Displacement of Chelate Ligands from Planar Four-co-ordinate Complexes. Part I. Reactions of Some Gold(III) Complexes of 2,2′-Bipyridyl

By **Giuliano Annibale, Lucio Cattalini, Abbas A. El-Awady,** and **Giovanni Natile,*** Istituto di Chimica Generale ed Inorganica, University of Venice, Italy

The kinetics of nucleophilic displacement of the chelate 2,2′-bipyridyl ligand (bipy) from the complex $[Au(bipy)X_2]^+$ by X^- (X = Cl or Br) have been measured in aqueous methanol solution at 25 °C. The rate constant shows dependences on hydrogen-ion concentration and on the first and third power of chloride-ion concentration. Details of the mechanism are discussed and compared with others involving replacement of chelate ligands from planar complexes of d^8 transition-metal ions.

KINETIC studies of the displacement of polydentate ligands from d^8 transition-metal ions have seldom been reported in recent literature.[1-5] In every case the mechanism involves opening of the chelate ring followed by competition between ring closure and displacement of the ligand, often complicated by possible protonation of unco-ordinated donor sites. Therefore simple kinetic expressions are not common, even if the mechanism must obviously be consistent with those known for simpler displacements of unidentate ligands in these systems.[6]

In this context we decided to investigate displacement of 2,2′-bipyridyl (bipy) from gold(III), bearing in mind that the relatively high reactivity of cationic gold(III) complexes can be partially counterbalanced by the relative inertness of the chelate molecule, which is believed to be strongly bonded due to possible formation of a pseudo-aromatic five-membered ring including the metal.[7] In this paper we report the kinetics of the

$$[Au(bipy)X_2]^+ + H^+ + 2X^- \longrightarrow [AuX_4]^- + bipyH^+ \quad (1)$$

processes (1) (X = Cl or Br), and discuss possible mechanisms.

EXPERIMENTAL

Except for $HAuCl_4,3H_2O$ (Johnson, Matthey and Co.), 2,2′-bipyridyl (bipy), perchloric acid, NaBr, LiCl, LiBr, $LiClO_4$, and methanol were all reagent-grade products. The complex $[Au(bipy)Cl_2]ClO_4$ was prepared according to the

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[1] R. G. Pearson and D. A. Johnson, *J. Amer. Chem. Soc.*, 1964, **86**, 3983.

[2] A. J. Poë and D. H. Vaughan, *Inorg. Chim. Acta*, 1967, **1**, 255.

[3] J. S. Coe, J. R. Lyons, and M. D. Hussain, *J. Chem. Soc.* (*A*), 1970, 90.

[4] A. Giacomelli and A. Indelli, *Inorg. Chem.*, 1972, **11**, 1033.

[5] J. S. Coe and J. R. Lyons, *J. Chem. Soc.* (*A*), 1971, 829.

[6] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' Benjamin, New York, 1966.

[7] P. Haake and P. A. Cronin, *Inorg. Chem.*, 1964, **2**, 879.

method reported for preparation of $[\mathrm{Au(phen)Cl_2}]\mathrm{ClO_4}$ (phen = 1,10-phenanthroline)[8] and characterized through i.r. spectra and elemental analysis, m.p. 298 °C (decomp.) {Found: C, 22·8; H, 1·70; Cl, 20·35; N, 5·15. $[\mathrm{Au(bipy)Cl_2}]\mathrm{ClO_4}$ requires C, 22·9; H, 1·55; Cl, 20·3; N, 5·35%}.

The complex $[\mathrm{Au(bipy)Br_2}]\mathrm{Br}$ was prepared by the action of a large excess of NaBr on $[\mathrm{Au(bipy)Cl_2}]\mathrm{Cl}$ in hot aqueous solution (the product precipitated as dark red crystals) and characterized in the same way as the chloro-complex, m.p. 200 °C (decomp.) {Found: C, 20·0; H, 1·30; Br, 40·4; N, 4·50. $[\mathrm{Au(bipy)Br_2}]\mathrm{Br}$ requires C, 20·2; H, 1·35; Br, 40·45; N, 4·70%}.

Kinetics.—Separate solutions of the complex and reagents were prepared in methanol containing 5% water. The concentrations of chloride and bromide ions and perchloric acid were determined by standard titrimetric methods. $\mathrm{LiClO_4}$ was also added in order to maintain constant ionic strength. The reagent solutions were separately brought to reaction temperature, then mixed in the thermostatted cell of an Optica CF4R double-beam recording spectrophotometer, and the kinetics followed by observing absorption changes in the u.v. region of the spectrum. Preliminary experiments showed that all absorbing species obeyed Beer's law in the solvent used. All kinetic runs were carried out with concentrations of the reagents X^- and H^+ large enough to provide pseudo-first-order conditions; the concentration of the gold complex in the reaction mixture was always less than 10^{-4}M. In every case the appearance of well defined isosbestic points indicated that single-stage processes take place. Pseudo-first-order rate constants, k_{obs}, were obtained from semi-logarithmic plots of $\ln(\mathrm{OD}_\infty - \mathrm{OD}_t)$ against time, where OD_t and OD_∞ are absorbances at a given wavelength at time t and at the end of the reaction respectively. These plots were linear for at least three half-lives. The experimentally determined rate constants, k_{obs} (s^{-1}), are summarized in Tables 1 and 2.

