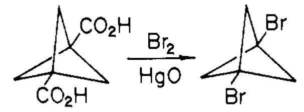
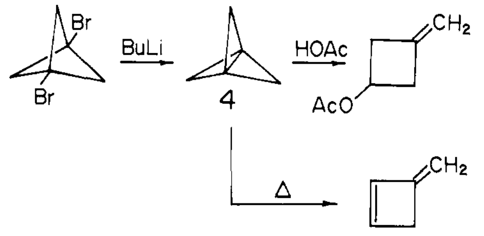
[2.2.2]propellane (**1**), which has a half-life of only an hour at 20 °C.[4]

We are now able to present a striking confirmation of these conclusions. 1,3-Dibromobicyclo[1.1.1]pentane (eq 1) was prepared from bicyclo[1.1.1]pentane-1,3-dicarboxylic acid, described by Applequist and Wheeler,[13] via a Hunsdiecker reaction (mp 119.5-120.5 °C; NMR ($CDCl_3$) δ 2.57 (s); Anal. C, H, Br). The product of the reaction of the dibromide with *tert*-butyllithium in pentane-ether was examined by GC (15 ft, 20% Apiezon L, 50 °C, 50 mL/min). Besides the peaks due to solvent and *tert*-butyl bromide, there appeared only one component, having a retention time of 3.6 min.



The $^1H$ NMR spectrum of this material had only a singlet at δ 2.06 ($CDCl_3$ solution). The $^{13}C$ NMR spectrum had bands at 1.0 ppm (quaternary carbon) and 74.2 ppm (methylene carbon, $J_{^{13}C-H}$ = 165 Hz). The mass spectrum had a peak at $m/e = 66$, suggesting that it is $C_5H_6$. It reacted with acetic acid to form 3-methylenecyclobutyl acetate.[14] In the gas phase, it rearranged with an approximate half-life of 5 min at 114 °C to give 3-methylenecyclobutene[15] (eq 2).



These data show that the compound is [1.1.1]propellane (**4**). Addition of a proton may give either the bicyclo[1.1.1]pentyl cation or the bicyclo[1.1.0]butyl-1-carbinyl cation. We have previously shown that both ions will give the 3-methylenecyclobutyl cation.[16,17] The thermolysis product may be derived by cleavage to 3-methylenecyclobutylidene (the reverse of adding a carbene to an alkene) followed by a hydrogen migration to give 3-methylenecyclobutene.[18]

The downfield shift of the methylene protons may appear surprising since they are formally part of a cyclopropane ring. However, one of the methylene protons of bicyclobutane appears at relatively low field (δ 1.5),[17] and this trend may easily be accentuated in **4**. The $^{13}C$ NMR spectrum is in accord with the observation that the bridgehead carbon of bicyclo[1.1.0]butane is shifted upfield and the methylene carbon is shifted downfield in comparison to other cycloalkanes.[19] The infrared spectrum ($CS_2$ solution) had strong bands at 3069, 3006 (CH stretch), 1093 (CCH bend), and 603 $cm^{-1}$ (antisym CC stretch), which may be compared with the corresponding bands of [2.2.1]propellane (3056, 2997, 1044, 530 $cm^{-1}$),[5] [2.1.1]propellane (3050, 2995, 1101, 574 $cm^{-1}$),[20] and bicyclo[1.1.0]butane (3055, 2954, 1113, 735 $cm^{-1}$).[21] A very intense band occurring between 500-600 $cm^{-1}$ appears to be characteristic of the small ring propellanes.[5]

Thus, despite the pessimism previously expressed concerning the preparation and stability of **4**,[22] it is the most easily prepared and the most stable of compounds **1-4**. The properties and reactions of **4** continue to be investigated. The nature of the central bond is of special interest with regard to theories of chemical bonding. Localized orbital calculations suggest that it has a bond order close to zero.[1] How can this be reconciled with an apparent bond dissociation energy close to that of the π bond in ethylene? This question is being explored. In addition, the energy changes on going from the propellanes to their singlet diradicals are being calculated by using the GVB[23] formalism which permits correct dissociation.

**Acknowledgment.** This investigation was supported by National Science Foundation Grant No. CHE-81-21421. We also acknowledge the support of the NSF Northeast Regional NMR facility at Yale University, which is funded by Grant No. CHE-79-16210 from the Chemistry Division of NSF. We especially appreciate the invaluable assistance of S. Kass in obtaining the NMR spectra.

**Registry No. 4**, 35634-10-7; bicyclo[1.1.1]pentane-1,3-dicarboxylic acid, 56842-95-6; 1,3-dibromobicyclo[1.1.1]pentane, 82783-71-9; 3-methylenecyclobutyl acetate, 18218-27-4; 3-methylenecyclobutene, 27538-13-2.

