Solvent Extraction Studies on Copper(II) and Silver(I) Complexes of Bis(4-hydroxypent-2-ylidene)diaminoethane: Composition of Extracted Copper(II) Species

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Abstract: Copper(II) complexes of bis(4-hydroxypent-2-ylidene)diaminoethane (BHPDE) were prepared by extractive method. Job's continuous variation and equilibrium constant methods, as well as spectral and elemental analyses were applied in the determination of the nature of extracted species. The results indicate the formation of mixed ionic complexes of the types $\text{Cu}(\text{H}_2\text{L})\text{X}_2$, $\text{Cu}(\text{H}_2\text{L})_2\text{X}_2$ and CuL (where H_2L = BHPDE and $\text{X} = \text{NO}_3^-$, ClO_4^- , Cl^- or $\frac{1}{2}\text{SO}_4^{2-}$). $\text{Cu}(\text{H}_2\text{L})\text{X}_2$ and $\text{Cu}(\text{H}_2\text{L})_2\text{X}_2$ predominate at low pH extractions while CuL chelate predominates at high pH extraction. The complexes exist in two isomeric forms, the blue readily-water-soluble and the violet less water-soluble forms. Both complexes show maximum absorption at 540 nm and molar absorptivity values of about $2.0 \times 10^2 \text{ dm}^3 \text{ mole}^{-1} \text{ cm}^{-1}$.

Keywords: Extraction, Copper(II), Bis(4-hydroxypent-2-ylidene)diaminoethane, UV-Vis

Introduction

Bis(4-hydroxypent-2-ylidene)diaminoethane (BHPDE) has been synthesised and characterized via UV-Vis^{1,2}, FTIR³⁻⁵ and NMR^{6,7}. Through these means it was established to exist in three tautomeric forms⁸. The coordination chemistry of BHPDE with divalent metal ions and the potentials of BHPDE as a photometric reagent and as extractant for Cu(II) and many other metal ions have been documented⁹⁻¹².

In our previous effort we had reported a comprehensive scheme for the extraction of Cu(II) and Ag(I) using BHPDE in various media¹³. Also we pursued an extensive study

towards establishing the effect of medium pH, complexing agents, acid concentration and salting-out agents on the extraction of the two metals¹⁴. A scheme for the separation of Ag(I) from Cu(II) in a synthetic mixture using BHPDE was proposed^{13,14}.

The present effort is an attempt at characterizing the extracted Cu(II) species formed at the various conditions that afforded quantitative extraction. This is with the aim to gaining insight into the various extraction profiles presented by Cu(II) at high and low pH as well as in concentrated and dilute acid solutions.

Experimental

Bis(4-hydroxypent-2-ylidene)diaminoethane (BHPDE) was prepared as reported elsewhere^{13,14} and was characterized based on melting point, UV-Vis, IR and NMR spectra. Stock solutions of Cu(II) were prepared using CuCl₂ (Merck, Analar grade). Buffer solutions were prepared following the Clark and Lubbs method¹⁵. Stock solutions of mineral acids (HNO₃, HCl, HClO₄ and H₂SO₄) were prepared by diluting the concentrated acids and were standardized using appropriate primary standard bases.

Electronic spectra of ligand and complexes were obtained on Pye-Unicam UV-Vis spectrophotometer. Infra-red spectra of the compounds were recorded using Thermo electron corporation IR 100 series. NMR data were run on Varian mercury YH200 MHz NMR spectrometer. Microanalysis of ligand and complexes was done at the Department of Chemistry, University of Sussex, England.

Determination of composition of extracted species

Job's continuous variation or equimolar method was employed in determining the composition of extracted species as reported elsewhere¹⁶ and confirmed by the method of equilibration constant¹⁷.

