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The Reactions of Displacement, by Amines, of a Bidentate Sulphur Donor Coordinated to Palladium(II)

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The kinetics of the nucleophilic displacement of the chelate group, C_6H_5–S–CH_2CH_2–S–C_6H_5 (S–S) from the complex [Pd(S–S)Cl_2] by amines (am) of different basicity and steric hindrance have been measured in 1,2-dimethoxyethane at 25°. When pyridine or its 3, 4, 5 substituted derivatives are used, the displacement of the first sulphur atom, corresponding to the bimolecular opening of the chelate ring, is the rate determining step and a linear relationship is observed between the reactivity of the amine and its basicity. In the presence of two ortho *substituents in the pyridine ring the replacement of the second sulphur atom becomes the slow step. The rate of the reactions and the discrimination of the substrate between different amines are compared with data of the literature relative to other planar substrates.*

Introduction

The kinetics of displacement of ligands by thioethers in some planar complexes of platinum(II),[1] gold(III),[2] and palladium(II)[3] have recently been reported. The extension of this research to the behaviour of thioethers as leaving groups encounters difficulty in palladium(II) substrates, owing to the high speed of the reactions. In the course of some experiments with the complex [Pd(S–S)Cl_2] (S–S= C_6H_5–S–CH_2CH_2–S–C_6H_5) we found that the bidentate group, S–S, was displaced relatively slowly by amines. As one might expect, the lability of the sulphur ligand is decreased, to some extent, by the chelation and as a general rule simple nucleophilic displacement of a chelate from a planar complex is unusual. In the series of complexes [Pt(bipy)(C)Cl], even when C is a strong *trans* labilizing ligand, the nucleophilic attack leads to the replacement of the chloride.[4] Acid catalysis of the displacement of chelates, *e.g.* the displacement of chelate amines from Pd^{II} by hydrochloric acid,[5] is different in principle since protonation reduces or prevents the return, or ring closing process.

In this paper we report and discuss the kinetics of the reaction

$$[Pd(S{-}S)Cl_2] + 2am \rightarrow [Pd(am)_2Cl_2] + S{-}S$$

(where am is a heterocyclic amine) in 1,2-dimethoxyethane at 25°.

Results and Discussion

All the reactions were studied spectrophotometrically and appeared, kinetically, as single stage processes. The initial spectrum was identical to that of [Pd(S–S)Cl_2] and the final absorbance was small over the whole range of spectrum examined. This is consistent with the complete loss of the sulphide ligand and is not inconsistent with the formation of the [Pd(am)$_2$Cl$_2$] complex. There is no evidence for the accumulation of significant quantities of a strongly absorbing intermediate. It is not possible to say from these observations whether the final product is *cis* or *trans*, or whether indeed one form isomerizes to the other. As a rule, such palladium(II) complexes are *trans* but the general stereochemical consequence of planar substitution is retention of configuration. We have therefore tried to carry out the above reaction on a preparative scale and find that, when am=pyridine, a product, analyzed for [Pd(py)$_2$Cl$_2$] was obtained. The infrared spectrum was significantly different from that of an authentic sample of *trans*-[Pd(py)$_2$Cl$_2$] and had many characteristic of a *cis* isomer.[6]

The rates of reaction were determined in the presence of a large excess of the entering amine so that, in any single run, the kinetics were of a first-order form. The rate constants (k_{obs}), were obtained from the slope of the plot of $\log_{10}(D_t - D_\infty)$ against time, where D_t and D_∞ are the optical densities of the solution at time t and the end of the reaction respectively, and are collected in Table I. The reproducibility of k_{obs} was excellent and calculation at different wavelengths give the same value.

In all cases the reaction rate, k_{obs}, was dependent upon the concentration of the entering amine but three types of behaviour were observed. The first

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[1] L. Cattalini, M. Martelli, and G. Kirschner, *Inorg. Chem.*, 7, 1488 (1968).
[2] L. Cattalini, M. Martelli, and G. Marangoni, *Inorg. Chem.*, 7, 1492 (1968).
[3] L. Cattalini, G. Marangoni, and M. Martelli, *Inorg. Chem.*, 7, 1495 (1968).
[4] L. Cattalini and M. Martelli, *Inorg. Chim. Acta*, 1, 189 (1967).
[5] A. J. Poë and D. H. Vaughan, *Inorg. Chim. Acta*, 2, 255 (1967).

