Reactions between Tetrachlorogold(III) Ions and *N*-Cyclohexylthiobenzamide

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Kinetic and spectroscopic evidence is presented which shows that in aqueous solution tetrachlorogold(III) ions and *N*-cyclohexylthiobenzamide (S) interact stoicheiometrically to form the 1 : 1 complexes $[AuCl_2(OH)(S)]^0$, $[AuCl_2(H_2O)(S)]^+$, $[AuCl_3(S)]^0$, and $[AuCl_5(S)]^{2-}$. The complexes are in rapid equilibrium and their relative concentrations depend upon the free chloride and hydrogen ion concentrations. All the complexes decompose, probably *via* a slow reaction with water, to give the *O*-amide and gold sulphide. In this decomposition $[AuCl_5(S)]^{2-}$ is the most reactive and the addition of chloride ions to a reaction mixture can therefore provide catalysis based on the conversion of a four- to a six-co-ordinated species. A possible explanation is given.

FEW studies exist of the interactions between thioamides and gold compounds. For aqueous acid solutions there is evidence [1] that relatively stable complexes between thiobenzamide and gold species are formed and in aqueous alkaline solution the decomposition of related complexes has been observed.[2] We now report on the reactions between tetrachlorogold(III) ions and *N*-cyclohexylthiobenzamide in aqueous perchloric acid.

EXPERIMENTAL

Materials.—*N*-Cyclohexylthiobenzamide was a previous sample.[3] Ethanol, perchloric acid, and sodium chloride and perchlorate were all of AnalaR grade. Sodium tetrachlorogold(III) was the B.D.H. reagent grade material. The thioamide was used as a stock solution in ethanol and all reaction mixtures contained 2% (v/v) ethanol.[3]

U.v. Spectral Changes and Complex Formation.—The equilibria (1) have been established [4,5] for gold chloride species in aqueous acid solution. They are set up rapidly with K *ca.* 10^{-3} mol l^{-1} and K_a *ca.* 0.63 at 25°. The spectra

$$[AuCl_4]^- + H_2O \overset{K}{\rightleftharpoons} [AuCl_3(H_2O)]^0 + Cl^- \overset{H_2O,\,K_a}{\rightleftharpoons} [AuCl_3(OH)]^- + H_3O^+ + Cl^- \quad (1)$$

of $[AuCl_4]^-$ and of $[AuCl_3(H_2O)]^0$ are very similar (Figure 1), ε_{310} being 4200 for the former and 4700 for the latter. When both the chloride and hydrogen ion concentrations are low, equilibria (1) lie to the right; the spectrum of $[AuCl_3(OH)]^-$ has no maximum at 310 nm (Figure 1). At any chosen acidity ($\lesssim$1.0M) and chloride ion concentration ($\lesssim$0.1M) the addition of *N*-cyclohexylthiobenzamide leads to the rapid formation of 1 : 1 complexes with the gold species by displacement of chloride. The spectra of the complexes formed with $[AuCl_4]^-$ (*i.e.* at high $[H_3O^+]$ and $[Cl^-]$) and with $[AuCl_3(OH)]^-$ (*i.e.* at low $[H_3O^+]$ and $[Cl^-]$) are also shown in Figure 1. By making measurements, along lines previously described,[3,6] at 325 nm, where *N*-cyclohexylthiobenzamide absorbs only slightly, it is possible to show

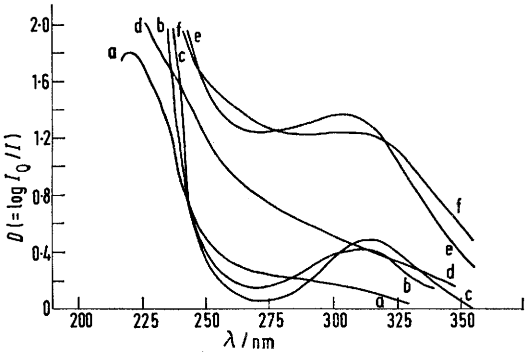
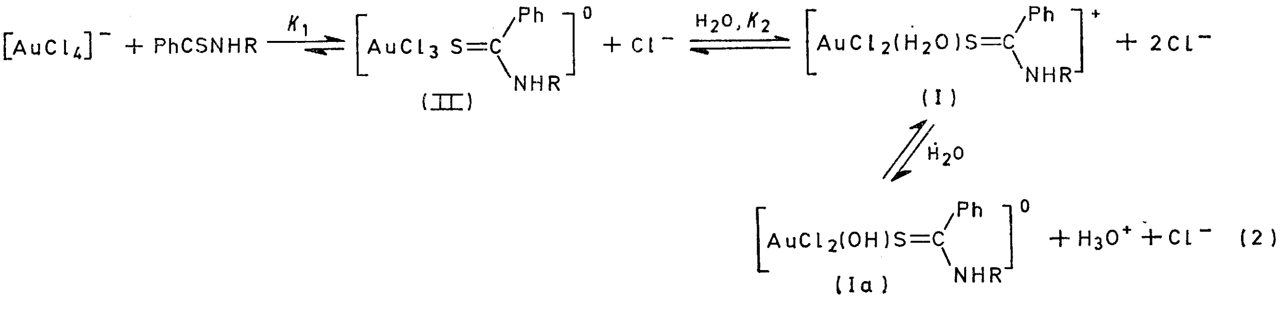