TABLE 1

Pseudo-first-order rate constants, k_{obs}, for the reaction $[\mathrm{Au(bipy)X_2}]^+ \longrightarrow [\mathrm{AuX_4}]^-$ at constant $[\mathrm{H}^+]$ and variable $[\mathrm{X}^-]$, and values of the intercepts, p(X), and gradients, q(X), obtained from plots of $(k_{\mathrm{obs}}/[\mathrm{X}^-])$ against $[\mathrm{X}^-]^2$ using a least-squares program

$[\mathrm{H}^+]$ = 0·20, I = 1·7M ($\mathrm{LiClO_4}$), 25 °C

$[\mathrm{Cl}^-]$/M	$10^4 k_{\mathrm{obs}}/\mathrm{s}^{-1}$
0·30	1·47
0·57	4·20
0·60	4·68
0·77	7·52
0·96	12·70
1·00	14·58
1·15	20·50
1·34	30·40

$p(\mathrm{Cl}) = (3{\cdot}80 \pm 0{\cdot}45) \times 10^{-4}\ \mathrm{l\ mol^{-1}\ s^{-1}}$

$q(\mathrm{Cl}) = (10{\cdot}50 \pm 0{\cdot}50) \times 10^{-4}\ \mathrm{l^3\ mol^{-3}\ s^{-1}}$

$[\mathrm{H}^+]$ = 1·00 × 10^{-2}, I = 0·2M ($\mathrm{LiClO_4}$), 25 °C

$10^2[\mathrm{Br}^-]$/M	$10^3 k_{\mathrm{obs}}/\mathrm{s}^{-1}$
0·50	2·77
1·00	6·85
1·50	11·11
2·00	18·70
2·50	28·80
3·00	39·50
3·50	56·40
4·00	78·50

$p(\mathrm{Br}) = (6{\cdot}68 \pm 0{\cdot}40) \times 10^{-1}\ \mathrm{l\ mol^{-1}\ s^{-1}}$

$q(\mathrm{Br}) = (8{\cdot}64 \pm 0{\cdot}50) \times 10^{2}\ \mathrm{l^3\ mol^{-3}\ s^{-1}}$

RESULTS

Kinetics of the Reaction of $[\mathrm{Au(bipy)Cl_2}]\mathrm{ClO_4}$.—(a) *At variable lithium chloride and constant acid concentrations.* The spectroscopic course of this reaction is shown in Figure 1. The final spectrum showed an intense peak with a maximum at 303 nm (ε 1·96 × 10^4 l $\mathrm{mol^{-1}\ cm^{-1}}$) which, apart from a small contribution from $[\mathrm{AuCl_4}]^-$ ions, resembled that of free bipy in acid medium ($[\mathrm{HClO_4}]$ = 0·2M) ($\lambda_{\mathrm{max.}}$ 300 nm, ε 1·68 × 10^4 l $\mathrm{mol^{-1}\ cm^{-1}}$), indicating that the studied reaction is replacement of bipy by halide ions. Observed rate constants at $[\mathrm{H}^+]$ = 0·1M are reported in Table 1 and plotted against $[\mathrm{Cl}^-]$ in Figure 2. The curvature in the latter plot indicated contributions from high-order chloride dependences, and the data were analysed graphically in a number of ways. A plot of $(k_{\mathrm{obs}}/[\mathrm{Cl}^-])$ against $[\mathrm{Cl}^-]^2$ gave a good straight line with finite intercept indicating a relation of the form (2) (gradient = q and intercept = p).

$$k_{\mathrm{obs}} = p[\mathrm{Cl}^-] + q[\mathrm{Cl}^-]^3 \qquad (2)$$

The absence of any significant second-order contribution was shown by plotting $\{(k_{\mathrm{obs}}/[\mathrm{Cl}^-]) - p\}[\mathrm{Cl}^-]$ against $[\mathrm{Cl}^-]$. A straight line with gradient q and zero intercept was obtained.

