gen chloride. The silane was then distilled through a trap cooled to −160°. The high-pressure (about 400 mm) infrared spectrum of the silane demonstrated that no hydrogen chloride was present.[3,4]

The thermal reactions were carried out in a 21-cm long cylindrical vessel of 1.5-cm radius surrounded by a heating tape and asbestos with a thermometer inserted between the tape and the vessel.

1. **Preparation of Chlorosilane-d_3.**—Chlorosilane-d_3 was prepared from the reaction of silane-d_4 and silver chloride as described for the reaction between silane and silver chloride.[5] The infrared spectrum of $ClSiD_3$ [1600 (s), 702 (vs), 540 (m) cm^{-1}] demonstrated that both silane-d_4[6] and dideuteriodichlorosilane[7] were absent. A mass spectrum of our sample confirmed that the compound was chlorosilane-d_3 and that the dichloro derivative was absent.

2. **Thermal Reaction of SiH_4 with HCl (362°).**—a. Silane (1.24 mmol) and hydrogen chloride (1.23 mmol) were allowed to react at 362° for 1 hr. The volatile fraction was then separated by trap to trap distillation. The fraction condensed in the −196° trap (1.62 mmol) was identified by an infrared spectrum to be a mixture of silane and hydrogen chloride. The fraction condensed in the −160° trap (0.065 mmol) was identified by an infrared spectrum and a mass spectrum to be a mixture of chlorosilane[8] and disilane[9] with $ClSiH_3:Si_2H_6 > 5:1$. The fraction condensed at −130° (0.17 mmol) was identified by an infrared spectrum and a mass spectrum to be primarily trichlorosilane[10] with some dichlorosilane.[11]

b. The inside of the reaction vessel was coated with silicon by the decomposition of 1 mmol of silane. Silane and hydrogen chloride (1.25 mmol each) were again allowed to react for 1 hr at 362°. For this run, the silane–hydrogen chloride fraction recovered was 2.26 mmol. The fraction condensed at −160° (0.032 mmol) was again a mixture of chlorosilane and disilane with $ClSiH_3:Si_2H_6 < 1:5$. No higher chlorosilanes were observed.

c. The inside of the reaction vessel was further coated by four decompositions (1 mmol each) of silane. Silane and hydrogen chloride (1.25 mmol each) were again allowed to react at 362°. The fraction condensed at −160° (0.043 mmol) consisted of disilane with some trisilane and at most a trace of chlorosilane. Nothing had condensed in the −130° trap.

3. **Thermal Reaction of SiD_4 with HCl.**—Silane-d_4 (1.24 mmol) and hydrogen chloride (1.24 mmol) were allowed to react in an uncoated reaction vessel at 360° for 1 hr. The fraction condensed at −196° (2.31 mmol) was a mixture of silane-d_4 and hydrogen chloride. The fraction condensed at −160° (0.023 mmol) was identified by an infrared spectrum to be a mixture of chlorosilane-d_3 and disilane-d_6 with a $ClSiD_3:Si_2D_6$ ratio of about 2. The fraction condensed at −130° (0.01 mmol) was identified by an infrared spectrum to be dichlorosilane-d_2. The silane-d_4 used in these experiments had as an impurity a very small amount of silane-d_3. The ratio of the intensity in the Si–H region (∼2180 cm^{-1}) compared to the intensity in the Si–D region (1600 cm^{-1}) was the same for the starting (silane-d_4 and silane-d_3) mixture and for the deuteriosilanes in the product fractions.

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(3) W. B. Steward and H. H. Nielsen, *Phys. Rev.*, **47**, 828 (1935).

(4) R. H. Pierson, A. N. Fletcher, and E. Gantz, *Anal. Chem.*, **28**, 1227 (1956).

(5) R. P. Hollandsworth, W. M. Ingle, and M. A. Ring, *Inorg. Chem.*, **6**, 844 (1967).

(6) J. H. Meal and M. K. Wilson, *J. Chem. Phys.*, **24**, 385 (1956).

(7) D. H. Christensen and O. F. Nielsen, *J. Mol. Spectry.*, **27**, 489 (1968).

(8) C. Newman, J. K. O. Loane, S. R. Polo, and M. K. Wilson, *J. Chem. Phys.*, **25**, 855 (1956).

(9) G. W. Bethke and M. K. Wilson, *ibid.*, **26**, 1107 (1957).

(10) N. A. Chumaevskii, *Opt. Spectry.* (U.S.S.R), **10**, 33 (1961).

(11) J. A. Hawkins and M. K. Wilson, *J. Chem. Phys.*, **21**, 360 (1953).

