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Vibrational Spectroscopic Studies of a Hydroxo-Bridged Dinuclear Copper Complex, a Potential Model for Multicopper Proteins

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Received January 9, 1992

The copper complex $[Cu_2(XYL{-}O{-})(OH)]^{2+}$, where XYL = *m*-xylene connected to two bis[2-(2-pyridyl)ethyl]amine ligands, serves as a potential model for the dinuclear copper sites in hemocyanin, tyrosinase, and the multicopper oxidases. Resonance Raman (RR) and infrared spectra of the complex reveal a ν_s(Cu–OH–Cu) mode at 465 cm^{-1} and a ν_{as}(Cu–OR–Cu) mode at 603 cm^{-1}. These represent the first such modes to be definitively identified by isotopic shifts and polarization behavior. These two vibrational modes have RR enhancement maxima at 430 and 460 nm, respectively, indicating that they are associated with different phenolate → Cu charge-transfer bands. Since no RR enhancement of ν_s(Cu–OH–Cu) was observed for the homologous μ-alkoxo, μ-OH complex, it appears that coupling to a chromophoric ligand such as phenolate may be important for the observation of M–OH vibrations in the RR spectra of such systems.

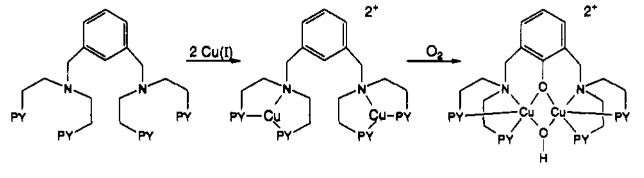
Introduction

A number of copper proteins contain EPR-silent, antiferromagnetically coupled Cu(II) ions.[2-4] These proteins include hemocyanin, the respiratory protein of molluscs and arthropods, and tyrosinase, a monooxygenase. Coupled copper sites are also found in multicopper oxidases such as laccase, ceruloplasmin, and ascorbate oxidase. In all of these proteins, the dinuclear copper sites appear to be directly involved in reactions with O_2.

Extensive chemical and spectroscopic comparisons of the hemocyanins and tyrosinases indicate that these proteins have similar dinuclear copper sites.[4] In the X-ray crystal structure of *Panulirus interruptus* deoxyhemocyanin, each Cu(I) is ligated to three histidines.[5] Resonance Raman spectroscopy of oxyhemocyanin has revealed that the dioxygen is bound as a symmetrical peroxide bridging the two copper ions,[6] and a similar structure is likely for oxytyrosinase.[7] Although recent modeling studies demonstrate that a single bridging peroxide could be responsible for the strong antiferromagnetic coupling in the oxy proteins,[8,9] it is also possible that an additional bridging group is present at the Cu(II) sites in these proteins.[4] In particular, methemocyanin (which does not react with O_2) appears to have a pH-sensitive, ionizable group coupling the two Cu(II) ions.[10] The X-ray data on deoxyhemocyanin exclude tyrosinate or other amino acids as the bridge between the two Cu(I) atoms, but the existence of a solvent-derived bridging ligand such as hydroxo or aqua cannot be ruled out at the present resolution of 3.2 Å.[5]

In the X-ray crystal structure of ascorbate oxidase,[11] each subunit has a type 1 (blue) copper site well-separated from a trinuclear copper cluster. The trinuclear cluster is composed of a type 2 copper (normal EPR) with two His and one aqua ligand and a spin-paired dimer with three His coordinated to each Cu. The X-ray refinement suggests that the dimer has at least one bridging O^{2-} or OH^- group.[11] Laccase and ceruloplasmin also contain all three types of copper sites and have homologous primary structures to ascorbate oxidase in the C-terminal part which contains ligand binding sites for the three types of copper atoms.[12]

Scheme I



XYL ligand, PY = 2-pyridyl $[Cu_2(XYL)]^{2+}$ $[Cu_2(XYL\text{-}O)(OH)]^{2+}$

This paper reports vibrational spectroscopic studies of a model complex for the dinuclear coupled copper site. This dinuclear cupric compound contains hydroxo (μ-OH) and phenoxo (μ-OR) bridges between the two Cu(II) atoms, with the μ-OR group being part of a dinucleating ligand (Scheme I). Both the hydroxo and phenoxo oxygen atoms were originally incorporated into the compound by reaction with molecular oxygen.[13] However, only the hydroxo oxygen is exchangeable with water. This makes it possible to investigate Raman and IR spectra of the complex with ^{18}O in either position. With isotope studies, we assign a ν(Cu–OH–Cu) mode at 465 cm^{-1} and a ν(Cu–OR–Cu) mode at 603 cm^{-1}. Raman polarization studies and IR absorption studies allow us to further assign them as symmetric and asymmetric vibrations, respectively.

