Evidence for a Strong Labilization Effect by Co-ordinated Sulphite in Amine Complexes of Palladium(II)

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Acidification of a chelated amine sulphito complex of palladium(II) to pH <6 results in dechelation and complete loss of the co-ordinated amine ligand in the presence of an excess of sulphite; this process is completely reversible on increasing the pH (>8) and reproduces the amine sulphito complex.

Amine ligands are generally used in mechanistic studies on the substitution behaviour of co-ordination complexes to block certain co-ordination sites. Such ligands are usually so strongly bound to the metal centre that they produce convenient, non-participating groups. However, in particular cases where the entering group is a very strong nucleophile or exhibits specific labilization effects once present in the co-ordination sphere, loss of these 'non-participating' ligands may occur in subsequent substitution reactions.

This was shown to be the case for S-bonded octahedral sulphito complexes. Investigations in this laboratory clearly demonstrated the dissociative loss of ammonia during the reaction of $Co(NH_3)_5SO_3^+$ with sulphite to produce *trans*-$Co(NH_3)_4(SO_3)_2^-$, or during its spontaneous aquation to produce *trans*-$Co(NH_3)_4(SO_3)(OH_2)^+$.[1] The corresponding O-bonded species, $Co(NH_3)_5OSO_2^+$, undergoes a subsequent redox reaction which presumably involves the initial release of the *trans* ammine ligand.[2] The strong labilization effect of co-ordinated sulphite has also been observed in closely related studies.[3—6] In contrast, very little is known about the behaviour of square-planar sulphite complexes. Some preliminary results[7,8] do indicate that Pd^{II} amine complexes with S-bonded ligands such as sulphite, thiosulphate, thiourea, and substituted thioureas, tend to decompose in subsequent reactions. However, no information on the nature of the decomposition products and the mechanism of this process is presently available.

We have now completed a detailed study[9] of the formation and reactivity of $Pd(Et_4dien)SO_3$, where Et_4dien = 1,1,7,7-tetraethyldiethylenetriamine. This complex can be generated in solution *via* anation of $Pd(Et_4dien)(OH_2)^{2+}$ or substitution of $Pd(Et_4dien)Cl^+$ by HSO_3^- or SO_3^{2-} at pH $\geqslant$7. A kinetic analysis showed that the anation reaction follows the normal substitution mechanism during which the aquo ligand is substituted, and does not proceed *via* SO_2 uptake by the hydroxo species as found for octahedral systems.[2—4,6,10] At pH <7, $Pd(Et_4dien)SO_3$ undergoes a subsequent reaction in the presence of an excess of sulphite (>1:1) which is accompanied by characteristic u.v.–visible spectral changes and isosbestic points at 263 and 315 nm (Figure 1). The $Pd(Et_4dien)SO_3$ species exhibits a characteristic absorption maximum at 271 nm (ε 20 400 dm^3 mol^{-1} cm^{-1}), and acidification of a solution of this complex prepared at pH >7 produces similar spectral changes. This complex can be stabilized at the lower pH in the absence of free sulphite, *i.e.* when it is prepared in solution from a 1:1 mixture of the reactants. The reaction product of the subsequent step was identified as $Pd(SO_3)_2^{2-}$, which exhibits identical spectral properties to an authentic sample of $Na_2Pd(SO_3)_2$. This means that the subsequent reaction involves total loss of the Et_4dien ligand. ^1H and ^{13}C n.m.r. spectra clearly indicate that the ligand is unco-ordinated at that stage of the process and so underline the validity of this suggestion.[11] The rate constant for the loss of Et_4dien reaches a limiting value of 5×10^{-3} s^{-1}

