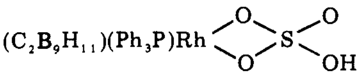

III

$$\xrightarrow{H_2} (C_2B_9H_{11})(Ph_3P)Rh(OSO_3H)(H)_2 \xrightarrow{Ph_3P} I + H_2SO_4 \quad (3)$$

$$III \xrightarrow[-H_2SO_4]{H_2} (C_2B_9H_{11})(Ph_3P)RhH \xrightarrow{Ph_3P} I \quad (4)$$

$$III \xrightarrow[-H_2SO_4]{RCH_2OH} (C_2B_9H_{11})(Ph_3P)RhOCH_2R$$

$$\xrightarrow{Ph_3P} I + RCHO \quad (5)$$

lytic dehydrogenation of alcohols are currently underway in these laboratories. The reactions of II with cyanide ion[11] and with phenylacetylene[11] produce species quite unlike those discussed above and they will be reported at a later data.

Acknowledgments. We thank the Office of Naval Research and the National Science Foundation (Grant No. CHE78-05679) for their generous support of this work. The authors thank Professor F. A. L. Anet for the use of the 80.5-MHz ^{11}B NMR spectrometer, Mr. Conrad A. O'Con for providing the ^{11}B and ^{31}P NMR, Mr. R. T. Baker for the ^{1}H NMR, and Dr. C. B. Knobler for help with the crystal structure.

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(3) One equivalent of triphenylphosphine was added to this reaction to suppress exchange of terminal B–H with D_2 catalyzed by I.
(4) Acetaldehyde was verified by its isolation as the 2,4-dinitrophenylhydrazone derivative. Propionaldehyde was verified by VPC. These reactions appear to be stochiometric in alcohol and complex II.
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Received February 17, 1979

Novel Applications of Chiral Polymer and Liquid Crystalline Polymer Hosts for the Characterization of Intramolecular Charge-Transfer and Exciton Bands in $Cs_2Pt(CN)_4$ by Circular Dichroism Spectropolarimetry

Sir:

Circular dichroism (CD) spectropolarimetry is an extremely useful tool for the characterization of optically isotropic chiral systems. CD provides both optical polarization information as well as the position of hidden transitions. Since CD can only be employed to probe chiral structures, its application is often limited because resolutions of enantiomeric structures may be difficult, time consuming, or impractical.

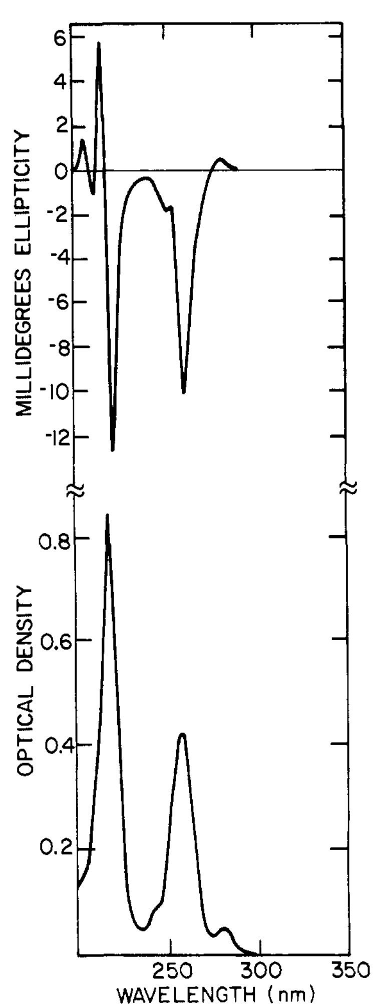

Figure 1. Absorption and circular dichroism spectra for dissolved $Cs_2Pt(CN)_4$ in hydroxypropyl cellulose (~20-μm film).

We have reported previously that *achiral* molecules display CD when ordered in a chiral manner in a fluid thermotropic[1] or lyotropic[2] cholesteric liquid crystalline host. More recently we have reported an in situ optical resolution and CD of potentially chiral crystallites (J-aggregate species) of *achiral dyes* in a rigid chiral polymeric host.[3,4] In this latter case the chiral polymer provides both the chiral perturbation for the optical resolution of chiral crystallites and the rigid matrix for an array of uniformly dispersed submicron- to micron-sized particles. The rigid matrix allows then for the elimination of linear dichroism as previously described.[3,5] Highly intense optical transitions can be probed quite simply by this technique when conventional single-crystal absorption or reflection techniques may be ineffective. The chiral polymer spectroscopic technique requires that a good solvent for both the chiral polymer and the chromophoric molecule be employed to ensure growth of the crystallites subsequent to film formation.

