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Electronic Spectra of Substituted Copper(II) Thioether Complexes

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Abstract: Electronic spectra over the 200–900-nm region are reported for mulls (80 K) and solutions (298 K) of $Cu(NH_2CH_2CH_2SCH_3)_2\cdot 2ClO_4$, $[Cu(BuSCH_2CH_2SBu)\cdot 2X]_2$ (X = Cl, Br), $Cu(BuSCH_2CH_2SBu)_2\cdot 2ClO_4$, $Cu(O_2CCH_2SCH_2CH_2SCH_2CO_2)\cdot H_2O$, $Cu(en)_2\cdot 2ClO_4$, $Cu(en)_2\cdot H_2O\cdot 2X$, and $[Cu(Me_2NCH_2CH_2NMe_2)\cdot 2X]_2$. Analyses of the ligand field and ligand to metal charge-transfer absorptions (LMCT) have been restricted to the mull spectra in order to exploit the structural information that was available from crystallographic studies. Particular attention has been devoted to the characterization of S(thioether) → Cu(II) LMCT. Identification of such absorptions in mixed ligand complexes was facilitated by characterizing the energies of N → Cu(II) and X → Cu(II) LMCT absorptions in the sulfur-free Cu(II) complexes studied. Additional indications of Cu(II)–S interactions were derived from NMR line-broadening and Raman studies. Approximately planar CuS_2N_2, CuS_2Cl_2, and CuS_4 ligand sets exhibit a strong absorption in the 22–26-μm^{-1} energy region which is assigned to $\sigma(S) \rightarrow Cu(II)$ LMCT. The observed variation in energy of this absorption may reflect the relative position of the Cu(II) d vacancy (i.e., ligand-field strength). Relative to the $\sigma(S) \rightarrow Cu(II)$ LMCT absorptions, those assignable in part to $\pi(S) \rightarrow Cu(II)$ LMCT were considerably less intense, red-shifted by ~0.5–0.7 μm^{-1}, and were not well separated in energy from interfering ligand field absorptions. Apparently LMCT absorption originating from the π orbital of thioether is considerably less intense than from the π orbitals of mercaptide.

A variety of studies have indicated that a S(cysteine)–Cu(II) chromophore is responsible for the intense coloration of the blue copper proteins.[2] As a result, the electronic structural nature of Cu(II) interactions with S donor ligands has acquired considerable research interest. Most sulfur ligands either undergo redox reactions with Cu(II) or have interfering optical spectra of their own. Simple mercaptides are instantaneously oxidized by Cu(II), while tertiary mercaptides such as $HSC(CH_3)_2CH_2NH_2$[3a] and $HSC(CH_3)_2CH(NH_2)CO_2H$[3b] react with Cu(II) to form complex $([Cu(I)]_6[Cu(II)]_6\ (ligand)_{12}Cl)$ cluster structures. Because of the availability of well characterized stable Cu(II) complexes with simple thioether ligands, they are an attractive vehicle for initiating an electronic structural investigation of Cu(II)–S bonding. This does not imply that Cu(II)–thioether complexes are appropriate bioinorganic models for the blue copper proteins, one of which (stellacyanin) does not contain any methionine residues.[4]

The study of Cu(II)–thioether bonding, until recently, largely has been restricted to solution equilibria and NMR line-broadening measurements.[5] A number of recent crystallographic studies have elucidated the structural parameters of Cu(II)–thioether bonding in a variety of complexes. These include: $Cu(Me_2NC(=O)CH_2SCH_2C(=O)NMe_2)\cdot 2Cl$,[6] $CuL\cdot 2ClO_4$ (L = a macrocyclic tetrathioether),[7] $Cu(NH_2CH_2CH_2SCH_3)_2\cdot 2ClO_4$,[8] $[Cu(BuSCH_2CH_2SBu)\cdot 2Cl]_2$,[9] and $[CuL'\cdot Cl\cdot ClO_4]_2$ (L′ = 3,4-bis(2-aminoethylthio)toluene).[10] In view of this available structural information, the nature of Cu(II)–thioether bonding now may be probed by electronic-spectral measurements.

We have been able to locate only two prior electronic spectral studies of Cu(II)–thioether complexes. A recent spectral study of Cu(II) complexes with various macrocyclic polythioether ligands was not accompanied by band assignments.[7] Also presented without detailed interpretation were the spectra of Cu(II) complexes with the series of ligands $^-O_2CCH_2S(CH_2CH_2S)_nCH_2CO_2^-$ (*n* = 0, 1, 2).[11]

We report here the measurement and partial assignment of the electronic spectra of $Cu(NH_2CH_2CH_2SCH_3)_2\cdot 2ClO_4$, $[Cu(BuSCH_2CH_2SBu)\cdot 2Cl]_2$, $[Cu(BuSCH_2CH_2SBu)\cdot 2Br]_2$, $Cu(BuSCH_2CH_2SBu)_2\cdot 2ClO_4$, and $Cu(O_2CCH_2SCH_2CH_2SCH_2CO_2)\cdot H_2O$. The molecular structures of the first two complexes are known from crystallographic studies; those of the latter complexes have been established in part by other means. Band assignments were facilitated by accompanying electronic spectral studies of $Cu(en)_2 \cdot 2ClO_4$, $Cu(en)_2 \cdot H_2O \cdot 2X$ (X = Cl, Br), and $[Cu(Me_2NCH_2CH_2NMe_2) \cdot 2X]_2$ (X = Cl, Br).

Experimental Section

Preparation of Complexes. (1) $Cu(NH_2CH_2CH_2NH_2)_2 \cdot 2ClO_4$ precipitated as purple needles from methanolic solutions containing $Cu(ClO_4)_2 \cdot 6H_2O$ and the ligand in a 1:2 molar ratio.[12] Anal. Calcd for $CuH_{16}N_4Cl_2O_8$: Cu, 16.61. Found: Cu, 16.68.

(2) $Cu(NH_2CH_2CH_2NH_2) \cdot H_2O \cdot 2Br$ precipitated as purple-blue crystals from ethanolic solutions containing $CuBr_2$ and the ligand in a 1:2 molar ratio.[12] Anal. Calcd for $CuH_{18}N_4OBr_2$: Cu, 17.57. Found: Cu, 17.60.

