

could also account for the negative results. Although the trigonally compressed "octahedral" sites in ZrCl would seem more suitable sites, the non-metal would then have two halides at 2.93 Å as second-nearest neighbors in the ccp slabs. This distance appears well less than probable van der Waals sums ($>3.3 \text{ \AA}^{30}$) but is not very different from oxygen-chlorine separations around the tetrahedral hole (Table V) where a repulsion may be inferred. In fact, a rearranged slab (AbaB) does accommodate carbon in the octahedral site in $1T\text{-Zr}_2\text{X}_2\text{C}$, $\text{X} = \text{Cl, Br}^{32,38}$. Mass transfer does not seem to be a likely barrier to reaction of ZrF_4 in view of its obvious volatility at temperature and neither does a size restriction (Table VI). But a second product is required by the reaction stoichiometry (eq 1), and in this case a favorable solution of fluoride in the metal analogous to that of the oxide⁴⁴ does not appear to be significant.

A distinctly larger expansion of the metal polyhedra takes place on oxidation of ZrX phases than with the stoichiometrically (and electronically) similar oxidation of the metal to $\text{Zr}(\text{O}_{0.42})$. Thus, the expansion of the metal volume is 1.89% to $\text{Zr}(\text{O}_{0.42})$, or 2.17% at the maximum in α (Figure 4) before onset of the contraction associated with ordering, while conversion of ZrX to $\text{ZrX}(\text{O}_{0.43})$ involves an overall volume increase of 5.9% (Cl) to 4.5% (Br), or 8.9% in the chloride when

just the volume of the subcell between the two metal layers is considered. Naturally the available interstitial volume in YCl is greater, and so only a 3.9% expansion in the comparable inter-metal subcell is necessary for conversion to $\text{K}_{0.08}\text{YCl}(\text{O}_{0.8})$.³⁸ In addition, the $\text{Zr}(\text{O}_x)$ solution exhibits a fair approximation to Vegard's rule up to about $x = 0.20$; that is, the lattice constants vary linearly with composition,²⁵ while those (and the cell volumes) of ZrCl and the three single crystals of $\text{ZrCl}(\text{O}_x)$ studied show substantial positive deviation from linearity with y . This appears to be further evidence of an expansion that is forced on the interlayer separation in the early stages, somewhat analogous to (but smaller than) that seen on the one-phase intercalation of lithium into MS_2 to form Li_xTiS_2 or Li_xTaS_2 where the initial "spacers" cause a relatively large change in the interslab separation.⁴⁵ Again, the coproduction of $\text{Zr}(\text{O}_x)$ may provide a significant driving force.

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Supplementary Material Available: Tables of structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

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Copper(II) Complexes with Tetradentate Bis(pyridyl)-Dithioether and Bis(pyridyl)-Diamine Ligands. Effect of Thioether Donors on the Electronic Absorption Spectra, Redox Behavior, and EPR Parameters of Copper(II) Complexes

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Eight copper(II) chelates containing a tetradentate bis(pyridyl)-dithioether ligand, $\text{py}(\text{CH}_2)_x\text{S}(\text{CH}_2)_y\text{S}(\text{CH}_2)_x\text{py}$, or a bis(pyridyl)-diamine ligand, $\text{py}(\text{CH}_2)_x\text{N}(\text{R})(\text{CH}_2)_y\text{N}(\text{R})(\text{CH}_2)_x\text{py}$, where $x = 1$ or 2, $y = 2$ or 3, and $\text{R} = \text{H}$ or CH_3 , were studied to determine the effect of thioether donors on the spectral and redox properties of the copper complexes. The systematic variation of the chelate ring sizes (5-5-5, 5-6-5, 6-5-6, and 6-6-6) allowed stereochemical trends in the observed properties to be ascertained as well as the effect of thioether substitution for the amine donors. The electronic absorption spectra of the $\text{Cu}^{\text{II}}[(\text{py})_2\text{S}_2]$ complexes differed from those of the $\text{Cu}^{\text{II}}[(\text{py})_2\text{N}_2]$ series by the presence of a $\text{S}(\sigma) \rightarrow \text{Cu}(\text{II})$ LMCT in the near-ultraviolet region and an enhanced intensity in the visible (d-d) bands which was attributed to an intensity-borrowing mechanism from the low-energy charge-transfer band. The Cu(I) complexes of both series of ligands exhibited an absorption band between 300 and 350 nm corresponding to a $\text{Cu}(\text{I}) \rightarrow \text{py}(\pi^*)$ MLCT transition. The Cu(II)/Cu(I) reduction potentials for the chelates typically showed little solvent dependence in acetonitrile and aqueous solutions as measured by cyclic and differential pulse voltammetry. The potentials for the $(\text{py})_2\text{S}_2$ series spanned a range ($E^\circ = +400$ to $+660$ mV vs. NHE) substantially higher than those exhibited by the $(\text{py})_2\text{N}_2$ series ($E^\circ = -170$ to $+320$ mV vs. NHE). The substitution of two thioether donors for two amine donors produced an increase in E° of 300-700 mV in pairs of the $(\text{py})_2\text{S}_2$ and $(\text{py})_2\text{N}_2$ complexes with the same chelate ring sizes. The reduction potentials for both series increase with increasing chelate ring size, suggesting that the larger chelate rings can more readily accommodate a pseudotetrahedral Cu(I) form. The anisotropic EPR parameters for the $\text{Cu}^{\text{II}}[(\text{py})_2\text{N}_2]$ series were nearly axial while the $\text{Cu}^{\text{II}}[(\text{py})_2\text{S}_2]$ series exhibited rhombic spectra representing the reduction in the effective donor atom symmetry of the complexes when the amine donors were replaced with thioether donors.

Introduction

With advances in the study of "blue" copper proteins there has been much interest in the spectroscopic features associated with copper-sulfur coordination. Recent X-ray crystal structures¹ of poplar plastocyanin and azurin indicate that the

coordination sphere of the "blue" copper consists of a methionine thioether, a cysteine mercaptide, and two histidine imidazole ligands. This result substantiated the growing spectral evidence for a distorted-tetrahedral geometry²⁻⁴ and

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for sulfur coordination^{2,5-7} at the "blue" copper site. The several transitions contained in the characteristic visible absorption band envelope of these proteins⁸ have been attributed to cysteine sulfur to copper(II) charge-transfer excitations of both σ and π symmetry.^{2,6,9} In addition, both the presence of sulfur donors and the tetrahedral copper site have been suggested to account for the high redox potentials (184–700 mV vs. NHE⁸) of the "blue" copper proteins.

