# A Thermodynamic Study of the Complexation and Coordinated Ligand Deprotonation Reactions for a Series of Tryosine Isomers with Copper(II)[1]

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**Abstract:** The thermodynamic parameters for the complexation reactions of tyrosine, *m*-tyrosine, *o*-tyrosine, and β-phenylserine with copper(II) in aqueous solution at 25° and $\mu = 0.16$ *M* are reported. The thermodynamic data indicate the formation of amino-carboxyl chelates for these amino acids with copper(II) in the pH range 3.5 to 6.5. In addition, the deprotonation reactions of the bis copper(II) complexes of tyrosine, *m*-tyrosine, and *o*-tyrosine were studied to determine the sites of deprotonation. The proton dissociations for the copper(II) complexes were postulated to occur from the phenolic oxygens of the bound amino acids. No bonding of the phenolic oxygen to the copper(II) was postulated for the tyrosine and *m*-tyrosine complexes. For the bis copper(II) complex of *o*-tyrosine the thermodynamic data are consistent with the formation of chelate rings involving the negatively charged phenolic oxygens and the amino nitrogens with copper(II).

Formation constants for the complexation reactions of tyrosine with copper(II) seem to indicate the formation of chelates involving the amino nitrogen and the carboxyl oxygen with the metal ion.[2,3] The monoprotonated form of tyrosine is thought to act as the chelating molecule in these reactions. The free energy changes obtained from the formation constants are not diagnostic of the type of bonding in metal ion complexes without consideration of the enthalpy change, $\Delta H$, and the entropy change, $\Delta S$, associated with the reaction.[4] Therefore a thermodynamic study involving the determination of formation constants and calorimetric heats of reaction of a series of tyrosine isomers with copper(II) was initiated. The ligands used in this study were tyrosine, *m*-tyrosine, *o*-tyrosine, and β-phenylserine.

The deprotonation reactions of the bis copper(II) complexes were also studied. In the formation of the bis copper(II) complexes of tyrosine, *m*-tyrosine, and *o*-tyrosine there is still one ionizable proton remaining on each of the complexed ligand molecules. Thus the possibility for coordinated ligand–proton dissociation reactions to occur does exist. There are two major areas of interest in studying these deprotonation reactions: (1) the site of the proton dissociation of the copper(II) complexes, and (2) the possibility of the amino acid bonding through the phenolic oxygen to the copper(II). By using different isomers of tyrosine the steric impediments to phenolic oxygen bonding can be varied. From heat data the extent of deprotonation at a specific site of the coordinated ligand can be determined.

## Experimental Section

**Materials.** The preparation of the sodium hydroxide, nitric acid, and metal ion solutions has been previously described.[5,6]

The amino acids L-tyrosine and DL-β-phenylserine were obtained from Nutritional Biochemicals Corporation. The amino acids DL-*m*-tyrosine and DL-*o*-tyrosine were obtained from the Aldrich Chemical Company. All the amino acids were obtained as the free base. They were used without further purification after drying for 8 hr at 100°.

**Potentiometric Titrations.** The potentiometric titrations have been described.[6] All the titrations were performed in a constant temperature cell at 25 ± 0.05°. Presaturated nitrogen was kept over the surface of the cell to prevent carbon dioxide absorption.

The pH data from the addition of standard sodium hydroxide to a 2.00:1.00 mole ratio of amino acid to copper nitrate were used to evaluate the formation constants of the copper(II) complexes, and the proton dissociation constants for the coordinated ligands. Two or three independent titrations were performed for each system, with between 9 and 22 points per titration.

**Calorimetric Titrations.** A volume of about 100 ml of solution was used in the calorimeter, and each addition of titrant consisted of 0.4–1.5 ml. From three to seven heat measurements were made during each titration.

