$\nu_{OH}$ 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]

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[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.

[4] (a) J. A. Schellman, *Accounts Chem. Res.*, **1**, 144 (1968); (b) J. A. Schellman, *J. Chem. Phys.*, **44**, 55 (1966).

[5] K. M. Wellman, W. Mungall, T. G. Mecca, and C. R. Hare, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, No. O-38; *Chem. Eng. News*, **45**, 48 (Oct 2, 1967).

[6] An "octant sign" rule has been proposed by C. J. Hawkins and E. Larsen, *Acta Chem. Scand.*, **19**, 185 (1965), but the authors' prediction that square-planar, bis complexes of simple D-amino acids and D-propylenediamine would yield negative d–d Cotton effects is opposite to observation (see ref 1, 7, and 8). The utility of this rule is further complicated by the attempt to use it to define the chirality of a complex in addition to predicting Cotton-effect signs.

[7] R. B. Martin, J. M. Tsangaris, and J. W. Chang, *J. Am. Chem. Soc.*, **90**, 821 (1968).

[8] T. Yasui, *Bull. Chem. Soc. Japan*, **38**, 1736 (1965); T. Yasui, J. Hidaka, and Y. Shimura, *J. Am. Chem. Soc.*, **87**, 2762 (1965).

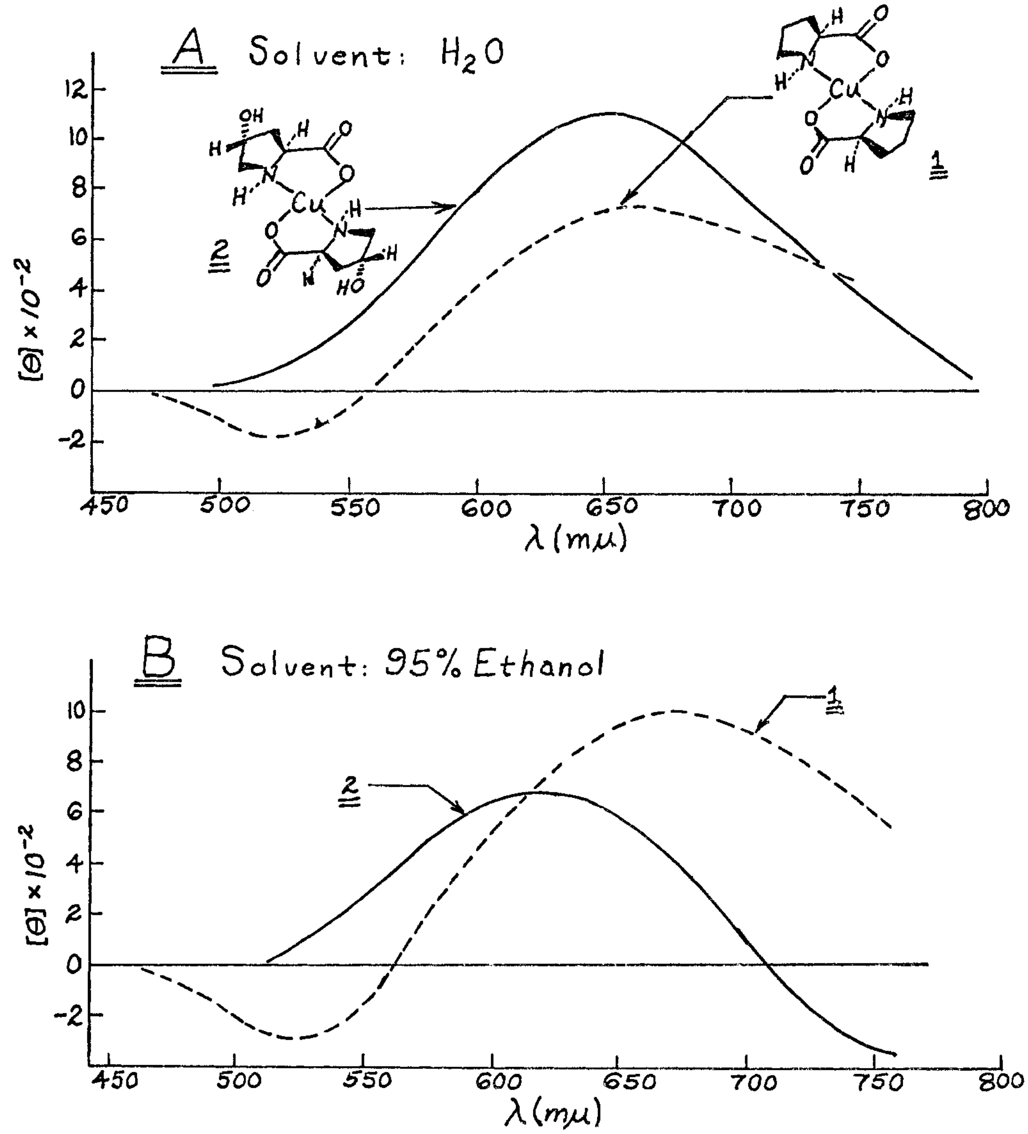

Figure 1.—Visible-region circular dichroism spectra for bis(L-prolinato)copper(II) and bis(hydroxy-L-prolinato)copper(II) in (A) water and (B) 95% ethanol.

