Dynamic NMR as a Nondestructive Method for the Determination of Rates of Dissociation. XVI. Mechanism of Sulfur Inversion in Platinum(II)-Thioether Complexes Revisited[1)]

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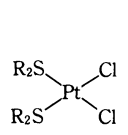
The mechanism of sulfur inversion in some platinum(II)–thioether complexes was reinvestigated with the use of the dynamic NMR technique. Activation parameters for the sulfur inversion in [(isopropylthio)acetato-*O*,*S*]bis(triphenylphosphine)platinum(II) perchlorate in $CDCl_3$ were obtained by taking advantage of the line shape changes in its ^1H NMR spectra at various temperatures as follows: ΔH^* 18.0±0.4 kcal mol^{-1}, ΔS^* 4.0±1.4 cal mol^{-1} K^{-1}. The kinetic parameters varied little, though the rates of inversion were determined in other solvents. The entropy of activation and the solvent effects together with the presence of coupling between the phosphine-^{31}P and the methine-^1H throughout the temperature range of investigation evidence the sulfur inversion without breaking the Pt–S bond. The sulfur inversion in dichlorobis(dialkyl sulfide)platinum(II) in nonpolar solvents was also concluded to take place without bond breakage.

While it is well known that the sulfur inversion in organic sulfonium ions is slow to make it possible to isolate enantiomers at room temperature,[2)] if they are properly substituted, that in coordination compounds is much faster to make it amenable to dynamic NMR study and consequently isolation of isomers due to the sulfur inversion impossible at room temperature. The typical examples among the coordination compounds are *cis*-dichlorobis(dialkyl sulfide)platinum(II) (**1**) and *trans*-dichlorobis(3,3-dimethylthietane)platinum(II) (**2**).



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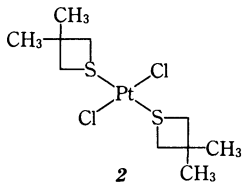

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Dynamic NMR spectral study on the inversion of the thioether ligands in compound **1** was carried out and it was concluded that the inversion did not involve the scission of the Pt–S bond by observing the coupling between ^{195}Pt and ^1H nuclei even at temperatures where coalescence of diastereotopic proton signals took place.[3,4)] However, close examination of the published figure discloses that the peaks attributed to the coupling are rather broad. In addition, it might be possible to argue that, since the compounds in question possess a pair of dialkyl sulfide ligands, one of the sulfur-ligands may be bonded to the platinum during the process of sulfur-detachment, thus the coupling being observed always.

We have shown in our previous works that, if the process involves bond-breakage in compounds of which ground state is ionic, the entropy of activation must be large positive, whereas it is large negative, if the compound in question is of covalence in its ground state.[5)] Using this generalization, we have shown that sulfur compounds are no exceptions. The entropy of activation for sulfur inversion in a thioether–borane and another complex was shown to be large negative, because the mechanism involves bond-dissociation,[1)] suggesting that the thioether complex possesses ionic nature at its ground state. By contrast, sulfonium salts, in which bond-dissociation was not likely, showed nearly zero entropy of activation by both classical[6)] and dynamic NMR method.[7)]

Actually, the dynamic NMR study of compounds **1** and **2** has been carried out. However, the method used for compound **1** was the line-width method which is known to tend to give erroneous entropy of activation.[8)] The total line shape analysis was carried out for compound **2**.[9)] However, due to the simplicity of the line shapes of the diastereotopic gem-dimethyl group,[10)] the reliability of the entropy of activation can be questioned.

Based on these experiences, we felt it would be appropriate to apply the total line shape analysis with the use of probes which would give complex signals[10)] for diagnosis of the mechanism of sulfur inversion in platinum–thioether complexes. This paper is to report the results of such investigation.

