are given in Table II. All the bands, especially in the ν(CS) region, are much narrower than those of $Cr(CO)_5(CS)$, indicating that the crystal is ordered at ambient conditions. The local symmetry of the $Cr(CO)_2(CS)$ moiety is C_s, for which two CO stretching modes (a′ + a″) are expected and observed in the solution IR spectra.[17] In the solid-state IR spectrum (KBr disk), four ν(CO) peaks are detected (Table II). These peak doublings undoubtedly arise from solid-state splitting.

Five binary ν(CO) combination bands, initially at 3902, 3861, 3854, 3825, and 3771 cm^{-1}, were monitored with increasing pressure (Figure 1). These combinations are assigned to 1962 + 1943, 1962 + 1908, 1943 + 1908, 1962 + 1856, and 1908 + 1856 cm^{-1}, respectively. Following the same procedure for $Cr(CO)_5(CS)$, we calcualted the pressure dependences of the parent ν(CO) fundamentals (Table II and Figure 1). The negative dν/dP values for certain of these ν(CO) modes again indicate that pressure leads to a significantly strengthening of the π-back-bonding between the metal and the carbonyl groups.

The behavior of the CS stretching region in the high-pressure IR spectra of (η-C_6H_6)$Cr(CO)_2(CS)$ is different from that in $Cr(CO)_5(CS)$. Instead of shifting to lower wavenumbers, the strong ν(CS) band, originally positioned at 1192 cm^{-1} (together with an obvious shoulder at 1211 cm^{-1}), moves to higher wavenumber with increasing pressure (Figure 2). Replacement of a CO group in (η-C_6H_6)$Cr(CO)_3$ by CS leads to an increase in the average CO force constant, but the CS force constant is smaller[17] and the ν(Cr–CS) and δ(CrCS) force constants are greater than those for $Cr(CO)_5(CS)$. The CS ligand should, therefore, be a better π-acceptor in the benzene complex than in $Cr(CO)_5(CS)$. However, the pressure dependences of the CS stretching modes are positive and dν/dP for the Cr–CS stretching frequency is much smaller, which implies a weaker π-acceptability. This might be due to the interaction between the filled π-bonding orbitals of CS and the filled d orbitals of the metal[18,19] and/or the higher anharmonicity of the thiocarbonyl stretch, both of which would lead to a positive pressure dependence. The high dν/dP values for the Cr–CO stretching modes in (η-C_6H_6)$Cr(CO)_2(CS)$ are consistent with the metal–carbonyl π-back-bonding being enhanced by pressure. There also appears to be no pressure-induced phase transition in this complex.

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Studies on Gold(II) Complexes with Hard and Soft Donor Ligands. 2.[1] Complexes with *o*-(Methylthio)aniline and 1,2-Bis((*o*-aminophenyl)thio)ethane

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The synthesis and properties of gold(II) complexes with *o*-(methylthio)aniline (Hmta) and 1,2-bis((*o*-aminophenyl)thio)ethane (dae) are reported. *o*-(Methylthio)aniline forms both mononuclear and binuclear complexes depending on the preparative conditions. The isomeric pair of monomeric gold(II) complexes $[Au(mta)_2Cl]Cl$ (**1a,b**), both of which give a four-line EPR multiplet in CH_2Cl_2 solution, undergo dimerization in DMF leading to the formation of $[Au(mta)_2Cl]_2Cl_2$ (**1c**), which exhibits a well-resolved seven-line EPR pattern possibly originating from two ^{197}Au nuclei. The corresponding dimeric bromo (**1d**) and thiocyanato (**1e**) complexes also exhibit similar EPR profiles. A temperature-dependent susceptibility measurement indicates that the two spins are ferromagnetically coupled within the dimer, while a weak antiferromagnetic coupling exists between the dimers. The cyclic voltammetric results are in line with EPR results.

Introduction

Paramagnetic complexes of gold in the formal oxidation state II are very rare,[3-6] and only two monomeric gold(II) complexes with the unsaturated sulfur donor ligands *N*,*N*-dialkyldithiocarbamate (dtc)[3] and maleonitriledithiolate (mnt)[5] are well established.[7-10] In all the reported dimeric complexes[11-21] of gold(II), a strong Au–Au bond is present, and consequently these complexes are diamagnetic. We have reported[1] an isomeric pair of isovalent gold(II) dimeric complexes which give a well-resolved seven-line EPR multiplet originating from two ^{197}Au nuclei (I = $^3/_2$) and a monomeric complex of gold(II) with the ligand *o*-aminobenzenethiol (Habt). While continuing our studies on stabilization of the formal oxidation state II for gold by complex formation with hard–soft donor ligands having an extended π-system, we have synthesized and isolated an isomeric pair of monomeric as well as a few dimeric complexes of gold(II) with *o*-(methylthio)aniline (Hmta) and two monomeric gold(II) complexes with 1,2-bis((*o*-aminophenyl)thio)ethane (dae) by the

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successful utilization of the redox reactions between AuX_4^- (X = Cl, Br) and the corresponding ligand. The present work describes in detail the preparation, characterization, and properties of these compounds.

Experimental Section

Chemicals. $HAuCl_4 \cdot xH_2O$ was obtained from Johnson Matthey, London. $NaAuCl_4 \cdot 2H_2O$ and $KAuBr_4 \cdot 2H_2O$ were prepared from $HAuCl_4 \cdot xH_2O$ using standard methods.[22] *o*-Aminobenzenethiol was obtained from E. Merck and was used without further purification. Distilled methyl iodide and 1,2-dibromoethane were used. All other chemicals were of reagent grade and were used as such. All solvents were distilled and dried according to standard procedures. Tetraethylammonium perchlorate (TEAP) was prepared from tetraethylammonium bromide (Fluka AG) by following a reported procedure.[23]

Ligands. *o*-(Methylthio)aniline (Hmta) was prepared by following the procedure described by Livingstone.[24] 1,2-Bis((*o*-aminophenyl)thio)ethane (dae) was prepared by a method described in the literature.[25]

Complexes. $[Au(mta)_2Cl]Cl$ (1). A 0.835-g (6.0-mmol) sample of *o*-(methylthio)aniline (Hmta) in 10 mL of dry and degassed methanol was added rapidly to a solution of 1.20 g (3.0 mmol) of $NaAuCl_4 \cdot 2H_2O$ in 25 mL of degassed dry methanol in dry dinitrogen atmosphere at room temperature. The reaction mixture turned blue, and a deep blue compound separated out from the solution. This was immediately filtered off and the solid was washed with methanol and air dried. The dry compound was then thoroughly washed with water until free from any acid and sodium chloride. It was finally washed with methanol followed by benzene and dried in vacuo. Yield 70%.

