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Synthesis, spectroscopic studies, molecular modeling and antimicrobial activity of binuclear Co(II) and Cu(II) complexes of 4,6-diacetylresorcinol

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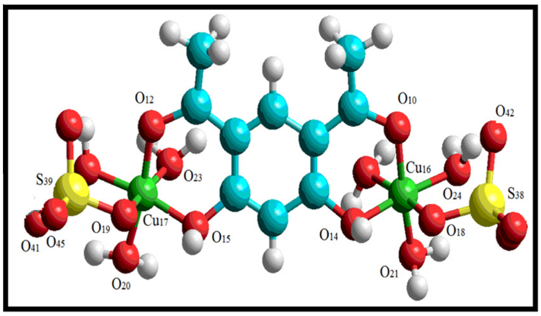
HIGHLIGHTS

- A new series of metal complexes of 4,6-diacetylresorcinol with Co(II) and Cu(II) have been synthesized.
- Complexes have been characterized by the analytical and spectral methods.
- The spin Hamiltonian parameters of the complexes were calculated and discussed.
- Molecular orbital calculations were performed.
- Some complexes showed antibacterial and antifungal activities.

GRAPHICAL ABSTRACT



$[(H_2L)Cu_2(SO_4)_2(H_2O)_6].4H_2O$

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ABSTRACT

Reactions of 4,6-diacetylresorcinol with different cobalt(II) and copper(II) salts *viz*., OAc^-, Cl^-, NO_3^- and SO_4^{2-}, yielded a new series of binuclear metal complexes. Reactions of the ligand with these metal ions in the presence of a secondary ligand (L′) [O,O-donor; acetylacetone, N,O-donor; 8-hydroxyquinoline or N,N-donor; 1,10-phenanthroline and *N,N,N′,N′*-tetramethylethylenediamine] in 1:2:2 (L:M:L′) molar ratio yielded mixed-ligand complexes with different molar ratios. The metal complexes were characterized by elemental and thermal analyses, IR, electronic, ESR and mass spectra as well as conductivity and magnetic susceptibility measurements. The analytical and spectroscopic data suggested that the H_2L ligand behaves as a neutral, monobasic or dibasic tetradentate ligand, depending on the type of the anion and secondary ligand used, through the two phenolic and two carbonyl groups. Electronic spectra, magnetic and conductivity measurements showed that all complexes are octahedral with non-electrolytic nature. The profile of ESR spectra of copper(II) complexes suggested the octahedral geometry and the spin Hamiltonian parameters of the complexes were calculated and discussed. Molecular orbital calculations were performed for metal complexes using *Hyperchem* 7.52 program on the bases of *PM3* level and the results correlated with the experimental data. The free ligand and some of its metal complexes showed antimicrobial activity towards some of Gram-positive and Gram-negative bacteria, yeast (*Candida albicans*) and fungus (*Aspergillus fumigatus*).

Introduction

Many researchers have focused their interests on transition metal complexes because of their extensive applications in wide ranging areas. These complexes have shown antibacterial, antifungal and antitumor activity [1–11]. Bimetallic coordination compounds serve as model systems for variety of biological reactions such as oxygen transport [12], oxygen activation, photocatalytic water splitting [13], electron transfer process [14], and metal–metal iteraction. The presence of two metal ions in close proximity can lead to a spin-exchange and unusual magnetic properties.

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Mixed-ligand complexes have been extensively studied following recognition that they play an important role in biological processes and serve as suitable models for valuable information in the elucidation of enzymatic processes of biological relevance [15,16]. Also, these complexes showed significant antifungal, antibacterial and anticancer activity [17,18].

In our previous studies [19–25], 4,6-diacetylresorcinol (DAR) has been used as a starting material for the generation of different polydentate ligands. These ligands are flexible and afford different transition metal complexes with different modes of bonding. However, literature survey revealed that few papers [26–28] reporting the synthesis and characterization of mixed-ligand complexes including 4,6-diacetylresorcinol as a primary ligand.

