ELECTROCHEMICAL AND COMPUTATIONAL STUDY OF COPPER (II) ALKYLPIRAZOLONE BASED ENAMINE COMPLEX

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ABSTRACT

The cyclic voltammograms (CV) of the copper complex CuL₂, L: C₁₉H₂₆N₃O [1-(n-hexyl)-3-methyl-4-[1-phenylaminopropylidene]-2-pyrazolin-5-one] have been studied. The CV profiles of CuL₂ show one or two reduction and oxidation wave. The energy level corresponding to the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of CuL₂ have been determined experimentally from the first oxidation and reduction onset potential, respectively. These values were also estimated from Density Functional calculations. The electrochemical energy gap deduced from these measurements (E_g ~ 1.03 eV) agrees quite well with the theoretical value.

INTRODUCTION

Pyrazolones are an important family of organic compounds.^{1,2} They have been widely studied as a consequence of their numerous applications³⁻⁶ and in particular as chelating agents for solvent extraction of various metal ions.^{7,8} Schiff bases⁹ and enamines derived from pyrazolones¹⁰ are known but they present solubility problems. To overcome this lack of solubility, convenient syntheses of 1-n-alkyl derivatives of pyrazolones were reported a few years ago.¹¹

The electrochemical methods are very important tools to characterize organic or inorganic systems. In this field, cyclic voltammetry (CV) is recognised as an important technique for measuring band gaps, electron affinities (*i.e.* the energy of LUMO, ϵ_{LUMO}) and ionization potential (*i.e.* the energy of HOMO, ϵ_{HOMO}).¹²⁻¹⁴ In this case, the oxidation process corresponds to removal of an electron from the HOMO energy level whereas the reduction cycle corresponds to electron addition to the LUMO.

Electrochemical studies using metal complexes with ligand based on 1-phenylpyrazolone Schiff bases have been reported.¹⁵ However the electrochemical behaviour of 1-alkylpyrazolone was not totally established,¹⁶ since it was not achieved to assign the nature of the voltammetric peaks observed.

In the present work we have determined several electronic properties of a copper (II) alkylpyrazolone based enamine complex (scheme 1) by electrochemical measurements (ϵ_{LUMO} , ϵ_{HOMO} and E_g). Furthermore we have compared the experimental with theoretical values obtained from density-functional calculations. For this we have calculated the electron density frontier orbitals and the natural charges.¹⁷

Scheme 1: Molecular structure of copper (II) alkylpyrazolone based enamine complex.

EXPERIMENTAL

Copper complex synthesis

The copper (II) complex shown in the scheme 1 was prepared from 0.1000 g (0.32 mmol) of protonated ligand HL (C₁₉H₂₇N₃O) and 0.032g (0.16 mmol) of Cu(CH₃COO)₂·H₂O dissolved in ethanol (10mL) and heated under reflux for 1 h. The solution was then evaporated to a final volume of 5 ml and allowed to cool at room temperature. The solid was filtered off and crystallized by slow evaporation from a chloroform-hexane mixture, 1:1 v/v (yield 0.08g, 73%; m.p. 396(2) K.^{18,19}

Electrochemical setup

The experimental method to carry out the cyclic voltammetry (CV) has been described in the literature.^{20,21} A glassy carbon disc of 0.07 cm² geometric area was used as working electrode. The reference electrode was Ag/AgCl in solution of tetraethylammonium chloride (Et₄NCl). The potential was adjusted to 0.197 V versus normal hydrogen electrode (NHE).²² Platinum gauze was used as counter-electrode.

Prior each experiment, the working electrode was polished with alumina slurry (particle size 0.3 μm) and the rinsed with bidistilled water and acetonitrile. Acetonitrile anhydrous (Aldrich Chemical Co) was used as solvent and it was manipulated with syringes. Tetrabutylammonium perchlorate (TBAClO₄) (Aldrich Chemical Co) was used as supporting electrolyte and it was dried under vacuum at 40°C for 24 h.

The electrochemical profiles were obtained from 0.001 M copper complex and ligand solutions containing 0.1 M supporting electrolyte at 100 mV/s scanning rate.

