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The Mechanism of Displacement of Thioethers Coordinated to Platinum(II) Complexes

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Ligand displacement reactions in d^8 square-planar complexes are usually discussed[1] in terms of a mechanism involving intermediates or transition states with five donor atoms. When an intermediate is formed, the reaction profile has two maxima. The experimental detection of such intermediates is generally impossible and, to our knowledge, has been shown in only one case.[2] For some platinum(II) complexes there is indirect kinetic evidence[3] that two energetically independent maxima occur in the reaction profile so that the bond-making and bond-breaking aspects of the substitutions can be considered separately. Even in these circumstances, however, the problem remains of determining which of the two maxima occurs at higher energy. In studying the replacement of anionic monodentate ligands X and Y by thioethers from complexes of the type Pt(bipy)XY it was concluded[4] that the first maximum in the reaction profile is of higher energy than the second. In order to provide further tests of this conclusion we have studied the processes

$$\mathrm{Pt(bipy)Cl(RSR')^+ + Y^- \longrightarrow Pt(bipy)Cl(Y) + RSR'} \quad (1)$$

i.e., the reverse of those reported previously.

Experimental Section

Materials.—The complex Pt(bipy)Cl$_2$, prepared according to the method reported in the literature,[5] was the starting material to obtain the cationic substrates. These, [Pt(bipy)Cl(RSR′)]NO$_3$ (RSR′ = C$_6$H$_5$CH$_2$–S–CH$_3$, C$_6$H$_5$–S–CH$_3$, C$_2$H$_5$–S–C$_2$H$_5$, C$_2$H$_5$–S–CH$_3$), were prepared by adding to a methanolic solution of [Pt(bipy)Cl(CH$_3$OH)]NO$_3$, obtained from Pt(bipy)Cl$_2$ and AgNO$_3$, the required amount of thioether. Evaporation of the solution to a small volume and addition of ether gave the product in the form of a pale yellow-white precipitate, which was recrystallized from methanol. The analytical data are summarized in Table I. The thioethers used were commercial products, reagent grade, with the exception of C$_6$H$_5$CH$_2$–S–CH$_3$ which was obtained according to a method reported in the literature.[6] The solvent methanol was dried by distillation over Mg(OCH$_3$)$_2$. Conductivity measurements, carried out by means of an LKB 3216B conductivity bridge, confirm that all the substrates are 1:1 electrolytes.

TABLE I
ANALYTICAL DATA FOR THE COMPLEXES
[Pt(bipy)Cl(RSR′)]NO$_3$

RSR′	% C		% H		% N		% S	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
C$_2$H$_5$–S–C$_2$H$_5$	33.4	33.2	3.57	3.61	8.34	8.31	6.36	6.41
C$_2$H$_5$–S–CH$_3$	31.9	31.8	3.27	3.27	8.58	8.55	6.54	6.54
C$_6$H$_5$CH$_2$–S–CH$_3$	39.2	39.4	3.27	3.26	7.62	7.58	5.81	5.78
C$_6$H$_5$–S–CH$_3$	38.0	38.2	2.98	2.96	7.82	7.84	5.96	6.01

Kinetics.—Experimental conditions and procedures were as reported previously[4] except that the ionic strength of each reaction mixture was maintained at 0.1 *M* by addition of LiNO$_3$.

Results

The spectra of the reaction mixtures showed relatively rapid changes (similar for Cl$^-$, Br$^-$, and I$^-$ as entering groups with a given substrate) and well-defined isosbestic points. The rate constants in Table II were calculated from these changes in spectra in the range 270–360 nm. In the reactions with Br$^-$ and I$^-$ the initial spectral changes were followed by much slower ones. The latter were not observed in the reactions with Cl$^-$ which showed changes in spectra exactly the reverse of those observed for the reactions of Pt(bipy)Cl$_2$ with thioethers.[4] In parallel with the initial spectral changes the conductance of all reaction mixtures decreased.

