TABLE I
HYDROXYL INFRARED STRETCHING FREQUENCIES (CM.$^{-1}$)

	$[Ni(CH_3OH)_6]$-$[ClO_4]_2$	$[Ni(C_2H_5OH)_6]$-$[ClO_4]_2$	$[Ni(H_2O)_6]$-$[ClO_4]$
$\nu_{\text{free O—H}}$	3622	3610	3760
$\nu_{\text{complex O—H}}$	3360	3380	3470

TABLE II
SPECTRAL DATA FOR THE OCTAHEDRAL NICKEL(II) COMPLEXES OF ETHANOL AND METHANOL
(ν IN UNITS OF CM.$^{-1}$ × 10^3)

	$[Ni(CH_3OH)_6]$-$[ClO_4]_2$	$[Ni(C_2H_5OH)_6]$-$[ClO_4]_2$
ν_1 ($^3A_{2g} \rightarrow {}^3T_{2g}$)	8.431	8.18
ϵ_1[a]	2.4	2.7
ν_2 ($^3A_{2g} \rightarrow {}^3T_{1g}(F)$)	14.226	13.404
ϵ_2	4	3
ν_3 ($^3A_{2g} \rightarrow {}^3T_{1g}(P)$)	25.000	24.795
ϵ_3	6.3	7.1
ν_2 calcd.	14.017	13.656
% difference in ν_2	1.5	1.8
$15B$	13.936	13.650
β	0.88	0.86

[a] Calculated from $\epsilon = A/bc$ where b, the cell thickness, is 1 cm., c, the concentration, is in moles/l., and A is the absorbance.

Electronic Spectra.—The spectra of the two alcohol complexes in this region are quite similar to that of the octahedral water complex, showing three transitions with some doublet character to the middle band. The values listed in Table II for ν_2 are the weighted averages of the doublet maxima.

The transitions in question are all Laporte-forbidden d–d transitions and hence weak in pure octahedral symmetry. The band frequencies and intensities indicate that the complexes have essentially octahedral symmetry.

The ground-state term of the gaseous divalent nickel ion is a ^3F which splits in the influence of the ligand field into a $^3A_{2g}$, $^3T_{2g}$, and $^3T_{1g}$ in order of increasing energy. The first excited triplet state in the gaseous ion is a ^3P which becomes a $^3T_{1g}$ in the ligand field. Energies are measured from the $^3A_{2g}$ as ground The secular determinants involved are (for a general review see ref. 6)

$$^3A_{2g}[-12Dq];\ ^3T_{2g}[-2Dq];\ ^3T_{1g}\begin{bmatrix} 6Dq & 4Dq \\ 4Dq & 15B \end{bmatrix}\begin{matrix} ^3F \\ ^3P \end{matrix}$$

where B is a Racah parameter. The distances between terms of maximum S are simple multiples of B. In this case $15B$ represents the ^3P–^3F term splitting.

The energy of the $^3T_{1g}(P)$ level above the ground $^3A_{2g}$ can be found simply by subtracting the energy of the $^3A_{2g}$ ($12Dq$) from the observed band maximum for ν_3. If this energy is substituted into the expanded $^3T_{1g}$ determinant (quadratic in E) a value for $15B$ for the complex can be obtained. This value can then be used to calculate the other eigenvalue which is the energy of the $^3T_{1g}(F)$ above the ground state. The value of the band maximum for ν_2 calculated in this way gives a check on the accuracy of the band assignments; see Table II.

The lowest energy transition in these complexes is from ground to $^3T_{2g}$. It follows directly from the secular determinants that the energy of this transition gives $10Dq$ immediately. Thus from Table II it can be seen that the Dq values for methanol and ethanol toward nickel(II) are 843 and 818 cm.$^{-1}$, respectively.

The calculations of $15B$ described above give a value somewhat lower than the value of the free gaseous ion,[7] 15,840 cm.$^{-1}$. This is the nephelauxetic effect caused by the lowering of interelectronic repulsions through some form of covalency. The nephelauxetic parameter is simply the ratio of a gas phase parameter to the value of the same parameter in a complex. In this case it is the ratio of B for the free and complexed nickel ion.

