2,9-Dimethyl-1,10-phenanthroline Copper(I) Complexes with some Sulphur-containing Amino Acids

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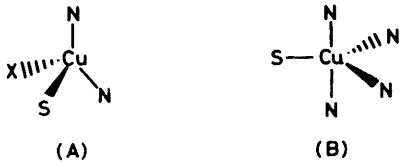
Complexes of $[Cu(dmphen)_n]^+$ (dmphen = 2,9-dimethyl-1,10-phenanthroline; n = 1 or 2) with several of the biologically relevant sulphur amino acids L (L = cysteine, penicillamine, methionine, *N*-acetylcysteine, and *N*-acetylpenicillamine) have been synthesized and characterised. I.r. and ^1H n.m.r. spectral results indicate that the amino group is protonated in the complexes containing sulphydryl amino acids; the carboxylic group remains unionised in complexes isolated from strongly acidic media while that in complexes isolated from nearly neutral solution ionises and co-ordinates to the Cu^I centre through one of the oxygen atoms. The Cu^I–S(sulphydryl) interaction in all complexes is exclusively one of sulphur ⟶ copper(I) σ donation, as supported by the relative magnitudes of the Cu–S stretching frequencies.

Many detailed physicochemical [1,2] studies have been conducted to probe the structure of the blue active sites in the type 1 cuproproteins. Two possible basic structural units, (A) (X = O or S) and (B), have thus been suggested.[3]



In these units, two of the co-ordinated nitrogen atoms are from the imidazole groups of the histidine residue while the sulphur atom is from the cysteinate functionality. As related examples of such analogues and also as part of our continuing interest in the mixed-ligand systems of copper(I) and copper(II),[4–6] mixed-ligand complexes of copper(I) containing 2,9-dimethyl-1,10-phenanthroline (dmphen) as the first ligand and a sulphur-containing amino acid as the second ligand have been prepared and studied in the present investigation. The dmphen is selected as the nitrogenous base since it is known to stabilise Cu^I relative to Cu^{II}. The amino acids used are those that provide the sulphydryl sulphur functionality and in several cases, the oxygen donor as well, thus completing a co-ordination geometry resembling that of type (A).

We report the synthesis, chemistry, and spectroscopy of several mixed-ligand complexes of copper(I) containing dmphen and one of the following amino acids: cysteine, penicillamine, *N*-acetylcysteine, *N*-acetylpenicillamine, and methionine (see Table 1).

Table 1. Microanalytical data (%) with calculated values in parentheses

Complex	C	H	N
(1) $[Cu(dmphen)(Cys)]Cl\cdot\frac{1}{3}MeCN$	47.65 (48.0)	5.2 (4.8)	10.15 (10.55)
(2) $[Cu(dmphen)(CysO)]\cdot HCl$	47.2 (47.6)	4.5 (4.4)	10.3 (9.9)
(3) $[Cu(dmphen)(Acys)]\cdot HCl\cdot\frac{1}{2}C_6H_6$	48.5 (49.0)	4.9 (5.05)	8.65 (8.2)
(4) $Na[Cu(dmphen)(AcysO)]\cdot 2HCl$	42.2 (41.8)	4.5 (4.2)	7.5 (7.65)
(5) $[Cu(dmphen)_2(Pen)]Cl\cdot 2HCl\cdot\frac{1}{6}C_6H_6$	52.35 (52.15)	5.3 (5.0)	9.4 (9.05)
(6) $[Cu(dmphen)(Apen)]\cdot HCl\cdot\frac{1}{2}C_6H_6$	53.15 (53.65)	5.75 (5.5)	8.05 (7.8)
(7) $Na[Cu(dmphen)(ApenO)]\cdot 4HCl\cdot\frac{1}{2}C_6H_6$	39.1 (39.15)	4.1 (4.5)	6.45 (6.0)
(8) $[\{Cu(dmphen)\}_2(Met)]Cl_2\cdot\frac{1}{2}C_6H_6$	54.25 (53.85)	4.25 (4.7)	8.95 (8.7)

