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Synthesis and characterization of water-soluble zinc(II) Schiff-base complexes derived from amino acids and 3-formyl-4-hydroxybenzyl-triphenylphosphonium chloride

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Tridentate Schiff-base ligands derived from condensation of 3-formyl-4-hydroxybenzyltriphenylphosphonium chloride with glycine, L-alanine, L-valine, L-leucine and L-phenylalanine in the presence of $Zn(OAc)_2 \cdot 2H_2O$ form five new water-soluble Zn(II)complexes, which were characterized by elemental analyses, IR, electronic absorption and ¹H, ¹³C NMR spectroscopies. In the IR spectra of the complexes, the difference between the asymmetric and the symmetric carboxylate stretching frequencies is larger than ~210 cm⁻¹, which implies that the carboxylate groups are monodentate. UV-Vis electronic absorption studies show that Zn(II) functions as a trap for the Schiff-base intermediate. Schiff-base complexes formation were confirmed by the appearance of new signals in the ¹H NMR for the azomethine hydrogen at ~8 ppm and condensed L-amino acids at 3.4–3.8 ppm (C(3)–H). These complexes are formed through coordination of the ONO from the carboxyl, imino and phenoxy groups of the ligands to Zn(II).

Keywords: Schiff-base complexes; 3-Formyl-4-hydroxybenzyl-triphenylphosphonium chloride; Amino acids; Zn(II) complexes

1. Introduction

Transition metal complexes of salicylaldehyde-amino acid Schiff bases are of considerable research interest due to their enzymatic model studies such as metalpyridoxal-amino acids and/or amine systems [1–6]. For example, γ -aminobutyric acid (GABA) aminotransferase is a pyridoxal 5'-phosphate (PLP)-dependent enzyme that catalyzes the transamination of GABA and R-ketoglutarate to give succinic semialdehyde and L-glutamate [7]. Hemoglobin reacts with PLP to form a Schiff base [8]. Pyridoxal and aminoguanidine Schiff base is a good inhibitor of formation of advanced glycation end products [9] and is considered to be promising for the treatment of diabetic complications. Transamination and racemization reactions involve the formation of an intermediate Schiff base [10]. PLP-dependent enzymes are also involved

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in α , β and γ -elimination reactions of amino acids [11, 12]. In general, however, these reactions are extremely slow in the absence of metal ions. Both metal ions and H⁺ concentration increase the rate of such reactions and stabilize the resulting products; the metal complex provides a planar structure which permits facile electron transfer via the extended π -orbital system [13, 14]. In nonenzymatic systems, the minimum structural requirements for reaction of pyridoxal with amino acids are the presence of the 2-formyl group and the 1-hydroxy subsistent on the phenyl ring [15].

Metal complexes of tridentate Schiff bases derived from salicylaldehyde derivatives and amino acids is of considerable interest due to their structural, magnetic and electrochemical properties as well as being potential models for a number of important biological systems. These complexes exhibit antimicrobial [16], antiproliferative [17], chemotherapeutic [18], antimalarial [19], radiopharmaceutical [20] and insulin-mimetic properties [21].

There is not much information about preparation of amino acid Schiff-base complexes derived from the water-soluble salicylaldehyde, 3-formyl-4-hydroxybenzyl-triphenylphosphonium chloride, Schiff-base anion, as a model system for PLP-dependent enzymes in aqueous solutions.

In earlier work, we synthesized and characterized Schiff-base complexes of transition metals [22, 23] and studied the interaction of these complexes as model complexes with biomolecules by using spectrophotometrical techniques [24–26].

Here, we report the preparation and characterization of water-soluble zinc(II) Schiff-base complexes derived from amino acids and 3-formyl-4-hydroxybenzyl-triphenylphosphonium chloride (figure 1).



Figure 1. Water-soluble Zn(II) Schiff-base complexes prepared from amino acids and 3-formyl-4-hydroxybenzyl-triphenylphosphonium chloride.

2. Experimental

2.1. Materials and measurements

All chemicals and solvents were reagent grade, obtained from either Merck or Fluka and used without further purification. 3-formyl-4-hydroxybenzyl-triphenylphosphonium chloride was synthesized according to the literature procedure [27].

