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Electronic and Spectroscopic Properties of Some Carbamate Derivatives as Chelating Ligands for Removing Ni^{2+} Ions from Biological Systems

IRAN SHEIKHSHOAIE* and S. JAMILLADDIN FATEMI
Chemistry Department, Shahid Bahonar University of Kerman, 76175-133, Iran
E-mail: i_shoaie@yahoo.com

The interactions of some carbamate derivatives, such as diethylcarbamate, dithiooxamide and ammonium N,N′-tetramethylene dithiocarbamate with Ni^{2+} have been studied in our laboratory. In the present study, by some semi-empirical calculations, we have investigated the electronic properties and also the electronic spectra of the above carbamate compounds in order to provide better understanding about the behaviour of these compounds for binding to Ni^{2+}. The mentioned compounds have potential coordination sites for binding to the metal ions; so these compounds are good chelating agents for removing Ni^{2+} from biological systems.

Key Words: Carbamates, Transferrin, Apotransferrin, Semi-empirical, Electronic property.

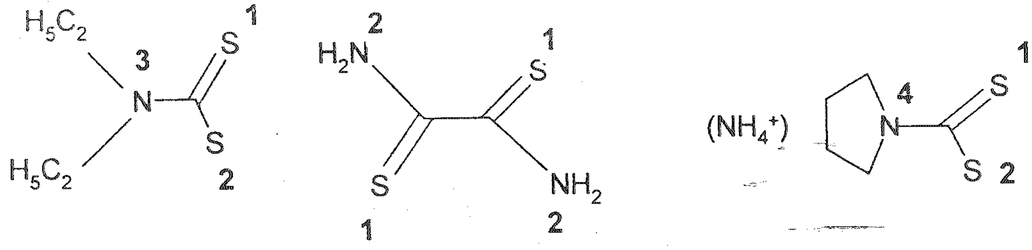
INTRODUCTION

Nickel is a toxic element that may cause different diseases in human body, such as allergic reactions, lung and nasal sinus cancers[1].

According to our earlier studies it is obvious that apotransferrin and transferrin have a tendency to bind rapidly with Ni^{2+}. Furthermore, competitive equilibrium studies between Nii^{2+} and Fei^{2+} for the binding site of transferrin indicate that Nii^{2+} replaces Fei^{2+}. With regard to existent evidence, it seems that*in vivo* Ni disturbance could take place by human serum transferrin through the interface in Fe transfer mechanism. For decades desferrioxamin (desferal) has been an Fe chelator choice for Fe overload treatment despite numerous problems associated with desferal use[2]. Transferrin is iron transport protein and serum transferrin is the principal iron transport protein in the blood of vertebrates and it plays a main role in internal ion exchange[2–5].

In the present study, we have investigated the electronic spectra and electronic properties by some semi-empirical methods for diethylcarbamate (I), dithiooxamide (II) and ammonium N,N′-tetramethylene dithiocarbamate (III) (Fig. 1) and their complexes. Here we have calculated the minimum energies for all of these compounds by AM1 semi-empirical methods[6] to obtain optimized configuration. For our investigation carbamate derivatives are good compounds for removing Ni^{2+} from biological systems.

All measurements and the results of absorption spectra were recently obtained. The absorption spectra of all compounds were recorded in dilute sodium hydroxide solution at pH 7.4.

