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^{1}H NMR Kinetic Study of Ligand Exchange on Bis(1,4-dithiane)platinum(II), Bis(1,4-dithiane)palladium(II), and Tetrakis(dimethyl sulfide)Platinum(II)[1]

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Ligand exchange on square-planar Pt(1,4-dithiane)$_2^{2+}$, Pd(1,4-dithiane)$_2^{2+}$, and Pt(Me$_2$S)$_4^{2+}$ has been studied as a function of temperature and pressure by ^{1}H NMR line-broadening, isotopic labeling, and magnetization transfer experiments with deuteriated nitromethane as solvent. Second-order rate constants and activation parameters are as follows: for 1,4-dithiane exchange on Pt(1,4-dithiane)$_2^{2+}$, $k_2^{298} = 28.8 \pm 4.8$ m^{-1} s^{-1}, $\Delta H^* = 32.9 \pm 3.6$ kJ mol^{-1}, $\Delta S^* = -106 \pm 11$ J K^{-1} mol^{-1}, and $\Delta V^* = -12.6 \pm 1.1$ cm^3 mol^{-1}; for 1,4-dithiane exchange on Pd(1,4-dithiane)$_2^{2+}$, $k_2^{298} = 9780 \pm 300$ m^{-1} s^{-1}, $\Delta H^* = 22.9 \pm 0.6$ kJ mol^{-1}, $\Delta S^* = -91.6 \pm 2.1$ J K^{-1} mol^{-1}, and $\Delta V^* = -9.8 \pm 0.4$ cm^3 mol^{-1}; for Me$_2$S exchange on Pt(Me$_2$S)$_4^{2+}$, $k_2^{298} = 1.54 \pm 0.07$ m^{-1} s^{-1}, $\Delta H^* = 42.1 \pm 0.7$ kJ mol^{-1}, $\Delta S^* = -100.2 \pm 2.2$ J K^{-1} mol^{-1}, and $\Delta V^* = -22.0 \pm 1.3$ cm^3 mol^{-1}. Second-order kinetics and negative entropies and volumes of activation indicate associative, I$_a$ or A, exchange mechanisms. For both metal centers, exchange of the chelated and strongly bound 1,4-dithiane, corrected for statistics, is faster than that of Me$_2$S, probably due to steric factors. The ratio in reactivity for Pd/Pt is only ca. 1300 for Me$_2$S and 340 for 1,4-dithiane, indicating a more pronounced sensitivity of Pt(II) to the electronic properties of the coordinated and entering ligands. Accordingly, activation volumes are more negative in the case of platinum. ΔV^* for the Me$_2$S exchange on Pt(II) is the most negative one reported so far for a square-planar solvent exchange.

Introduction

In contrast to octahedral systems, high-pressure data for solvent exchange on square-planar tetrasolvated cations MS$_4^{2+}$ are limited.[3,4] The first available data concern water exchange on Pt(H$_2$O)$_4^{2+}$ and Pd(H$_2$O)$_4^{2+}$ studied by oxygen-17 NMR.[5,6] Very recently, it has been shown[7] that the exchange rates of a series of square-planar palladium(II) solvates with amide, nitrile, isonitrile, and sulfide ligands span almost 8 orders of magnitude as a result of large changes in nucleophilicity of entering ligands, trans effects, and different steric hindrance of ligands and complexes. Consistently negative volumes of activation in these systems indicated an associative mode of activation, regardless of the nature of the ligands.[7]

Activation volumes for exchange of O-bonded ligands on the square-planar solvates studied so far are negative and small, $|\Delta V^*| \leq 4.6$ cm^3 mol^{-1}. The recent work on solvent exchange on Pd(Me$_2$S)$_4^{2+}$ and Pd(Et$_2$S)$_4^{2+}$, however, showed that activation volumes for exchange of these S-bonded dialkyl thioethers are significantly more negative.[7] It was therefore considered to be of interest to extend those studies to some similar platinum(II) complexes for which even larger activation volumes should be expected. We here report studies of solvent exchange on Pt(Me$_2$S)$_4^{2+}$, Pt(1,4-dithiane)$_2^{2+}$, and—for comparison—Pd(1,4-dithiane)$_2^{2+}$, where 1,4-dithiane denotes the cyclic dithioether S(CH$_2$CH$_2$)$_2$S. Structural studies of the solid triflate salts[8,9] show that 1,4-dithiane is bonded to the metal as a chelate with the ligand in a boat conformation and with a shorter and stronger metal–sulfur bond than that of the dimethyl sulfide complex. Conformational changes of the ligand can be expected to contribute to the free energy of activation in the case of 1,4-dithiane exchange.