Elemental analyses were performed using a Heraeus Elemental Analyzer CHN-O-Rapid (Elementar-Analyses system, GmbH). IR spectra were recorded on a FT-IR JASCO 460 spectrophotometer with KBr pellets. Electronic spectra were recorded using a CARY 100 Bio VARIAN UV-Vis spectrophotometer. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker FT-NMR 500 (500 MHz) Ultra Shield spectrometer at ambient temperature. Proton chemical shifts in DMSO-d₆ and D₂O were referenced to DMSO-d₆ (¹H NMR, $\delta_{DMSO} = 2.49$ ppm; ¹³C NMR, $\delta_{DMSO} = 40.5$ ppm) and D₂O (¹H NMR, $\delta_{H2O} = 4.70$ ppm) using tetramethylsilane (TMS) as an internal standard. Melting points were determined on a BUCHI melting point B-540.

2.2. Preparation of the complexes: general procedure

The new water-soluble amino acid Schiff-base complexes of Zn(II) were prepared as shown in scheme 1.

To a warm solution of the corresponding amino acid in water, 3-formyl-4-hydroxybenzyl-triphenylphosphonium chloride in ethanol was added. The resulting solution was stirred for 0.5 h. A solution of zinc(II) acetate dihydrate (5 mmol, 1.1 g) dissolved in minimal water (10 ml) was added dropwise; during the addition, the pH was adjusted to 7 by dropwise addition of 0.5 M KOH. The solution was stirred for 1 h and the yellowish-white precipitate obtained was filtered, washed with diethylether and air dried.

2.3. Synthesis of 1

Glycine (5 mmol, 0.375 g) in 10 mL of water and 3-formyl-4-hydroxybenzyltriphenylphosphonium chloride (5 mmol, 2.16 g) in 10 mL hot ethanol (70°C) gave analytically pure yellowish-white precipitate, collected by suction filtration, washed with diethylether and air dried (65% yield), m.p. 265–270°C (decomp). Anal. Calcd for $C_{28}H_{23}NO_3ZnPCl2.5H_2O$: C, 56.30; H, 4.70; N, 2.40%. Found: C, 56.22; H, 4.60; N, 2.22. IR (cm⁻¹): 3431(m), 3060(m), 2899(m), 1644(s), 1615(s), 1548(s), 1480(s),



Scheme 1. Synthesis of the water-soluble amino acid Schiff-base complexes of Zn(II).

1438(s), 1380(m), 1294(s), 1220(m), 1162(m), 1110(m), 1080(w), 999(w), 927(w), 907(m), 842(w), 818(w), 745(s), 720(m), 691(w), 602(w), 557(m), 496(w), 448(w). UV-Vis (H₂O): λ 359 nm (ε 5.05 × 10³ dm³ mol⁻¹ cm⁻¹), 267 nm (sh), 228 nm (ε 4.9 × 10⁴ dm³ mol⁻¹ cm⁻¹). ¹H NMR (DMSO-d₆ and D₂O, 293 K): δ 7.9 (s, 1H, CH=N), 7.6–7.78 (m, 15H, Ar), 6.6–6.8 (m, 3H, Ar), 4.95 (d, 2H, CH₂P), 3.79 (s, 2H, CH₂). ¹³C NMR (DMSO-d₆ and D₂O, 293 K): 69.2, 124.9, 124.5, 133.4, 136.5, 170.1, 172.1, 181.6. $\Lambda_{\rm M}$ (Ω^{-1} cm² mol⁻¹) (10⁻³ mol dm⁻³ in H₂O, 22°C) 1.2.

