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Mechanism of Olefin Metathesis and Cyclopropanation

Robert H. Grubbs

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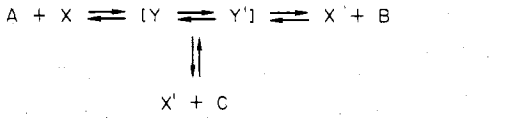
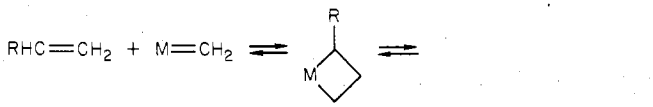
A serious objection to the Chauvin[1] mechanism for olefin methathesis has recently been raised by Mango.[2] He calculated that more cyclopropane than is observed should be present in olefin metathesis systems at equilibration conditions. Since Gassman and Johnson[3] have reported that cyclopropanes can undergo "metathesis" reactions, the cyclopropane to olefin interconversion is a kinetically accessible pathway. If this is the case, the calculation can be based on the following scheme where A and B are related olefins, C is related cyclopropanes, X and X′ are catalytic species, and Y and Y′ are intermediates.



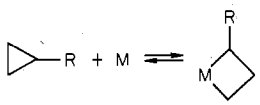
If, as by definition, the catalyst remains unchanged and therefore its free energy change is 0, the equilibrium constant is easily calculated from $\Delta\Delta G^\circ = 3(\Delta G^\circ(\text{ethylene})) - 2(\Delta G^\circ(\text{cyclopropane}))$. The resulting equilibrium constant as calculated is 0.17, and 20% of ethylene should be converted to cyclopropane.[2] Since only traces of cyclopropanes are observed[4,5] in metathesis reactions, the Chauvin mechanism appears incorrect. However, as will be shown below, it is the analysis that is in error.

The important steps in metathesis as required by the Chauvin mechanism are

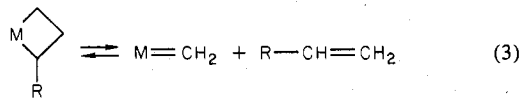


(1)

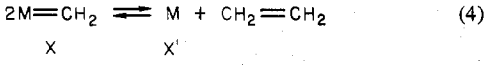
In order for there to be a related catalytic process to convert cyclopropanes into olefins as suggested in the earlier analysis, steps 2–4 are required. The key reaction is step 4. Without



(2)

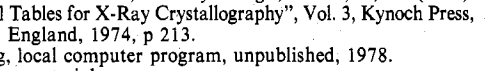


(3)



(4)

this reaction the metal is not a catalyst and does not cancel from the calculation. Gassman's results analyzed in these terms are instead described by reaction 5, an apparent common



(5)

fate of tungsten catalysts without sufficient olefin present.[5] This reaction does not relate olefin and X′ to X as is required by eq 4.[6] Reaction 4 can be considered equivalent to an initiation mechanism for metathesis.[7] In all cases observed to date, initiation of metathesis requires added reagents and is very slow relative to the catalytic reaction itself. The information of cyclopropane is a chain-termination step, and the *concentration of cyclopropane cannot be greater than the concentration of X*. This being the case, the final concentration of cyclopropane cannot be calculated exactly since the necessary equilibrium is

$$X + A \rightleftarrows X' + C$$

$$\Delta\Delta G = (\Delta G^\circ(\text{ethylene}) + \Delta G^\circ(X)) - (\Delta G^\circ(\text{cyclopropane}) + \Delta G^\circ(X'))$$

$$\Delta = (\Delta G^\circ(X) - \Delta G^\circ(X')) = \text{unknown}$$

On the basis of studies of related organometallic catalysts, the value of Δ would be expected to vary greatly.[8] At one extreme would be excellent catalysts for the cyclopropanation of olefins with diazo compounds but very poor metathesis catalysts while the opposite extreme would give outstanding metathesis systems.

If a complex formed cyclopropanes in significant amounts, it would give low yields of metathesis products and be a very short-lived catalyst.[9]

As can be seen, the Chauvin mechanism is not inconsistent with the thermodynamic calculations and remains as the mechanism most compatible with a large body of other experimental investigations.[7]

Acknowledgment. The author acknowledges the helpful discussions of J. Halpern and F. Mango and the financial aid of the National Science Foundation and Dow Chemical Co.

