(5) The pertinent nmr data for the new compounds reported are as follows: compound **2** (CS$_2$), τ 8.50 (m, 2 H), 6.95 (t, 2 H), 6.64 (t, 2 H), 6.30 (s, 6 H), 4.46 (m, 2 H); compound **4** (acetone-D_6), τ 6.90 (d, 2 H), 6.70 (m, 2 H), 6.18 (m, 4 H), 6.20 (s, 6 H), 4.16 (m, 2 H); compound **6** (CCl$_4$), τ 8.19 (d, 1 H), 7.45 (m, 1 H), 6.43 (t, 2 H) 3.60–44.35 (m, 4 H), 2.92 (s, 10 H); compound **7** (R = Ph) (C$_6$D$_6$), τ 6.48 (m, 2 H), 3.65–4.40 (m, 6 H), 2.7–3.15 (m, 10 H); compound **7** (R = COOCH$_3$) (CDCl$_3$), τ 6.30 (m, 2 H), 6.25 (s, 6 H), 3.6–4.4 (m, 6 H); compound **8** (CS$_2$), τ 8.5–8.8 (m, 4 H), 6.40 (m, 2 H), 6.33 (s, 6 H), 4.2–4.8 (m, 4 H).

(6) Crystals of **2** from ether–pentane are monoclinic, $P2_1/c$, a = 12.360 Å, b = 9.295 Å c = 14.195 Å, β = 102.2°, and Z = 4. Structure solution was by the heavy-atom method, followed by full-matrix least-squares refinement with 2583 reflections to a final R = 0.056, R_w = 0.050. Details of the structure will be reported elsewhere (T. A. Dodds and R. E. Davis, to be submitted for publication).

(7) In the formation of the free ligand an iron carbonyl fragment is released which conceivably could be reused in the reaction sequence. When diphenylacetylene and cycloheptatriene were added to an irradiated solution of **1**, the hydrocarbon **6** was obtained in 170% yield based on 1. The configuration **10** can apparently also be reached in a purely thermal manner; when diphenylacetylene and cycloheptatriene are heated with 1,5-cyclooctadiene Fe(CO)$_3$ the hydrocarbon **6** is produced in low yield. These results suggest that some metal system could be found which would catalyze [2 + 6] addition under mild conditions.

(8) This compound is a yellow solid: mp 130–131°; nmr (acetone-d_6) 3.89 (m, 2), 4.72 (m, 2), 5.77 (d, 1), 5.88 (m, 1), 6.36 (s, 3), 6.45 (s, 3), 6.72 (d, 1), 6.92 (m, 1), 8.43 (t, 1), and 9.37 (m, 1); ir (KBr) 2010 (vs), 1955 (vs), 1720 (s), and 1675 (s) cm^{-1}.

(9) Crystals of **12** from ether–pentane are monoclinic, a = 11.781 Å, b = 12.891 Å, c = 15.407 Å, β = 139.7°, Z = 4. A disordered crystal structure has been partially refined in space group $P2_1/c$; the chemical structure **12** is firmly established on the basis of bond distances and angles. A report of the solution, refinement, and disordered structure will be published elsewhere (T.-H. Hseu and R. E. Davis, to be submitted for publication).

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Molecular Sructure of Bis[(hydridotris(1-pyrazolyl)borato)copper(I)] and Implications for Certain Copper-Containing Proteins

Sir:

Polypyrazolylborate ligands have afforded a large number of interesting organometallic and coordination compounds.[1-3] In addition, they offer possible synthetic models of histidine chelating sites[4-6] in some metalloproteins. Among these are the copper-containing,[7,8] dioxygen-activating proteins hemocyanin[9] (a dioxygen carrier), tyrosinase[10] (an oxygenase), and possibly others[11] where copper atoms occur in pairs, histidine (imidazole) is implicated in metal ion binding,[9d] and a reduced form involves Cu(I). The fact that Cu[HBpz$_3$][12] (I) is dimeric in solution and reacts with CO to form a carbonyl complex,[12,13] with ν(CO) nearly as low as in carboxyhemocyanin,[14] has prompted us to investigate thoroughly the properties of I. We communicate here the first example of a pyrazolylborate ligand bridging two metals, of the pyrazolyl segment also bridging two metals, and of a new type of fluxional process for polypyrazolylborate complexes. We also report the oxygenation of I to produce what we formulate as a copper-dioxygen complex.

