Electronic and Circular Dichroism Spectra of Gold(I) Complexes having Sulphur- and Phosphorus-containing Ligands

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The electronic and circular dichroism spectra of some gold(I) complexes of the type [AuX(PR_3)] (R = Ph or Et; X = Cl, L-cysteinate, D-penicillaminate, or thiomalate), together with gold(I) complexes of the sulphur ligands alone, have been examined. Between 33 000 and 50 000 cm^{-1} the spectra are complex but appear to be dominated by transitions arising from molecular orbitals located mainly on the PR_3 and gold moieties. At lower energies, spectra due to sulphur-to-gold transitions are observed which appear to form a consistent pattern characteristic of this type of bond.

GOLD(I) forms a range of reputedly linear complexes with ' soft ' ligands containing sulphur or phosphorus as donor atoms but comparatively little has been done to determine the nature of their electronic spectra. Some complexes of this type are used in the treatment of rheumatoid arthritis and there has recently been renewed interest in the differences in therapeutic activity between different complexes. As part of a study of the mechanism of action of these drugs [1-4] we required an understanding of the electronic spectra of linear gold complexes so that the spectra might be used as probes to follow solution reactions involving these or related complexes.

The selected complexes are based on the thiomalato-(2—)aurate(I) ion, which is widely used as a drug,[5] chloro(triethylphosphine)gold(I), which is claimed to have therapeutic effects in animal studies,[6] and on complexes containing cysteine and penicillamine as ligands. The actual selection of complexes is determined to some extent by the chemistry of the system. Triphenylphosphinegold complexes with sulphur ligands, for example, form stable monomeric molecules in solution more readily than gold complexes of the sulphur-containing ligands themselves.

There are neither sufficient comparable studies to the present one nor an adequately developed and available theory to allow a rigorous interpretation of the results presented here. We use a molecular-orbital (m.o.) approach, which has already been applied to complexes of Mo^V and Mo^{VI} (ref. 7) and Au^{III} (ref. 4) with substantial agreement between theory and experiment, to obtain a plausible energy diagram which is in agreement with the spectroscopic observations. Circular dichroism (c.d.) measurements for those complexes which contain optically active ligands help to confirm this analysis.

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[1] H. Kamel, D. H. Brown, J. M. Ottaway, and W. E. Smith, *Analyst*, 1976, **101**, 790.

[2] H. Kamel, D. H. Brown, J. M. Ottaway, and W. E. Smith, *Arthritis and Rheumatism*, 1976, **19**, 1386.

[3] H. Kamel, D. H. Brown, J. M. Ottaway, and W. E. Smith, *Talanta*, 1977, **24**, 309.

[4] D. H. Brown and W. E. Smith, *J.C.S. Dalton*, 1976, 848.

[5] D. T. Walz, M. J. DiMartino, and B. M. Sutton, ' Medicinal Chemistry,' vol 13, eds. R. A. Scherrer and M. W. Whitehouse, Academic Press, New York, 1974.

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[7] D. H. Brown, P. G. Perkins, and J. J. P. Stewart, *J.C.S. Dalton*, 1972, 1105.

EXPERIMENTAL

The complexes were prepared by previously described methods [8-10] and in each case the analysis was satisfactory.

Electronic spectra were recorded on a Pye Unicam SP 1800 spectrophotometer by transmission in solution and by reflectance in the solid state. Circular dichroism (c.d.) spectra were measured by transmission in solution and by transmission through KCl discs for the solid. A number of discs containing different amounts of the optically active material were prepared in each case, and the most suitable were selected for study after an assessment of the degree of dispersion of the material and an initial spectrum. To check for strain effects, a number of discs were rotated through 30, 60, and 90° and the spectrum recorded after each rotation. There was some variation in the absolute values of $\Delta\varepsilon$ but no appreciable variation in the peak position or relative $\Delta\varepsilon$ values. The solid-state spectra were less well resolved than those in solution, which are therefore reported in detail. However, in the case of the cysteinatogold(I) complex, which is more strongly optically active, the solid-state result is given with an arbitrary $\Delta\varepsilon$ scale.

