

Theoretical study on the electronic spectrum of $[\text{M}(\text{CN})_2]_n^{-n}$ ($\text{M} = \text{Au}(\text{I}), \text{Ag}(\text{I}); n = 1-3$) complexes

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Abstract

The electronic structure and the spectroscopic properties of $[\text{M}(\text{CN})_2]_n^{-n}$ ($\text{M} = \text{Au}(\text{I}), \text{Ag}(\text{I}); n = 1-3$) were studied using density functional theory (DFT) at the B3LYP level. The absorption spectrums in these complexes were calculated by single excitation time-dependent (TD) method. The di- and trinuclear models shown a ${}^1(n\text{d}\sigma^* \rightarrow (n+1)\text{p}\sigma)$ transition associated with a metal–metal charge transfer, which is strongly interrelated with the gold–gold and silver–silver contacts. The values obtained are in agreement with the experimental range.

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1. Introduction

Two of the typical metal that form compounds with the cyanide ion are the heavy metal ions Au(I) and Ag(I) [1]. The physical chemistry of gold(I) and silver(I) dicyanide complexes have been of considerable interests due to their importance in industrial applications [2–4]. The $[\text{Au}(\text{CN})_2]^-$ and $[\text{Ag}(\text{CN})_2]^-$ are representative linear two coordinate complexes thereby attracting much attention on the molecular and electronic structures.

Patterson and co-workers have shown that both $[\text{Au}(\text{CN})_2]^-$ and $[\text{Ag}(\text{CN})_2]^-$ ions undergo self-association in a variety of conditions, particularly in solutions [5–8]. Oligomerization of both ions is due to aurophilic Au–Au and argentophilic Ag–Ag interactions [9]. The aggregated forms are readily detected by their absorption and luminescent spectrums. Thus, the electronic spectra from solutions of $\text{K}[\text{Au}(\text{CN})_2]$ and $\text{K}[\text{Ag}(\text{CN})_2]$ varies from 180 to 450 nm depending upon the concentration. The experimental data are shown in Table 1 [5,6]. The absorption spectrums show a progressive red shifts with an increase in concentration. These results have been attributed to excited state interactions in oligomeric forms of

these anions. Electronic structure calculations extended Hückel and MP2 suggest that this behavior is attributed to metal–metal interactions between neighboring $[\text{Au}(\text{CN})_2]^-$ or $[\text{Ag}(\text{CN})_2]^-$ ions [5–8].

The complexes studied here show evidence of metallophilic interactions. Closed-shell metallophilic interactions ($\text{d}^{10}\text{--}\text{d}^{10}$) are estimated to be energetically similar to hydrogen bonds (10–50 kJ/mol) [9,10]. At theoretical level, the attraction is estimated when electronic correlation effects are taken into account, strengthened by relativistic effects when the present heavy metals as the gold [11,12]. The mechanism behind such attraction is the dispersion (van der Waals) interaction, with additional allowance for virtual charge-transfer terms [13]. The optical properties of Ag(I) and Au(I) complexes have been calculated from CIS and higher levels [14,15]. Such properties have also been described efficiently through the Density Functional Theory (DFT) with the time-dependent (DFT-TD) approach, makes it the method of choice. Several works have shown an excellent association with experimental absorption and emission spectrums [16–20].

The objective of the present work is to study theoretically the excitation spectrums for systems of the type $[\text{M}(\text{CN})_2]_n^{-n}$ ($\text{M} = \text{Au}(\text{I}), \text{Ag}(\text{I}); n = 1-3$) at B3LYP level. These systems could be used as models of the small oligimers responsible for electronic spectra observed from solutions of $\text{K}[\text{Au}(\text{CN})_2]$ and $\text{K}[\text{Ag}(\text{CN})_2]$. Thus far, no systematic DFT investigations have been carried out in models proposed.

