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Physical Properties of Soft Donor Complexes of Copper

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The electronic absorption spectra, magnetic moments, and, in some instances, e.s.r. spectra of several copper complexes containing "soft" nitrogen and sulphur donors are examined. The presence of high intensity absorptions in the visible region of the electronic spectrum is discussed and compared with recently published work. A mixed d → d charge transfer component is argued for the transition. Assignment of electronic absorption bands is made.

Introduction

A renewed interest in the co-ordination chemistry of sulphur-containing ligands has been stimulated in recent years by the search for biological model compounds and especially by attempts to duplicate the unusual physical properties of some cupro-proteins [1, 2, 3]. We now report a study of a number of copper complexes with sulphur donors in which we have attempted to assess the effect of thio-ethers and thiols in conjugated and aliphatic systems. Since this work was begun the studies of Rorabacher and co-workers on the spectral [2] and redox [3] properties of copper–sulphur complexes have been published; our results add new ligand examples and, we believe, throw some light on the electronic processes involved at the metal centre in "blue" copper proteins.

The ligands we have prepared are shown in the Figure and we find that their reactions with cupric salts produce a variety of products, some clearly of interest in the context of bioinorganic models. A study of their u.v.–vis. spectra proved particularly helpful both in assessing the effect of soft [4, 6], and particularly sulphur, donors on the normal expectations for copper(II) and in the search for the intense absorption in the visible region of the spectrum characteristic of the so-called Type 1 centres [15]. In the event the compounds fell into two classes, those with normal spectra (a low broad band in the 12,000–20,000 cm^{-1} range) and those showing a much more intense absorption in this region.

Experimental

Preparations of all the complexes have been described elsewhere [1, 6, 7]. Ligands were; N,N′-ethylenebis(thiophene-2-aldimine) (L_1), N-2-aminoethyl-thiophene-2-aldimine (L_2), N,N′-ethylenebis(pyridine-2-aldimine) (L_3), 1,8-diamino-4-methyl-3,6-dithiaoctane (L_4), 3,4-bis(3-amino-1-thiopropyl)toluene (L_5), 1,10-diamino-4,7-diaza-5,6-dimethyldecane (L_6), 1,4,8,11,15,18,22,25-octathiacyclooctacosane (L_7), S,S′-bis(2-aminophenyl)propane-1,3-dithiol (L_8), 3,6-diaza-4,5-dimethyloctan-1,8-dithiol ($H_2(T_1)$), N,N′-bis(2-thiophenyl)butan-2,3-diimine ($H_2(T_2)$), 2-aminothiophenol ($H(T_3)$), N-(2-thiophenyl)pyridine-2-aldimine ($H(T_4)$), N-(2-thiophenyl)thiophene-2-aldimine ($H(T_5)$).

All visible and ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer. Solution spectra were obtained using 1 cm quartz cells, methanol being the preferred solvent because of solubility and hydrolysis considerations. Magnetic moments were obtained for solid samples by means of a Gouy balance and selected electron spin resonance spectra were run on a Varian E4 X-band spectrometer.

Discussion

We have categorised our observations into those reflecting "normal" behaviour for cupric complexes and those which do not. The latter group is likely to prove of interest in the search for biological models and can be compared with the former in order to identify special features. Tables I and II list the electronic absorption spectra of the "normal" complexes and magnetic moment and electron spin resonance data are listed in Tables III and IV. Data for the second class of compounds are presented in Tables V and VI.

The magnetic moments of the normal complexes were measured at room temperature and nearly all were in the range 1.74–1.83 B.M. Three exceptions had slightly depressed moments of 1.67, 1.68 and