Experimental Section

The μ-hydroxo, μ-phenoxo dinuclear copper complex $[Cu_2(XYL{-}O{-})(OH)](PF_6)_2$ was synthesized by the addition of O_2 to the dicopper(I) complex of $[Cu_2(XYL)](PF_6)_2$, as described previously[13] (Scheme I). After precipitation with dry diethyl ether, the compound was recrystallized twice from wet CH_2Cl_2–ether (1:3). A μ-^{18}OR complex $[Cu_2(XYL\text{-}^{18}O{-})(OH)]^{2+}$ was synthesized using $^{18}O_2$ instead of $^{16}O_2$ in the process. A μ-^{18}OH complex $[Cu_2(XYL{-}O{-})(^{18}OH)]^{2+}$ and a μ-OD complex $[Cu_2(XYL{-}O{-})(OD)]^{2+}$ were prepared by adding 1% $H_2{}^{18}O$ and 1% D_2O, respectively, to CH_3CN solutions of the μ-OR complex $[Cu_2(XYL{-}O{-})(OH)]^{2+}$, sealing in capillaries, and equilibrating for 1-2 h prior to measuring the Raman spectra. For IR spectra, these samples were evaporated to dryness on NaCl plates under argon and examined in an N_2-purged instrument.

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Table I. Vibrational Spectroscopic Properties of the $[Cu_2(XYL\text{-}O^-)(OH)]^{2+}$ Complex

frequency,[a] cm^{-1}	spectroscopic activity	isotope shift,[b] cm^{-1} ΔOD	Δ^{18}OH	Δ^{18}OR	Raman depolarization ratio (ρ)	Raman enhancement max, nm	assignment
465	RR	−16	−12	0	0.5	430	ν_s(Cu–OH–Cu)
603	RR, IR	0	0	−11	0.7	460	ν_{as}(Cu–OR–Cu)
623	RR, IR	0	0	−3	0.3	460	δ(phenolate)
1310	RR, IR	*c*	*c*	−8	*c*	460	ν(C–O) phenolate

[a] Frequencies from RR spectra of samples in acetonitrile. Similar values were observed in the IR spectra of solid samples in KBr pellets. [b] Average of values obtained by RR and IR spectroscopy. [c] Not determined.

Infrared spectra were recorded on a Perkin-Elmer 1800 FT-IR spectrophotometer connected to a Perkin-Elmer 7500 Professional Computer. Raman spectra were recorded either on a computerized Jarrell-Ash spectrophotometer equipped with a cooled RCA C31034 photomultiplier tube and an ORTEC Model 9302 amplifier-discriminator or a Dilor Z-24 spectrophotometer having a cooled Hamamatsu 943-02 PMT. Excitation sources were Spectra-Physics 164-05 (Ar) and 2025-11 (Kr) lasers. Raman spectra of solutions were obtained in a 90°-scattering geometry, whereas those for solid samples in an ~150°-backscattering geometry using a spinning disk. Peak frequencies were corrected using indene as a standard and are accurate to ±1 cm^{-1}.

Depolarization ratios of Raman features were measured in a 90° scattering geometry with the scattered light passing through an analyzer and a polarization scramber placed ahead of the entrance slit. For each sample, two spectra were obtained sequentially under the same conditions except that one was with the polarization analyzer in the parallel position (0°) and the other with the polarization analyzer in the perpendicular position (90°). The ρ value of a specific peak was determined by the ratio of $I_\perp/I_\parallel$.

Results

Raman studies of the $[Cu_2(XYL\text{-}O^-)(OH)]^{2+}$ complex in the 1100–1700-cm^{-1} region have been reported previously and show a number of resonance-enhanced phenolate vibrational modes.[14] A ν(C–O) vibration at 1307 cm^{-1} was identified from the shift of −8 cm^{-1} for the ^{18}OR-substituted complex. Our Raman studies in this high-frequency region with ^{18}OR-substituted sample gave similar results (Table I). In order to observe Cu–O–Cu vibrations, we conducted resonance Raman and infrared studies in the region below 1100 cm^{-1}. Although such vibrations are expected to occur between 200 and 600 cm^{-1},[15,16] no specific vibrations of Cu–OH–Cu or Cu–OR–Cu have been definitively identified in the literature. The $[Cu(XYL\text{-}O^-)(OH)]^{2+}$ complex has a 2-fold axis of symmetry perpendicular to the Cu···Cu axis.[13] Since the OH$^-$ and OR$^-$ bridging groups have markedly different chemical character, four vibrational modes are expected arising from symmetric and asymmetric motions of the Cu(μ-O)$_2$Cu core: ν_s(Cu–OH–Cu), ν_s(Cu–OR–Cu), ν_{as}(Cu–OH–Cu), and ν_{as}(Cu–OR–Cu). The resonance Raman spectrum (Figure 1A) exhibits a large number of features in the low-frequency region which can be assigned to Cu–O–Cu and/or phenolate modes through the use of isotopic substitution and excitation profiles.