FIGURE 1 Spectra of gold complexes $\{10^4[AuCl_4^-]$ 1.0M; solvent, 2% (v/v) $EtOH-H_2O$; $S = PhCSNHC_6H_{11}\}$: a, $[AuCl_3(OH)]^-$; b, $[AuCl_4]^-$; c, $[AuCl_3(H_2O)]^0$; d, $[AuCl_2(OH)(S)]^0$; e, $[AuCl_2(H_2O)(S)]^+$; f, $[AuCl_3(S)]^0$



$$[AuCl_4]^- + PhCSNHR \overset{K_1}{\rightleftharpoons} \left[AuCl_3\ S{=}C\begin{matrix}Ph\\NHR\end{matrix}\right]^0_{(II)} + Cl^- \overset{H_2O,\,K_2}{\rightleftharpoons} \left[AuCl_2(H_2O)S{=}C\begin{matrix}Ph\\NHR\end{matrix}\right]^+_{(I)} + 2Cl^-$$

$$\left[AuCl_2(H_2O)S{=}C\begin{matrix}Ph\\NHR\end{matrix}\right]^+_{(I)} \overset{H_2O}{\rightleftharpoons} \left[AuCl_2(OH)S{=}C\begin{matrix}Ph\\NHR\end{matrix}\right]^0_{(Ia)} + H_3O^+ + Cl^- \quad (2)$$

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[1] F. Kasparek and J. Mallin, *Coll. Czech. Chem. Comm.*, 1960, **25**, 2919.

[2] S. A. Voznesenskii, I. Pazel'skii, and I. M. Tsinn, *Trans. Inst. Pure Chem. Reagents, U.S.S.R.*, 1939, **16**, 98.

[3] A. J. Hall and D. P. N. Satchell, *J.C.S. Perkin II*, 1975, 778.

[4] W. Robb and I. van Z. Bekker, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 849.

[5] B. I. Peshchevitskii, V. I. Belevantsev, and N. V. Kurbatova, *Russ. J. Inorg. Chem.*, 1971, **16**, 1007.

[6] A. E. Harvey and D. Manning, *J. Amer. Chem. Soc.*, 1950, **72**, 4488.

that under all conditions the interactions are 1 : 1 and effectively stoicheiometric. The spectral observations as a whole indicate the existence of equilibria (2) in which K_1 is very large. When $[Cl^-] \geqslant 0.1$M further small spectral changes are seen which suggest that complex (II) is possibly being converted into another species. For complexes (I) and (II), ε_{310} = 13 200 and 12 600 respectively. Complex (Ia) has no maximum near 310 nm. Measurements at, or near, 310 nm, using a series of solutions of different hydrogen ion concentrations in the range 10^{-3}—3×10^{-2}M, permit the calculation of pK_a for the acid dissociation (I) $\rightleftharpoons$ (Ia); we find pK_a 1.55 ± 0.05 at 25°.

All the complexes decompose to the *O*-amide; this relatively slow decomposition does not prevent accurate observation of the initial complex formation.

Products.—Preparative scale experiments, using various concentration conditions, show that the *S*-amide–gold complexes decompose to give the corresponding *O*-amide and (normally) Au_2S_3 in high (>90%) yield. In reaction mixtures containing a large excess of the tetrachlorogold(III) ion more than the stoicheiometric quantity of this species is consumed and the inorganic product under these conditions is uncertain.

Kinetic Arrangements.—The rate of disappearance of the (total) 1 : 1 complex was measured spectroscopically at 310 nm, using various free tetrachlorogold(III), chloride, and perchloric acid concentrations. In all runs $[AuCl_4^-]_{stoich} \geqslant [PhCSNHR]_0$, so that the whole of the *S*-amide was present as 1 : 1 complex. All runs were at 25° and at a constant ionic strength of 2.5M maintained by sodium perchlorate. The loss of 1 : 1 complex was an accurately first-order process over two half-lives and the observed first-order rate constant, k_{obs}, was calculated from the slope of the plot of log $(D - D_\infty)$ against time. Values of k_{obs} (Table) were reproducible to within ±5%. The reaction mixtures remained homogeneous throughout all runs, gold sulphide being eventually precipitated in some cases.