The compound was dissolved in a small volume of dichloromethane and was subjected to chromatography on a silica gel (BDH) column (15 cm). On elution with dichloromethane a small yellow band separated out; this was rejected. Then a deep blue band was eluted with acetonitrile–benzene mixture (9:1 v/v); upon evaporation of the eluate a deep blue compound (**1a**) was obtained. This was purified by recrystallization from dichloromethane.

After the elution of **1a** another deep blue band remained at the top of the chromatographic column, which could be eluted only with methanol. Upon evaporation of the blue eluate **1b** was obtained.

$[Au(mta)_2Cl]_2Cl_2$ (1c). A 50-mg sample of **1a** was dissolved in 20 mL of dry and degassed DMF and stirred for 24 h at room temperature in dinitrogen atmosphere. The solvent was then dried up in vacuo. The compound was recrystallized from dichloromethane–methanol solution. Yield: 70%.

$[Au(mta)_2Br]_2Br_2$ (1d). To a solution of 1.19 g (2.0 mmol) of $KAuBr_4 \cdot 2H_2O$ in 25 mL of degassed dehydrated ethanol was added slowly 0.55 g (4.0 mmol) of *o*-(methylthio)aniline (Hmta) in 10 mL of degassed dehydrated ethanol in a dinitrogen atmosphere over 80 min. The reaction mixture gradually turned blue, and a deep blue compound was precipitated from the solution. This was filtered, washed with ethanol, and air-dried. It was then washed thoroughly with water followed by ethanol and finally with benzene and dried in vacuo giving a 40% yield. The compound was recrystallized from methanol and then from dichloromethane.

$[Au(mta)_2SCN]_2(SCN)_2$ (1e). This compound could be synthesized by reacting any of the compounds **1a–d** with an excess of NH_4SCN or KSCN in methanol. The resultant blue solution was stirred at room temperature for 24 h and evaporated, and the solid mass was thoroughly washed with water and dried in vacuo over fused $CaCl_2$. The compound was recrystallized from dichloromethane as blue powder, 80% yield.

$[Au(dae)Cl]Cl$ (2a). To a solution of 1.20 g (3.0 mmol) of $NaAuCl_4 \cdot 2H_2O$ in 30 mL of degassed methanol was added rapidly 0.835 g (3.0 mmol) of 1,2-bis((*o*-aminophenyl)thio)ethane (dae) dissolved in 15 mL of degassed methanol in a dinitrogen atmosphere. A deep blue compound separated out from the solution, it was immediately filtered off, washed with methanol, and air-dried. It was then thoroughly washed with water followed by ethanol and dried over fused $CaCl_2$. The compound was recrystallized from methanol. Yield: 40%.

Table I. Analytical Data for the Complexes

	anal. found (calcd)				
compound (formula)	% C	% H	% N	% X	% Au
$[Au(mta)_2Cl]Cl$ (**1a**)	29.97	2.86	4.98	12.80	36.78
($C_{14}H_{16}N_2S_2Cl_2Au$)	(30.88)	(2.94)	(5.15)	(13.05)	(36.21)
$[Au(mta)_2Cl]Cl$ (**1b**)	31.28	2.90	5.23	12.91	35.88
($C_{14}H_{16}N_2S_2Cl_2Au$)	(30.88)	(2.94)	(5.15)	(13.05)	(36.21)
$[Au(mta)_2Cl]_2Cl_2$ (**1c**)	30.08	2.87	5.01	12.82	36.56
($C_{28}H_{32}N_4S_4Cl_4Au_2$)	(30.88)	(2.94)	(5.15)	(13.05)	(36.21)
$[Au(mta)_2Br]_2Br_2$ (**1d**)	26.22	2.43	4.52	*a*	29.99
($C_{28}H_{32}N_4S_4Br_4Au_2$)	(26.54)	(2.53)	(4.42)	(25.27)	(31.12)
$[Au(mta)_2SCN]_2(SCN)_2$ (**1e**)	32.46	2.78	9.61	...	32.74
($C_{32}H_{32}N_8S_8Au_2$)	(32.60)	(2.71)	(9.50)	...	(33.45)
$[Au(dae)Cl]Cl$ (**2a**)	31.16	2.91	5.02	13.21	35.76
($C_{14}H_{16}N_2S_2Cl_2Au$)	(30.88)	(2.94)	(5.15)	(13.05)	(36.21)
$[Au(dae)Br]Br$ (**2b**)	26.70	2.60	4.57	*a*	29.67
($C_{14}H_{16}N_2S_2Br_2Au$)	(26.54)	(2.53)	(4.42)	(25.27)	(31.12)

[a] Not estimated.

Table II. Decomposition Temperature, Conductance Values, Magnetic Moments, and EPR Spectral Results

compound	dec temp, °C	Λ, Ω^{-1} cm^2 mol^{-1}	μ_{eff} at 300 K, μ_B	g_{iso}	A_{iso}, G
$[Au(mta)_2Cl]Cl$ (**1a**)	100–105	123^a	1.84	2.0033	6.5^c
$[Au(mta)_2Cl]Cl$ (**1b**)	100–103	126^a	1.84	2.0033	6.25^c
$[Au(mta)_2Cl]_2Cl_2$ (**1c**)	103–105	132^b	1.06	2.0033	$4.0^{b,c}$
$[Au(mta)_2Br]_2Br_2$ (**1d**)	95–98	121^b	1.03	2.0030	4.0^c
$[Au(mta)_2SCN]_2(SCN)_2$ (**1e**)	105–108	142^b	1.05	2.0033	4.0^b
$[Au(dae)Cl]Cl$ (**2a**)	125–130	129^a	1.85	2.0031	6.0^b
$[Au(dae)Br]Br$ (**2b**)	120–122	68^b	1.79	2.0033	5.5^b

[a] In CH_3CN. [b] In DMF. [c] In CH_2Cl_2.

