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Preparation and Spectral Studies of some Ternary 2,2′-Bipyridine and 1,10-Phenanthroline Copper(II) Dipeptide Complexes

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Several adducts of 1,10-phenanthroline and 2,2′-bipyridine with Cu(II) dipeptides were prepared and characterised. The visible and infrared spectra of these complexes indicate that they are five coordinate having square pyramidal geometry around Cu(II) with dipeptides behaving as tridentate ligands. The EPR spectra of these complexes at room and liquid nitrogen temperatures were analysed and the magnetic and bonding parameters were calculated. The square pyramidal geometry of Cu(II) in these complexes seems to be highly distorted. These complexes have been reduced with mercaptoethanol and possible modes of their action with cancer cells have been suggested. These complexes can also act as models of protein–metal–inhibitor complexes.

Introduction

Recently, the degradation of DNA by a copper(II) complex of 1,10-phenanthroline in the presence of rducing agents such as ascorbate, thiol or xanthine oxidase-hypoxanthine and oxygen has been reported. This degradation of DNA involves the hydroxyl radical [1, 2]. The copper(II) complex of 3,4,7,8-tetramethyl-1,10-phenanthroline significantly inhibits the growth of Landschutz ascites tumor in mice [3]. The 1,10-phenanthroline and 2,2′-bipyridine have shown retardation of growth of a Sarcoma-37 tumor [4], and the 1,10-phenanthroline inhibits the cell proliferation of Ehrlich ascites [5]. These chelating agents may show better antitumor activity if the hydrophilic groups of the chelating agents are masked by metal ions to form neutral chelate compounds. These neutral chelate compounds will be more permeable through the cell membrane [6, 7], and eventually behave as carriers of antitumor agents. In view of the importance of copper(II) complexes of 1,10-phenanthroline and 2,2′-bipyridine, we report here the synthesis and spectral studies of some ternary complexes of 1,10-phenanthroline and 2,2′-bipyridine with copper(II) dipeptides.

Experimental

Materials

Glycylglycine (Gly•Gly), glycyl-L-tyrosine (Gly•Tyr) and glycyl-L-phenylalanine (Gly•Phe) were purchased from Sigma Chem. Co., USA. 1,10-Phenanthroline (phen) and 2,2′-bipyridine (bipy) were bought from B.D.H., U.K. Other reagent grade chemicals were used without further purification.

Physical Measurements

The electronic absorption spectra of the Cu(II) complexes in different solvents were measured using a Perkin-Elmer Model-402 spectrophotometer in the range of 400 to 850 nm. The reflectance spectra of the complexes were recorded on a Varian Superscan-3 spectrophotometer. The infrared spectra of the complexes were recorded in Nujol mulls using a Perkin-Elmer Model-577 spectrophotometer in the range 4000 to 650 cm^{-1}. The electron paramagnetic resonance (EPR) spectra of the complexes were recorded on a Varian E-112 ESR spectrometer (X-band) using TCNE ($g = 2.00277$) as g marker. The EPR spectra of the frozen solutions at 77 K and solutions at room temperature were recorded by dissolving the complexes in ethanol. The molar conductances of the complexes in water and methanol at room temperature were measured with a Systronic's conductivity bridge Model-305 with a cell having a cell constant of 0.63.

Synthetic Procedures

$Cu(Gly{\cdot}Gly){\cdot}3H_2O$ *(Ia)*

This complex was prepared by adding glycylglycine (0.132 g, 10^{-3} *M*) to an aqueous suspension of copper hydroxide (1.25×10^{-3} *M*) at pH 6.5 according to the published method [8]. The product was recrystallised from water and dried in a vacuum desiccator over anhydrous calcium chloride.

