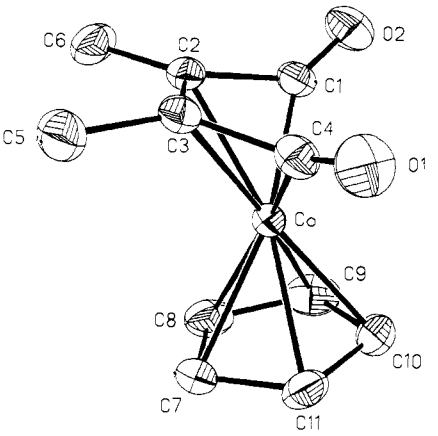
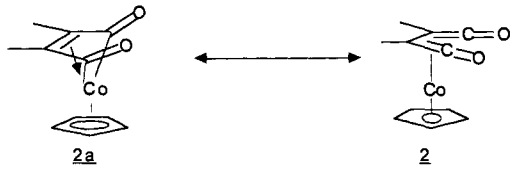


Figure 1. ORTEP diagram of η^5-CpCo(η^4-dimethylbisketene) showing 30% probability thermal ellipsoids with numbering scheme for the atoms. $R = 0.0409$, $R_w = 0.0438$. Distances: Co-C1, 1.868 (4) Å; Co-C2, 2.045 (3) Å; Co-C3, 2.065 (4) Å; Co-C4, 1.860 (4) Å; C1-C2, 1.455 (5) Å; C2-C3, 1.415 (5) Å; C3-C4, 1.445 (5) Å. Angles: C2-C1-O2, 137.8 (3)°; Co-C1-O2, 145.5 (3)°; C3-C4-O1, 138.5 (4)°; Co-C4-O1, 142.8 (3)°.

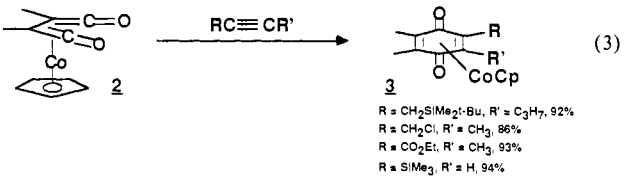
of the four carbons defining the bisketene backbone, and the fact that the bonds between these carbon atoms have similar lengths (1.455, 1.415, 1.445 Å) suggests some diene-like bonding for the structure of **2**.[3] However, the C-C-O bond angles (145.5°, 142.8°) indicate substantial rehybridization of the carbonyl carbon from sp toward sp^2 and the slightly shorter bond length for C2-C3 (compared to C1-C2 and C3-C4) both argue for a significant contribution of limiting geometry **2a** to the structure of this



2a **2**

bisketene complex.[3] Other studies relevant to this work include the characterization of η^2-monoketene complexes,[4] vinylketene complexes,[5] a diiminocobaltacyclopentene complex,[6] and a η^4-bis(*tert*-butylimino)diphenylbuta-1,3-diene complex.[7]

Bisketene complex **2** reacted under mild conditions with a variety of alkynes to give excellent isolated yields of η^5-CpCo-(η^4-1,4-benzoquinone) compounds **3** which are all very polar, air-stable, red-brown solids (eq 3).[2,8] Triphenylphosphine,



(3)

R = CH_2SiMe_2t-Bu, R' = C_3H_7, 92%
R = CH_2Cl, R' = CH_3, 86%
R = CO_2Et, R' = CH_3, 93%
R = $SiMe_3$, R' = H, 94%

pyridine, and diethyl sulfide all reacted quickly to convert the bisketene complex back to the maleoylcobalt structure **1**.[9] Although it is tempting to suggest a direct reaction of alkynes with **2** to give the quinone complexes **3**, the facile conversion of **2** back to the maleoyl form **1** with simple ligands implies that quinone complex formation may occur from a maleoylcobalt species **1** with L = alkyne. The reactions of bisketene complex **2** obviously have a bearing on the mechanism of our previously published studies of quinone complex formation from **1**.[2]

