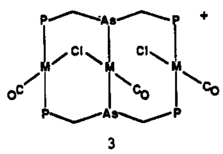
ions is quite normal. The elongation of the Ir–Cl bonds that are trans to the Au–Ir bonds relative to the cis Ir–Cl bonds is consistent with the high structural trans influence of metal–metal bonds and previous observations.[10]

An Au(III) ion coordinated between two Ir(I) centers may be regarded (after oxidative addition) as an Ir(II)–Au(I)–Ir(II) system, in which the electron count around each Ir(II) is 18 and that around the Au(I) is 16. Planar coordination, however, is highly unusual for Au(I), but four-coordinate gold complexes with 16 electrons are planar whereas those with 18 electrons are tetrahedral,[11] so **2** follows the general pattern.

The behavior of $Ir_2(CO)_2Cl_2(\mu\text{-dpma})_2$ and its rhodium analogue, $Rh_2(CO)_2Cl_2(\mu\text{-dpma})_2$, toward other d^8 metal complexes shows different reactivity. Addition of Rh(I) or Ir(I) complexes produces **3** in which a stack of three d^8 ions forms and no oxidative addition occurs.[12] Reaction with Pd(II) (from $(PhCN)_2PdCl_2$) produces **4** in which one Pd–Cl bond has been added to one, but only one, of the two metal centers; the metal ion at the other end of the molecule is left unaffected.[5,13] Since with Au(III) the three-fragment, two-center oxidative addition occurs, there appears to be a simple trend in which increasing the oxidation state of the added metal increases the number of oxidative-addition reactions.



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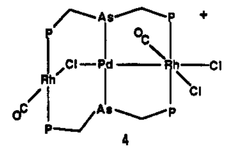

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Supplementary Material Available: Tables summarizing the data collection and refinement, atom coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen coordinates (10 pages). Ordering information is given on any masthead page.

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(11) (a) Puddephatt, R. J. *The Chemistry of Gold*; Elsevier: Amsterdam, 1978. (b) The salt $TlAu(CN)_2$ is somewhat of an exception since short Au–Au contacts, 3.037 (4) and 3.068 (4) Å, about each $Au(CN)_2^-$ produce a planar coordination environment (Blom, N.; Ludi, A.; Burgi, H.-B.; Tichy, K. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 1767), $[AuOs_6(CO)_{20}H_2]^{2-}$ contains a planar $AuOs_4$ unit (Johnson, B. F. G.; Kaner, D. A.; Lewis, J.; Ruithby, P. R. *J. Chem. Soc., Chem. Commun.* **1981**, 753), and $Au_2[Ph_2PCH(CH_2OCH_3)\text{-}PPh_2]_2Cl^+$ contains one planar $Au(P_2ClAu)$ unit with long Au–Au (3.002 (1) Å) and Au–Cl (2.963 (3) Å) distances (Schmidbaur, H.; Pollok, T.; Herr, R.; Wagner, F. E.; Bau, R.; Riede, J.; Muller, G. *Organometallics*, **1986**, *5*, 569).

(12) Balch, A. L.; Fossett, L. A.; Olmstead, M. M.; Reedy, P. E., Jr. *Organometallics* **1986**, *5*, 1929.

(13) Bailey, D. A.; Balch, A. L.; Fossett, L. A.; Olmstead, M. M.; Reedy, P. E., Jr. *Inorg. Chem.*, in press.

Articles

Contribution from the Institute for Physical and Theoretical Chemistry,
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Formation and Reactivity of Palladium(II) Sulfito Complexes in Aqueous Solution. 1. Spectroscopic Evidence for the Labilization of a Chelated Amine

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Received November 19, 1986

The reactions of $Pd(Et_4dien)Cl^+$ and $Pd(Et_4dien)OH_2^{2+}$ (Et_4dien = 1,1,7,7-tetraethyldiethylenetriamine) with bisulfite/sulfite were studied as a function of pH and sulfite concentration with use of spectroscopic techniques, viz. UV-vis, IR, and ^1H and ^{13}C NMR spectroscopy. The results clearly demonstrate the formation of $Pd(Et_4dien)SO_3$, which is stable at pH >7 but dechelates in acidic medium (pH <6) to produce a mixture of $Pd(SO_3)_2^{2-}$ and $Pd(SO_3)_3^{4-}$ depending on the sulfite concentration employed. The dechelation reaction is reversible; i.e., addition of base to pH >8 regenerates the $Pd(Et_4dien)SO_3$ species completely. The results are interpreted in terms of the labilization effect of coordinated sulfite and stabilization of the released amine ligand via protonation to prevent the reverse chelation reaction.

Introduction

We have a longstanding interest in the chemistry and mechanistic behavior of transition-metal carbonate and sulfite complexes in aqueous solution.[1-6] Our earlier work focused on octahedral complexes of Co(III), Rh(III), and Cr(III), and we recently extended these studies to square-planar complexes of Pt(II) and Pd(II). Surprising was our finding[3] that, in contrast to the case for octahedral complexes, the carbonato complexes of diethylenetriamine (dien) and substituted dien species of Pd(II) are not formed via the well-known CO_2 uptake by the metal hydroxo species but rather via anation of the metal aquo species by HCO_3^- or CO_3^{2-}. In a subsequent study[7] we could find no evidence for the formation of the corresponding Pt(II) carbonato complexes. These observations were partly ascribed to the nature of the

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* Author to whom all correspondence should be addressed.

(1) See Tables XXXI and XXXII in: Palmer, D. A.; van Eldik, R. *Chem. Rev.* **1983**, *83*, 651 and literature cited therein.

(2) See section IV in: van Eldik, R. *Adv. Inorg. Bioinorg. Mech.* **1984**, *3*, 275 and literature cited therein.

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(6) Schneider, K. J.; Roodt, A.; Leipoldt, J. G.; van Eldik, R. *Inorg. Chim. Acta* **1986**, *122*, 1.