Cys = $^-SCH_2CH(NH_3^+)COOH$ AcysO = $^-SCH_2CH(NHCOCH_3)COO^-$

CysO = $^-SCH_2CH(NH_3^+)COO^-$ Apen = $^-SCMe_2CH(NHCOCH_3)COOH$

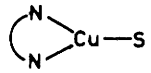
Pen = $^-SCMe_2CH(NH_3^+)COOH$ ApenO = $^-SCMe_2CH(NHCOCH_3)COO^-$

Acys = $^-SCH_2CH(NHCOCH_3)COOH$ Met = $MeSCH_2CH_2CH(NH_2)COOH$

Results and Discussion

Synthetic and Solution Studies.—As the amino acids selected for this study possess three potential binding sites, attempts have been made to monitor the modes of co-ordination through the use of three different reaction media: (a) acetonitrile–absolute ethanol (1 : 1) acidified with a small quantity of methanolic HCl (pH 1.40); (b) acetonitrile–ethanol–aqueous 0.10 HCl mol dm^{-3} (4 : 4 : 1) (pH 6.0); (c) an aqueous buffer of physiological pH 6.25 containing NaH_2PO_4. From (a), complexes (1), (3), (5), (6), and (8) (Table 1) are isolated while complexes (2), (4), and (7) (Table 1) are obtained using (b). Attempts to synthesize analytically pure samples from (c) are generally unsuccessful, probably due to the ease of oxidation of Cu^I in an aqueous medium. The stoicheiometries of the two complexes isolated from (a) and (b) are the same for Cys in (1) and (2), for Acys in (3) and (4) and Apen in (6) and (7); however, the modes of binding of each of these amino acids are found to be different in the two complexes, as manifested by i.r. and ^1H n.m.r. absorption characteristics. The stoicheiometry of the mixed-ligand complex of Pen, $[Cu(dmphen)_2(Pen)]Cl$, is unexpected as it involves the introduction of Pen into the apparently crowded co-ordination sphere of copper(I) in $[Cu(dmphen)_2]^+$. Nevertheless, the recently published *X*-ray crystallographic structures [7–9] of $[Cu(dmphen)_2]NO_3$ and of bis(6,6′-dimethyl-2,2′-bipyridyl)copper(I) tetrafluoroborate reveal a ' flattened ' tetrahedral geometry around the

copper(I) ion. Spectroscopic evidence further suggests [7] that this structure persists in solution. The 'flattened' structure probably leads to the fifth co-ordination site of copper(I) being more accessible to an incoming ligand. The fact that Cys does not yield a similar complex may well be due to the much more pronounced tendency of its sulphur atom to bridge metal centres,[10] resulting in formation of more complex species. Such copper(I) systems have been demonstrated by Kroneck and co-workers [11] to be highly unstable and are likely to undergo dissociation to yield three-co-ordinate Cu^{I} complexes of the type shown below, where $\widehat{N\ N}$ represents dmphen and S is *S*-bound cysteinate. This could conceivably



achieve a tetrahedral co-ordination through the formation of a Cu–O(carboxylate) or a Cu–Cl bond at the fourth co-ordination site of Cu^{I}. For Acys and Apen the acetyl group at the ^{-}NH end probably hinders co-ordination of these amino acids to the metal centre in the complexes containing $[Cu(dmphen)_2]^{+}$. Met forms the only complex in this study consisting of two $[Cu(dmphen)]^{+}$ units to one thioether sulphur.

