

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
UNIVERSITY OF VIRGINIA, CHARLOTTESVILLE, VIRGINIA 22901Circular Dichroism of Palladium(II) Complexes of Amino Acids and Peptides¹

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Palladium(II) induces the ionization of peptide hydrogens near pH 3.5 to yield tetragonal complexes with amide nitrogen donor atoms similar to copper(II) and nickel(II) peptide complexes. Promotion of peptide hydrogen ionization increases in the series Co(II) < Ni(II) < Cu(II) < Pd(II). As previously demonstrated for the analogous copper(II) and nickel(II) complexes, the circular dichroism results of sign identity and magnitude additivity in a series of tripeptide complexes of palladium(II) rule out the applicability of any octant or quadrant rules as descriptions of optical activity in ligand field bands of these tetragonal complexes. Several lines of evidence suggest that a hexadecant (D_{1h}) rule best describes the optical activity in the case of small side chains. A homologous series of potentially tridentate L- α,ω -diaminocarboxylates are only bidentate with palladium(II). 2,3-Diaminopropionate and 2,4-diaminobutyrate chelate primarily through two nitrogen donor atoms and lysine chelates through the five-membered chelate ring α -amino and carboxylate groups, while ornithine chelates by a mixture of both binding modes despite the seven-membered chelate ring required for binding through the two nitrogen donor atoms. Vicinal effects of substituents rather than chelate ring puckering appear to be the primary source of optical activity in these complexes.

As a result of a series of titration, spectrophotometric,² and, most recently, X-ray diffraction studies³ the structures of copper(II) complexes of amino acids and simple peptides are well understood. Both copper(II) and nickel(II) induce the ionization of the amide hydrogen atoms of peptides to yield complexes with peptide nitrogen donor atoms. In the presence of peptides containing three or more amino acid residues nickel(II) undergoes a stereochemical change from octahedral to planar upon peptide hydrogen ionization.⁴ Thus, these complexes are similar in structure to the corresponding tetragonal copper(II) tripeptide complexes. These tetragonal metal ion-peptide complexes provide a relatively unpuckered system of chelate rings to which amino acid side chains are attached in known dispositions. The results of circular dichroism measurements on both⁵ the copper(II)⁶ and tetragonal nickel(II)⁷ complexes of peptides have been shown to render inapplicable any octant or quadrant rules as descriptions of the optical activity in ligand field bands.

In this paper we undertake a circular dichroism (CD) study of the palladium(II) complexes of amino acids and peptides. We find that palladium(II) is the most effective metal ion for inducing peptide hydrogen ionizations, with the result that complexes with peptide nitrogen donor atoms are also obtained for this metal ion. Previous conclusions regarding optical activity in tetragonal metal ion complexes are substantiated by the results reported for palladium(II).

Experimental Section

All the amino acids and peptides used in this study, purchased

from Calbiochem, Mann Research Laboratories, or Cyclo Chemical Corp., were of the highest purity available. The Na_2PdCl_4 was obtained from Alfa Inorganics, Inc. Titration data showed it to be at least 99% pure.

The pH titrations were performed on a Radiometer TTT1a titrator-SBR2b titrigrph combination. Absorption measurements were made with a Cary 11 spectrophotometer, and CD measurements were taken with a JASCO Model ORD/UV-5 optical rotatory dispersion recorder having a Roussel-Jouan CD attachment. CD results are presented as differential molar absorptivities between left and right circularly polarized light, $\Delta\epsilon = \epsilon_L - \epsilon_R$.