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0020-1669/87/1326-1837$01.50/0

metal–hydroxo bond, which seems to differ significantly from that for octahedral complexes, and the weak nucleophilicity of the HCO_3^- and CO_3^{2-} species.

In general, sulfite is a significantly stronger nucleophile than bicarbonate or carbonate, and SO_2 uptake is faster and more efficient than CO_2 uptake. We have, therefore, undertaken a detailed study[8] of the formation and reactivity of a substituted dien sulfito complex of palladium(II), viz. $Pd(Et_4dien)SO_3$, where Et_4dien = 1,1,7,7-tetraethyldiethylenetriamine. This particular sterically hindered dien complex was selected on the basis of our experience with the general substitution behavior of $Pd(Et_4dien)Cl^+$, $Pd(Et_4dien)H_2O^{2+}$, and closely related complexes.[9-11] In this paper we report our spectroscopic observations regarding the formation and reactivity of $Pd(Et_4dien)SO_3$, as well as evidence for the labilization of the dien ligand by coordinated sulfite. A preliminary account of the latter finding has been reported.[12]

Experimental Section

Materials. $[Pd(Et_4dien)(Cl]ClO_4$ was prepared as described in the literature.[9,13] It was subjected to chemical analyses (Hoechst Analytical Laboratory, Frankfurt, West Germany), and the results were in excellent agreement with the theoretically expected values.[8] The chloro complex was converted into the aquo analogue in solution by adding an equivalent amount of $AgClO_4$, heating to 40 °C for 1 h, and removing the AgCl precipitate by filtering through a 0.1 μm pore membrane filter. Great care was taken to ensure that the resulting solution was free of Ag^+ ions and that the chloro complex had been converted completely into the aquo species.

$Na_2Pd(SO_3)_2\cdot H_2O$ was prepared through the reaction of $PdCl_4^{2-}$ with HSO_3^- at pH ~4. A slight excess of bisulfite is needed for the reaction to go to completion, and the product precipitates on cooling in an ice bath. Chemical analyses were in close agreement with the expected values. Other sulfito complexes were only prepared in solution, and details are given in the following paragraphs. Chemicals of analytical reagent grade and doubly distilled water were used to prepare all test solutions. McIlvaine phosphate–citric acid buffers[14] were employed to stabilize the pH in the range 2–8.

Measurements. UV–visible absorption spectra were recorded on Perkin-Elmer 555, Perkin-Elmer Lambda 5, and Shimadzu UV 250 spectrophotometers. IR absorption spectra (KBr disk) were recorded on a Beckman spectrometer. ^1H and ^{13}C NMR spectra were measured on Varian XL 100 and Bruker AM 300 instruments. A Radiometer PHM 64 instrument, whose reference electrode was filled with a 3 M NaCl solution, was used for all pH measurements.

Results and Discussion

In our preliminary communication[12] we reported that $Pd(Et_4dien)Cl^+$ and $Pd(Et_4dien)H_2O^{2+}$ can undergo ligand substitution and anation by sulfite, respectively, to produce $Pd(Et_4dien)SO_3$. This species exhibits interesting subsequent reactions that include labilization and dechelation of the amine ligand in weakly acidic medium and acid-catalyzed aquation to regenerate the aquo complex. The various reactions will now be treated in more detail.

Formation of $Pd(Et_4dien)SO_3$. The UV–vis absorption spectra of $Pd(Et_4dien)Cl^+$, $Pd(Et_4dien)H_2O^{2+}$, and $Pd(Et_4dien)OH^+$ found in this study are in excellent agreement with those reported before.[13,15] Addition of $S_2O_5^{2-}$ or SO_3^{2-} to a solution of $Pd(Et_4dien)H_2O^{2+}$ or $Pd(Et_4dien)Cl^+$ results in the formation of $Pd(Et_4dien)SO_3$, which exhibits absorption maxima at 271 (ϵ = 20400 M^{-1} cm^{-1}) and 232 nm. The intensity of the latter band strongly depends on the composition of the solution and is affected by the sulfite concentration, pH, and buffer concentration of the solution. A typical example of the formation of the 271-nm band is given in Figure 1, from which it can be seen that a shoulder at ca. 360 nm is also formed due to the partial formation of subsequent reaction products (see further discussion). The $Pd(Et_4dien)SO_3$ species can be produced in high yields in the presence of an excess of sulfite (1:10) at pH >7. At lower pH, an excess of sulfite (>1:1) results in subsequent decomposition, which is treated separately. However, a 1:1 mixture of $Pd(Et_4dien)H_2O^{2+}$ or $Pd(Et_4dien)Cl^+$ and sulfite does produce a stable product at pH 3–5. The observed spectral characteristics of $Pd(Et_4dien)SO_3$ are in close agreement with those reported for an isolated sample,[15] viz. 273 (ϵ = 13900) and 232 nm (ϵ = 11250 M^{-1} cm^{-1}). The higher extinction coefficient at 271 nm found in this study can be ascribed to the appropriate conditions selected to stabilize the sulfito complex. It is expected that the spectrum of the isolated sample[15] will strongly depend on the conditions under which it is recorded. We were unable to isolate a pure sample of $Pd(Et_4dien)SO_3$; our samples[8] were all contaminated with the subsequent decomposition product. However, ion-exchange experiments clearly indicated that we are dealing with a neutral species in solution. The most likely composition in line with all the mentioned observations is $Pd(Et_4dien)SO_3$, and its formation can be summarized as in Scheme I. In basic medium at pH >10 the formation of $Pd(Et_4dien)SO_3$ competes with the formation of the very inert $Pd(Et_4dien)OH^+$ species and the sulfito complex can only be formed with a large excess of sulfite.

