peculiar in these respects is not yet clear and research is in progress to investigate the problem further.

Experimental Section

The complexes Pt(bipy)(C)X (C, X = Cl, Cl; N_3, Cl; NO_2, Cl; NO_2, NO_2; NO_2, N_3) were prepared according to the methods reported in the literature.[6,9] The complex [Pt(bipy)Cl$((C_2H_5)_2S)$]NO_3 was obtained from the dichloro complex. Pt(bipy)Cl_2 (845 mg), dissolved in the minimum amount of dimethylformamide, was treated with 340 mg of $AgNO_3$. After 30 min the solution, separated from AgCl, was treated with 250 ml of benzene. The precipitate was separated and dissolved in the minimum amount of methanol, containing 180 mg of $(C_2H_5)_2S$, and the product was then obtained as a precipitate by adding ether. *Anal.* Calcd for $PtC_{14}ClH_{18}N_3O_3S$: C, 31.15; H, 3.36; N, 7.80; S, 5.94. Found: C, 31.2; H, 3.14; N, 7.7; S, 5.8. The thioethers were commercial products, reagent grade. The methanol was dried by distillation over $Mg(OCH_3)_2$.

Kinetics.—The complexes obey Beer's law and are stable in methanol. Known volumes of methanolic solutions of the substrate and reagent were brought separately to 25° and mixed in the thermostated cell of a double-beam recording spectrophotometer, Optica CF4. The reactions were followed by measuring the changes in optical density in the ultraviolet region of the spectrum over a period of time. Conductivity measurements were carried out by means of an LKB 3216B conductivity bridge.

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The Reactivity of Thioethers toward Neutral Gold(III) Complexes

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The rates of displacement of amines (am) from complexes of the type $AuCl_3(am)$ by a variety of thioethers have been measured in acetone at 25°. The discrimination of the entering reagent between the various substrates decreases as the reactivity increases, and it reaches a constant value. This is discussed in terms of an increasing importance of the bond-making aspects of the substitution. A comparison of the nucleophilicity of thioethers toward Au(III) and Pt(II) substrates is reported and the part played by steric hindrance is also discussed.

Introduction

In a previous paper[1] the kinetics of the forward and reverse reactions

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

(Bz_2S = dibenzyl sulfide, am = pyridine derivatives) were studied in detail for a range of complexes containing amines of different basicity and steric hindrance. Having established the kinetic properties of dibenzyl sulfide, it was then desirable to study the nucleophilicity of other thioethers toward gold(III) substrates, in order to attempt to correlate the reactivity with nonkinetic properties and to clarify the role of steric hindrance. Furthermore, a set of data concerning the nucleophilicity of thioethers toward platinum(II) substrates is now available[2] and it is therefore possible to compare the data of thioethers reacting on the isoelectronic substrates of the two d^8 transition metal ions.

In this paper we report the kinetics of replacement of amines from a series of complexes of the type $AuCl_3$(am), by various thioethers, RSR′. The systematic study of the changing of both the entering and the leaving groups requires a relatively large amount of kinetic data, but it does enable us to compare not only the reaction rates but also the ability of each reagent to discriminate between substrates containing different replaceable amines.

Results

The progress of the reaction was examined spectrophotometrically and the course of the reaction was much the same as was reported previously[1] for the reactions with dibenzyl sulfide. Since the reactions were carried out in the presence of an excess of thioethers, reduction may be likely. The change of optical density with time at 340 mμ takes places in two stages. In the first the absorbance increases from that of the amino to that of the sulfide complex, as experienced in the case of $(C_2H_5)_2S$ by comparison of the spectrum with that of an original sample of $AuCl_3((C_2H_5)_2S)$. In the second step, which is much slower, there is a decrease of optical density. The complex $AuCl_3((C_2H_5)_2S)$ can be obtained, in almost quantitative yield, by carrying out the reaction in more concentrated solution (preparative conditions) and using equimolar quantities of $AuCl_3$(am) and $(C_2H_5)_2S$, when the least basic amines are displaced, as previously reported for the entry of dibenzyl sulfide. The first stage therefore corresponds to the replacement of the coordinated amine by $(C_2H_5)_2S$ (or Bz_2S) and we assume it is the same also for the other thioethers. The second stage corresponds to the reduction from Au(III) to Au(I), and the stoichiometry and mechanism of the reaction are under investigation.

