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# CONFORMATIONAL ANALYSIS OF METAL COMPLEXES OF N-ACETYL ALANINE METHYL ESTER BY CNDO/2 METHOD

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## ABSTRACT

*The CNDO/2 calculations on Li(I)/Na(I)-N-acetylalanine methyl ester do not give satisfactory agreement with ab initio results. The ab initio method predicts the chelate conformation with simultaneous binding of metal ion to $O_9-O_{10}$ to be the most stable conformation, and the binding energies to decrease in the order:*

$$O_9-O_{10} > O_8-O_{10} > O_{10} > O_9 > O_8 > O_8-O_9$$

*whereas CNDO/2 calculations predict preferential binding sites as following:*

$$O_8-O_{10} > O_9-O_{10} > O_8-O_9 > O_8 > O_{10} > O_9$$

In our previous study,[1] the conformation of N-acetylalanine methyl ester and its complexes with Li(I) and Na(I) were investigated by ab initio method with minimal GLO basis sets. The results indicated the most favourable conformation to be a chelate structure.

In this work, we have used one of the most applied semi-empirical calculation procedure, the CNDO/2 method.[2] This method seems to predict fairly satisfactory bond angles for the ligand,[3] but the calculated bond lengths are not in very good agreement with experimental values.[4] It has been reported[5-8] that CNDO/2 calculations fail on metal-ligand complex systems, but only few studies on such systems have been carried out so far. Therefore, conformational changes of N-acetylalanine methyl ester under metal ion influence were investigated by the CNDO/2 method in order to test the effectiveness of this method in predicting the conformation of metal-ligand complexes where the ligand contains both peptide and ester functional groups.

The geometries of N-acetylalanine methyl ester are the same as in our previous investigation.[1] Metal positions near $O_8$, $O_9$, $O_{10}$ (Figure 1) and in the chelate geometry (Figure 2) have been optimized by CNDO/2 method. All calculations were performed at the IBM 3031/08 computer of Chulalongkorn University.

Table 1 shows binding energies and optimized intermolecular geometrical parameters for all systems.

The binding energies show the order Li(I)..$O_8$ < Li(I)..$O_{10}$ < Li(I)..$O_9$ with the optimized distance Li(I)..$O_8$ being 1.98 Å, while the preferential binding site optimized by ab initio method is $O_{10}$ with a metal–ligand distance of 1.76 Å.

The chelate geometry in which Li(I) is binding to both $O_8-O_{10}$ (Figure 2b) with the optimized angles $\Theta$ , $\phi$ , $\psi$ = 0,180,78 and the dihedral angle ($C_5O_{10}C_2O_8$) = 106.1 degrees is predicted to be the most favourable conformation. The $O_8$..Li(I) and $O_{10}$..Li(I) distances are both 2.12 Å.The ab initio has shown however, that simultaneous binding to $O_9-O_{10}$ with a metal..O distance of 1.90 Å(Figure 2c) is the most stable arrangement.[1]

The CNDO/2 optimization also predicts the chelate geometry for the Na(I)–complex (Figure 2) to be more stable than any conformation where Na(I) binds to one acceptor atom only (Figure 1). The favoured binding site is $O_8-O_{10}$ (Figure 2b) corresponding to conformational angles of 0,180,76 and a dihedral angle of 107.3 degrees. The distances $O_8$..Na(I) and $O_{10}$..Na(I) are 2.13 Å. The most stable binding site obtained by ab initiocalculation[1] is $O_9-O_{10}$ with metal distances of 2.18 Å. CNDO/2 actually leads to Na(I) binding distances approximately identical to those for Li(I), which indicates the method to be rather unsuitable for such a system.

## SUMMARIZING

From the results one can conclude that the approximations inherent in the CNDO/2 method make this method unsuitable for the study of metal complex conformations. One of the main reasons for this failure is assumed to be the neglect of inner electrons, leading to artificial charge transfer and hence to much too high binding energies and wrong bond lengths and thus, to the wrong structure.

## ACKNOWLEDGEMENT

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## REFERENCES

1. Kokpol, S.U., Hannongbua, S.V., Limtrakul, J.L. and Rode, B.M.(1986). *Inorganica Chimica Acta* **125**, 107.
2. Pople, J.A., Sautry, D.P. and Segal, G.A.(1965). *J. Chem. Phys.* **43**, s136.
3. Klopman, G. and Leary, B.O.(1970). *Topics Current Chem.* **15**, 445.
4. Davidson, R.B., Jorgensen, W.L. and Allen, L.C.(1970). *J. Am. Chem. Soc.* **92**, 749.
5. Rode, B.M.(1975). *Monatsch. Chem.* **106**, 339.
6. Russegger, P., Lischka, H. and Schuster, P.(1972). *Theor. Chim. Acta* **24**, 191.
7. Rode, B.M. and Sagarik, K.P.(1982). *Chem. Phys. Lett.* **88**, 337.
8. Schuster, P.(1969). *Int. J. Quantum Chem.* **3**, 851.