Cu–OH–Cu Vibration. The bridging hydroxo group was exchanged with solvent by dissolving $[Cu_2(XYL\text{-}O^-)(OH)](PF_6)_2$ in CH_3CN containing 1% water. This treatment did not result in any structural change other than bridge replacement as evidenced by the constancy of the electronic spectra (in $CH_3CN \pm H_2O$) and the RR spectra (solid vs CH_3CN solution). As can be seen in Figure 1, the 465-cm^{-1} peak of the μ-OH complex shifts to 453 cm^{-1} with $H_2{}^{18}O$ exchange and to 449 cm^{-1} with D_2O exchange. This peak is attributed to a Cu–OH–Cu vibrational mode. Although Figure 1 shows spectra restricted to the 400–700-cm^{-1} region, we also collected Raman data from 100 to 1100 cm^{-1} on solids and in CH_2Cl_2 and CD_3CN solutions, which would have revealed any modes obscured by the CH_3CN solvent peaks.

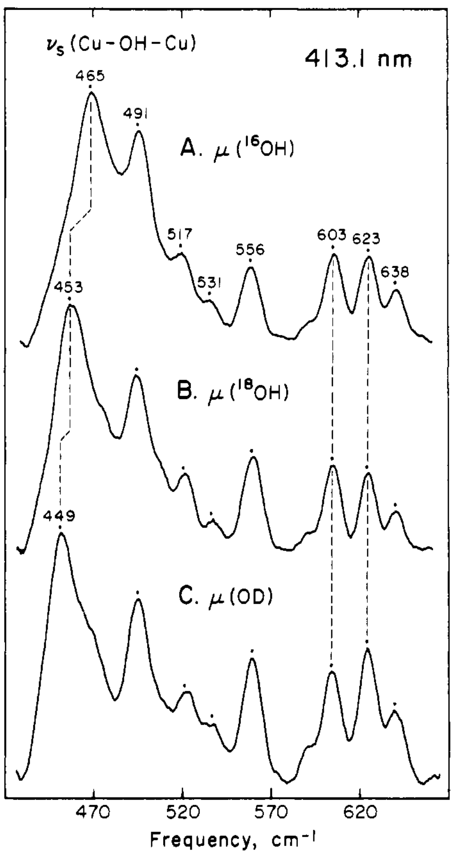

Figure 1. Resonance Raman spectrum of $[Cu_2(XYL\text{-}O^-)(OH)](PF_6)_2$ in CH_3CN (1 mg/mL) containing (A) 1% $H_2{}^{16}O$, (B) 1% $H_2{}^{18}O$, and (C) 1% D_2O. Spectra were obtained at 273 K (ice bath) with 413.1-nm excitation (20 mW) using a spectral resolution of 8 cm^{-1}, scan rate of 1 cm^{-1}/s, and an average of six scans.

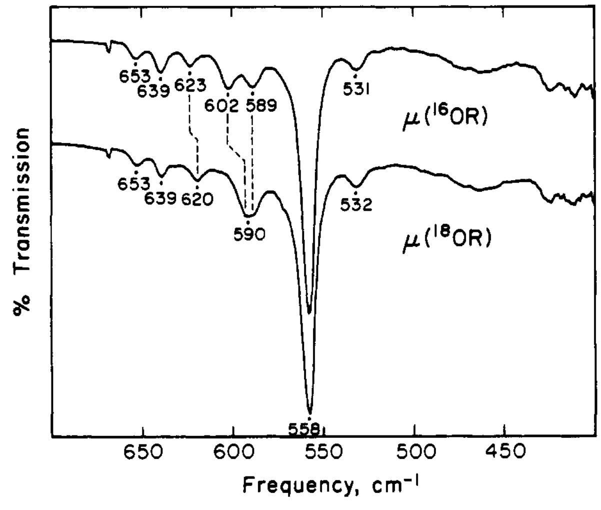

Figure 2. Infrared spectra of $[Cu_2(XYL\text{-}{}^{16}O^-)(OH)](PF_6)_2$ and $[Cu_2(XYL\text{-}{}^{18}O^-)(OH)](PF_6)_2$ in KBr pellets. Each spectrum is an average of 20 scans.

