

The fluorine nmr spectrum also consists of a 1:1 doublet ($\delta +53$ ppm from CCl_3F) caused by coupling of the fluorine with phosphorus. The P-F coupling constant is identical within experimental error to that of the uncomplexed ligand, 1194 cps.

Although $\{\text{CuCl}[(\text{CH}_3)_2\text{NPF}_2]\}_4$ is quite soluble in nonpolar organic solvents, several attempts to obtain the phosphorus nmr spectrum were unsuccessful. The difficulty can be traced to two obstacles. First, owing to the low magnetogyric ratio of phosphorus, the signal is about 10 times less intense than either hydrogen or fluorine. Second, because phosphorus is directly attached to the copper atom, the signal is expected to be broadened as a result of the quadrupole relaxation induced by copper. The signal is so broad that it cannot be located.

Copper(II) Chloride.—The oxidation-reduction re-

action between $(\text{CH}_3)_2\text{NPF}_2$ and copper(II) chloride is not surprising. All phosphines⁸ and some amines³⁰ also undergo oxidation by copper(II) halides. In the reaction of $(\text{CH}_3)_2\text{NPF}_2$ with CuCl_2 the formation of a new compound, $(\text{CH}_3)_2\text{NPF}_2\text{Cl}_2$, clearly indicates that any scheme used to rationalize the oxidation-reduction reaction must involve both an electron and an atom transfer. The mechanism of this reaction is not yet understood.

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(30) J. T. Yoke, J. F. Weiss, and G. Tollin, *Inorg. Chem.*, **2**, 1210 (1963).

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The Effect of Hydroxylic Solvents on the Kinetic Behavior of Gold(III) Complexes

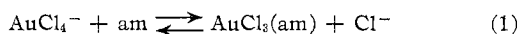
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The role of seven hydroxylic solvents ($\text{C}_6\text{H}_5\text{CH}_2\text{OH}$, CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, $\text{C}_3\text{H}_7\text{OH}$, *i*- $\text{C}_3\text{H}_7\text{OH}$, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$, $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OH}$) on the rates of the reactions in which heterocyclic amines (pyridine, 3-methylpyridine, 3,4-dimethylpyridine) are either the leaving or entering group in processes of the type $\text{AuCl}_3(\text{am}) + \text{Y}^-$ and $\text{AuCl}_4^- + \text{am}$ have been studied. The results indicate that the sequence of solvent effect upon the second-order rate constants is unaffected by the nature of the amine but is quantitatively reversed on going from the reactions of AuCl_4^- with amines to those of the neutral $\text{AuCl}_3(\text{am})$ with chloride and, to a smaller extent, bromide anion. This is discussed in terms of relative solvation of the charged species in the ground and transition states.

Introduction

The displacement of the coordinated amine from complexes of the type $\text{AuCl}_3(\text{am})$ by various nucleophiles was studied^{1,2} in methanol at 25°. Linear relationships between the free energy of activation and the basicity of the leaving amine were found when the entering nucleophiles are essentially σ bonded (e.g., Cl^- and Br^-), whereas biphilic reagents (NO_2^- and N_3^-) cause a more complicated behavior. The work was extended³ to a study of the reverse reactions, namely, the displacement of chloride from tetrachlorogold(III) anion by various pyridine derivatives under the same experimental conditions. The equilibrium constants for the process



were calculated from the ratio of the second-order rate constants of the reverse and forward reactions. The results were discussed in terms of the influence of the

basicity and, in some cases, of the steric hindrance of the amines upon both the kinetic and equilibrium constants.

