Displacement of Chelate Ligands from Planar Four-co-ordinate Complexes. Part III.[1,2] Displacement of 5-Nitro-1,10-phenanthroline from Dichloro(5-nitro-1,10-phenanthroline)gold(III) Ion

By **Giuliano Annibale, Giovanni Natile,*** and **Lucio Cattalini,** Istituto di Chimica Generale ed Inorganica, University of Venice, Italy

The kinetics of nucleophilic displacement of the chelate 5-nitro-1,10-phenanthroline (5-NO_2phen) from the complex $[AuCl_2(5\text{-}NO_2phen)]^+$ have been studied in 5% water–methanol solutions at 25 °C. At constant $[H^+]$ the reaction rate is second order in the chloride-ion concentration, and, at constant $[Cl^-]$, there is a linear dependence on the hydrogen-ion concentration with a finite intercept at $[H^+] = 0$. This dependence on $[Cl^-]$ differs from that found in the displacement of 2,2′-bipyridyl from $[AuCl_2(bipy)]^+$ and has been interpreted in terms of a mechanism in which there is no competition between co-ordination of an extra chloride and ring closing (as found in the bipy case). The effect of $[H^+]$ is smaller than that found in the bipy complex, indicating that in the present case the formation of protonated intermediates with the ligand still bonded to the metal is less favoured.

In Part I we reported a kinetic study of the displacement of 2,2′-bipyridyl from $[AuX_2(bipy)]^+$ (X = Cl or Br) by excess of halide in an acidic water–methanol medium.[1] In order to account for a third-order dependence of the reaction rate on the concentration of the entering halide, we postulated the axial interaction of two halide ions above and below the plane of the substrate leading to the formation of a six-co-ordinate intermediate. One end of the bidentate ligand then dissociated and there was subsequent competition between co-ordination of a third halide and reclosing of the chelate ring. This stepwise dissociation of a chelate ligand, which is likely to occur with bipy and other flexible bidentate ligands such as the substituted diamines studied in Part II,[2] is more difficult with the rigid ligand 1,10-phenanthroline. We therefore decided to investigate the displacement of 5-nitro-1,10-phenanthroline (5-NO_2phen) from $[AuCl_2(5\text{-}NO_2phen)]^+$ in order to test indirectly the validity of the previously suggested mechanism (the 5-nitro-derivative was chosen

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[1] Part I, G. Annibale, L. Cattalini, A. A. El Awady, and G. Natile, *J.C.S. Dalton*, 1974, 802.

[2] Part II, G. Annibale, L. Cattalini, and G. Natile, *J.C.S. Dalton*, 1975, 188.

because the ligand is less strongly bonded and the kinetics are, therefore, faster).

EXPERIMENTAL

Hydrogen tetrachloroaurate(III) trihydrate was purchased from Johnson, Matthey and Co.; 5-nitro-1,10-phenanthroline, $HClO_4$, LiCl, Li[ClO_4], and methanol were all reagent-grade products. The complex [$AuCl_2$(5-NO_2phen)]-[ClO_4] was prepared by the method reported[3] for the preparation of [$AuCl_2$(phen)][ClO_4] and characterized through its i.r. spectrum and elemental analysis, m.p. 296 °C (decomp.) {Found: C, 24.4; H, 1.2; Cl, 17.7; N, 7.3. [$AuCl_2$(5-NO_2phen)][ClO_4] requires C, 24.3; H, 1.35; Cl, 17.9; N, 7.1%}.

TABLE 1

Values of $k_{obs.}$ for the reaction [$AuCl_2$(5-NO_2phen)]$^+$ $\longrightarrow$ [$AuCl_4$]$^-$ at constant [Cl^-] and variable [H^+], and at constant [H^+] and variable [Cl^-], $I = 1.7$ mol dm^{-3} (Li[ClO_4]) and 25 °C

[Cl^-]/mol dm^{-3}	[H^+]/mol dm^{-3}	$10^5k_{obs.}$/s^{-1}
0.34	0.06	2.02
	0.12	3.04
	0.24	4.85
	0.36	6.34
	0.48	8.14
	0.60	9.50
0.81	0.024	9.43
	0.060	13.9
	0.12	16.1
	0.24	26.2
	0.36	35.7
	0.48	45.4
	0.60	54.0
1.19	0.024	23.0
	0.06	30.0
	0.12	37.7
	0.24	57.8
	0.36	77.8
	0.48	99.6
0.57	0.12	8.79
	0.24	12.6
	0.30	14.6
	0.36	17.2
	0.48	22.4
	0.60	25.3
1.00	0.05	18.0
	0.10	24.0
	0.12	25.0
	0.20	34.6
	0.24	39.0
	0.35	51.1
	0.36	53.0
	0.48	68.0
[H^+]/mol dm^{-3}	[Cl^-]/mol dm^{-3}	$10^5k_{obs.}$/s^{-1}
0.082	0.47	4.93
	0.75	11.5
	1.13	28.1
	1.32	37.5