The calorimeter standardization has been previously described.[6,7]

Heats of complexation of the amino acids with copper(II) were measured by either adding sodium hydroxide to a solution of the amino acid and copper nitrate or adding copper nitrate to a solution of the completely deprotonated amino acid. Corrections to the observed heat were made using the appropriate equilibrium constants, the pH readings, and the measured heats of deprotonation and neutralization.

The heats of deprotonation for the coordinated amino acids were determined from the titration of 2.00:1.00 mole ratios of amino acid to copper nitrate with sodium hydroxide between pH 6.5 and 9.5.

**Spectrophotometry.** Qualitative spectral measurements were made in order to obtain further information about the metal ion complexes. A Bausch and Lomb Spectronic 20 was used to measure absorbances in the visible region of the spectrum. A 1.0-cm cell was used in the spectrophotometer. The temperature during the measurements ranged from 22 to 24°.

## Results and Discussion

**Ligand Deprotonation Reactions in the Absence of Copper(II).** The equilibria that must be considered here are

$$H_2L \rightleftharpoons HL^- + H^+ \qquad pK_{a1} \qquad \Delta H_{a1} \qquad (1)$$

$$HL^- \rightleftharpoons L^{2-} + H^+ \qquad pK_{a2} \qquad \Delta H_{a2} \qquad (2)$$

where $H_2L$ is the zwitterion, $HL^-$ is the monoprotonated anion, and $L^{2-}$ is the completely deprotonated lig-

(1) Based on the dissertation of J. E. Letter submitted to the Graduate School of the University of Missouri, Columbia, in partial fulfillment for the degree of Doctor of Philosophy, Aug 1969.
(2) A. Albert, *Biochem. J.*, 50, 690 (1952).
(3) C. G. Birch and S. E. Manahan, *Anal. Chem.*, 39, 1182 (1967).
(4) G. H. Nancollas, "Interactions in Electrolyte Solutions," Elsevier Publishing Co., Amsterdam, 1966.
(5) J. L. Meyer, Ph.D. Thesis, University of Missouri, Columbia, Mo., 1968.
(6) J. E. Letter, Jr., and J. E. Bauman, Jr., *J. Amer. Chem. Soc.*, 92, 437 (1970).
(7) J. D. Hale, R. M. Izatt, and J. J. Christensen, *J. Phys. Chem.*, 67, 2608 (1963).

Table I. Thermodynamic Parameters for Amino Acid Deprotonations[a]

| Amino acid | Functional group | p$K_a$ | $\Delta G$, kcal/mole | $\Delta H$, kcal/mole | $-\Delta S$, cal/(mole deg) | Ref |
|---|---|---|---|---|---|---|
| Tyrosine | Amino | 9.21 | 12.56 | 10.14 | 8.1 | *b* |
| | | 9.11 | | | | *c* |
| | | 9.19 | | | | *d* |
| | Phenol | 10.13 | 13.81 | 5.83 | 26.8 | *b* |
| | | 10.13 | | | | *c* |
| | | 10.43 | | | | *d* |
| | | 10.05 | | 6.0 | | *e* |
| | | 9.92 | | | | *f* |
| *m*-Tyrosine | Amino | 9.09 | 12.40 | 10.10 | 7.7 | *b* |
| | Phenol | 10.11 | 13.79 | 6.39 | 24.8 | *b* |
| *o*-Tyrosine | Amino | 8.60 | 11.73 | 9.61 | 7.1 | *b* |
| | Phenol | 10.66 | 14.54 | 6.84 | 25.8 | *b* |
| $\beta$-Phenylserine | Amino | 8.79 | 11.99 | 9.33 | 8.9 | *b* |

[a] 25°, $\mu$ = 0.16. [b] Present study. [c] Reference 11; 25°, $\mu$ = 0.16. [d] Reference 2; 20°, $\mu$ = 0.01. [e] C. Tanford and G. L. Roberts, *J. Amer. Chem. Soc.*, **74**, 2509 (1952); 25°, $\mu$ = 0.15. [f] W. Stenstromm and N. Goldsmith, *J. Phys. Chem.*, **30**, 1683 (1926); 18–24°.

