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Research Article

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Synthesis, Characterization, Electrochemical Studies and Antioxidant Activity of some New Dimethylglyoxime Copper (II) Complexes with Purine Bases and Ortho-Phenylenediamine

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ABSTRACT

Mixed ligand complexes of copper (II) with dimethylglyoxime as primary ligand and purines bases (adenine, guanine) and ortho-phenylenediamine as a secondary ligands were prepared and characterized by elemental analysis, conductivity measurements, IR and UV-visible spectroscopy and cyclic voltametric. The compounds obtained are solids, insoluble in water, ethanol and methanol, but soluble in dimethylsulfoxide (DMSO) and dimethylformamide (DMF). The values of the molar conductivities reveal that all the complexes are non - electrolytes, the IR spectra show that ligands are coordinated to the metal ion in a bidentate manner with NN donor sites of dimethylglyoxime, adenine and orth-phenylenediamine and NO donor sites of guanine. UV-visible spectral data suggest that the complexes are in a square-planar, square pyramidal or octahedral geometry. The electrochemical behavior of the mixed ligands complexes of Cu(II) prepared indicates an irreversible process corresponding to the Cu^{I}/Cu redox pair and an irreversible oxidation of Cu^{+} to Cu^{2+}.These compounds were screened for their in-vitro antioxidant properties, these properties have been studied using 2, 2–diphenyl-picrylhydrazyl (DPPH) free radical scavenging. Only the complexes with ortho-phenylenediamine and mononuclear complex with adenine reveal the significant antioxidant activity in comparison to the butylhydroxytoluene (BHT, positive control).

Keywords: Mixed ligands; Copper (II); Spectroscopic studies; Cyclic voltammetry; Antioxidant activity

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INTRODUCTION

Copper is an important trace element for plants and animals and is involved in mixed ligand complex formation in a number of biological processes [1] and is involved also in redox metalloenzymes, in oxygenation and oxygen carrying proteins. Copper (II) forms many complexes with ligands having donor nitrogen atoms. Tetracordinated complexes are generally much more stable than hexacoordinated complexes, although many of these exist. For example $(Cu(NH_3)_4)^{+2}$ and $(Cu(en)_2)^{+2}$ are very stable while $(Cu(NH_3)_6)^{+2}$ and $(Cu(en)_3)^{+2}$ are less stable.
Dimethylglyoxime (H_2dmg) is a dibasic acid, which has been used as a typical analytical precipitating reagent for Ni(II) ion, it forms three types of metal complexes with divalent transition metal ions, $(M(Hdmg)_2)$, $(M(H_2dmg)_2)^{2+}$, $(M(dmg)_2)^{2-}$[2]. Adenine (Ade) and guanine (Gua), two purine bases, are the building blocks in both DNA and RNA that play crucial role in the storage of genetic information and in protein biosynthesis [3]. Metal complexes with these purine bases have many applications in molecular recognition [4], magnetism [5], luminescence [6], catalysis [7], molecular electronics [8] and gas absorption [9]. The complexation of metal ions with adenine has been well studied and its binding sites have also elucidated. Various coordination sites have been observed for adenine in copper complexes as indicated by X-ray studies. Among the four nitrogens N_1, N_3, N_7 and N_9 for adenine (Figure 1), the N_9 is the most basic and hence bears a proton rendering it the most preferred metal binding sites [10].

Ortho-phenylenediamine (OPD) is an organic compound with the formula C_6H_4 $(NH_2)_2$ this aromatic diamine is an important precursor to many heterocyclic compounds. It is isomeric with m-phenylenediamine and p-phenylenediamine and is commonly referred to as OPD [11]. The complexes of OPD and Schiff base derived from this ligand have a variety of applications including biological, clinical and analytical [12]. The OPD is used in the copper catalytized of quinoxalines [13]. Schiff bases of OPD are used in the synthesis of insecticides, dyestuff fungicides, corrosion inhibitors and pigments [14].

This article describes the synthesis and characterization of four mononuclear and two binuclear complexes of Cu (II) using dimethylglyoxime as the primary ligand and the purine bases and OPD as secondary. The complexes were characterized by elemental analysis, conductivity, electron and infrared spectroscopy and cyclic voltammetry. The antioxidant potential of all the complexes was determined using DPPH assay. The results of this assay show that some complexes possess good antioxidant activity in comparison to the positive control (BHT).