The c.d. spectrometer was constructed in this laboratory. It consists of a 150-W xenon lamp, Spex 1870 monochromator, Glan Taylor prism, and Morvue photoelastic modulator, and a photomultiplier and lock-in amplifier detection system together with appropriate optics. The machine was calibrated using a number of standards and was regularly checked against a camphorsulphonic acid standard. Wavelength calibration was within 1 nm at all the points checked with a mercury lamp, and repeat scans with the camphorsulphonic acid standard were within 5% in $\Delta\varepsilon$ at 290 nm.

RESULTS AND DISCUSSION

Calculations.—The SCF MO method was employed to calculate ground-state properties. Its method of parametrisation has been described previously.[7] The orbitals considered were the valence orbitals, namely *s*, *p*, and *d* for gold, phosphorus, and sulphur, *s* and *p* for carbon, oxygen, and nitrogen, and *s* for hydrogen. The diagonal Hamiltonian-matrix elements for gold were taken as: I_{6s}, 9.22; I_{6p}, 4.35; and I_{5d}, 11.11 eV.*

In order to reduce the size of the calculation as far as possible, detailed calculations were carried out for the hypothetical molecule [Au(PH$_3$){SCH$_2$CH(NH$_2$)-CO$_2$H}]. The dimensions of cysteine are those described previously for the molybdenum complex.[7] Sulphur–gold and phosphorus–gold distances were taken as 2.26 and 2.30 Å, respectively. Table 1 lists the energy levels of the five filled orbitals of highest energy and the five virtual orbitals of lowest energy. The filled orbitals lie mainly on the sulphur atom and the virtual ones on the gold atom. The first filled molecular orbitals containing a significant amount of phosphorus atomic orbitals lie significantly below filled m.o.s containing sulphur orbitals, and the first virtual orbitals with significant phosphorus content lie slightly above the lowest-energy virtual orbitals. Thus, we predict that the lowest-energy transitions are associated with the gold–sulphur system. This is consistent with the results of Figures 2—5. The orbital occupancies of gold, phosphorus, and sulphur are listed in Table 2. For the isolated gold(I) ion, the formal electronic configuration is $(6s)^0(6p)^0(5d)^{10}$ and the partial occupancy of the 6*s* and 6*p* orbital sets reflects the orbital mixing in the bonding of the ligand to the gold atom. The resulting, almost negligible, charge of −0.02 on gold suggests that the bonding between gold, sulphur, and phosphorus is mainly covalent with little ionic character, as would be expected for a relatively large ' soft ' metal ion.

TABLE 1

Energies (eV) and character of the highest bonding and lowest virtual orbitals

n	E_n	Character
1	−6.88	*p* on S
2	−6.66	delocalised over CO$_2$H
3	−5.49	*p* on S
4	−4.20	*p* on S
5	−2.69	*s* on Au, *p* on S
−1	4.33	*s* on Au
−2	5.44	*p* on Au
−3	5.45	*p* on Au
−4	6.27	*p* on Au
−5	6.99	*p* on carbon of CO$_2$H groups

TABLE 2

Orbital occupancies

	ns	*np*	*nd*
Au	1.17	0.23	9.62
P	1.03	4.33	0.03
S	1.32	4.67	0.25

Configuration-interaction calculations were carried out to establish the probable nature and intensity of the transitions. The results, using 5×5 and 20×20 matrices, are not completely consistent in energy and so this calculation and the one above were combined to give a qualitative diagram (Figure 1) which forms the basis for a reasonable interpretation of the lower-energy transitions (up to *ca.* 35 000 cm^{-1}). Higher-energy transitions are between more complex m.o.s and so it is necessary to rely solely on experimental observations for an interpretation.