and. The equilibrium in (2) was not measured for $\beta$-phenylserine, since the hydroxy proton dissociation for this amino acid could not be measured by our potentiometric techniques. For $\beta$-phenylserine p$K_{a1}$ and $\Delta H_{a1}$ were calculated in the manner previously described.[6]

For tyrosine, *m*-tyrosine, and *o*-tyrosine the two acid dissociation constants p$K_{a1}$ and p$K_{a2}$ are too close to neglect overlap in the two respective buffer regions. Therefore these constants were calculated from a linear equation. A function $\bar{n}_H$ was defined as the average number of protons bound per ligand.

$$\bar{n}_H = \frac{2[H_2L] + [HL^-]}{[H_2L] + [HL^-] + [L^{2-}]} \quad (3)$$

Substituting the equilibria of (1) and (2) into (3), the following expression can be obtained

$$\bar{n}_H = \frac{2[H^+] + K_{a1}[H^+]}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \quad (4)$$

which can be arranged to

$$\frac{[H^+]^2(\bar{n}_H - 2)}{\bar{n}_H} = \frac{K_{a1}[H^+](1 - \bar{n}_H)}{\bar{n}_H} - K_{a1}K_{a2} \quad (5)$$

A linear least-squares procedure was used to fit the data to eq 5, where a plot of $[H^+]^2(\bar{n}_H - 2)/\bar{n}_H$ *vs.* $[H^+](1 - \bar{n}_H)/\bar{n}_H$ gives a line of slope $K_{a1}$ and an intercept of $-K_{1a}K_{a2}$. Values for $\bar{n}_H$ were obtained from

$$\bar{n}_H = \frac{2C_L - C_B + [H^+] + [OH^-]}{C_L} \quad (6)$$

where $C_L$ is the total concentration of amino acid, $C_B$ is the concentration of base, and $[H^+]$ and $[OH^-]$ can be obtained from pH readings. Equation 6 can be obtained from proton balance relationships.

The deprotonation heats for tyrosine, *m*-tyrosine, and *o*-tyrosine were calculated from a linear equation also. A function $\overline{\Delta H}$ was defined as the average heat per mole of ligand deprotonated

$$\overline{\Delta H} = \frac{\Delta H_2[HL^-] + [\Delta H_{a1} + \Delta H_{a2}][L^{2-}]}{[HL^-] + 2[L^{2-}]} \quad (7)$$

which can be written using equilibria 1 and 2 as

$$\overline{\Delta H} = \frac{\Delta H_{a1} + (\Delta H_{a1} + \Delta H_{a2})(K_{a2}/[H^+])}{1 + 2K_{2a}/[H^+]} \quad (8)$$

Equation 8 can be rearranged to a linear form

$$\overline{\Delta H}(1 + \theta) = \Delta H_{a2}\theta + \Delta H_{a1} \quad (9)$$

where

$$\theta = \frac{K_{a2}/[H^+]}{1 + K_{a2}/[H^+]}$$

From a plot of $\overline{\Delta H}(1 + \theta)$ *vs.* $\theta$, values for $\Delta H_{a1}$ and $\Delta H_{a2}$ could be obtained. $\overline{\Delta H}$ was calculated by dividing the total corrected heat observed by the total moles of amino acid deprotonated. The thermodynamic parameters for the deprotonation of the ligands in the absence of copper(II) are given in Table I. Literature values are also given. The precision of the p$K_a$ values is estimated at ±0.05 and the precision of the $\Delta H_a$ values ±0.20.