The stoicheiometry of the complexes of $[Cu(dmphen)]^{+}$ with each of the amino acids (L) was studied in solution by Job's method of continuous variation [12] in the three media (a), (b), and (c). Solutions of [Cu(dmphen)Cl] as well as of L in accurately known concentrations were mixed such that the mol fraction of one of the reactants was varied from 0.10 to 0.90 while the total volume as well as the total concentration of the two reactants were kept constant. Plots of the absorbances measured at $\lambda = 430$, 450, and 470 nm, against the mol fractions are approximately symmetrical and show maxima at the mol ratio [Cu(dmphen)] : L of 1 : 1 for L = Cys, Pen, Acys, and Apen and of 2 : 1 for L′ = Met in media (a) and (b). Using (c), a maximum is observed at a mol ratio of 2 : 1 for L = Pen, Acys, Apen, and Met. Cysteine, however, displays a non-integral mol fraction of 1.75 : 1 at this pH, indicative of polymeric species formation. This is yet another manifestation of the stronger tendency of the cysteinate sulphur to bridge metal centres.

All the complexes isolated (Table 1) display an intense absorption band near 450 ± 10 nm which presumably is due to copper→ligand (dmphen) π^{*} transition.[13] The absence of the strong absorption band due to $\sigma(S)\rightarrow Cu^{II}$ at 530 nm [14] demonstrates that these complexes are of Cu^{I} and not of mixed valences. Solid-state spectra in Nujol display a much broadened absorption band at *ca.* 465 nm.

The molar conductivities of the complexes in dimethyl sulphoxide (dmso) are in the range [15] 40—90 Ω^{-1} cm^2 mol^{-1} for complexes (1)—(7). The high values may well be due to the release of HCl.[16]

I.R. Spectral Studies.—Studies in the i.r. spectral region 200—4 000 cm^{-1} were carried out by comparing the spectra of dmphen, the amino acids, and the mixed-ligand complexes, as well as those of the binary complexes. Careful comparisons reveal that the absorption peaks due to dmphen in complexes (1)—(4) and (6)—(8) (Table 2) display a pattern resembling that of [Cu(dmphen)Cl] [6] while those of complex (5) give a pattern bearing closer resemblance to that of $[Cu(dmphen)_2]Cl$.[6,*]

The disappearance of the S–H stretch at 2 550 cm^{-1} upon complex formation in (1)—(7) demonstrates that each of these amino acids bonds to the Cu^{I} centre through the sulphydryl S atom. In complex (8), the large shift of the C–S(thioether) stretch is consistent with the thioether sulphur bridging two Cu^{I} centres.[17] The characteristic absorptions of the protonated amino group at 3 000, *ca.* 1 600, and 1 490 cm^{-1} are found in complexes (1), (2), and (5). That the carboxyl group remains undissociated and unco-ordinated in complexes (1), (3), (5), (6), and (8) is supported by absorptions at *ca.* 1 730, *ca.* 1 225, and *ca.* 1 200 cm^{-1}. Replacement of these bands by those at *ca.* 1 615, *ca.* 1 590, and *ca.* 1 400 cm^{-1} in complexes (2), (4), and (7) strongly suggest co-ordination of the carboxylate oxygen to copper(I) in these cases. Met in (8) most probably bonds to Cu^{I} through the thioether sulphur only; this is manifested by the absorptions at 1 740 and 3 420 cm^{-1}. Thus the co-ordination mode of the sulphydryl amino acids changes from monodentate *via* the S-(sulphydryl) atom only to a bidentate mode *via* the S and O(carboxylate) atoms in going from a strongly acidic non-aqueous medium to a weakly acidic one.

Cysteine in Zn^{II} complexes has been shown [18] to exhibit two different co-ordination modes *via* (*a*) the S(sulphydryl) and the $^{-}NH_2$ atoms at pH 4 and (*b*) the S(sulphydryl) and the $^{-}COO^{-}$ atoms at pH 2. The differences in the modes of binding of Cys to Zn^{II} and to Cu^{I} in our case may well be a consequence of introducing the dmphen into the co-ordination sphere of Cu^{I}. Various attempts were made in our laboratory to effect co-ordination at the $^{-}NH_2$ end by employing reaction media at pH 6—8. However, only intractable solids were recovered in each case, probably due to the greater ease of oxidation of Cu^{I} as well as the increased tendency of the potentially tridentate amino acids to form polymeric species at higher pH.