(b) *At constant lithium chloride and variable perchloric acid concentrations.* Observed rate constants are given in Table 2. Each set of values of k_{obs} at a given chloride-ion concentration gave a good straight line when plotted against $[\mathrm{H}^+]$ (Figure 3). The intercepts (r) and gradients

TABLE 2

Values of k_{obs} for the reaction $[\mathrm{Au(bipy)X_2}]^+ \longrightarrow [\mathrm{AuX_4}]^-$ at constant $[\mathrm{X}^-]$ and variable $[\mathrm{H}^+]$

I = 1·7M ($\mathrm{LiClO_4}$), 25 °C

$[\mathrm{Cl}^-]$ = 0·30M		$[\mathrm{Cl}^-]$ = 0·60M	
$[\mathrm{H}^+]$/M	$10^4 k_{\mathrm{obs}}/\mathrm{s}^{-1}$	$[\mathrm{H}^+]$/M	$10^4 k_{\mathrm{obs}}/\mathrm{s}^{-1}$
0·10	1·20	0·05	2·25
0·20	1·47	0·10	2·90
0·30	1·96	0·20	4·68
0·40	2·29	0·30	5·67
0·50	2·54	0·40	7·40
		0·50	8·79

$[\mathrm{Cl}^-]$ = 1·00M		$[\mathrm{Cl}^-]$ = 1·40M	
0·025	4·00	0·012	5·50
0·05	5·82	0·025	7·80
0·10	8·40	0·05	12·50
0·20	14·58	0·10	21·02
0·30	20·60	0·20	38·04
		0·30	54·01

I = 0·2M ($\mathrm{LiClO_4}$), 25 °C

$[\mathrm{Br}^-]$ = 0·50 × 10^{-2}M		$[\mathrm{Br}^-]$ = 1·00 × 10^{-2}M	
$10^2[\mathrm{H}^+]$/M	$10^3 k_{\mathrm{obs}}/\mathrm{s}^{-1}$	$10^2[\mathrm{H}^+]$/M	$10^3 k_{\mathrm{obs}}/\mathrm{s}^{-1}$
0·50	1·97	0·56	5·80
1·00	2·77	1·00	6·85
2·00	3·22	2·00	10·20
3·00	3·95	3·10	13·80
5·00	6·30	5·00	19·20
10·00	10·10	10·00	33·60
15·00	13·40	15·00	48·00
20·00	18·30	19·00	62·20

$[\mathrm{Br}^-]$ = 2·00 × 10^{-2}M		$[\mathrm{Br}^-]$ = 2·50 × 10^{-2}M	
0·30	11·50	0·20	14·00
0·50	14·00	0·40	18·00
1·00	18·70	0·50	19·70
2·00	31·70	1·00	28·80
3·00	41·50	2·00	51·50
5·00	67·40	3·00	72·87

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[8] C. M. Harris, *J. Chem. Soc.*, 1959, 682.

(s) were evaluated by an unweighted least-squares program and are collected in Table 3. Since the intercepts r were small, there are rather large uncertainties in their values, whereas values of s are given with much smaller fractional uncertainties. r Values vary with halide-ion concentration and despite the uncertainties a plot of r against $[Cl^-]$ gave a reasonably good line with zero intercept and gradient r' (Figure 4). This value of r' is reported in Table 4. s Values also depend on halide-ion concentrations and plotting ($s/[Cl^-]$) against $[Cl^-]^2$ gave a straight line (Figure 5). Since the uncertainty in the s values is quite small, an

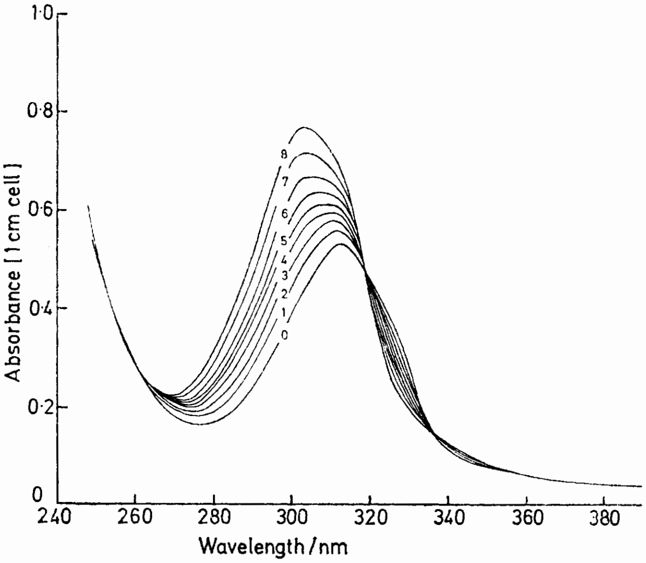


FIGURE 1 Spectroscopic course of the reaction $[Au(bipy)Cl_2]^+ + 2Cl^- + H^+ \longrightarrow [AuCl_4]^- + bipyH^+$: $[Au(bipy)Cl_2^+]_0 = 0{\cdot}45 \times 10^{-4}$; $[H^+] = 0{\cdot}296$; $[Cl^-] = 0{\cdot}768$; $I = 1{\cdot}7$M ($LiClO_4$); and 25 °C. Curves 0—8 show, respectively, spectra at zero time and after 3, 6·25, 10·5, 14·5, 20, 29, 50, and 100 min. It has been shown (see text) that the original band, with maximum at 312 nm, is of co-ordinated 2,2′-bipyridyl and that the final one, at 303 nm, is of protonated bipy

