

Synthesis and Characterization of Mixed Ligand Complexes of $\text{Cu}(\text{Phen})_2(\text{ClO}_4)_2$ with Some Aromatic Ligands

F. A. O. ADEKUNLE* and O. A. ODUNOLA

Department of Pure and Applied Chemistry, Ladoké Akintola University of Technology, Ogbomoso, Nigeria

fnnmy2001@yahoo.com

Received 26 October 2012 / Accepted 12 November 2012

Abstract: Five mixed-ligand complexes of copper(II) with 1, 10-phenanthroline and some selected aromatic ligands such as imidazole, 2-aminopyridine, 4- dimethylaminobenzonitrile, 2,2'-dipyridylketone, 4-methylimidazole-5-carboxaldehyde have been synthesized and characterized by microanalyses, spectroscopic and room temperature magnetic susceptibility measurements. The microanalyses data is satisfactory with the formation of the prepared complexes. The infrared spectra of the complexes reveal the involvement of the donor groups of the selected aromatic compounds attached to the copper metal in the formation of the mixed-ligand complexes. The electronic spectra in the visible region show the high energy, high intensity peaks between $13,647\text{ cm}^{-1}$ and $15,322\text{ cm}^{-1}$. The mass spectra of the complexes are supportive of the microanalytical data.

Keywords: Mixed-ligands, Aromatic ligands, Mass spectra, Microanalysis

Introduction

The nitrogen donor ligand 1,10-phenanthroline and its congener 2,2' bipyridine have been studied widely for their coordination ability due to their stability in biochemical processes¹⁻⁶. 1,10-Phenanthroline (phen) is a versatile polypyridine ligand in coordination chemistry. This nitrogen donor sp^2 ligand and its congener 2,2' bipyridine have been studied widely for their coordination ability due to their stability in biochemical processes³⁻⁶. Recently, copper-phenanthroline complexes have been used to study the interaction of DNA and protein⁶ and $[(\text{phen})_2\text{Cu}]^+$, $[(\text{phen})_2\text{Cu}]^{2+}$, $[(\text{phen})\text{Cu}]^+$ have been reported⁶ to be the active species for DNA cleavage. The mixed -ligand complex $[\text{Cu}(\text{hsm})(\text{nal})\text{H}_2\text{O}]\text{Cl}\cdot 3\text{H}_2\text{O}$ was demonstrated to alter bacterial DNA structure⁷. The binary Cu(II) complex of H_2L (where H_2L is 2-carboxyphenylhydrazo-benzoylacetone) have been reported to form mixed-ligand complexes with 1,10-phenanthroline and 2-aminopyridine⁸. In this work, we have synthesized mixed ligand complexes of $[\text{Cu}(\text{phen})_2\text{H}_2\text{O}](\text{ClO}_4)_2$ with some selected aromatic ligands, characterized and studied their physicochemical properties.

Experimental

$[\text{Cu}(\text{phen})_2\text{H}_2\text{O}](\text{ClO}_4)_2$ was prepared according to a literature procedure⁹.

[Cu(phen)₂H₂O](ClO₄)₂ with 1,3-diaza-2,4-cyclopentadiene (A)

128 mg (0.2 mmole) Cu(phen)₂OH₂(ClO₄)₂ was dissolved in 25 mL acetonitrile with stirring. To this 14 mg (0.2 mg) 1,3-diaza-2,4-cyclopentadiene (imidazole) was added. A deep blue coloured solution was obtained immediately and was stirred for 2 h, and then the clear blue solution was kept on the bench for crystallization to take place. Blue crystals were obtained after about 5 days. (Yield = 120 mg, 85%). ESIMS (CH₃CN) *m/z*: 422.7 {100%; [Cu(phen)²⁺]}.