The complexes studied were prepared in the following manner. Appropriate amounts of amino acid or peptide were weighed accurately and transferred into a volumetric flask. A small amount of water was added to dissolve the sample. Because several solutions containing different ligands were usually studied during the same time interval, the Na_2PdCl_4 was weighed into a volumetric flask, and, after all the ligands were weighed and dissolved, the Na_2PdCl_4 was diluted and quickly measured into the ligand-containing flasks to avoid hydrolysis of the palladium(II) ions. Finally, the appropriate amount of 2 *N* NaOH was added to each solution to give the neutral or negatively charged complex, taking into account in each case whether the ligand was in the form of the free base or the mono- or dihydrochloride. All measurements were made within a maximum of 5 hr after mixing. The absorbancies of the solutions were adjusted to respond within the linear portion of the CD by varying the concentrations from 1×10^{-3} to 5×10^{-3} *M* and the cell path lengths from 1 to 50 mm.

Results

Titration curves for aqueous solutions of palladium(II) and several ligands of net zero charge are presented in Figure 1. A solution containing 4 mol of glycine per mole of PdCl_4^{2-} yields a sharp end point near pH 5 after the addition of 2 equiv of base, indicating chelation of two glycinate ligands about palladium(II) rather than simple coordination of two or more amino acid ligands. The titration curve in Figure 1 shows that half of the glycine in the original solution loses an ammonium proton at pH ~ 9.5 corresponding to the value expected for unbound glycine molecules. Chelated 2:1 amino acid-palladium(II) complexes were prepared for CD measurements by adding 2 mol of each neutral amino acid

(1) This research was supported by a grant from the National Science Foundation.

(2) W. L. Koltun, R. H. Roth, and F. R. N. Gurd, *J. Biol. Chem.*, **238**, 124 (1963).

(3) H. C. Freeman, *Advan. Protein Chem.*, **22**, 337 (1967).

(4) R. B. Martin, M. Chamberlin, and J. T. Edsall, *J. Am. Chem. Soc.*, **82**, 495 (1960); H. C. Freeman, J. M. Guss, and R. L. Sinclair, *Chem. Commun.*, 485 (1968).

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

(6) J. M. Tsangaris and R. B. Martin, in preparation.

(7) J. W. Chang and R. B. Martin, *J. Phys. Chem.*, **73**, 4277 (1969).

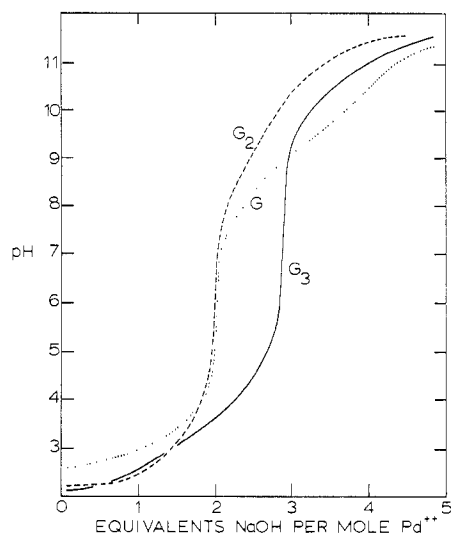


Figure 1.—Titration with 2 *M* NaOH of solutions containing 5 *mM* Na_2PdCl_4 and 20 *mM* glycine (G), 5 *mM* glycylglycine (G_2), and 5 *mM* glycylglycylglycine (G_3).

per mole of PdCl_4^{2-} and titrating with 2 equiv of base to sharp end points near pH 5.

Figure 1 also shows titrations of solutions containing equimolar amounts of PdCl_4^{2-} and either diglycine or triglycine. In the last case addition of 3 equiv of base to a solution containing neutral tripeptide and PdCl_4^{2-} is required to obtain a sharp end point near pH 6. No other titratable protons appear below pH 9. Evidently each neutral tripeptide ligand undergoes one ammonium and two peptide nitrogen ionizations to yield at neutral pH a planar palladium(II) complex with three nitrogen and one carboxylate oxygen donor atoms. Two equivalents of base is required to give a sharp end point near pH 4 in solutions containing equimolar amounts of dipeptide and PdCl_4^{2-} . Titration removes protons from the ammonium and peptide nitrogens, yielding a dipeptide chelated in a plane about palladium(II) coordinated by amino and peptide nitrogens and carboxylate oxygen. The fourth coordination position about palladium(II) is occupied by H_2O or Cl^- ; reference to Figure 1 shows that OH^- is not evident as a ligand until $\text{pH} > 8$. Absorption and CD measurements for both di- and tripeptides were made in the region of the equivalence points in Figure 1 from pH 6 to 7. In this pH region the ligand configuration is identical with that established by titration and X-ray studies for copper(II) and nickel(II) complexes of peptides that have undergone amide hydrogen ionization.²⁻⁴