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A New Series of Imidazole Thioether Chelating Ligands for Bioinorganic Copper

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Authentic synthetic analogues of the "blue" copper proteins (type I)[1] would be valuable in understanding the detailed geometrical and electronic structure of copper in its biological environment. All copper(II) model compounds reported so

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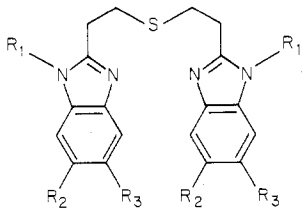
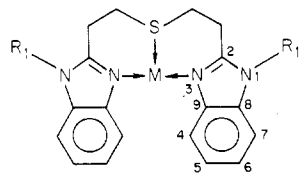
far,[2] although very instructive, have fallen short of close resemblance chiefly because of four problems: the incomplete knowledge of the four-donor ligand set in the protein, the difficulty of constraining a specific four-donor ligand set to a distorted tetrahedral geometry, the reluctance of Cu(II) to coordinate thioether ligands, and the facile oxidation of thiolate to disulfide by Cu(II). The recent X-ray crystal structure of a plastocyanin[3] has resolved the first problem, at least for the majority of "blue" copper proteins, by identifying the ligands as two histidine imidazoles, one methionine thioether, and one cysteine thiolate. This prompts us to communicate the facile one-step synthesis of a new group of chelating ligands within the general 2N,S donor class[4] containing a bis(benzimidazole) thioether donor set:



L_1: $R_2 = R_3 = H$
L_2: $R_2 = Me$; $R_3 = H$
L_3: $R_2 = R_3 = Me$
R_1 = H, Me, Et, *n*-Pr, Bzl

The reluctance of hard metals such as Cu(II) to bind soft thioether ligands in the absence of a chelate effect is well documented.[4a,5] By intentional design of the bond connectivity at the 2-position of the benzimidazole, the chelate effect has been exploited to enforce thioether coordination to the metal (M) once mononuclear bis(imidazole) coordination occurs. The N–S chelates of these ligands form the favored six-membered ring



Also by design, benzimidazoles rather than imidazoles were chosen so that the steric bulk of the aromatic ring, particularly at the 4-position, might lead to obligatory nonplanar geometry when four-coordination occurs. Thus, these ligands have the potential to overcome three of the four major obstacles to achieving a "blue" copper synthetic analogue.

Experimental Section

Tetrahydrofuran was distilled from sodium/benzophenone, heptane was distilled from CaH_2, and all other solvents were dried over molecular sieves. In order to protect Cu(I) complexes from dioxygen oxidation, we carried out all reactions involving Cu(I) in a He- or N_2-filled inert-atmosphere box. Magnetic susceptibility measurements were made on a Cahn Faraday System (Model 7600) and were experimentally corrected for diamagnetism by using closely related diamagnetic materials. IR spectra were taken on a Perkin-Elmer infrared spectrometer (Model 281), and visible spectra were measured on a Beckman spectrometer (Acta MVI). Shock sensitivity of any perchlorate salt has not been observed, but caution against explosion is warranted.

Synthesis of Ligands. L_1. To a mixture of 3,3′-thiodipropionic acid (8.3 g, 0.046 mol) and *o*-phenylenediamine (10.0 g, 0.093 mol) was added 4 M aqueous HCl (250 mL). The solution was refluxed for 24 h, followed by immediate filtration. As the filtrate cooled, large blue crystals formed. These were collected, dried in a vacuum desiccator, and identified as the dihydrochloride $L_1 \cdot 2HCl \cdot 2H_2O$. Anal. Calcd for $C_{18}H_{24}N_4Cl_2O_2S$: C, 50.11; H, 5.56; N, 12.99; S, 7.42; Cl, 16.47. Found: C, 50.16; H, 5.52; N, 12.94; S, 7.28; Cl, 16.38. NMR spectrum (Me_2SO-d_6): δ 3.33 (4, 4 H), 7.4 (m, 4 H). The free base was obtained by treatment of the dihydrochloride with excess aqueous ammonia. The dark oil and precipitate which separated were dissolved in ethanol, decolorized with charcoal at reflux for 10 min, and crystallized by gradual addition of water. Fine colorless needles were deposited when the solution was left standing. These needles were isolated and dried under vacuum (10.36 g, 70%). Anal. Calcd for $C_{18}H_{18}N_4S$: C, 67.08; H, 5.59; N, 17.39; S, 9.93. Found: C, 67.29; H, 5.74; N, 17.32; S, 9.77. NMR spectrum (Me_2SO-d_6): δ 3.0 (m, 4 H), 7.1 (m, 4 H).

