

Supplementary Information

AdcA lipoprotein involved in Zn(II) transport in *Streptococcus mutans* – is it as metal-specific as expected?

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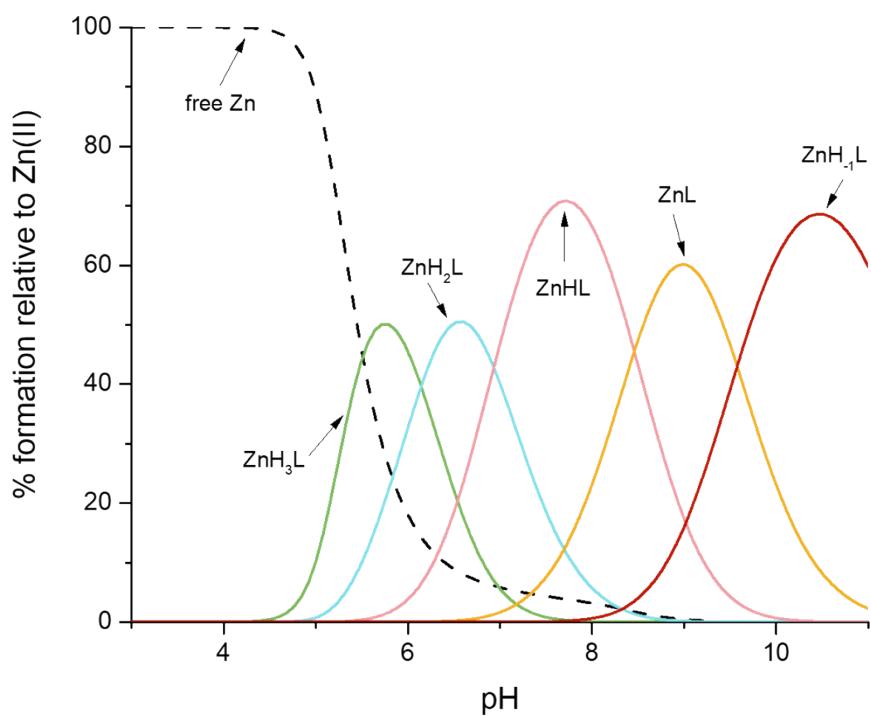
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*Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

10	20	30	40	50
MRKKPFIIVS	LLLVLAVVI	AFLLAKDGEK	RSNGKLNVVT	TFYPMYEFTK
60 NVVGDQGKVS	70 LLIKAGTEVH	80 DFEPSTKDVT	90 RIQEADTFVY	100 DSDSMETWVK
110 SVKKSVDTQK	120 VPFVKATGNM	130 ILAPGVTEE	140 E GHGHKGHHHA	150 YDPHVWLSPK
160 RAIKLVENIR	170 DALSKKFPHR	180 AKIFKKNAAN	190 YIDKLQTLDK	200 EYAEGLANAK
210 QKSFVTQHAA	220 FGYLALDYGL	230 TQIPITGLTA	240 ESEPSAKRLA	250 ELSKYVKEYG
260 INYIYFEENA	270 SSAVSKTLAD	280 ETGVKTAVLS	290 PLESLTQKQM	300 DAGENYFSVM
310 RANLKALKKT	320 TDSAGKEIKP	330 EMDSDKTVAN	340 GYFKDKSVKN	350 RKLSDWSGKW
360 QSIYPYLENG	370 TLDSVWDYKA	380 KSKKDMTAQE	390 YKEYYTGYK	400 TDVEKITIDG
410 KKNTITFVQK	420 GKEHKYTYKY	430 VGYKILTYKK	440 GNRGVRYLFE	450 TKDKGAGEFK
460 YVQFSD HGIK	470 SQKAEHFH LF	480 WGSESQDKLL	490 EEMGNWPTYY	500 PANLTGRQIA
510 QEIVAH				

Figure 1. Amino acid sequence of AdcA protein from *Streptococcus mutans*, probable Zn(II) binding sites are highlighted in red

A)



B)