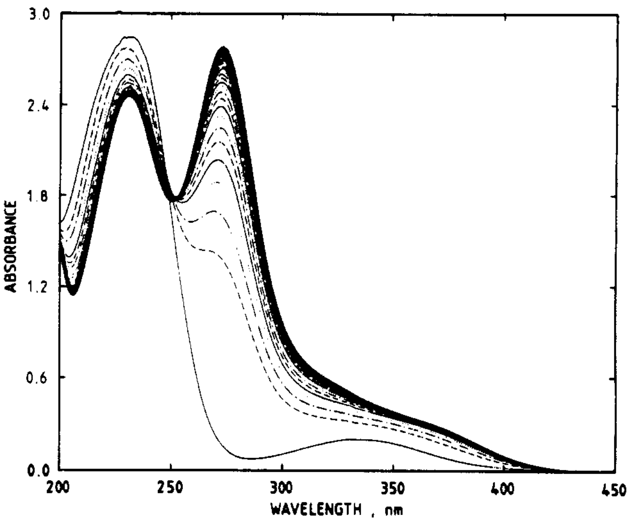
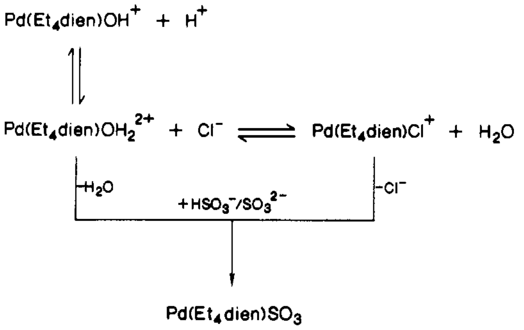


Figure 1. Repetitive scan spectra for the reaction $Pd(Et_4dien)Cl^+ + HSO_3^- \rightarrow Pd(Et_4dien)SO_3 + H^+ + Cl^-$. Conditions: [Pd] = 2.2 × 10^{-4} M; [total S] = 2.2 × 10^{-4} M; optical path length 0.88 cm; pH 5.0; temperature 25 °C; ionic strength 0.5 M; Δ*t* = 2 min.

Scheme I



Further evidence for the formation of the $Pd(Et_4dien)SO_3$ complex was obtained from ^{13}C NMR spectroscopy. The free Et_4dien ligand in D_2O exhibits four signals as shown in Figure 2a, which can be assigned to CH_2 attached to N_4 (52.5 ppm), CH_2 of the ethyl groups (48.2 ppm), CH_2 attached to N_1 (47.0 ppm), and CH_3 of the ethyl groups (12.0 ppm). These signals shift slightly on protonation of the amines in the absence of Me_2SO (Figure 2b). During complexation the ethyl substituents are no longer symmetrical and six signals of equal intensity are observed. In the case of the well-characterized $Pd(Et_4dien)Cl^+$ species, the

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(8) Mahal, G. Ph.D. Dissertation, University of Frankfurt, 1986.
(9) Breet, E. L. J.; van Eldik, R.; Kelm, H. *Polyhedron* **1983**, *2*, 1181.
(10) van Eldik, R.; Breet, E. L. J.; Kotowski, M.; Palmer, D. A.; Kelm, H. *Ber. Bunsen-Ges. Phys. Chem.* **1983**, *87*, 904.
(11) Breet, E. L. J.; van Eldik, R. *Inorg. Chem.* **1984**, *23*, 1865.
(12) Mahal, G.; van Eldik, R. *J. Chem. Soc., Chem. Commun.* **1987**, 328.
(13) Baddley, W. H.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 2944.
(14) Elving, P. J.; Markowitz, J. M.; Rosenthal, I. *Anal. Chem.* **1956**, *28*, 1179.
(15) Goddard, J. B.; Basolo, F. *Inorg. Chem.* **1968**, *7*, 936.

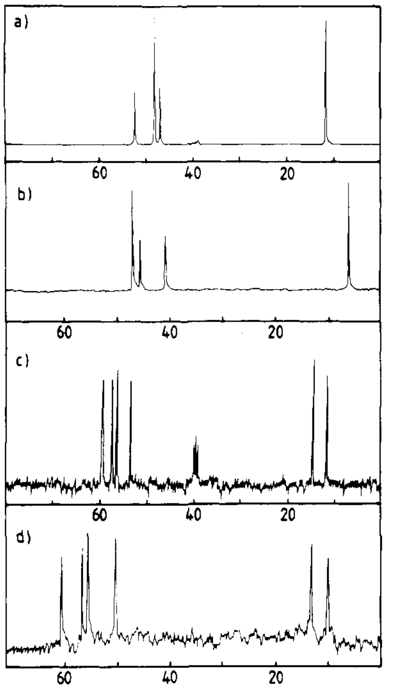


Figure 2. ^{13}C NMR spectra for various species: (a) Et_4dien in D_2O at pH 11; (b) Et_4dien in D_2O at pH 1; (c) Pd(Et_4dien)Cl^+ in D_2O and some Me_2SO; (d) Pd(Et_4dien)SO_3 in D_2O at pH 9.

^{13}C spectrum (Figure 2c) indicates the splitting of the signals at 12.0 and 48.2 ppm due to this effect. A very similar spectrum was obtained for the Pd(Et_4dien)SO_3 species (Figure 2d), indicating that the ligand geometry is identical with that for the chloro complex. Acidification of this solution to pH <5 resulted in a spectrum identical with that in Figure 2b, indicating that complete dechelation had occurred (see further discussion).