## บทคัดย่อ

ผลการคำนวณโดยวิธี CNDO/2 ของสารประกอบ Li(I)/Na(I)–N–acetylalanine methyl ester ให้ผลไม่ตรงกับวิธี ab initio วิธี ab initio ทำนายว่าคอนฟอร์เมชันแบบคีเลทโดยที่โลหะไอออน ยึดเหนี่ยวกับ $O_9-O_{10}$ เป็นคอนฟอร์เมชันที่อยู่ตัวที่สุดและพลังงานยึดเหนี่ยวลดลงเป็นลำดับดังนี้

$$O_9-O_{10} > O_8-O_{10} > O_{10} > O_9 > O_8 > O_8-O_9$$

ขณะที่การคำนวณแบบ CNDO/2 ทำนายว่า ตำแหน่งการยึดเหนี่ยวที่เรียงลำดับตามความชอบของไอออนโลหะเป็นดังนี้

$$O_8-O_{10} > O_9-O_{10} > O_8-O_9 > O_8 > O_{10} > O_9$$


**TABLE 1** Energy data and optimized geometrical parameters calculated with CNDO/2 and ab initio methods

| system | binding site of metal ion | optimized distance M(I)..O (Å) | | binding energy (a.u.) | |
|---|---|---|---|---|---|
| | | CNDO/2 | ab initio | CNDO/2 | ab initio |
| Li(I) complex | $O_8$ | 1.93 | 1.85 | −0.2648 | −0.03354 |
| | $O_9$ | 2.00 | 1.80 | −0.1725 | −0.04277 |
| | $O_{10}$ | 2.04 | 1.76 | −0.1811 | −0.06596 |
| | $O_9-O_{10}$ | 2.12 | 1.90 | −0.7657 | −0.06930 |
| | $O_8-O_{10}$ | 2.12 | 1.91 | −1.0415 | −0.06649 |
| | $O_8-O_9$ | 2.12 | 2.05 | −0.5310 | −0.01425 |
| Na(I) complex | $O_8$ | 2.12 | 2.19 | −0.5575 | −0.02749 |
| | $O_9$ | 2.12 | 2.11 | −0.4268 | −0.03204 |
| | $O_{10}$ | 2.12 | 2.09 | −0.4344 | −0.05284 |
| | $O_9-O_{10}$ | 2.12 | 2.18 | −1.2034 | −0.06103 |
| | $O_8-O_{10}$ | 2.13 | 2.23 | −1.2515 | −0.05701 |
| | $O_8-O_9$ | 2.12 | 2.29 | −0.6165 | −0.01219 |

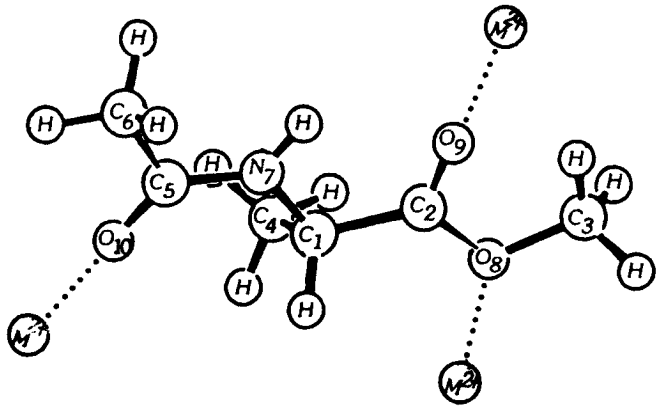
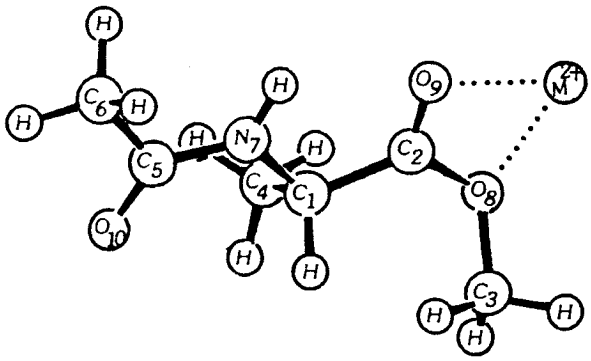
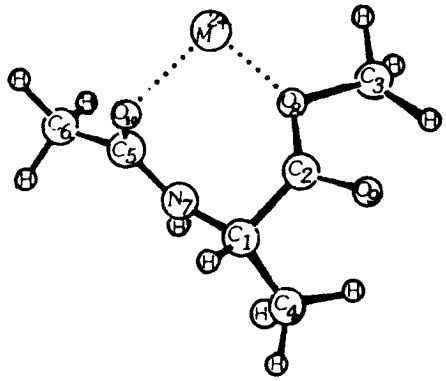


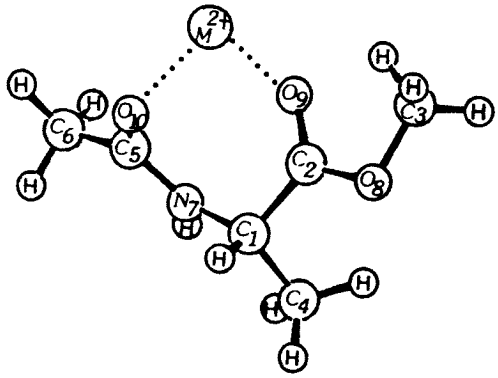

**Fig. 1** Conformation of metal/N–acetylalanine methyl ester complex where metal ion is binding to $O_8$, $O_9$ or $O_{10}$.




2a




2b




2c

**Fig. 2** Chelate conformation in which metal ion is binding to

| | |
|---|---|
| **2a** | $O_8-O_9$ |
| **2b** | $O_8-O_{10}$ |
| **2c** | $O_9-O_{10}$ |