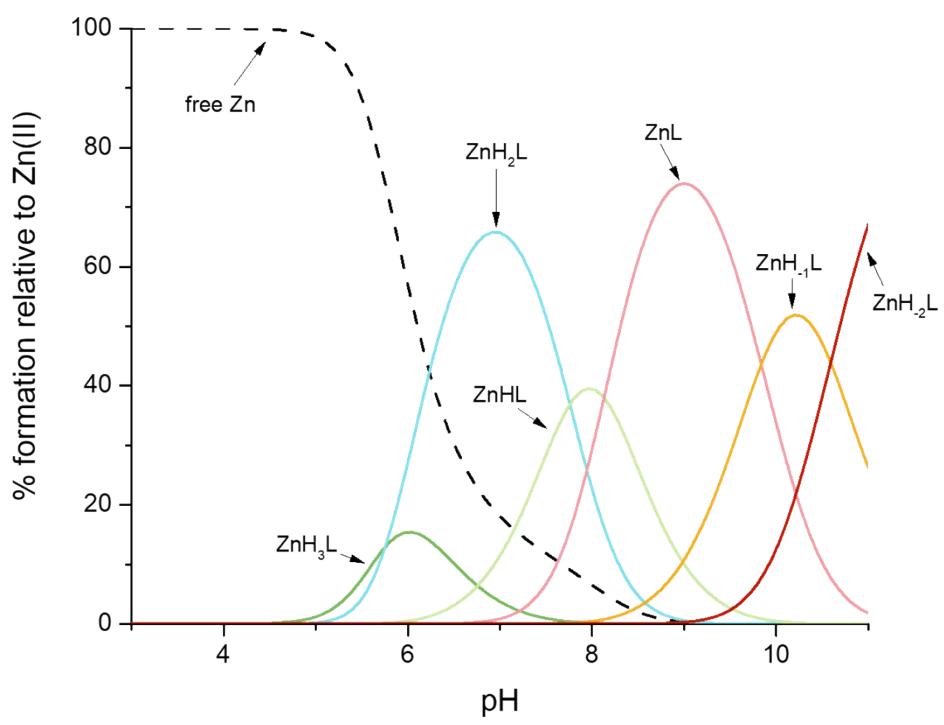
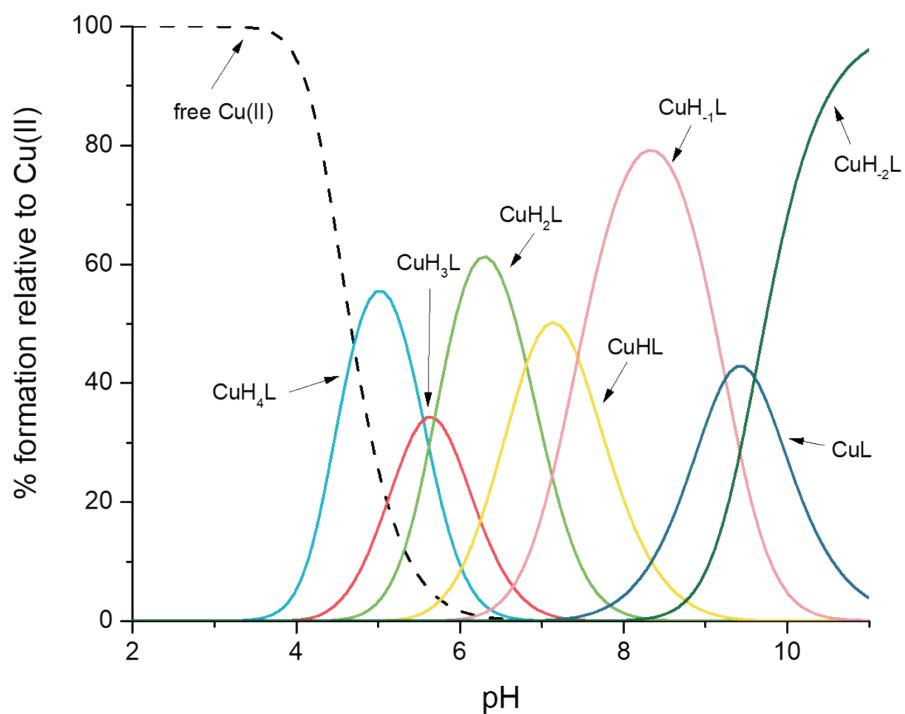


Figure 2. Species distribution diagrams for the formation of A) Zn(II) complexes with the Ac-EGHGHKGHHHA-NH₂; B) Zn(II) complexes with the Ac-HGIKSQKAEHFH-NH₂; T = 298 K; I = 0.1 M; [L] = 0.0005 M; M(II)/L molar ratio = 0.8 : 1

A)



B)