2.4. Synthesis of 2

Alanine (5 mmol, 0.445 g) gave analytically pure yellowish-white precipitate by suction filtration, washed with diethylether and air dried (65% yield), m.p. 255–260°C (decomp). Anal. Calcd for C₂₉H₂₅NO₃ZnPCl3.5H₂O: C, 55.65; H, 5.03; N, 2.24%. Found: C, 55.50; H, 4.90; N, 2.03. IR (cm⁻¹): 3427(m), 3064(m), 2988(m), 2936(m), 2896(m), 1636(s), 1607(s), 1551(s), 1480(s), 1438(s), 1385(m), 1349(m), 1297(s), 1217(m), 1161(m), 1112(m), 1056(w), 996(w), 927(w), 907(m), 883(m), 838(w), 814(w), 748(s), 720(m), 691(w), 605(w), 556(m), 499(w), 444(w). UV-Vis (H₂O): λ 359 nm (ε 4.26 × 10³ dm³ mol⁻¹ cm⁻¹), 271 nm (sh), 226 nm (ε 4.39 × 10⁴ dm³ mol⁻¹ cm⁻¹). ¹H NMR (DMSO-d₆ and D₂O, 293 K): δ 7.91 (s, 1H, CH=N), 7.6–7.9 (m, 15H, Ar), 6.5–6.8 (m, 3H, Ar), 4.7 (d, 2H, CH₂P), 3.8 (m, 1H, CH), 1.3 (d, 3H, CH₃). ¹³C NMR (DMSO-d₆ and D₂O, 293 K): 71.2, 79.2, 123.1, 124.3, 134.1, 137.0, 169.1, 172.4, 180.5. $\Lambda_{\rm M}$ (Ω^{-1} cm² mol⁻¹) (10⁻³ mol dm⁻³ in H₂O, 22°C) 1.5.

2.5. Synthesis of 3

Valine (5 mmol, 0.585 g), after the evaporation of the solvent, gave yellow precipitate recrystallized by ether diffusion to a methanolic solution. The resulting analytically pure yellowish-white precipitate was collected by suction filtration, washed with diethylether and air dried (45% yield), m.p. 179–185°C (decomp). Anal. Calcd for $C_{31}H_{29}NO_3ZnPCl2H_2O$: C, 58.97; H, 5.23; N, 2.22%. Found: C, 58.97; H, 5.20; N, 2.15. IR (cm⁻¹): 3431(m), 3064(m), 2968(m), 2932(m), 2899(m), 1631(s), 1603(s), 1527(s), 1478(s), 1438(s), 1386(m), 1334(m), 1309(m), 1217(s), 1076(m), 1036(w), 996(w), 899(m), 842(w), 818(w), 754(s), 722(m), 689(w), 613(w), 545(m), 499(w), 448(w). UV-Vis (H₂O): λ 360 nm (3.87 × 10³ dm³ mol⁻¹ cm⁻¹), 274 nm (sh), 228 nm (4.01 × 10⁴ dm³ mol⁻¹ cm⁻¹). ¹H NMR (DMSO-d₆ and D₂O, 293 K): δ 7.88 (s, 1H, CH=N), 7.5–7.7 (m, 15H, Ar), 6.59–6.7 (m, 3H, Ar), 4.9 (d, 2H, CH₂P), 3.4 (d, 1H, CH), 2.03 (m, 1H, CH), 0.75 (d, 6H, CH₃). ¹³C NMR (DMSO-d₆ and D₂O, 293 K): 21.4, 22.3, 42.5, 77.4, 119.3, 125.2, 129.7, 130.9, 132.3, 132.9, 134.9, 135.8, 140.0, 173.4, 175.6. Λ_M (Ω^{-1} cm² mol⁻¹) (10⁻³ mol dm⁻³ in H₂O, 22°C) 1.0.

2.6. Synthesis of 4

Leucine (5 mmol, 0.657 g) solution, after reaction, was left undisturbed overnight to reduce the volume of the solvent to about dryness and then ethylacetate was added to produce precipitate, which was then recrystallized by ether diffusion to a methanolic solution. The resulting analytically pure yellowish-white precipitate was collected by

