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}Pt–^{1}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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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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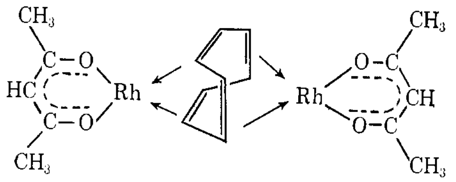
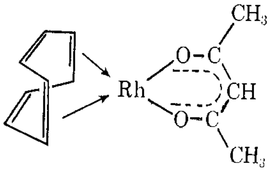
for such measurements to be possible. The purpose of this work was to confirm the proposed structures of these molecules (A and B) and to provide information on the polarity of the olefin–rhodium bond.



A



B

Experimental Section

μ-Cyclooctatetraene-2,4-pentanedionatodirhodium(I) and 2,4-pentanedionato(cyclooctatetraene)rhodium(I) were prepared as previously reported.[2] The apparatus, techniques, symbols used, and methods of calculation have been described by Le Fèvre, *et al.*[3-6] Microwave absorption measurements were undertaken at both 3109 and 9400 Mc. Benzene, as solvent, was dried and half frozen, and the remelted solid was stored over fresh sodium wire. The constants required for benzene at 25° are $\epsilon_1 = 2.2725$, $d_1 = 0.87378$, and $(n_1)_D = 1.4973$; increments to these values and to tan δ caused by weight fractions w_2 of the solute are listed in Table I. Polarizations, refractions, dipole moments, etc., are given in Table II.

TABLE I

INCREMENTAL DIELECTRIC CONSTANTS, DENSITIES, REFRACTIVE INDICES, AND DIELECTRIC ABSORPTIONS FOR SOLUTIONS IN BENZENE AT 25°

μ-Cyclooctatetraene-2,4-pentanedionatodirhodium(I)

$10^5 w_2$	403	480	904
$10^4 \Delta\epsilon$	29	35	. . .
$10^5 \Delta d$	. . .	224	422
$10^4 \Delta n$	4	4	10

$\Sigma\Delta\epsilon/\Sigma w_2 = 0.72$, $\Sigma\Delta d/\Sigma w_2 = 0.467$, $\Sigma\Delta n/\Sigma w_2 = 0.101$, and at 3109 and 9400 Mc Δ tan δ is zero for concentrations up to $10^5 w_2 = 904$

2,4-Pentanedionato(cyclooctatetraene)rhodium(I)

$10^5 w_2$	333	445	1118
$10^4 \Delta\epsilon$	29	38	. . .
$10^5 \Delta d$	137	177	447
$10^4 \Delta n$	3	4	11

$\Sigma\Delta\epsilon/\Sigma w_2 = 0.86$, $\Sigma\Delta d/\Sigma w_2 = 0.401$, $\Sigma\Delta n/\Sigma w_2 = 0.095$

$10^5 w_2$	1118	1277	1646
$10^3\Delta$ tan δ (at 3109 Mc)	0.887	0.911	0.959
$10^3\Delta$ tan δ (at 9400 Mc)	0.353	0.511	0.589

$\psi_{3109} = \Sigma\Delta \tan \delta/\Sigma w_2 = 0.068$, $\psi_{9400} = \Sigma\Delta \tan \delta/\Sigma w_2 = 0.036$

Results and Discussion

For both these compounds the total polarization and molecular refraction (see Table II) are such that it is uncertain from these results alone whether the molecules are actually polar or whether the differences $({}_\infty P_2 - R_D)$ are attributable entirely to atomic polarization.[7-9] Fortunately the dielectric loss measurements resolve this difficulty unequivocally.

TABLE II

POLARIZATIONS AND RESULTING DIPOLE MOMENTS (FROM OBSERVATIONS IN BENZENE AT 25°)

	$C_8H_8Rh_2(acac)_2$	$C_8H_8Rh(acac)$
$\alpha\epsilon_1$	0.72	0.86
β	0.534	0.459
γ	0.067	0.063
${}_\infty P_2$, cm^3	149.5	106.0
R_D, cm^3	108.6	72.2
μ, D[a]	0	0.82

[a] For method of calculation see text.

