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TERNARY COMPLEXES OF COPPER(II) CONTAINING INOSINE (Ino), GUANOSINE (Guo) AND THE DIPEPTIDES, GLY–GLY, GLY–L-ALA, GLY–L-VAL AND GLY–L-LEU

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Abstract—Ternary complexes of formulae $[Cu(dipeptide)(nucl)_2]Cl_2 \cdot xH_2O$ with dipeptides glycyl–glycine (Gly–Gly), glycyl–L-alanine (Gly–Ala), glycyl–L-valine (Gly–Val), glycyl–L-leucine (Gly–Leu) and nucl inosine (ino) and guanosine (guo) were isolated from a water : ethanol (2 : 1) solution and characterized with elemental analysis, conductivity measurements, IR, electronic and ESR spectra. At low pH values (<4) the dipeptides coordinate through the ($—NH_2$) terminal and peptide (C=O) groups and the nucleosides through the N_7 atoms. At pH > 4 the dipeptides coordinate through the ($—NH_2$) terminal and the deprotonated amide ($—N^-$) groups. The pK_a values for these deprotonations were estimated with electronic spectra and increase with the increase of the side chain of the dipeptides, due to steric reasons. At higher pH values one nucleoside molecule is liberated and replaced by the terminal deprotonated carboxylate group of the dipeptides. The pK values for these transformations were calculated with ESR spectra and follow the same trend as for the deprotonation constants and for the same reason.

Metal ions in biological systems may promote among others, selective interaction of proteins and nucleic acids, simultaneously coordinated with the same metal ion.[1–3] For example, Cu^{2+} and Zn^{2+} ions are known to mediate interactions between polypeptides containing glutamic acid and tyrosine residues and polynucleotides.[4] Another ubiquitous example is the so-called "zinc finger proteins" known to bind through Zn^{2+} ions to nucleic acids during replication of DNA, *via* hydrophobic residues.[5–7]

Using various techniques, several investigators attempted to study amino acids–peptides and nucleobases–nucleosides–nucleotides interactions, in their ternary complexes containing metal ions.[2,8–12] In all cases, hydrophobic or stacking ligand–ligand interactions between the simultaneously coordinated to the same metal ion ligand molecules, were detected.

More recently, we have been interested in studying ternary complexes of Pt^{2+} and Pd^{2+} with amino acids–peptides and nucleobases–nucleosides, as models of the DNA–platinum–protein crosslinks, known to take place with the antitumour drug *cis*-DDP and its inactive *trans*-DDP analogue.[13–19] Similar hydrophobic ligand–ligand interactions, increasing with the aliphatic side chain of the aminoacids were also detected, mainly with ^1H NMR spectroscopy.[13–19]

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Continuing our studies on similar ternary systems, we report on the characterization and properties of complexes of Cu^{2+} of the general formulae [Cu(dipeptide)(nucl)$_2$]Cl$_2$, where dipeptide is, glycyl–glycine (Gly–Gly) or glycyl–L-alanine (Gly–Ala) or glycyl–L-valine (Gly–Val) or glycyl–L-leucine (Gly–Leu) and nucl is inosine (ino) or guanosine (guo).

RESULTS AND DISCUSSION

Ternary complexes of formulae [Cu(dipeptide)(nucl)$_2$]Cl$_2 \cdot x$H$_2$O were easily isolated as solid adducts, from mixtures of ethanol : water (1 : 2). Their elemental analysis agree with the assigned formulae (Table 1). Their room temperature molar conductance (Λ_M) values suggest 1 : 2 electrolytes in aqueous solutions, in agreement with the general formulae.