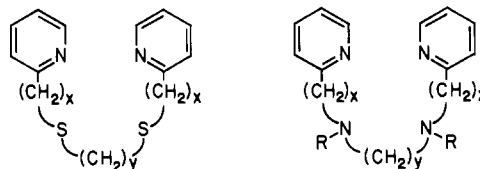
Discussion of the electronic absorption spectra observed for copper(II) complexes with thioether donors^{7,10-12} has focused on the nature of the sulfur to copper charge-transfer transitions. Bosnich¹⁰ assigned an intense band in the 350-nm region of the spectra of square-planar, square-pyramidal, and tetrahedral amine-thioether donor arrays to a $R_2S(\sigma) \rightarrow Cu(II)(x^2 - y^2)$ ligand to metal charge-transfer (LMCT) transition. Unusually intense d-d transitions at 600 nm in the thioether-containing complexes were said to arise by an intensity-borrowing mechanism from this low-energy charge-transfer band. Schugar¹¹ also observed an intense $R_2S(\sigma) \rightarrow Cu(II)$ LMCT for a series of bidentate thioether-containing chelates and assigned the unusual intensity in the visible region to intensity borrowing from the $S(\sigma) \rightarrow Cu(II)$ LMCT absorption and/or a contribution from $S(\pi) \rightarrow Cu(II)$ LMCT. An intense absorption band at ~ 600 nm¹² for some copper(II)- S_4 macrocyclic complexes was assigned as a $S(\pi) \rightarrow Cu(II)$ LMCT transition on the basis of resonance Raman studies⁷ and led to the suggestion that a methionine-copper(II) chromophore contributed to the intense color of the "blue" copper proteins. Solomon and Gray¹³ presented a detailed spectral assignment of the "blue" copper chromophore in which a high-energy shoulder (~ 526 nm) on the characteristic "blue" band was assigned originally to a methionine $S(\sigma) \rightarrow Cu(II)$ transition. Subsequent polarized single-crystal spectra¹⁴ of plastocyanin placed the methionine $S(\sigma) \rightarrow Cu(II)$ transition at 429 nm and totally excluded the thioether-copper(II) chromophore from the region of the "blue" band.

Previous electrochemical studies¹⁵⁻¹⁹ have reported high potentials for the Cu(II)/Cu(I) couple in chelates containing thioether donors and have attributed this effect to the π -acceptor ability of thioether donors in stabilizing the copper(I) state. Rorabacher and co-workers¹⁶ observed very high potentials for the reduction of some Cu(II)- S_4 macrocycles and noted these high potentials could be achieved without a tetrahedral distortion. This led to the suggestion that the methionine donor gives rise to the high reduction potential for

the blue copper site. This suggestion has been challenged by other workers,¹⁸ who observed that high redox potentials may be achieved without thioether donors. The rate constants for electron self-exchange furthermore indicate that up to two thioether ligands do not appreciably enhance rates of electron transfer.¹⁸ An additional suggestion² has been made that the low ligand field stabilization energy associated with the approximately tetrahedral site makes an important contribution to the high reduction potentials and this geometry allows facile electron transfer with minimal stereochemical changes between the copper(II) and copper(I) states.

EPR studies of copper(II) chelates have sought to relate bonding and coordination geometry to spectral parameters. Maki and McGarvey²⁰ and later Gersmann and Swalen²¹ constructed molecular wave functions from the EPR parameters calculated from the spectrum of copper(II) bis(acetylacetonate) and examined the covalency of the metal-ligand σ -bond and the nature of metal-ligand π -bonding. Peisach and Blumberg²² related a decrease in g_{\parallel} and an increase in A_{\parallel} to a diminished net charge for a series of copper(II) complexes having the same donor atoms. By observing these trends in varying donor atom arrays, they concluded that in non-"blue" copper proteins the copper is coordinated by oxygen and nitrogen but not by sulfur. Addison^{17,23} observed that increasing tetrahedral distortion increases g_{\parallel} and decreases A_{\parallel} for various N_4 , N_2S_2 , and S_4 donor arrays around Cu(II). The quotient $|g_{\parallel}/A_{\parallel}|$ was suggested as an empirical index of distortion of the donor set from planar toward tetrahedral, and the g_{\parallel} and A_{\parallel} values for "blue" copper proteins were found to be in the range for a tetrahedrally coordinated N_2S_2 donor array.

We have undertaken a systematic spectroscopic and electrochemical study of a series of copper complexes containing the bis(pyridyl)-dithioether open-chain tetradentate ligands **1a-d** and the analogous bis(pyridyl)-diamine ligands **2a-d**. By



- 1a: $x = 1, y = 2$; pdthx 2a: $x = 1, y = 2, R = H$; pdahx
 b: $x = 1, y = 3$; pdthp b: $x = 1, y = 3, R = H$; pdahp
 c: $x = 2, y = 2$; pdtto c: $x = 2, y = 2, R = CH_3$; pdao
 d: $x = 2, y = 3$; pdtn d: $x = 2, y = 3, R = CH_3$; pdan

substituting thioether donors for the innocent amine donors, we have evaluated the spectral and redox contributions of the thioether donors. The terminal pyridyl donors are constant throughout both series and serve to ensure the coordination of the internal thioether donors to copper. X-ray crystal structures reported by Brubaker et al.²⁴ have shown that the ligand pdto achieves tetradentate coordination to both copper(II) (square pyramidal with axially coordinated perchlorate) and copper(I) (tetrahedral).

Experimental Section

Materials. $Cu(CH_3CN)_4BF_4$ was prepared by a variation of the literature procedure for $Cu(CH_3CN)_4ClO_4$.²⁵ 2-Vinylpyridine (Aldrich) was freshly distilled prior to use. All other materials were reagent grade or better and used as received.