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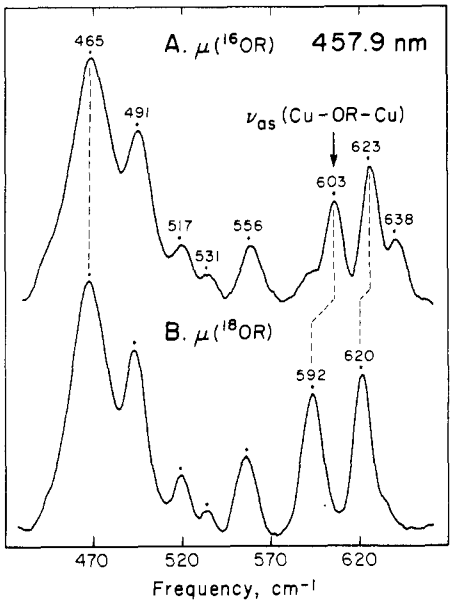

Figure 3. Resonance Raman spectra of $[Cu_2(XYL\text{-}^{16}O\text{-})(OH)](PF_6)_2$ and $[Cu_2(XYL\text{-}^{18}O\text{-})(OH)](PF_6)_2$ in CH_3CN (0.02 M). Spectra were obtained at room temperature with 457.9-nm radiation (25 mW) using a spectral resolution of 7.2 cm^{-1}, scan rate of 1 cm^{-1}/s, 3-s integration per point, and an average of four scans.

Only the feature at 465 cm^{-1} showed sensitivity to D_2O and $H_2{}^{18}O$ isotope exchange.

To establish the symmetry of the 465-cm^{-1} Cu–OH–Cu vibrational mode, we determined the depolarization ratio of the Raman feature and investigated the low-frequency FT-IR spectra. The former established that the 465-cm^{-1} peak is polarized (ρ = 0.5; Table I), and no corresponding absorption was observable in the IR spectrum (Figure 2). Examination of the ν(O–H) stretching region in the IR region did reveal isotopic exchange from the decreased intensity at 3625 cm^{-1} upon ^{18}O substitution. These results support the assignment of the 465-cm^{-1} peak as the symmetric vibration of the Cu–OH–Cu moiety.

Cu–OR–Cu Vibration. Two Raman peaks in the low-energy region are sensitive to ^{18}O substitution of the XYL ligand (Figure 3). Comparing RR spectra of μ-^{18}OR and μ-^{16}OR complexes, it can be seen that the 603-cm^{-1} peak of μ-^{16}OR complex shifts to 592 cm^{-1} and the 623-cm^{-1} peak shifts to 620 cm^{-1}. We assign the 603-cm^{-1} peak to a Cu–OR–Cu vibration on the basis of its −11-cm^{-1} isotopic shift. Previous studies on ferric phenoxo complexes show the existence of a phenolate ring mode near 630 cm^{-1}.[17] It is likely, therefore, that the 623-cm^{-1} peak of the $[Cu(XYL\text{-}O)(OH)]^{2+}$ complex is predominantly due to a phenolate ring vibration and that its −3-cm^{-1} isotope shift arises from motion of the phenolate oxygen in this mode.

The 603- and the 623-cm^{-1} peaks also appear in the IR spectrum (Figure 2). On ^{18}O substitution into the XYL–O bridge, these peaks exhibit the same isotopic shifts that were seen in the Raman spectrum. (The fact that the 639-cm^{-1} peak is unshifted in Figure 2 indicates that its decrease in intensity in Figure 3B is merely a consequence of RR intensity borrowing from the 623-cm^{-1} peak.) The appearance of the 603-cm^{-1} Cu–OR–Cu mode in both Raman and IR spectra, as well as its depolarization ratio of 0.7 (Table I), suggests that it be assigned as ν_{as}(Cu–OR–Cu). In contrast, the 623-cm^{-1} peak has a much smaller isotope shift and is strongly polarized (ρ = 0.3). These results indicate that this phenolate ring vibration is a symmetric mode. As a further probe of the assignment of the 603-cm^{-1} band as an asymmetric Cu–OR–Cu vibration, we looked for the presence of the overtone of this frequency. In oxo-bridged dinuclear metal complexes, weak ν_{as}(M–O–M) modes are often accompanied by quite intense $2\nu_{as}$ overtones.[18] However, in the present case, we observed no Raman feature near 1206 cm^{-1} ($2\nu_{as}$) or 930 cm^{-1} ($2\nu_s$). The absence of distinct overtones indicates that Cu–OX–Cu modes are less susceptible to overtone progressions than M–O–M systems.