All solutions were kept under flowing argon during 30 min before each experiment. The gas flux was inverted to keep an inert atmosphere over the solution while the electrochemical perturbation was applied. The electrochemical data were recorded in a BAS CV-50W system.

Computational calculations

The calculations were performed by using effective core pseudopotentials (ECP) basis set on the copper atom, and the standard basis set 6-31G** for carbon, oxygen, nitrogen, and hydrogen atoms.²³ The Ar core electrons of Cu were replaced by an ECP and DZ quality Hay and Wadt Los Alamos ECP basis set (LANL2DZ)²⁴ was used for the valence electrons. The LANL2DZ basis set has been successfully used in calculation on metalloporphyrins and derivatives and transition metal complexes.^{25,26}

Electron correlation effects were considered employing density functional theory (DFT) methods, which have been considered as a practical and effective computational tool, especially for organometallic compounds.^{27,28} Among these functional procedures, the most reliable approximation is often thought to be the hybrid HF/DFT method using a combination of the three nonlocal correlation functional; this method is called B3LYP.²⁹ GAUSSIAN 03W package³⁰ was used in the calculations. The geometry optimization was carried out with the unrestricted B3LYP functional^{29,31} and using the above basis sets. The molecular structures were fully optimized in gas phase, without symmetry

restrictions, and compared with single crystal X-ray structure.^{19,32} To plot the electron densities of HOMO and LUMO levels, we used the MacSpartanPro software.³³ The natural population analysis was performed using the NPA keyword implemented in the GAUSSIAN 03W.³⁴

RESULTS AND DISCUSSION

Electrochemical characterization

The electrochemical behaviour of the CuL_2 complex and the ligand L were studied by cyclic voltammetry (CV) (see figure 1). The CVs profiles were performed in the potential range of -1.60 to +1.35 V. The CuL_2 and L profiles in acetonitrile show one or two reduction and oxidation waves depending on the potential limits imposed.

For the ligand, two irreversible anodic peaks were observed at +0.775 and +1.250 V in the anodic scan (-1.025 and -1.540 V for the cathodic scan). Other authors have studied similar enamines ligands (e.g. 1-(n-hexyl)-3-methyl-5-pyrazolone¹⁶) and they found only one irreversible anodic peak. In our situation, if the anodic potential limit is increased, another peak can be observed. This feature is more representative of a molecular system with several redox sites because the ligand used in this study is a more reactive enamine. On the other hand, the copper (II) complex shows anodic peaks potentials at +0.590 and +0.690 V for the anodic scan and -0.850 and -1.100 V for the cathodic scan respectively. The onset potentials (E_{on}) for the first oxidation and reduction waves are situated at +0.416 V and -0.615 V, respectively. The onset potentials were obtained from the intersection of the two tangents drawn at the raising current and the background charging current of the CVs. The feature found is very similar to that found for the ligand; nevertheless anodic peaks appear at a less anodic potential and, in addition, both peaks correspond only to the ligand.

Figure 1. Cyclic voltammogram of CuL_2 and L in acetonitrile: (a, b) anodic and cathodic profiles of copper complex. (c, d) anodic and cathodic profiles of ligand.

An important aspect to emphasize is that during the formation of the copper complex a change in the ligand structure takes place, which allows the formation of new bonds with the copper (II) ion. In order to make a correct allocation of the observed electrochemical phenomena it is necessary to calculate the energy of the frontiers orbital in the complex so as to determine the most reactive sites in this molecule.