[6] A recent investigation, including X-rays diffraction studies, clearly indicates that the product is the *cis* isomer (L. Cattalini and M. Martelli, *Gazz. Chim. Ital.*, 98, 832 (1968).

Table I. Experimental first order rate constants (k_{obs}) relative to the displacement of the chelate S—S from $[Pd(S—S)Cl_2]$ by amines, in 1,2-dimethoxyethane at 25°

Amine	$10^2 \times [am], M$	$10^2 \times k_{obs}$, sec^{-1}
3-cyanopyridine	6.5	5.1
	10.3	9.0
	12.9	10.6
	20.6	17.0
4-cyanopyridine	1.48	2.0
	2.96	3.45
	5.5	6.1
	11	11.6
3-chloropyridine	1.6	3.1
	4.0	8.2
	8.0	14.7
	16	27.5
pyridine	0.56	4.5
	1.12	7.5
	3.0	21.5
	5.95	40.5
3,5-dimethylpyridine	0.38	4.6
	0.76	8.5
	1.54	17.0
	4.5	48.5
2-methylpyridine	1.12	0.31
	5.6	0.73
	11.2	1.06
	28	2.15
	56	3.91
	84	5.6
2,3-dimethylpyridine	0.46	0.13
	4.57	0.79
	22.8	2.44
	34.2	3.4
	45.7	4.36
	81.4	7.2
2,4-dimethylpyridine	0.106	0.107
	1.06	0.44
	1.95	0.57
	5.8	1.09
	11.6	1.72
	14.1	1.85
	29	3.22
	58	6.0
	71	7.2
	97	9.8
2,6-dimethylpyridine	1.05	0.207
	11.8	0.25
	20.9	0.472
	28.6	0.71
	68.2	2.20
	71.5	2.37
	82	2.78
	95.5	3.55
	118	5.1
	125	5.35
	143	6.45
	165	8.5
2,4,6-trimethylpyridine	10.1	0.275
	20.2	0.610
	28.1	0.92
	50.5	1.97
	70.4	3.22
	101	5.5

The concentration of the substrate in the reaction mixture wal always less than 10^{-4} M.

type, favoured by pyridine and its 3,4,5-substituted derivatives is of the form $k_{obs} = k_1 + k_2[am]$ which is usual for planar substitution (Figure 1). The second, which is favoured by pyridines with a single *o*-methyl substituent, achieves a linear dependence at high reagent concentration (Figure 2), and the third type, which is found for the 2,6-dimethyl-substituted pyridines, is of higher than first order dependence on amine (Figure 3).

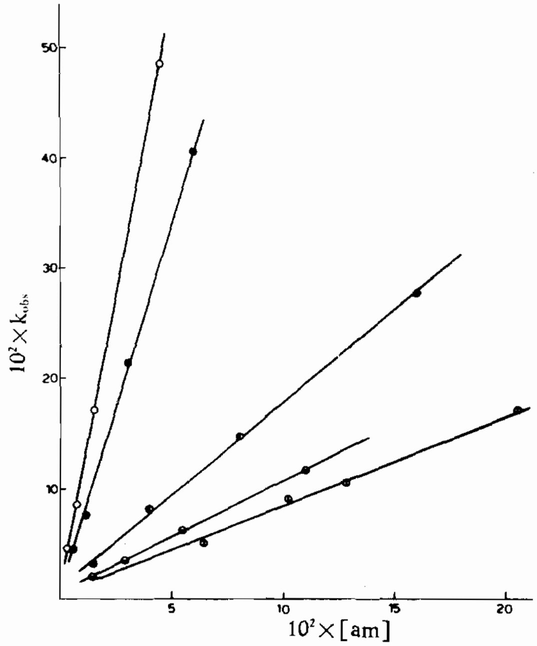


Figure 1. Plot of k_{obs} against [am] for the reactions of $[Pd(S—S)Cl_2]$ with unhindered pyridines. ◑ = 3-cyano-pyridine; ◒ = 4-cyanopyridine; ⊗ = 3-chloropyridine; ● = pyridine; ○ = 3,5-dimethylpyridine.