The CD of 2:1 amino acid complexes of palladium(II) display maxima near 355 nm and minima near 310 nm. Differential molar absorptivities ($\Delta\epsilon = \epsilon_L - \epsilon_R$) for these chelated complexes are presented in Table I. The net charge on the 2:1 amino acid complexes in Table I is zero except for the aspartic and glutamic acid complexes where it is -2 due to the carboxylate side chains. All of these amino acid complexes exhibit an absorption maximum near 320 nm with ϵ about 300, consistent with a two nitrogen, two carboxylate oxygen donor

TABLE I
CD OF Pd(II) COMPLEXES OF L-AMINO ACIDS AND GLYCYL DIPEPTIDES

| L-Amino acid, X | 2X | | Gly-X | | X-Gly | |
|--------------------|---------------|---------------|-----------|-----------|-----------|-----------|
| | 345-370 nm | 305-315 nm | 375 nm | 320 nm | 375 nm | 320 nm |
| Alanine | +0.26 | -0.68 | -0.80 | +0.25 | | +0.05 |
| Serine | +0.26 | -1.09 | -0.56 | +0.09 | -0.04 | +0.18 |
| Threonine | +0.23 | -1.45 | | | -0.10 | +0.25 |
| Leucine | | | -0.96 | +0.07 | -0.08 | +0.23 |
| Aspartate | +0.95 | -0.88 | -0.55 | +0.22 | | |
| Glutamate | +0.25 | -1.29 | -1.10 | +0.15 | | |
| Valine | +0.06 | -1.79 | -1.10 | +0.56 | -0.10 | +0.13 |
| Phenylalanine | | | -0.76 | -0.50 | +0.12 | +0.45 |
| Tyrosine | | | -0.80 | -0.63 | | +0.63 |
| Proline | +0.58 | -1.17 | | | -0.24 | +1.25 |

system. In addition to the data presented in Table I, the 2:1 palladium complex of L- α -aminobutyrate gives $\Delta\epsilon = +0.08$ and -1.20 at 360 and 312 nm, respectively, and the 2:1 L-hydroxyproline complex yields $\Delta\epsilon = +0.50$ and -0.58 at 363 and 317 nm, respectively.

Circular dichroism of potentially tridentate L-amino acids is shown in Table II. These complexes were pre-

TABLE II
CD AND ABSORPTION OF 2:1 Pd(II) COMPLEXES OF ZERO NET CHARGE WITH L-AMINO ACIDS

| | Absorption | | Circular dichroism | | | |
|-------------------------|-----------------|------------|--------------------|------------------|-----|------------------|
| | nm ^c | ϵ | nm | $\Delta\epsilon$ | nm | $\Delta\epsilon$ |
| 2,3-Diaminopropionate | 288 | 327 | | | 288 | +0.70 |
| 2,4-Diaminobutyrate | 292 | 416 | 355 | +0.04 | 289 | +0.59 |
| Ornithine | 294 | 352 | 343 | +0.11 | 271 | +0.28 |
| | | | | | 304 | -0.30 |
| Lysine ^a | 320 | 315 | 365 | +0.10 | 312 | -1.40 |
| Histidine | 280 sh | 460 | 313 | -0.63 | 252 | +2.9 |
| Cysteinate ^b | 415 sh | 80 | 429 | -0.16 | 295 | -2.5 |
| | 337 | 1300 | | | | |
| S-Methylcysteine | 310 sh | 2000 | 395 | +0.04 | 318 | -0.56 |
| Methionine | 315 | 2220 | 379 | +0.32 | 300 | -1.8 |