$[Au(dae)Br]Br$ (2b). A solution of 0.56 g (2.0 mmol) of 1,2-bis((*o*-aminophenyl)thio)ethane (dae) in 10 mL of degassed absolute ethanol was slowly added to a solution of 1.19 g (2.0 mmol) of $KAuBr_4 \cdot 2H_2O$ in 25 mL of degassed absolute ethanol in dinitrogen atmosphere over 70 min. The blue compound that separated out from the blue solution was collected by filtration, washed with ethanol, and air-dried. This was washed thoroughly with water followed by ethanol and dried over fused $CaCl_2$ in vacuo. The compound was recrystallized from dichloromethane. Yield: 35%. This compound could also be synthesized from **2a** by reacting it with an excess of LiBr in methanol with 80% yield.

Physical Measurements. Microanalyses (C,H,N) were performed in a Perkin-Elmer 240C elemental analyzer. Thermogravimetric (TG) and differential thermal analysis (DTA) were done in a Shimadzu DT-30 thermal analyzer. UV–vis spectra were recorded by using a Pye Unicam SP8 UV/VIS 150 spectrophotometer. Infrared spectra were measured with a Perkin-Elmer Model 783 spectrophotometer using the KBr wafer technique. Far-infrared spectra were recorded with a Polytech FIR-30 FT-FIR spectrometer using a polyethylene pellet. Static susceptibility measurements were made with a PAR 155 vibrating-sample magnetometer, and a temperature-dependent susceptibility measurement was made using a Model MPMS SQUID magnetometer from Quantum Design. 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. DPPH was used as an internal field marker. Variable-temperature EPR studies were done using a Varian E-257 variable-temperature accessory. Temperature was calibrated using a copper–constantan thermocouple and controlled to an accuracy of ±1 K. The simulations of the spectra have been performed on a Varian 620L computer. Electrochemical measurements were done with the help of a PAR Model 370-4 electrochemistry system incorporating the following instruments: Model 174A polarographic analyzer; Model 175 universal programmer; Model RE 0074 X-Y recorder. All experiments were carried out under 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)

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Table III. Most Relevant Infrared Bands (cm^{-1}) of the Ligands and the Complexes

compound	ν_{as}(N–H)	ν_s(N–H)	δ(NH$_2$)	ν(Au–N)	ν(Au–S)	ν(Au–X)	ν_{as}(X–Au–X)	ν_s(X–Au–X)
Hmta	3435	3340	1605					
dae	3365	3270	1620					
[Au(mta)$_2$Cl]Cl (**1a**)		3280		460	400	358		
[Au(mta)$_2$Cl]Cl (**1b**)		3270		455	395	350		
[Au(mta)$_2$Cl]$_2$Cl$_2$ (**1c**)		3280		460	385		365	350
[Au(mta)$_2$Br]$_2$Br$_2$ (**1d**)		3260		465	380		260	235
[Au(mta)$_2$SCN]$_2$(SCN)$_2$ (**1e**)		3280		458	380			
[Au(dae)Cl]Cl (**2a**)	3300	3190	1615	478	390	360		
[Au(dae)Br]Br (**2b**)	3305	3200	1610	480	390	210		

were used in the three electrode configurations. All cyclic voltammetric data were collected at 298 ± 1 K and are uncorrected for junction contribution.

Results and Discussion

Analytical data (Table I) indicate that the compounds **1a–c** have identical composition. Compounds **1a–e** are moderately soluble in dichloromethane, methanol, ethanol, and acetonitrile while compounds **2a,b** are moderately soluble in methanol and acetonitrile, but all these compounds are highly soluble in DMF and DMSO. The compounds **1a,b** and **2a** appear to be 1:1 electrolytes in acetonitrile while **2b** is a 1:1 electrolyte in DMF, but compounds **1c–e** are 1:2 electrolytes in DMF. The conductance values, magnetic moments, and decomposition temperatures for all these complexes are given in Table II. The compounds decompose without melting. Thermogravimetric (TG) analysis indicates that the rate of weight loss above decomposition point is slow and the loss is completed around 800 °C for most of these compounds. Differential thermal analysis (DTA) shows that the decomposition process is exothermic as indicated by the broad exotherm observed in each of the DTA traces.

Infrared Spectra. The most relevant infrared bands of the ligands and their complexes are listed in Table III. In the IR spectrum of *o*-(methylthio)aniline (Hmta) two strong bands observed[26,27] at 3435 and 3340 cm^{-1} are due to asymmetric and symmetric stretching frequencies of the NH$_2$ group but only one sharp band is noticed[27] near 3280 cm^{-1} for the complexes **1a–e** indicating the deprotonation of the NH$_2$ groups of the ligands during coordination to the metal ion. But in the case of the compounds **2a,b**, two strong bands located at 3300 and 3190 cm^{-1} arise due to ν_{as}(N–H) and ν_s(N–H) modes, respectively.[27] The corresponding δ(NH$_2$) mode occurs near 1615 cm^{-1}. A strong band at 2115 cm^{-1} and a medium-intensity band at 2055 cm^{-1} indicate[28] the presence of two different SCN$^-$ groups in compound **1e**. The band at 2055 cm^{-1} is characteristic of free SCN$^-$ while that at 2115 cm^{-1} is indicative[28] of bridging SCN$^-$. A medium-intensity band at ~460 cm^{-1} observed[1,29–31] in the spectra of **1a–e** probably arises due to ν(Au–N) while the ν(Au–N) for **2a,b** occurs around 480 cm^{-1}. These bands are absent in the IR spectra of the corresponding ligands. The bands observed in the region 400–380 cm^{-1} for all these complexes, assigned[32–35] to the terminal ν(Au–S) band, are very weak in intensity. A medium-intensity band around 360 cm^{-1} observed for **1a,b** and **2a** is assigned[30,31] as ν(Au–Cl). This band is absent in the bromo and thiocyanato complexes. The ν_{as}(Cl–Au–Cl) and ν_s(Cl–Au–Cl) modes are observed at 365 and 350 cm^{-1}, respectively, for compound **1c** while the asymmetric and symmetric Br–Au–Br modes occur at 260 and 235 cm^{-1}, respectively, for **1d**.[34–38] On the other hand, the ν(Au–Br) band for **2b** is located[34–38] at 210 cm^{-1}.

