Inorganica Chimica Acta, 32 (1979) 117–121

The Electronic Spectra of Some Gold(III) Complexes

D. H. BROWN, G. C. McKINLAY and W. E. SMITH

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, U.K.

Received June 1, 1978

The electronic spectra of a number of gold(III) complexes with amine, phosphine and halide ligands have been measured. The positions and intensities of the lowest energy bands appear to depend on the nature of the complexing species and in particular a wide variation in intensity which was related to the nature of the complexing ligands was observed.

Introduction

Many planar four coordinate gold(III) complexes give a characteristic spectrum on the low energy side of the main charge transfer band edge. However, in contrast to the situation with square planar complexes of platinum(II) [1], these spectra have only rarely been used to help characterise such complexes. Part of the problem is that there is as yet no clear picture of the nature of the transitions observed and no consistent ligand field effects have been observed. The polarised and temperature dependent single crystal spectra of sodium tetrachloroaurate indicated [2] that the intensity of the spectrum was reduced with temperature, and that it consisted of three components. The most intense component was assigned to a $^1A_{1g} \rightarrow {}^1E_g$ band corresponding to the $d_{xy} \rightarrow d_{xz}, d_{yz}$ transition but significant amounts of ligand mixing into the orbitals would seem to be indicated by the high oscillator strength of the band. This paper reports an investigation, both theoretical and experimental, of the spectra of a range of four coordinate, planar gold(III) complexes in solid and solution in an attempt to assess the effect of different ligands on the energy and intensity of the bands. Molecular orbital calculations of systems as large and complex as these gold compounds are insufficiently exact to aid in fixing the absolute energy positions of the states which give rise to the absorption bands; but where the states have been assigned experimentally they can give an estimate of the relative ligand and metal contributions to each state and therefore a calculation was carried out on suitable model systems in order to help rationalise the experimental observations.

TABLE I. Compounds Prepared and Analyses.

Compound[a]	Experimental %				Theoretical %			
	C	H	N	Hal	C	H	N	Hal
(py)$AuCl_3$	15.8	1.3	3.9	27.3	15.7	1.3	3.6	27.8
(α-pic)$AuCl_3$	18.3	1.8	3.5	26.5	18.1	2.0	3.5	26.8
(2,6-lut)$AuCl_3$	19.8	2.3	3.3	26.5	20.4	2.6	3.4	25.9
(Ph_3P)$AuCl_3$	38.9	2.7	–	18.9	38.2	2.7	–	18.8
(Et_3P)$AuCl_3$	16.9	3.4	–	25.1	17.0	3.5	–	25.2
$(py)_2AuCl_3$	25.0	2.5	6.2	22.9	26.0	2.2	6.1	23.0
(bipy)$AuCl_3$	25.8	1.8	5.8	23.4	26.1	1.7	6.1	23.1
$(en)_2AuCl_3$	11.6	3.8	13.4	24.3	11.3	3.8	13.2	25.1
$(lpd)_2AuCl_3$	15.0	4.1	11.4	24.0	15.9	4.4	12.4	23.6
$(pd)_2AuCl_3$	15.5	4.4	11.8	23.4	15.9	4.4	12.4	23.6
(py)$AuBr_3$	11.8	1.0	3.2	46.2	11.6	0.97	2.7	46.4
(α-pic)$AuBr_3$	13.8	1.3	3.2	45.0	13.6	1.3	2.6	45.3
(Ph_3P)$AuBr_3$	31.4	2.3	–	34.9	2.1	–	–	34.3
$(py)_2AuBr_3$	19.7	1.5	4.3	41.4	20.1	1.7	4.7	40.3
(2,6-lut)$AuBr_3$	15.7	1.7	3.1	44.3	15.4	1.7	2.6	44.1
(Et_3P)$AuBr_3$	13.0	2.6	–	42.8	12.8	2.7	–	43.7

[a] py, pyridine; α-pic, 2-methylpyridine; 2,6-lut, 2,6-dimethylpyridine; Ph_3P, triphenylphosphine; Et_3P, triethylphosphine; bipy, bipyridyl; en, ethylenediamine (1,2-diaminoethane); pd, 1,2-diaminopropane.