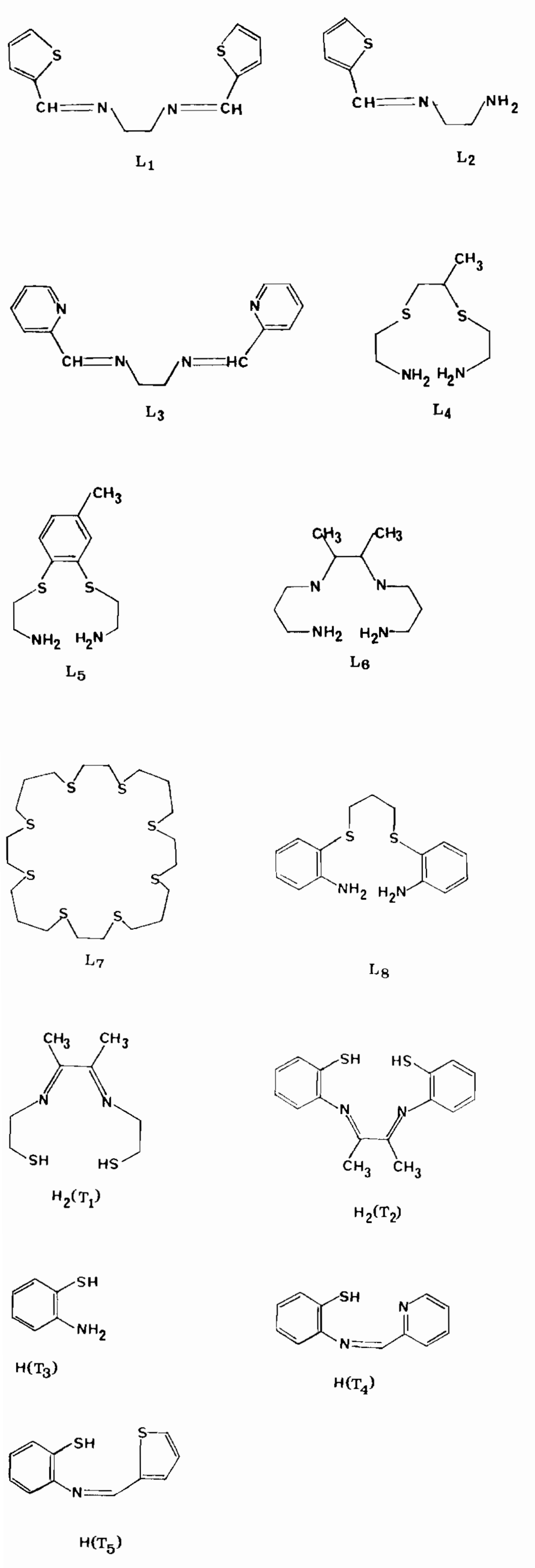

Figure. The Ligands.

1.69 B.M. which could be explained, for $Cu(L_5)Cl$-ClO_4 at least, by its dimeric nature [8] in the solid. This was substantiated by the e.s.r. spectrum which showed considerable line broadening. An interesting feature is the low value of $A_{\parallel}$, although $g_{\parallel}$ is similar to those found in other complexes. This decrease is, of course, observed for the Type 1 [5] copper ions of biological systems and is one of their defining characteristics.

All the normal complexes produced a broad absorption band in the visible region of the electronic spectrum and the position of the maximum allowed some of the complexes to be sorted into the various stereochemistries of Hathaway's correlation scheme [9]. Thus square-planar complexes are said to produce band maxima between 16 000 and 20 000 cm^{-1} and on this assumption $Cu(L_1)_2(ClO_4)_2$, $Cu(L_2)_2(ClO_4)_2$, $Cu(L_3)(ClO_4)_2$ and $Cu(L_6)ZnCl_4$ qualify. Similarly it can be determined that $Cu(L_1)$-Cl_2, $Cu(L_2)Cl_2$ and $Cu(L_3 \cdot H_2O)Cl_2$ are probably five-co-ordinate. It is possible that some of these complexes could contain six-co-ordinate copper, there being dangers in particularising a general trend, but the deductions are consistent with the observation that poorly co-ordinating anions such as perchlorate are likely to ensure four-co-ordination in solution, whereas with chloride an increased covalency can be expected. Confidence is reinforced by some structural data. Thus $Cu(L_2)Cl_2$ has been shown to have a square-pyramidal geometry [10] since it is dimeric with a chlorine bridge. On the other hand $Cu(L_2)_2$-$(ClO_4)_2$ is six-co-ordinate in the solid state [10] but since this is attained by perchlorate bonding it seems reasonable to suppose that a planar complex is present in solution. Complexes derived from L_1 and L_2 therefore give well-defined results, the band maxima for the (presumably five-co-ordinate) chloro species being at lower energies than the perchlorates.

