workers who used D labeling to study the stereochemistry of H shifts when carbenes rearrange to alkenes (**1** → **2**) have had to presume that k_H/k_D values for axial and equatorial pathways are equal.[1a-f] To our knowledge, the validity of this presumption has not been tested but perhaps deserves reconsideration in view of our present findings on the **2** → **1** process.

The factors responsible for the dissimilarity in isotope effects for the ax and eq trajectories in the photic **2** → **1** process are not clear. The extent of bond breaking, bond making, etc., for the two transition states could differ, in which case zero-point energy considerations would be relevant. Alternatively, H tunneling[12] might play a significant role, and if so, our isotope effects imply greater H tunneling for the equatorial trajectory. Inasmuch as D is far less subject to tunneling than H,[12,13] our D_{ax}/D_{eq} ratio may be the more genuine indicator of any inherent stereoelectronic factor in the alkene → carbene rearrangement.

Tunneling and isotope effect considerations may also be relevant in discussions of experimental H_{ax}/H_{eq} ratios[1f,14] in carbene → alkene (i.e., **1** → **2**) rearrangements.[1,2,15]

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X-ray Structure of Thiolatocopper(II) Complexes Bearing Close Spectroscopic Similarities to Blue Copper Proteins

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The synthesis and structural characterization of a thiolatocopper(II) complex which closely mimics the spectroscopic characteristics of blue copper proteins have been longtime goals in bioinorganic chemistry.[1-3] We recently reported the preparation of Cu(S*t*Bu)(HB(3,5-*i*Pr$_2$pz)$_3$) (**1**) which bears a close resemblance in its spectroscopic properties to blue copper proteins.[4] In this communication, we describe the crystal structure of an analogous thiolato complex Cu(SC$_6$F$_5$)(HB(3,5-*i*Pr$_2$pz)$_3$) (**2**). The preliminary structure of Cu(SCPh$_3$)(HB(3,5-*i*Pr$_2$pz)$_3$) (**3**) is also presented.

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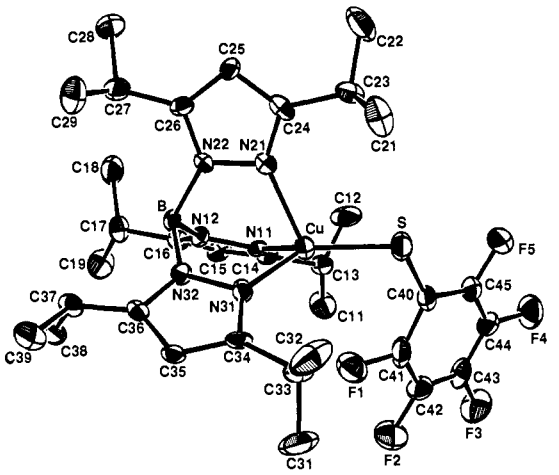

Figure 1. ORTEP view of Cu(SC$_6$F$_5$)(HB(3,5-*i*Pr$_2$pz)$_3$) (**2**). The octane molecule of crystallization is omitted for clarity. Selected bond distances (Å) and angles (deg): Cu-S, 2.176 (4); Cu-N11, 2.037 (9), Cu-N21, 2.119 (8), Cu-N31, 1.930 (9); S-Cu-N11, 122.7 (3); S-Cu-N21, 112.7 (2); S-Cu-N31, 134.6 (3); N11-Cu-N21, 90.9 (3); N11-Cu-N31, 93.9 (4); N21-Cu-N31, 90.2 (3); Cu-S-C40, 111.7 (4).

Reactions of a bis(μ-hydroxo) complex [Cu(HB(3,5-*i*Pr$_2$pz)$_3$)]$_2$(OH)$_2$ with a variety of thiols were surveyed to ascertain whether they could afford a stable thiolatocopper(II) complex. Thus 1-4 equiv of the thiol was added into a solution of the bis(μ-hydroxo) complex in CH_2Cl_2 at -78 °C. This reaction method effected the preparation of **1** as we reported previously.[4] The thiols surveyed include almost all of the aliphatic and aromatic thiols commercially available. With most of the thiols, the addition caused instantaneous decoloration of the solution, presumably due to the facile reduction to form a copper(I) complex. With C_6F_5SH and Ph_3CSH, however, moderately stable complexes Cu(SC$_6$F$_5$)(HB(3,5-*i*Pr$_2$pz)$_3$) (**2**) and Cu(SCPh$_3$)(HB(3,5-*i*Pr$_2$pz)$_3$) (**3**) were successfully obtained, and both of the complexes were isolated and crystallized.[5] The absorption and EPR spectra of **2** and **3** are comparable to those of **1**, and the close spectroscopic resemblance between **1**-**3** and blue copper proteins, azurin (Az) and plastocyanin (Pc), is evident.[6]

