

# Proton Magnetic Resonance Spectra of Platinum(II) Complexes. I. Pyramidal Configuration and Inversion at Sulfur in *cis*-Bis(dibenzyl sulfide)dichloroplatinum(II). Temperature and Solvent Effects on AB Chemical Shifts<sup>1-3</sup>

Paul Haake and Patricia Cronin Turley

Contribution No. 2071 from the Department of Chemistry, University of California, Los Angeles, California 90024. Received March 14, 1967

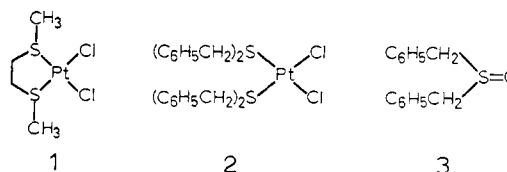
**Abstract:** Nuclear magnetic resonance spectra of *cis*-bis(dibenzyl sulfide)dichloroplatinum(II) indicate that in the ground state the sulfur atoms are pyramidal. Dynamic structure is also found: the sulfur atoms invert with a rate constant of  $10.3 \text{ sec}^{-1}$  at  $34.5^\circ$ , and the inversion process does not involve dissociation of the Pt-S bond. The activation energy,  $E_a$ , required for inversion at sulfur is 18.0 kcal/mole; the logarithm of the frequency factor is 13.8. These results come from study of the methylene region of the nmr spectra. The methylene resonance was proven to be an AB (66.3% due to Pt with  $I = 0$ ) + ABX (33.7% due to  $^{195}\text{Pt}$  with  $I = 1/2$ ) pattern by three experiments: double irradiation, inducement of a double-quantum transition, and amplification of the normal spectrum with a time-averaging computer. The two vicinal platinum-proton coupling constants are 29.3 and 55.7 cps at  $35^\circ$ . The AB chemical shift in this complex and in dibenzyl sulfoxide is dependent on temperature and solvent polarity.

The compound under study in this paper is *cis*-bis(dibenzyl sulfide)dichloroplatinum(II) (2). It is well known that platinum(II) complexes are planar, leading to the possibility of *cis* and *trans* isomers. But there are important structural questions beyond that. Which rotamers are favored in rotation about carbon-sulfur and sulfur-platinum bonds? What is the configuration at sulfur? If sulfur is pyramidal as in sulfides, how fast is inversion? Is there any barrier to rotation about sulfur-platinum bonds? This paper provides some experimental evidence bearing on these questions.

Although many metal-organosulfur complexes are known, there are very little structural data available. Crystallographic studies indicate that in a diethyl sulfide-mercury complex<sup>4</sup> and a nickel mercaptide polymer<sup>5</sup> the sulfur atom is pyramidal. In solution, recent nmr studies<sup>3,6</sup> show that sulfur is pyramidal when bonded to platinum and palladium. Moreover, inversion at sulfur is much faster than in sulfoxides<sup>7-10</sup> and sulfonium ions.<sup>11</sup> A study by Abel, Bush, Hopton,

and Jenkins<sup>6</sup> involved a sulfur chelate (1). In 1, inversion at sulfur could occur by breaking one S-Pt bond and re-forming it with the other configuration at sulfur.

This paper describes in detail the nmr behavior of *cis*-bis(dibenzyl sulfide)dichloroplatinum(II) (2). The dependence of the AB chemical shift (nonequivalent methylene protons) of 2 on temperature and solvent polarity is compared with that of the corresponding system in dibenzyl sulfoxide (3).



## Experimental Section

**Nmr Spectra.** The nmr spectra were recorded with two Varian A-60's, one of which was equipped with a variable-temperature probe, and a Varian HR-60 equipped with a temperature probe and a frequency-sweep unit. Spectra were calibrated by the side-band technique<sup>12</sup> using Hewlett-Packard 200AB or 200CD wide-range oscillators and a Hewlett-Packard 5233L frequency counter. Chemical shifts were measured relative to internal tetramethylsilane.

**Preparation of *cis*-Bis(dibenzyl sulfide)dichloroplatinum(II).** A mixture of benzyl sulfide and  $\text{K}_2\text{PtCl}_4$  (mole ratio 3:1) in water was shaken for 24 hr. The solid was filtered off and triturated with benzene. Evaporation of the benzene extract produced the yellow complex which was recrystallized from acetone several times; decomposition occurs at  $150\text{--}157^\circ$  (lit.<sup>13</sup>  $150^\circ$ ).

**Anal.** Calcd for  $\text{C}_{28}\text{H}_{28}\text{Cl}_2\text{PtS}_2$ : C, 48.40; H, 4.06. Found: C, 48.53; H, 4.31. Infrared: two broad Pt-Cl bands at 324 and  $314 \text{ cm}^{-1}$ .

