were recorded on a VG Mark II ESCALAB spectrometer equipped with a twin anode of Al and Mg. The resolution in this instrument is 0.2 eV. The Ag(3d) (368.2, 374.2 eV) levels were used as a standard. All measurements were made at room temperature of 298 K and at 10^{-9} Torr pressure. Samples were studied by using Mg Kα, and satellites due to the nonmonochromatic source were subtracted. Furthermore, the raw data were corrected for the experimental broadening functions by using a Fourier deconvolution program;[11] thereby, an enhanced resolution was obtained.

Results and Discussion

We have chosen a redox system where Au(III) ($AuCl_4^-$ or $AuBr_4^-$) is reduced by 2-(2-pyridyl)benzothiazole to Au(II) and simultaneously stabilized by complex formation with the ligand *N*-(2-pyridylmethyl)-2-mercaptoaniline (Hpma) generated in the medium. However, the products obtained from these reactions are dependent on experimental conditions such as the medium of the reaction, reagent concentrations, temperature, and the total time utilized for the reaction during the synthesis of the complexes. It is very difficult to purify these complexes since their solubility is extremely low in common organic solvents. So, an extraction method has been employed for the purification of these complexes. This accounts for the low yield of the pure compounds.

Table I. Conductance Values, Magnetic Moments, and EPR Results[a]

compound	Λ, Ω^{-1} cm^2 mol^{-1}	μ_{eff} at 300 K, μ_B	g_{iso}	A_{iso}, G
Au(pmc)Cl (**1a**)	2.5,[a] 28[b]	1.84	2.011	7.0
Au(pma)Br (**1b**)	2.8,[a] 23[b]	1.79	2.011	7.0
Au_2(pma)Cl_4 (**1c**)	3.2,[a] 43.3[b]	1.89	2.007	6.6
Au_2(pma)Br_4 (**1d**)	2.9,[a] 39.6[b]	1.86	2.007	6.6
[Au(pma)Cl]$_2$ (**1e**)	2.2,[a] 29[b]	2.14	2.010	*c*

[a] In nitrobenzene. [b] In DMF. [c] Not resolved.

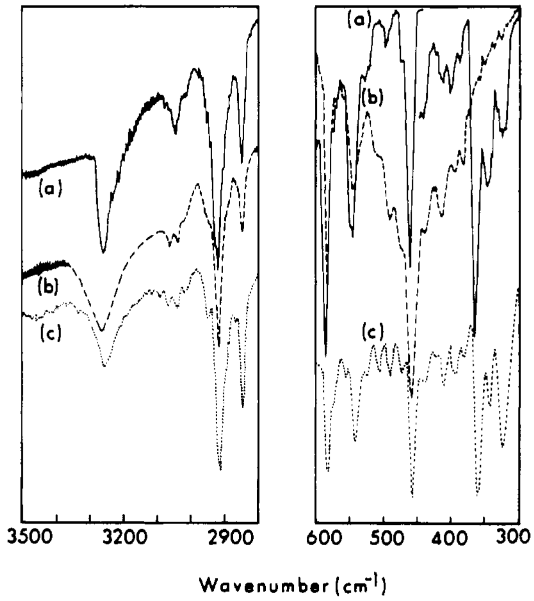

Figure 1. Infrared spectra. Spectra a–c are for compounds **1a–c**, respectively.

The solubility of these complexes is poor in dichloromethane, chloroform, and acetonitrile, moderate in nitrobenzene, but high in coordinating solvents like DMF and DMSO. All five compounds are nonelectrolytes in nitrobenzene, but appreciable conductance values are observed in DMF (Table I), indicating a partial dissociation of the halides from the coordination sphere of the complexes in this solvent. All these neutral complexes are intensely colored in the solid state (almost black) as well as in solution (deep purple).

