the square of the mixing coefficient divided by the square of the separation between the spin-allowed and spin-forbidden transitions. Thus while we would expect a $z$ component, based upon our selection rules, the intensity of this component is dependent upon a coupling coefficient and the proximity of a spin-allowed transition containing the equivalent representation. The polarization behavior of the 21,500-cm$^{-1}$ grouping is then explainable in terms of the behavior of the neighboring $^3T_2$ spin-allowed transition.

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## Pt–O Stretching and OH Wagging Frequencies in Trimethylplatinum Hydroxide[1]

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There has been considerable recent interest in the characterization of trimethylplatinum hydroxide $(CH_3)_3PtOH$, first prepared by Pope and Peachey.[2] Several workers have investigated the infrared and nmr spectra of this compound,[3–6] and very recently the assumed tetrameric structure upon which their analyses were based has been confirmed.[7–9] In this structure the four platinum atoms lie at the corners of a tetrahedron, with the four oxygen atoms forming a slightly smaller, interpenetrating tetrahedron, each OH group bridging three platinum atoms.

In the course of a detailed Raman and infrared study[10] of the compounds $[(CH_3)_3PtX]_4$ (where X = OH, Cl, I), we found reason to question previous interpretations of the infrared spectrum of $[(CH_3)_3PtOH]_4$, specifically in regard to the assignment of bands at 719 and 365 cm$^{-1}$ to Pt–O stretching and PtO deformation modes, respectively. Hoechstetter[3] originally assigned the band at 719 cm$^{-1}$ to Pt–O stretching on the basis of a small shift upon deuteration of the hydroxyl group. Morgan, *et al.*,[4] accepted this assignment and in addition attributed a band at 365 cm$^{-1}$ (beyond the range of the earlier work) to PtO deformation. In neither of these studies was a value assigned for the expected OH wagging mode.

Although the availability of vibrational spectra and assignments for metal–hydroxy complexes is limited, it is clear that the great majority of M–O stretching frequencies in such complexes appear well below the 719 cm$^{-1}$ assigned here. The range 300–625 cm$^{-1}$ includes most M–O stretching frequencies for simple hydroxy complexes[11] and complexes in which hydroxyl groups bridge two metals.[12,13] For hydroxyl or alkoxyl groups briding three metal atoms, one can compare the present case with $Pb_4(OH)_4^{4+}$[14] and $Tl_4(OR)_4$,[15] which have structures analogous to that of trimethylplatinum hydroxide and which show M–O stretching frequencies between 290 and 510 cm$^{-1}$. In $Tl_2Pt_2O_7$, where one also has Pt(IV) in octahedral coordination but where the Pt–O distances are considerably shorter (2.08 Å *vs.* 2.22 Å in $[(CH_3)_3PtOH]_4$), the highest infrared band is still only 684 cm$^{-1}$.[16] The structure of trimethylplatinum hydroxide shows no features which might account for an abnormally high Pt–O stretching frequency.

Clegg and Hall[17] have reported Raman spectra for aqueous solutions of $(CH_3)_3PtX$, where X is a poorly coordinating anion such as $NO_3^-$, $ClO_4^-$, or $SO_4^{2-}$. They interpreted the results in terms of a common cationic species, $(CH_3)_3Pt(OH_2)_n^+$, and assigned the value 357 cm$^{-1}$ to a Pt–O stretching mode. It has since been shown[18] that, for the perchlorate at least, $n = 3$, as expected. The Pt environment in this species is thus very similar to that in trimethylplatinum hydroxide, and we would expect Pt–O stretching frequencies near 357 cm$^{-1}$ for the latter.