$Cu(Gly{\cdot}Gly)(bipy){\cdot}3H_2O$ *(Ib)*

6N Sodium hydroxide in excess was added to a solution of 0.170 g of copper(II) chloride in 15 ml of water. The blue precipitate of copper hydroxide was filtered and washed with distilled water till the washings were free from chloride ions. The precipitate was suspended in 50% methanol and 0.132 g of glycylglycine and 0.156 g of 2,2′-bipyridine were added to it. The solution was stirred for one hour and then filtered. The filtrate was concentrated to a small volume on a water bath and cooled in a freezer for 24 hours when dark blue crystals were obtained. These crystals were filtered. The complex was recrystallised using 50% methanol. The crystals were filtered and washed with cold water followed by methanol and diethyl ether. They were finally dried in air. *Anal.* Found: C, 42.2; H, 4.8; N, 13.9%. Calcd. for $Cu(C_{14}H_{14}O_3N_4)\cdot 3H_2O$: C, 41.64; H, 4.96; N, 13.87%.

Cu(Gly·Gly)(phen)·3H$_2$O (Ic)

This complex was prepared by a method similar to that of the preparation of Ib except that 1,10-phenanthroline was used in place of 2,2′-bipyridine. The product was recrystallised from 70% ethanol. The crystals were washed with ethanol followed by diethyl ether and dried in air. *Anal.* Found: C, 44.7; H, 4.8; N, 13.2; Cu, 14.8%. Calcd. for $Cu(C_{16}H_{14}O_3N_4)\cdot 3H_2O$: C, 44.96; H, 4.68; N, 13.10; Cu, 14.85%.

Cu(Gly·Tyr)·4H$_2$O (IIa)

This complex was prepared by the method of Dehand and coworkers [9], and was further recrysallised from water.

Cu(Gly·Tyr)(bipy)·4H$_2$O (IIb)

The complex IIa (0.371 g, 10^{-3} *M*) was dissolved in 30 ml of water. A solution of 2,2′-bipyridine (0.156 g, 10^{-3} *M*) in 25 ml of ethanol was added to it. The mixture was stirred for two hours and then filtered. The deep blue filtrate was concentrated to a small volume using a rotary evaporator at 40 °C. The solution was kept in a refrigerator for 2 days when sky blue crystals were obtained. These crystals were filtered and washed with cold water followed by ethanol and diethyl ether. The crystals were finally dried in air. *Anal.* Found: C, 47.5; H, 5.4; N, 10.4%. Calcd. for $Cu(C_{21}H_{20}O_4N_4)\cdot 4H_2O$: C, 47.77; H, 5.31; N, 10.61%.

Cu(Gly·Tyr)(phen)·3H$_2$O (IIc)

This complex was obtained using the method of preparation of complex IIb except that 1,10-phenanthroline was used in place of 2,2′-bipyridine. The product was recrystallised from 50% ethanol. The crystals were dried in a vacuum desiccator over anhydrous calcium chloride. *Anal.* Found: C, 50.6; H, 4.5; N, 10.3%. Calcd. for $Cu(C_{23}H_{20}O_4N_4)\cdot 3H_2O$: C, 51.71; H, 4.87; N, 10.49%.

Cu(Gly·Phe)(bipy)·4H$_2$O (IIIa)

The freshly prepared copper hydroxide (1.1 m*M*) was suspended in 20 ml of water and glycyl-L-phenylalanine (0.222 g, 1 m*M*) was added to it. The pH of the solution was adjusted to 7. This solution was stirred for 2 hours and then filtered. The filtrate was mixed with 0.156 g (1 m*M*) of 2,2′-bipyridine in 20 ml of ethanol and the resulting solution was stirred for one hour. The solution was concentrated to a small volume using a rotary evaporator at 40 °C. On cooling this solution, plate-like crystals were obtained. These crystals were filtered and recrystallised from 30% ethanol. The crystals were washed first with cold water and then with cold ethanol. Finally, they were dried in a vacuum desiccator over anhydrous calcium chloride. *Anal.* Found: C, 49.8; H, 5.5; N, 10.8%. Calcd. for $Cu(C_{21}H_{20}O_3N_4)\cdot 4H_2O$: C, 49.27; H, 5.47; N, 10.94%.