Experimental

Complexes were prepared using previously described methods but with different phosphines and amines. The pyridine and substituted pyridine complexes were prepared by the method given in reference [3]; the phosphines by the method in reference [4]; the diaminoethane and diaminopropane complexes by the method in reference [5]. The bipyridyl complex by the method in reference [6]. The optically active diaminopropane was prepared by Dwyer's method [7]. The analyses of the complexes prepared are given in Table I. Carbon, hydrogen, nitrogen and halide analyses were carried out by standard microanalytical techniques. Electronic spectra were measured by transmission in solution on a Beckman Acta IVM uv–visible/near ir spectrometer and by reflectance in the solid-state on a Pye-Unicam SP1800. Solution spectra were obtained from chloroform solutions to minimise the risk of hydrolysis $Auen_2Cl_3$ and $AubipyCl_3$ solution spectra were recorded in aqueous solution since they were insufficiently soluble in chloroform. The circular dichroism spectrometer has been previously described [8]. Far infrared spectra were run on a Beckman interferometer and Raman spectra on a Cary 81. The molecular orbital approach used in the calculations has previously been applied to gold(III) [1], gold(I) [8] and to compounds of molybdenum(V) and (VI) [9] with reasonable agreement between theory and experiment.

TABLE II. Electronic Spectra (nm)[a].

Compound				
$NaAuCl_4$		300	390	
		308	410	485
$(py)AuCl_3$		312(1400)	364	
		320	380	480
$(\alpha\text{-pic})AuCl_3$		310(2600)	364	
		324	385	
$(2,6\text{-lut})AuCl_3$		320(3800)	390	
		330	410	470
$(Ph_3P)AuCl_3$		338(16,000)		
		320	358	
$(Et_3P)AuCl_3$		315(9000)		
		330	375	480
$(py)_2AuCl_3$		330	410	460
$(bipy)AuCl_3$		314(12,000)	326	
		310	320	440
$(en)_2AuCl_3$ (pH 3.1)		332(80)		
(pH 9.9)		335(1600)		
		330		
$(pd)_2AuCl_3$		328(60)		
		330		
$NaAuBr_4$	305	380(3900)	460	550
		380	450	540
$(py)AuBr_3$	340	398(1500)	455	520
	350	400		510
$(\alpha\text{-pic})AuBr_3$	335	396(1800)	444	520
	320	400		520
$(2,6\text{-lut})AuBr_3$	322	392(1840)	444	510
$(Et_3P)AuBr_3$	314	378(5,000)	410	510
$(Ph_3P)AuBr_3$	300	350	400	520
$(py)_2AuBr_3$		340	410	500

[a] Extinction coefficients are given in parenthesis in each case, lower energy bands are shoulders. For each compound the top line is absorption in solution and the second line reflectance in the solid. For the bispyridine complexes only reflectance spectra are given due to the insolubility of the complexes. Key to abbreviations used is given in Table I.

Results and Discussion

The solution spectra of a representative selection of the gold(III) complexes listed in Table II, illustrate the small shifts in energy and the wide variations in intensity found (Figure 1). On a superficial examination, the spectra have roughly the same shape with the predominant peak appearing at approximately the same wavelength. On the basis that the assignments made in the single-crystal study are essentially correct, these results probably indicate a variation in the amount of ligand mixing with the gold d orbitals which appears to be dependent on charge as well as the nature of the complexing ligands. Only the most intense band of three identified in these spectra is resolved in the solution spectra of the chloride complexes illustrated in Figure 1. The bands are resolved in the solid-state as demonstrated previously for sodium tetrachloroaurate [1].