L_2. This was prepared in a manner similar to that for L_1. Solvation by 2 H_2O was detected by NMR. Anal. Calcd for $C_{20}H_{26}N_4SO_2$: C, 62.15; H, 6.78; N, 14.50; S, 8.30. Found: C, 61.96; H, 6.69; N, 14.38; S, 8.46. NMR spectrum (acetone-d_6): δ 2.3 (1, 3 H), 3.0 (3, 4 H), 7.0 (m, 3 H).

L_3. This was prepared as above. Solvation by approximately 0.25 H_2O and 0.25 C_2H_5OH was detected by NMR. Anal. Calcd for $C_{22.5}H_{28}N_4SO_{0.5}$: C, 68.39; H, 7.17; N, 14.15. Found: C, 68.35; H, 6.99; N, 14.23. NMR spectrum (Me_2SO-d_6): δ 2.3 (1, 6 H), 2.95 (m, 4 H), 7.1 (1, 2 H).

N-Alkylation of L_1 and L_3 with methyl, ethyl, *n*-propyl, and benzyl groups to form **L_1–Me**, **L_1–Et**, **L_1–Pr**, **L_1–Bzl**, **L_3–Me**, **L_3–Et**, and **L_3–Pr**, respectively, was achieved by deprotonation of the free base with NaH followed by treatment with the appropriate alkyl bromide or iodide. The following procedure for L_1–Pr is typical.

L_1–Pr. To a suspension of recrystallized, dry L_1 (1 g, 3.1 mmol) in dry THF (925 mL) was slowly added, with stirring, NaH (0.28 g, 6.6 mmol of 57% paraffin suspension, prewashed with dry heptane). After H_2 evolution had ceased (~1 h), *n*-propyl iodide (1.6 g, 11.3 mmol) was added via syringe to the off-white crystalline suspension. The solution was stripped to dryness under reduced pressure, dissolved in $CHCl_3$, and filtered with the aid of Celite. The $CHCl_3$ filtrate was stripped to a thick oil which was purified by passage through a short alumina (80 g, 80–325 mesh, MCB activated) column using $CHCl_3$ as the eluent. The UV-active fraction was collected and stripped to a pale yellow oil which crystallized on standing (1 g, 79%).

L_1–Pr. Anal. Calcd for $C_{24}H_{30}N_4S$: C, 70.93; H, 7.44; N, 13.89; S, 7.88. Found: C, 70.68; H, 7.34; N, 13.62; S, 7.81. NMR spectrum ($CDCl_3$): δ 0.95 (3, 3 H), 1.8 (6, 2 H), 3.2 (m, 4 H), 4.0 (3, 2 H), 7.4 (m, 4 H).

L_1–Me. NMR spectrum ($CDCl_3$): δ 3.1 (m, 4 H), 3.4 (1, 3 H), 7.4 (m, 4 H).

L_1–Et. Anal. Calcd for $C_{22}H_{26}N_4S$: C, 69.80; H, 6.87; N, 14.80; S, 8.47. Found: C, 69.58; H, 6.89; N, 14.65; S, 8.41. NMR spectrum ($CDCl_3$): δ 1.25 (3, 3 H), 3.05 (m, 4 H), 4.0 (4, 2 H), 7.3 (m, 4 H).

