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Inversion at the Sulfur Atom in Bis(diethyl sulfide)-(1,1,2,2-tetraacetylethane-*C*,*O′*)platinum(II)

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Synopsis. Variable temperature ^{1}H NMR suggests that the metal-carbon bonded Pt(II) complex of 1,1,2,2-tetraacetylethane(dahd=3,4-diacetyl-2,4-hexadiene-2,5-diol), [Pt(dahd-C^3,O')(SEt$_2$)$_2$] undergoes two distinct rearrangements at the sulfides, one of which is accompanied by an anomalous dissociation process. From a comparison of the estimated kinetic parameters for inversion, an arrangement of the two sulfides in planar geometry is proposed.

A number of studies concerning internal exchange processes of pyramidal sulfur have been done on Pt(II) and Pt(IV) complexes with symmetry.[1–6] ^{1}H NMR spectral change of methylene hydrogens from the AB(ABCD) to the A$_2$ spin system in *trans*-[MCl$_2${S(CH$_2$SiMe$_3$)$_2$}$_2$] (M=Pd, Pt),[3] [MCl$_2${S(Ph)(CH$_2$SiMe$_3$)}$_2$] (M=Pd, Pt),[3] *cis*-[PtCl$_2$(SEt$_2$)$_2$][6] has been sufficiently explained by the inversion process on the assumption of fast M–S and S–C bond rotations. Still, sulfur inversion in a Pt(II) complex with low symmetry is relatively elusive.

The authors have recently prepared several anomalous 1,1,2,2-tetraacetylethane Pd(II) and Pt(II) complexes, in which the ligand links a metal with the (*C*,*O′*)-chelate; [M(dahd-C^3,O')L$_2$]{M=Pd, L$_2$=1,10-phen;[7] M=Pt, L=SEt$_2$, PMe$_2$Ph, L$_2$=2,9-R$_2$-1,10-phen (R=H, Me)}.[8] They have formerly been characterized by means of ^{1}H, ^{13}C NMR {^1J(^{195}Pt-C^3)=489 Hz} and Fast Atom Bombardment Mass Spectroscopy (M$^+$= 572).[8] Of them, ^{13}C NMR of [Pt(dahd-C^3,O')(SEt$_2$)$_2$] at the ambient temperature unexpectedly shows an absence of ^{195}Pt satellites in resonances due to one SEt$_2$. These findings led us to investigate the rearrangement dynamics of pyramidal sulfides arranged unsymmetrically in square planar geometry, one of which may possibly proceed via some dissociation.

This note will deal with the inversion processes of two distinct sulfides in [Pt(dahd-C^3,O')(SEt$_2$)$_2$], as studied by variable-temperature ^{1}H NMR; moreover, from a comparison of the activation parameter of inversion, an arrangement of the sulfides will also be discussed.

Results and Discussion

^{1}H NMR pattern of [Pt(dahd-C^3,O')(SEt$_2$)$_2$] in CDCl$_3$ changes with the temperature, as is shown in Fig. 1. The changes are remarkable in resonances due to methylene hydrogen of SEt$_2$ (δ 2.4—3.3). Throughout the temperature change, two distinct resonance patterns (S^1, S^2) were obtained. This finding is, as expected, consistent with no mutual exchange of the sulfides. The signals arising from S^1 show a quartet with no ^{195}Pt satellite at 308 K, consistent with its ^{13}C NMR. On the other hand, the resonances arising from S^2 obviously show the ^{195}Pt satellite {J(^{195}Pt-H)=28.8Hz}, though the coupling constant is relatively small compared with those of 46.4 and 37.2 Hz