Throughout this work no evidence for the formation of an O-bonded sulfito species, as reported for octahedral complexes,[2,4,5] could be found. Such species are usually characterized by subsequent linkage isomerization to the S-bonded species or by rapid loss of SO_2 via O–S bond cleavage on acidification, neither of which was observed in this study. In general, O-bonded sulfito complexes are produced via SO_2 uptake by the metal hydroxo species in a way similar to that for carbonato complexes.[1,2] The inability of the Pd(Et_4dien)OH^+ species to take up SO_2 is in agreement with our earlier finding that such species do not form carbonato complexes via CO_2 uptake but rather via anation of the aquo species by HCO_3^- or CO_3^{2-}.[3]

Stability and Decomposition of Pd(Et_4dien)SO_3. Solutions of Pd(Et_4dien)SO_3 at pH ≥8 are stable for unlimited periods of time. On acidification to pH <6 a decomposition reaction sets in and a product with absorption maxima at 251 and 363 nm is formed. A typical example of such a reaction is given in Figure 3, for which a McIlvaine buffer was used to adjust the pH from 8.3 to 3.3. Clean isosbestic points are produced at 262 and 322 nm only when a buffer is used to stabilize the pH following acidification. However, similar spectral changes are also obtained on acidification with $HClO_4$, i.e. in the absence of a buffer, indicating that the observed reaction does not involve the direct participation of the buffer. This is important since such labile Pd(II) complexes could exhibit reactions with the buffer components. According to the ^{13}C NMR spectra recorded during this process (see Figure 2), the acidification involves complete dechelation of the Et_4dien ligand and the formation of a Pd(II) sulfito species that exhibits the characteristic bands at 251 and 363 nm. The released Et_4dien ligand is presumably protonated under these conditions, since its protonation constants (expressed as pK) are 9.66, 8.62, and 3.55 at 20 °C,[16] and so partly prevents the reverse complex formation reaction. However, this cannot be the only effect since dien complexes are generally synthesized in acidic medium,[9,13] indicating that the presence of the sulfite ligand must play an important role.

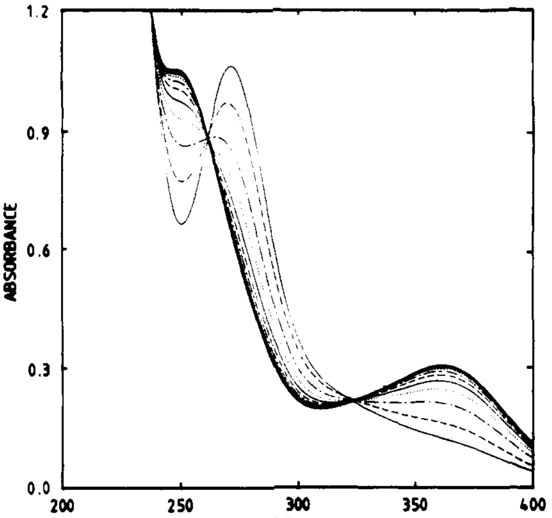
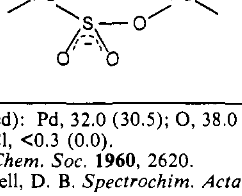


Figure 3. Repetitive scan spectra for the reaction Pd(Et_4dien)SO_3 + $HSO_3^- \rightarrow Pd(SO_3)_2^{2-}$ + Et_4dien·$x$$H^+$. Conditions: [Pd] = 6.2×10^{-5} M; [total S] = 6.2×10^{-4} M; optical path length 0.88 cm; pH 3.3; temperature 25 °C; ionic strength 0.5 M; Δt = 90 s.

The loss of the Et_4dien ligand is a reversible process, and on addition of base the Pd(Et_4dien)SO_3 species is regenerated in solution (see further discussion). The nature of the Pd(II) sulfite product, produced during the decomposition reaction, was identified by an alternative preparation of such species via the reaction of $PdCl_4^{2-}$ with sulfite at pH ~2. On addition of $Na_2S_2O_5$ to a dark red solution of $PdCl_4^{2-}$, a color change to yellow occurs and the produced species exhibits absorption maxima at 251 and 363 nm. The complex isolated when the solution was concentrated gave analyses[17] in fair agreement with the overall composition $Na_2Pd(SO_3)_2 \cdot H_2O$. We found that it was impossible to recrystallize this raw product, in agreement with earlier observations[18] and presumably due to the oxidation (Pd catalyzed) of sulfite. With the aid of a weak basic anion exchanger it was demonstrated that the Pd(II) sulfite species carries a negative charge in solution. In contrast, the addition of a weak acid cation exchanger to a solution of $Na_2Pd(SO_3)_2 \cdot H_2O$ had no meaningful effect on the spectral characteristics of this species. The UV-vis absorption spectrum of this species is in excellent agreement with that observed during the decomposition process (see Figure 3), viz. 251 (ϵ = 18 000) and 363 nm (ϵ = 5600 M^{-1} cm^{-1}).

IR spectra were recorded in an effort to clarify the bonding mode of the sulfite ligand in the isolated product, which could be Pd–SO_3, Pd–OSO_2, or various bidentate and bridged configurations.[2,4-6] Spectra of closely related species have been reported in the literature, viz. $K_2Pd(SO_3)_2$, $K_2Pt(SO_3)_2 \cdot 2H_2O$, and $K_6Pt(SO_3)_4 \cdot 2H_2O$,[18,19] and a detailed comparison[8] indicated close correspondence between the spectra of the bis(sulfito) species. From this comparison it can be concluded that the sulfite ligand is probably coordinated via an oxygen atom to one palladium center and via a sulfur atom to another palladium center in a bridging way as suggested before:[19]



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[16] Sillen, L. G. *Spec. Publ.—Chem. Soc.* **1971**, *No. 17*, 680.

[17] Anal. Found (calcd): Pd, 32.0 (30.5); O, 38.0 (36.7); S, 19.7 (18.4); Na, 11.0 (13.2); Cl, <0.3 (0.0).

[18] Earwicker, G. *J. Chem. Soc.* **1960**, 2620.

[19] Newman, G.; Powell, D. B. *Spectrochim. Acta* **1963**, *19*, 213.

