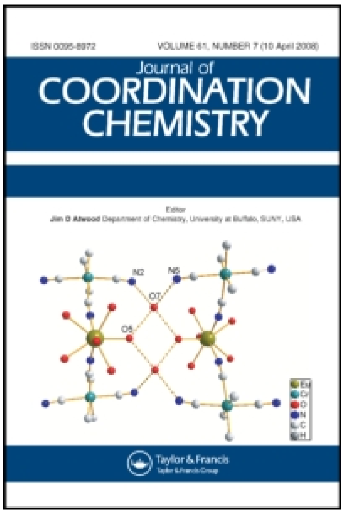

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SPECTROSCOPIC and REDOX BEHAVIOUR OF SOME COPPER(II) - THIOETHER COMPLEXES

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The features of electronic spectra and redox chemistry of a number of Cu(II)-thioether complexes have been examined. The origin of the intense absorption in the region around 14,000–16,000 cm^{-1} is attributed to $(\pi)S \rightarrow d(Cu^{2+})$ CTB, that obscures the less intense *d-d* (Cu^{2+}) band. The relationship between spectral characteristics and redox potentials of $CuL^{2+/+}$ couples values is discussed.

KEYWORDS: copper(II)-thioether complexes, redox-potentials.

INTRODUCTION

The puzzling spectral and redox behaviour of blue copper proteins has stimulated efforts to mimic these active sites with synthetic copper-thioether complexes. The growing interest in biomimetic chemistry of blue copper proteins has promoted the synthesis and physico-chemical studies of several groups of copper-thioether complexes.[1–10] The authors have attempted to model spectral and redox properties of 'blue' copper mainly by tetrathia- (CuS_4), dithiadiamino (aliphatic, $CuS_2N_2{}^a$, heterocyclic $CuS_2N_2{}^h$) and different polythiacontaining pentadentate Cu(II) complexes. Such donor sets resemble the composition of the cupredoxines and mimic, with different degrees of success, the unique spectral features and high redox potential values $CuL^{2+/+}$ of blue copper sites.

Despite considerable progress in the preparation of different blue copper protein models much less success has been achieved in understanding the origin of unusual physico-chemical properties of those proteins. Moreover, the nature of the intense band in the region around 14,000–16,000 cm^{-1} is still under discussion and causes controversy in the literature.[1,8,11–15] The redox behaviour of model copper complexes is much clearer.[10,16–21] The high values of redox potentials $CuL^{2+/+}$, shown by blue copper proteins and their synthetic model complexes are generally attributed to the presence of copper – sulfur coordination in which in such systems. But the relationship between ligand structure and the values of the redox potentials' $CuL^{2+/+}$ is not clear yet. The purpose of this paper is to critically overview some recent data reported for blue copper protein biomimetic model complexes and to