[Cu(phen)₂H₂O](ClO₄)₂ with 4- dimethyl aminobenzonitrile (B)

29 mg (0.2 mmole) 4-Dimethylaminobenzonitrile was added to 128 mg (0.2 mmole) Cu(phen)₂OH₂(ClO₄)₂ solution in 25 mL acetonitrile. The green coloured solution obtained was stirred for 2 h after which it was kept on the bench for crystal formation. Green crystals were obtained after 6 days. (Yield = 74 mg, 47%). ESIMS (CH₃CN) *m/z*: 211.6{55%; [Cu(phen)₂]²⁺}, 522{15%; [Cu(phen)₂(ClO₄)⁺]}.

[Cu(phen)₂H₂O](ClO₄)₂ with 2-aminopyridine (C)

19 mg (0.2 mmole) 2-Aminopyridine and 128 mg (0.2 mmole) Cu(phen)₂OH₂(ClO₄)₂ mixture in 25 mL acetonitrile was refluxed for 4 h. The clear deep green solution obtained was transferred to a beaker in hot condition for crystallization to take place. At the end of 4 days, bluish- green crystalline compounds were obtained (Yield = 124 mg, 84%). ESIMS (CH₃CN) *m/z*: 211.5{22%, [Cu(phen)₂]²⁺}, 522{12%; [Cu(phen)₂(ClO₄)⁺]}.

[Cu(phen)₂H₂O](ClO₄)₂ with 2,2'dipyridylketone (D)

74 mg (0.4 mmole) 2,2'Dipyridylketone(DPK) was added to 100 mL methanol solution of Cu(phen)₂OH₂(ClO₄)₂ (256 mg, 0.4 mmole). The resulting cloudy blue solution was stirred for 24 h, after which the solution was filtered by gravity and the filtrate kept on the bench for crystallization to take place. A blue compound with blue crystals was obtained after 9 days and was filtered by suction and dried in the air (Yield = 122 mg, 37%). ESIMS(CH₃CN) *m/z*: 211.3 {45%;[Cu(phen)₂]²⁺}, 422.6 {30%; [Cu(phen)₂]⁺}, 522 {12%; [Cu(phen)₂(ClO₄)⁺]}.

[Cu(phen)₂H₂O](ClO₄)₂ with 4-methylimidazole-5-carboxaldehyde (E)

44 mg (0.4 mmole) 4-Methylimidazole-5-carboxaldehyde was added to a 50 mL acetonitrile solution of Cu(phen)₂OH₂(ClO₄)₂ (256 mg, 0.4 mmole). The clear blue coloured solution obtained was stirred for 4 h, after which it was kept on the bench. The blue compound obtained after 7 days was recrystallised from methanol. (Yield = 200 mg, 67%). ESIMS (CH₃CN) *m/z*: 211.4{100%; [Cu(phen)₂]²⁺}, 522 {48%; [Cu(phen)₂(ClO₄)⁺]}.

Physical measurements

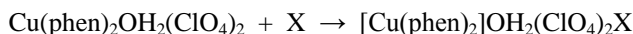
Microanalyses were performed by a Perkin-Elmer 2400II CHNS analyzer. Room temperature magnetic moments were measured by a magnetic susceptibility balance procured from Sherwood Scientific, UK. The diamagnetic corrections were evaluated using Pascal's constants. UV-Vis spectra were recorded on a Perkin Elmer Lambda 950 spectrophotometer, FTIR spectra (KBr) on a Shimadzu FTIR-8400S spectrometer and ESI mass spectra on a Waters Qtof Micro YA263 spectrometer.

Results and Discussion

The formation of the five - coordinate complexes proceeded in appreciable yields as shown in the following equation:



Where Y = 1,3-diaza-2,4-cyclopentadiene (IMID), 2,2'-dipyridylketone (DPK), 4-methylimidazole-5-carboxaldehyde (DMC).



Where X = 4-dimethylaminobenzonitrile (DAB), 2-aminopyridine (AMPY),

The analytical data are presented in Table 1. The complexes were obtained in different shades of colours ranging from green to blue. The complexes were soluble in acetonitrile.