^a Net charge of $+2$ as zero net charge complex is less soluble but exhibits a similar absorption spectrum. ^b Net charge of -2 . ^c sh signifies shoulder.

pared by mixing 2 mol of ligand per mole of palladium(II) in water and titrating to the equivalence point. Sharp end points were obtained corresponding to single negative charge on each ligand molecule near pH 5, 6, and 9, respectively, for the first three ligands of Table II. Lysine behaves like the simple bidentate amino acids reported in Table I. Attempts to neutralize the ϵ -ammonium group of lysine gave precipitates in the presence of palladium(II). The 2:1 histidine complex also yields a sharp end point near pH 6 corresponding to zero net charge on the complex. The last three entries in Table II, all sulfur-containing amino acids, display high molar extinction coefficients in absorption spectra, indicating involvement of the sulfur atoms in chelation.

Tables I and III list the CD $\Delta\epsilon$ values for 1:1 complexes of palladium(II) and dipeptides obtained near pH 6 where amino nitrogen, ionized amide nitrogen, and carboxylate oxygen donor atoms are presented to the metal ion. The dipeptide complexes exhibit absorption maxima near 330 nm with ϵ about 700. In addition to the results reported in Table I, L-isoleucylglycine gives a CD similar to that for L-valylglycine; the first amino acid of each dipeptide undergoes branching at the β -carbon atom. The glycyl-L-histidine complex with a ligand charge of -2 and a structure

TABLE III
 CIRCULAR DICHROISM OF Pd(II) COMPLEXES OF DIPEPTIDES

| Dipeptide | Obsd | | Calcd from Table I | |
|-------------|--------|--------|--------------------|--------|
| | 375 nm | 320 nm | 375 nm | 320 nm |
| L-Ala-L-Ala | -0.81 | +0.34 | -0.80 | +0.30 |
| L-Ala-D-Ala | +0.82 | -0.20 | +0.80 | -0.20 |
| L-Leu-L-Leu | -1.08 | +0.12 | -1.04 | +0.30 |
| L-Leu-D-Leu | +1.02 | +0.25 | +0.88 | +0.16 |
| L-Ala-L-Leu | -1.02 | +0.16 | -0.96 | +0.12 |
| L-Leu-L-Ala | -0.88 | +0.36 | -0.88 | +0.48 |
| L-Leu-L-Tyr | -0.87 | -0.65 | -0.88 | -0.40 |
| D-Leu-L-Tyr | -0.81 | -0.85 | -0.72 | -0.86 |
| L-Phe-L-Val | -1.07 | +0.98 | -0.98 | +1.01 |
| L-Val-L-Phe | -1.00 | -0.62 | -0.86 | -0.37 |

presumably similar to that of the copper(II) complex⁸ yields $\Delta\epsilon = -0.48$ and $+0.79$ at 345 and 285 nm, respectively, and an absorption maximum at 314 nm with ϵ 450. The CD does not change appreciably upon titration of the carboxylic acid side chains in the glycyl-L-aspartic acid and glycyl-L-glutamic acid complexes suggesting that these side-chain carboxylate groups do not interact directly with palladium(II). A similar result and conclusion are also obtained for the noninvolvement of the carboxylate side chains in the 2:1 complex of the L-amino acids with palladium(II).

