Studies on Gold(II) Complexes with Hard and Soft Donor Ligands. Part I. Complexes with *o*-Aminobenzenethiol†

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The synthesis and characterisation of gold(II) complexes with *o*-aminobenzenethiol is reported. The e.s.r. results indicate that the highest occupied molecular orbital has appreciable contribution from the sulphur donors of the ligands. It is the first time that binuclear gold(II) complexes giving well resolved seven-line e.s.r. patterns originating from two ^{197}Au nuclei have been reported.

Although the oxidation state 2+ is rare for gold, there are several reports[1-13] of gold complexes in which a formal oxidation state of 2+ for gold is established. In all the reported dimeric complexes,[5-13] gold(II) is stabilised by the presence of a strong Au–Au bond and consequently these are diamagnetic. Monomeric gold(II) complexes with some unsaturated sulphur-donor ligands such as *N*,*N*-dialkyldithiocarbamate[1] (dtc) and maleonitrile dithiolate[3] (mnt) are reported to be stabilised by delocalisation of the unpaired electron over the unsaturated ligand.[14] Also there is strong evidence[15-17] that Au^{II} species are formed as transient intermediates in redox reactions between the stable oxidation states 1+ and 3+.

Studies[18-21] on complexes related by electron-transfer reactions have demonstrated that it should be possible to stabilise new magnetic states using ligands having nitrogen- or oxygen-group donor atoms and appropriately extended π-systems. We have chosen such a system where Au^{III} is reduced by the ligand *o*-aminobenzenethiol (Habt) to Au^{II} and simultaneously stabilised by this extended π-system ligand containing soft as well as hard donor atoms and the unpaired electron is found to be highly delocalised (see below).

We report the preparation, characterisation, and properties of the isomeric pair of isovalent gold(II) dimeric complexes and a monomeric complex of Au^{II} with the ligand abt. It should be noted that no paramagnetic dimeric compound of gold in the formal oxidation state 2+ hitherto has been reported.

Experimental

Chemicals.—*o*-Aminobenzenethiol was obtained from E. Merck and was used without further purification. The compound $HAuCl_4{\cdot}3H_2O$ was obtained from Johnson Matthey; $NaAuCl_4{\cdot}2H_2O$ was prepared from $HAuCl_4{\cdot}3H_2O$ using a standard method.[22] All other chemicals were of reagent grade and were used without further purification. All the solvents were dried and distilled before use. Tetraethylammonium perchlorate (teap) was prepared from tetraethylammonium bromide (Fluka AG) by using a standard procedure.[23]

Preparation of the Compounds.—$[\{Au(abt)_2\}_2]$ (**1**). To a solution of $NaAuCl_4{\cdot}2H_2O$ (1.20 g, 0.003 mol) in degassed absolute ethanol (30 cm^3) was added rapidly Habt (0.75 g, 0.006 mol) in degassed absolute ethanol (15 cm^3) under a dry dinitrogen atmosphere. The reaction mixture turned blue-violet and a deep violet (almost black) compound separated out from the solution. This was immediately filtered off and the precipitate was washed with alcohol and air dried. The compound was then thoroughly washed with distilled water until it was free from any acid and sodium chloride. Finally the compound was washed with ethanol followed by diethyl ether and dried over fused calcium chloride *in vacuo*. One portion of this compound was purified from dichloromethane. Total yield *ca.* 40%; decomp. 160 °C (Found: C, 32.50; H, 2.70; Au, 43.95; N, 6.40. Calc. for $C_{24}H_{24}Au_2N_4S_4$: C, 32.35; H, 2.70; Au, 44.25; N, 6.30%).

$[\{Au(abt)_2\}_2]$ (**2**). Compound (**1**) (50 mg) was refluxed in dry degassed methanol (100 cm^3) for 2 h. The colour of the solution changed from purple to blue. This blue solution was cooled to room temperature, filtered through a G-4 sintered glass crucible, and the volume of the solution was reduced to *ca.* 10 cm^3 *in vacuo*. A deep blue (almost black) compound separated out. This was collected by filtration, washed thoroughly with benzene, and dried *in vacuo*. Yield 40%; decomp. 165 °C (Found: C, 31.95; H, 2.65; Au, 43.90; N, 6.20. Calc. for $C_{24}H_{24}Au_2N_4S_4$: C, 32.35; H, 2.70; Au, 44.25; N, 6.30%).

$[Au(abt)_2(dmf)_2]$ (**3**). Compound (**1**) (100 mg) was dissolved in *N*,*N*-dimethylformamide (dmf) (30 cm^3) and slowly refluxed (under low pressure) for 1 h; the solution turned deep blue. This was cooled to room temperature and filtered through a G-4 sintered glass crucible. The blue solution was collected and the solvent completely evaporated off *in vacuo*; the compound was washed with benzene and dried *in vacuo*. Yield 70%, relative to amount of (**1**) used; decomp. 155 °C (Found: C, 36.30; H, 4.50; Au, 33.80; N, 9.25. Calc. for $C_{18}H_{26}AuN_4O_2S_2$: C, 36.55; H, 4.40; Au, 33.35; N, 9.45%).