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Proton Magnetic Resonance Spectrum of Diammineplatinum(II) Perchlorate in Dimethyl Sulfoxide

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Complexes of some transition metal and actinide ions with dimethyl sulfoxide (DMSO) as a ligand exhibit metal–DMSO bonding through the sulfur atom in the solid phase. Infrared[1–3] and X-ray[4] studies of *trans*-$PdCl_2 \cdot 2DMSO$, infrared studies of $PtCl_2 \cdot 2DMSO$[2] and of $PtCl_2 \cdot x DMSO$,[3] X-ray studies of *cis*-$Pd(NO_3)_2 \cdot 2DMSO$[5] and of $(C_{15}H_{13}O)IrCl_2 \cdot 2DMSO$,[6] and the color of $[Rh(OAc)_2]_2 \cdot 2DMSO$[7] have shown or indicate that metal–sulfur bonding occurs. Although it is likely that the metal–sulfur bonding is retained when the complex is dissolved (if DMSO is retained as a ligand), there are no studies of solutions to support this expectation at present. Indeed, some studies indicate that changes from metal–oxygen to metal–sulfur bonding can occur when the composition of the compound is altered. Presumably the opposite change could also occur in some cases. For example, infrared studies of $Th(ClO_4)_4 \cdot 12DMSO$[8] and of $UO_2(ClO_4)_2 \cdot 5DMSO$[9] indicate that there are two types of DMSO in these compounds, namely, lattice DMSO and coordinated DMSO. The latter is bound to the metal through the oxygen atom. When the complexes are heated to drive off the lattice DMSO, the compounds $Th(ClO_4)_4 \cdot 6DMSO$ and $UO_2(ClO_4)_2 \cdot 4DMSO$ are formed. In these, lattice DMSO is absent and the infrared spectra indicate metal–sulfur rather than metal–oxygen bonding. In this note we report the results of pmr studies of DMSO solutions of $Pt(NH_3)_2(ClO_4)_2$.

Results and Discussion

The pmr spectrum, taken with an A-60 spectrometer equipped with a Hewlett-Packard 373 A counter, of *cis*-diammineplatinum(II) perchlorate dissolved in DMSO showed three different kinds of protons: those in the free, unbound DMSO, those in coordinated DMSO, and those in the coordinated ammonia molecules. The bound-DMSO proton absorption was a triplet with 1:4:1 intensity ratio. The center peak of this triplet was due to the methyl protons of DMSO bound to

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(1) F. A. Cotton and R. Francis, *J. Am. Chem. Soc.*, **82**, 2986 (1960).

(2) F. A. Cotton, R. Francis, and W. D. Horrocks, Jr., *J. Phys. Chem.*, **64**, 1534 (1960).

(3) J. Selbin, W. E. Bull, and L. H. Holmes, Jr., *J. Inorg. Nucl. Chem.*, **16**, 219 (1961).

(4) M. J. Bennett, F. A. Cotton, D. L. Weaver, R. J. Williams, and W. H. Watson, *Acta Cryst.*, **23**, 788 (1967).

(5) D. A. Langs, C. R. Hare, and R. G. Little, *Chem. Commun.*, 1080 (1967).

(6) M. McPartlin and R. Mason, *ibid.*, 545 (1967).

(7) S. A. Johnson, H. R. Hunt, and H. M. Neumann, *Inorg. Chem.*, **2**, 960 (1963).

(8) V. Krishnan and C. C. Patel, *J. Inorg. Nucl. Chem.*, **26**, 2201 (1964).

(9) V. Krishnan and C. C. Patel, *Indian J. Chem.*, **2**, 416 (1964).

platinum with zero nuclear spin and was 213.5 Hz downfield from sodium trimethylsilylpropanesulfonate (DDS). The two outside lines of the triplet were due to methyl protons of DMSO bound to ^{195}Pt, $I = {}^1/_2$, present in 33.7% natural abundance. The nuclear spin–nuclear spin coupling constant, $J(^{195}\text{Pt}{-}^{1}\text{H})$, was 23.2 Hz. Determination of the number of coordinated DMSO molecules in 0.643 and 0.733 M solutions of the platinum(II) salt by integration of the coordinated and free DMSO resonances gave results of 1.9 ± 0.1 and 2.0 ± 0.1, respectively, for five determinations on each solution. The free DMSO resonance, at 152.5 Hz downfield from DDS, was not shifted or broadened, compared to the pure solvent resonance, in the presence of the salt indicating a negligible exchange rate between the coordinated and free solvent at 35°. The solvation number of 2 and the absence of broadening of the free DMSO resonance indicated that there was either no solvation in the axial positions of the assumed planar complex or that solvent occupying these positions was magnetically equivalent to the bulk solvent. A solvation number of 2 has also been determined for *cis*-diammineplatinum(II) perchlorate in acetonitrile[10] and in water.[11]

The proton resonance of the coordinated ammonia molecules was a triplet with a 1:1:1 intensity ratio centered at 415.3 Hz downfield from DDS. The nuclear spin–nuclear spin coupling constant, $J(^{14}\text{N}{-}^{1}\text{H})$, was 50.5 Hz. Comparison of the intensities of the ammonia proton and the coordinated DMSO proton peaks gave a solvation number of 2.0 ± 0.1 for the bound DMSO in agreement with the solvation number obtained by comparison of the intensities of the coordinated and free DMSO peaks.