Complexes with Four Similar Complexing Groups

Solution and solid reflectance spectra of both sodium tetrachloroaurate and sodium tetrabromoaurate are in reasonable agreement with respect to energy position and relative intensity of each band. The solids both contain gold in a square planar environment, and the ions in solution are presumably similar [1]. The positions of the strongest low energy transitions for the ions $AuCl_4^-$ [10] suggest that for these ions a ligand field effect is observed.

The amine complexes $Au(en)_2Cl_3$ and $Au(pd)_2Cl_3$ which involve coordination of four nitrogen groups to the gold, are colourless solids which on dissolution in dilute acids give colourless solutions and in dilute bases give yellow solutions. It would appear that the colour change is produced by a change in extinction coefficient rather than by a significant change in peak position. The compound $Au(en)_2Cl_3$ is reported to act as a weak acid (pKa = 6.5) [5] resulting from the loss of a proton from a coordinated $-NH_2$ group. The change in colour in alkaline solution could result from this ionisation. The spectra of these solids show only the most intense peaks at approximately 330 nm. The circular dichroism spectra of the optically active

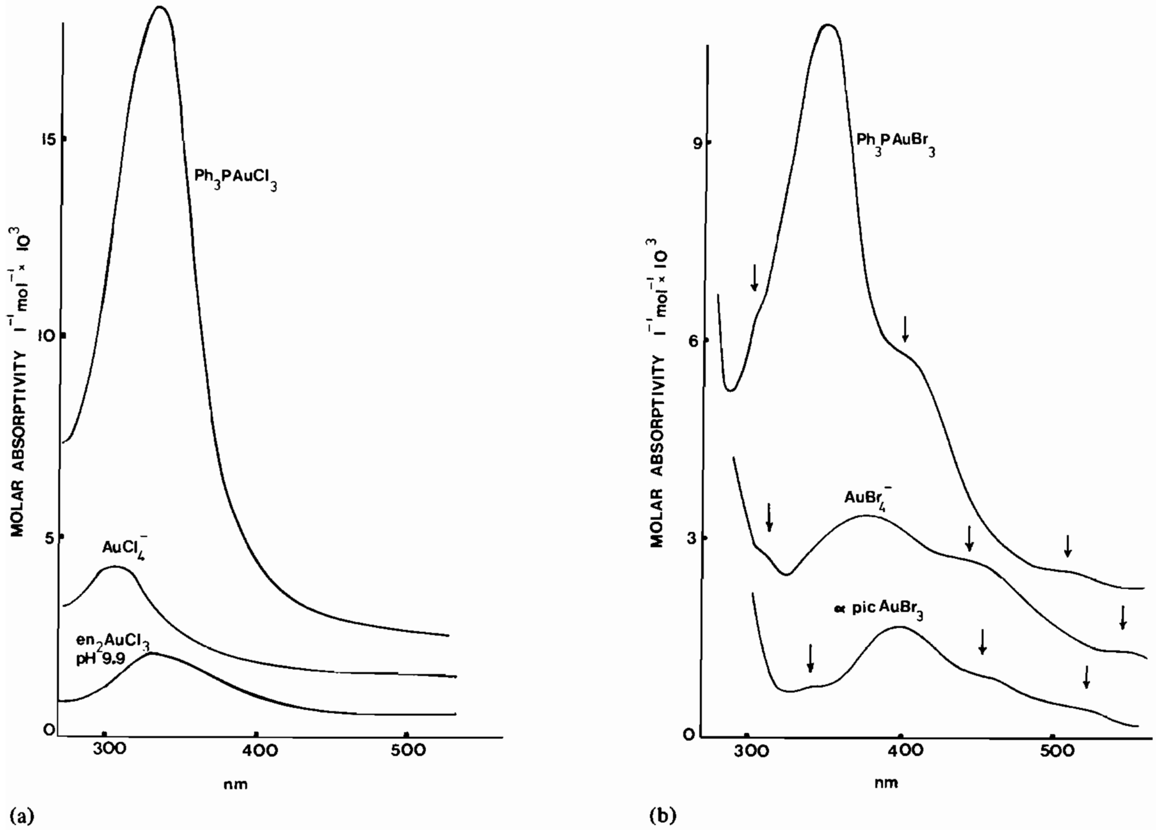

Figure 1. Representative selection of the uv–visible spectra in solution of the chloride (a) and bromide (b) complexes studied. Arrows indicate subsidiary maxima in the bromide spectra. Similar maxima are found in the solid reflectance spectra of the chloride complexes but are only observed with difficulty in solution [1]. Baselines are staggered for clarity.