Physical Measurements.—Carbon, hydrogen, and nitrogen analyses were performed on a Perkin-Elmer 240 C,H,N-analyser. Thermogravimetric (t.g.a.) and differential thermal analysis (d.t.a.) were done in a Shimadzu DT-30 thermal analyser. Electronic spectra were recorded using a Pye Unicam SP8 UV/VIS 150 spectrophotometer. Spectroscopic grade solvents were used throughout. 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 conductances were determined with a Philips PR 9500 bridge, using a cell calibrated with 0.02 mol dm^{-3} KCl solution. Proton n.m.r. spectra were recorded on a Varian XL 100 FT-NMR spectrometer.

Electrochemical measurements were done with the help of a

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† *Non-S.I. unit employed:* G = 10^{-4} T.

Table 1. Most relevant i.r. bands (cm^{-1}) of the free ligand and its complexes

Free ligand (Habt)	$[\{Au(abt)_2\}_2]$ (**1**)	$[\{Au(abt)_2\}_2]$ (**2**)	$[Au(abt)_2(dmf)_2]$ (**3**)	Assignment
3 450vs	3 420s	3 420s	3 430s	$\nu_{asym.}$(N–H)
3 355vs	3 330s	3 330s	3 320s	$\nu_{sym.}$(N–H)
2 520m				ν(S–H)
			1 660m	ν(C=O)
1 610vs	1 600vs	1 600vs	1 595vs	δ(NH_2)
750vs	765(sh) 755vs	750vs 745(sh)	748vs	π(C–H)
	470w 450m	475m 455m	490m 455w	ν(Au–N)
	385w	380w 335w	390w	ν(Au–S)

PAR model 370–4 electrochemistry system: 174A polarographic analyser, 175 universal programmer, RE 0074 X-Y recorder. All experiments were carried out under a dry nitrogen atmosphere in a three-electrode configuration. A planar Beckman model 39273 platinum electrode was used as a working electrode. The results were collected at 298 ± 1 K and are referenced to a saturated calomel electrode (s.c.e.); the reported potentials are uncorrected for junction contribution.

Electron spin resonance spectra were recorded on Varian E-4 *X*-band and Varian E-112 *X*/*Q*-band e.s.r. spectrometers; diphenylpicrylhydrazyl (dpph) was used as an internal field marker. The simulations of the spectra were performed on a Varian 620L computer.

Results and Discussion

The most relevant i.r. bands of the complexes and the ligand (Habt) are presented in Table 1; magnetic moments of the complexes are given in Table 2. Thermogravimetric analysis indicates that the compounds decompose at high temperatures without melting. The thermogram shows that the rate of weight loss of the compounds above decomposition point is very slow and the loss is completed only around 1 000 °C leaving pure metallic gold as the residue. The thermogram does not show any further weight loss with increase in temperature but the d.t.a. exhibits an endotherm corresponding to the melting point of metallic gold.

The solubility of the compounds in common organic solvents like dichloromethane, chloroform, acetonitrile, and ethanol is very poor but they are moderately soluble in co-ordinating solvents such as dmf, Me_2SO, and pyridine. The compounds are non-electrolytes in dmf. All three neutral complexes are intensely coloured in solution and their electronic spectra are highly rich (Table 3). However, the extremely low solubility of the complexes in common organic solvents does not permit molecular weight determination.

When a portion of compound (**1**) was refluxed in dry methanol, the purple solution turned blue and the deep blue compound (**2**) obtained on concentrating the blue solution has also the same composition as that of the parent compound (**1**). Also, a purple solution of (**1**) in dmf was found to turn blue on standing at room temperature over a period of 48 h. When compounds (**1**) or (**2**) are refluxed in dmf, a blue solution is obtained from which the complex $[Au(abt)_2(dmf)_2]$ (**3**) is isolated.

Infrared Spectra.—The $\nu_{asym.}$(N–H) and the $\nu_{sym.}$(N–H) bands of the free ligand (Habt) are observed[24] at 3 450 and 3 355 cm^{-1} respectively. In the i.r. spectra of both complexes (**1**) and (**2**) these two bands are located at 3 420 and 3 330 cm^{-1} while these bands are found at 3 430 and 3 320 cm^{-1} in the spectrum of compound (**3**). It is evident from these results that during complexation the $\nu_{asym.}$ and $\nu_{sym.}$ modes of the NH_2 group are shifted to low frequency by 20—30 cm^{-1}. The strong δ(NH_2) band of the free ligand[24] located at 1 610 cm^{-1} is found to be shifted to *ca.* 1 600 cm^{-1} in all three complexes. These results indicate the involvement of the NH_2 group in co-ordination to the metal acceptor centre in all these complexes.

The medium intensity band located at 2 520 cm^{-1} in the i.r. spectrum of the free ligand, assigned[24] as ν(S–H), is absent in the spectra of all the complexes confirming the deprotonation of the thiol group during complexation. This observation along with the absence of any other anion in these complexes confirms the co-ordination of the S^- to the metal ion.

