TABLE III

THE VISIBLE ABSORPTION SPECTRA OF THE BIS COMPLEXES

	Spectral bands ($\bar{\nu}$)			Dt',	Dq(amine),
	I_a	I_b	II	cm^{-1}	$cm^{-1} \times 10^{-3}$
cis-$H[Co(IDA)_2] \cdot H_2O$	1.779^a	2.008	2.618	−152	2.0
	$(145)^b$	sh $(38)^c$	(131)		
trans-$H[Co(IDA)_2] \cdot 4H_2O$	1.602	2.008	2.740	382	2.6
	sh $(11)^c$	(57.5)	(58.5)		
trans-$H[Co(MIDA)_2] \cdot 2H_2O$	1.607	1.969	2.717	304	2.5
	sh $(11)^c$	(59.2)	(67.5)		

[a] All $\bar{\nu}$ in $cm^{-1} \times 10^{-4}$. [b] Extinction coefficients (ϵ) in parentheses; those of shoulders are estimated. [c] The wavelengths for the shoulders are determined assuming a symmetrical-shaped curve for the main peaks.

shoulder somewhat lower than the *cis*. The theory also predicts that the less symmetric *cis* isomer should have a more intense spectrum than the *trans* isomer,[13] as is observed.

Wentworth and Piper[14] have discussed the splitting patterns found in terms of a splitting parameter Dt' related to the Dq of the ligands involved. In this case

$$Dt' = 4/7(Dq(\text{amine}) - Dq(\text{carboxylic acid}))$$

where

$$Dt'(trans) = 4/35(\text{band Ib} - \text{band I(acid)})$$
$$Dt'(cis) = 8/35(\text{band Ia} - \text{band I(acid)})$$

The approximate values of Dt' and Dq(amine) as tabulated in Table III are calculated using approximately a Dq(acid) of 2200 cm^{-1} found for the mixed complexes with dien and IDA and a value of C of 3800 cm^{-1} to give a band I(acid) of 18,200 cm^{-1}. The lower value of Dq(amine) for the *trans*-MIDA complex compared to *trans*-IDA is in agreement with the lower stability on N-alkyl substitution as observed with similar substituted amine carboxylic acid compounds.[4] The low value found for the *cis* complex is expected because of the amine repulsions indicated in the equilibrium distribution and the nmr measurements.

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(13) S. Yamada and R. Ysuchida, *Bull. Chem. Soc. Japan*, **26**, 15 (1953).

(14) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

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The Mechanism of the Replacement of Heterocyclic Amines from Some Aminotrichlorogold(III) Complexes

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Received January 3, 1966

A series of complexes of the type $[AuCl_3am]^0$, where am is a heterocyclic nitrogen base, has been prepared and the kinetics of the reactions with chloride, azide, and nitrite ions in methanol at 25° have been studied. In each case the first step is the replacement of the organic base, and the kinetics of this substitution follow the normal square-planar rate law: rate = $(k_1 + k_2[Y^-])$[complex]. k_1, the rate constant for the bimolecular solvolysis of the complex, is not very sensitive to the nature of the substrate, but the dependence of k_2 upon the natures of the substrate and the entering group indicates that the nucleophilic discrimination ability of Au(III) in these complexes is good and is influenced markedly by the nature of the leaving group. A linear free energy relationship is observed between the basicity of the leaving group and the rate constant for its replacement by chloride, but this simple behavior is not followed by azide and nitrite, and the more complicated relationship is discussed in terms of polarizability and π bonding in the transition state.

Introduction

Kinetic studies of the mechanism of the substitution reactions of square-planar complexes have been confined exclusively to complexes of d^8 transition metal ions. Nearly all of the systematic investigations have been carried out with complexes of Pt(II) and little has been reported about analogous complexes of other metals. It is of interest to compare the reactions of Au(III) complexes with those of Pt(II) in order to assess the relative importance of two possible factors that might be working in opposition to one another. On one hand it has been suggested[1] that the tendency to form stable trigonal-bipyramidal five-coordinate complexes of low-spin d^8 metal ions decreases as the oxidation state increases, *i.e.*, Cr(−II) > Mn(−I) > Fe(0) > Co(I) > Ni(II) > Cu(III), with a similar relationship for the isovalent elements of the second and third transition series. This argument should be equally valid when applied to the five-coordinate transition state for bimolecular substitution in a square-planar complex and would suggest that the bimolecular transition state is less readily formed by Au(III) than it is by Pt(II). On the other hand, the increased nuclear charge of Au(III) might attract the electron pair of the incoming nucleophile more strongly and thereby provide compensation. Under these circumstances the five bonds in the transition state are less likely to be equivalent and the three nonchanging bonds might be more covalent than the other two. A third point of interest is the extent to which the increased effective nuclear charge has made the nonbonding d electrons insensitive to electrophilic attack and thereby reduced the "biphilicity" of the process.