propylene diamine compound however, gave Cotton effects at 395(–) and 500(+) nm, suggesting that the other peaks present in the $AuCl_4^-$ spectrum are also present in these compounds but are of low intensity.

The position of the strongest peak at 332 nm for the complex $(en)_2AuCl_3$ does not fit into the expected ligand field series but the charge on the ligand has changed. A calculation of the orbital energies for the ion $Au(NH_3)_4^{3+}$ (Table III) suggests that the gold d_{z^2} atomic orbital, which in contrast to $AuCl_4^-$, occurs in this case amongst the highest filled orbitals, will contribute to the lowest energy transitions. Calculations for the ion $Au(H_2O)_4^{3+}$ show similar results. Thus the charge on the complexed gold(III) ion appears to be significant in that it affects both the position of the peaks and their intensities – the former through its effect on energies of the gold – 'd' orbitals and the latter through the degree of mixing in of ligand orbitals.

The spectrum of the $AuBr_4^-$ ion shows an extra peak at 310 nm. This occurs as a shoulder in the trough between the intense charge transfer band in the ultra-violet and the transition at 320 nm. This peak could arise from the first of the singlet → triplet transitions which occur as weak peaks in platinum(II) complexes at longer wavelengths than the spin-allowed transitions but which, in the case of gold(III) compounds, appear to occur at higher energies [1].

Mono Substituted Complexes

A range of compounds of formula $AuLX_3$ has been prepared with L a nitrogen or phosphorus ligand and X a chloride or bromide. The structure of triphenylphosphine gold(III) trichloride indicates that the gold is four coordinate and planar [11]. It seems likely that the other complexes have the same arrangement and again the agreement between solid and solution spectra is quite reasonable. The solution spectra were obtained in chloroform solution and conductivity measurements in chloroform indicated that the complexes were not dissociated. For example, the conductance of the complex $(\alpha\text{-pic})AuCl_3$ was 0.74×10^4 ohms^{-1} cm^2 compared to a value of 50×10^4 ohms^{-1} cm^2 for tetraethylammonium gold tetrabromide.

The spectra of the chloro complexes all consist of a dominant peak around 320 nm with two weaker peaks at higher wavelengths except in the cases of the

TABLE III. Highest Bonding and Lowest Virtual Orbitals.[a]

$AuCl_4^-$	$Au(NH_3)_4^{3+}$	$AuCl_3NH_3$	$AuCl_3PH_3$
Virtual			$p_z(P)d_{x^2-y^2}(P)d_{xz}(P)d_{z^2}(P)$
p_xp_y	p_xp_y	p_x	p_x
p_z	p_z	p_y	p_y
S	S	$d_{x^2-y^2}p_z$	$d_{x^2-y^2}p_x(P)p_x(Cl)p_x(Cl)$
			p_z
$d_{x^2-y^2}$	$d_{x^2-y^2}$	S	$Sp_xS(P)p_x(P)p_x(Cl)$
Filled			
d_{xy}	d_{xy}	$p_y(Cl)$	$p_xp_y(Cl)p_x(P)$
			$p_xp_y(Cl)p_x(P)$
$d_{yz}d_{xz}$	$d_{z^2}S$	$d_{xy}p_x(Cl)$	$d_{xy}p_x(Cl)$
$d_{yz}d_{xz}$	$d_{xy}d_{z^2}d$	d_{yz}	$d_{yz}p_z(Cl)$
$p_yp_y(Cl)$	$d_{xz}d_{yz}$	d_{xz}	$d_{xz}p_x(Cl)$
$p_xp_x(Cl)$	$d_{xz}d_{yz}$		
Charges on Atoms			
Au +0.89	Au +1.31	Au +0.95	Au +0.92
Cl −0.47	N −0.31	Cl(*trans*) −0.27	Cl(*trans*) −0.35
		Cl(*cis*) −0.43	Cl(*cis*) −0.40
		N −0.24	P −0.32
Covalent Bond Orders			
Au–Cl 0.78	Au–N 0.44	Au–Cl(*trans*) 0.82	Au–Cl(*trans*) 0.75
		Au–Cl(*cis*) 0.70	Au–Cl(*cis*) 0.67
		Au–N 0.17	Au–P 0.33