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(12) For bicyclo[1.1.0]butane, $\Delta H_f$ = 51.9 kcal/mol (Wiberg, K. B.; Fenoglio, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 3395) and with a normal methylene equivalent of -4.9 kcal/mol, $\Delta H_f \sim 47$ kcal/mol for 1-methylbicyclobutane. A C-H bond dissociation energy of ~104 kcal/mol at the bridgehead and ~96 kcal/mol at the methyl group was used.

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# Three-Coordinate Binuclear Copper(I) Complex: Model Compound for the Copper Sites in Deoxyhemocyanin and Deoxytyrosinase

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Tyrosinase and hemocyanin are metalloproteins that contain electronically coupled binuclear copper active sites.[1-4] These are often classified together with the binuclear sites in laccase, ascorbate oxidase, and ceruloplasmin as type 3 copper.[5] Both proteins are known to interact with dioxygen as part of their physiological function: hemocyanins[1,6] function as $O_2$ carriers in

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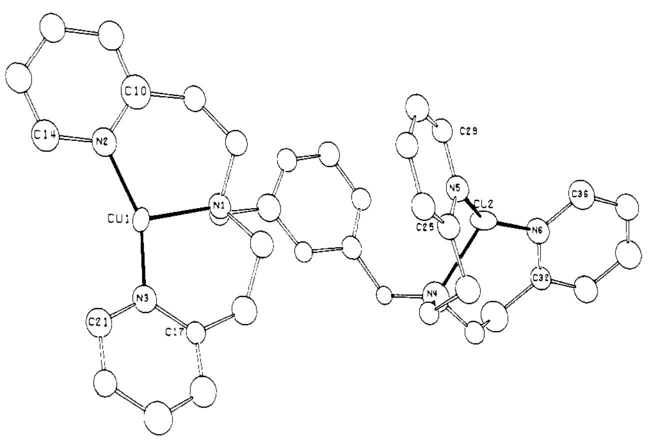


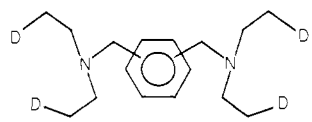
**Figure 1.** ORTEP diagram of the $[Cu_2(m\text{-}XYL(py))]^{2+}$ cation, showing the atom labeling scheme. Relevant bond lengths (Å) and angles (deg) are as follows: Cu···Cu, 8.940 (2); Cu1-N1, 2.120 (8); Cu1-N2, 1.931 (10); Cu1-N3, 1.932 (9); Cu2-N4, 2.195 (7); Cu2-N5, 1.903 (9); Cu2-N6, 1.917 (9); N1-Cu1-N2, 102.7 (4); N1-Cu1-N3, 104.1 (4); N2-Cu1-N3, 151.1 (4); N4-Cu2-N5, 99.8 (3); N4-Cu2-N6, 104.3 (3); N5-Cu2-N6, 150.7 (3).

the hemolymph of arthropods and molluscs, whereas tyrosinase[1,7] is a monooxygenase utilizing dioxygen in the hydroxylation of monophenols (monophenol → *o*-diphenol) and further functions as a two-electron oxidase (*o*-diphenol → *o*-quinone). A substantial body of chemical and spectroscopic information exists for the oxygenated (oxy) and oxidized (met) forms of hemocyanin and tyrosinase.[1,8,9] Strong parallels exist between the active sites of these proteins[1,8,10] consistent with the notion that binding and fixation of dioxygen are related.

Since dioxygen interaction occurs with the reduced state of these proteins,[11] a complete understanding of the structures and reactivity of the deoxy sites is required. From utilization of Extended X-ray Absorption Fine Structure (EXAFS) data combined with other information, two models for the copper sites in deoxyhemocyanin have recently been proposed. Two Cu(I) ions coordinated trigonally by three imidazole nitrogen ligands from histidine are separated by 3.4 Å in one model,[12] while in the other it is suggested that the two copper atoms are each coordinated to only two histidines and that the cuprous ions are separated by at least 4.5 Å.[13] In both models, substantial changes occur upon oxygenation, giving rise to tetragonally coordinated Cu(II) ions separated by ~3.6 Å, bridged by an exogenous $O_2^{2-}$ ligand (derived from $O_2$) and another oxygen-containing endogenous ligand.[12-14]