Infrared Spectra. The compound 2-(2-pyridyl)benzothiazoline exhibits a strong band at 3190 cm^{-1} due to the N–H stretching frequency.[12,13] In all of the metal complexes, a single band of medium intensity located around 3260 cm^{-1} is observed (Figure 1), and this band is assigned as ν(N–H). The IR spectra of these complexes indicate the presence of a CH_2 group since strong ν(C–H) bands are observed (Figure 1) at 2920 and 2845 cm^{-1}, respectively. The presence of the CH_2 group is confirmed by ^{1}H NMR spectra (δ 1.26 ppm, 2 H); the NH signal is observed at δ 2.64 ppm. No S–H band is observed in the region 2500–2600 cm^{-1} for all of these complexes. One of the two ν(Au–N) modes

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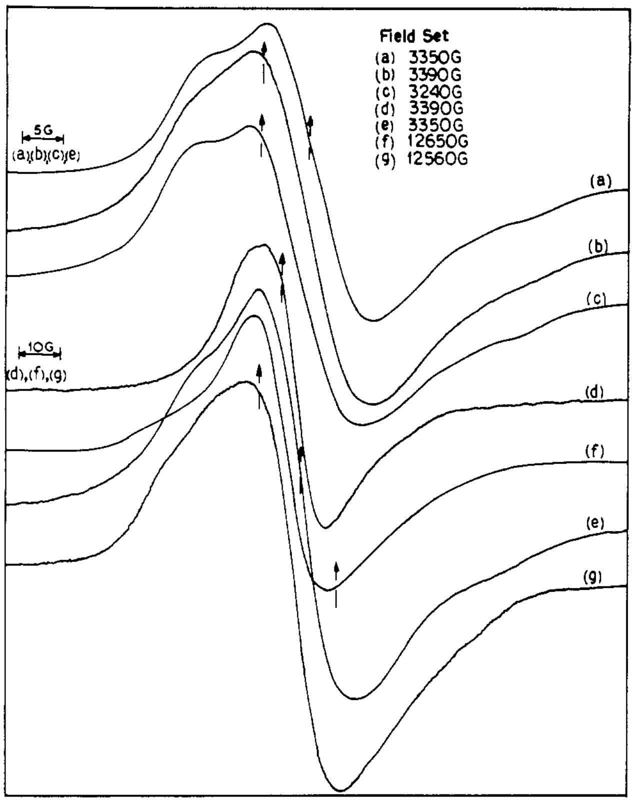

Figure 2. Powder EPR spectra at room temperature. Spectra a–e are for compounds **1a–e**, respectively, recorded at X-band frequency; spectra f and g are for **1a** and **1c** recorded at Q-band frequency.

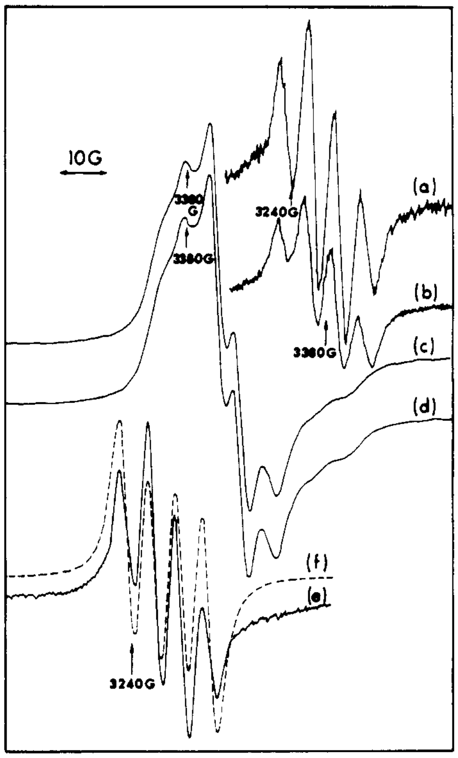

Figure 3. Solution EPR spectra recorded at X-band frequency at room temperature. Spectra a–d are the experimental spectra for **1a–d**, respectively, in nitrobenzene. Spectrum e is the experimental spectrum for **1c** after its conversion to the monomer in nitrobenzene, and spectrum f is the corresponding simulated spectrum.

