Table II. Calculated and Observed IR Bands of C_4H_4 and C_4D_4[a]

		C_4H_4			C_4D_4	
Type	No. in Chart I	Calcd frequencies, SCF	Calcd rel intensities, $(dD/dq_i)^2$	Obsd bands	Calcd frequencies, SCF	Calcd rel intensities
asym C═C	**1**	1697	0.08		1612	0.10
asym C—C	**2**	790	0.21		661	0.24
CH	**3**	3287	0.37	(3040)	2466	0.14
CH	**4**	3270	0.06		2407	0.03
CCH	**5**	1129	0.00		823	0.00
CCH	**6**	1377	0.86	1240	1161	0.33
Out of plane	**7**	692	4.20	570	508	2.26

[a] In cm^{-1}.

and the mass matrix **M**, the harmonic vibration frequencies $\lambda_i = \omega_i/2\pi$ and IR-vibration vectors $\mathbf{C}_i$ are calculated from the eigenvalue equation

$$\mathbf{FC}_i = \lambda_i^2\mathbf{MC}_i$$

The vectors $\mathbf{C}_i$ are then used to estimate the relative intensities of the IR-active fundamentals by calculating the square of the dipole moment change along the corresponding normal vibration.

To test the numerical reliability of our results we performed the same type of calculation for ethylene using the same basis set. The results are collected in Table I, where we have also included both the observed fundamentals and harmonic frequencies[11] which should be compared with our calculated SCF values. Obviously, the SCF approximation leads only to a rather poor agreement with experiment[12] for some ω_i. This is particularly true for the out-of-plane bending vibration ω_7; inclusion of electron correlation by means of the CEPA formalism lowers the force constant by ~15%, reducing the SCF harmonic frequency of 1092 to 998 cm^{-1} which is in reasonable agreement with the experimental value of 969 cm^{-1}. The reason for the rather large deviation of the asymmetric HCH bending vibration ω_{12} is not known so far. Our calculated relative intensities reproduce the experimental results fairly well.

Table II contains the results for cyclobutadiene for the seven IR-active vibrations. Only two of them are expected to give strong bands in the IR spectrum; the CH stretch is already rather weak, much more so the asymmetric C–C stretch. The assignment of the band at 570 cm^{-1} to the out-of-plane deformation and of the band at 3040 cm^{-1} to the CH stretch is evident, particularly since the deviations of observed and SCF frequencies are practically the same as in ethylene. The two IR-active CCH bending vibrations at 1129 and 1377 cm^{-1}, respectively, differ very strongly in their intensities. Only the one in which the two easily polarizable C═C double bonds are deformed along their main axis (B_{2u}, compare Chart I) gives rise to a large dipole moment and to a strong band. Its calculated frequency is almost 140 cm^{-1} higher than that of the observed band at 1240 cm^{-1}. That is about the same deviation from experiment as in the case of ethylene.

Thus, we assign the observed band at 1240 cm^{-1} to an in-plane CCH bending vibration of rectangular cyclobutadiene rather than to the asymmetric C–C stretching vibration of a hypothetical square cyclobutadiene.[1] Though the C–C stretching vibration might appear at that frequency, the strong band of the CCH bending must appear in that region and there is no other band available to account for it (the band at 661 cm^{-1} originally assigned to the CCH bending does not belong to the cyclobutadiene at all[3]). Very recently, Krantz et al.[13] reported the IR spectrum of a ^{13}C substituted cyclobutadiene. The very small shift of 4 cm^{-1} which they found for the band at 1240 cm^{-1} supports also our assignment. Only the spectrum of the so far unknown perdeuteriocyclobutadiene could give the final answer to the assignment of the CCH bending vibration since in this species the CCH bending vibration should be shifted by ~200 cm^{-1} to longer wavelengths, whereas the C–C stretching vibrations should be much less affected.

Acknowledgment. All the computations have been performed on a minicomputer of the type Interdata 8/32. We thank the "Deutsche Forschungsgemeinschaft" for granting this computer to our group. We are grateful to Professor Davidson for valuable comments.