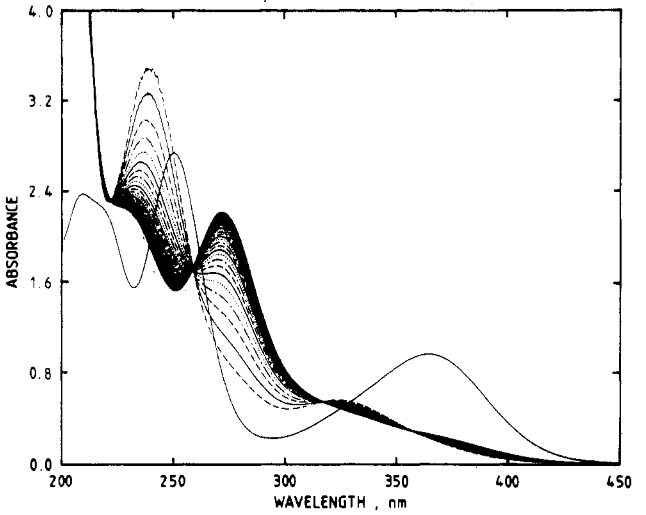


Figure 4. Repetitive scan spectra for the reaction $Pd(SO_3)_2^{2-} + Et_4dien \rightarrow Pd(Et_4dien)SO_3 + SO_3^{2-}$. Conditions: [Pd] = 2×10^{-4} M; [Et_4dien] = 2×10^{-4} M; optical path length 0.88 cm; pH 10.9; temperature 25 °C; ionic strength 0.5 M; Δt = 5 min.

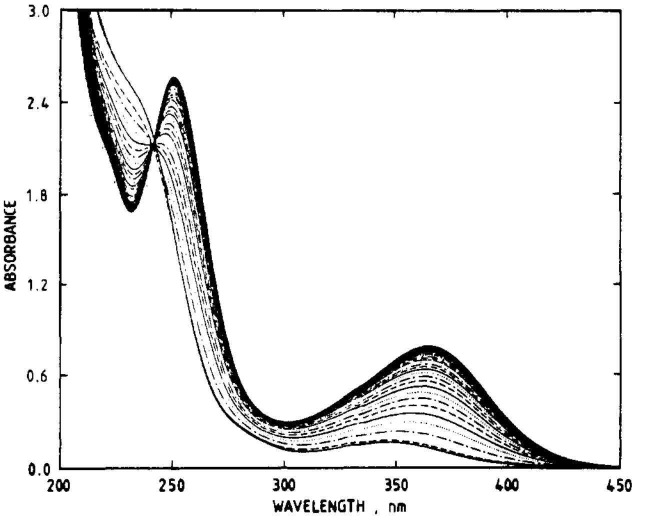


Figure 5. Repetitive scan spectra for the reaction $Pd(Et_4dien)Cl^+ + HSO_3^- \rightarrow Pd(SO_3)_2^{2-} + Et_4dien{\cdot}xH^+ + Cl^-$. Conditions: [Pd] = 1.5×10^{-4} M; [total S] = 2.1×10^{-3} M; optical path length 0.88 cm; pH 3.3; temperature 25 °C; ionic strength 0.5 M; Δt = 2 min.

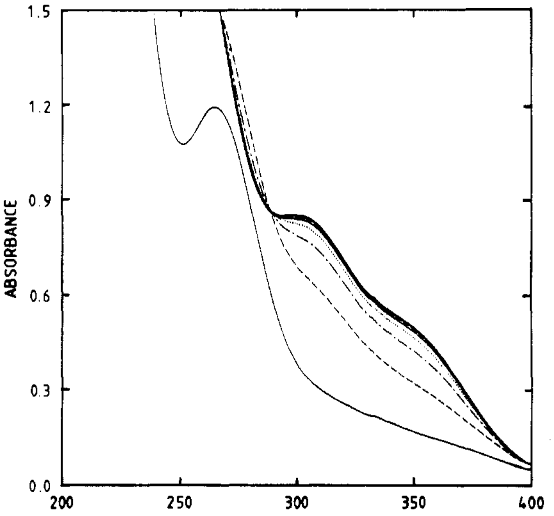
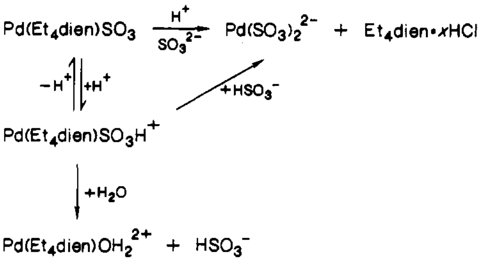


Figure 6. Spectral evidence for the formation of $Pd(SO_3)_2^{2-}$ and $Pd(SO_3)_3^{4-}$ (see text). Conditions: [Pd] = 8.7×10^{-5} M; [total S] = 2.4×10^{-2} M; optical path length 0.88 cm; pH 5; temperature 25 °C; ionic strength 0.5 M; Δt = 2 min.

Scheme II



The $Pd(SO_3)_2^{2-}$ species reacts with Et_4dien at pH >7 to form the $Pd(Et_4dien)SO_3$ complex as shown in Figure 4. On addition of the base, partial formation of an unstable hydroxo–sulfito species (λ_{max} = 239 and 327 nm) of unknown composition occurs, which subsequently produces the $Pd(Et_4dien)SO_3$ species accompanied by isosbestic points at 222, 259, 317, and 356 nm. The formation of the hydroxo–sulfito intermediate occurs to a smaller degree at pH 8, where $Pd(Et_4dien)SO_3$ is produced almost instantaneously.[8] Evidence for the formation of a hydroxo–sulfito species can also be observed when the pH of a solution containing $Pd(SO_3)_2^{2-}$ is increased to 11 in the absence of Et_4dien, which results in the formation of bands at 239 and ca. 330 nm. Subsequent addition of Et_4dien resulted in the rapid formation of $Pd(Et_4dien)SO_3$.

