Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2013, 5(8):69-73

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Synthesis, characterization and antibacterial studies of some copper (II) complexes of 2,2'-bipyridine and 1.10-phenanthroline

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ABSTRACT

Six copper (II) complexes of 2,2'-bipyridine and 1,10-phenanthroline have been synthesized and characterized using metal analysis, infrared and electronic spectra and the results indicated that the copper ion coordinated to the ligands to give octahedral complexes. The complexes and ligands have been screened for in-vitro antibacterial activity against a range of gram positive and gram negative bacteria. The antibacterial screening showed that the 1,10-phenanthroline ligand had the greatest antimicrobial activity with very high zones of inhibition against the various bacterial species ranging from 26mm to 31mm while the 2,2-bipyridine ligand had very low antimicrobial activity with very low zones of inhibition ranging between 8mm and 18mm. All the copper (II) phenanthroline complexes had reduced activity towards the various bacteria when compared with the free ligand while the copper(II) 2,2-bipyridine complexes had increased activity when compared with the free ligand. The microbial activity of the phenanthroline complexes compared well with that of streptomycin, the reference antibiotic, although they are significant enough to indicate some antibacterial properties inherent in the complexes. In general, the results indicated that the complexes have potential and promising antibacterial activity.

Key words: 2,2'-bipyridine, 1,10-phenanthroline, complexes, antibacterial property, ligands, copper (II)

INTRODUCTION

A lot of metal ions like copper (II) play very vital roles in biological process in humans. These metals including their complexes inhibit antimicrobial activities apart from being found at active sites or as structural components of many enzymes. 2,2-bipyridine and 1,10-phenanthroline are strong bidentate ligands which form stable chelates with many transition metals. These ligands have a starring role in the field of chemistry and molecular recognition due to their usefulness in medicine and in the industry[1,2]. Various mixed ligand complexes containing these ligands have been synthesized and their antibacterial and antifungal activity studied [3,4,5,6]. The ESR, IR, Raman and electronic spectra of some bipyridyl and 1,10-phenanthroline compounds have also been studied[7,8,9]. Binuclear copper complex $[Cu(OH)_2L_2]^{2+}$ was formed as the major hydrolysed species in a rear neutral solution of Cu^{2+} containing 1: 1 molar ratio of 2,2'-bipyridine, 1,10-phenanthroline; their instability and formation constants were calculated[10]. The dissociation constant of $Cu[C_5H_4N_2]^+$ have been studied using a semi-neutralization method and the instability constant was also calculated to be 1.75 x 10^{-7} [11]. Metal (II) β-diketone complexes and their adducts with 2,2-bipyridine and 1,10-phenanthroline have been synthesized and characterized[12,13,14]. Although similar work on copper(II) complexes of these ligands have been reported earlier[15,16], this study present cases of complexes with different compositions from that of the earlier ones.

EXPERIMENTAL SECTION

The following reagents used were all of analytical grade: 2,2'-bipyridine, 1,10-phenanthroline, copper(II) acetate, copper(II) nitrate and copper (II) sulphate. The solvents used were purified by standard methods [[17].

SYNTHESIS OF THE COMPLEXES

Synthesis of the Copper (II) complex of 1,10-phenanthroline from Sulphate.

0.92g (0.0038moles) of the $CuSO_4.5H_2O$ in 12cm^3 of distilled water was added in drops to a 13cm^3 solution of 1.5g (0.0078moles) of 1,10-phenanthroline in 50% methanol on a magnetic stirrer. The precipitate formed was left to stir for one hour, filtered and washed with 50% methanol before drying in a dessicator over calcium chloride. This same procedure was used for the synthesis of the other two phenanthroline complexes.

Synthesis of the Copper (II) Complex of 2,2'-bipyridine from Acetate.