Intensities of Transitions up to 35 000 cm^{-1}.—The exact geometry of these complexes, particularly in solution, is difficult to define. Rotation about, and small distortion away from, the line of centres of the atoms may require only slight energy changes and the effect of solvent or packing forces round the molecule may be very significant. Further, the nature of the symmetry ensures that each m.o. can contain contributions from many atomic orbitals and the calculation results show that the m.o.s contain minor but significant contributions from orbitals on atoms which are not collinear with the P–Au–S bond system. Intensities more than energies are likely to be affected significantly by these factors and considerable variation in intensity of

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* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

[8] N. J. DeStefano and J. L. Burmeister, *Inorg. Chem.*, 1971, **10**, 998.

[9] F. G. Mann, A. F. Wells, and D. Purdie, *J. Chem. Soc.*, 1937, 1828.

[10] G. E. Coates, C. Kowala, and J. M. Swan, *Austral. J. Chem.*, 1966, **19**, 539.

particular bands in the spectra even of closely related complexes is to be expected and is found. The above arguments also suggest that rigorous selection rules based on symmetry arguments are unlikely to be applicable to linear complexes of this type.

Calculated transition probabilities indicate that the lowest-energy transition S(p_x)S(p_z)Au(s)$\rightarrow$Au(s)Au(p_x)S(p_x) will be more intense (transition probability 0.32) than the transitions S(p_y)$\rightarrow$Au(s)Au(p_x)S(p_x) and $CO_2H$$\rightarrow$Au($s$)Au($p_x$)S($p_x$) (calculated transition probability 0.02 and 0.04, respectively). The m.o.s are expressed throughout in terms of the largest contributing atomic orbitals in decreasing order of contribution. The above results are physically reasonable; the lowest-energy transition involves orbitals which are substantially in the same plane, are spread between the sulphur and the gold, and contain both s and p orbitals, so that the transition can be regarded as at least partially allowed. The transition from S(p_y) is likely to be weak, since the ground-state wavefunction is orthogonal to the plane of the excited-state one. However, this transition will be rotationally allowed, and therefore its relative intensity may be much greater and it may well appear in the c.d. spectra. There is unlikely to be much overlap between ground and excited states for transitions between a m.o. on the CO_2H group and one mainly on gold. Similar arguments apply to the next highest-energy transition S(p_x)S(p_z)Au(s)$\rightarrow$Au(p_x)Au(p_z) (calculated transition probability 0.41).

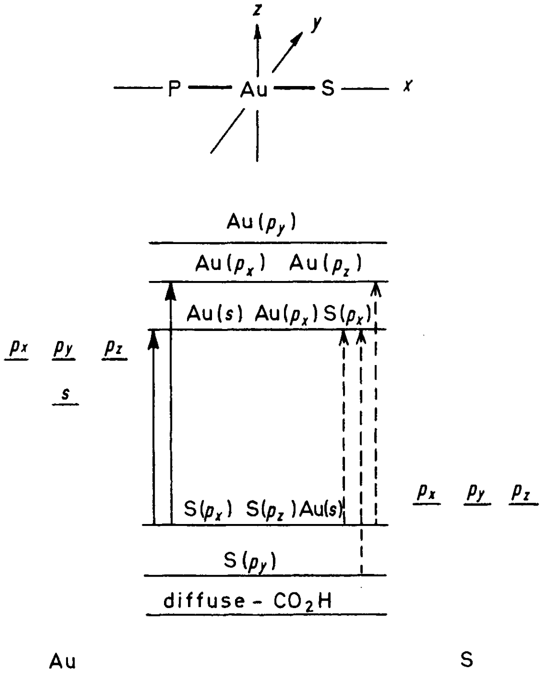

FIGURE 1 Molecular-orbital diagram for [AuX(PR_3)] complexes (X = cysteinato, penicillaminato, or thiomalato; R = Ph or Et). Solid arrows are transitions expected to be intense in the u.v.–visible spectra, dotted arrows are allowed intense transitions in c.d. spectra. The molecular orbitals are labelled in terms of the main contributing atomic orbitals in order of decreasing contribution

Circular dichroism intensities also require a consideration of the magnetic-dipole part of the intensity expression [11] and this should certainly be true with the non-rigorous nature of the u.v.–visible selection rules. Thus, the two transitions allowed under u.v.–visible rules and the transition S(p_y)$\rightarrow$Au(s)Au(p_x)S(p_x) contain suitable orbitals to give some magnetic-dipole intensity and therefore this latter band may well appear in the c.d. spectra, in a relatively more intense form than in the u.v.–visible spectra.

