Table II. Electronic Spectra of Chromium(III) and Vanadium(II) Complexes

complex[a]	absorptions ($\tilde{\nu}_{max}$, cm^{-1}) $^4A_2 \rightarrow {}^4T_2$	$^4A_2 \rightarrow {}^2E$	ref
Al_2O_3:Cr^{3+}	18 000	14 410	10
$Cr(en)_3{}^{3+}$	21 400	15 000	11
$Cr(phen)_3{}^{3+}$	23 400	13 750	1
MgO:V^{2+}	14 300	11 500	8
$V(en)_3{}^{2+}$	15 600	*b*	9
$V(phen)_3{}^{2+}$	17 800[c]	11 000[d]	2, 5

[a] See text for ligand abbreviations. [b] Data not available. [c] Calculated;[5] obscured by MLCT absorption. [d] Predicted; see text.

10^4 M^{-1} cm^{-1} [6]), in agreement with the $M(bpy)_3{}^{2+/3+}$ electrode potentials (V, 0.09 V;[2] Ru, 0.87 V;[7] both vs. Fc/Fc$^+$ in CH_3CN). On the basis of the "tail" of the MLCT absorption band in $V(phen)_3{}^{2+}$ ($\epsilon_{900} \sim 10$ M^{-1} cm^{-1}), the equilibrium energy of the lowest lying quartet MLCT excited state, "^{4}MLCT", is probably no higher than 11 000 cm^{-1}.

The d–d transitions $^4A_2 \rightarrow {}^4T_2$ and $^4A_2 \rightarrow {}^2E$ in $V(NN)_3{}^{2+}$ are probably obscured by the broad, nearly featureless MLCT bands. König and Herzog have estimated that the energy of $^4T_2$ is ca. 17 800 cm^{-1};[5] this is a region of intense MLCT absorption in all of these complexes. We have estimated the ^2E energy in $V(NN)_3{}^{2+}$ using data for other V^{2+} and Cr^{3+} species (Table II). Since ^2E lies below $^4T_2$ in MgO:V^{2+},[8] the same order should hold in the stronger field environments of $V(en)_3{}^{2+}$ (en = ethylenediamine)[9] and $V(phen)_3{}^{2+}$. Also, the ^2E energy in $Cr(phen)_3{}^{3+}$ [1] is slightly less than that in ruby[10] and $Cr(en)_3{}^{3+}$.[11] Thus, we believe that the ^2E energy in $V(phen)_3{}^{2+}$ is ca. 11 000 cm^{-1}.

Measurement of luminescence or excited-state lifetimes should allow us to determine whether ^2E or ^{4}MLCT is the lowest energy excited state in $V(NN)_3{}^{2+}$. (The two states might mix substantially, especially under the influence of spin–orbit coupling, but it should still be possible to evaluate their relative contributions.) We have observed no luminescence (700–1200 nm) from $V(phen)_3{}^{2+}$ or $V(bpy)_3{}^{2+}$ in the solid state or in solution, either at room temperature or at 77 K.[2] The very short excited-state lifetimes in Table I (compared to 24 ms for ^2E in MgO:V^{2+} at room temperature[8b]) can be explained in two ways. The lowest energy excited state could be ^{4}MLCT; the spin-allowed ^{4}MLCT $\rightarrow {}^4A_2$ decay should be very rapid. Alternatively, ^2E could be lowest lying, with the short-lived ^{4}MLCT state slightly higher in energy. This latter scheme would allow for rapid decay of ^2E by thermally activated back intersystem crossing to ^{4}MLCT. In this case, a low-temperature measurement should reveal a lifetime characteristic of ^2E, since the thermally activated process would be inhibited. However, the lifetime we observe at 5 K, less than 10 ns, is still far too short for ^2E. Thus, the back-intersystem-crossing model is ruled out, and the lowest energy excited state in $V(phen)_3{}^{2+}$ must be primarily ^{4}MLCT in character (Figure 3b).

Fluorescence from ^{4}MLCT will probably be very difficult to observe in $V(NN)_3{}^{2+}$. The breadth of the MLCT absorption band (fwhm ca. 4000 cm^{-1}) suggests that a large Stokes shift can be anticipated between the absorption and fluorescence maxima. Thus, even if fluorescence does occur, it will be very broad, and its maximum intensity will probably occur at wavelengths greater than 1000 nm (where the sensitivity of photomultiplier detectors is very low).