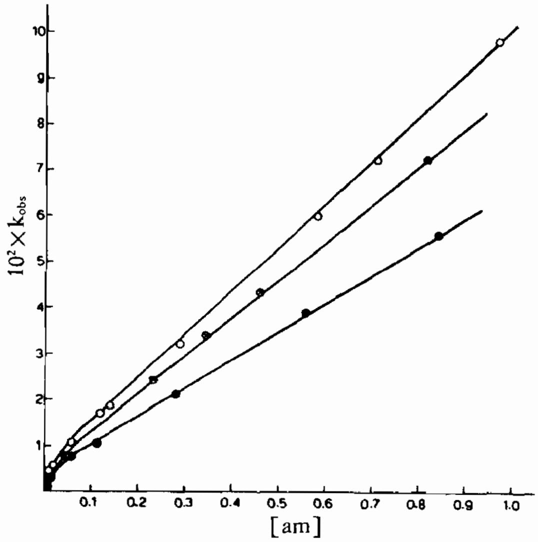


Figure 2. Plot of k_{obs} against [am] for the reactions of $[Pd(S—S)Cl_2]$ with 2-methylpyridine (●), 2,3-dimethylpyridine (⊗), and 2,4-dimethylpyridine (○).

The complication in the rate law arises from the partial reversibility of the displacement of the chelate.

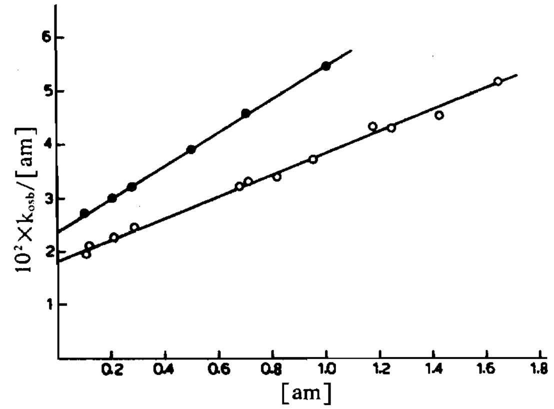
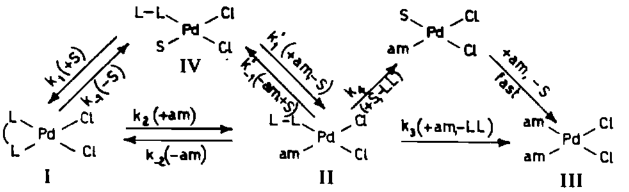


Figure 3. Plot of $k_{osb}/[am]$ against [am] for the reactions of $[Pd(S\text{—}S)Cl_2]$ with 2,6-dimethylpyridine (○) and 2,4,6-trimethylpyridine (●).

The spectrophotometric evidence indicates that the chelate is replaced by two molecules of amine without any detectable accumulation of a monosubstituted intermediate. The overall process can be indicated as follows (am = amine, S = solvent, L–L = $C_6H_5\text{—}S\text{—}CH_2CH_2\text{—}S\text{—}C_6H_5$):



In this scheme we take account of the normal bimolecular displacement of the first and second sulphur atoms of the chelate, the alternative solvolytic substitution paths (represented by the first order rate constants k_1 and k_4) and also include competitive ring closing displacement of am and S by processes involving the first order rate constants k_{-1} and k_{-2}.