0.96g (0.0048 moles) of the $Cu(CH_3COO)_2.H_2O$ in 12cm^3 of distilled water was added in drops to a solution of 13cm^3 of 1.5g (0.0096moles) of 2,2-bipyridine in 50% methanol dried in a dessicator over calcium chloride. The other complexes of copper (II) 2,2-bipyridine were synthesized using the same procedure except that in the case of the complex synthesized from nitrate, a few drops of ammonia solution was added to raise the pH of the solution in order to induce precipitation.

PHYSICAL MEASUREMENTS

The percentage copper in the complexes was determined titrimetrically using EDTA[18]. The electronic spectra of the compounds were recorded on a Lambda 3B UV/visible spectrophotometer while the infrared spectra were measured as KBr discs on a pye-unicam SP3-300 spectrophotometer.

Antimicrobial Screening

Media used.

The nutrient agar and nutrient broth were used for culturing the bacterial isolates while diagnostic sensitivity test agar (oxoid Ltd) was used for sensitivity.

Microorganisms used

The following microorganisms were used :
Gram positive: *Bacilus anthracis*, *staphylococcus aureus*, *Bacilus cereus*, *Staphylococcus faecalis*.
Gram Negative: *Escherichia coli*, *Staphylococcus typhi*, *Klebsiella Pneumonia*, *Pseudomonas aeruginiosa*, *Pseudomonas fluorescens*.

Antibacterial Screening

The antibacterial activity of the six complexes was determined at a concentration of 100ppm against five positive and five gram negative bacteria. In vitro antibacterial screening was generally performed by disc diffusion methods for the primary selection compounds as therapeutic agents. In this method, activity of the test compounds was expressed by measuring the diameter of zone of inhibition. Generally, the more susceptible the organisms, the bigger the zone of inhibitions. This method indicates the sensitivity or resistance of the microorganisms to the test material as well as bacteriostatic or bacteriocidal activity of a compound[19]. The plates were observed for zones of inhibition after 24hrs incubation at 37^{0}C. The diameters of the zone of inhibition produced by the complexes were compared with a standard antibiotic streptomycin at a concentration of 10000ppm

RESULTS AND DISCUSSION

The general equation for the formation of the complexes can be represented as shown below

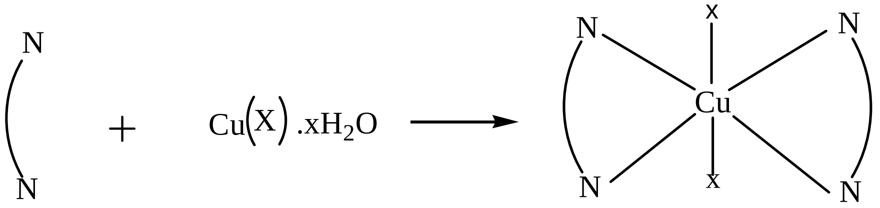

Table 1: Analytical data of the complexes

S/No	Compound	M.M	COLOUR	%YIELD	$\mu_{eff.}$ B.M	% METAL	
						EXPTD	OBSD
1	Cu(bipy)$_2$ (NO$_3$)$_2$	499.88	Blue	71	1.97	12.70	12.71
2	Cu(bipy)$_2$ SO$_4$	471.88	Blue	66	2.00	13.46	13.57
3	Cu(bipy)$_2$(CH$_3$COO)$_2$	493.88	Blue	76	1.99	12.86	12.90
4	Cu(phen)$_2$ SO$_4$	544.50	Ash	62	2.21	11.66	11.84
5	Cu(phen)$_2$ (CH$_3$COO)$_2$	560.07	Blue	80	2.31	11.34	1132
6	Cu(phen)$_2$ (NO$_3$)$_2$	572.50	Blue	68	2.18	11.09	11.20

Table 2: Relevant Infra-red spectra bands of the ligands and complexes (cm^{-1})