In the far-i.r. spectra of both the compounds (**1**) and (**2**), the medium intensity bands observed in the region 475—450 cm^{-1} may be assigned[25–28] as the ν(Au–N) modes. The ν(Au–N) bands for compound (**3**) are located at 490 and 455 cm^{-1}. The terminal ν(Au–S) appears[29–33] as a weak intensity band around 390 cm^{-1} in the spectra of compounds (**1**) and (**3**) while two weak bands observed at 380 and 355 cm^{-1} in the spectrum of compound (**2**) may be assigned as terminal ν(Au–S). However, we could not locate any ν(Au–S–Au) mode, probably because it is very weak. These results are consistent with the observations on ν(Au–N) and ν(Au–S) described in the literature.[25–33] Thus i.r. data clearly indicate that all the donor sites of the ligands are involved in co-ordination to the metal acceptor centre.

E.S.R. Results.—The powder e.s.r. spectra for all three compounds were recorded at room temperature at *X*-band frequency and these are shown in Figure 1. Compounds (**1**) and (**2**) were dissolved in dmf and the solution e.s.r. spectra recorded at room temperature; they gave almost identical seven-line e.s.r. spectra. The seven-line pattern is presumed to arise from two interacting gold nuclei (100% ^{197}Au, $I = \frac{3}{2}$). Both the spectra were simulated by assuming interaction of the unpaired electron with two gold nuclei and the agreement between experimental and simulated spectra is satisfactory (Figure 2). The purple dmf solution of (**1**), when allowed to stand at room temperature for *ca.* 48 h, turned blue; this also exhibits a seven-line e.s.r. spectrum identical with that previously obtained for (**2**) in dmf solution. Addition of pyridine did not change the e.s.r. spectra even after allowing the solution to stand for one month at room temperature in air. Compound (**3**) gives a four-line e.s.r. spectrum in dmf solution [Figure 2(*d*)] being characteristic of an interacting gold nucleus. The isotropic *g* values for compounds (**1**)—(**3**) are close to 2.003 and the isotropic *A* values are 4.25, 4.0, and 5.5 G respectively.

The most important evidence regarding the nature and structure of the complexes has been obtained from e.s.r. investigations. The strong e.s.r. signal given by powder samples

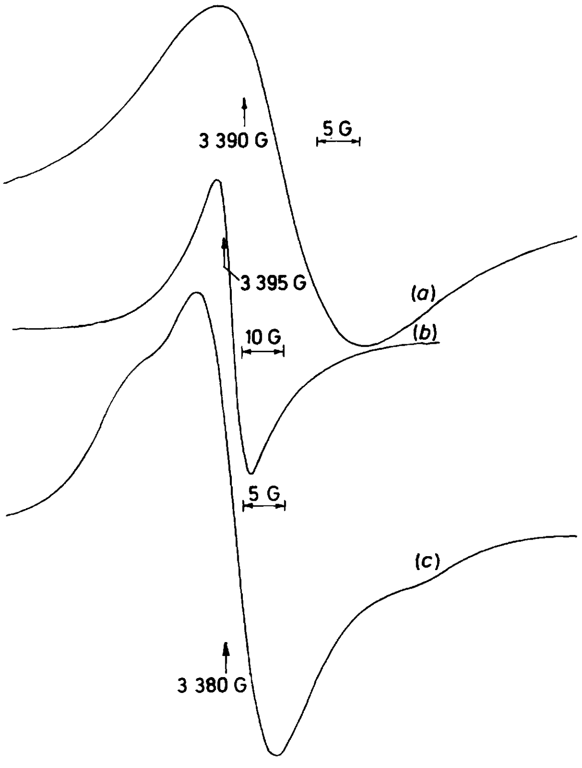

Figure 1. Powder e.s.r. spectra recorded at *X*-band frequency at room temperature: (*a*) compound (**1**), (*b*) (**2**), and (*c*) (**3**)

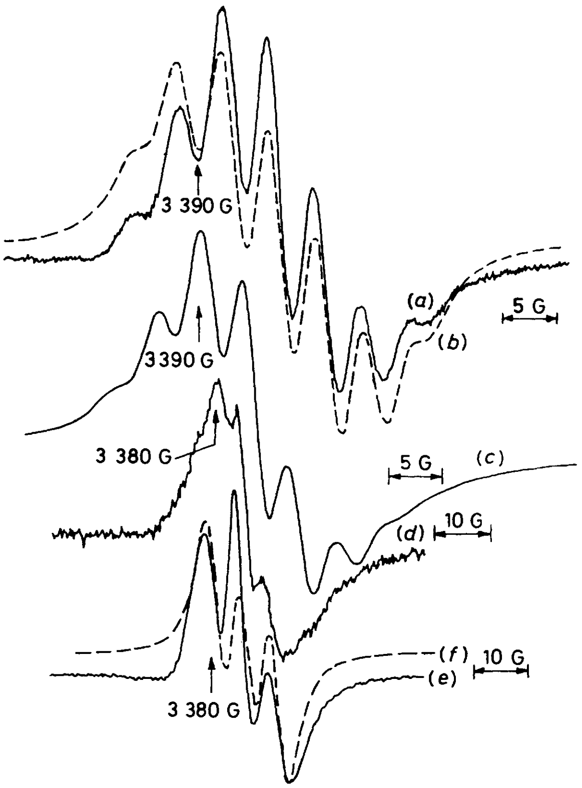

Figure 2. Solution e.s.r. spectra recorded in dmf at *X*-band frequency at room temperature: (*a*) and (*b*), experimental and simulated spectra for compound (**1**); (*c*) and (*d*), experimental spectra for compounds (**2**) and (**3**) respectively; (*e*) and (*f*) experimental and simulated spectra for the CN^- reaction product of compound (**3**)

indicates that they are paramagnetic. This implies either a d^9 or a d^7 low-spin configuration for the metal ion. Considering the stoicheiometry of the complexes it is unlikely that the metal exists in oxidation state +4 in these compounds; also, complexes of gold(IV) are hitherto unreported.