Reduction of Ic by Mercaptoethanol

The Ic (0.025 g) was dissolved in 5 ml of water and 2.5 ml of 0.1 *M* solution of mercaptoethanol (molar ratio of Ic to mercaptoethanol is 1:5) was added to it. This solution was quickly diluted to 25 ml. The first spectrum of the solution was recorded after five minutes of mixing Ic with mercaptoethanol. Subsequently, the spectra were recorded after an interval of three minutes. The decrease in the intensity of the 425 nm peak was recorded with time. A similar experiment was carried out in 3% sodium dodecylsulphate (SDS) solution instead of water. The decrease in the intensity of the 440 nm peak was recorded with time in SDS.

Results and Discussion

Five mixed complexes (Ib, Ic, IIb, IIc and IIIa) of phen and bipy with three Cu(II) dipeptides were prepared. They were characterised by elemental chemical analysis and infrared spectroscopy. The selective infrared bands of these complexes are discussed below.

The electronic absorption spectra of these Cu(II) complexes in the visible region were recorded in water, methanol and dimethyl sulphoxide (DMSO) and the wavelength maxima (λ_{max}) are given in Table I. These spectral bands showed appreciable absorption at 850 nm, and the percentage of ratio of extinction coefficient at λ_{max}, ϵ_{max}, and extinction coefficient at λ_{850}, were also measured. These data are also given in Table I. The Ia and IIa complexes show values of $\epsilon_{850}/\epsilon_{max}\%$ as 10 and 14 respectively, whereas the mixed complexes of phen and bipy such as Ib, Ic, IIb and IIIa, also show values of $\epsilon_{850}/\epsilon_{max}\%$ ranging from 26 to 45. These higher values in the presence of phen and bipy suggest that the Cu(II) in these complexes is five coordinate with a nitrogen donor in a near-apical

TABLE I. Electronic Absorption Spectral Data and Molar Conductivity of Copper(II) Complexes in Different Solvents.

Complex	Solvent	^{a} λ_{max}	^{b} ϵ_{max}	$\frac{\epsilon_{850}}{\epsilon_{max}}$ %	Molar^c conductivity at room temperature
Ia	Water^d	640	(85)	10	4.88
	Methanol	–		–	2.32
		660^e	–	–	–
Ib	Water	644	(113)	45	22.3
	Methanol	634	(131)	40	6.7
		630^e		–	–
Ic	Water	640	(102)	43	25.9
	Methanol	630	(120)	36	6.3
	DMSO	629	(112)	34	–
		632^e		–	–
IIa	Water	635	(76)	14	5.2
	Methanol	–		–	4.1
IIb	Water	638	(100)	33	16.3
	Methanol	630	(121)	36	5.2
IIc	Water	638	(90)	27	17.6
	Methanol	626	(124)	26	4.3
IIIa	Water	635	(85)	33	15.6
	Methanol	630	(119)	34	2.9

[a] λ_{max} is the wavelength maximum in nm. [b] ϵ_{max} is the extinction coefficient at wavelength maximum in M^{-1} cm^2. [c] Mohs cm^2 mol^{-1}. [d] The pH of complexes in water was *ca.* 8. [e] The peak position is observed in reflectance spectrum.

position. The similarity of the absorption maximum and intensity of Cu(II) dipeptide complexes and their adducts with phen and bipy further suggests that the structures of these Cu(II) complexes are five coordinate with the dipeptide behaving as a tridentate ligand [10].

The ternary complexes show no change in their absorption maxima in the presence of 1:3 mol of excess of phen or bipy or sodium salt of dipeptide in water at pH 8. This suggests that the extra added ligands are not displacing ligands already coordinated in the complexes.

In order to check the same structures of the ternary Cu(II) complexes in solution and in solid state, the reflectance spectra of Ia, Ib and Ic in solid state were measured and their spectral maxima are given in Table I. The values of $\epsilon_{850}/\epsilon_{max}\%$ were also measured and they show that Ib and Ic have higher values than Ia A similar trend is already observed in solution. These data confirm the earlier conclusion that the structures of Ic in solid and solution states have the same five coordinate square pyramidal geometry around Cu(II) [10].