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A Novel 5-Fluorouracil–Copper(II)–Peptide Ternary Complex

Sir:

The pyrimidine derivative 5-fluorouracil (5-FU) is presently used as a carcinostat in humans.[1] As a first step in the elucidation of the interactions between a metal ion, a peptide, and a carcinostat related to the natural occurring nucleic acids, we

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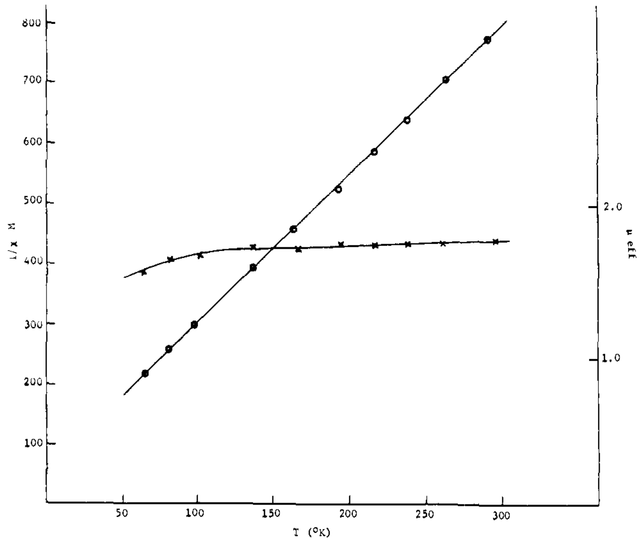

Figure 1. Magnetic susceptibility data of Cu(glygly)(5-FU)·H_2O. O and x are experimental points for the inverse susceptibility and magnetic moment, respectively. — is a Curie–Weiss line.

have isolated the 5-fluorouraciloglycylglycinocopper(II) monohydrate, Cu(glygly)(5-FU)·H_2O complex. This ternary compound can be considered a model of study for the more complicated metal–protein–nucleic acid interactions such as those in the synaptosomes.[2] This compound also opens the field to compare its carcinostatic activity with that of plain 5-fluorouracil.[3] It should be noted that a great flexibility for variation or attachment of functional groups existed at the peptide end of this ternary complex. Finally, this report is also a start in the solid state spectroscopic study of peptide–nucleic acid interactions mediated by a metal ion.[4] This type of interaction has been suggested[5] as potentially helpful in the stacking of the aromatic species and the concomitant stabilization of the compound via an additional "bond" of the charge-transfer type.

We wish to present here the method of synthesis, elemental analysis as well as the electron paramagnetic resonance spectra, electronic spectra, and static magnetic susceptibility measurements on Cu(glygly)(5-FU)·H_2O.

The complex was prepared by dissolving a 1:1 molar ratio of bisglycylglycinocopper(II) previously prepared[6] (0.1955 g) and 5-fluorouracil (0.1300 g) in 30 mL of 30% aqueous ethanol. The solution was constantly stirred and heated to 70 °C for 3 h allowing about half the solvent to evaporate. To the remaining solution was added an equal volume of ethyl acetate and this was placed in a freezer for a week. The crystals of Cu(glygly)(5-FU)·H_2O formed; they were filtered, washed with cold water, and dried at 60 °C. The yield was quantitative. Anal. Calcd for Cu(glygly)(5-FU)·H_2O ($CuC_8H_{11}N_4O_6F$): C, 28.07; H, 3.22; N, 16.37. Found: C, 27.99; H, 3.41; N, 16.35. The color of the compound was marine blue and the melting point was 222–238 °C with decomposition. The electron paramagnetic resonance spectra were obtained in a Varian HFE-12 spectrometer at 77 K (sample immersed in liquid nitrogen) and room temperature using X-band frequencies, the magnetic susceptibility in a Faraday balance setup previously described,[7] and the electronic spectra in a Beckman DK-2A spectrophotometer. All of the measurements were made on polycrystalline material.

The synthesis and stability of this compound reflect the possibility of the formation of this or similar compounds in vivo. The electronic spectrum had a maximum at relatively low energy, 14 000 cm^{-1}, which is characteristic[8] of weak ligand fields surrounding the copper(II) ion, possibly five coordination. The electron paramagnetic resonance spectrum consisted of two bands which can be assigned[9] to the $g_{\|}$ and $g_{\perp}$ of the usual axial spectrum of copper(II) with values of 2.26 and 2.06, respectively. These values indicate that the immediate environment of the copper(II) ion is axially distorted, and, considering the electronic spectra data, the bonding to the metal can be postulated as square-pyramidal five coordination (C_{4v} symmetry). There was no evidence of the presence of H_{MIN} or any other bands corresponding to spin-coupled triplet-state species.