Bisketene complex **2** is stable in the solid state and can be stored in that form; however, in solution exposed to air slow decomposition occurs. On heating a benzene solution of **2** to 80 °C under nitrogen in a sealed system, decomposition occurs to give η^5-$CpCo(CO)_2$,[10] η^5-$(CpCoCO)_3$,[10] η^5-CpCo(η^4-duroquinone),[11] and η^5-CpCo(CO)(dimethylmaleoyl) **1**, L = CO. These results point to decarbonylation of the bisketene complex as the major mode of thermal decomposition, since the liberated CO and 2-butyne (possibly complexed) can react with **2** to give the latter two observed products.

In a preliminary set of reactions we have prepared the η^5-C_5Me_5 analogues of **1**, L = CO, and **2** and found the pentamethyl bisketene complex to be more stable toward decomposition than its nonmethylated analogue. Attempts to convert both of the bisketene complexes into other interesting compounds (reaction with RLi, with Wittig or Tebbe reagents) and a study of the reaction chemistry of the functionalized quinone complexes are currently under way. Complete experimental details for the chemistry described in this manuscript can be found in the supplementary material.

Acknowledgment. This investigation was supported in part by PHS Grants CA 26374 and CA 40157 awarded by the National Cancer Institute, DHHS, and in part by the National Science Foundation under Grant CHE-8305055.

Supplementary Material Available: Experimental details for the synthesis and reactions of bisketene complexes and complete data for the X-ray crystal structure determination (25 pages). Ordering information is given on any current masthead page.

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(9) Identified by comparison with known compounds prepared according to the procedures described in ref 2.

(10) Identified after chromatography by comparison of infrared data with the values described in: Vollhardt, K. P. C.; Bercaw, J. E.; Bergman, R. G. *J. Organomet. Chem.* **1975**, *97*, 283.

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Resonance Raman Spectroscopy of Metalloproteins under Extreme Conditions: Cryogenic Diamond-Cell Study of Azurin

Stephen F. Agnew, Jon R. Schoonover, Basil I. Swanson,* and William H. Woodruff*

Los Alamos National Laboratory, Inorganic and Structural Chemistry Group, Isotope and Nuclear Chemistry Division, University of California Los Alamos, New Mexico 87545

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There are numerous cases in the physiological functioning of proteins where volume changes or other transformations that may be induced or affected by pressure are known to be important. Considerable spectrophotometric study (primarily of hemoglobin and its derivatives) has been devoted to such phenomena at hydrostatic pressures in the 1-8 kbar range (ref 1 and references therein). However, protein behavior under the extreme pressures available by current diamond-cell technology has not been investigated. In particular, no structure-specific spectroscopic probes (e.g., vibrational spectroscopy) have been utilized to determine whether the structural integrity of any protein remains intact under

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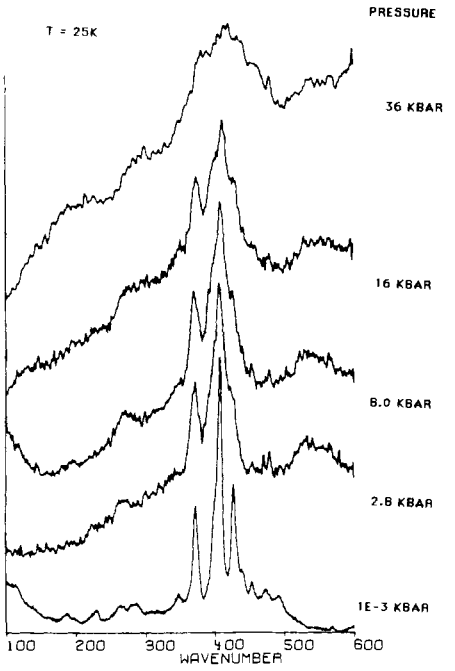