As a first approach, it is possible to determine the energy of the frontier orbital from the electrochemical parameters. The HOMO and LUMO energies can be determined from the first oxidation and reduction onset potentials, respectively. The potential difference can be used to estimate the energy gap of the copper complex, that is, the $E_g = \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}$. The energy level of the normal hydrogen electrode (NHE) is situated 4.5 eV below the zero vacuum energy level.³⁵ From this value and the redox potential of the reference electrode used in the present work Ag/AgCl (0.197 V), a simple relation can be

written which allows estimating both energy values.^{36,37}

The experimental energies values of HOMO and LUMO levels for CuL_2 are -4.28 and -5.31 eV respectively; therefore the band gap estimated from the electrochemical measurements is 1.03 eV (table 1). The electrochemical energy gap deduced from these measurements is mayor than calculated theoretical value. This result is not strange, because it is well-known that the calculated band gap in many cases does not agree with the experimental value.^{38,39}

Table 1: Electrochemical parameters for L and CuL_2 obtained from cyclic voltammetry

System	First anodic peak potential (mV)	First cathodic peak potential (mV)
L	775	-1025
CuL_2	590	-850
	Anodic onset potential	Cathodic onset potential
CuL_2	416	-615
Experimental gap energy (eV)		
CuL_2	1.03	

Computational calculation

As a first approach we have carried out the geometry optimization of the ligand (L) and the complex (CuL_2). However, during the geometric optimization process, convergence problems took place, increasing the calculation time; furthermore, it was not found a minimum energy conformation in both cases. This is due to the great number of conformers that can exist in ligand and complex respectively. Due to this, in both the ligand and the complex, we have eliminated the aliphatic flexible chains and they were replaced by methyl groups, this allowed to avoid the problem of convergence and to find a minimum (see scheme 2).

to this new model as CuL_2S_2 ($\text{S} = \text{CH}_3\text{CN}$). In this way, in the optimization process we considered the effect of two solvent molecules on the equilibrium geometric parameters. We consider that this modification should not affect significantly the validity of the electrochemical parameters. The equilibrium geometries of the ligand L and of the complex CuL_2S_2 obtained through DFT calculations were compared with those reported in literature.^{19,32} Table 2 shows values of bond length for the optimized ligand model employed in this study, which are in agreement with the experimental data obtained by X ray diffraction (XRD). In addition table 2 shows the values of the optimized geometric parameters for the CuL_2S_2 complex model. The results are quite close to the values reported in the literature³² since the errors found in bond distances and angles are less than 0.2%, e.g. 0.04 Å and 0.5 degrees.

Table 2: Comparison between single crystal X-ray diffraction (XRD) measurements and DFT calculations of ligand model (L) and copper (II) complex with two acetonitrile axial molecules (CuL_2S_2 model).

Ligand			Copper (II) Complex		
Distance	XRD	DFT	Distance	XRD	DFT
O1-C1	1.253(2)	1.251	Cu1-O1	1.879 (2)	1.875
N1-C1	1.355(2)	1.370	Cu1-O1'	1.879 (2)	1.877
N1-N2	1.385(2)	1.385	Cu1-N3	2.036 (3)	2.038
N1-C10	1.452(3)	1.443	Cu1-N3'	2.036 (3)	2.040
N2-C3	1.312(2)	1.311	O1-C1	1.282 (4)	1.285
N3-C5	1.330(2)	1.354	N3-C5	1.317 (4)	1.314
N3-C8	1.434(2)	1.411	C2-C5	1.420(5)	1.419
C1-C2	1.438(3)	1.466	C1-C2	1.409(5)	1.409
C2-C5	1.394(2)	1.391	C2-C3	1.430(5)	1.429
C2-C3	1.439(2)	1.449	N2-C3	1.314(4)	1.314
C3-C4	1.477(3)	1.500	N1-N2	1.375(4)	1.376
Copper (II) Complex					
Angle	XRD	DFT	Angle	XRD	DFT
O1-Cu1-O1'	180.00(7)	179.8	C1-O1-Cu1	122.5(2)	122.4
O1-Cu1-N3	92.24(11)	92.4	O1-C1-C2	131.7(3)	131.7
O1'-Cu1-N3	87.76(11)	87.8	C1-C2-C5	122.8(3)	122.7
O1-Cu1-N3'	87.76(11)	87.6	C2-C5-N3	120.3(6)	120.8
O1'-Cu1-N3'	92.24(11)	92.2	C5-N3-Cu1	126.6(2)	126.5
N3-Cu1-N3'	180.0(13)	179.9			

Once the geometries for the ligand L and the CuL_2S_2 complex were optimized, we have calculated the electron density maps of HOMO and LUMO states for these models (see figure 2). Also, we calculated the electron density maps of the CuL_2 complex, our aim being to observe the effect of solvent molecules (CH_3CN) on the electronic properties of the complex.

