Figure 3.—Potentiometric titration of the bis(2-pyridyl-methyl)amine ligand under the conditions: A, 0.002 M ligand; B, 0.004 M ligand and 0.002 M Cu(II); C, data of curve B replotted to show monodentate coordination of second ligand; D, 0.004 M ligand and 0.002 M Ni(II); E, data of curve D replotted to show tridentate coordination of second ligand.

formation of the 1:1 complex only. To place emphasis upon the coordination of the *second* ligand alone, the dotted curve C is shown. Curve C was obtained by replotting the data of curve B after correction of the a

values to eliminate the effect of the first ligand. (That it, the pH at $a = 1.5$ on curve B corresponds, stoichiometrically, to the beginning of the titration of the second ligand and is thus transposed to a value of $a = 0$ on curve C. Likewise, the pH at $a = 2$ is transposed to $a = 1$, etc. This procedure leads to the most meaningful results in those cases where the coordination of the first ligand is substantially complete prior to the beginning of the coordination of the second ligand.) From curve C it is observed that the titration of the *second* ligand, in the presence of the already formed 1:1 complex, follows the titration of the ligand itself until the two pyridine protons have been almost completely removed thus indicating little, if any, coordination. During the neutralization of the third (amine) proton, coordination is occurring as evidenced by the departure of curve C from curve A. These results indicate that for the second ligand there is negligible coordination until the amine nitrogen becomes involved in a monodentate fashion. This agrees with the explanation based upon enthalpies given by Fernelius for dien and Cu(II). Similar 2:1 titrations for 2-DPA and the other metal ions indicated that only for Ni(II) and Cd(II) does the second ligand appear to coordinate in a tridentate manner. Curves D and E are similarly obtained in the case of Ni(II).

The Mechanistic Role of Dibenzyl Sulfide as an Entering and Leaving Group in Neutral Gold(III) Systems

BY L. CATTALINI, G. MARANGONI, AND M. MARTELLI

The kinetics of displacement of amines (am) from a series of complexes of the type AuCl₃(am) by dibenzyl sulfide and of the reverse reactions have been measured in acetone at 25° and compared with the data relative to other reactions of the same substrates. The discrimination between complexes containing amines of different basicity is related to the relative influence of the bond-making and bond-breaking aspects of the substitution process. The steric effects observed with pyridine derivatives having methyl group(s) *ortho* to the nitrogen are discussed in terms of steric perturbations in the transition state.

Introduction

The range of reagents which have been used in the study of the kinetics of displacement of ligands from planar gold(III) complexes[1] is limited because the rates and nature of the reaction of Au(III) substrates are extremely sensitive to the nature of the nucleophile. In many cases the reactions are too fast to measure by conventional techniques and in many others reduction occurs in preference to substitution.

In order to extend the range of nucleophiles examined

and also to obtain systematic information about the reactivity of thioethers toward planar d⁸ substrates we have examined the kinetic behavior of dibenzyl sulfide.

A preliminary study indicated that the tetrachloroaurate(III) anion reacts rapidly with dibenzyl sulfide and other thioethers in methanol at 25° and is reduced.[2] However, in acetone at 25° it is possible to study the forward and reverse steps of reactions of the type

$$\text{AuCl}_3(\text{am}) + \text{Bz}_2\text{S} \rightleftharpoons \text{AuCl}_3(\text{Bz}_2\text{S}) + \text{am}$$

(1) L. Cattalini, A. Orio, and M. L. Tobe, *J. Am. Chem. Soc.*, **89**, 3130 (1967), and references therein.
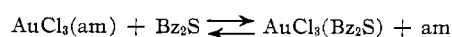
(2) V. Ricevuto, unpublished results.

(am = a heterocyclic nitrogen base, Bz₂S = dibenzyl sulfide) under conditions where reduction does not cause undue interference. The kinetics of these reactions are reported and discussed in this paper.

Results

A solution of $AuCl_3(Bz_2S)$ in dry acetone is stable for at least 1 week and only undergoes reduction in the presence of a large excess of the thioether. In the reactions

$$AuCl_3(Bz_2S) + am \longrightarrow AuCl_3(am) + Bz_2S \qquad (1)$$
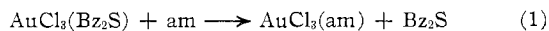
the dibenzyl sulfide is never present in sufficient amount to interfere and the complex undergoes substitution in the presence of excess amine without any reduction. The final spectra are identical with the sum of the spectra of $AuCl_3(am)$ and Bz_2S (in the region where the amine does not absorb significantly) thus indicating that, under the experimental conditions, the reaction went to completion.