Having established the factors governing the effect of the entering and leaving groups upon this type of reactions, it appeared necessary to investigate, in detail, the role played by the solvent. In this paper we report and discuss the kinetics and equilibria of process 1 (in the cases where $\text{am} = \text{pyridine}$, 3-methylpyridine, and 3,4-dimethylpyridine) in a series of hydroxylic solvents. In addition, we report the effect of changing the solvent upon the reaction



Results and Discussion

In the case of the reactions involving the entry of chloride, the ultraviolet spectra at the beginning and at the end of the reactions correspond exactly to those of authentic samples of $\text{AuCl}_3(\text{am})$ and AuCl_4^- (and *vice versa* for the reverse processes) in each of the examined solvents. During the reactions isosbestic

(1) L. Cattalini and M. L. Tobe, *Inorg. Chem.*, **5**, 1145 (1966).

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

(3) L. Cattalini, M. Nicolini, and A. Orio, *ibid.*, **5**, 1674 (1966).

TABLE I
PSEUDO-FIRST-ORDER RATE CONSTANTS (k_{obsd}) FOR THE DISPLACEMENT OF THE HETEROCYCLIC AMINE FROM THE COMPLEXES
 $\text{AuCl}_3(\text{am})$ BY CHLORIDE (25°) AND BROMIDE (10°) IONS IN VARIOUS SOLVENTS

Solvent	am					
	3,4-Dimethylpyridine		3-Methylpyridine		Pyridine	
(a) Reactions with Cl^- (LiCl) at 25°						
	$10^2[\text{Cl}^-], M$	$10^2k_{\text{obsd}}, \text{sec}^{-1}$	$10^2[\text{Cl}^-], M$	$10^2k_{\text{obsd}}, \text{sec}^{-1}$	$10^2[\text{Cl}^-], M$	$10^2k_{\text{obsd}}, \text{sec}^{-1}$
$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	0.665	1.55	1.95	4.0	0.665	2.0
	1.33	2.0	3.9	5.6	1.33	3.2
	2.66	2.5	7.8	10.5	2.66	6.1
CH_3OH	1.07	1.5				
	2.15	2.9		<i>a</i>		<i>a</i>
	4.50	5.9				
$\text{CH}_3\text{CH}_2\text{OH}$	1.15	2.3	1.15	10.5	1.15	14
	2.30	5.1	2.30	14.2	2.30	23
	4.60	8.8	4.60	25	2.30 ^b	25
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$					4.60	42
	1.05	3.25	1.11	6.6	1.05	15.5
	2.10	6.5	2.22	12	2.1	29.2
$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	4.21	12	4.44	23	4.21	52
	0.78	4.8	0.78	15	0.78	23
	0.78	5.1	1.56	22.5	1.56	32
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$	3.12	11.8	3.12	32	3.12	53
	0.79	4.1	0.79	12	0.79	17.5
	1.58	6.2	1.58	22	0.80 ^b	17.3
$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$	3.15	13.2	3.15	41.5	1.58	28.5
					3.15	57.5
	1.06	7.5	1.06	18	1.00 ^b	27
	2.12	13	2.12	30	1.06	28
	4.25	25	4.25	57	2.12	52
					4.25	103
(b) Reactions with Br^- ($n\text{-C}_4\text{H}_9\text{N}$) ₄ Br at 10°						
	$10^2[\text{Br}^-], M$	$10^2k_{\text{obsd}}, \text{sec}^{-1}$	$10^2[\text{Br}^-], M$	$10^2k_{\text{obsd}}, \text{sec}^{-1}$	$10^2[\text{Br}^-], M$	$10^2k_{\text{obsd}}, \text{sec}^{-1}$
$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	2.05	2.8	2.05	3.4	1.05	3.6
	4.10	4.6	4.10	6.7	2.10	5.6
	8.20	8.3	8.20	14	4.20	11.8
CH_3OH	1.07	1.6	1.07	3.0	1.07	4.15
	2.15	3.2	2.15	5.95	2.15	8.20
	4.30	6.4	4.30	11.6	4.30	16.3
$\text{CH}_3\text{CH}_2\text{OH}$	1.03	4.21	1.03	4.8	1.03	6.0
	2.06	6.31	2.06	8.6	2.06	13
	4.12	10.7	4.12	16.0	4.12	23.4
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$	0.945	3.2	0.945	5.9	0.945	6.5
	1.89	6.0	1.89	10.7	1.89	19
	3.78	12.1	3.78	23	3.78	33

