ing the conversion of the orange isomer to the yellow isomer in boiling tetrachloroethane (bp 146°) is consistent with the reversible formation of such a three-coordinate platinum(II) intermediate which would be expected to be unstable.

Since one of the main applications of *trans*-$[(PPh_3)_2Pt_2Cl_4]$ is in bridge cleavage reactions of the type

$$[(PPh_3)_2Pt_2Cl_4] + 2L \rightarrow 2[(PPh_3)PtLCl_2]$$

it was of interest to compare the reactions of the present yellow isomer with those of the orange isomer. Previous work has shown that *trans*-$[(PPh_3)_2Pt_2Cl_4]$ reacts with amines to yield a trans monomeric product,[12] whereas with carbon monoxide *cis*-$[(PPh_3)Pt(CO)Cl_2]$ is obtained[11,13] probably due to rearrangement of the trans product formed initially. By comparison we found that the yellow isomer (*cis*-$[(PPh_3)_2Pt_2Cl_4]$) reacts much faster than the trans isomer with *p*-toluidine to yield *cis*-$[(PPh_3)Pt(p\text{-toluidine})Cl_2]$ rather than the expected trans product. This most unexpected result was carefully checked by a number of physical techniques, and although we have no explanation for it, it does provide strong evidence that the compound we have described as *cis*-$[(PPh_3)_2Pt_2Cl_4]$ is truly an isomer of, and not a crystalline modification of, *trans*-$[(PPh_3)_2Pt_2Cl_4]$. The yellow isomer reacted with carbon monoxide to yield *cis*-$[(PPh_3)Pt(CO)Cl_2]$ as expected, and although the yield was low, in our hands it was higher than that obtained from *trans*-$[(PPh_3)_2Pt_2Cl_4]$ which failed to react at room temperature and atmospheric pressure.

Registry No. *cis*-$[(PPh_3)_2PtCl_2]$, 15604-36-1; *trans*-$[(PPh_3)_2Pt_2Cl_4]$, 17522-96-2; $[(PPh_3)_2Pt_2Cl_4]$, 40192-47-0; *cis*-$[(PPh_3)Pt(p\text{-toluidine})Cl_2]$, 40192-48-1; *trans*-$[(PPh_3)Pt(p\text{-toluidine})Cl_2]$, 15604-91-8; *cis*-$[(PPh_3)Pt(CO)Cl_2]$, 19618-78-1.

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Circular Dichroism of D-(−)-Quinic Acid and Some of Its Metal Ion Complexes[1]

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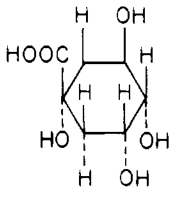
Through circularly dichroic absorption spectra (CD) it has been possible to follow 1:1 chelate complex formation between hydroxylic aliphatic carboxylic acids possessing optical activity and metal ions such as Ni(II), Co(II), and rare earths.[2-4] For most cations, the sign of the dichroism in a given optical transition of the visible spectrum correlates with the configuration at the α carbon of the optically active acid, when the hydroxyl group of the chelant remains protonated. This holds whether the hydroxyl coordinated is on the γ carbon, as tends to be the preferred position for the rare earths, the β carbon (preferred by the Ni(II)), or the α carbon.

In D-(−)-quinic acid (hexahydro-1,3,4,5-tetrahydroxybenzoic acid) (I) one of the hydroxyls is attached to the same carbon as is the carboxyl group, but this is not an asymmetric carbon in the usual sense. (If the 3 and 5 hydroxyl groups were on the same side of the ring, there would be a mirror plane through the 1 and 4 carbons.) The 3 and 5 carbons are themselves conventional asymmetric carbons, and when the corresponding hydroxyls are on the opposite sides of the ring, as in the natural product,[5] the compound is optically active. The hypothetical form I with both hydroxyls on the same side is recognizable as a meso acid. The 4 carbon, like the 1 carbon, is not asymmetric, but the cis or trans position of the hydroxyl relative to the carboxyl group differentiates isomers.