Gold-Phosphorus Spectra.—Solid and solution spectra of both [AuCl(PR_3)] (R = Ph or Et) are in reasonable agreement in each case and so we consider the better-resolved solution results to be indicative of the spectra of these molecules. In the case of the triphenylphosphine complex, the chloro- and nitrato-derivative were prepared and the spectra compared. Except at higher concentrations, where nitrate bands could be seen, there was no difference between the spectra. Thus, the possibility of chloride-to-gold transitions with significant intensity in this energy region can be ruled out.

The spectra of arylphosphines have previously been assigned on the basis of three possible bands: the $\pi\rightarrow\pi^*$ transitions of benzene extended to allow a phosphorus contribution to the orbitals and which are equivalent to the ${}^1A_{1g}\rightarrow{}^1B_{1u}$ (K band) and ${}^1A_{1g}\rightarrow{}^1B_{2u}$ (B band) of benzene, and a band due to an $n\rightarrow\pi^*$ transition between the lone pair on the phosphorus and the π system (R band). In PPh_3 the usual assignment of the bands observed is to the K and R bands, with the latter being intense due to s and p mixing on the phosphorus to give a transition with some s-to-p character. In PPh_3O, on the other hand, the R band is shifted and the weaker B band, which often exhibits fine structure similar to the well studied benzene vibronic structure, can be seen.[12,13]

In the spectrum of [AuCl(PPh_3)] (Figure 2) the situation appears to be similar. The R band is shifted hypsochromically to reveal the weaker, structured B band. Raman spectra of this complex and of the silver analogue give a strong A_{1g} band at $1\,000 \pm 2$ cm^{-1}. The interval in the fine structure of the B band is *ca.* 970 cm^{-1}. This compares with 995 and 925 cm^{-1} for the ground and excited states of benzene. Therefore the B band appears to be clearly assigned. The R band shifts to higher energies, as is the case in spectra of phosphine oxide. Thus, the most obvious effect of gold on the spectra of PPh_3 is to act as an electron-withdrawing agent.

The spectrum of [AuCl(PEt_3)] is much weaker. Triethylphosphine has one band, presumably an $n\rightarrow\pi$ transition of the ethyl groups, but triethylphosphine oxide does show a second band at 260 nm. This is probably due to a transition from the phosphorus lone

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[11] R. D. Gillard, *Progr. Inorg. Chem.*, 1966, **7**, 215.

[12] B. I. Stepanov, A. I. Bokarov, and B. A. Korolev, *Teor. i eksp. Khim.*, 1968, **4**, 354.

[13] C. N. R. Rao, J. Ramachandran, and A. Balasubramanian, *Canad. J. Chem.*, 1961, **39**, 171.

pair to a much less developed phosphorus–oxygen π system analogous to the *R* band of PPh_3. Similar behaviour is found for the gold complex and so we assign the two peaks to an $n \rightarrow \pi^*$ transition on the ethyl groups (220 nm) and to an $n \rightarrow \pi^*$ transition on P and P–Au orbitals (260 nm).

Phosphorus–Gold–Sulphur Complexes.—Both u.v.–visible and, where appropriate, c.d. spectra were obtained in the solid and solution states for these complexes. There is good agreement between solid and solution spectra but the latter (Figures 3 and 4) are better resolved and are reported in detail. A system of bands appears at lower energy than in the previous case and in agreement with the calculated results is assigned as mainly due to sulphur-to-gold transitions. The complex $[Au(PEt_3)\{SCH_2CH(NH_2)CO_2H\}]$ is not stable for more than a few hours and if the solution is left to stand for 2 d, a precipitate of $[Au\{SCH_2CH(NH_2)CO_2H\}]$ appears. The other spectra are stable over a period of days. Circular dichroism spectra below 290 nm are less accurate due to light-level problems associated with the strongly absorbing solutions. Those below 300 nm were run using solutions having absorbances between 0.5 and 1.5 and at similar light levels to the calibration standard and thus are reasonably accurate.

