

Synthesis, characterisation and antimicrobial studies of Copper(II) mixed ligand complexes of β -diketone with, N, N, N', N'-tetramethylethylenediamine

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Abstract

Mixed ligand copper(II) complexes of β -diketones [dibenzoylmethane (dbmH), benzoylacetone (bzacH) and acetylacetone (acacH)] and N, N, N', N'-Tetramethylethylenediamine (tmen) have been synthesised and characterised by metal analysis, conductance measurement, magnetic susceptibility measurement, infrared spectroscopy, electronic spectroscopy and antimicrobial studies. The β -diketones and N,N,N',N'-Tetramethylethylenediamine both acted as bidentate ligands with the β -diketones coordinating through the enolic oxygen, while tmen coordinated through the two nitrogen atoms. The electronic spectra measurements are corroborative of five-coordinate square pyramidal geometry for the complexes. The magnetic moments for the complexes were observed in the range 1.78-2.10 B.M, which is in support of a normal paramagnetic moment. The antimicrobial activities of the compounds, suggested their potential utilization as antimicrobial agents.

Key words: β -diketones; N, N, N', N'-Tetramethylethylenediamine; paramagnetic; antimicrobial studies.

Introduction

β -diketones have been used as ligands for almost 120 years and have remained one of the ligands of choice in coordination chemistry [1]. This is primarily due to the wide range of applications [2] both in science and industry. The compounds are often used in polymer technology e.g. as substrates for the manufacture of homogeneous and heterogeneous catalysts, as polymerization catalysts and substances which modify the properties of resulting polymer [3]. They are used as shift reagents for the structural determination of steroids and other complex molecules [4,5]. They have also been widely used in pharmaceutical industries [6]. Furthermore, metal complexes of β -diketones are also used in the manufacturing of silicon resin which is used for electronic devices [7].

The survey of the literature shows that a series of mixed ligand copper(II) complexes containing acetylacetone (acacH), benzoylacetone (bzacH), dibenzoylmethane (dbmH), trifluoroacetylacetone (TFAH), hexafluoroacetylacetone(HFAH) and N, N, N', N'-Tetramethylethylenediamine(tmen) with

counter ions such as ClO_4^- and NO_3^- have been prepared [8] but the activity of these complexes have not been tested against fungi and bacteria. In addition, the Cl^- counter ion has not been synthesised with the different mixed ligands. Hence, this paper presents the spectroscopic properties and the antimicrobial study of the mixed ligand copper(II) complexes of β -diketones and N, N, N', N'-Tetramethylethylenediamine in continuation of our studies on β -diketones and their derivatives [9-15].

Materials and methods

Reagents and Solvents

Acetylacetone, benzoylacetone, dibenzoylmethane, copper (II) nitrate trihydrate, copper(II) chloride monohydrate, N, N, N', N'-tetramethylethylenediamine, methanol, chloroform and ethanol. They are of analytical grade obtained from Aldrich Chemicals and British Drug House (BDH) Chemicals Limited and were utilised without further purification.



Preparation of [Cu(bzac)(tmen)NO₃]

A solution of Copper nitrate hexahydrate (0.4392 g, 1.8 mmol) dissolved in 2 mL water was added directly to a mixture of tmen (0.3 mL) and BzacH (0.3 g, 1.8 mmol) in methanol in 3 mL ethanol. The mixture was allowed to stir for over one hour and 2 drops of ammonia were added to maintain the pH at 6. The precipitate obtained was filtered using a suction pump and dried in a vacuum desiccator over silica. Similar procedure was used in the preparation of other complexes [8,16].

Biological Studies

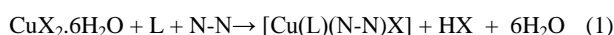
The antimicrobial screening of the synthesised complexes were investigated using Gram-positive bacteria, *Staphylococcus aureus* and *Bacillus subtilis*, Gram-negative bacteria, *Pseudomonas aeruginosa*, *Salmonella enterica*, *Escherichia coli* and *Klebsiella pneumonia* and four fungi (*Candida albicans*, *Aspergillus niger*, *Penicillium notatum*, *Rhizopus stolonifer*). Each of the six compounds was used at a concentration of 100 mg/ml, prepared by dissolving 0.5 g in 5 ml of either sterile distilled water or methanol. Plate cultures were prepared either by seeding (bacteria and yeasts) or spread-plate (mould) using 0.1ml of 10⁻² dilution from 18 to 24 hour-old broth culture of each bacterium or 24 to 72 hour-old broth culture of each fungus, in Nutrient agar (bacteria) or Sabouraud dextrose agar (fungi) [18].

Physical Measurements

The percentage copper in the prepared complexes was determined by complexometric titration using EDTA solution while the solid reflectance spectra of the complexes were recorded on a Perkin-Elmer λ25 spectrophotometer. The infrared spectra were recorded as KBr disc on a Perkin-Elmer FT-IR spectrum BX spectrometer in the range of 4000-350 cm⁻¹. The room temperature magnetic susceptibilities were measured on a Sherwood Susceptibility balance MSB Mark 1 at 303 K. The melting points were obtained using Gallenkamp melting point apparatus.