Recently, the ligational behavior of 4,6-diacetylresorcinol towards the alkaline earth metal and nickel(II) ions [29,30] has been studied. As a part of our continuing study of metal complexes of 4,6-diacetylresorcinol, the aim of the current work is to investigate the effect of anions and secondary ligands on the structures of the formed complexes through reactions of 4,6-diacetylresorcinol with various cobalt(II) and copper(II) salts in absence and presence of secondary ligands. The synthesized complexes have been characterized by elemental analyses, spectral, molar conductance and magnetic studies as well as thermal gravimetric analysis (TGA). Molecular modeling was carried out for the metal complexes and the theoretical results were correlated with the experimental data. The metal complexes were also screened for their antimicrobial activity.

Experimental

Materials

4,6-Diacetylresorcinol was prepared as cited in the literature [31]. Metal salts, lithium hydroxide, acetylacetone (acac), 8-hydroxyquinoline (8-HQ), 1,10-phenanthroline (phen), *N,N,N′,N′*-tetramethylethylenediamine (tmen), EDTA disodium salt, ammonium hydroxide, mureoxide and nitric acid were either Aldrich, BDH or Merck products. Organic solvents (ethanol, diethylether, dimethylformamide (DMF) and dimethylsulfoxide (DMSO)) were reagent grade chemicals and were used without further purification.

Synthesis of the metal complexes

Lithium hydroxide dissolved in the least amount of bidistilled water was added gradually with constant stirring to the solution of the ligand, in ethanol, in molar ratio 2:1 (LiOH:H_2L). The metal ion dissolved in ethanol was added to the above mixture in the molar ratio 2:1 (M:L) and the reaction mixture was heated under reflux for 7 h. The resulting precipitates were filtered off, washed with bidistilled water, ethanol then ether and finally air-dried. The following detailed preparations are given as examples and the other complexes were obtained similarly.

Synthesis of the $[(L)_2Co_2(H_2O)_4]\cdot 3H_2O\cdot EtOH$, complex (**4**)

Lithium hydroxide monohydrate, $LiOH\cdot H_2O$ (0.216 g, 5.15 mmol) in the least amount of bidistilled water (10 mL) was added gradually with constant stirring to the solution of the ligand, H_2L, (0.5 g, 2.58 mmol) in ethanol (30 mL), in molar ratio 2:1 (LiOH:H_2L). Cobalt(II) nitrate hexahydrate, $Co(NO_3)_2\cdot 6H_2O$, (1.498 g, 5.15 mmol) in ethanol (30 mL) was added gradually with constant stirring to the above mixture. The resulting mixture was heated under reflux for 7 h. A dark yellow precipitate was formed, filtered off and washed several times with small amounts of bidistilled water, ethanol then diethylether and finally air-dried. The yield was 0.7 g (81%), m.p. > 300 °C.

Synthesis of the $[(HL)_2Co_2(8\text{-}HQ)_2]$, complex (**6**)

Lithium hydroxide monohydrate, $LiOH\cdot H_2O$ (0.216 g, 5.15 mmol) in the least amount of bidistilled water (10 mL) was added gradually with constant stirring to the solution of the ligand,

Table 1
Analytical and physical data of Co(II) and Cu(II) complexes of the H_2L ligand.