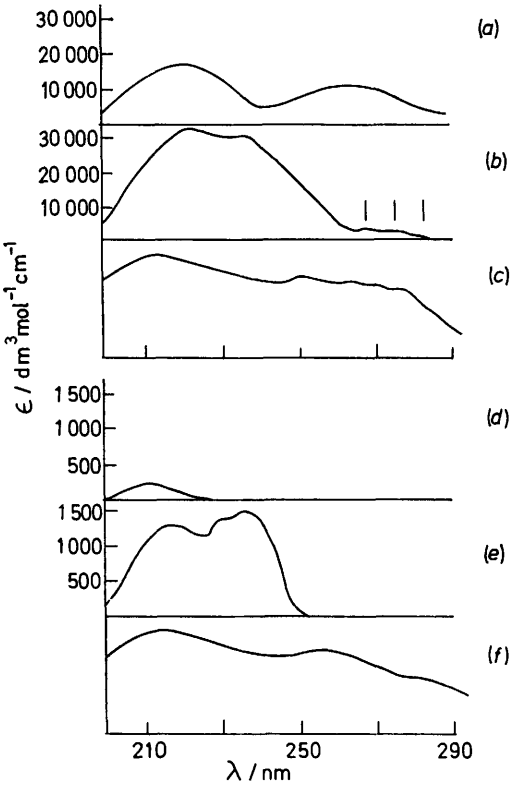

FIGURE 2 U.v.–visible spectra in the solid (reflectance) and solution states: (*a*) PPh_3 (solution); (*b*) and (*c*) $[AuCl(PPh_3)]$ in solution and solid; (*d*) PEt_3 (solution); (*e*) and (*f*) $[AuCl(PEt_3)]$ in solution and solid

In the high-energy region (below 280 nm) the spectra of complexes containing PPh_3 are of lower overall intensity than $[AuCl(PPh_3)]$, presumably due to a decreased electron density in the π system caused by the sulphur ligand. The possibility of a transition which

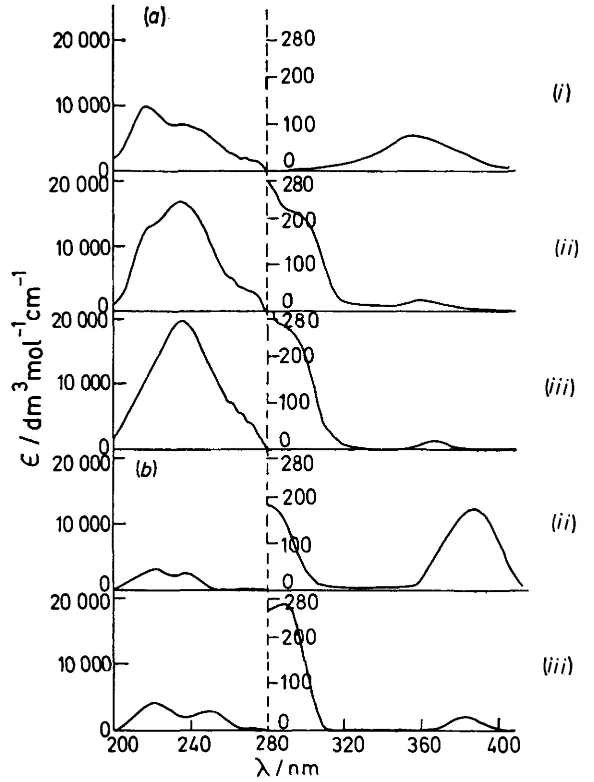

FIGURE 3 U.v.–visible spectra in solution of (*a*) $[AuX(PPh_3)]$, (*b*) $[AuX(PEt_3)]$ where X = thiomalate (*i*), cysteinate (*ii*), or penicillaminate (*iii*)

