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Scientific paper

Ab-Initio Study of Citrate Ion as an Oxygen-Rich Complexing Agent

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Abstract

Theoretical studies on conformational analysis, geometry optimizations and frequencies for citrate at the MP2/LAN-L2DZ level portrait it as a promising candidate for a complexing agent for cadmium (II) ion (Cd^{2+}) and cadmium sulfide (CdS). Natural Bond Orbital (NBO) charges, Delocalization Indices, HOMO/LUMO gaps and surfaces along with absolute electronegativity values were employed to analyze the interactions among the configurations obtained. The most stable structures involved the interaction between the LUMO of Cd^{2+}/CdS and the most dense region of the HOMO of the citrate ion.

Keywords: HOMO/LUMO surfaces; complexing agent; CdS; citrate ion

1. Introduction

The synthesis of CdS films, which are used on solar cells through a cheap technique such as chemical bath deposition (CBD) [1] is highly dependable on the complexing agent used. The optimum semiconductor films are produced modulating temperature [2], pH [3] and reactive concentration [4]. In this technique, the thin films are deposited on substrates in contact with dilute chemical baths containing metallic ions. Thus, the morphology of the film is highly dependent on the precipitation of the solid phase. Therefore, the complexing agents play a crucial role on the structure of the thin film being deposited. One of the complexing agents used experimentally is ammonia [5]. However, its volatility and toxicity have contributed to a search for other materials. Among them, are ethylene-diamine (ED) [6], ethylenediaminetetraacetic acid (EDTA) [6], polyethyleneimine [7], acetylacetone [8] and glycine [9]. There are only a handful of complexing agents proposed and few studies on the interactions involved between complexing agents and CdS. Our aim is to propose new complexing agents that can show a good affinity with CdS to enhance the homogeneity of the morphology and structure of the film. We propose citrate ion as a complexing agent for CdS based on our previous studies [9,10] that show a high relationship between the stability of CdS and an oxygen-rich complexing agent. The main goal of this paper is to analyze the participation of the oxygens in the citrate ion on the interaction between it and Cd²+/CdS through charges, delocalization indices, HOMO/LUMO and absolute electronegativity.

2. Methodology

We employed Gaussian 09 [11] software for ab-initio quantum mechanical calculations at the second order perturbation Møller Plesset MP2 [12] level of theory in conjunction with the LANL2DZ [13] basis set. We used global orbital cutoffs and fine convergence criteria. We examined the Hessian matrix to confirm the energy minima configurations had only positive vibrational frequencies which

pertain to energy minima and not transition states. Basis set superposition error (BSSE) [14] calculations and zero-point energies were employed to correct the energies.

Dissociation energies (ΔE) were obtained from:

$$\Delta E = E_{system} - E_{citrate\ ion} - E_{Cd^{2+}/CdS}, \quad (1)$$

where system refers to the system formed by Cd^{2+} or CdS and the citrate ion. The terms $E_{citrate\ ion}$ and $E_{Cd}^{2+}/_{CdS}$ refer to the energy in kcal/mol of the optimized structures of the citrate ion, Cd^{2+} and CdS on an individual level, respectively. In the first set of results, we studied the systems Cd^{2+} -citrate ion, while the second set of results pertain to the CdS-citrate ion systems. For all the systems, we calculated the difference between the Lowest Unoccupied Molecular Orbital (LUMO) and the Highest Occupied Molecular Orbital (HOMO) referred to as GAP in eV in Table 1.

We calculated absolute electronegativity, χ , for all the systems [15],

$$\chi = \frac{I + A}{2} \tag{2}$$

where $-\varepsilon_{\text{HOMO}} = I$ and $-\varepsilon_{\text{LUMO}} = A$.

In addition, we report charges in au obtained via Natural Bond Orbital (NBO) analyses [16] using Gaussian 09. Delocalization indices, DI(A,B) between atoms A and B, were calculated through the AIMALL software [17] to analyze bonds and interactions between the atoms in the molecular species.