$C_8H_8Rh_2(acac)_2$.—Since no difference in dielectric absorption could be detected between solutions and pure solvent, this molecule is essentially nonpolar[10] and such a result is entirely consistent with the proposed centrosymmetric structure (A). Hence the observed atomic polarization of 40.9 cm^3 (38% of R_D) must be attributed to the rhodium atoms and coordinated groups. Finn, *et al.*,[7] have examined various nonpolar metal acetylacetonates in nonpolar solvents and found that the atomic polarization varies from 30 to 62% of the electronic polarization and that, in general, an atomic polarization of ~14 cm^3 can be considered to arise from each metal–acac grouping. Thus in $C_8H_8Rh_2(acac)_2$ ~28 cm^3 of the atomic polarization is accounted for by the rhodium–oxygen bonds, and, bearing in mind the conclusions of Coop and Sutton,[8] the remaining 12.9 cm^3 probably results from the polar olefin–rhodium bonds, which are capable of being bent relative to one another.

$C_8H_8Rh(acac)$.—The nonzero Δ tan δ values of Table I definitely indicate that this molecule is polar. Furthermore, assuming that the Debye equation is applicable, the observed relaxation data can be fitted to a calculated loss curve defined by the dipole moment (μ) and the relaxation time (τ).[5] The Debye model has been shown[11] to describe satisfactorily the dielectric behavior in nonpolar, low-viscosity solvents of solute molecules possessing a fixed dipole moment. Calculations using an IBM 7040 computer showed that the Debye curve having $\mu = 0.9$ D and $\tau = 51.0 \times 10^{-12}$ sec was in good agreement with the observed values of ψ. The experimental error in ψ could lead to an error of no more than ±0.1 D in the dipole moment. A relaxation time of 51.0×10^{-12} sec is of the order expected for a relatively large solute species such as $C_8H_8Rh(acac)$ (*cf.* C_6H_5Cl, $\tau = 8.3 \times 10^{-12}$ sec; $(C_6H_5)_2CO$, $\tau = 17.4$

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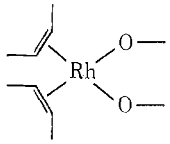
$\times 10^{-12}$ sec; $(C_6H_5)_3CCl$, $\tau = 62 \times 10^{-12}$ sec[12]). Using the data of Table II it is noteworthy that if an atomic polarization of 14 cm^3 is attributed to the rhodium–acac grouping and one of 12.9/2 cm^3 to the olefin–metal bonds, then the total atomic polarization is 20 cm^3 and the dipole moment becomes 0.82 D. Thus it seems reasonable to conclude that the dipole moment of $C_8H_8Rh(acac)$ is 0.9 ± 0.1 D and this result is in accord with the proposed structure B.

Smith and Wilkins[13] have shown that the chemical shifts of the CH and CH_3 protons in the nmr spectra of many acetylacetonates are dependent upon the molecular dipole moment; *e.g.*, in $Sn(acac)_2Cl_2$ for which μ is 8.8 D, the CH chemical shift changes by −0.29 ppm relative to the average nonpolar value of τ, while for $B(acac)F_2$ the CH and CH_3 chemical shifts change by −0.59 and −0.26 ppm, respectively, owing to a dipole moment of 6.7 D. With $C_8H_8Rh(acac)$ the CH and CH_3 proton shifts (τ 4.55 and 8.02, respectively[2]) are not greatly different from the average values found for nonpolar molecules (τ 4.56 and 7.98, respectively[13]) and this is consistent with the small dipole moment observed.