Ligands. The ligands 1,6-bis(2-pyridyl)-2,5-dithiahexane, pdthx (**1a**), and 1,7-bis(2-pyridyl)-2,6-dithiaheptane, pdthp (**1b**), were ob-

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Table I. Analytical and Magnetic Data for the Copper Complexes

complex	% C		% H		% N		% S		$\mu_{\text{eff}}(25^\circ\text{C})$, μ_{B}
	calcd	found	calcd	found	calcd	found	calcd	found	
Cu(pdthx)(ClO ₄) ₂	31.20	31.10	3.00	3.06	5.00	5.35	11.90	11.67	1.80
Cu(pdthp)(ClO ₄) ₂	32.58	32.84	3.29	3.48	5.07	5.24	11.60	11.80	1.79
Cu(pdto)(ClO ₄) ₂	33.89	34.62	3.56	3.53	4.94	4.89	11.30	11.21	1.77
Cu(pdtn)(ClO ₄) ₂	41.11	41.85	4.31	4.44	5.99	5.97			dia ^a
Cu(pdtn)(ClO ₄) ₂ · ¹ / ₂ CH ₃ CN	43.06	42.74	4.73	4.70	6.97	6.96	12.77	12.81	dia ^a
Cu(pdahx)(ClO ₄) ₂ ^b									1.82
Cu(pdahp)(ClO ₄) ₂ ^b									1.79
Cu(pdao)(ClO ₄) ₂ ·H ₂ O	37.34	37.31	4.89	4.83	9.67	9.54			1.83
Cu(pdan)(ClO ₄) ₂	39.69	39.89	4.92	5.03	9.75	9.53			1.83

^a Diamagnetic. ^b Literature preparations; see Experimental Section.

tained as oils from the reaction of 2-(chloromethyl)pyridine (Aldrich) and 1,2-ethanedithiol or 1,3-propanedithiol (Aldrich) by the method of Livingstone and Nolan.²⁶ ¹H NMR (Me₂SO-*d*₆): pdthx (**1a**) δ 3.26 (s, 4), 3.90 (s, 4), 7.40 (m, 6), 8.44 (d, 2); pdthp (**1b**) δ 1.94 (m, 2), 2.54 (t, 4), 3.82 (s, 4), 7.40 (m, 6), 8.44 (d, 2). The ligands 1,8-bis(2-pyridyl)-3,6-dithianone, pdto (**1c**), and 1,9-bis(2-pyridyl)-3,7-dithianone, pdtn (**1d**), were prepared from 2-vinylpyridine (Aldrich) and 1,2-ethanedithiol or 1,3-propanedithiol by the method of Goodwin and Lions.²⁷ ¹H NMR (Me₂SO-*d*₆): pdto (**1c**): δ 2.64 (s, 4), 2.86 (s, 8), 7.40 (m, 6), 8.44 (d, 2); pdtn (**1d**) δ 1.86 (m, 2), 2.56 (t, 4), 2.96 (s, 8), 7.40 (m, 6), 8.44 (d, 2). 1,6-Bis(2-pyridyl)-2,5-diazahexane, pdahx (**2a**), and 1,7-bis(2-pyridyl)-2,6-diazahexane, pdahp (**2b**), were prepared by the method of Goodwin and Lions.²⁷ The ligands 1,8-bis(2-pyridyl)-3,6-dimethyl-3,6-diazocane, pdao (**2c**), and 1,9-bis(2-pyridyl)-3,7-dimethyl-3,7-diazocane, pdan (**2d**), were synthesized by the addition of *N,N'*-dimethylethylenediamine or *N,N'*-dimethyl-1,3-propylenediamine to 2-vinylpyridine according to the following method. To a solution of freshly distilled 2-vinylpyridine (7.3 g, 69 mmol) in methanol was added 5.8 g of concentrated HCl under nitrogen. A stoichiometric amount (34.5 mmol) of the *N,N'*-dimethyl-substituted diamine was added dropwise, and the solution was refluxed under nitrogen for 1 h. An excess of NaOH in methanol was added, and the precipitated NaCl was filtered off. After evaporation of the solvent, the residue was extracted with anhydrous diethyl ether. The ether solution was dried over CaSO₄, filtered, and evaporated to a pale yellow oil. This oil was taken up in ether, treated with decolorizing carbon, and filtered, and the ether solution was evaporated to a pale yellow oil.

Complexes. *Caution!* Several of these complexes containing perchlorate counterions exhibited shock sensitivity²⁴ and detonated during grinding or removal from glass-frit funnels. The complexes should be handled cautiously in small amounts. The bis(pyridyl)-dithia complexes [Cu(pdthx)](ClO₄)₂, [Cu(pdthp)](ClO₄)₂, and [Cu(pdto)](ClO₄)₂ were synthesized by the addition of an ethanol solution of the appropriate ligand (1.8 mmol in 100 mL) to an aqueous solution of Cu(ClO₄)₂·6H₂O (1.8 mmol in 10 mL). Blue precipitates of the crude products were collected by suction filtration and washed with cold ethanol. Recrystallization was accomplished from methanol [Cu(pdto)](ClO₄)₂ from hot water). The copper(I) complex [Cu(pdtn)]ClO₄·0.5CH₃CN was prepared by the addition under N₂ of [Cu(CH₃CN)₄]BF₄ (0.49 g, 1.6 mmol) in 150 mL of ethanol to a solution of pdtn (0.50 g, 1.6 mmol) in 50 mL of ethanol. The solution was stirred for 1 h and then evaporated to a pale green oil. The oil was dissolved in degassed acetonitrile, and an excess of NaClO₄·H₂O was added. Water was added to the point of incipient precipitation. Evaporation of this solution over a few days afforded colorless crystals of the copper(I) complex.

[Cu(pdto)]ClO₄ was prepared by adding [Cu(CH₃CN)₄]BF₄ (0.56 g, 1.8 mmol) to a solution of pdto (0.54 g, 1.8 mmol) in ethanol (100 mL). The solution was stirred for 1/2 h, and the resulting white precipitate was isolated by suction filtration. The crude product was dissolved in acetonitrile and a two-fold excess of NaClO₄·H₂O was added, followed by the addition of water to the point of incipient precipitation. Slow evaporation yielded white crystals of the copper(I) complex. Copper(I) complexes of pdthx and pdthp were not isolated. For spectral studies, the copper(I) forms of these complexes were generated by controlled-potential reduction followed by an anaerobic

transfer to a spectrophotometer cell.

The bis(pyridyl)-dithia complexes of ligands **2a** and **2b** were synthesized by the addition of a solution of Cu(ClO₄)₂·6H₂O (0.75 g, 2.0 mmol) in 50 mL of methanol to a solution containing the stoichiometric amount of appropriate ligand in 50 mL of methanol. Complexes of **2c** and **2d** were prepared similarly except that ethanol was employed as the solvent. The immediate blue precipitates that formed were collected by suction filtration and recrystallized from methanol ([Cu(pdahx)](ClO₄)₂ from water). The copper(I) forms of the bis(pyridyl)-dithia series of ligands were not isolated but were generated by controlled-potential reductions for spectral studies.