3. Results and Discussion

The interaction between citrate ion and cadmium (pale yellow) can be considered an acid-base one. The calculated values of χ for the citrate ion and cadmium were of 4.78 $\times~10^{-20}$ J and 1.87 $\times~10^{-20}$ J, respectively. It is expected that Cd²+ attracts electrons and the citrate ion donates them. This is confirmed by NBO charges and delocalization indices.

Figure 1 shows the optimized geometry of citrate ion and the CdS in conjunction with their HOMO and LUMO surfaces. The energy minima configurations formed by the interaction between citrate ion and Cd²⁺ are depicted in Figure 2 in order of stability whereas the first structure is the most stable.

In structure 1, the citrate ion displays 3 hydrogen bonds involving its deprotonated carboxyl groups with de-



Figure 1. Selected geometrical parameters of citrate ion and CdS whereby bond lengths are in angstroms (Å). HOMO and LUMO surfaces are depicted for both substances.

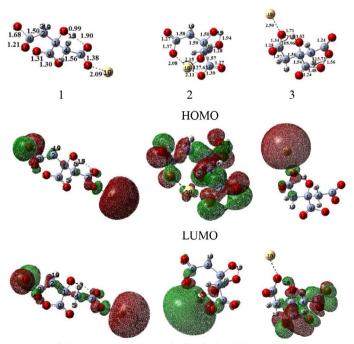


Figure 2. Selected geometrical parameters of the systems citrate ion-Cd whereby bond lengths are in angstroms (Å) and angles in °. HOMO and LUMO surfaces are depicted for all the configurations.

localization indices of DI(H6,O11) = 0.04, DI(O13,H15) = 0.10 and DI(H5,O16) = 0.04 and distances of 2.48 Å, 1.77 Å and 2.37 Å, respectively. The first structure of Fig. 2 has a dissociation energy of -1065.20 KJ/mol. To form this structure, C4 and C7 moved their attached atoms to interact with cadmium. It shares one hydrogen bond with citrate ion from Fig.1, yet with a smaller DI(O13,H15) = 0.06. The transfer of electrons from the citrate ion to cadmium is confirmed by its decrease in charge to 0.85 au and DI(O12,Cd18) = 0.51. Structure 2 has a dissociation energy of -798.36 KJ/mol. It does not retain any of the hydrogen bonds the lone citrate ion had, which could account for an increase in energy compared to structure 1. However, its high stability is most likely supported by the interaction of Cd with the ion on the region where most of the citrate ion's HOMO is located. It forms 1 hydrogen bond with DI(H15,O16) = 0.06 and shows charge transfer between Cd and 3 oxygens with DI values of DI(O11,Cd18) = 0.47, DI(O12,Cd18) = 0.48, DI(O17,Cd18) = 0.39 and

Table 1. MP2/LANL2DZ dissociation energies with zero point corrections, HOMO/LUMO gaps and absolute electronegativity (X) are listed under $\Delta E(0K)$ in kJ/mol; GAP and χ in (× 10^{-19} J), respectively, shown on Figs. 1–3.

System	ΔΕ	GAP	X	
1	-1065.20	2.40	0.16	
2	-798.36	17.6	0.15	
3	-283.34	2.68	0.15	
4	-518.36	14.7	0.38	
5	-514.16	14.8	0.38	
6	-506.40	14.7	0.38	
7	-499.44	14.8	0.31	
8	-478.53	14.9	0.32	
9	-470.91	14.9	0.32	
10	-241.98	18.0	0.33	

Table 2. Delocalization Indices of citrate ion and structures 1-3.

A	В	DI(A,B) citrate	1	2	3
C8	O10	1.24	1.51	1.41	1.14
H6	O11	0.04	_	_	_
C8	O11	1.28	0.75	1.04	1.38
C7	O12	1.28	1.02	1.05	1.53
C7	O13	1.21	1.34	1.44	0.82
O10	H15	_	_	_	0.10
O13	H15	0.10	0.06	_	_
H5	O16	0.04	_	_	_
C9	O16	1.25	1.30	1.37	0.83
O13	O16	_	_	_	1.08
H15	O16	_	_	0.06	_
C9	O17	1.27	1.30	1.11	1.54
O10	Cd18	_	_	_	0.26
O11	Cd18	_	_	0.47	_
O12	Cd18	_	0.51	0.48	_
O17	Cd18	-	-	0.39	-

distances of 2.08 Å, 2.11 Å and 2.15 Å, leaving Cd with a charge of 1.65 au. Structure 3 is the least stable system. It does not retain any of the lone citrate ion's hydrogen bonds. It forms a hydrogen bond with DI(O10,H15) = 0.10. It also forms a single bond between 2 oxygens, with DI(O13,O16) = 1.08 which increases the repulsion between them, rising