Synthesis of Cu(II) - BHPDE complexes

The complexes were synthesized from pre-determined high and low pH of quantitative extraction^{13,14} in order to ascertain the nature of extracted species. CuCl₂ was dissolved in pH 9.0 buffer and evaporated to dryness and redissolved in the same buffer solution to obtain 20 mL of 0.001 M metal ion solution. This solution was reacted with 2.23×10^{-3} mole of freshly prepared BHPDE at 40 °C and stirred for 300 s. The crystals formed were recrystallised in H₂O/Dioxane (40/60), dried and characterized. The same procedure was followed in preparing the complex from low pH solution (0.001 to 0.1 M H₂SO₄, HNO₃, HCl and HClO₄). The above procedures were repeated at room temperature and complexes formed extracted using CHCl₃. The organic extracts were evaporated to dryness, the products recrystallised using H₂O/dioxane, dried and characterized.

Results and Discussion

Job's continuous variation method was employed in investigating the metal-ligand mole ratio of copper(II)-BHPDE complexes extracted from acid solutions. The results as summarized in Figure 1 shows a metal-ligand mole ratio of 2:3 in all the acids studied. The result differs from what was obtained (1:1 metal-ligand ratio) in the log-log plot of BHPDE against distribution ratio (D) in Figure 2. This variation is likely due to the fact that at the conditions of extraction two types of complexes are formed having 1:1 and 1:2 metal-ligand ratio respectively. A combination of these gives a mixture of ionic complexes with 2:3 metal-ligand mole ratio especially at high ligand concentrations. Formation of ionic complexes of BHPDE with lanthanides^{18,19} and zinc²⁰ has been documented. Our results seem to be in conformity with these.

Figure 1. Jobs curve for Cu(II) - BHPDE complex. Metal ligand mole ratio = 2:3. (a) 0.001M HCl; (b) 0.001M HNO₃; (c) 0.001M H₂SO₄; (d) 0.001M HClO₄

Figure 2. Effect of initial concentration of BHPDE on the distribution of Cu(II)

The slope of the curve in Figure 2 gives the value of 1.0 implying 1:1 Cu-BHPDE mole ratio. This result is supported by the fact that at low pH (10^{-3} - 10^{-1} M, acid) the ligand is protonated and can complex with copper as a neutral molecule²⁰⁻²¹. On the basis of this, extraction of copper(II) could be explained using the following equations.

$$K_{\text{ex}} = \frac{[\text{Cu}(\text{H}_2\text{B})_2 \cdot \text{X}_2] \cdot [\text{H}^+]^2}{[\text{Cu}(\text{H}_2\text{O})_6]^{2+} \cdot [\text{H}_3\text{B}^+]^2 \cdot [\text{X}^-]^2} \quad (2)$$

$$= D \times \frac{[\text{H}^+]^2}{[\text{X}^-]^2 [\text{H}_3\text{B}^+]^2} \quad (3)$$

(K_{ex} = extraction constant; D = distribution ratio). As reported previously^{14,15}, the first base dissociation constant K_{lb} is given as

$$K_{\text{lb}} = \frac{[\text{H}_3\text{B}^+]}{[\text{H}_2\text{B}][\text{H}^+]}$$

$$\therefore [\text{H}_3\text{B}^+] = K_{\text{lb}} [\text{H}_2\text{B}][\text{H}^+] \quad (4)$$

Substituting equation (4) into (3) gives

$$K_{\text{ex}} = \frac{D}{[\text{X}^-]^2 K_{\text{lb}}^2 [\text{H}_2\text{B}]^2} \quad (5)$$

$$\therefore \log K_{\text{ex}} = \log D - 2\log [\text{X}] - 2\log [\text{H}_2\text{B}] - 2\log K_{\text{lb}} \quad (6)$$

$$\therefore \log D = 2\log [\text{X}] + 2\log [\text{H}_2\text{B}] + 2\log K_{\text{lb}} + \log K_{\text{ex}} \quad (7)$$

(H_2B = BHPDE and X = NO_3 , Cl , or $\frac{1}{2}\text{SO}_4$)

The determined extraction constant, K_{ex} , from equation (7) as depicted in Figure 2 is $10^{15.9}$. The ligand behaves as a weak acid and in high pH media^{13,14} formation of a chelate will probably be according to equation (8).