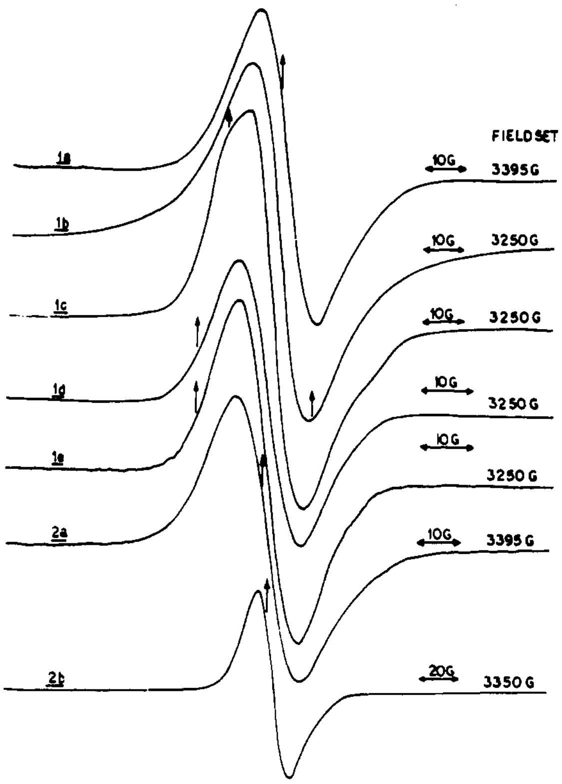

Figure 1. Powder EPR spectra recorded at X-band frequency at room temperature.

The results of conductance measurements in solutions have already revealed that one of the two halides (or SCN$^-$ for **1e**) present per metal ion is coordinated to the metal acceptor center in all these complexes. This is further supported by the IR and far-IR spectra of the complexes, and this indicates that the metal ion is at least five-coordinated in these compounds. Since **1a** and **1b** have identical composition and conductance values, they are isomeric. From the order of their separation by column chromatography and the nature of the eluant used, it is evident that **1a** is less polar than **1b**. Hence, it is expected that **1a** should have a trans structure while **1b** should be the cis form. On the other hand, both **2a** and **2b** obviously are of cis configuration. It is evident from the infrared spectra of the complexes that the NH$_2$ group of the Hmta ligand is deprotonated during coordination to the metal ion in the complexes **1a–e** while the NH$_2$ groups of the dae ligand are coordinated as such in the complexes **2a,b**. But as the driving force for the deprotonation is not clear, it is difficult to state why the dae ligand does not undergo deprotonation during

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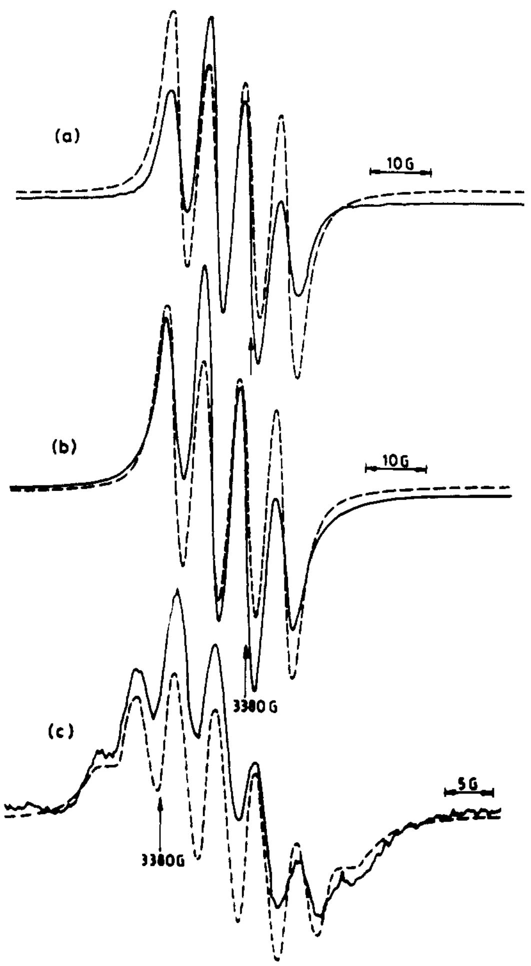

Figure 2. Solution EPR spectra recorded at X-band frequency at room temperature: (a) experimental (—) and simulated (---) spectra for compound **1a** in CH_2Cl_2, (b) experimental (—) and simulated (---) spectra for **1b** in CH_2Cl_2, and (c) experimental (—) and simulated (---) spectra for **1c** in DMF.

complexation while the Hmta ligand does.

EPR Results. The powder spectra recorded at X-band frequency at room temperature for these complexes are shown in Figure 1. The strong signal exhibited by powder samples implies that the compounds are paramagnetic. This leaves us with either a d^9 or a d^7 low spin configuration for the metal ion, the latter being very unlikely.