Crystals of I suitable for diffraction were grown from toluene solution at −40°. The compound crystallizes in the triclinic space group $P\bar{1}$ with one dimeric molecule in a unit cell of dimensions a = 9.264 (1) Å, b = 7.638 (1) Å, c = 8.181 (1) Å, α = 92.96 (1)°, β = 101.71 (1)°, γ = 89.40 (1)°. Intensity data were collected on a diffractometer, and the structure was solved by standard Patterson and Fourier methods. It was refined by full-matrix least-squares techniques to an R index of 0.037 for 2111 observations above
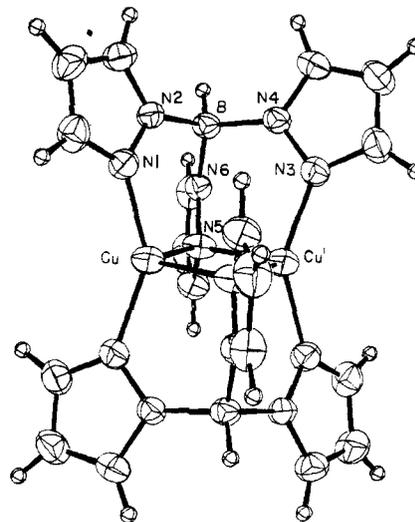
Figure 1. The molecular geometry of the centrosymmetric dimer [Cu(HBpz$_3$)]$_2$.

background. The molecular structure consists of a centrosymmetric dimer with each HBpz$_3$ unit contributing two terminal pyrazole ligands (one to each copper) and one crosswise bridging pyrazole ligand (Figure 1). A listing of positional and thermal parameters will appear in the microfilm edition; see paragraph at end of paper regarding supplementary material. The two bridging pyrazole rings lie in a noncrystallographic molecular mirror plane. Major features of the structure are (1) each copper ion is in a highly distorted tetrahedral environment, with N–Cu–N angles ranging from 93.74 (9) to 144.75 (10)°, (2) the Cu–Cu distance of 2.660 (1) Å is somewhat longer than in the ligand-bridged Cu(I) acetate structure (2.544 Å),[15] (3) the dimensions within the bridging pyrazole ring do not differ significantly from those in the terminal rings, and (4) the Cu–N bond distances are some 0.3 Å longer for the bridging nitrogen atoms (2.254 (2) and 2.224 (2) vs. 1.948 (2) and 1.946 (2) Å). In complexes containing both amino and bridging amido ligands, the corresponding metal–N distances are nearly equal.[16] Features (3) and (4) lead us to suggest that the bridge involves three-center two-electron bonding. These results also suggest that imidazole may be capable of functioning as a bridging ligand in bimetallic copper proteins.

Despite the existence of two kinds of pyrazole rings in the solid state, the rings are magnetically equivalent in the solution pmr spectrum down to −130° (90 MHz).[17] Barring a major structural change on dissolution or accidental spectral degeneracy, the results can be interpreted in terms of rapid intramolecular rotational movement of the HBpz$_3$ ligand about the B–H bond axis, which serves to interconvert bridge and terminal pyrazole rings. This rearrangement involving nitrogen heterocycles represents a new and potentially large class of bridge-terminal ligand interchange processes.[18]

