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Resonance Raman Studies of Phenolate-Bridged Binuclear Copper Complexes. Relevance to Hemocyanin and Tyrosinase

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Phenolate-bridged binuclear complexes serve as models for proposed active site structures in the met forms of hemocyanin and tyrosinase. The resonance Raman spectra of these complexes have been investigated and compared with corresponding mononuclear analogues. The phenolate ν_{C-O}'s for the binuclear complexes occur above 1300 cm^{-1} and are significantly higher in energy than those for the mononuclear analogues. Comparisons of the crystal structures of mononuclear and binuclear complexes suggest that the higher ν_{C-O} values for the binuclear complexes may result from the larger Cu–O–C(Ph) angles enforced by the bridging structure.

Hemocyanin and tyrosinase are binuclear copper proteins that bind molecular oxygen.[1-5] In a series of spectroscopic experiments involving a variety of protein complexes, Solomon and co-workers have elucidated much of the coordination chemistry of these binuclear copper centers.[6-8] One aspect of the coordination chemistry yet to be determined is the nature of the endogenous ligand that acts as a bridge between the two coppers in the met forms of these proteins. The copper centers in this oxidation state are strongly coupled antiferromagnetically.[9] Monoalkoxy bridges in model complexes have been shown to mediate the appropriate antiferromagnetic coupling and are thus suitable candidates for the endogenous bridge.[10-13] Solomon has proposed that tyrosine may serve as the bridging ligand[6,14] because of the presence of absorption bands in the region near 400 nm, which is typical for phenolate-to-copper(II) charge-transfer bands.[15,16] Resonance Raman spectroscopy has proven useful in recent years as a probe for charge-transfer bands. The involvement of phenolate in a charge-transfer transition is manifested by the enhancement of characteristic features at ca. 1170, 1270, 1500, and 1600 cm^{-1}, corresponding to phenolate-ring deformations.[17,18] Such studies probing the potential phenolate-to-copper(II) charge-transfer region in the binuclear copper proteins are in progress. In anticipation of this, we have examined the resonance Raman spectra of recently synthesized phenolate-bridged binuclear copper complexes to serve as a basis for comparisons with the proteins.

Experimental Section

The resonance Raman data for the complexes studied are summarized in Table I.[19] Complexes A–G[25-30] were synthesized according to procedures developed by Karlin and Sorrell. CuMCl (E) was prepared by mixing equimolar quantities of $CuCl_2$ and the phenolate ligand (M) in methanol. The compound was precipitated by the addition of diethyl ether and recrystallized from methanol/ether, giving brown crystals (64%). $CuMN_3$ (D) was prepared by the reaction of CuMCl with NaN_3 in methanol. The complex was precipitated with ether and recrystallized from CH_2Cl_2/ether (85%). Both complexes gave satisfactory analyses. Further details on the synthesis and characterization of these complexes are forthcoming.[28] The tetradentate ligand for compound H was synthesized in the following manner: 3-methylsalicylaldehyde was synthesized by the Reimer–Tiemann reaction[31] from *o*-cresol; this was then reacted with 1,2-diaminoethane to yield the Schiff base adduct, which was then reduced with sodium borohydride in ethanol. The identity of the ligand was confirmed with NMR and mass spectra. The copper complex was synthesized according to literature procedures.[32]