OOG curves not apparent in water. The apparent shifts of the band maxima in Figure 1A and B are a function of the parameters of the parent overlapping curves.[9] The qualitative but important points to note are that the short-wavelength bands for **1** and **2** are opposite in sign as are the long-wavelength bands. This sign reversal is even more clearly defined in the aqueous solution spectra of the N-methylated derivatives shown in Figure 2A. Thus, one is left with a dichotomy: either the argument[7] used to predict like signs for the CD bands of the L-proline and hydroxy-L-proline is wrong (they exhibit oppositely signed curves) or the $D_{4h}$ rule is not applicable. In either case, the proline-like complexes do not appear to be suitable models to establish the correctness of one symmetry rule over another at this time.[10] In this connection, the suggestions that L-proline is unique because of its cyclic nature[11] or the formation of a second chiral center on chelating[8] seem unfounded, since the ligand N,N-dimethylleucine also exhibits a distinct OOG curve for its cupric complex (see Figure 2A). It appears that N-alkylation is the structural feature which makes the CD spectra in Figure 2A unusual (though they are by no means unique according to continuing work in our laboratory).

Application of the $D_{4h}$ rule to square-planar copper(II) complexes of L-prolylglycylglycineamide and L-prolineamide[12] (*cis* or *trans*) predicts like-signed Cotton

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(9) (a) K. M. Wellman, P. H. A. Laur, W. S. Briggs, A. Moscowitz, and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 66 (1965); T. Burer and L. I. Katzin, *J. Phys. Chem.*, **70**, 2663 (1966); (b) D. W. Urry, *Ann. Rev. Phys. Chem.*, **19**, 477 (1968).

(10) By appropriate conformational and configurational changes in the proline-like ligands, it may be possible to accommodate the results, in a fashion, by the $D_{4h}$ or $D_{2h}$ rule. This is hardly a satisfying procedure, since it has no basis in experiment, and it only serves to reduce further the validity of the proline complexes as useful models.

(11) R. D. Gillard, H. M. Irwing, R. M. Parkins, N. C. Payne, and L. D. Pettit, *J. Chem. Soc.*, *A*, 1159 (1966).