Molecular formulae of complexes

Table 1 shows some physical properties and microanalytical data of both ligand and complexes. Complexes prepared in high pH media show sharp melting point ($\approx 145^\circ\text{C}$) while those prepared at low pH decompose at about 240°C . This indicates that at high pH, 1:1 complexes of the form CuB are formed and their nature is not dependent on whether they are extracted or synthesized.

At low pH of the aqueous mixture the complexes formed are either 1:2 or 2:3 metal-ligand ratio. The 2:3 complexes being a mixture of 1:1 and 1:2 as stated above. The complexes formed at high pH are mostly greenish or violet whereas at low pH, violet and blue (purple) complexes are obtained. The violet form predominates in organic solvents and is the most stable. Other forms tend to give violet colour in organic solvents. The violet form crystallizes more readily from aqueous preparation media than the blue form.

From Table 1, it is also noticeable that the number of anions attached to the complex seems to depend on the anion concentration. This is quite evident in the complexes prepared in HCl media.

Table 1. Physical and microanalytical data of ligand and complexes

Molecular formula	preparation Condition	m.p, °C	Yield, %	Colour	Required, %			Found, %		
					C	H	N	C	H	N
$C_{12}H_{20}N_2O_2$	-	111-112	95.5	White	64.24	8.93	12.50	63.98	7.45	12.43
$CuC_{12}H_{18}N_2O_2$	pH 9 (Ext)	114-112	56	Violet	50.41	7.03	9.80	50.15	6.18	9.32
$CuC_{12}H_{18}N_2O_2$	pH 9 (Synth)	146	48	Violet	50.41	7.03	9.80	49.74	6.15	9.36
$Cu(C_{12}H_{20}N_2O_2)_3$ $Cl_3(OH)$	10^{-3} M HCl (Synth)	239(Dec)	62	Purple	49.42	6.93	9.60	49.74	6.15	7.32
$Cu_2(C_{12}H_{20}N_2O_2)_3$ $Cl_3(OH)$	10^{-3} M HCl (Ext)	240(Dec)	59	Purple	46.81	6.67	9.10	46.02	5.67	Not det
$Cu(C_{12}H_{20}N_2O_2)_2$ (NO_3) (OH)	10^{-3} M HNO_3 (Ext)	235(Dec)	43	Blue	48.75	7.00	11.84	48.41	6.69	Not det
$Cu(C_{12}H_{20}N_2O_2)_2$ (NO_3) (OH)	10^{-2} M HNO_3 (Ext)	235(Dec)	50	Blue	48.75	7.00	11.84	47.88	6.63	Not det
$Cu_2(C_{12}H_{20}N_2O_2)_3$ Cl_2SO_4	10^{-3} M H_2SO_4 (Synth)	236(Dec)	45.9	Violet	44.7	6.30	8.69	45.71	5.25	Not det
$Cu_2(C_{12}H_{20}N_2O_2)_3$ $Cl_2(OH)_2$	10^{-3} M H_2SO_4 (Ext)	236(Dec)	42.3	Violet	47.8	6.92	9.30	47.68	6.06	8.65
$Cu_2(C_{12}H_{20}N_2O_2)_3$ $Cl_2(OH)_2$	10^{-3} M $HClO_4$ (Ext)	235(Dec)	47.2	Violet	47.8	6.92	9.30	47.88	5.43	8.83
$Cu_2(C_{12}H_{20}N_2O_2)_3$ $Cl_3(OH)_2$	10^{-3} M $HClO_4$ (Synth)	235(Dec)	46.0	Purple	47.8	6.92	9.30	47.11	5.19	9.00

Legend: Ext = Extracted; Synth = Synthesized; Dec = Decomposes; Not det = Not determined