The solution e.s.r. spectra for complexes (**1**) and (**2**) consist of seven-line patterns indicating an interaction with two nuclei with $I = \frac{3}{2}$. This can arise from two gold nuclei (100% ^{197}Au, $I = \frac{3}{2}$). The possibility of hyperfine coupling originating from protons is ruled out since ^{1}H n.m.r. spectra indicate the presence of aromatic protons at usual field (however, the lines are broadened). Had there been radicals localised on the aromatic ring, there should be considerable shifts in the resonance field positions for the aromatic protons. It is, therefore, reasonable to assume that the unpaired electrons interact with two gold nuclei giving a seven-line multiplet. Compound (**3**) gives a four-line multiplet in dmf solution. Here, it is reasonable to suggest that the hyperfine coupling arises from only one interacting gold nucleus.

The conversion of compound (**1**) to (**2**) in methanol at high temperature and in dmf solution on standing at room temperature is of interest. Since these two compounds have almost identical e.s.r. spectra it is logical to propose an intramolecular conversion involving a change from centrosymmetric [(**1**)] to non-centrosymmetric [(**2**)] structure. Since the unpaired electron is confined to the $d_{x^2-y^2}$ orbital of the metal ion, and the conversion does not involve any change in the in-plane bonding, there would be no change in the energy of the h.o.m.o. for these compounds. Consequently they give almost identical e.s.r. results.

These results indicate that while compounds (**1**) and (**2**) are dimeric, compound (**3**) is monomeric in solution. There are many instances of chelating ligands having a thiol group which form thiolato-bridged complexes containing two or more metal ions,[34–41] as is proposed for both compounds (**1**) and (**2**). Since all the donor sites of the ligands are involved in co-ordination, a distorted square-pyramidal environment is expected for each of the two metal ions in the dimeric molecules. On the other hand, the monomeric compound (**3**) should have a distorted octahedral geometry. The proposed structures of the complexes on the basis of the e.s.r. and i.r. spectra and stoicheiometry are shown in Figure 3.

It is important to note that the hyperfine coupling constant observed for these complexes is quite small compared with that for analogous gold(II) complexes with dtc[1] and mnt ligands.[3] We propose that the molecular orbital containing the unpaired electron has major contributions from ligand sulphur orbitals apart from the metal; we will examine this in future reports. The very small hyperfine splitting observed in the e.s.r. spectra of these complexes is strongly indicative of the low metal character of the semi-occupied molecular orbital.[20,42]

Electrochemical Results.—The redox activities of the complexes were examined in acetonitrile solution (0.1 mol dm^{-3} teap) at a platinum electrode using cyclic voltammetry (c.v.); results are given in Table 2. All potentials are referenced to s.c.e. Both compounds (**1**) and (**2**) show two reversible oxidative couples while compound (**3**) shows one reversible oxidative response. An irreversible reductive response is invariably seen in all the complexes. Compounds (**1**) and (**2**) display a broad reductive response at E_{pc} −1.22 and −1.18 V respectively while complex (**3**) exhibits a sharp reductive response at −1.0 V. The ligand (Habt) alone does not show any redox behaviour in the potential range studied. The relevant voltammograms are shown in Figure 4.

