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Proton Magnetic Resonance Study of Diammineplatinum(II) Perchlorate in Acetonitrile and Propionitrile

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Many platinum(II) complexes exhibit square-planar coordination and exchange ligands rather slowly.[2] Hence these complexes should be useful for determining solvation numbers when the number of ligands (exclusive of solvent) is less than 4. Furthermore, a study of the nmr spectrum of the solvent is potentially able to reveal labile bonding of solvent at the fifth and sixth coordination positions through a shift of the bulk solvent line. In this note we report the isolation of the acetonitrile and propionitrile complexes [*cis*-$Pt(NH_3)_2(CH_3CN)_2](ClO_4)_2$ and [*cis*-$Pt(NH_3)_2(C_2H_5CN)_2](ClO_4)_2$. The solvation number of the acetonitrile complex and its Pt–H coupling constant were determined in acetonitrile solution.

Experimental Section

Chemicals.—Reagent grade acetonitrile was purified by repeated (*ca.* 5 times) distillation from P_2O_5, followed by simple distillation. It was stored in brown bottles under a dry nitrogen atmosphere.

Eastman isonitrile-free propionitrile was distilled from P_2O_5 and then fractionated. The fraction coming over at 97° was collected.

Spectra.—The proton nmr spectra were obtained on a Varian Associates A-60 spectrometer equipped with a V 6020 heat exchanger and a V 6040 variable-temperature controller. A Hewlett-Packard 3300 A function generator and a Hewlett-Packard 373 A counter were employed in measuring the chemical shifts. Temperatures were measured with an iron–constantan thermocouple using a Leeds and Northrup millivolt potentiometer.

The ir spectra were obtained on a Perkin-Elmer Model 521 grating spectrometer. The samples were split mulls. CsI windows were used.

Analyses were performed by the University of Minnesota Microanalytical Laboratory. *Anal.* Calcd for $(NH_3)_2Pt(CH_3CN)_2(ClO_4)_2$: N, 10.98; H, 2.35; C, 9.41. Found: N, 10.44; H, 2.84; C, 9.56. Calcd for $(NH_3)_2Pt(CH_2CH_3CN)_2(ClO_4)_2$: N, 10.40; H, 2.97; C, 13.38. Found: N, 10.38; H, 3.10; C, 13.38.

Results and Discussion

The proton nmr spectra were taken of two solutions (0.805 and 0.472 *m*) of *cis*-$(NH_3)_2Pt(ClO_4)_2$[3] in acetonitrile. It was found that CH_3CN coordinated to the Pt and exchanged with bulk solvent so slowly that separate resonances for bound and free solvent were observed. These separate resonances persisted, with no indication of broadening, to the boiling point of CH_3CN, 81°. The resonance for bound acetonitrile appeared as a triplet centered 36 cps downfield from the bulk solvent peak. The averages of the ratios of the area of the center peak to the area of one of the outside peaks were 4.01 ± 0.10 and 4.07 ± 0.10, respectively, for the two samples. This indicates that the triplet was indeed due to the coupling of ^{195}Pt (33.7% natural abundance) with the CH_3CN protons. The coupling constant, J_{Pt-H}, was 12.1 cps.

To obtain the solvation number from the 0.805 *m* solution, the ^{13}C satellite of the bulk solvent resonance was integrated with respect to one of the side peaks of the bound triplet. The result of six integrations was a solvation number of 2.0 ± 0.1. One peak of the triplet was used in order to obtain integrals of comparable size for the peaks. To verify this solvation number, the triplet was integrated with respect to the NH_3 peak, and a solvation number of 2.0 ± 0.1 was obtained. The same integrations were performed for the 0.472 *m* solution. The ^{13}C integration gave a solvation number of 1.8 ± 0.2; the NH_3 integration gave 1.9 ± 0.2. The bulk solvent peak was unshifted indicating either that there was no appreciable solvation at the fifth and sixth coordination sites of Pt(II) or that, if there was solvation at these two sites, this solvation did not give rise to an appreciable chemical shift of the proton resonance.

The spectrum for $(NH_3)_2Pt(ClO_4)_2$ dissolved in propionitrile was complex. The limited solubility in this solvent, the overlapping of bound solvent peaks with ^{13}C satellites of bulk solvent, and spin–spin coupling of the Pt with the bound protons prevented determination of the solvation number by integration. As well as could be determined, both the bound methyl and methylene resonances were 37 cps downfield from the bulk peaks.

Both the acetonitrile and the propionitrile solutions were evaporated to dryness. The resulting solids were analyzed for C, H, and N. The results of these analyses (*vide supra*) indicate solvation numbers of 2.

The ir spectra were taken to determine whether the compounds had retained their *cis* configurations and whether the perchlorate group was bonding to the Pt. Diammineplatinum(II) compounds have the symmetric NH_3 deformation in the 1300–1400-cm^{-1} region.[3,4] In *trans* compounds it is a singlet; in *cis* it is a doublet.[4] When the perchlorate group enters into bonding, its symmetry is changed from T_d to C_{3v}. The ν_3 around 1100 cm^{-1} splits, ν_4 around 625 cm^{-1} splits, and ν_1 in the 800–1000-cm^{-1} region appears.[3,5] Our data for these regions are given in Table I. It is seen that the ir spectra show that the complex has the *cis* configuration and that the perchlorate group is not bonded to the metal. This result is consistent with the fact that Pt(II) diammines retain their *cis* structure upon solution.[6]

When a 0.108 *m* solution of $(NH_3)_2Pt(CH_3CH_2CN)_2(ClO_4)_2$ in CH_3CN was prepared, it was found that the

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[1] NASA Predoctoral Fellow.

