ments may be made about the pentagonal-pyramidal and cis octahedral structures.

**Pentagonal Pyramid.** The known pentagonal-pyramidal molecules are restricted to bis(peroxo) complexes, in which the peroxo ligands form part of the puckered pentagonal plane. The maximum deviations from the best least-squares plane through ABCDE are ±12, ±3, and ±7°, respectively, for the three compounds listed in Table II, which are less than the predicted value of ±16°. This may be partly due to the very short metal-apical oxygen bonds and/or to the quasi-pentagonal-bipyramidal nature of these molecules. In $(NH_4)_4[(V(O_2)_2O)_2O]$ there are six vanadium-oxygen bonds in the range 1.61-2.01 Å, but one of the peroxo oxygen atoms bonded to the other vanadium atom in the dimeric anion approaches to 2.50 Å to complete the pentagonal bipyramid. Similarly in $(NH_4)[V(O_2)_2O(NH_3)]$ there are five vanadium-oxygen bonds in the range 1.61-1.88 Å, but the vanadyl oxygen atom of an adjacent molecule occupies the seventh position creating a vanadium-oxygen distance of 2.93 Å.

**Cis Octahedral Structures.** These calculations lead to the interesting prediction that the cis octahedral structure will be distorted in a way which is significantly different from that which might have been intuitively expected.

Commencing with a regular octahedral *cis*-M(bidentate)$_2$(monodentate)$_2$ with a normalized bidentate bite of 1.414, at first sight it might be expected that a decrease in bite would simply result in the atoms A and B (and also the symmetry-related C and D) moving toward one another along the AB edge (and CD edge, respectively). That is, there would be expected to be an increase in $\phi_A$ and a decrease in $\theta_A$, with a simultaneous decrease in $\phi_B$ and increase in $\theta_B$. The effect on the bond angles about the metal atom M would be to increase AMC and AME, whereas AMF, BMC, and BMF would be relatively unchanged. The coordinate $\phi_E$ and the bond angle EMF (which is equal to twice $\phi_E$) would also be expected to increase as the other four donor atoms become more crowded together.

However an important prediction from these calculations is that this contraction in the bite from 1.414 to 0.7 is accompanied by a rotation of the bidentates about the twofold axis of the molecule resulting in a much larger distortion of the polyhedron. That is, in addition to the expected increase in $\phi_A$, there is an initial *increase* in $\theta_A$ (Figure 2). The increase in $\theta_B$ is consequently fairly large, whereas $\phi_B$ is approximately constant. (These results have been anticipated in Figure 1). In terms of bond angles, the increase in $\theta_A$ and $\theta_B$ results in an increase in AMF as well as in AMC and AME, whereas BMF remains close to 90°. No prediction can be made about BMC, since the ligand-ligand repulsion energy is relatively insensitive to this angle and also because the angle corresponding to minimum energy depends upon the assumed value of $n$ in the repulsive law.

This predicted increase in $\theta_A$ and $\theta_B$ on shrinking the bidentate is confirmed by experiment. The stereochemistry of the cis octahedral complex containing bidentates of smallest normalized bite, namely, $[Co(NO_3)_2(Me_3PO)_2]$, cannot be adequately described as "distorted octahedral." In this case $\theta_A = 17°$, and the relevant bond angles are AMC = 105°, AME = 96°, AMF = 96°, BMF = 91°, and BMC = 85°.

**Acknowledgments.** This work was carried out while on leave at the University Chemical Laboratories, University of Cambridge, and thanks are due to Professor J. Lewis and his colleagues for their hospitality.

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## Dimeric Triphenylphosphine Complexes of Platinum(II)

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During the course of attempting to prepare *trans*-$[(PPh_3)_2Pt_2Cl_4]$, which is orange, by a modification of the method described in ref 1, we prepared a new pale-yellow isomer which we consider to be *cis*-$[(PPh_3)_2Pt_2Cl_4]$. Since one of the main uses[2] of these bridged complexes involves their reaction with a further ligand to yield monomeric complexes $[(PPh_3)PtLCl_2]$, we investigated the reaction of the new isomer with *p*-toluidine and carbon monoxide.

### Experimental Section

**Preparation of $[(PPh_3)_2Pt_2Cl_4]$. Method 1.** *cis*-$[(PPh_3)_2PtCl_2]$[3] (10 mmol) and $PtCl_2$ (11 mmol) were refluxed in tetrachloroethane (150 ml) for 6 hr. After filtering to remove unreacted $PtCl_2$ the solution was cooled to 0° and treated with animal charcoal to remove the small amount of colloidal platinum formed. Light petroleum (*ca.* 200 ml, bp 60-80°) was then added with vigorous stirring to give a pale-yellow precipitate in 75% yield. *Anal.* Calcd for $[(PPh_3)_2Pt_2Cl_4]$: C, 41.0; H, 2.9. Found: C, 41.0; H, 3.0. The principal parent ion peak in the mass spectrum was at 1056 (calcd mol wt = 1056.6).

