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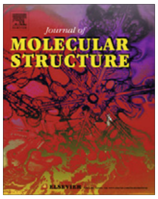

Synthesis, spectroscopic characterization and antimicrobial activity of mono-, bi- and tri-nuclear metal complexes of a new Schiff base ligand

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ABSTRACT

Condensation of *o*-acetoacetylphenol and 1,2-diaminopropane in 1:1 molar ratio under condition of high dilution yielded the mono-condensed dibasic Schiff base ligand with a N_2O_2 donors. The mono-condensed ligand has been used for further condensation with 2-hydroxy-5-nitrobenzaldehyde to obtain the new asymmetrical dicompartmental Schiff base ligand, H_3L, with N_2O_3 donors. The structure of the ligand was elucidated by analytical and spectroscopic tools (IR, ^1H and ^{13}C NMR spectra) which indicated that the coordinating sites are oxygen atoms of the phenolic OH groups, nitrogen atoms of the azomethine groups and the oxygen atom of the ketonic group. Reactions of the ligand with metal salts yielded mono- and homo-bi-nuclear complexes formulated as [M(HL)], where M=Co(II), Ni(II) and Cu(II), $[Fe(H_2L)Cl_2(H_2O)]\cdot 2½H_2O$, $[Fe_2(HL)(ox)Cl_3(H_2O)_2]\cdot 5H_2O$, $[UO_2(H_2L)(OAc)(H_2O)_2]$, $[VO(H_3L)(SO_4)(H_2O)]\cdot H_2O$, $[M_2(L)Cl(H_2O)_2]\cdot ½H_2O$, where M=Co(II) and Ni(II) and $[Cu(H_2L)Cl]$. The mononuclear Ni(II) complex, [Ni(HL)], was used to synthesize homo- and hetero-bi- and tri-nuclear complexes with the molecular formulae $[Ni_2(L)Cl(H_2O)_2]$, $[Ni_2(L)_2FeCl(H_2O)]\cdot H_2O$ and $[Ni_2(HL)_2CoCl_2]$. The structures of the complexes were characterized by various techniques such as elemental and thermal analyses, IR, ^1H and ^{13}C NMR, mass and electronic spectra as well as conductivity and magnetic moment measurements. Square-planar and octahedral geometries are suggested for the Cu(II), Co(II) and Ni(II) complexes, octahedral geometry for the Fe(III) and VO^{2+} complexes while uranium(VI) ion is octa-coordinated in its complex. The Schiff base and its metal complexes were evaluated for antimicrobial activity against Gram positive bacteria (*Staphylococcus aureus*), Gram negative bacteria (*Escherichia coli*) and fungi (*Candida albicans* and *Aspergillus flavus*). The ligand and some of its complexes were found to be biologically active.

1. Introduction

Schiff base ligands are considered privileged ligands, because they are easily prepared by a simple one-pot condensation of aldehydes and primary amines in an alcohol solvent. Metal complexes of these bases have numerous applications including antibacterial, antifungal [1–6] and antiviral activities [7,8] as well as other biological applications [9–12]. Several applications have been related for these complexes in chemical analysis [13], absorption and transport of oxygen [14], in pesticides [15] and heterogeneous and homogeneous catalysis for oxidation and polymerization of organic compounds [16–19]. The term “dinucleating ligands” was first introduced in 1970 by Robson [20] to describe the class of polydentate chelating ligands which able to bind simultaneously two metal ions. Among many different types of dinucleating ligands, the phenol-based compartmental ligands attracted particularly wide attention of scientists. The term “compartmental” was introduced to indicate a ligand containing two adjacent, but dissimilar coordinating sites [21]. Particular interest in this type of ligands resulted from the recent recognition of the asymmetric nature of a number of bimetallic biosites [22,23].

Thus, in the present work, a new asymmetric dicompartmental Schiff base ligand, H_3L, which contains N_2O_3 coordinating sites was synthesized. Using this dicompartmental ligand, mono-, homo- and hetero-bi- and tri-nuclear complexes were synthesized and characterized. Indeed, the biological activity of the ligand and its complexes was screened against selected kinds of bacteria and fungi.

2. Experimental

2.1. Reagents and materials

$CuCl_2\cdot 2H_2O$, $NiCl_2\cdot 6H_2O$, $CoCl_2\cdot 6H_2O$, $FeCl_3\cdot 6H_2O$, $Cu(OAc)_2\cdot H_2O$, $Ni(OAc)_2\cdot 4H_2O$, $Co(OAc)_2\cdot 4H_2O$, $UO_2(OAc)_2\cdot 2H_2O$, $VOSO_4\cdot H_2O$,

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$LiOH \cdot H_2O$, oxalic acid, ethylacetate, sodium metal, *o*-hydroxyacetophenone, 1,2-diaminopropane and 2-hydroxy-5-nitrobenzaldehyde were either BDH or Merck chemicals. *o*-Acetoacetylphenol was prepared following the literature procedure [24]. Organic solvents were spectroscopic grade and used without further purification.