Table 3. NBO charges in a.u. for citrate ion and systems 1-3.

	citrate	1	2	3
C1	0.28	0.28	0.25	0.25
C2	-0.54	-0.57	-0.54	-0.53
H3	0.23	0.32	0.24	0.25
C4	-0.56	-0.53	-0.56	-0.54
H5	0.23	0.25	0.21	0.24
H6	0.25	0.22	0.27	0.28
C7	1.00	1.08	0.98	0.99
C8	1.00	1.01	0.99	0.99
C9	1.00	0.95	0.97	0.98
O10	-0.98	-0.64	-0.76	-1.00
O11	-0.93	-0.47	-1.05	-0.80
O12	-0.93	-1.05	-1.04	-0.64
O13	-0.97	-0.84	-0.74	-0.34
O14	-0.93	-0.88	-0.87	-0.87
H15	0.52	0.54	0.53	0.56
O16	-0.95	-0.89	-0.79	-0.38
O17	-0.93	-0.88	-1.00	-0.63
Cd18	_	0.86	1.65	-0.02
H19	0.20	0.24	0.26	0.23

Table 4. Delocalization Indices of structures 4-10

		DI(A,B)						
A	В	4	5	6	7	8	9	10
Н6	O10	_	_	_	0.04	_	_	_
C8	O10	1.27	1.27	1.10	1.20	1.25	1.19	1.54
H6	O11	0.04	0.04	_	_	_	_	_
C8	O11	1.27	1.27	1.35	1.19	1.27	1.22	0.91
C9	O11	_	_	_	_	_	_	0.76
H3	O12	_	_	0.05	_	_	_	_
C7	O12	1.29	1.33	1.27	1.28	1.16	1.25	1.27
C7	O13	1.15	1.09	1.26	1.23	1.24	1.28	1.06
O10	H15	_	_	_	_	0.07	_	_
O12	H15	0.06	_	_	_	_	_	_
O13	H15	_	_	_	0.09	_	_	_
C9	O16	1.09	1.34	1.37	1.24	1.24	1.30	0.54
O13	O16	_	_	_	_	_	_	1.04
H15	O16	_	_	-	_	_	_	-
C9	O17	1.36	1.10	1.08	1.31	1.32	1.24	1.29
H15	O17	_	0.07	0.05		_	0.07	_
O10	Cd19	_	_	0.33	0.28	_	0.30	_
O11	Cd19	_	_	_	0.30	_	0.27	_
O12	Cd19	_	_	_	_	0.30	_	0.30
O13	Cd19	0.30	0.31	_	_	0.30	_	_
O14	Cd19	_	_	_	_	_	_	0.30
O16	Cd19	0.32	_	_	_	-	_	_
O17	Cd19	_	0.30	0.31	-	_	-	_
S18	Cd19	1.22	1.23	1.22	1.33	1.32	1.32	1.02

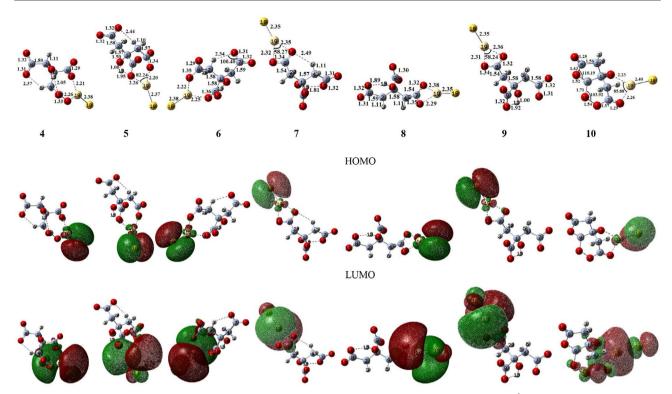


Figure 3. Selected geometrical parameters of the systems citrate ion-CdS whereby bond lengths are in angstroms (Å) and angles in °. HOMO and LUMO surfaces are depicted for all the configurations.