Discussion

The Dq values for the methanol and ethanol complexes are very close to that for water. For purposes of comparison these values and those for some common solvents are[2,3]: NH_3 (1060); H_2O (860); $HC(O)N(CH_3)_2$ (850); CH_3OH (843); C_2H_5OH (818); $(CH_3)_2SO$ (773); $CH_3C(O)N(CH_3)_2$ (769).

It is interesting that the spectrochemical order $H_2O > CH_3OH > C_2H_5OH$ parallels the magnitude of the O–H infrared frequency shift of the solvent on complexation ($\Delta\nu_{O-H}$ of Table I). The spectrochemical order does not parallel the inductive order of the substituent, $C_2H_5 > CH_3 > H$, nor does it parallel the dipole moments of these three molecules (H_2O = 1.82, CH_3OH = 1.71, C_2H_5OH = 1.73).

The positions of water and methanol in the nephelauxetic series are very close (H_2O, β = 0.89; CH_3OH, β = 0.88) while a slightly lower value, β = 0.86, is found for ethanol.

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CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH
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Preparation and Properties of Dichlorobis(1-octene)platinum(II)

BY J. F. HARROD

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Complexes of platinum in which more than one monoolefin is bound to the same metal atom have been

TABLE I

H^1 N.M.R. DATA FOR PLATINUM–OCTENE COMPLEXES

	δ^a			
Compound	—CH═C	C═CH$_2$	—CH$_2$C═	CH$_3$(CH$_2$)$_4$—
1-Octene	5.5–6.0 (1)	4.8–5.2 (2)	1.8–2.2 (2)	0.6–1.5 (11)
$(C_8H_{16})_2Pt_2Cl_4$	4.7–5.5 (1)	3.8–4.5 (2)	?–1.4	0.6–1.7 (13)^b
$(C_8H_{16})_2PtCl_2$	3.9–5.5 (3)		?–2.5	0.6–2.5 (13)^b

^{a} Chemical shifts expressed as δ (p.p.m.) relative to tetramethylsilane. ^{b} The allyl and methylene protons were not sufficiently resolved and were counted together. Figures in parentheses are the number of protons per octene molecule.

described for the ethylene–platinum(II) system.[1] Chatt prepared a thermally unstable complex analyzing for $(C_2H_4)_2PtCl_2$ which, by virtue of its color and solubility in low dielectric solvents, was assigned the *trans* configuration. He also prepared a gray, unstable complex with an analysis corresponding to $(C_2H_4)_2PtCl_2$ + 10% Pt. To this material he tentatively assigned the *cis* structure. An unstable bis(1-butene) complex has been described by Jonassen and Field.[2]

In the course of studying the chemistry of the higher 1-olefin complexes of Pt(II) it was observed that a white crystalline solid was very slowly precipitated from a concentrated solution of di-μ-chloro-dichlorobis(1-octene)diplatinum(II) in 1-octene. This complex proved to be dichlorobis(1-octene)platinum(II). The dipole moment of the complex was not measured but its color and insolubility in paraffins strongly suggested a *cis* structure.

The bis octene complex was sufficiently stable to be dissolved and recovered from a variety of organic solvents, but in the course of several days both the solid complex and solutions underwent extensive decomposition to bridged dimer and free olefin. The recovered olefin from decomposition of the complex was found to have undergone some isomerization (*ca.* 20 mole % internal isomers).[3]

The infrared spectra of the bridged dimer and the bis octene complex were superficially very similar. The $\nu_{C=C}$ band for the bis complex was found to occur at 1510 ± 1 cm.$^{-1}$, whereas the same band for the bridged dimer occurred at 1498 ± 1 cm.$^{-1}$. This shift of 12 cm.$^{-1}$ is indicative of slightly weaker binding of the olefin to the metal in the bis olefin complex. The only other major difference between the infrared spectra was the splitting of the strong band at 1020 cm.$^{-1}$ into a doublet in the bis olefin complex. This band is probably the out of plane deformation mode of the —HC═ group, and in both complexes the absorption occurs at higher energy ($\sim$30 cm.$^{-1}$) than in the free olefin.