Table 1. Analytical data of the complexes

Compound	Molecular formula	M.W	Yield %	Colour	μ_{eff} (B.M)	% Observed (Calculated)		
						C	H	N
Cu(phen)_2 (IMID)(ClO_4) ₂	$\text{C}_{27}\text{H}_{20}\text{N}_6\text{O}_8\text{Cl}_2\text{Cu}$	690.74	85	Blue	2.09	47.01 (46.91)	2.82 (2.92)	11.84 (12.17)
Cu(phen)_2 (DAB)(ClO_4) ₂ · H_2O · HClO_4	$\text{C}_{33}\text{H}_{29}\text{N}_6\text{O}_{13}\text{Cl}_3\text{Cu}$	887.31	47	Green	2.13	45.21 (44.63)	2.72 (3.29)	8.65 (9.47)
Cu(phen)_2 (AMPY) (ClO_4) ₂ ·0.5 H_2O	$\text{C}_{29}\text{H}_{23}\text{N}_6\text{O}_{8.5}\text{Cl}_2\text{Cu}$	725.77	84	Bluish-green	1.88	47.95 (48.55)	3.19 (3.09)	11.58 (11.73)
Cu(phen)_2 (DPK)(ClO_4) ₂	$\text{C}_{35}\text{H}_{24}\text{N}_6\text{O}_9\text{Cl}_2\text{Cu}$	806.77	37	Blue	1.80	53.72 (52.04)	2.95 (3.00)	10.70 (10.41)
Cu(phen)_2 (DMC)(ClO_4) ₂	$\text{C}_{29}\text{H}_{22}\text{N}_6\text{O}_9\text{Cl}_2\text{Cu}$	732.76	67	Blue	1.90	47.41 (47.49)	3.07 (3.03)	10.90 (11.47)

IMID = 1,3-diaza-2,4-cyclopentadiene, DAB = 4-dimethylaminobenzonitrile, AMPY = 2-aminopyridine, DPK = 2,2'-dipyridylketone, DMC = 4-methylimidazole-5-carboxaldehyde.

IR spectra

The mixed – ligand 1,3-diaza-2,4-cyclopentadiene complex (A), showed a band at 1518 cm^{-1} due to the coordinated C=N group of 1,3-diaza-2,4-cyclopentadiene^{8,10}. The stretching vibration due to C≡N of the nitrile group usually¹⁰ at ca 2250 cm^{-1} appears at ca 1998 cm^{-1} in the 4-dimethylaminobenzonitrile. This indicates that the group is involved in the formation of the mixed-ligand complex (B)¹⁰. The mixed 2-aminopyridine complex (C) showed the two bands at ca 3067 cm^{-1} and 999 cm^{-1} . The second band is assigned to the skeletal vibration of the pyridine ring, the breathing mode, while the first is due to the coordinated⁸ NH_2 . The $\nu(\text{C}=\text{O})$ of the 2, 2'-dipyridylketone was observed in the IR spectrum of the complex (D) at ca 1626 cm^{-1} . This indicates the participation of the carbonyl group of the ketonic compound in coordination to the central metal ion. The C=N group of the 4-methylimidazole-5-carboxaldehyde complex (E) showed a band at 1585 cm^{-1} due to the coordination to the Cu metal ion of the $[\text{Cu(phen)}_2\text{H}_2\text{O}](\text{ClO}_4)_2$ compound⁸. The $\nu(\text{OH})$ frequency of the lattice water molecules in the complexes was observed at 3418 cm^{-1} for complex (B) and at 3356 cm^{-1} for the complex (C)⁸.

Electronic spectra and magnetic moments

The UV-Visible spectra of the complexes were carried out in acetonitrile (10^{-3} mol L^{-1}) solution. The value of the band positions (cm^{-1}) are listed in Table 2. The visible bands of

these complexes exhibit the high energy, high intensity peaks at 15,309 cm⁻¹ for the complex (A), 13,647 cm⁻¹ for the complex (B), 14,175 cm⁻¹ for the complex (C) 14,734 cm⁻¹ for the complex (D) and 15,322 cm⁻¹ for the complex (E). The order of one-electron ground-state configurations is $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz} = d_{yz}$ and the transitions may be assigned as the $d_{xz} = d_{yz} \rightarrow d_{x^2-y^2}$ for the high-energy peak¹¹.