[a] The molecular orbitals are labelled in terms of the main contributing atomic orbitals. These are gold in origin except where otherwise shown.

α-picoline and triethylphosphine complexes in which the peak is not resolved. The spectra all show a strong resemblance to that of the parent $AuCl_4^-$ ion with no evidence of extra bands due to a splitting of the d_{xz}, d_{yz} molecular orbital. The spectra of the bromide series are similar.

The positions of the phosphine complexes of the gold(III) chloride and bromide ions do not follow the same trend in energies as the nitrogen ligands relative to the parent tetrahaloanion. This could be due to the contributions of phosphorus orbitals to the otherwise mainly gold virtual orbitals. Thus triphenylphosphine in particular appears to exert a greater influence on peak positions than do the pyridine-type ligands.

The intensities of the dominant peaks vary considerably. The intensity order in the chlorides (py < α-pic < Cl^- < lut < Et_3P < Ph_3P) and in the bromides (py < α-pic < lut < Br^- < Ph_3P) differs only in the position of the halide ion, but the intensity range is much greater for the chlorides (1,400 → 16,000) than the bromides (1550 → 9,400).

Bi-substituted Complexes

Two structures are likely for such compounds – planar four coordinate with a non-complexed anion and five coordinate. Most structures so far described for gold(III) complexes are square planar and the two five coordinate structures which have been published [12] are sterically hindered from forming the expected square planar complexes. Thus, although the possibility of five or even six coordinate gold(III) cannot be ruled out, the most likely structures for the compounds examined here would be square planar. Again the similarity of the electronic spectra of the complexes to those of the parent tetrahalide gold complexes further supports square planar structures. The spectra of (bipy)$AuCl_3$ in solution is the least satisfactory of all the spectra both because the second band appears to be of quite high intensity and could indicate a splitting of the d_{xz}, d_{yz} orbital in the *cis* configuration and because the conductivity in water of the (bipy)$AuCl_3$ complex suggested that a limited amount of hydrolysis of the complex had occurred.

Two square planar isomers – *cis* and *trans*-$(AuL_2X_2)^+X^-$ – can in theory be prepared. Using bipyridyl, the *cis* isomer is most likely. The comparable bromo complex could not be isolated, presumably because of the greater stability of the gold–bromide bond. With the bis pyridine complex, however, the structure is less obvious. It is prepared by treating the mono pyridine complex with excess pyridine and washing with chloroform and water to remove the more soluble mono pyridine complex. It is very much less soluble in water than the bipyridyl complex and this suggests that it could be the *trans* isomer. *Trans* isomers have negligible dipole moments, are less polar, less solvated and hence less soluble. The corresponding bromide complex was made by the same method.

The infrared and Raman spectra appear to confirm this suggestion [13]. There is no evidence of coincidences or near coincidences in the spectra of the bis pyridine gold(III) trihalide complex but in the bipyridyl complex, a number of near coincidences, which are probably not exact due to solid state effects were observed. The compounds are insufficiently soluble for solution spectra to be obtained.