Polarity of the Olefin–Rhodium Bond.—Few data are available on the polarity of olefin–metal bonds and, in particular, there appear to have been no previous studies of the dipole moments of compounds containing olefin–rhodium bonds. If a square-planar arrangement of ligands about the rhodium atom with bond angles of 90° is assumed for structure B (the OMO bond angle is near 90° in most acetylacetonates[14]), then the olefin–rhodium polarity can be calculated provided we have an estimate of the moment of the $C_5H_7O_2Rh$ group. Such an estimate has been given by Coop and Sutton,[8] who successfully used in atomic polarization calculations an experimentally based value of 7.5 D for the moment of an acetylacetonate chelate ring including a metal atom. Use of this value and the experimental resultant moment (μ_R = 0.9 D) leads to two estimates (depending on moment directions) of $\mu(\| \rightarrow Rh)$, 4.7 or 5.9 D. Chatt and Duncanson[15] have proposed that the moment of the olefin–platinum bond is ~4 or 8 D and the former value is favored. The present work indicates that in the olefin–rhodium bond there is a similar large degree of electrical asymmetry and that, as with Pt(II) complexes,[16] back-donation of electrons from the metal to the olefinic bond is probably not a major effect.



$$\mu(\text{acac}-\text{Rh})\text{-}2\mu(\,\| \longrightarrow \text{Rh})\cos 45^\circ = \pm\mu_R$$

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Preparation and Some Properties of Tetramethylammonium Dihydrogen Trifluoride[1a]

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In the course of an investigation to develop an electrochemical method of fluorination, the need arose for a fluoride salt soluble in acetonitrile. Tetramethylammonium dihydrogen trifluoride was prepared and it proved to be a useful salt for this purpose.

The preparation of the salt involved treatment of tetramethylammonium chloride with an excess of anhydrous hydrogen fluoride. This procedure is based on the first step in the preparation of tetramethylammonium fluoride described by Urban and Doetzer,[2] in which the hydrogen fluoride bound to the fluoride ion was removed by treatment with sodium ethoxide in methanol, yielding the normal fluoride.

We have found that the removal of excess hydrogen fluoride, without attempting to prepare the normal fluoride, produces a white solid, the composition of which corresponds to $(CH_3)_4NH_2F_3$. With the usual precautions for the exclusion of water, the same composition was observed in five preparations.

It is not surprising that the compound containing $H_2F_3^-$ results from the action of excess HF on $(CH_3)_4NCl$ in view of the high heat of the hydrogen bond in HF_2^-, −37 kcal/mol, reported by Harrell and McDaniel.[3]

Experimental Section

In a typical preparation, tetramethylammonium chloride (Matheson Coleman and Bell, 99+%) was dried at 120° for 12 hr. To 10.04 g (94.0 mmol) of the chloride in a polyethylene beaker 56 ml of liquid hydrogen fluoride was added at room temperature. The fuming mixture was allowed to stand overnight in a hood. When the fuming had subsided (8–12 hr), the beaker and contents were placed in a plastic vacuum desiccator which was attached to a vacuum pump, protected by scrubbers filled with sodium fluoride pellets and a trap at −78°. Evacuation was continued until a white solid, mp 103–105°, was formed. A yield of 12.20 g, 95.58%, was obtained. Larger batches of up to 50 g have been made.

Anal. Calcd for $C_4H_{14}NF_3$: C, 36.08; H, 10.60; N, 10.52; F, 42.80. Found (average of elemental analyses[4] of samples from five preparations): C, 35.72; H, 10.38; N, 10.18; F, 42.09.

The HF content of two samples from different preparations was determined by titration with standard sodium hydroxide. *Anal.* Calcd for $(CH_3)_4NF \cdot 2HF$: HF, 30.04. Found: HF, 29.63 and 30.19, which correspond to HF:$(CH_3)_4NF$ ratios of 1.959 and 2.013.

An infrared curve was obtained from the anhydrous salt in a KBr pellet on a Perkin-Elmer Model 421 spectrophotometer.

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[1] (a) Presented at the First Northeast Regional Meeting of the American Chemical Society, Boston, Mass., Oct 1968. (b) NDEA Fellow, 1965–1968. (c) Person to whom inquiries may be directed.

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