2.2. Synthesis of the ligand

2.2.1. Synthesis of o-acetoacetylphenol

o-Acetoacetylphenol was prepared as cited in the literature [24].

2.2.2. Synthesis of [(E)-3-(1-aminopropan-2-ylimino)-1-(2-hydroxyphenyl)butan-1-one] (H.U.)

A solution of *o*-acetoacetylphenol, 15 g (84.3 mmol) in 250 mL chloroform was added dropwise to a solution of 1,2-diaminopropane, 6.24 g (84.3 mmol) in 150 mL chloroform. After complete addition, the solution was stirred for an additional 18 h and chloroform was removed under reduced pressure, yielding the half-unit ligand as a viscous liquid which solidifies to form yellow precipitate upon addition of heptane. The yellow solid was filtered off, washed with least amount of chloroform and air-dried. Yield: 16.5 g, 83.7%, m.p. 78 °C.

2.2.3. Synthesis of the asymmetric Schiff base ligand

The new Schiff base (*E*)-3-(1-((*E*)-2-hydroxy-5-nitrobenzylideneamino)propan-2-ylimino)-1-(2-hydroxyphenyl)butan-1-one (H_3L) was prepared by condensation of (*E*)-3-(1-aminopropan-2-ylimino)-1-(2-hydroxyphenyl)butan-1-one dissolved in $CHCl_3$ with 2-hydroxy-5-nitrobenzaldehyde. A yellow solid product is formed upon cooling the solution slowly to room temperature and the precipitate was filtered off, washed with chloroform then diethyl ether and finally air-dried. The analytical and physical data for the ligand and its metal complexes are listed in Table 1. Scheme 1 represents the synthetic outline of the asymmetric Schiff base ligand.

2.3. Syntheses of the metal complexes

A general method has been used for the preparation of all complexes. A hot 20 mL ethanolic solution of the metal salt of VO^{2+}, Fe(III), Co(II), Ni(II), Cu(II) and UO_2^{2+} was gradually added to a chloroform solution of the ligand (30 mL) in 1:1 or 1:2 molar ratio and the solution was heated under reflux for 3 h on a water bath during which the solid complex precipitated. The precipitate was filtered off, washed with ethanol then diethyl ether and finally air-dried. In case of VO^{2+} complex, water was added to ensure complete dissolution of $VOSO_4 \cdot H_2O$. The uranyl complex was prepared in methanol. The following detailed preparations are given as examples and the other complexes were obtained similarly.

2.3.1. [Co(HL)], **6**

Cobalt(II) acetate tetrahydrate, $Co(OAc)_2 \cdot 4H_2O$ (0.39 g, 1.57 mmol) in ethanol (20 mL) was added gradually with constant stirring to the solution of the ligand, H_3L, (0.6 g, 1.57 mmol) in chloroform (25 mL). The reaction mixture was heated under reflux for 3 h. The precipitate was filtered off, washed with ethanol then ether and finally air-dried. Yield: 0.5 g (72.5%).

2.3.2. [$Fe_2(H_2L)(ox)Cl_3(H_2O)_2$]·$5H_2O$, **5**

Lithium hydroxide monohydrate, $LiOH \cdot H_2O$ (0.197 g, 4.7 mmol) in methanol (10 mL) was added gradually with constant stirring to the solution of the ligand, H_3L, (0.6 g, 1.57 mmol) in chloroform (25 mL). Oxalic acid (0.197 g, 1.57 mmol) in ethanol (15 mL) was added gradually to the above mixture then iron(III) chloride hexahydrate, $FeCl_3 \cdot 6H_2O$ (0.85 g, 3.15 mmol) in ethanol (20 mL) was added and the reaction mixture was heated under reflux for 3 h.

Table 1
Analytical and physical data for the Schiff base, H_3L, ligand and its metal complexes.