Experimental Section

Chemicals and Solutions. [Pt(Me$_2$S)$_4$](CF$_3$SO$_3$)$_2$ and [Pt(1,4-dithiane)$_2$](CF$_3$SO$_3$)$_2$ were synthesized as described elsewhere[8,9] from Pt(H$_2$O)$_4^{2+}$,[10] Me$_2$S (Merck, zur Synthese), 1,4-dithiane (dithio 1,4-dioxane) (Aldrich 97%), and CF$_3$SO$_3$H (Merck, zur Synthese). [Pd(1,4-dithiane)$_2$](BF$_4$)$_2$ was prepared by adding an excess of 1,4-dithiane to a solution of [Pd(MeCN)$_4$](BF$_4$)$_2$ (Fluka, purum) in nitromethane; the complex separates immediately as a lemon yellow precipitate, which was washed with ether and dried under vacuum. Its purity was checked by ^{1}H NMR spectroscopy.

The solutions used for NMR measurements were freshly prepared in a nitrogen-filled glovebox. All solvents were used as received but were stored and dried over 4-Å molecular sieves for 48 h before use. Deuteriated dimethyl sulfide S(CD$_3$)$_2$ (Glaser AG, 99.9% D) was dried for ca. 1 day in the dark over 4-Å molecular sieves. Deuteriated nitromethane (CD$_3$NO$_2$, Ciba-Geigy) was added to the solutions as both an inert diluent and an internal lock substance. Also, 2% CH$_2$Cl$_2$ was used as an internal line-width and chemical shift reference (5.30 ppm referred to TMS). TMS could not be used because it reduces the palladium solvates to palladium metal. All concentrations are expressed in moles per kilogram of solvent (m = mol kg^{-1}). The coordination number, n_c, of the complexes in solution was obtained by integration of the NMR signals for free and coordinated ligands, by use of solutions of known composition. In all three cases n_c was found to be 4.

NMR Measurements. Ambient pressure ^{1}H NMR spectra were recorded on a Bruker AC-200 spectrometer (cryomagnet 4.7 T) working at 200 MHz. The temperature was measured before and after accumulation of spectra by substituting the sample with a Pt-100 resistor[11] and was constant within ±0.2 K.

Spectra at variable pressures were recorded using a Bruker AM-400 spectrometer working at 400 MHz. Measurements were made up to 200 MPa using a home-built high-pressure probe which has been described previously.[12] A built-in platinum resistor allows temperature measurements with an accuracy of ±1 K after all corrections.[13] Thermostated synthetic oil was pumped through the bomb, allowing the temperature to be stabilized to ±0.2 K. For relatively slow exchange, a fast-injection apparatus described elsewhere was used.[14]

The magnetization transfer measurements were performed using the "inversion–recovery technique" as described in the literature.[15] Selective inversion of the free or bound signal was achieved, using the so-called "1,–3,3,–1" pulse train.[16] After a variable time, t, a nonselective 90°

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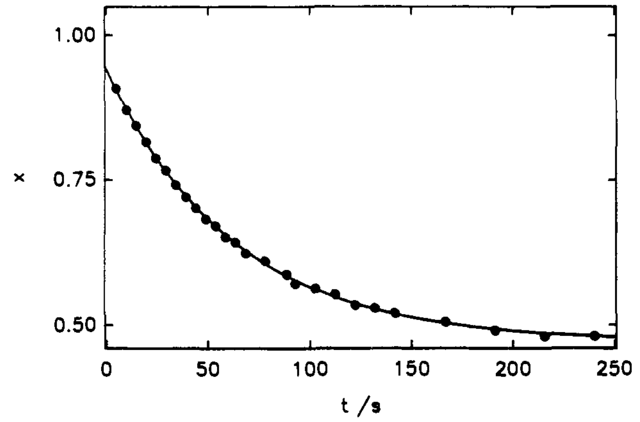

Figure 1. Mole fraction x of bound Me_2S, as a function of time, after addition of a solution of Me_2S-d_6 to a solution of $Pt(Me_2S)_4(CF_3SO_3)_2$ in CD_3NO_2 at 246.8 K. $[Pt(Me_2S)_4(CF_3SO_3)_2]$ = 0.0548 *m*, $[Me_2S]$ = 0.248 *m*.

pulse allows observation of the signal.

Computation Method. The analysis of the experimental data using the required equations was done by a nonlinear least-squares program fitting the values of the desired parameters. Reported errors are 1 standard deviation.

Results

Dimethyl Sulfide Exchange on $Pt(Me_2S)_4^{2+}$. The Me_2S exchange (eq 1) was followed as a function of temperature (246–371 K) using three techniques to obtain the rate constants.

$$Pt(Me_2S)_4^{2+} + 4{}^*Me_2S \rightleftarrows Pt({}^*Me_2S)_4^{2+} + 4Me_2S \quad (1)$$

(i) At *low temperatures* (246–253 K), where the rate constants are small (<0.1 s^{-1}) on the NMR time scale, fast-injection experiments (FI) were used. The reaction was followed by monitoring the increase in intensity of the proton NMR signal of free Me_2S and the decrease of the signal from the coordinated Me_2S, after fast injection of a Me_2S-d_6 solution to a solution of $Pt(Me_2S)_4^{2+}$ in CD_3NO_2. The time dependence of the mole fraction $x = [Me_2S]_c/([Me_2S]_c + [Me_2S]_f)$ of bound nondeuteriated dimethyl sulfide, obtained by integration of the signals (Figure 1), was fitted to eq 2, where k_{obs} is the observed first-order rate

$$x = x_\infty + (x_0 - x_\infty) \exp[-k_{obs}t/(1 - x_\infty)] \quad (2)$$

constant (s^{-1}) for the exchange of a particular dimethyl sulfide molecule in $Pt(Me_2S)_4^{2+}$ according to eq 1, and x_0 and x_∞ are the values of x at $t = 0$ and ∞, respectively. The adjustable parameters were k_{obs}, x_0, and x_∞.