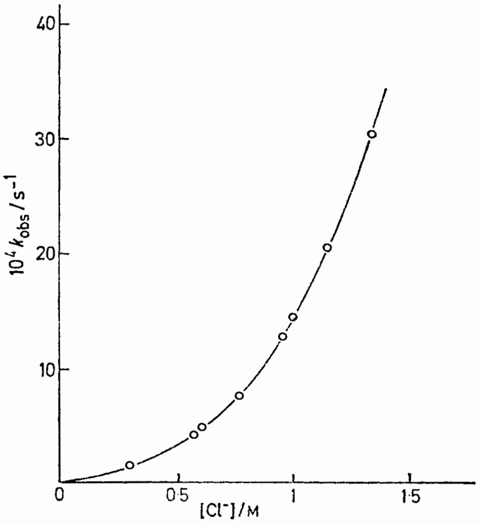


FIGURE 2 Dependence of k_{obs} on $[Cl^-]$ for the reaction $[Au(bipy)Cl_2]^+ \longrightarrow [AuCl_4]^-$: $[H^+] = 0{\cdot}2$; $I = 1{\cdot}7$M ($LiClO_4$); 25 °C

TABLE 3

Values of intercepts, r (at $[H^+] = 0$), and gradients, s, of plots of k_{obs} against $[H^+]$ at constant $[X^-]$, using values from Table 2. (These parameters were obtained from least-squares calculations.)

$[Cl^-]$/M	$10^4r/s^{-1}$	10^4s/l mol^{-1} s^{-1}
0·30	0·84 ± 0·23	3·50 ± 0·70
0·60	1·53 ± 0·37	14·50 ± 1·00
1·00	2·58 ± 0·40	60·00 ± 2·00
1·40	3·90 ± 0·60	168·00 ± 5·00
$10^2[Br^-]$/M	$10^3r/s^{-1}$	s/l mol^{-1} s^{-1}
0·50	1·74 ± 0·45	0·082 ± 0·004
1·00	4·04 ± 0·88	0·30 ± 0·01
2·00	7·56 ± 1·77	1·18 ± 0·07
2·50	9·10 ± 1·40	2·11 ± 0·09

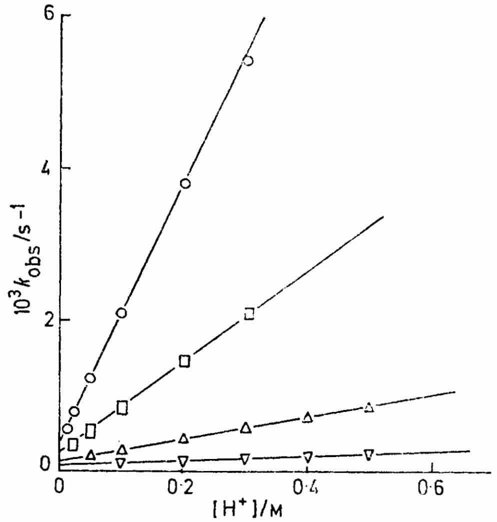


FIGURE 3 Plots of pseudo-first-order rate constants, k_{obs}, against $[H^+]$ at constant $[Cl^-]$ for the reaction $[Au(bipy)Cl_2]^+ \longrightarrow [AuCl_4]^-$: $[Cl^-] = 0{\cdot}30$ (▽), 0·60 (△), 1·00 (□), 1·40 (○); $I = 1{\cdot}7$M ($LiClO_4$), 25 °C

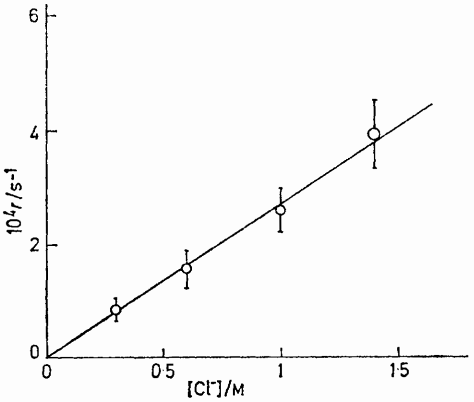


FIGURE 4 Dependence of r (see text) on $[Cl^-]$ for the reaction $[Au(bipy)Cl_2]^+ \longrightarrow [AuCl_4]^-$

TABLE 4

Values of the constants of equation (3) derived (see text) from results in Table 3

$r'(Cl)$/l mol^{-1} s^{-1} = $2{\cdot}8 \times 10^{-4}$
$s'(Cl)$/l^2 mol^{-2} s^{-1} = $4{\cdot}12 \times 10^{-4}$ $s''(Cl)$/l^4 mol^{-4} s^{-1} = $5{\cdot}24 \times 10^{-3}$
$r'(Br)$/l mol^{-1} s^{-1} = 0·37
$s'(Br)$/l^2 mol^{-2} s^{-1} = 19·22 $s''(Br)$/l^4 mol^{-4} s^{-1} = $1{\cdot}03 \times 10^5$

unweighted least-squares method was used in the evaluation of the intercept s' and gradient s'' of the linear plot. The calculated values of s' and s'' are also reported in Table 4. The intercept of the plot of s against halide-ion concentration is small and thus the value of s' is largely uncertain, as is clear from Figure 5.

