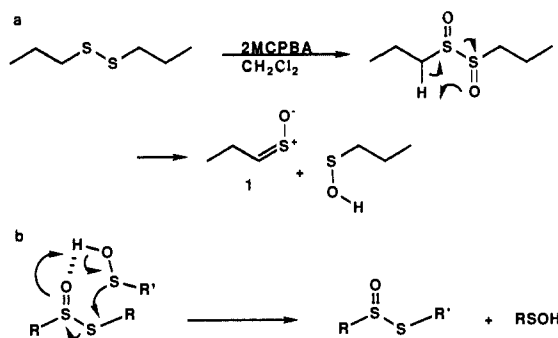


Scheme IV



CH₂Cl₂ at -60 °C followed by warming up to -40 °C during 1 h, rapid workup with ice-cold NaHCO₃ solution, drying over K₂CO₃, and concentration in vacuo at 0 °C gave **6** in 34% yield. Compound **6** is a colorless solid of formula C₆H₁₀S₂O₂ (decomposition point 48 °C; high-resolution EI-MS 178.0121, calcd 178.0122; FD-MS also indicates the parent ion at 178) with IR bands at 1103 and 1120 cm⁻¹. The ¹H and ¹³C NMR spectra in CDCl₃ are identical with those of **6** isolated from onion. Upon changing of the solvent to C₆D₆, the ¹H NMR spectrum of **6** showed peaks at δ 7.06 (d, *J* = 9.6 Hz, 2 H), 3.3 (m, 2 H), and 0.60 (d, 6.3 Hz, 6 H). The ¹³C and ¹H NMR data for **6** in CDCl₃ and C₆D₆ are in good agreement with analogous data for **1**^{2b} and are consistent with **6** having *all-Z* stereochemistry at the C=S bonds. Sequential treatment of synthetic **6** with ozone/-50 °C, H₂O₂-HCOOH, and MeOH-H₂SO₄ gave in 88% yield a compound identical by GC-MS and ¹³C NMR with authentic *d,l*-dimethyl 2,3-dimethylsuccinate (*d,l*-**12**) and different from authentic *meso*-**12**,⁷ thereby establishing synthetic/natural **6** as (*Z,Z*)-*d,l*-2,3-dimethyl-1,4-butanedithial *S,S'*-dioxide (*d,l*-**6**). Compound **6** shows moderate *in vitro* inhibition of 5-lipoxygenase in porcine leucocytes.⁸

We suggest that in the presence of excess oxidant (*E,E*-**9**) is converted into **10**. The anti conformation of the oxygen atoms depicted in **10**, which correlates upon rearrangement with *Z* CSO geometry, follows theoretical predictions that this conformation represents an energy minimum.^{6b} Compound **10** should undergo a particularly facile [3,3]-sigmatropic rearrangement due to the weakness of the S-S bond (ca. 36 kcal)^{6b} and the rate-enhancing effect of the two zwitterionic sulfinyl functions.^{5b} The exclusive formation of *d,l*-**6** from dioxidation of (*E,E*-**9**) is consistent with concerted [3,3]-sigmatropic rearrangement of **10** and with previous observations on the stereospecificity of products from *mono-oxidation* of isomers of **9**.^{3b,9} Unexpectedly, dioxidation of (*E,Z*-) and (*Z,Z*-)**9** gives mixtures of *d,l*- and *meso*-**6**,¹⁰ suggesting a change to a stepwise mechanism when the disulfide oxidation and/or [3,3]-process is retarded by *Z* C=C stereochemistry.¹⁰

How is bis(sulfine) **6** formed in onion extracts? An attractive possibility would involve "thiophilic" addition of **2** to **1** (see Scheme III, path a) followed by nucleophilic attack of a second molecule of **2** on α -disulfoxide intermediate **13**. The formation of (*E*)-1-propenyl propyl *vic*-disulfoxide (**13**) illustrated in Scheme III, path a, is the reverse of the reaction observed in the decomposition of aliphatic *vic*-disulfoxides (Scheme IV, path a)^{6a,11} while the reaction of **13** with **2** is analogous to the reaction of sulfenic acids

(7) Prepared by methylation of authentic samples of *d,l*- and *meso*-2,3-dimethylsuccinic acids purchased from Aldrich Chemical Company.