**Preparation of Dibenzyl Sulfoxide.** Dibenzyl sulfide was oxidized with sodium metaperiodate in 50% aqueous ethanol according to Leonard and Johnson's method,<sup>14</sup> mp  $132\text{--}133^\circ$ .

(12) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

(13) v. K. A. Jensen, *Z. Anorg. Allgem. Chem.*, **231**, 365 (1937).

(14) N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).

- (1) Dedicated to the late Dr. A. J. R. Bourn.
- (2) Research supported in part by Grant GP-3726 from the National Science Foundation, by Grant AM-6870 from the U. S. Public Health Service, and by an Alfred P. Sloan Research Fellowship to P. H.
- (3) A preliminary report of this work has appeared: P. Haake and P. C. Turley, *Inorg. Nucl. Chem. Letters*, **2**, 173 (1966).
- (4) C.-I. Branden, *Arkiv Kemi*, **22**, 83 (1964).
- (5) P. Woodward, L. F. Dahl, E. W. Abel, and B. C. Crosse, *J. Am. Chem. Soc.*, **87**, 5251 (1965).
- (6) E. W. Abel, R. P. Bush, F. J. Hopton, and C. R. Jenkins, *Chem. Commun.*, 58 (1966).
- (7) (a) K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965; (b) C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Co., New York, N. Y., 1962.
- (8) K. Mislow, M. Axelrod, D. R. Rayner, H. Gotthardt, L. M. Coyne, and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 4958 (1965).
- (9) (a) H. B. Henbest and S. A. Kahn, *Proc. Chem. Soc.*, 56 (1964); (b) K. Mislow, P. Schneider, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **86**, 2957 (1964); (c) C. R. Johnson and D. McCants, Jr., *ibid.*, **86**, 2935 (1964).
- (10) (a) K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *ibid.*, **86**, 1452 (1964); (b) C. R. Johnson and D. McCants, Jr., *ibid.*, **87**, 5404 (1965).
- (11) (a) M. P. Balfe, J. Kenyon, and J. Phillips, *J. Chem. Soc.*, 2554 (1930); (b) D. Darwish and G. Tourigny, *J. Am. Chem. Soc.*, **88**, 4303 (1966).

## Results

The probe temperature proton magnetic resonance spectrum of **2** (methylene region only) is shown in Figure 1a. The methylene protons are represented by five peaks having a mean chemical shift at  $-230$  cps. The large, closely spaced doublet integrates for four times the area of the single downfield peak. The separation between the most upfield and the most downfield peaks is 50 cps, and the midpoint falls within the "center" doublet. The distance between the second upfield peak and the single downfield peak is 36 cps with a midpoint coinciding with the downfield half of the center doublet. Since 33.7% of naturally occurring platinum is  $^{195}\text{Pt}$  ( $I = 1/2$ ), the spectrum can be interpreted as an ABX (34%) pattern superimposed upon an AB (66%) pattern with  $J_{\text{AX}} (\sim 50 \text{ cps}) \neq J_{\text{BX}} (\sim 36 \text{ cps})$ .

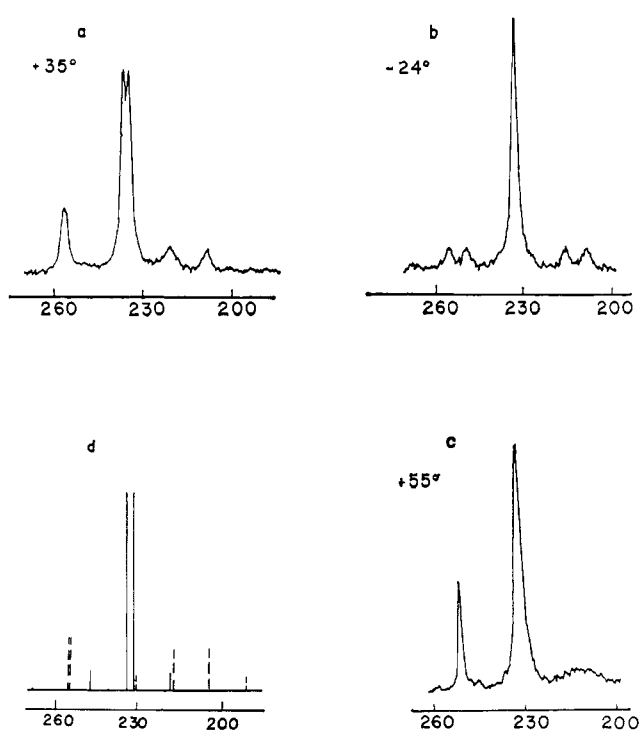
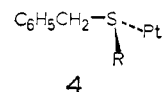


Figure 1. Methylene region of nmr spectra of *cis*-bis(dibenzyl sulfide)dichloroplatinum(II) (**2**): (a) at normal probe temperature; (b) at  $-24^\circ$ ; (c) at  $+55^\circ$ ; (d) calculated spectrum for AB (—, 66.3%) and ABX (---, 33.7%).