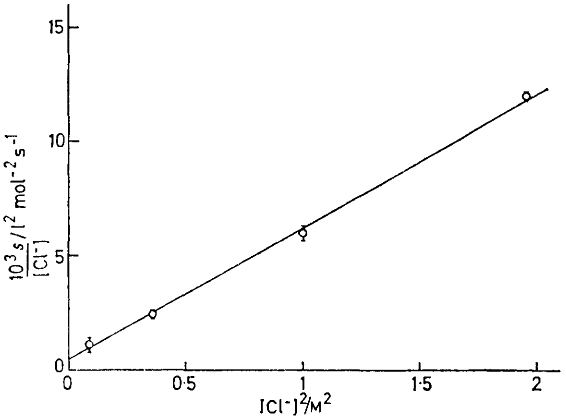


FIGURE 5 Dependence of $s/[Cl^-]$ (see text) on $[Cl^-]^2$ for the reaction $[Au(bipy)Cl_2]^+ \longrightarrow [AuCl_4]^-$

The experimental data are therefore adequately expressed by equation (3) which gives k_{obs} in terms of $[H^+]$ and $[X^-]$.

$$k_{obs} = (r' + s'[H^+])[X^-] + s''[H^+][X^-]^3 \qquad (3)$$

This equation, obtained by evaluating k_{obs} as a function of $[H^+]$ at different halide-ion concentrations, is completely analogous to that of (2), obtained at constant $[H^+]$ and varying halide-ion concentration, and the estimated values of p and q (constant $[H^+] = 0{\cdot}2$M) agree within the limits of experimental error respectively with the values of $(r' + s'[H^+])$ and $(s''[H^+])$ calculated for the same hydrogen-ion concentration.

Kinetics of the Reaction of [Au(bipy)Br$_2$]Br.—(a) *At variable lithium bromide and constant perchloric acid concentrations.* This system is similar to the analogous chloride reaction with a dependence of k_{obs} on bromide-ion concentration shown in Figure 6. The plot of $(k_{obs}/[Br^-])$ against $[Br^-]^2$ gave a straight line with intercept p(Br) and gradient q(Br). Values of q(Br) and p(Br) obtained by a least-squares program are given in Table 1. Since the bromide reaction is much faster than the chloride, a much smaller ionic strength ($I = 0{\cdot}2$M) and wider range of $[Br^-]$ were used. At bromide-ion concentrations less than 2×10^{-3}M the plot of $(k_{obs}/[Br^-])$ against $[Br^-]^2$ showed small departure from linearity (the chloride reaction could not be studied under these conditions) and so the given rate law may require minor corrections at low anion concentrations.

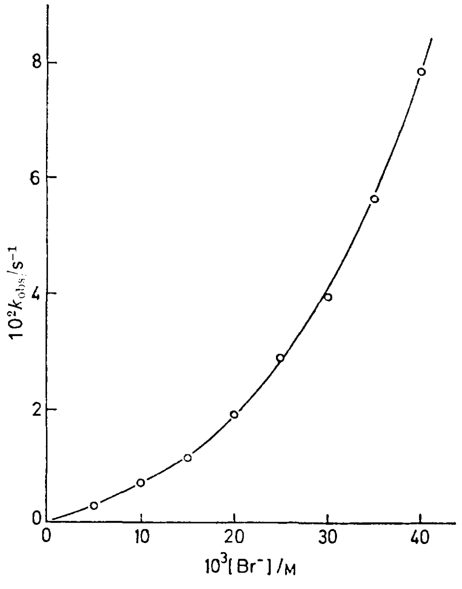


FIGURE 6 Dependence of k_{obs} on $[Br^-]$ for the reaction $[Au(bipy)Br_2]^+ \longrightarrow [AuBr_4]^-$: $[H^+] = 0{\cdot}01$; $I = 0{\cdot}2$M (LiClO$_4$); 25 °C

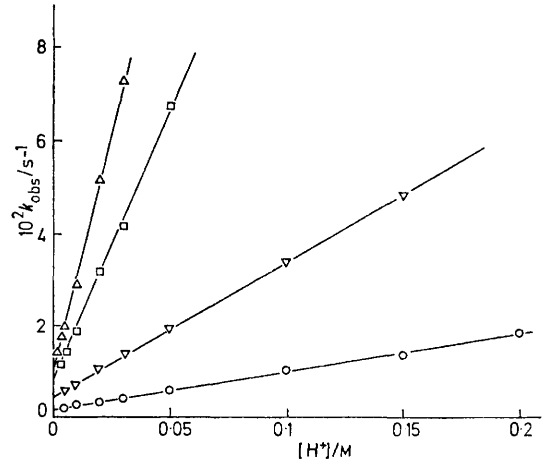


FIGURE 7 Plots of pseudo-first-order rate constants, k_{obs}, against $[H^+]$ at constant $[Br^-]$ for the reaction $[Au(bipy)Br_2]^+ \longrightarrow [AuBr_4]^-$: $[Br^-] = 0{\cdot}005$ (○), 0·01 (▽), 0·02 (□), 0·025 (△); $I = 0{\cdot}2$M (LiClO$_4$); 25 °C