Compounds derived from L_3 are less well-defined. With chloride as anion the d $\rightarrow$ d band has a maximum at 14 400 cm^{-1} consistent with the value of 13 300 cm^{-1} found in nitromethane solution [11] when solvent shifts are taken into account. With water as solvent, however, the maximum occurs at 16 000 cm^{-1}. Whether or not this is due to hydrolysis or to a change in stereochemistry could not be established. Attempts to recrystallise $Cu(L_3 \cdot H_2O)$-Cl_2, even from methanol, yielded only $CuenCl_2$. With perchlorate as anion the spectrum could only be measured in water because of solubility problems and here the band maximum recorded at 16 500 cm^{-1} a value consistent with a four-co-ordinate structure. This assumption is given credence by noting that the band position is almost identical with that found for the perchlorate in nitromethane. Thus these compounds can be tentatively said to be four- or five-co-ordinate.

TABLE I. Electronic Absorption Spectra of "Normal" Complexes.[a]

Complex	Absorption Bands (cm^{-1})						Solvent
$Cu(L_1)_2(ClO_4)_2$	ν 16100		34700	38800			MeOH
	ε[b] 40		20500	33500			
$Cu(L_1)Cl_2$	15200		34100	38300			MeOH
	50		19800	27400			
$Cu(L_1)Cl_2$	15400		34000	38000			H_2O
	50		12400	24800			
$Cu(L_2)_2(ClO_4)_2$	18300		34400	38600			MeOH
	80		14900	29800			
$Cu(L_2)_2(ClO_4)_2$	18700		34000	38200			H_2O
	90		19300	37000			
$Cu(L_2)Cl_2$	15500		34000	39200			MeOH
	60		5100	5600			
$Cu(L_3)(ClO_4)_2$	16500		33500	34800	36100	37600	H_2O
	150		10200	15600	16900	15600	
$Cu(L_3 \cdot H_2O)Cl_2$	14400	(26700)	32900	35300	39700	43900	MeOH
	100	140	3000	10900	14800	16400	
$Cu(L_3 \cdot H_2O)Cl_2$	16000	(27000)	33400	34800	38800	42900	H_2O
	100	100	10000	12000	10000	20000	
$Cu_2(L_4)Cl_4$	(13000)	17000	30700		38300		MeOH
	50	80	3200		440		
$Cu_2(L_4)Cl_4$	16500		30900		38000		H_2O
	35		1900		2200		
$Cu(L_5)ClClO_4$	17300		30000		36200	43500	MeOH
	150		2600		8000	13800	
$Cu(L_5)ClClO_4$	16300		30300		36600	43500	H_2O
	50		1800		8800	14800	
$Cu(L_6)ZnCl_4$	16800					47500	MeOH
	120					10000	

[a]Brackets indicate a shoulder on a more intense absorption. [b]ε in M^{-1} cm^{-1} calculated on the assumption that all the metal is complexed.

TABLE II. Position of the visible band in the solid state and solution.

Complex	KBr disc (cm^{-1})	Water[a] (cm^{-1})	Methanol[a] (cm^{-1})
$Cu(L_1)_2(ClO_4)_2$	15 900	16 100	–
$Cu(L_1)Cl_2$	14 800	15 400	15 200
$Cu(L_3)(ClO_4)_2$ Blue	15 200	16 500	–
$Cu(L_3)(ClO_4)_2$ Green	15 300	–	–
$Cu(L_3)Cl_2$	14 200	16 000	14 400
$Cu_2(L_4)Cl_4$	15 700	17 000	–
$Cu(L_5)ClClO_4$	15 400	16 300	17 300
$Cu(L_6)ZnCl_4$	16 700	–	16 800

[a]Omission of a value means that substances were insoluble in the solvent or underwent obvious changes.

TABLE III. Magnetic Moments of "Normal" Copper Complexes.

Complex	Magnetic Moment (B.M.)
$Cu(L_1)Cl_1$	1.76
$Cu(L_1)_2(ClO_4)_2$	1.78
$Cu(L_2)_2(ClO_4)_2$	1.83
$Cu(L_3)(ClO_4)_2$ (Blue)	1.77
$Cu_2(L_3)Cl_4$	1.69
$Cu(L_3 \cdot H_2O)Cl_2$	1.81
$Cu_2(L_4)Cl_4$	1.74
$Cu(L_5)ClClO_4$	1.67
$Cu(L_6)ZnCl_4$	1.68

We have not attempted to characterise the remaining complexes of this group since supporting data are not available and criticism [12] of the assignment of co-ordination numbers from spectra stresses the difficulty of particularising overall trends.