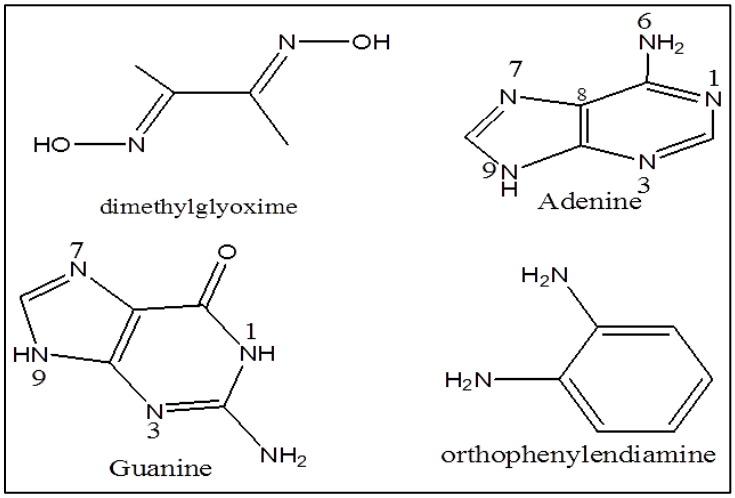

Figure 1: Structures of ligands

EXPERIMENTAL SECTION

Materials

All chemical reagents and solvent used in the synthesis of complexes were Fluka products and used without further purification.

Physical Measurements

The elemental microanalyses were carried out at the service of microanalyses, Faculty of Pharmacy University Paris South. Melting points were measured using melting point meter-series MPM-H2. The conductometric measurements were obtained with a CONSORT C3030 etalons at room temperature in 10^{-3} M solutions of the complexes in DMSO. The IR spectra of solid samples (KBr discs) in the range 400-4000 cm^{-1} were recorded on a Shimadzu FTIR-8400M spectrophotometer. The electronic absorption spectra of solutions of the complexes in DMSO were recorded on a Shimadzu 6800 spectrophotometer in the range 200-900 nm. The electrochemical measurements were recorded using Potentiostat/ Galvanosta model EGG-273A.

Preparation of Complexes

Complexes ($Cu_2(Hdmg)(Ade)_2(NO_3)(H_2O)$) (1) and ($Cu_2(Hdmg)(Gua)_2(NO_3)(H_2O)$ (2)

The complexes were prepared by mixing a solution of H_2dmg (5 mmol, 0.58 g) in 30 ml of hot absolute ethanol with (10 mmol, 2.42 g) of Cu $(NO_3)_2$, $3H_2O$ dissolved in 10 ml of distilled water. The mixture is left under magnetic stirring for about 30 min. Then adenine (10 mmol, 1.36 g) (1) or guanine (10 mmol, 1.52 g) (2) dissolved in a solution (40 ml of ethanol absolute+40 ml of KOH), were added (Figure 2) to the mixture with constant stirring. The mixture was refluxed for two hours. The precipitates obtained were filtered, washed successively with water and ethanol and dried in air.

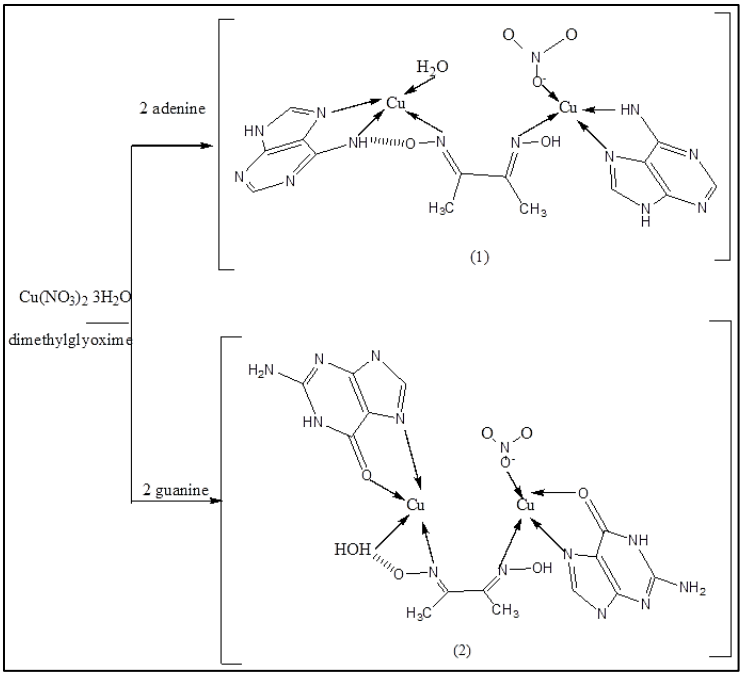

Figure 2: Synthesis of complexes 1and 2

Complexes ($Cu(H_2dmg)(Ade)(NO_3)_2$) (3) and ($Cu(Hdmg)(Gua)(NO_3)$) (4)

These complexes were prepared using the method described above but using 5 mmol of Cu $(NO_3)_2$, $3H_2O$ and 5mmol of each ligands (Figure 3).