Raman spectra of *solid* $[(CH_3)_3PtOH]_4$[10] also show a line near 719 cm$^{-1}$ and another one at 706 cm$^{-1}$. However, these bands are evidently shifted in benzene solution, since no intensity is observed between 700 and 740 cm$^{-1}$. This is further evidence against the assignment of the 719-cm$^{-1}$ frequency as Pt–O stretching (*i.e.*, a "cage" motion) since the remainder of the solution spectrum, as well as nmr results,[4] strongly indicates that the tetrametric cage structure is maintained in benzene solutions. New Raman lines are found at 744, 790, and 829 cm$^{-1}$ in benzene solution. These frequencies may include one or both of the modes shifted from 706 and 719 cm$^{-1}$.

We now present evidence from a new deuteration experiment that the 719-cm$^{-1}$ band (observed here at 724 cm$^{-1}$) in trimethylplatinum hydroxide is in fact due to OH wagging.

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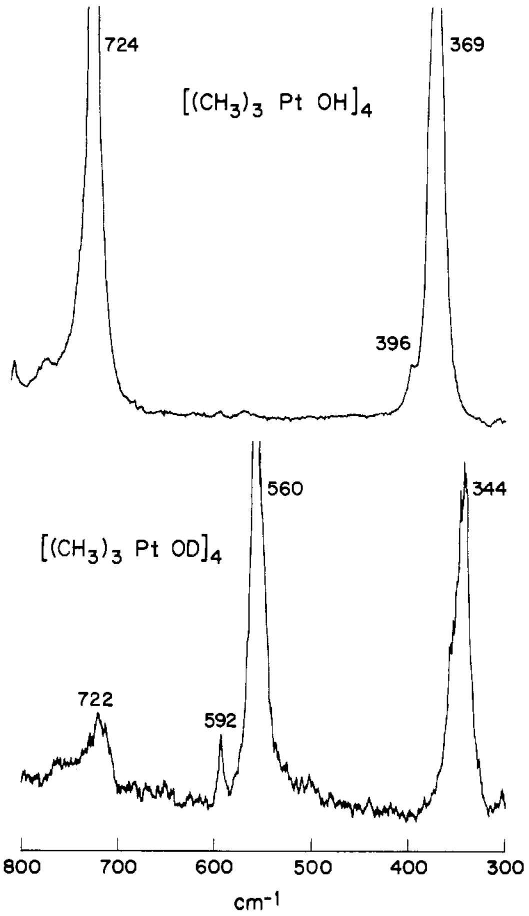

Figure 1.—Infrared spectra of Nujol mulls of $[(CH_3)_3PtOH]_4$ and $[(CH_3)_3PtOD]_4$.

### Experimental Section

$[(CH_3)_3PtI]_4$ was prepared by the method of Pope and Peachey.[2] $[(CH_3)_3PtOH]_4$ and $[(CH_3)_3PtOD]_4$ were prepared from $[(CH_3)_3PtI]_4$ as described by Pope and Peachey,[2] using $D_2O$ instead of $H_2O$ in the latter case. This was also the method used by Hoechstetter[3] in his deuteration experiment.

Infrared spectra were recorded as Nujol mulls between CsI plates on a Beckman IR-12 in the region 300–1100 $cm^{-1}$ for the hydroxide and 300–4000 $cm^{-1}$ for the deuterated compound. For the hydroxide, the spectrum was also obtained from a KBr pellet in the region 250–4000 $cm^{-1}$.

Raman spectra were obtained with He–Ne (6328 Å) laser excitation on an instrument which has been described previously.[19] Samples were microcrystalline solids pressed between glass plates.

### Results and Discussion

Infrared spectra in the region 300–800 $cm^{-1}$ are shown in Figure 1. Clearly the 724-$cm^{-1}$ band has shifted to 560 $cm^{-1}$ on deuteration, while the 369-$cm^{-1}$ band has shifted only to 344 $cm^{-1}$. It is possible that all or part of the residual intensity at $\sim$724 $cm^{-1}$ in the –OD spectrum can be attributed to the Nujol medium, which has a weak line in this area. The band at 592 $cm^{-1}$ in the spectrum of the deuterated compound also appears in spectra of more concentrated samples of $[(CH_3)_3PtOH]_4$ and has previously been assigned to Pt–C stretching.[3–5] In addition, $[(CH_3)_3PtOH]_4$ has an O–H stretching band at 3595 $cm^{-1}$ as previously reported,[3,4] while the deuterated compound shows an O–D stretching band at 2655 $cm^{-1}$ and only slight intensity at 3595 $cm^{-1}$. Otherwise the spectra are nearly identical.