Electronic spectra

UV spectral data of BHPDE and its synthesized and extracted Cu(II) complexes are displayed in Table 2. The ligand absorbs at 321.9 nm with a shoulder at 237 nm and molar absorptivities are 5.3×10^4 and 1.1×10^4 L mol⁻¹ cm⁻¹ respectively. This has been attributed to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. The complexes absorb between 297 and 310 nm with molar extinction between 10^4 to 10^6 L mol⁻¹ cm⁻¹. Another prominent peak at about 241 nm also appears in the complexes extracted from high pH media. From what has been reported for other Schiff base complexes¹⁸ the peak at 321.9 nm in the ligand and now at 297 nm and 310 nm in the complexes is due to electronic transition in the hydrogen-bonded chelate rings. Hypsochromic shift in the complexes is likely the result of interaction of the metal ion with the non-bonding electrons of ketoamine nitrogens.

The visible spectra of complexes (Table 2) present a maximum absorption at 540 nm and molar absorptivity of about 10^2 . Although three bands should be expected for tetragonally distorted Cu(II) complexes for the transitions ${}^2B_{1g} \rightarrow {}^2A_2$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$, and ${}^2B_{1g} \rightarrow 2E_g$ in order to increasing energy, but in general one broad band is obtained with or without shoulder at about 1400-800 cm⁻¹. This is likely due to d←d transitions or d←d transitions coupled with charge transfer spectra¹⁸. Table 3 shows that the complexes formed under various conditions absorbed between 540 nm to 545 nm with molar absorptivities of 200 to 252 L mol⁻¹ cm⁻¹ confirming the fact that the mode of preparation (extracted or synthesized) did not confer extra properties on the complexes.

Table 2. Ultra-Violet spectra of BHPDE and its copper(II) complexes in chloroform

Molecular formula	Preparation Condition	$\lambda_{\max}1$, nm	$\epsilon_{\max}1$, L mole ⁻¹ cm ⁻¹	$\lambda_{\max}2$, nm	$\epsilon_{\max}2$, L mole ⁻¹ cm ⁻¹	$\lambda_{\max}3$, nm	$\epsilon_{\max}3$, L mole ⁻¹ cm ⁻¹
BHPDE	-	321.9(s)	5.3×10^4	327(sh)	1.1×10^4	-	-
Cu B	pH 9 (Ext)	311.6(s)	4.9×10^4	272.5(b)	4.8×10^4	241.9(sh)	4.3×10^4
Cu B	pH 9 (Synth)	311.7(s)	2.0×10^4	277.2(sh)	1.0×10^4	240.7(s)	1.4×10^4
Cu(H ₂ B) ₂ .Cl ₂	10 ⁻³ M HCl (Synth)	310.9(s)	2.1×10^5	242.7(s)	1.4×10^5	-	-
Cu ₂ (H ₂ B) ₃ .Cl ₂ (OH)	10 ⁻² M HCl (Ext)	297.3(s)	8.3×10^4	245(s)	6.7×10^4	-	-
Cu(H ₂ B) ₂ .NO ₃ .(OH)	10 ⁻³ M HNO ₃ (Ext)	310.4(s)	6.8×10^4	243.5(s)	5.6×10^4	-	-
Cu(H ₂ B) ₂ .NO ₃ (OH)	10 ⁻² M HNO ₃ (Synth)	307.4(s)	1.5×10^4	242.4(s)	1.2×10^4	-	-
Cu ₂ (H ₂ B) ₃ .Cl ₂ . (OH) ₂	10 ⁻³ M H ₂ SO ₄ (Ext)	296.8(s)	8.9×10^4	246.4(s)	7.6×10^4	-	-
Cu ₂ (H ₂ B) ₃ .Cl ₂ .SO ₄	10 ⁻¹ M H ₂ SO ₄ (Synth)	309.6(s)	5.4×10^4	243.1(s)	4.1×10^4	-	-
Cu ₂ (H ₂ B) ₃ .Cl ₂ . (OH) ₂	10 ⁻³ M HClO ₄ (Synth)	298.1(s)	2.0×10^5	246.4(s)	1.3×10^5	-	-
Cu ₂ (H ₂ B) ₃ .Cl ₂ . (OH) ₂	10 ⁻³ M HClO ₄ (Ext)	296.8(s)	1.1×10^6	247.5(s)	8.9×10^4	-	-