Figure 1. RR spectra of azurin at 25 K and the pressures indicated. The ambient-pressure spectrum was obtained at 12 K. RR spectra were obtained using the apparatus described elsewhere.[10] Temperature control was provided by an Air Products Displex cryostat. The diamond cell, which has been described in detail elsewhere,[12] is capable of generating pressures up to approximately 100 kbar. The pressures were measured by observing the wavelength of the ^2E emission of microscopic ruby chips within the cell. The sample volume of the diamond cell is defined by an inconel gasket with an aperture approximately 200 μm in diameter squeezed between two brilliant-cut diamonds with the bases cut flat. The optical path length between the two flat diamond surfaces was approximately 50 μm. To load the protein, the cell was disassembled and a drop of *Pseudomonas aeruginosa* azurin solution (0.01 M, pH 5.5) was introduced into the aperture of the inconel gasket. The solution was allowed to evaporate to a paste. The cell was reassembled, and the desired pressure was established. The azurin was prepared and purified by procedures described elsewhere.[10] Raman spectra were collected in 180° backscattering geometry from the diamond cell, using 25 mW of 647.1-nm excitation from a Spectra Physics 171 Kr^+ laser. Spectral slit width was 5 cm^{-1}. Peak positions were determined digitally, by curve resolution where necessary, and have an estimated precision of ±1 cm^{-1}.

pressures of tens of kilobars and, if it does, what effects may be observed.

We report the first vibrational study of a metalloprotein under extreme pressure (3–70 kbar) and cryogenic temperatures. The spectroscopic probe employed is resonance Raman (RR) spectroscopy. We have chosen as an initial system for study the blue copper protein azurin, because (unlike, for example, heme proteins wherein the chromophore is a prosthetic group whose structure may persist even if the protein structure is denatured) the structural integrity of the blue copper chromophore is dependent upon the primary, secondary, and tertiary structures of the protein remaining intact.[2-4] In addition, extensive ambient-pressure RR studies of blue copper proteins[5-10] are available.

The protein residues proximate to copper in azurin[3,4] and also in plastocyanin[2] have been shown to be two imidazole residues from histidines, mercaptide sulfur from cysteine, and thioether sulfur from methionine. These liganding amino acids are parts of the polypeptide backbone of the protein. Although in plastocyanin protein constraints may hold the methionine sulfur too far from the copper atom for Cu–S(met) bonding to occur,[2,9,11] making Cu(II) effectively three-coordinate, this may not be the case in azurin.[9,10]

The azurin RR spectra between ambient pressure and 36 kbar (Figure 1) show intense vibrational fundamentals below 600 cm^{-1}, which include the symmetric Cu–N(his-Im) stretch and the Cu–S(cys) stretch strongly mixed with ligand deformations.[8-10] Except for irreversible photodecomposition at 70 kbar, the pressure effects on the RR spectra were reversible. The 70-kbar spectrum showed catastrophic line broadening and frequency upshifts, showing only broad features at ca. 350 and 500 cm^{-1} and a strong peak at 200 cm^{-1} which is probably due to photodecomposed protein. These effects were reversible upon lowering pressure to ≤36 kbar if the protein was not illuminated with laser light while at 70 kbar.

The spectra show the same major features from ambient pressure up to 36 kbar, namely, the three prominent peaks at approximately 370, 410, and 430 cm^{-1}, the shoulder at 400 cm^{-1}, and the weaker feature near 270 cm^{-1}. The precise frequencies are pressure-dependent, as are the relative intensities and linewidths. However, it can be stated with confidence that the relatively similar frequencies at 36 kbar and below indicate that the normal vibrational modes of the blue copper chromophore are essentially independent of pressure up to 36 kbar. This conclusion, combined with the established sensitivity of these modes to structure,[10] strongly suggests that the structure of the blue copper chromophore does not change substantially over this pressure range. Accordingly, it may be inferred that no radical changes in protein secondary or tertiary structure occur at or below 36 kbar. This observation alone is remarkable inasmuch as no known terrestrial organism lives at hydrostatic pressures greater than the deepest ocean trenches (ca. 1 kbar): therefore, there is no obvious evolutionary reason for protein structures to survive extreme pressure.