L_1–Bzl as Approximately the 0.16 CH_2Cl_2 Solvate. Anal. Calcd for $C_{32.16}H_{30.33}Cl_{0.33}N_4S$: C, 74.76; H, 5.92; N, 10.84; S, 6.21. Found: C, 74.70; H, 5.93; N, 10.73; S, 5.78. NMR spectrum ($CDCl_3$): δ 3.05 (m, 4 H), 5.3 (1, 2 H), 7.4 (m, 9 H).

L_3–Me. NMR spectrum ($CDCl_3$): δ 2.45 (1, 6 H), 3.15 (m, 4 H), 3.65 (1, 3 H), 7.21 (2, 2 H).

L_3–Et. Anal. Calcd for $C_{26}H_{34}N_4S$: C, 71.85; H, 7.89; N, 12.89; S, 7.38. Found: C, 71.19; H, 7.77; N, 12.50; S, 7.06. NMR spectrum ($CDCl_3$): δ 1.45 (3, 3 H), 2.4 (1, 6 H), 3.2 (m, 4 H), 4.1 (4, 2 H), 7.25 (2, 2 H).

L_3–Pr. Anal. Calcd for $C_{28}H_{38}N_4S$: C, 72.68; H, 8.28; N, 12.11; S, 6.93. Found: C, 72.42; H, 8.17; N, 11.96; S, 6.88. NMR spectrum ($CDCl_3$): δ 1.05 (3, 3 H), 1.95 (6, 2 H), 2.50 (1, 6 H), 3.26 (m, 4 H), 4.05 (3, 2 H), 7.25 (2, 2 H).

Synthesis of Cu(II) Complexes. All Cu(II) complexes of general formula $[Cu(L)(H_2O)(OClO_3)][ClO_4]$ were prepared by equimolar addition of ligand to $Cu(ClO_4)_2 \cdot 6H_2O$ in a small volume of ethanol. The resulting green solution soon deposited green crystals which were collected in high yield and dried under vacuum.

$[Cu(L_1)(H_2O)(OClO_3)][ClO_4] \cdot H_2O \cdot 0.25EtOH$. Anal. Calcd for $C_{18.5}H_{23.5}N_4CuCl_2O_{10.25}S$: Cu, 9.97; C, 34.89; H, 3.79; N, 8.79; Cl, 11.13. Found: Cu, 10.0; C, 35.07; H, 3.62; N, 9.02; Cl, 10.94. IR spectrum (KBr): $\nu(ClO_4)$ 1100 (s, br), 620 cm^{-1}. μ_{eff} = 1.87 μ_B (25 °C). λ_{max}(acetone) 645 nm (2.46 × 10^2 L/(mol cm)).

$[Cu(L_1\text{–Me})(H_2O)(OClO_3)][ClO_4] \cdot H_2O \cdot {}^1/_2EtOH$. Anal. Calcd for $C_{21}H_{29}N_4CuCl_2O_{10.5}S$: Cu, 9.46; C, 37.53; H, 4.35; N, 8.34; Cl, 10.55. Found: Cu, 9.51; C, 37.63; H, 4.19; N, 8.34; Cl, 10.55. IR spectrum (KBr): $\nu(ClO_4)$ 1100 (s, br), 620 cm^{-1}. μ_{eff} = 1.92 μ_B (25 °C). λ_{max}(acetone) 645 nm (2.14 × 10^2 L/(mol cm)).

$[Cu(L_1\text{–Pr})(H_2O)(OClO_3)][ClO_4] \cdot EtOH$. Anal. Calcd for $C_{26}H_{38}N_4CuCl_2O_{10}S$: Cu, 8.67; C, 42.59; H, 5.22; N, 7.64; Cl, 9.67. Found: Cu, 8.51; C, 42.26; H, 5.23; N, 7.57; Cl, 9.92. IR spectrum (KBr): $\nu(ClO_4)$ 1100 (s, br), 620 cm^{-1}. μ_{eff} = 1.81 μ_B (25 °C).

λ_{max}(acetone) 640 nm (2.16×10^2 L/(mol cm)). ESR (acetone–THF): $g_\perp = 2.10$, $g_\parallel = 2.26$, $A_\parallel = 0.013$ cm^{-1}.