IR spectra

Characteristic IR bands of all the complexes are included in Table 2. All the ternary complexes containing ino and guo, show the bands in the region 1600–1700 cm^{-1} slightly shifted to lower frequencies, possibly due to a Cu^{2+}–N_7 monodentate coordination, similar to the analogous Pd^{2+} and Pt^{2+} complexes.[20–22] In a N_1, a simultaneous N_1N_7, a chelate N_7O_6 or a chelate N_1O_6 coordination, the C_6=O would not retain its double bond character and as a result a new band would have been observed at about 1620–1640 cm^{-1}.[22, 23] That was the case of the complex [Cu$_4$(5′-IMPH$_1$)$_2$(*o*-phen)$_4$(H$_2$O)$_4^{2+}$](NO$_3$)$_2 \cdot$ 14H$_2$O,[24] where Cu^{2+} was bound to all three sites of IMP (N_1,N_7,O_6) simultaneously, showing a band at 1620 cm^{-1}.

On the other hand, Gly–GlyOMe(O-methyl-ester) and Gly–Gly[25] when bound to Cu^{2+} ions through the terminal amino group and the amide C=O group, in acidic pH values, show bands at 1634 cm^{-1} and 1625 cm^{-1}, respectively, assigned to the Cu^{2+} coordinated amide I band. In our ternary systems the amide I band is shown at 1625–1640 cm^{-1} in the various complexes, indicating again a peptide amide carbonyl coordination with Cu^{2+}, in all cases, besides the terminal amino coordination.[14,25] The coordination of the latter is

Table 1. Elemental analysis and molar conductance values of the compounds

Compound	Cu%		Cl%		C%		H%		N%		Λ_M (20°C, H$_2$O, 10^{-3} M)
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
[(ino)$_2$Cu(Gly–Gly)]Cl$_2 \cdot$ 4H$_2$O, **1A**	7.3	7.7	8.1	8.1	33.0	33.0	4.5	4.1	16.0	16.1	185
[(ino)$_2$Cu(Gly–Ala)]Cl$_2 \cdot$ 9H$_2$O, **2A**	6.5	6.5	7.3	8.0	30.7	30.5	5.2	4.5	14.3	14.1	204
[(ino)$_2$Cu(Gly–Val)]Cl$_2 \cdot$ 9H$_2$O, **3A**	6.3	6.5	7.1	7.9	32.2	31.5	5.6	4.7	13.9	13.2	209
[(ino)$_2$Cu(Gly–Leu)]Cl$_2 \cdot$ 9H$_2$O, **4A**	6.2	6.3	7.0	7.8	32.9	32.9	5.7	4.9	13.7	13.6	216
[(guo)$_2$Cu(Gly–Gly)]Cl$_2 \cdot$ 4H$_2$O, **1B**	7.0	7.8	7.9	8.1	31.9	31.4	4.5	4.5	18.6	18.5	249
[(guo)$_2$Cu(Gly–Ala)]Cl$_2 \cdot$ 7H$_2$O, **2B**	6.5	6.4	7.3	7.2	30.9	31.0	5.0	4.4	17.3	16.9	205
[(guo)$_2$Cu(Gly–Val)]Cl$_2 \cdot$ 7H$_2$O, **3B**	6.3	6.9	7.1	7.0	32.3	32.3	5.4	4.8	16.8	16.6	213
[(guo)$_2$Cu(Gly–Leu)]Cl$_2 \cdot$ 7H$_2$O, **4B**	6.3	6.9	7.0	7.9	33.1	33.3	5.5	4.9	16.6	16.8	222

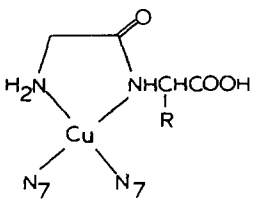
Table 2. Characteristic IR bonds of the complexes

Complex	ν(C=O) of nucl ν(COOH) of peptide	Amide I	Ring stretchings ν(C=C) ν(C=N)	δNH$_2$ of peptide	Amide II	Sugar modes
1A	1695	n.i	1595	n.i	n.i	820,800
2A	1705	n.i	1585	n.i	n.i	820,795
3A	1695	n.i	1595	n.i	n.i	820,800
4A	1695	n.i	1595	n.i	n.i	825,800
1B	1700	1625	1595	1560	1525	820,800
2B	1695	1630	1595	1565	1540	825,800
3B	1700	1625	1595	1560	1545	825,800
4B	1705	1625	1595	1560	1530	825,800

n.i = not identified.