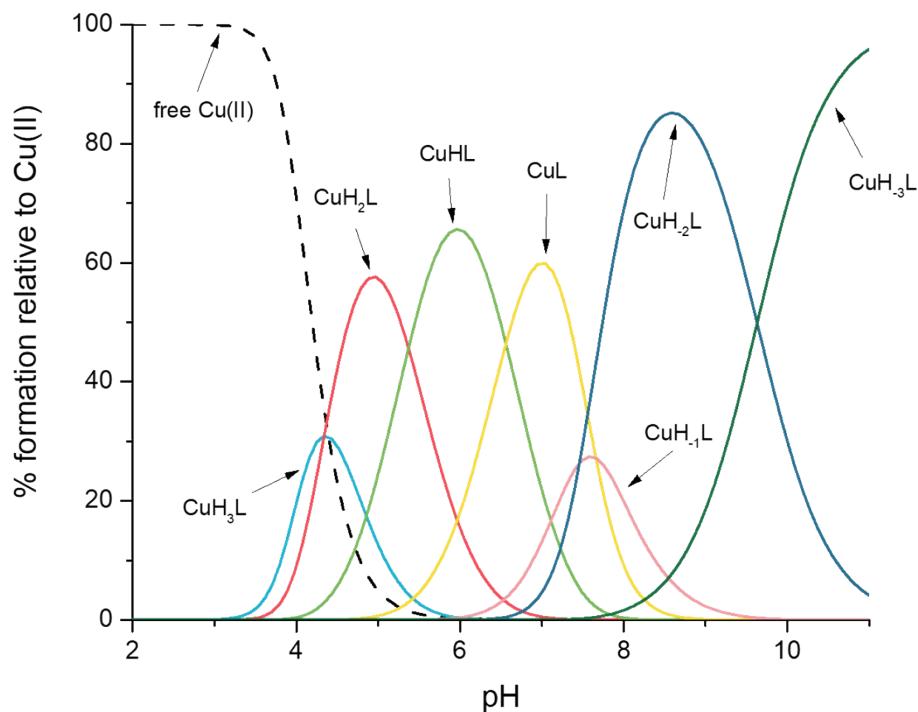


Figure 3. Species distribution diagrams for the formation of A) Cu(II) complexes with the Ac-EGHGHKGHHHA-NH₂; B) Cu(II) complexes with the Ac-HGIKSQKAEHFH-NH₂; T = 298 K; I = 0.1 M; [L] = 0.0005 M; M(II)/L molar ratio = 0.8 : 1

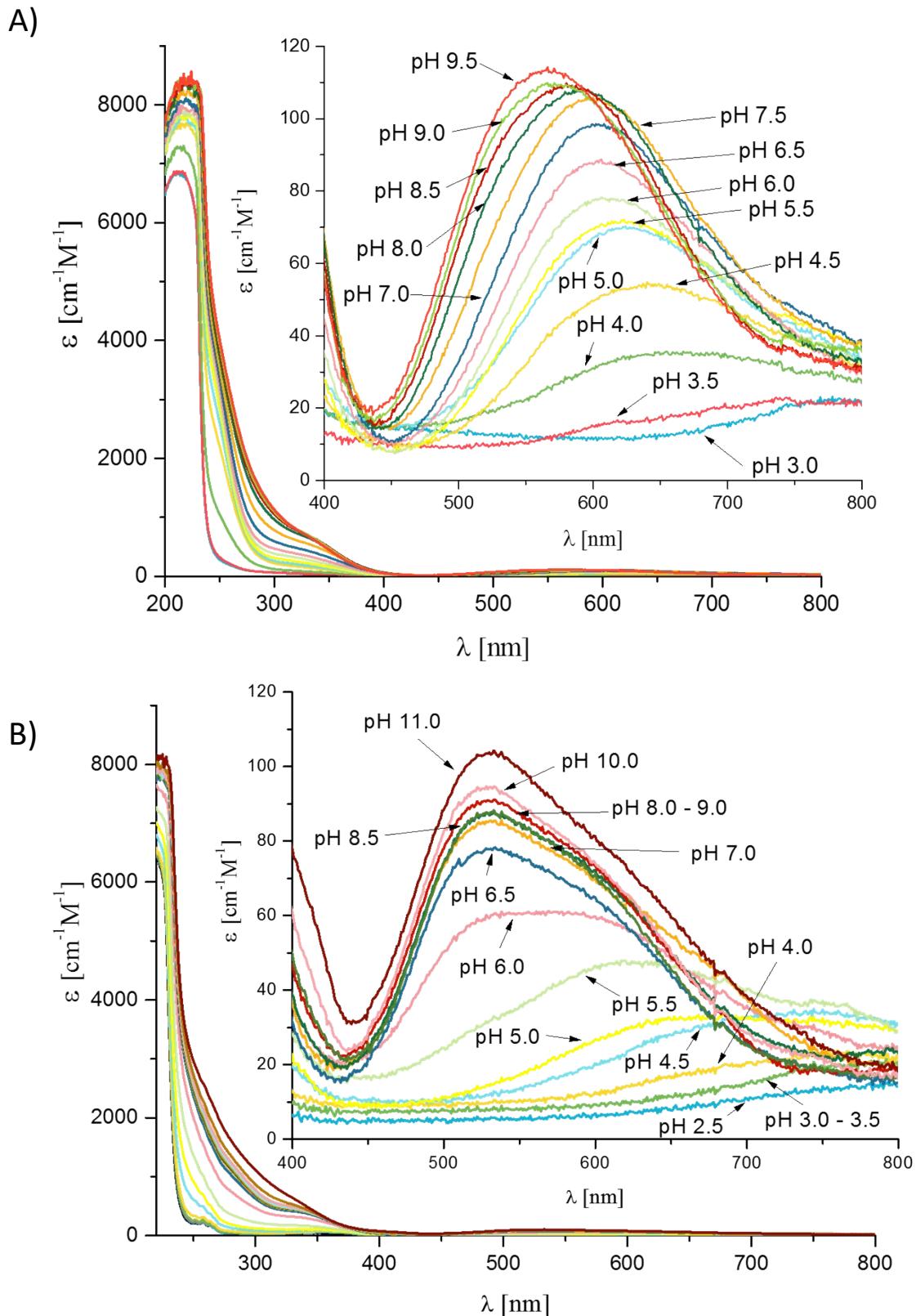


Figure 4. UV-Vis spectra of Cu(II) complexes with A) the Ac-EGHGHKGHHHA-NH₂; B) the Ac-HGIKSQKAHFH-NH₂ in the range 200-800 nm and pH range 2.0-11.0; T = 298 K; optical path = 1 cm; [L] = 0.0005 M; M(II)/L = 0.8 : 1