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TABLE I

SELECTED IR DATA FOR Pt COMPLEXES (CM^{-1})

$(NH_3)_2Pt(CH_3CH_2CN)_2(ClO_4)_2$	$(NH_3)_2Pt(CH_3CN)_2(ClO_4)_2$
621 (singlet)	623 (singlet)
800–1000 (no peaks)	800–1000 (no peaks)
1090 (singlet)	1090 (singlet)
1348 and 1364 (NH_3 sym def)	1343 and 1363 (NH_3 sym def)

nmr spectrum of the solution exhibited the triplet due to bound CH_3CN. The central peak of this triplet was integrated with respect to the ^{13}C satellite of bulk CH_3CN and the value of the solvation number was found to be 1.95 ± 0.1. Thus two acetonitrile molecules had displaced the two propionitrile molecules. This result confirms the existing evidence that acetonitrile displaces propionitrile completely from the Pt coordination shell.[7] The position of the CH_3CH_2CN methyl triplet, 64, 72, and 80 cps downfield from TMS, showed that this resonance was due to free propionitrile. Furthermore, when the methyl peak of CH_3CH_2CN was integrated with respect to the ^{13}C satellite of bulk CH_3CN, the number of free CH_3CH_2CN molecules was calculated using eq 1. The ratio of the propionitrile to

$$\frac{\text{free } CH_3CH_2CN}{\text{free } CH_3CN} = \frac{\text{area of } CH_3CH_2CN}{(178.5)(\text{area of } ^{13}C)} \qquad (1)$$

^{13}C areas was 1.73. Thus 0.254 mol of free CH_3CH_2CN was found, in reasonable agreement with the 0.216 mol expected.

The ^{195}Pt–^{1}H coupling is transmitted through four bonds. The value of the coupling constant, 12.1 cps, is smaller than those reported for coupling through two or three bonds.[8–15] Lewis, *et al.*,[10] used values of coupling constants to assign bonding sites in Pt–acac complexes. The basis for their assignments was that coupling constants should decrease as the interacting nuclei are separated by more bonds. Thus, it becomes important to determine coupling constants for a variety of systems. The coupling in the Pt–CH_3CN system is slightly larger than that of other systems where the interaction is through four bonds.[16,17] In fact, four-bond Pt–H couplings range from our 12.1 cps down to 2 cps.[10] The persistence of the coupling up to the boiling point (81°) indicated that the acetonitrile molecules were strongly bonded to the platinum. This was consistent with the observation of no broadening of the bound triplet even at the higher temperatures and indicated that the solvent-exchange rate was too slow to be measurable by this method.

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The Mass Spectrum of Trifluorosilyltetracarbonylcobalt[1a]

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Recently published reports[2,3] on the infrared spectrum and force constants of trifluorosilyltetracarbonylcobalt, $SiF_3Co(CO)_4$, have suggested that there might be significant $(d \rightarrow d)\pi$ bonding between the silicon and cobalt in this and other silicon tetracarbonylcobalt compounds. This paper reports the fragmentation pattern of $SiF_3Co(CO)_4$ and the appearance potential measurement of selected ions from which the standard heats of formation of the positive ions of $SiF_3Co(CO)_4$, $\Delta H_f°(SiF_3Co(CO)_4)$, and the silicon–cobalt bond energy in $SiF_3Co(CO)_4$ have been calculated.

Experimental Section

Trifluorosilyltetracarbonylcobalt was prepared from $HSiF_3$ and $Co_2(CO)_8$.[4] The identity and purity of the compound were ascertained by partial elemental analysis, Dumas molecular weight determination, and infrared and mass spectral measurements. Decomposition was minimized by storage of the compound at the temperature of boiling liquid nitrogen. Trifluorosilyltetracarbonylcobalt was introduced into the mass spectrometer by the following procedure. The tube containing $SiF_3Co(CO)_4$ was warmed slowly from −196 to −78° and traces of any volatile materials, *e.g.*, CO and SiF_4, were removed by evacuation; the sample tube was then warmed slowly to 0°, distilling $SiF_3Co(CO)_4$ into the mass spectrometer.

All of the mass spectral data were obtained on a modified 12-107 Bendix TOF mass spectrometer previously described.[5] The reasons for the selection of this mass spectrometer have been cited elsewhere.[6] A fresh sample of $SiF_3Co(CO)_4$ was introduced into the mass spectrometer for each measurement, since some thermal decomposition did occur on standing at room temperature.

Results and Discussion

Fragmentation Patterns.—The fragmentation pattern of $SiF_3Co(CO)_4$, corrected for the background in the mass spectrometer, is given in Table I. Some of the salient features of the mass spectrum are the moderately intense parent ion current at m/e 256 and the fact that CO is fragmented from the parent ion more readily than F. Like other transition metal carbonyls,[7,8]

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