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Reactivity of Amines towards Dichloro[biacetylbis(N-methyl, N-phenyl)osazone]platinum(II)

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We have investigated the kinetics of substitution with amines of one of the coordinated chlorides in the complex Pt(Oz)Cl₂, where Oz = Biacetylbis(N-methyl,N-phenyl)osazone. The results obtained are compared with those relative to the complex Pt(bipy) Cl₂ and indicate that the greater reactivity of Pt(Oz) Cl₂ can be attributed to a labilizing effect due to an interaction in the transition state between one of the ortho hydrogens of one of the phenyl rings of the ligand and the developping chloride.

Introduction

A number of investigations dealing with reactivity of amines towards square planar complexes of d^8 transition metal ions have been published in the past.[1–8] However, the majority of available data refer to gold (III) and palladium(II) derivatives and the dependence of reactivity on the basicity of the entering amine has proved to be low in the case of Pt(II) systems.[1] The ligand Biacetylbis(N-methyl,N-phenyl)osazone (Oz) is known to act as chelate with Pd(II) and Pt(II) forming the complex $M(Oz)Cl_2$ (Figure 1), which, under appropriate experimental conditions, undergoes hydrogen chloride elimination and *ortho*-metallation at one of the phenyl groups.[9–12]

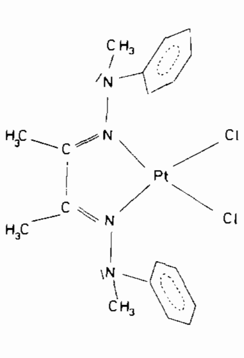

Figure 1. Reaction substrate.

In order to see if the chemical and steric characteristics of the phenyl groups also influence the substitution reactions of the chloride ions we decided to investigate the reactivity of $Pt(Oz)Cl_2$ with amines comparing the data with those of the analogous $Pt(bipy)Cl_2$.
The results are reported and discussed in this paper.

Results

Examination of the changing spectrum of a methanolic solution of $Pt(Oz)Cl_2$ containing an excess of amine shows that two stages of reaction are involved, the second one being much slower than the first one, which is characterized by a well defined isosbetic point. The final product of the first stage has been isolated in the case of the reaction with pyridine and the analysis indicates that it is $[Pt(Oz)(Py)Cl]^+$. Conductivity measurements in methanol at 25°C also indicate clearly that this first stage corresponds to the formation of a 1:1 electrolyte. In fact the initial conductivity which is very low, as expected for a non ionic system, in the presence of excess amine increases with time in a first order fashion and the final molar conductivity (89 ohm^{-1} cm^{-1}) is very close to that expected for a 1:1 electrolyte under this condition ($5 \times 10^{-4} M$). Therefore it is clear that the experimentally determined first-order rate constants are those corresponding to the displacement of the first chloride:

$$Pt(Oz)Cl_2 + am \rightarrow [Pt(Oz)(am)Cl]^+ + Cl^-$$

Preliminary studies show that the complexes obey Beer's law and are stable towards solvolysis; moreover addition of $NaNO_3$ to the reacting system did not alter significantly the observed rate constants as expected for processes involving neutral compounds where there is no primary salt effect.

All the reactions were carried out in the presence of a large excess of amine in order to achieve in any particular run pseudo first-order conditions. The rate constants were obtained from the slope of the semilogarithmic plot of log(D_t–D_∞) *vs.* time, where D_t and D_∞ are the optical densities of the solution at an appropriate wavelength at time t and at the end of the first stage respectively. Measurements carried out at different wavelengths in the range 360–300 mμ, where there is an adequate change of optical density, gave the same values for the rate constants.

As usual in the substitutions at square planar complexes,[1] the observed pseudo first-order rate constants depend upon the concentration of the entering amine according to the expression:

$$k_{obsd} = k_1 + k_2[am]$$

The k_{obsd} values are reported in Table I, the corresponding second order rate constants, k_2, together with the corresponding values for the reactions of Pt(bipy)Cl_2 (carried out under the same experimental conditions and reported for comparison) are summarized in Table II.