The overall reaction sequence, viz. dechelation and reverse formation of $Pd(Et_4dien)SO_3$, could be clearly followed by using ^1H and ^{13}C NMR techniques. The free Et_4dien ligand at pH 10 in D_2O exhibits a triplet proton signal for the CH_3 moiety between 1.1 and 1.4 ppm and an overlap of a quartet and a triplet between 2.6 and 2.9 ppm for the two types of CH_2 groups. The intensity ratio of these signals is 3:4 in agreement with the CH_3:CH_2 ratio. Addition of $Pd(SO_3)_2^{2-}$ produces two new triplets for the CH_3 groups between 1.5 and 1.9 ppm. These signals are assigned to the formation of $Pd(Et_4dien)SO_3$ and completely disappear on acidification of the solution to pH <5. The final spectrum is identical with that of the free ligand. Similar conclusions can be drawn from the ^{13}C NMR spectra in Figure 2.

This dechelation reaction can also be observed for the $Pd(Et_4dien)Cl^+$ complex during the reaction with HSO_3^-/SO_3^{2-} at pH ≤5. The corresponding repetitive scan spectra (Figure 5) exhibit no evidence for the formation of the $Pd(Et_4dien)SO_3$ species, indicating that the subsequent dechelation reaction is a fast, non-rate-determining step. The $Pd(SO_3)_2^{2-}$ species undergoes subsequent substitution in the presence of a large excess of sulfite to presumably produce the $Pd(SO_3)_3^{4-}$ species, which exhibits a characteristic absorption at 309 nm (ϵ = 18 500 M^{-1} cm^{-1}). The absorptions at 251 nm are almost identical for both complexes. The $Pd(SO_3)_2^{2-}$ and $Pd(SO_3)_3^{4-}$ species exist in equilibrium and are produced at the same rate during the decomposition of $Pd(Et_4dien)SO_3$ as can be seen from the spectra in Figure 6. We therefore have good reason to believe that the sulfito species absorbing at 309 nm is a higher substituted complex and is probably of ligand geometry different from that suggested for $Pd(SO_3)_2^{2-}$.

Acidification of $Pd(Et_4dien)SO_3$ in strongly acidic medium ($[H^+] \geq 1$ M) leads to the partial formation of $Pd(Et_4dien)OH_2^{2+}$ and $Pd(SO_3)_2^{2-}$. Repetitive scan spectra demonstrated (a typical example for this process is given in Figure 7) that the extent of aquation compared to dechelation strongly depends on $[H^+]$. In 6 M $HClO_4$ almost no dechelation and only aquation occurs. It follows that the sulfito species can undergo acid-catalyzed aquation presumably via a bisulfito complex, $Pd(Et_4dien)SO_3H^+$, for which the acid dissociation constant (pK) is expected to be ca. 2. The latter value is based on our experience with related carbonato complexes and their protonation constants.[1-3] Such a bisulfito complex could on the one hand be significantly more labile to allow for aquation of the sulfite ligand and on the other hand exert a weaker labilization effect on the chelated amine ligand to dis-

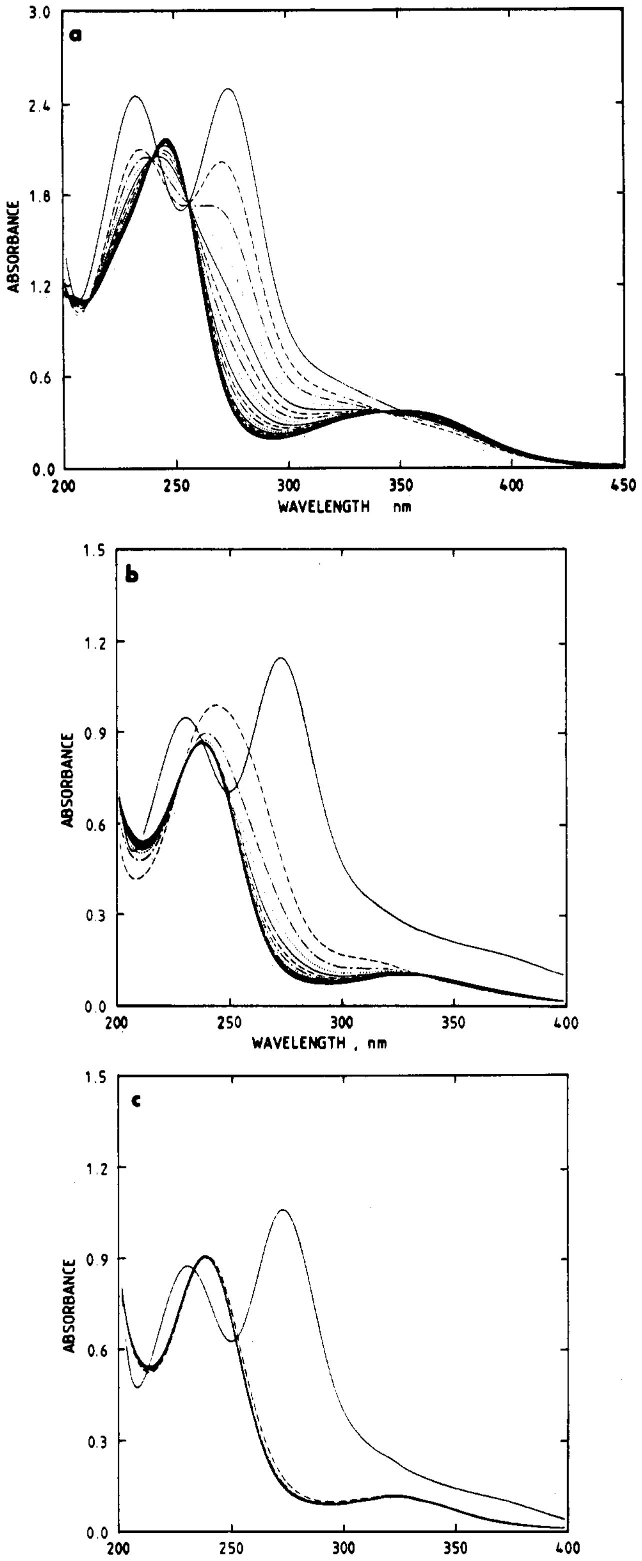


Figure 7. Repetitive scan spectra for the acidification of Pd(Et$_4$dien)SO$_3$ to produce Pd(Et$_4$dien)OH$_2$$^{2+}$ and Pd(SO$_3$)$_2$$^{2-}$: (a) [Pd] = 2×10^{-4} M, [total S] = 4×10^{-4} M, 0.1 M HClO$_4$; (b) [Pd] = 1×10^{-4} M, [total S] = 2×10^{-4} M, 2.9 M HClO$_4$; (c) [Pd] = 1×10^{-4} M, [total S] = 2×10^{-4} M, 5.8 M HClO$_4$. Conditions: optical path length 0.88 cm; temperature 25 °C; Δt = 45 s.

courage dechelation. The various decomposition reactions of Pd(Et$_4$dien)SO$_3$ can be summarized as shown in Scheme II.