Complex ($Cu(Hdmg)(OPD)(NO_3)$) (5)

The complex was prepared using the following method:

Dimethylglyoxime (5 mmol, 0.58 g) is introduced in to 30 ml of hot absolute ethanol, to this solution is added the Cu $(NO_3)_2$, 3H2O (5 mmol, 1.21 g) dissolved previously in 5 ml of distilled water. The mixture was refluxed for 1hour. Then a solution of orthophenylenediamine (5 mmol, 0.54 g) dissolved in hot water (30 ml) was added (Figure 3) with magnetic stirring. The reaction mixture was heated again at reflux for 1hour. The resulting precipitated was filtered, washed successively with water and ethanol and dried in air.

Complex ($Cu(H_2dmg)(OPD)(Br)_2$) (6)

This complex was prepared using the same procedure as complex (5) but using in addition solid NaBr (10 mmol, 1.02 g).

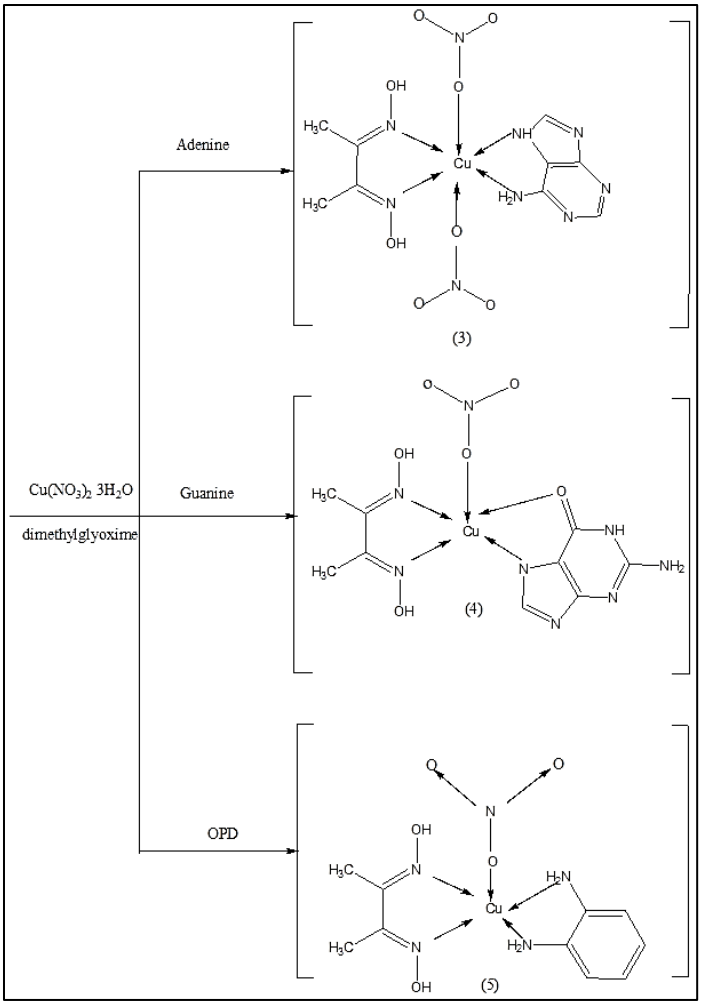

Figure 3: Synthesis of complexes 3-5

RESULTS AND DISCUSSION

The physical properties and analytical data of complexes are summarized in Table 1. All the complexes are insoluble in water, ethanol, and methanol, but soluble in dimethylsulfoxide, and dimethylformamide. The non-electrolyte nature of the complexes was confirmed by the low molar conductance values measured at 25°C (10^{-3} M) in DMSO solution. The results of the elemental analysis of the mixed ligand complexes are in good agreement with those required by the proposed formula.

Table 1: Characteristic and analytical data of the complexes

Compound formula	Color	M.P(C°)	R (%)	% C		%H		% N		%Métal		% Br		Λ_M (Ω^1cm2.mole$^-$)
				Cal	Exp	Cal	Exp	Cal	Exp	Cal	Exp	Cal	Exp	
(Cu_2 (Hdmg) $(Ade)_2(NO_3)(H_2O)$1	Brown	>410	53	28.45	28.05	2.87	2.48	30.82	30.75	21.45	21.52			10
(Cu_2 (Hdmg) $(Gua)_2(NO_3)(H_2O)$2	Olive	>360	65	27	27.82	2.73	2.52	29.24	29.13	20.41	21.07			8.93
($Cu(H_2dmg)$ $(Ade)(NO_3)_2$) 3	Darkgreen	>360	75	24.62	24.61	2.02	2.96	28.05	28.72	14.48	14.22			59
(Cu(Hdmg) (Gua)(NO_3) 4	Palegreen	>360	56	27.57	27.8	3.06	3.59	28.59	28.13	16.22	16.7			4.2
Cu(Hdmg)(OPD)(NO_3)	Saddlebr	289	47	34.	34.	4.3	3.8	20.	20.	18.	18.			40