Legend: S = Sharp; Sh = Shoulder; B = Broad; Ext = Extracted; Synth = Synthesized

Table 3. Visible spectra of some of Cu-BHPDE complexes in chloroform

Molecular formula	Method of Preparation	$\lambda_{\max}$, nm	$\epsilon_{\max}2$, L mole ⁻¹ cm ⁻¹
Cu B	pH 9 (Ext)	540	200.1
Cu B	pH 9 (Synth)	543	202.3
Cu ₂ (H ₂ B) ₃ .Cl ₂ .SO ₄	10 ⁻¹ M H ₂ SO ₄ (Synth)	541	240
Cu ₂ (H ₂ B) ₃ .Cl ₂ (OH) ₂	10 ⁻² M HClO ₄ (Ext)	545	252

Legend: H₂B = BHPDE; Ext = Extracted; Synth = Synthesized

FTIR spectra

Table 4 gives the essential peaks of ligand and complexes and presents a scheme for determining the mode of ligation of the ligand. The peak at 3100 cm⁻¹ due to hydrogen-bonded OH or NH in the ligand appears with weaker intensities at 2900 cm⁻¹ in complexes prepared from low pH but is absent in complexes prepared from high pH media. This is indicative of ligation to the nitrogen and oxygen atoms of the undissociated ligand at low pH, -NH and -OH vibrations being limited by the presence of the metal. At high pH deprotonation takes place before complexation thereby leading to absence of $\nu(\text{NH})$ or $\nu(\text{OH})$.

Free OH peaks at 3550 cm⁻¹ in the complexes extracted and prepared from pH 9 and 10⁻³ M HCl is not likely due to coordinated water since it is not supported by elemental analysis. It is probably due to presence of moisture in the Nujol mulls. The bands at 1600-1645 cm⁻¹ in both ligand and complexes extracted and synthesized from pH 9 is likely due to hydrogen-bonded carbonyl stretch. On chelation the carbonyl stretch suffers only slight distortion as only the imino hydrogens are removed before chelation. The band between 1600-1560 cm⁻¹ is ascribed to $\nu(\text{C}=\text{C})$ and 1560-1430 cm⁻¹ due to $\nu(\text{C}=\text{N})$. The lower frequencies of some of these bands is due to intramolecular hydrogen-bonding.

