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Mono-, Di- and Trinuclear Copper(II) Complexes of a Schiff Base Ligand, 2-{(*E*)-[(6-{[(1*E*)-(2-hydroxyphenyl)methylene]amino}pyridin-2-yl)imino]-methyl}phenol

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A Schiff base ligand, 2-{(E)-[(6-{[(1E)-(2-hydroxyphenyl)methylene]amino}-pyridin-2-yl)imino]-methyl} phenol (H_2PySAL), was prepared by condensation of 2,6-diaminopyridine and salicylaldehide in EtOH. The Schiff base ligand was checked by elemental analyses, ^{1}H-NMR, ^{13}C-NMR, IR, UV/Vis, and mass spectral studies. Three new mono-, di-, and trinuclear copper(II) complexes of the Schiff base ligand, formula [Cu(H_2PySAL)]Cl_2, [Cu_2(PySAL) (Phen)]Cl_2, [Cu_3(PySAL)$_2$]Cl_2, were prepared and characterized by elemental analyses, magnetic moment, and IR, Uv/Vis, and mass spectral studies. The spectroscopic data of the complexes indicate that the copper(II) ions are coordinated by the oxygen atoms and nitrogen atoms (C=N) of the ligand. In the dinuclear complex, in which the first Cu(II) ions were complexed with oxygen and nitrogen atoms of the Schiff base ligand, the second Cu(II) ions are bridged by dianionic oxygen atoms of the phenolate groups and are linked to the 1,10-phenanthroline nitrogen atoms. The data support the proposed structure of H_2PySAL and its complexes.

Key Words: Schiff bases, mono-, di- and trinuclear copper(II) complexes.

Introduction

In principle, the central transition metal atoms of different soft and hard Lewis acidity usually need to be satisfied in the most suitable fashion. Hence heterodentate ligands have the greatest possibility to form polynuclear complexes[1,2] according to many available reports for the preparation of model copper complexes containing mimic copper metalloproteins such as hemocyanine and tyrosinase. In order to elucidate the factors that determine the function and activation of metalloproteins, several studies have focused on understanding the correlation between the active site of metalloproteins with their metallocenters.[3,4] A number of dinuclear complexes from various type ligand systems have been prepared and examined in terms

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of their oxygen uptake[4−15] or redox processes of oxygen.[16−19] In addition, dinucleating macrocycles have been synthesized by combining chelating acyclic subunits[20] or by functionalizing a macrocyclic structure by attaching side chains.[21,22] It has been reported that the derivatized macrocyclic systems exhibited the characteristics of mono- and dinuclear complexes such as catalysis and molecular recognition.[23−25] Furthermore, various mononuclear metal complexes from Schiff base ligands modified with benzo-15-crown-5 have been shown to possess enzyme-like activities.[26]

In this paper, the synthesis and characterization of mono-, di- and trinuclear copper(II) complexes (**4-6**) of a Schiff base ligand, 2-{(E)-[(6-{[(1E)-(2-hydroxyphenyl)methylene]amino}pyridin-2-yl)imino]-methyl} phenol (H_2PySAL), are reported and characterized by elemental analyses; mass, UV-Vis, and IR spectra; and magnetic susceptibilities.

Experimental

Electronic spectra were obtained on an ATI Unicam UV2 Model UV-Vis spectrophotometer. IR spectra were recorded on an ATI Unicam Matson 1000 Model FTIR spectrophotometer as KBr pellets. Room temperature magnetic susceptibility measurements were obtained on a PAR model 155 vibrating sample magnetometer. C, H and N contents were determined microanalytically on a Hewlett Packard 85 CHN analyzer, and metal contents were estimated spectrophotometrically. The metal contents of Cu(II) complexes were determined by complexometric titration against EDTA.[27] ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian Gemini 200 spectrometer. DMSO-d_6 was used as the solvent. Chemical shifts (δ) are reported in ppm relative to Me_4Si, using the solvent signal as internal reference. Mass spectra (ESI) were recorded on a Micromass LC-MS/MS. All chemicals were of the highest quality available, obtained from local suppliers, and used as received.

2-{(E)-[(6-{[(1E)-(2-hydroxyphenyl)methylene]amino}-pyridin-2-yl)imino]-methyl}phenol (H_2PySAL; $C_{19}H_{15}N_3O_2$)

This ligand has been previously reported.[28] 2,6-Diaminopyridine (1.09 g, 10 mmol) and salicide aldehyde (2.5 g, 20 mmol) were mixed and dissolved in absolute EtOH (25 cm^3). After being stirred for 2 h at room temperature, the solution was boiled under reflux for 1 h. The resulting red-yellow solution was filtered while hot and concentrated slowly. When this solution cooled, a red-yellow crystalline product was precipitated. This product was isolated by vacuum filtration, washed with EtOH and dried in air in that order to yield a yellow solid product. Yield: 2.65 (80%). mp 186 °C. MS: (ESI) m/s = 320 (30), 221(60), 169(100), 159(70).