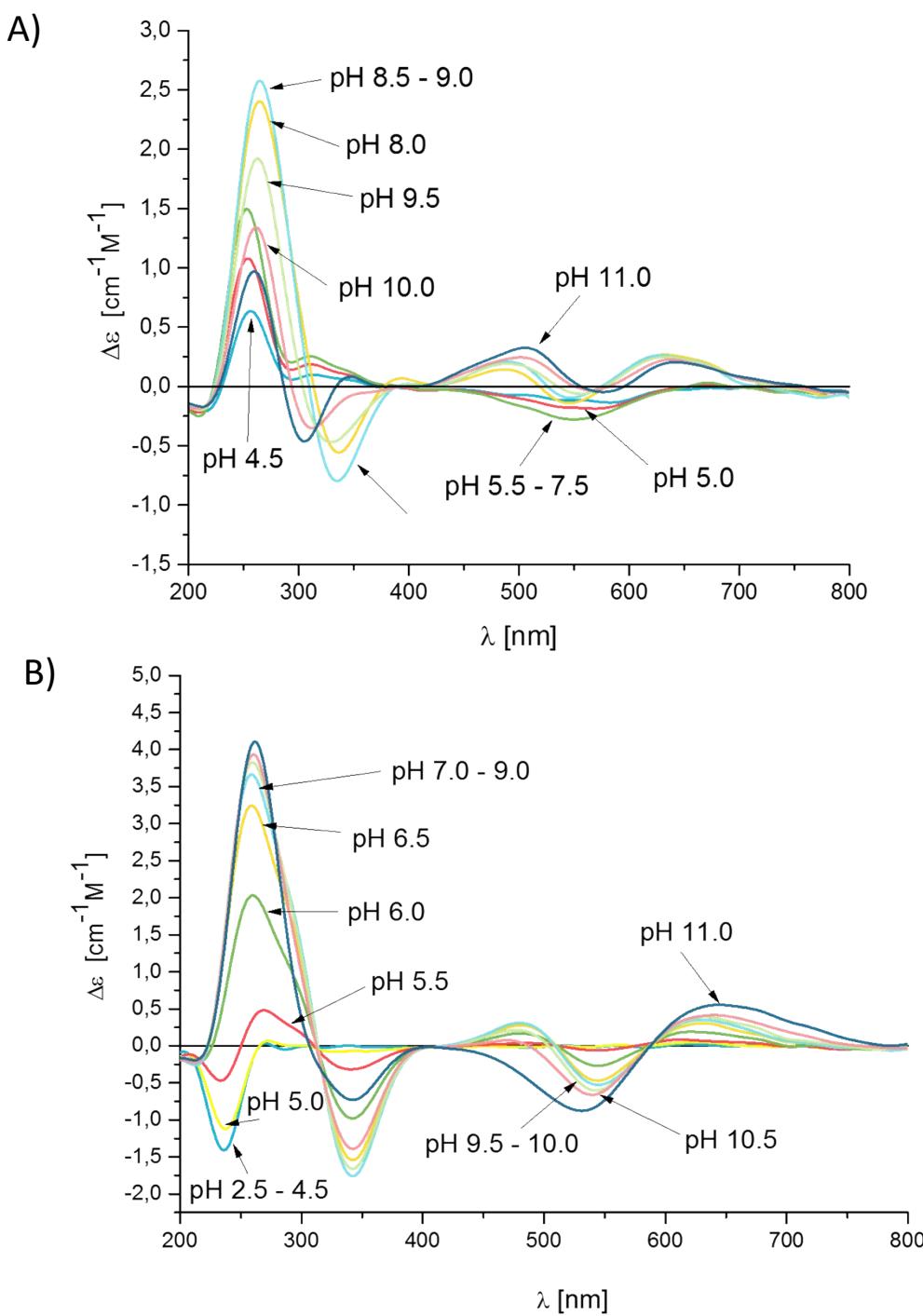
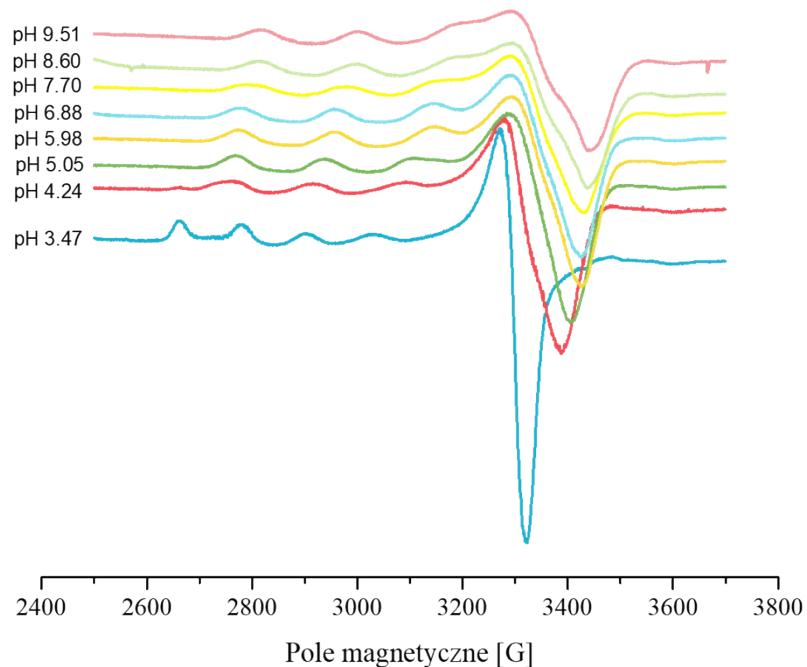