(ii) At *intermediate temperatures* (325–340 K), between those accessible by fast-injection and line-broadening NMR, the magnetization transfer NMR technique (MT) was used to study the exchange rates. In systems in which the longitudinal relaxation rate, $1/T_1$, is less than or equal to the exchange rate, it is possible to deduce the exchange rate between two sites by selectively inverting the signal of one site and monitoring the intensity of the signal of both sites as a function of time between the inversion and monitoring pulses. The return of the magnetization to equilibrium is then governed by both the $1/T_1$ of the exchanging species and the exchange rate between the sites.[17,18] In this work the two sites are that of the Me_2S coordinated to platinum(II) and that of the free Me_2S. A complication arises from the tripletlike structure of the signal for the bound ligands. The two satellites correspond to the solvent bound to the spin $^1/_2$ platinum-195 isotope and the central line to the solvent bound to spin 0 platinum isotopes. The satellites contribute 33.8% and the central line contributes 66.2% to the total intensity. To perform fine selective inversion we need well-separated signals, which is the case. The chemical shifts, δ, of free and bound Me_2S and the coupling constant, $J(^{195}Pt-^1H)$, of the solvent bound to Pt are, respectively, 2.07 ppm, 2.76 ppm, and 45.3 Hz for $[Pt(Me_2S)_4](CF_3SO_3)_2$ in nitromethane. Figure 2a shows a typical magnetization transfer experiment performed at 312 K, with the high-pressure probe at 175 MPa and 400 MHz. The experimental magnetizations were obtained by direct measurements of the signal heights from the spectra and were fitted to the equations given by Led and Gesmar.[17] The contribution of the satellites to the height of the central line and the ratio between the signal line widths were taken into account. Seven parameters were adjusted: the final and initial signal heights of free and coordinated ligand, their spin–lattice relaxation rates ($1/T_{1F}$ and $1/T_{1C}$), and the exchange rate constant k_{obs}. An example of a fit is show in Figure 2b.

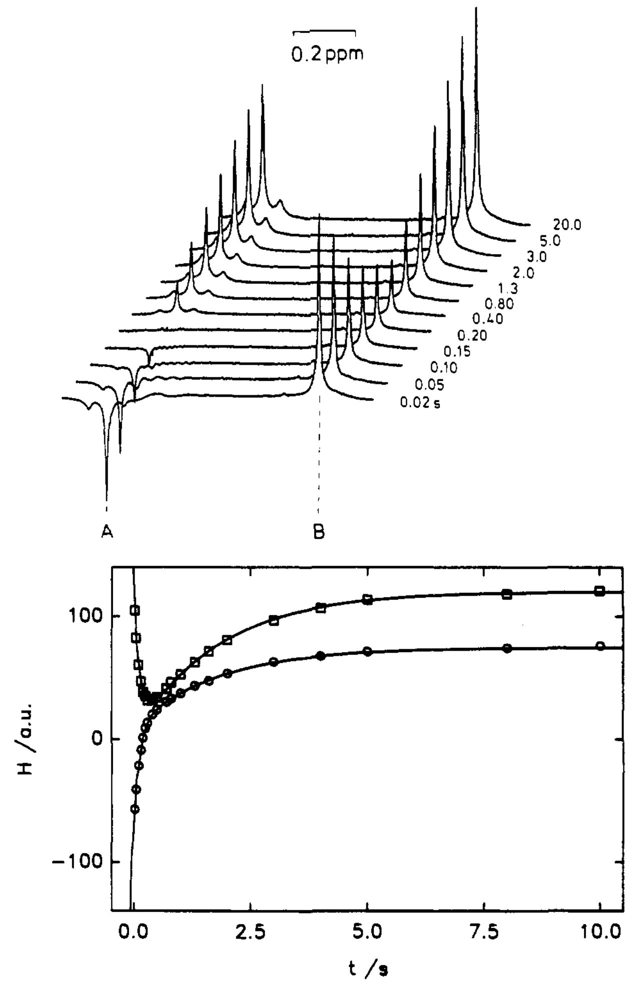

Figure 2. (a) 400-MHz ^1H NMR spectra of a 0.0997 *m* $Pt(Me_2S)_4(CF_3SO_3)_2$ and 0.360 m Me_2S solution in CD_3NO_2 at 312.2 K and 148 MPa as a function of the time interval *t* between the inversion pulse train and the observation pulse: (A) coordinated Me_2S (δ_C = 2.76 ppm, $J(^{195}Pt-^1H)$ = 45.3 Hz); (B) free Me_2S (δ_F = 2.07 ppm). The pulse sequence employed was the following: $(25.5°-D_1-67.5°-D_1-67.5°-D_1-25.5°-t-D_2)$ where the delays D_1 = 1.82 ms and D_2 = 40 s and the 90° pulse = 79 μs. (b) Calculated curve from the experiment shown in part a: (○) signal height of the central line from Me_2S bound to Pt; (□) signal height of the free Me_2S. The lines are generated by the equations given in ref 17 and are fitted to the experimental values.