TABLE I. Pseudo First Order Rate Constants for the Displacement of One Chloride From the Complex Pt(Oz)Cl_2 in Methanol at 25 °C.[a]

Entering Amine	$10^2 \times$ [am],*M*	$10^3 \times k_{obsd}$, sec^{-1}
3-Cyanopyridine	0.10	1.35
	0.20	1.65
	0.30	2.32
	0.40	2.74
	0.50	3.38
	0.60	4.41
	0.70	4.78
	0.80	5.48
	0.90	6.16
	1.00	6.51
4-Cyanopyridine	0.21	1.46
	0.35	2.15
	0.42	2.61
	0.70	4.40
	1.05	6.90
	1.75	8.71
	2.27	11.52
	3.15	15.50
	3.50	18.21
Pyridine	0.33	2.95
	0.50	4.41
	0.83	6.60
	1.66	12.21
	2.50	19.23
3-Methylpyridine	0.28	3.55
	0.43	4.80
	0.55	6.21
	0.95	10.10
4-Methylpyridine	0.26	2.41
	0.52	4.13
	0.59	5.20
	0.88	7.02
	1.15	9.51
	1.48	11.82
	1.78	15.20
	2.45	20.10
3.5-Dimethylpyridine	0.38	4.71
	0.51	6.10
	0.77	8.02
	1.16	12.51
	1.44	15.82
	1.93	20.04
Morpholine	0.32	4.92
	0.79	11.03
	1.20	16.50
	1.53	20.52
	1.69	22.03
	1.97	25.51
Cyclohexylamine	0.15	6.56
	0.31	13.80
	0.48	22.21
	0.62	25.02
	0.72	32.53
	0.95	41.52
	1.19	51.30
2-Methylpyridine	10.3	1.24
	13.7	1.38
	17.2	1.66
	27.5	2.50
	34.4	2.75
	46.6	3.65
2,3-Dimethylpyridine	19.8	2.06
	26.4	2.35
	33.0	2.84
	39.6	3.30
	47.0	3.70
	62.7	4.90
	78.3	6.00
2,4-Dimethylpyridine	17.1	2.91
	20.6	3.22
	34.2	4.60
	51.3	6.90
	60.0	8.11
	85.5	11.40

[a] The concentration of the complex in the reaction mixture was always less than 5×10^{-4} *M*.

The k_1 which was practically negligible in the case of Pt(bipy)Cl_2 is 5×10^{-4} sec^{-1} in the present case and, as expected, is independent on the nature of the entering group.

Discussion

By plotting the values of logk_2 against the pK_A of the entering amine a linear relationship is found as far

TABLE II. Second Order (M^{-1} sec^{-1}) Rate Constants for the Displacement of a Coordinated Chloride from $Pt(Oz)Cl_2$ and $Pt(bipy)Cl_2$ in Methanol at 25° C.

Entering Amine	pK_a[a]	$Pt(Oz)Cl_2$	$Pt(bipy)Cl_2$
3-Cyanopyridine	1.39	0.61 ± 0.04	–
4-Cyanopyridine	1.90	0.48 ± 0.04	0.0041
Pyridine	5.17	0.73 ± 0.05	0.0058
3-Methylpyridine	5.68	0.97 ± 0.01	0.0062
4-Methylpyridine	6.02	0.82 ± 0.01	0.0064
3,5-Dimethylpyridine	6.34	1.01 ± 0.08	0.0065
Morpholine	8.40	1.25 ± 0.06	0.009
Cyclohexylamine	10.64	4.30 ± 0.34	0.012
Quinoline	4.95	–	0.00050
2-Methylpyridine	6.10	0.0067 ± 0.0007	0.00058
2,3-Dimethylpyridine	6.60	0.0068 ± 0.0004	–
2,4-Dimethylpyridine	6.99	0.0125 ± 0.0008	0.00079
Diethylamine	11.00	–	0.00121

[a] pK_a of the conjugate acid in water.

as pyridines substituted in 3, 4 and 5 positions are concerned (Figure 2).