Physical Measurements. Elemental analyses (Table I) were performed by Galbraith Laboratories, Inc., Knoxville, TN. Infrared spectra were measured on a Beckman IR-10 spectrophotometer. Proton NMR spectra were recorded on a Varian A-60A spectrometer in a suitable solvent with tetramethylsilane (Me₄Si) as an internal standard. Electronic absorption spectra were recorded on a Cary Model 14 spectrophotometer. Magnetic susceptibilities at room temperature were determined via the Faraday method with a Varian V-4004 electromagnet and a Cahn RG electrobalance. Hg[Co(NCS)₄] and [Ni(en)₃]S₂O₃ were used as standards, and diamagnetic corrections were calculated from a table of Pascal's constants.²⁸ Cyclic voltammetry and differential pulse voltammetry were performed on a Princeton Applied Research (PAR) Model 170 potentiostat. Controlled-potential electrolyses were carried out with an apparatus consisting of a PAR Model 373 potentiostat, a Houston Model 2000 xy recorder, and a three-compartment cell, which was adapted to allow the anaerobic transfer of the electrolyzed solution into quartz cells so that the electronic absorption spectrum of the product could be recorded. The electrochemical cells were constructed to conform with accepted concepts in cell design,²⁹ and cell resistance was electronically compensated. All electrochemical potentials were measured relative to a saturated calomel electrode constructed according to accepted design,³⁰ and the nonaqueous electrochemical potentials were corrected for liquid-junction potentials via the use of the ferrocenium/ferrocene couple as an internal redox standard.³¹ The corrected potentials were then referenced to the normal hydrogen electrode (NHE) by the addition of +400 mV.³¹ Platinum electrodes were cleaned by treatment with hot concentrated nitric acid and then with aqua regia, followed by a thorough rinsing with distilled water. Wax-impregnated graphite (WIG) electrodes were rubbed with carborundum paper and rinsed with the appropriate solvent. The hanging mercury drop electrode (HMDE) was a PAR Model 9323, and a fresh mercury drop was used for each voltammogram. Anisotropic EPR spectra were observed on Varian E-3 and E-112 spectrometers in dilute 9:1 methanol/ethanol glasses³² with DPPH (Aldrich) as an external calibrant. EPR sim-

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Table II. Electronic Spectra of the Copper(II) Complexes in Several Solvents

complex	solvent	λ_{\max} , nm (ϵ , M ⁻¹ cm ⁻¹)				
Cu(pdthx) ²⁺	H ₂ O	990 (90)	926 (94)	637 (103)	333 (2360)	262 (12 600)
	CH ₃ CN		925 (165)	610 (185)	344 (2260)	263 (12 300)
	CH ₃ OH		960 (66)	640 (96)	338 (1090)	260 (11 100)
Cu(pdthp) ²⁺	H ₂ O			663 (218)	351 (2860)	264 (10 900)
	CH ₃ CN			670 (342)	360 (3430)	263 (11 100)
	CH ₃ OH			662 (327)	358 (3380)	263 (10 500)
Cu(pdto) ²⁺	H ₂ O			602 (540)	350 (3960)	260 (9730)
	CH ₃ CN			595 (902)	360 (5560)	270 (sh), 260 (11 300)
	CH ₃ OH			599 (615)	356 (3990)	262 (13 100)
Cu(pdtn) ²⁺ ^a	CH ₃ CN			610 (453)	380 (5020)	263 (13 900)
Cu(pdahx) ²⁺	H ₂ O			603 (152)		255 (11 400)
	CH ₃ CN			599 (182)		256 (12 500)
	CH ₃ OH			599 (182)		256 (11 800)
Cu(pdahp) ²⁺	H ₂ O			603 (143)		255 (15 500)
	CH ₃ CN			596 (145)		255 (15 200)
	CH ₃ OH			599 (153)		255 (14 100)
Cu(pdao) ²⁺	H ₂ O			589 (245)		292 (sh), 263 (12 100)
	CH ₃ CN			628 (277)		282 (sh), 262 (12 000)
	CH ₃ OH			599 (277)		282 (sh), 263 (12 400)
Cu(pdan) ²⁺	H ₂ O			659 (274)		290 (sh), 264 (10 200)
	CH ₃ CN			653 (285)		291 (sh), 264 (11 700)
	CH ₃ OH			645 (340)		295 (sh), 265 (12 500)

^a Cu(II) species generated by controlled-potential oxidation.

ulations were run on a DEC PDP-11/45 minicomputer using an adaptation of the program KUSKA.³³ The simulated and experimental spectra were plotted together to examine the fit of the simulations.

Results and Discussion

Synthesis, Magnetism, and Infrared Spectra of the Complexes. Preparations of the tetradentate ligands yielded oils (except for crystalline pdto) which were characterized by NMR and used without further purification for the synthesis of the copper(II) complexes. Except for pdtn all the ligands produced copper(II) complexes of 1:1 stoichiometry as indicated by the analytical data (Table I). When pdtn was added to an alcohol solution of copper(II), the initial deep green color faded slowly and only an impure copper(I) complex could be isolated. Similar results occurred when the synthesis of Cu(pdtn)(ClO₄)₂ was attempted in aqueous solution. A pure sample of Cu^I(pdtn)ClO₄·0.5CH₃CN was prepared by the addition of tetrakis(acetonitrile) copper(I) perchlorate to a solution of the ligand in ethanol. For spectral studies the species Cu^{II}(pdtn)²⁺ was generated by controlled-potential oxidation and measurements were made quickly. Magnetic susceptibility measurements for all of the complexes yielded values of μ_{eff} (25 °C) (Table I) indicative of mononuclear Cu(II) species.

Characteristic vibrational modes for pyridine were exhibited by all of the complexes at ~1600 and 800 cm⁻¹. Typically weak carbon-sulfur stretching frequencies were not apparent in the dithia complexes. All of the complexes displayed absorption bands at 1119 and 625 cm⁻¹ attributed to ν_3 and ν_4 of the perchlorate counterions.³⁴ Cu(pdao)(ClO₄)·H₂O gave a strong absorption at 3400 cm⁻¹, which confirmed the presence of coordinated water. A sharp, weak band at 2280 cm⁻¹ for Cu^I(pdtn)(ClO₄)·0.5CH₃CN indicated the presence of acetonitrile solvation.