TABLE II
FIRST-ORDER RATE CONSTANTS FOR REACTIONS 1
IN METHANOL AT 25° (μ = 0.1 *M*)[a]

Leaving group RSR′	10^3[entering group], *M*	10$^3k_{\text{obsd}}$, sec^{-1}	10^3 [entering group], *M*	10$^3k_{\text{obsd}}$, sec^{-1}
	Entering Group I$^-$			
C$_2$H$_5$–S–C$_2$H$_5$	2.0	3.06	1.0	1.53
	1.4	2.15	0.4	0.63
C$_2$H$_5$–S–CH$_3$	8.0	23	2.0	5.74
	4.0	11.8	1.0	2.84
C$_6$H$_5$CH$_2$–S–CH$_3$	0.5	9.4	0.2	4.6
	0.35	6.8	0.133	3.4
	Entering Group Br$^-$			
C$_2$H$_5$–S–C$_2$H$_5$	100	2.91	50	1.15
	75	2.21	10	0.23
C$_2$H$_5$–S–CH$_3$	100	5.5	50	2.70
	75	4.04	20	1.03
C$_6$H$_5$CH$_2$–S–CH$_3$	10	3.61	5	1.8
	7.5	2.68	2	0.73
C$_6$H$_5$–S–CH$_3$	10	38.2	5	19
	7.5	28.5	1	3.8
	Entering Group Cl$^-$			
C$_2$H$_5$–S–C$_2$H$_5$	100	9.95	50	4.93
	80	7.83	20	1.92
	66.6	6.15		
C$_2$H$_5$–S–CH$_3$	100	0.202	50	0.096
	75	0.141	20	0.042
C$_6$H$_5$CH$_2$–S–CH$_3$	100	1.095	33.3	0.375
	75	0.81	20	0.22
	50	0.55		
C$_6$H$_5$–S–CH$_3$	100	10.5	50	5.4
	75	7.7	10	1.1

[a] In all cases the complex concentration was less than 2 × 10^{-6} *M*.

Second-order rate constants (k_2) were calculated from plots of k_{obsd} against [Y$^-$] and are given in Table III to-

TABLE III
SECOND-ORDER RATE CONSTANTS, k_2, RELATIVE TO THE
REPLACEMENT OF RSR′ FROM THE COMPLEXES
Pt(bipy)Cl(RSR′)$^+$ IN METHANOL AT 25° (μ = 0.1 *M*),
BY ANIONIC REAGENTS, Y$^-$

RSR′	$-\Sigma\sigma^*$	k_2, M^{-1} sec^{-1}		
		Y$^-$ = I$^-$	Y$^-$ = Br$^-$	Y$^-$ = Cl$^-$
C$_2$H$_5$–S–CH$_3$	−0.6	...	3.81	0.105
C$_6$H$_5$CH$_2$–S–CH$_3$	−0.215	19	0.361	0.011
C$_2$H$_5$–S–CH$_3$	+0.1	3.0	0.055	0.0019
C$_2$H$_5$–S–C$_2$H$_5$	+0.2	1.53	0.0291	0.00098

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[1] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1968, Chapter II. See also L. Cattalini in "Inorganic Reaction Mechanisms," J. O. Edwards, Ed., Wiley, New York, N. Y., 1970, pp 263–327.

[2] L. Cattalini, R. Ugo, and A. Orio, *J. Amer. Chem. Soc.*, **90**, 4800 (1968).

[3] L. Cattalini and M. Martelli, *Gazz. Chim. Ital.*, **97**, 498 (1967).

[4] L. Cattalini, M. Martelli, and G. Kirschner, *Inorg. Chem.*, **7**, 1488 (1968).

[5] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 965 (1934).

[6] G. Braum and E. P. Engeldertz, *Ber.*, **56**, 1573 (1923).

gether with values of $-\Sigma\sigma^*$, the sum of Taft σ^* constants[7] for the groups (R, R′) present in the thioethers.

Discussion

The spectroscopic and conductance measurements referred to above suggest that the rate constants in Table II refer to reactions 1 and that, with $Y^- = Br^-$ or I^-, these reactions are followed by the much slower processes

$$\mathrm{Pt(bipy)Cl(Y)} + \mathrm{Y}^- \longrightarrow \mathrm{Pt(bipy)Y_2} + \mathrm{Cl}^- \qquad (2)$$

The $-\Sigma\sigma^*$ values are a measure of the inductive effect of R and R′ and it has been shown that they are in linear relationship with the free energy of activation, in processes where thioethers act as entering groups.[4,8]

As one might expect for the attack at these "soft" substrates, the order of nucleophilicity is $I^- > Br^- > Cl^-$. Moreover, there is a linear decrease of the reactivity, expressed in terms of log k_2, as the σ-donor ability of the thioethers, measured in terms of $-\Sigma\sigma^*$, increases. In fact, plots of log k_2 against $-\Sigma\sigma^*$ for each entering group give three parallel straight lines. This indicates that the ability of each substrate to discriminate between the various reagents does not depend upon the nature of the displaceable thioether, and the ability of the entering group to discriminate between the various substrates does not depend upon its own nature. It also indicates that, as might be expected in these reactions, the bond-making and bond-breaking aspects of the substitution can be discussed separately.