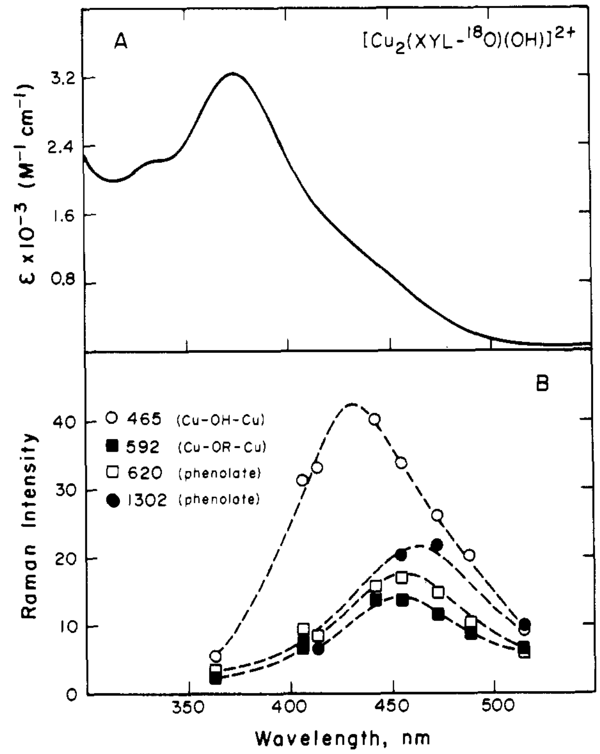

Figure 4. Resonance Raman enhancement profiles for the $[Cu_2(XYL\text{-}^{18}O\text{-})(OH)]^{2+}$ complex: (A) absorption spectrum in CH_3CN; (B) relative molar Raman scattering intensities. A solid sample of the μ-^{18}OR complex, $[Cu_2(XYL\text{-}^{18}O\text{-})(OH)](PF_6)_2$, was mixed with a 3× excess of $NaNO_3$, and its Raman spectrum was obtained at a series of excitation wavelengths. The intensities (areas) of the peaks at 465, 592, 620, and 1302 cm^{-1} were determined relative to $\nu_1(NO_3^-)$ at 1055 cm^{-1} and corrected for differences in molar concentrations.

Raman Enhancement Profiles. The electronic absorption spectrum of the $[Cu_2(XYL\text{-}O\text{-})(OH)]^{2+}$ complex has an intense maximum at 375 nm and a broad shoulder at ~430 nm (Figure 4A). A comparison of the RR spectra obtained with different excitation wavelengths (Figures 1 and 3) reveals that ν_s(Cu–OH–Cu) is more strongly enhanced with higher energy excitation relative to ν_{as}(Cu–OR–Cu). To further investigate the nature of the electronic absorption bands, intensity enhancement profiles of the 465- [ν_s(Cu–OH–Cu)], 592- [ν_{as}(Cu–^{18}OR–Cu)], 620- [ν(phenol(^{18}O)ate)], and 1302-cm^{-1}]ν(C–^{18}O)phenolate] modes were obtained relative to $\nu_1(NO_3^-)$ of $NaNO_3$ used as an internal standard (Figure 4B). It is clear that the three Raman features at 592, 620, and 1302 cm^{-1} share a similar profile with an enhancement maximum at ~460 nm. In contrast, the ν_s(Cu–OH–Cu) mode at 465 cm^{-1} belongs to a different chromophore with an enhancement maximum near 430 nm. Although the Raman enhancement profiles in Figure 4B were obtained on a solid sample, similar enhancement behavior was observed for a solution sample with intensities quantitated relative to an acetonitrile solvent peak.

On the basis of the Raman enhancement behavior of the three phenolate modes in the $[Cu_2(XYL\text{-}O\text{-})(OH)]^{2+}$ complex, the 460-nm component under the broad shoulder in the absorption spectrum can reasonably be assigned to a phenolate → Cu(II) charge-transfer (CT) band. This assignment is in agreement with Raman studies on several other phenoxo-bridged dinuclear Cu(II) complexes which indicate that the phenolate vibrational modes are more enhanced with blue excitation (457.9 nm) than with green excitation (514.5 nm).[14,15] Electronic spectral comparisons between phenoxo-bridged and mononuclear complexes have also

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suggested the presence of phenolate → Cu(II) CT bands between 445 and 465 nm in the dinuclear complexes.[19,20] However, many other phenoxo-bridged Cu(II) complexes exhibit an intense absorption between 360 and 390 nm,[15,19,21] similar to the major 375-nm band in the XYL–O complex. Although these absorption bands also have been attributed to phenolate → Cu CT, the lack of Raman enhancement of phenolate modes for the XYL–O complex in the 350–400-nm spectral range (Figure 4) makes such an assignment problematic. In ferric phenolate complexes, Raman enhancement maxima have been observed to be red-shifted by 40–70 nm relative to the position of the phenolate → Fe(III) CT bands.[22] This raises the possibility that 375- and 430-nm absorptions are both phenolate → Cu(II) CT bands, giving rise to the Raman enhancement maxima at 430 and 460 nm, respectively.