evidenced from its appearance at lower frequencies in the complexes with ino ($\approx 1565\ cm^{-1}$), compared to the free peptides.[14] The amide II band appears near 1525–1545 cm^{-1} in the ternary complexes and this indicates its protonation and not an involvement in bonding with Cu^{2+}.[14,26] The terminal carboxylate group of the dipeptides on the other hand, should also be protonated and not involved in bonding with Cu^{2+}, since their ν(C=O) frequencies appear near the ν(C=O) frequencies of the carbonyl groups at the sixth position of both nucleosides as shoulders.[14] Many bands in the complexes with guo cannot be seen due to being obscured by the strong absorptions of the ligand in the 1500–1700 cm^{-1} region.

Based on these observations, the most probable structures of the solid state ternary complexes isolated in the present study will be:



The sugar conformation of the coordinated nucleosides should be both $^2E(\approx 40\%)$, and $^3E(\approx 60\%)$ as this is seen from the relative intensities of the bands near 800 and 825 cm^{-1}. In free guo and ino the ^2E conformation predominates.[14,27] Similar is the case in the complexes with palladium(II)[14] and platinum(II).[27–29]

Visible spectra

The binding of Cu^{2+} ions with dipeptides depends on pH in aqueous solutions and the equilibria shown in Fig. 1 are established.[30–33]

Deprotonation of the amide nitrogen with simultaneous coordination with Cu^{2+} occurs at pH > 4. This has been determined by various methods, including electronic spectroscopy.[31,32] Thus, the carbonyl oxygen coordination replacement by a deprotonated amide coordination is accompanied by a shift of the λ_{max} of about 730 nm of the former, to about 620 nm in the latter.[31–33]

In our case it was interesting to try to determine spectrophotometrically the pK_a value of the amide deprotonation of our ternary complexes isolated as solid adducts and containing two nucleoside molecules. In fact, the aqueous solutions of our complexes were a green colour and had a maximum at about 790 nm (see Table 3) at low pH values, in support of structure **I**, but they turned gradually to a blue colour upon increasing the pH, showing maxima near 640 nm. These bands are most probably due to the $^2E \rightarrow {}^2T$ transition of Cu^{2+} complexes, in a distorted octahedral environment,[34] the two axial positions being occupied by either water molecules or interacting weakly with two oxygen atoms of the carbonyls at the sixth position of the nucleosides, as this happens in the crystal structure of the ternary complex (glygly)Cu(Cyt)·$2H_2O$.[35]

The pK_a values were calculated from the plots $pH = f(\lambda_{max})$ (Fig. 2). The results are given in Table 3, which also includes the values for the binary Cu(dipeptide) system taken from the literature[30] for comparison.

From the calculated values the following observations are made:

(i) They are increasing with increasing aliphatic chain in both series of complexes containing guo and ino, following the same trend as in the corresponding binary systems.[30,33] This has been interpreted as the result of steric difficulties in the conformation restructuring of the peptide, increasing with the bulkier side chain.[30,33]

(ii) The deprotonation of the amide proton is facilitated by the presence of the nucleosides, most probably through their proton accepting groups and/or intervening water molecules. This is more pronounced in the case of the complexes with ino.

(iii) The difference of the pK_a values between the binary and the ternary system decreases with the aliphatic side chain of the peptides, emphasizing again the importance of the steric effects.

Increasing the pH of the solution a precipitate appears at pH > 6, depending on the complex. This is due to the equilibrium shown in Fig. 3.