The electrochemical behaviour of these complexes is in good

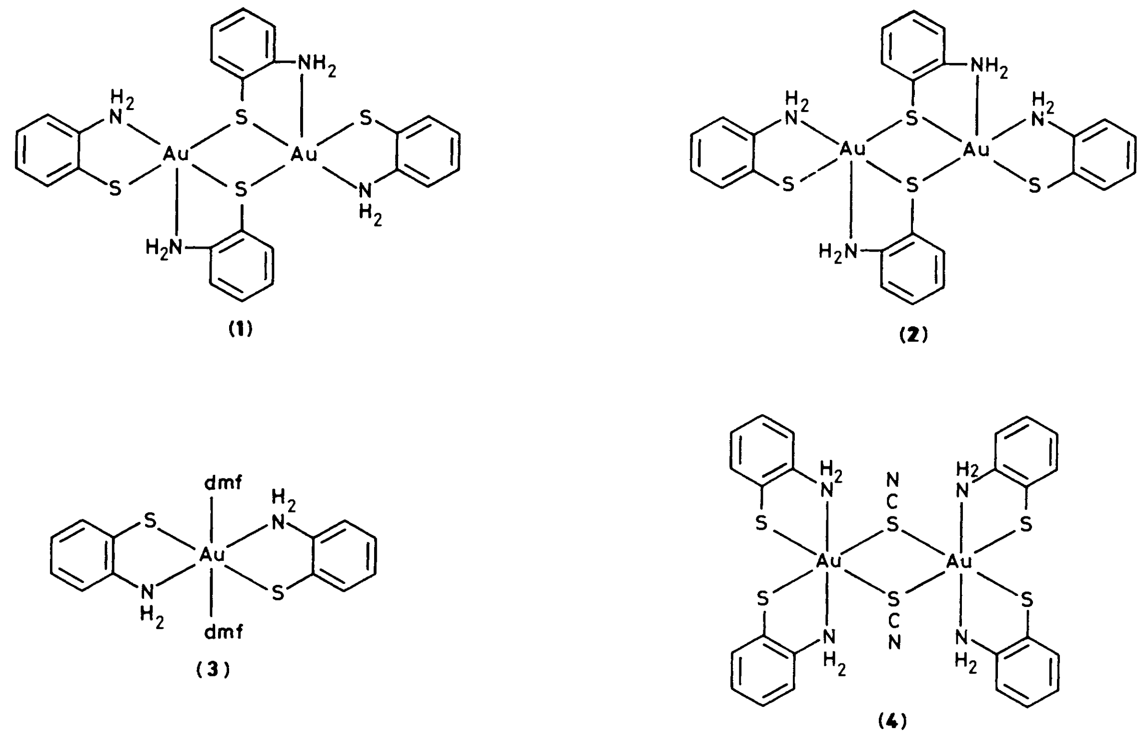

Figure 3. Structures of the compounds (1)—(4) [(4) is the SCN$^-$ reaction product of (3)]

agreement with the proposed structures. Complexes (1) and (2) display two overlapping but distinct (Figure 4) $Au^{III/II}$ couples (below). The presence of significant ligand-mediated metal–metal interaction [$\mu_{eff.}$ = 2.66 and 2.60 for (1) and (2) respectively] in each case is thus demonstrated. Detailed temperature-dependent susceptibility measurements to determine the nature and magnitude of interaction are in progress.

$$[\{Au(abt)_2\}_2]^+ + e^- \rightleftharpoons [\{Au(abt)_2\}_2]$$

$$[\{Au(abt)_2\}_2]^{2+} + e^- \rightleftharpoons [\{Au(abt)_2\}_2]^+$$

Compounds (1) and (2) are an isomeric pair; the small difference in peak potentials is evidence of this. At a relatively slow scan rate (v = 50 mV s^{-1}), the current heights for both couples have the required value for a one-electron transfer. The pair of couples is diagnostic of binuclear species which is in line with the e.s.r. results. In (1) and (2), the difference of $E_{298}(2)$ and $E_{298}(1)$ is almost constant (*ca.* 300 mV) which is a general characteristic of binuclear species.

The mononuclear complex (3) exhibits a reversible (peak to peak separation, ΔE_p, in c.v. 60 mV at scan rates 50, 100, 200, and 300 mV s^{-1}) one-electron oxidative response with well-defined anodic and cathodic peaks of equal height corresponding to the couple below. On multiple scan reversal, the nature of the waves retains the original shapes indicating high reversibility of the electrode reaction [Figure 4 (*c*)]. The nearly Nernstian behaviour and reversible nature of this response are good indications that the gross stereochemistry in both oxidation states is the same though the electronic state of the metal ion changes (Au^{II}, d^9; Au^{III}, d^8).

$$[Au(abt)_2(dmf)_2]^+ + e^- \rightleftharpoons [Au(abt)_2(dmf)_2]$$

The irreversible cathodic response around −1.0 V in this series of complexes is presumably due to metal-centred reduction, $Au^{II} \rightarrow Au^{I}$. The corresponding anodic response is not observed indicating slow electron-transfer kinetics[43] for this process. The reduced species is unstable on the voltammetric time-scale studied (up to 500 mV s^{-1}) and does not survive to undergo reoxidation. However, the reductive response for both the dimers (1) and (2) is quite broad which may be due to two successive overlapping reductions of the two different moieties.

Table 2. Cyclic voltammetric data[a] at 298 K, magnetic moments,[b] and e.s.r. data[c]

	E^0_{298}/V (ΔE_p/mV)				
Compound	$E^0_{298}(1)$	$E^0_{298}(2)$	$\mu_{eff.}$	g_{iso}	A_{iso}/G
(1)	0.26 (80)	0.59 (100)	2.66	2.0033	4.25
(2)	0.32 (80)	0.68 (80)	2.60	2.0029	4.00
(3)	0.65 (60)		1.76	2.0032	5.50

[a] Solvent, CH_3CN; supporting electrolyte, teap (0.1 mol dm^{-3}); solute concentration, *ca.* 0.5 × 10^{-4} mol dm^{-3}; platinum working electrode, s.c.e. reference electrode. $E^0_{298} = 0.5\,(E_{pa} + E_{pc})$ where E_{pa} and E_{pc} are anodic and cathodic peak potentials respectively. [b] At 300 K. [c] In dmf at room temperature.