^a Data available from the literature.¹ ^b Cl^- provided as $(\text{C}_6\text{H}_5)_4\text{AsCl}$.

points can be observed, which are the same found in the reverse reactions. These two facts together indicate clearly that the observed process is the replacement of the coordinated amine by chloride or of chloride by amine. The reactions were carried out in the presence of a sufficient excess of the entering ligand to ensure (a) complete reaction and (b) pseudo-first-order kinetics.

The pseudo-first-order rate constants (k_{obsd}) were obtained from the change of optical density of the reaction mixture with time at a suitable wavelength in the range 310–330 $m\mu$ in the way previously reported¹ for the reactions in methanol.

In the reaction $\text{AuCl}_3(\text{am}) + \text{Br}^- \rightarrow \text{AuCl}_3\text{Br}^- + \text{am}$ the changes in spectra follow much the same course as when the process was studied in methanol and the evidence that the amine is displaced in the first slow step is precisely the same presented in the previous work.²

The dependence of the observed rate constant upon the concentration of the entering reagent Y^- (or Y) can

be expressed by the usual two-term expression $k_{\text{obsd}} = k_1 + k_2[\text{Y}]$. The values of k_{obsd} and the experimental conditions are reported in Table I and the values of the rate constants k_1 and k_2 are summarized in Table II. It should be pointed out that the values of k_1 are very approximate since the rate is controlled almost entirely by the k_2 term.

In order to provide an empirical measure of solvent properties, an attempt was made to correlate the rate data with the sum of the Taft values⁴ for the inductive effects of the individual groups attached to the oxygen of the solvent. In a preliminary communication⁵ it was observed that there was a linear relationship between the $-\Sigma\sigma^*$ values and $\log k_2$. These values (where available) are also reported in Table II. The assign-

(4) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956. See also H. K. Hall, Jr., *J. Am. Chem. Soc.*, **79**, 5441 (1957), and references therein.

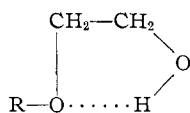
(5) L. Cattalini, M. Martelli, and A. Orio, *Chim. Ind. (Milan)*, **49**, 623 (1967).

TABLE II
FIRST-^a AND SECOND-ORDER RATE CONSTANTS FOR THE DISPLACEMENT OF THE HETEROCYCLIC AMINE FROM AuCl₃(am)
BY CHLORIDE (25°) AND BROMIDE (10°) IONS IN VARIOUS SOLVENTS

Solvent	$\Sigma\sigma^{*b}$	$10^3k_1, \text{sec}^{-1}$	$10^3k_2(\text{Cl}), M^{-1} \text{sec}^{-1}$	$10^2k_{-2}(\text{Cl}), M^{-1} \text{sec}^{-1}$	K^d	$k_2(\text{Br}), M^{-1} \text{sec}^{-1}$
am = 3,4-dimethylpyridine						
C ₆ H ₅ CH ₂ OH	0.71	1.25	4.75	830	175	0.94
CH ₃ OH	0.49	0.2	13.1	270	20.6	1.51
CH ₃ CH ₂ OH	0.39	0.6	18.0	174	9.7	2.08
CH ₃ CH ₂ CH ₂ OH	0.37	0.7	23.6	144	6.1	...
CH ₃ CH(OH)CH ₃	0.30	2.5	29.5	107	3.63	...
CH ₃ OCH ₂ CH ₂ OH	(0.2) ^e	0.4	40.6	55	1.36	3.15
CH ₃ CH ₂ OCH ₂ CH ₂ OH	(0.1) ^e	1.5	55.5	34.2	0.62	...
am = 3-methylpyridine						
C ₆ H ₅ CH ₂ OH	0.71	1.4	11.6	1.71
CH ₃ OH	0.49	0.7 ^f	19.5 ^f	2.75
CH ₃ CH ₂ OH	0.39	5 ^f	42	3.4
CH ₃ CH ₂ CH ₂ OH	0.37	1	50
CH ₃ CH(OH)CH ₃	0.30	10	72.5
CH ₃ OCH ₂ CH ₂ OH	(0.2) ^e	3	120	6.1
CH ₃ CH ₂ OCH ₂ CH ₂ OH	(0.1) ^e	4	130
am = pyridine						
C ₆ H ₅ CH ₂ OH	0.71	0.5	21	525	25	2.8
CH ₃ OH	0.49	0.75 ^f	41.7 ^f	160	3.84	3.78
CH ₃ CH ₂ OH	0.39	5	81.5	113	1.39	5.1
CH ₃ CH ₂ CH ₂ OH	0.37	4	110	90	0.84	...
CH ₃ CH(OH)CH ₃	0.30	13	122	65	0.53	...
CH ₃ OCH ₂ CH ₂ OH	(0.2) ^e	1.5	170	34.5	0.2	8.8
CH ₃ CH ₂ OCH ₂ CH ₂ OH	(0.1) ^e	1.2	236	20	0.085	...