A tridentate chelate structure with the peptide is formed and the nucleoside is liberated. The amount of the nucleoside liberated was determined in the case of guo, which is practically insoluble at almost neutral pH values, by filtration, drying and weighing. The 1 : 1 : 1 complexes formed were also isolated in a few cases and their elemental analysis corresponded to the assigned formulae. Liberation of the chelated 2,2′ bipyridine (bpy) was also observed in the Cu(dipeptide) (bpy) ternary system upon increasing the pH.[33,36]

Due to precipitation we could not use the visible spectra to determine the pK_a for equilibrium (2). We have instead used ESR spectra.

ESR spectra

The Cu^{2+} ion species formed in solution with Gly–Gly and Gly–His where studied with ESR

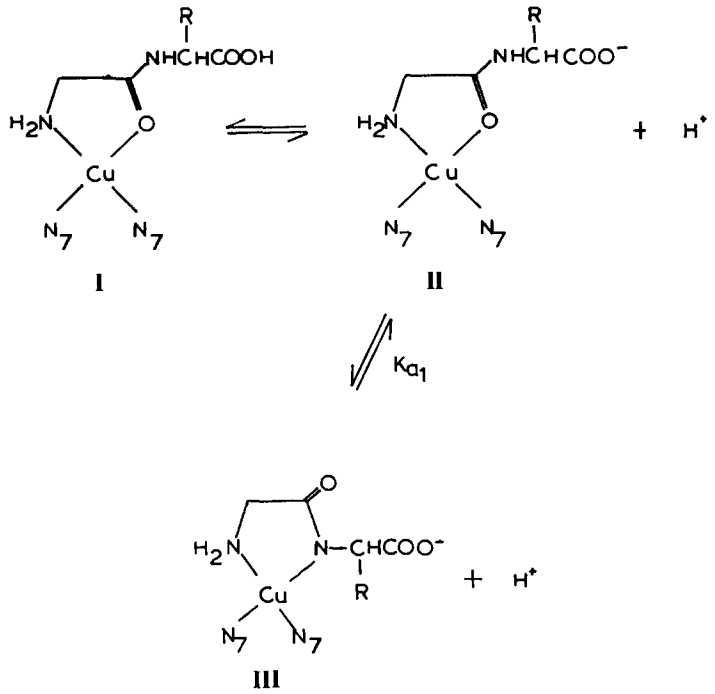


Fig. 1. Various equilibria of the complexes [Cu(dipeptide) (nucl)$_2$]Cl$_2$ · xH$_2$O.

Table 3. Electronic spectral data and pK_a values of the complexes

Complex	pH, λ_{max}, (nm), (ε)						pK_a	Δ^c
1A	3.05,[a] 786(36)	3.52, 719(40)	3.96, 677(45)	4.44, 656(58)	5.10, 646(65)	5.80, 643(78)	3.52	0.67
2A	3.05, 790(39)	3.50, 790(40)	3.84, 781(43)	4.20, 729(57)	4.77, 640(66)	5.99, 630(105)	3.83	0.52
3A	2.84, 801(40)	3.46, 800(39)	3.77, 790(43)	4.40, 678(59)	4.86, 649(68)	5.58, 634(102)	4.12	0.53
4A	3.07, 805(38)	3.80, 797(40)	4.18, 775(41)	4.58, 656(59)	5.10, 639(68)	5.64, 634(101)	4.28	0.48
1B	3.08, 785(37)	3.55, 715(40)	4.01, 708(42)	4.50, 680(59)	5.19, 645(67)	5.80, 638(102)	3.72	0.47
2B	2.95, 803(38)	3.57, 798(39)	3.82, 784(44)	4.45, 690(60)	4.95, 638(68)	5.50, 635(104)	4.15	0.20
3B	3.10, 804(38)	3.68, 801(39)	4.10, 760(43)	4.52, 648(64)	5.07, 637(68)	5.70, 636(103)	4.28	0.37
4B	3.02, 803(38)	3.99, 800(39)	4.03, 795(43)	4.50, 710(60)	5.10, 651(66)	5.72, 635(102)	4.77	0.29
Cu(Gly–Gly)	—	—	—	—	—	—	4.19[b]	
Cu(Gly–Ala)	—	—	—	—	—	—	4.35[b]	
Cu(Gly–Val)	—	—	—	—	—	—	4.65[b]	
Cu(Gly–Leu)	—	—	—	—	—	—	4.76[b]	

[a] These were the pH values followed by the values of λ_{max} and ε in parenthesis.
[b] Taken from ref. 30.
[c] Δ = pK_a (binary) − pK_a (ternary).

spectroscopy previously[37,38] and various species were identified.