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(1) L. Cattalini, G. Marangoni, and M. Martelli, *Inorg. Chem.*, **7**, 1145 (1968).

(2) L. Cattalini, M. Martelli, and G. Kirschner, *ibid.*, **7**, 1488 (1968).

TABLE I

FIRST-ORDER RATE CONSTANTS, DETERMINED IN ACETONE AT 25°[a]

	10^2[RSR′], M	10^2k_{obsd}, sec^{-1}
(1) $AuCl_3(am) + C_6H_5SCH_3 \longrightarrow AuCl_3(C_6H_5SCH_3) + am$		
3-Cyanopyridine	0.4	1.7
	0.72	3.0
	0.82	3.5
	1.45	5.5
	3.6	14
4-Cyanopyridine	0.174	0.45
	0.7	1.68
	1.45	3.6
	1.74	4.4
3-Chloropyridine	1.5	2.3
	2.9	4.2
	3.6	5.0
	5.6	8.0
	7.2	10.3
	11.4	16.0
4-Chloropyridine	2.4	1.5
	4.5	3.0
	7.2	4.4
	13.0	8.1
Pyridine	17.5	4.8
	28.5	7.4
	42	11.5
	57	15.2
(2) $AuCl_3(am) + ClCH_2CH_2SCH_3 \longrightarrow AuCl_3(ClCH_2CH_2SCH_3) + am$		
3-Cyanopyridine	0.063	0.78
	0.126	1.48
	1.26	11.4
	2.52	23.0
4-Cyanopyridine	0.155	1.0
	0.772	4.75
	1.55	9.5
	3.86	24.0
3-Chloropyridine	0.126	0.55
	1.26	5.05
	2.52	10.1
4-Chloropyridine	0.7	1.5
	1.55	3.2
	3.86	8.4
(3) $AuCl_3(am) + (i\text{-}C_3H_7)_2S \longrightarrow AuCl_3(i\text{-}C_3H_7)_2S + am$		
3-Cyanopyridine	0.18	2.0
	0.36	3.9
	0.72	7.9
4-Cyanopyridine	0.36	2.52
	0.72	5.2
	2.16	15.6
	3.6	24.3
3-Chloropyridine	0.21	0.8
	0.42	1.62
	2.11	8.5
4-Chloropyridine	0.422	0.81
	0 844	1.61
	2.11	4.3
Pyridine	0.515	0.414
	1.03	0.855
	1.18	0.99
	2.3	1.38
	3.6	2.64
	7.2	5.34
	10.2	7.7
(4) $AuCl_3(am) + C_2H_5SCH_3 \longrightarrow AuCl_3(C_2H_5SCH_3) + am$		
3-Cyanopyridine	0.0222	1.85
	0.0444	3.8
	0.0888	7.74
	0.177	14.5
	0.444	37.3
4-Cyanopyridine	0.0138	1.0
	0.138	9.8
	0.163	12.2
	0.326	24.0
3-Chloropyridine	0.089	3.45
	0.178	6.35
	0.444	17.9
	0.888	34.5
4-Chloropyridine	0.114	2.67
	0.57	13.6
	1.14	27.4
Pyridine	0.141	1.61
	0.282	3.22
	0.564	6.55
3,5-Dimethylpyridine	0.444	3.35
	0.888	6.65
	1.77	13.8
(5) $AuCl_3(am) + (C_2H_5)_2S \longrightarrow AuCl_3((C_2H_5)_2S) + am$		
3-Cyanopyridine	0.071	7.0
	0.142	13.6
	0.426	41.0
4-Cyanopyridine	0.071	4.5
	0.142	9.2
	0.426	26.4
3-Chloropyridine	0.071	2.98
	0.142	6.3
	0.426	18
	0.71	31
4-Chloropyridine	0.071	1.9
	0.142	3.55
	0.244	6.44
	0.426	11.3
Pyridine	0.092	1.15
	0.184	2.42
	0.368	4.35
3,5-Dimethylpyridine	0.157	1.2
	0.314	2.3
	0.628	5.0
	1.57	11.5
(6) $AuCl_3(am) + (CH_2)_4S \longrightarrow AuCl_3(C_4H_8S) + am$		
3-Cyanopyridine	0.024	4.4
	0.06	11.5
	0.12	22
4-Cyanopyridine	0.024	3.0
	0.06	8.05
	0.12	16
	0.24	34
3-Chloropyridine	0.024	2.04
	0.06	5.28
	0.12	10.5
	0.42	37
4-Chloropyridine	0.12	6.6
	0.6	32.1
	0.24	12.6
Pyridine	0.12	3.6
	0.24	7.0
	0.6	18
3,5-Dimethylpyridine	0.24	4.1
	0.6	10
	1.2	21