The slope of the line can be estimated to be 0.05 and is almost the same as that found for $Pt(bipy)Cl_2$.

As usual, pyridines containing one methyl group in the position 2 are considerably less reactive and the Δ parameter (defined as the difference of $\log k_2$ for unhindered and hindered amines) which is a measure of the steric retardation effect is in this case $\simeq 2.0$ and can be compared with the value $\Delta \simeq 1.0$ obtained for $Pt(bipy)Cl_2$. In addition, cyclohexylamine which normally behaves like an unhindered pyridine in this case is slightly more reactive than expected. The following peculiar facts arise from the experimental results:

(i) The reactivity of unhindered pyridines is considerably larger towards $Pt(Oz)Cl_2$ than towards $Pt(bipy)Cl_2$.

(ii) The discriminating ability of the two substrates between amines of different basicities is almost the same.

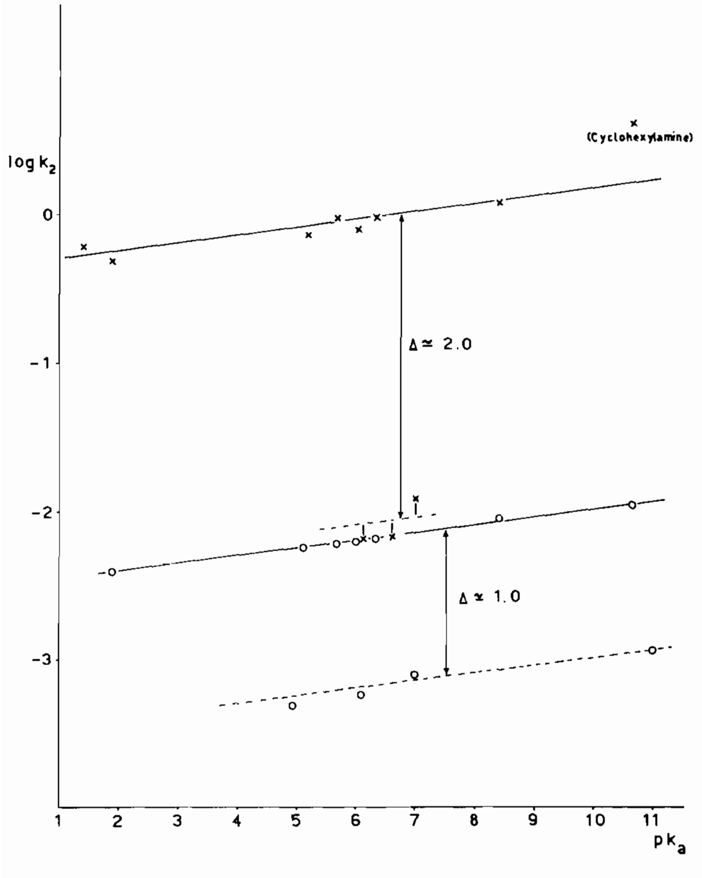

Figure 2. Diagram of $\log k_2$ against pk_a of the entering amine for the $Pt(Oz)Cl_2$ substrate (×) and for the $Pt(bipy)Cl_2$ complex (O); the continuous and dotted lines refer to unhindered and hindered amines respectively.

(iii) $Pt(Oz)Cl_2$ is largely more sensitive to steric retardation than is $Pt(bipy)Cl_2$.