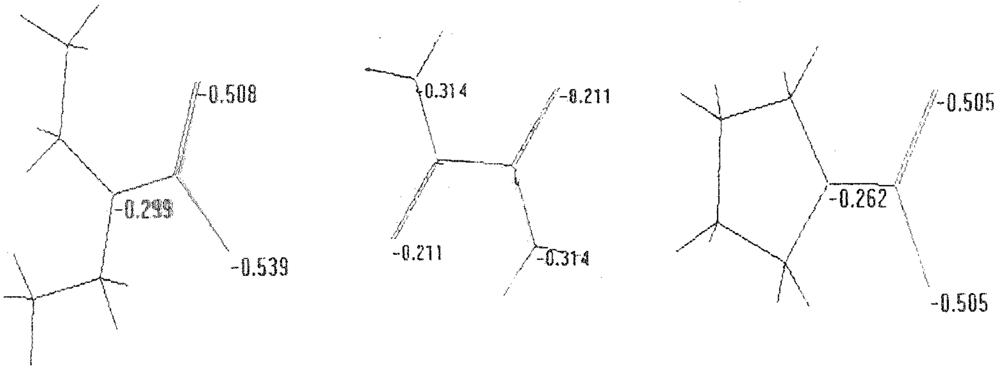


I II III

Fig. 1. Structures of diethylcarbamate (I), dithiooxamide (II) and ammonium N,N′-tetramethylene dithiocarbamate (III)

EXPERIMENTAL

AM1 calculations were performed with MOPAC 7.0[7] to estimate the atomic partial charges, optimization energy of all molecules and predict energy. Each SCF calculation was carried out until the change in energy on successive iterations was less than 0.00001 kcal/mol. Configuration interaction calculations were performed to study the excited-state properties of all three carbamate compounds (**I**, **II** and **III**). Finally the energies of the HOMO and LUMO orbitals, dipole moments and heat of formation are reported in Table-1. All compounds are good electron donors (Fig.2).



I II III

Fig. 2. The optimized geometry of diethylcarbamate (I), dithiooxamide (II) and ammonium N,N′-tetramethylene dithiocarbamate (III) compounds by using AM1 semi-empirical method

TABLE-1
SOME OF THE CALCULATED PROPERTIES FOR THREE CARBAMATE COMPOUNDS I, II AND III USING AM1 SEMI-EMPIRICAL METHOD

Compound	Total energy (kcal/mol)	Heat of formation (kcal/mol)	μ (debye)	E_{HOMO} (eV)	E_{LUMO} (eV)
I	–31706.0781	–15.2943	9.263	–3.0961	4.7780
II	–25679.0680	31.9332	0.000	–8.8041	–1.4409
III	–31078.3894	–17.4151	9.638	–3.3333	4.6099

TABLE-2
MULLIKEN CHARGES ON THE COORDINATION SITES FOR THREE CARBAMATE COMPOUNDS I, II AND III, ACCORDING TO AM1 SEMI-EMPIRICAL CALCULATION METHOD

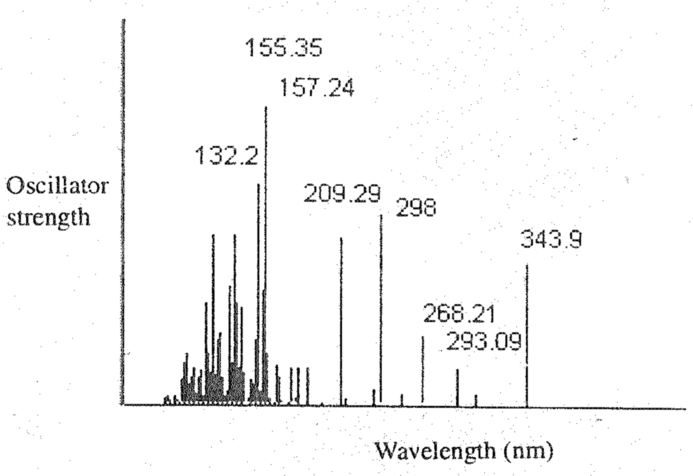
Atom	I	II	III
$S_{(1)}$	–0.508	–0.211	–0.505
$S_{(2)}$	–0.539	–	–0.505
$N_{(2)}$	–	–0.314	–
$N_{(3)}$	–0.299	–	–
$N_{(4)}$	–	–	–0.262

TABLE-3
COMPARISON OF AM1 THEORETICAL AND EXPERIENTIAL TRANSITION ENERGIES IN WATER (λ_{max} in nm) OF THREE CARBAMATE COMPOUNDS

Compound No.	λ_{max} (Calcd.)	λ_{max} (Expt.)
I	157.05	260.00
II	166.80	225.00
III	157.24	250.00

RESULTS AND DISCUSSION

1. Table-3 shows that the theoretical data for λ_{max} of the three carbamate compounds **I**, **II** and **III** have good agreement with experimentat data.
2. Fig. 2 shows the coordination sites for **I**, **II** and **III** carbamate compounds are S and N atoms.
3. All the three above mentioned carbamate compounds are two bidentate ligands, so these compounds are suitable reagents for removing Ni^{2+} from biological media.