Electronic Absorption Spectra of the Cu(II) Complexes. The UV-vis spectra of the bis(pyridyl)-dithia and bis(pyridyl)-diazia complexes with Cu(II) in water, acetonitrile, and methanol solutions are summarized in Table II. All of the Cu(II) complexes, except Cu(pdthx)(ClO₄)₂, exhibit a single,

broad absorption band envelope with λ_{\max} in the range 595–670 nm, typical of d-d absorption bands for Cu(II) in a weakly tetragonal field.³⁵ A slight solvent dependence of band position suggests weak axial coordination by solvent molecules, and extinction coefficients were found to be slightly concentration dependent as reported previously for Cu(pdto)(ClO₄)₂.¹⁰ The markedly different visible absorption spectrum for Cu(pdthx)(ClO₄)₂, consisting of two well-separated bands, implies a coordination geometry for this complex different from that of the remaining members of the series. From considerations of the strain energies present in the possible arrangements of linear tetradentate ligands it has been noted previously that the square-planar configuration is highly strained for these ligands, which generate three five-membered chelate rings.³⁶ The large size of the internal sulfur donors and the unsaturated bonds in the terminal pyridine donors serve to exaggerate this strain in Cu(pdthx)²⁺. It is not surprising, therefore, that a similar spectrum (λ_{\max} (ϵ) = 854 (146), 595 nm (254); methanol solvent)^{10,37} is observed for the Cu(II) complex of the analogous ligand 1,8-diamino-3,6-dithiaoctane (eee), which also produces three five-membered chelate rings. In six-coordinate Co(III) complexes,³⁸ eee prefers the cis- α (sym-cis) configuration, **3**. A similar arrangement of the eee ligand is found in the five-coordinate complex [(1,8-diamino-3,6-dithiaoctane)(1-methylimidazole)]copper(II) perchlorate,³⁹ which exhibits a distorted square pyramidal geometry, **4**, with the imidazole in the basal position and one of the thioether donors providing axial coordination.

In donor solvents, Cu(pdthx)²⁺ probably adopts a similar square-pyramidal structure, **5**, in which a solvent molecule occupies a basal coordination site. The favored sym-cis folding of the tetradentate ligand places a thioether donor at the axial site. Support for this structure is obtained by examining the spectra of the known square-pyramidal Cu(II) complexes with ligands of comparable ligand field strength. Two-component d → d spectra with splitting comparable to that observed for Cu(pdthx)(Sol)²⁺ are given by Cu(NH₃)₅²⁺,⁴⁰ Cu(eee)(im)²⁺,¹⁰

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four bis(pyridyl)-dithia complexes. In acetonitrile solution, the separation $\nu_{CT} - \nu_{vis}$ decreases systematically through the series but the oscillator strengths⁴⁹ of ν_{CT} are in the order $\text{Cu}(\text{pdthx})^{2+} < \text{Cu}(\text{pdthp})^{2+} < \text{Cu}(\text{pdto})^{2+} \approx \text{Cu}(\text{pdtn})^{2+}$. The observed intensities of the visible band increase as predicted for the first three members of the series, $\text{Cu}(\text{pdthx})^{2+} > \text{Cu}(\text{pdthp})^{2+} > \text{Cu}(\text{pdto})^{2+}$, but $\text{Cu}(\text{pdtn})^{2+}$ shows a visible band diminished in intensity in acetonitrile, the only solvent where spectral data were obtained for this electrogenerated form of the complex. This qualitative agreement of the intensity of the visible band with eq 1 supports intensity borrowing as the mechanism by which the visible band becomes enhanced in the bis(pyridyl)-dithia complexes. An alternative explanation based on increasing pseudotetrahedral distortion giving rise to greater allowedness of the d-d bands is apparently ruled out (at least through $\text{Cu}(\text{pdto})^{2+}$) by the EPR data (see below), which reveal no distortions from tetragonal geometries.

A smaller intensity enhancement of the visible band is observed for the two bis(pyridyl)-diazia complexes containing the largest chelate ring sizes. The tertiary amine donors present in these two ligands produce a lowering of the $\text{N}(\sigma) \rightarrow \text{Cu}(\text{d}_{x^2-y^2})$ charge-transfer band by $\sim 4000 \text{ cm}^{-1}$ (see below). The enhanced intensities of the d-d bands in these two complexes may result from increased intensity borrowing with the lower energy $\text{N}(\sigma) \rightarrow \text{Cu}(\text{d}_{x^2-y^2})$ charge-transfer band.

Less controversy arises over the assignments of the remaining bands in the electronic spectra of these complexes. The band of moderate intensity observed for the bis(pyridyl)-dithia Cu(II) complexes between 330 and 380 nm has been reported for a variety of Cu(II) species in which thioether is coordinated in the tetragonal plane and is assigned as the $\text{S}(\sigma) \rightarrow \text{Cu}(\text{II})(\text{d}_{x^2-y^2})$ charge-transfer transition. The energy of this transition decreases with the increasing reduction potentials observed as the chelate ring sizes become larger. This observation supports the band assignment since, as the Cu(II) ion becomes more oxidizing, the electronic transition from the sulfur to the Cu(II) ion becomes easier. Schugar and co-workers⁵⁰ have shown recently that the $\text{S}(\sigma) \rightarrow \text{Cu}(\text{II})(\text{d}_{x^2-y^2})$ charge-transfer transition is not observed for Cu(II) complexes containing axial thioether donors. The loss of intensity for this transition probably results from poor overlap characteristics between the $\text{S}(\sigma)$ and the half-empty $\text{d}_{x^2-y^2}$ orbital on the Cu(II). This effect provides a rationalization for the significantly lower intensity of the charge-transfer band at $\sim 340 \text{ nm}$ for the complex $\text{Cu}(\text{pdthx})(\text{ClO}_4)_2$, to which we assign the square-pyramidal geometry 5.

High-energy bands (250–292 nm) in the spectra of the Cu(II) complexes are also observed in the spectra of the corresponding ligands but with greatly reduced intensities ($\epsilon = 2000\text{--}8000$). The bands in the free-ligand spectra are attributed to pyridine $\pi\text{--}\pi^*$ transitions, and the enhanced intensities and additional bands observed in the spectra of the complexes are assigned to overlapping $\text{N}(\sigma) \rightarrow \text{Cu}(\text{II})(\text{d}_{x^2-y^2})$ transitions. For $\text{Cu}(\text{pdao})^{2+}$ and $\text{Cu}(\text{pdan})^{2+}$, which contain tertiary amine donors, the $\text{N}(\sigma) \rightarrow \text{Cu}(\text{II})$ LMCT occurs at lower energies owing to the electron-releasing nature of the methyl substituent.

Jørgensen⁵¹ has introduced the concept of optical electronegativity in discussing the nature of LMCT transitions and has developed the empirical expression

$$\nu^{\text{cor}} = [\chi(\text{L}) - \chi(\text{M})](30.0 \times 10^3 \text{ cm}^{-1})$$

(49) Oscillator strengths of the charge-transfer bands were approximated by the expression $f \approx (4.6 \times 10^{-9})\epsilon_{\text{max}}\Delta\nu_{1/2}$; Reference 32, p 108.