Lowering the temperature causes the downfield platinum satellite to split into two broad peaks as is shown in Figure 1b. The center doublet collapses to a singlet although the methylene protons must still be nonequivalent since there are four platinum satellites. Raising the temperature produces coalescence; Figure 1c ( $55^\circ$ ) is near the coalescence temperature for the upfield satellites, although the center absorption is a fairly sharp singlet at this temperature. The single platinum proton coupling at  $55^\circ$  is  $\pm 43.0$  cps, the average of the two frequency separations found at lower temperatures.

These nmr observations can be explained by an AB system caused by a pyramidal sulfur and the molecular environment shown in **4**. An averaging process such

as inversion would produce an  $A_2$  system as is observed at higher temperatures. However, some of the signals predicted for the AB region in an AB + ABX system<sup>12</sup> are not observed, so this explanation cannot be confirmed from the spectra.



There are two other possible explanations which do not require the presence of more transitions than those observed. (1) The methylene groups could be nonequivalent because of restricted rotation about the Pt-S bond. Models make steric inhibitions to rotation seem unlikely, but double bond character caused by d-d  $\pi$  bonding in the square-planar complex (the filled platinum d orbitals are not all degenerate) might be involved.<sup>15</sup> (2) There could be two different sulfide groups caused by a distorted square-planar geometry,<sup>16</sup> but this seems unlikely.

Three methods have been used to detect hidden resonances and demonstrate the presence of an A-B system. First, we have utilized the effects of indirect spin-spin interactions. Figure 2 records the pmr spectra of the methylene protons of **2** when subjected to weak irradiation according to the method of Freeman

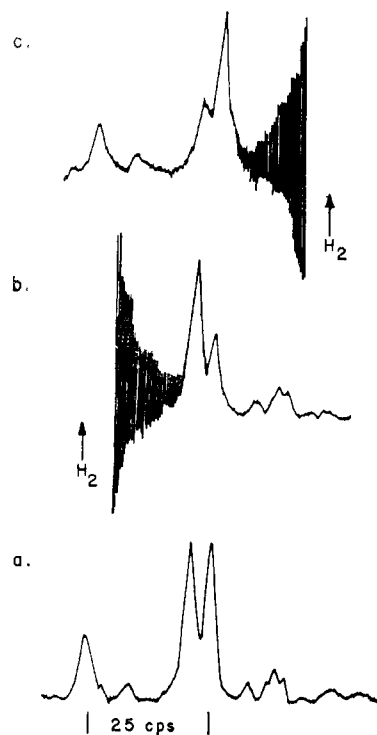


Figure 2. Methylene region in nmr spectrum of *cis*-bis(dibenzyl sulfide)dichloroplatinum(II) (**2**);  $+11.8^\circ$ ; solvent is  $\text{CHCl}_3$ - $\text{C}_6\text{H}_5\text{NO}_2$  (1:1). Some impurity peaks are present (see Figure 1a): (a) frequency-sweep spectrum; (b) irradiation of low-field side of center doublet; (c) irradiation of high-field side of center doublet.

(15) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 332 (1954).

(16) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962).

and Anderson.<sup>17</sup> The alteration in line shape of the center doublet is due to irradiation of the weak hidden, outer resonances of the center AB quartet.<sup>17</sup> The transition regressive to the irradiated transition is not cleanly split as is often true,<sup>17</sup> probably because the magnitude of splitting is proportional to the square root of the intensity of the irradiated line.<sup>17,18</sup> The irradiated lines are very weak in this case, and only broadening of the regressive transition is observed.<sup>19</sup>

Secondly, a technique has recently been developed for assigning progressive transitions in an energy-level diagram.<sup>18</sup> If the radiofrequency power is increased until single-quantum transitions saturate and double-quantum transitions begin to appear, then the frequencies of the double-quantum transitions must correspond closely to the average of two progressively related single-quantum transitions. This method is applicable to the dibenzyl sulfide complex. The two energy diagrams (AB + ABX) constructed from the results of the double-resonance experiment predict double-quantum transitions at about -233 cps for the AB system and at -255 and -211 cps for the ABX system in the proton spectrum. Figure 3 shows the dependence of the pmr spectra of the methylene protons

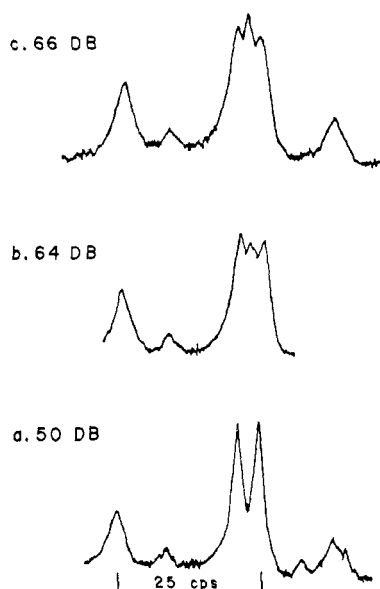


Figure 3. Double-quantum transitions in the nmr spectra of the methylene region of *cis*-bis(dibenzyl sulfide)dichloroplatinum(II) (2). Some impurity peaks are present (see Figure 1a): (a) normal spectrum with radiofrequency = 50 db; (b) radiofrequency = 64 db; (c) radiofrequency = 66 db.

upon radiofrequency power; one of the predicted double-quantum transitions was observed. Its existence and position is in agreement with the proposed AB system.