(3) $Cu(NH_2CH_2CH_2NH_2)_2 \cdot H_2O \cdot 2Cl$ precipitated as purple-blue crystals from ethanolic solutions containing $CuCl_2$ and the ligand in a 2:1 molar ratio.[12]

(4) $[Cu(Me_2NCH_2CH_2NMe_2) \cdot 2X]_2$, where X = Cl^- and Br^-, were prepared by a published method.[13] Anal. Calcd for $CuC_6H_{16}N_2Br_2$: Cu, 18.71. Found: 18.61. Anal. Calcd for $CuC_6H_{16}N_2Cl_2$: Cu, 25.35. Found: 25.38.

(5) $[CuBBTE \cdot 2Cl]_2$ (BBTE = $BuSCH_2CH_2SBu$) crystallized as green-black needles from solutions of $CuCl_2$ and BBTE in absolute CH_3OH (0.2 M in each reactant). The crystals were collected by filtration and dried under a stream of N_2. The complex melted sharply at 117 °C; it could be recrystallized from dry CH_3CN, CH_2Cl_2, and CH_2ClCH_2Cl. Anal. Calcd for $CuC_{10}H_{22}S_2Cl_2$: C, 35.24; H, 6.51; S, 18.81. Found: C, 35.45; H, 6.67; S, 18.77.

The BBTE ligand was prepared by the reaction of $ClCH_2CH_2Cl$ with 2 equiv of freshly prepared BuS^-Na^+ in absolute CH_3OH. After the CH_3OH was removed by rotoevaporation, water and ether were added to the residue. The ether extract was dried over $MgSO_4$ and concentrated to an oil by rotoevaporation. BBTE was recovered as a viscous colorless liquid that distilled at 70 °C (0.1 mmHg). Anal. Calcd for $C_{10}H_{22}S_2$: C, 58.19; H, 10.74; S, 31.07. Found, C, 58.07; H, 10.66; S, 31.25.

(6) $[CuBBTE \cdot 2Br]_2$ rapidly crystallized as green-black needles (mp 108 °C) from solutions of $CuBr_2$ and BBTE in absolute CH_3OH. Although solutions of the above chloro derivative in dry CH_2Cl_2 were stable for at least 2 weeks at 25 °C, those of $[Cu(BBTE) \cdot 2Br]_2$ gradually turned colorless over a period of several hours. Similar relative stabilities have been observed for the $CuCl_2$ and $CuBr_2$ complexes of $CH_3SCH_2CH_2SCH_3$.[14] Bleaching of simple solvated Cu(II)-bromo species also has been observed.[15] Anal. Calcd for $CuC_{10}H_{22}S_2Br_2$: C, 27.95; H, 5.16; S, 14.92. Found: C, 28.03; H, 5.16; S, 14.92.

(7) $Cu(BBTE)_2 \cdot 2ClO_4$ was prepared by adding a solution of 1.29 g of BBTE in 20 ml of *tert*-amyl alcohol to a solution of 1.09 g of $Cu(ClO_4)_2 \cdot 6H_2O$ in 20 ml of *tert*-amyl alcohol and 5 ml of 2,2-dimethoxypropane. The solution of $Cu(ClO_4)_2 \cdot 6H_2O$ first was allowed to "dehydrate" at 25 °C for 6 h. The product separated as black needles, which were collected by filtration and dried in a stream of N_2. The crystals were not shock sensitive, but *detonated* upon heating to ~118 °C. The product could be recrystallized without apparent decomposition by allowing its solutions in either 1-octanol or 1-octanol/CH_2Cl_2 to evaporate slowly. Anal. Calcd for $CuC_{20}H_{44}S_4O_8Cl_2$: C, 35.57; H, 6.57; S, 18.89. Found: C, 35.68; H, 6.50; S, 18.87.

(8) $CuEDDA \cdot H_2O$, MnEDDA, and $NiEDDA \cdot 2H_2O$ (EDDA = $^-O_2CCH_2SCH_2CH_2SCH_2CO_2^-$) were prepared by published methods[11] and recrystallized from H_2O as pale green needles, white microcrystals, and deep green prisms, respectively. Anal. Calcd for $CuC_6H_{10}O_5S_2$: C, 24.87; H, 3.48; S, 22.10. Found: C, 25.23; H, 3.48; S, 21.92. Anal. Calcd for $NiC_6H_{12}O_6S_2$: C, 23.78; H, 3.98. Found: C, 24.09; H, 3.95. Anal. Calcd for $MnC_6H_8O_4S_2$: C, 27.38; H, 3.06. Found: C, 26.81; H, 3.13.

The free ligand (H_2EDDA) was prepared by a published method from $ClCH_2CH_2Cl$ and $HSCH_2CO_2H$.[16] The white crystalline material melted at 108–109 °C after recrystallization from ethyl acetate (lit. 108–109 °C).[16] Anal. Calcd for $C_6H_{10}O_4S_2$: C, 34.27; H, 4.53. Found: C, 34.27; H, 4.79.

Spectral Measurements. (1) Electronic spectra were recorded on a Cary Model 14 spectrophotometer. Solid state spectra were obtained for the complexes dispersed in mineral oil mulls contained between quartz disks. Mull spectra at 80 K were made using an evacuable Dewar of standard design. The combination of the quartz disks and mineral oil films was spectrally transparent over the 210–800 nm range.

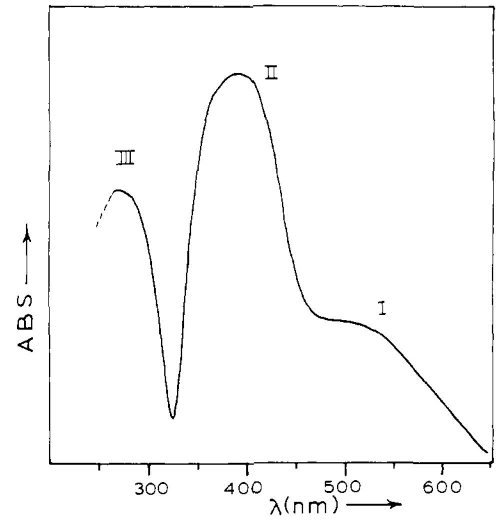

Figure 1. Mull spectra of $Cu(NH_2CH_2CH_2SCH_3)_2 \cdot 2ClO_4$ at 80 K.

(2) Raman spectra were recorded on a Cary Model 82 spectrophotometer using the 4880-Å line of a Coherent Radiation Model 52 argon/krypton laser as the excitation source. Disks of the neat compounds were prepared with a standard KBr die and rotated at ~3000 rpm in order to prevent photodecomposition.

(3) Infrared spectra were recorded on a Perkin-Elmer Model 225 spectrophotometer using both the KBr pellet and mineral oil mull techniques.