I

On adding $CoCl_2$, $NiCl_2$, or $PrCl_3$ to a solution of largely neutralized quinic acid, complexes form, signaled by the CD which appears in the metal ion absorption peaks. The CD is strong for Co(II), is relatively weak for Ni(II), and is of medium intensity for the Pr(III) system (Figure 1), compared with complexes of aliphatic hydroxy acid chelants.[2-4] In all three cases, the spectrum is characteristic for interaction of that metal ion with a levo α-hydroxy acid,[2-4] to give a 1:1 complex. The CD spectrum in the carboxyl absorption region of the free quinic acid is positive, the same sign as that for levo α-hydroxy (or α-amino) aliphatic acids,[6] though about 0.1 the intensity, so the behavior parallels the aliphatic acid case.

In the aliphatic α-hydroxylic acids, as mentioned, the asymmetry around the α carbon exerts the greatest influence on the carboxyl chromophore. In addition to any averaging-out of the effects of these more remote dissymmetries, due to rotations possible along the skeletal carbon chain, the short-distance dissymmetry of spatial field from the presence of hydrogen atom, hydroxyl group, and alkyl chain attached to the same carbon as the carboxyl can be expected to be overwhelming. This field is also transmitted to the metal ion which may be attached to the ionized carboxyl, even though the metal ion chelation may be completed by binding to a hydroxyl group attached to a different carbon atom which has its own local dissymmetry of substituents.

There is thus a difference in the influence of the environment which is quantitatively related to the nature of the bonding, as well as to spatial arrangements *per se*. In cases where the hydroxyl is deprotonated, the influence may shift so that the configuration around the carbon to which the

[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

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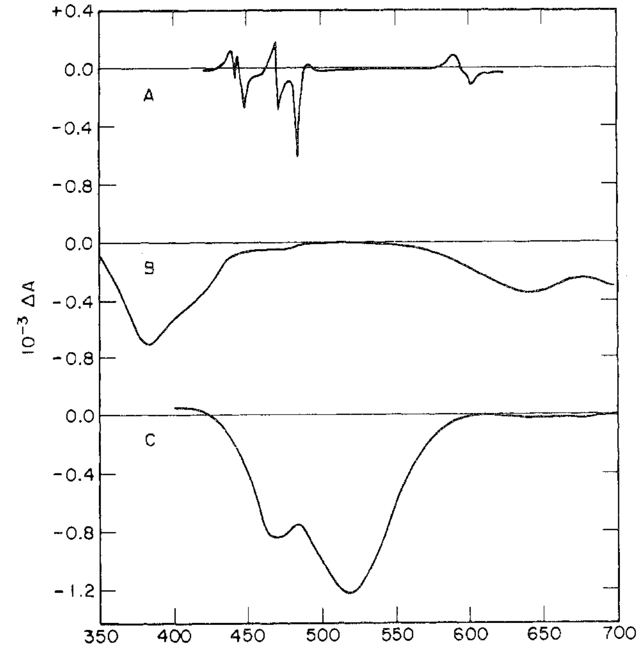

Figure 1. CD spectra of metal ion–D-(–)-quinic acid 1:1 complexes: (A) Pr^{3+} complex–upper states of transitions are $^3P_2$ (443.5 nm), $^3P_1$ (469 nm), $^3P_0$ (482 nm), and $^1D_2$ (590 nm); (B) Ni(II) complex–upper states of transitions are $\Gamma_1(^1G)$ (385 nm), $\Gamma_4(^3P)$ (408 nm), $\Gamma_5(^1D)$ (464 nm), and $\Gamma_4(^3F)$ (665 nm); (C) Co(II) complex–upper states of transitions are $^2T_{1g}$ (465 nm), $^4T_{1g}$ (517 nm), and $^4A_{2g}$ (646 nm).

hydroxyl is attached has the greater influence on the dichroism of the metal ion. With at least some metal ions, the influence of the hydroxyl ion attachment may override that of the carboxyl attachment even without deprotonation.[3]