The electron density maps suggest that the oxidation of the ligand involves mainly the pirazolone moiety (see figure 2a). The presence of several reactive sites in this molecule must be due to the presence of conjugated double bonds, which influences the distribution of the electronic density (the HOMO level is delocalized over several atoms). In the copper complex (figure 2c), the situation

is very similar to that of the ligand; however it exists a location of the electronic density between the C1, C2, N2, C1', C2' and N2' atoms. This location must be mainly the effect of the copper ion. The electron density map for the complex which includes the two acetonitrile axial molecules is a little different, because the localization is now over C3, C5, C3' and C5' atoms.

For the LUMO level the electronic density maps indicate that these molecules may suffer a nucleophilic addition to α,β unsaturated double bonds. However the effect of the copper ion has modified the distribution of the MO and it participates in the LUMO. Under these features it is possible to identify two oxidation processes that involve only ligand double bonds carbon-carbon, carbon-nitrogen and carbon-oxygen. In the reduction process, besides the ligand double bonds, it also involves the metal ion; in this case three reduction processes will exist, two for the ligand and one for the metal ion.

Table 3 shows the atomic charges from the natural population analysis (NPA) ¹⁷ for ligand L and CuL_2 and CuL_2S_2 model complexes. We have included natural charges associated to atoms that are directly bonded to copper ion. The calculated charge on the copper ion is lower than the formal charge +2. It results from charge donation from the nitrogen and oxygen atoms of the ligand.

Table 3: Atomic charges from the natural population analysis (NPA) for the model complexes: (CuL_2S_2), (CuL_2), and the ligand (L).

Atom	CuL_2S_2	CuL_2	L
Cu1	1.26	1.13	-
O1	-0.81	-0.83	-0.68
C1	0.64	0.64	0.63
C2	0.17	0.19	0.20
C3	-0.26	-0.26	-0.29
C5	0.23	0.24	0.33
N3	-0.68	-0.69	-0.57
O1'	-0.81	-0.83	-
C1'	0.64	0.64	-
C2'	0.17	0.18	-
C3'	-0.26	-0.26	-
C5'	0.23	0.24	-
N3'	-0.68	-0.70	-

The atomic charge presented by the atoms O1 and N3 in the ligand decreases after complex formation. This is because oxygen and nitrogen have the electron-donor's behavior on the copper ion (an electrophilic site). For the copper complex the negative region involved by the bonds of the ligand and the positive region is located in the metal ion and over C1 and C5. These results are coherent with those obtained with HOMO and LUMO electron densities.

The band gap energy values calculated for CuL_2S_2 and CuL_2 from DFT UB3LYP/6-31G**/LANL2DZ level theory calculations are 0.66 and 0.61 eV respectively.

Figure 2. Electronic densities maps of HOMO and LUMO levels for copper complexes and ligand obtained from B3LYP/6-31G**/LANL2DZ calculations: (a, b) ligand; (c, d) CuL_2 and (e, f) CuL_2S_2 .

CONCLUSION

Cyclic voltammograms of copper complex CuL_{25} , L: $\text{C}_{19}\text{H}_{26}\text{N}_3\text{O}$ [1-(n-hexyl)-3-methyl-4-[1-phenylaminopropylidene]-2-pyrazolin-5-one] show one or two reduction and oxidation waves. The electrochemical oxidation process involves only ligand double bond but the reduction involves the ligand and also the copper ion. The energy levels corresponding to HOMO and LUMO levels have been determined experimentally from the first oxidation and reduction onset potential respectively, and their values were estimated using DFT UB3LYP/6-31G**/LANL2DZ level theory. The electrochemical energy gap deduced from these measurements ($E_g \sim 1.03$ eV) it is something different than the calculated theoretical value, although it falls inside the expected range.

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Supplementary data

Supplementary data for this paper are available from the IUCr electronic archives (reference: OB1229)

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