Electronic Structures and Spectral Properties.—The low symmetry of the molecules (1) and (2) does not provide a suitable co-ordinate system for the purpose of interpretation of optical spectra. Though the molecules are dimeric, they can be considered as two weakly interacting five-co-ordinate monomers for the purpose of interpreting the optical spectra. Hence, we have considered that each gold ion has a distorted square-pyramidal environment in which the co-ordinate axes are chosen roughly along the bond axes as shown in Figure 5(*a*). Since gold is a 5*d* element, the ligand-field splitting of *d* orbitals is much greater than that in copper. The order of *d*-orbital energies for square-planar $[AuX_4]^-$ (X = halide) is found[44—47] to be $d_{x^2-y^2} > d_{xy} > d_{xz}, d_{yz} > d_{z^2}$ and except for $d_{x^2-y^2}$ all

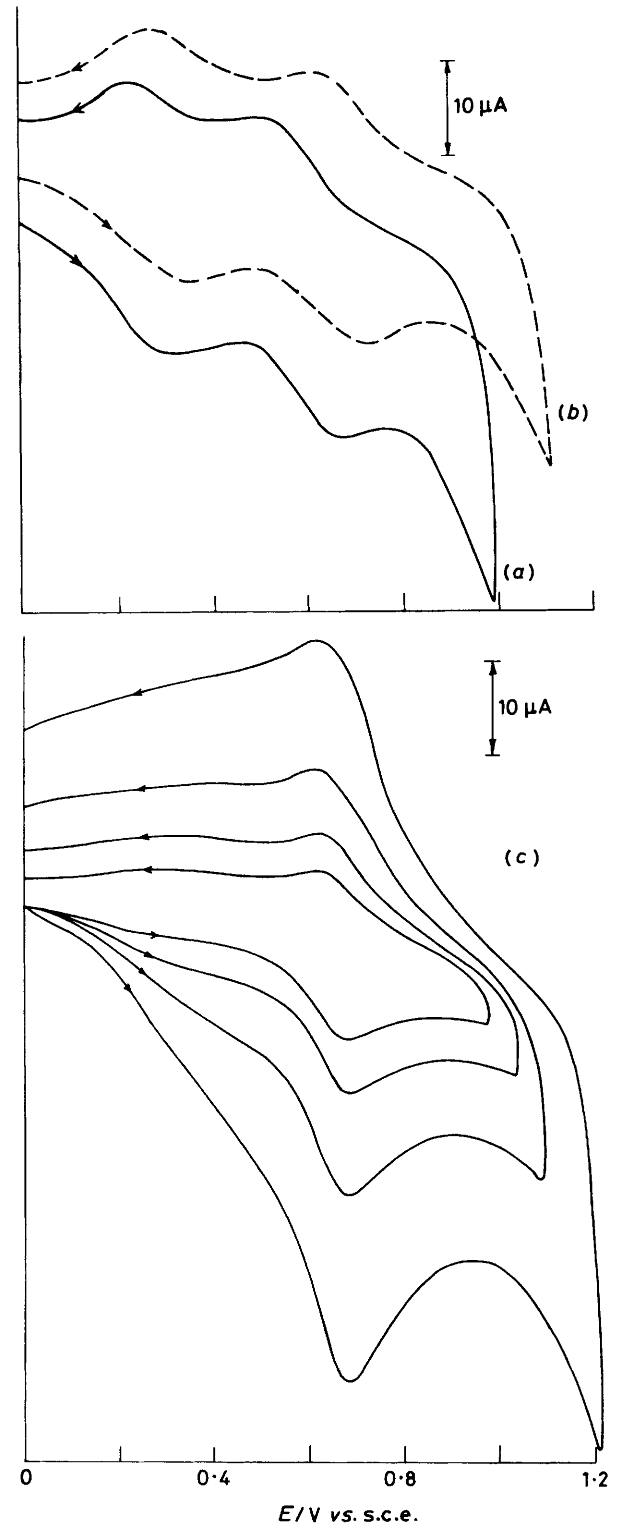

Figure 4. Cyclic voltammograms of: (*a*) compound (**1**), and (*b*) (**2**), in CH_3CN (0.1 mol dm^{-3} teap), scan rate 50 mV s^{-1}; (*c*) (**3**), in CH_3CN (0.1 mol dm^{-3} teap), scan rates 50, 100, 200, and 300 mV s^{-1}. Solute concentration *ca.* 0.5 × 10^{-4} mol dm^{-3}

are doubly occupied in the ground state (Au^{III}, 5d^8). A d^9 Au^{II} complex would be strongly distorted tetragonally and the ninth electron would occupy the highly unfavourable $d_{x^2-y^2}$ orbital, which will be raised correspondingly higher in energy.

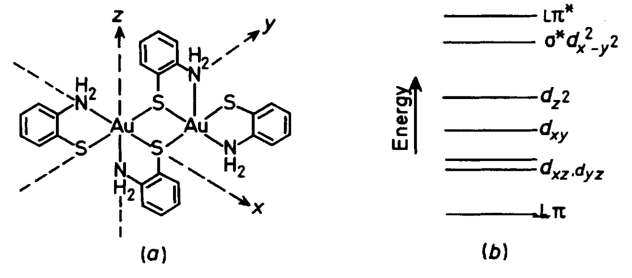

Figure 5. (*a*) Co-ordinate system for compound (**1**) for designation of molecular orbitals. (*b*) Qualitative energy level diagram for (**1**)

The d-orbital energy levels for a Au^{II} ion in tetragonal field are shown[48] to be in the order $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{xz}, d_{yz}$. But the ordering of the relative energies of d_{z^2} and d_{xy} for the present set of complexes is probably a matter of debate. Electronic and e.s.r. (see later) spectral studies reveal the fact that there is significant interaction in the fifth and/or sixth co-ordination positions of these complexes with solvents or other additional ligands. Since the additional ligand approaches along the z axis of the complex, the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition should be significantly affected. The lowest energy band of compound (**1**) at 14 300 cm^{-1} in dichloromethane is found to be shifted to 13 700 cm^{-1} when the spectrum is recorded in dmf and this band is not observed at all when CN^- is added to this dmf solution. On this basis, the relative energies of d orbitals is proposed to be in the order $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{yz} \sim d_{xz}$.