Kinetics.—Separate solutions of the complex and reagents were prepared in methanol containing 5% water. The concentrations of the chloride ion and perchloric acid were determined by standard titrimetric methods. Lithium perchlorate was added in order to maintain a constant ionic strength. The reagent solutions were separately brought to the reaction temperature, then mixed in the thermostatted cell of an Optica CF4R double-beam 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 sufficient excess of the reagents, Cl^- and H^+, to provide pseudo-first-order conditions; the concentration of the gold complex in the reaction mixture was always less than 10^{-4} mol dm^{-3}. In each case the appearance of well defined isosbestic points indicated that a single-stage process was being observed. Pseudo-first-order rate constants, $k_{obs.}$, were obtained from semi-logarithmic plots of $\ln(A_\infty - A_t)$ against time, where A_t and A_∞ are the 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 are summarized in Table 1. From the values of $k_{obs.}$ the parameters B_0, B_1, and B_1' shown in Table 2 were calculated by least-squares methods. The constants r and s (see text) were derived from these parameters using an unweighted least-squares program and the error in their values was derived from the standard deviations of B_0, B_1, and B_1' using the formula for indirect error.

TABLE 2

Values of the intercepts, B_0 (at [H^+] = 0), and gradients, B_1, of straight lines obtained from plots of $k_{obs.}$ against [H^+] at constant [Cl^-], and values of gradients, B_1', of straight lines with zero intercept obtained from plots of $k_{obs.}$[Cl^-] against [Cl^-] at constant [H^+], using the values from Table 1 (the parameters were obtained from least-squares calculation)

[Cl^-]/mol dm^{-3}	10^4B_1/dm^3 mol^{-1} s^{-1}	10^5B_0/s^{-1}
0.34	1.38 ± 0.10	1.35 ± 0.36
0.57	3.59 ± 0.43	4.26 ± 1.60
0.81	7.78 ± 0.26	7.61 ± 0.89
1.00	11.50 ± 0.45	11.76 ± 1.24
1.19	16.62 ± 0.78	18.75 ± 2.11
[H^+]/mol dm^{-3}	10^4B_1/dm^6 mol^{-2} s^{-1}	
0.082	2.19 ± 0.52	
0.24	4.02 ± 0.48	
0.36	5.46 ± 0.45	
0.48	6.98 ± 0.54	

RESULTS

The spectroscopic course of the reaction showed the presence of two well defined isosbestic points at 297 and 278 nm, clearly indicating that the reaction takes place in one step. The final spectrum corresponded to that of a solution of [5-NO_2-Hphen][$AuCl_4$] in the same medium, indicating that the reaction studied is the displacement of the chelate ligand by chloride.

The observed rate constants are given in Table 1. At a given chloride concentration the rate of reaction increased linearly as the acid concentration was increased in accord with the two-term rate expression (1); B_0 and B_1 are

$$k_{obs.} = B_0 + B_1[H^+] \qquad (1)$$

respectively the intercept and gradient of a plot of $k_{obs.}$ against [H^+] at constant [Cl^-] (Figure 1), and their values, calculated by least-squares methods, are given in Table 2. These parameters depend on the concentration of chloride.

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

A plot of $B_0[\mathrm{Cl}^-]^{-1}$ against $[\mathrm{Cl}^-]$ was linear and passed through the origin. The gradient [r in equation (2)] was

$$B_0 = r[\mathrm{Cl}^-]^2 \qquad (2)$$

$(1.24 \pm 0.25) \times 10^{-4}$ dm^6 mol^{-2} s^{-1}. The parameters B_1 also increased as $[\mathrm{Cl}^-]$ was increased, and a plot of $B_1[\mathrm{Cl}^-]^{-1}$ against $[\mathrm{Cl}^-]$ was also linear and passed through the origin.