Table I. Resonance Raman Data for Copper Phenolate Complexes

compd	enhanced phenolate vib, cm^{-1}			ref
$[Cu_2L(OH)]^{2+}$ (A) ^{16}O soln	1307 (s)	1473 (s)	1596 (s)	*a*
^{18}O soln	1299 (s)	1473 (s)	1596 (s)	*a*
^{18}O solid	1298 (m)	1472 (s)	1594 (s)	*a*
$[Cu_2L(OMe)]^{2+}$ (B) soln	1308 (s)	1474 (s)	1584 (s)	*a*
			1596 (s)	
$[Cu_2L(N_3)]^{2+}$ (C) soln	1304 (s)	1474 (s)	1596 (s)	*a*
$[CuMN_3]$ (D) solid	1273 (m)	1483 (m)	1598 (m)	*a*
[CuMCl] (E) soln	1262 (s)	1482 (m)	1578 (m)	*a*
	1274 (s)		1598 (s)	
	1284 (s)			
solid	1278 (s)	1482 (s)	1572 (m)	*a*
$[Cu_2L'(OH)]^{2+}$ (F) soln	1314 (s)	1486 (s)	1613 (s)	*a*
solid	1310 (m)	1484 (s)	1610 (m)	*a*
[CuM'Br] (G) soln	1266 (s)	1482 (m)	1598 (m)	*a*
solid	1266 (s)	1480 (s)	1572 (m)	*a*
			1596 (s)	
$[CuM''(MeOH)_2]$ (H) soln	1286 (s)	1434 (m)	1593 (s)	*a*
		1464 (m)		
$Cu(Im)_2(OC_6H_2\text{-}2,4,6\text{-}Cl_3)_2$ (I)				
soln	1316 (m)	1463 (s)	1562 (s)	20
solid	1304 (s)	1460 (s)	1569 (s)	20
Cu(II)/(L-Lys,L-Tyr)$_n$	1250 (s)	1501 (s)	1602 (s)	21
	1320 (w)			
Cu(II)/(L-Glu,L-Tyr)$_n$	1258 (s)	1500 (w)	1603 (s)	22
Cu(II) serotransferrin	1281 (s)	1506 (m)	1608 (s)	23
	1277 (s)	1500 (m)	1601 (s)	20
Cu(II) lactoferrin	1275 (s)	1501 (m)	1603 (s)	24

[a] This work; solution spectra in CD_3CN except for compound H, which was done in CD_3OD solution.

Optical spectra were obtained in acetonitrile on a Cary 219 UV–vis spectrophotometer at room temperature. Resonance Raman spectra were obtained with an argon ion laser using available lines for excitation at a power output of between 50 and 200 mW. The spectra were

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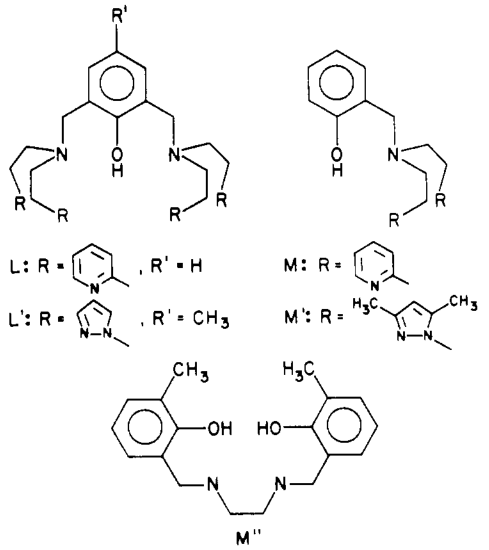
recorded on SPEX Raman spectrometers interfaced with a microprocessor or a microcomputer for data handling. The solutions at millimolar concentrations were placed in a spinning cell to minimize sample degradation and collected at 90° with use of a spectral slit width of 4 cm^{-1}. Features obtained in solution were referenced to an acetonitrile-d_3 vibration at 1102 cm^{-1}. Raman spectra of solid samples were obtained on 5% pellets in a KBr matrix also utilizing a spinning cell.

