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Mono- and binuclear copper(II) complexes of new hydrazone ligands derived from 4,6-diacetylresorcinol: Synthesis, spectral studies and antimicrobial activity

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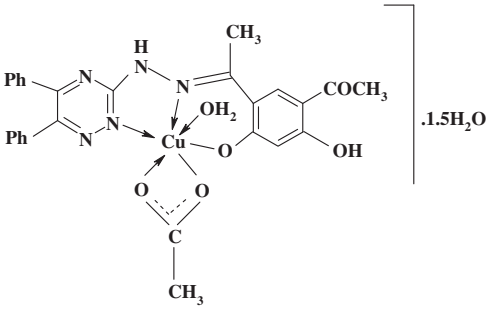
HIGHLIGHTS

- Two new hydrazone ligands were synthesized and characterized.
- Copper(II) complexes were synthesized and characterized by analytical and spectral methods.
- The spin Hamiltonian parameters of some complexes were calculated and discussed.
- The complexes exhibited octahedral and square planar geometrical arrangements.
- The ligands and some complexes showed antimicrobial activity.

GRAPHICAL ABSTRACT



[(HL¹)Cu(OAc)(H₂O)].1.5H₂O

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ABSTRACT

Two new hydrazone ligands, H_2L^1 and H_2L^2, were synthesized by the condensation of 4,6-diacetylresorcinol with 3-hydrazino-5,6-diphenyl-1,2,4-triazine and isatin monohydrazone, respectively. The structures of the ligands were elucidated by elemental analyses, IR, ^{1}H NMR, electronic and mass spectra. Reactions of the ligands with several copper(II) salts, including AcO^-, NO_3^-, SO_4^{2-}, Cl^- and Br^- afforded mono- and binuclear metal complexes. Also, the ligands were allowed to react with Cu(II) ion in the presence of a secondary ligand (L′) [N,O-donor; 8-hydroxyquinoline, N,N-donor; 1,10-phenanthroline or O,O-donor; benzoylacetone]. Characterization and structure elucidation of the prepared complexes were achieved by elemental and thermal analyses, IR, electronic, mass and ESR spectra as well as conductivity and magnetic susceptibility measurements. The ESR spin Hamiltonian parameters of some complexes were calculated. The spectroscopic data showed that the H_2L^1 ligand acts as a neutral or monobasic tridentate ligand while the H_2L^2 ligand acts as a bis(monobasic tridentate) ligand. The coordination sites with the copper(II) ion are phenolic oxygen, azomethine nitrogen and triazinic nitrogen (H_2L^1 ligand) or isatinic oxygen (H_2L^2 ligand). The metal complexes exhibited octahedral and square planar geometrical arrangements depending on the nature of the anion. The ligands and some metal complexes showed antimicrobial activity.

Introduction

Hydrazones and their metal complexes form an interesting class of compounds which find extensive applications in antibacterial, antifungal and antitumor agents [1–3]. Also, they are used in extraction of some metal ions using different buffer solutions [4], micro determination of metal ions [4], determination of titanium in bauxite, Portland cement, amphibolites and granites [5].

Triazine is an important class of heterocyclic compounds found in many synthetic and natural products with a wide range of

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biological activities, such as adenosine receptor antagonist [6], antiamoebic [7], antimalarial [8], antiviral [9], antitubercular [10] and carbonic anhydrase inhibitor [11].

Isatin is a versatile lead molecule for designing potential bioactive agents and its derivatives were reported to possess a broad spectrum of antiviral activities [12]. Ligands containing isatin moiety are known to possess a wide range of pharmacological properties that include antibacterial, antifungal [13], anticonvulsant [14] and anti-HIV [15] activities.

The bifunctional carbonyl compound; 4,6-diacetylresorcinol (DAR) serves as precursor for the construction of different polydentate ligands [16–20]. In our previous studies, metal complexes of polydentate ligands derived from 4,6-diacetylresorcinol [21–27] have been synthesized and fully characterized. The most motivating features of these ligands are the possibility of use them to synthesize polynuclear complexes with different modes of bonding. Also, mixed-ligand complexes including 4,6-diacetylresorcinol as a primary ligand have been studied [28–30].