^a The first-order rate constants, k_1 , have been obtained at 25° and are very approximate. ^b Sum of the Taft σ^* values (see text). ^c Second-order rate constants for the reactions $\text{AuCl}_4^- + \text{am} \rightarrow \text{AuCl}_3(\text{am}) + \text{Cl}^-$, from ref 5. ^d Equilibrium constants, calculated from the ratio $k_{-2}(\text{Cl})/k_2(\text{Cl})$; $K = [\text{AuCl}_4^-][\text{am}]/[\text{AuCl}_3(\text{am})][\text{Cl}^-]$. ^e See text. ^f Data from ref 1.

ment of $-\Sigma\sigma^*$ values to the bifunctional solvents 2-methoxyethanol and 2-ethoxyethanol presents some difficulty since values are not available for 2-alkoxyethyl groups and since an interaction between the two oxygens by way of hydrogen bonding



cannot be ruled out. In order to utilize the data for the ether alcohols we have simply assigned effective $-\Sigma\sigma^*$ values, which place the points for the reaction between AuCl_4^- and 3,4-dimethylpyridine on the straight line. On using these values it is found that the linear relationship is maintained in all of the other reactions reported. It is of interest to note that the values of $\Sigma\sigma^*$ thus obtained are virtually identical with those calculated for the ether oxygen but it would be rash to conclude that this is evidence that the ether oxygen is the one specifically involved in the solvation processes.

The relationship between $\log k_2$ and $-\Sigma\sigma^*$ for the solvent is shown in Figure 1 where it will be seen that a linear behavior is found for both the forward and reverse processes of eq 1. The same is true for the reactions of the nonelectrolyte complexes with bromide (Figure 2). In all cases the slopes appear to be independent of the nature of the amine. This is in agreement with a previous observation that the ability of