Results and Discussion

Synthetic binuclear copper complexes with phenolate bridges have recently been reported by Karlin[25-27] and Sorrell[29] (Table I). The binucleating ligands, together with other ligands used in this study, are shown:



Compound A has been shown by X-ray crystallography to be a binuclear complex consisting of two copper square pyramids sharing a basal edge with phenolate and hydroxide bridging the copper centers.[25] Compounds B[26] and C[27] have structures similar to that of compound A, with methoxide and azide (1,1-bridge) replacing the hydroxide bridge, respectively. Compound F consists of two copper centers, one square pyramidal and the other trigonal bipyramidal; the two centers share a phenolate and hydroxide edge.[29] Compounds D,[28] E,[28] and G[30] are mononuclear analogues of the binuclear complexes, while compound H is a mononuclear copper complex having 2,6-dialkylated phenols as ligands (Table I). The visible spectra of some of the complexes studied are shown in Figure 1. All exhibit absorption features near 400 nm, the region expected for phenolate-to-copper(II) charge-transfer transitions.[15,16]

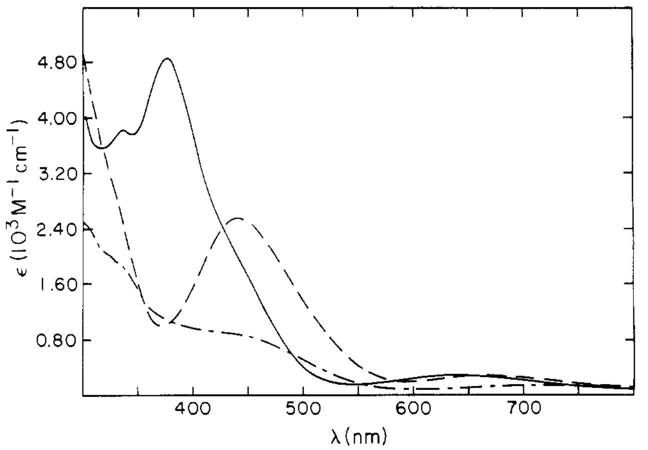


Figure 1. UV-visible spectra of copper complexes in CH_3CN: compound A (—); compound E (- - -); compound F (–·–).

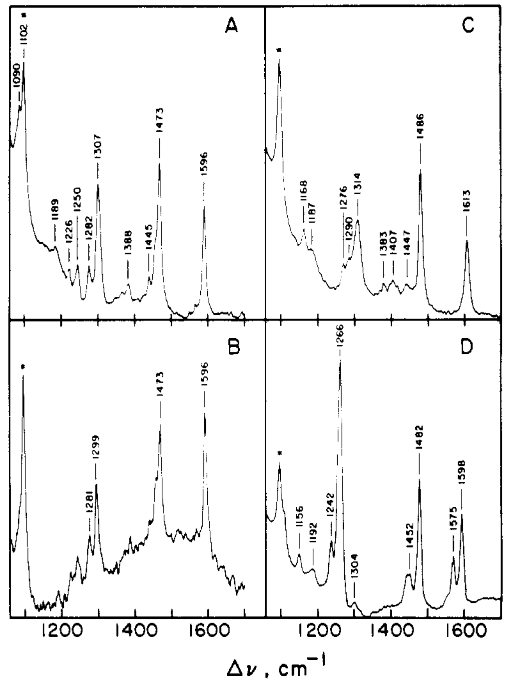


Figure 2. Resonance Raman spectra of copper complexes in CD_3CN: A, compound A-^{16}O; B, compound A-^{18}O; C, compound F; D, compound G. Conditions: 488.0-nm excitation, 100-mW power. Asterisk denotes 1102-cm^{-1} feature of CD_3CN.

Resonance Raman spectra of the synthetic complexes have been obtained and are shown in Figure 2. Prominent features in the spectrum of compound A at 1596, 1473, and 1307 cm^{-1} correspond to two ν_{C-C}'s associated with ring deformations and the phenolate ν_{C-O}, respectively. These are found at energies similar to those observed for other phenolate complexes.[17,18] The ν_{C-H} mode normally found near 1170 cm^{-1} for para-substituted phenols is apparently lost upon 2,6-dialkylation of the phenol; this mode shifts 100 cm^{-1} to lower energy in the spectrum of *p*-cresol when the 2,6-H's are deuterated.[33] An

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(19) Abbreviations: Im, imidazole; Lys, lysine; Tyr, tyrosine; Glu, glutamic acid.