appears[6,14,15] as a medium-intensity band near 460 cm^{-1}, which is independent of X (Cl, Br). However, we are unable to locate the other ν(Au–N) band. The ν(Au–S) mode for the present set of complexes appears[1,6,16,17] as a weak but prominent band in the region 415–380 cm^{-1}, but assignment of ν(Au–S–Au) is very difficult.[6] Compound **1a** exhibits the ν(Au–Cl) mode as a medium-intensity band at 365 cm^{-1} with a shoulder at 350 cm^{-1}. These bands are absent in the corresponding bromo analogue **1b**, which exhibits a medium-intensity band at 258 cm^{-1} due to ν(Au–Br). Compound **1c** shows a medium-intensity band at 358 cm^{-1} with a shoulder at 350 cm^{-1} probably arising due to ν_{as}(Cl–Au–Cl) and ν_s(Cl–Au–Cl) modes, respectively, and another band at 320 cm^{-1}, which may be assigned as ν(Au–Cl). Another medium-intensity band observed at 257 cm^{-1} may be due to ν_{as}(Au–Cl–Au), and a weak band at 242 cm^{-1} is assignable to ν_s(Au–Cl–Au). All of these values are in good agreement with those reported in the literature.[15-22] These bands are absent in the far-infrared spectrum of the corresponding bromo complex **1d**. This bromo analogue **1d** exhibits two medium-intensity bands at 248 and 223 cm^{-1}, which are assigned to the ν_{as}(Br–Au–Br) and ν_s(Br–Au–Br) modes, respectively. The ν(Au–Br) band occurs at 205 cm^{-1}. Two weak bands observed at 172 and 160 cm^{-1} may be due to ν(Au–Br–Au) asymmetric and symmetric stretching modes respectively.[15,23] On the other hand, compound **1e** exhibits a medium-intensity band at 365 cm^{-1} with a shoulder at 348 cm^{-1} and another band at 330 cm^{-1}, which are probably arising due to ν(Au–Cl) modes.

Thus, the presence of NH and CH_2 groups confirms that all of these metal complexes contain the reduced form[8] of the classical Schiff base ligand. It should be mentioned here that 2-(2-pyridyl)benzothiazoline, which is not directly a Schiff base ligand, forms Schiff base complexes with the metal ions reported so far.[13] However, it is difficult to state how the reduced form of the Schiff base is formed in the present case. Since no S–H band is located for any of these complexes, it is likely that the thiol group is deprotonated and coordinated to the metal ion in the S$^-$ form.[6]

EPR Results. The powder EPR spectra for the complexes were recorded at room temperature at X-band and Q-band frequencies and these are shown in Figure 2. The solution EPR spectra were recorded at X-band frequency in nitrobenzene. The chloro compound **1a** and its bromo analogue **1b** exhibit almost identical spectra (A_{iso} = 7 G) consisting of four lines (Figure 3a,b). Compounds **1c** and **1d**, on the other hand, exhibit unsymmetrical EPR spectra, which are identical to each other, and each of these spectra consist of seven lines (Figure 3c,d). The nitrobenzene solutions of **1c** and **1d**, when allowed to stand at room temperature for about 72 h, give a four-line multiplet in each case, and these are found to be identical to those obtained for **1a** and **1b** in nitrobenzene solutions. Assuming an interaction with one gold nucleus, the four-line spectrum for **1c** is simulated and found to be in very good agreement with the experimental one (Figure 3e,f). However, both these compounds, when dissolved in DMF, directly give rise to a four-line multiplet in each case. Compound **1e**, when dissolved in nitrobenzene or in DMF, produces a broad EPR spectrum without showing any structure. The EPR results are summarized in Table I.

The intense EPR signal displayed by powder samples indicates that they are paramagnetic. This observation along with the stoichiometric results of the complexes suggests a d^9 configuration for the metal ion. Though the stoichiometries of compounds **1a** and **1e** are identical, their structural differences are reflected in their solution EPR spectra.

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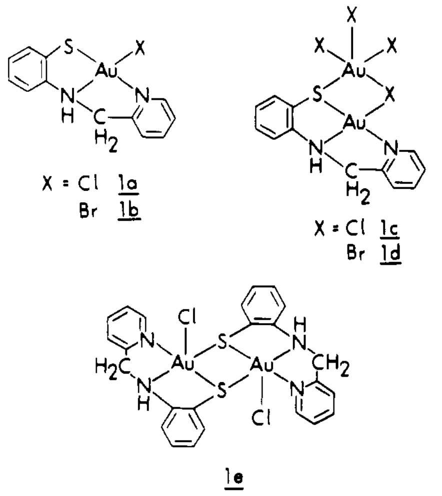

Figure 4. Structures of compounds **1a–e**.