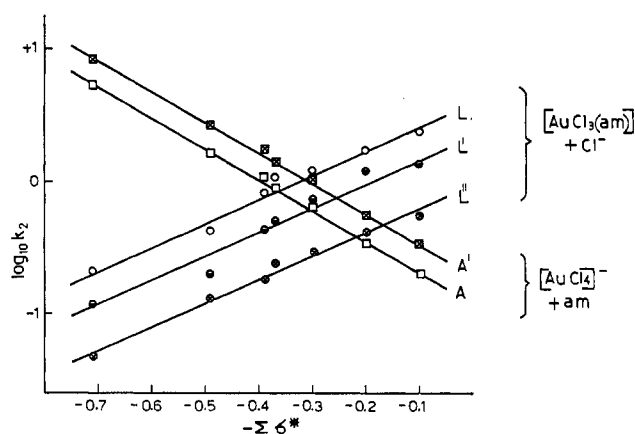


Figure 1.—Plot of $\log k_2$ against the value of $-\Sigma\sigma^*$ for the reactions: L, O, $\text{AuCl}_3(\text{py}) + \text{Cl}^-$; L', \bullet , $\text{AuCl}_3(3\text{-Mepy}) + \text{Cl}^-$; L'', \otimes , $\text{AuCl}_3(3,4\text{-Me}_2\text{py}) + \text{Cl}^-$; A', \boxtimes , $\text{AuCl}_4^- + 3,4\text{-Me}_2\text{py}$; A, \square , $\text{AuCl}_4^- + \text{py}$.

AuCl_4^- to discriminate between amines of different basicity is much the same in methanol and acetone.⁶

The effect of the solvent upon the rate of the reaction arises from the difference in the solvation of the reagents in the ground state and the transition state. This is, of course, a composite effect and any attempt to assign contributions to the various aspects must be approached with caution. Nevertheless one might consider separately the specific and general sol-

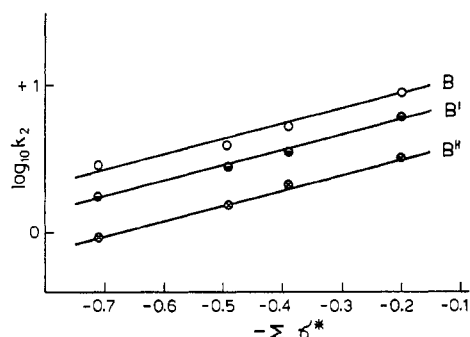


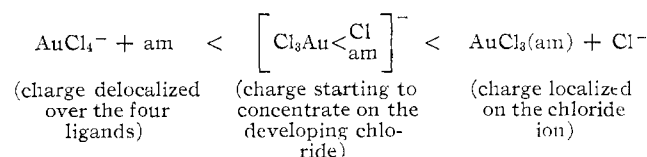
Figure 2.—Plot of $\log k_2$ against the value of $-\Sigma\sigma^*$ for the reactions: B, O, $\text{AuCl}_3(\text{py}) + \text{Br}^-$; B', ●, $\text{AuCl}_3(3\text{-Me-py}) + \text{Br}^-$; B'', ⊙, $\text{AuCl}_3(3,4\text{-Me}_2\text{-py}) + \text{Br}^-$.

vent effects associated with the ground state and the transition state.

It has been suggested that, in a planar complex, the axial positions are strongly and specifically solvated and that changes in this type of solvation on going to the transition state contribute considerably to the overall solvation effect.^{5,7} This interaction, which might be looked upon as a form of weak coordination between the electron-accepting metal ion and suitable donor sites on the solvent molecules can be quite important in the exposed axial positions of the planar complex, as shown by solvent effect upon spectra⁸ and by solvent-induced circular dichroism.⁹ In the trigonal-bipyramidal structure the central atom is more shielded by the five surrounding ligands, and the two solvent molecules specifically associated with the axial positions of the square plane will therefore be expelled on going to the transition state.

When considering the general solvent effects in this polar solvent, it is to be expected that the most important contribution comes from the charged species and the extent to which this charge is localized. This appears to be borne out by the observation that the solvent has little effect upon the ability of the substrate to differentiate between the various amines. The change in solvation experienced by these uncharged reagents on entering the transition state should not be large in comparison with the other effects. The absence of any change of rate constants when the chloride is provided as tetraphenylarsonium chloride (Table I) indicates that the solvation of the cation that is necessarily introduced with the chloride plays no part in the process and can be excluded from any discussion.

If we consider the extent of charge localization to the systems under study, we have the sequence



(7) U. Belluco, M. Graziani, M. Nicolini, and P. Rigo, *Inorg. Chem.*, **6**, 721 (1967), and references therein.

(8) C. M. Harris, S. E. Livingstone, and I. H. Reece, *J. Chem. Soc.*, 1505 (1959).