[Cu(L$_3$–Me)(H$_2$O)(OClO$_3$)][ClO$_4$]·2H$_2$O. Anal. Calcd for $C_{24}H_{36}N_4CuCl_2O_{11}S$: Cu, 8.78; C, 39.86; H, 5.02; N, 7.75. Found: Cu, 8.81; C, 40.20; H, 4.83; N, 7.69. IR spectrum (KBr): ν(ClO$_4$) 1100 (s, br), 620 cm^{-1}. $\mu_{eff} = 1.86\ \mu_B$ (25 °C). λ_{max}(acetone) 645 nm (2.26×10^2 L/(mol cm)).

[Cu(L$_3$–Et)(H$_2$O)(OClO$_3$)][ClO$_4$]·H$_2$O·$^1/_2$EtOH. Anal. Calcd for $C_{27}H_{41}N_4CuCl_2O_{10.5}S$: Cu, 8.40; C, 42.89; H, 5.46; N, 7.41; Cl, 9.37. Found: Cu, 8.23; C, 42.65; H, 5.39; N, 7.33; Cl, 8.68. IR spectrum (KBr): ν(ClO$_4$) 1100 (s, br), 620 (sp) cm^{-1}. $\mu_{eff} = 1.80\ \mu_B$ (25 °C). λ_{max}(acetone) 643 nm (2.41×10^2 L/(mol cm)).

[Cu(L$_3$–Pr)(H$_2$O)(OClO$_3$)][ClO$_4$]·EtOH. Anal. Calcd for $C_{30}H_{46}N_4CuCl_2O_{10}S$: Cu, 8.05; C, 45.65; H, 5.87; N, 7.09; Cl, 8.98. Found: Cu, 8.11; C, 45.92; H, 5.77; N, 7.12; Cl, 9.67. IR spectrum (KBr): ν(ClO$_4$) 1100 (s, br), 620 cm^{-1}. λ_{max}(acetone) 643 nm (2.21×10^2 L/(mol cm)).

Synthesis of Cu(I) Complexes. All Cu(I) complexes were prepared by equimolar addition of ligand and Cu(MeCN)$_4$BF$_4$[6] in a small volume of dry acetone. The solution was stirred until all reactants were dissolved and then filtered through a medium frit. Heptane was then added until a slight turbidity was produced. Colorless crystals were slowly deposited and identified as the following compounds. All compounds were diamagnetic.

[Cu(L$_1$–Pr)][BF$_4$]. This compound was vacuum dried. Anal. Calcd for $CuC_{24}H_{30}N_4SBF_4$: Cu, 11.40; C, 51.75; H, 5.42; N, 10.06; S, 5.75. Found: Cu, 11.40; C, 51.93; H, 5.40, N, 9.98; S, 4.89. NMR spectrum (Me$_2$SO-d_6): δ 0.8 (3), 1.65 (6), 1.95 (1), 3.15 (m), 4.15 (3), 7.4 (m). IR spectrum (KBr): ν(BF$_4$) 1060 (s, br) cm^{-1}.

[Cu(L$_3$)][BF$_4$]. Anal. Calcd for $CuC_{22}H_{26}N_4SBF_4$: Cu, 12.20; C, 50.73; H, 5.03; N, 10.75. Found: Cu, 12.00; C, 50.56; H, 5.09; N, 10.56. NMR spectrum (Me$_2$SO-d_6): δ 2.2 (1, 6 H), 3.1 (m, 4 H), 7.2 (2, 2 H). IR spectrum (KBr): ν(BF$_4$) 1050 (s, br) cm^{-1}.

[Cu(L$_3$–Pr)][BF$_4$]. Anal. Calcd for $CuC_{28}H_{28}N_4SBF_4$: Cu, 10.36; C, 54.85; H, 6.25; N, 9.14; S, 5.23. Found: Cu, 10.30; C, 54.75; H, 6.18; N, 8.98; S, 4.99. NMR spectrum (Me$_2$SO-d_6): δ 0.79 (3, 3 H), 1.64 (6, 2 H), 2.20 (1, 6 H), 3.14 (m, 4 H), 4.1 (3, 2 H), 7.35 (2, 2 H). IR spectrum (KBr): ν(BF$_4$) 1050 (s, br) cm^{-1}.