Results and discussion

The reaction of the β-diketones and tmen with the metal(II) gave coloured complexes in good yields (50-80%) according to equation 1



(X=NO₃ and Cl), (L=acacH, bzacH and dbmH) and (N-N= tmen)

The metal complexes decomposed in the range 200-300°C. The complexes were of varying solubility in methanol, chloroform, dimethylformamide, dimethylsulphoxide, acetone, petroleum ether, nitromethane and n-hexane, ranging from readily soluble to insoluble. However, all the complexes were soluble in DMSO and DMF. The colours, % metal, melting points, and room temperature magnetic moments for the complexes are presented in Table 1.

Table 1. Analytical data of the Mixed ligand copper(II) complexes

Complexes	Molar mass	Colour	% Yield	Melting pt.(°C)	%Exp. (Calculated)	μ _{eff.}
[Cu(acac)(tmen)NO ₃]	340.9	Blue	72.00	273-275	17.71(18.64)	2.10
[Cu(acac)(tmen)Cl].H ₂ O	314.3	Blue	68.00	284-286	19.20(19.11)	1.78
[Cu(bzac)(tmen)NO ₃]	402.9	Green	19.79	185-187	15.96(15.76)	2.01
[Cu(bzac)(tmen)Cl]	376.4	Green	33.89	192-194	15.89(16.10)	1.78
[Cu(dbm)(tmen)NO ₃]	465.0	Light green	86.81	271-273	12.97(13.67)	1.90
[Cu(dbm)(tmen)Cl]	468.5	Green	52.91	275	12.86(13.67)	2.09

Infrared Spectra

The relevant infrared spectra data of the complexes are presented in Table 2. In the complexes studied, the frequencies of the asymmetric C=O and C=C stretching vibrations were lowered from their free ligand values (Table 2). The ν(C=O)+ν(C=C) vibrations of the copper(II) complexes occurred as multiple bands in the 1593-1517 cm⁻¹ region characteristic of the mixed

mode of vibration arising due to the normal coordinates having the contribution from ν(C=O) and ν(C=C) indicating the presence of coordinated β-diketones [19]. The band at 1384 cm⁻¹ confirmed the presence of NO₃⁻ counter ion and this has been assigned as symmetric stretching of the NO₂ group. The coupled vibrations of M-O and M-N stretching modes appeared below 700 cm⁻¹ in the mixed ligand complexes [20,21].

Table 2. Relevant Infrared Spectra bands (cm^{-1}) of the Mixed ligand copper(II) complexes

Complexes	ν_{OH}	$\nu_{\text{as}}(\text{C}=\text{O}+\text{C}=\text{C})$	$\nu_{\text{sym}}\text{NO}_2$
acacH	3413b	1713s, 1614s	
bzacH	3422b	1599m, 1540b	
dbmH	3464b	1594m, 1579m	
[Cu(acac)(tmen)NO ₃]		1578w, 1531m	1384s
[Cu(acac)(tmen)Cl]		1589m, 1557, 1517m	
[Cu(bzac)(tmen)NO ₃]		1589s, 1552s, 1515	1384s
[Cu(bzac)(tmen)Cl]		1589s, 1557, 1517m	
[Cu(dbm)(tmen)NO ₃]		1593s, 1545s, 1526s	
[Cu(dbm)(tmen)Cl]		1593s, 1544s, 1525s	1384w

Electronic Spectra

The electronic solution spectra of the ligands and the complexes were studied in chloroform and methanol and the assignments are presented in Tables 3. Upon chelation, $\pi_3-\pi_4^*$ hypsochromic shift ($34,483 \text{ cm}^{-1} \rightarrow 34,602 \text{ cm}^{-1}$) was observed in [Cu(dbm)tmenCl] in chloroform while $\pi_3-\pi_4^*$ bathochromic shift ($34,364 \text{ cm}^{-1} \rightarrow 33,333 \text{ cm}^{-1}$) was observed in [Cu(dbm)tmenCl] in methanol. The ligand field

spectra bands of the [Cu(dbm)tmenCl] and [Cu(dbm)(tmen)NO₃] in chloroform were typically of a square pyramidal geometry [22].

The electronic solid reflectance spectra of the ligands, complexes and the assignments are presented in Table 4. The ligands showed a single band of $\pi_3-\pi_4^*$ transition in the region $31,250-35,210 \text{ cm}^{-1}$ while bands in the $37,450-44,640 \text{ cm}^{-1}$ region have been assigned as benzenoid/ $\sigma_{\text{L}}-3d_{\text{xy}}$ transitions [22].