**Method 2.** Following the procedure in ref 1, *cis*-$[(PPh_3)_2PtCl_2]$[3] (0.92 mmol) and $PtCl_2$ (1.10 mmol) were refluxed with stirring under nitrogen in tetrachloroethane (25 ml) for 1 hr. After filtering to remove unreacted $PtCl_2$, treating the solution with animal charcoal, and evaporating to 5 ml under reduced pressure, a pale yellow crystalline solid contaminated with some colloidal platinum was obtained. Further pale yellow crystals were obtained by the addition of pentane. Following the procedure in ref 1, the product was purified by dissolving in chloroform, treating the solution with animal charcoal, and adding pentane to precipitate orange $[(PPh_3)_2Pt_2Cl_4]$ in 50% yield. *Anal.* Calcd for $[(PPh_3)_2Pt_2Cl_4]$: C, 41.0; H, 2.9. Found: C, 40.8; H, 2.8.

**Isomerization of $[(PPh_3)_2Pt_2Cl_4]$. Yellow Isomer.** When a solution of yellow $[(PPh_3)_2Pt_2Cl_4]$ was warmed in chloroform it rapidly turned orange with precipitation of the orange isomer. After boiling for 5 min quantitative conversion of the yellow isomer to the orange was achieved. The orange isomer was shown to be *trans*-$[(PPh_3)_2Pt_2Cl_4]$ by comparison with an authentic sample prepared as described by Goodfellow and Venanzi.[4]

**Orange Isomer.** When a solution of orange $[(PPh_3)_2Pt_2Cl_4]$ was refluxed in tetrachloroethane, it darkened due to the formation of a little colloidal platinum. After refluxing for 1 hr the solution was cooled to room temperature and treated with animal charcoal and the resulting yellow filtrate cooled in an ice bath to yield pale yellow crystals of $[(PPh_3)_2Pt_2Cl_4]$. Further pale yellow crystals were obtained by the addition of light petroleum to the mother liquor. The infrared spectra were identical with that of the yellow isomer of $[(PPh_3)_2Pt_2Cl_4]$.

**Reaction of $[(PPh_3)_2Pt_2Cl_4]$ with *p*-Toluidine. 1. Yellow Isomer.** When a solution of the yellow isomer of $[(PPh_3)_2Pt_2Cl_4]$ (0.187 mmol) in acetone was treated with a solution of *p*-toluidine (0.373 mmol) in acetone, a yellow precipitate of *cis*-$[(PPh_3)Pt(p\text{-toluidine})Cl_2]$ was obtained in 98% yield. The precipitate was filtered off, dried, and recrystallized from an acetone-petroleum ether (bp 60-80°) mixture. *Anal.* Calcd for $[(PPh_3)Pt(p\text{-toluidine})Cl_2]$: C, 47.3; H, 3.8; N, 2.2. Found: C, 47.1; H, 3.7; N, 2.0. The melting point was 247-249° (without decomposition). The observation of two Pt-Cl stretching vibrations in the far-infrared (Nujol mull) at 348.5 and 327 cm$^{-1}$, together with a dipole moment (in benzene at 25.2°) of 2.47 D, indicated that the product was the cis isomer.

**2. Orange Isomer.** A suspension of the orange isomer of

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(1) A. C. Smithies, P. Schmidt, and M. Orchin, *Inorg. Syn.*, 12, 240 (1970).

(2) F. R. Hartley, *Organometal. Chem. Rev., Sect. A*, 6, 119 (1970).

(3) L. Malatesta and C. Cariello, *J. Chem. Soc.*, 2323 (1958).

(4) R. J. Goodfellow and L. M. Venanzi, *J. Chem. Soc.*, 7533 (1965).

$[(PPh_3)_2Pt_2Cl_4]$ (0.185 mmol) in acetone was shaken vigorously with a solution of *p*-toluidine in acetone for 3 days at room temperature. After filtering off unreacted *trans*-$[(PPh_3)_2Pt_2Cl_4]$, the yellow filtrate was evaporated to dryness *in vacuo* and recrystallized from a mixture of acetone and petroleum ether (bp 60–80°) to give a 70% yield of pale yellow *trans*-$[(PPh_3)Pt(p\text{-toluidine})Cl_2]$. *Anal.* Calcd for $[(PPh_3)Pt(p\text{-toluidine})Cl_2]$: C, 47.3; H, 3.8; N, 2.2. Found: C, 47.8; H, 4.1; N, 2.8. The melting point was 196–198° (without decomposition). The observation of only one Pt–Cl stretching frequency in the far-infrared (Nujol mull) at 345.5 $cm^{-1}$, together with a dipole moment (in benzene at 25.2°) of 1.61 D, indicated that the product was the trans isomer.