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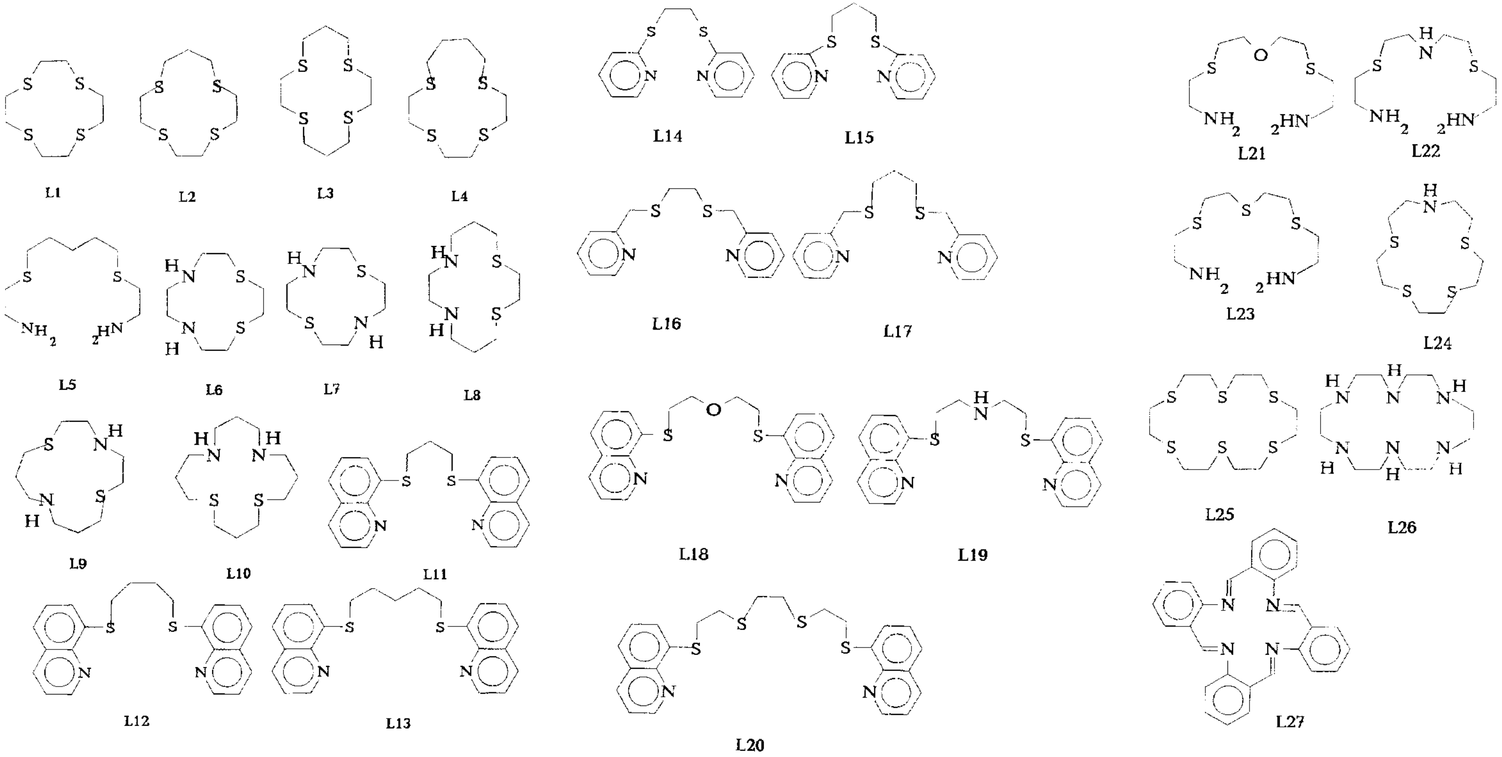

Figure 1 The ligands treated in this paper.

elucidate the influence of ligand structure on their electronic spectra and redox potentials.

ELECTRONIC SPECTRA OF POLYTHIACOPPER(II) COMPLEXES

The characteristic features of the electronic spectra of some thiacontaining Cu(II) complexes are listed in Table 1. Spectroscopic studies of blue copper proteins models reveal that Cu(II) thioether complexes show two intense bands in the visible spectra. These absorption bands are observed in high (24,000–30,000 cm^{-1}) and low (13,000–18,000 cm^{-1}) energy regions. The large molar extinction coefficients of the violet band indicate this transition as $\sigma(S) \rightarrow d(Cu^{2+})$ charge transfer. Whereas, the attribution of this transition is well recognized, the nature of low-energy band is still moot. The somewhat lower intensity of this band ($\sim$160–800 $M^{-1}cm^{-1}$) militates against it being mainly $(\pi)S \rightarrow d(Cu^{2+})$ charge transfer. Although, this transition may be considered as a *d-d* band that increases its intensity by borrowing some intensity from the neighboring $\sigma(S) \rightarrow d(Cu^{2+})$ charge transfer[7] band, this explanation is not convincing, because the mechanism of such borrowing has not been elucidated.

We apply here Jørgensen's concept of charge-transfer bands(CTB)[25] to calculate the optical negativities of the Cu(II) central ions in the different coordination sets (Table 1). In this concept,[25,26] the excitation energy of the CTB depends on the difference between the optical electronegativities of the thioether donor atom ($\chi(S)$] and Cu(II) [$\chi(Cu^{2+})$]:

$$\nu = 30{,}000\,[\chi(S) - \chi(Cu^{2+})] \tag{1}$$

Recently, it was pointed out that $\chi\ (Cu^{2+})$ varies with twisting of the $CuL_4{}^{2+}$ chromophore topology from square planar toward tetrahedral geometry.[14] Such angular dependence of $\chi\ (Cu^{2+})$ values somewhat resembles the concept of orbital electronegativities[27] and thus, $\chi\ (Cu^{2+})$ values can be considered as a measure of Cu(II) orbital negativity in its compounds and used as a measure of the relative electronic density at the Cu(II) atom.