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(1) R. S. Nyholm, *Proc. Chem. Soc.*, 273 (1961); R. S. Nyholm and M. L. Tobe, *Experientia, Suppl.*, **9**, 112 (1965).

Little systematic work has been done on the way in which the nature of the leaving group affects the rate of any square-planar substitution reaction, and there is only one report dealing with the dependence of rate upon the nature of the entering group in a Au(III) complex.[2] The present paper reports the kinetics of the reaction

$$[AuCl_3am]^0 + Y^- \longrightarrow [AuCl_3Y]^- + am$$

where am is a heterocyclic amine (pyridine, 3- or 4-methylpyridine, 3,5- or 2,6-dimethylpyridine, quinoline, or isoquinoline) and Y^- is Cl^-, NO_2^-, or N_3^-. The reactions were studied spectrophotometrically in methanol at 25°.

Results

(1) **Kinetics of the Reaction with Chloride.**—This reaction is the simplest to characterize spectrophotometrically. Examination of the changing spectrum of a methanolic solution originally containing $[AuCl_3am]^0$ and excess lithium chloride showed, through the development of well-defined isosbestic points whose position depended only upon the spectrum of the starting compound, that a single-stage process was involved. There was no evidence for the reduction of the complex to Au(I) or metallic gold under the experimental conditions (metallic gold was slowly deposited from solutions left exposed to light for long periods of time), and since the only other possible substitution reaction, namely the displacement of chloride by chloride, could not change the spectrum, it was reasonable to assume that the observed reaction was the displacement of the amine by chloride. In every case the final spectrum corresponded closely to that of the $[AuCl_4]^-$ anion.

All the reactions were carried out in the presence of a large excess of chloride so that, in any particular run, the kinetics were of a first-order form. The rate constants were obtained from the slope of the semilogarithmic plot of log $(D_t - D_\infty)$ against time, where D_t and D_∞ are the optical densities of the solution at the wavelength of maximum change (in the region of 320 mμ, depending upon the complex studied) at times t minutes and after ten half-lives, respectively. These pseudo-first-order rate constants varied with the concentration of chloride in the way that is now usual in square-planar substitution, *i.e.*, $k_{obsd} = k_1 + k_2[Cl^-]$, and the values of k_1 and k_2, obtained from the intercept and slope of the linear plot of k_{obsd} against $[Cl^-]$, are collected in Table I. Addition of a neutral salt ($LiClO_4$) indicated that primary salt effects were absent and secondary effects were negligible, and no further attempt was made to maintain constant ionic strength. The rate of reaction was not sensitive to the presence of adventitious traces of oxidation–reduction catalysts, as was the case in the exchange of chloride with $[AuCl_4]^-$,[3] and extensive purification of the substrates and reagents did not significantly change the rate of reaction.

Preliminary studies of the spectra of the complexes in methanol in the absence of added chloride showed that they obeyed Beer's law and indicated that they were stable toward solvolysis. Therefore, it was not necessary to add acid to prevent proton loss from the solvento complex, $[PtCl_3CH_3OH]$.