With the second class of complexes, for the moment labelled anomalous – in the sense of not showing normal magnetic moments or visible absorption

TABLE IV. Electron Spin Resonance Parameters.

Complex	$g_{\parallel}$	$A_{\parallel}$ (cm^{-1})	$W_{\parallel}$ (Gauss)[a]	$g_{\perp}$	$A_{\perp}$ (cm^{-1})	$W_{\perp}$ (Gauss)[a]
$Cu(L_1)Cl_2$	2.289	0.0179	40	2.065	0.0008	55
$Cu(L_3 \cdot H_2O)Cl_2$	2.221	0.0193	55	2.055	0.0019	60
$Cu(L_5)ClClO_4$	2.235	0.0107	50	2.100	0.0018	75
$Cu(T_4)Cl$	–	~0.010	–	–	–	–

[a] W is the half-width.

TABLE V. Magnetic Moments of "Anomalous" Copper Complexes.

Complex	Magnetic Moment (B.M.)
$Cu(T_1)$	1.27
$Cu(T_2)$	1.36
$Cu(NO_3)_2 + H(T_3)$	1.46
$CuCl_2 + H(T_3)$	0.93
$Cu(ClO_4)_2 + H(T_3)$	1.00
$Cu(ClO_4)_2 + H(T_3)/Na$	0.61
$Cu(T_4)Cl$	1.79
$CuCl_2 + H(T_5)$	0.54
$Cu_2(L_7)(ClO_4)_4$	1.32
$Cu(L_8)ClClO_4$	1.06

spectra – no correlation between molecular structure and physical data can be made and each compound must be treated separately. Either of these anomalies are of interest, the former because of its connection with the Type 3, "e.s.r. non-detectable" copper centres [5], the latter as an approximation to the behaviour of Type 1 copper – as well as for other purely chemical reasons [13]. That these features are found together in some compounds is not to be regarded as evidence of a relationship between them although we shall suggest later that both are likely to be seen in small model compounds.

The compound $Cu(T_4)Cl$ which has a normal moment but a high intensity band at 19 000 cm^{-1} (ϵ = 900 in methanol, 2 000 in DMF) shows just one of these features as, at first sight, does $Cu_2(L_7)$-$(ClO_4)_4$ with a depressed moment and an arguably normal spectrum (ϵ = 300). When compared with the recent work of Rorabacher and his co-workers on cupric complexes of sulphur-containing polydentate and macrocyclic ligands [3, 4] which are characterised by intense absorptions in the 16 000 cm^{-1} ($\epsilon \cong 1.5 \times 10^3$) and 25 000 cm^{-1} ($\epsilon \cong 7 \times 10^3$) regions this extinction coefficient does seem low;

TABLE VI. Electronic Absorption Spectra of "Anomalous" Complexes.[a]

Compound		Absorption Bands (cm^{-1})					
$Cu_2(L_7)(ClO_4)_4$	ν	17300	25600				37500
	ϵ[c]	300	1300				1300
$Cu(NO_3)_2 + H(T_3)$		16100	21400		32300		
	Ratio[b]	1	3		19		
$CuCl_2 + H(T_3)$		16200	21300		32700	38800	42700
	Ratio[b]	1	1.5		24	33	40
$Cu(ClO_4)_2 + H(T_3)$		16000	21000		33200	38800	42200
		1500	2100		7400	6300	7000
$Cu(ClO_4)_2 + H(T_3)/Na$		16000	21600		33000		41200
	Ratio[b]	1	1.5		14		25
$Cu(L_8)ClClO_4$		16400	19700	25200	33100		42000
		1000	1000	1000	3500		6000
$Cu(T_4)Cl$		19000		28600	32800	39800	43100
		900		5700	13400	15000	15500
$Cu(T_5)Cl$		18800		30100	(33900)	38500	
		300		21700	2300	31000	

[a] All spectra obtained in methanol solution. [b] Complexes not sufficiently soluble for extinction coefficients to be obtained. [c] ϵ in M^{-1} cm^{-1} calculated on the assumption that all the metal is complexed. This is unlikely to be true [4] and sets a lower limit to the intensity of the absorption.

nevertheless it is greater than the value expected for simple cupric complexes and since $Cu_2(L_7)(ClO_4)_4$ is unlikely to have a large formation constant it is probable that the measured values, being based on the overall copper concentration, are significantly low. We thus describe this compound as being similar to the remaining complexes in Table VI in showing higher than normal absorption in the visible region. It will be noted that in some instances in Table VI the extinction coefficient could not be determined because of the very low solubility of compounds. Instead, the ratio of the peak heights in the 16 000 cm^{-1} region and 25 000 cm^{-1} region is shown. These are in the 1:1.5–1:3 range which is also typical of the compounds described by Rorabacher [3].