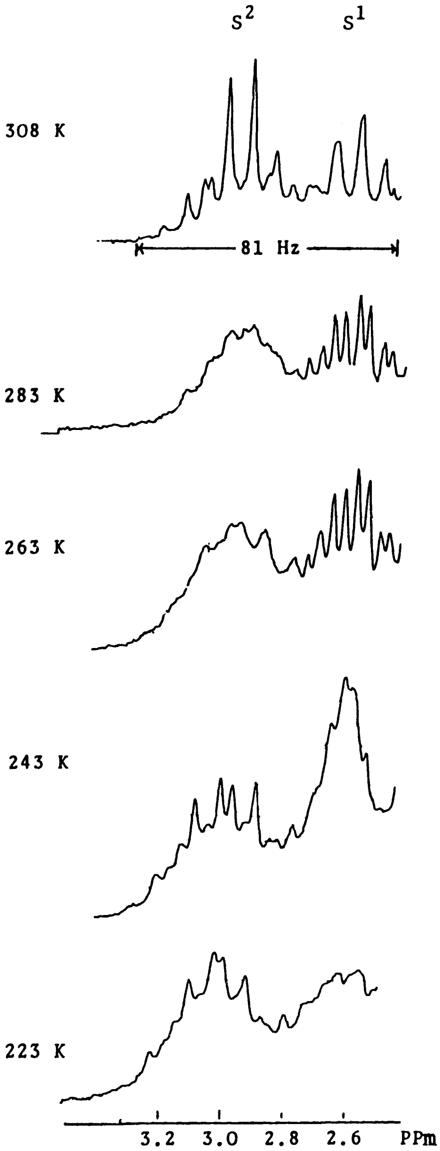

Fig. 1. Variable temperature ^{1}H NMR (resonances due to methylene proton of SEt$_2$) of Pt(dahd-C^3,O')(SEt$_2$)$_2$ in CDCl$_3$. The spectra were recorded using Hitachi R-90H FT NMR (90.04 MHz) operating Fourier transform mode. Deviation of temperature control was ±2%±1° on the centigrade temperature scale.

found for *cis*- and *trans*-$[PtCl_2(SEt_2)_2]$[6] respectively over the coalescence temperature.

The resonances due to S^2 at 283 K are very close to coalescence, but below 283 K the resonaces separate. At 243 K, four predominant quartets could be discerned with $J(H,H')=7.2$ Hz, although the complete analysis of $J(^{195}Pt\text{-}H)$ could not be performed. However the spectrum is in good agreement with the simulated lines of ABM_3 spin system with $J_{AB}=11.7$ and $J_{AM}=J_{BM}=7.2$ Hz. A spin-system change, $ABM_3 \rightleftarrows A_2M_3$, thus arising from S^2 corresponds to an averaging process of two pairs of methylene hydrogen. This mutual exchange of methylene hydrogen cannot be explained by rotation about the Pt–S and S–C bonds. The only process causing such an exchange is inversion at the pyramidal sulfur atom. The effect of inversion is shown in Fig. 3 as a preferred conformation, [A] or [B]. The symmetry plane bisecting the pyramidal sulfide ligand for both conformations is in coplanar with the coordination plane where the two conformations are enantiometrically related and where the methylene protons between the two groups are indistinguishable magnetically. The [B] conformation is obtained by the inversion of S^2 in [A] together with a 180° rotation about the Pt–S^2 bond and 120° rotation about the S^2–C bond; the net effect is a mutual exchange of methylene hydrogen. Concerning the so-called hindered rotation, no firm spectral evidence has been obtained in the Pt(II) and Pd(II) complexes so far