The rate of formation of the products, (III), which is the same as the rate of disappearance of (I) since no significant accumulation of an intermediate occurs, is:

$$-d[I]/dt = d[III]/dt = k_3[II][am] + k_4[II] \qquad (1)$$

Also

$$d[IV]/dt = k_1[I] + k'_{-1}[II] - k_{-1}[IV] - k_1'[IV][am] \qquad (2)$$

$$d[II]/dt = k_2[I][am] + k_1'[IV][am] - k_{-2}[II] - k'_{-1}[II] - k_4[II] - k_3[II][am] \qquad (3)$$

Under stationary state conditions, $d[IV]/dt = 0$ and $d[II]/dt = 0$ so that one can calculate the appropriate expression for [II]. Substituting this expression into (1) we obtain:

$$\text{rate} = \frac{[k_2[am](k_{-1}+k_1'[am]) + k_1k_1'[am]](k_4+k_3[am])[I]}{k_{-1}(k_{-2}+k_4+k'_{-1}+k_3[am]) + k_1'[am](k_{-2}+k_4+k_3[am])}$$

Under the pseudo-first order conditions used,

$$k_{osb} = -\frac{1}{[I]} \times \frac{d[I]}{dt} =$$

$$\frac{[k_2[am](k_{-1}+k_1'[am]) + k_1k_1'[am]](k_4+k_3[am])}{k_{-1}(k_{-2}+k_4+k'_{-1}+k_3[am]) + k_1'[am](k_{-2}+k_4+k_3[am])} \qquad (4)$$

When am is an unhindered amine it is likely that once the ring is open the reaction will proceed rapidly so that $k_4 + k_3[am] \gg k_{-2} + k'_{-1}$, $k_4 + k_3[am] \gg k_1 + k_2[am]$, and $k_1'[am] \gg k_{-1}$. Expression (4) then reduces to

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

This is in accord with the behaviour which has been observed for such amines (Figure 1). It appears that in each case the reaction is mainly controlled by the k_2 term and the appropiate values are collected in Table II.

When am is a doubly hindered amine a different approach can be made, since the reaction of II, which is now a sterically hindered substrate, is likely to become the rate determining step, so that $k_{-2} \gg k_4 + k_3[am]$, $k_{-1} \gg k_1'[am]$. Moreover, according to the known lability[3] of monodentate thioethers as compared to amines as leaving groups, $k_4 \gg k'_{-1}$. Expression (4) then reduces to

$$k_{obs} = \frac{(k_2k_{-1} + k_1k_1')(k_4 + k_3[am])[am]}{k_{-1}k_{-2}}$$

which is in accord with the behaviour which has been observed for 2,6-dimethyl and 2,4,6-trimethylpyridine. The plot of $k_{obs}/[am]$ against [am] gives a straigth line (Figure 3) and the ratio between the slope and the intercept is k_3/k_4 (Table II).

In the general case, expression (4) must be applied and it is possible to show, by examining the differential expression $d(k_{obs})/d[am]$ that, at high values of [am] the relationship between k_{obs} and [am] is expected to become linear, with a slope $= k_2$. It

Table II. Kinetic parameters relative to the replacement by amines of the chelate group $C_6H_5\text{—}S\text{—}CH_2CH_2\text{—}S\text{—}C_6H_5$ from the complex $[Pd(S\text{—}S)Cl_2]$ in 1,2-dimethoxyethane at 25°

amine	pK_a [a]	k_2 $M^{-1} \times sec^{-1}$	k_3/k_4 M^{-1}
3-cyanopyridine	1.38	0.79	—
4-cyanopyridine	1.90	1.0	—
3-chloropyridine	2.84	1.74	—
pyridine	5.17	6.8	—
3,5-dimethylpyridine	6.34	10.6	—
2-methylpyridine	6.1	0.06	—
2,3-dimethylpyridine	6.6	0.082	—
2,4-dimethylpyridine	6.9	0.092	—
2,6-dimethylpyridine	6.75	—	1.14
2,4,6-trimethylpyridine	7.48	—	1.32

[a] The values of pK_a refer to the acid amH^+ in water. The value of k_1 can be estimated to be in the range 5×10^{-3}–10^{-2} sec^{-1}.

corresponds to the behaviour which has been observed with 2-methyl, 2,3-dimethyl, and 2,4-dimethylpyridine (Figure 2). The values of k_2 are collected in Table II. One can observe that, whereas with the unhindered amines k_1 is almost negligible compared to $k_2[am]$, in this case a larger part of the process goes *via* the k_1 path, owing to the steric retardation effect acting on the path controlled by k_2.