(iii) At *high temperatures* (T > 350 K) the NMR signals start to broaden and the rate constants were determined from the width of the NMR signals at half-height using eq 3, where τ_j^r is the

$$1/\tau_j^r = \pi(W_j - W_j^0) = k_{obs} \quad (3)$$

residence time in site j, and W_j and W_j^0 are the full width at half-height in the presence and absence of exchange.

The second-order rate law of eq 4, was assumed for this exchange reaction. The second-order rate constants were fitted to the Eyring equation (Figure 3), leading to k_2^{298} = 1.54 ± 0.07

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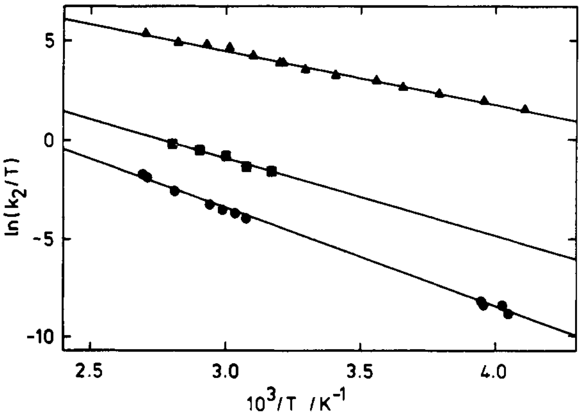

Figure 3. Plot of ln (k_2/T) vs reciprocal temperature for ligand exchange on (●) Pt(Me$_2$S)$_4^{2+}$, (■) Pt(1,4-dithiane)$_2^{2+}$, and (▲) Pd(1,4-dithiane)$_2^{2+}$ in CD$_3$NO$_2$.

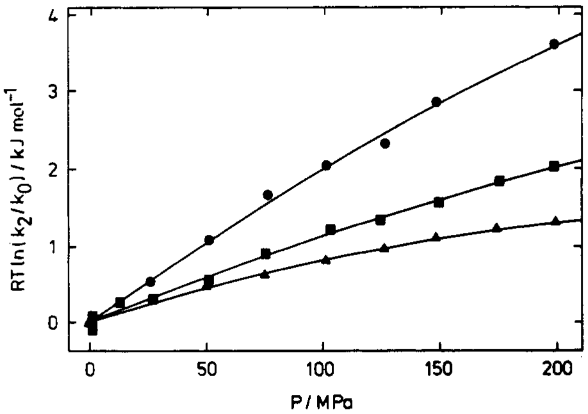

Figure 4. Pressure effect on the normalized natural logarithm of the second-order rate constant for ligand exchange on (●) Pt(Me$_2$S)$_4^{2+}$ (312.2 K), (■) Pt(1,4-dithiane)$_2^{2+}$ (330.3 K), and (▲) Pd(1,4-dithiane)$_2^{2+}$ (282.2 K) in CD$_3$NO$_2$. The equation $\ln k_2 = \ln k_0 - (\Delta V^{\ddagger}P/RT) + (\Delta\beta^{\ddagger}P^2/2RT)$, where k_0, $\Delta V^{\ddagger}$, and $\Delta\beta^{\ddagger}$ are adjustable parameters, was fitted to the data, using a least-squares routine.

m^{-1} s^{-1}, $\Delta H^{\ddagger}$ = 42.1 ± 0.7 kJ mol^{-1}, and $\Delta S^{\ddagger}$ = −100.2 ± 2.2 J K^{-1} mol^{-1}.

$$k_{\text{obs}} = -\text{d}[\text{Pt}(\text{Me}_2\text{S})_4^{2+}]/\text{d}t[\text{Pt}(\text{Me}_2\text{S})_4^{2+}] = k_2[\text{Me}_2\text{S}] \quad (4)$$

The pressure dependence of the rate constants was obtained by magnetization transfer experiments at 312 K. The data were fitted to eq 5 (Figure 4), where k_0 is the rate constant at zero

$$\ln k_2 = \ln k_0 - \Delta V^{\ddagger}P/RT + \Delta\beta^{\ddagger}P^2/2RT \quad (5)$$

pressure, $\Delta V^{\ddagger}$ the activation volume, and $\Delta\beta^{\ddagger}$ the compressibility coefficient of activation. This leads to $\Delta V^{\ddagger}$ = −22.0 ± 1.3 cm^3 mol^{-1}, k_0 = 3.27 ± 0.06 m^{-1} s^{-1}, and $\Delta\beta^{\ddagger}$ = (−4.0 ± 1.3) × 10^{-2} cm^3 mol^{-1} MPa^{-1}.