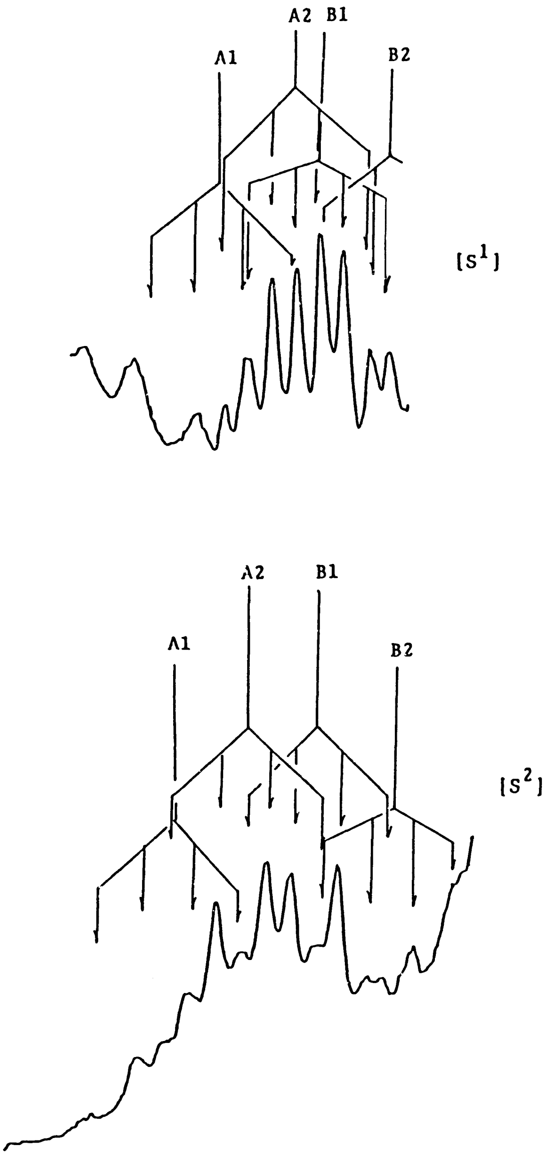

Fig. 2. AB part of ABM_3 spin system assigned to methylene hydrogen at; S^1 at 263 K and S^2 at 243 K.

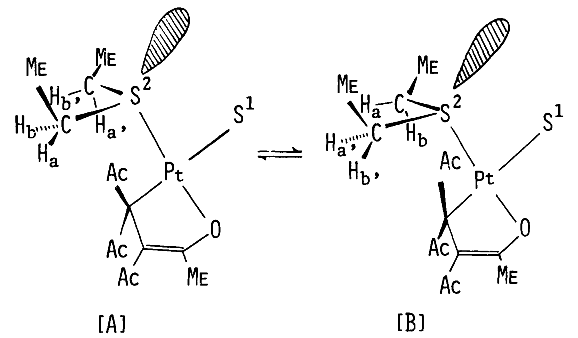

Fig. 3. A conformation [B] is obtained by inversion at S^2 in [A] together with 180° rotation about Pt–S bond and 120° rotation about S–C bond.

Table 1. Variable-Temperature ^{1}H NMR Data

T/K	$\Delta\nu$/Hz[a)]		J_{AB}/Hz[b)]		ΔG^*/kJ·mol^{-1}[c)]		k/s^{-1}[d)]	
	S^1	S^2	S^1	S^2	S^1	S^2	S^1	S^2
308					67.7			
	}[T_c]				|		}21.7(±0.4)	
283		[T_c]			62.0	65.8(±0.1)		45.0(±0.2)
263	9.70(±0.2)		11.3(±0.5)					
243		20.1(±0.1)		11.7(±0.1)				

a) Spacing estimated by $\sqrt{(A1-B2)(A2-B1)}$, where A1, A2, B1, and B2 are the chemical shifts due to the ABM_3 spin system observed for methylene hydrogen in the order of low-field resonances. b) Coupling constant $J_{H,H}$ within the methylene group. c) Calculated by the use of $\Delta G^*/RT_c=22.96+\ln(T_c/\Delta\nu)$, where ΔG^* is the activation parameter for the inversion of sulfide at the coalescence temperature; R. J. Abraham and P. Loftus, "Proton and Carbon-13 NMR spectroscopy-An Integrated Approach," Heydon and Son (1978). d) Inversion rate calculated by the use of $k=RT_c/Nh\exp(-\Delta G^*/RT_c)$. e) Coalescence may exist between 283—308 K, and its ΔG^* was arbitrarily estimated, with 283 K as its lower limit and 308 K as its upper limit. f) Coalescence temperature.