The shift of the center peak of the coordinated DMSO triplet was 61.0 Hz downfield with respect to the free solvent peak. The shift of the coordinated DMSO peak with respect to the free solvent peak was 25.0 Hz downfield for $[\text{Al(DMSO)}_6](\text{ClO}_4)_3$ dissolved in DMSO.[12] The larger shift for the DMSO bound to platinum(II) as compared to the shift for the DMSO bound to aluminum(III) is evidence indicating that there may be fewer bonds between the metal and the methyl proton in the case of platinum(II) than in the case of aluminum(III). In the case of aluminum(III) the coordinated DMSO was most probably bonded to the metal through the oxygen so that there were four bonds between the metal and the methyl proton. If the coordinated DMSO was bonded to platinum(II) through the sulfur atom, there would be three bonds between the metal and the methyl protons. The larger observed shift for platinum(II) is consistent with platinum(II)–DMSO bonding through the sulfur atom in DMSO solution. Furthermore, the $^{195}\text{Pt}{-}^{1}\text{H}$ coupling constant usually has a value of 2–16 Hz for four intervening bonds,[10,13–16] of 20–48 for three intervening bonds,[15–19] and of 62–123 Hz for two intervening bonds.[13,14,19] The value of 23.2 Hz obtained in this work indicates three intervening bonds, *i.e.*, bonding of platinum(II) to the sulfur atom of DMSO in the DMSO solutions.

The infrared spectrum of the solid $\text{Pt(NH}_3)_2(\text{ClO}_4)_2 \cdot 2\text{DMSO}$ in Nujol mull taken on a Perkin-Elmer Model 521 spectrometer showed bands at 1085 and 620 cm^{-1} (*cf.* 1090 and 621 cm^{-1} for $[cis\text{-Pt(NH}_3)_2(\text{CH}_3\text{CN})_2](\text{ClO}_4)_2$[10]) which can be assigned to ν_3 and ν_4, respectively, of ClO_4^- with essentially T_d symmetry. Hence the perchlorate ion did not appear to be coordinated to platinum(II) in the solid. Bands at 730 and 690 cm^{-1} were assigned to the asymmetrical and symmetrical C–S stretching motions, respectively (*cf.*, 736 and 689 cm^{-1} in $\text{PtCl}_2 \cdot 2\text{DMSO}$[2]), and indicate bonding between platinum(II) and sulfur. The manner of assignment of bands in the region 950–1150 cm^{-1} is not completely clear[2,3,20] partly because of the coupling of the CH_3 rocking and S–O stretching motions which are found in this region. Since assignments of bands observed in this region for the perchlorate salt would only be tentative, such assignments will not be made.

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(10) J. F. O'Brien, G. E. Glass, and W. L. Reynolds, *Inorg. Chem.*, **7**, 1664 (1968).

(11) G. E. Glass, W. B. Schwabacher, and R. S. Tobias, *ibid.*, **7**, 2471 (1968).

(12) S. Thomas and W. L. Reynolds, *J. Chem. Phys.*, **44**, 3148 (1966).

(13) J. Lewis, R. F. Long, and C. Oldham, *J. Chem. Soc.*, 6740 (1965).

(14) A. R. Brause, F. Kaplan, and M. Orchin, *J. Am. Chem. Soc.*, **89**, 2661 (1967).

(15) W. McFarlane, *J. Chem. Soc., A*, 1922 (1967).

(16) J. M. Jenkins and B. L. Shaw, *ibid.*, *A*, 770 (1966).

(17) E. W. Abel, R. P. Bush, F. J. Hopton, and C. R. Jenkins, *Chem. Commun.*, 58 (1966).

(18) P. D. Kaplan, P. Schmidt, and M. Orchin, *J. Am. Chem. Soc.*, **89**, 4537 (1967).

(19) B. F. G. Johnson, C. Holloway, G. Hulley, and J. Lewis, *Chem. Commun.*, 1143 (1967).

(20) R. S. Drago and D. Meek, *J. Phys. Chem.*, **65**, 1446 (1961).

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Dipole Moments of Cyclooctatetraene–Rhodium(I) Complexes

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In a recent paper[2] the preparation and properties of a number of cyclooctatetraene–rhodium(I) complexes were described and probable structures were deduced from infrared and proton nmr spectroscopic data. We now report dipole moment and dielectric absorption results for two of these complexes, $\text{C}_8\text{H}_8\text{Rh}_2(\text{acac})_2$ and $\text{C}_8\text{H}_8\text{Rh(acac)}$; the other compounds noted previously[2] are either insoluble or insufficiently stable in solution

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(2) M. A. Bennett and J. D. Saxby, *Inorg. Chem.*, **7**, 321 (1968).