Table 3. Electronic Solution Spectra of the Mixed ligand copper(II) complexes (cm^{-1})

dbmH	[Cu(dbm)tmenCl]	[Cu(dbm)tmenNO ₃]	Tentative Assignment
<u>Methanol</u>			
43,668*	37,879	39,216	Benzenoid band/ $\sigma_{\text{L}}-3d_{\text{xy}}$
39,841			
34,364	33,333*		$\pi_3-\pi_4^*$
	27,778	28,169	π -d
	-----	-----	d-d
<u>Chloroform</u>			
46,948			$\pi_3-\pi_5^*$
45,455			
44,248			Benzenoid band/ $\sigma_{\text{L}}-3d_{\text{xy}}$
42,735	37,594	37,313	
39,526			
34,483	34,602		$\pi_3-\pi_4^*$
	28,571	28,409	π -d
	16,155	15,601	d-d

Table 4. Solid Electronic Spectra of the Mixed ligand copper(II) complexes (cm^{-1})

Complexes	C.T/ π - π^* transitions (cm^{-1})	d-d transitions/assignment (cm^{-1})
acacH	31,250, 45,454	-
bzacH	31,060, 37,450, 44,640	-
dbmH	35,210, 42,920	-
[Cu(acac)(tmen)NO ₃]	29,762, 30,395, 46,729, 50,251	14,286
[Cu(acac)(tmen)Cl]	29,851, 30,488, 47,619	14,815

[Cu(bzac)(tmen) NO ₃]	30,300	15,400
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Table 5. Antimicrobial activity of the Mixed ligand copper(II) complexes

Complexes	<i>S. aur</i>	<i>E. coli</i>	<i>B. sub</i>	<i>P. aer</i>	<i>S. typhi</i>	<i>K. pne</i>	<i>Ca</i>	<i>An</i>	<i>Pen</i>	<i>Rs</i>
[Cu(acac)(tmen)NO ₃]	S	S	S	S	MS	S	MS	MS	MS	MS
[Cu(acac)(tmen)Cl]	MS	S	S	MS	R	R	MS	MS	R	R
[Cu(bzac)(tmen) NO ₃]	MS	MS	MS	ND	ND	MS	ND	MS	MS	MS
[Cu(dbm)(tmen)NO ₃]	S	S	S	S	S	S	R	MS	MS	R
[Cu(dbm)(tmen)Cl]	MS	MS	MS	MS	MS	R	MS	R	R	R
Gentamycin	MS	ND	MS	MS	ND	MS	ND	ND	ND	ND
Tioconazole	ND	ND	ND	ND	ND	ND	MS	MS	ND	ND
Methanol	No activities									

S. aur = *Staphylococcus aureus*; *B. sub* = *Bacillus subtilis*; *K. pne* = *Klebsiella pneumonia*; *E. coli* = *Escherichia coli*; *S.typhi*=*Serovar typhi*; *P. aer* = *Pseudomonas aeruginosa*; *Ca* = *Candida albicans*; *An* = *Aspergillus niger*; *Pen* = *Penicillium notatum*; *Rs*=*Rhizopus stolonifer*; R= organism resistant to the extract; MS=organism moderately sensitive to extract; S=organism adequately sensitive to extract; ND=not done

The bulk of copper (II) from literature consist of complexes with single broad, poorly resolved, absorption band in the visible region [23]. All the complexes showed a single broad band in the visible region with varying λ_{\max} between 15,400-14,286 cm^{-1} region, which is consistent with a square pyramidal geometry [16].

Magnetic moments

A moment of 1.9-2.2 B.M. is usually observed for mononuclear copper(II) complexes, regardless of stereochemistry, expectedly higher than the spin only moment due to orbital contribution and spin-orbit coupling[24]. A moment of 1.7-2.2 B.M. is observed for all the complexes which indicate that the Cu(II) complexes are mononuclear.

Antibacterial activities

[Cu(acac)(tmen)NO₃] and [Cu(dbm)(tmen)NO₃] showed pronounced activity on the tested bacteria except [Cu(acac)(tmen)NO₃] on *Serovar typhi* with moderate sensitivity. [Cu(acac)(tmen)Cl], [Cu(bzac)(tmen) NO₃] and [Cu(dbm)(tmen)Cl] were moderately sensitive on the tested bacteria except [Cu(acac)(tmen)Cl] on *Escherichia coli* and *Bacillus subtilis* with pronounced sensitivity. [Cu(dbm)(tmen)Cl] was resistant on *Serovar typhi*. All the complexes were moderately sensitive on the fungi strains except [Cu(acac)(tmen)Cl] on *Penicillium notatum* and *Rhizopus stolonifer*; [Cu(dbm)(tmen)NO₃] on *Candida albicans* and *Rhizopus stolonifer* which lacked antifungi activity and [Cu(dbm)(tmen)Cl] with pronounced activity on *Aspergillus niger*. [Cu(acac)(tmen)NO₃] and [Cu(dbm)(tmen)NO₃] had stronger activity than the standard drug (gentamicin) while [Cu(dbm)(tmen)Cl] and [Cu(bzac)(tmen) NO₃] compared favourably with that of gentamicin used at 8 and 4

mg/mL . All the complexes compared favourably with Tioconazole in *Candida albicans* and *Aspergillus niger* except [Cu(dbm)(tmen)NO₃] and [Cu(dbm)(tmen)Cl] which showed resistance in *Candida albicans* and *Aspergillus niger* respectively.

Conclusion

β -Diketone coordinates to the copper through two oxygen and the N, N, N', N'-Tetramethylethylenediamine coordinates through two nitrogen while the chloride or the nitrate takes the fifth position giving each complex a probable square pyramidal geometry.

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