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excitation profile study of these vibrations shows that the features are increasingly more enhanced as the excitation wavelength is varied from 514.5 to 457.9 nm.[34] Compound A exhibits two strongly absorbing features near 400 nm in its electronic spectrum (Figure 1), and the assignment of either feature as the phenolate-to-copper(II) charge-transfer band would be consistent with the excitation profile data. We, however, favor the assignment of the lower energy shoulder as the charge-transfer transition because its extinction coefficient is in better agreement with the range of extinction coefficients observed for the phenolate charge-transfer bands in copper complexes (~500–2000 M^{-1} cm^{-1} per phenolate).[15,16]

The circumstances leading to the synthesis of compound A allowed the convenient incorporation of ^{18}O into the phenolate moiety.[25,26] Raman spectra of the ^{18}O-labeled complex unequivocally assign the 1307-cm^{-1} feature as principally ν_{C-O}, since this is the only peak in the 1100–1700-cm^{-1} region that is significantly affected by the introduction of ^{18}O. The 8-cm^{-1} shift observed can be compared with the 6- and 22-cm^{-1} shifts for the ν_{C-O} of phenol[35] and phenolate anion[36] upon ^{18}O substitution. The Raman spectra of the other binuclear complexes, B, C, and F, exhibit similar features, with the ν_{C-O}'s also found above 1300 cm^{-1}.

Several mononuclear copper complexes with similar ligands, D, E, and G, were studied for comparison. Complex D has been shown to be a trigonal-bipyramidal copper complex, with N_3 occupying an axial position.[28] These compounds, which are mononuclear equivalents of the binuclear complexes, exhibit ν_{C-C} values similar to those of the binuclear complexes but ν_{C-O} values that are smaller. Compound H, a mononuclear complex with 2,6-dialkylated phenolate ligands, exhibits a ν_{C-O} similar to those observed for the other mononuclear species. In Table I are also included previously published data on copper transferrins and copper phenolate complexes. These complexes exhibit a range of ν_{C-O}'s from 1264 to 1286 cm^{-1} with one exception. The trichlorophenolate complex (I) exhibits a ν_{C-O} at 1316 cm^{-1}, which may be attributed to the presence of three electron-withdrawing groups on the phenolate ligand. The parent phenol exhibits a ν_{C-O} at 1284 cm^{-1}, which shifts to 1324 cm^{-1} upon deprotonation. The values of the ν_{C-O}'s in the binuclear copper complexes thus appear to be high. The data for the corresponding mononuclear complexes show that neither the 2,6-dialkyl substitution nor the five-coordinate copper environment gives rise to the increased ν_{C-O} values. Our data thus suggest that the higher value for the ν_{C-O} in the phenolate-bridged binuclear complexes is a consequence of the bridging mode.

Resonance Raman studies of metal phenolate proteins have demonstrated that the ν_{C-O} is the most variable of the four characteristic enhanced tyrosinate vibrations.[17,18,37] These variations have been explained on the basis of observations that the ν_{C-O}'s of phenol and phenolate are 1249 and 1281 cm^{-1}, respectively. Ionization to phenolate introduces substantial double-bond character to the C–O bond, thereby shortening it and increasing its stretching frequency.[20] When extended to the metal complexes, the value of the ν_{C-O} is suggested to reflect the strength of the metal phenolate interactions—the weaker the metal phenolate interaction, the more phenolate-like the tyrosine, the higher the frequency of the ν_{C-O}. However, since the phenolate oxygen is coordinated to the two copper centers in the binuclear complexes, it is difficult to argue that the metal phenolate interactions are weakened in these complexes to give rise to the higher ν_{C-O}. Comparisons of Cu–O bond lengths of binuclear and mononuclear copper phenolate complexes show no consistent variations to indicate a trend.