Table I

Second-Order Rate Constants (M^{-1} sec^{-1}) for the Displacement of the Heterocyclic Amine from the Complex $[AuCl_3am]^0$ in Methanol at 25°

		Entering ligand			
am	pK_a[a]	CH_3OH[b]	Cl^-	NO_2^-	N_3^-
Quinoline	4.95	3.0×10^{-4}	0.245	1.47	29.1
Isoquinoline	5.14	5.8×10^{-4}	0.245	6.82	72
Pyridine	5.17	7.5×10^{-4}	0.417	6.75	108
3-Methylpyridine	5.68	7.0×10^{-4}	0.195	41.4	78
4-Methylpyridine	6.02	6.1×10^{-4}	0.096	43.0	68
3,5-Dimethylpyridine	6.34	7.0×10^{-4}	0.090	34.5	51
2,6-Dimethylpyridine	6.75	6.2×10^{-4}	0.039	26.1	24.7

[a] pK_a of the conjugate acid. [b] The solvolytic data are expressed as first-order rate constants (sec^{-1}).

(2) **Kinetics of Substitution by Nitrite and Azide.**—Preliminary observations once again confirmed that there was no significant reduction of the complex in the course of the reaction. The spectrophotometric evaluation of the kinetics was complicated by the fact that displacement of the chloride as well as displacement of amine would cause a change in spectrum and, since the concentrations of complex used were far too low to allow a direct chemical identification of the leaving group, it was necessary to deduce the nature of the leaving group spectrophotometrically. By rapidly measuring the spectrum of the reaction mixture over the range 250–350 mμ from time to time in the course of the reaction it was possible to show that the reaction occurred in more than one stage. When azide was the reagent, four separate stages of the reaction could be identified and an isosbestic point, the wavelength (290 mμ) and extinction coefficient (4×10^4 cm^2 mole^{-1}) of which were independent of the parent substrate, developed in the second stage. In the substitution by nitrite the individual stages of the later part of the reaction could not all be resolved and the process was characterized by two steps. In all cases the rate of the first step depended upon the nature of the substrate whereas that of the second and subsequent stages did not. In every case the subsequent stages of the reaction were very sensitive to the ionic strength of the medium whereas the first stage was not. All of these observations are consistent with the idea that the first stage of the reaction between $[AuCl_3am]^0$ and N_3^- or NO_2^- was the displacement of the neutral heterocyclic ligand and that the subsequent reactions involved the same anionic complexes since they were independent of the nature of the amine displaced. Chemical confirmation of the identity of the first stage was not possible and a spectrophotometric evaluation was ruled out because the possible intermediates, $[AuCl_{4-n}(NO_2)_n]^-$ and $[AuCl_{4-n}(N_3)_n]^-$, have never been characterized. An attempt was made to obtain a product from the reaction between equimolar amounts of $[AuCl_3py]$ and NaN_3, but only a very small quantity of a very explosive solid was isolated.

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[2] W. H. Baddley and F. Basolo, *Inorg. Chem.*, **3**, 1087 (1964).

[3] R. L. Rich and H. Taube, *J. Phys. Chem.*, **58**, 6 (1954).

Substitution by azide was conveniently studied at the isosbestic point of the second step (290 mμ) and the pseudo-first-order rate constant was determined from the slope of the semilogarithmic plot, as in the case of chloride substitution. In the nitrite substitution reactions, where only two stages could be observed, the two rates were so different that the first stage could be studied without significant interference from the second. The rates were determined from the change of optical density at 270 mμ and the rate constants determined graphically as before; however, because of the slight interference of the second stage at the very end of the reaction, the infinity value used was the optical density after six half-lives. Measurements carried out at other wavelengths where there was an adequate change of optical density gave the same value for the rate constant. This confirms that the first stage of the reaction is essentially complete before the second stage has developed. Although there is no supporting evidence, it seems reasonable to believe that the first stage was the replacement of the amine and one chloride, *i.e.*

$$[AuCl_3am]^0 + NO_2^- \xrightarrow{slow} [AuCl_3NO_2]^- + am \xrightarrow[+NO_2^-]{fast} [AuCl_2(NO_2)_2]^- + Cl^-$$

and

$$[AuCl_2(NO_2)_2]^- + NO_2^- \xrightarrow{slow} [AuCl(NO_2)_3]^- + Cl^- \xrightarrow[+NO_2^-]{fast} [Au(NO_2)_4]^- + Cl^-$$

This formulation is in accord with the accepted *trans effect* behavior of coordinated nitrite and suggests that the dinitrodichloroaurate(III) anion is the *trans* isomer.