(4) ^1H NMR spectra at ~32 °C were recorded on a Varian Model T-60 spectrometer in either D_2O or CD_2Cl_2. H_2EDDA was neutralized with an appropriate amount of a NaOD solution obtained from Merck and Co., Rahway, N. J. For the line-broadening studies, $CuCl_2$ was added as a solid to the BBTE/CD_2Cl_2 solutions, and as small aliquots of concentrated $CuCl_2/D_2O$ solutions to the EDDA/D_2O solutions.

Electronic Spectral Results and Discussion

The electronic spectral results are summarized in Table I and are discussed below for each compound studied.

(1) $Cu(NH_2CH_2CH_2SCH_3)_2 \cdot 2ClO_4$. The molecular structure of this discrete monomeric complex has been described elsewhere.[8] Briefly, the tetragonal $CuN_2S_2O_2$ ligand set consists of a trans-planar N_2S_2 unit and two relatively long bonds to the weakly bound ClO_4^- groups. The observed Cu–N, Cu–S, and Cu–O bond distances were 1.977, 2.366, and 2.599 Å, respectively. Mull spectra of this complex at 80 K are presented in Figure 1; spectra obtained at 298 K essentially were identical in appearance.

The lowest energy absorptions of free primary amines and of free alkyl thioethers involve excitation of their lone pair(s), and occur at ~47 000 and ~44 000 cm^{-1}, respectively.[17] Since complexation by Cu(II) should stabilize the lone pairs of $NH_2CH_2CH_2SCH_3$, ligand-localized transitions are not expected at wavelengths longer than ~230 nm.

Electronic spectra of the bis-Cu(II) complexes of $NH_2CH_2CH_2NH_2$(en) and its alkyl derivatives have been studied in detail by others.[18,19] The parent $Cu(en)_2^{2+}$ complex exhibited $\sigma(N) \rightarrow Cu(II)$ LMCT at ~240 nm; alkylation of the ligand resulted in a systematic red shift of this absorption. An observed correlation between the position of this band and the estimated first ionization potential (IP) of the free diamines supported a LMCT assignment.[18] Mull spectra (Table I) of $Cu(en)_2 \cdot 2ClO_4$, which has a tetragonal CuN_4O_2 ligand set,[12] consist of a ligand field absorption at ~520 nm along with a single UV absorption at ~250 nm. Thus, the above LMCT spectra of $Cu(en)_2^{2+}$ complexes are not perturbed by apical Cu(II)–ClO_4 interactions. By analogy, then, we assign the

Table I. Summary of Spectral Results and Assignments

	CH_2Cl_2, 298 K			Mull, 80 K		
Complex	λ, nm	μm^{-1}	ε	λ (nm)	μm^{-1}	Assignment
$Cu(NH_2CH_2CH_2SCH_3)_2 \cdot 2ClO_4$				~550	1.82	LF + $\pi(S) \rightarrow d_{x^2-y^2}$
				~390	2.56	$\sigma(S) \rightarrow d_{x^2-y^2}$
				~270	3.70	$\sigma(N) \rightarrow d_{x^2-y^2}$
$Cu(BBTE)_2 \cdot 2ClO_4$	~570	1.75	1 050	~565	1.77	$\pi(S) \rightarrow d_{x^2-y^2}$ + LF(?)
	440	2.27	11 240	442	2.27	$\sigma(S) \rightarrow d_{x^2-y^2}$
	346	2.89	790	~340	2.94	
	273	3.66	2 400	277	3.61	
	227	4.40	2 000	~228	4.38	
$[Cu(BBTE) \cdot 2Cl]_2$	750	1.33	460	~800	1.25	LF
				~570 (sh)	1.75	$\pi(S) \rightarrow d_{x^2-y^2}$
	449	2.23	2 740	448	2.23	$\sigma(S) \rightarrow d_{x^2-y^2}$
	363	2.80	6 380	387	2.59	$Cl \rightarrow d_{x^2-y^2}$
	272	3.68	3 830	292	3.42	$Cl \rightarrow d_{x^2-y^2}$
				~240	4.17	$Cl \rightarrow d_{x^2-y^2}$
				215	4.65	thioether (Rydberg)
$[Cu(Me_2NCH_2CH_2NMe_2) \cdot 2Cl]_2$	~850 (sh)	1.18	~80			
	690	1.45	145	~675	1.48	LF
	393	2.55	1 020	370	2.70	$Cl \rightarrow d_{x^2-y^2}$
	294	3.40	6 980	315	3.17	$Cl \rightarrow d_{x^2-y^2}$
				~275	3.63	$\sigma(N) \rightarrow d_{x^2-y^2}$ + Cl(apical) $\rightarrow d_{x^2-y^2}$
	216	4.63	1 800	212	4.72	$Cl \rightarrow d_{x^2-y^2}$
$Cu(en)_2 \cdot H_2O \cdot 2Cl$				~535	1.87	LF
				~280	3.57	Cl(apical) $\rightarrow d_{x^2-y^2}$
				~235	4.25	$\sigma(N) \rightarrow d_{x^2-y^2}$
$Cu(en)_2 \cdot 2ClO_4$				~520	1.92	LF
				~250	4.00	$\sigma(N) \rightarrow d_{x^2-y^2}$
$Cu(en)_2 \cdot H_2O \cdot 2Br$				~530	1.89	LF
				~300	3.33	Br(apical) $\rightarrow d_{x^2-y^2}$
				~230	4.35	$\sigma(N) \rightarrow d_{x^2-y^2}$
$[Cu(Me_2NCH_2CH_2NMe_2) \cdot 2Br]_2$	~900 (sh)	1.12	~120			
	710	1.42	240	~655	1.53	LF
	505	1.96	596	~490	2.04	$Br \rightarrow d_{x^2-y^2}$
	~410 (sh)	2.44	2 000	~390	2.56	$Br \rightarrow d_{x^2-y^2}$
	327	3.06	6 540	~340	2.94	$Br \rightarrow d_{x^2-y^2}$
				~280	3.57	$\sigma(N) \rightarrow d_{x^2-y^2}$
	228	4.39	2 330	228	4.39	
$[Cu(BBTE) \cdot 2Br]_2$				~800	1.25	LF
				544	1.84	$Br \rightarrow d_{x^2-y^2}$
				~420	2.38	$\sigma(S) \rightarrow d_{x^2-y^2}$ + $Br \rightarrow d_{x^2-y^2}$
				358 (sh)	2.79	$Br \rightarrow d_{x^2-y^2}$
				310	3.23	$Br \rightarrow d_{x^2-y^2}$
				260	3.85	
				236	4.24	
$Cu(EDDA) \cdot H_2O$	~780	1.28	62[a]	~800	1.25[b]	LF
	325	3.08	2 600[a]	340	2.94[b]	$\sigma(S) \rightarrow Cu$
	267	3.65	4 000[a]	275	3.64[b]	$CO_2 \rightarrow Cu$