(8) (a) Wagner, H.; Breu, W., unpublished results. Determination of the IC₅₀ of **6** and structure-activity studies are in progress. (b) 5-Lipoxygenase inhibitors are of interest as potential antiinflammatory agents: Cashman, R. *Pharm. Res.* **1985**, *253*.

(9) Monooxidation of (*E,E*-**9**), (*Z,Z*-**9**), and (*E,Z*-**9**) affords, respectively, *trans*-**5**, *4b-trans*-**5**, and *4a-cis*-**5**, by processes that must involve cyclization by two competitive concerted mechanisms (a modification of our earlier mechanism^{3b}).¹⁰

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with thiosulfonates (Scheme IV, path b).¹² The alternative "carbophilic" mode of addition of **2** to **1** (Scheme III, path b) would generate an α -(alkenylsulfinyl)propanesulfenic acid **14**, a likely intermediate in the formation of "cepaene" **15**.^{13,14}

Compound **6** could also originate via homolytic decomposition of **13** into *n*-propanesulfinyl and (*E*)-1-propenesulfinyl radicals followed by self-coupling of the latter. However, the likelihood of the occurrence of such radical recombination on a significant scale in onion extracts is small. Furthermore, model studies¹⁰ involving **13** generated by oxidation of 1-propenyl propyl disulfide indicate formation of characteristic products in addition to **6** and in amounts comparable to **6**, which we have been unable to detect in onion extracts. Efforts to establish the mechanisms of formation, determine biological properties and reactions, and achieve syntheses of the remarkable organosulfur compounds found in onion extracts are continuing.

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(13) (a) Bayer, T.; Wagner, H.; Wray, V.; Dorsch, W. *Lancet* **1988**, 906. (b) Bayer, T.; Breu, W.; Seligmann, O.; Wray, V.; Wagner, H. *Phytochemistry* **1989**, *28*, 2373. (c) For a related compound which in our opinion should also be termed a "cepaene" (RS(O)CHETS(SR')), see: Kawakishi, S.; Morimitsu, Y. *Lancet* **1988**, 330.

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Insulin Stabilizes Copper(II)-Thiolate Ligation That Models Blue Copper Proteins

Mark L. Brader and Michael F. Dunn*

Department of Biochemistry
University of California, Riverside
Riverside, California 92521

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Blue (or type 1) copper proteins¹ are characterized by two unique spectroscopic properties,^{2,3} an intense absorption envelope

* Author to whom correspondence should be addressed.

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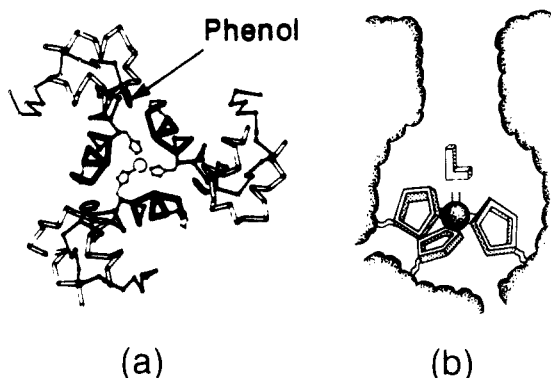


Figure 1. (a) View down the 3-fold symmetry axis of one-half of the Zn(II)-R₆ insulin hexamer showing the structural arrangement of the three subunits that form one zinc site. The locations of the protein-bound phenol molecules are shown also. Reprinted with permission from ref 9. Copyright 1989 Nature. (b) A schematic representation of one metal chelate site in the R₆ insulin hexamer showing the ~8-Å-long channel which extends from the metal to the hexamer surface. The metal is coordinated by three insulin B10 histidine residues and an exchangeable fourth ligand (denoted L) in a distorted tetrahedral geometry.