The molar conductivities of these Cu(II) complexes in water and methanol were also measured and they are given in Table I. These Cu(II) complexes show very low molar conductivities in methanol solution suggesting the presence of neutral species. The molar conductivities of Cu(II) dipeptide adducts with phen and bipy show more conductivities in water than Cu(II) dipeptides. This suggests that the adducts are slightly dissociated into ionic species in water.

The Ia, Ic and IIa have five coordinate square pyramidal geometry around Cu(II) in the solid state [10–12]. The IIa, Ia and Ic also retain the same structure in solution (see above) as was found in the solid state. One of the common features of these structures is that the dipeptides behave as tridentate ligands with amino, ionised amide nitrogen and carboxylate oxygen donor atoms approximately tetragonally disposed about Cu(II). In the solid state, the infrared spectra of Cu(II) complexes show a strong band between 1600 and 1569 cm^{-1}. This band is assigned to the peptide carbonyl stretching band with ionisation of the peptide N–H hydrogen [12]. The N–H bending vibrations were observed between 1606 and 1630 cm^{-1}. The NH_2 vibrations in the Cu(II) complexes have been observed in the range of 3120 to 3355 cm^{-1} which indicates that the NH_2 group is involved in the bonding [14].

The EPR spectra of Cu(II) complexes were recorded in solution at room temperature. They are isotropic due to tumbling motion of the molecules in solution [15]. The isotropic g value, g_o, was calculated at the centre of four lines observed in the spectrum. The isotropic nuclear hyperfine coupling constant, A_0, expressed in cm^{-1}, was calculated from the spacing between two consecutive lines of the

TABLE II. Magnetic Parameters of Copper(II) Complexes.

Complex	$g_\parallel$	$g_\perp$	go	$A_\parallel \times 10^4$ cm^{-1}	$A_\perp \times 10^4$ cm^{-1}	$A_o \times 10^4$ cm^{-1}
Ia	2.250	2.055	2.120	185	16	70
Ib	2.243	2.058	2.120	157	6	53
Ic	2.243	2.057	2.119	162	6	55
IIa	2.243	2.059	2.120	175	18	70
IIb	2.232	2.064	2.120	175	10	62
IIc	2.232	2.061	2.118	172	15	65
IIIa	2.236	2.058	2.118	172	10	61

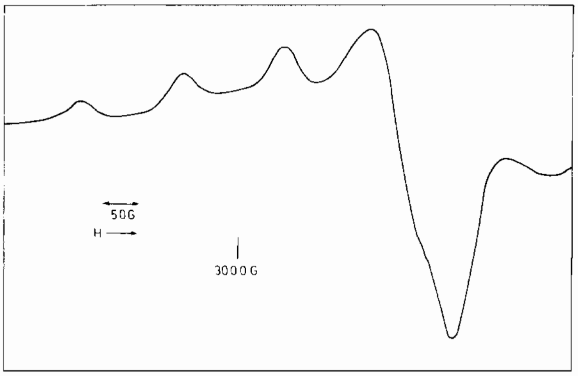

Fig. 1. Frozen solution EPR spectrum of Cu(Gly•Gly)(bipy)•$3H_2O$ complex at 77 K.

spectrum. Both are given in Table II. The EPR spectra of Cu(II) complexes in glassy state at liquid nitrogen temperature were anisotropic and one of the spectra is shown in Fig. 1. These spectra suggest that the Cu(II) complexes have typical square pyramidal geometry (or elongated octahedron). The low field side of the spectra was well resolved to allow accurate calculation of $g_\parallel$ and $A_\parallel$. The high-field spectra were not well resolved and so $g_\perp$ and $A_\perp$ were calculated using the equations $g_\perp = \frac{3g_o - g_\parallel}{2}$ and $A_\perp = \frac{3A_o - A_\parallel}{2}$. The EPR parameters of these Cu(II) complexes at 77 K are also given in Table II.