With quinic acid, however, the spatial field at the carboxyl arises in asymmetries at the γ carbons. From the distance function implied in the dominance of the α carbon effect in the aliphatic acids, in which rotational and bending averagings along the chain are implicit in diminishing effects of more remote asymmetries, the strength of the quinic dichroism would be surprising. Presumably, then, the relative rigidity of positionings which the six-membered ring structure enforces on the carboxyl-asymmetry relation is very significant. Because of tetrahedral bonding at the 1 carbon, the carboxyl group is at an angle to the plane of the 6,1,2 carbon trio. The metal chelates, when formed between the two substituents on the 1 carbon, place the metal ion essentially *in* that plane, and presumably therefore in position to experience the maximum of the dissymmetric field. As the quantitative and qualitative effects on the metal ion transitions seem the same as those for the aliphatic α carbon asymmetric acids, the apparent lesser effects on the free carboxyl can be ascribed to geometric distribution of the field. We are left with the problem (and opportunity) of analyzing how the two different atomic situations give the same resultant asymmetric field at the α and 1 carbons.

The answer to this problem is not yet at hand. But some aid toward its answer may lie in observing that the carbonyl group of the optically active substituted cyclohexanones[7] functions as an indicator for the field asymmetry at the 1 position, parallel to the chelated metal atom of the quinic acid complexes and to the carboxyl group of the free acid (with allowance for the geometrical difference in position already cited). This comparison on spatial bases is not entirely free of questions of the influence of bonding differences. The bonds of the carbonyl carbon to the 2 and 6 carbons of the ring differ from those linking normal tetrahedral carbon at the 1 position, and even in the geometry-centered generalizations developed for the cyclohexanone systems there are definitely effects specific to the chemical nature of substituents.[8] This implies that detailed electron distribution (*i.e.*, bonding) plays a role here as it does with the metal ion chelates.

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Stoichiometric Study of the Chromium(II)-Chromium(VI) Reaction in Acidic Aqueous Chloride Media[1a]

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We are reporting a stoichiometric study of reaction 1, in acidic aqueous chloride-containing solutions, where Cr(III) includes the species $Cr(H_2O)_6^{3+}$, $Cr(H_2O)_5Cl^{2+}$ and $Cr_2(H_2O)_8(OH)_2^{4+}$

$$3Cr(II) + Cr(VI) = 4Cr(III) \tag{1}$$

The mechanism of the reaction in aqueous chloride-free media is not yet established,[2] but it is generally thought[2-5] to include the one-electron transfers indicated in eq 2-4.

$$Cr(VI) + Cr(II) \rightarrow Cr(V) + Cr(III) \tag{2}$$

$$Cr(V) + Cr(II) \rightarrow Cr(IV) + Cr(III) \tag{3}$$

$$Cr(IV) + Cr(II) \rightarrow Cr_2(H_2O)_8(OH)_2^{4+} \tag{4}$$

Additional steps are suggested by some observations, however. Hegedus and Haim[5] observed some ^{51}Cr label in $Cr(H_2O)_6^{3+}$ product, after labeling only the Cr(VI) reactant. These authors suggest that the two-electron transfer shown in eq 5,

$$^*Cr(V) + Cr(II) \rightarrow {}^*Cr(III) + Cr(IV) \tag{5}$$

using about 20% of the Cr(V), may account for their observation. Experiments[3,5] in which stoichiometric ratios of Cr(II) and Cr(VI) were used gave close to the 50% monomer product that is predicted by eq 2-4, or by eq 2-5. King, *et al.*,[4] working with excess Cr(VI) and low total reactant concentrations, found monomer yields ranging up to 71% of the total product. It was suggested[4] that reactions 6a and 6b may

$$Cr(IV) + H_2O \rightarrow Cr(III) + H^+ + OH \tag{6a}$$

$$Cr(II) + OH \rightarrow Cr(III) + OH^- \tag{6b}$$

account for the higher monomer yield. Additional steps that could lead to greater than 50% monomer have been proposed;[5] these are indicated by eq 7 and 8.

$$Cr(V) + Cr(IV) \rightarrow Cr(VI) + Cr(III) \tag{7}$$

$$Cr(IV) + Cr(IV) \rightarrow Cr(V) + Cr(III) \tag{8}$$

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