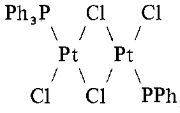
**Reaction of $[(PPh_3)_2Pt_2Cl_4]$ with Carbon Monoxide.** Suspensions of both the yellow and the orange isomers of $[(PPh_3)_2Pt_2Cl_4]$ (0.187 mmol) in benzene (20 ml) were stirred vigorously at room temperature for 10 days while a slow stream of carbon monoxide was bubbled in. The solutions were filtered to remove unreacted starting material and evaporated to dryness *in vacuo*. The solution from orange $[(PPh_3)_2Pt_2Cl_4]$ yielded no carbonyl complex, while that from yellow $[(PPh_3)_2Pt_2Cl_4]$ yielded a small quantity of a white precipitate which was recrystallized from a mixture of dichloromethane and hexane. The product exhibited a single carbonyl stretching band at 2117 $cm^{-1}$ in $CHCl_3$ solution and at 2077 $cm^{-1}$ in a Nujol mull and decomposed between 218 and 232° indicating that it was *cis*-$[(PPh_3)Pt(CO)Cl_2]$.

**Physical Measurements.** Infrared spectra were recorded on a Beckman IR11 spectrometer. Dipole moments were obtained in AnalaR benzene by the method of Chatt and Shaw[5] using a W.T.W. Dipolmeter fitted with a DM01 cell and an Abbe refractometer manufactured by Bellingham and Stanley, both of which were thermostated at 25.2°. X-Ray powder diffraction patterns were recorded on a Unicam S25 crystal goniometer using Cu Kα radiation. Mass spectra were obtained from an A.E.I. MS12 instrument.

## Results and Discussion

In addition to the properties listed in Table I, the yellow isomer of $[(PPh_3)_2Pt_2Cl_4]$ gives a very different X-ray powder diffraction pattern to the orange isomer. While this does not completely preclude the possibility that the yellow complex is a crystalline modification of the known trans isomer, it strongly supports the data in Table I, particularly the electronic spectrum, which was obtained in solution and the reaction with *p*-toluidine in suggesting that the two compounds are isomers and not different crystalline forms of the same compound.

In view of the known structure of the orange isomer **1**,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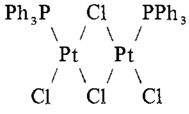
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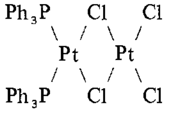
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there are two likely structures for the yellow isomer, **2** and **3**.[6] The only difference between the electronic spectra of the yellow and orange isomers lies in the intensities of the bands. Since it has previously been noted[7] that the bands in $[PtCl_4]^{2-}$ and $[Pt_2Cl_6]^{2-}$ are at similar energies in the d-d transition region, indicating no interaction between the two platinum atoms in the dimeric complex, we favor structure **2** for the yellow isomer of $[(PPh_3)_2Pt_2Cl_4]$. This would result in each platinum atom in **1** and **2** being surrounded by one triphenylphosphine ligand and one terminal and two bridging chlorine atoms. Structure **2** is also consistent with our observation that yellow $[(PPh_3)_2Pt_2Cl_4]$ can be quantitatively isomerized to the orange form on warming in chloroform[8] and that the reverse isomerization takes place in tetrachloroethane. A rather high activation energy would be expected for the interconversion of **3** and **1**.

**Table I.** Properties of *cis*- and *trans*-$[(PPh_3)_2Pt_2Cl_4]$

| Property | *cis*-$[(PPh_3)_2Pt_2Cl_4]$ | *trans*-$[(PPh_3)_2Pt_2Cl_4]$ |
|---|---|---|
| Color | Pale yellow | Orange |
| Mp, °C | 320 with dec | 270–280[a] |
| Pt–Cl stretching frequencies in the ir spectrum, $cm^{-1}$ | 355 | 358 (Pt–Cl terminal) |
| | 325 | 319.5 (Pt–Cl bridging trans to Cl) |
| | 268 | 259 (Pt–Cl bridging trans to $PPh_3$) |
| Electronic spectrum[b] | 21,500 (60) | 21,500 (90) |
| | 26,500 (500) | 26,500 (750) |
| | 30,000 (1,400) | 30,000 (1,500) |
| | 36,360 (11,000) | 36,360 (13,000) |
| | 37,310 (12,500) | 37,310 (15,000) |
| | 38,310 (13,000) | 38,310 (16,000) |
| Product of rxn with *p*-toluidine | *cis*-$[(PPh_3)Pt(p\text{-toluidine})Cl_2]$ | *trans*-$[(PPh_3)Pt(p\text{-toluidine})Cl_2]$ |
| Product of rxn with CO | *cis*-$[(PPh_3)Pt(CO)Cl_2]$ | *cis*-$[(PPh_3)Pt(CO)Cl_2]$[c] |

[a] Present work, which is in agreement with that of ref 2. [b] Band positions given in $cm^{-1}$ with approximate molar extinction coefficients in parentheses. [c] A. C. Smithies and M. Orchin, private communication.