Among the $V(NN)_3{}^{2+}$ complexes in Table I, the electron-withdrawing Ph_2phen gives the shortest lifetime and the electron-donating Me_4phen the longest. This trend may be due to changes in the energies of the ^{4}MLCT states: the intense MLCT absorption band occurs at significantly lower energy in $V(Ph_2phen)_3{}^{2+}$ than in the other complexes. Our lifetime and electronic spectral data are also consistent with the energy-gap law.[12]

The excited-state lifetime for $V(phen)_3{}^{2+}$ (EtOH/MeOH, 4:1 v/v) approximately doubles as the temperature is lowered from 293 to 117 K (Table I). An Arrhenius plot of these data gives a slope corresponding to an activation energy of ca. 100 cm^{-1}. This is much smaller than the values obtained for excited-state decay in other polypyridine complexes (1040 cm^{-1} for $Cr(phen)_3{}^{3+}$ in CH_3OH;[13] 3200 cm^{-1} for $Ru(phen)_3{}^{2+}$ in CH_2Cl_2[14]). Our small activation energy could be associated with thermal excitations to other close-lying MLCT states or with low-energy vibrations of the complex framework.[15] However, the very short ^{4}MLCT lifetime we observe at 5 K shows that thermally activated processes do not play a major role in excited-state decay even at higher temperatures.

Previous studies of $Cr(NN)_3{}^{3+}$,[1,16] $Ru(NN)_3{}^{2+}$,[6] and $Os(NN)_3{}^{2+}$ [17] excited-state nonradiative decay all found larger rates for NN = bpy than for NN = phen. Our lifetimes for $V(bpy)_3{}^{2+}$ and $V(Me_2bpy)_3{}^{2+}$ (Table I) are also shorter than those for the phenanthroline derivatives. In all of these cases, then, the more flexible bpy ligands appear to permit faster excited-state decay.

Photoredox reactions of metal complexes have generally involved phosphorescent excited states. Our experiments, on the other hand, have shown that the redox-active lowest energy excited state in vanadium(II) polypyridine complexes is a MLCT state of the same spin multiplicity as the ground state.

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Copper-Promoted Autoxidation of a Binucleating Ligand

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Hemocyanin is a copper protein that reversibly binds molecular oxygen.[2] When viewed in the light of the now well-understood and well-modeled oxygen-carrying chemistry of iron in hemoglobin,[3] this apparently simple reaction of copper might not seem

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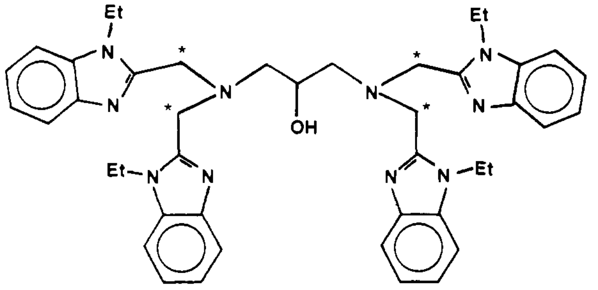
particularly remarkable. And yet, despite more than a decade of effort, it has proved to be exceedingly difficult to mimic with model compounds. Oxyhemocyanin has a thermal stability and a cleanly reversible oxygen-binding capacity that is unmatched by even the most promising model systems.[4-6]