1,4-Dithiane Exchange on M(1,4-dithiane)$_2^{2+}$ (M = Pt, Pd). Figure 5 shows the ^{1}H NMR spectra in absence of exchange of Pt(1,4-dithiane)$_2^{2+}$ and Pd(1,4-dithiane)$_2^{2+}$ in nitromethane with an excess of free 1,4-dithiane present. The rate constants for the exchange reaction (6) were obtained using eq 3, except for the

$$\text{M(dithiane)}_2^{2+} + 2{}^*\text{dithiane} \rightleftarrows \text{M}({}^*\text{dithiane})_2^{2+} + 2\,\text{dithiane} \quad (6)$$

temperature dependence of the 1,4-dithiane exchange on Pd(1,4-dithiane)$_2^{2+}$, where calculated spectra were least-squares fitted to the spectra, using a program derived from EXCNG.[19]

The exchange is first order with respect to free ligand with negligible intercepts in the linear plots of k_{obs} versus [1,4-dithiane] (Table I). The rate law therefore follows the form shown in eq 4. The variable-temperature (Figure 3) rate constants were fitted to the Eyring equation, leading to k_2^{298} = 9780 ± 300 m^{-1} s^{-1}, $\Delta H^{\ddagger}$ = 22.9 ± 0.6 kJ mol^{-1}, and $\Delta S^{\ddagger}$ = −91.6 ± 2.1 J K^{-1} mol^{-1} for Pd(1,4-dithiane)$_2^{2+}$ and k_2^{298} = 28.8 ± 4.8 m^{-1} s^{-1}, $\Delta H^{\ddagger}$ = 32.9 ± 3.6 kJ mol^{-1}, and $\Delta S^{\ddagger}$ = −106 ± 11 J K^{-1} mol^{-1} for Pt(1,4-dithiane)$_2^{2+}$. The variable pressure data (Figure 4) were fitted to eq 5 leading to $\Delta V^{\ddagger}$ = −9.8 ± 0.4 cm^3 mol^{-1}, k_0 = 5800 ± 40 m^{-1} s^{-1}, and $\Delta\beta^{\ddagger}$ = (−3.3 ± 0.4) × 10^{-2} cm^3 mol^{-1} MPa^{-1} for Pd(1,4-dithiane)$_2^{2+}$ at 282 K and $\Delta V^{\ddagger}$ = −12.6 ± 1.2 cm^3 mol^{-1}, k_0 = 191 ± 3 m^{-1} s^{-1}, and $\Delta\beta^{\ddagger}$ = (−2.4 ± 1.2) × 10^{-2} cm^3 mol^{-1} MPa^{-1} for Pt(1,4-dithiane)$_2^{2+}$ at 330 K.

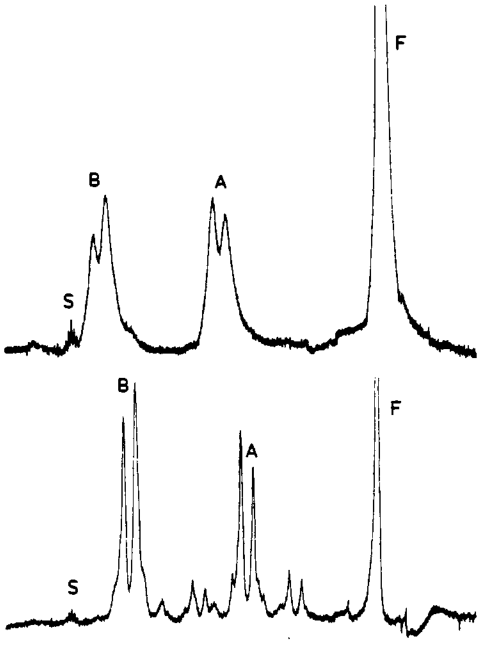

Figure 5. 200-MHz ^{1}H NMR spectra: (upper spectrum) [Pd(1,4-dithiane)$_2$(BF$_4$)$_2$] = 0.00478 m, [1,4-dithiane] = 0.0119 m, at 252.6 K; (lower spectrum) [Pt(1,4-dithiane)$_2$(CF$_3$SO$_3$)$_2$] = 0.0855 m, [1,4-dithiane] = 0.443 m, at 303.7 K. Key: (F) free dithiane (2.70 ppm); (A and B) coordinated dithiane (for Pd, δ_C = 3.27 ppm (A) and 3.70 ppm (B), $^2J(^1\text{H}-^1\text{H})$ = 9.3 Hz; for Pt, δ_C = 3.19 ppm (A), $J(^{135}\text{Pt}-^1\text{H})$ = 70.0 Hz, and δ_C = 3.61 ppm (B), $^2J(^1\text{H}-^1\text{H})$ = 8.8 Hz); (S) satellite ^{13}C–^{1}H of CHD$_2$NO$_2$.