in the region 600–630 nm ($\epsilon = 3000\text{--}5000\text{ M}^{-1}\text{ cm}^{-1}$) and an ESR spectrum possessing an unusually small hyperfine coupling constant ($A_{\parallel} < 70 \times 10^{-4}\text{ cm}^{-1}$). These curious spectral features are markedly different from those exhibited by normal copper(II) complexes and appear to be associated intimately with the properties essential to the redox function of blue copper proteins. The important goal of understanding the behavior of blue copper proteins in biochemical systems has provided much of the impetus for scrutinizing the origins of the unusual spectroscopic features. The challenge to develop model systems has consequently generated much activity;^{4,5} however, success in this area has been severely limited, largely due to the intractability of the Cu(II)–S(thiolate) interaction. We report the preparation of a Cu(II)-substituted human insulin hexamer complex incorporating coordinated pentafluorothiophenol (PFTP) which constitutes a remarkably accurate facsimile of the blue copper center.

We have reported recently⁶ that the Co(II)-substituted insulin hexamer undergoes the phenol-induced T₆ to R₆ conformational transition⁷ in solution. This transition involves the binding of phenol to six well-defined, hydrophobic pockets within the hexamer, extensive structural changes in the hexamer surface topography, and large geometrical changes in the coordination environment of the metal ions.^{8,9} In our study,⁶ we concluded

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Table I. UV-Visible Electronic Absorption Data for the M-R₆-Thiolate Complexes

compd	M	L ^a	color	λ_{max} , nm (ϵ_{max} , ^b M ⁻¹ cm ⁻¹)
1	Cu(II)	PFTP	blue	377 (1400), 408 (1400), 626 (2000), 910 (500)
2	Co(II)	PFTP	purple	333 (3400), 374 (1200), 398 (sh) (900), 528 (500), 596 (br) (700)
3	Cu(II)	TP	green	370 (400), 442 (300), 696 (900), 910 (400)
4	Cu(II)	TC	green	390 (sh) (1400), 430 (sh) (900), 702 (1800), 910 (1200)
5	Co(II)	TP	green	345 (2000), 402 (1600), 524 (500), 610 (br) (700)
6	Co(II)	TC	green	350 (2600), 410 (2100), 522 (800), 610 (br) (700)
7	Co(II)	azurin		330 (2600), 380 (1100), 531 (300), 641 (500) ^c

^a PFTP = pentafluorothiophenol, TP = thiophenol, TC = *p*-thiocresol. ^b ϵ_{max} , extinction coefficient calculated with respect to metal ion concentration; br = broad, sh = shoulder. ^c Reference 14.

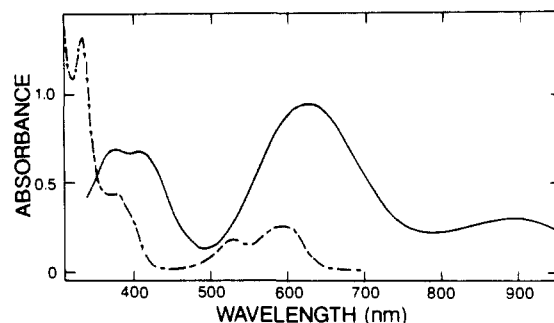


Figure 2. The electronic absorption spectrum of 1 (—) and 2 (---), each $0.2 \times 10^{-3}\text{ M}$ prepared in 25 mM Tris-ClO₄⁻ buffer, pH = 8.0.¹³