[a] H_2O at 298 K. [b] Reflectance at 298 K.

absorption at ~270 nm (band III) of $Cu(NH_2CH_2CH_2SCH_3)_2 \cdot 2ClO_4$ to $\sigma(N) \rightarrow Cu(II)$ LMCT. We assume that the first IP of the NH_2CH_2-ligand fragment may be approximated by the value of 78 240 cm^{-1} reported for CH_3NH_2, and the first IP of the CH_3SCH_2-ligand fragment may be approximated by the value of 70 400 cm^{-1} observed for CH_3SCH_3.[14] On this basis, we estimate that $\sigma(S) \rightarrow Cu(II)$ LMCT should be red shifted ~8000 cm^{-1} relative to $\sigma(N) \rightarrow Cu(II)$ LMCT. The intense absorption at ~390 nm (band II) is appropriate in energy for $\sigma(S) \rightarrow Cu(II)$ LMCT; the energy separation between bands II and III is ~11 400 cm^{-1}. These results indicate that the thioether donor has a considerably lower optical electronegativity than the amine donor, and are consistent with estimates derived from the spectra of Ir(III)- and Ir(IV)-thioether complexes.[20,21]

Other workers have observed that the ligand field strength of thioether is greater than that of H_2O, but less than those of pyridine and NH_3.[20,22] The trans-planar CuN_2O_2 ligand sets of $Cu(amino\ acid)_2$ complexes result in ligand-field absorptions at ~600 nm;[23] this λ_{max} is not shifted drastically by additional (apical) ligation. The above results indicate that the broad absorption roughly centered at 550 nm (band I) is appropriate in energy for the ligand-field absorptions of the *trans*-$CuN_2S_2O_2$ ligand set. The nearby intense $\sigma(S) \rightarrow Cu(II)$ LMCT absorption at ~390 nm may perturb band I in two ways. First, intensity enhancement of band I may be expected from the usual intensity "borrowing" mechanisms. Second, a $\pi(S) \rightarrow Cu(II)$ LMCT absorption may contribute to the intensity of band I. The π-symmetry lone pair of thioether should, relative to the σ lone pair, be less stabilized by complexation and have less overlap with the Cu(II) orbitals. Thus, $\pi(S) \rightarrow Cu(II)$ LMCT should be weaker and red shifted relative to $\sigma(S) \rightarrow Cu(II)$ LMCT. The actual spectroscopic importance of the π symmetry lone pair of thioether is difficult

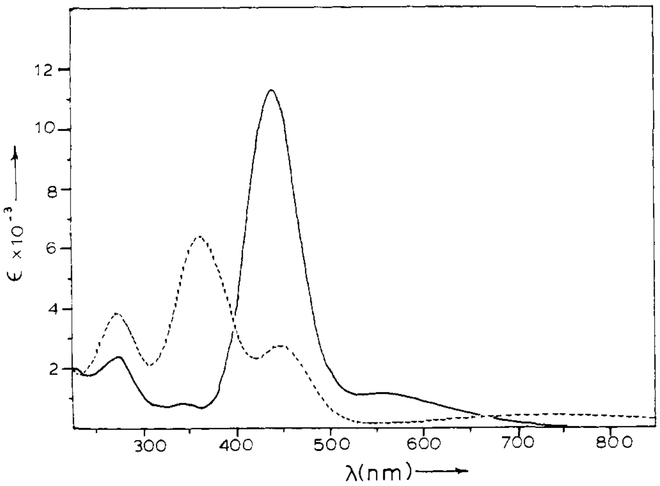

Figure 2. Spectra of Cu(BBTE)$_2$·2ClO$_4$ (—) and [CuBBTE·2Cl]$_2$ (- - - -) in CH$_2$Cl$_2$ at 298 K.

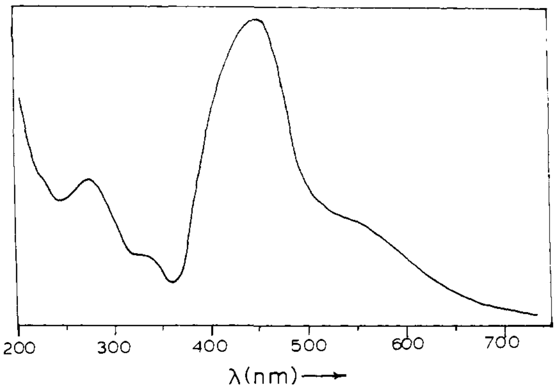

Figure 3. Mull spectra of Cu(BBTE)$_2$·2ClO$_4$ at 80 K.

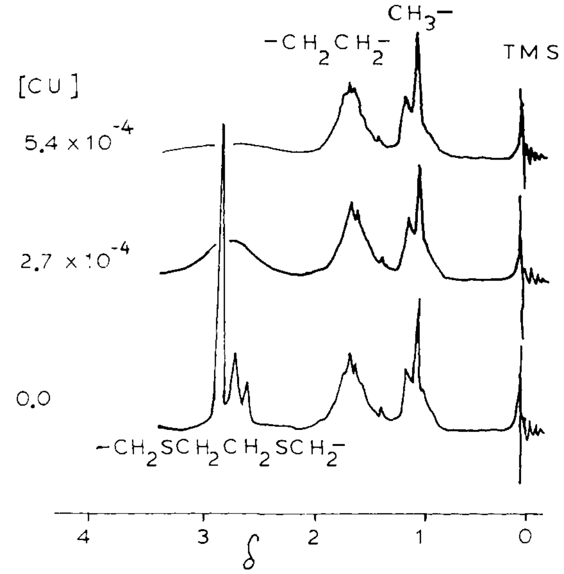

Figure 4. Effect of added CuCl$_2$ on the NMR spectra of BBTE in CD$_2$Cl$_2$ at ~305 K.

to establish. The observed spectrochemical ordering[20,22] of NH$_3$ > R$_2$S > H$_2$O > F$^-$ indicates R$_2$S is intermediate between NH$_3$ (σ bonding only) and H$_2$O (σ bonding plus reduced ligand field attributable to one filled π orbital).