The appearance of almost equally intense four-line pattern EPR spectra for **1a** and **1b** may arise due to the interaction of the unpaired electron with a nucleus with $I = {}^3/_2$. Since the hyperfine coupling constants are found to be the same in both the chloro and bromo compounds **1a** and **1b**, it is very unlikely that the hyperfine coupling is arising from halogens which also have $I = {}^3/_2$ nuclei in 100% natural abundance. So, it is reasonable to propose that the hyperfine coupling arises from the interaction of the unpaired electron with the magnetic moment of one gold nucleus (100% ^{197}Au, $I = {}^3/_2$) in complexes **1a** and **1b**. The unsymmetrical seven-line EPR spectra for **1c** and **1d** show the interaction of one unpaired electron with two inequivalent ^{197}Au nuclei. The occurrence of a four-line multiplet from the nitrobenzene solutions of **1c** and **1d**, when allowed to stand for about 72 h, clearly indicates that the dinuclear structure of the compounds **1c** and **1d** is not stable in solution and becomes monomeric on standing at room temperature. Since the four-line EPR spectra obtained after the spontaneous dissociation of **1c** and **1d** are found to be identical to those for **1a** and **1b** in nitrobenzene solutions (Figure 3), it is reasonable to propose that one of the dissociation products is Au(pma)X, which exhibits the four-line spectrum. The other product is most probably the EPR-silent gold(III) compound AuX_3. It should be noted here that the dissociation process in a coordinating solvent like DMF is fast and a four-line EPR spectrum is immediately obtained. Compound **1e**, however, exhibits only a broad spectrum in solution. But since the stoichiometry of this compound is identical with that of **1a** and a terminal halogen, i.e., ν(Au–Cl), mode is located in the far-infrared spectrum, a sulfur-bridged dimeric structure is proposed for **1e**. The electrochemical results (vide infra) obtained for this compound provide a further compelling evidence in favor of this dimeric structure. The proposed structures of complexes **1a–e** on the basis of stoichiometry and IR, NMR, and EPR spectra are shown in Figure 4.

It is important to note here that the hyperfine coupling constant (A_{Au}) for compounds **1a–e** is quite small (Table I). The very small A_{Au} values observed for these complexes are strongly indicative[24-26] of a large delocalization of the unpaired electron onto the ligands. The ground-state parameters most sensitive to delocalization are the EPR *g* and superhyperfine coupling values. It should be mentioned here that we do not see any nitrogen superhyperfine splitting even at 77 K. Had there been even a fractional unpaired electron density on the nitrogen atom, it would have definitely been manifested on the EPR spectrum. Therefore, in complexes **1a–e**, it appears that the delocalization occurs mainly over the sulfur ligands. Since only ^{33}S (natural abundance 0.76%) has nonzero nuclear spin among naturally occurring sulfur isotopes, no superhyperfine splitting from the sulfur is observed. The experimentally observed EPR *g* values (Table I) are, in spite of the large spin–orbit coupling parameter for the gold nucleus, found to be very close to the free radical *g* value. This seems to be due to the low metal d character of the HOMO,[27] which is responsible for lowering the contribution of the spin–orbit coupling constant in shifting the *g*.

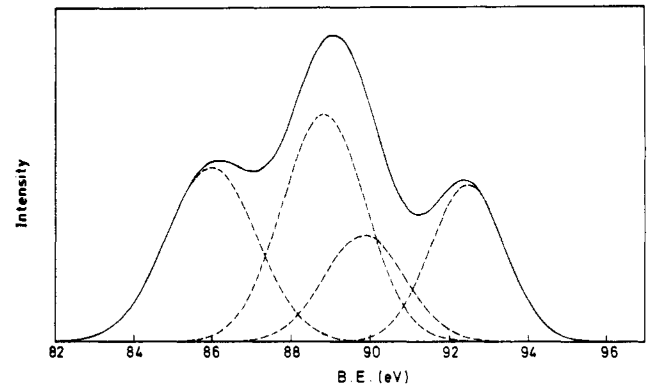

Figure 5. Au(4f) ESCA spectra of $Au_2(pma)Cl_4$. Both the experimental (—) and the Gaussian fitted peaks (- -) are shown.