5	own			41	04	1	1	07	36	22	4			
Cu(H_2dmg) (OPD)($Br)_2$ 6	Brown	272	67	26. 81	27. 2	3.5 7	3.2 3	12. 51	11. 95	14. 19	13. 83	35. 7	35. 3	29

The Infrared Spectra

The important IR bands of the free ligands and their metal complexes are shown in Tables 2,3 respectively, and the IR spectrum of (Cu(H_2dmg)(Gua)(NO_3)) is shown in Figure 4. The infrared spectra of the prepared complexes are compared with those of the free ligands in order to determine the changes that might have taken place during the complexation. The spectrum of dimethylgloxime shows a band with a medium intensity at 1447 cm^{-1}, attributed to υ (C=N) of the oxime. This band is shifted to lower frequencies (1386-1416 cm^{-1}) in all the mixed-ligand complexes. The adsorption band observed at 1144 cm^{-1} due to υ (NO) in the H_2dmg spectrum is shifted to higher frequencies (1150-1193 cm^{-1}) in all complexes. While the appearance of a band in all complexes spectra in the 714-783 cm^{-1} region is assigned to the NO deformation vibration of H_2dmg. All these characteristics indicate that dimethylglyoxime is coordinated with the metal ion by the nitrogen atom of the oxime function [15-18].

Another band observed at 1606 cm^{-1} in the spectra of complexes 1 and 3 is assigned to the C = N stretching vibrations of adenine. The five possible nitrogen binding sites of adenine are the pyrimidine N_1 and N_3, the imidazole N_7 and N_9 ring nitrogen and N_6 nitrogen of the exocyclic NH_2 group [19]. The asymmetric and symmetric NH_2 vibration frequency bands of adenine at 3286 and 3114 cm^{-1}, respectively were shifted to higher wavenumbers in complexes 1 and 3. Deformation frequency δ NH_2 of free adenine observed at 1668 cm^{-1} is shifted to a lower value of the wavenumber in complex 1 and to a higher value in complex 3. Moreover, the band at 1250 cm^{-1} in the spectrum of adenine attributed to δ (C-NH_2) or δ (NH) is shifted to a higher wavenumber in complex 1 and weaker in complex 3. This confirms that the exocyclic NH_2 group of adenine is coordinated with the metal ion in these complexes [19, 20]. The adenine spectrum shows an absorption band at 1230 cm^{-1} assigned to υ (C_8-N_7), the latter is shifted to lower wavenumber at 1189 cm^{-1} in complex 1 and at 1198 cm^{-1} in complex 3, indicating that the binding of the adenine to the metal was carried out with the ring nitrogen. Another band at 1502 cm^{-1} in the adenine spectrum due to υ (C = C) is instead displaced in these complexes to the region of larger wave numbers.

The IR spectrum of guanine has two bands at 3320 and 1630 cm^{-1}, the latter being due to the different modes of vibration υ, δ, respectively of NH_2. These bands are not displaced in complexes 2 and 4, indicating that the amino group is not involved in the complexation. The spectrum of guanine also displays a strong band split into two distinct peaks at 1695 and 1 670 cm^{-1}, which corresponds to υ (C = O) of the amide, these two peaks were slightly shifted during complexation with the metal (Table 2), which shows that copper is bound to guanine by the oxygen atom of the carbonyl group. The band at 1410 cm^{-1} in guanine due to υ (C-N_7) of the amide is shifted slightly to larger numbers waves in complexes 2 and 4, indicating that the N atom of the amide is involved in complexation [21]. This confirms that N_7 is more donor than N_3, due to the resonance stabilization of N_7. Therefore, it can be deduced that the guanine is bonded to the metal by the O atom of the C = O group and the N atom of the amide in the complexes 2 and 4.