No.	Reactions	Complexes M.F. [F.W.]	Color	Yield (%)	M.P. (°C)	Elemental analysis, % Found/(Calc.)				
						C	H	N	Cl (S)	M
1	H.U.	[$C_{13}H_{18}N_2O_2$] [234.30]	Yellow	83.8	78	66.7 (66.64)	7.5 (7.74)	12.1 (11.96)	–	–
2	H_3L	[$C_{20}H_{21}N_3O_5$] [383.41]	Yellow	77.0	137	62.7 (62.65)	5.5 (5.52)	11.1 (10.96)	–	–
3	$H_3L + VOSO_4 \cdot H_2O$	[$VO(H_3L)(SO_4)(H_2O)$]·H_2O [$C_{20}H_{25}N_3O_{12}SV$] [582.44]	Pale brown	60.0	>342	41.0 (41.24)	4.1 (4.33)	7.3 (7.21)	5.5 (5.51)	8.7 (8.75)
4	$H_3L + FeCl_3 \cdot 6H_2O$	[$Fe(H_2L)Cl_2(H_2O)$]·$2\frac{1}{2}H_2O$ [$C_{20}H_{27}N_3O_{8\frac{1}{2}}Cl_2Fe$] [572.21]	Deep brown	77.0	>342	42.1 (41.98)	4.6 (4.76)	7.3 (7.34)	12.5 (12.39)	9.7 (9.76)
5	H_3L + Oxalic acid + $LiOH \cdot H_2O + FeCl_3 \cdot 6H_2O$	[$Fe_2(HL)(ox)Cl_3(H_2O)_2$]·$5H_2O$ [$C_{22}H_{34}N_3O_{16}Cl_3Fe_2$] [814.58]	Reddish brown	51.7	>342	32.2 (32.44)	4.0 (4.21)	5.3 (5.16)	12.8 (13.06)	13.7 (13.71)
6	$H_3L + Co(OAc)_2 \cdot 4H_2O$	[Co(HL)] [$C_{20}H_{19}N_3O_5Co$] [440.32]	Bick red	72.5	>342	54.5 (54.56)	4.4 (4.35)	9.5 (9.54)	–	13.3 (13.38)
7	$H_3L + Ni(OAc)_2 \cdot 4H_2O$	[Ni(HL)] [$C_{20}H_{19}N_3O_5Ni$] [440.10]	Red	70.0	308	54.5 (54.58)	4.3 (4.35)	9.3 (9.55)	–	13.4 (13.34)
8	$H_3L + Cu(OAc)_2 \cdot H_2O$	[Cu(HL)] [$C_{20}H_{19}N_3O_5Cu$] [444.94]	Pale violet	83.5	>342	53.8 (53.99)	4.4 (4.30)	9.3 (9.44)	–	14.2 (14.28)
9	$H_3L + CoCl_2 \cdot 6H_2O + LiOH \cdot H_2O$	[$Co_2(L)Cl(H_2O)_2$]·$\frac{1}{2}H_2O$ [$C_{20}H_{23}N_3O_{7\frac{1}{2}}ClCo_2$] [578.74]	Brown	66.7	>342	41.5 (41.51)	4.2 (4.01)	7.2 (7.26)	6.2 (6.13)	20.5 (20.37)
10	$H_3L + NiCl_2 \cdot 6H_2O + LiOH \cdot H_2O$	[$Ni_2(L)Cl(H_2O)_2$]·$\frac{1}{2}H_2O$ [$C_{20}H_{23}N_3O_{7\frac{1}{2}}ClNi_2$] [578.29]	Pale brown	80.0	>342	41.3 (41.54)	3.9 (4.01)	7.4 (7.27)	6.3 (6.13)	20.3 (20.30)
11	$H_3L + CuCl_2 \cdot 2H_2O + LiOH \cdot H_2O$	[$Cu(H_2L)Cl$] [$C_{20}H_{20}N_3O_5ClCu$] [481.40]	Brown	75.0	>342	49.8 (49.90)	4.3 (4.19)	8.7 (8.73)	7.4 (7.36)	13.0 (13.20)
12	[Ni(HL)] + $FeCl_3 \cdot 6H_2O + LiOH \cdot H_2O$	[$Ni_2(L)_2FeCl(H_2O)$]·H_2O [$C_{40}H_{40}N_6O_{12}ClNi_2Fe$] [1005.52]	Brownish red	82.0	>342	47.5 (47.78)	4.0 (4.01)	8.4 (8.36)	3.6 (3.53)	Ni;11.5 (11.68), Fe; 5.4 (5.55)
13	[Ni(HL)] + $CoCl_2 \cdot 6H_2O + LiOH \cdot H_2O$	[$Ni_2(HL)_2CoCl_2$] [$C_{40}H_{38}N_6O_{10}Cl_2Ni_2Co$] [1010.04]	Reddish brown	69.5	>342	47.5 (47.57)	3.8 (3.79)	8.4 (8.32)	6.8 (7.02)	Ni;11.7 (11.63), Co; 5.6 (5.83)
14	[Ni(HL)] + $NiCl_2 \cdot 6H_2O + LiOH \cdot H_2O$	[$Ni_2(L)Cl(H_2O)_2$] [$C_{20}H_{22}N_3O_7ClNi_2$] [569.29]	Brown	71.0	>342	42.3 (42.20)	3.7 (3.90)	7.4 (7.38)	6.2 (6.23)	20.5 (20.63)
15	$H_3L + UO_2(OAc)_2 \cdot 2H_2O$	[$UO_2(H_2L)(OAc)(H_2O)_2$] [$C_{22}H_{27}N_3O_{11}U$] [747.50]	Orange	81.0	144	35.1 (35.35)	3.5 (3.64)	5.8 (5.62)	–	31.4 (31.84)