The pseudo-first-order rate constants, k_{obsd}, varied with the concentration of anionic reagent according to the expression $k_{obsd} = k_1 + k_2[Y^-]$, and the values of k_1 and k_2 obtained from the intercept and slope of the linear plot of k_{obsd} against $[Y^-]$ are collected in Table I. For any one complex the value of k_1 obtained was independent of the nature of the entering anion, which is further proof that the amine is displaced in the first step of the reaction with azide and nitrite as well as in the reaction with chloride, where it is the only possible reaction.

Discussion

The general kinetic form of all these substitution reactions is in agreement with previous observations on square-planar substitution, *i.e.*, $-d[complex]/dt = (k_1 + k_2[Y])[complex]$. It is now generally agreed that all the stages are bimolecular, the first-order term representing bimolecular solvolysis by methanol and the second-order term direct bimolecular attack by Y. It is not possible within this group of reactions to make a direct comparison between Au(III) and Pt(II) because the analogous reaction, involving the displacement of the neutral ligand in preference to the usually labile chloride, is, at first sight, a rather startling observation. However, it is of interest to compare the data in Table I with the rate constants for the reaction of *trans*-$[Pt(py)_2Cl_2]$, now considered as the reference substrate for the n_{Pt} scale of nucleophilicity with respect to platinum.[4] These, in methanol at 30°, are: CH_3OH, 1.0×10^{-5} sec^{-1}; Cl^-, 4.5×10^{-4} (estimated); N_3^-, 1.55×10^{-3}; NO_2^-, 6.8×10^{-4} (the last three are second-order rate constants in M^{-1} sec^{-1}). Although the coordination shells of the Au(III) and Pt(II) ions are different and the leaving group is neutral in the first case and anionic in the second, the reactions of neutral complexes with some charge separation in the transition state are being compared in both cases. It will be seen that the Au(III) complexes are considerably more reactive than the Pt(II) complexes toward the anionic reagents, and this is in accord with previously published data.[2,5] The rate of the solvolytic reaction does not change much from substrate to substrate, nor does it reflect the enhanced reactivity as much as the anionic reagents: this is also in agreement with previous work.

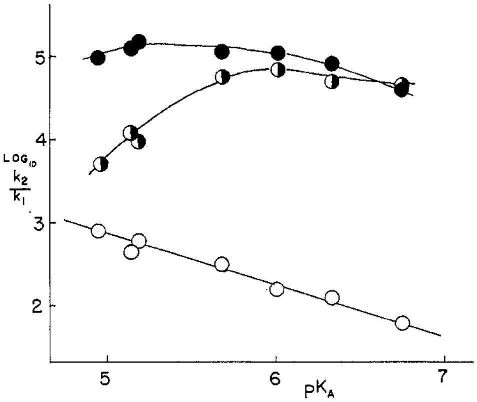

Figure 1.—Log k_2/k_1 plotted as a function of the pK_a of the leaving group: ○, chloride entry; ◑, nitrite entry; ●, azide entry.

Of the three reagents used, the chloride ion is the least polarizable and possesses little or no biphilic properties, functioning only as a σ-bonding nucleophile; therefore, it is convenient to discuss the reaction with chloride first and then consider the reactions with azide and nitrite in order to assess the contributions made by the polarization and electrophilic aspects of the reaction. In general, it can be seen from Table I that the rate constants for the solvolytic part of the reaction are not very dependent upon the nature of the leaving group. In order to correlate the results we have used the ratio k_2/k_1 as a measure of the relative reactivity of the different substrates toward, in this case, chloride, thereby making it possible to neglect certain factors concerning the leaving group which, in the first approximation, are independent of the nature of the entering group. In Figure 1 log k_2/k_1, which is a measure of the relative free energies of activation, is plotted against the pK_a of the conjugate acid of the leaving group, which is a measure of the free energy of protonation of the base. A reasonably good straight-line relationship is obtained, and it is of interest to note that this is the first time, in square-planar substitution, that a linear free-energy

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(4) U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, **87**, 241 (1965).