The reverse reactions, *i.e.*

$$AuCl_3(am) + Bz_2S \longrightarrow AuCl_3(Bz_2S) + am \qquad (2)$$
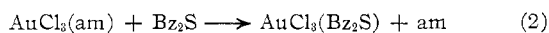
were carried out in the presence of an excess of thioether in order to ensure pseudo-first-order conditions and force the reaction to completion. These are conditions where reduction may be likely but the change of optical density with the time at 340 mμ takes place in two stages. In the first the absorbance increases from that of the amine to that of the sulfide complex. In the second step, the absorbance decreases more slowly. The first stage therefore corresponds to the replacement of the coordinate amine by Bz_2S. If the reaction was carried out in more concentrated solution (preparative conditions) using equimolar quantities of $AuCl_3(am)$ and Bz_2S, it was possible to obtain the thioether complex in almost quantitative yield, when the least basic amines were displaced. The second step corresponds to the reduction of Au(III) to Au(I) and the stoichiometry and mechanism of the reaction are under investigation. In a few cases, where the most basic amines were being displaced and the concentration of thioether was insufficient to push the reaction to completion, the rate constant was obtained from the initial rate of the reaction.

All of the reactions were followed spectrophotometrically and carried out in the presence of a large excess of the entering reagent to ensure that, wherever possible, the reaction went to completion and that, in any particular run, the kinetics were of a first-order form. The rate constants (k_{obsd}) were obtained from the slope of the plot of log $(D_t - D_\infty)$ vs. time, where D_t and D_∞ are the optical densities of the reaction mixture at 340 mμ at time t and at the end of the reaction, respectively. Measurements carried out at other wavelengths, where there is an adequate change of optical density, give the same value for the rate constants. The values of k_{obsd} are summarized in Table I.

The rate constants were generally reproducible to ±5% except for the reactions where sterically hindered amines were leaving groups, where the error is greater

Table I[a]

FIRST-ORDER RATE CONSTANTS DETERMINED IN ACETONE AT 25°

$$AuCl_3(Bz_2S) + am \longrightarrow AuCl_3(am) + Bz_2S$$

$10^2[am]$, M	10^2k_{obsd}, sec⁻¹	$10^2[am]$, M	10^2k_{obsd}, sec⁻¹
3-Cyanopyridine		**Quinoline**	
1.0	0.45	0.61	0.78
5.0	2.05	1.21	1.46
7.5	3.0	1.33	1.61
10.0	3.95		
4-Cyanopyridine		**2-Methylpyridine**	
1.0	1.2	0.65	2.9
5.0	5.1	1.30	5.5
6.0	5.2	2.60	10.2
10.0	9.6	5.20	21
3-Chloropyridine		**2,3-Dimethylpyridine**	
0.53	2.1	0.3	1.87
2.65	5.5	0.6	3.68
5.3	12		
4-Chloropyridine		**2,4-Dimethylpyridine**	
0.33	2.37	0.11	1.4
0.65	4.95	0.28	3.9
1.31	9.95	0.56	7.6
		0.84	9.9
Pyridine		**2,6-Dimethylpyridine**	
0.088	5.5	1.25	1.1
0.148	8.4	2.5	2.5
		5.0	4.95
		10.0	10.1
3-Methylpyridine		**2,4,6-Trimethylpyridine**	
0.09	8.5	3.33	8.85
0.121	11.5	5.0	12.4
0.181	16.8	2.5	5.6
		1.25	2.6
3,5-Dimethylpyridine			
0.068	15		
0.137	32		