[a] The concentration of the substrate in the reaction mixture was always in the range 5×10^{-5}–10^{-4} M. The reproducibility of the rate constants was excellent, and the experimental error is generally not greater than 4–5%.

As a rule, the displacement of the amine from $AuCl_3$(am) by RSR′ goes to completion under the experimental conditions used. However, in the cases where the most basic amines were replaced by the least reactive thioethers, it was necessary to use a large excess of RSR′. For the same reason, it was not possible to obtain data for certain of the reactions of the complexes containing pyridine and 3,5-dimethylpyridine. An attempt was made to use diphenyl sulfide as reagent, but the reactions were quite slow and, apart from the problem of reversibility, it seemed that the rate of reduction was comparable to the rate of substitution.

The rate constants, k_{obsd}, obtained in the presence of an excess of the entering nucleophile in order to ensure pseudo-first-order conditions, were calculated from the

TABLE II

SECOND-ORDER RATE CONSTANTS, k_2 (M^{-1} SEC^{-1}), RELATIVE TO THE REPLACEMENT BY THIOETHERS OF AMINES FROM $AuCl_3$(am) COMPLEXES, IN ACETONE AT 25°

		Entering groups[b]						
Amine	pK_a[a]	$C_6H_5SCH_3$ (−0.6)	(i-C_3H_7)$_2$S (+0.38)	Cl$(CH_2)_2SCH_3$ (−0.385)	Bz_2S[c] (−0.43)	$C_2H_5SCH_3$ (+0.1)	$(C_2H_5)_2S$ (+0.2)	$(CH_2)_4S$ (+0.18)
3-CN-py	1.38	4.1	11.5	9.1	13.9	84	97	186
4-CN-py	1.90	2.5	7.0	6.2	10.4	72	63.5	135
3-Cl-py	2.84	1.4	3.9	4.0	7.2	38	42.5	87
4-Cl-py	3.84	0.62	1.95	2.12	4.7	24	27	53
py	5.17	0.27	0.80	...	2.4	11.5	12.3	30
3,5-$(CH_3)_2$-py	6.34	...	...	...	1.55	7.5	7.5	17.1

[a] Values relative to the acid amH$^+$ in water. [b] The values in parentheses are the sum of the Taft σ^* values, $-\Sigma\sigma^*$, relative to the inductive effects of the radicals R and R′ in RSR′. Values of σ^* from R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, and from H. K. Hall, Jr., *J. Am. Chem. Soc.*, **79,** 5442 (1957). [c] Data from ref 1.

slope of the semilogarithmic plot of the change of optical density of the reaction mixture *vs.* time and are summarized in Table I.

Discussion

The plots of k_{obsd} against [RSR′] are linear and pass through the origin. The slopes of these lines can be used to calculate the second-order rate constants, k_2, for the bimolecular displacement of the amines by thioethers, which are summarized in Table II. The plots of log k_2 *vs.* the pK_a of the leaving amines are linear (see Figure 1) and the reactivity decreases, as expected, with increasing basicity of the amine.