(9) B. Bosnich, *J. Am. Chem. Soc.*, **88**, 2606 (1966).

and, therefore, if the extent of the general solvation is related to this, it follows that the change from $\text{AuCl}_4^- + \text{am}$ to the transition state is accompanied by an overall increase in solvation whereas the change from $\text{AuCl}_3(\text{am}) + \text{Cl}^-$ to the same transition state is accompanied by a decrease in solvation. Thus, if the general solvent effects are of overwhelming importance, it would be expected that the effects of changing solvent on the forward reaction would be entirely reversed in the backward reaction.

On the other hand, the specific solvation effects associated with the axial positions of the square plane would require that desolvation occurs on going from the ground state to the transition state irrespective of the nature of the reagents and that the solvent effect should be in the same direction in both the forward and the backward reaction.

The results in Figure 1 show clearly that the solvent effect is reversed in the backward reaction and one must conclude, therefore, that at least in this type of system, the specific solvation effects are very much less important than the general electrostatic effects. Perhaps in a system in which the reagents and products are all neutral species it might be possible to examine

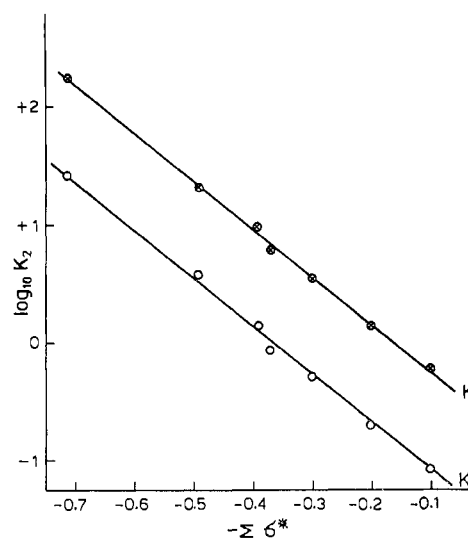


Figure 3.—Plot of $\log K$ against the value of $-\Sigma\sigma^*$: $K' = [\text{AuCl}_3(3,4\text{-Me}_2\text{py})][\text{Cl}^-]/[\text{AuCl}_4^-][3,4\text{-Me}_2\text{py}]$; $K = [\text{AuCl}_3(\text{py})][\text{Cl}^-]/[\text{AuCl}_4^-][\text{py}]$.

the effect of the specific axial solvation on the rates of the reactions. The bromide ion is less solvated than chloride in these hydroxylic solvents and so the amount of desolvation involved in reaching the transition state will be less. This is reflected in the data on Figure 2 where it can be seen that the slope of $\log k_2$ for bromide entry in $\text{AuCl}_3(\text{am})$ against $-\Sigma\sigma^*$ (0.5) is markedly less than that for chloride entry (1.76).

The equilibrium constants relative to the systems of (1) have been calculated from the ratio of the second-order rate constants and are also reported in Table II. Owing to the different direction of the effect of the change of solvent on the forward and backward reac-

tions, the equilibrium constants are much more influenced by the nature of the solvent than the rate constants, as can be seen in the slope (2.26) of the lines in Figure 3, which is, in fact, the difference between the slopes of the lines in Figure 1.

Experimental Section

All of the complexes used in this study were prepared and purified in ways previously described.^{1,5} The solvents were pure commercial samples (chromatographic grade), dried according to

the methods reported in the literature. The methods used to follow the kinetics were similar to those reported previously.¹ Known volumes of thermostated solutions of the complex and the reagent were mixed in the spectrophotometer cell which was placed in the thermostated compartment of an Optica CF-4 recording spectrophotometer. The spectrum changes characteristic of the reacting system were first determined by scanning the near-ultraviolet region at known intervals. Once the spectra changes were characterized and suitable wavelengths were chosen to study the reaction, the kinetics were followed by looking at the wavelength at the chosen value and recording the change of optical density as a function of time.