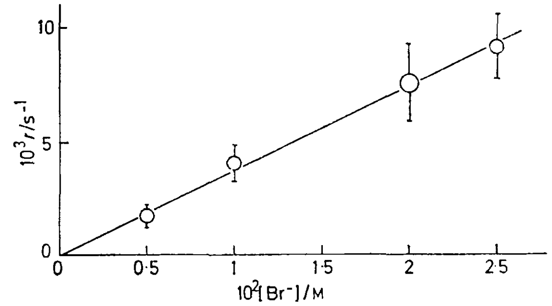


FIGURE 8 Dependence of r (see text) on $[Br^-]$ for the reaction $[Au(bipy)Br_2]^+ \longrightarrow [AuBr_4]^-$

(b) *At constant lithium bromide and variable perchloric acid concentrations.* Each set of values of k_{obs} at a given bromide-ion concentration gave a good straight line on plotting k_{obs} against $[H^+]$ (Figure 7). Values of k_{obs} and those of r(Br) and s(Br), obtained respectively from intercepts and gradients of linear plots of k_{obs} against $[H^+]$, using a least-squares program, are collected in Tables 2 and 3 respectively. The rather large uncertainties in some of the values of r(Br) are due mainly to their small size compared to those of the corresponding s constants. A plot of r(Br) against $[Br^-]$ (Figure 8) gave a good straight line with zero intercept and gradient r'(Br), evaluated by a graphical method. A plot of $\{s(\mathrm{Br})/[\mathrm{Br}^-]\}$ against $[\mathrm{Br}^-]^2$ gave a straight line and the intercept $s'(\mathrm{Br})$ and gradient $s''(\mathrm{Br})$ were evaluated using an unweighted least-squares treatment (see Table 4 and Figure 9).

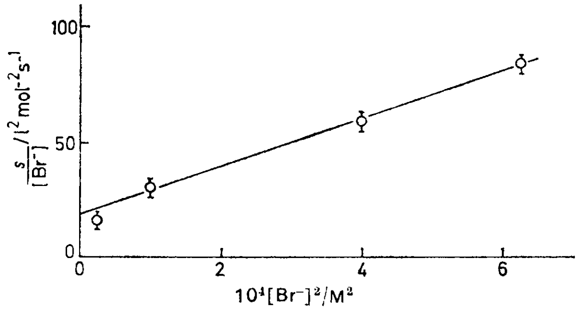


FIGURE 9 Dependence of $r/[\mathrm{Br}^-]$ (see text) on $[\mathrm{Br}^-]^2$ for the reaction $[\mathrm{Au(bipy)Br_2}]^+ \longrightarrow [\mathrm{AuBr_4}]^-$

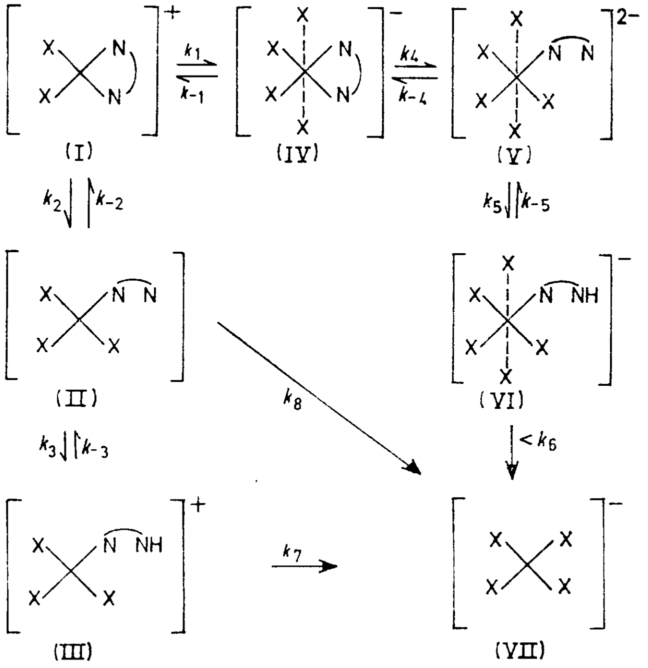
The experimental data once again are in accordance with equation (3). The agreement between the values of $p(\mathrm{Br})$ and that calculated from $\{r'(\mathrm{Br}) + s'(\mathrm{Br})[\mathrm{H}^+]\}$ ($[\mathrm{H}^+] = 0{\cdot}01\,\mathrm{M}$), and that between the value of $q(\mathrm{Br})$ and that obtained from $\{s''(\mathrm{Br})[\mathrm{H}^+]\}$ ($[\mathrm{H}^+] = 0{\cdot}01\,\mathrm{M}$), is within experimental error. The ratio $s'' : s'$ in the bromide case is some 500 times larger than in the chloride reaction, and since the ratio $r' : s'$ does not change much with changing halide, the third-order halide dependence is most marked in the bromide reaction.