To probe the application of these techniques to inorganic complexes we have investigated cesium tetracyanoplatinate ($Cs_2Pt(CN)_4{\cdot}H_2O$, I). This compound is unique among the tetracyanoplatinate salts which form one-dimensional stacks in the solid state because the $Pt(CN)_4{}^{2-}$ units, individually achiral, are organized into helical arrays which confer chirality on the crystal.[6,7] The optical properties of the one-dimensional tetracyanoplatinate salts are quite different from those of the individual $Pt(CN)_4{}^{2-}$ units. In dilute aqueous solution $Pt(CN)_4{}^{2-}$ has absorption bands at 280, 258, 242, and 218 nm which have been assigned by magnetic circular dichroism[8,9]

0002-7863/79/1501-5419$01.00/0

(MCD) to electric-dipole-allowed intramolecular charge transfer ($Pt5d_{z^2} \rightarrow CN\pi^*$) and metal localized ($Pt5d_{z^2} \rightarrow Pt6p_z$) transitions. When the anions are brought together in a crystal, these intramolecular excited states form the basis of Frenkel excitons which propagate along the chains.[10,11] Because the molecular transition dipoles are so large and the distance between neighbors in the chain is relatively small, the resulting band of exciton states is unusually wide for a molecular crystal (up to ~2 eV). Consequently in the crystal the lowest allowed transition to the $k = 0$ exciton state is red shifted very strongly from its position in solution to an extent which varies as R^{-3}, where R is the near neighbor Pt-Pt spacing along the chain.[12]

A ~10-μm-thick film of hydroxypropyl cellulose (purchased from Polysciences, Inc., Rydal, Pa. 19046), prepared by draw-bar coating a 2.5 wt % polymer solution (in 80:20 methanol-water) containing 15 wt % I/polymer onto a 1 × 3 in. quartz slide and air drying at room temperature for 1 h, indicated the presence of only the monomeric form of I. The dissolved species of I did not exhibit CD. However, CD could be observed within the absorption bands of the monomeric form of I (see Figure 1) after the polymer film was heated to 40 °C for 1 min in a vessel saturated with water vapor. This treatment converted the initially unordered amorphous layer into a birefringent cholesteric liquid crystal film. Only while the film was in this mesomorphic phase could CD be observed in monomeric I. The 280-nm electronic transition exhibits positive CD, while the 258- and 242-nm bands exhibit negative CD. The 218-nm absorption band is composed of two electronic transitions with opposite CD, negative at 222 and positive at 217 nm. There are also two transitions of opposite CD at ~210 nm. This is the first observation of CD in an achiral Pt complex with an achiral molecular unit.

Preferred orientation in the helical environment is the origin of the CD induced in the absorption bands of individual achiral solute molecules dissolved in a cholesteric solvent. At a particular wavelength, the magnitude of the CD is proportional to the difference between the extinction coefficients of absorption polarized parallel and perpendicular to the direction of a nematic layer.[13] Consequently, for a planar molecule like $Pt(CN)_4{}^{2-}$, the sign of the induced CD gives an indication whether the band in question is polarized parallel or perpendicular to the molecular plane. In the D^*_{4h} double-point group appropriate to $Pt(CN)_4{}^{2-}$, transitions are electric dipole allowed to A_{2u} and E_u upper states for incident light with its electric vector respectively parallel and perpendicular to the fourfold axis. Detailed assignments of the ultraviolet transitions of $Pt(CN)_4{}^{2-}$ have long been under discussion, but, mainly as a result of magnetic circular dichroism measurements, there is now general agreement on two points: the longest wavelength band (280 nm) is defined as E_u, while both the major bands (258 and 218 nm) should contain contributions from A_{2u} as well as E_u.[8,9] If we take it from the positive sign of the induced CD at 280 nm that a positive CD characterizes an E_u state, the remainder of the CD spectrum can be used to define the assignments of the other bands. Thus the bands at 258 and 242 nm must be predominantly A_{2u}, while the intense 218-nm band is a composite of A_{2u} and E_u, the former lying at longer wavelength.

In the hydroxypropyl cellulose matrix (Figure 2) microcrystals of I show absorption at 362 and 302 nm, in addition to three bands at shorter wavelength which correlate with absorption bands of monomeric $Pt(CN)_4{}^{2-}$, and may probably originate from some isolated molecules of the complex dissolved in the matrix overlapping the microcrystallite bands. The microcrystals of I within the chiral film were further characterized by measuring their emission spectrum, which agreed with that reported for macroscopic single crystals of I.[14] As well as the absorption, Figure 2 also shows the CD spectrum of the film containing the microcrystals. The bands at shorter wavelength than 280 nm all exhibit CD of relative sign and magnitude similar to those of monomeric $Pt(CN)_4{}^{2-}$ shown in Figure 1,[5] though superimposed on a monotonically increasing negative background. In view of the fact that the monomeric species was found not to exhibit CD in the amorphous polymer film prior to crystallization, the CD spectrum shown in Figure 2 is believed to originate solely from the microcrystallites. The CD at longer wavelength than 300 nm demonstrates that partial resolution of the chiral crystals has been achieved. This is the first time that a chiral inorganic crystal has been resolved in this way.