$$AuCl_3(am) + Bz_2S \longrightarrow AuCl_3(Bz_2S) + am$$

$10^2[Bz_2S]$, M	10^2k_{obsd}, sec⁻¹	$10^2[Bz_2S]$, M	10^2k_{obsd}, sec⁻¹
3-Cyanopyridine		**3-Methylpyridine**	
0.33	5.1	0.5	0.9
0.50	7.7	1.0	1.81
1.0	14.0	2.0	3.7
4-Cyanopyridine		**3,5-Dimethylpyridine**	
0.25	2.53	2.0	3.1
0.50	5.56	2.7	4.24
1.0	10.5	5.0	7.8
3-Chloropyridine		**Quinoline**	
0.33	2.54	0.625	0.264
0.50	3.68	1.25	0.391
1.0	7.3	2.5	0.66
4-Chloropyridine		**2-Methylpyridine**	
0.33	1.55	2.0	0.207
0.50	2.34	5.0	0.384
1.0	4.8	6.66	0.495
		10.0	0.69
Pyridine		**2,3-Dimethylpyridine**	
0.33	0.92	2.5	0.216
0.50	1.2	5.0	0.372
1.0	2.3	10.0	0.70
2.0	4.9		
2,4-Dimethylpyridine			
5.0	0.506		
10.0	0.69		

[a] The concentration of the complexes in the reaction mixture was always in the range 5×10^{-5}–10^{-4} mole/l.

(8–10%) because the reactions are slow and overlap the reduction process. For this reason, it was not possible to study the reactions of Bz_2S with the complexes containing 2,6-dimethyl- and 2,4,6-trimethylpyridine.

The dependence of the observed rate constant upon the concentration of the entering reagent, Y, follows the usual[3] form, $k_{obsd} = k_1 + k_2[Y]$. However, in most of the cases reported here, the k_1 term is not detectable. It appears only in the reactions where sterically hindered amines are the leaving groups, with values of the order of magnitude of 10^{-3} sec^{-1}.

Discussion
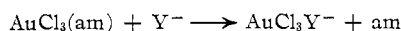
The second-order rate constants, k_2, relative to reactions 1 and 2 are summarized in Table II, together with the values of pK_a of the amines in water, which we assume to be a measure of their σ-donor properties.

TABLE II
SECOND-ORDER RATE CONSTANTS, k_2,
FOR REACTIONS 1 AND 2 IN ACETONE AT 25°

		k_2, M^{-1} sec^{-1}	
Amine	pK_a	Bz_2S as entering group	Bz_2S as leaving group
3-Cyanopyridine	1.38	13.9	0.42
4-Cyanopyridine	1.90	10.4	0.96
3-Chloropyridine	2.84	7.2	2.17
4-Chloropyridine	3.84	4.7	7.65
Pyridine	5.17	2.4	56
3-Methylpyridine	5.68	1.86	94
3,5-Dimethylpyridine	6.34	1.55	225
Quinoline	4.95	0.103	1.2
2-Methylpyridine	6.1	0.061	4.0
2,3-Dimethylpyridine	6.6	0.065	6.2
2,4-Dimethylpyridine	6.99	0.04	12.9
2,6-Dimethylpyridine	6.75	...	0.78
2,4,6-Trimethylpyridine	7.48	...	2.4

In Figure 1, the logarithms of the second-order rate constants are plotted against the pK_a values of the amines concerned. The parallel lines link amines having the same form of steric hindrance, which are listed in the three groups in Table II. When the amines act as entering groups, the reactivity increases with their σ-donor ability, and when they are leaving groups, the opposite is true.

It is of interest to compare the behavior of dibenzyl sulfide with that of other reagents that are known to displace amines from these complexes.[4,5] In the reactions