Table II. Binding Energy (BE) and ΔE (eV) for the Compounds Au(pma)Cl and $Au_2(pma)Cl_4$

		Au(pma)Cl		$Au_2(pma)Cl_4$	
		BE	ΔE	BE	ΔE
Au(1)	$4f_{7/2}$	86.38	2.58	86.14	2.34
	$4f_{5/2}$	90.04		89.84	
Au(2)	$4f_{7/2}$			88.94	5.14
	$4f_{5/2}$			92.45	
S	2p	163.78	−1.02	163.98	−0.82
Cl(1)	2p	198.50	−2.50	198.21	−2.79
Cl(2)[a]	2p			199.35	−1.65
N(1)	1s	398.27	−3.33	398.50	−3.10
N(2)[b]	1s	400.26	−1.34	400.34	−1.26
C(1)	1s	284.19	−0.61	284.35	−0.45
C(2)	1s	285.48	0.68	285.21	0.41
C(3)	1s	287.49	2.69	287.21	2.41

[a] Cl(2), bridging. [b] N(2), in pyridine ring.

The magnetic data (Table I) for the monomeric species Au(pma)X (X = Cl, Br) are consistent with a d^9 complex having only one unpaired electron, and this is further supported by the EPR results. The magnetic moment values for the dinuclear compounds **1c** and **1d** indicate that these also possess only one unpaired electron. The corresponding EPR spectra for $Au_2(pma)X_4$ is consistent with a mixed-valent Au(II)/Au(III) species with an unpaired electron delocalized over both Au centers. The presence of two different Au centers in these dinuclear complexes has been clearly observed from the ESCA study of **1c**.

ESCA Results. The observed ESCA spectra were initially corrected for the instrumental broadening. However, in most cases, the signal appears as an overlap of several peaks, indicating the presence of a particular type of atom in different chemical environments. These peaks were resolved by using a Gaussian deconvolution program following a similar procedure described

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(27) In order to understand the nature of the highest occupied molecular orbital for the mononuclear compounds **1a** and **1b**, a spin-restricted self-conssistent-field-Xα-scattered-wave (SCF-Xα-SW) calculation[26] has been carried out for a model compound, $Au(NH_3)_2(SCH_3)Cl$, assuming a C_s symmetry (vide infra) for the molecule. The calculation indicates that the highest occupied molecular orbital has a contribution of about 67.5% from sulfur pπ orbital and only 21.6% of gold d character. Hence the significant feature of this level is the large contribution of the sulfur 3p orbitals, indicating that the ground state is very covalent, and this can account for the large delocalization of the electron. However, in the absence of structural parameters, calculations are performed only on the basis of a number of approximations based on spectroscopic results for the compounds **1a,b**. Hence this should be taken as preliminary and tentative.

Table III. Cyclic Voltammetric Results[a,b] at 298 K

compound	E_{pc}, V	E_{pa}, V	ΔE_p, mV	$E_{1/2}$, V
Au(pma)Cl[c] (**1a**)	+0.15	+0.35	200	+0.25
Au(pma)Br (**1b**)	+0.16	+0.32	160	+0.24
$Au_2(pma)Cl_4$ (**1c**)	−1.07	−0.77	300	−0.92
$Au_2(pma)Br_4$ (**1d**)	−0.85	−0.75	100	−0.80
$[Au(pma)Cl]_2$ (**1e**)	−0.03, −0.36	+0.23[d]	*e*	*e*

[a] Solvent, CH_3CN; supporting electrolyte, TEAP (0.1 M); solute concentration, $\approx 10^{-4}$ M; working electrode, platinum; reference electrode, SCE. [b] $E_{1/2} = 0.5(E_{pa} + E_{pc})$ where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively. [c] An irreversible oxidative response is observed at E_{pa} +1.15 V. [d] Only one oxidative response is observed, corresponding to two successive reductive responses at E_{pc}'s of −0.03 and −0.36 V. [e] Undefined.

by Manoharan and his co-workers.[28] The Au(4f) ESCA spectrum in the region 82–96 eV for **1c** and the Gaussian fitted peaks are shown in Figure 5.