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Table III. Electronic Spectra of the Copper(I) Complexes in Acetonitrile

complex	λ_{max} , nm (ϵ , $\text{M}^{-1} \text{ cm}^{-1}$)	
$\text{Cu}(\text{pdthx})^{+a}$	310 (sh) ^b	258 (7500)
$\text{Cu}(\text{pdthp})^{+a}$	317 (4100)	250 (8300)
$\text{Cu}(\text{pdto})^{+c}$	307 (3800)	250 (8400)
$\text{Cu}(\text{pdtn})^{+c}$	295 (3000)	250 (7000)
$\text{Cu}(\text{pdahx})^{+a}$	342 (3200)	284 (sh), ^b 250 (8200)
$\text{Cu}(\text{pdaph})^{+a}$	356 (5000)	252 (12 100)
$\text{Cu}(\text{pdao})^{+a}$	357 (6700)	252 (11 500)
$\text{Cu}(\text{pdan})^{+a}$	340 (4700)	292 (sh), ^b 244 (10 900)

^a Cu(I) species generated by controlled-potential reduction and anaerobically transferred to spectrophotometer cell. ^b Shoulder.

^c For measurement, solid copper(I) complexes were dissolved in acetonitrile.

to predict the energy of these transitions, where ν^{cor} = the energy of the charge-transfer transition in 10^3 cm^{-1} , corrected for ligand field strength, and $\chi(\text{L})$, $\chi(\text{M})$ are empirical parameters for the optical electronegativities of the ligand and metal, respectively. With our spectral data we can determine values of orbital optical electronegativities for Cu^{2+} and the donors and can correct the observed LMCT energy by approximating Δ as the band maximum of the ligand field envelope. Analysis of the $\text{N}(\sigma) \rightarrow \text{Cu}(\text{II})$ LMCT transition for each of 16 linear tetradentate chelates, including 8 terminal amine-containing analogues³⁷ of the ligands presented here, gives us a value of 2.48 ± 0.04 for the orbital optical electronegativity of copper(II), which agrees with Jørgensen's results of ~ 2.4 . By a similar analysis of the $\text{S}(\sigma) \rightarrow \text{Cu}(\text{II})$ LMCT transition we obtain a value of 2.91 ± 0.06 for $\chi(\text{R}_2\text{S})$ in agreement with Jørgensen's result of 2.90 from a study of the spectrum of *trans*- $\text{IrCl}_4(\text{Et}_2\text{S})_2$.⁵¹ This confirmed value of the orbital optical electronegativity parameter for a thioether donor allows the energy of a thioether \rightarrow metal ion charge-transfer band to be estimated and should be useful in transition assignments^{51b} in complexes containing thioether groups.

Electronic Absorption Spectra of the Cu(I) Complexes. The Cu(I) complexes of both the bis(pyridyl)-dithia and the bis(pyridyl)-diazia series of ligands exhibit two absorption bands (Table III). The high-energy band centered at $\sim 250 \text{ nm}$ occurs also in the free ligands and is assigned to $\pi\text{--}\pi^*$ transitions within the pyridine rings. A lower energy band which occurs at $\sim 310 \text{ nm}$ for the bis(pyridyl)-dithia complexes and at $\sim 350 \text{ nm}$ for the bis(pyridyl)-diazia complexes is assigned as a $\text{Cu}(\text{I}) \rightarrow \text{py}(\pi^*)$ metal to ligand charge-transfer (MLCT) transition. This $\text{Cu}(\text{I}) \rightarrow \text{L}(\pi^*)$ MLCT transition has been previously observed with the 390-nm band in the spectrum of tetrakis(pyridine)copper(I)⁵² and with the bands in the region 435–455 nm in the spectra of Cu(I) complexes of substituted *o*-phenanthroline and bipyridyl ligands.⁵³ Further support for the assignment of this band as a $\text{Cu}(\text{I}) \rightarrow \text{py}(\pi^*)$ transition comes from the observation that the transition occurs at a lower energy for the bis(pyridyl)-diazia series of complexes which have lower reduction potentials than the bis(pyridyl)-dithia series. This trend is in agreement with the assignment as a MLCT transition since a more reducing Cu(I) ion could more easily transfer an electron to the pyridine antibonding orbital.

Electrochemistry. The electrochemical behavior of the Cu(II)/Cu(I) couple for the chelates was investigated by cyclic voltammetry and differential pulse voltammetry in acetonitrile and aqueous solutions (Table IV). Values of $E^{\circ'}$ were measured vs. the ferrocenium/ferrocene couple as an internal redox standard to minimize the contributions of liquid junction potentials and are reported vs. NHE for ease of comparison.

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Table IV. Electrochemical Results for the Bis(pyridyl)-Dithia and Bis(pyridyl)-Diaza Complexes of Cu(II) in Water and Acetonitrile

complex	solvent	cyclic voltammetry ^a			differential pulse ^b E, mV ^e	electrode material ^c	coulometry ^d n
		E ^{o'} , mV ^e	ΔE _p , mV ^f	i _a /i _c ^g			
Cu(pdthx) ²⁺	H ₂ O	+396 ± 7	100	1.34	+403	Pt	0.95
	CH ₃ CN	+510 ± 3	78	0.97	+506	WIG	
Cu(pdthp) ²⁺	H ₂ O	+473 ± 1	66	1.19	+480	Pt	0.98
	CH ₃ CN	+547 ± 6	70	1.07	+544	WIG	
Cu(pdto) ²⁺	H ₂ O	+586 ± 3	102	1.51	+596	WIG	0.95
	CH ₃ CN	+609 ± 3	84	1.13	+617	WIG	
Cu(pdtn) ²⁺	H ₂ O ^h	+592 ± 1	134	2.11	+625	WIG	0.99
	CH ₃ CN ⁱ	+659 ± 3	90	0.99	+654	WIG	
Cu(pdahx) ²⁺	H ₂ O	-196 ± 1	138	0.96	-193	Pt	0.97
	CH ₃ CN	-169 ± 4	70	0.88	-171	HMDE	
Cu(pdahp) ²⁺	H ₂ O	-106 ± 10	78	0.81	-129	HMDE	0.96
	CH ₃ CN	-148 ± 8	72	0.60	-146	WIG	
Cu(pdao) ²⁺	H ₂ O	+99 ± 4	115	1.07	+93	HMDE	0.97
	CH ₃ CN	+83 ± 16	196	1.09	+109	WIG	
Cu(pdán) ²⁺	H ₂ O	+275 ± 1	74	1.02	+277	HMDE	1.00
	CH ₃ CN	+310 ± 8	94	1.15	+318	WIG	