(17) (a) R. Freeman and W. A. Anderson, *J. Chem. Phys.*, **37**, 2053 (1962); (b) *ibid.*, **39**, 806 (1963).

(18) W. A. Anderson, R. Freeman, and C. A. Reilly, *ibid.*, **39**, 1518 (1963).

(19) Alternatively, the decreased intensity could be due to a transmission of saturated protons from the irradiated site to the observed site by the inversion process.<sup>20a</sup> The nuclear Overhauser effect seems less likely.<sup>20b</sup> All of these possibilities support an AB explanation for the nmr spectra of 2.

(20) (a) S. Forsen and R. A. Hoffman, *J. Chem. Phys.*, **39**, 2892 (1963); (b) K. Kuhlmann and J. D. Baldeschwieler, *J. Am. Chem. Soc.*, **85**, 1010 (1963).

Thirdly, the Varian time-averaging computer was used and a low-intensity peak was observed at -191 cps corresponding to an outer peak of the upfield AB system. This experiment enabled a more accurate determination of the geminal coupling constant. A final, theoretical, computed spectrum (Figure 1d) gave agreement with all observations using the following parameters (cps):  $\Delta\nu_{AB} = 8.4$ ,  $J_{AB} = -13.0$ ,  $J_{AX} = 55.7$ ,  $J_{BX} = 29.3$ .

**Rate Process.** A temperature dependence of the methylene protons in 2 was observed (Figure 1c). Above 55°, only one 1:4:1 methylene system is observed, indicating rapid exchange of protons between the A and B sites leading to an A<sub>2</sub> system. This exchange could occur by inversion at sulfur. Exchange of ligands would lead to loss of Pt-S-C-H coupling (still present in Figure 1c), so this cannot explain the observations at higher temperature. The spectra can be broken down into three AB patterns corresponding to platinum spins of +1/2, 0, and -1/2, and the AB group furthest downfield will be assigned arbitrarily to  $I_{Pt} = +1/2$ . A graph of temperature vs. chemical shift separation is shown in Figure 4. The least-

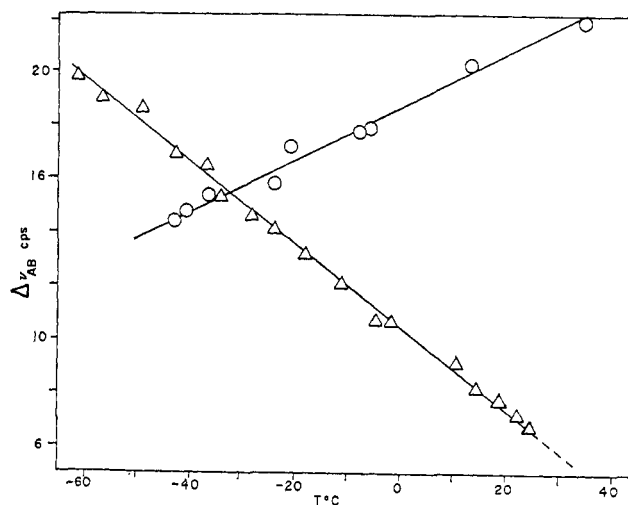


Figure 4. Dependence of chemical shift on temperature in *cis*-bis(dibenzyl sulfide)dichloroplatinum(II):  $\Delta$ , downfield AB system; O, upfield AB system.

squares equations for cps separation between A and B protons are for  $I_{Pt} = +1/2$  and  $T = -62$  to  $+25^\circ$

$$\Delta\nu_{AB}^+ = \nu_B^+ - \nu_A^+ = -0.153T + 10.41 \quad (1)$$

$$\sigma_{\text{slope}} = 0.002 \quad \sigma_{\text{intercept}} = 0.08$$

and for  $I_{Pt} = -1/2$  and  $T = -43$  to  $+13^\circ$

$$\Delta\nu_{AB}^- = \nu_A^- - \nu_B^- = 0.106T + 18.92 \quad (2)$$

$$\sigma_{\text{slope}} = 0.007 \quad \sigma_{\text{intercept}} = 0.18$$

The temperature range in which the peak separation of the center AB pattern could be determined experimentally was quite small; therefore, the net  $\Delta\nu_{AB}$  for 2 was determined from the data displayed in Figure 4 and eq 1 and 2.