Since the Cu–OH–Cu stretch is selectively enhanced near 430 nm, an alternative assignment for this spectral region could be to a hydroxo → Cu(II) CT. Such a suggestion has been made for alkoxo-bridged dicopper(II) complexes where the dinucleating ligand N3OH is derived from 2-hydroxypropane connected to two bis[2-(2-pyridyl)ethyl]amine groups.[23] The $[Cu_2(N3\text{–}O\text{–})(OH)]^{2+}$ and the $[Cu_2(N3\text{–}O\text{–})(OCH_3)]^{2+}$ complexes have their respective absorption maxima at 418 and 375 nm ($\epsilon \sim 800\ M^{-1}\ cm^{-1}$). However, the Raman spectrum of the $[Cu_2(N3\text{–}O\text{–})(OH)]^{2+}$ complex obtained with 413-nm excitation gives no indication of an ^{18}O-dependent Cu–OH–Cu mode. Furthermore, no spectral feature has a molar scattering intensity greater than 2 relative to $\nu_1(NO_3^-)$, whereas the RR peaks in the homologous XYL–O complex are enhanced 15- to 40-fold relative to those for nitrate (Figure 4).

A similar lack of resonance enhancement occurs with the $(\mu\text{-}OH)_2$ complex, $Cu_2(L_2)(OH)_2$, where L = hydrotris(3,5-diisopropyl-1-pyrazolyl)borate.[24] This compound is altogether lacking in electronic spectral features in the 300–500-nm region, and no Raman peaks with molar scattering greater than 1 relative to nitrate are observed. Similarly, the $Cu_2(L_2)(^{18}OH)_2$ complex shows no isotope-dependent Cu–OH–Cu modes between 350 and 650 cm^{-1}. These results suggest that the relatively strong enhancement of ν_s(Cu–OH–Cu) in the $[Cu_2(XYL\text{–}O\text{–})(OH)]^{2+}$ complex derives from its association with an additional phenolate → Cu(II) CT band at 430 or 375 nm. Other probable phenolate modes such as the peaks at 491 and 557 cm^{-1} also show maximum enhancement near 430 nm (Figures 1 and 3).

Discussion

Vibrational Assignments. In this report, we present the first definitive identification of Cu–OH–Cu and Cu–OR–Cu vibrations in a dinuclear copper complex by oxygen isotope substitutions. Analogous M–O–M vibrations are well-known for oxo-bridged metal clusters in both metalloproteins and inorganic model complexes. Examples include Fe–O–Fe,[25] Ru–O–Ru, Os–O–Os, Re–O–Re, W–O–W, Cr–O–Cr, Sn–O–Sn, and V–O–V.[16,26] However, data for hydroxo-bridged systems are far less extensive. Previous IR and Raman studies on hydroxo-bridged Pt, Co, Cr, and Cu complexes placed symmetric M–OH–M vibrations at 290–370 cm^{-1} (Raman)[16,27] and asymmetric M–OH–M vibrations at 480–580 cm^{-1} (IR),[16,28] but these assignments were not based upon ^{18}O isotope shifts and, thus, have remained unsubstantiated.

For the $[Cu_2(XYL\text{–}O\text{–})(OH)]^{2+}$ complex, we have observed two three-atom vibrational modes, ν_s(Cu–OH–Cu) and ν_{as}(Cu–OR–Cu). From ^{18}O and D isotope data, these are distinct, localized vibrations with no indication of any coupling between them. Moreover, these modes have different Raman enhancement profiles, indicating that they are associated with different chromophores. Since the Cu–O–Cu angles are known,[13] the expected ^{18}O isotope shift of each ν(Cu–OX–Cu) can be calculated using secular equations.[29] For a Cu–OH–Cu angle of 104°, ν_s(Cu–OH–Cu) at 465 cm^{-1} is predicted to shift $-18\ cm^{-1}$ with $\mu\text{-}^{18}OH$ and $-10\ cm^{-1}$ with μ-OD (assuming that the μ-OH group behaves as a point mass). The observed shifts are -12 and $-16\ cm^{-1}$, respectively, with the $\Delta^{18}O$ value being anomalously small and the ΔD value being anomalously large. For the known Cu–OR–Cu angle of 102°, a ν_{as}(Cu–OR–Cu) at 603 cm^{-1} is predicted to shift by $-28\ cm^{-1}$ (considering only the oxygen atom of the phenolate), whereas a shift of only $-11\ cm^{-1}$ is observed.