Calculation

A theoretical study was carried out using an established CNDO programme which has been described previously [9]. In order to reduce the size of the calculation, NH_3 and PH_3 adducts were used in place of the amines and phosphines used experimentally. Table III lists in order the energy levels of the highest filled and lowest virtual orbitals. The virtual orbitals are mainly gold in origin except in the case of the phosphine complex where *p* and *d* orbitals of the ligand atom occur in the lowest virtual set. With the three chloride complexes, ligand orbitals are amongst the highest filled orbitals and, as has been reported for $AuCl_4^-$, contribute to the essentially gold transitions, conferring some ligand → metal charge transfer character. With the tetraamine complex, nitrogen orbitals lie at a lower level and thus will contribute less to the low-energy transitions. The appearance of the d_{z^2} orbital above the d_{xz} and d_{yz} orbitals in the tetraamine complex, but not in the chloro complexes, could be a product of the more ionic character of the tetraamine complex. With the phosphine complex, calculations show that there is significant ligand mixing in both filled and virtual orbitals. This will result in a greater ligand contribution to the low energy electronic transitions. Using phenyl dimethyl phosphine as ligand, a further calculation showed a similar orbital ordering but with a greater contribution from the phosphorus atomic orbitals to the lowest virtual orbitals. Experimentally the comparative similarity of the spectra of the complexes Ph_3PAuCl_3 and Ph_3PAuBr_3 indicate that the triphenyl phosphine ligands are playing a greater part in determining the spectra than say triethylphosphine in its trihalo complexes. The greater mixing in of ligand orbitals is probably also reflected in the variation in intensity of the strong peak between 300 and 400 nm.

The calculated charges on the atom are also given in Table III. In the tetraamine complex the higher charge on the gold suggests a greater degree of ionic character in the gold–nitrogen bond. The covalent bond orders show the Au–P bond to be approximately twice that of the Au–N bond in the complexes $AuCl_3L$.

Thus the calculations reaffirm the experimental information discussed above – that low-energy gold(III) spectra in the visible and near ultraviolet are produced by electronic transitions which, although basically gold in origin, are strongly affected by the charge on the ligands and also by the ability of the ligand orbitals to mix with the gold orbitals.

These results both experimental and theoretical suggest that gold(III) spectra are not likely to be as useful as, say, first-row transition-metal-ion spectra in developing a simple comprehensive spectrochemical series since the change in the position of the major peak in the spectra is not sufficiently large. However, the solution spectra were run in chloroform to minimise the risk of hydrolysis or solvolysis and the intensity changes observed are large and ligand dependent. This property may provide a useful indicator in experimental studies. Certainly the changes in solution from yellow to colourless may arise from a number of possible coordination changes as well as reduction from gold(III) to gold(I).

References

1 D. H. Brown and W. E. Smith, *J. Chem. Soc. Dalton*, 848 (1976), and refs. therein.
2 R. F. Kroenig, R. M. Rush, D. S. Martin and J. C. Clardy, *Inorg. Chem.*, *13*, 1366 (1974), and refs. therein.
3 C. S. Gibson and W. M. Colles, *J. Chem. Soc.*, 2407 (1931).
4 F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1235 (1940).
5 B. P. Bloch and J. C. Bailar, *J. Am. Chem. Soc.*, *73*, 4722 (1951).
6 C. M. Harris and T. N. Lockyer, *J. Chem. Soc. A*, 3083 (1959).
7 F. P. Dwyer, F. L. Garvan, A. Schulman, *J. Am. Chem. Soc.*, *81*, 290 (1959).
8 D. H. Brown, G. McKinlay and W. E. Smith, *J. Chem. Soc. Dalton*, 1874 (1977).
9 D. H. Brown, P. G. Perkins and J. J. P. Stewart, *J. Chem. Soc. Dalton*, 1105 (1972).
10 A. K. Gangopadhayay and A. Chakravorty, *J. Chem. Phys.*, *35*, 2206 (1961).
11 G. Bandoli, D. A. Clemente, G. Marangoni and L. Cattalini, *J. Chem. Soc. Dalton*, 886 (1973).
12 W. T. Robinson and E. Sinn, *J. Chem. Soc. Dalton*, 726 (1975).
13 D. H. Brown and W. E. Smith, unpublished data.