(5) R. L. Rich and H. Taube, *J. Phys. Chem.*, **58**, 1 (1954).

relationship between a free energy of activation and an equilibrium property of either the entering or the leaving group has been obtained. Therefore, when chloride is the entering group there is a clear relationship between the rate of reaction and the strength of the breaking bond. This does not appear to be true for the reaction with methanol. The data for the reactions with azide and nitrite have been treated in a similar way and are also plotted in Figure 1, where it will be seen that the simple linear relationship does not hold. Not only does the discriminating power of the gold depend upon the nature of the leaving group, but the relative nucleophilicites are also changed. For the displacement of the least basic amine, nitrite is some six times more reactive than chloride, and azide is some twenty times more reactive than nitrite, indicating a much greater discrimination than is usually observed in the reactions of similar Pt(II) complexes. As the basicity of the leaving group increases, the rates of its displacement by nitrite or azide also increase, the effect being more marked in the case of nitrite so that, for the displacement of 2,6-dimethylpyridine, nitrite is the better reagent. The rates of displacement of the more basic ligands do tend to decrease as their basicity increases, but it has not yet been possible to obtain complexes with suitable ligands of high enough basicity to see whether the dependence of log k_2/k_1 upon pK_a becomes linear in this region.

The similarity of the kinetic forms of these and other square-planar substitution reactions indicates that the same bimolecular mechanism is operating. Any discussion concerning relative reactivities must take into account the energetics of the five-coordinate transition state and, for a start, it is convenient to consider the factors affecting the occurrence of stable five-coordination and then relate them to the formation of the transition states. For the isoelectronic sequence of d^8 metal ions, the tendency to form stable, trigonal-bipyramidal, five-coordinate complexes appears to decrease as the formal oxidation state of the metal increases. This has been attributed to the increase in the relative energy separation between $(n-1)$d–ns and ns–np orbitals as the charge on the metal increases, so that the combination of the $(n-1)d_{x^2-y^2}$, the ns, and the *three* np orbitals to form a set of five equivalent orbitals becomes progressively more difficult.[1,6] If the transition state contains essentially covalent bonds, one might expect Au(III) to be less reactive than Pt(II). However, in spite of these arguments, five, and even six, coordination can be found in certain low-spin Pt(II) and Au(III) complexes, *e.g.*, $[Pt(diars)_2I]ClO_4$,[7] $[Au(diars)_2I](ClO_4)_2$,[8] and $[Au(diars)_2I_2]ClO_4$,[8] where diars = *o*-phenylenebisdimethylarsine, both in the solid state and in solution. It was suggested that the bonding of the anions differs from that of the arsenics and makes use of $6p_z$–$6d_{z^2}$ hybrid orbitals,[8] but, although a purely electrostatic type of interaction was rejected because of the large changes in spectrum caused by adding the anions, there is little doubt that the axial bonds have much more ionic character than the four in the square plane. It is noteworthy that the increase in coordination number above four in Pt(II) and Au(III) complexes is generally found when the metal is coordinated to ligands that are able to leave a relatively high positive charge upon the metal and that the complexes are generally, but not invariably, square bipyramidal or octahedral. Consequently, five and six coordination again becomes likely in the highest oxidation states of the d^8 isoelectronic series, but there the electrostatic aspects become more important.

The application of these arguments to the five-coordinate transition state is only valid insofar as it applies to the trigonal bipyramid. This is so because, if somewhere along the reaction coordinate, the system adopts a square-pyramidal form with the entering group in the axial position, it must, further on, adopt an equivalent form with the leaving group in the axial position. If we have a truly synchronous bimolecular mechanism, Figure 2a, neither of these can be the *single* transition state that is required and which must have some intermediate geometry. However, it has been suggested, quite reasonably, that substitution in square-planar complexes is an addition process with a five-coordinate *intermediate*, Figure 2b,[9] and two transition states, one involving bond making and the other involving bond breaking. Although the entering and leaving group could affect both halves of the profile, it is clearly possible that either transition state could have the higher energy and therefore be rate determining. If the intermediate is trigonal bipyramidal it is not likely that these two transition states will be square pyramidal since this would imply that the square pyramid was less stable than the trigonal bipyramid, which is not in accord with known fact. For example, only when steric limitations are applied, as in the complexes of tris(*o*-diphenylarsinophenyl)arsine (QAS), does one find trigonal-bipyramidal complexes of the type $[M(QAS)X]^+$, M = Pd or Pt.[10,11] Four arsenics without steric restriction, as in $[Pt(diars)_2X]^+$, occupy the four corners of the square plane and the anion occupies the axial position of the square pyramid. The square-pyramidal form can therefore be found lower down the slopes of the reaction profile, Figure 2c, and, although it may be present in large amounts in the reaction solution, it will not affect the rate of reaction except insofar as a pre-equilibrium will affect the kinetic form. It is of interest to note that, whereas the fifth ligand in this type of complex is extremely labile,[12] the axial bromide in $[Pt(QAS)Br]^+$ is inert and its displacement is a bimolecular process.[13] This adds support to the idea that the

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(6) R. S. Nyholm, private communication.