In order to address the question of whether the low-energy band can be attributed to the $\pi(S) \rightarrow d(Cu^{2+})$ CT, one can account $\chi\ (Cu^{2+})$ values from the position of this band. Using a value of 2.9 for the orbital optical negativity of the thioether donor for a $\pi(S) \rightarrow d(Cu^{2+})$ CTB,[14,26] we calculated $\chi\ (Cu^{2+})$ values, which are listed in Table (1). However $\chi(S)$ values for $\sigma(S) \rightarrow d(Cu^{2+})$ are not present in the literature. Normally the χ values for $\sigma(L) \rightarrow d(M^{n+})$ CTB exceed those values for $\pi(S) \rightarrow d(Cu^{2+})$ charge transfer bands by 0.4.[26] Thus we suppose, that the $\chi(S)$ value for $\sigma(S) \rightarrow d(Cu^{2+})$ CTB should be 3.3. This approach yields the $\chi\ (Cu^{2+})$ values from the low-energy band (Table 1) using equation (*1*). The accuracy of proposed χ (S) values for $\sigma(S) \rightarrow d(Cu^{2+})$ CTB confirms the rough coincidence in $\chi\ (Cu^{2+})$ values calculated from both bands (Table 1). This agrees well with the charge transfer nature of both bands. The CT nature for these two bands is also supported by the existence of a crude correlation for $\nu_\pi(S) \rightarrow d(Cu^{2+})$ *vs.* $^{\nu}\sigma(S) \rightarrow d(Cu^{2+})$ (Fig. 2).

The absence of such a correlation for $CuL11^{2+}$–$CuL13^{2+}$ and $CuL18^{2+}$ – $CuL20^{2+}$ proves our recent suggestion that the high-energy bands in these complexes are $\sigma(N) \rightarrow d(Cu^{2+})$ charge transfer bands obscuring the $\sigma(S) \rightarrow d(Cu^{2+})$ CTB of less

Table 1 Characteristic properties of the complexes.

Complex	ν_{max},cm^{-1}	$\chi_{Cu}{}^{a}$	$E_{CuL}{}^{2+/+}$,V	Reference
	CuS_4	*Donor*	*Set*	
$CuL1^{2+}$	25 317	2.36	0.98	4
	16 529	2.35		
$CuL2^{2+}$	25 000	2.37	0.95	4
	15 291	2.39		
$CuL3^{2+}$	25 641	2.35	0.86	9
	18 080	2.30		
$CuL4^{2+}$	23 640	2.40	1.12	4
	16 695	2.34		
	$CuS_2N_2{}^{a}$	*Donor*	*Set*	
$Cu_2(L5)_3{}^{2+}$	26 316	2.32	0.5	2
	16 502	2.35		
$CuL6^{2+}$	29 155	2.23	0.164	6
	16 129	2.36		
$CuL7^{2+}$	25 641	2.35	0.132	6
	16 129	2.36		
$CuL8^{2+}$	29 762	2.33	0.012	6
	18 975	2.27		
$CuL9^{2+}$	26 810	2.31	0.172	6
	18 051	2.30		
$CuL10^{2+}$	27 027	2.30	0.368	6
	17 123	2.33		
	$CuS_2N_2{}^{h}$	*Donor*	*Set*	
$CuL11^{2+}$	32 787		0.83	3
	31 746	2.14		
	15 873	2.40		
$CuL12^{2+}$	32 468		0.845	3
	31 447	2.15		
	15 625	2.38		
$CuL13^{2+}$	32 787		0.870	3
	31 746	2.14		
	14 124	2.43		
$CuL14^{2+}$	29 064	2.23	0.510	7
	16 393	2.35		
$CuL15^{2+}$	27 778	2.27	0.547	7
	14 925	2.40		
$CuL16^{2+}$	27 778	2.27	0.609	7
	16 806	2.34		
$CuL17^{2+}$	26 316	2.32	0.659	7
	16 393	2.35		
	Pentadentate	*Donor*	*Sets*	
$CuL18^{2+}$	32 787		0.670	3
	31 746	2.14		
	13 889	2.43		
$CuL19^{2+}$	32 787		0.703	3
	31 746	2.14		
	16 129	2.36		
$CuL21^{2+}$	28 571	2.25	0.451	2
	17 391	2.32		
$CuL22^{2+}$	25 641	2.35	0.216	2
	16 129	2.32		