Figure 1 indicates the molecular structure of **2**, which definitely establishes the monomeric structure of **2**.[7] The coordination structure of **2** is described as distorted tetrahedral, or more precisely trigonal pyramidal, with a N_3S ligand donor set. Accordingly, the copper positions close to the basal trigonal plane consisting of N11, N31, and S; the distance between the copper and the basal plane is 0.34 Å, whereas a ca. 0.70-Å separation is expected for a regular tetrahedron. The copper(II)-thiolate sulfur distance of 2.18 Å is distincly shorter than those of the synthetic copper(II) thiolato complexes reported so far (2.23-2.94 Å)[8] and comparable to those found in blue copper proteins (see

(5) Complex **2** was isolated as crystalline solids from a mixture of CH_2Cl_2/pentane/octane at -20 °C. Anal. Calcd for $C_{33}H_{46}N_6BCuF_5S$: C, 54.43; H, 6.37; N, 11.54. Found: C, 55.14; H, 6.28; N, 10.71. UV-vis (CH_2Cl_2, at 20 °C, nm, ϵ/cm^{-1} M^{-1}): 420 (630), 665 (5960), 1020 (1200). EPR (toluene, at -160 °C): $g_\parallel$, 2.30; $g_\perp$, 2.10; $A_\parallel$, 54 × 10^{-4} cm^{-1}. Complex **3** was isolated in a similar manner. Satisfactory elemental analysis was obtained. UV-vis (CH_2Cl_2, at 20 °C, nm, ϵ/cm^{-1} M^{-1}): 440 (340), 625 (6600), 910 (1230). EPR (toluene, at -160 °C): $g_\parallel$, 2.23; $g_\perp$, 2.07; $A_\parallel$, 74 × 10^{-4} cm^{-1}.

(6) Pc (spinach) UV-vis: 460 (590), 597 (4900), 770 (1670) nm. EPR: $g_\parallel$, 2.23; $g_\perp$, 2.06; $A_\parallel$, 63 × 10^{-4} cm^{-1}. Az (*A. denitrificans*) UV-vis: 460 (580), 619 (5100), 780 (1040) nm. EPR: $g_\parallel$, 2.26; $g_\perp$, 2.06; $A_\parallel$, 60 × 10^{-4} cm^{-1}. Aniscough, E. W.; Bingham, A. G.; Brodie, A. M.; Ellis, W. R.; Gray, H. B.; Loehr, T. M.; Plowman, J. E.; Norris, G. E.; Baker, E. N. *Biochemistry* **1987**, *26*, 71.

(7) **2**·0.5(*n*-C$_8$H$_{18}$) crystallized in the monoclinic space group P_{21}/a with a = 25.364 (7) Å, b = 16.166 (3) Å, c = 9.924 (3) Å, β = 90.52 (3)°, V = 4069 (3) Å^3, and Z = 4. The structure was solved by the direct method and refined anisotropically for all non-hydrogen atoms by block-diagonal least-squares techniques (TEXSAN). All hydrogen atoms except those on the octane molecule were calculated and fixed in the final refinement cycles. The current $R(R_w)$ factor is 7.28(6.29)% for 2573 reflections collected at -45 °C ($3° \le 2\theta \le 45°$, $|F_o| \ge 3\sigma|F_o|$).