DISCUSSION

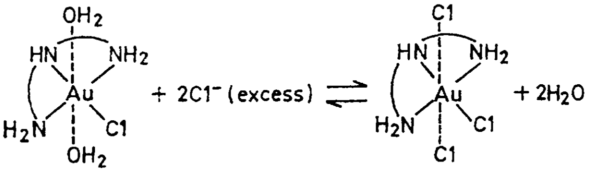
The experimental results indicate a clear difference between the displacement of the bidentate amine, 2,2′-bipyridyl (bipy), and that of unidentate amines from $\mathrm{Au^{III}}$ complexes. The latter ligands show a dependence on the entering group, Y, typical of planar d^8 complexes,[6] with a rate law of the form rate = $(k_1 + k_2[\mathrm{Y}])$[substrate]. The absence of a dependence on $[\mathrm{H}^+]$ in the reactions $[\mathrm{Au(am)X_3}] + \mathrm{X}^- \longrightarrow [\mathrm{AuX_4}]^- + \mathrm{am}$, suggests that the role of the hydrogen ion may be only to protonate the amine (am) released and hence suppress the reverse reaction. The behaviour of the bipy complexes, however, is rather different, the most striking features being the dependence of the rate constant on $[\mathrm{H}^+]$ and the term with third-order dependence on $[\mathrm{X}^-]$ (X = Cl or Br). Similar acid dependences of the rate constant to those observed for the bipy complexes have been found for other bidentate chelate complexes, and intermediates with single-bonded protonated bifunctional ligands have been postulated.[1-3] The third-order dependence in the chloride case could arise in principle from medium rather than mechanistic effects because, even if the ionic strength is maintained at $1{\cdot}7\,\mathrm{M}$, there are large changes in composition over the range of concentrations studied. But since the same relation has been found also for the bromide complex, in which the experimental conditions are much different, this possibility has been ruled out.

In the study of the reaction $[\mathrm{Pd(acac)_2}] \longrightarrow [\mathrm{Pd(acac)Cl_2}]^-$ (acac = acetylacetonate ion), Pearson and Johnson[1] postulated steady-state intermediates with single-bonded acac groups. Poë and Vaughan[2] and Coe *et al.*,[3] however, adopted a mechanism involving a preliminary equilibrium with a single-bonded ethylenediamine (en) intermediate for the reactions $[\mathrm{Pd(en)Cl_2}] \longrightarrow [\mathrm{PdCl_4}]^{2-}$ and $[\mathrm{Pd(en)_2}]^{2+} \longrightarrow [\mathrm{Pd(en)Cl_2}]$. Substitution of $\mathrm{SCN^-}$ for $\mathrm{C_2O_4}^{2-}$ in the reaction $[\mathrm{Pt(C_2O_4)_2}]^{2-} \longrightarrow [\mathrm{Pt(SCN)_4}]^{2-}$ was explained by a two-stage process in which entry of the first two $\mathrm{SCN^-}$ groups gave an intermediate with two single-bonded oxalato-groups in *trans*-position to one another, followed by slow replacement of one oxalato-group and fast replacement of the second. In the reaction of *cis*- and *trans*-bis(glycinato)-palladium(II) in acid solution each glycinato-ligand is completely replaced in turn and protonation equilibria of the free end of a single-bonded ligand in the course of its replacement is invoked.

As far as the results obtained in this investigation are concerned we propose the mechanism given below, in which two reaction paths occur simultaneously leading to formation of the products. Reaction path one [(I) ⟶ (II) ⟶ (III) ⟶ (VII)] has a first-order dependence on halide-ion concentration and can occur through the normal associative nucleophilic attack known for planar complexes. The second path [(I) ⟶ (IV) ⟶ (V) ⟶ (VI) ⟶ (VII)] leads to a third-order dependence on halide-ion concentration. Here we propose that the reactant (substrate) is in equilibrium with a six-co-ordinate species with two halide ions occupying axial positions, leading to formation of a distorted octahedral configuration.