Wave-length	Oscillator strength
343.09	0.212
293.09	0.058
268.21	0.101
298.00	0.301
209.29	0.282
157.24	0.397
155.25	0.251
132.30	0.283
122.00	0.227

Fig. 3. Theoretical UV spectra for ammonium N,N′-tetramethylene dithiocarbamate (**III**)

4. The HOMO molecular orbitals for all three **I**, **II** and **III** carbamate compounds are located on S atoms, so more probably S atoms in these structures are the selective coordination sites[9–10].
5. For laboratory investigation of the ability of these carbamate compounds to remove nickel(II) ions from biological systems, studies have to be carried out on rats as a biological model in future.

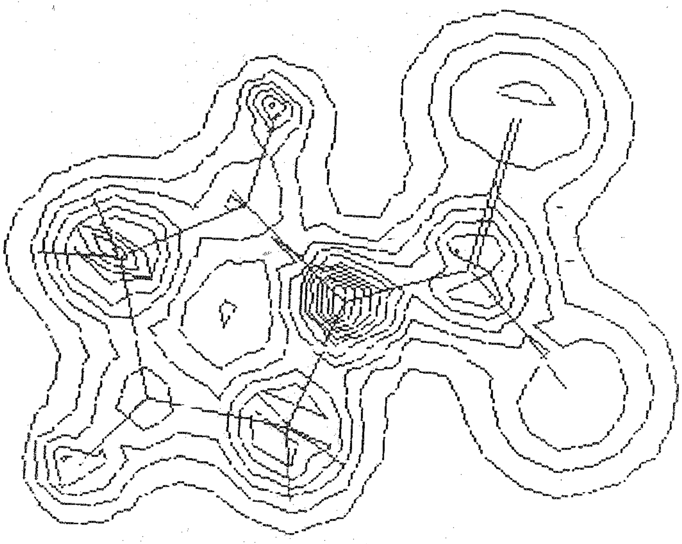


Fig. 4. The distribution of molecular charge density on the optimized **III** carbamate structure

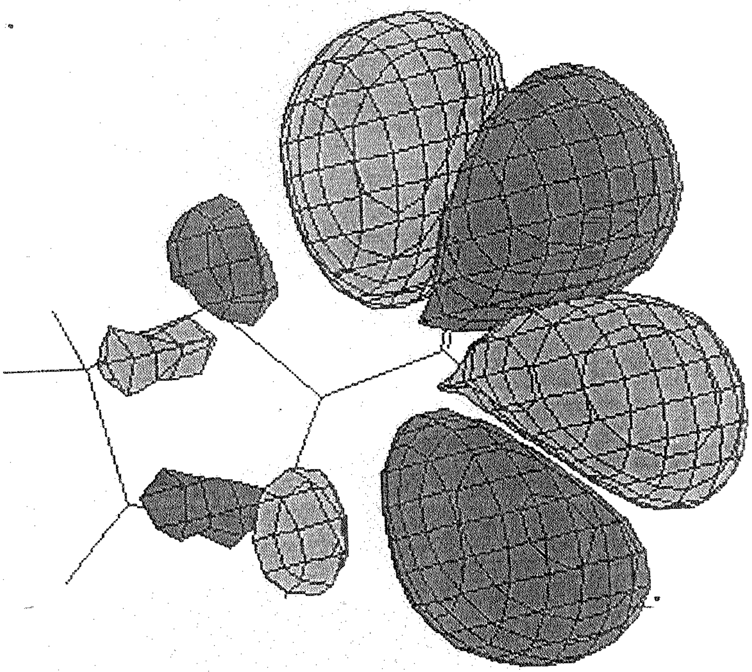
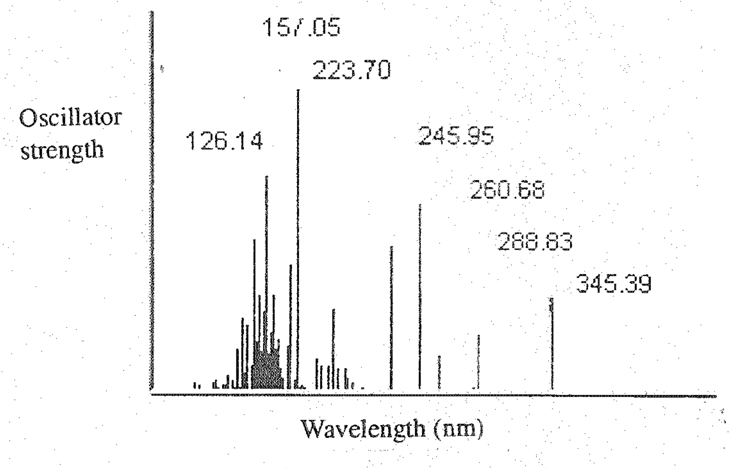