suction filtration and air dried (44% yield), m.p. 176–183°C (decomp). Anal. Calcd for C₃₂H₃₁NO₃ZnPCl2H₂O: C, 59.55; H, 5.43; N, 2.17%. Found: C, 59.46; H, 5.37; N, 2.07. IR (cm⁻¹): 3431(m), 3064(m), 2954(m), 2936(m), 2907(m), 2883(m), 1627(s), 1602(m), 1539(s), 1476(s), 1438(s), 1388(m), 1338(m), 1305(m), 1213(s), 1160(w), 1111(m), 1072(m), 1027(w), 999(w), 931(m), 840(w), 818(w), 749(s), 722(m), 691(w), 609(w), 541(m), 500(w), 448(w). UV-Vis (H₂O): λ 361 nm (ε 3.3 × 10³ dm³ mol⁻¹ cm⁻¹), 274 nm (sh), 226 nm (ε 3.6 × 10⁴ dm³ mol⁻¹ cm⁻¹). ¹H NMR (DMSO-d₆ and D₂O, 308 K): δ 7.91 (s, 1H, CH=N), 7.6–7.8 (m, 15H, Ar), 6.55–6.67 (m, 3H, Ar), 4.9 (d, 2H, CH₂P), 3.6 (t, 1H, CH), 2.09 (m, 2H, CH₂), 1.74 (m, 1H, CH), 0.88 (d, 6H, CH₃). ¹³C NMR (DMSO-d₆ and D₂O, 308 K): 20.8, 21.1, 31.5, 42.8, 73.2, 124.7, 129.2, 130.8, 134.9, 140.0, 173, 175.1, 176.2. $\Lambda_{\rm M}$ (Ω⁻¹ cm² mol⁻¹) (10⁻³ mol dm⁻³ in H₂O, 22°C) 1.3.

2.7. Synthesis of 5

Phenylalanine (5 mmol, 0.825 g) gave analytically pure yellowish-white precipitate, collected by suction filtration, washed with diethylether and air dried (55% yield). m.p. 206-207°C (decomp). Anal. Calcd for C35H29NO3ZnPCl3H2O: C, 60.27; H, 5.02; N, 2.01%. Found: C, 60.30; H, 4.90; N, 2.10. IR (cm⁻¹): 3423(m), 3060(m), 3028(m), 2927(m), 2899(m), 1631(s), 1601(m), 1533(s), 1476(s), 1437(s), 1378(m), 1301(m), 1204(s), 1110(m), 1032(w), 996(w), 895(m), 838(w), 814(w), 751(s), 720(m), 363 nm 691(w). 605(w), 556(m), 499(w), 444(w). UV-Vis (H_2O) : λ $(\varepsilon 4.52 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$, 274 nm (sh), 225 nm ($\varepsilon 4.28 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). ¹H NMR (DMSO-d₆ and D₂O, 308 K): δ 7.89 (s, 1H, CH=N), 7.6–7.8 (m, 20H, Ar), 6.25– 6.67 (m, 3H, Ar), 4.9 (d, 2H, CH₂P), 3.6 (m, 1H, CH), 2.5 (t, 2H, CH₂). ¹³C NMR (DMSO-d₆ and D₂O, 308 K): 51.4, 76.5, 100.4, 118.8, 119.4, 128.7, 130.6, 130.9, 134.8, 135.7, 138.3, 151.2, 170.5, 176.6, 179.1. Λ_{M} (Ω^{-1} cm² mol⁻¹) (10⁻³ mol dm⁻³ in H₂O, 22°C) 1.1.

3. Results and discussion

Zinc(II) Schiff-base complexes were prepared by metal ion template condensation of the carbonyl compound and amino acids; the Schiff-base ligands obtained from the reaction between amino acids and 3-formyl-4-hydroxybenzyl-triphenylphosphonium chloride are unstable in the absence of metal ions and Zn(II) is required both as a template and as a trap to stabilize the resulting product [28–30]. The Schiff-base complexes are soluble in methanol, DMF, DMSO and water and stable in air. In all cases we have obtained amorphous samples that were unsuitable for single crystal X-ray diffraction. The complexes are characterized by elemental analysis, IR, ¹H NMR, ¹³C NMR, UV-Vis spectra and conductivity measurements.

3.1. IR spectra

Infrared spectra of these complexes provide insight into the mode of bonding of the Schiff-base ligand to the metal ion. Solid state infrared spectra of 3-formyl-4-hydroxybenzyl-triphenylphosphonium chloride, glycine and 1 in the double bond stretching region (C=C), (C=O) are compared in figure 2.