The significant pressure-dependent changes in the RR spectra include general frequency upshifts, increased intensity of the weaker peaks in the 370–450-cm^{-1} region compared to the strong peak near 410 cm^{-1}, and monotonic peak width increase with increasing pressure. The frequency shifts can be understood in terms of general increases in the nonbonding forces and internal force constants as pressure is increased. The shifts in the 370–450-cm^{-1} region are all similar in magnitude. However, the frequency of the peak near 270 cm^{-1} (previously assigned as Cu–N(his-Im) stretch[10]) is much more sensitive to pressure than the higher frequency modes.

The intensities of the peaks at 370 and 430 cm^{-1} and the shoulder at 400 cm^{-1}, relative to the major peak at 410 cm^{-1}, increase by approximately 50% between ambient pressure and 16 kbar. This increase continues in the 36-kbar spectrum and, in addition, the weak feature near 450 cm^{-1} gains substantial intensity. These intensity changes are probably due to pressure-induced constraints on the displacements which occur in the S(cys) → Cu^{2+} LMCT excited state. Apparently coordinate displacements in going from the ground to the excited state change as a function of pressure, becoming more uniformly projected upon the RR-active ground-state normal coordinates as pressure increased.

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The line-width increases with increasing pressure are typical in high-pressure Raman spectroscopy. We ascribe the line widths primarily to homogeneous broadening of the Raman transitions due to enhanced intraprotein vibrational dephasing at high pressure. Thus, pressure and temperature effects upon line width tend to cancel one another in these experiments. Indeed, in the 2–8-kbar range, the main effect of elevated *pressure* is to produce a spectrum which mimics the one observed at ambient rather than cryogenic *temperature*, including the line-width increases and the coalescence of the two peaks in the 270–280-cm^{-1} range.[9,10]

The absence of profound changes in the azurin RR spectrum up to 36 kbar suggests that no substantial changes in the coordination of copper at the active site occur in this pressure range. We have previously suggested[9,10] that in azurin all four potential ligands (vide supra) form significant bonds to copper, while in plastocyanin the Cu–S(met) bond is effectively nonexistent at room temperature. We may expect that elevated pressure might force significant Cu–S(met) bonding in plastocyanin and that such an effect will be observable in the RR spectrum. In general, we have demonstrated the applicability of this powerful combination of high-pressure, cryogenic, and spectroscopic techniques to metalloproteins. Related investigations are continuing in these laboratories.

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Registry No. Azurin, 12284-43-4.

Long-Lived Reactive Excited States of Zero-Valent Phosphine, Phosphite, and Arsine Complexes of Nickel, Palladium, and Platinum

Jonathan V. Caspar

Contribution No. 3744, Central Research and Development Department, Experimental Station E. I. du Pont de Nemours and Co. Wilmington, Delaware 19898

Received May 7, 1985

We wish to report here the first examples of d^{10} metal phosphine and phosphite complexes of nickel, palladium, and platinum which possess long-lived emissive excited states at room temperature in fluid solution.[1] In addition we have found that these complexes are photochemically reactive toward organic substrates, an observation that we believe represents an important new consideration in the interpretation of the mechanisms of oxidative addition reactions of this class of compounds. Furthermore in the light of the extensive use of these zero-valent metal complexes in a variety of catalytic and stoichiometric synthetic organic transformations, our observations may lead to a new and general approach to expanding the scope of the reactivity of this class of reagents.