^a Measured in H₂O for 1–2 mM solutions of the complex in 0.5 M NaNO₃ vs. SCE; converted to NHE scale by addition of 244 mV. Measured in CH₃CN for 1–2 mM solutions of the complex in 0.1 M TEAP vs. SCE with internal ferrocene standard. See Experimental Section for conversion to NHE scale. ^b Scan rate 1 mV/s; modulation amplitude 10 mV. ^c Pt = Pt bead; WIG = wax-impregnated graphite; HMDE = hanging mercury drop electrode. ^d Pt-gauze electrode. ^e Vs. NHE, averaged values for scan rates from 20 to 200 mV/s. ^f Reported for scan rate 50 mV/s. ^g Nicholson, R. S. *Anal. Chem.* 1966, 38, 1406. ^h Measured for 1:1 freshly prepared solutions of Cu(ClO₄)₂·6H₂O and pdtn. ⁱ Measured for 2.2 mM Cu(pdtn)ClO₄.

Instrumental *iR* compensation was employed for all measurements in this study. Two main trends are apparent in the observed values of the Cu(II)/Cu(I) potential. The substitution of two thioethers for two amine donors results in increased values of E^{o'} by 300–700 mV in corresponding pairs of bis(pyridyl)-dithia and bis(pyridyl)-diaza complexes. This result is in agreement with previous observations that thioether donors produce high values for the Cu(II)/Cu(I) couple,^{15–17} an effect which is attributed to the ability of the thioether donor to stabilize the Cu(I) state via a π-acceptor interaction. The second major trend is the monotonic increase in the redox potentials as the chelate ring sizes are increased. This trend presumably results from the increased ability of the more flexible chelate rings to accommodate a pseudotetrahedral geometry, which is favorable for the Cu(I) state and destabilizes Cu(II). The ability of the thioether ligands to raise the redox potential diminishes with increasing chelate ring size. This effect occurs primarily because the potentials for the bis(pyridyl)-diaza complexes increase much more dramatically than the bis(pyridyl)-dithia series with increasing ring size. The origin of this effect is likely to reside in a greater flexibility of the diaza ligands compared to their dithia counterparts. The potentials of the diaza series span a range of almost 500 mV, a remarkable change considering that the donor atom set remains constant.

The redox potentials for the Cu(II)/Cu(I) couple were essentially the same for different working-electrode materials, but the reversibility of the electrode processes as judged by peak separations varied as a function of the electrode. A few of the complexes approach nearly reversible electrochemical behavior as judged by the peak separations (ΔE_p) and current ratios (i_a/i_c), but most of the redox changes must be considered quasi-reversible by these criteria. Electrochemical irreversibility in copper chelates with flexible ligands is generally attributed to the configurational change accompanying electron transfer, and the X-ray structures reported by Brubaker et al.²⁴ for the Cu(II) and Cu(I) complexes of pdto support this concept. Coulometry results for all members of the bis(pyridyl)-dithia and bis(pyridyl)-diaza series in acetonitrile confirmed that the redox process involved a 1e change. All of the reduced complexes were stable toward disproportionation and could be reoxidized by 1e back to the Cu(II) species.

When the effects of liquid-junction potentials are minimized, there is little difference between the potentials observed in

Table V. Anisotropic Parameters Obtained from the Simulation of the EPR Spectra^a of the Copper(II) Complexes

complex	g _x	g _y	g _z	A _x ^b	A _y ^b	A _z ^b	g _z /A _z ^c
Cu(pdthx) ²⁺	2.050	2.115	2.280	0.8	1.0	18.3	119
Cu(pdthp) ²⁺	2.006	2.108	2.272	0.1	0.2	18.0	126
Cu(pdto) ²⁺	2.048	2.085	2.197	0.5	0.1	20.2	109
Cu(pdtn) ²⁺ ^d							
Cu(pdahx) ²⁺	2.075	2.085	2.205	0.5	0.5	19.3	114
Cu(pdahp) ²⁺	2.053	2.053	2.215	0.5	0.5	19.6	112
Cu(pdao) ²⁺	2.068	2.083	2.212	0.5	0.5	18.4	114
Cu(pdán) ²⁺	2.100	2.100	2.225	0.2	0.2	15.8	141

^a Experimental spectra obtained in 9:1 methanol/ethanol glasses at ~77 K. ^b In cm⁻¹ × 10³. ^c In cm. ^d Spectrum not reproducible.

acetonitrile compared to those in water. This result indicates that there is little effect of solvent coordination on the redox potentials in this series of complexes. Acetonitrile would be expected to make the observed redox potential more positive owing to its well-known ability to stabilize the Cu(I) state. This effect does occur for the one member of the series Cu^{II}(pdthx)²⁺, which shows a large solvent dependence on the spectra and for which we propose the five-coordinate structure, **5**, in solution. The potentials of the remaining bis(pyridyl)-dithia complexes are increased to a lesser extent in acetonitrile, and the bis(pyridyl)-diaza complexes show no significant differences in the two solvents.

Electron Paramagnetic Resonance Spectra. The anisotropic EPR spectra of the copper(II) chelates obtained in 9:1 methanol/ethanol glasses at 77 K have the usual line shape for mononuclear copper(II) complexes with a d_{x²-y²} ground state. The g_z values are greater than the g_x and g_y values and are in the range seen for copper in axially elongated octahedral, square-planar, or square-pyramidal geometries.⁵⁴ This agrees with our interpretation of the ligand field spectra and supports our view that these chelates adopt a tetragonal symmetry in solution.

The anisotropic values for g_x and g_y were poorly resolved so the EPR parameters (Table V) were determined by the best fit of the computer-simulated spectra. The alcohol solvent may axially coordinate the copper(II) chelates and increase the value of g_{||}.⁵⁵ This may explain the difference between our

value of $g_z = 2.197$ for $[\text{Cu}(\text{pdto})](\text{ClO}_4)_2$ and a previously reported¹⁷ result of $g_{\parallel} = 2.164$ in nitromethane.

The immediate observation of the influence of thioether donors on the EPR spectra is that rhombic g factors are required to fit the observed spectra. Boas et al.⁵⁶ discussed the effect of various square-planar donor arrays about copper(II) on the EPR line shape. The suggestion was that a square-planar N_4 array would give rise to an axial spectrum, while a cis-rectangular N_2S_2 array, as in the $(\text{py})_2\text{S}_2$ series, would result in a rhombic distortion. The source of the rhombic distortion has been shown theoretically⁵⁴ to arise from a mixing of excited ligand field states with the ground state in C_{2v} symmetry that was not available in D_{4h} symmetry. Thus we interpret the nearly axial EPR spectra for our $(\text{py})_2\text{N}_2$ series as indicative of the pseudotetrahedral symmetry of these chelates, while the rhombic spectra of the $(\text{py})_2\text{S}_2$ series can be ascribed to a reduction in apparent symmetry from D_{4h} to C_{2v} .

