Journal of Thermal Analysis, Vol. 44 (1995) 1493-1498

THERMAL STABILITIES, ELECTRONIC PROPERTIES AND STRUCTURES OF METFORMIN-METAL COMPLEXES

Molecular orbital investigation

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Abstract

The atomic superposition and electron delocalization molecular orbital (ASED-MO) theory was used to calculate structures and relative stabilities of metformin-metal complexes. The relative stabilities and decomposition pathways were discussed in terms of bond order, binding energy and the nature of charge on the central metal atom. The electronic transitions and their energy gaps were also studied. The optimization of the structures shows that the most stable state is distorted from planarity for Co^{II} and Ni^{II} complexes.

Keywords: complexes, metformin-metal complexes, molecular orbital investigation, thermal stabilities

Introduction

Metformin has clinical importance as an analgesic, antidiabetic and antimalarial [1, 2] agent. It also lowers the blood sugar level to the minimum physiological limit. Recently, cobalt(II), nickel(II) and copper(II)-metformin complexes (with stronger antibiotic properties than that of metformin) have been prepared and studied [3]. These complexes show a phase change upon heating in the solid state. The phase change has been investigated by means of DTA, TG, electrical conductivity, X-ray powder diffraction and IR spectroscopy [4, 5]. It was suggested that the phase transition observed may be attributed to geometrical isomerization (*cis-trans*) of the two chelate rings around the metal ion, and/or conformation changes (boat-chair) of the individual six-membered chelate rings. The aim of this paper is to use the atomic superposition and electron delocalization molecular orbital (ASED-MO) theory [6, 7] to calculate

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0368-4466/95/ $ 4.00

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structures and relative stabilities of metformin-metal complexes, and try to understand their electronic properties.

Experimental

Theoretical method

The ASED-MO technique is a semiempirical approach based on a partioning of molecular electronic density functions into atomic and delocalization components. Using the electrostatic theorem, the forces on the nuclei are integrated as the atoms are brought into a molecular configuration to yield a repulsive energy due to rigid atom densities and an attractive energy due to electron delocalization. The sum is the exact molecular binding energy. In the ASED-MO method the atom superposition energy (E_R) is calculated from the actual atomic densities whereas the electron delocalization attractive energy is approximated as the change in the total one-electron valence orbital energy (ΔE_{MO}) obtained by using a modified extended Hückel-Hamiltonian:

$$E = E_R + \Delta E_{MO}$$

This technique is used to predict molecular structures, stabilities, electronic properties and reactions pathways. The input data consist of valence state Slater orbital exponents [8] and ionization potentials [9] (VSIP) for the constituent atoms. These parameters are sometimes altered (particularly in treating ionic heteronuclear molecules) to ensure reasonably accurate calculations of ionicities and bond lengths in diatomic fragment molecules. In this way electronic charge-self-consistency is taken into account [7]. The diatomic parameters are used in studying larger molecules. In the present work unshifted atomic parameters are used for N, C and H atoms (Table 1). The ionization potentials of Co, Ni and Cu are increased by 2.9, 2.0 and 1.8 eV, respectively to give reasonable charge transfer to the ligands. The bond lengths given in this paper are variationally optimized to the nearest 0.01 Å and the bond angles to the nearest degree. The N–H bonds are kept constant in all calculations at 1.0 Å.

Measurement of thermal stability

The thermal stabilities of the complexes were measured in air with a Shimadzu XD-30 thermal analyzer at a heating rate of 10 deg·min^{-1}. The initial temperatures of decomposition (Table 2) were taken from the DTA curves.

Results and discussion

We started the ASED-MO calculations on a planar structure of metformin-metal complexes where the two chelate rings are in the same plane with the met-

Table 1 Atomic parameters used in the calculations: principle quantum numbers, *n*; ionization potentials, *IP* (eV); orbital exponents, ζ(au), and respective linear coefficients, *C*, for double- ζd orbitals

Atom	*s*			*p*			*d*					
	n	*IP*	ζ	*n*	IP	ζ	*n*	IP	ζ_1	C_1	ζ_2	C_2
Co	4	9.86	1.7500	4	6.93	1.450	3	11.0	5.55	0.5560	1.90	0.6461
Ni	4	9.44	1.8000	4	6.25	1.500	3	11.8	5.75	0.5683	2.00	0.6292
Cu	4	10.63	1.8500	4	6.84	1.550	3	13.3	5.95	0.5819	2.10	0.6120
C	2	16.59	1.6580	2	11.26	1.618						
N	2	20.33	1.9237	2	14.54	1.917						
H	1	13.60	1.2000									

Table 2 Binding energy (*B.E.*), energy gap (ΔE), charge density on the metal atom and DTA decomposition temperature for complexes