Table III also tabulates CD magnitudes for dipeptides calculated from the sums of observed values for the two relevant glycyl dipeptides in Table I. The observed results for L-alanyl-glycine are added to those for glycyl-L-alanine to obtain the calculated sums for L-alanyl-L-alanine in Table III. For L-alanyl-D-alanine the results in Table I for glycyl-L-alanine are subtracted from those for L-alanyl-glycine. Agreement is excellent between the observed and calculated results at 375 nm and only slightly less good at 320 nm, where contributions from an electron-transfer band at shorter wavelengths affect the magnitudes. The excellent agreement between the observed results for dipeptides composed of two optically active amino acid residues and the value calculated from the sum of the two corresponding glycyl dipeptides demonstrates that contributions to optical activity in ligand field bands of palladium(II) complexes of dipeptides are additive functions of independent contributions from each amino acid residue. This statement holds even when D-amino acid residues appear in the peptides.

 TABLE IV
 CIRCULAR DICHROISM OF Pd(II) COMPLEXES OF TRIPEPTIDES COMPOSED OF L-AMINO ACID RESIDUES

| | 335 nm | | 290 nm | | | 335 nm | | 290 nm |
|-------------|-------------|-------|-------------|-------------|-------|--------|--|--------|
| | Ala-Gly-Gly | -0.10 | +0.15 | Leu-Gly-Leu | | -1.20 | | |
| Gly-Ala-Gly | -1.50 | +0.15 | Gly-Ala-Leu | -2.60 | | | | |
| Gly-Gly-Ala | -1.00 | +0.37 | Val-Gly-Gly | -0.24 | +0.47 | | | |
| Ala-Ala-Ala | -2.50 | +0.30 | Phe-Gly-Gly | +1.20 | | | | |
| Leu-Gly-Gly | -0.30 | +0.30 | Gly-Phe-Gly | -1.45 | +0.38 | | | |
| Gly-Leu-Gly | -1.70 | | Gly-Gly-Phe | | -1.60 | | | |
| Gly-Gly-Leu | -1.30 | | | | | | | |

The CD of tripeptide complexes of palladium(II) are presented in Table IV. These data were obtained in

neutral solutions where the four positions about the palladium(II) plane are occupied by three nitrogen and one carboxylate oxygen ligand donor atoms so that each complex possesses a net charge of -1 . These solutions yield an absorption maximum at 300 nm with ϵ about 1300, nearly ten times greater than for the corresponding nickel(II) complexes.⁷ The substantial CD magnitude observed when the carboxyl terminal residue of a di- or tripeptide complex contains a side chain provides additional evidence that the last residue is chelated and a carboxylate oxygen coordinated to palladium(II). The sum (-2.60) of the CD magnitudes at 335 nm for the first three peptides of Table IV, each containing a single L-alanyl residue, is nearly identical with the value obtained for the trialanine complex. Two other such additions are possible within Table IV; it is unfortunate that the trileucine and triphenylalanine complexes were insufficiently soluble to obtain a CD. As for the dipeptides we conclude that each amino acid residue contributes independently to optical activity of the ligand field bands of the tripeptide complexes.

Discussion

Addition of base to solutions containing palladium(II) and an equimolar amount of di- or tripeptides results in the titration of 2 and 3 equiv of protons, respectively, before the end points near pH 6. No breaks occur in the titration curve below pH 6 where the ammonium and one or two amide hydrogens undergo removal to solvent. The pK_a value for palladium(II)-induced deprotonation of the amide hydrogens in peptides is about 3.5. This value is approximately 2, 5, and 7 pK_a units less than for the respective copper(II)-,² nickel(II)-,⁴ and cobalt(II)-promoted⁹ peptide hydrogen ionizations. Thus palladium(II) is the most effective metal ion yet measured in promoting peptide hydrogen ionizations. The wavelengths of absorption spectra maxima are consistent with amide nitrogens serving as donor atoms after amide hydrogen ionization. Therefore the structures of the palladium(II) peptide complexes may be taken as similar to those established for copper(II)³ and nickel(II)⁴ complexes.