Within each series there is no discernible trend in either g or A values. For the $(\text{py})_2\text{S}_2$ series our values of A_z and g_z did not fall in the same ranges as those in the plot of A_{\parallel} as a function of g_{\parallel} for Peisach and Blumberg's N_2S_2 series.²² This lack of correlation may be due to the effect of axial solvent coordination on our spectra or, more likely, to the fact of their sulfur donors including only thiosemicarbazones and mercaptides, but not thioethers. Our values of A_{\parallel} and g_{\parallel} for the $(\text{py})_2\text{N}_2$ series, on the other hand, correlate well with their plot for CuN_4 complexes.

We report the quotient $|g_z/A_z|$ for both series as another indication of the stereochemistry of our chelates in solution. Addison¹⁷ has suggested that this quotient may be an empirical index of tetrahedral distortion from tetragonal geometry. He observed values from 105 to 135 cm for square-planar structures and from 150 to 250 cm for tetrahedrally distorted complexes. The range of our values, 109–141 cm, indicates that in alcohol solution the chelates exhibit little or no tetrahedral distortion from tetragonal symmetry.

Conclusions. The present systematic comparison of the properties of a series of bis(pyridyl)-dithia complexes with their bis(pyridyl)-diaz analogues leads to the following conclusions regarding the influence of equatorially bonded thioether donors on the spectral and redox properties of tetragonal copper(II) complexes. (1) A moderately intense band in the region 320–380 nm is reasonably assigned as a $\text{S}(\sigma) \rightarrow \text{Cu}(\text{d}_{x^2-y^2})$ ligand to metal charge transfer, as has been suggested previously.^{10,11} Good overlap between the sulfur σ orbital and the half-filled $\text{d}_{x^2-y^2}$ orbital accounts for the intensity of this band. (2) The presence of thioether donors in a Cu(II) complex does not always produce intense visible absorption bands such as those seen for the $\text{Cu}^{\text{II}}\text{S}_4$ macrocycles¹² since only a modest enhancement of the bands at ~ 600 nm occurs in the present set of thioether complexes. (3) No unique band which may be attributed to a $\text{S}(\pi) \rightarrow \text{Cu}(\text{d}_{x^2-y^2})$ transition is observed separate from the $\text{d} \rightarrow \text{d}$ transitions. Overlap considerations predict that such a transition would be much weaker than the transition originating in the $\text{S}(\sigma)$ orbital. (4)

The enhanced intensities of the $\text{d} \rightarrow \text{d}$ bands in the presence of thioether donors appears to arise from intensity borrowing from the $\text{S}(\sigma) \rightarrow \text{Cu}(\text{d}_{x^2-y^2})$ charge-transfer band. (5) Thioether donors present a ligand field strength toward Cu(II) that is intermediate between secondary and tertiary amine donors. (6) The substitution of two thioether donors for two amine donors consistently raises the potential of the Cu(II)/Cu(I) couple by 300–700 mV, an effect which is qualitatively attributed to the ability of the thioether donors to accept electron density into vacant 3d orbitals and stabilize the Cu(I) state.

Owing to the difference in geometry between the tetragonal bis(pyridyl)-dithia complexes studied here and the pseudotetrahedral copper(II) site in the "blue" copper proteins, it is not possible to relate directly their spectral properties. The methionine thioether donor in the "blue" copper site occupies an apical position at the abnormally long distance of 2.90 Å in a distorted pseudotetrahedral coordination shell, and the ground state of the copper(II) ion has the unpaired electron in the $\text{d}_{x^2-y^2}$ orbital as determined by EPR.² These two factors in the "blue" copper site suggest that charge-transfer transitions from either the $\text{S}(\sigma)$ or the $\text{S}(\pi)$ orbitals to the $\text{Cu}(\text{d}_{x^2-y^2})$ orbital will be weak because of very poor overlap arising from the long bond length and symmetry considerations. In addition, if thioether $\rightarrow \text{Cu}(\text{II})$ charge-transfer transitions do occur in the "blue" copper spectra they would be expected to appear at lower energies in the pseudotetrahedral site than in the tetragonal complexes^{51b} and would probably be shifted into the visible region. Whereas the location of the $\text{S}(\sigma) \rightarrow \text{Cu}(\text{d}_{x^2-y^2})$ transition and the apparent absence of a transition originating from the $\text{S}(\pi)$ orbital are now well established for tetragonal Cu(II) complexes containing thioether donors in equatorial positions, thioether to Cu(II) charge-transfer transitions in pseudotetrahedral complexes remain relatively unexplored.⁵⁷ Although it appears unlikely that thioether to Cu(II) charge-transfer bands contribute to the unique spectra of the "blue" copper site, the question is not yet resolved. We have explored further the nature of thioether-copper orbital interactions and the assignment of charge-transfer transitions using molecular orbital calculations, and these results are published elsewhere.⁵⁸

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Registry No. $\text{Cu}(\text{pdthx})(\text{ClO}_4)_2$, 72783-95-0; $\text{Cu}(\text{pdthx})^+$, 72783-98-3; $\text{Cu}(\text{pdthp})(\text{ClO}_4)_2$, 72783-97-2; $\text{Cu}(\text{pdthp})^+$, 72784-00-0; $\text{Cu}(\text{pdto})(\text{ClO}_4)_2$, 64685-83-2; $\text{Cu}(\text{pdto})(\text{ClO}_4)$, 72784-02-2; $\text{Cu}(\text{pdtn})^{2+}$, 86902-78-5; $\text{Cu}(\text{pdtn})(\text{ClO}_4)$, 72883-00-2; $\text{Cu}(\text{pdahx})(\text{ClO}_4)_2$, 32592-71-5; $\text{Cu}(\text{pdahx})^+$, 80291-82-3; $\text{Cu}(\text{pdahp})(\text{ClO}_4)_2$, 32593-55-8; $\text{Cu}(\text{pdahp})^+$, 86902-79-6; $\text{Cu}(\text{pdao})(\text{ClO}_4)_2$, 72784-04-4; $\text{Cu}(\text{pdao})^+$, 86902-80-9; $\text{Cu}(\text{pdan})(\text{ClO}_4)_2$, 72784-06-6; $\text{Cu}(\text{pdan})^+$, 86902-81-0.

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