An alternate rationale may arise from a consideration of the hybridization at oxygen in the complexes. The variability of the ν_{C-O} reflects variations in the C–O bond strength, which is a function of the percent s character in the oxygen hybrid orbital involved in the C–O bond. The percent s character of the oxygen hybrid orbital would depend on the Cu–O–C(Ph) angle: the larger the angle, the greater the s character of the oxygen hybrid orbital involved in the C–O bond. Mononuclear complexes exhibit Cu–O–C(Ph) angles in the range of 117–122°;[38-40] that of complex D in this study is 121.9 (16)°.[28] These complexes give rise to ν_{C-O}'s under 1300 cm^{-1}. The binuclear complexes A–C and F, all of which are structurally characterized, exhibit Cu–O–C(Ph) angles in the range of 126–130°, due to structural requirements of the cluster.[25-27,29] The presence of two single-atom bridges between the copper centers results in a small (102–108°) Cu–O(phenolate)–Cu angle; this and the near trigonal planarity of the phenolate oxygen give rise to the larger Cu–O–C(Ph) angles. The larger angles in the binuclear complexes would be expected to enhance the s character of the oxygen hybrid orbital involved in the phenolate C–O bond, thereby increasing the C–O bond strength and the ν_{C-O}. The ν_{C-O} of 1316 cm^{-1} observed for mononuclear complex I is also consistent with its larger Cu–O–C angle (129.6°).[41] Similar arguments have been used to explain the relative strengths of the C–H bond in alkanes, alkenes, and alkynes.[42]

In detailed studies of the spectroscopy of the binuclear copper sites in hemocyanin and tyrosinase, Solomon has argued for the presence of an endogenous ligand bridge in the met and oxy forms of these proteins.[6-8,14] The strong antiferromagnetic interaction between the copper centers[43,44] and the absence of sulfur in the first coordination shell of copper as indicated by EXAFS analysis[45,46] limit the possibilities[2] for the endogenous bridge to phenolate, alkoxide, and hydroxide. The competitive displacement of the endogenous bridge by specific exogenous anions at low pH indicates that the bridging ligand has an intrinsic $pK_a > 7$.[14] The presence of a ligand-to-Cu(II) charge-transfer band near 400 nm attributed to the endogenous ligand[6,8] in the met and oxy forms of hemocyanin and tyrosinase suggests that phenolate is the most likely candidate for this bridge.[2]

The charge-transfer band near 400 nm observed in the proteins has an extinction coefficient of ca. 500 M^{-1} cm^{-1}.[2]

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(34) Excitation profiles of Compounds A, F, and G. Compound A. Intensities of the 1307-, 1473-, and 1596-cm^{-1} peaks relative to the 1102-cm^{-1} CD_3CN peak: at 514.5 nm, 0.79, 0.90, 1.02; at 488.0 nm, 1.59, 1.70, 1.84; at 457.9 nm, 3.16, 3.84, 3.50. Compound F. Intensities of the 1314-, 1486-, and 1613-cm^{-1} peaks relative to solvent: at 514.5 nm, 0.38, 0.61, 0.35; at 496.5 nm, 0.82, 1.4, 0.76; at 476.5 nm, 2.4, 5.0, 2.5; at 457.9 nm, 5.4, 13.7, 6.7. Compound G. Intensities of the 1266-, 1482-, and 1598-cm^{-1} peaks relative to solvent: at 514.5 nm, 0.29, 0.17, 0.13; at 496.5 nm, 0.68, 0.47, 0.40; at 476.5 nm, 1.3, 0.85, 0.67; at 457.9 nm, 3.5, 1.8, 1.8. All complexes exhibit vibrations that are increasingly enhanced as the excitation wavelength becomes shorter.

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This is small compared to those of the synthetic complexes we have studied but still within the range observed for copper phenolate complexes.[15,16] Among the binuclear complexes, the phenolate-bridged pyridine complex exhibits a significantly larger extinction coefficient than does the phenolate-bridged pyrazole complex. Both complexes exhibit well-enhanced phenolate vibrations in their Raman spectra, so resonance Raman experiments on the binuclear copper proteins should yield valuable insights.