EPR investigation in solution has afforded the most important evidence regarding the nature and structure of the complexes. Compounds **1a–d** are dissolved in dichloromethane and the solution EPR spectra are recorded at room temperature. Both compounds **1a** and **1b** give identical EPR spectra, each of which consists of four lines (Figure 2). The four-line pattern is presumed to arise from one interacting gold nucleus (100% ^{197}Au, $I = {}^3/_2$). The simulated spectrum is found to be in good agreement with the experimental one (Figure 2a,b). Again the solution EPR spectra of both complexes **1c** and **1d** are also identical to each other, consisting of a seven-line pattern. On the other hand, the thiocyanato complex **1e** also gives a seven-line multiplet in DMF solution, indicating an interaction with two nuclei with $I = {}^3/_2$. This can arise from two gold nuclei. Since the isotropic hyperfine coupling constant for the chloro compound **1c** and its bromo analogue **1d** are identical, it is unlikely that the hyperfine coupling arises from halogens which also have $I = {}^3/_2$ in 100% abundances though made up of two different magnetic moments with different abundances. It is also noted that the seven-line multiplet of the thiocyanato complex **1e** is identical with that of **1c** in DMF solution, which is strongly indicative of an interaction with two gold nuclei. The possibility of hyperfine coupling originating from aromatic protons is ruled out since the ^{1}H NMR spectra confirm the presence of aromatic protons in their usual positions, but the lines are somewhat broadened.

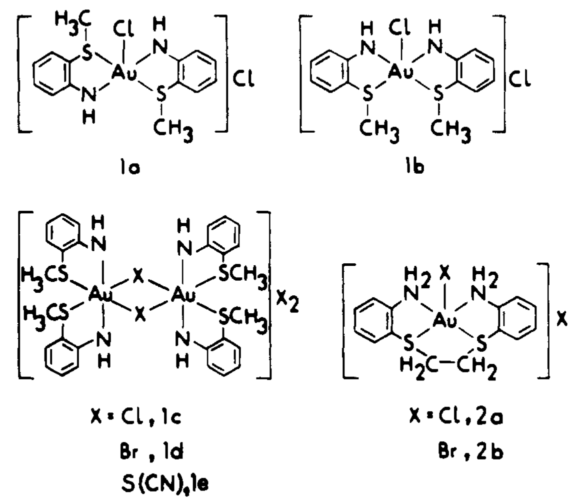

Figure 3. Structures of the compounds.

When complexes **1a,b** are dissolved in DMF and the solution EPR spectra are recorded at room temperature, both compounds give identical EPR spectra which consist of seven lines and this seven-line multiplet is found to be identical with that obtained for **1c** in DMF. The hyperfine coupling (4.0 G) is found to be much less than that observed in the four-line multiplet of the corresponding dichloromethane solutions. This suggests that these compounds, **1a,b**, undergo dimerization in DMF solutions, leading to the formation of **1c**. Assuming an interaction with two gold nuclei, the simulated spectrum obtained is in very good agreement with the experimental one (Figure 2c). The EPR results are summarized in Table II.

The chloro compound **2a** and its bromo analogue **2b**, when dissolved in DMF, yield identical spectra which consist of four lines, indicating an interaction with one gold nucleus. These results indicate that while compounds **1a,b** and **2a,b** are monomeric, compounds **1c–e** are dimeric in solution. The interesting feature of our investigations is the spontaneous dimerization of the monomeric complexes **1a,b** in DMF leading to the formation of **1c**, and the dimeric complexes **1c–e** retain their dimeric structure in DMF solution. This indicates that the metal ion has a tendency to achieve higher coordination in these complexes which is rare in the coordination chemistry of gold.[1]

Moreover, all the isolated compounds are highly stable in the solid state as well as in solution in the presence of air. The structures of the compounds that are consistent with EPR results, stoichiometry, conductance data, and IR spectra are presented in Figure 3.

The assignment of a metal ion oxidation state to compounds **1a–e** is ambiguous because of the π-delocalized nature of the ligands. It may be mentioned here that the 1,2-dithiolene-type ligands form a wide variety of compounds[39–42] with metals in apparently many different oxidation states. Undoubtedly in such cases considerable delocalization accounts for the ability of these complexes to exist with a range of electron populations. However, in the present case, the observed EPR results are more consistent with Au(II)-stabilized radical structures containing the oxidized ligands where the unpaired electron is highly delocalized onto the ligand. The magnetic data (Table II) for the monomeric complexes **1a,b** are consistent with a d^9 complex having only one unpaired electron, and this is further supported by the EPR results.

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This leads to a spin-doublet ground state for the mononuclear complexes **1a**,**b**. It may be noted here that the detailed MO calculations of the $[Ni(mnt)_2]^n$ system are found to be consistent with the Ni(II)–radical-ligand formulation for the $n = 0$ and -1 complexes[39] containing the oxidized ligands, and the ground state for the $n = -1$ complex is shown to be

$$...(2b_{1g})^2(4b_{2g})^2(4a_g)^1(3b_{1g})^0$$

with $4b_{2g}$ and $4a_g$ levels having large ligand character. The other possibility that the product **1a** or **1b** could alternatively involve one anionic mta ligand, a Au(III) d^8 ion, and a ligand radical with one unpaired electron can be ruled out due to the following reasons. Though this formulation explains the magnetic moment, it is inconsistent with the observed EPR results. In the EPR spectra of the complexes, we do not see any nitrogen superhyperfine resonance 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. Thus on the basis of the magnetic moment data and EPR results, we could say that the two electrons of the two oxidized mta ligands are residing in the same molecular orbital if the complete MO diagram of the system is considered, leading ultimately to a "$S = {}^1/_2$" system. A similar situation is expected for the dinuclear complexes **1c**–**e**, wherein there are four oxidized mta ligands and two Au(II) ions. As with the monomers, it is expected, in the absence of any nitrogen superhyperfine resonance in the EPR spectra of the dinuclear complexes, that the four electrons of the four oxidized ligands are actually paired up when the MO is considered, leading to a triplet ground state due to the interaction of two unpaired electrons, one each in the two Au(II) ions. The fact that there is such an exchange interaction is evident from the seven-line EPR multiplet with an intensity ratio 1:2:3:4:3:2:1 for the dimers **1c**–**e** in solution. The variable-temperature susceptibility studies (discussed below) on **1c** clearly indicate a triplet ground state for this compound. This is only a conjecture, and rigorous calculations are required to see the electronic distributions for the compounds **1a**–**e**.