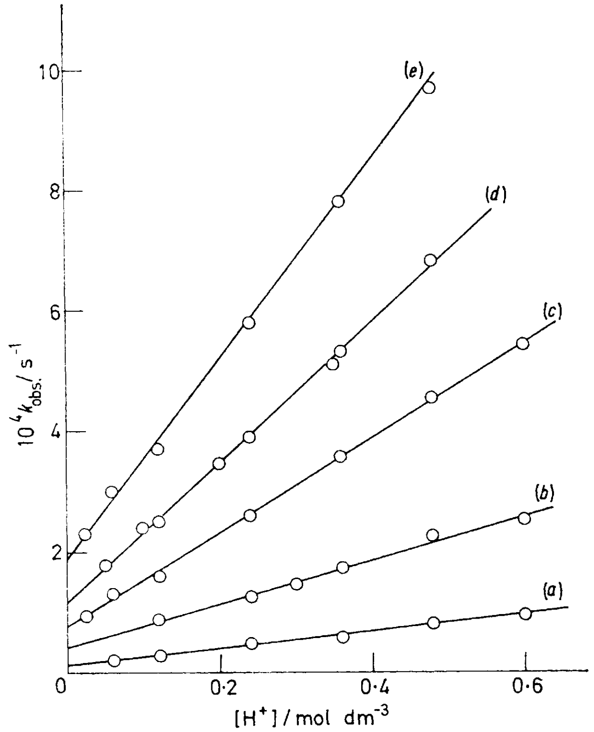


FIGURE 1 Plots of pseudo-first-order rate constants, $k_{\mathrm{obs.}}$, against $[\mathrm{H}^+]$ at constant $[\mathrm{Cl}^-]$ for the reaction $[\mathrm{AuCl_2(5\text{-}NO_2phen)}]^+ \longrightarrow [\mathrm{AuCl_4}]^-$. $[\mathrm{Cl}^-]$ = 0.34 (*a*), 0.57 (*b*), 0.81 (*c*), 1.00 (*d*), and 1.19 mol dm^{-3} (*e*); I = 1.7 mol dm^{-3} (Li[ClO$_4$]), 25 °C

The gradient [s in equation (3)] was $(1.18 \pm 0.05) \times 10^{-3}$ dm^9 mol^{-3} s^{-1}.

$$B_1 = s[\mathrm{Cl}^-]^2 \qquad (3)$$

From equations (1)—(3) we can write expression (4) for the overall dependence of $k_{\mathrm{obs.}}$ on $[\mathrm{H}^+]$ and $[\mathrm{Cl}^-]$. It

$$k_{\mathrm{obs.}} = r[\mathrm{Cl}^-]^2 + s[\mathrm{Cl}^-]^2[\mathrm{H}^+] \qquad (4)$$

follows that on plotting $k_{\mathrm{obs.}}[\mathrm{Cl}^-]^{-1}$ against $[\mathrm{Cl}^-]$ at constant $[\mathrm{H}^+]$, straight lines passing through the origin and having gradient $B_1' = r + s[\mathrm{H}^+]$ should be obtained (Figure 2). The values of B_1' obtained for $[\mathrm{H}^+]$ = 0.08, 0.24, 0.36, and 0.48 mol dm^{-3} using the values of $k_{\mathrm{obs.}}$ reported in Table 1 are also summarized in Table 2. A plot of B_1' against $[\mathrm{H}^+]$ (Figure 3) gave the values $(1.17 \pm 0.56) \times 10^{-4}$ dm^6 mol^{-2} s^{-1} and $(1.20 \pm 0.18) \times 10^{-3}$ dm^9 mol^{-3} s^{-1} for r and s respectively. The agreement of these values with those obtained independently from the previous treatment of the experimental data provides good support for rate expression (4).

DISCUSSION

Contrary to what was found with the displacement of bipy, it is necessary, on the basis of the experimental results, to exclude the participation of a third halide ion in the displacement of 5-nitro-1,10-phenanthroline from $[\mathrm{AuCl_2(5\text{-}NO_2phen)}]^+$. This is consistent with the view that it is almost impossible for the rigid 5-NO$_2$phen to be unidentate in a complex with a third halide taking