In the reactions of the type

$$\mathrm{Pt(bipy)(X)Y} + \mathrm{RSR'} \longrightarrow \mathrm{Pt(bipy)(RSR')Y}^+ + \mathrm{X}^-$$

the effect of the nature of the leaving group on the reaction rate was relatively small (increasing by a factor of 7 on going from $X = N_3$ to $X = Cl$) whereas the effect of the nature of the entering group was significant. In the case of the reactions reported here, the natures of both the entering and leaving groups are of importance. The increase of the reaction rate with the nature of the entering anion is greater than 3 orders of magnitude on going from $Y^- = Cl^-$ to $Y^- = I^-$, and its dependence upon the nature of the displaced thioether is also extremely marked. These facts are consistent with the view that, in these reactions, the second maximum in the reaction profile is of higher energy. If the converse were true, the rate of these asynchronous processes might markedly depend on the degree of bond formation in the activated complex between the metal and the entering group but not on the nature of the leaving group, which would still be strongly bonded to the metal as it was in the ground state. However, if the second maximum is of higher energy, the rate might depend on the degree of bond rupture in the activated complex and therefore upon the nature of the leaving group, as well as on the nature of the entering reagent which becomes firmly bonded to the metal in the activated complex.

A plausible explanation for the behavior of thioethers in these and other reactions[9,10] may be given in terms of a stereoelectronic hindrance arising from interference between the nonbonded lone pairs of electrons on the sulfur and the distribution of charge on the complex. In the case of the entry of thioethers this hindrance arises in the formation of the activated complex and makes bond formation more difficult so that the degree of bond making will be rate determining. When thioethers are the leaving groups, they are present both in the ground and transition states and a relatively higher degree of bond rupture in the activated complex should favor the reaction rate.

Finally, if the rate constants for the forward reactions do not vary significantly with ionic strength, we can combine the present results with those obtained earlier[4] and calculate equilibrium constants for the reactions

$$\mathrm{Pt(bipy)Cl_2} + \mathrm{RSR'} \rightleftharpoons \mathrm{Pt(bipy)Cl(RSR')}^+ + \mathrm{Cl}^- \quad (3)$$

where $R = CH_3$ and $R' = C_6H_5$, CH_3, or C_2H_5.

Assuming that the free energy of the reactants does not depend markedly on the nature of the thioether, the relative free energies of the products may be determined from these three equilibrium constants. The relative free energies of activation may also be calculated from the rate constants reported earlier.[4] A comparison of the total and activation free energies shows that the nature of the thioether affects the ground-state energy of the system $\mathrm{Pt(bipy)Cl(RSR')}^+ + \mathrm{Cl}^-$ to a greater extent than it affects the energy of the transition state. This is in accord with the conclusion that the Pt–S bond is partially broken in passing from the ground state to the transition state for the reverse of (3).

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Circular Dichroism and Polarized Crystal Spectra of Cobalt(II) L-Histidinate Complexes[1]

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The importance of simple transition metal complexes of the essential amino acid histidine as "model" systems for metal-activated enzymes has been discussed previously.[2] Interest in histidine complexes of the cobaltous ion has been particularly widespread stimulated by the reversible oxygen-carrying capacity of cobalt(II)–histidine solutions.[3] Complementing the extensive solution investigations, a few reports of specific solid-state compounds have also been made. Isolation of the oxy-

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[7] R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newmann, Ed., Wiley, New York, N. Y., 1965.

[8] L. Cattalini, G. Marangoni, and M. Martelli, *Inorg. Chem.*, **7**, 1495 (1968).

[9] L. Cattalini, G. Marangoni, and M. Martelli, *Proc. Symp. Coord. Chem., 1970*, 347 (1970).

[10] L. Cattalini, G. Marangoni, J. S. Coe, and M. Martelli, *J. Chem. Soc. A*, 593 (1971).

[1] (a) Presented in part at the 155th National Meeting, of the American Chemical Society, San Francisco, Calif., 1968; see Abstracts, No. M124. (b) Taken in part from the Ph.D. thesis of P. L. Meredith, Duke University, 1970.

[2] P. L. Meredith and R. A. Palmer, *Inorg. Chem.*, **10**, 1049 (1971).

[3] J. Z. Hearon and D. Burk, *J. Nat. Cancer Inst.*, **9**, 337 (1949).