Some H^1 n.m.r. data for the two complexes are summarized in Table I. The vinyl protons of the bridged dimer gave two broad but clearly separated peaks corresponding to terminal and penultimate protons. With the bis complex these two peaks were not resolved but the observation of an integrated intensity corresponding to three vinyl protons was important in eliminating several structural possibilities such as internal olefin complexes or π-allyl complexes. All of the protons on the vinyl and allylic carbon atoms showed the increased shielding expected when the double bond is partially saturated by complexing to the metal ion.

Attempts to prepare bis complexes of other 1-olefins, including 1-heptene and 1-nonene, were not successful. Attempts at preparing the octene complex *in vacuo* did not meet with success, and it is believed that oxygen may play a role in assisting the cleavage of the bridged dimer. Examination of the residual solution after crystallization of the bis complex revealed the presence of an appreciable quantity of aliphatic ketone in the mother liquor. Chatt has previously discussed the bridge splitting role of acetone in the preparation of the bis ethylene complexes.[1] The crystallization of the octene complex may be the result of a fortuitous combination of effects, such as solubility, rate of oxidation of olefin, and equilibrium distribution of isomers (the bis complex is not precipitated quantitatively, a considerable amount of orange platinum complex remains in solution), which is not satisfied in the case of the other 1-olefins tried.

The preparation of *cis*-bis olefin complexes is of interest in view of the interesting possibilities of geometrical isomerism. Because the >C═C< is perpendicular to the plane of the complex, three isomers are possible; one *meso* form in which the pendant alkyl groups are directed toward the same side of the molecular plane and two enantiomers with the pendant alkyl groups directed toward opposite sides of the plane. The recent isolation of enantiomers of platinum olefin complexes[4] leaves little doubt that this type of isomerism is feasible for the *cis*-bis complexes, but the resolution of such isomers may prove a difficult problem.

Experimental

Di-μ-chloro-dichlorobis(1-octene)diplatinum(II) (2.0 g.) was dissolved in freshly purified 1-octene (10 ml.). The solution was divided into two equal portions, A and B.

Solution A was evaporated to dryness *in vacuo* and pumped out at 10^{-5} torr for 5 days. The product, a dark brown, waxy solid, gave the following analysis. *Anal.* Calcd. for $(C_8H_{16})_2Pt_2Cl_4$: C, 25.3; H, 4.2. Found: C, 25.6; H, 4.3.

Solution B was left standing in a 50-ml. beaker, covered to minimize evaporation, for 1 week. The solution was periodically agitated to assist nucleation. The supernatant liquor was decanted and the residual crystals were washed several times with small aliquots of *n*-hexane. The product was a pale yellow crystalline material. Recrystallization from hot 10% benzene in *n*-hexane gave a pure white crystalline compound, yield 0.2 g;

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[2] H. B. Jonassen and J. E. Field, *J. Am. Chem. Soc.*, **79**, 1275 (1957).

[3] J. F. Harrod and A. J. Chalk, *ibid.*, **86**, 1776 (1964).

[4] G. Pajaro, P. Corradine, R. Palumbo, and A. Panunzi, *Makromol. Chem.*, **71**, 184 (1964).

m.p. 72–73°. *Anal.* Calcd. for $(C_8H_{16})_2PtCl_2$: C, 39.1; H, 6.5; Pt, 40. Found: C, 39.1; H, 6.4; Pt, 39.2.

Infrared spectra were measured in KBr disks; n.m.r. spectra in perdeuteriobenzene.

CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY,
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H, H Coupling in Diene–Iron Carbonyl Complexes[1]

BY H. S. GUTOWSKY AND J. JONÁŠ[2]

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High resolution nuclear magnetic resonance spectra recently have been used extensively for the study of transition metal complexes of various organic unsaturated compounds.[3] Among such applications, the iron carbonyl complexes of different dienes[4] have been investigated and several interesting features have been observed in their high resolution proton spectra. In a diene–iron carbonyl complex, shown schematically in Figure 1, the "terminal" hydrogens X, X′, which are nearest to and most directly affected by the bonding to iron, exhibit a large upfield shift.[4] On the other hand, the resonance of the central hydrogens A, A′ appears in the normal region for olefinic protons (usually around 5.0 p.p.m. downfield from TMS). The two central and two terminal hydrogens give proton spectra characteristic of A_2X_2 spin systems as reported for a number of these complexes,[4] such as cyclohepta-1,3-dieneiron tricarbonyl, cyclohexa-1,3-dieneiron tricarbonyl, and bicyclo[4.2.0]octa-2,4-dieneiron tricarbonyl. Besides the chemical shifts, the magnitudes of the H, H coupling constants have been reported[4] for protons in the diene moiety, and it has been noted[5] that the vicinal coupling constants are "smaller than usual."