It should be mentioned here that though there can be solutions with different intensities of bands, the peak positions remain at the same value. It is important to note that the standard deviation between the experimental and the fitted spectra in the present cases was about 0.02. The binding energy shifts (ΔE's) were calculated by taking the $E°$ values for Au($4f_{7/2}$), S(2p), Cl(2p), N(1s), and C(1s) as 83.8, 164.8, 201.0, 401.6, and 284.8 eV, respectively,[28,29] and they are presented in Table II. From our experimental data, we are able to identify three peaks for C(1s) and two peaks for N(1s) corresponding to the complex and two peaks for Cl(2p) and two pairs of peaks for Au($4f_{7/2,5/2}$) corresponding to **1c**.

The ESCA data reveals a pronounced influence of the Au oxidation state on the Au($4f_{7/2}$) binding energies. The difference between the Au($4f_{7/2}$) binding energies for the two different Au centers in **1c** is found to be as much as 2.8 eV, clearly indicating the presence of two different oxidation states. On the other hand, the Au($4f_{7/2}$) binding energy corresponding to **1a** is more or less the same as that for the similar gold center in **1c**, revealing that they have the same formal oxidation state, which is presumed to be +2. It may be pointed out here that the Au($4f_{7/2}$) binding energies observed for these two Au(II) centers are comparable with those for the gold(II) complexes reported in the literature.[30] However, the Au($4f_{7/2}$) binding energy for the Au(III) center (88.94 eV) in the dinuclear complex **1c** is higher than that (87.59 eV) for $KAuCl_4$,[30] indicating a less positive charge on the Au atom in the anionic complex $AuCl_4^-$. The Cl(2p) binding energy (198.21 eV) for the terminal Cl atoms in **1c** is almost the same as that obtained (198.10 eV) for the Cl atoms in $KAuCl_4$, but the binding energy (199.35 eV) for the bridging Cl atom is much higher than that for terminal Cl atom, indicating a less negative charge on the former. The difference between the N(1s) binding energies of the two different N atoms present in a complex is about 2 eV, clearly indicating the significant difference in the charge densities on the N atoms. However, ΔE_S seems to be affected very little when going from a terminal (**1a**) to a bridging (**1c**) sulfur donor atom. Similarly, there is no appreciable change in the corresponding ΔE_C's and ΔE_N's while the compound is changed from **1a** to **1c**.

Electrochemical Results. The redox behavior of complexes **1a–e** has been studied in CH_3CN containing 0.1 M TEAP at a platinum working electrode using cyclic voltammetry (CV). Results are given in Table III. Compounds **1a** and **1b** exhibit (Figure 6) the quasi-reversible reductive couple shown in eq 1 near +0.25 V vs

$$\mathrm{Au(pma)X} + e^- \rightleftharpoons [\mathrm{Au(pma)X}]^- \qquad (1)$$

SCE, indicating that the reduced species is not stable. The dinuclear compounds **1c** and **1d** are reduced at much more negative potentials, indicating that both these compounds are difficult to reduce as compared to the monomers **1a** and **1b**.

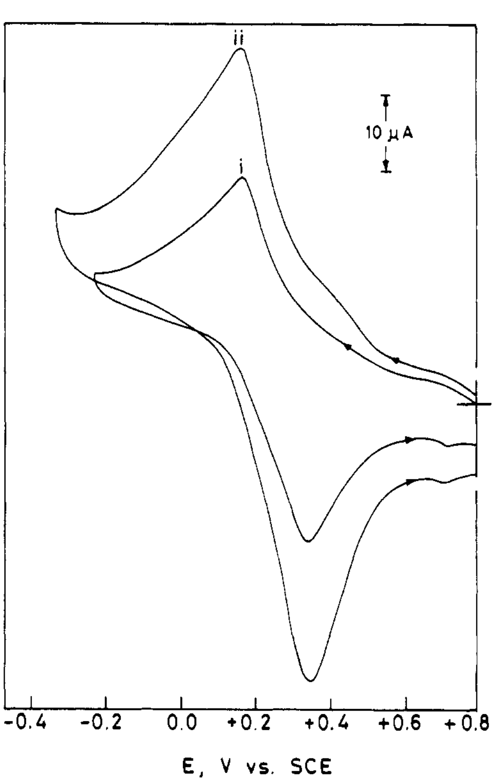

Figure 6. Cyclic voltammograms for ~1 × 10^{-4} M compound **1a** in CH_3CN containing 0.1 M TEAP at scan rates of (i) 50 and (ii) 100 mV s^{-1}, respectively.