Figure 5. CD spectra of Cu(II) complexes with A) the Ac-EGHGHKGHHHA-NH₂; B) the Ac-HGIKSQKAEHFH-NH₂ in the range 200-800 nm and pH range 2.0-11.0; T = 298 K; optical path = 1 cm; [L] = 0.0005 M; M(II)/L = 0.8 : 1

A)



B)

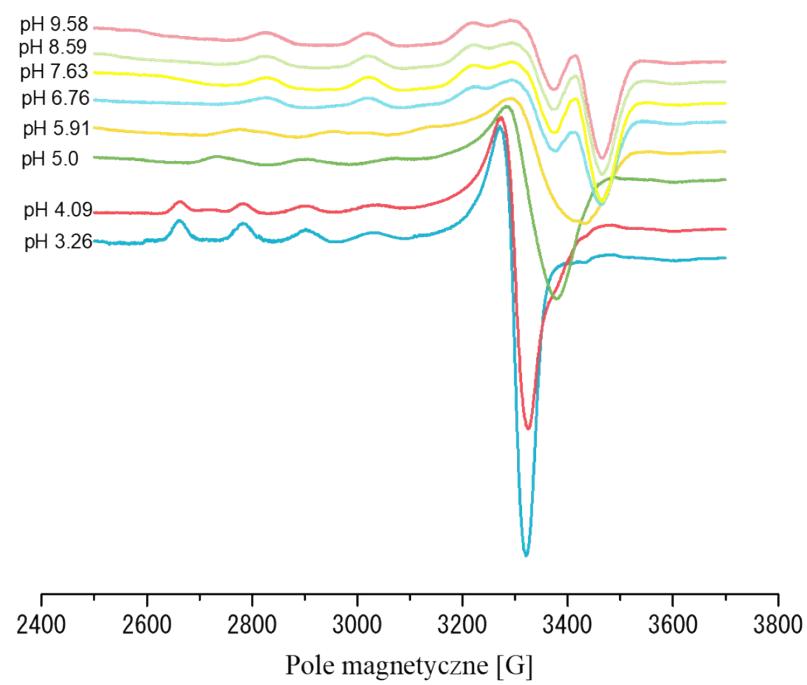


Figure 6. EPR spectra of Cu(II) complexes with A) the Ac-EGHGHKGHHHA-NH₂; B) the Ac-HGIKSQKAEHFH-NH₂