Before discussing these results, however, we briefly outline present understanding by noting that two schools of thought are evident. On the one hand Gray and co-workers [14, 15] and Tang and Spiro and their collaborators [16, 17] have presented experimental evidence supporting a charge-transfer description of the absorption band which they infer occurs under rather special circumstances. Those working with proteins generally agree that the donor must be electron rich and is, in fact, a thiol (cysteine). There is evidence that the ligand field is weak – Williams suggests as a consequence that the co-ordination geometry will be tetrahedral [18] whereas Tang and Spiro favour a trigonal bipyramidal arrangement. Substantial delocalisation of the sulphur density on to the copper atom is inferred. On the other hand Rorabacher *et al.* assume that their compounds are modelling Type 1 behaviour, and the redox values and absorption intensities indeed suggest that they are, and come to the conclusion that this behaviour is not at all uncommon. Thus they demonstrate that thiols or thio-ethers are equally acceptable, that the co-ordination arrangement is not important and can be planar and, by implication, that strong sulphur–copper orbital overlap may not occur. In assessing these divergent views one conclusion is that the Rorabacher compounds are not models for biological behaviour but coincidentally give that appearance through processes which are not necessarily related to those occurring in enzymes. Alternatively the information could be supposed to suggest that Type 1 behaviour is not such a specialised manifestation of copper(II) chemistry as is generally supposed. Our thesis is that, to some extent, these views represent the extremes of the actual situation. We will argue that copper–sulphur orbital overlap is important but not restricted to thiols nor, on the other hand, guaranteed merely by the presence of a sulphur atom.

It can be seen that all the examples of "anomalous" spectra occur with sulphur-containing compounds. However, the question of $Cu_2(L_7)(ClO_4)_4$ apart, there are two exceptions to the inference that the presence of sulphur ensures the intense absorption in the visible region. These are $Cu_2(L_4)Cl_4$ and $Cu(L_5)ClClO_4$. They contain aliphatic as well as partially aromatic thio-ethers and neither are dissimilar in ligand design from $Cu(L_8)ClClO_4$ and some of Rorabacher's compounds. The L_5 complex also has the same stoichiometry as the "anomalous" L_8. Without knowing the structure of all three of these compounds – that for $Cu(L_5)ClClO_4$ is available [8] – it is not possible to provide a detailed explanation for this difference in behaviour in the 16 000 cm^{-1} band but a number of comments seem pertinent. The first is that $Cu(L_5)ClClO_4$ is a "copper sulphate blue" crystalline compound clearly "normal" in appearance as well as in measured spectrum. The observation cannot, therefore, be dismissed as reflecting a low formation constant – as we have suggested, perhaps wrongly, for $Cu_2(L_7)(ClO_4)_4$. Thus we conclude, contrary to Rorabacher *et al.* that it does matter how the donors are bonded although it may be that the exact geometry is not crucial.

In considering the electronic processes we are struck by the fact that the typical spectrum [3] of a model compound looks, in the visible region, remarkably like that of a simple cupric species, being broad and tailing into the i.r., except for its exceptional intensity. We refer again to the "normal" behaviour of $Cu(L_5)ClClO_4$ even though the structural results show the presence of sulphur donor atoms in *cis*-octahedral sites. When the Cu–S distances of 2.445(6), 2.609(6) and 2.431(6), 2.565(6) Å in the dimeric species present in the solid [8] are compared with the 2.30 Å reported [19] for one of the planar compounds of Rorabacher it is tempting to think that the intensity of the absorption envelope in the visible region has been lost as a result of decreased overlap with metal orbitals. We suggest, therefore, that in these sulphur-containing compounds the metal–donor back-bonding is often very significant and that as the copper d-orbitals become more "sulphur-like", and more stabilised, the original d–d transition (we are supposing a d_{xz}, $d_{yz} \rightarrow d_{xy}$ change in planar geometry) becomes more intense and moves from the red end of the envelope toward the 16 000 cm^{-1} position where the visible region maximum is usually seen. An associated increase in the σ-bonding and destabilisation of the highest metal d-orbital may also occur to help the energy shift. In the limit the transition approximates a charge transfer and would be described as an $S_\pi \rightarrow Cu_d$ transition. As indicated a concomitant strengthening of the donor bond could be expected, accounting for some of the electron drift to the copper seen in the proteins. This effect would clearly be aided if the sulphur atom were a thiol rather than a thio-ether.