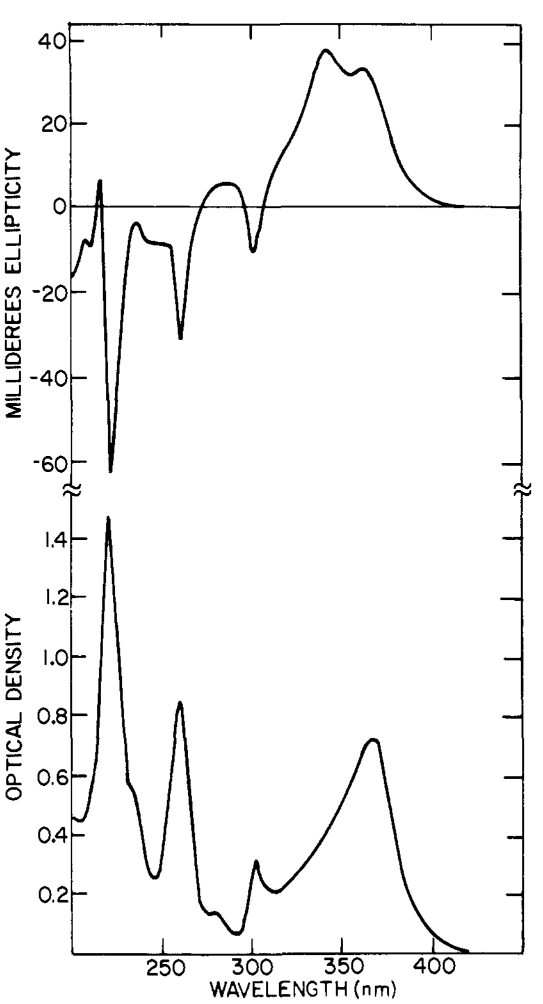

Figure 2. Absorption and circular dichorism spectra of crystalline $Cs_2Pt(CN)_4 \cdot H_2O$ (~20 wt %) in hydroxypropyl cellulose (~20-μm film).

Interpolating the R^{-3} law mentioned above with the known Pt-Pt spacing, the longest wavelength intense absorption band in crystalline I is predicted to be at 364 nm and polarized substantially parallel to the c axis, which is the direction of the helix.[15] Unfortunately we do not know the absolute configuration of the crystals which have formed preferentially; so it is not possible to interpret the sign of the CD under the two crystal absorption bands. We anticipate that the chiral arrangement of $Pt(CN)_4{}^{2-}$ groups in I confers rotational strength on the Frenkel exciton absorption and emission bands in very much the same way as in helical polymers like proteins and DNA.[16] In further work we intend to apply theory of the Moffitt type[16] to explain the sign and magnitude of the rotational strength in this unusual one-dimensional inorganic crystal. We shall also explore the application of chiral polymeric matrices to the spectroscopy of other inorganic and metal-organic compounds.

Acknowledgment. We thank Arthur Smith for assistance in synthesizing I. This work was done while P.D. was a Visiting Scientist at Xerox. He thanks the members of Webster Research Center for their hospitality.

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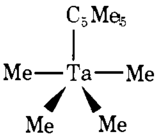
Reaction of CO with Ta(η^5-C_5Me_5)Me_4. Intramolecular Reductive Coupling of Carbon Monoxide via an "η^2-Acetone" Intermediate

Sir:

Since one of the most sought after catalytic reactions today is the selective reductive coupling of two molecules of CO with H_2,[1,2] it is important to know under what circumstances and how CO carbon atoms couple. One documented method consists of coupling oxycarbene-like Zr acyl ligands.[3,4] We report here another using Ta (η^5-C_5Me_5)Me_4 as the reducing agent which proceeds via an "η^2-acetone" or oxytantallacyclopropane intermediate.