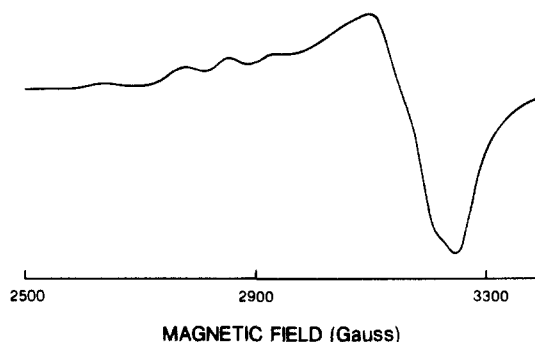


Figure 3. ESR spectrum (77 K, $\nu = 9.21\text{ GHz}$) of 1; $A_{\parallel} = 80 \times 10^{-4}\text{ cm}^{-1}$, $g_{\parallel} = 2.281$, $g_{\perp} = 2.079$. Recorded for a $0.3 \times 10^{-3}\text{ M}$ solution of hexamer complex¹⁴ prepared in 25 mM Tris-ClO₄⁻ buffer, pH = 8.0.

that the Co(II)-substituted T- and R-state hexamers, Co(II)-T₆ and Co(II)-R₆, respectively, are structurally analogous to the crystallographically identified Zn(II)-T₆⁸ and Zn(II)-R₆⁹ (Figure 1) hexamers. The coordination of Zn(II)⁹ or Co(II)⁶ in the R₆ structure is afforded by a tetrahedral arrangement of three histidine nitrogen atoms and one aqua ligand or chloride ion. In Co(II)-R₆, the Co(II) center undergoes ligand-exchange reactions

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in which the aqua ligand can be replaced by a variety of coordinating anions.^{6,10}

Copper-substituted insulin has been crystallized and studied in detail¹¹ via X-ray diffraction and ESR spectroscopy under T-state conditions (octahedral Cu(II) coordination). From these studies it has been concluded that Cu(II)-insulin crystals are isomorphous with Zn(II)-T₆ crystals and that the crystal structures of copper and zinc insulin are essentially the same. Our results indicate that in solution the Cu(II)-insulin hexamer¹² undergoes the T₆ to R₆ conformational transition in a manner analogous to that established for the Co(II) and Zn(II) hexamers, producing a Cu(II)-R₆ species upon the addition of a methanol solution of PFTP. This gives rise to an intense blue color, which is attributable to the PFTP complex of the Cu(II)-R₆ hexamer¹³ (compound 1). The UV-visible absorption spectrum of 1 (Figure 2, Table I) displays an intense band at 626 nm and is similar to those reported for blue copper proteins. The ESR spectrum of 1 (Figure 3)¹⁴ displays a hyperfine coupling constant A_{||} of 80 × 10⁻⁴ cm⁻¹, a value significantly lower than those usually reported for low molecular weight copper(II) complexes (viz., A_{||} = 130-220 × 10⁻⁴ cm⁻¹).^{1e}

Cobalt(II) substitution is well recognized to give an extremely sensitive spectroscopic probe of the geometrical and donor characteristics of the metal chelate sites in many metalloproteins.¹⁵ The UV-visible absorption spectrum obtained for the Co(II)-R₆ complex of PFTP (compound 2) is given in Figure 2 and Table I. There is an extraordinary resemblance between this spectrum and those of the Co(II)-substituted blue copper proteins, azurin (Table I), plastocyanin, and stellacyanin.¹⁶ Spectral data for the Cu(II)-R₆ and Co(II)-R₆ complexes obtained with several thiophenol derivatives (compounds 3-6) are presented in Table I. The spectral variation displayed by this series shows that substitutions in the aromatic ring of thiophenol alter the donor properties of the coordinated thiolate sulfur atom and thereby influence the spectroscopic features of the copper(II) center.