Table 1 *Continued.*

Complex	ν_{max},cm^{-1}	$\chi_{Cu}{}^{a}$	$E_{CuL}{}^{2+/+}$,V	Reference
CuL23^{2+}	29 240	2.23	0.321	2
	17 857	2.30		
CuL24^{2+}	24 390	2.39	0.740	19
	16 208	2.36		
	Hexadentate	*Donor*	*Sets*	
CuL20^{2+}	32 787		0.760	3
	24 096	2.4		
	15 873	2.40		
CuL25^{2+}	31 250	2.15	1.05	4
	27 322	2.29		
	24 213	2.39		
	13 908	2.43		
CuL26^{2+}			-0.53	19
	CuN$_4$	*Donor*	*Set*	
CuL27^{2+}		12	0.375	19

intensity. From examination of the high-energy band position in $CuN^{h}{}_{2}S_{2}{}^{2+}$ complexes it can be readily deduced that increasing π - delocalization in ligands (quinoline derivatives, CuL11^{2+}-CuL13^{2+} and CuL18^{2+}-CuL20^{2+} *vs.* pyridine derivatives, CuL14^{2+}-CuL17^{2+}) shifts this band toward lower frequencies. In other words, the position of the $\sigma(N) \rightarrow d(Cu^{2+})$ CTB shifts to longer wavelength with "softening" of the nature of the heterocyclic amine donor atom. There is a remarkable influence of *cis-trans* isomerism in $CuN^{a}{}_{2}S_{2}{}^{2+}$ complexes (CuL6^{2+} and CuL7^{2+}) on the position of the violet band whereas the position of the red band in these complexes remains unchanged.

Recent semi-empirical MO calculations,[28] as well as near-IR molecular circular dichroism investigations,[30] also proved the charge-transfer nature of the "red" band in "blue" copper proteins and their synthetic models. So, these data and optical electronegativity approach convincingly support the $\pi(S) \rightarrow d(Cu^{2+})$ CT nature for the low-energy band in copper-thioether chromophores. It is likely, that this CTB obscures a weak absorption arising from the forbidden LF band.

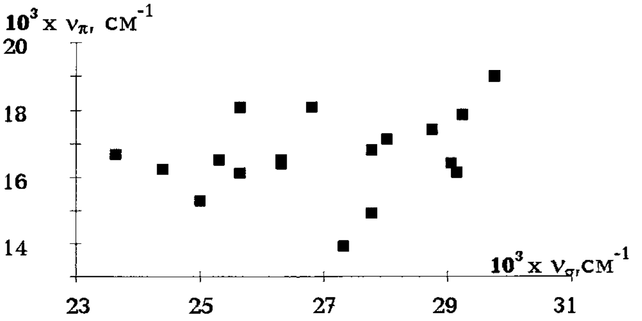

Figure 2 Map of $\nu\ \pi(S) \rightarrow d(Cu^{2+})$ *vs.* $\nu\ \sigma(S) \rightarrow d(Cu^{2+})$

REDOX POTENTIALS $E_{CuL}{}^{2+/+}$ OF POLYTHIACOPPER COMPLEXES

The redox potentials of some $CuL^{2+/+}$ couples are listed in Table 1. It was estimated before that incorporation of a thioether donor into the ligand structure induces a positive shift in the redox potentials of $CuL^{2+/+}$ couples.[10,16-21] This statement is supported by the stabilization of copper(I)-thioether species with respect to Cu(II) due to thioether π-acceptor ability.[9-10] Moreover, recently the possibility of σ-metal-thioether backbond formation was proved;[28] and undoubtedly such an interaction also increases the redox potential value. As evident from Table 1, the replacement of aliphatic amine donors with heterocyclic ones, causes positive shifts in $E_{CuL}{}^{2+/+}$ values. It is noteworthy that increasing π-electron delocalization (quinoline *vs.* pyridine moieties) raises the redox potential values.

Recently, several approaches for the accounting of redox potential $E_{CuL}{}^{2+/+}$ values were proposed.[18-21] It was shown that $E°_{CuL}{}^{2+/+}$ values are mainly dependent on the nature of donor atoms that bind to copper:

$$E°_{CuL}{}^{2+/+} = \Sigma n_D E°(D) \quad (2)$$

where n_D – is the number of donors and E°(D) is a contribution related to the donor nature. It is easy to deduce from the data collected in Table 1, that in acetonitrile solution such increments are:

S (thioether)	0.244 V
N (quinoline)	0.180 V
N (azomethine)	0.009 V
N (pyridine)	0.005 V
N (aliphatic)	-0.132 V.