Compound	Water O-H stretch (cm^{-1})	C-H stretch (cm^{-1})	Aromatic ring stretch (cm^{-1})	C=C phen/bipy (cm^{-1})	C-H phen/bipy(cm^{-1})
2,2-bipyridine	3387s	2975m 2905m 2527w	1621m 1598w	1438s 1319w	627s 877s 748s
1,10-phenanthroline	3467s	2613m 2356m	1638m	1493s 1405m	856s 730s
Cu(bipy)$_2$ (NO$_3$)$_2$	3460s	2925m 2858w	1605m	1453s 1380m 1308w	833s 736s 766s
Cu(bipy)$_2$ SO$_4$		2925m 2365m	1612m	1453s 1374m 1320m	852s 772s 730s
Cu(bipy)$_2$(CH$_3$COO)$_2$	3375s	2931m 2347b 2858m	1575m	1465s 1374m	772s 736s
Cu(phen)$_2$ SO$_4$		2925m	1593m	1460s 1374m	852s 730s
Cu(phen)$_2$ (CH$_3$COO)$_2$	3458s	2896m 2681m	1674s 1589m	1377m	849s 714s
Cu(phen)$_2$ (NO$_3$)$_2$		2927m 2341m	1581m 1526w	1460s 1352m	852s 718s

b- broad, s- strong, w- weak, m- medium

Table 3: UV-Visible spectra of the ligands and complexes

S/No	Compound	d-d (nm)	n-π * (nm)
1	2,2-bipyridine		242, 229
2	1,10-phenanthroline		246, 230
3	Cu(bipy)$_2$ (NO$_3$)$_2$	692 , 736	234,221
4	Cu(bipy)$_2$ SO$_4$	684, 741, 767	232,224
5	Cu(bipy)$_2$(CH$_3$COO)$_2$	689, 743, 770	236,224
6	Cu(phen)$_2$ SO$_4$	690, 740	237,221
7	Cu(phen)$_2$ (CH$_3$COO)$_2$	686, 709, 727	238, 268, 226
8	Cu(phen)$_2$ (NO$_3$)$_2$	682, 701,	235, 222

Table 4: Results of the antibacterial screening of the ligands and complexes

	DMSO	2,2-bipy	1,10-phen	Cu(bipy)$_2$ SO$_4$	Cu(bipy)$_2$ (CH$_3$COO)$_2$	Cu(bipy)$_2$ (NO$_3$)$_2$	Cu(phen)$_2$ SO$_4$	Cu(phen)$_2$ (CH$_3$COO)$_2$	Cu(phen)$_2$ (NO$_3$)$_2$	Streptomycin
Bacillus anthracis	0	10	28	18	19	14	24	25	20	27
Bacillus cereus	0	11	30	20	21	15	27	29	22	29
Staphylococcus faecalis	0	16	30	19	21	18	26	27	21	28
Staphylococcus lutea	0	12	29	18	20	14	24	26	20	27
Escherichia coli	0	18	29	19	20	20	24	27	21	25
Samonella staphylococcus typhi	0	16	31	21	23	18	25	28	23	26
Klebsiella Pneumonia	0	13	26	16	19	15	20	24	18	22
Pseudomonas aeruginosa	0	8	30	20	18	11	22	26	22	27
Pseudomonas Fluorescens	0	10	29	19	17	13	21	25	21	24

DISCUSSION

Table 1 shows the analytical data, colours, percentage yield and room temperature magnetic moments ($\mu_{eff.}$) of the prepared complexes. The elemental analysis was in good agreement with those calculated for the proposed formula. All the complexes were obtained as various shades of green. The magnetic moment data which ranged between 1.90-2.31 BM shows the paramagnetic nature of the compounds. A moment of 1.73-2.2BM is usually observed for magnetically dilute copper II compounds whose geometry approaches octahedral having moments at the lower end while those approaching tetrahedral geometry are at the higher end [20].