Reliable extinction coefficients could not be obtained for bands I–III. The complex was essentially insoluble in poorly ligating solvents such as CH$_2$Cl$_2$. Although this dark red-purple complex was readily soluble in CH$_3$CN, CH$_3$C(=O)-CH$_3$, DMF, and other polar organic compounds, the resulting blue solutions implied that dissolution was accompanied by a change in coordination structure. Solutions in CH$_3$NO$_2$ (UV cutoff ~380 nm) initially were red-purple, but noticeably faded upon standing.

As most sulfur-containing ligands either undergo redox reactions with Cu(II) or have interfering electronic spectra of their own, only limited spectral comparisons can be made between Cu(NH$_2$CH$_2$CH$_2$SCH$_3$)$_2$·2ClO$_4$ and other C(II) complexes of sulfur donor ligands. Another complex having a planar N$_2$S$_2$ ligand set is the Cu(II) complex of diacetyl bis(thiosemicarbazone).[24] The electronic spectra of this complex includes an intense band (ϵ 5800) at 480 nm, which we consider likely to originate from σ(S) → Cu(II) LMCT. Finally, we have characterized a cluster complex which contains approximately planar *cis*-Cu(II)N$_2$S$_2$ units (the ligand is $^-$SC(CH$_3$)$_2$CH$_2$NH$_2$).[3] Additional complexation of the mercaptide by two Cu(I) species suggests the sulfur donors have a chemical character intermediate between that of mercaptide and thioether. The optical spectra of this cluster complex are dominated by an intense absorption ($\epsilon \simeq 3400$ *per* Cu(II)) at ~520 nm. Our justification for drawing spectral comparisons to these latter two complexes is the observation by others that σ(S) → Co(III) LMCT occurred at approximately the same energies for a variety of S donor ligands.[25]

2. Cu(BBTE)$_2$·2ClO$_4$ (BBTE = BuSCH$_2$CH$_2$SBu). Preliminary studies[26] of this complex show that it crystallizes from *n*-octanol/CH$_2$Cl$_2$ mixtures as dark brown rectangular plates in the space group $P2_1/_a$ with a = 24.83, b = 17.44, and c = 25.47 Å, and β = 117.8°. Based upon the similarity between the spectra of this complex (Figures 2 and 3) and those reported over the 300–700 nm range for a Cu(II)-macrocyclic tetrathioether complex of known structure,[7] it would appear that both materials have comparable equatorial CuS$_4$ ligand sets. The similarity of the mull and solution spectra of Cu(BBTE)$_2$·2ClO$_4$ indicates that the solution and solid state coordination structures are not grossly different. That some degree of Cu(II)–BBTE interaction persists in solution is evidenced by our NMR line-broadening studies (Figure 4). Addition of small amounts of CuCl$_2$ to solutions of BBTE (0.1N) in CD$_2$Cl$_2$ caused selective broadening of the eight methylene hydrogens adjacent to the S donors. Under these conditions, the NMR adsorptions of the terminal -CH$_2$CH$_2$CH$_3$ fragments remained essentially unchanged.

The spectra of Cu(BBTE)$_2$·2ClO$_4$ are dominated by the intense (ϵ 11 240) absorption at 440 nm. Based upon our analysis of the Cu(NH$_2$CH$_2$CH$_2$SCH$_3$)$_2$·2ClO$_4$ spectra ($\lambda_{max} \simeq 390$), this intense absorption of Cu(BBTE)$_2$·2ClO$_4$ may be assigned to σ(S) → Cu(II) LMCT. If the symmetry of the presumed CuS$_4$ ligand set may be approximated by D_{4h}, a single orbitally allowed charge-transfer transition, $^2B_{1g} \rightarrow {}^2E_u$, is expected.[19] The large intensity of the 440-nm absorption is consistent with it being the expected allowed transition, having essentially $\sigma \rightarrow \sigma^*$ character.

As noted in the discussion of the Cu(NH$_2$CH$_2$CH$_2$S-CH$_3$)$_2$·2ClO$_4$ spectra, thioethers lie between oxygen and nitrogen ligands in the spectrochemical series. Since the ligand-field band of Cu(CH$_3$OCH$_2$CH$_2$OCH$_3$)$_2$·2ClO$_4$ was observed at ~800 nm,[27] that expected for Cu(BBTE)$_2$·2ClO$_4$ should be well removed toward higher energy. Thus, ligand-field excitations likely contribute to the lowest energy optical absorption of Cu(BBTE)$_2$·2ClO$_4$ at ~570 nm. The relatively high intensity of the 570-nm band (ϵ ~1050) may result from intensity borrowing from the σ(S) → Cu(II) LMCT absorption at 440 nm and/or a contribution from π(S) → Cu(II) LMCT. These hypotheses imply that the intensity of the ligand-field bands should decrease if they are well separated in

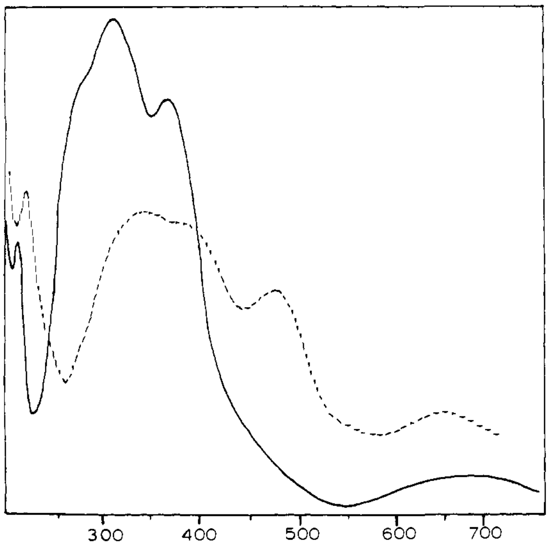

Figure 5. Mull spectra of $[Cu(Me_2NCH_2CH_2NMe_2)\cdot 2Cl]_2$ (—) and $[Cu(Me_2NCH_2CH_2NMe_2)\cdot 2Br]_2$ (- - - -) at 80 K.

energy from the σ,π(S) → Cu(II) LMCT absorptions. Such spectral behavior has been observed for the $Cu(O_2CCH_2SCH_2CH_2SCH_2CO_2)\cdot H_2O$ complex (vide infra). Alternatively, the broad absorption at ~570 nm may be dominated by π(S) → Cu(II) LMCT and obscure weaker LF absorptions at somewhat lower energy. The difference in energy (~0.3 μm^{-1}) between σ(S) → Cu(II) LMCT in $Cu(NH_2CH_2SCH_3)_2\cdot 2ClO_4$ and $Cu(BBTE)_2\cdot 2ClO_4$ may arise from a roughly comparable difference in energy between their respective LF absorptions (vide infra).