By noting the similarity of observed and calculated values for CD magnitudes of dipeptides in Table III and from comparisons of tripeptides within Table IV we have already concluded that the optical activity generated in the ligand field bands of palladium(II) complexes of peptides are composed of additive and independent contributions from each amino acid residue. The same conclusion has also been reached for nickel(II)⁷ and copper(II)⁶ complexes of peptides provided that the side chain is not too large, particularly if it is located in the amino terminal position. This additivity relationship is important because it suggests that the conformation adopted by the side chains in a di- or tripeptide complex is independent of the side chains present in other residues of the peptide.

As has already been demonstrated for nickel(II) and copper(II) complexes of peptides,⁵⁻⁷ the sign identity as

(8) J. F. Blount, K. A. Fraser, H. C. Freeman, J. T. Szymanski, and C. H. Wang, *Acta Cryst.*, **22**, 396 (1967); *Chem. Commun.*, 23 (1966); R. B. Martin and J. T. Edsall, *J. Am. Chem. Soc.*, **82**, 1107 (1960).

(9) M. S. Michailidis and R. B. Martin, *ibid.*, **91**, 4683 (1969).

observed in the first three alanyl peptides or the three monoacyl-containing peptides of Table IV rules out the applicability of any octant rule to these tetragonal complexes. No matter how octants are drawn in these complexes of well-defined structure, the Gly-X-Gly tripeptide must have a sign opposite that of the other two tripeptides containing a single optically active amino acid residue. Sign identity for a set of three tripeptides may be accommodated either by constructing hexadecants, which divide the plane of the chelate ring into eight wedge-shaped regions of alternating sign, or by simply assigning one sign to the region above the chelate plane and the other to that below.⁵⁻⁷ Both sector rules have support if the one-electron perturbation model of optical activity is applicable, as the former is the pseudoscalar representation for molecules belonging to the D_{4h} symmetry point group and the latter that for the C_{2h} or C_s point groups.¹⁰ The former rule predicts little difference in CD signs and magnitudes for *cis* and *trans* isomers of chelated L-amino acid complexes, while the latter rule predicts near-zero magnitude for *cis* isomers of chelated L-amino acid complexes since the two side chains appear in sectors of opposite sign. The observation that the *cis* and *trans* complexes of bis(L-alanineamidato)palladium(II) each display a total $\Delta\epsilon = -0.98$ within 4% of each other¹¹ supports the hexadecant (D_{4h}) sector rule for the d-d transitions in tetragonal transition metal ion complexes. Alternatively a C_{2v} rule may be applied to the *cis* complex. The palladium(II) complexes reported in this paper represent the third divalent transition metal ion for which octant and quadrant rules are eliminated as general descriptions of the results of optical activity in the ligand field bands of tetragonal complexes.

Results recorded in Table II were obtained in order to find the ring size at which a transition occurs from N,O to N,N donors in tetragonal palladium(II) complexes. The first four L-amino acids may be viewed as substituted glycines with the possibility of chelating through a five-membered ring with α -amino nitrogen and carboxylate oxygen donor atoms. They may also chelate through two amino nitrogen donor atoms with five-, six-, seven-, and eight-membered rings, respectively. Simultaneous chelation by all three donor atoms in a plane about one palladium(II) ion is sterically impossible. Two lines of evidence suggest that no apical chelation occurs in these potentially tridentate ligands and that only two of three possible donor atoms are coordinated to palladium(II). The 2:1 lysine complex exhibits an absorption spectrum and CD consistent with the other amino acids in Table I that must have two α -amino and two carboxylate oxygen donor atoms. Second, the L-2,3-diaminopropionate complex exhibits an absorption maximum at 288 nm identical with that of the bis-($-$)-1,2-diaminopropane complex, which must possess four amino donors.¹² The CD for

the lysine complex is characterized by a large negative peak at 312 nm, and that of L-2,3-diaminopropionate, by a smaller positive peak at 288 nm. Examination of Table II reveals that the ornithinate complex exhibits a CD that is most nearly characteristic of an equal mixture of N,N and N,O donors. Thus for palladium(II) the crossover from a five-membered N,O donor system occurs at ornithine with its seven-membered ring system composed of N,N donors. That such a large ring is competitive with a five-membered ring containing N,O donors is due to the preference of palladium(II) for nitrogen over oxygen donor atoms. Involvement of the sulfur atom of methionine in chelation indicates that palladium(II) prefers chelation involving an amino nitrogen and an ether sulfur in a six-membered ring to chelation involving a five-membered ring with amino nitrogen and carboxylate donors.