The principal IR absorption bands of the complexes are listed in table 2. In the infrared spectra of the 2,2-bipyridine and 1,10-phenanthroline, the band around 3387-3460cm^{-1} has been assigned to O-H stretching vibration of water which supports the presence of lattice water molecules in all the ligands and complexes. The band around 2975 in 2,2-bipy and 261cm^{-1} in 1,10-phen have been assigned to the C-H stretch vibration. These shifted to lower frequencies on complexation. The aromatic ring stretching vibration found around 1621 and 1638cm^{-1} in the 2,2-bipyridine and 1,10-phenantroline respectively also shifted to lower frequencies on complexation suggesting that both the nitrogens of the ligands are coordinated to the metal ion[21]. Similarly the C=C stretching bands around 1438 in 2,2-bipyridine shifted to higher frequency while it shifted to lower frequency(from 1493) in 1,10-phenanthroline, the C-H deformation band around 877 in the ligand moved to lower frequency in the complexes. In the complexes, bands around 641cm^{-1} have been assigned to Cu-O bands while those around 450cm^{-1} have been assigned to Cu-N band.

The electronic reflectance spectra of the ligands and complexes in the ultraviolet region exhibited peaks around 238nm -268nm which may be assigned to charge transfer and n-π* intraligand transitions. The visible region of the spectra of the complexes show bands around 689-770nm which may be assigned to d-d transitions of a distorted octahedral copper (II) chromophore and it may be assigned to $^2E_g - ^2T_{2g}$ transition[22]. Tetragonal copper (II) complexes are expected to show three transitions namely $^2B_{1g--}{}^2A_{Ig,}$ $^2B_{Ig}$-$^2B_{2g}$ and $^2B_{Ig}$-^2E_g but band due to those transitions usually overlap to give a broad absorption band. The broad band around 536nm indicates a tetragonally distorted octahedral configuration around Cu(II) ion[23]. Hence, the band around 689nm may be taken as 10Dq.

Antibacterial Activity

The results of the antibacterial activity of the 2,2-bipyridine, 1,10-phenanthroline, their copper complexes and a reference antibiotic, streptomycin against ten bacteria are listed in table 4. Metal complexes are generally more effective in many cases than the free ligands[24]. Tweedy's chelation theory[25] predicts that chelation reduces the polarity of the metal atom mainly because of partial sharing of its positive charge with donor groups and possible electron delocalization over the whole ring. This consequently increases lipophilic characters of the chelates, favouring its permeation through lipid layers of bacterial membrane. The 1,10-phenanthroline ligand had the greatest antimicrobial activity with very high zones of inhibition against the various bacterial species ranging from 26mm to 31mm while the 2,2-bipyridine ligand had very low antimicrobial activity with very low zones of inhibition ranging between 8mm and 18mm. All the copper (II) phenanthroline complexes had reduced activity towards the various bacteria when compared with the free ligand while the copper (II) 2,2-bipyridine complexes had increased activity when compared with the free ligand. In comparing the complexes, the complexes with the carboxylate ion COO^- had increased activity when compared with the other complexes from the same ligand. The zones of inhibitions for the 1,10-phenanthroline complexes was in the order $Cu(phen)_2 (CH_3COO)_2 > Cu(phen)_2 SO_4 > Cu(phen)_2 (NO_3)_2$ while that of the 2,2-bipyridine complexes was in the order $Cu(bipy)_2(CH_3COO) > Cu(bipy)_2 SO_4 > Cu(bipy)_2 (NO_3)_2$. The microbial activity of the phenanthroline complexes compared well with that of the reference antibiotic, although they are significant enough to indicate some antibacterial properties inherent in the complexes. In general, the results indicated that the complexes have potential and promising activity.

CONCLUSION

Six new copper(II) complexes of 1,10-phenanthroline and 2,2-bipyridine have been synthesized and characterized. The complexes have probable octahedral geometry. The complexes exhibited antibacterial activities comparable to a standard antibiotic streptomycin.

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