The high-energy absorptions visible in both the mull spectra and the solution spectra at approximately 340, 280, and 230 nm cannot be assigned with confidence until the molecular structure of $Cu(\mathbf{BBTE})_2\cdot 2ClO_4$ has been established. For example, a polynuclear structure would permit both apical and equatorial ligation by thioether. By analogy to the results described below for Cl^- and Br^-, the LMCT absorptions of apical thioether ligands should be both weaker and blue shifted relative to those of equatorial thioethers at 440 and possibly 570 nm. As noted above, the Rydberg transitions of BBTE should appear at no longer wavelengths than 230 nm. Also, we have carefully eliminated any possible attribution of "extraneous" absorption bands to either impurities or decomposition products. Possibly Cu(II) localized transitions (i.e., 3d → 4p) may appear in the UV region; absorptions of this type have been identified in the UV spectra[28] of $PtCl_4^{2-}$. Alternatively, ClO_4 → Cu(II) LMCT might be involved.

We wish to emphasize that the identification of Cu(II) Rydberg transitions in these complexes is a subject for future research, and not an assignment for the high-energy bands in Figures 2 and 3. Finally, the absence of low-energy (λ > 260 nm) absorption bands in the spectra (not shown) of Cu(I)–BBTE complexes indicates that the absorptions at ~277 and ~340 nm exhibited by $Cu(BBTE)_2\cdot 2ClO_4$ are not attributable to metal → ligand CT.

3. $[Cu(BBTE)\cdot 2Cl]_2$. Crystallographic studies of this complex show that it is a μ-dichloro-bridged dimer.[9] The CuS_2Cl_3 ligand set consists of a cis-puckered S_2Cl_2 equatorial unit along with apical ligation by a weakly bound Cl. Observed bond distances within the ligand set were: Cu-S (2.37 Å), Cu-S (2.31 Å), Cu-Cl (2.24 Å), Cu-Cl (2.27 Å), and apical Cu-Cl (2.83 Å). Charge-transfer absorptions a priori may originate from the σ and π thioether orbitals as well as from the σ, π, and nonbonding orbitals of both types of Cl. We adopt an empirical approach to this potentially complex electronic structural situation. The structural similarity between $[Cu(BBTE)\cdot 2Cl]_2$ and $[Cu(Me_2NCH_2CH_2NMe_2)\cdot 2Cl]_2$[29] allows spectral comparisons to be made between the respective CuS_2Cl_3 and CuN_2Cl_3 ligand sets.

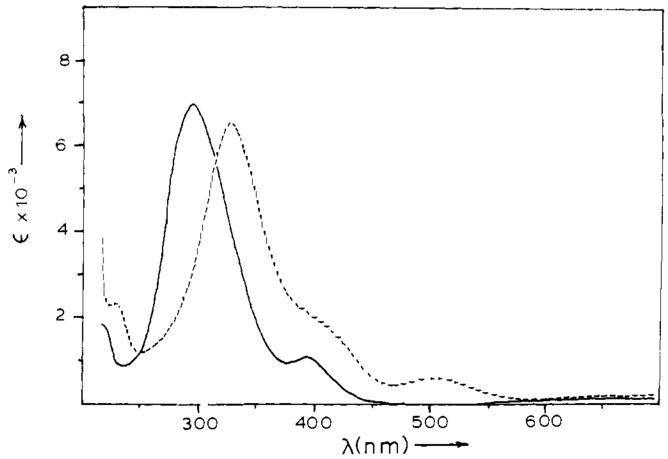

Figure 6. Spectra of $[Cu(Me_2NCH_2CH_2NMe_2)\cdot 2Cl]_2$ (—) and $[Cu(Me_2NCH_2CH_2NMe_2)\cdot 2Br]_2$ (- - - -) in CH_2Cl_2 at 298 K.

We first consider the electronic spectral differences between equatorial and apical Cl. Mull spectra at ~80 K of $Cu(en)_2\cdot 2ClO_4$ and $Cu(en)_2\cdot 2Cl\cdot H_2O$ are listed in Table I. Crystallographic studies show that the complexes have comparable CuN_4 equatorial bonding.[12] Replacement of the two apical ClO_4 ligands by apical Cl and H_2O ligands gives rise to an electronic absorption (shoulder) at ~280 nm. Since this absorption is not exhibited by aqueous $Cu(en)_2^{2+}$, it may be assigned to Cl(apical) → Cu(II) LMCT.

The relative weakness of this band is expected because the Cu(II) d vacancy $(x^2 - y^2)$ is equatorially directed and has poor overlap with the apical Cl orbitals. Thus, the apical ligands of the Cu(II) complexes studied here are expected to contribute only weak spectral features at relatively high energies. Such absorptions should in general be dominated by those associated with the equatorial ligation. Both of the above bisethylenediamine Cu(II) complexes exhibit σ(N) → Cu(II) LMCT at ~250 nm. Complexes of Cu(II) with $NH_2CH_2CH_2NEt_2$ and related ligands exhibit absorptions at ~244 and ~283 nm which have been attributed to σ(N) → Cu(II) LMCT involving the primary and tertiary amine ligand fragments, respectively.[19] Thus, the shoulder at ~275 nm in the mull spectra of $[Cu(Me_2NCH_2CH_2NMe_2)\cdot 2Cl]_2$ (Figure 5) is appropriate in energy for both Cl(apical) → Cu(II) and σ(N) → Cu(II) LMCT. The remaining high-energy absorptions at ~370, ~315, and ~212 nm bear a close resemblance to the spectra of $CuCl_4^{2-}$, a somewhat flattened pseudotetrahedral species.[30,31] On this basis, the above three bands may be assigned to Cl → Cu(II) LMCT. With the exception of the shoulder at ~275 nm, the solution (Figure 6) and mull spectra (Figure 5) of $[Cu(Me_2NCH_2CH_2NMe_2)\cdot 2Cl]_2$ exhibit the same absorption maxima; the relative peak heights in the mull spectra bear only a superficial resemblance to the true values. Our focus is, however, limited to the spectra of mulled solids for which structural information is available.