Figure 2. A comparison of the infrared spectra of (a) glycine, (b) complex and (c) 3-formyl-4-hydroxybenzyl-triphenylphosphonium chloride.

The four peaks in the spectrum of glycine, $\nu_{as}(COO)$, 1608 cm⁻¹; $\nu(N-H)$, 1590 cm⁻¹; $\nu(N-H)$, 1510 cm⁻¹; $\nu_s(COO)$, 1413 cm⁻¹ [31], are not seen in the spectrum of the Schiffbase complex. The same changes can be seen for the carbonyl at 1672 cm⁻¹, figure 2(c), and the band assigned to N–H at 1510 cm⁻¹, figure 2(a), which disappear upon Schiffbase complex formation.

The IR spectra of complexes show prominent stretching vibration of the azomethine band (HC=N) at 1644 cm^{-1} [32–34], in agreement with the proposed formation of Schiff-base complexes. Further support for the above assignments comes from NMR spectra, which show a chemical shift at 8 ppm, assigned to the iminic proton.

The $v_{as}(COO)$ is assigned to the strong band at $1601-1615 \text{ cm}^{-1}$, broadened because of overlap with aromatic ring-carbon stretches at 1600 cm^{-1} . In some cases, 1644 and 1615 cm^{-1} emerge from the broad band corresponding to v(C=N) and $v_{as}(COO)$, respectively. The symmetric carboxylate stretch, $v_s(COO)$, is a medium/strong peak in the range $1378-1388 \text{ cm}^{-1}$. The shift from 1413 cm^{-1} in glycine to $\sim 1380 \text{ cm}^{-1}$ in complexes show carboxylate is coordinated to Zn. The difference between v_{as} and v_s modes ($v_{as}(COO)-v_s(COO)$) is $217-235 \text{ cm}^{-1}$, typical for monodentate coordination of the ionized carboxylate with metal cations [35, 36]. The absorption at 3400 cm^{-1} is associated with the O–H stretch of intermolecular hydrogen bonds or water [37]. Other bands possibly related to the Schiff-base moiety and observed in the complexes could be tentatively assigned; a medium/strong band at $1530-1550 \text{ cm}^{-1}$ related to the vibration

Compound	ν (C=N)	$v_{as}(COO)$	$\nu_{\rm s}({\rm COO})$
1	1644	1615	1380
2	1636	1607	1385
3	1631	1603	1386
4	1627	1602	1388
5	1631	1601	1378

Table 1. The major IR spectral data (cm^{-1}) of the complexes.

Table 2. The main electronic spectral data of the complexes.

Compound	λ, nm (10 ⁻⁴ ε, M ⁻¹ cm ⁻¹) Aromatic ring $\pi \to \pi^*$	λ , nm (10 ⁻³ ε , M ⁻¹ cm ⁻¹) Imine $\pi \rightarrow \pi^*$	
1	228 (4.90)	359 (5.05)	
2	226 (4.39)	359 (4.26)	
3	228 (4.01)	360 (3.87)	
4	226 (3.60)	361 (3.30)	
5	225 (4.28)	363 (4.52)	

of the (Ph–)C–C(=N) group is typical for salicylaldehyde derivatives [38, 39]. A medium band in the range $2840-2980 \text{ cm}^{-1}$ is due to the aliphatic C–H stretching. Selected IR spectral data for the complexes are given in table 1.

3.2. Electronic absorption and NMR spectra

Electronic spectral data for the complexes in H₂O are summarized in table 2. The spectra show bands at 227 nm, 270 nm and 360 nm. The bands in the range 200–370 nm are assigned to $n \rightarrow \pi^*/\pi \rightarrow \pi^*$ transitions of the salicylidene chromophore [39].