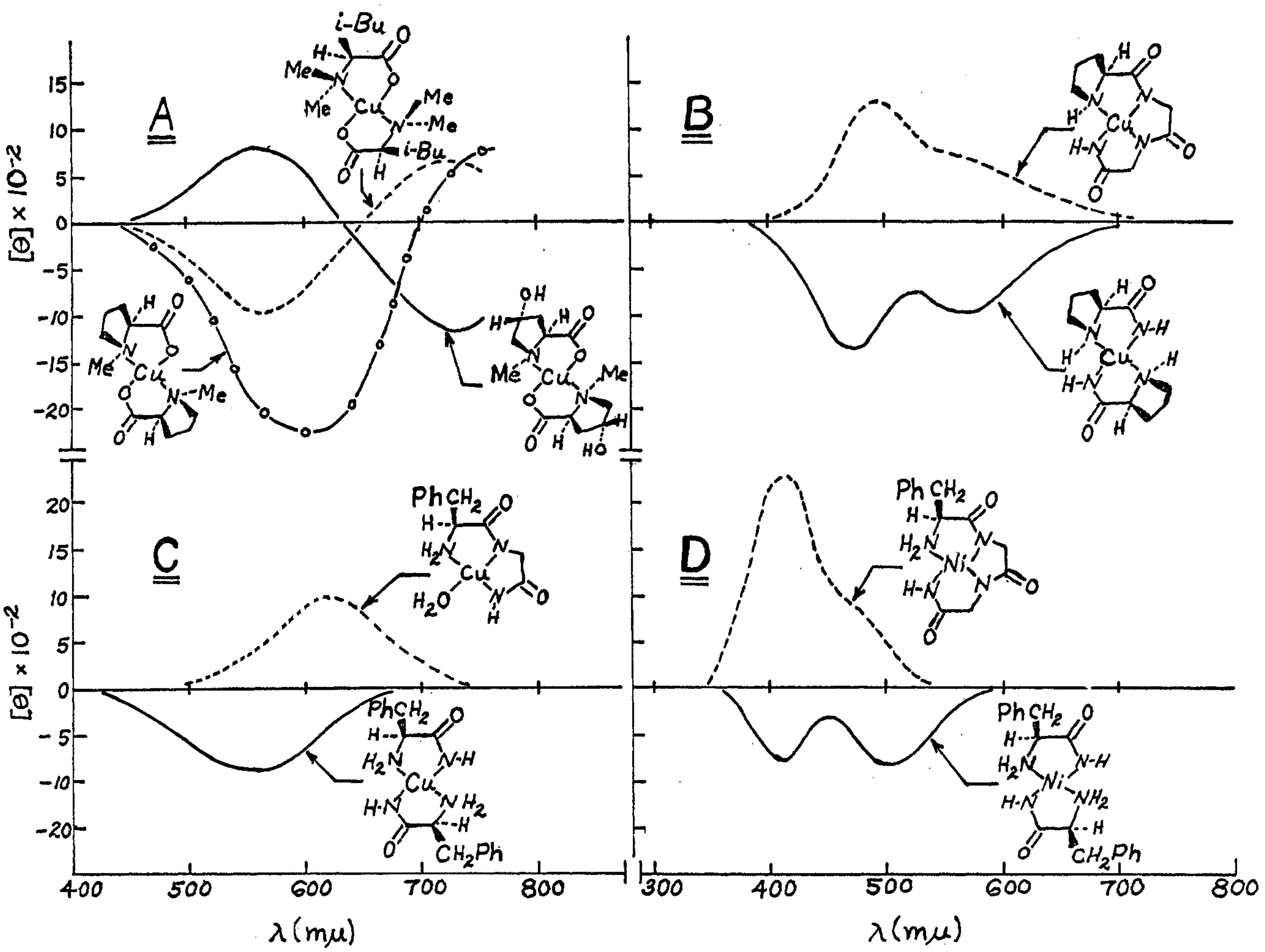

Figure 2.—Visible-region circular dichroism spectra for several metal complexes. Concentrations: copper(II) complexes, *ca.* 1 × $10^{-3}$ *M;* nickel(II) complexes, *ca.* 2 × $10^{-3}$ *M.*

effects. In point of fact the curves are almost mirror images as shown in Figure 2B. There is no experimental evidence to indicate that differences in chelate ring puckering cause the marked CD differences in these complexes.[13] Interestingly, the bis(proline)amide complex exhibits two negative d–d bands (Figure 2B) in contrast to a positive and negative band in the corresponding bis-proline complex.[8] Again, it is not clear how the $D_{4h}$ rule would accommodate this contrast if both complexes have approximate $D_{4h}$ symmetry as suggested previously.[7] Figure 2C shows the CD curves for the copper(II) complexes of L-phenylalanylglycineamide and the corresponding bis amide. Since the benzyl side chains lie in negative-contributing regions according to the tenets of the $D_{4h}$ rule, the mirror image relationship observed in Figure 2C is not predicted. The shift of the d–d transition envelope to longer wavelength for the dipeptide complex is consistent with the coordination of a water molecule in a square-planar position. Square-planar nickel complexes also show anomalies when attempting to apply the $D_{4h}$ rule as shown (see Figure 2D) by Cotton-effect sign changes as the coordinating atoms are varied while keeping the side chain in negative-contributing regions.

From the foregoing results, a $D_{4h}$ rule is clearly inadequate for even qualitative predictions over the structural variations covered. This conclusion is apparently independent of which d–d transition is concerned since the whole d–d Cotton-effect bands invert in most of the comparisons made. Furthermore, other likely symmetry rules, the "planar" rule ($C_{2h}$), "quadrant" rule ($C_{2v}$), and "octant" rule ($D_{2h}$), are similarly unsatisfying. At this point it is reasonable to ask: Should any symmetry rule based on the one-electron theory[4b] correlate the CD spectra of square-planar, transition metal complexes? The answer to this question is intimately involved with the degree of coplanarity of the metal and the coordinating atoms[14] (idealized coplanarity *cannot* be assumed in the peptide complexes[13]) and in the degree of coupling between the weak d–d transitions and the strong ligand–metal charge-transfer bands.[15] If these latter enhancement

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[12] Spectra of peptide and bis-amide complexes were measured at pH 10.5–11.5. The CD curves exhibit a slight pH dependence above pH 9; however, only the amplitude and not the sign of the curves is affected.

[13] A survey of X-ray crystallographic measurements shows that amino acid–metal complexes do not exhibit significantly more chelate ring deformation than do the peptides in the solid state. These observations will be discussed fully elsewhere.

[14] A. D. Liehr, *J. Phys. Chem.*, **68**, 665, 3629 (1964); R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 202 (1965).

mechanisms are operative, a complex situation arises which can (hopefully!) be comprehended only by quantitative treatment. A vibronic coupling mechanism[16] for rotatory strength enhancement in these cases of OOG curves cannot be dismissed without detailed consideration. Work is continuing.

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(15) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965); S. F. Mason and B. J. Norman, *Chem. Commun.*, 48 (1965).

(16) O. E. Weigang, Jr., *J. Chem. Phys.*, **43**, 3609 (1965).