No.	Reaction	Complex M. F. [F. Wt]	Color	Yield (%)	M.P. (°C)	Elemental analysis, % Found/(Calc.)				
						C	H	N	CI/S	M
(1)	$H_2L + Co(OAc)_2 + LiOH$	$[(L)_2Co_2(H_2O)_4]\cdot 2H_2O\cdot 0.5EtOH$ $C_{21}H_{31}O_{14.5}Co_2$ [633.34]	Dark yellow	61	>300	39.5(39.83)	4.76(4.93)	–	–	18.3(18.61)
(2)	$H_2L + CoCl_2 + LiOH$	$[(L)Co_2Cl_2(H_2O)_4(EtOH)_2]\cdot 1.5H_2O$ $C_{14}H_{31}Cl_2O_{11.5}Co_2$ [572.17]	Beige	38	>300	29.01(29.39)	5.1(5.46)	–	12.60(12.39)	20.2(20.6)
(3)	$H_2L + CoSO_4 + LiOH$	$[(H_2L)_2Co_2(SO_4)_2]\cdot EtOH$ $C_{22}H_{26}O_{17}S_2Co_2$ [744.44]	Beige	82	>300	35.75(35.5)	3.8(3.52)	–	8.35(8.61)	15.5(15.83)
(4)	$H_2L + Co(NO_3)_2 + LiOH$	$[(L)_2Co_2(H_2O)_4]\cdot 3H_2O\cdot EtOH$ $C_{22}H_{36}O_{16}Co_2$ [674.39]	Dark yellow	81	>300	39.04(39.18)	5.27(5.38)	–	–	17.2(17.48)
(5)	$H_2L + Co(NO_3)_2 + acac + LiOH$	$[(HL)_2Co_2(acac)_2]\cdot 1.5H_2O$ $C_{30}H_{35}O_{13.5}Co_2$ [729.47]	Beige	90	>300	49.15(49.4)	4.98(4.84)	–	–	15.9(16.16)
(6)	$H_2L + Co(NO_3)_2 + 8\text{-}HQ + LiOH$	$[(HL)_2Co_2(8\text{-}HQ)_2]$ $C_{38}H_{30}N_2O_{10}Co_2$ [792.54]	Brownish orange	79	>300	57.68(57.59)	3.93(3.82)	3.9(3.53)	–	14.5(14.87)
(7)	$H_2L + Co(NO_3)_2 + phen + LiOH$	$[(L)Co_2(NO_3)_2(phen)_2(H_2O)_2]\cdot 5H_2O$ $C_{34}H_{38}N_6O_{17}Co_2$ [920.58]	Pale brown	42	>300	44.7(44.36)	4.33(4.16)	8.9(9.13)	–	12.6(12.8)
(8)	$H_2L + Co(NO_3)_2 + tmen + LiOH$	$[(L)Co_2(NO_3)_2(tmen)(H_2O)_4]$ $C_{16}H_{32}N_4O_{14}Co_2$ [622.32]	Yellowish green	57	>300	30.88(30.88)	4.80(5.18)	8.74(9.00)	–	18.6(18.94)
(9)	$H_2L + Cu(OAc)_2 + LiOH$	$[(L)Cu_2(OAc)_2(H_2O)_4]\cdot 1.5H_2O\cdot 0.5EtOH$ $C_{15}H_{28}O_{14}Cu_2$ [559.47]	Dark green	43	>300	32.5(32.2)	4.8(5.04)	–	–	23(22.72)
(10)	$H_2L + CuCl_2 + LiOH$	$[(L)Cu_2Cl_2(H_2O)_4(EtOH)_2]\cdot H_2O$ $C_{14}H_{30}O_{11}Cl_2Cu_2$ [572.39]	Green	31	>300	29.2(29.38)	5(5.28)	–	12.00(12.39)	22.4(22.2)
(11)	$H_2L + CuSO_4 + LiOH$	$[(H_2L)Cu_2(SO_4)_2(H_2O)_6]\cdot 4H_2O$ $C_{10}H_{30}O_{22}S_2Cu_2$ [693.56]	Pale green	89	>300	17(17.32)	4.04(4.36)	–	9.60(9.25)	18.1(18.32)
(12)	$H_2L + Cu(NO_3)_2 + LiOH$	$[(L)_2Cu_2(H_2O)_4]$ $C_{20}H_{24}O_{12}Cu_2$ [583.50]	Green	74	>300	40.8(41.17)	4.04(4.15)	–	–	21.4(21.78)
(13)	$H_2L + Cu(OAc)_2 +$ $+ acac + LiOH$	$[(HL)_2Cu_2(acac)_2]\cdot 2.5H_2O$ $C_{30}H_{37}O_{14.5}Cu_2$ [756.71]	Green	87	>300	47.3(47.62)	5.03(4.93)	–	–	16.6(16.8)
(14)	$H_2L + Cu(OAc)_2 + 8\text{-}HQ + LiOH$	$[(L)Cu_2(8\text{-}HQ)_2(H_2O)_4]\cdot 3H_2O$ $C_{28}H_{34}N_2O_{13}Cu_2$ [733.68]	Pale green	39	282	45.7(45.84)	4.4(4.67)	3.5(3.82)	–	17.2(17.32)