The palladium(II) complexes of L-amino acids recorded in Table I and that for L-lysine in Table II exhibit a predominantly negative CD for their ring systems with N and O donors. The positive CD values for L-2,3-diaminopropionate and L-2,4-diaminobutyrate recorded in Table II for ligands which chelate through two N donors may be accounted for by noting that the position of the carboxylate side chain in these chelated systems corresponds to that of a side chain in a D-amino acid with N and O donors. The positive $\Delta\epsilon = +1.22$ at 282 nm recorded for the 2:1 complex of ($-$)-1,2-diaminopropane with palladium(II)¹² is consistent with the CD sign pattern, as the configuration of this ligand corresponds to that of D-amino acids. Both the wavelength of the absorption maximum and the CD pattern indicate that histidine chelates through two nitrogen donor atoms.

The magnitudes of the CD in the 1:2 palladium(II) complexes of ($-$)-1,2-diaminopropane and that recorded in Table II for L-2,3-diaminopropionate, two ligands with puckered chelate rings, are similar to the magnitudes in Table I for amino acids and peptides which possess nearly planar chelate rings. Similar CD magnitudes have also been noted for ($-$)-1,2-diaminopropane and amino acid complexes of copper(II)⁶ and nickel(II).⁷ The CD of a d-d transition in the necessarily unchelated complex *trans*-dichlorobis(($-$)-1-phenylethylamine)palladium(II) is a significant $\Delta\epsilon = -0.5$ ¹³ presumably due to a favored ethanic rotamer with *trans* palladium(II) and phenyl groups and little rotational averaging. All the CD magnitudes are minimal due to the cancellation of oppositely signed components. The sign correspondences pointed out in the previous paragraph and the similarity of CD magnitudes of complexes with puckered, nearly planar, and no chelate rings suggest that those proposals for generation of optical activity in d-d transitions of metal ions by some form of chelate ring puckering are incomplete. The nearly identical CD magnitudes for *cis* and *trans* isomers of bis(L-alanineamidato)palladium(II)¹¹ indicate that disposition or configuration of these ligands about tetragonal transition metal ions is not an im-

(10) J. A. Schellman, *J. Chem. Phys.*, **44**, 55 (1966).

(11) T. Komorita, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Japan*, **41**, 854 (1968).

(12) H. Ito, J. Fujita, and K. Saito, *ibid.*, **40**, 2584 (1967).

(13) B. Bosnich, *J. Chem. Soc., A*, 1394 (1966).

portant contributor to optical activity in d-d transitions. Similar CD magnitudes observed for puckered, planar, and no chelate rings also suggest a low contribution from chelate ring puckering in the complexes discussed in this paper. Vicinal effects of substituents remain as the primary source of optical activity in ligand field bands of most tetragonal transition metal ion complexes displaying relatively weak CD.

The relative energies of the 4d orbitals in tetragonal palladium(II) are difficult to determine because they are closely spaced, and because electron-transfer transitions interfere at short wavelengths. A likely order of increasing energies for the 4d orbitals of palladium(II) in these systems is $z^2 < xz \sim yz < xy < x^2 - y^2$.¹⁴ In the D_{4h} symmetry point group the above ordering is described by the representations $a_{1g} < e_g < b_{2g} < b_{1g}$. In d^8 palladium(II) the three spin-allowed one-electron d-d transitions in order of increasing energy are $b_{2g} \rightarrow b_{1g}$ ($A_{1g} \rightarrow A_{2g}$), $e_g \rightarrow b_{1g}$ ($A_{1g} \rightarrow E_g$), and $a_{1g} \rightarrow b_{1g}$

(14) W. R. Mason and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 5721 (1968).