Results and Discussion

Platinum(II) Complexes with One Thioether Ligand. Clearly, a compound which has only one thioether ligand is desirable to avoid the complexity. A recent publication described the preparation of compound **3**, of which thioether ligand showed the dynamics in its NMR spectra, though the free energies of activation only have been reported.[11)]

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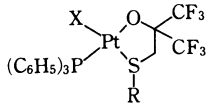

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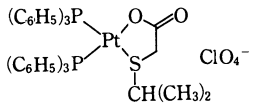

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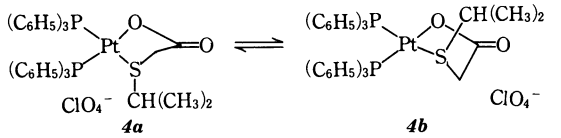
We decided to use this type of compounds for our investigation and prepared compound **4** by treating *cis*-dichlorobis(triphenylphosphine)platinum(II) with potassium (isopropylthio)acetate followed by silver perchlorate. We have selected this compound because the isopropyl probe for the exchange of their magnetic sites on inversion should not show coupling with platinum to make it much easier to carry out the line shape simulation and the isopropyl-methyls give complex enough signals to assure the reliability of the data thus obtained.

Although similarly prepared chloro[(isopropylthio)-acetato-*O,S*](triphenylphosphine)platinum(II) did show the change in the line shapes on heating at above 100 °C, decomposition set in at the same time. Compound **4** by contrast showed the desired line shape change without decomposition, thanks to the trans influence.[12] The process may be written as in the following scheme.



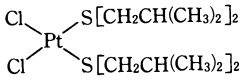
4a 4b

Kinetic parameters obtained by simulation of the line shapes are shown in Table 1. The feature of the kinetic parameters is the near zero entropy of activation. From our experience in the past, the results support the idea that the sulfur inversion in the platinum complex takes place without bond dissociation, namely the simple inversion of sulfur. Further support for the mechanisms proposed is obtained from the following observations.

One is the coupling between the isopropyl-methine proton and one of the phosphorus atoms in the ligands. This coupling was observed at room temperature and was persistent at 90 °C where the coalescence of the signals due to the isopropyl-methyl group took place.

The other piece of evidence is the solvent effects. The activation parameters obtained with **4** in various solvents are listed in Table 1. The data clearly show that the activation parameters are not dependent on the solvent used and entropy of activation is always close to zero. If the mechanism of the sulfur-inversion involved the S–Pt bond scission, the inversion would have been fast in the solvents of which affinity toward platinum was high.

Platinum(II) Complexes with Two Thioether Ligands. Coming back to the problem of the platinum complexes that contain two molecules of sulfur ligands, we were interested in knowing whether these compounds as well demonstrate the near zero entropy of activation for sulfur inversion. We selected *cis*- and *trans*-dichlorobis(diisobutyl sulfide)platinum(II) (**5** and **6** respectively) for our investigation. These compounds were prepared by the known method from potassium tetrachloroplatinate(II) and diisobutyl sulfide. Their cis- and trans-isomers were assigned by the behavior in chromatography as well as the coupling constants between the platinum and the α-proton of the isobutyl group: the cis compound gives a larger coupling constant than the trans.[13]



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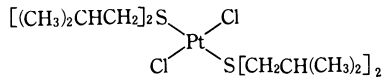

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The kinetic parameters obtained by total line shape analysis of these compounds are shown in Table 2, in which rate constants rather than free energies of activation are shown to demonstrate small differences in the rates. The results clearly show that the inversion of the thioether ligands in the trans isomer is more facile than in the cis, again due to the trans influence. The entropy of activation is not very far from zero.

The results can be interpreted on the basis of sulfur inversion without bond dissociation and that the complexity in the sulfur-inversion due to the presence of two thioether ligands can be ruled out. The existence of coupling between ^{195}Pt and ^{1}H at the α-position of the thioether ligand at temperatures higher than the coalescence point of the isopropyl-methyl

Table 1. Kinetic Parameters for Sulfur Inversion in Compound **4** in Various Solvents[a]

Solvent	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/kcal mol^{-1} K^{-1}	$\Delta G^{\ddagger}_{298}$/kcal mol^{-1}
$CDCl_3$	18.0±0.4	4.0±1.4	16.8
$(CD_3)_2CO$	18.5±0.7	4.8±2.0	17.1
CD_3NO_2	17.8±0.3	3.6±1.0	16.7
$(CD_3)_2SO$	17.9±0.4	2.6±1.3	17.1

a) 1 cal=4.184 J.