Several authors have commented on the significance of the n.m.r. results. For example, Sternhell[5] has suggested that the small vicinal coupling constants result from delocalization of the π-electrons, and Manuel[6] has proposed that the proton spectra of tricarbonyl-(1,1′-bicycloalkenyl)iron(0) complexes favor a structure involving 1,4 addition of the iron atom across the dienic system, as implied in Figure 1. However, in the previous discussions, no consideration seems to have been given to the effects upon the proton spectra of the nonplanarity of the H and C atoms in the diene–iron carbonyl complex. The main purpose of this note is to call attention to the existence and importance of such effects in these complexes.

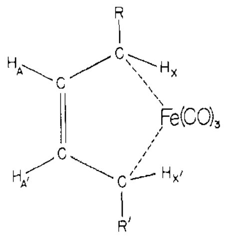

Figure 1.—The diene–iron carbonyl complex. The four carbon atoms which were the 1,4-diene before complex formation are in the plane of the paper, the Fe is below, H_X and $H_{X'}$ are above, and H_A and $H_{A'}$ are perhaps somewhat below.

Our interest in this type of system was stimulated by Frankel,[7] who very kindly gave us a sample of the iron carbonyl complex obtained from methyl linoleate as well as a spectrum of it obtained with a Varian Associates A-60 spectrometer. At that time, only the magnitudes of the coupling constants had been reported. However, it is possible to obtain the relative signs of J_{AX} and $J_{AX'}$ from an A_2X_2 spectrum,[8] and we thought it worthwhile to make such an analysis. Therefore, we reran the A_2X_2 part of the proton spectrum of the linoleate complex on the A-60 spectrometer in our laboratory and analyzed it by means of the Swalen–Reilly computer programs.[9] The appearance and assignment of the spectrum are very similar to those reported[4] for other diene–iron carbonyl complexes. The central hydrogen atoms (A and A′ in Figure 1) give a well-defined low-field multiplet 5.00 p.p.m. downfield from TMS, whereas the terminal hydrogens (X and X′ in Figure 1) give the high-field half of the A_2X_2 spectrum, which overlaps the intense structureless bands of the CH_2 groups. Further details of the spectrum and of the properties of the complex have been reported by Frankel.[7]

Our analysis, based mainly on the unobscured low-field multiplet, gave the following results: $\nu_A = -300.0 \pm 2.0$, $\nu_X = -110.3 \pm 20.0$, $J_{AA'} = 4.4 \pm 0.2$, $J_{XX'} = 0.0 \pm 0.2$, $J_{AX} = J_{A'X'} = +8.4 \pm 0.2$, $J_{AX'} = J_{A'X} = -1.7 \pm 0.2$, all in c.p.s. with the ν values referred to TMS. The large uncertainty in ν_X is due to overlap of the high-field half (X_2) of the spectrum by the strong CH_2 bands. The widths of the downfield lines were exceptionally large, about 3 c.p.s. at half-maximum intensity. In spite of the broadening and the fact that only the downfield multiplet could be analyzed, the results show conclusively that J_{AX} and $J_{AX'}$ are of opposite sign. The broadening of the A_2X_2 lines most likely results from the fact that the sample is actually a mixture of diene–iron carbonyl complexes, with slightly different shifts and coupling constants which give overlapping transitions. That is, in Figure 1, R and R′ are[7] $CH_3(CH_2)_y$– and $-(CH_2)_x$-$COOCH_3$ with $x + y = 12$ and $x, y = 4, 8; 5, 7; \ldots 10, 2$.

In any event the chemical shifts and coupling constants obtained in our analysis are comparable with

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[1] Supported in part by the U. S. Office of Naval Research and by the National Science Foundation.

[2] On leave of absence from the Czechoslovak Academy of Science, Institute of Organic Chemistry and Biochemistry, Prague.

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