Resonance Raman studies have provided evidence for dioxygen binding in oxyhemocyanin[47,48] and oxytyrosinase[49] and for azide binding in corresponding azide complexes.[2] However, current efforts to probe the 400-nm region of the proteins appear to be hampered by fluorescence problems.[2] Should these difficulties be alleviated, our studies suggest that the observation of a phenolate ν_{C-O} at ca. 1300 cm^{-1} or higher in resonance Raman experiments on these proteins would support the proposal for an endogenous phenolate bridge in the met and oxy forms of hemocyanin and tyrosinase.

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Registry No. A, 86593-50-2; B, 79846-28-9; C, 93531-98-7; D, 93531-99-8; E, 93532-00-4; F, 82281-85-4; G, 93532-01-5; H, 93532-02-6; M″, 93532-03-7; 3-methylsalicylaldehyde, 824-42-0; 1,2-diaminoethane, 107-15-3; ^{18}O, 14797-71-8; tyrosinase, 9002-10-2.

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Three-Coordinate Metal Amides of Manganese(II) and Cobalt(II): Synthesis and X-ray Structure of the First Tris(silylamide) of Manganese and the X-ray Crystal Structures of $[M_2(N(SiMe_3)_2)_4]$ (M = Mn, Co)

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Three low-coordinate metal amides containing the bis(trimethylsilyl)amido group have been characterized by X-ray diffraction and elemental analysis. The molecular structures of $[Mn(N(SiMe_3)_2)_3Li(THF)]$ (**1**), $[Mn_2(N(SiMe_3)_2)_4]$ (**2**), and $[Co_2(N(SiMe_3)_2)_4]$ (**3**) have the amido group acting as both a bridging and a terminal ligand. The crystal data [Mo Kα ($\lambda = 0.71069$ Å)] at 140 K are as follows: (**1**) $a = 11.678$ (2) Å, $b = 19.362$ (2) Å, $c = 17.020$ (3) Å, $\beta = 108.77$ (1)°, $Z = 4$, space group $P2_1/n$; (**2**) $a = 17.997$ (2) Å, $b = 14.942$ (1) Å, $c = 18.636$ (2) Å, $\beta = 121.24$ (1)°, $Z = 4$ (dimers), space group $C2/c$; (**3**) $a = 17.907$ (3) Å, $b = 14.644$ (2) Å, $c = 18.633$ (3) Å, $\beta = 120.47$ (2)°, $Z = 4$ (dimers), space group $C2/c$. For **1**–**3** $R = 0.031$, 0.031, and 0.037, respectively. Complex **1** is the first homoleptic tris(silylamide) of manganese. Both **2** and **3** are dimeric in the solid state. All three complexes exhibit the coordination number 3 at the metal centers.

Introduction

The bis(trimethylsilyl)amido group has been used extensively to stabilize low coordination numbers and oxidation states throughout the periodic table.[1] The ligand was initially employed for this purpose with the first-row transition elements by Wannagat and Bradley.[2-8] This work resulted in the synthesis of the trivalent complexes $[M(N(SiMe_3)_2)_3]$[5], where M = Sc, Ti, V, Cr, and Fe, along with the bivalent compounds $[M(N(SiMe_3)_2)_2]$,[6-8] where M = Mn, Fe,[9] Co, and Ni.

X-ray structural reports have been published for the tris((trimethylsilyl)amides) of Ti, V, Cr, Fe, and many f-block elements.[4,5,10-12] Spectroscopic data for the remaining trivalent derivatives point to similar trigonal-planar structures although some trigonal-pyramidal structures have been found for Nd, Sc, Yb, and Eu.[13,14]

The X-ray crystal structure of $[Mn_2(N(SiMe_3)_2)_4]$ is the only reported structural example of a homoleptic[15] bivalent bis(silyl)amide complex.[6] However, structures of a few heteroleptic bis(silylamido) derivatives have been described. Three examples of these are the complexes [Cr(N-

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