Simultaneous Formation and Decomposition of Pd(Et$_4$dien)SO$_3$. When sulfite is added to a solution of Pd(Et$_4$dien)OH$_2$$^{2+}$ at pH ≤5, the relatively fast formation of Pd(Et$_4$dien)SO$_3$ is followed by the subsequent dechelation step. In this case the intermediate

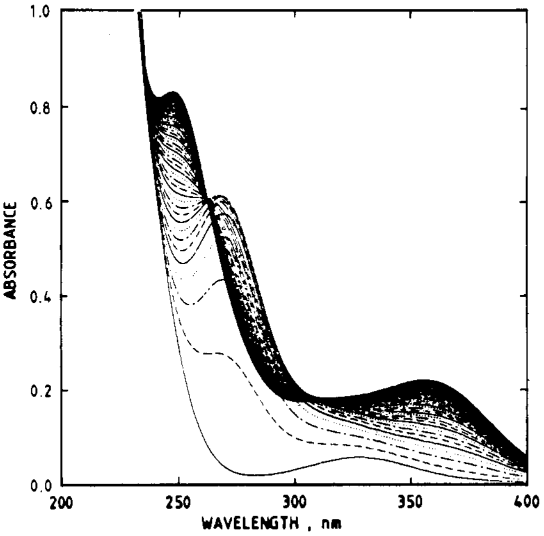


Figure 8. Repetitive scan spectra for the reactions Pd(Et$_4$dien)OH$_2$$^{2+}$ + HSO$_3$$^-$ → Pd(Et$_4$dien)SO$_3$ + H$^+$ + H$_2$O and Pd(Et$_4$dien)SO$_3$ + HSO$_3$$^-$ → Pd(SO$_3$)$_2$$^{2-}$ + Et$_4$dien·H$^+$. Conditions: [Pd] = 5×10^{-5} M; [total S] = 7×10^{-4} M; optical path length 0.88 cm; pH 4.5; temperature 25 °C; ionic strength 0.5 M; Δt = 55 s.

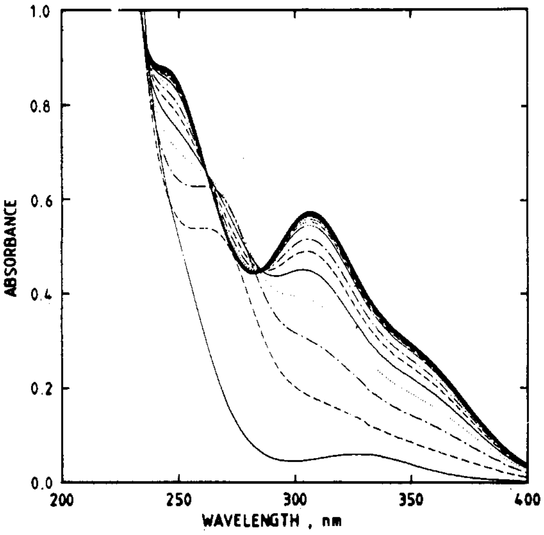


Figure 9. Repetitive scan spectra for the reactions Pd(Et$_4$dien)OH$_2$$^{2+}$ + HSO$_3$$^-$ → Pd(Et$_4$dien)SO$_3$ + H$^+$ + H$_2$O and Pd(Et$_4$dien)SO$_3$ + HSO$_3$$^-$ → Pd(SO$_3$)$_2$$^{2-}$ + Pd(SO$_3$)$_3$$^{4-}$ + Et$_4$dien·H$^+$. Conditions: [Pd] = 6×10^{-5} M; [total S] = 1.6×10^{-2} M; optical path length 0.88 cm; pH 4.5; temperature 25 °C; ionic strength 0.5 M; Δt = 57 s.

Pd(Et$_4$dien)SO$_3$ species is only produced partly before it reacts to give the final product, viz. Pd(SO$_3$)$_2$$^{2-}$, with isosbestic points at 265 and 310 nm (see Figure 8 for a typical example). The latter strongly depend on the pH and sulfite concentration of the reaction mixture. It is important to note that Pd(Et$_4$dien)SO$_3$ decomposes completely to Pd(SO$_3$)$_2$$^{2-}$ at $0 < \mathrm{pH} < 5$, only partly at $5 < \mathrm{pH} < 7$, and not at all at pH >7, where it is very stable.

It is quite understandable that we can observe the Pd(Et$_4$dien)SO$_3$ species as a reaction intermediate when the aquo complex is used as starting material since anation is usually much faster than ligand substitution and a buildup of this species can occur. This is not the case when the chloro complex is used as starting material and no buildup occurs (see Figure 5). When a large excess of sulfite is used, the intermediate species produces both Pd(SO$_3$)$_2$$^{2-}$ and Pd(SO$_3$)$_3$$^{4-}$ as demonstrated by the repetitive scan spectra in Figure 9.