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Table 1
Experimental absorption spectra versus concentration of $K[Au(CN)_2]$ and $K[Ag(CN)_2]$ in aqueous solutions [5]

Concentration (M)	λ (nm)	Absorbance	
$K[Au(CN)_2]$ 1×10^{-4}	196	1.3	
	204	1.5	
	219	1.3	
	228	0.5	
	236	0.4	
	209	4.1	
1×10^{-2}	228	4.4	
	236	4.3	
	210	4.3	
0.10	233	4.8	
	288	4.7	
	$K[Ag(CN)_2]$ 5×10^{-4}	199	1.1
1×10^{-3}		205	2.6
		207	3.1
0.30		223	2.6
		206	3.6
		249	3.5
0.80	278	2.9	
	208	4.1	
	250	3.8	
	279	3.2	
	296	2.6	

2. Models and methods

Models proposed $[M(CN)_2]_n^{-n}$ ($M = Au(I), Ag(I); n = 1-3$) used in our study are depicted in Fig. 1. The geometries were fully optimized to the indicated symmetry by the B3LYP method. Single point calculations of these geometries were simulating to study the excitation spectrums with TD-DFT. We have chosen for the models $[M(CN)_2]_2^{-2}$ (D_{2d}) and $[M(CN)_2]_3^{-3}$ (D_{2h}) the orientation staggered linear. This is due to the studied based on dimers of gold with orientation eclipsed show a strong repulsive term (quadrupole–quadrupole interaction) [21], while the models with staggered orientations are found to give a dispersive character in the metallophilic attraction.

Calculations using the GAUSSIAN 98 package were done [22]. The 19 valence-electron (VE) of Au and Ag quasi-relativistic (QR) pseudo-potential (PP) of Andrae [23] was employed. We used two f-type polarization functions on gold ($\alpha_f = 0.20, 1.19$) and silver ($\alpha_f = 0.22, 1.72$) [11]. Also, the atoms C and N were treated through PPs, using double-zeta basis sets with the addition of one d-type polarization function [24].

The energies excitation were obtained at the B3LYP level by using the time-dependent perturbation theory approach (TD-DFT) [25,26], which is based on random-phase approximation (RPA) method [27]. The TD-DFT approach provides an alternative to computationally demanding multi-reference configuration interaction methods in the study of excited-

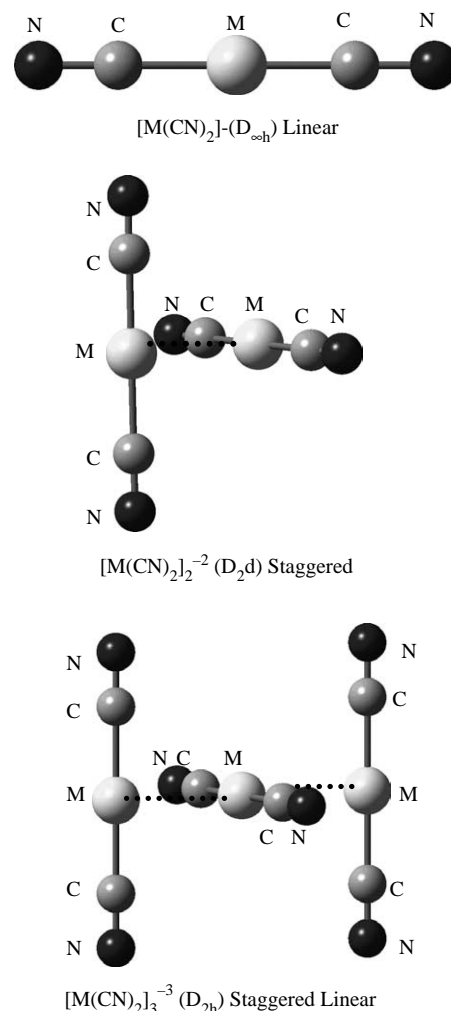


Fig. 1. Models: $[M(CN)_2]^-$, $[M(CN)_2]_2^{-2}$ and $[M(CN)_2]_3^{-3}$ ($M = Au, Ag$).

states. The TD-DFT calculations do not evaluate the spin–orbit splitting, the values are averaged.

3. Results and discussion

3.1. Molecular geometry

Table 2 shows the main parameters of the models proposed. The theoretical results are in agreement with the experimental and theoretical data on the metal–metal contacts [28–31]. It is maintained in the experimental trend.

These results should be analyzed with caution, since DFT calculations using B3LYP do not describe rightly the metallophilic attraction; though DFT can reproduce the distance metallophilic [32,33]. The reason behind could be the specific form of the correlation energy, which it is not adequately described [11–13]. Moreover, the B3LYP functional is able to mimic the process near to the gold–gold and silver–silver equilibrium distance [29]. Our goal here is not to describe the metallophilic interaction and its magnitude, but the electronic spectrums for the systems mentioned.

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