$$\begin{aligned} \Delta\nu_{AB} &= \nu_A - \nu_B = (\nu_A^+ + \nu_A^- - \nu_B^+ - \nu_B^-)/2 = \\ &(\Delta\nu_{AB}^- - \Delta\nu_{AB}^+)/2 = 0.130T + 4.26 \quad (3) \end{aligned}$$

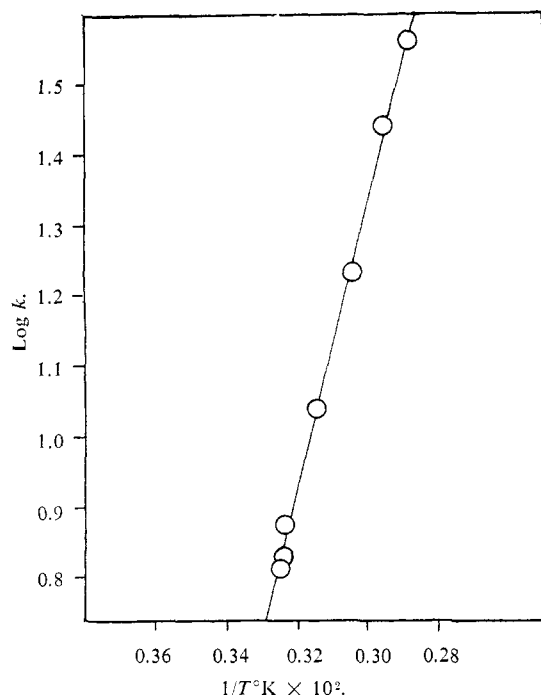


Figure 5. Arrhenius plot of the rate of sulfur inversion in *cis*-bis(dibenzyl sulfide)dichloroplatinum(II).

Note that temperature for eq 1-3 is in  $^\circ\text{C}$ . Therefore  $\Delta\nu_{\text{AB}}$  (eq 3) becomes negative at  $\sim -33^\circ$  (Figure 4). These linear relationships,<sup>21</sup> in the absence of exchange, allow the true AB chemical shifts to be obtained at any temperature within the valid range of the equations. The three AB systems coalesce at different temperatures, permitting several rate constants to be determined.

At a peak separation,  $\Delta\nu_e$ , sufficiently different from the actual chemical shift separation,  $\Delta\nu$ , the rate constant,  $k$ , for inversion was calculated from<sup>23</sup>

$$k = \frac{\pi}{\sqrt{2}}(\Delta\nu^2 - \Delta\nu_e^2)^{1/2} \quad (4)$$

At coalescence eq 4 reduces to

$$k = \pi\Delta\nu/\sqrt{2} \quad (5)$$

Above the coalescence temperature, the peak width,  $W^*$  (in cps), was used to evaluate the rate constant for the averaging process<sup>23b</sup>

$$k = \frac{\pi\{W'' + W^*[1 + 2(W^*/\Delta\nu)^2 - (W^*/\Delta\nu)^4]^{1/2}\}}{2[(W^*/\Delta\nu)^2 - (W''/\Delta\nu)^2]} \quad (6)$$

where  $W''$  = line width at half-maximum signal amplitude in the absence of exchange,  $W^*$  = observed line

(21) Although an exponential rather than a linear relationship would be expected ( $\Delta\nu = \sum_i a_i \Delta\nu_i e^{-E_i/RT}$ ), it has been shown<sup>22</sup> in substituted ethanes that the curvature is small. Over a  $100^\circ$  temperature range, a straight line is a reasonable approximation of the actual curve.

(22) H. S. Gutowsky, G. G. Belford, and P. E. McMahon, *J. Chem. Phys.*, **36**, 3353 (1962).

(23) (a) H. S. Gutowsky and C. H. Holm, *ibid.*, **25**, 1228 (1956); (b) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. Meinzer, *J. Am. Chem. Soc.*, **88**, 3185 (1966).

width at half-height. When  $W^* \gg W''$ , eq 6 reduces to

$$k = \frac{\pi}{2}\Delta\nu[(\Delta\nu/W^*)^2 - (W^*/\Delta\nu)^2 + 2]^{1/2} \quad (7)$$

The free energy of activation,  $\Delta F^*$ , was calculated from rate constants determined by this method and from the Eyring equation (eq 8). The activation

$$\Delta F^* = 2.3RT[\log(B/h) + \log T - \log k] \quad (8)$$

energy,  $E_a$ , was calculated from the Arrhenius relationship (eq 9). The enthalpy and entropy values were

$$2.3 \log k = -E_a/RT + 2.3 \log A \quad (9)$$

calculated from

$$\Delta H^* = E_a - RT \quad (10)$$

$$\Delta S^* = (\Delta H^* - \Delta F^*)/T \quad (11)$$

An Arrhenius plot is shown in Figure 5. Therefore, the activation parameters for inversion at sulfur in **2** are:  $\Delta F^* = 16.6 \pm 0.3$  kcal/mole,  $E_a = 18.0 \pm 0.5$  kcal/mole,  $\log A = 13.8 \pm 0.3$ ,  $\Delta S^* = 3$  eu,  $\Delta H^* = 17.4$  kcal/mole. The rate constant for inversion is  $10.3 \text{ sec}^{-1}$  at  $34.5^\circ$ .