(7) C. M. Harris, R. S. Nyholm, and D. J. Phillips, *J. Chem. Soc.*, 4379 (1960).

(8) C. M. Harris and R. S. Nyholm, *ibid.*, 63 (1957).

(9) H. B. Gray, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 103.

(10) J. A. Brewster, C. A. Savage, and L. M. Venanzi, *J. Chem. Soc.*, 3699 (1961).

(11) G. A. Mair, H. M. Powell, and L. M. Venanzi, *Proc. Chem. Soc.*, 170 (1961).

(12) A. Peloso and M. L. Tobe, unpublished results.

(13) R. G. Pearson, M. M. Muir, and L. M. Venanzi, *J. Chem. Soc.*, 5521 (1965).

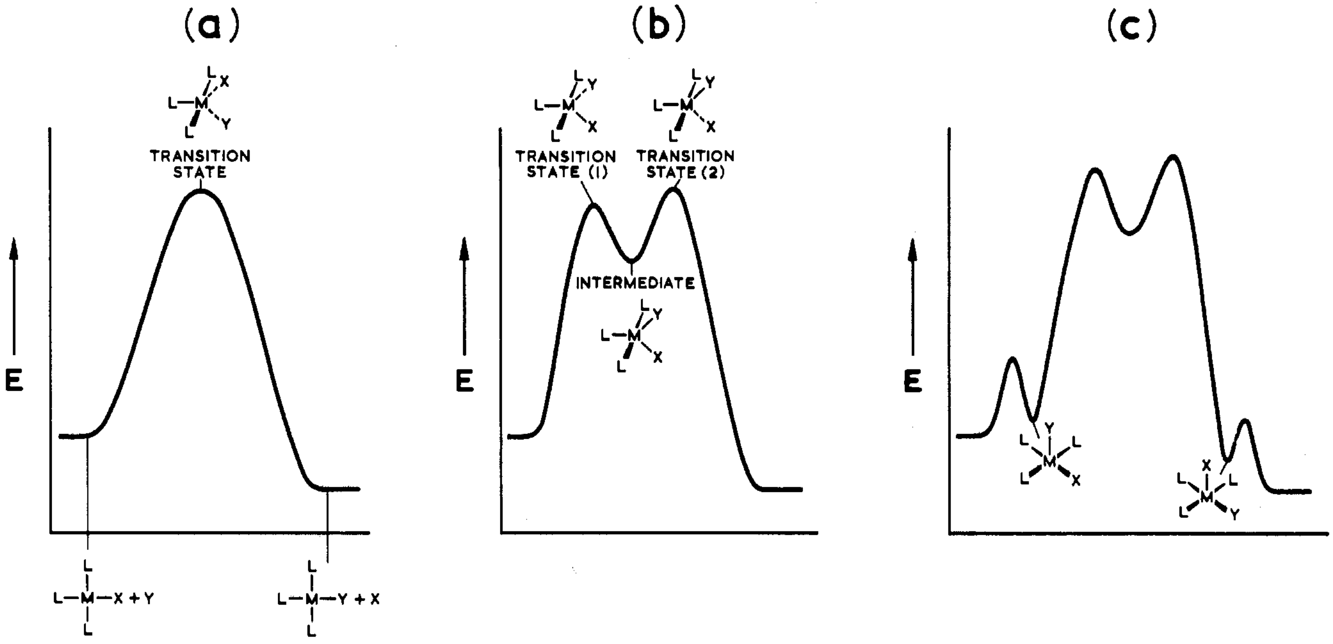

Figure 2.—Diagrammatic representation of energy relationships for progress along the reaction coordinate (the ordinate) for (a) a synchronous bimolecular substitution of X by Y, (b) an "addition" mechanism with a five-coordinate intermediate, and, (c) an "addition" mechanism with possible preequilibrium association of the reagents to form a labile square-pyramidal intermediate. For simplicity the parts of the curve that are common to more than one figure are labeled only once.

five bonds in the trigonal bipyramid are more nearly equivalent than those in the square pyramid where the axial bond is much more ionic than the other four. The two transition states therefore probably have a distorted trigonal-bipyramidal structure.