Table I. Observed, k_{obs}, and Second-Order, k_2, Rate Constants for 1,4-Dithiane Exchange on Pt(1,4-dithiane)$_2$(CF$_3$SO$_3$)$_2$ and Pd(1,4-dithiane)$_2$(BF$_4$)$_2$ as a Function of Concentration of Free 1,4-Dithiane in CD$_3$NO$_2$

[M(1,4-dithiane)$_2^{2+}$]/m	[1,4-dithiane]/m	k_{obs}/s^{-1}	k_2/m^{-1} s^{-1}
	M = Pt (T = 330.4 K)		
0.0587	0.0581	6.46	111
0.0575	0.122	16.2	132
0.0635	0.247	26.6	108
0.0601	0.316	32.6	103
	M = Pd (T = 290.1 K)		
0.00343	0.00196	6.47	3300
0.00344	0.00412	14.7	3570
0.00348	0.00690	21.2	3080
0.00396	0.00937	30.4	3240
0.00349	0.0102	34.8	3400
0.00339	0.0199	62.9	3150

Discussion

The exchange rates of both Me$_2$S and 1,4-dithiane on platinum(II) were found to be slower than those of the corresponding palladium(II) analogues (see Table II). This is in agreement with what is normally observed when exchange of ligands on the two metal centers are compared. The second-order rate law and the negative values found for both the entropies and volumes of

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Table II. Exchange Rate Constants and Activation Parameters for Ligand and Solvent Exchange on PdL_4^{2+} and PtL_4^{2+} Complexes[a]

complex	$k_2^{298}/m^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1} (T range/K)	$\Delta V^{\ddagger}$/cm^3 mol^{-1} (T/K)	ref[b]
$Pd(NH_3)_4^{2+}$[b]	1.6×10^{-2}[i]	67.3	−54.1 (273–298)		27
$Pd(Et_2S)_4^{2+}$[c]	5.0 ± 0.6	50.4 ± 2.4	−62.8 ± 6.9 (323–369)	−11.6 ± 0.4 (358)	7
$Pd(H_2O)_4^{2+}$[d]	10.2 ± 0.7	49.5 ± 1.9	−60 ± 6 (239–345)	−2.2 ± 0.2 (324)	6
$Pd(DMA)_4^{2+}$[c]	34.8 ± 1.0	43.2 ± 1.3	−76.2 ± 4.2 (275–332)	−2.8 ± 0.2 (303)	7
$Pd(MeCN)_4^{2+}$[c]	48.8 ± 1.3	45.4 ± 0.8	−60.1 ± 2.4 (285–368)	−0.1 ± 0.4 (336)	7
$Pd(CN)_4^{2-}$[e]	124 ± 11[i]	17 ± 3	−147 ± 9 (303–333)		26
$Pd(DMF)_4^{2+}$[c]	153 ± 6	41.9 ± 1.0	−62.3 ± 3.4 (272–345)	−0.2 ± 0.6 (305)	7
$Pd(Me_2S)_4^{2+}$[c]	2140 ± 53	31.9 ± 0.6	−74.3 ± 1.9 (248–355)	−9.4 ± 0.3 (303)	7
$Pd(1,4\text{-dithiane})_2^{2+}$[c]	9780 ± 300	22.9 ± 0.6	−91.6 ± 2.1 (243–370)	−9.8 ± 0.4 (282)	this work
$Pd(MeNC)_4^{2+}$[f]	$(10.6 \pm 0.7) \times 10^5$	16.4 ± 1.1	−74.5 ± 4.1 (234–314)	−3.1 ± 0.1 (264)	7
$Pt(H_2O)_4^{2+}$[d]	$(7.1 \pm 0.5) \times 10^{-6}$	89.7 ± 2.4	−43 ± 8 (273–334)	−4.6 ± 0.2 (297)	5
$Pt(Me_2S)_4^{2+}$[c]	1.54 ± 0.07	42.1 ± 0.7	−100.2 ± 2.2 (246–371)	−22.0 ± 1.3 (312)	this work
$Pt(DMSO)_4^{2+}$[c,g]	2 ± 1	47 ± 4	−74 ± 10 (248–284)	−5 ± 3 (360)	28
$Pt(CN)_4^{2-}$[e]	25 ± 2[i]	24 ± 3	−137 ± 10 (303–333)		26
$Pt(1,4\text{-dithiane})_2^{2+}$[c]	28.8 ± 4.8	32.9 ± 3.6	−106 ± 11 (315–356)	−12.6 ± 1.1 (330)	this work
$Pt(DMSO)_4^{2+}$[c,h]	$(3.2 \pm 0.1) \times 10^3$	32.8 ± 0.2	−62.0 ± 0.7 (238–292)	−2.5 ± 0.3 (265)	28
$Pt(MeNC)_4^{2+}$[f]	$(6.2 \pm 0.4) \times 10^5$	13.8 ± 1.1	−87.9 ± 3.9 (231–316)	−3.7 ± 0.1 (264)	7

[a] Quoted errors are one standard deviation. [b] In diluent H_2O. [c] In diluent CD_3NO_2. [d] Rate constant and $\Delta S^{\ddagger}$ for the exchange of a particular water molecule recalculated to second-order units, i.e.: $k_{ex}^{298}/55$. [e] In diluent EtOH. [f] In diluent CD_3CN. [g] S bonded. [h] O bonded. [i] k_2 in L mol^{-1} s^{-1}.