The kinetics of the displacement of the amine from the same type of gold(III) complexes by Cl$^-$, Br$^-$, NO_2^-, and N_3^- have been reported in the literature.[3,4] Linear relationships between log k_2 and the pK_a of the amine were observed in the reactions with the essentially σ nucleophiles Cl$^-$ and Br$^-$, but the biphilic reagents NO_2^- and N_3^- showed considerable departures from linearity. This behavior was discussed in terms of π interactions in the transition state. Applying the same criteria to the reactions with thioethers we must conclude, as in the case of dibenzyl sulfide,[1] that in these reactions there is not any significant contribution from back-donation from the metal to the sulfur atom in the transition state. The same conclusions have been reached in the investigation on the nucleophilicty of thioethers toward platinum(II) complexes,[2] and from some preliminary experiments it seems to be true also in reactions with planar palladium(II) substrates.

A remarkable point is that the discrimination between the complexes containing different amines (measured from the slope of the lines in Figure 1) decreases as the reactivity of the thioethers increases and reaches a constant value (0.2) with the most reactive ones. In this case there is a strong similarity with the ligand displacement reactions at platinum(II) substrates, where it was always found that the change of reactivity due to the different nature of the leaving group is not dependent (except in the case of biphilic reagents) upon the nature of the entering nucleophile.[1,5] This has been interpreted as an indication that the intimate mechanism of the substitution is not a synchronous interchange but rather an associative process in which a minimum, corresponding to the formation of a five-coordinate intermediate, will appear in the energy profile for the reaction.[6,7]

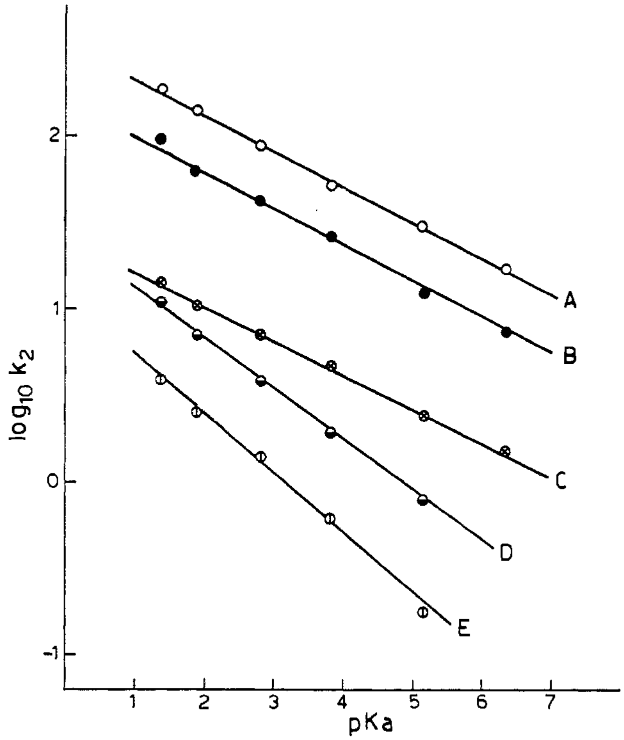

Figure 1.—Plot of log k_2 against the pK_a of the leaving amine for some of the reactions $AuCl_3$(am) + RSR′ → $AuCl_3$(RSR′) + am, in acetone at 25°: ○, RSR′ = $(CH_2)_4S$ (A); ●, RSR′ = $(C_2H_5)_2S$ (B); ⊗, RSR′ = BzSBz (C); ◒, RSR′ = (i-C_3H_7)$_2$S (D); ⦶, RSR′ = $C_6H_5SCH_3$ (E).

However, in the case of platinum(II) derivatives, it was usually difficult to establish in any particular case if the minimum lies before or after the rate-determining transition state. With the reactions of the Au(III) complexes, the fact that an increase in the reactivity

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(5) (a) U. Belluco, R. Ettore, F. Basolo, R. G. Pearson, and A. Turco, *ibid.*, **5**, 591 (1966); (b) U. Belluco, M. Graziani, M. Nicolini, and P. Rigo, *ibid.*, **6**, 721 (1967); (c) L. Cattalini and M. Martelli, *Gazz. Chim. Ital.*, **97**, 498 (1967).