Table 4. Infrared Absorption Bands (cm^{-1}) of Nujol Mulls

Assignment	-OH, from water	OH,	NH,	CH_3 , CH_2	C = O	C = C	C=N	C – CH_3 ,	C – N	C – O	C=C – H	Cu – O
BHPDE	-	3100 (br)	2900(br)	2820(w)	1625(w)	1590(br)	1500(s)	1440(w) 1355(w)	1340(s)	1270(s) 1125(w)	920(w)	
Cu B. pH 9 (ext)	3500 (br)		2890(w)	2820(w)	1630(w)	1525(m)	1490(w)	1440(br) 1360(br)	1335(w)	1260(w) 1100(w)	930(s)	235(w)
Cu B. pH 9 (synth)	3500 (br)		2890(w)	2820(br)	1640(w)	1570(w)	1500(w)	1450(w) 1400(br)	1335(br)	1250(w) 1100(s)	930(s) 300(s)	265(w)
$(\text{Cu}(\text{H}_2\text{B})_2.\text{Cl}_2)$ 10^{-2} M HCl (synth)	3500 (br)		2900(w)	2820(w)		1560(w)	1500(w)	1400	1335(w)	1260(m) 1100(s)	930(vs) 280(m)	200(w)
$(\text{Cu}(\text{H}_2\text{B})_3.\text{Cl}_2$ (OH)) 10^{-2} M HCl (synth)			2900(m)	2820(w)		1560(m)	1510(m)	1440(m) 1395(w)	1340(w)	1260(s) 1175(w)	920(s) 270(m)	250(w)
$(\text{Cu}(\text{H}_2\text{B})_2.\text{NO}_3$ (OH)) 10^{-3} M HNO ₃ (ext)			2890(s)	2820(w)		1560(s)	1510(m)	1440(w) 1360(w)	1340(w)	1260(s) 1100(w)	920(m) 270(m)	200(w)
$(\text{Cu}(\text{H}_2\text{B})_2.\text{NO}_3$ (OH)) 10^{-3} M HNO ₃ (ext)			2895(vs)	2820(s)		1560(s)	1510(m)	1440(m) 1360(w)	1340(w)	1260(s) 1100(w)	920(m) 275(m)	200
$(\text{Cu}_2(\text{H}_2\text{B})_3.\text{Cl}_2\text{S}$ $\text{O}_4)$ 10^{-1} M H ₂ SO ₄ (synth)			2895(br)	2820(s)		1560(s)	1510(m)	1440(m) 1360(w)	1340(w)	1260(s) 1100(w)	920(s) 280(s)	299(m)
$(\text{Cu}_2(\text{H}_2\text{B})_2.\text{Cl}_2$ (OH) ₂) 10^{-2} M H ₂ SO ₄ (ext)			2900(br)	2820(s)		1560(w)	1510(w)	1440(m) 1400(w)	1340(w)	1260(s) 1200(w)	925(m) 270(s)	200(m)
$(\text{Cu}_2(\text{H}_2\text{B})_3.\text{Cl}_2$ (OH) ₂) 10^{-3} M HClO ₄ (ext)			2895(br)	2820(s)		1560(m)		1440(m) 1360(w)	1340(w)	1260(s)	920(m) 275(m)	200(w)
$(\text{Cu}_2(\text{H}_2\text{B})_3.\text{Cl}_2$ (OH) ₂) 10^{-3} M HClO ₄ (synth)			2900(m)	2820(w)		1560(m)	1510(m)	1440(m) 1395(w)	1360(w)	1260(s) 1170(m)	920(s) 280(m)	200(w)

Legend: S = Strong; Vs = Very Strong; M = Medium; Synth = Synthesized complex; W = Weak; Ext = Extracted complex; Br = Broad

NO₃ vibrational mode appeared at 1360 and 700 cm⁻¹ for complexes prepared in HNO₃. Presence of absorption bands in the far IR between 440 and 250 cm⁻¹ are due to Cu-O and Cu-N vibrations. C-O stretching frequencies between 1150-1020 cm⁻¹ are apparent in the ligand and in the complexes in high pH medium.

NMR Data

Proton NMR data of the ligand in CDCl₃ with TMS as internal reference is on Table 5. The sharp doublet at 1.87 integrated for 12 protons is assigned to the slightly non-equivalent CH₃C-N and CH₃C-O protons. The 4 H, triplet at 3.9 ppm is due to the ethylene bridge protons whereas the singlet at 4.91 (2 H) is attributed to the vinyl hydrogens. This is related to the broad band at 10.60 integrated for 2 H which likely arises from the strongly hydrogen-bonded enolic form. This shows that in this solvent the structural form of this ligand is strongly hydrogen-bonded.

Table 5. Proton resonance data for the ligand in CDCl₃ relative to tetramethylsilane as internal reference

Signal, ppm	Assignment
10.60 (br) 2 H	Sym. O-H, <i>N-N</i> proton, - hydrogen bonded
4.91 (s) 2H, 3.38	Sym. -CH =, methylene protons
3.39 (t) 4H, 2.30	-CH ₂ - CH ₂ , methylene bridge protons
1.91 (d) 12H, 1.82	Sym. CH ₃ C - O Non-equivalent

Legend: d = doublet; t = triplet; br = broad; s = singlet; Sym = synthesized

Most of the complexes showed single and broad absorption. This has been attributed to paramagnetic effect. This effect is observed in all the complexes implying that they likely have the same structural forms.

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