the dissociation energy to -283.34 KJ/mol and the charge of Cd to -0.02 au. Structures 1-3 all showed similar absolute electronegativity values of 1.60×10^{-20} J, 1.53×10^{-20} J and 1.52×10^{-20} J, respectively. HOMO/LUMO gaps of structures 1 and 3 were very similar, with values of 2.40×10^{-19} J and 2.68×10^{-19} J, respectively, while that of structure 2 was of 1.76×10^{-18} J indicating its lower ability as a conductor in comparison.

The next set of structures (4–10) are the energy minima geometries of the interaction between citrate ion and CdS. As in structures 1–3, the transfer of electrons happens from the citrate ion to CdS. Observing Fig. 1, the LUMO is denser on Cd, which indicates it is prone to accepting electrons. It can also be seen that the HOMO of the citrate ion lies mostly on the deprotonated carboxyl groups from (O16-C9-O17)⁻, to a lesser extent on (O10-C8-O11)⁻ and on (O12-C7-O13)⁻. The most stable structures of this set (4-6) show interactions between Cd19 and the (O16-C9-O17)⁻ group.

Configuration 4 is the most stable structure of this set with a dissociation energy of –518.36 KJ/mol. The interaction of Cd19 is with O13 and O16, with delocalization indices of DI(O13,Cd19) = 0.30 and DI(O16,Cd19) = 0.32. The charges of Cd and S were of 1.21 au and –1.38 au, respectively. Structure 5 has a dissociation energy of –514.16 KJ/mol, very close to that of structure 4. Its interactions also occur with oxygens of different deprotonated carboxyl groups. Its DI values were of DI(O13,Cd19) = 0.31 and DI(O17,Cd19) = 0.30. The charges of Cd and S

Table 5. NBO charges in a.u. for systems 4-10.

	4	5	6	7	8	9	10
C1	0.29	0.28	0.29	0.28	0.28	0.29	0.15
C2	-0.52	-0.52	-0.53	-0.52	-0.53	-0.51	-0.27
H3	0.22	0.21	0.27	0.23	0.19	0.23	0.14
C4	-0.54	-0.53	-0.53	-0.55	-0.51	-0.53	-0.27
H5	0.21	0.21	0.22	0.22	0.25	0.23	0.15
H6	0.27	0.26	0.22	0.23	0.20	0.20	0.12
C7	1.01	1.03	1.00	1.00	1.05	1.00	0.52
C8	1.00	0.99	1.00	1.05	1.00	1.04	0.48
C9	0.98	0.99	0.98	0.96	0.96	0.97	0.50
O10	-0.94	-0.94	-1.00	-0.94	-0.93	-0.95	-0.32
O11	-0.93	-0.93	-0.84	-0.94	-0.93	-0.92	-0.34
O12	-0.89	-0.86	-0.93	-0.92	-0.96	-0.96	-0.42
O13	-0.97	-1.02	-0.95	-0.94	-0.90	-0.92	-0.20
O14	-0.87	-0.88	-0.87	-0.90	-0.90	-0.91	-0.49
H15	0.51	0.51	0.50	0.54	0.54	0.53	0.29
O16	-1.02	-0.84	-0.81	-0.96	-0.96	-0.90	-0.16
O17	-0.82	-1.01	-1.02	-0.89	-0.88	-0.94	-0.43
S18	-1.38	-1.38	-1.38	-1.33	-1.34	-1.33	0.27
Cd19	1.21	1.21	1.20	1.14	1.15	1.15	0.66
H20	0.20	0.21	0.19	0.24	0.23	0.22	0.13

showed the same values as in structure 4. In structure 6, Cd interacts with 2 oxygens of different groups, with DI values of DI(O10,Cd19) = 0.33 and DI(O17,Cd19) = 0.31. Its dissociation energy is very close to that of structures 4 and 5, with a value of -506.40 kcal/mol. The charges of Cd

and S were almost the same as in the last two structures, with values of 1.20 and -1.38 au, respectively. Structures 4-6 had similar values of HOMO/LUMO gaps and absolute electronegativities.