In the far-i.r. region the Cu–S stretches [19,20] (Table 2) display an interesting trend in that those of Cys or Acys absorb at significantly lower frequencies than the corresponding vibrations of Pen and Apen. This is actually in agreement with the conclusions of Kroneck and co-workers [11] who pointed out that the S(sulphydryl) atom in four-co-ordinate copper(I) complexes is exclusively σ donating towards Cu^{I}. The higher Cu^{I}–S stretching frequencies in (5)—(7) are accompanied by lower values of the Cu^{I}–N stretching vibration [21,22] in the region 380—360 cm^{-1}, compared to those of Cys and Acys. This further supports the $S\rightarrow Cu^{I}$ σ donation.

Hydrogen-1 N.M.R. Spectra.—Sharp and well defined peaks are observed in the ^{1}H n.m.r. spectra of complexes (1)—(7) (Table 3), indicative of the negligible concentration of Cu^{II} in solution. The absorption peaks of dmphen in complex (8), though somewhat broadened, display chemical shifts that are comparable to those of complexes (1)—(7).

The observed downfield shifts [23–25] of the methylene and methine protons of Cys and Acys and of the methine proton of Apen demonstrate that each of these amino acids binds to the Cu^{I} through the S(sulphydryl) atom and the carboxylate oxygen in (2), (4), and (7). As appreciable shifts are observed only for the methylene protons, the Cys ligand in (1) and Acys in (3) are bound to Cu^{I} through the S(sulphydryl) atom only. The paramagnetic shift of the methine ^{1}H of Pen in (5) is approximately half the magnitude of those found for complexes (2), (4), and (7). It would appear that there exists appreciable interaction between Cu^{I} and the carboxylate oxygen in (5). Thus the ^{1}H spectral data indicate that Cys, Acys, and Apen continue to display the two different co-

* This complex is represented as $[Cu(dmphen)_2]Cl$ here, rather than $[Cu(dmphen)_2Cl]$ given in ref. 6, in view of the reported *X*-ray crystal structure of $[Cu(dmphen)_2]NO_3$.[7]

Table 2. Selected i.r. and far-i.r. absorptions (cm^{-1}) and probable assignments [a]

Complex								
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	Probable assignments
		3 400w,br	3 300w,br		3 360s,br	3 300w,br	3 420s	$\nu(NH_2)$ or ν(NH) (amide)
3 000s,br	3 000s,br			2 960s,br				$\nu(NH_3^+)$
1 726s,sp		1 725s,br		1 727s,sp	1 710s,sp		1 740m,sp	ν(C=O) (un-ionised carboxyl)
1 620m,sp	1 615s,sp	1 620m,br	1 620s,sp	1 660s,sp	1 617w,sp	1 605s,sp	1 620m,sp	dmphen or $\nu_{asym}(COO^-)$ (co-ordinated carboxyl)
1 590m,sp	1 580s,sp	1 590s,sp	1 590s,sp	1 625s,br	1 580m,sp	1 590w,sp	1 595s,sp	
1 490s,sp	1 495s,sp		1 490s,sp	1 600m,sp		1 490s,sp		
				1 530w,sp				
				1 490s,sp				
1 425m,sp	1 430m,sp	1 425m,sp	1 430m,sp	1 430w,sp	1 426w,sp	1 430m,sp	1 435m,sp	dmphen or $\nu(COO^-)$
1 410m,br	1 406m,br		1 406m,sp			1 405w,sp	1 424m,sp	(co-ordinated carboxyl)
1 225m,sp		1 228m,sp		1 230m,sp	1 230m,sp		1 227m,sp	ν(C–O) (un-ionised
1 205m,sp		1 210m,sp		1 210m,sp	1 200m,sp		1 210m,sp	carboxyl)
849s,sp	848vs,sp	860vs,sp	850vs,sp	850vs,sp	841w,br	845m,sp	851vs,sp	dmphen
775s,sp	770s,sp	770m,sp	770m,sp	780m,sp	765w,sp	760m,sp	760s,sp	
725s,sp	720s,sp	730s,sp	730m,sp	730s,sp	730m,sp	720m,sp	730s,sp	
685w,sp	685w,sp	675m,sp		676m,sp	680m,sp	678w,sp	723w,sp	ν(C–S)
385w,sp	388s,sp	380w,br	380w,br	373m,sp	365m,sp	366w,sp	332s,sp	ν(Cu–N) (dmphen)
330m,sp	328s,sp	330m,sp	335w,sp	350m,sp	325m,sp	330m,sp		
295m,sp		298m,sp			295w,sp		297m,sp	ν(Cu–Cl) [b]
287m,sp	280m,br	280w,br	280w,br	280w,sp	284m,sp	285m,sp	280m,sp	ν(Cu–N) (dmphen)
265w,sp	260w,sp	260w,sp	260w,sp	268w,sp	270w,sp	270w,sp		ν(Cu–S)
	230w,sp		235w,sp			233w,sp		ν(Cu–O) [c]
	212w,sp		215w,sp			215w,sp		