A feature of the Rorabacher compounds is the correlation between their redox potentials and the number of sulphur donors present. The potential of *ca.* –0.3V jumps to *ca.* +0.3V when one or two

TABLE VII. Absorption Spectra of Ligands.

Ligand			Absorption Bands (cm^{-1})		
L_1	ν	35000		38800	
	ϵ (in M^{-1} cm^{-1})	23700		26200	
L_3		35000		37000	42900
		5300		12600	19900
L_4	No absorption <40000 cm^{-1}				
L_5		33800		40000	46700
		1500		8400	19300
L_7	No absorption <40000 cm^{-1}				
L_8		33000		38800	42200
		7700		4700	21100
$H(T_3)$	28700	33400			45500
	1800	2200			26100
T_3^-	29300	33300			46300
	5500	2400			21600
$H(T_4)$		32600		(40000)	43900
		23900		5500	22600
T_4^-	27800	32200		40200	43900
	800	19200		8000	20000
$H(T_5)$		31500		41700	46900
		12400		17200	28900
T_5^-	26600	31000	36500	39400	43100
	1200	17000	3500	8000	10000

sulphurs are co-ordinated in *cis*-planar positions and then to +0.8 V with four sulphurs [3]. The destabilisation of the planar cupric state when donors displaying a *trans*-effect are opposite one another is thus emphasised and would seem to lend some support to the view that metal–sulphur π-bonding is present.

Finally we report our assignments of the ultraviolet bands made on similar lines to those successfully employed in co-ordination chemistry by recording the spectra of the ligands (Table VII) and their anions for comparison with those of the complexes. Two ligands, L_4 and L_7, showed no absorption below 40 000 cm^{-1} so that their respective bands at 30 700 and 38 300, and 25 600 and 37 500 cm^{-1} in their copper(II) complexes are assigned as arising from charge transfer mechanisms. As the similar complex $Cu(L_6)ZnCl_4$ in which the donors are all nitrogens showed no substantial absorption below 45 000 cm^{-1} it would appear that the charge transfer bands associated with L_4 and L_7 must involve sulphur donor orbitals. Much more tentatively it can be assumed that one of the absorptions is a $S_\sigma \rightarrow Cu_d$ transition and the other a $S_n \rightarrow Cu_d$. This can be argued since L_4 and L_7 each have two charge transfer bands whereas L_5 and L_8, in which the sulphur atoms are bonded to a benzene ring and are more likely to be in sp^2 hybridisation, have only one. We ascribe the 25 000 to 30 000 cm^{-1} region as $S_\sigma \rightarrow Cu_d$ (*cf.* 34 000 cm^{-1} for a $\sigma \rightarrow d$ transition in salicylaldimine complexes of copper(II) [20]) and that at 38 000 cm^{-1} to the $S_n \rightarrow Cu_d$ alternative. By comparing the spectra of L_4 and L_5, two similar ligand systems differing only in the addition of an aromatic ring to the latter, the π-π* intra-ligand bands can also be located and distinguished from charge transfer bands. This process can be continued until the assignments of Table VIII are made. Suggestions for some of the "anomalous" spectra are the most dubious because practical difficulties connected with the insolubility of some of the thiol complexes led to poor resolution of some bands. Nevertheless, complexes derived from $H(T_3)$ gave consistent bands at 33 000 and 42 000 cm^{-1}, as well as in the visible region. The assignment of bands for the complex $Cu(T_4)Cl$ was made by use of hydrolysis spectra [1] as well as by comparison with the spectrum of the anion. The intense band in the visible region is assigned as a mixed transition for all complexes where it occurs in the sense already discussed.