Collectively, the present results strongly suggest that the peculiar spectra exhibited by 1 arise from the combination of copper(II)-thiolate (PFTP) ligation in conjunction with the ligand field imposed by the His-B10 site of the R₆ insulin hexamer. According to all the spectroscopic criteria thus far examined, this particular donor arrangement evidently generates a chemical environment in which the electronic energy states of the copper(II) ions in 1 are very similar to those of the copper(II) ions in blue copper proteins.

We conclude that complexes formed via the interaction of thiophenol derivatives with the Cu(II)-R₆ insulin hexamer provide a useful model system through which the spectrochemical features of the blue copper center may be systematically probed.¹⁷ Current investigations¹⁸ indicate that similar experiments performed using copper(II)-substituted carbonic anhydrase manifest spectroscopic information that will enhance these studies.

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(12) Solutions of M(II)-R₆ were prepared as described in ref 6 by using 25 mM Tris-ClO₄⁻ buffer, pH = 8.0. Insulin concentrations were determined from the absorbance measured at 280 nm (ε₂₈₀ = 5.7 × 10⁵ per insulin subunit, MW 5800).

(13) M-R₆-thiolate complexes were prepared by using a M:thiolate ratio of 1:1.1. Solutions of 1 gradually faded to a pale blue color over a period of approximately 30 h. This bleaching is indicative of slow reduction to Cu(I).

(14) The ESR spectrum of Figure 3 displays a minor feature at 2640 G. Control experiments indicate that this feature is attributable to a small fraction of T₆ complex present in the T₆ ⇌ R₆ equilibrium.

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(17) Studies to characterize a series of Cu(II)-R₆ complexes incorporating thiophenol derivatives as ligands via electrochemical and a range of spectroscopic techniques will be reported in a full paper.

(18) Brader, M. L.; Dunn, M. F. Manuscript in preparation.

for assistance with recording spectra and to the Novo-Nordisk Research Institute (Denmark) for the provision of insulin. This work was supported by the California Affiliate of the American Diabetes Association, Grants ADACA/DUNN/88 and ADA-CA/87, and by the National Institutes of Health, Grant 1R01DK42124-01.

Ligand-Induced Selective Stabilization of the Anti Isomer in (η³-Allyl)palladium Complexes: An Attempt To Control the E-Z Stereochemistry in Palladium-Promoted Allylic Substitutions

Björn Åkermark* and Sverker Hansson

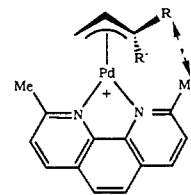
Department of Organic Chemistry
Royal Institute of Technology
100 44 Stockholm, Sweden

Aldo Vitagliano*

Dipartimento di Chimica
Università di Napoli, via Mezzocannone 4
80134 Napoli, Italy

Received July 3, 1989

Except in special cases, (η³-allyl)palladium complexes tend to adopt a syn configuration (s), while the less stable anti isomer (a) is generally present in less than 10%.¹ It appeared to us that a rigid bidentate ligand, shaped to "embrace" the metal as in 1, should interfere more sterically with a syn substituent, leading to a preference for the anti configuration.² Provided isomerization



1

a R = H, R' = Me
s R = Me, R' = H

is sufficiently fast, this offers the possibility of obtaining Z products in palladium-promoted reactions of allylic substrates, irrespective of the configuration of the starting material. Following this idea, we prepared complexes of general formula Pd(N-N)(CH₂=CH-CRR')⁺ (1, R = H, R' = Me; 2, R = H, R' = Et; 3, R = H, R' = n-Pr; 4, R = H, R' = i-Pr; 5, R = Me, R' = CH₂CH₂CH=CMe₂),³ from the η³-allyl-chloride complexes, AgBF₄, and 2,9-dimethyl-1,10-phenanthroline (dmphen) using established procedures.⁴ Except for the geranyl-neryl complex 5, which has a disubstituted allyl group, the syn isomer was indeed the less stable, and at equilibrium, the anti/syn ratio was about 70/30. The pure syn complex could be obtained by addition of

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