Such a species is in fact not abnormal and several six-co-ordinate gold(III) complexes have been proposed throughout the literature, *e.g.* $[Au(diars)_2X_2]^+$ [9] [X = Br and I; diars = *o*-phenylenebis(dimethylarsine)]. Furthermore Wieck and Basolo [10] compared the kinetics of substitution of various anions in $[Au(dien)Cl]^{2+}$ (dien = diethylenetriamine) with those of planar Pt^{II} showing that axial interaction was also possible in solution, *e.g.* equation (4). Baddley and Basolo [11] have also measured equilibrium constants for the reactions $[Au(dien)Cl]^{2+} \rightleftharpoons [Au(dien - H)Cl]^+ + H^+$, p$K_a$ 4·7, and $[Au(Et_4dien)Cl]^{2+} \rightleftharpoons [Au(Et_4dien - H)Cl]^+ + H^+$, p$K_a$ 2·2.* The differences in pK_a values were attributed to reduced positive charge on the central ion due to axial interaction with solvent molecules or chloride ions above and below the plane of the ion $[Au(dien)Cl]^{2+}$. This interaction would be less in the sterically hindered Et_4dien system and is enhanced if halide ion instead of a solvent molecule is co-ordinated to the central metal ion. In addition, the inertness of bipy in the complexes studied in this investigation made it possible to study the reaction at chloride- and bromide-ion concentrations much greater than those used in the reactions with complexes containing unidentate amines. The pseudo-octahedral species can then release one end of the bidentate ligand through a dissociative mechanism, with subsequent competition between co-ordination of a third halide ligand and reclosing of the chelate ring or, alternatively, undergo direct attack by the third halide ligand in a competition stage analogous to that drawn for the parallel path first order in $[X^-]$. Once one end of the chelating ligand is released, protonation of the free nitrogen atom occurs. Protonation of the single-bonded bidentate ligand weakens the remaining metal–ligand bond and promotes complete dissociation of the ligand.



(4)

The reaction path (I) ⟶ (II) ⟶ (VII) is essentially analogous to that found in displacements of non-chelated ligands in square-planar complexes and which gives rise to the second-order term in the rate expression. The step (IV) ⟶ (V) in the reaction path (I) ⟶ (IV) ⟶ (VII) on the other hand resembles the path which gave rise to the second-order rate contribution in the displacement reaction of one bidentate ligand from $[Fe(bipy)_3]^{2+}$ in the presence of OH^- and CN^- ions.[12,13]

Making the approximation of the steady state for all the intermediates equation (5) may be deduced from the

$$-\frac{1}{[Au(bipy)X_2{}^+]_0}\frac{d[Au(bipy)X_2{}^+]_0}{dt} = \frac{k_2k_8(k_{-3}+k_7)[X^-]}{(k_{-2}+k_8)(k_{-3}+k_7)+k_3k_7[H^+]} + \frac{k_2k_3k_7[H^+][Cl^-]}{(k_{-2}+k_8)(k_{-3}+k_7)+k_3k_7[H^+]} + \frac{k_1k_4k_5k_6[H^+][Cl^-]^3}{k_{-1}k_{-4}(k_{-5}+k_6)+k_{-1}k_5k_6[H^+]+k_4k_5k_6[H^+][Cl^-]} \quad (5)$$

reaction scheme. This expression implies the approach to a limiting rate at high hydrogen-ion concentration. The linearity of the experimental dependence of rate constant on $[H^+]$ can be explained assuming that approach to the limiting value occurs at inaccessibly high proton concentrations. In fact if we assume that $k_3 \simeq k_{-3}$ and $k_5 \simeq k_{-5}$ (as expected from the low value of pK_a for $bipyH_2{}^{2+}$ [14]), and also that $k_{-2} \gg k_7[H^+]$, $k_{-4} \gg k_6[H^+]$, and $k_{-1}k_{-4} \gg k_4k_6[H^+][Cl^-]$ (as expected, ring closing being much faster than the other processes), the denominators in the above expression become acid independent.

As shown previously (see Results section) the bromide complex is much more reactive than the chloride (10^4—10^8 times faster). This may be the result of two separate effects: (i) the labilizing effect of *trans*-halogen, which is stronger for bromide than it is for chloride; and (ii) the stronger co-ordinating ability of Br^- which would favour formation of the six-co-ordinate species. We have also shown that the ratio $s'' : s'$ is larger in the second case (bromide complex) than it is in the first (chloro-complex) (although the data have been evaluated at different ionic strengths, this fact does not interfere with direct comparison of the two sets of data). This result strongly supports the hypothesis that direct interaction of the halide with the central metal ion occurs in the reaction path leading to the term with a third-order dependence on $[X^-]$ in the rate expression; if an ion-pair mechanism was operative the inverse trend would have been found.

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* Systematic names for dien and Et_4dien are 1,5-diamino-3-azapentane and *NNN′N′*-tetraethyl-1,5-diamino-3-azapentane; the abbreviations dien − H and Et_4dien − H indicate removal of the H atom at the 3-position.

[9] C. M. Harris and R. S. Nyholm, *J. Chem. Soc.*, 1957, 63; U. F. Duckworth and N. C. Stephenson, *Inorg. Chem.*, 1969, **8**, 1661.

[10] C. F. Wieck and F. Basolo, *Inorg. Chem.*, 1966, **5**, 576.

[11] W. H. Baddley and F. Basolo, *Inorg. Chem.*, 1963, **2**, 921.

[12] J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1965, 6061.

[13] J. Burgess, *J.C.S. Dalton*, 1972, 1061.

[14] J. H. Baxendale and P. George, *Trans. Faraday Soc.*, 1950, **46**, 55.