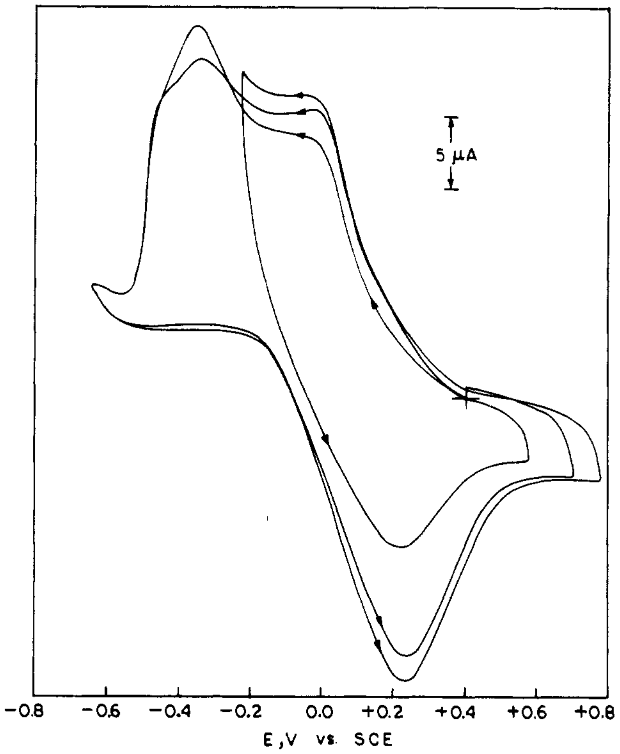

Figure 7. Cyclic voltammograms for ~1 × 10^{-4} M compound **1e** in CH_3CN containing 0.1 M TEAP at a scan rate of 50 mV s^{-1}.

Compound **1e**, on the other hand, undergoes two successive reductions as evident from the two cathodic peaks at E_{pc}'s of −0.03 and −0.36 V, respectively. The corresponding single anodic peak at E_{pa} +0.23 V is probably due to a one-step oxidation of the two successive reductions. This is supported by the fact that the same

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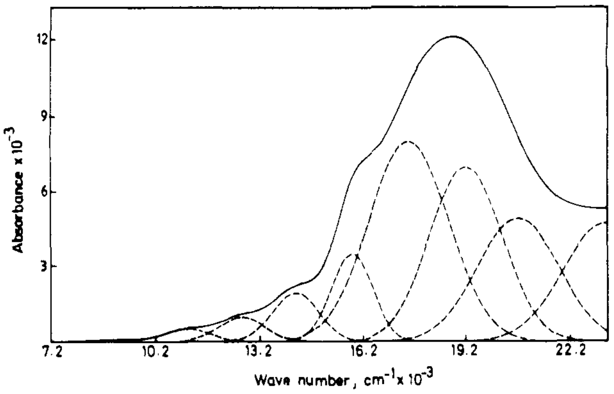

Figure 8. Electronic spectrum of **1a** in nitrobenzene at room temperature in the near-IR and visible regions (—) along with their Gaussian analyses (- -).

anodic wave is observed if the potential is scanned in such a manner as to cycle only the first reductive response (Figure 7), and also the anodic current (i_{pa}) is found to be decreased. However, the separation between the two cathodic peaks is 330 mV, which reflects the reduction of two different metal centers in the same molecular entity. The other possibility of stepwise reduction of the same metal center is thus nullified. This separation is a characteristic feature[6] of many dinuclear transition metal complexes. Thus, the proposition of the dimeric structure for **1e** is supported by electrochemical investigations.

Electronic Structures and Spectral Properties. Compounds **1a–e** produce intense purple colors in solutions, which exhibit highly rich optical spectra (Figure 8). The spectra of compounds **1a**, **1b**, and **1e** are found to be very similar while those for **1c** and **1d** are similar to each other, and the overall spectral features for all these complexes are comparable. The typical feature of the electronic spectrum of any one of these complexes is the occurrence of four weak bands in the red and near-infrared regions followed by intense absorption[31] in the visible region (Table 4; supplementary material).