The $g_\parallel$ values are greater than the $g_\perp$ values in these Cu(II) complexes as $g_\parallel > g_\perp > 2.04$. Thus they have a ground state of $d_{x^2-y^2}$ (or more rarely d_{xy}) [14]. Considering an approximate D_{4h} symmetry of square pyramidal Cu(II) complexes, the bonding parameters from their EPR spectra were calculated using a modified semiempirical LCAO–MO method of Kevilson and Neiman [16–18]. It was assumed in the Kevilson and Neiman method that the Fermi contact term, K, is constant. Certain rules were derived based on this assumption. These rules were later found to be inconsistent with certain experimental data [19, 20] including ours (see Table II). Recently, Rockenbauer and coworkers [16, 17] have shown that the hyperfine contact term, K, is not a constant but depends on the isotropic hyperfine coupling constant, A_o. Their method was employed for calculating the hyperfine contact term K and σ-bonding parameter α^2. The charge density in the 4s orbital or the 4s contribution to ground state can be represented by ϵ'^2 and is calculated by the method of Rockenbauer [18]. However, the Kevilson and Neiman method [16] was used to calculate the in-plane π-bonding parameter β_1^2 and out-of-plane π-bonding parameter β^2. These bonding parameters are given in Table III.

The α^2 values represent the covalency of in-plane σ-bonding. The metal ligand σ-bond is totally ionic if $\alpha^2 = 1$ and is totally covalent if $\alpha^2 = 0.5$. The α^2 values of the Cu(II) complexes fall in the range of 0.76 to 0.82 depicting appreciable covalency of the in-plane σ-bonding [18, 21]. The α'^2 values increase with corresponding decrease of α^2. This indicates that the axial σ-bonding is decreasing with corresponding increase in the in-plane σ-bonding. The β_1^2 values are found in the range of 0.79 to 0.85 and indicate appreciable in-plane π-bonding in the Cu(II) complexes. The α^2 and β_1^2 follow opposite trends in the Cu(II) complexes. These observations can be explained in terms of competition between the in-plane σ- and π-bonds in the Cu(II) complexes. The β^2 values vary in the range of 0.77 to 0.90, indicating strong to weak out-of-plane π-bonding.

The theoretical plot of ϵ'^2 against α^2 for molecules in approximate D_{4h} symmetry was obtained by using the equation $\epsilon'^2 = 1.06\ \alpha^2 - 0.567$, suggested by Rockenbauer [18]. This plot of ϵ'^2 against α^2 for the Cu(II) complexes gives a straight line by joining the points, (●), as shown in Fig. 2. The points (■) of adducts of phen and bipy in the plot of ϵ'^2 against α^2 were obtained using equation 15 from Rockenbauer's paper [18]. The points of phen and bipy adducts fall far above the theoretical straight line whereas the points of Ia and IIa fall very near the theoretical straight line. This indicates that the phen and bipy adducts have appreciable distortion to rhombic symmetry [10].

The chelating agents such as phen and bipy are employed to inhibit several metalloenzymes possibly

TABLE III. Ligand Field Energies, Bonding Parameters and ϵ'^2 of Copper(II) Complexes.

Complex	ΔE, cm^{-1}	α^2	α'^2	β_1^2	β^2	ϵ'^2
Ia	15625	0.82	0.27	0.80	0.86	0.32
Ib	15750	0.76	0.33	0.85	0.81	0.39
Ic	15625	0.78	0.31	0.83	0.77	0.40
IIa	15750	0.81	0.28	0.79	0.90	0.31
IIb	15675	0.79	0.30	0.79	0.86	0.35
IIc	15675	0.76	0.33	0.83	0.86	0.29
IIIa	15750	0.79	0.30	0.80	0.79	0.36