To summarize the findings of the present investigations, we draw attention to the remarkable labilization effect of coordinated sulfite in a square planar chelated amine complex of Pd(II). This effect strongly depends on the pH of the solution, i.e. the ability to protonate the leaving ligand and to prevent the reverse chelation reaction. Addition of base, i.e. deprotonation of the amine ligand, results in chelation and the formation of the sulfito complex. Aquation of the sulfite ligand in $Pd(Et_4dien)SO_3$ only occurs in strongly acidic medium and competes with the dechelation reaction. A detailed kinetic study of the various reaction steps has been completed and will be reported in a subsequent paper.[20]

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Stereoselective Electron-Transfer Reactions of (Ethylenediaminetetraacetato)cobaltate(III), (Propylenediaminetetraacetato)cobaltate(III), and (1,2-Cyclohexanediaminetetraacetato)cobaltate(III) with Tris(ethylenediamine)cobalt(II)

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The stereoselectivities of the electron-transfer reactions of $[Co(edta)]^-$, $[Co(pdta)]^-$ (pdta = propylenediaminetetraacetate), and $[Co(cdta)]^-$ (cdta = 1,2-cyclohexanediaminetetraacetate) with $[Co(en)_3]^{2+}$ in aqueous solution and Me_2SO ([en] = 0.3 M, [Co(III)] = [Co(II)] = 0.01 M) have been determined by studying the optical purity of the $[Co(en)_3]^{3+}$ product. In aqueous solution, the ratio of the rate constants of the Δ-Λ and Δ-Δ reactions, $k_{\Delta\Lambda}/k_{\Delta\Delta}$, is 1.2 for all three reactions, and in Me_2SO, the ratios are 2.0, 2.1, and 2.1, respectively. The rate constants of the reactions in aqueous solution ([en] = 1.6 M, [enHCl] = 0.10 M, μ = 1.00 M, 25 °C) were found to be 5.2, 5.2, and 5.0 $M^{-1}\ s^{-1}$, respectively. For the $[Co(edta)]^-/[Co(en)_3]^{2+}$ reaction, the degree of stereoselectivity is strongly solvent dependent, with $k_{\Delta\Lambda}/k_{\Delta\Delta}$ increasing for the solvent series water < ethylene glycol < methanol ≃ ethanol ≃ formamide < ethylenediamine < DMF < Me_2SO < sulfolane. In addition, the effect of the ethylenediamine concentration on the rate constant of the $[Co(edta)]^-/[Co(en)_3]^{2+}$ reaction was studied. As the ethylenediamine concentration is raised from 0.085 to 0.985 M, the second-order rate constant rises from 4.66 to 5.79 $M^{-1}\ s^{-1}$. To account for the similarity in reactivity of the three oxidants with $[Co(en)_3]^{2+}$, a model is proposed for the orientation of the reactants in the activated complex in which the carboxylate groups of the oxidant face the reductant.

Introduction

Stereoselectivity effects offer opportunities for probing subtleties of the activated complexes of reactions. In the study of electron-transfer reactions of metal complexes, little is known about the relative orientation of the reactants in the transition state. Not even the intermetal distance in the transition state in simple electron-transfer reactions is known with certainty. The discovery of stereoselectivity in these reactions had provided a tool that may provide considerable information about their mechanistic details.

What appear to be well-established instances of stereoselective electron-transfer reactions are described in recent reports by Geselowitz and Taube[1,2] on the reactions of $[Co^{II}(en)_3]^{2+}$ with $[Co^{III}(edta)]^-$ and of $[Co^{II}(edta)]^{2-}$ with $[Ru^{III}(bpy)_3]^{3+}$ and several other oxidants. Lappin et al.[3] observed stereoselectivity in the reaction of a Ni^{IV} oxime complex with $[Co(edta)]^{2-}$, and Creaser et al.[4] noted the effect in the reaction of $[Co^{II}(sepulchrate)]^{2+}$ with $[Co^{III}(diamsarH_2)]^{5+}$. Stereoselectivity has also been reported for photochemical reactions in the quenching of excited-state $[Ru(bpy)_3]^{2+}$ by $[Co^{III}(acac)_3]$ found by Porter and Sparks[5] and quenching by $[Co(edta)]^-$ reported by Kaizu et al.[6] Moreover, the opportunities for practical applications of this class of reactions is evident in the recent work of Barton and coworkers,[7] which has revealed stereoselective binding and redox reactions of metal complexes with DNA.

The goal of the work reported here was to improve our understanding of the stereoselectivity of the $[Co(en)_3]^{2+}/[Co(edta)]^-$ reaction. We report the results of a study of the solvent dependence of the stereoselectivity of this reaction and the effects observed when $[Co(pdta)]^-$ (pdta = propylenediaminetetraacetate) and $[Co(cdta)]^-$ (cdta = 1,2-cyclohexanediaminetetraacetate) are substituted for $[Co(edta)]^-$. Additionally, kinetic data are presented for the reactions.

Experimental Section

Preparation of Materials. Reagents. Commercial analytical grade reagents were used unless otherwise specified. Ethylenediamine was distilled over sodium.

$Co(O_3SCF_3)_2$. Cobalt trifluoromethanesulfonate hexahydrate was prepared by neutralizing $CoCO_3$ with aqueous CF_3SO_3H and evaporating to dryness. The residue was converted to the anhydrous form by drying it in vacuo at 110 °C.

$(+)_{589}$- and $(-)_{589}$-*cis*-$[Co(en)_2(NO_2)_2]Br$. *cis*-$[Co(en)_2(NO_2)_2]NO_2$ was prepared from $[Co(en)_2(CO_3)]Cl$ and resolved with $Na_2[Sb_2((+)\text{-}tart)_2]\cdot 2H_2O$, and the enantiomers were crystallized as the bromide salts by using the method of Dwyer and Garvan.[8] Specific rotation data for the less soluble diastereoisomer, $(-)_{589}$-*cis*-$[Co(en)_2(NO_2)_2][Sb_2((+)\text{-}tart)_2]$, and the $(+)_{589}$ and $(-)_{589}$ bromide salts of the complex (all 0.3% in water) are given in Table I.

$(-)_{546}$- and $(+)_{546}$-$K[Co(edta)]\cdot 2H_2O$. These complexes were prepared and resolved according to literature methods.[9,10] Specific rotation data

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