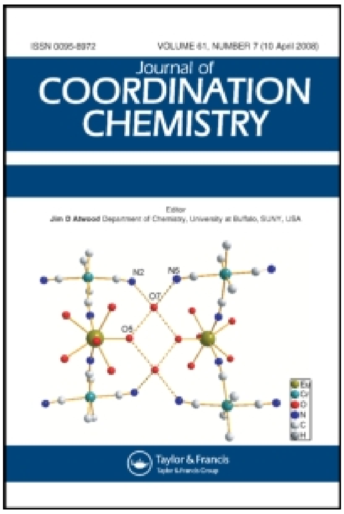

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SYNTHESIS AND CHARACTERIZATION OF Fe(III), Co(III), Cu(II) AND Zn(II) COMPLEXES OF *N*-2,4-HYDROXYBENZAL-*D*-GLUCOSAMINE

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The Schiff base *N*-2,4-dihydroxybenzal-*D*-glucosamine (L), and its Fe(III), Co(III), Cu(II) and Zn(II) complexes have been synthesized and characterized. Magnetic moments suggest that all complexes are high-spin. The Cu(II) chelate in DMF solution has a distorted tetrahedral structure, as shown by ESR and electronic spectra. Detailed studies have been made concerning the solution equilibrium of L with transition metal ions. Stabilities of the complexes are in accord with the Irving–Williams series.

Keywords: *D*-glucosamine; Schiff base; complex; synthesis; stability constants

INTRODUCTION

The ability of sugars to sequester metals is of current interest in terms of the development of models for biologically important compounds and clinical use. These studies could be advanced by the development of methods by which metals can be readily attached to sugars.[1,2] Amino sugars derived from Schiff bases with aromatic aldehydes have been known since 1922.[3–6] Nevertheless, few transition metal complexes of these ligands have been reported,[7] but they do show strong anti-bacterial activity.[8–10] Here we report

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the synthesis of a Schiff base of 2,4-dihydroxybenzaldehyde with *D*-glucosamine (L), along with several of its transition metal complexes. In addition, we report solution equilibrium involving L with five transition metal ions.

EXPERIMENTAL

Analytical grade chemicals were used throughout. Carbon, hydrogen and nitrogen analyses were performed using a Perkin-Elmer 240 instrument. Conductivity measurements were performed in methanol using a Shanghai DDS-11A apparatus at 25°C. Thermoanalyses were carried out using a SDT 2960C TA instrument. EI mass spectra of L in ethanol were obtained with an HP spectrometer. IR spectra were recorded in KBr (L) and CsI pellets (complexes) on a Perkin-Elmer 983 spectrophotometer. Electronic spectra were obtained using a Shimadzu UV-265 spectrophotometer. ^{1}H NMR spectra in DMSO were recorded on a Varian XL-200 spectrometer; all peak positions are related to TMS. ESR spectra of the copper(II) complex was measured on a JES-FEIXG JEOL ESR spectrometer at X-band frequencies at 77 K (frozen DMF solution). Magnetic moments were measured by the Evans method, using t-butyl alcohol as internal standard.

Preparation of N-2,4-dihydroxybenzal-D-glucosamine (L)

N-2,4-dihydroxybenzal-*D*-glucosamine was prepared by a method given in the literature.[3] Light yellow needle crystals were collected by filtration, washed with ether, recrystallized from ethanol and vacuum dried over $CaCl_2$. Yield: 95%. Physical and spectroscopic data were in agreement with literature values.

General Method for Preparation of Complexes of L

An ethanolic solution (30 cm^3) of metal acetate (0.005 mol) was added dropwise to a stirred solution of L (0.005 mol) in ethanol (30 cm^3). After three hours, the mixture was concentrated at 40°C on a rotary evaporator. Addition of excess ether gave a precipitate, which was kept in a refrigerator for two days. The product was collected by filtration, washed with ether and dried in a vacuum desiccator overnight. The Co(III) complex was obtained with oxygen bubbling through the reaction mixture for 6 h. The Fe(III) complex was synthesized using ferric chloride as starting material.

$[Cu(H_{-2}L)(H_2O)]\cdot H_2O$ (**1**): green, yield 1.10 g (54.6%), mp > 250°C (decomp.). *Anal*: calcd. for $C_{13}H_{19}O_8$ NCu(%): C, 39.34; H, 4.79; N, 3.53; Cu, 16.02. Found: C, 39.60; H, 4.88; N, 3.10; Cu, 16.50.

[Co $(H_{-2}L)(OAc)] \cdot H_2O$ (**2**): dark brown, yield 0.87 g (41.3%), mp > 250°C (decomp.). *Anal*: calcd. for $C_{15}H_{20}O_{10}NCo$(%): C, 41.57; H, 4.62; N, 3.23; Co, 13.63. Found: C, 41.91; H, 4.64; N, 3.12; Co, 13.71.

$[Fe(H_{-2}L)(H_2O)Cl] \cdot H_2O$ (**3**): violet, yield 1.11 g (50.4%), mp >250°C (decomp.). *Anal*: calcd. for $C_{13}H_{19}O_9NClFe$(%): C, 36.80; H, 4.48; N, 3.30; Fe, 14.25. Found: C, 37.40; H, 5.16; N, 3.31; Fe, 13.92.

$[Zn(H_{-1}L)_2(H_2O)] \cdot 4H_2O$ (**4**): pale yellow, yield: 0.93 g (50.7%), mp > 250°C (decomp.). *Anal*: calcd. for $C_{26}H_{42}O_{19}N_2Zn$(%): C, 41.54; H, 5.59; N, 3.73; Zn, 8.52. Found: C, 41.50; H, 5.89; N, 3.26; Zn, 9.04.