The most relevant absorption bands in the IR spectra of Complexes 5 and 6 with OPD are listed in Table 3. These complexes show the characteristic bands due to the NH and CH elongation vibrations of the OPD ligand in the regions 3187- 3400 cm^{-1} and 3102-3167 cm^{-1}, respectively. In the spectrum of free OPD, the bands observed in the 3185-3374 cm^{-1} region are due to ν (NH) and that at 3032 cm^{-1} is due to ν (CH). These shifts show the involvement of NH_2 in coordination with the metal [22]. Moreover, the absorption band centered at 1500 cm^{-1} in the complex 5 and at 1510 cm^{-1} in the complex 6, assigned to the vibrational mode of υ (CN) of the OPD ligand is displaced to higher frequencies compared with this of the free ligand which appears at 1492 cm^{-1}. On the other hand, the band corresponding to the vibrational mode υ (C = C) located at 1605 cm^{-1} for the complex 5 and at 1604 cm^{-1} for the complex 6 is clearly shifted to lower frequencies that υ (C = C).) in the free OPD which is at 1626 cm^{-1} [23]. The IR spectrum of complex 6 shows a new band at 430 cm^{-1} that is absent in the spectra of the ligands, this band is attributed to the stretching vibrational frequency of the metal-Br bond [24].

A nitrate ligand can coordinate to the metal ion in two types, as monodentate or bidentate ligand [25].

In the IR spectra of complexes (1-5) there are three bands assigned to NO_3^- coordinate bound to Cu (II) centre: υ_1 at (1479-1453), υ_2 at (1375-1336), and υ_3 at (1066-950) [25-28]. The complexes (1-5) give a $|\upsilon_2 - \upsilon_1|$ separation at 104-122 cm^{-1} [25,26,28] suggesting monodentate bonding for the nitrate group. On the other hand, the band at 3267 cm^{-1} in complex 1 and at 3233 cm^{-1} in complex 2 may be attributed to υ (OH) of water molecules coordinated [29-32].

The studied of Cu(II) complexes (1-6) gave new IR bands at 448-515 cm^{-1} corresponding to υ (Cu-N) while the band at 557 cm^{-1} in the complexes 2 and 4 is assigned to υ (Cu-O) [33,34].

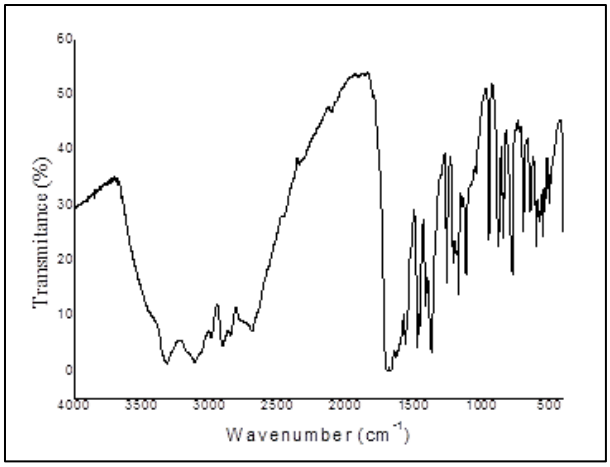

Figure 4: Infrared spectrum of Cu(H_2dmg)(Gua)(NO_3)

Table 2: Relevant IR data (cm^{-1}) of the ligands

Compound	ν (C==N)	ν (NO)	σ (NO)	ν_{as} (NH_2)	ν_s (NH_2)	σ (NH_2)	ν (C==O)	ν (C-NH_2)	ν (C==C)	ν (C-H)
H_2dmg	1447	1144	750							
Ade	1600			3286	3114	1668		1250	1502	2976
Gua				3320	3120	1630	1695(d)	1150		2910
							1670			
OPD				3373	3185			1492	1626	3032
				3303						

Table 3: Relevant IR data (cm^{-1}) of the complexes

Compound	ν(C==N)	ν (NO)	σ (NO)	ν_{as} (NH_2)	ν_s (NH_2)	σ (NH_2)	ν (C==O)	ν (C-NH_2)	ν(C==C)	ν (C-H)	ν (NO_3) coord	ν (Cu-O)	ν (Cu-N)
Complex 1	1404	1155	743	3324	3178	1658		1271	1506	2884	1465-1343-1038		468
	1606												
Complex 2	1414	1193	781	3320		1630	1700	1147		2907	1479-1375-950	557	499
							1675						
Complex 3	1416	1150	714	3340	3158	1672		1236	1528	2781	1454-1336-1055		477
	1606												
Complex 4	1416	1169	783	3320		1630	1687	1147		2909	1469-1365-1038	557	496
							1660						
Complex 5	1386	1150	743	3400	3187			1500	1605	3102	1453-1339-1066		448
				3281									497
Complex 6	1416	1187	761	3349	3280			1510	1604	3167			478
				3291									515

Electronic Absorption Spectra

The UV-VIS spectra of the complexes obtained in DMSO, were measured in the 200-900 nm domain, comprising two distinct regions, the first one being specific to the intra-ligand electronic transitions, ranging from 269 to about 317 nm corresponding to the transition $\pi \rightarrow \pi^*$, the second region is specific to charge transfer (CT) and d – d transitions (411-750 nm). The electron spectral data of all the complexes are listed in Table 4 with those of the free ligands for comparison and the electron absorption spectrum of (Cu(H_2dmg)(Ade)(NO_3)$_2$) is given in Figure 5.