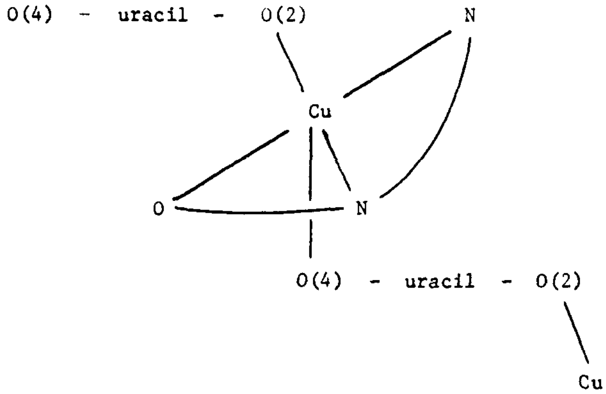

Figure 2. Suggested structure of the Cu(glygly)(5-FU)·H_2O coordination compound.

The static magnetic susceptibility from room temperature to 77 K is shown in Figure 1 where O and x represent the experimental points for the inverse magnetic susceptibility and magnetic moment, respectively, and the — a Curie–Weiss[10] behavior with $\theta = -20$ K. The value for θ is sufficiently large, and also the magnetic moment dips enough in Figure 1, so that a weak lattice antiferromagnetic coupling is indicated. The strength of these spin–spin interactions must be small,[11] <40 cm^{-1}, judging from the temperature where the effect becomes noticeable and the lack of any $S = 1$ electron paramagnetic resonance spectrum.

Finally, a comparison of the infrared spectra of free 5-fluorouracil and that of the coordination compound showed significant changes in the carbonyl area.[12] The C(2)=O and C(4)=O stretches have been assigned[13] in the free ligand to strong bands at 1724 and 1681 cm^{-1}, respectively. These bands disappear upon complexation and there is no absorption at all in the area between 2000 and 1650 cm^{-1}. This is produced by the formation of coordination bonds by both oxygens. These data, together with the results of the electronic spectra, electron paramagnetic resonance, and susceptibility measurements, suggest a structure, as shown in Figure 2, where the 5-fluorouracil acts as a weak bridge between copper(II) ions completing the square-pyramidal coordination via carbonyl coordination. We are presently expanding the susceptibility measurements down to 12 K to establish the type of intermolecular magnetic interactions in effect in this compound. We are also trying to obtain single crystals of this compound in order to look for nitrogen superhyperfine and to do a structural x-ray study.

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Enantiomer Recognition and Conformational Equilibria in Platinum(0) Complexes of 2,3-Isopropylidene-2,3-*trans*-dihydroxy-1,4-bis(diphenylphosphino)butane (diop)

Sir:

We report that the asymmetric chelating ligand (*R,R*)-diop (**1**) forms a mononuclear platinum(0) complex (**2**) which exhibits conformational isomerism observable by ^{31}P NMR. This is pertinent to the role of diop complexes in asymmetric homogeneous catalysis[1] and particularly to their optical efficiency when compared with chelate complexes derived from chiral diphosphinoethane derivatives.[2] Furthermore there is considerable stereoselectivity in ligand binding favoring the optically active bis(diop) complex over its meso diastereomer in solution.

Bis(cyclooctadiene)platinum(0)[3] reacts with (*R,R*)-**1** in C_6H_6 or C_7D_8 giving complex **2**, isolable as a yellow crystalline solid. Anal. ($C_{62}H_{64}O_4P_4Pt$) C, H, P. Mol wt: obsd, 1132; calcd, 1191. The ^{31}P NMR spectrum of **2** (Figure 1) in C_7D_8 is a sharp singlet at δ −11.3 ppm[4] above 320 K with clearly defined platinum satellites ($J_{\text{P-Pt}}$ = 3751 Hz); *no* rapid intermolecular exchange process is seen in the presence of free phosphine.[5] Cooling the solution causes first broadening of the signals and then resolution into an AA′XX′ multiplet (δ_{P_A} −5.2, δ_{P_X} −19.1 ppm ($J_{P_A\text{-Pt}}$ = 3983, $J_{P_X\text{-Pt}}$ = 3521, $J_{P_AP_X}$ = $J_{P_AP_{X'}}$ = 50 Hz)). This dynamic process, for which $\Delta G^{\ddagger}_{250}$ = 48 KJ mol^{-1},[6] must be intramolecular in a monomeric complex because of the sharpness of the platinum satellite signals, even at 370 K. All other mechanisms would lead to satellite broadening by the process Pt ($I = \frac{1}{2}$) $\rightleftarrows$ Pt ($I = 0$) and the *minimum* free-energy of activation for this is 83 KJ mol^{-1}. Furthermore, line shapes are independent of concentration, or of added **1**, and the dynamic processes leading to broadening of both satellite peaks have similar rate constants[6] to the dynamic process leading to broadening of the main peak.