RESULTS AND DISCUSSION

The results in the Table show (i) that k_{obs} is unaffected by the presence of free tetrachlorogold(III) ions, (ii) that k_{obs} is effectively independent of the hydrogen ion concentration at all chloride ion concentrations, and (iii) that, at a fixed value of $[H_3O^+]$, as $[Cl^-]$ rises from 0.0 to 3.0M, k_{obs} first falls and then rises again, its value eventually levelling-out when $[Cl^-] \gtrsim 2.0$M (Figure 2). These kinetic results can be nicely rationalised if the rapidly established equilibria (2), which explain most of the spectroscopic measurements, are extended as in (3) to include the hexa-co-ordinated gold complex (III). It is assumed that complexes (I), (Ia), (II), and (III) can all lead to the *O*-amide *via* slow reactions in which water attacks the thiocarbonyl carbon atom.

Effects of hydrogen, tetrachlorogold(III), and chloride ion concentrations

$10^5[PhCSNHR]_0$ 5.0M; temperature 25°; ionic strength 2.50M; k_{obs} = observed first-order rate constant

(i) Effect of hydrogen ion concentration ($10^4[AuCl_4^-]$ 3.0M)

(a) $[Cl^-]$ 0.00

$10^3[H_3O^+]$/M	0.18	0.91	1.82	9.12	91.2	916
10^2k_{obs}/min^{-1}	5.32	5.44	5.51	5.50	5.42	5.60

(b) $[Cl^-]$ 0.04M

$10^2[H_3O^+]$/M	0.00	9.12	45.8	91.6
10^2k_{obs}/min^{-1}	1.92	2.10	2.10	2.02

(c) $[Cl^-]$ 1.00M

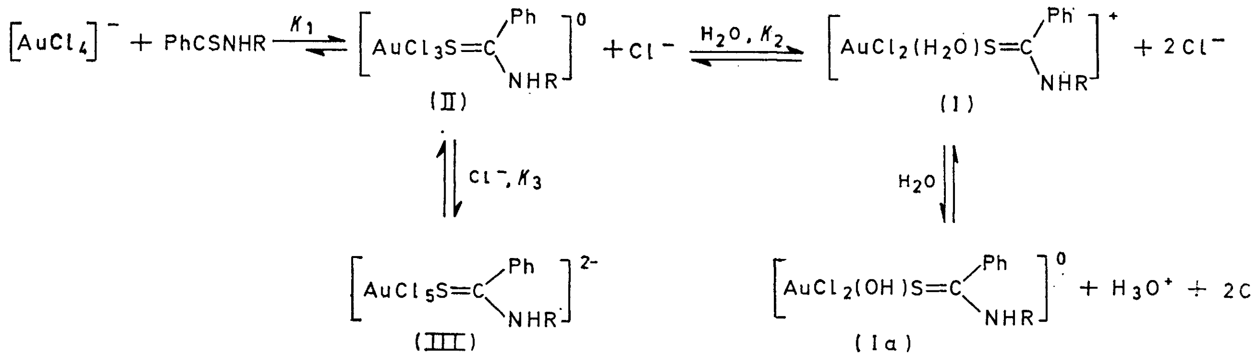
$10^3[H_3O^+]$/M	0.18	0.91	458	916
10^2k_{obs}/min^{-1}	1.71	1.80	1.62	1.80

(ii) Effect of tetrachlorogold(III) ion concentration ($[H_3O^+]$ 0.46M; $[Cl^-]$ 2.0M)

$10^5[AuCl_4^-]$/M	5.0	10	15	20	30
$10k_{obs}$/min^{-1}	1.62	1.81	1.80	1.72	1.74

(iii) Effect of chloride ion concentration ($[H_3O^+]$ 0.46M; $10^4[AuCl_4^-]$ 3.0M)

$10^4[Cl^-]$/M	0.00	0.20	0.50	0.80	1.20	2.40	4.00
10^2k_{obs}/min^{-1}	2.90	2.88	2.70	2.49	2.30	1.82	1.40
$10^4[Cl^-]$/M	8.00	20.0	40.0				
10^2k_{obs}/min^{-1}	1.09	0.905	0.690				
$[Cl^-]$/M	0.02	0.04	0.10	0.15	0.20	0.30	0.40
10^2k_{obs}/min^{-1}	0.690	0.898	2.01	2.67	4.04	5.11	8.20
$[Cl^-]$/M	0.60	9.00	1.00	1.20	1.50	1.75	
10^2k_{obs}/min^{-1}	11.8	14.6	15.5	16.1	16.9	17.0	



(3)

It is evident from (i) that only complexes containing one gold atom are involved in the slow process. That is compatible with the proposed scheme. Fact (ii) shows that the dissociation of the water proton in (I), to give (Ia), which occurs at low chloride and hydrogen ion concentrations, has little effect on k_{obs}. The reactivities of (I) and (Ia) towards decomposition to the *O*-amide are therefore taken to be similar. That seems possible.