Conclusion

Certain trends can be observed in the position and intensity of the d $\rightarrow$ d maxima of normal cupric com-

TABLE VIII. Assignment of Absorption Bands.[a]

Complex		Absorption Bands (cm^{-1})					
$Cu(L_1)_2(ClO_4)_2$	ν	16100			34700	38800	
	ϵ (M^{-1} cm^{-1})	40			20500	33500	
		mixed			$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	
$Cu(L_2)_2(ClO_4)_2$		18300			38600	38600	
		80			29800	29800	
		mixed			$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	
$Cu_2(L_4)Cl_4$		17000			30700	38400	
		80			3200	4400	
		mixed			c.t.	c.t.	
$Cu(L_5)ClClO_4$		17300			30000	36200	43500
		150			2600	8000	13800
		mixed			c.t.	c.t. or	$\pi \rightarrow \pi^*$
						$\pi \rightarrow \pi^*$	
$Cu(L_7)(ClO_4)_4$		17300		25600		37500	
		300		1300		1300	
		mixed		c.t.			
$Cu(L_8)ClClO_4$		16400	19700	25200	33100		42000
		1000	1000	1000	3500		6000
		mixed	$\pi \rightarrow d$	$S_n \rightarrow d$	$\pi \rightarrow \pi^*$		$\pi \rightarrow \pi^*$
$Cu(ClO_4)_2$ + H(T_3)		16000	21000	$\pi \rightarrow \pi^*$	33200	38800	42200
		1500	2100		7400	6300	7000
		mixed	$\pi \rightarrow d$		$\pi \rightarrow \pi^*$	$S_n \rightarrow d$	$\pi \rightarrow \pi^*$
$CuCl_2$ + H(T_3)		16200	21300		32700	38800	42700
			$\pi \rightarrow d$		$\pi \rightarrow \pi^*$	$S_n \rightarrow d$	$\pi \rightarrow \pi^*$
		mixed					
$Cu(NO_3)_2$ + H(T_3)		16100	21400		32300	38900	42600
			$\pi \rightarrow d$		$\pi \rightarrow \pi^*$	$S_n \rightarrow d$	$\pi \rightarrow \pi^*$
		mixed					
$Cu(ClO_4)_2$ + H(T_3)/Na		16100	21600		33000		41200
		mixed	$\pi \rightarrow d$		$\pi \rightarrow \pi^*$		c.t.
$Cu(T_4)Cl$			19000	28600	32800	39800	43100
			900	5700	13400	15000	15000
			mixed	$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
				& c.t.			
$Cu(T_5)Cl$		18800		30100	(33900)	38500	
		300		21700	(2300)	31000	
		mixed		$\pi \rightarrow \pi^*$	c.t.	$\pi \rightarrow \pi^*$	

[a]All spectra obtained in methanol solutoin. Brackets indicate a shoulder on a more intense absorption.

plexes which allow predictions about stereochemistry. Thus the energy orderings put forward by Hathaway [9] apply to the normal complexes studied in this work due heed being paid to the warnings of McKenzie [12]. The main division of stereochemistries into four- and five-co-ordinate complexes accords with chemical expectation, the increase occurring in the presence of soft donor groups when bonding anions such as chloride are also available. This increase in co-ordination number can be understood in a general sense in that the donation of electron density away from the copper atom through back-bonding with the softer donors renders the metal more able to add an extra donor atom in an axial position and also accounts for the dimerisation of some of these compounds in the solid state [8, 10]. Under this circumstance spin-pairing may occur so that lowered magnetic moments and intense electronic absorption bands in the visible region are likely to be an associated feature of small complexes containing sulphur donors without implying that they must necessarily feature together in biological systems or in acceptable model compounds. However, the fact that an increase to six-co-ordination does not often occur and the fact that the structural solution of the dimer of $Cu(L_5)Cl(ClO_4)$ [8] shows that whereas one copper is six-co-ordinate the other remains at five, suggests that five co-ordination is often a favourable state in "soft" donor complexes. Such a deduction was also made from imine hydrolysis studies of copper(II) complexes [6]. The importance of such a situation in biological systems is apparent in the consideration of dioxygen addition to copper ions, since it is likely that this must involve an increase in co-ordination number.

The visible spectra of the "anomalous" complexes also have a biological significance since the observed bands resemble the large absorptions found in some cuproproteins and extend the observations on model compounds beyond macrocyclic and quadridentate aliphatic ligands. It seems to us that it is now necessary to decide whether or not these compounds and those of Rorabacher and others [21], with their electronic and redox behaviour so similar to the proteins, are proper models in the sense of involving similar electronic processes. If they are, then further consideration and refinement of the suggested electron transitions seems desirable. If they are not, a clear distinction between the processes seems equally required.

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