Preparation of [Cu (PySAL)]Cl_2.H_2O, (4; $C_{19}H_{15}N_3O_3Cl_2Cu$)

A solution of $CuCI_2.2H_2O$ (0.85 g, 4.7 mmol) in dried EtOH (10 cm^3) was added to the ligand solution (1.5 g, 4.7 mmol) in 20 cm^{3}of EtOH, and the mixture was refluxed under stirring for 3 h. The resulting brown solution was filtered while hot and concentrated slowly. When the solution cooled, a pale brown crystalline product was precipitated. The brown product was filtered off and washed with EtOH and then Et_2O. Then the brown solid product was dried in vacuo. Yield: 0.9 g (50%). mp >300 °C, MS: (ESI) m/s = 470(35), 468(20), 366(45), 366(50), 364(100), 356(35).

Preparation of $[Cu_2[(PySAL)\ phen]\ Cl_2$, (5; $C_{31}H_{23}N_5O_2Cl_2Cu_2$)

The mononuclear copper complex (**4**) (470 mg, 1 mmol) was added to Et_3N (1 mmol) in dry MeOH (20 cm^3) and the mixture was stirred for 1 h. The separated solution of $CuCl_2.2H_2O$ (170 mg, 1 mmol) in MeOH (10 cm^3) and 1,10-phenanthroline monohydrate (200 mg, 1 mmol) in MeOH (10 cm^3) was successively added to the resulting mixture, which was boiled under reflux for 5 h. The dark-brown product was filtered off, washed with MeOH and Et_2O, and dried in vacuo. Yield: 0.42 g (60%). mp >300 °C, MS: (ESI) m/s = 693(15), 271(100), 243(55).

Preparation of $[Cu_3\ (PySAL)_2\ ]Cl_2$, (6; $C_{38}H_{26}N_6O_4Cl_2Cu_3$)

The mononuclear copper complex (**4**) (940 mg, 2 mmol) was added to Et_3N (1 mmol) in dry MeOH (25 cm^3) and this mixture was stirred for 1 h. The separated solution of $CuCl_2.2H_2O$ (170 mg, 1 mmol) in MeOH (10 cm^3) was added to a solution of the copper complex, which was heated under reflux for 8 h. The light-brown product was filtered off, washed with MeOH and Et_2O and dried in vacuo. Yield: 0.6 g (67%). mp >300 °C, MS (ESI) m/s = 891(10), 372(50), 354(45), 159(100).

Results and Discussion

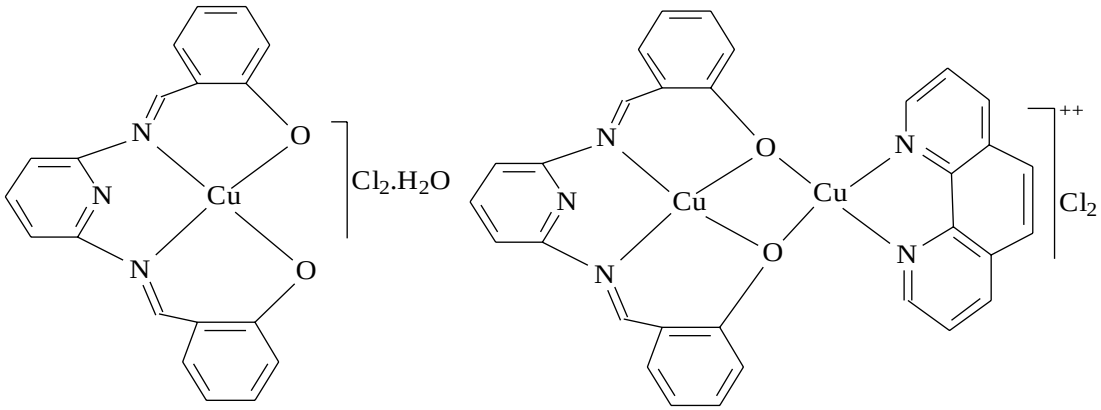
2-{(*E*)-[(6-{[(1*E*)-(2-hydroxyphenyl)methylene]amino}pyridin-2-yl)imino]-methyl}phenol (H_2PySAL) was prepared by condensation of 2,6-diaminopyridine and salicylaldehide in EtOH. The structural formula of (H_2PySAL) (**3**), which is a precursor of the (H_2PySAL), was checked by elemental analysis (Table 1), and IR data (Table 2). This ligand and its complexes have been previously reported and even structurally characterized.[28,29] The investigation included a study of the characteristics that are essential for solvent extraction and for spectrophotometric and spectrofluorimetric determinations.[29] In the ligand structure of (H_2PySAL) (**3**), N_2O_2 units are available for the complexation of metal ions in tetragonal coordination geometry. In this coordination mode, a square planar Cu(II) complex (**4**) was obtained through the reaction of the ligand and the $CuCl_2.2H_2O$ solution in the EtOH (1:1 metal:ligand ratio) (Figure). The corresponding copper complex (**4**) was prepared by the reaction of the ligand mixture in EtOH with copper(II) salts.