Table 2. Kinetic Parameters for Sulfur Inversion in Compounds **5** (Cis) and **6** (Trans) in Various Solvents

Form	Solvent	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}	k_{298}/s^{-1}
Cis	C_7D_8[a]	15.1±0.3	−2.6±0.8	15.1
	$CDCl_3$	17.2±0.5	4.7±1.4	17.3
	$(CD_3)_2CO$	17.6±0.6	7.5±1.8	33.6
	CD_3OD	16.6±0.4	3.6±1.3	26.3
Trans	C_7D_8[a]	12.6±0.3	−2.0±1.1	11.5×10^3
	CD_2Cl_2	11.7±0.3	−6.1±1.0	7.9×10^3

a) Toluene-d_8.

proton signals was confirmed.

Factors Affecting Sulfur-Inversion. Interesting is the fact that the solvent effect on the rates of sulfur-inversion in **5** is significant. The rates of inversion is larger in more polar solvents than in the less polar. We postulate that in these compounds solvent-assisted inversion of sulfur is involved to some extent. The difference between **4** and **5** may be attributed to the trans influence: if the Pt–S bond is weakened, the solvent assistance becomes more important.

The results provide a hint in considering the cause of the fast or slow inversion of sulfur. It was suggested in the literature[4] that the stabilization of the transition state for inversion due to the $p\pi$–$d\pi$ interaction would be the cause for more facile inversion in the platinum complexes than in the sulfonium ions. It may be argued that the sulfur inversion in the platinum complexes is easier than in organic sulfonium compounds because the pyramidality[14] of the sulfur which is connected to the platinum and two alkyl ligands is smaller in the ground state than the sulfonium ions because of the $p\pi$–$d\pi$ interaction. However, if it were the case, the thioethers that are bonded by a short bond should invert more rapidly than that connected by a long bond. Thus we agree with the old postulate as the explanation of the easier sulfur inversion in the platinum complexes.

The relatively slow inversion of the thioether ligand in compound **4**, despite the fact that the strong trans effect of the phosphine ligand[4] should reduce the barrier, deserves mention here. We believe this is due to the ring puckering of the ligand. The facts that the chemical shift difference between the two protons of the α-methylene group in the acetate ligand is as large as ca. 1 ppm and that only one of these protons shows couplings with ^{195}Pt and ^{31}P support that the five-membered ring made by the ligand and the platinum is fairly puckered. Probably the planar transition state for inversion in this compound is accordingly of high energy.

Experimental

***cis*-[(Isopropylthio)acetato-*O,S*]bis(triphenylphosphine)-platinum(II) Perchlorate (4).** (Isopropylthio)acetic acid[16] (34 mg or 0.25 mmol) was added to 19 mg (0.34 mmol) of potassium hydroxide in 20 mL of ethanol. To this solution was added 0.20 g (0.25 mmol) of *cis*-dichlorobis(triphenylphosphine)platinum(II)[17] in 10 mL of dichloromethane and the whole was stirred for 2.5 h at room temperature. The precipitate was removed by filtration and 60 mg (0.29 mmol) of silver perchlorate was added to the filtrate. The resulting silver chloride was immediately removed by filtration and the filtrate was stirred for 20 h. The solvent was evaporated and the residue was extracted with dichloromethane and the extract was washed with water. After evaporation of the solvent, the residue was recrystallized from ethanol to afford 0.12 g (49%) of the desired compound which contained 1/2 molecule of ethanol, mp 155—160 °C (decomp). Found: C, 51.72; H, 4.34%. Calcd for $C_{41}H_{39}ClO_6P_2PtS\cdot0.5C_2H_6O$: C, 51.45; H, 4.41%. ^{1}H NMR ($CDCl_3$, −20 °C) δ=0.98 (3H, d, J=6.8 Hz), 1.55 (3H, d, J=6.8 Hz), 2.74(1H, double septet, J=6.8 and 1.6 Hz), 3.36 (1H, dd, J=17.1 and 3.2 Hz), 4.26 (1H, d, J=17.1 Hz), 7.3—7.7 (30H, m).