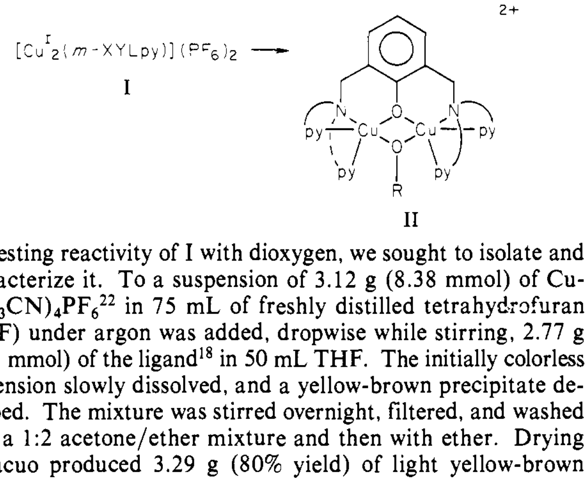
In contrast to the prevalence of binuclear Cu(II) complexes, few well-characterized low-coordinate binuclear Cu(I) model compounds exist.[15] In this communication, we report the synthesis and X-ray structural determination of a novel binuclear Cu(I) complex, I, containing well-separated trigonally coordinated Cu(I) centers that possess structural features common to both models proposed for deoxyhemocyanin. Its reactivity with dioxygen also makes it an excellent model system for the study of Cu(I)–$O_2$ interactions and $O_2$ activation.

As part of extensive investigations into the chemistry of binuclear copper complexes,[16-19] we are utilizing a new series of binucleating ligands, -XYL(D), D = nitrogen- or sulfur-donor group,



XYL(D)
D = py = 2-pyridyl (ref 17, 18)
D = SEt = ethylthio (ref 19)

where two tridentate ligand donor groups are separated by an *o*-, *m*-, or *p*-xylyl bridge.[20] Recently we reported the first example of a *m*-xylyl-containing copper complex showing that when a Cu(I) derivative of *m*-XYLpy (I) reacts with $O_2$ in methanol, hydroxylation of the xylyl ligand occurs, forming a phenolate bridged binuclear Cu(II) complex, II (R = methyl).[18] Because of this



II

interesting reactivity of I with dioxygen, we sought to isolate and characterize it. To a suspension of 3.12 g (8.38 mmol) of $Cu(CH_3CN)_4PF_6$[22] in 75 mL of freshly distilled tetrahydrofuran (THF) under argon was added, dropwise while stirring, 2.77 g (4.98 mmol) of the ligand[18] in 50 mL THF. The initially colorless suspension slowly dissolved, and a yellow-brown precipitate developed. The mixture was stirred overnight, filtered, and washed with a 1:2 acetone/ether mixture and then with ether. Drying in vacuo produced 3.29 g (80% yield) of light yellow-brown microcrystals of $Cu_2(m\text{-}XYLpy)(PF_6)_2$, I. Crystals suitable for X-ray diffraction were obtained by recrystallization from acetone/ether.

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The structure of the $(Cu_2(m\text{-XYLpy}))^{2+}$ cation is shown in Figure 1.[24,25] It consists of two crystallographically independent cuprous ion coordination environments. Each Cu(I) is three-coordinate with ligation from two pyridine and one tertiary amino donor groups. The chelating tridentate ligands cause considerable distortions from idealized trigonal planar coordination. The *N*-amino–Cu–*N*-py angles are acute (99–105°), resulting in large *N*-py–Cu–*N*-py angles of 151.1 (4) and 150.7 (3°) for Cu1 and Cu2, respectively. Some distortion from planarity occurs with Cu1 0.131 Å out of the N1,N2,N3 plane and Cu2 0.224 Å out of the N4,N5,N6 plane. The bonding distances are typical for three-coordinate Cu(I) with nitrogen donors[15a,26] while the Cu–*N*-py distances are shorter by ~0.08 Å than the bond lengths found in the monomeric tetracoordinate Cu(I) complex containing the same tridentate ligand.[27] The cuprous ion polyhedra extend away from each other (Cu1···Cu2 = 8.940 Å) as is found in $Cu_2Cl_4(p\text{-XYLpy})$.[17]

$Cu_2(m\text{-XYLpy})(PF_6)_2$, I, is the first example of a discrete Cu(I) binuclear complex containing three-coordinate copper ions with neutral nitrogenous ligands.[15c] It possesses a number of features postulated to occur in deoxyhemocyanin. There are two distorted trigonal planar Cu(I) moieties and unsaturated pyridine nitrogen donors to model imidazole coordination in the proteins. It also has well-separated copper ion groups which could move together upon oxygenation. This latter aspect has been suggested and is an attractive proposal, considering the abundance of evidence pointing to conformation changes upon oxygen binding in hemocyanins.[1,6,13b] $Cu_2(m\text{-XYLpy})^{2+}$ is very reactive, and introduction of $O_2$ to its dichloromethane solution results in the high yield $O_2$ incorporation via hydroxylation of the benzene ring of *m*-XYLpy and formation of a phenoxy and hydroxy doubly bridged Cu(II) binuclear complex (II, R = H) where the Cu(II)···Cu(II) separation is reduced to ~3.1 Å.[28]

Thus, I appears to be a good functional model compound for the deoxy state of the copper monooxygenases in that hydroxylation of an aromatic ring is effected. Studies of Cu(I)–$O_2$ interactions, mechanistic investigations of $O_2$ "activation", and reactivity with $O_2$/substrate (e.g., phenols) systems are presently in progress.