**Comparison of Sulfoxide and Complex.** In order to learn more about the meaning of these observations on **2**, dibenzyl sulfoxide, a compound with similar configuration at sulfur, was studied. We investigated the effects of both temperature and solvent on  $\Delta\nu_{\text{AB}}$  in **2** and **3**. Unfortunately the low solubility of *cis*- $\{[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{S}]_2\text{PtCl}_2\}$  sharply limited the choice of solvents. The dependence of the AB chemical shift is shown in Table I. In complex **2**, the geminal coupling constant is assumed to be  $-13.0$  cps in all solvents.

Table I. Effect of Solvent on the AB Chemical Shifts

| Solvent                         | $\epsilon$        | $\Delta\nu$ ,<br>cps | <b>3</b><br>$J_{\text{AB}}$ ,<br>cps | <b>2</b><br>$\Delta\nu_e$ ,<br>cps |
|---------------------------------|-------------------|----------------------|--------------------------------------|------------------------------------|
| Carbon tetrachloride            | 2.24 <sup>a</sup> | <2.0                 |                                      |                                    |
| Chloroform                      | 5.05 <sup>a</sup> | <2.0                 |                                      | 8.4                                |
| Nitrobenzene + chloroform (1:1) | 21 <sup>b</sup>   | 7.4                  | 12.7                                 | 11.7                               |
| Nitrobenzene                    | 36.1 <sup>a</sup> | 9.5                  | 13.0                                 | 15.8                               |
| Cyanobenzene                    | 25.2 <sup>c</sup> | 9.8                  | 13.0                                 | 16.5                               |
| Nitromethane                    | 37.5 <sup>a</sup> | 11.7                 | 13.1                                 |                                    |
| Dimethyl sulfoxide              | 48.9 <sup>d</sup> | 16.3                 | 13.0                                 |                                    |
| Dimethylformamide               | 36.7 <sup>a</sup> | 17.4                 | 13.1                                 |                                    |

<sup>a</sup> "Handbook of Chemistry and Physics," 46th ed, Chemical Rubber Co., Cleveland, Ohio, 1965. <sup>b</sup> Average of the dielectric constants of nitrobenzene and chloroform. <sup>c</sup> A. A. Maryott and E. R. Smith, National Bureau of Standards Circular No. 514, U. S. Government Printing Office, Washington, D. C., 1951. <sup>d</sup> H. L. Schlafer and W. Schaffernicht, *Angew. Chem.*, **72**, 618 (1960). <sup>e</sup>  $J_{\text{AB}}$  assumed to be 13.0 cps in all solvents.

A temperature study of dibenzyl sulfoxide was carried out to see if there was dimeric association at low temperatures<sup>24</sup> and if there was inversion at high temperatures. A plot of the chemical shift between the methyl-

(24) R. F. Watson and J. F. Eastham, *ibid.*, **87**, 664 (1965).

ene protons as a function of temperature is shown in Figure 6. No decrease in chemical shift between A and B protons was observed as the temperature was lowered in any solvent studied. Furthermore, as the temperature of the chloroform sample was raised, a gradual change from an A<sub>2</sub> to an AB system was not found. Therefore, we have found no evidence for dimerism<sup>24</sup> and inversion.<sup>25</sup>

## Discussion

**Pyramidal Sulfur and the Averaging Process.** The results of double-irradiation experiments and the detection by time-averaging of an outer peak of an AB system demonstrate that the magnetic nonequivalence in Figure 1 is due to AB methylene groups. Therefore, the sulfur atom in **2** must be pyramidal so that only one pair of electrons on sulfur participates in  $\sigma$  bonding to the platinum atom. This structural result extends the crystallographic observations on sulfide-metal compounds.<sup>4,5</sup> The results obtained in this study give no evidence for hindered rotation about the S-Pt bond. Since studies were carried to  $\sim -60^\circ$ , this places some limits on the possible barrier to rotation about this ligand-metal bond.

The averaging process which makes the two methylene hydrogens equivalent (on the nmr time scale) must be due to inversion at sulfur. Since we continue to observe Pt-S-C-H coupling above the coalescence temperature and the  $J$  above coalescence equals the average of the  $J$ 's below coalescence, the inversion process cannot involve dissociation of the sulfide ligand, for that would lead to exchange of sulfides and loss of Pt-S-C-H coupling. The activation entropy for the inversion process is within experimental error of zero as expected for a symmetrical, unimolecular reaction.<sup>26</sup>

**Dibenzyl Sulfoxide.** We examined dibenzyl sulfoxide (**3**) as a simple model for the more complex platinum(II) compounds. Both **2** and **3** have pyramidal sulfur atoms and both have  $\pi$  back-bonding because of d-d overlap in **2** and p-d overlap in **3**.