The enhanced reactivity of the Au(III) complexes suggests that the electrostatic factors promoting five-coordination are carried over to some extent into the transition states and become more important in the acts of bond making and bond breaking in Au(III) than in the lower-charged Pt(II). In this way it is possible to explain why the heterocyclic amine, which can only make an ion–dipole interaction in the transition state, is more readily displaced than the chloride, which makes an ion–ion interaction. One can also understand why the reactivity with anions is enhanced whereas the reactivity of methanol is much the same in the Pt(II) and Au(III) complexes. This electrostatic contribution is not of overriding importance and serves only to make a discrimination between essentially "hard" ligands.[14] The gold atom is still "soft," in the Pearson sense, and still discriminates in favor of the more polarizable ligands so that, in the case of the halide ions, the reactivity order toward Au(III) is still Cl < Br < I[2] and not the reverse, or "hard" acid–base sequence. Preliminary studies indicate that the [AuCl$_3$am] complexes react much more rapidly with bromide than with chloride, but the detailed kinetic study must await the availability of special fast reaction equipment.

In this work we have found that Au(III) shows a greater discrimination between chloride and azide in all the complexes studied and between chloride and nitrite in the complexes of the more basic amines than is shown by Pt(II) in many of the nonelectrolyte complexes.[4] However, a much larger discrimination factor has been reported for *trans*-[Pt(NH$_3$)$_2$Cl$_2$][15] and indicated for [PtCl$_4$]$^{2-}$,[16] although these data should be treated with caution since no attempt was made to identify the products of the reaction. It is possible to explain how the discriminating power of the gold atom is affected by the nature of the leaving group by considering the degree of assistance required to break the bond. The reaction with the essentially σ-bonding chloride shows a linear free-energy relationship between the rate of reaction and the basicity of the leaving group (presumably representing the strength of the metal–ligand bond). It should follow that, as the basicity of the leaving group increases, bond breaking becomes more difficult and requires more assistance from the incoming group, the rate-determining transition state becoming more compact. The ability of the gold atom to discriminate between the anionic reagents appears to be least in the complexes of the weakest bases, where the transition state is most open. Here, the gold atom bears the greatest positive charge and is, therefore, less polarizable than in the transition state with the more basic amines. Consequently, it will be less able to make use of the polarizability of the incoming group. The increase in the discrimination between chloride and nitrite as the basicity of the leaving group increases can be ascribed to a synergic effect in which, as the strength of the Au–NO$_2$ σ bond increases in the transition state, the gold becomes more polarizable and the nitrite is more able to make use of its electrophilic polarizability. At first, this effect outweighs the rate-decreasing bond-breaking contribution, which always

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[14] R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

[15] D. Banerjea, F. Basolo, and R. G. Pearson, *ibid.*, **79**, 4055 (1957).

[16] H. B. Gray, *ibid.*, **84**, 1548 (1962).

predominates for chloride entry, but, when the electrophilic contribution reaches its maximum, the rate starts to decrease as the strength of the bond between the metal and the leaving group increases. These effects can also be observed in the reaction with azide but they are less marked.

Experimental Section

Trichloropyridinegold(III) and trichloroquinolinegold(III) were first characterized by Renz,[17] but the other complexes are described here for the first time. All of the complexes were prepared by the following general method. Equimolar amounts of the appropriate organic heterocyclic base were added to a concentrated aqueous solution of chloroauric acid which had previously been carefully neutralized with sodium carbonate. A yellow precipitate formed almost immediately and was filtered off and washed repeatedly with water and methanol and then dried over phosphorus pentoxide under vacuum. The precipitate could be recrystallized from anhydrous methanol, but this led to considerable loss of yield and to further decomposition, and it was found to be preferable, for the kinetic studies, to use the original precipitate that had been washed repeatedly with water and methanol. The analyses are reported in Table II. Attempts to make analogous complexes with piperidine, toluidine, and naphthylamine resulted in the reduction of the complex to metallic gold.