When the values of k_2 can be derived from the complex kinetics it is found that there is a linear relationship between $\log_{10}k_2$ and the pK_a of the entering amine, a common occurence in this type of substitution.[7] The slope $(\alpha) = 0.22$ gives a measure of the ability of the complex $[Pd(S{-}S)Cl_2]$ to discriminate between the entering amines. Since all other studies of amine entry in the literature relate to chloride as leaving group, it is not possible yet to make a significant comparison.* Nevertheless attention should de drawn to the steric effect $(\Delta = 2.4)$ which is the largest found for the reactions of these amines with planar complexes of Pt^{II}, Pd^{II}, Au^{III}.

A final comment is that, in spite of chelation, the ligand S–S is displaced from the complex in preference to chloride and is therefore more labile. The same is true of the reactions of amines on the Au^{III} complex $[AuCl_3(Bz_2S)]$ (Bz_2S = dibenzylsulphide) in acetone[8] and there are indications that also Pt^{II} complexes behave in this way. In addition, we have evidence that amines can displace thioethers from *trans*-$[Pd(R_2S)_2Cl_2]$ and also from $[Pt(S{-}S)Cl_2]$. Therefore, the lability of thioethers coordinated to d^8 planar complexes seems to be a general feature. The possible role of the solvent in determining the nature of the leaving group is being investigated.

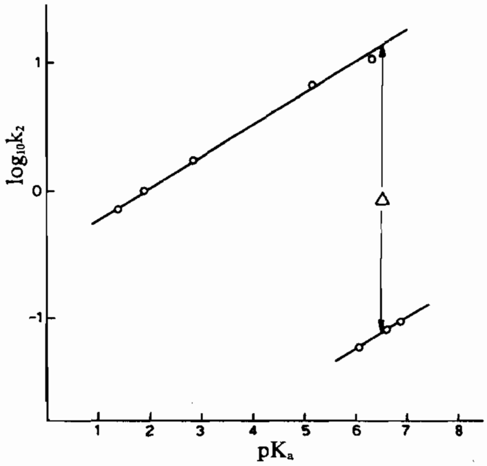


Figure 4. The relationship between $\log_{10}k_2$ and the pK_a of the amines entering on the substrate $[Pd(S{-}S)Cl_2]$ in 1,2-dimethoxyethane at 25°.

Experimental Section

The complex $[Pd(C_6H_5SCH_2CH_2SC_6H_5)Cl_2]$ was obtained as a yellow precipitate by adding an acetonic solution to an aqueous solution of K_2PdCl_4, in the molar ratio 1:1. The product, filtered off, washed with water and recrystallized from acetone has m.p. 280°, corresponding to the value reported in the literature[9] and is analitically pure. Solutions of the complex in acetone and 1,2-dimethoxyethane closely follow Beer's law. The amines were all reagent grade, and the solvent was distilled on sodium before the use.

Kinetics. The method used to follow the kinetics was the same previously reported.[1,2,3] Known volumes of thermostated solutions of the complex and reagent were brought separately to 25° and mixed in the thermostated cell of an Optica-CF4 double beam recording spectrophotometer. The spectra changes characteristic of the reacting system were first determined by scanning the near ultraviolet region at known intervals. Once the spectrum changes were characterized and suitable wavelengths chosen to study the reaction, the kinetics were followed by locking the wavelength at the chosen value (in the range 310-330 mμ) and recording the changes of optical density as a function of time.

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(*) A comparison with the corresponding Pt^{II} complex has been recently published [M. Martelli, G. Marangoni, and L. Cattalini, *Gazz. Chim. Ital.*, *98*, 1031 (1968)].

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

(9) G. M. Bennet, A. N. Mosses, F. S. Statham, *J. Chem. Soc.*, 1668 (1930).