**Solvent Effects on  $\nu_A - \nu_B$ .** The data in Table I and Figure 6 demonstrate a pronounced increase in  $\Delta\nu_{AB}$  for **3**, with increase in dielectric constant and decrease in temperature. Association may be important, since it has been reported that this leads to a negligible  $\Delta\nu_{AB}$  in sulfoxides.<sup>24</sup> In the more polar solvents, association would occur to a smaller extent. The changes in  $\Delta\nu_{AB}$  may also be dependent on conformational populations involved in rotation about the C-S bond, the orientation and anisotropy of the phenyl rings, and the anisotropy of the S=O bond.

Conformational studies have indicated that the lone pair of electrons on nitrogen has a preference for the equatorial position similar to that of a hydrogen or perhaps smaller.<sup>27</sup> In cyclic sulfoxides, the pair of electrons on sulfur apparently has a greater preference for the equatorial position than the sulfoxide oxygen.<sup>28</sup>

(25) Inversion rates of sulfoxides have been measured polarimetrically [D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *J. Am. Chem. Soc.*, **88**, 3138 (1966)] and are very much slower than required for observation by nmr.

(26) The mechanism of inversion is discussed fully in the accompanying paper: P. C. Turley and P. Haake, *ibid.*, **89**, 4617 (1967).

(27) (a) K. Brown, A. R. Katritzky, and A. J. Waring, *Proc. Chem. Soc.*, 257 (1964); (b) P. J. Brignell, A. R. Katritzky, and P. L. Russell, *Chem. Commun.*, 723 (1966).

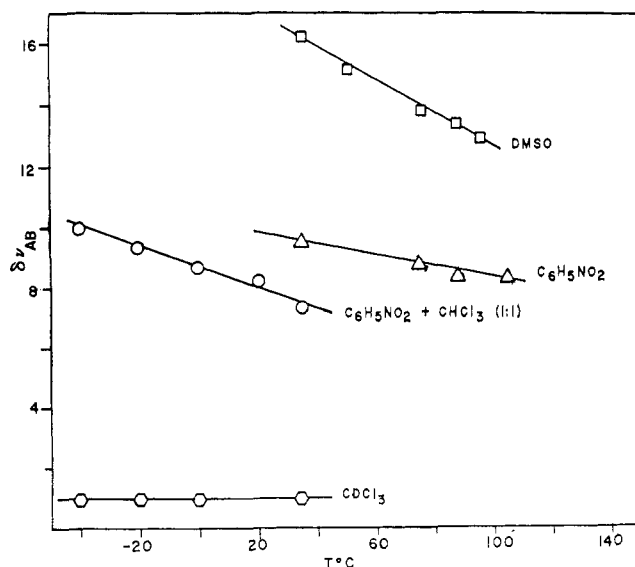
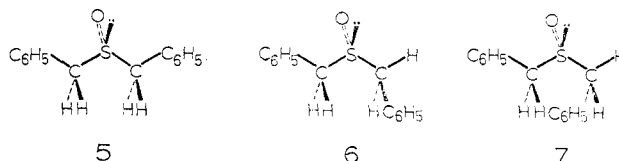


Figure 6. Temperature dependence of  $\Delta\nu_{AB}$  for the methylene groups of dibenzyl sulfide.

If these results can be extended to acyclic systems, the order of stabilities should be **5** > **6** > **7** for the conformations about the S-C bond on the right-hand side of those drawings.<sup>29</sup>



In **5**, the two benzyl hydrogen atoms are in different positions, *gauche* and *trans*, with respect to the S=O bond. The S=O bond has been treated in several ways to derive its diamagnetic anisotropic effect.<sup>30</sup> In some six-membered ring sulfoxides, treatment of the S=O bond as a triple bond has explained observed chemical shifts of nearby hydrogens.<sup>30c</sup>

It has been shown in benzyl ethers that  $\Delta\nu_{AB}$  is dependent on orientation of the phenyl ring of the benzyl group.<sup>31</sup> However, in those studies<sup>31</sup>  $\Delta\nu_{AB}$  decreased with increasing dielectric constant, but we have found the reverse (Table I). In **5**, the difference in size of the sulfur, oxygen, and unshared pair could cause a different orientation of the phenyl ring with respect to the two hydrogens.

The decreased  $\Delta\nu_{AB}$  in **3** with increasing temperature may be due to a change in the distribution of conformational populations or to the decrease in dielectric constant with increasing temperature.

**cis-Bis(dibenzyl sulfide)dichloroplatinum(II).** In **2**, conformational populations need to be considered for

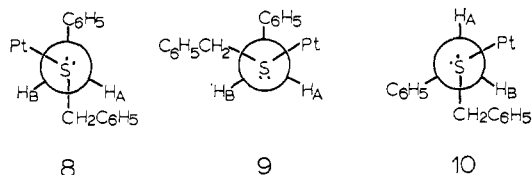
(28) C. R. Johnson and D. McCants, Jr., *J. Am. Chem. Soc.*, **86**, 2935 (1964); J. C. Martin and J. J. Uebel, *ibid.*, **86**, 2936 (1964).