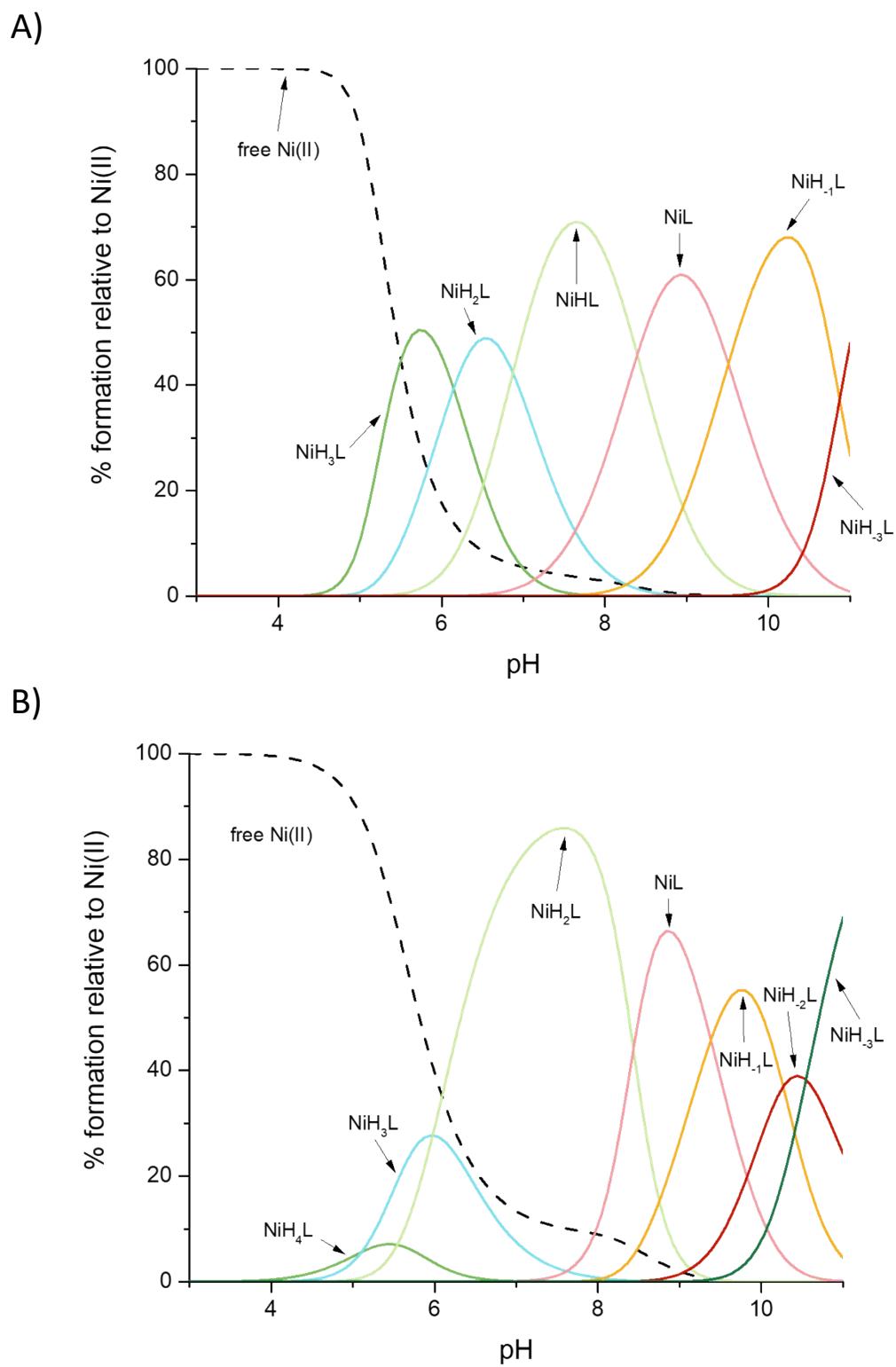


Figure 7. Species distribution diagrams for the formation of A) Ni(II) complexes with the Ac-EGHGHKGHHHA-NH₂; B) Ni(II) complexes with the Ac-HGIKSQKAEHFH-NH₂; T = 298 K; I = 0.1 M; [L] = 0.0005 M; M(II)/L molar ratio = 0.8 : 1