The enthalpy values for proton ionization from the amino group are more endothermic than the enthalpy values for phenolic deprotonation. This is a reflection of the differences in the two types of proton donor atoms involved. The large differences in $\Delta S$ for amino deprotonations and phenolic deprotonations seem to reflect the differences in proton ionization from a neutral molecule (amino ionization) and from an anionic molecule (phenolic ionization). The doubly charged anion formed in the phenolic ionizations seems to have a greater ordering effect on the surrounding water molecules than does the singly charged anion formed in the amino ionizations. The thermodynamic quantities for the phenolic deprotonations in Table I are very similar to those reported for phenol at 25° and $\mu$ = 0.0; p$K$ = 9.979, $\Delta H$ = 5.650 kcal/mole and $\Delta S$ = 26.7 cal/(mole deg).[8]

The p$K_a$ values for the phenolic acid dissociation reactions are quite similar to the p$K_a$ values for the amino deprotonations. This similarity of p$K_a$ values is the result of different factors, as evidenced by the differences in enthalpy and entropy data for the two types of ionizations. The p$K_a$ values alone give very little information as to the site of deprotonation.

**Copper(II) Complexation and Coordinated Ligand–Proton Ionization Reactions.** The significant equilibria for the copper(II)–amino acid systems are the following, in addition to (1) and (2).

$$Cu^{2+} + HL^- \rightleftharpoons Cu(HL)^+ \quad K_1, \Delta H_1 \quad (10)$$

$$Cu(HL)^+ + HL^- \rightleftharpoons Cu(HL)_2 \quad K_2, \Delta H_2 \quad (11)$$

(8) F. J. Millero, J. C. Ahluwalia, and L. G. Hepler, *J. Chem. Eng. Data*, **9**, 192 (1964).

Table II. Thermodynamic Parameters for the Complexation and Deprotonation Reactions with Copper(II)[a]

| Reaction | Amino acid | Log $K$ | $-\Delta G$, kcal/mole | $-\Delta H$, kcal/mole | $\Delta S$, cal/(mole deg) |
|---|---|---|---|---|---|
| $Cu^{2+} + HL^- \rightarrow CuHL^+$ | Tyrosine[b] | 7.92 | 10.80 | 5.42 | 18.1 |
| | *m*-Tyrosine | 7.82 | 10.66 | 5.51 | 17.3 |
| | *o*-Tyrosine | 6.92 | 9.44 | 4.36 | 17.0 |
| | β-Phenylserine | 7.76 | 10.58 | 5.01 | 18.7 |
| $CuHL^+ + HL^- \rightarrow Cu(HL)_2$ | Tyrosine | 6.94 | 9.46 | 5.65 | 12.8 |
| | *m*-Tyrosine | 6.83 | 9.31 | 5.74 | 12.0 |
| | *o*-Tyrosine | 5.64 | 7.69 | 4.82 | 9.6 |
| | β-Phenylserine | 6.34 | 8.65 | 5.49 | 10.6 |
| $Cu(HL)_2 \rightarrow Cu(HL)(L)^- + H^+$ | Tyrosine | −9.29 | −12.68 | −6.08 | −22.2 |
| | *m*-Tyrosine | −8.95 | −12.21 | −6.18 | −20.2 |
| | *o*-Tyrosine | −8.79 | −11.99 | −5.42 | −22.1 |
| $Cu(HL)(L)^- \rightarrow CuL_2^{2-} + H^+$ | Tyrosine | −10.18 | −13.88 | −6.43 | −25.0 |
| | *m*-Tyrosine | −10.29 | −14.03 | −6.51 | −25.2 |
| | *o*-Tyrosine | −9.71 | −13.24 | −5.71 | −25.3 |

[a] 25°, $\mu$ = 0.16. [b] Log $K_1$ = 7.60, log $K_2$ = 7.76 at 15°, $\mu$ = 0.10: S. G. Birch and S. E. Manahan, *Anal. Chem.*, **39**, 1182 (1967); log $K_1K_2$ = 15.0 at 20°, $\mu$ = 0.01: A. Albert, *Biochem. J.*, **50**, 690 (1952).