A qualitative molecular orbital energy level diagram indicating only the important levels is shown in Figure 5(*b*). The orbitals Lπ and Lπ* are essentially ligand levels. In the electronic ground state of the metal complexes under discussion here, Lπ will always be filled with electrons and Lπ* will generally be empty. The Lπ–Lπ* separation has been determined by the position of the first intraligand (Lπ → Lπ*) band in a complex. The $d_{x^2-y^2}$ orbital should be the highest occupied molecular orbital (h.o.m.o.) in the electronic ground state of the complexes. The same co-ordinate system is chosen for the monomeric complex (**3**) also. On the basis of these considerations, one would expect a maximum of four d–d transitions for these complexes, which have been observed experimentally. The single most significant aspect of the optical spectra is the observation of ligand-field transitions *not* masked by the intraligand charge-transfer (c.t.) bands which usually occurs in most other Au^{II} complexes. Reasonable transition assignments are given in Table 3. It should be noted here that though the lowest energy band for $[Au(S_4C_4)(CN)_4]^{2-}$ is observed[3] at 13 750 cm^{-1} (ε 368 dm^3 mol^{-1} cm^{-1}), a direct comparison is not possible since the electronic structure for this dianionic dithiolene complex is quite different from those of the non-planar complexes under investigation. However, tetragonal copper(II) and silver(II) complexes exhibit similar types of spectral features.[48,49]

It has been observed that the lowest energy band at 15 875 cm^{-1} (Table 3) arising from the transition $d_{z^2} \longrightarrow d_{x^2-y^2}$ for compound (**3**) has much higher energy than that obtained for the same transition (14 300 cm^{-1}) of compounds (**1**) and (**2**) which have a square-pyramidal ligand environment around each metal ion. This indicates that the interaction of the two axial ligands (*i.e.*, two dmf molecules along z axis) in compound (**3**) is much weaker than the interaction of the fifth ligand (NH_2 group) along the z axis in compounds (**1**) or (**2**) and consequently the former has a much higher energy gap between $d_{x^2-y^2}$ and d_{z^2} than that for the latter two compounds.

The bands in the u.v. region, which are located in positions similar to those in the free ligand (Habt) spectrum may be

Table 3. Electronic spectral band positions (cm^{-1}) and assignments for the complexes and the ligand

Compound[a]	Band positions (cm^{-1}) (ε/dm^3 mol^{-1} cm^{-1})	Assignments
(**1**)[b]	14 300 (1 674)	$d_{z^2} \longrightarrow d_{x^2-y^2}$
	16 650 (6 520)	$d_{xy} \longrightarrow d_{x^2-y^2}$
	18 350 (16 390)	$d_{yz} \longrightarrow d_{x^2-y^2}$
	19 400 (16 213)	$d_{xz} \longrightarrow d_{x^2-y^2}$
	38 450 (52 871)	$\mathrm{M} \longrightarrow \mathrm{L}\pi^*$
	30 300 (23 792)	$\mathrm{L}\pi \longrightarrow \mathrm{L}\pi^*$
	34 500 (40 314)	$\mathrm{L}\pi \longrightarrow \mathrm{L}\pi^*$
	43 500 (92 525)	$\mathrm{L}\pi \longrightarrow \mathrm{L}\pi^*$
(**2**)	14 300 (8 072)	$d_{z^2} \longrightarrow d_{x^2-y^2}$
	16 400 (13 660)	$d_{xy} \longrightarrow d_{x^2-y^2}$
	17 250 (14 488)	$d_{yz} \longrightarrow d_{x^2-y^2}$
	18 850 (12 625)	$d_{xz} \longrightarrow d_{x^2-y^2}$
	25 000 (10 762)	$\mathrm{M} \longrightarrow \mathrm{L}\pi^*$
	37 050 (46 914)	$\mathrm{M} \longrightarrow \mathrm{L}\pi^*$
	29 400 (20 697)	$\mathrm{L}\pi \longrightarrow \mathrm{L}\pi^*$
	34 500 (40 705)	$\mathrm{L}\pi \longrightarrow \mathrm{L}\pi^*$
	45 450 (82 790)	$\mathrm{L}\pi \longrightarrow \mathrm{L}\pi^*$
(**3**)	15 875 (9 015)	$d_{z^2} \longrightarrow d_{x^2-y^2}$
	17 550 (13 208)	$d_{xy} \longrightarrow d_{x^2-y^2}$
	18 850 (11 321)	$d_{xz},d_{yz} \longrightarrow d_{x^2-y^2}$
	29 400 (20 092)	$\mathrm{L}\pi \longrightarrow \mathrm{L}\pi^*$
	33 350 (36 167)	$\mathrm{L}\pi \longrightarrow \mathrm{L}\pi^*$
o-$NH_2C_6H_4SH$ (pure ligand)	29 400 (813)	$\mathrm{L}\pi \longrightarrow \mathrm{L}\pi^*$
	33 900 (2 635)	$\mathrm{L}\pi \longrightarrow \mathrm{L}\pi^*$
	43 100 (8 514)	$\mathrm{L}\pi \longrightarrow \mathrm{L}\pi^*$