***cis*- and *trans*-Dichlorobis(diisobutyl sulfide)platinum(II) (5 and 6).** To a solution of 0.88 g (2.1 mmol) of potassium tetrachloroplatinate(II) in 40 mL of water was added 0.31 g (2.1 mmol) of diisobutyl sulfide[18] in 6 ml of ethanol. The mixture was stirred for ca. 90 h at room temperature and an oily product was separated by decantation. The product was submitted to chromatography on silica gel with a 1:1 hexane–dichloromethane eluent. The trans form was eluted first and then came the cis form. The separated products were recrystallized from ethanol.

Cis-form, yellowish green crystals, mp 130 °C, was obtained in 21% yield. Found: C, 34.13; H, 6.57; Cl, 12.82; S, 11.79%. Calcd for $C_{16}H_{36}Cl_2PtS_2$: C, 34.41; H, 6.50; Cl, 12.69; S, 11.48%. ^{1}H NMR ($CDCl_3$, −20 °C) δ=1.00 (3H, d, J=6.6 Hz), 1.05 (3H, d, J=6.6 Hz), 2.20 (1H, app septet J=ca. 6.5 Hz), 2.43 (1H, dd, J=11.9 and 8.5 Hz), 3.19 (1H, dd, J=11.9 and 5.7 Hz).

Trans-form, yellow crystals, mp 106 °C, was obtained in 16% yield. Found: C, 34.12; H, 6.55; Cl, 12.85; S, 11.46%. Calcd for $C_{16}H_{36}Cl_2PtS_2$: C, 34.41; H, 6.50; Cl, 12.69; S, 11.48%. ^{1}H NMR (toluene-d_8, −18 °C) δ=0.94 (6H, d, J=6.4 Hz), 1.82 (1H, br s), 2.27 (1H, app septet, J=ca. 6.3 Hz), 3.08 (1H, br s).

Dynamic NMR Spectroscopy. The spectra were obtained with a JEOL GX270 spectrometer. The temperature was calibrated with a thermocouple. The sample was dissolved in appropriate solvents to make up a ca. 50 mmol L^{-1} solution. The simulation of the line shapes was performed with the use of DNMR3 program[19] by assuming the site exchange process of $A_3B_3X \rightleftarrows B_3A_3X$ which was approximated as $ABX \rightleftarrows BAX$.

Table 4. Rate Constants of Sulfur Inversion in Compounds **4**, **5**, and **6** in Various Solvents

Compound	Solvent	k/s^{-1} (temperature/°C)
4	$CDCl_3$	7.4 (33.9), 10.5 (37.9), 16.0 (41.9), 34.0 (49.9), 54 (55.4), 82 (60.4)
4	$(CD_3)_2CO$	7.4 (38.0), 11.2 (42.0), 16.5 (45.9), 22.0 (49.4), 28.5 (52.1), 38 (55.2)
4	CD_3NO_2	11.1 (37.9), 16.9 (41.9), 24.8 (46.0), 36.8 (50.0), 58 (55.4), 88 (60.4), 196 (70.4), 410 (80.4)
4	$(CD_3)_2SO$	7.6 (40.0), 12.0 (44.9), 19.2 (50.0), 32.5 (55.4), 51 (60.5), 112 (70.4), 235 (80.4), 460 (90.3)
5	C_7D_8[a]	6.1 (14.8), 8.2 (17.8), 10.6 (20.9), 13.9 (23.9), 18.0 (26.8), 23.4 (29.8)
5	$CDCl_3$	6.2 (14.8), 8.0 (17.3), 10.4 (19.8), 13.5 (22.4), 16.4 (25.2), 22.6 (27.9)
5	$(CD_3)_2CO$	3.8 (4.8), 5.1 (7.4), 6.5 (9.8), 8.5 (12.3), 11.1 (14.8), 15.2 (17.3)
5	CD_3OD	3.9 (6.9), 5.0 (8.8), 6.3 (10.9), 7.6 (12.9), 9.6 (15.1), 11.5 (16.9)
6	C_7D_8[a]	3.8 (−35.8), 4.5 (−34.4), 5.6 (−32.8), 6.5 (−31.4), 7.6 (−30.0), 11.5 (−26.,3)
6	CD_2Cl_2	3.7 (−36.9), 4.4 (−35.3), 5.4 (−33.1), 6.6 (−31.2), 8.4 (−29.1), 10.7 (−26.9)

a) Toluene-d_8.