The fact that the ^{18}OH and ^{18}OR shifts are smaller than expected can be explained if ν_s(Cu–OH–Cu) and ν_{as}(Cu–OR–Cu) are not pure, but mixed, vibrational modes. It is likely that ν_{as}(Cu–OR–Cu) at 603 cm^{-1} undergoes *kinematic* coupling with another phenolate mode. Previously, smaller-than-expected ^{18}O isotopic shifts for ν(Fe–O) of mononuclear phenoxo iron complexes have also been ascribed to the coupling of the ν(Fe–O)phenolate mode with a benzene ring mode.[30] The ν(C–O) phenolate stretch at 1310 cm^{-1} in the $[Cu_2(XYL\text{–}O\text{–})(OH)]^{2+}$ complex is similarly not a pure vibrational mode as it shifts by $-8\ cm^{-1}$ for ^{18}O (Table I) compared to a predicted value of $-26\ cm^{-1}$ (considering only C–O). This finding is in agreement with a normal-coordinate analysis for the 2,4,6-trichlorophenolate complex of Cu(II) where the vibrational mode at 1316 cm^{-1} was calculated to have only 43% C–O stretching character.[31] In addition to such kinematic coupling, *vibronic* coupling of Cu–OR–Cu motions with the electronically active phenolate moiety provides a mechanism for resonance enhancement[32] of ν_{as}(Cu–OR–Cu). The failure to observe the ν_s(Cu–OR–Cu) mode in the Raman spectrum underlines the importance of appropriate coupling with the phenolate chromophore in order to achieve resonance enhancement.

The ν_s(Cu–OH–Cu) mode at 465 cm^{-1} may undergo kinematic coupling with the δ(Cu–O–H) bend,[33] as suggested by the large shift of $-16\ cm^{-1}$ with deuterium. Alternatively, ν_s(Cu–OH–Cu) could be coupled with a pyridine ring deformation mode such as that observed at 440 cm^{-1} in mononuclear Cu(II) pyridine complexes.[34] Both the phenolate and pyridine ligands in $[Cu_2(XYL\text{–}O\text{–})(OH)]^{2+}$ may contribute to electron delocalization in the electronic excited state, thereby explaining the rather large Raman enhancement of the Cu–OH–Cu symmetric stretch. In a previous RR study of phenoxo- and hydroxo-bridged Cu(II) complexes in which the dinucleating ligands lacked aromatic nitrogens such as pyridine, no such strongly enhanced ν(Cu–OH–Cu) modes were detected.[15]

Applicability to Metalloproteins. The RR scattering intensity of the ν_s(Cu–OH–Cu) mode of the $[Cu_2(XYL\text{–}O\text{–})(OH)]^{2+}$ complex reaches a maximum value of 40 relative to a nitrate internal standard (Figure 4). Given typically available protein concentrations of ≤5 mM, a vibration with a relative scattering intensity of 40 would be just at the limit of being detectable by RR spectroscopy and, thus, could potentially be observed in a dinuclear copper protein. However, the failure to observe reso-

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nance-enhanced Cu–OH–Cu modes in a number of other dinuclear copper complexes that lack phenolate or pyridine ligands[15,23,24] suggests that the presence of **both** types of ligands may be important. For the multicopper proteins of known structure, hemocyanin and ascorbate oxidase, histidine ligands abound and are likely to have similar vibronic properties to pyridine. However, there is no evidence for phenolate ligation of copper in these proteins. On the basis of our studies of the μ-OH-bridged copper complexes, we feel that it will be difficult to use Raman spectroscopy to detect bridging OH groups in these proteins.

Hydroxo-bridged dinuclear metal clusters are also of relevance to dinuclear iron proteins where they have been implicated in the mixed-valence forms of hemerythrin, purple acid phosphatase, and methane monooxygenase.[35] The μ-oxo bridge that is found in the fully oxidized forms of the dinuclear iron proteins is readily detected by RR spectroscopy.[25] The oxo → Fe(III) CT transition is a dominant chromophore in the near-UV region and leads to strong enhancement of the ν_s(Fe–O–Fe) mode. However, no such chromophoric character exists in the corresponding hydroxo-bridged complexes. We have been unable to detect ν_s(Fe–OH–Fe) in the RR spectra of hydroxo-bridged diiron(III) complexes containing pyrazole[36] or benzimidazole[37] ligands. We have observed an Fe–OH vibration in the RR spectrum of the dinuclear iron protein, purple acid phosphatase, that may arise from a bridging OH group.[38] Interestingly, this Fe–OH mode is resonance-enhanced via a phenolate → Fe(III) CT band. Therefore, it is likely that an additional strong chromophore such as that provided by a phenolate ligand is required in order to obtain RR spectra from hydroxo-bridged metal systems.