In our case and knowing the pK_a values for the deprotonation of the amide hydrogen for all the ternary complexes from the electronic spectra, we have recorded their ESR spectra as a function of pH ($\approx$3–7) in aqueous solution and at room temperature. At low pH values the spectra were isotropic with $g \approx 2.19$ being the average of various orientations of the molecules in solution.[38] Increasing the pH results to a dramatic change in the spectra (Fig. 4) but has only a small effect on the ESR parameter ($g = 2.19 \pm 0.05$). The g_{II} tends to decrease with the rise in the negative charge of the ligand.[38,39] The spectrum does not change any further at pH $\approx$ 6–7 and resembles the one with Cu^{2+} and Gly–His, where the metal ion coordinates through the amino (NH_2), the amide (NH) deprotonated or a histidine nitrogen and the deprotonated carboxylate group,[37] stable at pH 4–5.2.

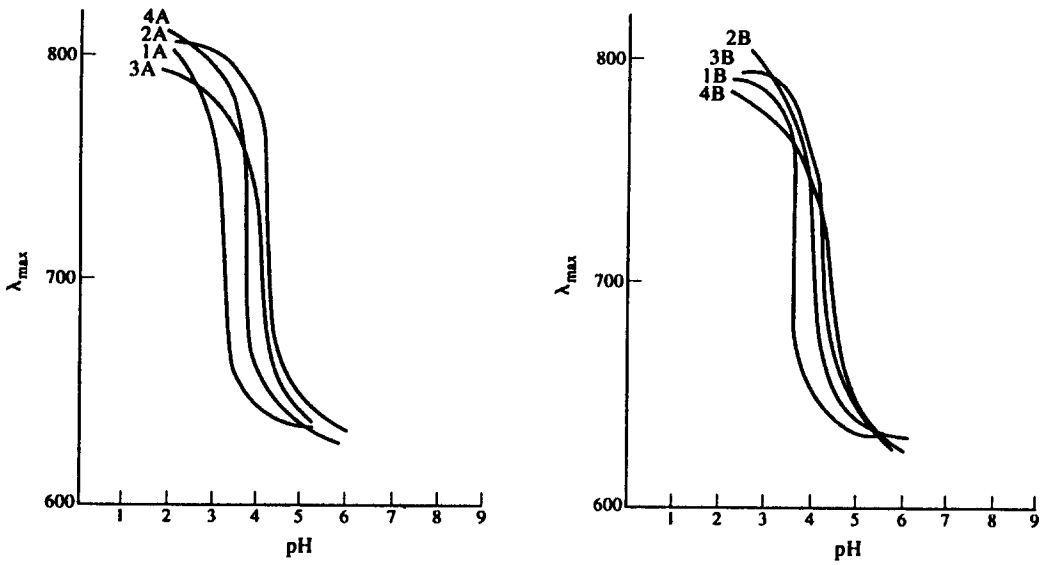
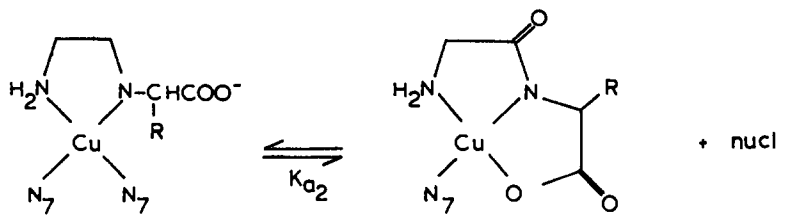


Fig. 2. Plots of $pH = f(\lambda_{max})$ of the complexes **A** (1–4) and **B** (1–4).