[a] Solvents: (**1**) in CH_2Cl_2, (**2**) in CH_3OH, (**3**) in dmf, and free ligand (Habt, *o*-$NH_2C_6H_4SH$) in CH_2Cl_2. [b] Identical optical spectrum in CH_3OH.

assigned as intraligand transitions. However, in the absence of a complete molecular orbital picture of the relevant complexes, exact interpretations of these bands are difficult at this stage.

Reactivity of the Complexes.—The reactions of the compounds (**1**), (**2**), and (**3**) with monodentate ligands like SCN^-, $SeCN^-$, NCO^-, and CN^- have been carried out in dmf solutions and their e.s.r. spectra have been studied. The compounds (**1**) and (**2**) readily react with SCN^-, $SeCN^-$, and NCO^- forming insoluble compounds, probably polymeric, which give broad e.s.r. signals in the powder state. However, reacting CN^- with (**1**) produces a highly soluble compound which gives a three-line e.s.r. spectrum in dmf solution. It is probable that the sulphur bridge is split when the compound reacts with CN^- producing a five-co-ordinate compound, $[Au(abt)_2(CN)]^-$, which is highly soluble. The unpaired electron interacts with the nitrogen nucleus ($I = 1$) of the incoming ligand (CN^-) producing a three-line e.s.r. spectrum because of a possible d_{z^2} ground state (created by the strong-field ligand CN^- in the axial position), also supported by entirely different optical features (band positions in the visible region are 18 100, 18 860, and 20 000 cm^{-1} respectively).

On the other hand, reaction of compound (**3**) with SCN^-, $SeCN^-$, NCO^-, and CN^- produces highly soluble compounds in each case. The dmf solutions of these reaction products, except that with SCN^-, give three-line e.s.r. spectra. The reaction products may be five-co-ordinate species where the unpaired electron interacts with the nitrogen nucleus ($I = 1$) of the incoming ligand giving three-line spectra in all the cases. The e.s.r. spectra of the product were simulated assuming that the unpaired electron is interacting with the nitrogen nucleus of the CN^- ligand and the agreement between experimental and simulated spectra is satisfactory [Figure 2(*e*) and (*f*)]. However with SCN^-, compound (**3**) reacts differently; the blue dmf solution gives a seven-line e.s.r. spectrum which originates from the interaction of the unpaired electron with two gold nuclei ($I = \frac{3}{2}$). This result, in contrast to those for CN^- and $SeCN^-$ is surprising. It is possible that a dimer $[\{Au(abt)_2(SCN)\}_2]^{2-}$ (**4**) is formed with bridging through S of SCN^-; a probable structure is shown in Figure 3.

All these reaction products are quite stable in solution in air, which is evident from the unchanged e.s.r. spectral profiles even if the solutions are allowed to stand at room temperature for a few days. The splitting due to interaction with N, whenever obtained (*e.g.*, CN^-, 5.5 G) is small, possibly indicating delocalisation of the unpaired electron over the whole complex with a low density at the nitrogen site compared with that of nitrogenous ligands in a d^9 system where $A_{\text{iso}} \approx 14$ G.

Conclusions

A careful analysis of the i.r. spectra of the complexes and the ligand indicates the co-ordination of all the donor sites of the ligands in the complexes. Crucial evidence regarding the nature of these complexes was obtained from their e.s.r. spectra. The appearance of an almost equally intense four-line pattern for the monomeric complex (**3**) in solution and a seven-line pattern with an intensity ratio 1:2:3:4:3:2:1 for the dimeric complexes (**1**) and (**2**), also in solution, is undoubtedly an indication of the interaction of the unpaired electron with the gold nucleus. When these complexes are reacted with chosen ligands containing nitrogen donors, the solution spectrum changes from a four-line/seven-line pattern to a three-line pattern with an intensity ratio 1:1:1. Such a change is thought to arise due to the interaction of the unpaired electron with the nitrogen nucleus of the incoming ligand. The interaction with the incoming ligand appears to lead to a mixing of the $d_{x^2-y^2}$ and d_{z^2} levels. The electron density is perhaps transferred significantly to the incoming ligand. However, no hyperfine structure originating from the interaction with the nitrogens of the ligand(s) abt is observed in the parent complexes (**1**), (**2**), and (**3**). Several attempts to prepare single crystals of any of these complexes failed, so all investigations were confined to powders and solutions of the complexes. From these investigations it may be concluded that in this series of complexes and their reaction products, the metal ion has a pronounced tendency to achieve higher co-ordination (five or six) which is rare in gold chemistry[50] and scarce for gold(II).

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