Since all four low-energy d–d transitions are observed for **1a–e**, we assume a flattened tetrahedral Au(II) unit in these complexes. As both mononuclear and dinuclear complexes exhibit similar spectral features, it is considered that the major contribution to the optical spectrum is originating from the gold(II) center of Au(pma)X in a flattened tetrahedral environment. We have chosen a coordinate system[31] in which the tetrahedral t_2 orbital set is (d_{xz}, d_{yz}, $d_{x^2-y^2}$). In this system a tetragonal distortion toward the square-planar configuration would be expected to yield a $^2B_2(d_{x^2-y^2})$ ground state for Au(II). The splitting of the E level (d_{xz}, d_{yz}) is probably due to some additional distortion to C_s. The relative energies of the gold d and selected ligand σ and π orbitals are based on the electronic spectroscopic results.[31] The thiolato sulfur and gold bonding is considered to involve one π- and two σ-type interactions.[26] The optical spectral band positions and a reasonable but tentative transition assignment picture are presented in Table 4 (supplementary material).

Concluding Remarks

Crucial evidence regarding the nature and structure of the compounds is obtained from the analysis of their EPR spectra. The very small A_{Au} values observed in the EPR spectra are strongly indicative[24–26] of the low metal character of the highest occupied molecular orbital. No hyperfine structure originating from the interaction with the nitrogen nuclei of the ligand pma is observed in the EPR spectra of complexes **1a–e**. Two pairs of ionizations are observed in the XPS spectrum of **1c**, consistent with the presence of both a Au(II) center and a Au(III) center. All attempts to prepare single crystals of any one of these complexes have failed, so all investigations were confined to powders and solutions of the compounds.

Acknowledgment. We thank the RSIC, IIT, Madras, India, for spectroscopic facilities. Thanks are due to Professor A. Chakravorty of IACS, Calcutta, India for providing electrochemical facilities. A.P.K. thanks Dr. B. Ghosh and Dr. S. Pal for help with the electrochemical studies.

Registry No. **1a**, 139944-30-2; **1b**, 139944-31-3; **1c**, 139944-32-4; **1d**, 139944-33-5; **1e**, 139944-34-6; A, 19257-96-6; $NaAuCl_4$, 15189-51-2; $KAuBr_4$, 14323-32-1; pyridine-2-carboxaldehyde, 1121-60-4; *o*-aminobenzenethiol, 137-07-5.

Supplementary Material Available: Table 4, giving electronic spectral band positions of the complexes, textual details of the molecular orbital calculations, and Table 5, giving input parameters for SCF–Xα–SW calculations for $Au(NH_3)_2(SCH_3)Cl$ (8 pages). Ordering information is given on any current masthead page.

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Vaporization and Vapor Complexation in the Gold(III) Chloride–Aluminum(III) Chloride System

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Received May 3, 1991

The vapors over solid gold(III) chloride and the vapor-phase equilibria of the gold(III) chloride–aluminum(III) chloride binary system have been investigated spectrophotometrically. The thermodynamic functions of the sublimation $2AuCl_3(s) = Au_2Cl_6(g)$ were determined: $\Delta H_S° = 114.2 \pm 1.8$ kJ mol^{-1} and $\Delta S_S° = 160.5 \pm 3.3$ J mol^{-1} K^{-1} ($480 < T < 580$K). One predominant vapor complex found in the binary system formed according to the reaction $AuCl_3(s) + {}^1/_2Al_2Cl_6(g) = AuAlCl_6(g)$ with $\Delta H_R° = 59.9 \pm 0.8$ kJ mol^{-1} and $\Delta S_R° = 91.5 \pm 1.6$ J mol^{-1} K^{-1} ($470 < T < 550$ K). At 470 K and 1 atm $Al_2Cl_6(g)$ pressure the volatility enhancement of $AuCl_3$ is ~300. The electronic absorption spectra of the $Au_2Cl_6(g)$ and $AuAlCl_6(g)$ molecules were interpreted in terms of a distorted square planar geometry of Au(III). "Bridged" and "terminal" ligand-to-metal charge-transfer bands were indentified in the spectra.

Introduction

The different solid and gaseous species formed during chlorination of gold have been the subject of investigation of some early publications.[1–4] It has been pointed out[1] that two solids $AuCl_3$ and AuCl are formed at different temperatures and chlorine pressures. At temperatures below 500 °C three distinct equilibria have been reported to occur[2,3] at a chlorine pressure of ~1 atm:

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