The electron spectra of complexes 1 and 3 with adenine display a band of high intensity in the UV region, centered at 290 nm with a molar extinction coefficient of 3600 l $mol^{-}cm^{-1}$ for complex 1 and 3940 l $mol^{-}cm^{-1}$ for complex 3, this band attributed to the $\pi \rightarrow \pi^*$ transition is also observed in the spectra of free ligands. The displacement of the position of this band towards higher frequencies confirms the coordination of the ligands with the metal ion. In addition, these complexes also have a 428 nm band for complex 1 and at 411 nm for complex 3, this band is assigned to the ligand charge transfer transition to metal (LMCT).

On the other hand, the complex 1 shows two distinct bands at 722 and 580 nm, the position of these two bands is an indication of a square planar geometry around the copper (II) [35,37], whereas the complex 3 displays a single band at 555 nm, the latter can be assigned to the transition $^2E_g \rightarrow {}^2T_{2g}$ and conforms to an octahedral geometry [38-40]. The absorption bands observed in the region 272-289 nm in the complexes 2 and 4 with guanine can be assigned to

the π → π * intra-ligand transitions associated with the ligands H_2dmg and guanine. These complexes also display a band at 411 nm (complex 2) and at 492 nm (complex 4), this band is associated with the transition of ligand charge transfer (LMCT). The electron spectrum of the complex 2 also shows two distinct bands of low intensity at 567 and 702 nm, the latter being characteristic of a plane square geometry [38-40]. On the other hand, the spectrum of the complex 4 has several bands, which are characteristic of the d-d and charge transfer transitions of a d^9 system. Therefore, a square base pyramidal geometry is proposed for this complex [41,42].

The spectra of complexes 5 and 6 show clear bands in the 269-317 nm region, the latter being due to π → π * intra-ligand transitions. Localized transitions at 427 and 443 nm, respectively, are attributed to LM charge transfer. The visible spectrum of complex 5 has a band whose maximum is 659 nm with a molar absorption coefficient of 540 $l.mol^{-}cm^{-1}$ (Table 4). The position of this absorption is typical of that of a square-based pyramidal geometry [43]. Moreover, the electron spectrum of the complex 6 shows a band whose maximum is located at 690 nm, this band is characteristic of a transition d-d similar to that of the Cu (II) ion in a deformed octahedral environment [44-46].

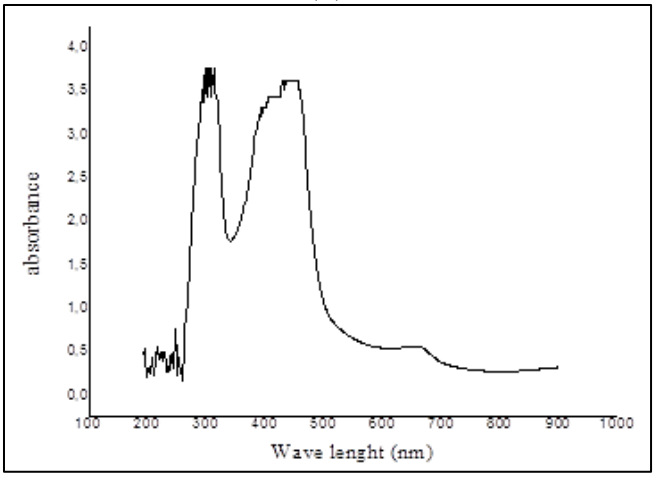

Figure 5: Electronic absorption spectrum of Cu (Hdmg)(OPD)(NO3)

Table 4: Electronic spectral data of the ligands and complexes

Compound	λ (nm)	ν (cm^{-1})	ε ($l\ mol^{-1}\ cm^{-1}$)	Transitions électronic
Dimethylglyoxime	290	34483	100	$\pi \rightarrow \pi^*$
	270	37037	1300	$\pi \rightarrow \pi^*$
Adenine	286	34965	2800	$\pi \rightarrow \pi^*$
Guanine	375	26667	200	$n \rightarrow \pi^*$
	300	33333	3450	$\pi \rightarrow \pi^*$
Ortho-phenylenediamine	305	32787	3410	$\pi \rightarrow \pi^*$
	269	37175	2120	$\pi \rightarrow \pi^*$
Complex 1	722	13850	600	d→d
	580	17241	990	d→d
	428	23364	440	charge- transfert (CT)
	311	32154	1360	$\pi \rightarrow \pi^*$
	289	34602	3600	$\pi \rightarrow \pi^*$
Complex 2	702	14245	1140	d→d
	567	17637	1940	d→d
	411	24331	3050	charge- transfert (CT)
	289	34602	3200	$\pi \rightarrow \pi^*$
Complex 3	555	18018	220	d→d
	411	24331	670	charge- transfert (CT)
	290	34483	3940	$\pi \rightarrow \pi^*$
Complex 4	750	13333	630	d→d
	666	15015	630	d→d
	534	18727	620	d→d
	492	20325	640	charge- transfer (CT)
	287	34843	3370	$\pi \rightarrow \pi^*$
	272	36765	4000	$\pi \rightarrow \pi^*$
Complex 5	659	15175	540	d→d
	443	22573	4900	charge- transfert (CT)