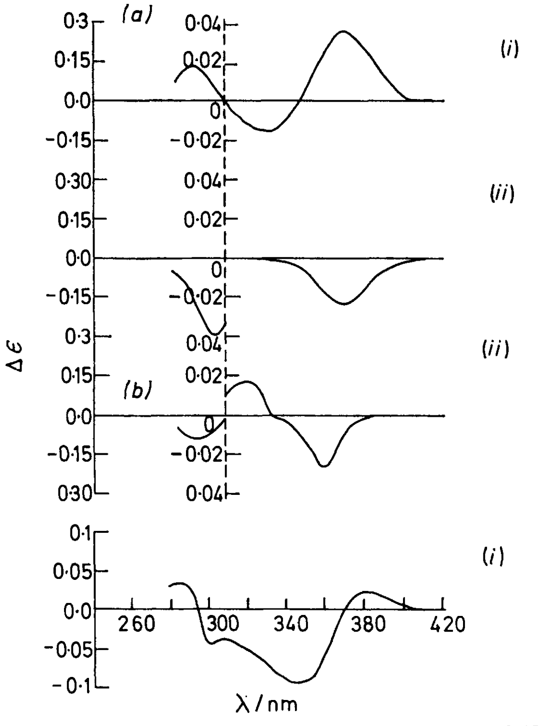

FIGURE 4 C.d. spectra in solution of (*a*) $[AuX(PPh_3)]$, (*b*) $[AuX(PEt_3)]$. X = Cysteinate (*i*) or penicillaminate (*ii*)

may be assigned solely to gold–sulphur or to the sulphur-containing ligand is unlikely, in view of the very much lower intensity of the spectra in the same energy region for triethylphosphine complexes of the same ligands. Levels at about the same energies as the *K*, *R*, and *B* bands are again present, together with the appropriate fine structure on the *B* band. The actual shape of the spectra is variable. The chemistry of the sulphydryl group of the three sulphur ligands is significantly different and so the spectroscopic differences are probably due to the different σ- and π-bonding characteristics of the ligands producing different electron densities in the gold–phosphorus bonds.

This argument is borne out by the triethylphosphine complexes. In this case the spectra are of comparable intensity to the spectrum of $[AuCl(PEt_3)]$ and are similar in shape. Thus, similar assignments are reasonable and the more localised Au–P system is less affected by the sulphur ligand than the more extensive π system in the triphenylphosphine complexes.

In the lower-energy region, in which the spectra are due to sulphur-to-gold transitions of lower intensity, the u.v.–visible spectrum shows two bands, one well resolved at *ca.* 360 nm and assigned to the $S(p_x)S(p_z)Au(s) \rightarrow Au(s)Au(p_x)S(p_x)$ transition and one appearing as a shoulder on the more intense, higher-energy system at *ca.* 290 nm, assigned to the $S(p_x)S(p_z)Au(s) \rightarrow Au(p_x)Au(p_x)$ transition. In the c.d. spectra these bands are also present and a third band, assigned $S(p_y) \rightarrow Au(s)Au(p_x)S(p_x)$, also appears.

Gold–Sulphur Complexes.—The chemistry of gold with the sulphur ligands alone is rather complex. Thiomalato(2—)aurate(I) is very soluble in aqueous solution; its spectrum is affected by chloride and hydroxide ions and there is evidence of the formation of polymeric species in solution.[14] Solutions of cysteinatogold(I), on the other hand, eventually precipitate an insoluble form of this complex. Penicillaminatogold(I) remains soluble but is easily oxidised to Au^{III}. Its solution might contain complexes analogous to the complicated compound recently crystallised from the copper–penicillamine system.[15]

We therefore studied cysteinatogold(I) and sodium thiomalato(2—)aurate(I) in more detail. The spectra consist of rather broad bands but there is reasonable agreement between the u.v.–visible spectrum of each complex in the solid and solution states (Figure 5) and similar assignments to those used for the $[AuX(PR_3)]$ complexes seem reasonable in the low-energy region. In the high-energy region the bands are broad and ill defined. If the contribution from predominantly Au–S bands is similar in the $[AuX(PR_3)]$ complexes, it would explain why the most prominent features appear to be due to the $Au(PR_3)$ moiety.