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

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parallels the decrease in the discrimination between the complexes containing different leaving groups suggests that in the processes with the more efficient thioethers bond formation in the transition state is the driving force of the reaction. A marked dependence of the rate upon the nature of the entering group is to be expected under these circumstances. A residual dependence of rate upon the nature of the leaving amine is not inconsistent with a situation with virtually no bond breaking in the transition state, since the σ-donor properties of the amine will influence the electrophilicity of the reaction center. It implies a fairly compact transition state, which might be related to the fact that in these reactions both the entering and leaving groups are neutral and therefore repel one another least of all.

It is of interest to compare the behavior of thioethers as nucleophiles toward these Au(III) species with that toward Pt(II) derivatives. It has been suggested[2] that also in the reactions of RSR′ toward Pt(II) substrates bond making is the driving force of the reaction. It seems that thioethers favor the formation of the new bond without promoting at the same time a significant breaking of the old one. There are however significant differences. Apart from the greater reactivity of the Au(III) species, which seems to be a general rule,[7] it is found that, whereas the discrimination between different leaving groups is independent of the nature of the entering thioether for the reactions at platinum(II) complexes, the limiting behavior is only achieved in the case of gold(III) complexes with the most reactive thioethers. This might be related to the greater ability of Pt(II) to support a nonsynchronous substitution mechanism.[7]

In addition, the nucleophilicity of RSR′ toward Pt(II) is related quite simply to the inductive effects of the radicals bonded to the sulfur atoms[2] (see Table II, note *b*), whereas the same is not true in the present case. This might be attributed to the steric hindrance effects, which are of greater importance in Au(III) than in Pt(II). The only reagent which, because of its structure, might be not significantly affected by steric hindrance is tetrahydrothiophene; this is the most reactive thioether that was used.

Experimental Section

The complexes of the type $AuCl_3(am)$ were prepared as described previously.[1] The complex $AuCl_3((C_2H_5)_2S)$ was obtained with the method described in the literature.[8] The thioethers were commercial samples, reagent grade. The solvent, acetone, was purified and dried by successive distillation over $KMnO_4$ and K_2CO_3.

Kinetics. The reactions were followed spectrophotometrically, as already described in the case of dibenzyl sulfide.[1] Known volumes of the complex and reagent in acetone were brought separately to the reaction temperature and mixed in the thermostated cell of an Optica CF4 double-beam recording spectrophotometer. The solutions of the complexes in acetone obey Beer's law and are stable. Once the spectrum changes characteristic of the reacting system were determined, the kinetics were followed by observing the wavelength at a chosen value (usually 340 mμ) and recording the change of optical density as a function of time.

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Reactivity of Thioethers toward Neutral Palladium(II) Complexes

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The rates of displacement of one amine (am) from complexes of the type *trans*-$Pd(am)_2Cl_2$ by a variety of thioethers have been measured in 1,2-dimethoxyethane at 25°. The reactivity increases linearly with the increasing σ-donor ability of the entering nucleophile, RSR′, and decreases linearly with the basicity of the amine. Moreover, the discrimination of each substrate between the various thioethers is independent of the nature of the amine, and the discrimination of each reagent between various substrates is independent of the nature of the thioether. This is discussed in terms of an associative mechanism of reaction.

Introduction

In previous works[1,2] the nucleophilicity of thioethers toward platinum(II) and gold(III) planar complexes has been investigated. The kinetics of the reactions

$$Pt(bipy)(C)X + RSR' \longrightarrow Pt(bipy)(C)(RSR')^+ + X^-$$

($C, X = NO_2, Cl;\ NO_2, NO_2;\ NO_2, N_3;\ N_3, Cl;\ Cl, Cl$) and

$$AuCl_3(am) + RSR' \longrightarrow AuCl_3(RSR') + am$$

(am = pyridine derivatives) have been studied for a variety of thioethers, RSR′, and complexes. The results indicate that these substitutions occur through an associative mechanism where the transition state is mainly determined by the formation of the new bond between the metal and the entering group. It implies that the

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