Figure 1 presents the observed absorption and emission spectra of $Pd(PPh_3)_4$ and $Pd_2(dppm)_3$ in THF solution. These relatively broad (~3000 cm^{-1} full width at half-maximum) unstructured room temperature emission spectra are typical of all of the Pd(0) and Pt(0) compounds that we have investigated. Neither $Pd_2(dppm)_3$ nor $Pd(PPh_3)_4$ exhibit any additional structure at 77 K. The emission spectra of the Ni(0) complexes show a very poorly resolved shoulder approximately 1000–2000 cm^{-1} higher in energy than the band maximum. Decay kinetics for the excited states were found to be unaffected by the addition of excess ligand and were cleanly first order as determined by both transient absorption and fluorescence spectroscopies.[2] Table I summarizes the observed spectroscopic and photophysical properties of a variety of ML_n complexes (M = Ni, Pd, Pt; L = tertiary phosphine or phosphite, n = 3, 4).[3] Also included in the table are the spectroscopic properties of two ligand-bridged dimeric complexes, $Pd_2(dppm)_3$[4] and $Pd_2(dpam)_3$[5] (see Table I for ligand abbreviations). The dimeric complexes in Table I are expected to have

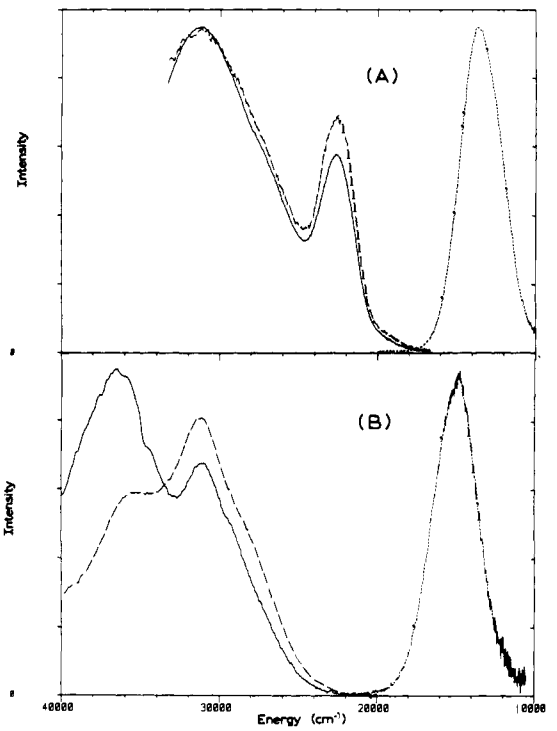

Figure 1. Absorption (—), corrected excitation (---), and corrected emission (•••) spectra of $Pd_2(dppm)_3$ (A) and $Pd(PPh_3)_4$ (B) at room temperature in tetrahydrofuran solution.

Table I. Spectroscopic and Photophysical Properties of d^{10} Metal Phosphine and Phosphite Complexes at 25 °C in Nitrogen-Saturated Tetrahydrofuran Solution

compound[a]	emission max, nm	excited-state lifetime, μs	emission quantum yield,[14] %	excited-state decay rates: radiative $s^{-1} \times 10^{-3}$	excited-state decay rates: nonradiative, $s^{-1} \times 10^{-5}$
$Pd(PEt_3)_3$	646	5.20	1.13	2.17	1.90
$Pd(PPh_3)_4$	660	3.61	1.66	4.60	2.72
$Pd(PMe_2Ph)_4$	690	1.39			
$Pd(PMePh_2)_4$	675		0.133		
$Pd_2(dppm)_3$	740	5.38	1.9	3.53	1.82
$Pd_2(dpam)_3$	710		7.53		
$Ni(P(O\text{-}o\text{-}tol)_3)_3$	~645 (sh), 745	5.13	0.293	0.57	1.94
$Ni(PPh_3)_4$	~740 (sh), 800				
$Pt(PPh_3)_4$	740	0.70	0.039	0.55	14.2

[a] Ligand abbreviations: triethylphosphine (PEt_3), triphenylphosphine (PPh_3), diphenylmethylphosphine ($PMePh_2$), dimethylphenylphosphine (PMe_2Ph), bis(dimethylphosphino)methane (dppm), bis(diphenylarsino)methane (dpam), tri-*o*-tolylphosphite ($P(O\text{-}o\text{-}tol)_3$).

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(5) Details of the preparation of this complex from allylpalladium chloride and bis(diphenylarsino)methane will be reported elsewhere.

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