$$Cu(HL)_2 \rightleftharpoons Cu(HL)(L)^- + H^+ \qquad K_{a1}', \Delta H_{a1}' \qquad (12)$$

$$Cu(HL)(L)^- \rightleftharpoons CuL_2^{2-} + H^+ \qquad K_{a2}', \Delta H_{a2}' \qquad (13)$$

All other reactions, such as the formation of CuL, were found to be negligible under the conditions of our experiments. The formation constants, $K_1$ and $K_2$, and the stepwise heats of complexation, $\Delta H_1$ and $\Delta H_2$, were determined by methods previously described.[6] The titration curves in Figure 1 for 2.0:1.0 mole ratios of tyrosine, *m*-tyrosine, and *o*-tyrosine to copper(II) indicate two distinct regions, the formation of the mono and bis copper(II) complexes, followed by the deprotonation reactions of the bis copper(II) complexes. The coordinated ligand–proton dissociation reactions for the bis copper(II) complexes were treated in a manner analogous to the ligand deprotonation reactions in the absence of copper(II). A function $\bar{n}_H'$ was defined as the number of ionizable protons bound per metal ion.

$$\bar{n}_H' = \frac{2[Cu(HL)_2] + [Cu(HL)(L)^-]}{[Cu(HL)_2] + [Cu(HL)(L)^-] + [Cu^{2+}]} \qquad (14)$$

By using (12) and (13) with (14) a linear equation of the form of eq 5, except that $K_{a1}$ is replaced by $K_{a1}'$ and $K_{a2}$ is replaced by $K_{a2}'$, can be obtained. Thus, acid dissociation constants for the coordinated ligands were calculated. In the same way an equation of the form of (9) can be obtained by defining a function $\overline{\Delta H}'$ as the average heat per mole of copper(II) complex deprotonated. Thus, values for $\Delta H_{a1}'$ and $\Delta H_{a2}'$ could be calculated. The coordinated ligands in the bis copper(II) complex of β-phenylserine were not found to undergo proton dissociation in the pH region of this study.

The thermodynamic parameters for the complexation and deprotonation reactions for the copper(II)–amino acid systems are given in Table II. Available literature values are also given. The thermodynamic data for the formation of the mono and bis copper(II) complexes are similar to the thermodynamic parameters for other α-amino acids with copper(II).[6,9,10] The enthalpy values for the stepwise complexation reactions in Table II are consistent with the formation of copper(II)–amino nitrogen bonds, while the entropy data for these reactions indicate the formation of copper(II)–carboxyl oxygen bonds.[4,6] The values for $\Delta H_1$ are more endothermic than the values for $\Delta H_2$, and $\Delta S_1$ values are considerably more positive than $\Delta S_2$ values. These facts are consistent with the breaking of additional copper(II)–water bonds, and the subsequent release of additional water molecules in the first step of complexation, as compared to the second step.[4]

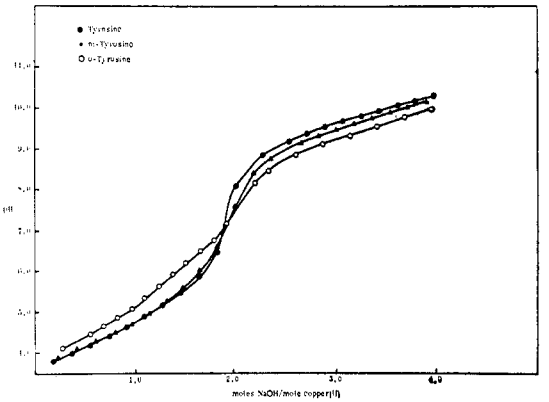


Figure 1. Titration curves for 2.0:1.0 mole ratios of tyrosine, *m*-tyrosine, and *o*-tyrosine to copper(II).