$$AuCl_3(am) + Y^- \longrightarrow AuCl_3Y^- + am$$

a linear free energy relationship between the logarithm of the second-order rate constants and the pK_a values of the leaving amines is observed when Y^- is essentially a σ-donor nucleophile, such as Cl^- and Br^-. When Y^- is a "biphilic" reagent (NO_2^-, N_3^-) the influence of back-donation from the metal to the entering group in the transition state leads to a more complicated rela-
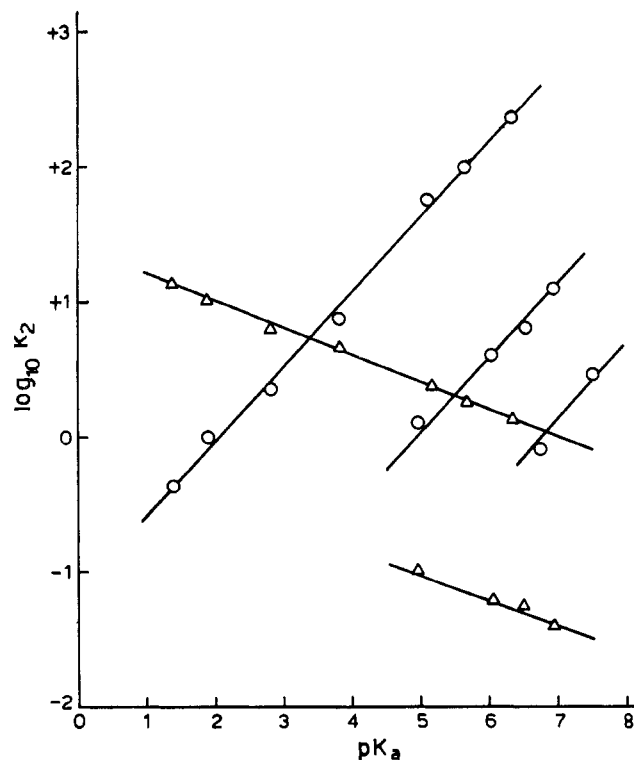

Figure 1.—Plot of log k_2 vs. pK_a for the reactions: O, $AuCl_3$-(Bz_2S) + am → $AuCl_3(am)$ + Bz_2S (the reactivity increases with the pK_a of the entering amine); △, $AuCl_3(am)$ + Bz_2S → $AuCl_3$-(Bz_2S) + am (the reactivity decreases by increasing the pK_a of the leaving amine).

tionship. Therefore, the linear relationship observed in the case of dibenzyl sulfide indicates that it behaves as a σ donor and that any possible π interactions do not contribute significantly to the free energy changes during the formation of the transition states. The absence of π interaction is not surprising. It agrees with preliminary observations which we have made on other d^8 systems (Pd(II) and Pt(II) complexes) as well as with evidence obtained by other authors.[6-8]

A quantitative comparison of the values of the rate constants for the displacement of the amines by Bz_2S and the above-mentioned anionic reagents cannot be made because different solvents have been used (acetone and methanol). However, it might be possible to compare the slopes of the plots of log k_2 vs. pK_a, that is the ability of the reagents to discriminate between substrates differing only in the nature of the leaving amine, since in fact it has been shown in the cases of

$$AuCl_4^- + am \rightleftharpoons AuCl_3(am) + Cl^- \qquad (3)$$
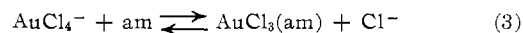
that the slope is the same in methanol and acetone[9] and also that the discrimination between the basicity of entering or leaving amines does not depend upon the nature of the reaction medium in seven different hydroxylic solvents.[10] The slopes are −0.68 and −0.37

(3) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter II and references therein.

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(5) L. Cattalini, A. Orio, and M. L. Tobe, *ibid.*, **6**, 75 (1967).

(6) R. Backhouse, M. E. Foss, and R. S. Nyholm, *J. Chem. Soc.*, 1714 (1957).

(7) G. Dyer and D. W. Meek, *Inorg. Chem.*, **4**, 1398 (1965).

(8) G. Dyer, M. O. Workman, and D. W. Meek, *ibid.*, **6**, 1404 (1967).

(9) L. Cattalini, A. Doni, and A. Orio, *ibid.*, **6**, 280 (1967).

(10) L. Cattalini, V. Ricevuto, A. Orio, and M. L. Tobe, *ibid.*, **7**, 51 (1968).

TABLE III

ANALYTICAL DATA FOR THE NEW COMPLEXES OF THE TYPE $AuCl_3(am)$

Amine	—————% Au—————		—————% C—————		—————% H—————		—————% N—————	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
3-Cyanopyridine	48.3	48.1	17.7	17.4	1.0	1.3	7.15	7.09
4-Cyanopyridine	48.3	48.3	17.7	17.6	1.0	1.1	7.15	7.05
3-Chloropyridine	47.3	47.0	14.4	14.1	0.96	1.1	3.36	3.18
4-Chloropyridine	47.3	47.4	14.4	14.6	0.96	0.91	3.36	3.42

for Cl^- and Br^-, respectively, and -0.2 for Bz_2S, indicating that the nature of the leaving group becomes less important in differentiating the rates of the reactions on going from Cl^- to Br^- and Bz_2S as entering reagents. This suggests that the relative importance of the bond-breaking aspects of the substitution compared to the bond-making aspects is less when Bz_2S is the entering group, which is in accord with the greater micropolarizability ("softness") of the sulfur atom, which is the most important factor in determining the reactivity at "soft" reaction centers[1,11] such as gold(III) complexes. It might be of interest to remember here that the order of reactivity toward platinum(II) substrates (which are also soft) is $R_2S > Br^- > Cl^-$.[12] Moreover, the fact that Bz_2S is a neutral reagent should also be of importance in promoting a better degree of bond making in the transition state, since it is known[1] that electrostatic factors also play a significant role in gold(III) substitution.