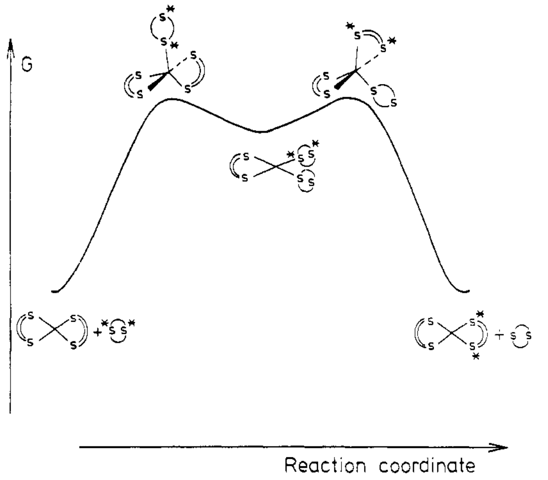

Figure 6. Reaction profile suggested for the ligand exchange on square-planar $M(1,4\text{-dithiane})^{2+}$ complexes (M = Pt and Pd).

activation indicate an associative mechanism, A or I_1, for the ligand exchange, as previously found for other substitution reactions on square-planar complexes.

The NMR spectra of the complexes $M(1,4\text{-dithiane})_2^{2+}$ (M = Pd, Pt) shown in Figure 5 indicate that the structure of these two complexes in solution are similar to the square-planar chelate structure of $Pt(1,4\text{-dithiane})_2^{2+}$ in the solid state.[9]

A tentative symmetrical reaction profile for the 1,4-dithiane exchange is shown in Figure 6. Exchange of the chelating ligand is assumed to occur in a two-step process through transition states with a trigonal-bipyramidal geometry. The first and rate-determining step results in formation of a square-planar intermediate with one chelating ligand and two monodentate ligands. Although the formation of this intermediate complex might be thermodynamically favored at high concentrations of 1,4-dithiane, it could not be observed. The succeeding replacement of one of the monodentate ligands and formation of the product chelate are therefore likely to be rapid.

A comparison of the solid-state structures[8,9] of the complexes $Pt(Me_2S)_4^{2+}$ and $Pt(1,4\text{-dithiane})_2^{2+}$ shows that the metal–sulfur bonds are 0.02 Å shorter and the bond correspondingly stronger in the chelate. The chelated ligand is also geometrically somewhat strained as compared to free dithiane in the boat conformation.[9,20] In spite of the stronger bonding, exchange of the chelate ligand is faster than that of dimethyl sulfide by a factor of ca. 5 for Pd and ca. 10 for Pt; cf. Table II. Even if a statistical correction for the number of donor S atoms on the ligands is made, the dithioether exchange is faster at both metal centers.

Since both the donor properties of Me_2S and 1,4-dithiane and their properties as trans-directing ligands are expected to be similar, the observed differences in reactivity most probably originate from differences in steric crowding on the complexes and/or different properties of Me_2S and 1,4-dithiane as leaving ligands. The steric crowding increases in the order 1,4-dithiane < Me_2S < Et_2S, which agrees with the observed order of reactivities cf. Table II.

Since the chelated 1,4-dithiane is geometrically strained in the ground state, even a slight weakening of the metal-leaving ligand bond in the transition state will allow the ligand to relax into a less strained boat conformation. This might contribute to lower the energy barrier for formation of the transition state. The effect on the activation parameters, in particular the activation enthalpy, should be almost independent on the nature of the metal ion. This is indeed the case, the enthalpies of activation being ca. 9 kJ mol^{-1} lower for exchange of dithiane compared to Me_2S both for Pd and Pt (see Table II).

For associative substitution reactions on square-planar complexes, there is an intricate interaction between the metal center and the trans and entering ligands.[21-24] Those are mainly responsible for the overall rate of reaction. A difficulty with chemically simple exchange reactions of the type listed in Table II is that the variables determining the reactivity, such as entering and leaving groups, trans and cis ligands, are not separable. A comparison between two exchange reactions always involves a simultaneous change of all those parameters. A separate evaluation of those effects requires a systematic variation of substrate complexes and entering ligands, which has been done previously for more simple systems.[25] Data relevant for the present systems are still lacking, however.

That interplay between the metal centers and the respective ligands are of importance in the reactions studied in the present work, is illustrated by the relatively small difference in reactivity between the Pd and Pt exchanges. The ratio for the S-bonded exchange investigated has decreased to 1300 for Me_2S and 340 for 1,4-dithiane, compared to the factor of ca. 10^6 that has been reported for exchange of O-bonded ligands.[5,6] This increase of reactivity of reactions of Pt(II) complexes relative to those of Pd(II) has been observed earlier for exchange of MeNC[7] and cyanide[26] and is in agreement with the more pronounced sensitivity

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of the Pt(II) center to the electronic properties of the coordinated and entering ligands.