When $[H_3O^+] = 0.46$M the concentration of (Ia) is negligible at all values of $[Cl^-]$ and the predicted rate equation is therefore (4), where k_{I}, k_{II}, and k_{III} are the pseudo-first order rate constants for the reactions of water with complexes (I), (II), and (III), respectively. Using the equilibrium constants defined by equation (3)

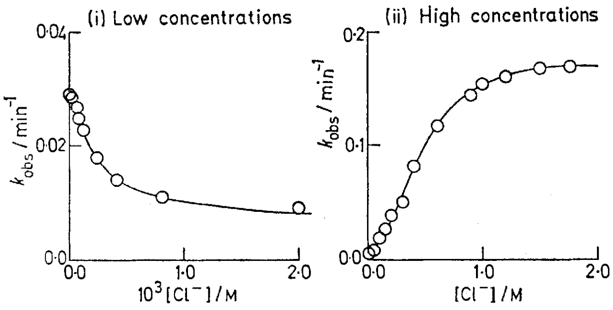


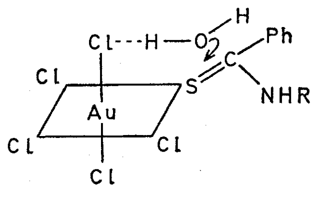
FIGURE 2 Effect of chloride ion concentration on k_{obs} at 25°: $10^5[S\text{-amide}]_{initial}$ 5.0M; $10^4[AuCl_4]^-_{initial}$ 3.0M; $[H_3O^+]$ 0.46M; ionic strength 2.5M

$$-d[1:1\ \text{complex}]_{total}/dt = k_{obs}\{[(I)] + [(II)] + [(III)]\} = k_I[(I)] + k_{II}[(II)] + k_{III}[(III)] \quad (4)$$

it can be shown that $k_{obs} = (k_I K_2 + k_{II}[Cl^-] + k_{III}K_3[Cl^-]^3)/(K_2 + [Cl^-] + K_3[Cl^-]^3)$. This expression with $10^2k_I = 3.2$ min^{-1}, $10^3k_{II} = 6.0$ min^{-1}, $k_{III} = 0.18$ min^{-1}, $10^4K_2 = 2.0$ mol l^{-1}, and $K_3 = 5.4$ mol^{-2} l^2 leads to values of k_{obs} represented by the continuous lines in Figure 2. The proposed scheme is clearly in good agreement with the effects of changes in $[Cl^-]$. The kinetic evidence for the existence of (III) is to that extent strong. The principal reactant at high chloride ion concentrations is thus probably (III).

Previous evidence [7,8] (largely spectroscopic) for hexa-co-ordinate gold is not compelling, except in work on chelated complexes.[9] However, a recent kinetic study [10] of the conversion of $[Au(bipy)X_2]^+$ into $[AuX_4]^{2-}$ (where $X = Cl^-$ or Br^-) strongly suggests the intermediacy of complexes similar to (III). As noted in the Experimental section, the spectral changes at high chloride ion concentrations are suggestive of further complexation of (II), but alone are insufficient to identify (III). There is no evidence for a penta-co-ordinate species in either the present, or the previous,[10] kinetic study.

We tentatively attribute the relative reactivities of the complexes [*i.e.* (III) > (I) > (II)] to the slow step being an attack on the thiocarbonyl carbon atom by outer-sphere water molecules hydrogen-bonded to the other resident ligands, *e.g.* (IV). We suggest this process could be easier in (I) than in (II), owing to one resident ligand being water already, and appreciably easier in (III) than in (II) owing to the hexa-co-ordination which will make the relevant intramolecular collisions more likely. The details of the steps following the slow step can only be guessed at. Whatever the true explanation of the relatively great reactivity of (III), it is clear that high chloride ion concentrations provide a catalysis of the present decomposition. This type of catalysis *via* hexa-co-ordinated ligands may well be relevant to the reactions of other square planar complexes.



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[7] C. M. Harris, S. E. Livingstone, and I. H. Reese, *Austral. J. Chem.*, 1957, **10**, 282.

[8] C. M. Harris and I. H. Reese, *Nature*, 1958, **182**, 1665.

[9] 'Comprehensive Inorganic Chemistry,' eds. J. C. Bailar, H. J. Emeléus, Sir Ronald Nyholm, and A. F. Trotman-Dickenson, Pergamon, New York, 1973, vol. 3.

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