[Cu(L$_1$–Me)][BF$_4$]. NMR spectrum (Me$_2$SO-d_6): δ 3.2 (m, 4 H), 3.75 (1, 3 H), 7.4 (m, 4 H). IR spectrum (KBr): ν(BF$_4$) 1050 (s, br) cm^{-1}.

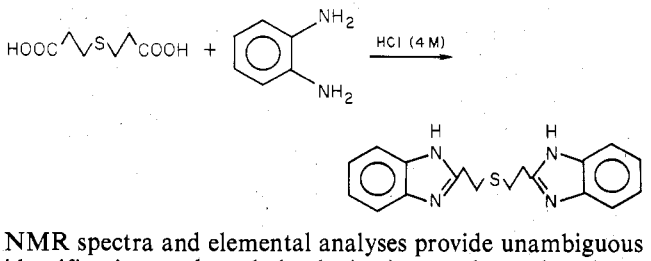
[Cu(L$_1$–Bz)][BF$_4$]. NMR spectrum (Me$_2$SO-d_6): δ 3.0 (m, 4 H), 5.30 (1, 2 H), 7.2 (m, 9 H). IR spectrum (KBr): ν(BF$_4$) 1055 (s, br) cm^{-1}.

[Cu(L$_3$–Me)][BF$_4$]. NMR spectrum (Me$_2$SO-d_6): δ 2.23 (1, 6 H), 3.13 (m, 4 H), 3.60 (1, 3 H), 7.15 (2, 2 H). IR spectrum (KBr): ν(BF$_4$) 1060 (s, br) cm^{-1}.

[Cu(L$_3$–Et)][BF$_4$]. NMR spectrum (Me$_2$SO-d_6): δ 1.2 (3, 3 H), 2.25 (1, 6 H), 3.15 (m, 4 H), 4.1 (4, 2 H), 7.10 (2, 2 H). IR spectrum (KBr): ν(BF$_4$) 1040 (s, br) cm^{-1}.

Discussion

The ligand synthesis is notable for its simplicity, purity, and good yield from commercially available precursors. It exploits the Phillips acid-catalyzed condensation[7] of a carboxylic acid with an *o*-phenylenediamine to yield a benzimidazole in one step:



NMR spectra and elemental analyses provide unambiguous identification, and methyl substitution on the *o*-phenylenediamine ring gives the closely related series of ligands L$_1$–L$_3$. Further elaboration of these basic benzimidazoles is achieved by N-alkylation with the alkyl group R = methyl, ethyl, *n*-propyl, and benzyl. This gives a gradation of solubilities and crystallizing abilities within the 15 different ligands. The *N*-*n*-propyl ligands L$_1$Pr and L$_3$Pr have the most convenient handling characteristics and have been mostly widely employed in complex formation reactions.

Copper(II) complexes of 1:1 stoichiometry form on mixing Cu(ClO$_4$)$_2$·6H$_2$O with the ligand in ethanol. The preliminary results of an X-ray structure of one derivative, [Cu(L$_3$)(H$_2$O)(OClO$_3$)][ClO$_4$], reveals a five-coordinate distorted square-pyramidal stereochemistry around the copper atom, where the donor atoms are comprised of the 2N,S chelate, a water molecule, and a monodentate perchlorate ion. Curiously, the coordinated perchlorate cannot be detected by the usual splitting of the ν(ClO$_4^-$) in the infrared spectrum (KBr or Nujol mull); it is apparently masked by the noncoordinated perchlorate ion. The designed reluctance of the chelate to allow square-planar coordination is confirmed by the crystal structure as is the coordination of the thioether. There is some literature disagreement over the assignment of the spectral region expected for the thioether S(σ) → Cu(d$_{\sigma^*}$) transition,[2c,2h,10,11] and, unfortunately, the high-energy region is obscured in our complexes by π–π^* transitions of the benzimidazoles. However, an absorption near 645 nm in all the Cu(II) complexes is consistent with a d–d transition whose intensity ($\epsilon \simeq 230$ M^{-1} cm^{-1}) is slightly enhanced by thioether coordination.[11]