Fig. 5. The plot of HOMO for optimized **III** structure



Wave-length	Oscillator strength
345.39	0.188
288.83	0.125
260.68	0.068
245.95	0.339
223.70	0.278
157.05	0.543
150.70	0.238
126.14	0.326

Fig. 6. Theoretical UV spectra for I carbamate compound

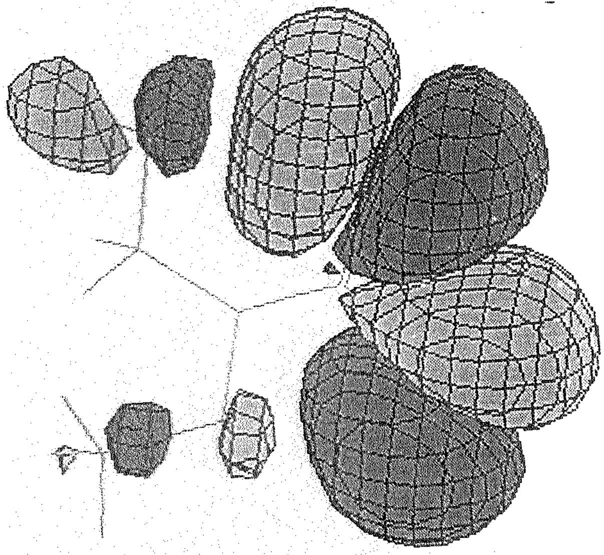


Fig. 7. The plot of HOMO for optimized I carbamate structure

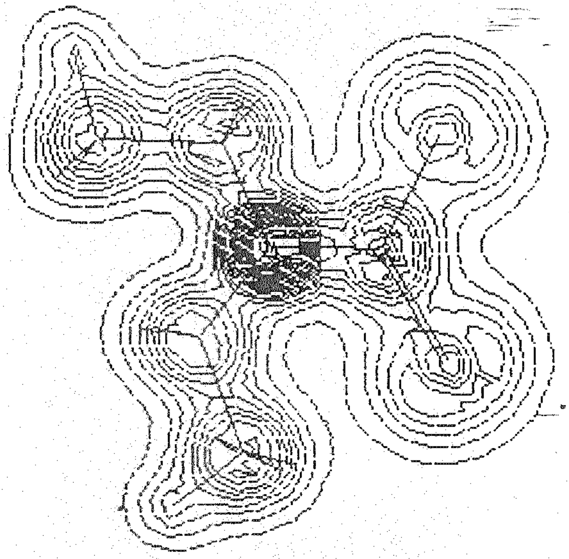
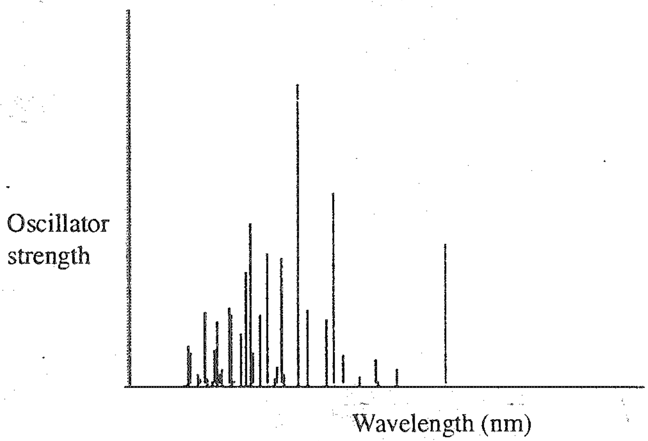