On the basis of stated facts, the present work is an extension to our work and is devoted to the synthesis of new hydrazone ligands, H_2L^1 and H_2L^2, by the condensation of 4,6-diacetylresorcinol with 3-hydrazino-5,6-diphenyl-1,2,4-triazine and isatin monohydrazone, respectively in the molar ratio 1:2 (DAR:hydrazino). The ligational behavior of the new ligands towards different copper(II) salts was investigated. The structures of the ligands and their metal complexes were characterized by elemental and thermal analyses, IR, ^{1}H NMR, electronic, ESR and mass spectra as well as conductivity and magnetic susceptibility measurements at room temperature. The biological activity of the ligands and their complexes was screened against selected kinds of bacteria and fungi.

Experimental

Materials

4,6-Diacetylresorcinol was prepared as cited in the literature [16]. 3-Hydrazino-5,6-diphenyl-1,2,4-triazine was prepared according to Ref. [31] and isatin monohydrazone was prepared according to Ref. [32]. Benzil, glacial acetic acid, thiosemicarbazide, hydrazine hydrate and isatin were BDH or Merck products. Metal salts, lithium hydroxide, 8-hydroxyquinoline (8-HQ), 1,10-phenanthroline (Phen), benzoylacetone (Bac), EDTA disodium salt, ammonium hydroxide, mureoxide and nitric acid were either Aldrich,

Table 1
Analytical and physical data of the hydrazone, H_2L^1 and H_2L^2, ligands and their copper(II) complexes.