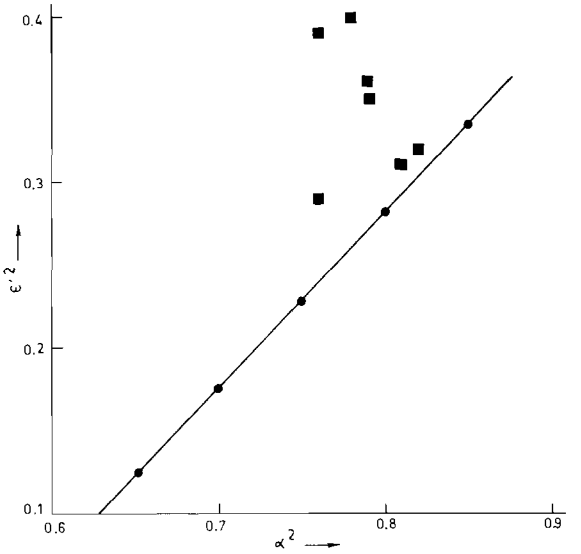

Fig. 2. Plot of α^2 against ϵ'^2 for the copper(II) complexes.

by forming ternary complexes [5, 22]. The 1:1 complexes of Cu(II) dipeptide with phen or bipy may act as models of the above ternary protein–metal–inhibitor complexes.

In addition, phen and bipy retard the growth of a Sarcoma-37 tumor possibly by binding the essential metals of the cancer cells [4]. The attachement of these ligands to a metal may greatly aid cell transport [7]. Therefore, the neutral adducts of the Cu(II) dipeptides with phen and bipy such as Ib, Ic, IIb, IIc and IIIa, were prepared. The presence of dipeptides in these chelates has the further advantage that they (amino acids) have active transport processes in the cells. In addition, the healthy cells tolerate them well, and have the means to use or dispose of them after the therapy [23]. When the phen and bipy adducts of Cu(II) dipeptides are inside cancer cells, the Cu(II) complexes may be reduced to Cu(I)–SR where SR is an anion of glutathione or cysteine or thiol with the liberation of phen or bipy. The Cu(I)–SR and the phen or bipy may then attack the specific cellular locations and thus kill the cancer cells [6, 24].

In order to verify that phen or bipy and Cu(I)–SR species would be released by the reduction of Cu(II) complexes inside the cancer cells, the reduction of Ic was carried out *in vitro* by mercaptoethanol in the molar ratio of 1:X (X = 15 to 50). A red product was obtained on this reduction, which was detected as Cu(I)–SR by the absence of the EPR spectrum of Cu(II) species at liquid nitrogen temperature. About 70% phen was also recovered from the reduced mixture by extracting it in diethyl ether. The Cu(I)–SR species also absorbs strongly at 425 nm. The reduced species, on air oxidation, gives a broad band at 640 nm which is characteristic of Cu(II) dipeptide species. This shows that the free phen is liberated with the formation of Cu(I) species on reduction of Ic with thiol.

Another mechanism of interaction of anticancer metal chelates and cancer cells might be to destroy the selective permeability of tumor cells [7]. In order to verify this mechanism, the reduction of Ic with mercaptoethanol in the molar ratio of 1:15 was studied in water and in 3% sodium dodecyl sulphate detergent. The reduced species of Ic shows a red shift to 440 nm in detergent. The rates of oxidation of reduced Ic by oxygen were studied in water and detergent under identical conditions. The rate of oxidation is faster in water than in detergent by a factor of 2.8. This suggests that Ic has penetrated in the hydrophobic region of the micelles. This lends further support to the theory of penetration of Cu(II) complexes into the hydrophobic region of tumor cells and thus favours the destruction of the selective permeability of the tumor cells.

The Cu(II) dipeptide complexes with 1,10-phenanthroline and 2,2'-bipyridine have distorted square pyramidal structures. The peptide occupies three coordination positions and one nitrogen of 1,10-phenanthroline and 2,2'-bipyridine occupies the fourth position in the tetragonal plane. The apical position is occupied by the second nitrogen of 1,10-phenanthroline or 2,2'-bipyridine. These adducts on reduction with mercaptoethanol liberate 1,10-phenanthroline or 2,2'-bipyridine with approximately 70% yield.

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