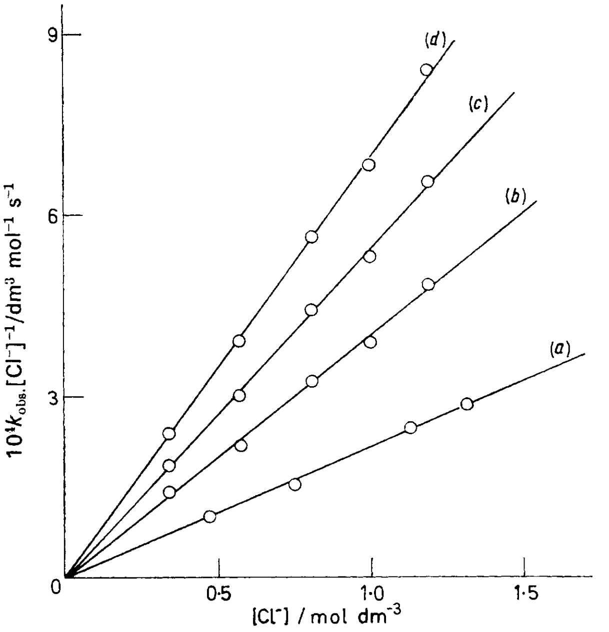


FIGURE 2 Plots of $k_{\mathrm{obs.}}[\mathrm{Cl}^-]^{-1}$ against $[\mathrm{Cl}^-]$ at constant $[\mathrm{H}^+]$ for the reaction $[\mathrm{AuCl_2(5\text{-}NO_2phen)}]^+ \longrightarrow [\mathrm{AuCl_4}]^-$. $[\mathrm{H}^+]$ = 0.08 (*a*), 0.24 (*b*), 0.36 (*c*), and 0.48 mol dm^{-3} (*d*); I = 1.7 mol dm^{-3}, 25 °C

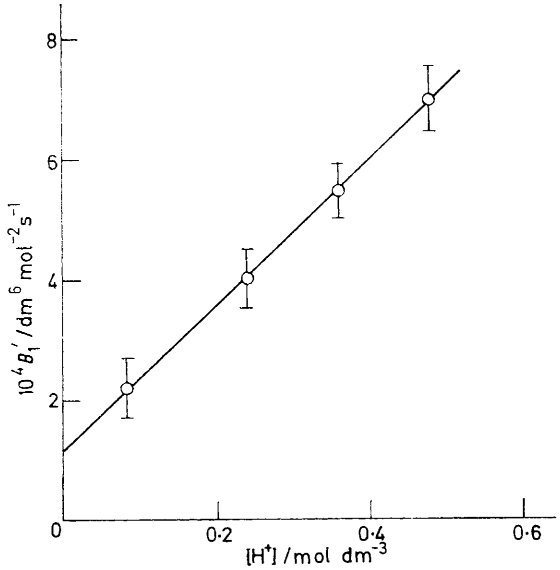
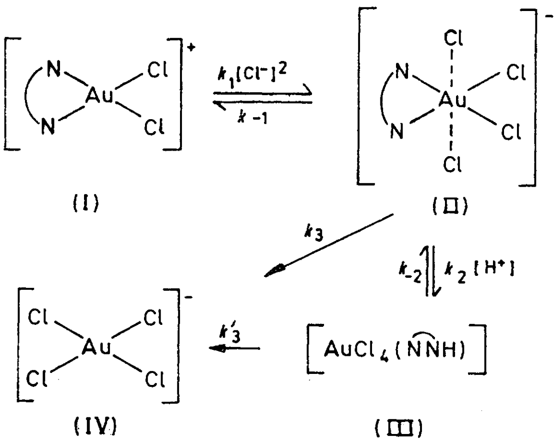


FIGURE 3 Plot of B_1 against $[\mathrm{H}^+]$ for the reaction $[\mathrm{AuCl_2(5\text{-}NO_2phen)}]^+ \longrightarrow [\mathrm{AuCl_4}]^-$

the place of the displaced nitrogen. In the bipy case, once one end of the chelate ligand has been displaced, protonation at the free nitrogen can take place, thus weakening the remaining metal–ligand bond and promoting complete dissociation of the ligand. The reaction rate is therefore proportional to the hydrogen-ion concentration. In the rate expression for the displacement of 5-NO_2phen there is a term which is proportional to $[H^+]$ and another which is independent of $[H^+]$. In the suggested mechanism we have therefore introduced an equilibrium between an unprotonated and a protonated species which both decompose to give the final products.