I is electrochemically active, and cyclic voltammetric measurements in dimethylformamide show a quasi-reversible one-electron (per copper) oxidation wave at $E = +0.16$ V vs. NHE. Compound I also reacts with "typical" Cu(I) ligands; thus it forms adducts with CO, olefins, phosphines, and phosphites to give compounds formulated as $Cu_2(m\text{-XYLpy})L_2(PF_6)_2$. These chemical investigations will be reported separately.

**Acknowledgment.** We are grateful to Research Corp. (K.D.K.), National Institutes of Health (K.D.K. GM28962; J.Z. GM22566 and GM27459) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (K.D.K.), for support of this work.

**Registry No.** I, 82731-39-3; $Cu(CH_3CN)_4PF_6$, 64443-05-6.

**Supplementary Material Available:** Listing of atomic coordinates and temperature factors, bond lengths, bond angles, and anisotropic temperature factors (9 pages). Ordering information is given on any current masthead page.

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[24] The complex crystallizes in the space group $P1$ with two molecules in a unit cell: $a = 11.251$ (3) Å, $b = 11.444$ (3) Å, $c = 15.721$ (4) Å; $\alpha = 95.71$ (2)°, $\beta = 102.06$ (2), $\gamma = 94.74$ (2); $\rho_{calcd} = 1.640$ g/cm³. The positional parameters of the copper atoms were determined by the Patterson method, and the other atoms were located on difference Fourier maps. With 2761 unique observed reflections ($3° < 2\theta < 40°$, $F_o > 6\sigma(F_o)$) taken at 22 °C on a Nicolet R3m diffractometer using Mo K$\alpha$ radiation, the structure was refined to a current value of 0.072 for the discrepancy index $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

[25] Supplementary material.

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# Electrically Stimulated Release of Neurotransmitters from a Surface. An Analogue of the Presynaptic Terminal

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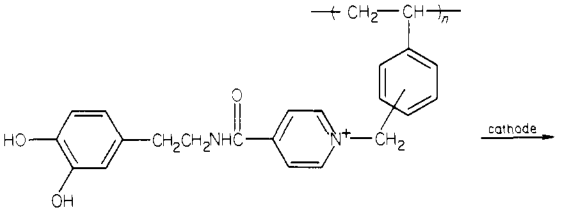
*Received May 27, 1982*

The conduction of electricity in vivo involves chemical communication between a presynaptic nerve cell and a postsynaptic nerve cell. The presynaptic terminal usually acts by liberating a transmitter substance in response to a change in its cell potential. We report that a solid electrode, modified with a thin layer of a suitable polymer, will similarly respond to a change in potential to release a neurotransmitter.

The experimental design is based upon recent work in which electrode surfaces have been modified to provide tailor-made molecular surface structures. It has been shown that polymers can be adsorbed or insolubilized onto electrodes.[1] If these polymers have suitable reducible or oxidizable groups, they are electroactive as expected. Our approach in this project was to synthesize a polymer that held a neurotransmitter via a cathodically cleavable bond. When adsorbed, this polymer could then be used to release the neurotransmitter. The controlled release of bound molecules from an electrode surface has not been previously reported. A device based upon this concept could have practical utility for the delivery of small amounts of material to specific locations at specific times.

The polymer **1** was chosen as a delivery agent for the neurotransmitter, dopamine. The polymer structure includes (a) a polystyrene backbone, which provides strong adsorption to the surface, (b) an isonicotinate unit, which allows reduction at rather positive potentials, and (c) the neurotransmitter, attached via a cathodically cleavable amide bond.



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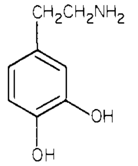
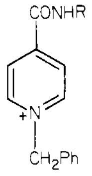


dopamine

It was previously demonstrated that the amide linkage of isonicotinamides would cleave upon reduction in DMF.[2] We have used aqueous solution, pH 7, to survey the reduction of several model pyridines and pyridinium salts. With use of a glassy carbon electrode, cyclic voltammetry (CV) showed that cationic *N*-alkylisonicotinamides, like compound **2**, reduced at potentials more



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