studied even at 213 K,[3] which can be assumed to be fast. In the present case also, the rotation about Pt–S^2 bond is tentatively presumed to be fast in the NMR time scale. The activation parameter for the inversion process at S^2 was thus estimated to be $\Delta G^*(T_c=283\ \mathrm{K})=65.8\ \mathrm{kJ\cdot mol^{-1}}$ and k (inversion rate at T_c)$=45.0\ \mathrm{s^{-1}}$. These activation parameters obtained for $[\mathrm{Pt(dahd}\text{-}C^3,O')(\mathrm{SEt_2})_2]$ are comparable with those of $\Delta G^*=70.3\ \mathrm{kJ\cdot mol^{-1}}$ and $k=64.7\ \mathrm{s^{-1}}$ ($T_c=333$ K) found for *cis*-$[\mathrm{PtCl_2(SEt_2)_2}]$ and those of $58.2\ \mathrm{kJ\cdot mol^{-1}}$ and $k=36.4\ \mathrm{s^{-1}}$ ($T_c=274$ K) for its trans form.

On the other hand, low-temperature ^{1}H NMR (resonances arising from S^1Et_2) shows an analogous and more explicit spectral change, while its ^{13}C NMR at the ambient temperature exhibits no ^{195}Pt satellites. The coalescence temperature is in the vicinity of 300 K. The resonances at 263 K, which seem to be two quartets overlapping, are, however, assigned to the AB part of the ABM_3 spin system; the spectrum accords well with lines simulated using the five-spin system with $J_{AB}=11.3$ and $J_{AM}=J_{BM}=7.2$ Hz. We could not, unfortunately, obtain precise information whether or not ^{195}Pt–H coupling exists at that temperature. The spin system change thus arising from S^1, $ABM_3 \rightleftarrows A_2M_3$, corresponds to an averaging process of methylene hydrogen and can also be explained only by an inversion process. However, this inversion cannot proceed intramolecularly, because the lack of ^{195}Pt–H and ^{195}Pt–C couplings indicates a bond breakage of the sulfide, S^1. In fact, on the addition of the free ligand SEt_2 into $[\mathrm{Pt(dahd}\text{-}C^3,O')(\mathrm{SEt_2})_2]$, only the broad resonances arising from S^1, whose spectrum is close to the coalescence temperature, became a sharp and single quartet with an increase in the intensity, while its chemical shift did not change. For the spectral change with the temperature due to S^1, T_c has not definitely been fixed. The activation free energy was arbitrarily estimated at the two temperatures, 283 and 308 K, to be 62.0 and $67.7\ \mathrm{kJ\cdot mol^{-1}}$ respectively. Although such a rough estimation for ΔG^* gives a fair deviation, the inversion rates k thus derived at both temperatures eventually approach $21.7\ \mathrm{s^{-1}}$, unaccompanied by any significant deviations. Accordingly, the inversion rate of S^1 estimated at 283 K can be compared with that of S^2, which unexpectedly results in one half of the rate of S^2. As has been established formerly,[8] S^1 in $[\mathrm{Pt(dahd}\text{-}C^3,O')(\mathrm{SEt_2})_2]$ is readily displaced by PPh_3 to give $[\mathrm{Pt(dahd}\text{-}C^3,O')(\mathrm{PPh_3})(\mathrm{S^2Et_2})]$, in which PPh_3 is arranged trans to $C^3\{J(^{31}P\text{–}C^3)=60\ \mathrm{Hz}\}$. By accounting for the trans labilizing effect: C(3)(from $acac^-$)> O(from $acac^-$),[8,9] S^1 undergoing rearrangement via a bond breakage should be arranged trans to C(3) from the $dahd^{2-}$. If an analogous intramolecular rearrangement can be presumed, the inversion of S^1 should proceed much faster than that of S^2. In contrast to this expectation, the inversion rate of S^1, accompanied by bond dissociation, is comparatively much slower than that of S^2. It is most likely that the rearrangement of S^1 proceeds via an intermolecular pathway.[10]

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