Ta(η^5-C_5Me_5)Me_4 (**1**)[6] reacts rapidly with 1 mol of CO at 25 °C to give (in 80% yield) an "η^2-acetone" complex,[7] monomeric **2** (eq 1).[10a] Its IR spectrum shows a peak at 1200 cm^{-1} which we believe is ν_{C-O}; **2** therefore may be more accurately described as an oxytantallacyclopropane complex. Since its ^1H and ^{13}C NMR spectra[10b] show only three types of methyl groups (5:2:2 ratio) and since the peak for the acetone methyl group broadens significantly at −80 °C in tol-d_8 in the 270-MHz ^1H NMR spectrum, we suggest the molecule has a ground-state pseudo-tetragonal-pyramidal geometry which rearranges rapidly under most conditions. Acetone is produced on treating **2** with oxygen, but bound acetone does not exchange readily with free acetone-d_6. η^2-Acetone is reduced to 2-propanol (appropriately labeled using D_2O) on treating **2** with water; 2 mol of methane is also formed. The reaction of **1** with 94% ^{13}C-enriched CO (*CO) gave Ta(η^5-C_5Me_5)(O=*CMe_2)Me_2 (**2**-**C*).[11] The peak we suspect is ν_{C-O} in **2** (at 1200 cm^{-1}) shifts to 1180 cm^{-1} in **2**-**C*. We could detect no intermediate between **1** and **2** in low-temperature ^{13}C NMR experiments.



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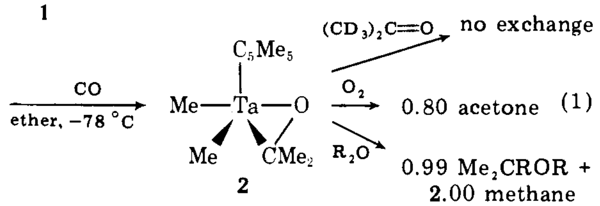
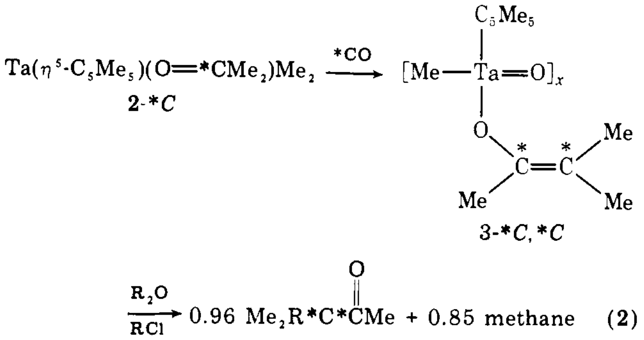


R = H or D

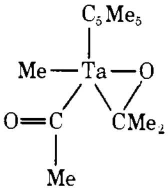
Ta(η^5-C_5Me_5)(acetone)Me_2 absorbs a second mole of CO more slowly at 25 °C to give another sublimable (180 °C, 1 μ) pale yellow complex (**3**,[12] 90% yield) whose ^1H and ^{13}C NMR spectra[13] suggest that five different methyl groups are present (5:1:1:1:1) and whose IR spectrum shows a medium strength band at 1670 cm^{-1}. Treating **2**-**C* with CO gave a product (**3**-**C,C*) in which the CO carbon atoms have not scrambled[14] and J_{C*C} = 88 Hz, consistent with a C(sp^2)-C(sp^2) coupling constant;[3,11b] the IR band shifts to 1640 cm^{-1}. Hydrolysis of **3**-**C*,**C* gives 1 mol of methane and 1 mol of appropriately labeled methyl isopropyl ketone-$^{13}C_2$ (eq 2). Therefore, we postulate that **3** contains an enolate ligand.[15] However, **3** is not a discrete monomer (mol wt 640 ± 40 in benzene; calcd 432) but, we believe, a mixture of linear or cyclic oligomers containing $\leftarrow$Ta-O-Ta-O$\rightarrow$ bonds. This is consistent with the fact that the region in which a metal-oxygen stretching frequency would be expected (1000-700 cm^{-1}) contains many relative weak peaks rather than a single strong peak, characteristic of (e.g.) $\nu_{Ta=O}$. We also know that **3** can be hydrolyzed with 1 equiv of ROH (R = Me or Me_3C) to give 1 equiv of methyl isopropyl ketone and pentane-soluble pale yellow products which are also inseparable mixtures of several complexes.



R = H or D

The reaction between a 1:1 mixture of Ta(η^5-C_5Me_5)-$(CH_3)_4$ and Ta(η^5-C_5Me_5)$(CD_3)_4$ (pre-mixed at 25 °C) in ether at −78 °C with 2 mol of CO followed by hydrolysis gave only $(CH_3)_2HCC(O)CH_3$ and $(CD_3)_2HCC(O)CD_3$ (54% d_0, 1% d_3, 2% d_6, 43% d_9). This suggests that the methyl groups in **1**-d_0 and **1**-$(CD_3)_4$ do not scramble readily and **3** is formed entirely intramolecularly.

The two most reasonable intermediate products of the reaction of **2** with CO are **4** and **5**. In either the acyl may be best



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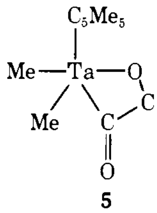

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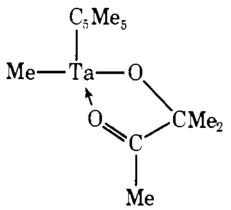

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