Table 1. Elemental analyses, UV-Vis spectral data of the ligand (H_2PySAL) and its complexes.

			Yield	Found (Calcd.) (%)				
Comp	Color	(%)	μ^a_{eff}	C	H	N	Cu	λ_{max}, nm[b]
(**3**)	Red-yellow	80	-	71.8(71.9)	4.9(4.8)	13.1(13.2)	-	278, 374
(**4**)	Pale brown	50	1.72	48.4(48.6)	3.4(3.2)	9.1(9.0)	13.7(13.5)	269, 323, 389, 465
(**5**)	Dark brown	60	1.80	53.8(53.7)	3.2(3.1)	10.0(10.1)	18.5(18.3)	275, 392, 479
(**6**)	Dark brown	67	1.79	51.2(51.1)	3.0(2.9)	9.3(9.4)	21.3(21.4)	323, 404, 510

[a]per molecule at 297K (BM)

[b]The spectra were obtained in DMF.



4 **5**

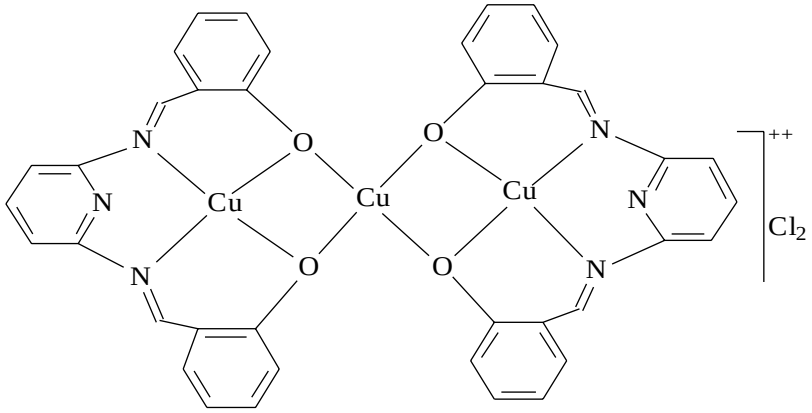


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Figure. Proposed structures for the copper(II) complexes.

The ligand (**3**) has been checked by ^{1}H-NMR spectra in $CDCl_3$ solution. The spectrum of the ligand (H_2PySAL) shows a broad singlet at 13.41(-OH, 2H), a singlet at 9.47 (H-C==N, 2H), a triplet at 7.82 ($J_{9,10}$= 7.8 Hz) (Py-H, C-10, 1H), a doublet of doublets at 7.55 ($J_{2,3}$= 7.6 Hz, $J_{2,4}$ = 1.2 Hz) (Ar-H, C-2, 2H), a doublet of triplets at 7.43 ($J_{2,3}$= $J_{3,4}$= 7.6 Hz, $J_{3,5}$ = 1.4 Hz) (Ar-H, C-3, 2H), a doublet at 7.23 ($J_{9,10}$= 7.8 Hz) (Py-H, C-9, 2H), a doublet of doublets at 7.03 ($J_{4,5}$ = 6.8 Hz, $J_{3,5}$ = 1.4 Hz) (Ar-H, C-5), and a doublet of triplets at 6.97 ($J_{3,4}$= $J_{4,5}$= 6.8 Hz, $J_{2,4}$ = 1.2 Hz) (Ar-H, C-4, 2H) ppm. There is one AB_2 system at 7.82 and 7.23 ppm belonging to pyridine protons and one AA'BB' system at 6.95-7.55 ppm belonging to aromatic protons in the ^{1}H-NMR spectral data of a $CDCl_3$ solution of H_2PySAL. The Schiff base ligand proton signals at 13.41 ppm disappear on deuterium exchange. In the ^{1}H-NMR spectra integrated data are consistent with the formula. The 10 resonances observed in the ^{13}C-NMR spectra of H_2PySAL (**3**) are also consistent with the formula.