Fig. 8. The distribution of molecular charge density on the optimized I structure



Wave-length	Oscillator strength
308.49	0.371
201.18	0.500
193.39	0.175
175.67	0.199
166.80	0.777
152.10	0.336
137.40	0.348
131.32	0.426

Fig. 9. Theoretical UV spectra for II carbamate compound

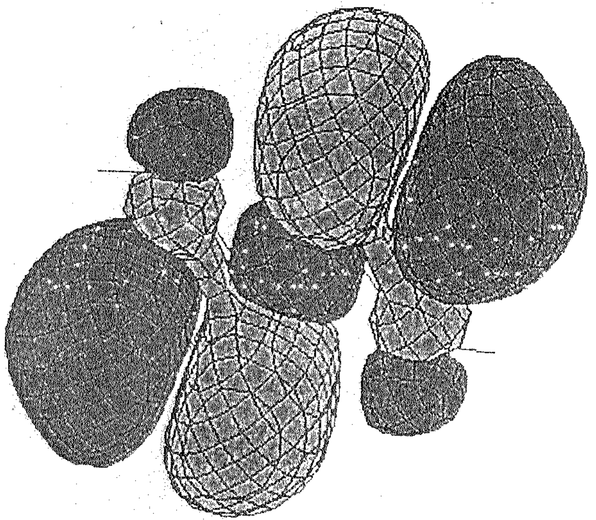


Fig. 10. The plot of HOMO for optimized II structure

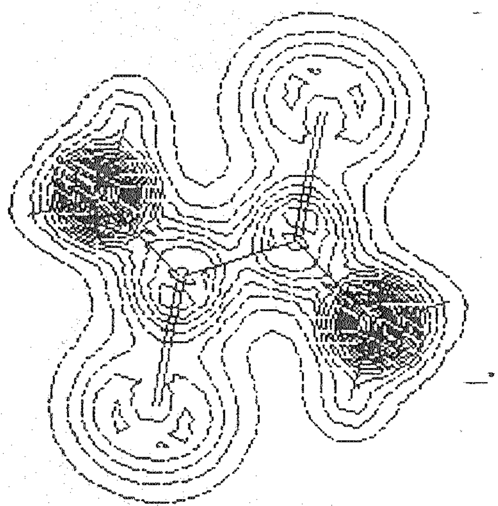


Fig. 11 The distribution of molecular charge density on the optimized II compound

REFERENCES

1. (a) D. Pascoe, Toxicology Studies in Biology, Edward Arnold Publishers, London, p. 231 (1983); (b) Zu D. Liu and R.C. Hidar, *Medical Res. Rev.*, **22**, 26 (2002); (c) I. Turcot, A. Stintzi, J. Xu and K.N. Raymond, *J. Biol. Inorg. Chem.*, **5**, 634,(2000).
2. W.R. Hariss, *Inorg. Bichem.*, **27**, 41 (1986).
3. S. Chasten, R.W. Evans, R. Garatt, B. Gorinsky, S. Hasnain, C. Horsburg and H. Jhoti, *J. Biochem.*, **27**, 5804 (1988).
4. P. Aisen and I. Listowsky, *Ann. Rev. J. Biochem.*, **49**, 357 (1980).
5. S. Baitley, *J. Biochem.*, **27**, 5704 (1988).
7. M.J.S. Dewar, E.G. Zoebisch, E.F. Healy and J.J.P. Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1985).
8. J.J.P. Stewart, MOPAC: A Semiempirical Molecular Orbital Program, in QCPE 455, **6**, 1990 (1983).
9. I. Sheikhshoaie and M.H. Mashhadizadeh, *Russ. J. Coord. Chem.*, **29**, 268 (2003).
10. I. Sheikhshoaie, *J. Coord. Chem.*, **53**, 463 (2003).

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