Potentiometric Titrations

An aqueous solution containing L and salt was titrated with carbonate-free 0.1647 mol dm^{-3} KOH. The pH values were measured with a pHS-3C (601B) pH meter equipped with a glass silver–silver chloride combination electrode, with a precision of ±0.01 pH. The electrode was standardized using buffer solutions of potassium hydrogenphthalate and mixed phosphates. Ionic strength was kept at 0.1 mol dm^{-3} with KCl and the temperature of solutions was maintained at 25 ± 0.1°C. Solutions were deoxygenated with pure nitrogen gas. The protonation constant of L was determined under the same conditions as stability constants. Values of β_{pqr} were calculated using the program MINIQUAD.[11]

RESULTS AND DISCUSSION

Elemental analyses (Table I) agree well with the proposed formulae for the complexes. Molar conductivities in methanol (Table I) at 25°C showed that all the compounds are non-electrolytes.[12] Thermoanalyses indicated the number of coordinated water molecules in the complexes. These data also agreed with the formulae of the complexes.

Spectroscopic Studies

EI mass spectra of L did not give a signal corresponding to the M^+ ion. Cleavage of the C=N bond causes the loss of a fragment, $C_7H_6O_2$, leading to the $[C_6H_{13}O_5N]^+$ ion at m/z 179.

IR spectra of the complexes show a shift in the C=N group absorption to lower frequency as compared with the parent ligand, indicating the coordination of the nitrogen atom to the metal ion. A band in the 300–400 and another in the 200–300 cm^{-1} region are attributed to $\nu_{(M-N)}$ and $\nu_{(M-O)}$, respectively. The broad absorption in the 3200–3400 cm^{-1} region for all

TABLE I Electronic absorption data for the compounds in methanol. Charges are omitted for clarity

Compound	λ/nm(log ϵ(M^{-1}cm^{-1}))			
L	219.6(4.11)	304.8(4.23)	372.8(3.84)	
$CuH_{-2}L$	226.0(4.13)	252.0(4.10)	291.0(4.05)	347.6(3.79)
$Zn(H_{-1}L)_2$	232.4(3.41)	250.4(3.46)	289.8(3.44)	348.4(3.20)
$CoH_{-2}L$	253.2(4.18)	285.0(2.90)	360.0(2.67)	
$FeH_{-2}L$	220.2(4.14)	246.4(4.06)	282.4(4.15)	506.0(3.13)

complexes substantiate the presence of water. In the IR spectrum of $CoH_{-2}L$, bands at 1542 cm^{-1} and 1338 cm^{-1} are due to v_a (CO_2^-) and v_s (CO_2^-), respectively, of coordinated acetate. The separation is 204 cm^{-1}, which is characteristic of binding as a monodentate.[13]

Evidence for a strong hydrogen bond between the nitrogen atom of the sugar and the hydroxyl function on the aromatic ring comes from the characteristic low field shift of the hydroxyl proton (14.07 ppm) in the ^{1}H NMR spectrum of L. Signals for the aromatic ring, imino group, lattice water and coordinated water are observed in the NMR spectrum of the zinc(II) complex, in which the hydroxyl protons of the aromatic ring are absent because of loss during coordination.

Electronic spectroscopic data are also shown in Table I. Compared to L, in the complexes the azomethine chromophore $\pi \rightarrow \pi^*$ transitions are shifted to higher energies, indicating that the imino nitrogen is coordinated to the metal ion. In the copper(II) complex the *d-d* absorption band at about 621 nm is broad and characteristic of a *pseudo*-tetrahedral structure.[14]

Solution magnetic moments could be determined by the Evans method. The magnetic moment of $FeH_{-2}L$ is 5.38 BM, which suggests that the Fe (III) complex is high-spin.

Values of $g_{\|}$, $g_{\perp}$ and $A_{\|}$ for $CuH_{-2}L$ are 2.38, 2.15 and 162.8 G, respectively. The ESR spectrum of $CuH_{-2}L$ exhibits the usual line shape for mononuclear Cu(II) complexes with $g_{\|} > g_{\perp} > 2.03$, indicating axial symmetry. The $g_{\|}/A_{\|}$ values can be used to estimate the distortion of the square planar complex toward the tetrahedron;[15] $g_{\|}/A_{\|}$ of $CuH_{-2}L$ is 145 cm^{-1} and reflects a distorted tetrahedron with a d_{x2-y2} ground state.

Solution Chemistry

The protonation constants of L in log units, $\log\beta_{101}$ and $\log\beta_{102}$, are 12.6 and 20.4, respectively, with errors of ± 0.1 log units. The buffer regions are rather extended in the titration curves of L plus metal ions, with a rapid increase at about $a = 2$ ($a = C_{OH}/C_L$). With the transition metal ions,

TABLE II Stability constants determined for the metal complexes (± 0.1 log units)

Metal ion	*Cu*^{II}	*Ni*^{II}	*Co*^{II}	*Zn*^{II}	*Fe*^{III}
$\log\beta_{110}$	11.2	8.5	7.2	8.6	12.6
$\log\beta_{120}$	19.1	15.4	13.6	15.4	20.4

$[MH_{-2}L]$ and $[MH_{-4}L_2]$ were formed. Equilibrium constants obtained are given in Table II. The stability sequence is $Zn^{II} < Cu^{II} > Ni^{II} > Co^{II}$, in agreement with the Irving–Williams series. The equilibrium constant for Fe^{III} is the largest. In neutral and weakly acid solutions, $[MH_{-2}L]$ predominates, amounting to almost 100% at pH 7–8, for Cu^{II}, Co^{II} and Ni^{II}. $[MH_{-4}L_2]$ exists only in basic solutions.

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