Acknowledgment. We are grateful to Dr. Nobumasa Kitajima for providing samples of the $Cu_2(L_2)(OH)_2$ complex[24a] and Dr. Roman Czernuszewicz for many helpful discussions. This work was supported by grants from the National Institutes of Health, Nos. GM 18865 (T.M.L. and J.S.-L.) and GM 28962 (K.D.K.).

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Cluster Synthesis. 38. Formation of High-Nuclearity Platinum–Osmium Cluster Complexes. Synthesis, Structural Characterizations, and Interrelationships of $Pt_4Os_6(CO)_{22}(COD)$, $Pt_5Os_6(CO)_{21}(COD)_2$, $Pt_4Os_6(CO)_{19}(COD)_2$, and $Pt_7Os_6(CO)_{21}(COD)_2$ (COD = Cycloocta-1,5-diene)

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Received December 27, 1991

Three new high-nuclearity platinum–osmium carbonyl cluster complexes $Pt_4Os_6(CO)_{22}(COD)$ (**2**), $Pt_5Os_6(CO)_{21}(COD)_2$ (**3**), and $Pt_4Os_6(CO)_{19}(COD)_2$ (**4**) were obtained in 17%, 13%, and 9% yields, respectively, from the pyrolysis of $Pt_2Os_3(CO)_{10}(COD)_2$ (**1**) under a CO atmosphere at 128 °C. Compounds **2**–**4** were characterized by IR, ^{1}H NMR, and single-crystal X-ray diffraction analyses. Compound **2** consists of two Pt_3Os_3 octahedra sharing a Pt_3 triangular face. A Pt(COD) group caps one of the Os_3 triangular faces. Compound **3** is structurally similar to compound **2** but has an additional Pt(COD) group capping one of the $PtOs_2$ triangular faces. The cluster of compound **4** can be viewed as a meta-bicapped Pt_2Os_4 octahedron with an additional Pt(COD) group capping a $PtOs_2$ triangle to one of the capping groups on the octahedron and a Pt(COD) group bridging the Pt–Pt edge of the octahedron. Compound **2** was converted to **4** in 65% yield, when it was irradiated in the presence of COD. When compound **2** was treated with 1 equiv of trimethylamine *N*-oxide and 2 equiv of $Pt(COD)_2$, compound **3** and a new higher nuclearity platinum–osmium carbonyl complex $Pt_7Os_6(CO)_{21}(COD)_2$ (**5**; 8% yield) were obtained. Compound **5** was characterized by a single-crystal X-ray diffraction analysis. It was formed by the loss of one CO from **2** and the addition of three Pt atoms and one COD ligand. The structure consists of layers of metal atoms. A platinum-capped Os_3 triangle sits next to a planar Pt_4 layer, which in turn lies next to a planar five atom layer consisting of three osmium and two platinum atoms. Compound **2** was converted to the known compound $Pt_4Os_6(CO)_{21}(COD)(\mu\text{-H})_2$ (**6**) in good yield (79%) by reacting with trimethylamine *N*-oxide and hydrogen. Crystal data: for **2**, space group $P2_1/n$, a = 20.404 (6) Å, b = 9.607 (5) Å, c = 24.171 (8) Å, β = 90.512 (3)°, Z = 4, and R = 0.040 for 2847 reflections; for **3**, space group $P2_1/m$, a = 12.023 (8) Å, b = 16.010 (9) Å, c = 13.902 (7) Å, β = 103.79 (5)°, Z = 2, and R = 0.037 for 2428 reflections; for **4**, space group $C2/c$, a = 45.67 (1) Å, b = 11.836 (4) Å, c = 17.444 (4) Å, β = 99.04 (2)°, and R = 0.034 for 3295 reflections; for **5**, space group $P2_1/n$, a = 21.061 (6) Å, b = 12.086 (3) Å, c = 21.348 (6) Å, β = 92.06 (2)°, and R = 0.039 for 3134 reflections.

Introduction

The chemistry of heteronuclear cluster complexes containing platinum has attracted a great deal of interest[1] because of the importance of platinum alloys to the process of catalytic petroleum re-forming.[2] Higher nuclearity mixed-metal clusters may serve as good models for such catalysts because the arrangement of the metal atoms on their surfaces may resemble those on the surfaces of real catalysts. To date, however, there are relatively few examples of high-nuclearity mixed-metal cluster complexes con-

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