Some comments may be made on this reaction scheme. In principle, the intermediates can be considered either as unstable, in which case the steady-state approximation is appropriate, or as in a pre-equilibrium with the reactant; the rate expressions in the two different cases would be (5) and (6), respectively. Both expressions

$$\text{Rate} = \frac{k_1k_3(k_{-2} + k_3')[Cl^-]^2 + k_1k_2k_3'[H^+][Cl^-]^2}{(k_{-1} + k_3)\,(k_{-2} + k_3') + k_3'k_2[H^+]} \quad (5)$$

$$\text{Rate} = \frac{k_1k_3k_{-2}[Cl^-]^2 + k_1k_2k_3'[H^+][Cl^-]^2}{k_{-1}k_{-2} + k_1k_{-2}[Cl^-]^2 + k_1k_2[H^+][Cl^-]^2} \quad (6)$$

reproduce the experimental rate law if the kinetic constants are such that in the denominator the terms which are functions of $[H^+]$ and/or $[Cl^-]$ are negligible in comparison to the others. In the first hypothesis, this implies that the protonation equilibrium is shifted towards the unprotonated species, and in the second hypothesis that the equilibria between species (I) and (II) and (II) and (III) both lie well to the left. It is clear that under these circumstances no distinction can be made between the two hypotheses and both are in accord with the presence, from the beginning of the experimental runs, of two good isosbestic points and the absence of any significant change in absorbance soon after the mixing of the reagents. The suggested mechanism implies two simultaneous reactions for the decomposition of species (II) to the final products, one involving direct participation of the hydrogen ion and the other not.

The effect of the hydrogen-ion concentration on the rate of dissociation of phenanthroline in transition-metal complexes has been observed in other cases.[4,5] In particular, for the dissociation of (1,10-phenanthroline)-nickel(II) the observed rate constant, k_d, is greatly dependent on $[H^+]$ and increased with increasing $[H^+]$ to a limiting value. It was suggested that in highly acidic solution (concentration greater than 0.5 mol dm^{-3}) a proton could be associated with the phen portion of the complex but not directly with the nitrogen, forming a new complex $[Ni(Hphen)(OH_2)_4]^{3+}$ or, alternatively, a unidentate phen intermediate with a protonated free nitrogen could be formed.[6] On the other hand, it is known that the phenanthrolinium ion forms a diprotonated species in strongly acidic solutions, and for the equilibrium $[H_2phen]^{2+} \rightleftharpoons [Hphen]^+ + H^+$ a constant of 5 mol dm^{-3} has been estimated in aqueous solution.[6] The analogy of the behaviour of a co-ordinated proton and a metal ion led us to suppose that, as $[Hphen]^+$ can fix another proton forming $[H_2phen]^{2+}$, a co-ordinated phen molecule can also be protonated.

The same experimental conditions (25 °C, $I = 1.7$ mol dm^{-3}) used in the displacement of bipy and 5-NO_2phen allows a direct comparison between the rates of the two reactions. In the displacement of bipy the term third order in $[Cl^-]$ in the experimental rate expression was $5.24 \times 10^{-3}[H^+][Cl^-]^3$; in the present case the contribution second order in $[Cl^-]$ is $(1.2 \times 10^{-4} + 1.2 \times 10^{-3}[H^+])[Cl^-]^2$. The individual constants cannot be compared since they refer to different processes; however, at equal $[H^+]$ and $[Cl^-]$ the rate was much smaller in the phen than in the bipy case. In metal complexes with a series of closely related chelate molecules it is expected that the relative order of stabilities of the metal–nitrogen bond is the same as that of the basic strength of the ligand.[7] The reported pK_a values of 5-NO_2phen [8] and bipy [9] are 3.57 and 4.33 respectively; therefore, from an electronic point of view, the metal–nitrogen bond should be stronger in the bipy than in the 5-NO_2phen case. The fact that the rates of dissociation do not parallel the weakness of the metal–nitrogen bond is a clear indication that the rigidity of the 5-NO_2phen ligand slows down the dissociation reaction; bipy and substituted ethylenediamines, unlike phen, can form unidentate complexes with metals and in part they owe their greater reactivity to their greater flexibility.[10]

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1,10-Phenanthroline differs from the other, more flexible, ligands also in its substitution into the square-planar substrates $[PtCl_4]^{2-}$ and $[PdCl_4]^{2-}$.[10-12] In these cases the reaction is unusually slow and insensitive to the basicity of the phen derivative used and to whether or not it was protonated. The slowness of the reaction can be assigned to the steric hindrance to bond formation by phen together with its inability to act as a simple unidentate ligand towards the metal ion, and related to this is the equal rate of reaction displayed by free and protonated phen. The activated complex would therefore have the same stoicheiometry as intermediates (II) and (III) in our reaction scheme with a phen molecule or a phenanthrolinium ion associated with a $[MCl_4]^{n-}$ moiety.

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