($A_{1g} \rightarrow B_{1g}$). These transitions are designated A, E, and B, respectively. Of these three transitions only the highest energy one labeled B is magnetic dipole forbidden to the extent that D_{4h} microsymmetry is maintained. Application of the above ordering leads to the assignment of the E transition to the positive CD peak observed in most tripeptide palladium(II) complexes near 290 nm and the A transition to the negative peak near 335 nm. The CD of the tripeptide complexes of palladium(II) bears a sign pattern similar to that of the tetragonal nickel(II) complexes. Both display a consistently negative CD peak at a wavelength 35 nm or greater than the absorption maximum and occasionally a positive CD peak nearer the absorption maximum. The assignments suggested above are consistent with those already made for the tetragonal nickel(II) complexes where the B transition may be at relatively lower energy.⁷ These assignments may also be applied to the other peptide, amide, and amino acid complexes of palladium(II).

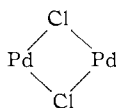
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Polynuclear Complexes of Palladium(II) with Halogen and Sulfur Bridges

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The reaction of $\text{Na}_2[\text{PdCl}_4]$ with diphenyl disulfide in methanol yields a polymeric compound of formula $[\text{Pd}(\text{SC}_6\text{H}_5)\text{Cl}]_n$ (I) containing alternating halogen and sulfur bridges. This compound is also formed by refluxing $[\text{Pd}((\text{C}_6\text{H}_5)_2\text{S}_2)\text{Cl}_2]_2$ in methanol. The characterization of I was based on its infrared spectra and on its bridge-splitting reactions. In the reaction of I with a neutral ligand L (L = pyridine, triphenylphosphine, triphenylarsine) S-bridged complexes of the type $[\text{Pd}(\text{SC}_6\text{H}_5)\text{LCl}]_2$ are formed. The reaction with ethylenediamine yields the cationic S-bridged complex $[\text{Pd}(\text{SC}_6\text{H}_5)(\text{en})_2\text{Cl}]_2$, whereas with $[\text{As}(\text{C}_6\text{H}_5)_4]\text{Cl}$ the cationic complex $[\text{Pd}(\text{SC}_6\text{H}_5)\text{Cl}]_2[\text{As}(\text{C}_6\text{H}_5)_4]_2$ is formed. The above reactions involve only splitting of the



bridges. When I reacts either with 1,2-bis(diphenylphosphino)ethane or with an excess of phosphine, both the halogen and sulfur bridges are cleaved. The nature of the products in the bridge-splitting reactions has been determined on the basis of elemental analysis, ir spectra, conductivity, and molecular weight measurements, where possible.

Introduction

Palladium(II) has a great tendency to form thiolato-bridged complexes which are usually very resistant to cleavage by reactions with neutral ligands.¹ Polymeric structures with only sulfur bridges have been obtained in the reactions of PdCl_4^{2-} with alkyl or aryl thiols.^{2,3} The present work reports the synthesis and the bridge-splitting reactions of new polymeric complexes of palladium(II) containing alternating

halogen and sulfur bridges, $[\text{Pd}(\text{SC}_6\text{H}_5)\text{X}]_n$. The aim was to study the course of the reaction between palladium(II) derivatives and diphenyl disulfide in order to investigate the cleavage of the sulfur-sulfur bond promoted by palladium(II) complexes and also to determine the nature of the reaction products in these reactions.

(1) L. F. Lindoy, *Coord. Chem. Rev.*, **4**, 41 (1969), and references therein.

(2) F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1549 (1935).

(3) R. G. Hayter and F. S. Humiec, *J. Inorg. Nucl. Chem.*, **26**, 807 (1964)