The c.d. spectrum of cysteinatogold(I) in solution is very intense (Figure 6). The solution, if left to stand for a few hours, precipitates a complex from which a good solid-state c.d. spectrum can be obtained, indicating an intense chromophore. Since gold(I) complexes of this type are usually quite soluble, the most reasonable

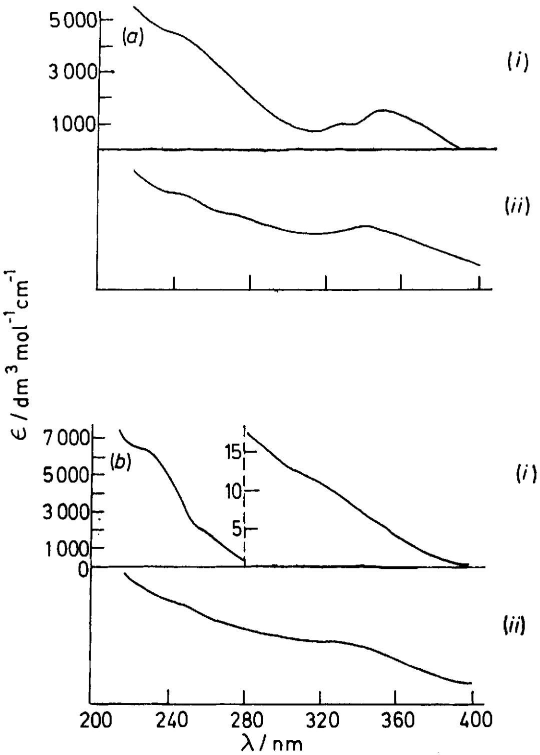

FIGURE 5 U.v.–visible spectra of (*a*) cysteinatogold(I) and (*b*) sodium thiomalato(2—)aurate(I) in the solution (*i*) and solid states (*ii*)

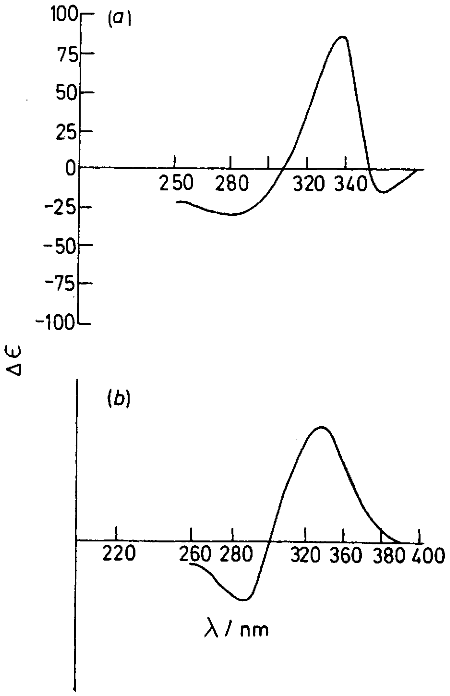

FIGURE 6 C.d. spectra of cysteinatogold(I) in the solution (*a*) and solid states (*b*)

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[14] A. A. Isab and P. J. Sadler, *J.C.S. Chem. Comm.*, 1976, 1051.

[15] P. J. M. W. L. Barker and H. C. Freeman, *J.C.S. Chem. Comm.*, 1976, 312.

explanation of the increased intensity is that the solution consists of small polymers of increased rigidity.

Thus, bands characteristic of this type of gold(I) complex, lying in an energy region rather lower than that of most intense transitions in proteins, have been observed and, in the case of cysteinatogold(I) at least, the c.d. spectrum is quite intense. It may well be that this type of spectrum can be used to study biologically important reactions of gold with naturally occurring sulphydryl groups at quite low (10^{-4} mol dm^{-3}) concentrations.

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