[a] sp = Sharp, br = broad. [b] M. Goldstein, E. F. Mooney, A. Anderson, and H. A. Gebbie, *Spectrochim. Acta*, 1965, **21**, 105; M. J. Campbell, M. Goldstein, and S. R. Grezeskowiak, *Chem. Commun.*, 1967, 778. [c] B. W. Cook, R. G. J. Miller, and P. F. Todd, *J. Organomet. Chem.*, 1969, **19**, 421; P. Battaglia, A. Bonamartini, Corradi, G. Marcotrigiano, L. Menabue, and G. C. Pellecani, *Inorg. Chem.*, 1981, **20**, 1075.

Table 3. Hydrogen-1 n.m.r. spectra (δ/p.p.m.) of the complexes in $[^2H_6]$dmso

Complex	Protons of dmphen: Methyl	Protons of dmphen: Aromatic	Methine $-CH-$ COOH	Methylene $HS-CH_2-$	Others	Integration [a]
(1)	2.54	8.42	3.85	3.45	7.80—6.30 (NH_3^+)	6 : 6 : 1 : 2
(2)	2.45	8.34	4.20	3.50		*b*
(3)	2.52	8.47	4.52	2.98	2.01 (CH_3 of amide group), 7.36 (benzene)	6 : 6 : 1 : 2 : 3
(4)	2.50	8.40	4.75	3.05	2.05 (CH_3 of amide group), 7.40 (benzene)	6 : 6 : 1 : 2 : 3
(5)	2.48	8.35 [c]	3.96		(*a*) 1.50 (CH_3 of carbon α to SH) (*b*) 7.75—5.80 (NH_3^+) (*c*) 7.36 (benzene)	12 : 1 [d]
(6)	2.48	8.40	4.51		(*a*) 1.97 (CH_3 of amide group) (*b*) 1.44 (CH_3 of carbon α to SH) (*c*) 7.36 (benzene)	6 : 6 : 1 : 3 : 6
(7)	2.55	7.80	4.97		(*a*) 1.90 (CH_3 of amide group) (*b*) 1.31 (CH_3 of carbon α to SH)	6 : 6 : 1 : 3 : 6
(8)	2.45	8.34	3.30		2.45 [e] [CH_3 of CH_3-S and CH_2 of $-S(CH_2)_2$]	
(9)	2.45	8.35				6 : 6
(10)	2.65	8.32 [c]				6 : 6

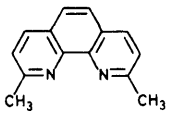
[a] Integration was carried out with respect to the methine proton. [b] Peaks generally weak due to low solubility of this complex. [c] Ill resolved multiplet. [d] Aromatic H : methine H. [e] Peaks due to methyl H of dmphen, as well as methylene H and methyl H of Met coalesce to give a multiplet structure centred at δ 2.45 p.p.m.

ordination modes manifested by the i.r. absorption characteristics of the complexes in the solid state.