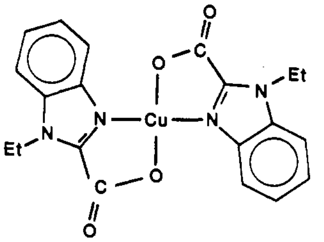
The most common problem encountered with oxyhemocyanin models is one of poor reversibility. Most, if not all, copper(I) complexes that are reported to form dioxygen adducts in solution quickly react further at ambient temperature to give irreversibly oxidized products. In some cases, copper(II) complexes can be isolated, usually containing the thermodynamically favored $[Cu_2(OR)_2]^{2+}$ core.[7,8] The ultimate fate of dioxygen is probably four-electron reduction to water. In a few cases, reactive dioxygen adducts have given rise to copper(II) complexes having oxidized ligands in high enough yield to allow isolation and characterization. Recent examples include aromatic hydroxylation,[9-11] oxidative dehydrogenation of amines,[12] and one case of aliphatic hydroxylation.[13] More frequently, however, oxygenation of binuclear copper(I) complexes causes oxidative degradation that is difficult to characterize. It appears that a strong oxidative capacity is intrinsic to the chemistry of a dicopper peroxide moiety and this is undoubtedly exploited by binuclear copper oxygenating enzymes such as tyrosinase.[14] In order for hemocyanin to function as a simple, reversible oxygen carrier, the active site must be designed to kinetically shut down this oxidative chemistry. Presently, it is unknown precisely how this is achieved but the growing knowledge of how copper promotes the oxidation of organic molecules is beginning to provide some clues.[15] This prompts us to report the isolation and structural characterization of a copper-promoted oxidative degradation product of the binucleating ligand HL-Et, which has recently been shown to be very useful in preparing methemocyanin models[16] (see structure I). We find that the benzylic-like methylene groups (labeled * in I) are susceptible to oxidative cleavage under a variety of conditions. The isolated product is a copper(II) bis complex of the 2-carboxylate of *N*-ethylbenzimidazole, $Cu(2\text{-}O_2CBz\text{-}Et)_2$ (II).



I

Table I. Crystal Data for $Cu(2\text{-}O_2CBz\text{-}Et)_2$

empirical formula: $C_{20}H_{18}N_4O_4Cu$
fw: 445.9
rhombohedral
space group: $R\bar{3}$
$a = b = 32.673$ (5) Å
$c = 4.698$ (1) Å
$\alpha = \beta = 90°$
$\gamma = 120°$
$V = 4341$ (1) Å^3
$Z = 9$
$F(000) = 2042$
$\mu = 11.66$ cm^{-1}
λ(Mo Kα) = 0.71069 Å
index range: $h = -36 \rightarrow 36$; $k = 0 \rightarrow 36$; $l = 0 \rightarrow 6$
no. of total reflcns: 2258
no. of unique reflcns: 1258
no. of obsd reflcns with $I > 2\sigma_I$: 765
systematic absences: $-h + k + l = 3n$
$R = 0.0627$
$R_w = 0.0492$



II

Experimental Section

All materials were AR grade and were used without purification. Acetonitrile (usually containing 0.005% H_2O) was purchased from Burdick and Jackson. The ligand HL-Et and its copper(II) complexes were prepared as previously described.[16] *N*-Ethylbenzimidazole was prepared via bromoethane alkylation of benzimidazole under previously described conditions[16] and characterized by ^1H NMR (90 MHz, $CDCl_3$): δ 1.5 (t, 3 H), 4.2 (q, 2 H), 7.2–7.8 (m, 5 H). *N*-Ethyl-2-carboxybenzimidazole[17] and $[Cu(MeCN)_4]ClO_4$[18] were prepared by literature methods.

Elemental analysis were performed by Chemical Analytical Services, Berkeley, CA. Infrared spectra were recorded as KBr disks on a Perkin-Elmer 281 spectrometer.

Caution! While none of the present perchlorate salts has proved to be shock-sensitive, precautions against explosion are recommended. Reactions were never performed on a scale larger than 0.3 g, and usually, lesser amounts were used.

Bis(2-carboxy-*N*-ethylbenzimidazole)copper(II), $Cu(2\text{-}O_2CBz\text{-}Et)_2$. Oxygen was bubbled through a bright yellow solution of HL-Et (0.1818 g, 0.25 mmol) and $[Cu(MeCN)_4]ClO_4$ (0.1645 g, 0.50 mmol) in acetonitrile (25 mL) for a few minutes. Purple crystals of product were deposited from the green solution over a period of a few days, and the yield continued to increase up to 0.023 g (20% based on HL-Et) over a period of 1 month. Anal. Calcd for $CuC_{20}H_{18}N_4O_4$: C, 54.36; H, 4.07; N, 12.7; Cu, 14.38. Found: C, 54.26; H, 4.02; N, 12.75; Cu, 14.6.