III IV

Fig. 3. Formation of this *tris*-chelate structure with subsequent liberations of nucl from the complexes.

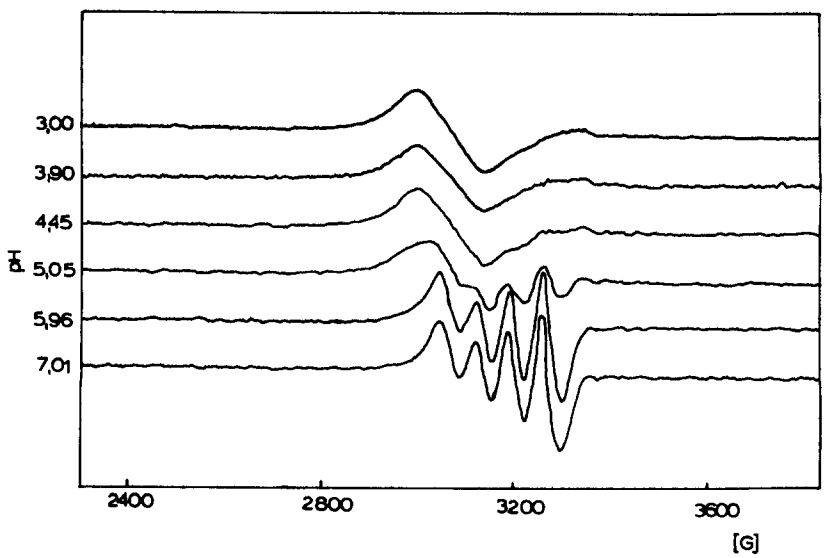


Fig. 4. ESR spectra of the complex $[Cu(Gly–Gly)(ino)_2]Cl_2$ as a function of pH.

Assuming structure **III** for the spectrum at pH ≈ 4 and structure **VI** (Fig. 3) at pH ≈ 7, where one nucleoside molecule was liberated and replaced by a carboxylate group, we were able to calculate the proportion of these two forms of the various complexes in equilibria by computer simulation of the spectra at various pH values as the sums of the spectra at pH ≈ 4 and pH ≈ 7 (structures **III** and **IV**) $[x(C_{pH-7}) + (1-x)(C_{pH-4})]$. From the plots of percentage of species $= f(pH)$ (Fig. 5) the pK_a values for equilibrium 2 (Fig. 5) were calculated. The results are included in Table 4. From these, it is concluded again that the pK_a values for this transformation increase with the aliphatic side chain of the peptides most probably due to steric phenomena.[30,33]

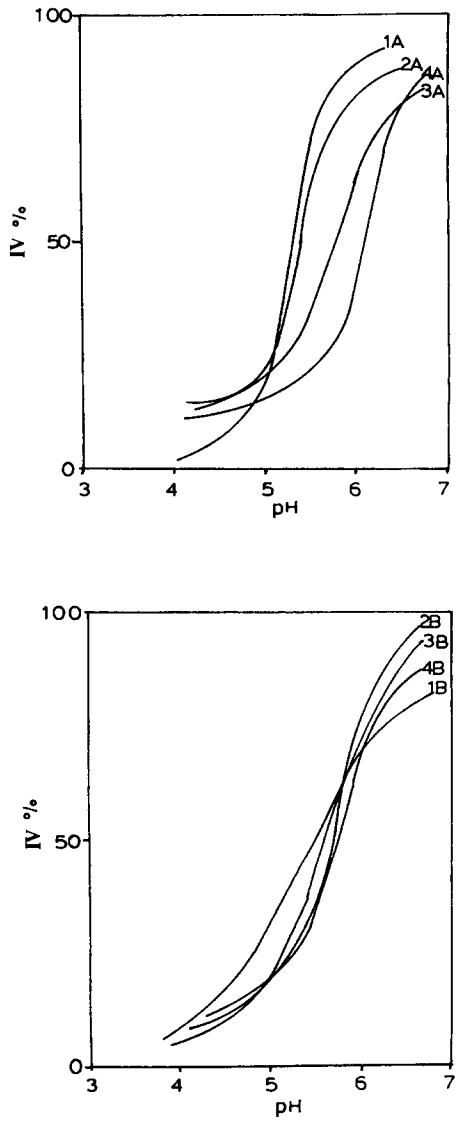


Fig. 5. Plots of pH $= f(\lambda_{max})$ of the complexes **A** (1–4) and **B** (1–4).