In complex (8), the ^1H n.m.r. absorptions due to the methyl and methylene protons of Met partially overlap with that of the methyl ^1H of dmphen giving rise to a complex multiplet structure centred at δ 2.45 p.p.m. The shifts observed for the methyl and methylene protons are consistent with the thioether sulphur bridging the two copper centres. It is interesting to note that Cu^I has been suggested,[26] from the results of solution studies, to be among the metal ions (others are Pd^{II}, Ag^I, and Au^I) which bind the $-CH_2CH_2SCH_3$ chain of Met. That the thioether sulphur is a better π-electron acceptor than the S(sulphydryl) atom may have contributed to its greater tendency to bridge the two Cu^I centres. Based on thermogravimetric behaviour, a similar structure has been suggested [27] for the related Pd^{II} complex.

The aromatic protons of dmphen in (1)—(4) and (6)—(8) display absorptions similar to that of [Cu(dmphen)Cl] (9). However, a more complex multiplet centred at δ 8.35 p.p.m. was observed for those of (5). A similar feature was also

Table 4. Hydrogen-1 n.m.r. spectra (δ/p.p.m.) of the ligands in [$^2H_6$]dmso

Ligand	Protons of dmphen: Methyl	Protons of dmphen: Aromatic	Methylene $HS-CH_2-$	Methine $-CH(NH_2)-COOH$	Methyl $HS-C(CH_3)-$	Methyl α to thioether sulphur H_3C-S-	Methylene α to thioether sulphur $-S-CH_2-$	Methyl of acetyl group $CH_3CO(NH)$
	2.92	7.74						
Cysteine			3.05	3.80				
Acetylcysteine			2.81	4.43				1.90
Penicillamine				3.68	1.60			
Acetylpenicillamine				4.45	1.40			1.92
Methionine				3.83		2.11	2.78	

found for [Cu(dmphen)$_2$]Cl (10). In the light of the published structure of [Cu(dmphen)$_2$]NO_3 this observed ^1H n.m.r. spectrum could have arisen from the non-equivalence of the two dmphen molecules in the flattened tetrahedral structure.

In the spectra of (3), (5), and (6) an additional resonance is found at δ 7.36 p.p.m. (Table 3), characteristic of the ^1H absorption of benzene. This lends support to the formulation of these complexes based on elemental analysis (Table 1).

Experimental

The ^1H n.m.r. spectra were recorded at 90 MHz on a Perkin-Elmer R32 spectrophotometer. The electronic spectra were run using a Hitachi 124 spectrophotometer. I.r. spectra were recorded on a Perkin-Elmer model 567 spectrophotometer which was calibrated with polystyrene film; KBr pellets and Nujol mulls were employed throughout.

The ligand 2,9-dimethyl-1,10-phenanthroline and the amino acids were obtained from the Aldrich Chemical Co.; 'Gold Label' samples were purchased where available. Solvents were purified and dried by the usual methods.[28]

Preparation of Complexes.—Freshly prepared copper(I) chloride (0.54 g) in dry acetonitrile [28] (40 cm^3) was slowly added to a warm ethanolic * solution (20 cm^3) of the amino acid of equimolar quantity. The resultant colourless solution was refluxed for 1 h. A near-boiling solution of 2,9-dimethyl-1,10-phenanthroline (0.40 g) in ethanol (20 cm^3) was added. The solution was then heated to reflux for *ca.* 20 h over an oil bath. An intense red solution was obtained. The solution was filtered and evaporated down to half its volume under N_2, whereupon the orange solid [Cu(dmphen)Cl] precipitated out of the solution. This was removed and further evaporation of the ensuing solution yielded a uniform and intense red solid. The product was recrystallised from benzene–ethanol (8 : 2) and washed with methanol.

* Cysteine, penicillamine, and methionine are only partially soluble in absolute ethanol. Methanolic HCl or aqueous 0.10 mol dm^{-3} HCl was slowly added to a suspension of the amino acid in absolute alcohol till a clear solution was obtained (see Results and Discussion section).

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