In nonprotonic solvents, I takes up (irreversibly) 1 mol of dry dioxygen to yield a green, paramagnetic substance (II), which analyzes (elemental analysis, mass spectrum, cryoscopic molecular weight in benzene) for Cu$_2$(HBpz$_3$)$_2$O$_2$. We have been unable to identify securely ν(^{16}O–^{16}O) or ν(^{18}O–^{18}O) in the vibrational spectra[19] (ir and laser Raman). However, we tentatively assign a ν(Cu–^{16}O)[19b,20] in the infrared at 520 cm^{-1} (ν(Cu–^{18}O) = 500 cm^{-1}). Compound II reacts with (CH$_3$)(C$_6$H$_5$)$_2$P according to eq 1. Decomposition to, or equilibrium with, Cu(HBpz$_3$)$_2$ (detected *via* epr and visible spectroscopy) has hampered ef-

$$II + 4R_3P \longrightarrow 2Cu(PR_3)(HBpz_3)^{12a} + 2OPR_3 \quad (1)$$
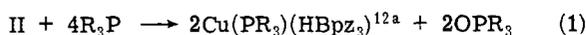
forts to grow crystals of II. Further investigations with both pyrazolylborate and physiologically more realistic synthetic ligands are underway.[21]

Supplementary Material Available. A listing of positional and thermal parameters will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-7564.

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Pentagonal Bipyramidal Complexes of Nickel(II) and Copper(II). The Relative Importance of Ligand Geometry vs. Crystal Field Effects

Sir:

Pentagonal bipyramidal complexes of the first-row transition elements are relatively rare. Until recently, the only seven-coordinate complexes involved the Mn(II)[1] and Fe(III)[2,3] ions, which have no crystal field stabilization energy. In fact, for transition metals with a nonspherical distribution of electrons, a planar pentagonal arrangement was considered unlikely because of crystal field effects.[4,5] However, the synthesis of pentagonal bipyramidal complexes of V(III)[6] and Fe(II), Co(II), and Zn(II)[7] suggested that other seven-coordinate complexes of the first-row transition metals might indeed be prepared. We now wish to report the first pentagonal-bipyramidal complexes of Ni(II) and Cu(II). Our results indicate that ligand geometry may be more important than crystal field effects.

The complexes were prepared by stirring and heating a slurry of DAPSC, 2,6-diacetylpyridinebissemicarbazone, in ethanol with an ethanol–water solution of either $Ni(NO_3)_2 \cdot 6H_2O$ or $Cu(NO_3)_2 \cdot 3H_2O$. The DAPSC slowly dissolves and after complete solution, slow evaporation of the solvent produces crystalline products. An analysis of the products suggested the stoichiometries $DAPSC \cdot Ni(NO_3)_2 \cdot 3H_2O$ (I), and $DAPSC \cdot Cu(NO_3)_2 \cdot 3H_2O$ (II). Since hydrolysis of the ligand could have occurred, X-ray crystal structure studies were undertaken.

Both complexes crystallize in the monoclinic system. The unit cell dimensions are $a = 11.493$ (2) Å, $b = 14.914$ (4) Å, $c = 12.154$ (4) Å, and $\beta = 104.94$ (2)° for I and $a = 10.977$ (4) Å, $b = 13.930$ (3) Å, $c = 6.977$ (3) Å, and $\beta = 104.55$ (3)° for II. The calculated densities of 1.697 g cm⁻³ for four molecules of I per unit cell and 1.669 g cm⁻³ for two molecules of II per unit cell are in good agreement with the values of 1.70 and 1.65 g cm⁻³ for I and II, respectively, measured by flotation. The systematic extinctions suggested that the space groups were $P2_1/n$ for I and either Pc or $P2/c$ for II. The intensity distribution for II favored $P2/c$, which requires the molecule to have a two-fold symmetry axis, and the successful analysis confirms this choice.

The intensity data for both complexes were measured using a Syntex P1̄ diffractometer with graphite monochromatized Mo Kα- radiation and a variable speed $\theta-2\theta$ scan technique. The nickel atom in I was located from a Patterson function. In II, the Cu atom is required to lie on a two-fold axis and the y- coordinate was determined from a Patterson function. Subsequent Fourier syntheses for both compounds were used to locate the lighter atoms. Refinement was by least-squares techniques to an R of 0.055 for the 1623 reflections used in the analysis for I and to an R of 0.056 for the 1647 reflections used in the case of II.

The pentagonal bipyramidal nature of the two complexes is easily seen in Figures 1 and 2. In both complexes the metal atom is surrounded by an approximately planar pen-