X-ray Structure Determination. Purple single crystals of $Cu(2\text{-}O_2CBz\text{-}Et)_2$ were selectively harvested from attempts to recrystallize $[Cu_2(NO_2)(L\text{-}Et)][ClO_4]_2$[16] from acetonitrile by ether vapor diffusion. A crystal of dimensions 0.29 × 0.07 × 0.06 mm was used for data collection at room temperature on a Nicolet R3m four-circle diffractometer. The unit cell parameters were determined by least-squares refinement using 25 accurately centered reflections ($21° < 2\theta < 25°$). Reflections were collected by using the θ–2θ scan technique ($3° < 2\theta < 45°$) and varible scan rate (4.88–29.3° min^{-1}). Crystal stability was monitored by recording 3 standard reflections every 100 reflections, and no significant variation was observed. Following data reduction, 765 reflections were used for the subsequent structural analysis. Intensities were corrected for Lorentz-polarization effects and for absorption. (Transmission factors varied between 0.893 and 0.938.) Elimination of space groups belonging to the $3m$ Laue class was done on the basis of photographs. Analysis of the data suggested that the space group was centrosymmetric, and since the only systematic absences were $(-h + k + l) = 3n$, the crystal was assigned to the rhombohedral space group $R\bar{3}$ with hexagonal settings. Crystal data are summarized in Table I.

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Table II. Atomic Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for $Cu(2\text{-}O_2CBz\text{-}Et)_2$

atom	*x*	*y*	*z*	U^a
Cu	5000	10000	0	40 (1)
N1	4368 (2)	9516 (2)	−1131 (13)	35 (3)
O1	4956 (2)	9512 (2)	2643 (13)	46 (3)
N2	3795 (2)	8777 (2)	−430 (13)	36 (3)
O2	4459 (2)	8766 (2)	3969 (13)	50 (3)
C1	4571 (3)	9112 (3)	2534 (19)	42 (5)
C3	4004 (3)	9438 (3)	−2921 (17)	30 (4)
C8	3641 (3)	8972 (3)	−2481 (17)	33 (4)
C2	4239 (3)	9118 (3)	326 (18)	40 (5)
C5	3533 (3)	9534 (3)	−6384 (18)	44 (5)
C4	3951 (3)	9724 (3)	−4913 (17)	39 (4)
C9	3541 (3)	8291 (3)	650 (19)	49 (4)
C7	3208 (3)	8775 (3)	−3950 (16)	37 (4)
C10	3658 (4)	7964 (3)	−1012 (23)	88 (7)
C6	3171 (3)	9067 (3)	−5898 (18)	46 (5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The structure was solved by direct methods. The metal atom (on a center of symmetry) and nine other atoms were located by using the program RANT.[19] The remaining non-hydrogen atoms were located from difference Fourier maps; blocked cascade least-squares refinement resulted in a conventional $R = 0.085$. Hydrogen atoms were included at calculated positions by using a riding model (C–H = 0.96 Å) with thermal parameters of $1.2U$ of their carrier atoms. The structure was further refined with all the non-hydrogen atoms anisotropic and converged with $R = 0.0627$, $R_W = 0.0492$. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = [\sigma^2(F_o)]^{-1}$. A final difference map showed no significant features; the ratio of maximum least-squares shift to error was 0.026. All the programs used for data reduction and structure solution are included in the SHELXTL (version 4.0) package.[19] A listing of the observed and calculated structure factors is available in the supplementary material.

Description of the Structure

The complex crystallizes as discrete molecules of $Cu(2\text{-}O_2CBz\text{-}Et)_2$. A packing diagram is included in the supplementary material. The asymmetric unit comprises half the molecule with the copper atom on a center of symmetry. Atomic coordinates are given in Table II. Anisotropic temperature factors and hydrogen coordinates are given in Tables III and IV in the supplementary material. Figure 1 shows the atom-numbering scheme and a perspective view that illustrates the essentially square-planar coordination geometry. Excluding the ethyl groups, the complex is planar to within ±0.03 Å. The N1–Cu–O1 and N1–Cu–O1 angles are 84.0 (3) and 96.0 (3)°, respectively. There are no significant axial interactions, the shortest distance of a heteroatom to copper being 3.78 Å to O1 of a neighboring molecule. The Cu–N distance is 1.944 (5) Å, which is at the low end of the range for Cu(II)–imidazole bond lengths,[20] presumably because of the low coordination number. The Cu–O distance is 1.968 (6) Å, which is again near the short end of the range typical of tetragonal copper(II) carboxylates.[21] All other bond lengths and bond angles are unexceptional and are listed in Table V of the supplementary material.