Table 3. Relationships between the Chemical Shift Differences of the Diastereotopic Protons and Temperature

Compound	Solvent	$\Delta\nu/s^{-1}=At/°C+B$	
		A	B
4	$CDCl_3$	−0.3512	145.55
4	$(CD_3)_2CO$	−0.2946	125.65
4	CD_3NO_2	−0.3153	136.34
4	$(CD_3)_2SO$	−0.2626	109.98
5	C_7D_8[a]	0.0274	13.52
5	$CDCl_3$	0.0351	12.69
5	$(CD_3)_2CO$	0.0009	5.36
5	CD_3OD	0.0347	9.38
6	C_7D_8[a]	0.150	3.63
6	CD_2Cl_2	0.0102	5.43

a) Toluene-d_8.

The coupling constants and the chemical shift differences at various temperatures were estimated by the tendency observed from the several points in the slow exchange limit. The coupling constants were constant throughout the temperature range to let us assume they were the same at temperatures where the line shapes changed. The chemical shift differences drifted when the temperature was changed and were correlated linearly with temperature. The relationships are given in Table 3. These lines were extrapolated to the temperature where the line shape change was observed. T_2 was estimated from the line width due to the protons which were not involved in the exchange and varied from 0.08 to 0.17 s for compound **4** and 0.14—0.24 s for compounds **5** and **6** according to the conditions of the measurement. The T_2 was adjusted, when necessary, to make the fit of the calculated line shapes better than the fixed value. The rate constants of site exchange thus obtained are compiled in Table 4.

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References

1) For Part XV of the series, see M. Ōki and Y. Yamada, *Bull. Chem. Soc. Jpn.*, **61**, 1191 (1988).
2) M. Mikolajczyk and J. Drabowicz, *Top. Stereochem.*, **13**, 333 (1982).
3) P. Haake and P. C. Turley, *J. Am. Chem. Soc.*, **89**, 4611 (1965).
4) P. C. Turley and P. Haake, *J. Am. Chem. Soc.*, **89**, 4617 (1965).
5) T. Morita and M. Ōki, *Bull. Chem. Soc. Jpn.*, **59**, 3603 (1986) and papers cited therein.
6) R. Scartazzini and K. Mislow, *Tetrahedron Lett.*, **1967**, 2719: M. Ōki, Y. Yamada, and S. Murata, *Bull. Chem. Soc. Jpn.*, **61**, 707 (1988).
7) M. Ōki and Y. Yamada, *Bull. Chem. Soc. Jpn.*, **61**, 1181 (1988).
8) M. Ōki, "Applications of Dynamic NMR Spectroscopy to Organic Chemistry," VCH Publishers, Deerfield Beach (1985), pp. 22—30.
9) E. W. Abel, M. Booth, and K. G. Orrell, *J. Chem. Soc., Dalton Trans.*, **1974**, 1994.
10) M. Nakamura, H. Kihara, N. Nakamura, and M. Ōki, *Org. Magn. Reson.*, **12**, 702 (1979): G. Binsch and H. Kessler, *Angew. Chem., Int. Ed. Engl.*, **19**, 411 (1980).
11) R. T. Boere and C. J. Willis, *Can. J. Chem.*, **64**, 492 (1986).
12) A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. A*, **1966**, 1707: T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).
13) S. M. Grim, R. L. Keiter, and W. McFarlane, *Inorg. Chem.*, **6**, 1133 (1967).
14) J. D. Dunitz, "X-Ray Analysis and the Structure of Organic Molecules," Cornell University Press, Ithaca (1979), pp. 366—384.
15) R. Gosling and M. L. Tobe, *Inorg. Chem.*, **22**, 1235 (1983). See also Ref. 12.
16) L. D. Petit and C. Sherrington, *J. Chem. Soc. A*, **1968**, 3078.
17) J. C. Bailar, Jr., and H. Itatani, *Inorg. Chem.*, **4**, 1618 (1965).
18) D. T. McAllan, T. V. Cullum, R. A. Dean, and F. A. Fidler, *J. Am. Chem. Soc.*, **73**, 3627 (1951).
19) G. Binsch, *Top. Stereochem.*, **3**, 97 (1968).