No.	Reaction	Complex M.F. [F. Wt]	Color	Yield [a] (%)	M.P. (°C)	Elemental analysis, % found/(calc.)				
						C	H	N	Cl/S	M
	H_2L^1	$C_{25}H_{21}N_5O_3$ [439.48]	Pale brown	89	>300	68.46 (68.33)	4.7 (4.82)	16.1 (15.94)	–	–
(1)	H_2L^1 + $Cu(OAc)_2{\cdot}H_2O$	$[(HL^1)Cu(OAc)(H_2O)]{\cdot}1.5H_2O$ $C_{27}H_{28}N_5O_{7.5}Cu$ [606.1]	Brown	83	>300	53.57 (53.51)	4.97 (4.66)	11.8 (11.55)	–	10.4 (10.48)
(2)	H_2L^1 + $Cu(NO_3)_2{\cdot}2.5H_2O$	$[(HL^1)Cu(H_2O)]NO_3$ $C_{25}H_{22}N_6O_7Cu$ [582.04]	Dark green	84	>300	51.66 (51.59)	3.8 (3.81)	14.56 (14.44)	–	11.0 (10.92)
(3)	H_2L^1 + $CuSO_4{\cdot}5H_2O$	$[(H_2L^1)Cu(SO_4)(H_2O)_2]{\cdot}1.5H_2O$ $C_{25}H_{28}N_5O_{10.5}SCu$ [662.14]	Brown	50	>300	45.42 (45.35)	4.0 (4.26)	10.47 (10.58)	4.6 (4.84)	9.4 (9.6)
(4)	H_2L^1 + $CuCl_2{\cdot}2H_2O$	$[(HL^1)CuCl]{\cdot}1.5H_2O$ $C_{25}H_{23}N_5O_{4.5}ClCu$ [564.49]	Green	75	281	52.9 (53.19)	4.2 (4.11)	12.29 (12.41)	6.0 (6.28)	11.1 (11.26)
(5)	H_2L^1 + $CuBr_2$	$[(HL^1)Cu(H_2O)_3]Br{\cdot}H_2O$ $C_{25}H_{28}N_5O_7BrCu$ [653.98]	Dark green	60	260	45.84 (45.92)	4.1 (4.32)	10.88 (10.71)	–	9.5 (9.72)
(6)	H_2L^1 + $Cu(OAc)_2{\cdot}H_2O$ + 8-HQ	$[(HL^1)Cu(8\text{-}HQ)(H_2O)]$ $C_{34}H_{28}N_6O_5Cu$ [664.19]	Chocolate brown	96	263	61.47 (61.49)	4.0 (4.25)	12.9 (12.65)	–	9.4 (9.57)
(7)	H_2L^1 + $Cu(OAc)_2{\cdot}H_2O$ + Phen	$[(HL^1)Cu(OAc)(Phen)]$ $C_{39}H_{31}N_7O_5Cu$ [741.27]	Dark brown	71	267	63.4 (63.19)	3.9 (4.22)	13.5 (13.23)	–	8.4 (8.57)
(8)	H_2L^1 + $Cu(OAc)_2{\cdot}H_2O$ + Bac	$[(HL^1)Cu(H_2O)(Bac)]{\cdot}2H_2O$ $C_{35}H_{35}N_5O_8Cu$ [717.24]	Dark brown	71	>300	58.3 (58.61)	4.7 (4.92)	9.9 (9.76)	–	8.7 (8.86)
	H_2L^2	$C_{26}H_{20}N_6O_4$ [480.49]	Brown	94	>300	64.8 (64.99)	4.5 (4.2)	17.2 (17.49)	–	–
(9)	H_2L^2 + $Cu(OAc)_2{\cdot}H_2O$	$[(L^2)Cu_2(OAc)_2(EtOH)_2]{\cdot}0.5H_2O{\cdot}0.5EtOH$ $C_{35}H_{40}N_6O_{11}Cu_2$ [847.83]	Dark brown	59	>300	49.6 (49.58)	4.5 (4.76)	9.79 (9.91)	–	14.8 (14.99)
(10)	H_2L^2 + $Cu(NO_3)_2{\cdot}2.5H_2O$	$[(L^2)_2Cu_2]{\cdot}EtOH$ $C_{54}H_{42}N_{12}O_9Cu_2$ [1130.10]	Chocolate brown	17	>300	57.37 (57.39)	3.77 (3.75)	14.6 (14.87)	–	11.20 (11.25)
(11)	H_2L^2 + $CuSO_4{\cdot}5H_2O$	$[(L^2)_2Cu_2]{\cdot}2H_2O$ $C_{52}H_{40}N_{12}O_{10}Cu_2$ [1120.07]	Chocolate brown	23	>300	55.57 (55.76)	3.92 (3.6)	15.4 (15.01)	–	11.30 (11.35)
(12)	H_2L^2 + $CuCl_2{\cdot}2H_2O$ + LiOH	$[(L^2)Cu_2Cl_2]{\cdot}H_2O{\cdot}EtOH$ $C_{28}H_{26}N_6O_6Cl_2Cu_2$ [740.55]	Dark brown	58	>300	45.59 (45.41)	3.55 (3.54)	11.1 (11.35)	9.3 (9.57)	17.0 (17.16)
(13)	H_2L^2 + $CuBr_2$	$[(L^2)Cu_2Br_2]$ $C_{26}H_{18}N_6O_4Br_2Cu_2$ [765.37]	Dark brown	53	>300	40.83 (40.80)	2.29 (2.37)	10.7 (10.98)	–	16.4 (16.61)
(14)	H_2L^2 + $Cu(OAc)_2{\cdot}H_2O$ + 8-HQ	$[(L^2)Cu_2(8\text{-}HQ)_2(EtOH)_2]$ $C_{48}H_{42}N_8O_8Cu_2$ [986.01]	Chocolate brown	79	>300	58.39 (58.47)	4.1 (4.29)	11.1 (11.36)	–	12.7 (12.89)
(15)	H_2L^2 + $Cu(OAc)_2{\cdot}H_2O$ + Phen	$[(L^2)Cu_2(OAc)_2(Phen)_2]{\cdot}3H_2O$ $C_{54}H_{46}N_{10}O_{11}Cu_2$ [1138.12]	Brown	40	>300	57.06 (56.99)	3.8 (4.07)	12.0 (12.31)	–	10.9 (11.17)
(16)	H_2L^2 + $Cu(OAc)_2{\cdot}H_2O$ + Bac	$[(L^2)Cu_2(H_2O)_2(Bac)_2]{\cdot}3H_2O$ $C_{46}H_{46}N_6O_{13}Cu_2$ [1018.00]	Reddish brown	64	>300	54.24 (54.27)	4.3 (4.55)	8.0 (8.26)	–	12.3 (12.48)

[a] The yield is calculated on the basis of ligands.