	317	31546	3780	$\pi \rightarrow \pi^*$
	298	33557	3780	$\pi \rightarrow \pi^*$
Complex 6	690	14493	330	d→d
	427	23420	3060	charge- transfert (CT)
	294	34014	840	$\pi \rightarrow \pi^*$
	269	37175	1140	$\pi \rightarrow \pi^*$

Electrochemical Studies

The electrochemical data of the ligands and their complexes were recorded in DMSO, with sodium perchlorate as the supporting electrolyte. The results of cyclic voltammograms (CV) are shown in Table 5 and the voltammograms of $Cu(NO_3)_2$ and ($Cu(Hdmg)(OPD)(NO_3)$) are illustrated in Figure 6. The cyclic voltammogram of Cu $(NO_3)_2 3H_2O$ shows an anodic single peak at 0.26 V with no cathodic response associated to the oxidation of Cu^I to Cu^{II}. The cyclic voltammogram of dimethylgloxime shows an anodic and cathodic process at Epa = -0.56 V and Epc = -0.70 V. The adenine and guanine ligands have waves with Epa values of 1.10 and 0.82 V, respectively corresponding to irreversible oxidations of the ligands. Furthermore, the voltammograms of these ligands display an irreversible cathodic peak with Epc values of -0.66 V and -0.65 V, respectively. Whereas the cyclic voltammogram of the OPD shows three irreversible anodic waves at -0.47, 0.38 and 1.14 V, these bands correspond to the oxidation of the ligand.

By comparing the cyclic voltammograms of the complexes with those of the ligands and the $Cu(NO_3)_2 3H_2O$ salt taken as references, it is easy to confirm the presence of the ligands and the metal cation in the complexes.

Experimental data for complexes 1-4 indicate an irreversible reduction process with the cathodic peak appearing between -1,08 and -1,37 V and the anodic peak appearing between -0,52 and -0,69 V. The cathodic peak is due to the reduction of Cu^I to Cu [1,33,47-51]. In addition, the cyclic voltammograms of these complexes show two anodic peaks without associated cathodic response, the first peak located in the 0.13 V - 0.15 V region is assigned to the oxidation of Cu^I to Cu^{II} [33,51,52] and the second peak observed in the region 0.82 V - 1.12 V could be attributed to the oxidation of the adenine or guanine ligands.

The cyclic voltammograms of complexes 5 and 6 show a well-defined redox process corresponding to the formation of an irreversible Cu^I/Cu couple, the anodic peak occur at Epa = -0.51 V and the associated cathodic peak is located at Epc = -1.14 V for complex 5. For complex 6, the anodic peak is observed at Epa = -0.58 V and the cathodic peak associated at Epc = -1.05 V. In addition, these complexes have also three anodic peaks without associated cathodic response, the first peak located at 0.15 V for the complex 5 and at 0.25 V for the complex 6, could be attributed to the oxidation of Cu^I to Cu^{II}, the other peaks could be assigned to the oxidation of the OPD. The oxidation of H_2dmg in all the complexes could be an overlap with a potential of couple Cu^I/Cu.

Antioxidant Activity of Complexes

The 2, 2-diphenyl-1-picrylhydrazyl radical ($DPPH^{\bullet}$) is a stable free radical, which has been widely accepted as a tool for estimating the free radical scavenging activities of potential antioxidants [53,54]. The lower IC_{50} value indicates a stronger ability of the tested compound to act as a DPPH scavenger while the higher IC_{50} value indicates a lower scavenging activity of the scavengers. On electron or hydrogen reception the purple colour of DPPH radical fades or disappears due to its conversion to 2, 2-diphenyl-1-picrylhydrazine resulting in decrease in absorbance at λ 517 nm. The more decrease the absorption in the presence of scavengers the more effective is its radical scavenging activity. Herein the antioxidant activity of complexes was expressed as IC_{50} (Figure 7). The complexes 3, 5 and 6 showed inhibitory concentrations of 50% free radicals (IC_{50}) of 24.45, 18.74 and 15.09 µg/ml respectively, while butylhydroxytoluene (BHT, positive control) presented a value of 10.46 µg/mL. This seems indicate that the radical scavenging activity of these complexes is due to an electron donating mechanism and not an hydrogen donating mechanism since there no hydrogen atoms to be given [55].