Anhydrous lithium chloride was recrystallized repeatedly from acetone and dried and stored in a vacuum desiccator. Sodium nitrite and sodium azide (AR grade) were recrystallized repeatedly from methanol and dried and stored in the dark in a vacuum desiccator.

AnalaR methanol was used without further treatment since small traces of water did not appear to have any effect upon the reactions.

TABLE II

ANALYTICAL DATA FOR THE COMPLEXES OF THE TYPE $[AuCl_3am]^0$

am	Complex	C, % Calcd	C, % Found	H, % Calcd	H, % Found	Cl, % Calcd	Cl, % Found
Pyridine	$C_5H_5NCl_3Au$	15.7	16.3	1.3	1.4	27.8	27.5
Quinoline	$C_9H_9NCl_3Au$	24.7	24.9	1.6	1.7	24.4	24.4
Isoquinoline	$C_9H_9NCl_3Au$	24.7	25.0	1.6	1.8	24.4	23.7
4-Methylpyridine	$C_6H_7NCl_3Au$	18.2	18.3	1.7	1.9	26.8	27.2
3-Methylpyridine	$C_6H_7NCl_3Au$	18.2	18.6	1.7	1.8	26.8	26.5
3,5-Dimethylpyridine	$C_7H_9NCl_3Au$	20.5	20.5	2.2	2.2	25.9	25.4
2,6-Dimethylpyridine	$C_7H_9NCl_3Au$	20.5	21.3	2.2	2.3	25.9	25.9

Kinetics.—Methanolic solutions of the complex (generally in the range 10^{-5}–10^{-4} M) and the appropriate reagent (10^{-5}–10^{-2} M) were prepared and stored separately in a thermostat. The reaction was started by mixing known volumes of the two solutions in the spectrophotometer cell, which was then placed in the thermostated compartment of the spectrophotometer. Most of the measurements were made with a Unicam SP 800 double-beam recording spectrophotometer. The slower reactions were followed by scanning the near-ultraviolet spectrum from time to time in the course of the reaction. In this way it was possible to separate and identify the individual stages of the reaction and then collect the appropriate optical density data. When the reaction was so fast that the time taken to scan an individual spectrum was a significant part of the time of the over-all reaction, the measurements were made at a single wavelength chosen after preliminary scanning experiments. The results were either recorded by allowing the chart to move at a known rate while the spectrophotometer was locked at the chosen wavelength or else obtained manually using a Unicam SP 500 spectrophotometer.

Acknowledgments.—L. C. wishes to thank the Italian Council for Research (C.N.R., Rome) for a fellowship and the Institute of General Chemistry of the University of Padua for a leave of absence.

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Trigonal Bipyramidal Complexes of Bivalent Manganese, Iron, and Zinc with Tris(2-dimethylaminoethyl)amine

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Received March 7, 1966

The quadridentate ligand tris(2-dimethylaminoethyl)amine (Me_6tren) forms 1:1 complexes with $MnBr_2$, MnI_2, $FeBr_2$, $ZnBr_2$, and ZnI_2. X-Ray powder photographs and conductivity and spectral data indicate that these complexes must be formulated as $[M(Me_6tren)X]X$. The metal is five-coordinated with an approximately trigonal bipyramidal configuration. Manganous and ferrous compounds are of the high-spin type. A simple crystal field model is employed in order to calculate the splitting of the ^5D ground terms of the d^4 and d^6 configurations in C_{3v} fields. The spectra of $[Fe(Me_6tren)Br]Br$ and of $[Cr(Me_6tren)Br]Br$ are discussed on this basis.

Introduction

Five-coordinated complexes of elements of the first transition group are still rather rare. In particular, those of manganese(II)[1] and of iron(II)[2,3] have only recently been isolated.

In this laboratory five-coordinated complexes of bivalent ions of the first transition group with ligands capable of giving high-spin configurations are being investigated. Previous studies have shown that the quadridentate amine $N[CH_2CH_2N(CH_3)_2]_3$, tris(2-di-

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