The infrared spectrum of the yellow isomer of $[(PPh_3)_2Pt_2Cl_4]$ is similar to that of the orange isomer. In both all three bands due to Pt–Cl stretching modes have weak shoulders on their low energy sides. A detailed comparison of the spectra of the two isomers (see Table I) shows that the highest Pt–Cl stretching frequencies, assigned to the terminal chlorine atom,[9] are similar in both isomers. By contrast, the other two bands, assigned to the bridging chlorine atoms,[9] are displaced slightly to higher energy in the yellow isomer. Such a spectrum is more likely for structure **2** than structure **3**.

An attempt to distinguish between structures **2** and **3** from the mass spectra fragmentation pattern failed because only the parent ion peaks could be observed. These peaks served, however, to confirm the formulation of the product as $[(PPh_3)_2Pt_2Cl_4]$. Although the present evidence strongly suggests that the yellow isomer has structure **2**, a single-crystal X-ray diffraction investigation is being undertaken to confirm this. The present rejection of structure **3** is in agreement with earlier work[10] on the structures of *cis*- and *trans*-$[(PPr_3)ClPt(SEt)_2PtCl(PPr_3)]$, where it was concluded that a cis structure analogous to **3** was thermodynamically unstable due to the large amount of electrical energy that would be stored in a molecule with a predicted dipole moment of about 20 D.

Insufficient data are given in ref 1 or in the same authors' earlier paper[11] to determine which isomer of $[(PPh_3)_2Pt_2Cl_4]$ they prepared. However, on repeating their preparation we obtained the yellow isomer initially but found that during the recommended recrystallization from chloroform it was quantitatively isomerized to the orange *trans*-$[(PPh_3)_2Pt_2Cl_4]$. It has been suggested previously[10] that such an isomerization occurs by reversible chloride bridge cleavage to yield two $[(PPh_3)PtCl_2]$ fragments. The decomposition observed dur-

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(5) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959).

(6) A referee has suggested that two further isomers, in which one and two triphenylphosphine molecules, respectively, are present as bridging ligands, should also be considered. We consider that such structures are most unlikely, firstly because triphenylphosphine ligands are not noted for their bridging ability and secondly because they appear incompatible with the present ultraviolet and visible and infrared spectral data.

(7) P. Day, M. J. Smith, and R. J. P. Williams, *J. Chem. Soc. A*, 668 (1968).

(8) Part of the driving force for the rapid isomerization of the yellow isomer in chloroform is the relatively low solubility of the orange isomer in this solvent.

(9) R. J. Goodfellow, P. L. Goggin, and L. M. Venanzi, *J. Chem. Soc. A*, 1897 (1967).

(10) J. Chatt and F. A. Hart, *J. Chem. Soc.*, 2363 (1953).

(11) A. C. Smithies, M. Rycheck, and M. Orchin, *J. Organometal. Chem.*, 12, 199 (1968).

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.

**Acknowledgments.** We thank the S.R.C. for a studentship (to G. W. S.), Dr. B. F. G. Johnson for carrying out the mass spectral investigation, Professor A. G. Davies for allowing us to use the microanalytical services at University College, London, and Johnson Matthey & Co. Ltd. for their generous loan of the platinum salts used during this investigation.

[12] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 3858 (1955).

[13] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1662 (1964).

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

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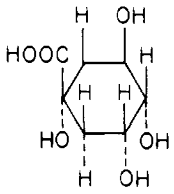
Through circularly dichroic absorption spectra (CD) it has been possible to follow 1:1 chelate complex formation between hydroxylic aliphatic carboxylic acids possessing optical activity and metal ions such as Ni(II), Co(II), and rare earths.[2-4] For most cations, the sign of the dichroism in a given 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.

[2] L. I. Katzin and E. Gulyas, *J. Amer. Chem. Soc.*, **92**, 1211 (1970).

[3] L. I. Katzin, *Inorg. Chem.*, **8**, 1649 (1969); **7**, 1183 (1968).

[4] L. I. Katzin, *Inorg. Chem.*, **12**, 649 (1973).

[5] B. A. Bohm, *Chem. Rev.*, **65**, 435 (1965).

[6] L. I. Katzin and E. Gulyas, *J. Amer. Chem. Soc.*, **90**, 247 (1968).