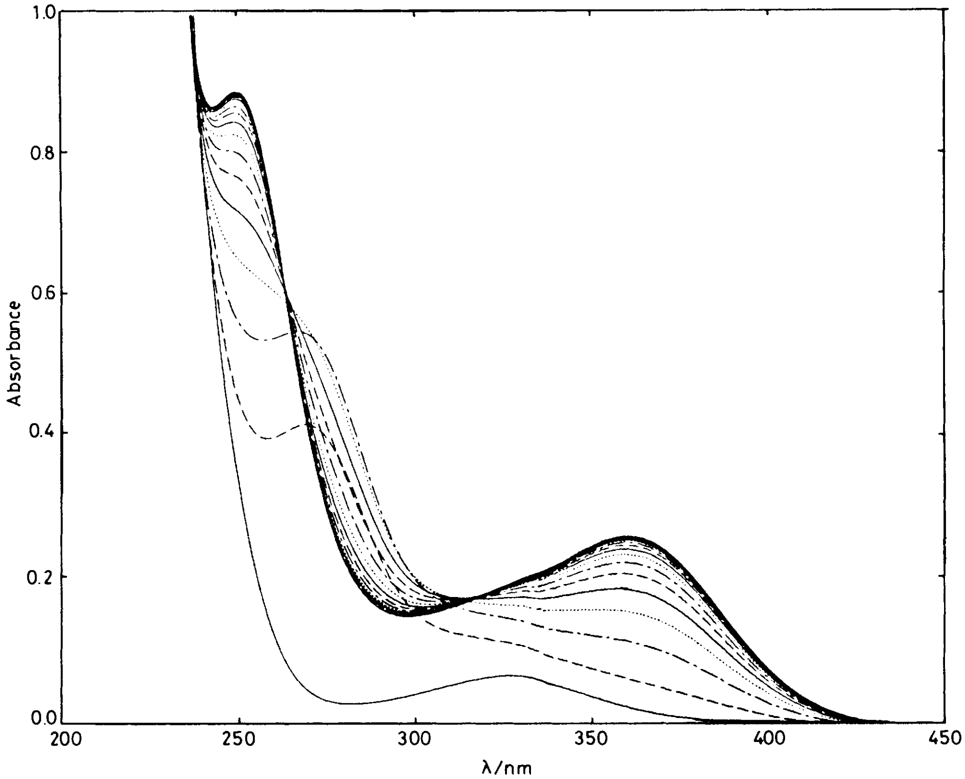

Figure 1. Successive u.v.–visible spectra for the reaction of $Pd(Et_4dien)OH_2^{2+}$ with sulphite in weakly acidic aqueous solution. The solid line is the spectrum of $Pd(Et_4dien)OH_2^{2+}$ before addition of sulphite, [Pd] = 5.2×10^{-5} M, [total S] = 7.3×10^{-4} M, pH = 4.15, Δt = 3 min, temperature = 298 K, ionic strength = 0.5 M, optical pathlength = 0.88 cm.

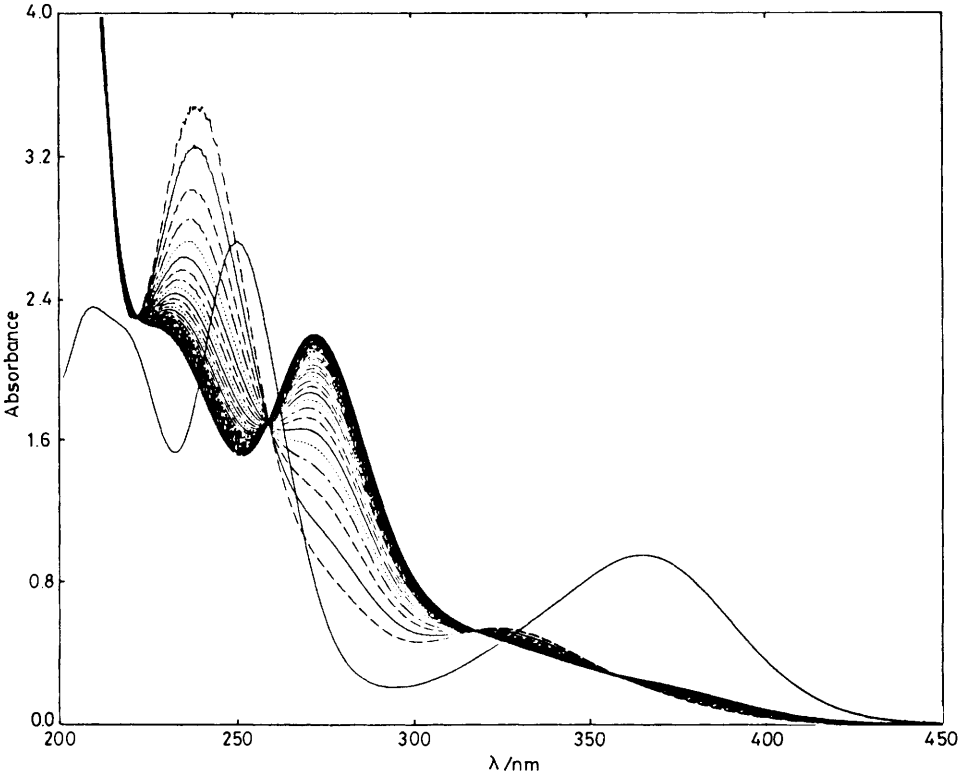

Figure 2. Successve u.v.–visible spectra for the addition of base to a solution consisting of $Pd(SO_3)_2^{2-}$ and Et_4dien. The solid line is the spectrum of the reaction mixture before addition of base, [Pd] = 2×10^{-4} M, [Et_4dien] = 2×10^{-4} M, final pH = 10.9, Δt = 5 min, temperature = 298 K, ionic strength = 0.5 M, optical pathlength = 0.88 cm.

at pH ~4, 25 °C and in the absence of a large excess of sulphite. Furthermore, the loss of the amine ligand is a reversible process, and on increasing the pH to above 8, $Pd(SO_3)_2^{2-}$ reacts with Et_4dien to produce $Pd(Et_4dien)SO_3$. A typical example is presented in Figure 2, where the immediate spectral change on the addition of base is ascribed to the partial formation of a sulphitohydroxo complex which subsequently produces $Pd(Et_4dien)SO_3$. Similar behaviour was observed when $Na_2Pd(SO_3)_2$ was used as starting material. The observed rate constant for the example in Figure 2 is 6×10^{-4} s^{-1} under the quoted conditions.

This is to our knowledge the first well-documented example of a system in which co-ordinated sulphite (S-bonded) can labilize a chelated amine to such an extent that protonation of the amine leads to dechelation and complete release of the amine. The dechelation is expected to occur in a number of steps of which the first is presumably acid-catalysed and rate-determining. This can account for the strong pH dependence of the process and the observed kinetic relationships.[9,11] Similar reactions are observed when $Pd(Et_4dien)Cl^+$ reacts with an excess of SO_3^{2-} at pH 5, although the formation of the $Pd(Et_4dien)SO_3$ intermediate, which is much slower than in the case of the aquo complex, can only be observed at low sulphite concentrations. In the presence of an excess of sulphite, the chloro complex produces directly $Pd(SO_3)_2^{2-}$ and the free amine. The reversibility of this process following a moderate increase in pH is presumably due to the deprotonation of the unco-ordinated ligand and its ability to then bind to the metal centre.

The earlier mentioned preliminary observations[7,8] indicate that other S-bonded nucleophiles could exhibit similar effects. In general, such reactions are of fundamental interest to biological (anti-tumour), environmental, and catalytic processes, since they may constitute alternative reversible reaction routes that involve species of significantly higher reactivity.

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Received, 28th July 1986; Com. 1060

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