It is important to note here that the hyperfine coupling constant (^{197}Au) for these complexes is quite small. The high A_{Au} values in $[AuS_4C_4(CN)_4]^{2-}$ and $Au(S_2CNEt_2)_2$ of 41.7 G and 29 G respectively,[43] as compared to the low A_{Au} values in the present set of complexes, are indicative of a large delocalization of the unpaired electron onto the ligands in the latter complexes. All of our complexes are nonplanar or rigorously of low symmetry. Consequently, the d character (expected from the planar dithiolenes) not only is considerably changed but also is more delocalized onto the ligand. The absence of nitrogen superhyperfine splitting on our complexes is puzzling; perhaps the spin delocalization exclusively takes place onto sulfur ligands. It is obvious that all the monomeric complexes have a spin-doublet ground state. The ground state of the dimeric complexes should originate from either a ferromagnetic interaction or an antiferromagnetic interaction between the two metal ions.

In order to get an insight into the nature of "magnetism" in the dimeric systems **1c**–**e**, we measured the susceptibility of **1c** as a function of temperature in the range 5–300 K, and the plot of molar susceptibility versus temperature is shown in Figure 4. No distinct maximum or cut off is seen in the plot. Though the plot of χ_M vs T indicates a coupling of ferromagnetic nature, we have found it difficult to fit it to perfection using the conventional Bleaney–Bowers equations inclusive of molecular field correction[44] as given by

$$\chi_M^{cor} = \chi_M/(1 - 2ZJ'\chi_M/Ng^2\mu_B^2)$$

χ_M is the simple Heisenberg susceptibility of the Bleaney–Bowers expression[45] for an exchange coupled pair of $S = {}^1/_2$ spins

$$\chi_M = \frac{2Ng^2\mu_B^2}{kT}[3 + \exp(-2J/kT)]^{-1}$$

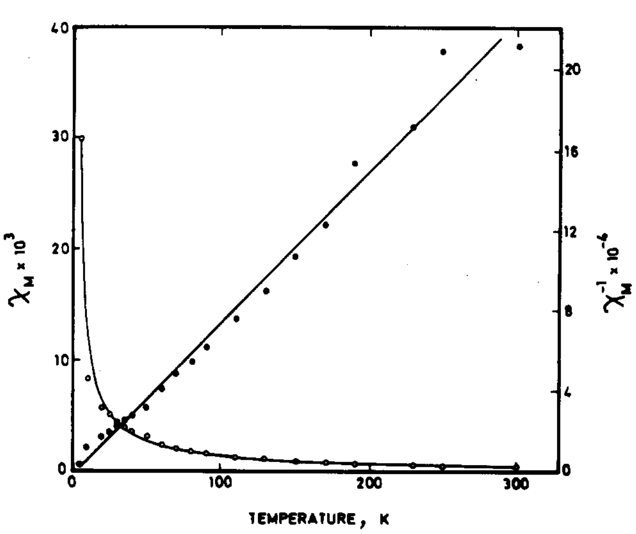

Figure 4. Temperature variation of susceptibility of **1c** at a field of 0.5 T. Both χ_M vs T and χ_M^{-1} vs T are plotted.

where g, μ_B, and k have the usual meaning and Z is the number of nearest neighboring spin centers, which is assumed to be 2 in the present case. Using the average g (2.003) from EPR results, a least-squares fit was performed by varying both J and J' to minimize the error function

$$f(g,J) = \frac{1}{N}\sum_{i=1}^{n}[\chi_M^{exptl}(T_i) - \chi_M^{calcd}(T_i)]^2T_i^2$$

which yielded $2J = 10$ cm^{-1} and $J' = -0.25$ cm^{-1}. Though we got a $2J$ value of +10 cm^{-1} and J' (interdimer exchange) of -0.25 cm^{-1}, the fitting has been less than perfect. Any fit away from these numbers (including Z other than 2) leads to gross errors. Hence the only inference that we could draw was that the two Au(II) ions within the dimer are ferromagnetically coupled with a possible weak interdimer antiferromagnetic coupling. The improper fit could also mean that the dimers could be some sort of one-dimensional or quasi-one-dimensional systems. But no specific conclusions can be arrived at without a crystal structure determination. The latter is hampered by our inability to get single crystals of reasonable size thus far.

Coming back to our EPR results, we must state that no half-field transition has been observed possibly because of low "D" values (since the unpaired electron has its origin from a metal-stabilized free radical). Frozen-glass EPR spectra are hyperfine broadened and do not show even "D separations", of course, again because of low "D". However, in the absence of definitive structural information, any interpretation of the data must be speculative. Therefore all discussions in this regard must be considered as tentative.

Another interesting aspect, which focuses on the dimeric nature of compound **1c**, has come out by studying the temperature-dependent EPR. Lowering of the temperature leads to increased EPR intensity for compound **1c**, which could be generally attributed to small changes in Zeeman population. However, the heating experiment is interesting, wherein the EPR intensity increases on heating accompanied by a slight decrease in line width. Also, the heated sample when cooled to room temperature gives an EPR spectrum with no reduction in the intensity of the heated sample. Furthermore, the EPR spectrum with reduced line width is identical to that of compound **1a**, and at the same time the total intensity is twice as much as the initial intensity of the dimeric sample **1c**. This probably indicates that each molecule of **1c**, which is weakly exchange coupled, is converted on heating to two monomer molecules of **1a** rather than **1b** (**1b** has a larger line width than **1a**). This is an additional proof for the dimeric nature of **1c**. The results are shown in Figure 5.