The formation constants for *o*-tyrosine in Table II are considerably smaller than the constants for the other amino acids. The heats of complexation for *o*-tyrosine are lower by about 1 kcal/mole than the heats for the other amino acids, while the entropy values are only slightly lower. The amino group of *o*-tyrosine is less basic (by about 0.5 log unit) than the amino groups of tyrosine and *m*-tyrosine. Therefore, the lower formation constants for *o*-tyrosine with copper(II) can be partially explained by the lower basicity of the amino nitrogen of this ligand. The formation constants for β-phenylserine are also somewhat lowered due to less exothermic values for $\Delta H_1$ and $\Delta H_2$ compared to the values of $\Delta H_1$ and $\Delta H_2$ for tyrosine and *m*-tyrosine.

The deprotonation data of Table II were obtained in order to try to determine the site of the coordinated ligand–proton dissociation reactions. The $pK_a'$ data in Table II are consistent with either amino or phenolic deprotonation. The enthalpy and entropy values for deprotonation of the bis copper(II) complexes of tyrosine and *m*-tyrosine are consistent with phenolic

(9) R. M. Izatt, J. J. Christensen, and V. Kothari, *Inorg. Chem.*, 3, 1565 (1964).
(10) V. S. Sharma and H. B. Mathur, *Indian J. Chem.*, 3, 475 (1965).

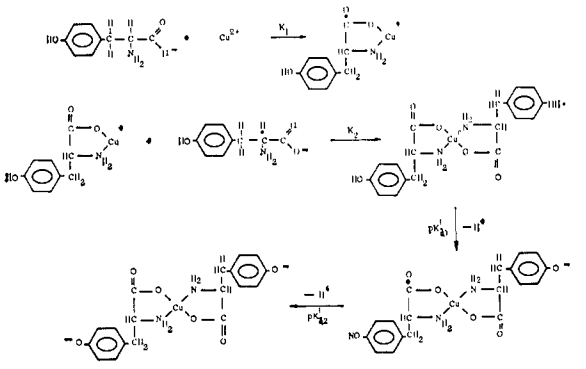

Figure 2. Some reactions of tyrosine with copper(II).

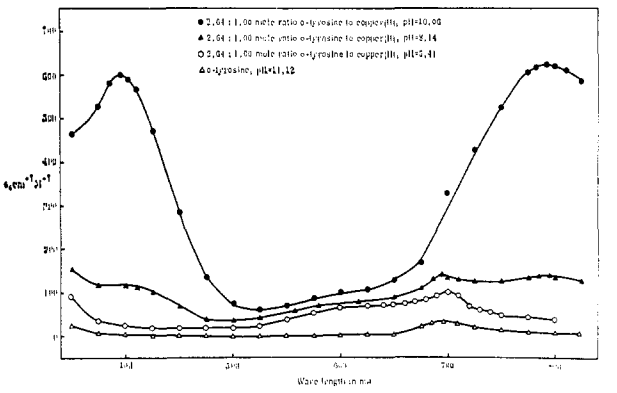

Figure 3. Visible absorption spectra of *o*-tyrosine and the bis complexes of *o*-tyrosine with copper(II).

proton dissociation reactions. This can be seen by comparison of the deprotonation heat and entropy data in Table I and Table II. The heat data can thus be effectively used to determine the site of proton dissociation of the coordinated ligand, whereas the $pK_a'$ values do not give this information. The $pK_{a1}'$ values for the bis copper(II) complexes are lower than the $pK_a$ values for the phenolic deprotonation of the ligand in the absence of copper(II). This is in agreement with the "microconstant" calculated for proton ionization from the phenolic group of tyrosine with the carboxyl and amino groups protonated. This microconstant was lower than the acid dissociation constant ("macroconstant") for the phenolic group with the amino and carboxyl groups deprotonated (microconstant = 9.42, macroconstant = 10.04).[11] Thus the decrease in basicity of the coordinated ligand compared to the free ligand seems reasonable. The thermodynamic data do not indicate any interactions of the deprotonated phenolic group in the tyrosine and *m*-tyrosine with copper(II). A reaction scheme consistent with the data for the copper(II)–tyrosine system is shown in Figure 2.