The reverse reaction indicates that dibenzyl sulfide is displaced from the complex in preference to chloride and is therefore more labile. The original observation that, in the $AuCl_3(am)$ complex, the amine was more labile than chloride was very surprising since in the analogous platinum(II) complexes the chloride was always more labile. The reaction

$trans$-$Pt((CH_3)_2S)_2Cl_2 + 2C_5H_{11}N \longrightarrow$
$\qquad\qquad trans$-$Pt(C_5H_{11}N)_2Cl_2 + 2(CH_3)_2S$

in n-butyl ether[13] indicates that, in this case, Pt(II) and Au(III) are similar. In addition, we have evidence that amines can displace thioethers from $trans$-$Pd(R_2S)_2$-Cl_2 in dimethoxyethane.

The plot of log k_2 against pK_a of the entering amine for reaction 3 in acetone[9] is a straight line of slope $+0.15$ whereas the slope of the analogous plot for reaction 1 (Figure 1) is $+0.55$. Thus, dibenzyl sulfide as a leaving group leads to a much greater discrimination than chloride, indicating, once again, the greater development of the bond making in the transition state when the "soft" and neutral species Bz_2S is present.

The parallel lines in Figure 1 refer to amines having different steric hindrance, $i.e.$, derivatives of pyridine, 2-methylpyridine (including quinoline), and 2,6-dimethylpyridine. Studies of reaction 3 showed[14] that

steric retardation only occurred in the forward reaction and not in the case when the amine was the leaving group. This was interpreted in terms of a compensation of steric perturbations in the ground and transition states for the reverse process. Moreover, it has been observed in several cases,[9,15-17] both in inorganic and organic systems, that steric retardation due to one or two methyl groups *ortho* to the nitrogen in the pyridine ring is additive. In other words, the decrease of reactivity due to two α-methyl groups is twice that due to one. In the present work, as can be seen in Figure 1, the steric effects are *not* additive and they are present *both* in the forward *and* the reverse reactions. This indicates that dibenzyl sulfide, being considerably more bulky than chloride, leads to a congestion in the trigonal-bipyramidal transition state $[AuCl_3(am)(Bz_2S)]$ that is greater than the congestion in either $[AuCl_3(am)]$ or $[AuCl_3(Bz_2S)]$, whereas no extra strain resulted in going from $[AuCl_3(am)]$ to $[AuCl_4(am)]$. Molecular models indicate that there will be significant interaction between the two bulky ligands (am and Bz_2S) in the trigonal plane. The departure from additivity is probably the consequence of the lower symmetry of the $(Bz_2S)Cl_3Au$–residue as compared with Cl_4Au–.

Experimental Section

The complexes $AuCl_3(am)$ were prepared by the standard procedure previously reported,[4] $i.e.$, by adding the amine to an aqueous solution of $HAuCl_4$, neutralized with $NaHCO_3$. Some of the complexes are new and the corresponding analytical figures are reported in Table III. The complex $AuCl_3(Bz_2S)$ was obtained with the method described in the literature.[18] Commercial amines were distilled over potassium hydroxide pellets, when necessary. Dibenzyl sulfide was a pure product, reagent grade. Anhydrous acetone was used in all of the kinetics studies.

Kinetics.—Acetone solutions of the appropriate complex and reagent were thermostated and mixed in the thermostated cell of an Optica CF4R double-beam recording spectrophotometer. The solutions of the complexes in acetone obey Beer's law and are stable, at least during the time required to follow the kinetics. The spectral changes characteristic of the reacting system were first determined by scanning the near-uv region at known intervals. Once the spectral changes were characterized, the kinetics were followed by looking at a chosen wavelength (usually 340 mμ) and recording the change of optical density as a function of time.

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