We assume that the equatorial Cl → Cu(II) LMCT bands roughly are invariant to the change from the diamine to the bisthioether ligation. However, a modest red shift of the σ(Cl) → Cu(II) LMCT absorption may be expected when the ligation is changed from diamine to bisthioether. As evidenced by the positions of the LF bands of $[Cu(Me_2NCH_2CH_2NMe_2)\cdot 2Cl]_2$ and $[Cu(BBTE)\cdot 2Cl]_2$ (Table I), the d vacancy is ~0.2 μm^{-1} lower in energy in the latter complex. A comparison of LMCT originating from the π- and nonbonding Cl orbitals in

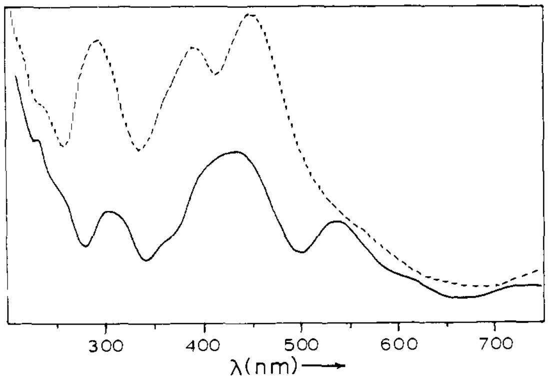

Figure 7. Mull spectra of $[CuBBTE{\cdot}2Br]_2$ (—) and $[CuBBTE{\cdot}2Cl]_2$ (- - - -) at 80 K.

both complexes is considerably more difficult. The energies of these latter absorptions also are sensitive to the extent to which the Cl valence orbitals are split in the above complexes. On this basis, the absorptions of $[Cu(BBTE){\cdot}2Cl]_2$ at ~387, ~292, and either 240 or 215 nm (Figure 7) may be assigned to Cl → Cu(II) LMCT. One of the latter high-energy absorptions may be due to an electronic transition localized on the thioether ligand.[17] By difference, the remaining strong absorption at ~448 nm (2.23 μm^{-1}) and the shoulder at ~570 nm may be assigned to σ(S) → Cu(II) and π(S) → Cu(II) LMCT, respectively. Consistent with this assignment is the blue shift of σ(S) → Cu(II) LMCT to 390 nm (2.56 μm^{-1}) that was observed for $Cu(NH_2CH_2CH_2SCH_3)_2{\cdot}2ClO_4$. This shift may reflect in part the larger ligand field of this latter complex. Our assignments of σ(S) → Cu(II) and Cl → Cu(II) LMCT yield an energy difference of ~2500 cm^{-1} for their respective absorptions at ~448 and ~387 nm. These results imply that Cl and thioether have closely similar optical electronegativities, and are supported by other studies.[20]

The ligand-field absorptions of the CuN_2Cl_3 and CuS_2Cl_3 chromophores occur in the 675–800 nm region, and reflect the low spectrochemical position[22] of Cl^-. The resulting energy separation between the LF and σ(S) → Cu(II) LMCT absorptions provides a spectral window for the suggested π(S) → Cu(II) LMCT absorption. The shoulder observed in the mull spectra (80 K) at ~570 nm is not visible in the solution spectra at 298 K; whether this results from differences in coordination structures or differences in spectral resolution is not known.

4. $[Cu(BBTE){\cdot}2Br]_2$. Since $[Cu(Me_2NCH_2CH_2NMe_2){\cdot}2X]_2$ (X = Br, Cl) and $[Cu(BBTE){\cdot}2Cl]_2$ are dimeric complexes,[9,29] it appears likely that $[Cu(BBTE){\cdot}2Br]_2$ has a comparable dimeric structure. This assumption has not yet been experimentally verified, but has little significance for our purposes. An approximate correspondence between the solution spectra (Figure 6) of $[Cu(Me_2NCH_2CH_2Me_2){\cdot}2Br]_2$ and those of $CuBr_4^{2-}$ [15] indicate that the bands of the former complex are dominated by its equatorial Cu–Br bonding.

Mull spectra of $Cu(en)_2{\cdot}H_2O{\cdot}2Br$, which has a CuN_4BrO ligand set,[12] indicate that apical Br → Cu(II) LMCT should occur at ~300 nm. Due to the instability of $[Cu(BBTE){\cdot}2Br]_2$ in CH_2Cl_2 solution, only mull spectra (Figure 7) were obtained. These spectra also appear to be dominated by Br → Cu(II) LMCT absorptions, and are not a promising vehicle for investigating S → Cu(II) LMCT. Based upon our studies of other Cu(II) complexes, the broad asymmetric absorption centered at ~430 nm probably is in part composed of σ(S) → Cu(II) LMCT.

5. $Cu(EDDA){\cdot}H_2O$ (EDDA = $^-O_2CCH_2SCH_2CH_2SCH_2CO_2^-$). The reflectance and solution spectra of $Cu(EDDA){\cdot}H_2O$ at 298 K are summarized in Table I and closely correspond to published values obtained for this complex formulated as a dihydrate.[11] Both of the fairly intense bands were attributed to CT absorptions; their origins were not specified further. Since the magnetic moment (2.19 μ_B, 298 K) of the dihydrate was not abnormally low,[11] UV absorptions originating from dimeric Cu(II)–carboxylate units cannot be present. Moreover, the broad band attributable to carboxylate → Cu(II) LMCT in Cu(II) acetate occurs at ~250–280 nm.[33] In view of these considerations and the results presented for complexes **1–3** (vide supra), σ(S) → Cu(II) LMCT is a probable origin of the intense absorption at 340 nm (Figure 8).

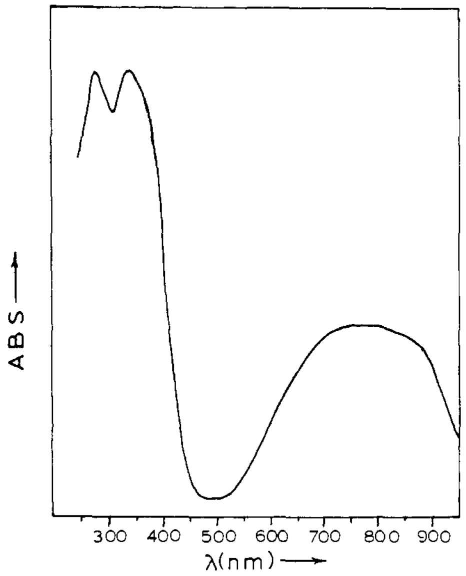

Figure 8. Reflectance spectra of $CuEDDA{\cdot}H_2O$ at 298 K.