Configuration 7, with a dissociation energy of -499.44 KJ/mol depicts the interaction between Cd19 and two oxygens of the same functional group with DI(O10,Cd19) = 0.28 and (DI(O11,Cd19) = 0.30. It shows two hydrogen bonds with DI(H6,O10) = 0.04 and DI(O13,H15) = 0.09. The charges of Cd and S were of 1.14 au and -1.33 au. Configuration 8 interacts with two oxygens of the functional group (O12-C7-O13)- with DI(O12,Cd19) = 0.30 and DI(O13,Cd19) = 0.30 but only has one hydrogen bond with DI(O10,H15) = 0.07. This could account for a smaller dissociation energy of -478.53 KJ/mol. The charges of Cd and S are similar to those of structure 7, with values of 1.15 au and -1.34 au, respectively. For Structure 9, similarly as in structure 7, the interaction between Cd and citrate is with the same functional group, with DI(O10,Cd19) = 0.30 and DI(O11,Cd19) =0.27. It only has one hydrogen bond with DI(H15,O17) = 0.07 with a dissociation energy of -470.91 KJ/mol. Absolute electronegativity for systems 7–9 have similar values of electronegativity (1.48 \times 10⁻¹⁸ J for 7 and 1.49 \times 10⁻¹⁸ J for structures 8 and 9). Their HOMO/LUMO gaps are quite similar, with values of 3.12×10^{-20} J, 3.20×10^{-20} J and 3.19×10^{-20} J.

The last structure, configuration 10 portrays the least stable structure with a dissociation energy of -241.98 KJ/mol. This great difference in energy could be due to a bond formed between O13 and O16 with DI(O13,O16) = 1.04. As for the interactions between Cd and oxygens, DI(O12,Cd19) = 0.30 and DI(O14,Cd19) = 0.30. The charges of Cd and S were of 0.66 and 0.27, greatly influenced by the O13-O16 bond. This last structure has an absolute electronegativity of 3.28×10^{-20} J and a larger HOMO/LUMO gap of 1.80×10^{-18} J.

4. Conclusions

The oxygens in the citrate ion played on important role on the interaction between it and Cd²⁺/CdS. This was described by NBO charges, delocalization indices, HOMO/LUMO surfaces, gap and electronegativity. The transfer of electrons occurs from the citrate ion to Cd²⁺ or CdS. The most stable structures are formed when the deprotonated carboxyl groups on the citrate ion with greater HOMO density participate. The calculations that support this were dissociation energies, charges, delocalization indices, HOMO/LUMO and electronegativity.

The most stable structure for citrate ion- Cd^{2+} was formed from the interaction DI(O12,Cd18) = 0.51, portraying 3 hydrogen bonds. The most stable structure for citrate ion-CdS displayed DI(O13,Cd19) = 0.30 and DI(O16,Cd19) = 0.32 with also 3 hydrogen bonds. The

least stable structures 3 and 10 both show the formation of a O13-O16 bond with DI's of 1.08 and 1.04 au, respectively and no hydrogen bonds.

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Povzetek

Teoretične študije o konformacijski analizi, geometrijski optimizaciji in frekvencah na ravni MP2/LANL2DZ predstavljajo citrat kot obetavnega kandidata za kompleksirajoče sredstvo za kadmijev (II) ion (Cd^{2+}) in kadmijev sulfid (CdS). Za analizo medsebojnih vplivov med pridobljenimi konfiguracijami so bili uporabljeni naravni naboji orbital (Natural Bond Orbital or NBO), indeksi delokalizacije, HOMO/LUMO vrzeli in površine ter absolutne vrednosti elektronegativnosti. Najbolj stabilne strukture so vključevale interakcijo med LUMO Cd^{2+}/CdS in najbolj gostim območjem HOMO citratnega iona.



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