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Table I. Structural Comparison of the CuN_2S Units in **2**, **3**, and Blue Copper Proteins

	$Cu(SC_6F_5)L$ (**2**)	$Cu(SCPh_3)L$ (**3**)	Az (*A. denitricans*)	Pc (*popula*)	Pc (*E. prolifera*)	PAz	CBP
Cu–N1 (Å)	1.930 (9)	1.97 (5)	2.08	1.91	1.89	2.16	1.90
Cu–N2 (Å)	2.037 (9)	2.03 (4)	2.00	2.06	2.17	2.13	2.13
Cu–S (Å)	2.176 (4)	2.12 (2)	2.15	2.07	2.12	2.16	1.99
S–Cu–N1 (deg)	134.6 (3)	135 (1)	135	132	125	136	139
S–Cu–N2 (deg)	122.7 (3)	124 (2)	119	123	120	112	110
N1–Cu–N2 (deg)	93.9 (4)	98 (2)	105	97	104	100	99
Cu/N1N2S plane (Å)	0.34	0.20	0.12	0.36[a]	0.37[a]	0.43	0.39[a]
Cu–S* (Å)	2.119 (8)[b]	2.05 (5)[b]	3.11	2.82	2.92	2.76	2.62
EPR	axial	axial	axial	axial	axial	rhombic	rhombic
ref	this work	this work	14	15	16	17	18

[a] The data were provided by H. C. Freeman. [b] The distance between the copper and the apical nitrogen atom.

Table I). Although the refinement is very poor, the X-ray analysis of **3** indicates that its coordination structure is essentially similar to that of **2**.[9]

Blue copper proteins may be classified into three groups on the basis of their spectroscopic properties: (I) proteins that give an axial symmetric EPR spectrum; (II) proteins exhibiting a rhombic EPR spectrum; and (III) nitrous reductase[10] and Cu_A in cytochrome *c* oxidase[11] which exhibit distinctive features in absorption and EPR spectra. Whereas the structure of class III blue copper proteins remains to be solved, the crystal structures of class I and II blue copper proteins are available. The coordination structures of both types of the proteins are generally referred as distorted tetrahedral with a N_2SS^* (S^* denotes methionine sulfur) ligand donor set. The relevant structural parameters of **2**, **3**, and the blue copper proteins are compared in Table I. The CuN_2S unit of **2** (or **3**) is geometrically close to those of Az and Pc. These coordination structures can be described as trigonal, since the separations between the copper and the N_2S basal plane are short (<0.4 Å). On the other hand, the Cu···(N_2S) distances in pseudoazurin (PAz) and cucumber basic blue copper protein (CBP) are more separated (~0.4 Å). It should be noteworthy that **2** (or **3**) gives an axial EPR spectrum as Az and Pc, whereas PAz and CBP exhibit a rhombic EPR signal. Hence, the distinct features in EPR may correlate with the Cu···(N_2S) separations.[12] Alternatively, the apical ligand seems not to affect the spectroscopic properties of blue copper proteins significantly when the copper positions closely to the N_2S plane. In **2**, the apical nitrogen ligand is apparently more tightly bound to the copper than the methionine sulfur in Az or Pc. Nevertheless, both exhibit an axial EPR spectrum, which is associated with a $d_{x^2-y^2}$ ground state of the unpaired d-electron.[13] Conversely, PAz and CBP give a rhombic EPR spectrum, although the copper ions are surrounded by N_2SS^* ligand donors as in Az and Pc.

In order to prove the hypothesis, more extensive structural characterization of blue copper model complexes is under continued investigation.

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Supplementary Material Available: Summary of X-ray analysis and tables of atomic coordinates, anisotropic thermal parameters, and bond distances and angles for **2**·0.5(C_8H_{18}) (6 pages); table of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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Synthesis of Novel Solid-State Compounds in Supercritical Solvents: Preparation and Structure of $K_2Ag_{12}Se_7$ in Supercritical Ethylenediamine

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One important aspect of the recent surge of interest in solid-state chemistry[1] has been the preparation of kinetically stabilized solids. These are prepared at relatively low temperatures and thus are not the thermodynamically stable products appearing on high-temperature phase diagrams. The synthetic challenge is to develop techniques whereby there is intimate contact between the (mostly solid) starting materials and sufficient thermal energy for them to react. A desirable side benefit would be the ability to grow single crystals of the product. A common technique is the use of fluxes or molten salts to dissolve reactants at a relatively low temperature. These are often low-melting metals, oxides, halides,[2] or sulfides[3] and are usually chemically inert under the reaction conditions. A recent novel modification is the use of low-melting alkali metal polychalcogenides as both reactant and molten salt

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