The deprotonation reactions for the bis copper(II) complex with *o*-tyrosine are somewhat confusing. The heat data seem to indicate phenolic proton dissociations, but the copper(II) complex deprotonation heats are notably less endothermic than the free *o*-tyrosine phenolic proton dissociations. To try and resolve these results the total heats of complexation for the *o*-tyrosine, *m*-tyrosine, and tyrosine doubly charged anion with copper(II) were determined.

$$Cu^{2+} + 2L^{2-} \longrightarrow CuL_2^{2-} \qquad \Delta H'_{0-2} \qquad (15)$$

Table III lists the values for $\Delta H'_{0-2}$ along with total heat values for the reaction of the monoprotonated anions with copper(II) for comparison. The precision of the $\Delta H'_{0-2}$ values is about ±0.30 kcal/mole. The enthalpy data in Table III indicate for tyrosine and *m*-tyrosine that the ligands are bonding to the copper(II) at the same sites for both the doubly charged and singly charged ligand anions.

**Table III.** Total Heats of Complexation for the Copper(II) Complexes[a]

| Reaction | Ligand | $-\Delta H$, kcal/mole |
|---|---|---|
| $Cu^{2+} + 2HL^- \rightarrow CuHL_2$ | Tyrosine | 11.07 |
| | *m*-Tyrosine | 11.35 |
| | *o*-Tyrosine | 9.25 |
| $Cu^{2+} + 2L^{2-} \rightarrow CuL_2^{2-}$ | Tyrosine | 10.48 |
| | *m*-Tyrosine | 10.87 |
| | *o*-Tyrosine | 11.77 |

[a] 25°, $\mu$ = 0.16.

For *o*-tyrosine the $\Delta H$ values in Table III are consistent with different bonding sites for the doubly and singly charged anions. The doubly charged anion of *o*-tyrosine could be acting as a tridentate chelate, with the amino nitrogen and phenolic oxygen bonding to the copper(II) in the *xy* plane of the metal, and the carboxyl oxygen bonding in the *z* axial position. It does not seem reasonable that the $L^{2-}$ form of the *o*-tyrosine ligand is bonding to the copper(II) only through the amino and carboxyl groups. Thus the position of the phenolic oxygen in the tyrosine isomers is critical in determining the interactions of this oxygen with the copper(II). For tyrosine and *m*-tyrosine the phenolic oxygen, even when it is deprotonated, does not bond to the copper(II) because of steric considerations. In the case of *o*-tyrosine the phenolic group is in closer proximity to the amino group, and the negatively charged phenolic group does seem to bond to the copper(II).

A change in color from blue-violet to green occurs in going from the $Cu(HL)_2$ to the $CuL_2^{2-}$ species (pH about 6–10) of *o*-tyrosine. The visible spectra between 350 and 825 mμ for a 2.64:1.00 mole ratio of *o*-tyrosine to copper(II) at various pH values is shown in Figure 3. Visible spectra for the bis copper(II) complexes of tyrosine and *m*-tyrosine did not show any major changes in going from pH 6 to pH 10. A band at about 620 mμ was observed for these species, in agreement with Laurie.[12] Gorton and Jameson,[13] using 10:1 mole ratios of L-β-(3,4 dihydroxyphenyl)alanine, DOPA, to copper(II), observed a spectral shift in $\lambda_{max}$ from 610 to 444 mμ in going from pH 5 to pH 9. These authors proposed that the DOPA was bonding to the copper(II) through the amino and carboxyl group at pH 5, and through the phenolic oxygens only at pH 9. They found no complexes chelated through both the amino and phenolic groups. This conclusion is consistent with the present thermodynamic and spectral observations for tyrosine and *m*-tyrosine with copper(II), where the phenolic groups are in similar positions as in the

(11) R. B. Martin, J. T. Edsall, D. B. Wetlaufer, and B. R. Hollingworth, *J. Biol. Chem.*, 233, 1429 (1958).