(29) Since it is not known why oxygen prefers the axial position in six-membered ring sulfoxides,<sup>28</sup> it is uncertain if **6** is preferred over **7**.

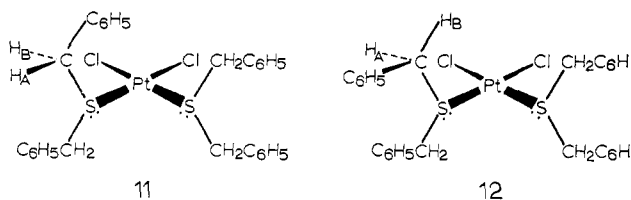
(30) (a) J. G. Pritchard and P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 2105 (1961); (b) Y. Y. Samitov and R. M. Aminova, *J. Struct. Chem. (USSR)*, **5**, 497 (1964); (c) K. W. Buck, A. B. Foster, W. D. Pardoe, M. H. Qadir, and J. M. Webber, *Chem. Commun.*, 759 (1966).

(31) (a) G. M. Whitesides, D. Holtz, and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 2628 (1964); (b) G. M. Whitesides, J. J. Grocki, D. Holtz, H. Steinberg, and J. D. Roberts, *ibid.*, **87**, 1058 (1965).

rotation about both C-S and S-Pt bonds. The steric requirements of the platinum group in **2** make it difficult to predict the preferred conformation for rotation about S-CH<sub>2</sub> bonds. Although the S-Pt bond is long (probably about 2.2 Å<sup>32</sup>), the S-Pt-S and S-Pt-Cl bond angles of 90° could make the Pt group sterically large. Models indicate that this is correct, and it appears impossible for all S-benzyl groups to be in conformation **8** at one time, but conformations **8** and **10** should certainly be the favored ones.



Relative sizes of groups indicate that the conformations shown in **11** and **12** should be favored in rotation about the S-Pt bond. These conformations minimize benzyl-benzyl and benzyl-chloro interactions that appear severe in rotated versions of **11** and **12**. The



two favored conformations for rotation about the S-C bonds are shown in **11** (conformation **8**) and **12** (conformation **10**).

**Temperature Effects on Coupling Constants in 2.** Since the absolute values of the slopes in eq 1 and 2 are different, the platinum proton coupling constants also vary with temperature. If eq 1 and 2 are added,  $J_{AX} - J_{BX}$  is obtained as a function of temperature.

(32) Based on the Pt-P bond length in a phosphine-platinum(II) complex: R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

$$J_{AX} - J_{BX} = (J_A^+ - J_A^-) - (J_B^+ - J_B^-) = -0.047T + 29.33 \quad (12)$$

Conformation **8** should have the greatest difference in coupling constants in the two preferred conformations, **8** and **10**, because in **10**, but not in **8**, both hydrogens are *gauche* to platinum. The negative slope of eq 12 requires that the population of **10** increase with increasing temperature.

**Temperature Effects on Chemical Shifts in 2.** Solvents with higher dielectric constant result in increased  $\Delta\nu_{AB}$  for **2** as is true for **3**. Temperature effects have been studied only in deuteriochloroform for **2**, but the dependence on temperature (eq 1-3 and Figure 4) has a negative slope;  $\Delta\nu_{AB}$  decreases with increasing temperature.

An important factor in chemical shifts should be the relation of the hydrogen to the plane of the platinum complex. From the screening anisotropy in square-planar platinum(II) complexes, a methylene proton out of the plane is expected to be shifted downfield relative to one closer to the plane of the complex.<sup>33</sup> Therefore, it is important to consider rotation about the S-Pt bond.

In **11** (conformation **8**), there should be little contribution to  $\Delta\nu_{AB}$  from the platinum anisotropy<sup>33</sup> since H<sub>A</sub> and H<sub>B</sub> are in similar positions with respect to the plane of the platinum complex. In **12** (conformation **10**), however, H<sub>B</sub> should be shifted downfield by the platinum anisotropy. Since the population of this conformer must increase with temperature (from coupling constants), the chemical shifts are in agreement with the proton assignments shown in **11** (**8**) and **12** (**10**). Therefore, we conclude that for Pt-S-C-H couplings, as in many other cases,  $J_{trans} > J_{gauche}$ . The consistency of this conclusion with other systems supports our proton assignments.

**Acknowledgment.** We are particularly indebted to the late Dr. A. J. R. Bourn and to Professor F. A. L. Anet for valuable discussions and help with the instrumentation.

(33) A. D. Buckingham and P. J. Stevens, *J. Chem. Soc.*, 4583 (1964).