The electronic spectra of the aldehyde, glycine-aldehyde mixtures (1:1) in ethanol-water solution and Zn(II) complex are given in figure 3. Aldehyde in ethanol (figure 3a) possesses low energy absorption bands in the wavelength region from 230 to 340 nm, and for glycine-water mixtures there is no absorption bands at 200-900 nm in the UV-Vis spectra. No changes in the spectrum of the glycinealdehyde mixtures (1:1) in ethanol-water solution (figure 3b) suggest that the desired ligand is not synthesized *in situ* within the study condition. Addition of an equivalent of zinc(II) acetate to glycine-aldehyde mixtures (1:1) in ethanol-water solution, followed by adjusting the solution to pH 7 by dropwise addition of 0.5 M KOH (figure 3c) led to the formation of the desired complex. An intense, broad absorption at 330 nm, assigned to $n \rightarrow \pi^*$ transition of the salicylaldehyde chromophore [39], disappears while a new band at 364 nm appeared upon formation of complexes. This band is assigned to a $\pi \rightarrow \pi^*$ transition originating mainly in the azomethine chromophore (imine $\pi \rightarrow \pi^*$ transition) [40-42], an indication that zinc(II) Schiff-base complexes have been synthesized.

The appearance of a new band in the lower energy region is related to an increase in conjugation upon formation of Schiff-base metal complex. The metal ion promotes



Figure 3. Electronic spectra of (a) 3-formyl-4-hydroxybenzyl-triphenylphosphonium chloride (aldehyde) (----), (b) glycine-aldehyde mixtures (1:1) in ethanol-water solution (---) and (c) complex 1 (-----)

	Glycine 1	L-Alanine 2	L-Valine 3	L-Leucine 4	L-Phenylalanine 5
С(3)–Н	3.79	3.80	3.40	3.60	3.60
C(5)–H	7.90	7.91	7.88	7.91	7.89
C(8)–H	6.60	6.50	6.59	6.55	6.25
C(9)–H	6.65	6.59	6.65	6.60	6.56
C(11)–H	6.80	6.80	6.70	6.67	6.89
С(12)–Н	4.95	4.70	4.90	4.90	4.90
C(2)	181.6	180.5	175.6	176.2	179.1
C(3)	69.2	79.2	77.4	73.2	76.5
C(5)	172.1	172.4	173.4	175.1	176.6

Table 3. Selected ¹H NMR and ¹³C NMR values of Zn(II) complexes.

Schiff-base formation and stabilizes the product [12, 28]. The band at higher energy is probably associated with benzene ring intraligand transitions [39]. The very low Λ_M (Ω^{-1} cm² mol⁻¹) values of 10⁻³ solution in H₂O at 22°C imply

non-electrolytes [43].

Selected ¹H NMR and ¹³C NMR spectral data for the complexes in DMSO-H₂O are given in table 3.

Complexes formation were confirmed by the appearance of new signals for the azomethine hydrogen at 7.9 ppm and condensed L-amino acids at 3.4–3.8 ppm (C(3)-H). The protons of the CH₂P group are a doublet at 4.7-4.9 ppm. Other aromatic protons were observed at 6.5–7.75 ppm [44–46].

The appearance of a new signal at 7.9 ppm, and disappearance of the aldehyde proton (HC=O) at 10.15 ppm, suggests the formation of the Schiff base. Disappearance of the signal at 11.4 ppm indicates deprotonation of the OH, confirming complexation of the ligand via the phenolate-O with the metal ion. The results of ¹³C NMR spectroscopy agree with the structure shown for the Zn(II) complexes.

4. Conclusion

Five water-soluble zinc(II) complexes of amino acid-salicylaldehyde Schiff base have been prepared by template synthesis in neutral solutions. The Schiff-base ligands obtained from reaction between amino acids and 3-formyl-4-hydroxybenzyl-triphenylphosphonium chloride are unstable in the absence of metal ions. Zn(II) promotes formation of the Schiff-base ligands and functions as a trap for the Schiff-base intermediate. Elemental analysis, IR, UV-Vis, ¹H NMR and ¹³C NMR spectral data for the complexes are in good agreement with similar studies in the literature, showing the presence of a tridentate amino acid Schiff-base ligand coordinating through the phenolato O, imine N, and carboxyl O [31, 46–49].

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