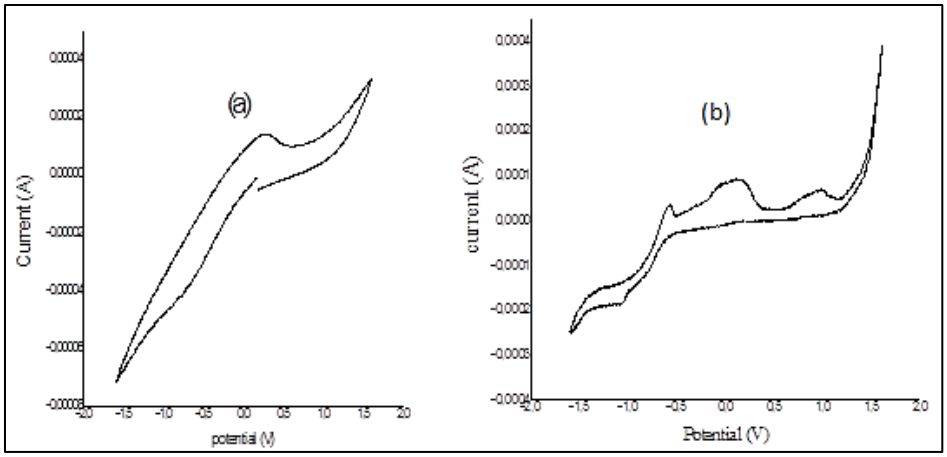

Figure 6: Cyclic voltammogram of (Cu2 (Hdmg)(Ade)2(NO3)(H2O)) (scan rate 50 mV/s)

Table 5: Electrochemical data of the ligands and the Cu(II) complexesa containing NaClO4 10-1 M in DMSO

Compound	E_{pa} (V)	E_{pc} (V)
Dimethylglyoxim	-0.5	-0.7
Adenine	1.1	-
	-	-0.66
Guanine	0.82	-
	-	-0.65
Ortho-phenylenediamine	-0.47	-
	0.38	-
	1.14	-
$Cu(NO_3)_2 3H_2O$	0.26	-
Complex 1	-0.52	-1.14
	0.15	-
	1	-
Complex 2	-0.69	-1.1
	0.15	-
	1.1	-
Complex 3	-	-1.35
	-0.56	-1.08
	0.13	-
	0.82	-
Complex 4	-0.59	-1.37
	0.13	-
	1.12	-
Complex 5	-0.51	-1.14
	0.15	-
	0.44	-
	1.13	-
Complex 6	-0.58	-1.05
	0.25	-
	0.59	-
	1.17	-

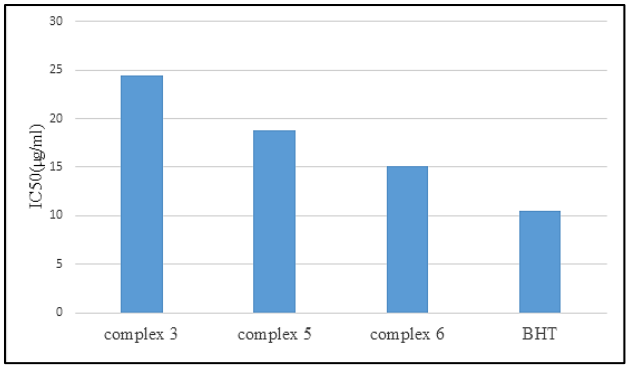

Figure 7: The antioxidant activity of complexes 3,5 and 6 using DPPH assay (IC50= µg/ml)

CONCLUSION

Copper (II) complexes with dimethylglyoxime as primary ligand and purine bases (adenine, guanine) and ortho-phenylenediamine as secondary ligands were synthesized and characterized by different physico-chemical and spectroscopic techniques. Conductimetric analysis shows that these complexes are non-electrolytes. The IR study reveals that all the ligands are bidentate. The electron absorption spectra indicate that the complexes have different geometries. The electrochemical behavior of the copper(II) complexes was determined by cyclic voltammetry, which shows an irreversible redox process corresponding to the Cu^{I}/Cu and irreversible oxidation Cu^{I} to Cu^{II}. The antioxidant potential of the complexes was determined using a DPPH assay. The IC50 value was determined for each complex having antioxidant activity. The results of this activity show that complex 6 has a strong antioxidant activity as BHT.

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