The mass (ESI) of H_2PySAL exhibited the molecular ion at m/z320 $[M + 3]^+$, which indicates formation of the H_2PySAL (**3**) and the molecular ion peak appeared at (m/z, ESI) 470 $[M+H_2O+1]^+$ for the mononuclear copper(II) (**4**), at 693 $[M]^+$ for the dinuclear copper(II) (**5**), and at 891$[M-1]^+$ for the trinuclear copper(II) (**6**), indicating the formation of the copper(II) complexes. The molecular ion peak of

the mononuclear copper(II) complex (**4**) was attributed to the fact that this molecule has 1 ligand molecule, and 1 copper and 2 chloride ions. The molecular ion peak of the dinuclear copper(II) complex (**5**) was attributed to the fact that this molecule has 1 mononuclear copper(II) complex, 1 copper and 2 chloride ions, and one 1,10-phenanthroline molecule. The molecular ion peak of the trinuclear copper(II) complex (**6**) was attributed to the fact that this molecule has 2 mononuclear copper(II) complexes, and 1 copper and 2 chloride ions.

In general, the complexes exhibited very comparable IR features, suggesting that they are of similar structure. The presence or absence of certain bands in the generally complicated IR spectra has been used to establish the nature of complexes. Relevant bands are given in Table 2. In the IR spectrum of the ligand (**3**), the –O-H stretching vibration band was observed at 3391 cm^{-1}, as well as the C-N band at 1486 cm^{-1}, the C=N a sharp band at 1610 cm^{-1}, and the C-O band at 1278 cm^{-1}. The sharp intensity bands in the 1608 cm^{-1} region of **4** were assigned to C=N stretching vibration, while the strong sharp band at 1225 cm^{-1} was due to C-O stretching vibration. The IR of complex **5** has shown the C=N sharp band, the C-N and the C-O band at 1608 cm^{-1}, 1456 cm^{-1}, and 1223 cm^{-1}, respectively. In the IR spectra of these complexes (-OH) stretching vibrations disappeared and there was no distinct shift in (C=N) stretches after complex formation. The band assigned to ν(C-O) shifted to lower frequency 50 cm^{-1} upon coordination in the complexes.[10,11] The band assigned to ν(C-N) shows a shift of 30 cm^{-1} towards a lower frequency.[10,11] IR data confirm the binding of the copper(II) by O and N donor groups of the present ligand and support the tentative structure of the complexes (Figure). In complex **5**, one copper-containing fragment was joined through one 1,10-phenantroline molecule to form a dimeric compound. However, in compound **6**, the bands belonging to C-N, C=N and C-O appeared at 1456 cm^{-1}, 1610 cm^{-1}, and 1226 cm^{-1}.[11,26]

Table 2. Observed i.r. frequencies (cm^{-1}) and proposed mode of assignments for the ligand (H_2PySAL) and its complexes.

Comp.	(O-H)	C-N	C=N	C-O	Cu-N	Cu-O
(3)	3391	1486	1610	1278		
(4)	-	1455	1608	1225	514	375
(5)	-	1456	1608	1223	517	355
(6)	-	1456	1610	1226	498	350

The room temperature magnetic moment of all the mono-, di- and trinuclear complexes showed a normal magnetic moment (Table 1). The magnetic moment of the mononuclear copper(II) complexes (**4**) is ca. 1.72 B.M., corresponding to one unpaired electron, of the dinuclear copper(II) complexes (**5**) is 1.80 B.M. and of the trinuclear copper(II) complexes is 1.79 B.M. The magnetic moment data of the all copper(II) complexes suggest square-planar geometry[10,11,26] for each.

The ligand and copper(II) complexes were dissolved in DMF. In the UV-Vis spectra were observed as characteristic bands of the metal complexes. The absorption bands are given in Table 1. The absorption λ_{max} of the free ligand H_2PySAL was seen at ca. 300 nm and is attributable to the $\pi - \pi^*$ transition of the C=N group. In addition, the electronic spectra of the complexes showed intense absorption at ca. 400 nm, which is assigned to charge-transfer (MLCT) transition from the p π orbitals of the donor atoms to d orbitals of the metal.[11,30,31] In all the complexes, d-d transitions were observed at ca. 500 nm and the energy of the d-d transition suggests distorted tetragonal geometry[10,11,26,30] for each.

In summary, the synthesis and characterization of complexes containing Cu(II) H_2PySAL have been described. In the mononuclear complexes Cu(II) ions were complex with nitrogen atoms and oxygen atoms of ligand a square-planar coordination geometry. In the dinuclear Cu(II) complex, the second Cu(II) ions are ligated with dianionic oxygen atoms of the ligand, which are linked to the 1,10- phenanthroline nitrogen atoms. However, the trinuclear Cu(II) complex (**6**) was formed by the coordination of the third Cu(II) ions with dianionic oxygen atoms of each of the 2 molecules of the mononuclear Cu(II) complexes (**4**). All the spectral and elemental analyses' data support the formation of the copper(II) complexes.

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