Indeed, one should note, surprisingly, more positive contributions for N(azomethine). The unexpectedly high $E°_{N(azomethine)}$ value was calculated from the $E°_{CuTAAB^{2+/+}}$ and can be explained by the TAAB ligand structure (L27), containing four azomethine bonds conjugated with the π-systems of four benzene rings. Indeed, the contribution from the azomethine moiety of approximate value 0.0V seems more reliable. Similarly $E°_{N(aliphatic)}$ (–0.09 V), calculated from the data measured for the hexadentate complex $CuL26^{2+}$ does not correlate smoothly with those data received for the tetradentate systems (–0.132 V). Equation 2 can be used as a rough guide to the evaluation of $E°_{CuL}{}^{2+/+}$ values. The differences between the calculated and experimental $E°_{CuL}{}^{2+/+}$ values do not exceed ±0.12 V., and these deviations can be attributed to the influence of ligand structure[17-20] and to the coordination core topology.[29]

One can easily estimate, that according to their $E°_{CuL}{}^{2+/+}$ values, tetragonal copper complexes follow the order:

$CuS_4 > cuS_2N_2(\text{quinoline}) > CuS_2N_2(\text{pyridine})\ CuN_4(\text{azomethine}) > CuN_4(\text{aliphatic})$

This row reflects also the increasing of donor set hardness from left to tright. So, this sequence can be considered as a working approach for the estimation of ligand set softness/hardness by measuring of $E°_{CuL}{}^{2+/+}$ values.

The linearity of plot $E°_{CuL}{}^{2+/+}$ *vs.* ν_{max} was proposed as a criterion for the CTB assignment.[26] The "Milky Way" character of plots of $E°_{CuL}{}^{2+/+}$ *vs.* ν_{max} would seem militate against the CT nature of these bands (Fig. 3 and Fig. 4). Nevertheless, the question is *why* should one expect the linear character of this plot? Whereas the electronic spectroscopy is a spectroscopy of the excited state,[13] the position of CTB

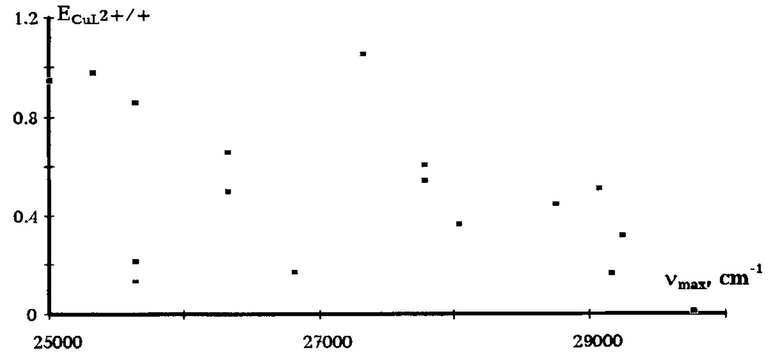

Figure 3 Reduction potentials $CuL^{2+/+}$ plotted against v $\sigma(S) \rightarrow d(Cu^{2+})$

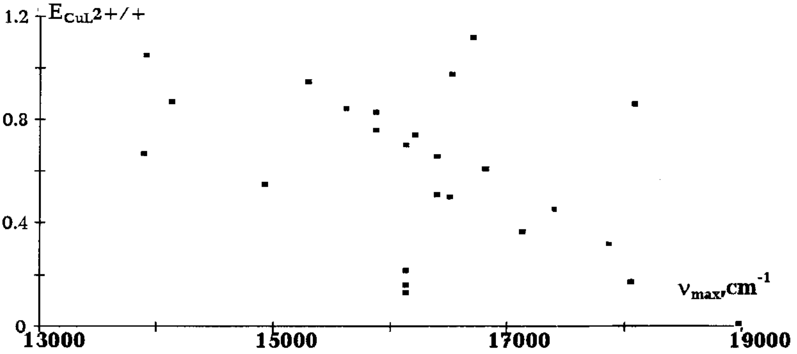

Figure 4 Reduction potentials $CuL^{2+/+}$ plotted against v $\pi(S) \rightarrow d(Cu^{2+})$

reflects the energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The redox potential value $E^{\circ}{}_{CuL}{}^{2+/+}$ depends only on LUMO's energy, which is in Cu(II) complexes state can also be considered as a single occupied molecular orbital (SOMO). Thus, one could not expect the linearity between the position of CTB in copper complexes and their redox potentials.

It should be mentioned here that Cu(II) complexes with 14-membered macrocycles exhibit different spectroscopic and redox behaviour when being compared with their closest analogues. This we can attribute to the well-known unique electronic structure of macrocyclic complexes with the 5-6-5-6 chelate ring sequence.[29]

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