(12) S. H. Laurie, *Aust. J. Chem.*, 20, 2609 (1967).

(13) J. E. Gorton and R. F. Jameson, *J. Chem. Soc., A*, 2615 (1968).

DOPA molecule. The appearance of a band at 390 mμ for the $CuL_2^{2-}$ complex of *o*-tyrosine is consistent with interaction of the phenolic oxygen with copper(II). The band at 790 mμ could be associated with copper(II)–nitrogen interactions. These proposals for the copper(II) complexes of tyrosine, *m*-tyrosine, and *o*-tyrosine are consistent with the thermodynamic data. The spectral parameters measured for the complexes are meant to act as further qualitative evidence for the conclusions based on the thermodynamic data.

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# Dipole Moments, Atomic Charges, and Carbon Inner-Shell Binding Energies of the Fluorinated Methanes

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**Abstract:** *Ab initio* self-consistent field molecular orbital (SCF-MO) wave functions for the series of molecules $CH_4$, $CH_3F$, $CH_2F_2$, and $CHF_3$ have been analyzed in terms of the simple concepts of bond dipoles and effective atomic charges. By assuming that the "true" C–H and C–F bond dipoles are proportional to bond dipoles calculated from the Mulliken populations, and by calibrating against the standard bond dipoles (C–H in $CH_4$ and C–F in $CH_3F$), we have calculated molecular dipole moments for the series $CH_3F$ to $CHF_3$ in good agreement with experimental values. The effective atomic charges based on the calibrated bond dipoles, as well as those based on Mulliken population analysis of the SCF-MO wave functions, do not exhibit charge alternation similar to that found by the semiempirical CNDO calculations of Pople and Gordon. The carbon 1s energy level shifts for multiple fluorination seem to be the sum of shifts which arise for a single fluorination. The binding energies of the carbon 1s electrons are essentially linear functions of the charge at carbon calculated by either of the above-mentioned ways. A consideration of this binding energy–charge correlation and others from the literature show that such correlations exist for several different definitions of atomic charge, and that they should consequently be regarded primarily as useful relationships allowing statements to be made about relative charges, but not necessarily reflecting the absolute physical situation.

Recent advances in *ab initio* quantum mechanical calculations for molecules of chemical interest have produced many opportunities for fresh insight into, and analysis of, molecular electronic structure. In this paper we use the simple concepts of bond dipoles and atomic charges to analyze the electronic structures of the series $CH_4$, $CH_3F$, $CH_2F_2$, and $CHF_3$, based on the SCF–MO wave functions determined by Ha and Allen.[1] These wave functions consist of molecular orbitals expanded as linear combinations of groups of Gaussian functions which are themselves accurate representations of the SCF atomic orbitals.

There are several reasons for this analysis. (1) The experimental values[2] of the molecular dipole moments for $CH_3F$, $CH_2F_2$, and $CHF_3$ do not follow a simple additive bond dipole relation.[3] This has been discussed and rationalized in the "bond polarizability" model.[3,4] Since the electronic structures described by the wave functions depend in a self-consistent way on all the electrons and nuclei in the systems, we hoped to extract this dipole moment behavior from the wave functions. (2) The charge distributions are also of interest, particularly in view of the results from the approximate CNDO calculations of Pople and Gordon,[5] which suggested that charge alternation may be characteristic of inductive and mesomeric effects. (3) The accessibility of inner shell binding energies by the ESCA techniques[6] and the apparent linear correlation of measured binding energy with atomic charge for sulfur[7] and nitrogen[8] in molecules suggest that a consideration be made of the carbon 1s binding energies and atomic charges.

## Dipole Moments and Atomic Charges

Table I presents the total dipole moments for $CH_3F$, $CH_2F_2$, and $CHF_3$ (i) from experiment,[2] (ii) from direct calculation of the expectation value of the dipole moment operator with the SCF–MO wave functions,[1]

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