Electrochemical Results. The redox behavior of the mononuclear complexes **1a**, **1b** and **2a** has been studied in CH_3CN/0.1M TEAP and that for the dimeric complexes **1c** and **1e** have been

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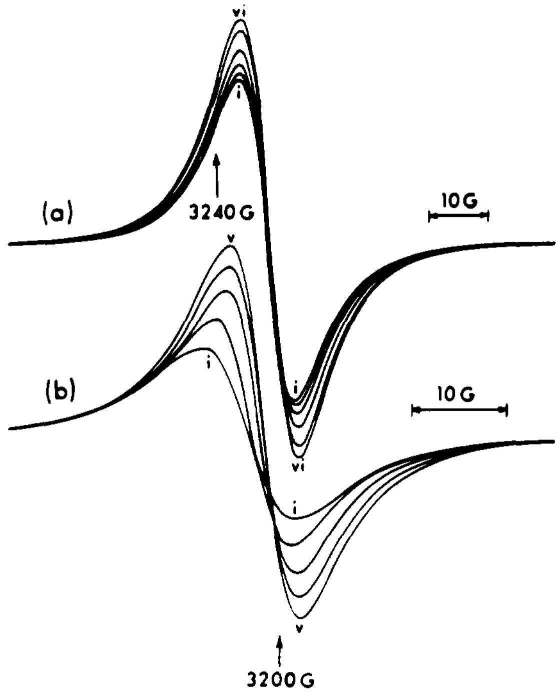

Figure 5. Variable-temperature EPR results for **1c**: (a) below room temperature at (i) 300 K, (ii) 260 K, (iii) 220 K, (iv) 180 K, (v) 140 K, and (vi) 110 K; (b) above room temperature at (i) 300 K, (ii) 315 K, (iii) 335 K, (iv) 355 K, and (v) 370 K.

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

compound[c]	$E_{1/2}$, V (ΔE_p, mV) $(E_{1/2})_1$	$(E_{1/2})_2$
[Au(mta)$_2$Cl]Cl (**1a**)	+0.08 (70)	*d*
[Au(mta)$_2$Cl]Cl (**1b**)	+0.10 (70)	*d*
[Au(mta)$_2$Cl]$_2$Cl$_2$ (**1c**)	−0.09 (220)	−0.87 (110)
[Au(mta)$_2$SCN]$_2$(SCN)$_2$ (**1e**)	−0.21 (280)	−0.92 (105)
[Au(dae)Cl]Cl (**2a**)	+0.145 (190)	*d*

[a] Conditions: solvent, CH$_3$CN for **1a,b** and **2a** and DMF for **1c,e**; supporting electrolyte, TEAP (0.1 M); solute concentration, $\sim 10^{-4}$ 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] One irreversible oxidation wave is observed at +1.20 V for **1a**, +1.24 V for **1b**, +1.20 V for **1c**, and +0.62 V for **1e**, respectively. [d] Does not arise.

examined in DMF/0.1M TEAP at a platinum working electrode using cyclic voltammetry (CV). Results are given in Table IV. Both the complexes **1a,b** are reduced at almost the same potential. The electrochemical natures of this isomeric pair are similar—reflecting that the geometry of the molecules has little effect on electrochemical properties. The isomers exhibit reductive couple (1) near +0.1 V vs SCE. Well-defined cathodic and anodic peaks

$$[\mathrm{Au(mta)_2Cl}]^+ + e^- \rightleftharpoons [\mathrm{Au(mta)_2Cl}]^0 \qquad (1)$$

of equal height are observed (Figure 6). At slow scan rate (v = 50 mV s^{-1}) the peak to peak separation, ΔE_p, is found to be 70 mV, showing that the process is nearly reversible and involves one-electron transfer. The nearly Nernstian behavior and reversible nature of couple (1) are good indications that the gross geometry of the isomers in both oxidation states are alike. With the increase in scan rates ΔE_p increases, but this increase in ΔE_p does not affect the $E_{1/2}$ value. Besides the reductive couple (1), two successive oxidative responses are observed within +0.8 V, which are coupled to a broad reduction wave near +0.35 V (Figure 6). Both the complexes are irreversibly oxidized near +1.2 V. The closeness of electrochemical behavior of this isomeric pair is also consistent with the similar chemical reactivity and identical EPR results.

The corresponding dimeric complex **1c** shows two quasireversible reductive responses (Figure 7) near −0.1 and −0.9 V vs

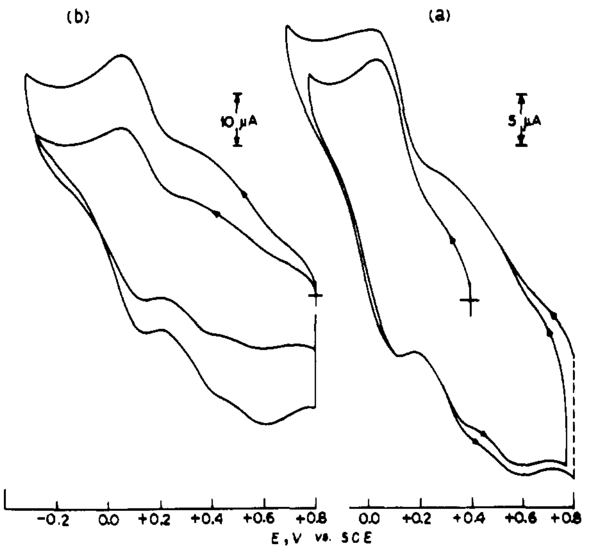

Figure 6. Cyclic voltammograms for $\sim 1 \times 10^{-4}$ M compound in 0.1 M TEAP/CH$_3$CN: (a) for **1a** at a scan rate of 50 mV s^{-1}; (b) for **1b** at scan rates of 50 and 100 mV s^{-1}, respectively.

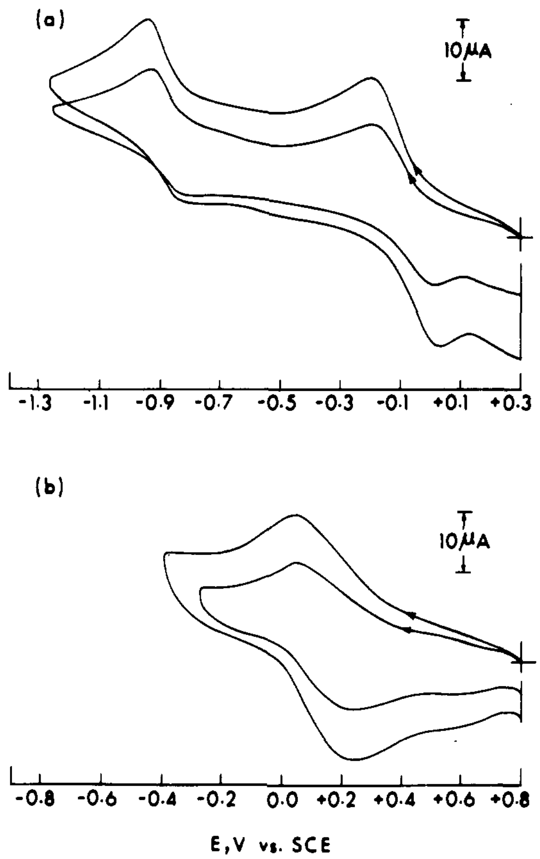

Figure 7. Cyclic voltammograms: (a) for **1c** in 0.1 M TEAP/DMF; (b) for **2a** in 0.1 M TEAP/CH$_3$CN at scan rates of 50 and 100 mV s^{-1}, respectively. Solute concentration $\sim 1 \times 10^{-4}$ M.