For the exchange reactions listed in Table II, there is no obvious correlation between the entropies and volumes of activation. The magnitudes of the activation volumes for the solvent exchange on Pd(II) are always smaller than for the corresponding exchange on Pt(II). With exception of the thioether complexes, the activation volumes reported so far are very small, generally not exceeding 20% of the molar volume of the entering ligand. This might indicate either that the associative character is weak or that additional effects such as bond stretching in the transition state or solvational changes decrease the volumes that should be expected for associative reactions. Exchange of thioethers display much larger activation volumes. However, it is still an open question whether this is due to changes in solvation, to an increasingly associative behavior expected for such sulfur-bonding ligands, or to a combination of both.

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Supplementary Material Available: Second-order rate constants and chemical shifts for the ligand exchange on ML_n^{2+} as a function of temperature (Tables SI–SIII) and pressure (Tables SIV–SVI) and observed rate constants and longitudinal relaxation rates obtained from the magnetization transfer experiments (Tables SVII and SVIII) (5 pages). Ordering information is given on any current masthead page.

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Direct Determination of the Self-Exchange Electron-Transfer Rate Constant for a Copper(II/I) Macrocyclic Pentathiaether Complex

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The value of the self-exchange electron-transfer rate constant for the macrocyclic pentathiaether complex $Cu^{II/I}([15]aneS_5)$ has been determined using ^1H NMR line-broadening measurements, both in D_2O and in 80% CD_3OD–20% D_2O (w/w). In the pure D_2O solvent studied over a range of 3 pD units and with varying amounts of excess $Cu^{2+}(aq)$ ion present, the best estimate of the 25 °C self-exchange rate constant is $k_{11} = 2 \times 10^5\ M^{-1}\,s^{-1}$ with activation parameters of $\Delta H^* = 14.0 \pm 4.0$ kJ mol^{-1} and $\Delta S^* = -103 \pm 11$ J mol^{-1} K^{-1}. On the basis of a single determination in 80% CD_3OD–20% D_2O, the corresponding values are $k_{11} = 0.8 \times 10^5\ M^{-1}\,s^{-1}$ (25 °C), $\Delta H^* = 19.6 \pm 1.1$ kJ mol^{-1}, and $\Delta S^* = -77 \pm 4$ J mol^{-1} K^{-1}. The 25 °C k_{11} value in D_2O is in virtual agreement with the corresponding calculated self-exchange rate constant value obtained by application of the Marcus cross relationship to the experimental rate constants previously reported for the *reduction* of $Cu^{II}([15]aneS_5)$ with ruthenium(II) and cobalt(II) complexes ($k_{11(\mathrm{Red})} = 3 \times 10^5\ M^{-1}\,s^{-1}$) but is considerably larger than a similar calculated value based upon an experimental rate constant previously determined for the *oxidation* of the corresponding $Cu^{I}([15]aneS_5)$ complex by an iron(III) complex ($k_{11(\mathrm{Ox})} = 8 \times 10^3\ M^{-1}\,s^{-1}$). These three k_{11} values appear to be consistent with our previous proposal that the Cu(II/I)–polythiaether complexes undergo electron transfer by a dual-pathway "square-scheme" mechanism in which the $Cu^{I}L$ metastable intermediate species is more stable than the corresponding $Cu^{II}L$ intermediate.

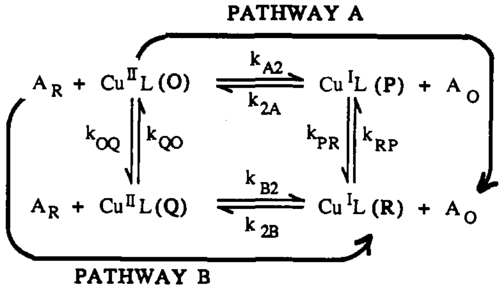
Introduction

In studying the kinetics of electron-transfer reactions involving various Cu(II/I) redox couples with selected counterreagents

$$Cu^{II}L + A_R \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} Cu^{I}L + A_O \qquad (1)$$

most investigators have reported only the reduction of $Cu^{II}L$ to $Cu^{I}L$ (i.e., only k_{12} values have generally been experimentally determined).[2] This reflects the fact that many $Cu^{I}L$ complexes are of low solubility, are subject to disproportionation, and/or are exceptionally sensitive to air oxidation, and, therefore, are more difficult to control as starting materials. For the few instances in which both the reduction and oxidation of a single redox couple have been reported, however, discrepancies have been noted in the self-exchange rate constant (k_{11}) values which are generated upon applying the Marcus relationship[3] to both the k_{12} and k_{21} values (i.e., $k_{11(\mathrm{Red})} \neq k_{11(\mathrm{Ox})}$).[4,5] This discrepancy is contrary to normal theoretical considerations for outer-sphere electron-transfer processes. Moreover, the direction of the discrepancy appears to depend upon the nature of the complex involved. For

Scheme I



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