Raman spectra of the solids give the same results. The lines found at 706 and 724 $cm^{-1}$ in $[(CH_3)_3PtOH]_4$ do not appear in the spectra of the deuterated compound, but a new line is found at 563 $cm^{-1}$. The OH and OD stretching frequencies are essentially identical with those found in the infrared spectrum.

On the basis of these results, the line which we locate at 724 $cm^{-1}$ in the infrared spectrum of $[(CH_3)_3PtOH]_4$, previously assigned to Pt–O stretching, is now assigned to OH wagging, $\delta_{OH}$(H–O–Pt bending). The observed ratio $\delta_{OH}/\delta_{OD} = 1.29$ is in the range found for many other hydroxy species.[20] We also assign the additional Raman line at 706 $cm^{-1}$ in the H compound to OH wagging. The infrared band which we find at 369 $cm^{-1}$ and the shoulder at 396 $cm^{-1}$ can then be assigned to Pt–O stretching, consistent with the frequency assigned for $(CH_3)_3Pt(H_2O)_3^+$.[17] For $[(CH_3)_3PtOH]_4$ (point group $T_d$), group theory predicts four Raman-active Pt–O stretching frequencies, two of these also appearing in the infrared spectrum. The Raman spectrum shows four lines between 340 and 430 $cm^{-1}$ which may be assigned to Pt–O stretching. Two of these are coincident with the infrared bands at 369 and 396 $cm^{-1}$. Complete Raman and infrared assignments for the cage modes of trimethylplatinum hydroxide will be published elsewhere.[10]

As to the previous deuteration results,[3] Hoechstetter stated that his infrared spectra indicated a mixture of OD and OH compounds, and we can only assume that the band he reported at 712 $cm^{-1}$ was a residue of the 719 $cm^{-1}$ line of the hydroxide and that the 560 $cm^{-1}$ OD line for some reason was not observed.

The OH wagging frequencies assigned here fall near the lower end of the range 600–1200 $cm^{-1}$,[11] usually associated with this mode. Two factors have been discussed[21] as being of primary importance in determining the location of the $\delta_{OH}$ mode: the per cent ionic character of the M–O bond (the more ionic the bond, the lower the frequency) and the O---O distance of any hydrogen bonds O–H---O associated with the hydroxyl proton (shorter O---O distances leading to higher frequencies). Tarte[21] studied a series of Cu(II)–hydroxy complexes, in which the first factor might be assumed to be reasonably constant, and found a nearly linear decrease of $\delta_{OH}$ as $\nu_{OH}$, the OH stretching frequency, increased. This was to be expected, since $\nu_{OH}$ is almost exclusively dependent on the second factor above, shorter O---O distances leading to lower $\nu_{OH}$ values. The data point for trimethylplatinum hydroxide (*i.e.*,

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(19) R. E. Miller, D. L. Rousseau, and G. E. Leroi, Technical Report No. 22, ONR Contract 1858(27), NR014-203, May 1967.

(20) E. Hartert and O. Glemser, *Z. Elektrochem.*, **60**, 746 (1956).