Since crystallographic studies have shown that EDDA is a tetradentate S_2O_2 donor in the pseudooctahedral $Ni(EDDA){\cdot}2H_2O$ complex,[34] precedent exists for expecting a ligand role of thioether in the Cu(II) complex. Our NMR studies (not shown) revealed that small amounts of Cu(II) effectively broadened the resonances of all methylene ligand protons. However, since EDDA lacks protons which are remote from potential donor sites and which may serve as internal references, these results are not as convincing as those for BBTE (Figure 4). Published NMR line-broadening studies of $EtSCH_2CO_2^-/Cu(II)/D_2O$ mixtures[35] demonstrated that the ligand is a S donor toward Cu(II). These results support a tetradentate role of EDDA towards Cu(II). Also, this conclusion is supported by our Raman studies (Figure 9) of free $H_2{\cdot}EDDA$ and its Ni(II), Mn(II), and Cu(II) complexes. Since EDDA is a 1,2-disubstituted ethane, its binding to Ni(II), as evidenced by x-ray crystallographic results,[34] necessarily involves a change in ligand conformation from predominantly trans to exclusively gauche. Published studies showed that the C–S mode(s) of *trans*-$RSCH_2CH_2SR$ (R = H, D, CH_3) were strongly Raman active, and appeared in the 680–750-cm^{-1} region.[36] The C–S mode(s) of the gauche isomers appeared in the 630–680-cm^{-1} region. The Raman spectra of H_2EDDA include an intense band at 747 cm^{-1} that we attribute to the C–S mode of the trans conformation; two less intense bands at 661 and 679 cm^{-1} may be attributed to the presence of the gauche isomer. Upon complexation to Ni(II), the absorption at 747 cm^{-1} vanished; the remaining absorptions at 658 (strong) and 670 cm^{-1} (weaker) are attributed to C–S modes of gauche EDDA. Although the crystallographic details of the MnEDDA structure are not known, a similar band pattern at 649 (strong) and 676 cm^{-1} (weaker) indicates that the ligand conformation is gauche. Probably analogous absorptions are exhibited by $Cu(EDDA){\cdot}H_2O$ at 649 (strong) and 675 cm^{-1} (weaker), *and* at 695 (strong) and

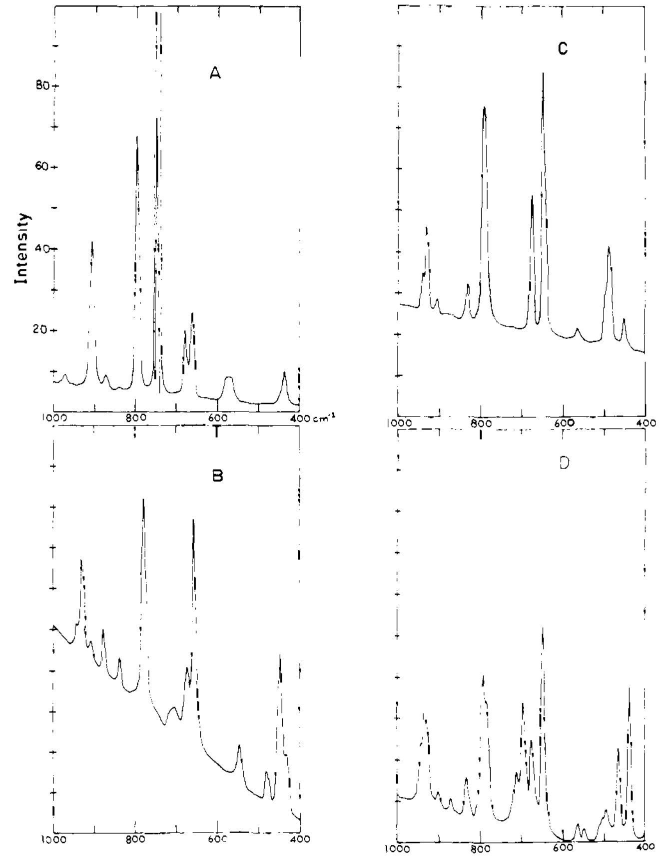

Figure 9. Raman spectra of H_2EDDA (A), $NiEDDA{\cdot}2H_2O$ (B), MnEDDA (C), and $CuEDDA{\cdot}H_2O$ (D).

710 cm^{-1} (weaker). Our interpretation of these results is that two types of crystallographically distinct EDDA are present; the conformation of at least one of them is gauche.

Our assignment of the electronic absorption at ~340 nm to σ(S) → Cu(II) LMCT thus is consistent with the probable tetradentate role of EDDA towards Cu(II). Since the LF absorptions of this complex (~800 nm) are well removed toward lower energy, a wide spectral window is provided for the π(S) → Cu(II) absorption. It was not located. We conclude that for thioether ligands, π(S) → Cu(II) LMCT is either relatively weak or absent.

Conclusions

Our results establish that equatorial Cu(II)–thioether bonding gives rise to an intense σ(S) → Cu(II) charge-transfer electronic transition in the 340–450-nm spectral region. The energy of this absorption for various Cu(II) complexes roughly correlates with the energy of the Cu(II) ligand-field absorptions. Coordination geometries and ligand donor sets, which raise the energy of the Cu(II) d vacancy, also cause a blue shift in the position of the σ(S) → Cu(II) LMCT absorption.

We have not observed intense electronic transitions of the type π(S) → Cu(II). This result is in harmony with the relatively high ligand-field strength of thioether. Thioether acts like a simple σ-donor ligand; it does not exhibit the multiple CT absorptions and weak ligand-field attributable to the lone pairs of Cl^-, even though both ligands have similar optical electronegativities.[20] Evidently, the π symmetry lone pair of ligated thioether does not interact strongly with Cu(II) d orbitals, at least in complexes of tetragonal symmetry. We should note that this inference may not apply to mercaptide ligands, which possess two π symmetry lone pairs.

We have tentatively identified a π(S) → Cu(II) LMCT transition only for the complex $[Cu(BBTE){\cdot}2Cl]_2$; the rather low symmetry of this complex may contribute to a higher transition intensity. This assignment leads to the inference that interactions within the cis-pseudoplanar CuS_2Cl_2 equatorial ligand set result in an energy difference of ~4800 cm^{-1} between the σ and π sulfur orbitals. Comparable splittings of ~3000 cm^{-1} have been suggested for the flattened pseudotetrahedral CuN_3S(mercaptide) unit thought to be the chromophore of the blue copper proteins.[2a,b] Spectral studies of the pseudotetrahedral $Co[SC(CH_3)_2CH_2NH_2]_2$ complex[32] indicate that the σ and π orbitals of the mercaptide sulfur have been split by ~8000 cm^{-1}.

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