Since the discriminating ability is related to the electrophilicity of the metal which is the center of reaction, it seems that bond formation is not very different in the two cases, apart from steric hindrance. Moreover steric retardation is larger for $Pt(Oz)Cl_2$ than for $Pt(bipy)Cl_2$ and this is easily understood on the basis of the bulkiness of the osazone. This larger hindrance could also explain the fact that cyclohexylamine is more reactive than expected since even unhindered pyridines having a hydrogen in position 2 could in this case suffer a small retardation effect.

In conclusion by comparing the osazone complex with the bipyridyl one we found that although the metal has almost the same electrophilicity and that the first complex is much more hindered than the second one, $Pt(Oz)Cl_2$ reacts about 10^2 times faster than $Pt(bipy)Cl_2$. The higher reactivity could be explained on the basis of electrophilic assistance to the leaving chloride by one of the *ortho* hydrogens of the phenyl groups in the ligand molecule. This can be related to the previous observation of HCl elimination.

Experimental

Preparation of cis-dichlorobiacetylbis(N-methyl, N-phenyl)osazonePt(II)

A methanol solution of the ligand (1 mmol in ≃40 ml) was added dropwise and at room temperature to a stirred solution of $K[PtCl_3(C_2H_4)]$ in the same solvent (1 mmol in ≃20 ml). A bright red colour due to the formation of dichloro[biacetylbis (N-methyl,N-phenyl)osazone]-π-ethylene-Pt(II)[11] immediately appears (the intermediate complex can partly precipitate under these experimental conditions). On standing the solution darkens and after 24 hr the precipitation is complete.

The product separates out as very dark green, shiny crystals: they were filtered, washed with methanol then with ether and dried (yield 95%. Calcd C 38.5; H 3.9; N 10.0; Cl 12.6. Found C 38.5; H 4.0; N 9.7; Cl 12.6. Mp 224–226° C d).

Acknowledgements

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References

1 C.H. Langford and H.B. Gray, "Ligand Substitution Processes", Benjamin, New York, 1966.
F. Basolo and R.G. Pearson, "Mechanism of Inorganic Reactions", 2nd edn, John Wiley, New York, 1967, p. 220.
L. Cattalini, "Reaction mechanism in Inorganic Chemistry", MTP International Review of Science, Series one, Volume 9, M.L. Tobe Editor, Butterworths (1972).
2 L. Cattalini, A. Orio, A. Doni, *Inorg. Chem., 5,* 1517 (1966).
3 L. Cattalini, M. Nicolini, A. Orio, *Inorg. Chem., 5,* 1674 (1966).
4 L. Cattalini, A. Doni, A. Orio, *Inorg. Chem., 6,* 280 (1967).
5 L. Cattalini, A. Orio, M. Martelli, *La Chim. e l'Ind., 49,* 625 (1967).
6 A. Orio, V. Ricevuto, L. Cattalini, *La Chim. e l'ind., 49,* 1337 (1967).
7 L. Cattalini, M. Martelli, G. Marangoni, *Inorg. Chim. Acta, 2,* 405 (1968).
8 G. Marangoni, M. Martelli, L. Cattalini, *Gazz. Chim. Ital., 98,* 1038 (1968).
9 G. Bombieri, L. Caglioti, L. Cattalini, E. Forsellini, F. Gasparrini, R. Graziani, P.A. Vigato, *Chem. Comm.,* 1415 (1971).
10 L. Caglioti, L. Cattalini, F. Gasparrini, M. Ghedini, G. Paolucci, P.A. Vigato, *Inorg. Chim. Acta, 7,* 538 (1973).
11 L. Cattalini, F. Gasparrini, L. Maresca, G. Natile, *Chem. Comm., 369 (1973).*
12 L. Caglioti, L. Cattalini, F. Gasparrini, L. Maresca, G. Natile, Unpublished results.
13 L. Baracco, L. Cattalini, J.S. Coe, E. Rotondo, *J. Chem. Soc. (A),* 1800 (1971).
14 E. Rotondo, V. Marsala, L. Cattalini, J.S. Coe, *J. Chem. Soc. (Dalton),* 2546 (1972).