Table 2. Selected IR vibrational bands and electronic spectral transitions for the compounds (cm⁻¹)

Compound	C=O str	N-H str	C-N str	C≡N str	C=N str	O-H str	Pyridine ring vibration	ClO ₄ ⁻ str	Electronic Spectra, cm ⁻¹
Cu(phen) ₂ (IMID)(ClO ₄) ₂	-	3190	-	-	1518	-	-	623, 1101	49,432 37,385 34,322 15,309 49,601
Cu(phen) ₂ (DAB) (ClO ₄) ₂ . H ₂ O. HClO ₄	-	-	1429	1998	-	3418	-	625, 1103	45,190 37,273 34,200sh 13,647 45,143
Cu(phen) ₂ (AMPY) (ClO ₄) ₂ 0.5H ₂ O	-	3067	1227	-	1628	3356	999	623, 1094	37,353 34,369sh 14,175 45,177
Cu(phen) ₂ (DPK)(ClO ₄) ₂	1626	-	-	-	1425	-	-	623, 1092	37,749 34,498 14,734 45,312
Cu(phen) ₂ (DMC)(ClO ₄) ₂	1661	3445	-	-	1585	-	-	623, 1090	37,611 34,318 15,322

From the literature, five-coordinate transition metal complexes without constraints of chelating ligands adopt the trigonal bipyramidal geometry; also ligand-ligand repulsion favours these arrangements¹². The electronic transitions of these mixed-ligand complexes are similar to those reported in the literature¹¹. The presence of chelating ligand constraints and the reduction in ligand-ligand repulsion since the 1,10-phenanthroline ligand will repel equally indicates that the geometry of the copper ion in the mixed-ligand complexes favours square pyramidal arrangement¹¹. The magnetic moments of the complexes (C), (D) and (E) at 1.88B.M, 1.80B.M and 1.90B.M respectively agree with that of similar systems in the literature^{8,13}. The moments observed for the complexes (A) and (B) with values 2.09B.M and 2.13B.M which is a little higher the spin –only value (1.83B.M.) is due to orbital contribution to the magnetic moments¹⁴. These values correspond to one unpaired electron and thus offer evidence for mononuclear structures of the complexes⁸. The proposed structures of the mixed-ligand complexes are shown in Figure 1.