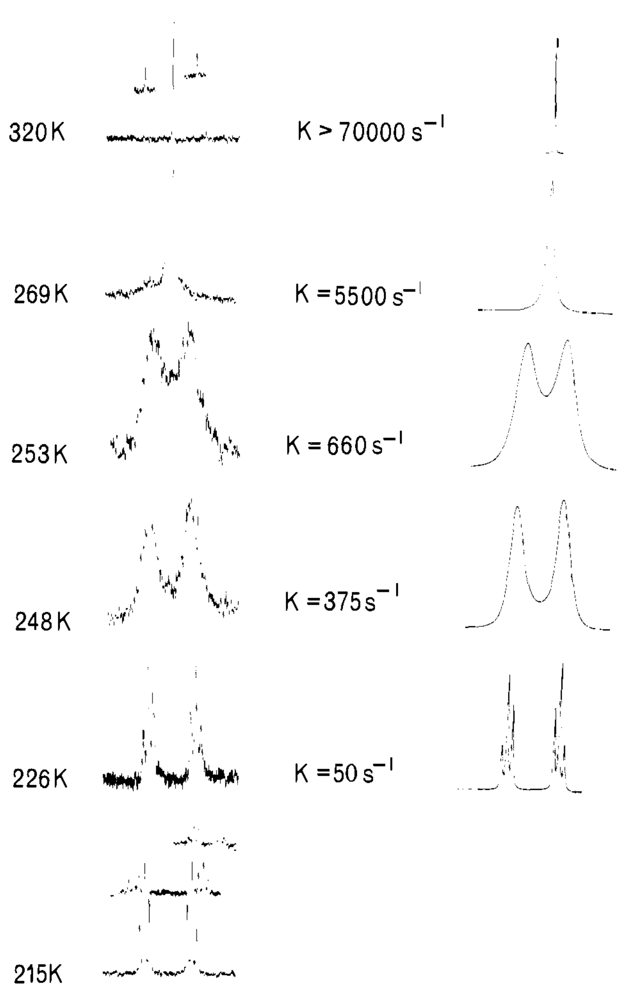
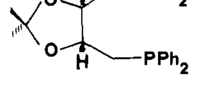


Figure 1. Variable-temperature proton-decoupled ^{31}P NMR spectra of **2** in C_7D_8 at stated temperatures, 36.43 MHz. Platinum-coupled satellites are inset where appropriate.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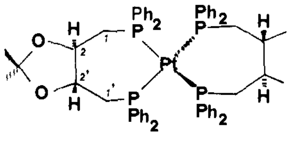
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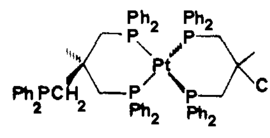
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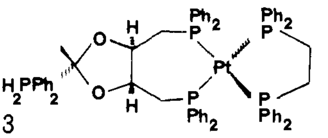
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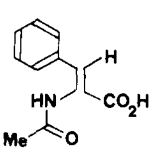
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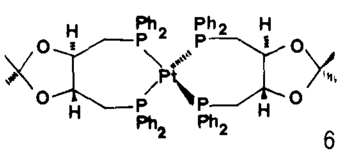
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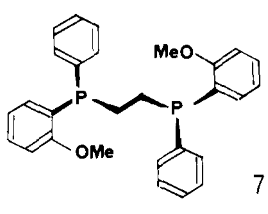
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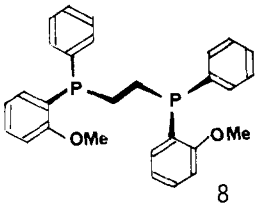
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Dynamic equilibria have previously been observed in the bis complex **3**[7] owing to site exchange in the six-membered chelate. When this complex is static on the NMR time scale, the two bound phosphines of a single ligand are inequivalent and the observed low-temperature spectrum approximates to an A_2X_2 pattern because $J_{AX} = J_{AX'}$. The phenomenon observed with **2** is different and stems from equivalencing of two bound ligand geometries rather than equivalencing of an intrinsically different pair of phosphorus atoms within the same ligand. This interpretation is supported by the observation that the mixed complex **4**, prepared in situ by addition of an equimolar quantity of $Ph_2PCH_2CH_2PPh_2$ to a solution of **2** in C_7D_8 at 300 K, shows a sharp A_2X_2 ^{31}P NMR spectrum throughout the range 220–320 K (δ_{P_A} 25.9, δ_{P_X} −6.6 ppm ($J_{P_A\text{-Pt}}$ = 3471, $J_{P_X\text{-Pt}}$ = 3996, $J_{P_A\text{-}P_X}$ $\mp$ 56 Hz), requiring that the two phosphines of diop in **4** are equivalent.

Inspection of molecular models reveals two low-energy

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