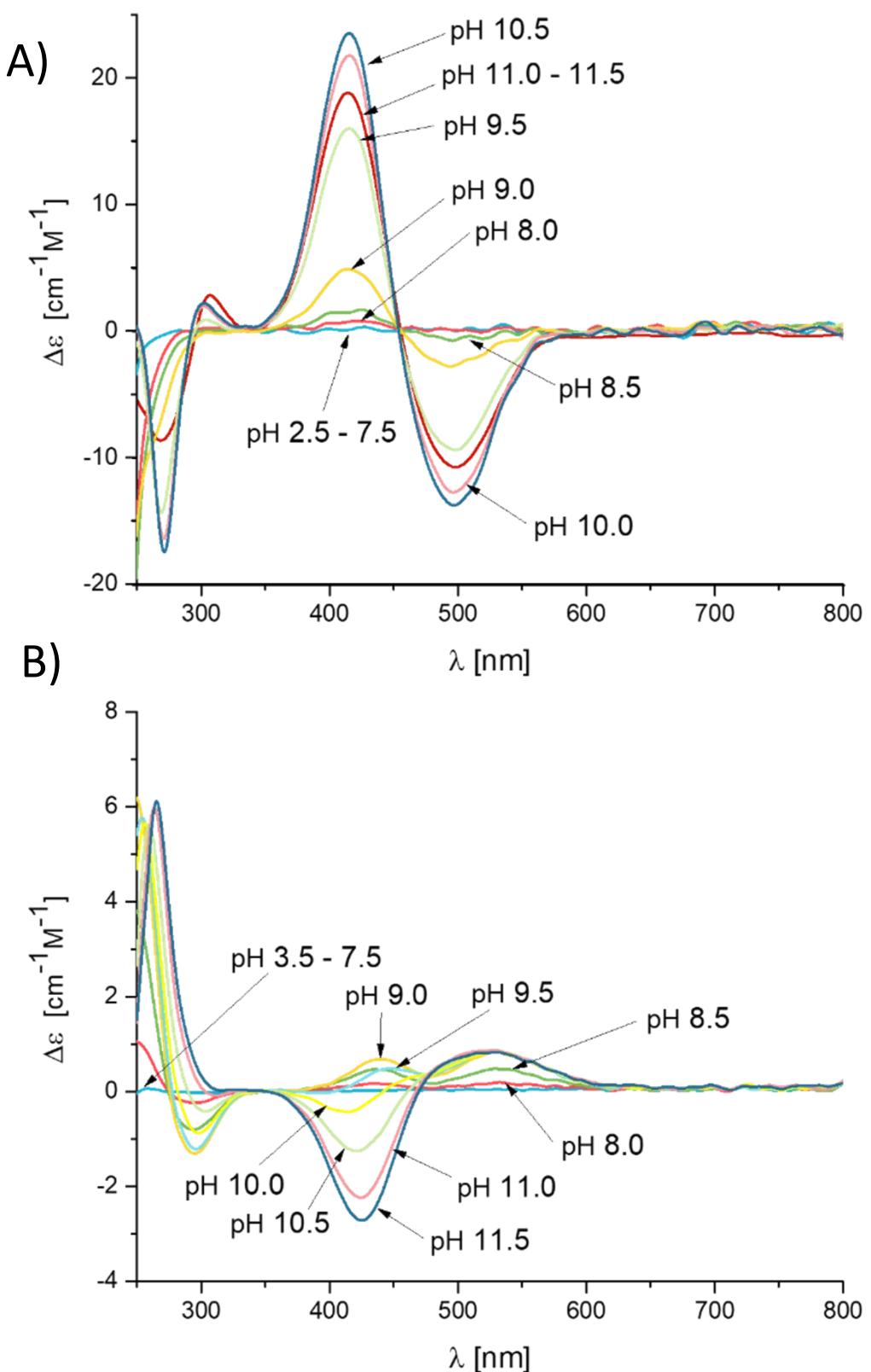
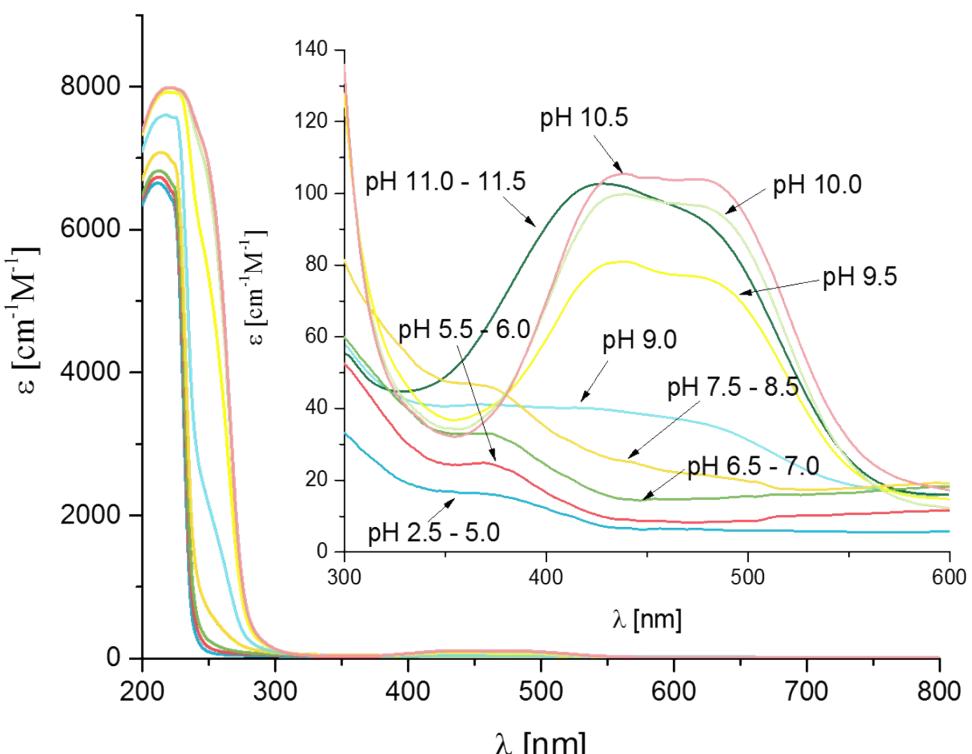


Figure 8. CD spectra of Ni(II) complexes with A) the Ac-EGHGHKGHHHA-NH₂; B) the Ac-HGIKSQKAHFH-NH₂ in the range 250-800 nm and pH range 2.5-10.5; T = 298 K; optical path = 1 cm; [L] = 0.0005 M; M(II)/L = 0.8 : 1

A)



B)