EXPERIMENTAL

Materials

The dipeptides glycyl–glycine (Gly–Gly), glycyl–L-alanine (Gly–Ala), glycyl–L-valine (Gly–Val) and glycyl–L-leucine (Gly–Leu) were purchased from Sigma Chemical Company and were used without further purification. $CuCl_2$ was from Alfa Inorganics.

Methods

(i) The elemental analysis for Cu and Cl were performed in our laboratory while those of C, H, N by the Laboratories of Chimie de Coordination, in Toulouse, France.

(ii) The conductivity measurements were made in our E 365 B Conductoscope Metrohm Ltd., Herisau, Switzerland.

(iii) The IR spectra were recorded on a Perkin–Elmer model 580 spectrophotometer.

(iv) The electronic spectra were obtained on a Perkin–Elmer Lambda 15 UV/vis spectrophotometer in rectangular quartz cells (1 cm).

(v) The ESR spectra were recorded on a Brucker ESP 300 E spectrometer at ≈9 GHz (*X*-Band).

Preparation of complexes

$CuCl_2$ (1 mmol) was dissolved in 6 cm^3 of a solution of ethanol : water (1 : 2) and 1 mmol of the corresponding dipeptide in an equal volume of the same solution. The two solutions were mixed and in the resulting blue solution 2 mmol of the corresponding nucleoside was added. The mixture was heated under stirring for 30 to 60 min at ≈70°C. After cooling to room temperature and filtering from any insoluble material, 10–15 cm^3 of ethanol were added to the solution and the resulting precipitate was filtered. It was then washed with a mixture of ice cold ethanol : water (8 : 2) and finally with ethanol and ether. Yields 35–65%.

UV/vis and ESR titrations

These were performed at $I = 0.1$ (KNO_3)[40] and the pH was adjusted by using dilute solutions of HNO_3 and KOH. Carbonate free dilute KOH solution was prepared under N_2 and standardized against standard potassium hydrogen phthalate. pH values were measured with a consort pH meter. Calibrations were made with Fluka AG standard buffer solutions (pH 4 and 7 at 25°C).

Table 4. ESR spectral data and calculated pK_a values of the complexes

Complex	pH	Percentage $C_{pH\sim4}$	Percentage $C_{pH\sim7}$	g_I	g_{II}	pK_a
1A	3.9	100	0	2.19	2.19	5.2
	4.45	97	3	2.19	2.19	
	5.05	77	23	2.19	2.19	
	5.9	13	87	2.19	2.14	
	7.01	0	100	2.19	2.14	
2A	3.9	100	0	2.19	2.19	5.3
	4.51	97	3	2.19	2.19	
	5.17	53	47	2.19	2.13	
	6.04	17	83	2.13	2.13	
	6.96	0	100	2.19	2.13	
3A	3.14	100	0	–	–	5.6
	4.10	86	14	–	–	
	4.55	82	18	–	–	
	5.01	78	22	–	–	
	5.99	–	–	–	–	
	6.97	15	85	–	–	
4A	3.18	100	0	–	–	6.0
	3.95	91	9	–	–	
	4.47	81	19	–	–	
	4.98	80	20	–	–	
	6.06	55	45	–	–	
	7.00	7	93	–	–	
1B	–	–	–	–	–	5.45
2B	–	–	–	–	–	5.60
3B	–	–	–	–	–	5.67
4B	–	–	–	–	–	5.75

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