Copper(I) complexes are readily prepared by anaerobic treatment of [Cu(CH$_3$CN)$_4$]BF$_4$ with the free ligands in acetone solution. Isolable as colorless, diamagnetic crystalline solids or powders, they are moderately air stable. In solution, however, rapid aerobic oxidation is evident from the formation of blue products. Infrared spectra suggest that the tetrafluoroborate counterion is noncoordinated although a ligand absorption on the higher frequency side of ν(B–F) may obscure some unusual asymmetry in this band. A structural assignment can only be very tentative at this time. Three-coordinate Cu(I) complexes are not without precedent,[8] but dimers are also quite possible.[9]

We are optimistic that such chelates as those reported here will contribute to the evolutionary improvement of structural models for the "blue" copper proteins—from so-called models to true synthetic analogues.[12] In this regard, we note that a series of cuprous thiolate complexes of general formula CuL(SR) can be isolated as colorless, diamagnetic, crystalline solids by treatment of the [CuL][BF$_4$] complexes with RS$^-$. Their properties will be reported once definitive structural data are in hand. The cupric complexes reported herein also react readily with thiolates at −77 °C in acetone–THF to give intensely blue solutions. The celebrated "blue" copper absorption band near 600 nm is observed with the high extinction coefficient (3190–5156 M^{-1} cm^{-1}) that is diagnostic of copper(II)–thiolate ligation,[10] suggesting that complexes of the type [CuL(SR)]ClO$_4$ are formed. Increasingly sophisticated ligand constraints to improve the model and make its isolation possible are our current synthetic goals.

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Registry No. L$_1$, 70813-89-7; L$_1$·2HCl, 70813-90-0; L$_1$-Me, 70813-91-1; L$_1$-Et, 70813-92-2; L$_1$-Pr, 70813-93-3; L$_1$-Bzl, 70813-94-4; L$_2$, 70813-95-5; L$_3$, 70813-96-6; L$_3$-Me, 70813-97-7; L$_3$-Et, 70813-98-8; L$_3$-Pr, 70813-99-9; [Cu(L$_1$)(H$_2$O)(OClO$_3$)][ClO$_4$], 70814-04-9; [Cu(L$_1$-Me)(H$_2$O)(OClO$_3$)][ClO$_4$], 70850-32-7; [Cu(L$_1$-Pr)(H$_2$O)(OClO$_3$)][ClO$_4$], 70850-34-9; [Cu(L$_3$-Me)(H$_2$O)(OClO$_3$)][ClO$_4$], 70814-06-1; [Cu(L$_3$-Et)(H$_2$O)(OClO$_3$)][ClO$_4$], 70814-08-3; [Cu(L$_3$-Pr)(H$_2$O)(OClO$_3$)][ClO$_4$], 70814-10-7; [Cu(L$_1$-Pr)][BF$_4$], 70814-12-9; [Cu(L$_3$)][BF$_4$], 70814-14-1; [Cu(L$_3$-Pr)][BF$_4$], 70850-40-7; [Cu(L$_1$-Me)][BF$_4$], 70814-16-3; [Cu(L$_1$-Bzl)][BF$_4$], 70814-18-5; [Cu(L$_3$-Me)][BF$_4$], 70814-20-9; [Cu(L$_3$-Et)][BF$_4$], 70814-22-1; 3,3′-thiodipropionic acid, 111-17-1; *o*-phenylenediamine, 95-54-5; *n*-propyl iodide, 107-08-4.

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(12) It may be useful to distinguish between a "synthetic model" and a "synthetic analogue". The latter is a very close structural facsimile of the metal coordination in a metalloprotein with respect to ligand type, geometry, and physical properties while a model may mimic certain aspects only.