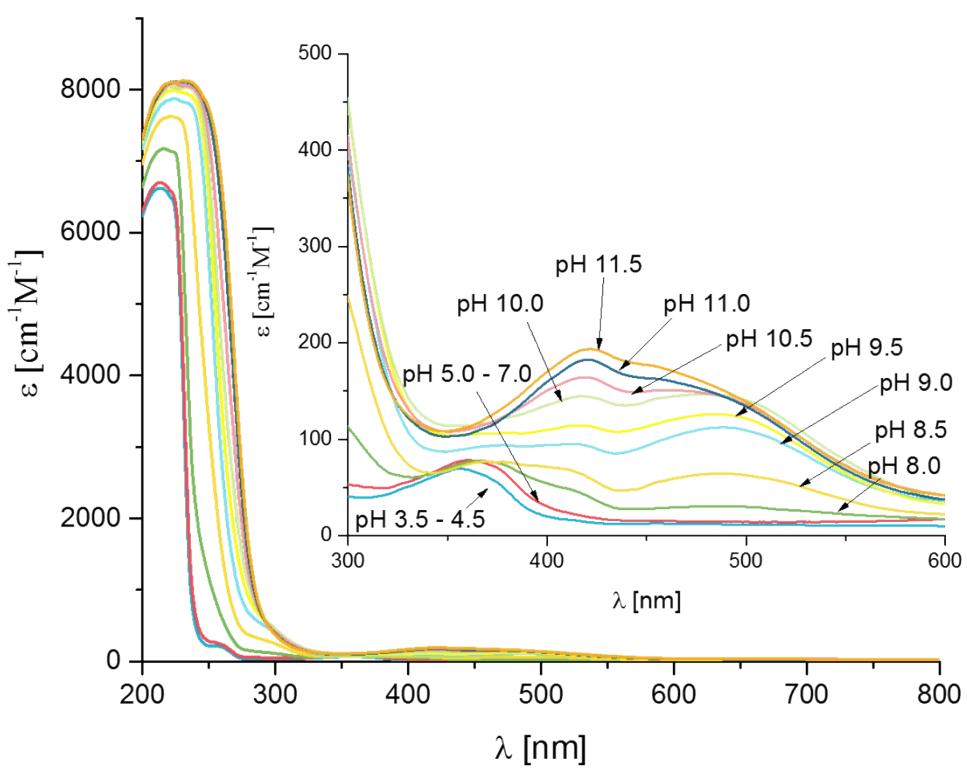


Figure 9. UV-Vis spectra of Ni(II) complexes with A) the Ac-EGHGHKGHHHA-NH₂; B) the Ac-HGIKSQKAHFH-NH₂ in the range 200-800 nm and pH range 2.5-10.5; T = 298 K; optical path = 1 cm; [L] = 0.0005 M; M(II)/L = 0.8 : 1

Table 1 Equilibrium constants for Ac-EGHGHKGHHHA-NH₂ ligand, spectroscopic parameters and proposed coordination modes for Cu(II) complexes at T = 298 K and I = 0.1 M (NaClO₄); M(II)/L = 0.8 : 1

Ac-EGHGHKGHHHA-NH ₂									
	Log β	Log K	UV-Vis	CD	EPR				
			λ [nm]	ε [M ⁻¹ ·cm ⁻¹]	λ [nm]	Δε [M ⁻¹ ·cm ⁻¹]	A _{II} [G]	g _{II}	
CuH ₄ L	36.62 (1)		328 640	154.16 54.81	256 314 540	0.64 0.10 -0.11	150	2.31	1N_{im}/2N_{im}
CuH ₃ L	32.28 (1)	4.34	328 627	188.17 69.96	254 311 554	1.08 0.19 -0.18	171	2.28	2N_{im}
CuH ₂ L	26.91 (2)	5.37	334 606	271.39 78.29	253 308 546	1.65 0.29 -0.30	188	2.25	3N_{im}
CuHL	20.35 (2)	6.56			256 385 545 643	1.53 0.04 -0.22 0.11	188	2.25	2N_{im}1N[·]
CuL	12.69 (3)	7.66			264 334 392 488 546 634	2.40 -0.55 0.07 0.14 -0.14 0.27	195	2.23	1N_{im}2N[·]
CuH _{.1} L	5.23 (3)	7.46			265 335 488 547 634	2.60 -0.76 0.20 -0.14 0.26	205	2.21	1N_{im}3N[·]
CuH _{.2} L	-4.40 (5)	9.63			263 329 490 556 633	1.92 -0.47 0.19 -0.06 0.25	205	2.21	1N_{im}3N[·]

Table 2 Equilibrium constants for Ac-HGIKSQKAEHFH-NH₂ ligand, spectroscopic parameters and proposed coordination modes for Cu(II) complexes at T = 298 K and I = 0.1 M (NaClO₄); M(II)/L = 0.8 : 1

Ac-HGIKSQKAEHFH-NH ₂									
	Log β	Log K	UV-Vis		CD	EPR		Binding mode	
			λ [nm]	ε [M ⁻¹ ·cm ⁻¹]	λ [nm]	$\Delta\varepsilon$ [M ⁻¹ ·cm ⁻¹]	A_{II} [G]	g_{II}	
CuH ₃ L	33.73 (3)		352 672	104.99 32.28	238	-2.19	152	2.31	1N_{im}/2N_{im}
CuH ₂ L	28.18 (5)	5.55	346 619	156.69 47.99	233 269 341	-0.47 0.48 -0.32	170	2.26	3N_{im}
CuHL	22.49 (4)	5.69	336 534	398.07 78.32	259 342 480 544 635	3.24 -1.54 0.32 -0.51 0.33	193	2.20	3N_{im}1N[·]
CuL	15.68 (5)	6.81	335 526	430.07 85.17	259 342 481 544 630	3.57 -1.71 0.29 -0.54 0.33	195	2.20	2N_{im}2N[·]
CuH ₁ L	8.24 (4)	7.44	331 528	452.75 87.72	259 342 479 545 633	3.71 -1.80 0.32 -0.55 0.35	206	2.20	1N_{im}3N[·]
CuH ₂ L	-1.00 (7)	9.24	327 528	476.53 91.57	259 342 479 544 635	3.79 -1.77 0.29 -0.56 0.35	206	2.20	1N_{im}3N[·]
CuH ₃ L	-10.60 (5)	9.60	337 528	552.11 103.49	262 342 531 644	4.11 -0.73 -0.88 0.55	206	2.20	1N_{im}3N[·]