SCE. The electrochemical behavior of this halo-bridged complex is quite different from that of the sulfur-bridged complexes[1] [Au(abt)$_2$]$_2$ (Habt = *o*-aminobenzenethiol), which display two reversible oxidative couples. The more negative value of the reduction potentials and large gap between the two responses (Table IV) may be due to the weak coupling and low stability of the dimer **1c**. However, only one irreversible oxidative response is observed near +1.2 V for this complex. The S-bonded thiocyanato-bridged dimer **1e** exhibits a similar electrochemical behavior except that the reductive steps shifted cathodically. The separation of the two potentials is more or less the same as com-

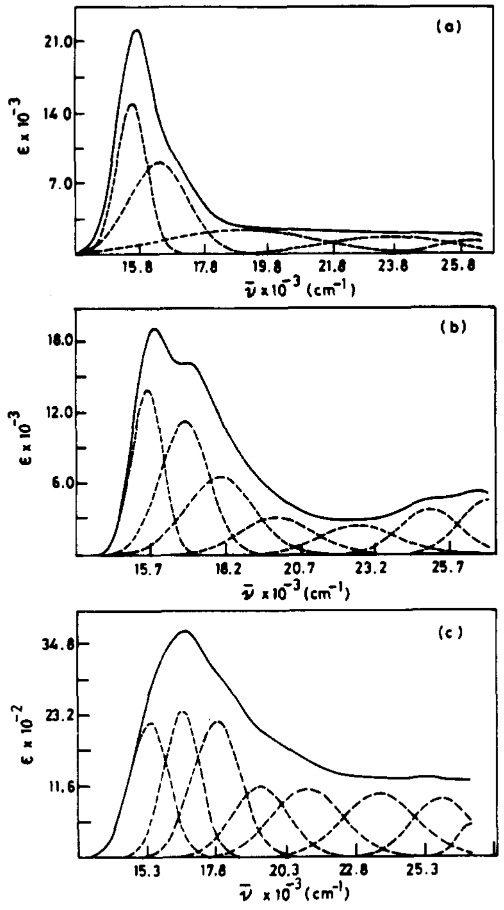

Figure 8. Electronic spectra for the compounds in CH_2Cl_2: in the visible region along with their Gaussian analyses: (a) **1a**; (b) **1c**; (c) **2a**.

pared to that observed in **1c**. An irreversible oxidation wave near +0.62 V is observed for **1e**.

The monomeric complex **2a** containing the open-chain diamine–dithioether ligand 1,2-bis((*o*-aminophenyl)thio)ethane (dae), undergoes quasireversible (Figure 7) one-electron reduction near +0.15 V vs SCE. A slightly positive shift of the reduction potential of this complex compared to that of **1a** or **1b** is seen. This probably happens due to greater ligand field stability and the chelate effect of the tetradentate ligand in **2a**. Except for this reductive couple, no other response is seen within +1.25 V.

Electronic Spectra. All the complexes produce intense blue color in solutions, which exhibit highly rich optical spectra. It is noted that the optical spectra of **1a,b**, which are similar to each other, differ considerably (Figure 8) from that of **2a**, although all of these three compounds are five-coordinate with the same donor atoms. This is a clear indication of the fact that the electronic structures of **1a,b** are different from that of **2a**. It should be mentioned here that **1a,b** involve the coordination of the oxidized ligand. However, in general, all these complexes exhibit at least two lowest energy bands which are much more intense than the higher energy ones in the visible region indicating that the first set corresponds to charge transfer (CT) of the type M → L and the second set is probably arising due to d–d transitions. It may be recalled here that all these complexes undergo facile reduction (Table IV) indicating that the energy of the lowest unoccupied molecular orbital (LUMO), which is probably of the ligand origin, is quite low, and since gold(II) is easy to oxidize, a low-energy M → L charge transfer is not unlikely for these compounds.

The spectra of the compounds **1c–e**, though they look similar to that of **1a** or **1b**, actually have a greater number of bands (Figure 8b) revealing the dimeric nature of the compounds **1c–e**. There is considerable resemblance in the optical spectra of **1a–e** to those of certain 1,2-dithiolene complexes where intense absorptions occur[43] at low energy in the visible and near-infrared regions. However, if one does not look into the molecular orbital picture, proper assignment of the electronic transitions for this series of compounds would be beset with difficulties.

Concluding Remarks

The appearance of almost equally intense four-line pattern EPR spectra for the monomeric complexes in solution and a seven-line multiplet with an intensity ratio 1:2:3:4:3:2:1 for the dimeric complexes, also in solution, is an indication of the interaction of the unpaired electron with the gold nucleus. The very small hyperfine splitting observed in the EPR spectra of these complexes is strongly indicative of the low metal character of the semioccupied molecular orbital.[43,46] No hyperfine structure originating from the interaction with the nitrogen nucleus/nuclei of the ligand(s) mta and dae is observed in the parent complexes **1a–e** and **2a,b**. However, the EPR results are widely different from those for the reported[3,5] gold(II) complexes; an exact explanation is not possible at this stage due to the rather unknown nature of the Au(II) acceptor center in five- or six-coordinate surroundings. The positive sign of $2J$ shows that the intradimer exchange interaction is of ferromagnetic nature, and the negative sign of J' indicates that the interdimer exchange interaction is of antiferromagnetic nature. All attempts to prepare single crystals of any one of these complexes have failed, so all investigations are confined to powders and solutions of the complexes.

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