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Homonuclear Bonds in Sulfur–Selenium Mixed Crystals: A Raman Spectroscopic Study

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Both sulfur and selenium have at least one allotropic form in which they exist as S_8 and Se_8 (eight-membered) rings, respectively. Also, they are known to form "mixed crystals" as compounds of general formula Se_nS_{8-n}.[1] Single-crystal X-ray studies, done at this institute[2] and other laboratories,[3] indicate that these mixed crystals also consist of eight-membered rings. Further information about the structure of the moieties present in these mixed crystals could not be obtained by the X-ray studies as the crystals were found to be disordered systems. The disorder is believed to be due to orientational disorder and/or the presence of different Se_nS_{8-n} species at the crystallographically equivalent sites. One of the important but still unresolved questions in this subject is whether homonuclear bonds are present in these mixed crystals, particularly in the systems with low selenium or low sulfur content. Mass spectroscopic studies are also not able to answer the above question as the Se_nS_{8-n} compounds are thought to rearrange in the mass spectrometer.[4,5] Vibrational spectroscopy can give direct information about the conformation of molecules by the observation of characteristic frequencies for the different bonds and groups. Therefore, we have started a study of the vibrational spectra of these mixed crystals in order to gain structural information about the molecular units in the Se_nS_{8-n} mixed crystals. Here we report a Raman spectroscopic investigation of these systems undertaken to investigate the presence of Se–Se and S–S homonuclear bonds in these mixed crystals.

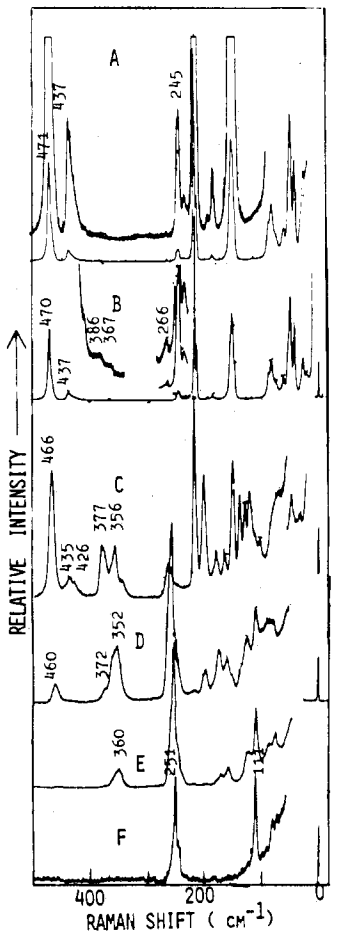

Figure 1. Raman spectra of polycrystalline samples at room temperature: (A) pure S_8 crystals (upper trace recorded at a gain 10 times that for the lower trace); (B) $Se_{0.05}S_{7.95}$ crystals (two upper traces recorded at gains 10 and 30 times, respectively, that for the lower trace); (C) $Se_{1.5}S_{6.5}$ mixed crystals; (D) $Se_{4.1}S_{3.9}$ mixed crystals; (E) $Se_{5.9}S_{2.1}$ mixed crystals; (F) pure Se_8 crystals. Exciting line is shown in spectra B–F.

Experimental Section

Materials. The polycrystalline samples were obtained by fractional crystallization of (a) commerical "SeS_2" obtained from Merck[2] and (b) the glassy products obtained from melts of equimolar amounts of sulfur and selenium.[3-5] The Se_nS_{8-n} mixed crystals were analyzed for their Se content by iodometric titrations. Many samples were double checked by gravimetric determination of their sulfur content as barium sulfate.

Spectra. Raman spectra of crystalline samples were obtained by using ~120 mW of 6328-Å radiation of a He–Ne laser (OIP, Gent). Cary 81 and Coderg PH1 monochromators were used. Both instruments are equipped with RCA C31034 photomultipliers, Servogor 5 strip-chart recorders, and necessary electronics. Spectra were recorded with a dc amplification system. Usual 90° scattering geometry was employed, but the incident laser radiation was focused as a line on the sample rather than as a point to avoid local heating of the colored samples. This was achieved with a combination of a cylinder lens and a convex lens in the incident beam. The polycrystalline samples were contained in a rectangular glass cell with flat walls which was placed at ~45° to both the incident radiation and the entrance slit. The frequency scale was calibrated by using the laser-emission lines and a Ne lamp.

Results and Discussion

Raman spectra of a few representative compositions of Se_nS_{8-n} mixed crystals, as polycrystalline samples, are shown in Figure 1. This figure also contains the spectra of pure S_8

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