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$\nu_{OH}$ 3595 cm$^{-1}$, $\delta_{OH}$ 724 cm$^{-1}$) falls very near the best straight line for the Cu(II) system, indicating that the $\delta_{OH}$ value assigned here is reasonable. The low $\delta_{OH}$ frequency observed in the present case can then be understood as resulting from the absence of hydrogen bonding, which is also reflected in the sharpness of $\nu_{OH}$ (half-width ~5 cm$^{-1}$). In the crystal structure of trimethylplatinum hydroxide, the closest intermolecular contact is H(hydroxyl)-H(methyl) = 2.2 Å.[9]

Hartert and Glemser[20] have put the relationship between $\nu_{OH}$ and $\delta_{OH}$ into more general terms, allowing for variations in the per cent ionic character of the M–O bond by introducing an "effective radius" for the OH group, $R_{OH}$, as a parameter. The resulting empirical equation relates $\delta_{OH}$, $\nu_{OH}$, and $R_{OH}$, and seems to be useful for a wide range of cases. From the experimental frequencies for trimethylplatinum hydroxide, $R_{OH}$ is calculated to be 1.32 Å, which requires a cation ionic radius of 0.90 Å. This seems to be in the right range, since the ionic radii of $Pt^{2+}$ and $Pt^{4+}$ are thought to be ~0.95 and ~0.70 Å, respectively.[22]

(22) C. S. G. Phillips and R. J. P. Williams, "Inorganic Chemistry," Vol. II, Oxford University Press, New York, N. Y., 1966.

# Correspondence

## On the Question of the Generality of Symmetry Rules for Optically Active, Square-Planar Transition Metal Complexes[1,2]

*Sir:*

Optical activity in transition metal complexes has long intrigued theoreticians and experimentalists alike; yet, there is no satisfactory quantitative treatment of their rotatory strengths.[3] Because of the intimate relationship between molecular geometry, chromophoric symmetry, and Cotton effect signs, empirical symmetry rules have much practical value in addition to providing theoretical stimulus.[4] It is of much interest, then, to note that an octant rule ($D_{2h}$ rule[4b]) for copper(II)–amino acid complexes has been proposed.[5,6] A more recent proposal[7] claims that a $D_{4h}$ rule[4b] correlates not only the copper(II) complexes of amino acids, tripeptides, and tripeptide amides, but also the corresponding nickel complexes. A valid $D_{4h}$ rule would be of much theoretical and practical interest; clearly it is necessary to establish the accuracy and generality of such a rule. We wish to present evidence here which bears on this question.

Bis(L-prolinato)copper (**1**) and bis(hydroxy-L-prolinato)copper (**2**) have previously occupied a unique position in copper(II) complexes since they were claimed[7,8] to exhibit like, positive d–d Cotton effects. We have found **1** and **2** do have positive circular dichroism (CD) maxima in the 630–650-mμ region (Figure 1A) in agreement with the earlier observations.[7,8] However, previous work[9] on overlapping, oppositely signed Gaussian curves (OOG curves) has pointed up the difficulty of quantitative analysis of such curves. Clearly, from Figure 1A, bis(L-prolinato)copper(II) in water exhibits a CD spectrum composed of OOG curves. The dangers of assuming from Figure 1A that **1** and **2** exhibit like-Cotton effects is illustrated in Figure 1B. This latter figure shows the CD spectra of **1** and **2** in 95% ethanol. Again **1** exhibits OOG curves in ethanol as in water, whereas **2** clearly shows

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(1) (a) Structure and Optical Activity in Metal Complexes. V. Part IV: K. M. Wellman, T. G. Mecca, W. Mungall, and C. R. Hare, *J. Am. Chem. Soc.*, **90**, 805 (1968). (b) A preliminary report of this work was presented at the 156th National Meeting of the American Cheimcal Society, Atlantic City, N. J., Sept 1968; see Abstract INOR 75.

(2) All CD measurements reported here were recorded on a Cary 60 spectropolarimeter at ambient temperatures fitted with the Cary CD attachment. The amino acid amides and peptides were used as obtained from Cyclo Chemical Corp.

(3) For pertinent comments, see F. Woldbye, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **24**, 197 (1963), and A. M. Sargeson, "Transition Metal Complexes," Vol. 3, R. L. Carlin, Ed., Marcel Dekker, Inc., New York, N. Y., 1966, pp 334–342.

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