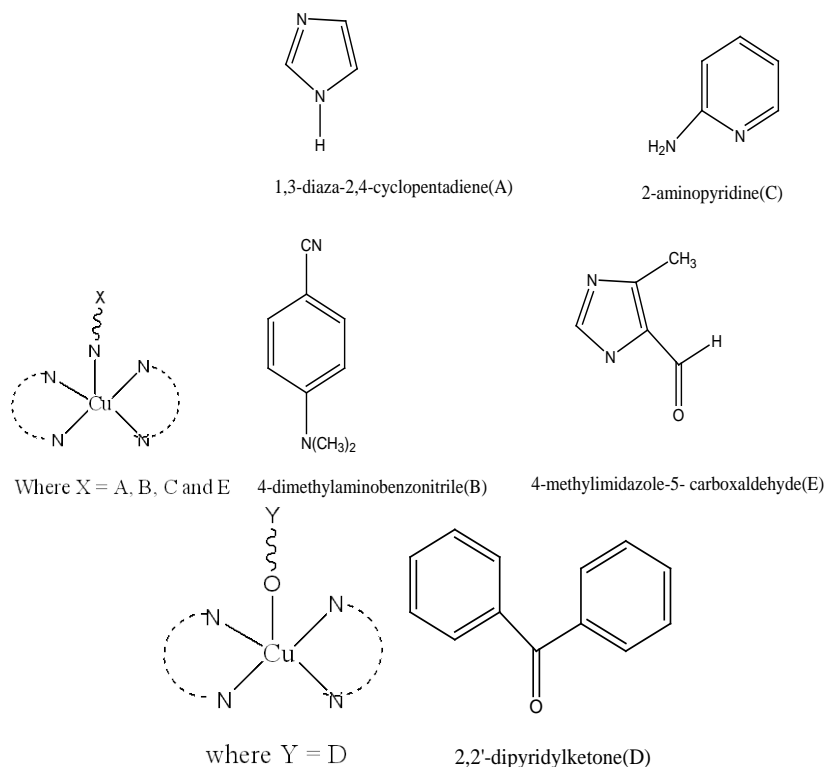


Figure 1. The proposed structure of the complexes

Conclusion

The reaction of $[\text{Cu}(\text{phen})_2 \text{H}_2\text{O}](\text{ClO}_4)_2$ with 1,3-diaza-2,4-cyclopentadiene, 4-dimethylaminobenzonitrile, 2-aminopyridine, 2,2'-dipyridylketone and 4-methylimidazole-5-carboxaldehyde yielded mixed –ligand complexes.

The infrared spectra indicates that all the coordinating groups behaved as monodentate ligands; through the nitrogen atom at the position 3 of the 1,3-diaza- 2,4-cyclopentadiene, the nitrogen of the –CN group in 4-dimethylaminobenzonitrile, nitrogen atom of the amino group in 2-aminopyridine and the nitrogen atom at position 3 of the 4-methylimidazole-5-carboxaldehyde while the oxygen atom of the carbonyl group of the 2,2'dipyridylketone also behaves similarly. The elemental analyses, electronic transitions, magnetic susceptibility measurements and the mass spectra data were all supportive of the formation of the mixed – ligand complexes.

Acknowledgement

F.A.O.A is grateful to Prof. Dipankar Datta of Indian Association for the Cultivation of Science, Calcutta for the use of his Laboratory and Third World Academy of Science Trieste, Italy for a post-doctoral fellowship.

References

1. Onawumi O O E, Faboya O O P, Odunola O A, Prasad T K and Rajasekharan M V, *Polyhedron*, 2008, **27**(1), 113-117.

2. Onawumi O O, Adekunle F A, Ibrahim A O, Rajasekharan M V and Odunola O A, *Synth React Inorg Met-Org Nano Met Chem.*, 2010, **40**, 78-83.
3. Siegel H, Huber P P and Pasternack R F, *Inorg Chem.*, 1971, **10**, 2226-2280.
4. Onawumi O O, Adeoye I O and Adekunle F A O, *Open J Inorg Chem.*, 2013, **3**, 26-33.
5. Poznanonic G and Sevaljevic L, *Mol Biol Rep.*, 1984, **9(4)**, 231-234.
6. Chen C H B, Miline L, Landgraf R, Perrin D M and Sigman D S, *Artificial Nucleases, Chembiochem.*, 2001, **2**, 735-740.
7. Bivian-Castro EY, Lopez M G, Pedraza-Reyes M, Bernes S and Mendoza-Diaz G, *Bioinorg Chem Appl.*, 2009.
8. Khalil M M H and Mashaly M M, *Chin J Chem.*, 2008, **26**, 1669-1677.
9. Murphy G, Murphy C, Murphy B and Hathaway B, *J Chem Soc., Dalton Trans.*, 1997, 2653-2660.
10. William Kemp, *Organic Spectroscopy*, 3rd Edition Edinburgh ELBS, 1991, 42-68.
11. Youngme S., Phuengphai P, Pakawatchai C, Kongsaree P and Chaichit N, *Acta Cryst Section B Struct Sci.*, 2008, **B64(3)**, 2008, 318-329.
12. Bodie Douglas, Darl McDaniel and John Alexander, *Concepts and Models of Inorganic Chemistry*, Wiley Indian Edition, 3rd Edition, 424-427.
13. Supriya S and Das S K, *Inorg Chem Commun.*, 2003, **6(1)**, 10-14.
14. Netra Pal Singh, Anu and Jagvir Singh, *J Chem.*, 2012, **9(4)**, 1835-1842.