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Electronic Structures and Spectra of Square-Planar Gold(III) Complexes

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The electronic spectra of AuCl_4^- , AuBr_4^- , and $\text{Au}(\text{SCN})_4^-$ have been measured in the visible and near-ultraviolet regions at 300 and 77°K in a 2:1 2-methyltetrahydrofuran-methyl alcohol solvent mixture. Improved resolution at low temperature revealed d-d transitions in each case, and the assignment of these transitions has been given based on a d-MO ordering of $b_{1g}(x^2 - y^2) > b_{2g}(xy) > e_g(xz, yz) > a_{1g}(z^2)$. The electronic spectrum of $\text{Au}(\text{CN})_4^-$ has also been measured to 54,000 cm^{-1} at room temperature in water and acetonitrile.

Introduction

The interpretation of the electronic spectra of gold(III) complexes has not been fruitful in aiding solution of the square-planar electronic structural problem.¹⁻³ One reason has been poor resolution of the ligand field spectra from which information regarding the d-MO leveling ordering can be extracted. For example, the d-d transitions are almost completely obscured by intense charge-transfer transitions in the AuCl_4^- and AuBr_4^- complexes.³ Another reason is that aqueous solution spectra of gold(III) complexes are subject to question because of the known tendency of these complexes to hydrolyze.⁴

In this paper, as part of our investigations of the electronic structures of a number of square-planar complexes, we present measurements of the electronic spectra of some gold(III) complexes of the type MX_4^- , where X is chloride, bromide, thiocyanate, and cyanide. To avoid the possibility of hydrolysis, our measurements were made in nonaqueous media. Also, where possible, measurements were made in a medium that forms a rigid, transparent glass when cooled to liquid nitrogen temperature. By cooling samples to near liquid nitrogen temperature, the resolution of the weaker ligand field spectra was markedly improved.

Experimental Section

The gold complexes, except $\text{Au}(\text{CN})_4^-$, were prepared from reagent grade hydrogen tetrachloroaurate(III), $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Mallinckrodt). Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

***n*-Butylammonium Tetrachloroaurate(III)**, $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{AuCl}_4]$.—An excess of concentrated hydrochloric acid was added to a concentrated aqueous solution of HAuCl_4 . A stoichiometric amount of *n*-butylammonium chloride as a concentrated aqueous solution was then added at ice-bath temperatures. Golden needles of product formed immediately. These were washed with cold water and then with ether and dried under vacuum. *Anal.* Calcd for $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{AuCl}_4]$: Au, 33.89; C, 33.06; H, 6.24. Found: Au, 33.66; C, 33.29; H, 6.45.

***n*-Butylammonium Tetrabromoaurate(III)**, $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{AuBr}_4]$.—An excess of concentrated hydrobromic acid was added to a concentrated aqueous solution of HAuCl_4 , followed by the addition of a stoichiometric amount of *n*-butylammonium bromide as a concentrated aqueous solution. Dark red plates formed immediately. These were collected and washed with cold water and then ether, and finally dried under vacuum. *Anal.* Calcd for $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{AuBr}_4]$: Au, 25.95; C, 25.32; H, 4.78. Found: Au, 26.20; C, 25.43; H, 4.62.

***n*-Butylammonium Tetracyanoaurate(III)**, $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Au}(\text{CN})_4]$.—This compound was prepared from $\text{K}[\text{Au}(\text{CN})_4]$. The potassium salt was prepared by the method of Smith and co-workers.⁵ The literature procedure was followed exactly except that the treatment of $\text{Au}(\text{CN})_2\text{Br}_2^-$ with potassium cyanide was carried out at ice-bath temperature. The *n*-butylammonium salt was then prepared by adding a solution containing a stoichiometric amount of *n*-butylammonium chloride to a concentrated aqueous solution of the potassium salt. A white microcrystalline precipitate formed immediately. This was

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(2) H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963).

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