Discussion

We have observed the purple crystalline product of autoxidation of copper complexes of the binucleating ligand HL-Et under a variety of circumstances. The synthesis of $Cu(2\text{-}O_2CBz\text{-}Et)_2$ reported herein involves oxygenation of a copper(I) complex. But the actual crystals used for the X-ray structure determination were separated as a minor product from atttempts to recrystallize $[Cu^{II}_2(NO_2)(L\text{-}Et)][ClO_4]_2$ from acetonitrile–ether. In fact, we have observed purple crystals having an IR spectrum identical with that of an authentic product in many solutions of copper(II) salts/HL-Et/base mixtures left to stand in air. We suspect that many organic solvents, particularly under basic conditions, are capable of reducing copper(II) complexes of HL-Et to copper(I) and that subsequent autoxidation occurs. For example, spontaneous reduction of copper(II) complexes in acetonitrile has been reported.[7,22] The insolubility of $Cu(2\text{-}O_2CBz\text{-}Et)_2$ greatly assists its isolation from a variety of conditions. It has meager solubility in all common solvents but does dissolve in concentrated acid. A direct synthesis of $Cu(2\text{-}O_2CBz\text{-}Et)_2$ in powder form has been briefly reported,[17] and we have repeated this preparation using sodium *N*-ethylbenzimidazole-2-carboxylate and copper(II) nitrate. Elemental analyses and IR spectra compare favorably to those of the crystalline form.

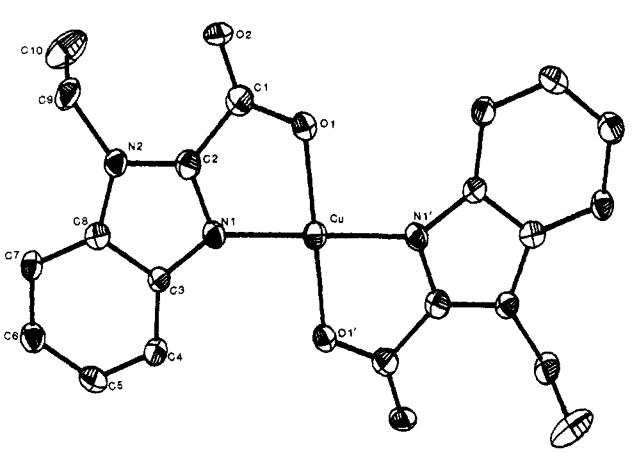

Figure 1. Atom-numbering scheme and perspective view of $Cu(2\text{-}O_2CBz\text{-}Et)_2$. Thermal ellipsoids are contoured at the 30% probability level.

The vulnerability of the methylene groups of HL-Et to copper-promoted autoxidation probably arises from their activation toward benzylic-like chemistry. The methylene group in question is adjacent to an aromatic ring *and* to an electronegative atom (N). It is therefore likely to be fairly acidic. Since dioxygen coordinated to copper is expected to be quite basic, it is tempting to think that bringing these functionalities together within the coordination sphere of copper initiates oxidation. Our results find a close parallel to the observation that copper-catalyzed autoxidation of organic substrates having the sequence $-N{=}C-CH_2-X$ occurs at the activated methylene group.[23] In the case where the substrate is bis(1-methylbenzimidazol-2-yl)methane[24] the methylene group is oxidized to a ketonic carbonyl. This suggests that the slow formation the final carboxylate complex in the present work may be due to slow hydrolysis of an amide formed this way.

The present observations provide a guide to linkages that should probably by avoided in ligands designed to mimic oxyhemocyanin or copper monooxygenases. They also suggest that the active sites of these proteins must isolate the Cu_2O_2 moiety from close contact with activated C–H bonds of the polypeptide. For this reason, we await with great interest, the further refinement of the crystal structure of a hemocyanin.[25]

Acknowledgment. This work was supported by the National Institutes of Health (Grant AM 30801 to C.A.R.). We thank Maruta Zvagulis for early assistance in this work.

Supplementary Material Available: Tables III–V, showing anisotropic thermal parameters, hydrogen atom coordinates, bond lengths, and bond angles, and a packing diagram (3 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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