Compound	*B.E.*/eV	ΔE of $d_{x-y} \rightarrow \pi^*_{C=N}$ /eV calcd. (Found)[a]	Charge density on the metal atom	DTA $T_{decomp.}$ °C
CoL_2	4.619	0.631 (0.625)	+0.967	250
NiL_2	4.148	0.217 (0.15)	+0.982	240
CuL_2	2.176	1.907 (very low conductivity)	+0.909	210

[a] Refs [4] and [5], *L*=metformin.

al ion. For simplicity, we used an NH_2 group in our models instead of $N(CH_3)_2$. The central metal ion (with approximately square planar arrangement) is coordinated to two N_2-bidentate ligands (Fig. 1). There are two different kinds of bond for coordinated nitrogen in the bidentate ligand: the covalent M–N bond and the coordinate M–NH_2 bond. The strength of M–N bonds accounts for their predicted higher bond orders when compared to the M–NH_2 bonds. The opti-

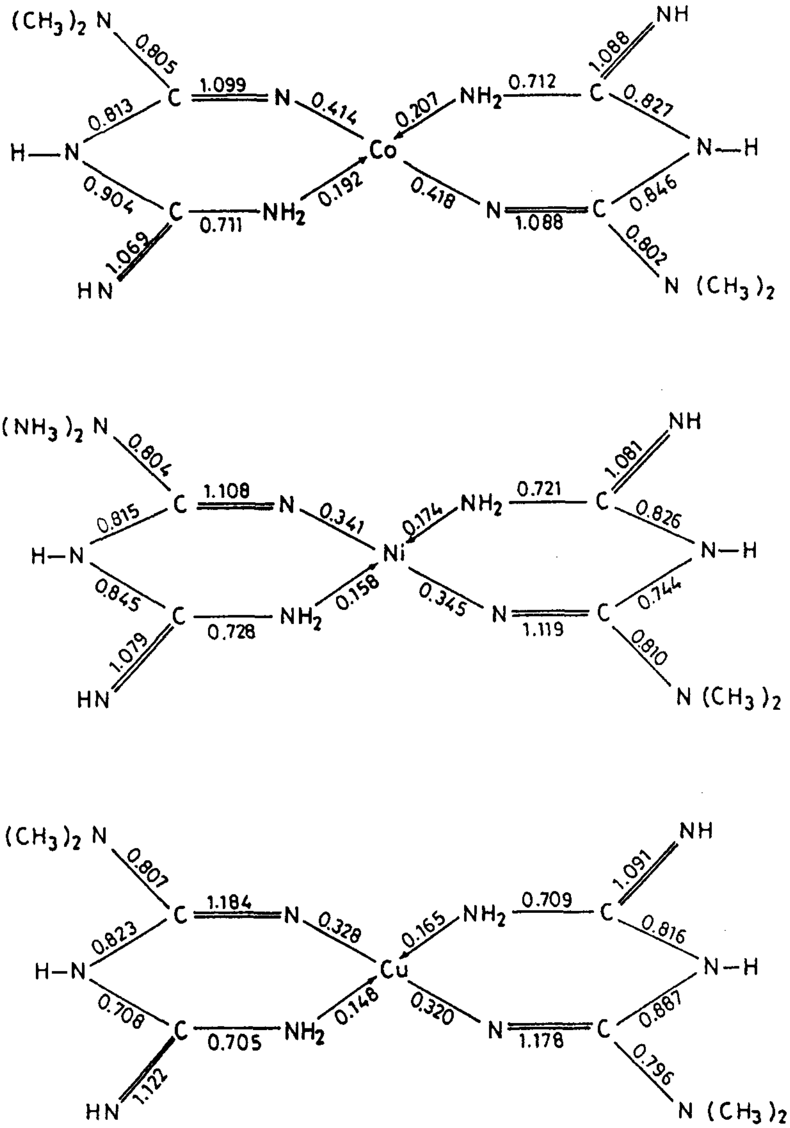

Fig. 1 Structures for the complexes with calculated bond orders

mized structures for complexes were calculated and gave bond orders as shown in Fig. 1. The M–N bond orders are nearly 0.416, 0.343 and 0.324 whereas M–NH_2 have values 0.199, 0.166 and 0.161 for cobalt, nickel and copper complexes, respectively. The other bonds (as CN) have higher bond orders ranging from 0.70 to 1.18. These values indicate that the weakest bond in the complexes is the coordinated M–NH_2, which suggests that decomposition may start by the scission of that bond, rather than the others. Moreover, the higher bond order for Co–NH_2 than that for nickel and copper is in agreement with the higher thermal stability of the cobalt complex as discussed later.

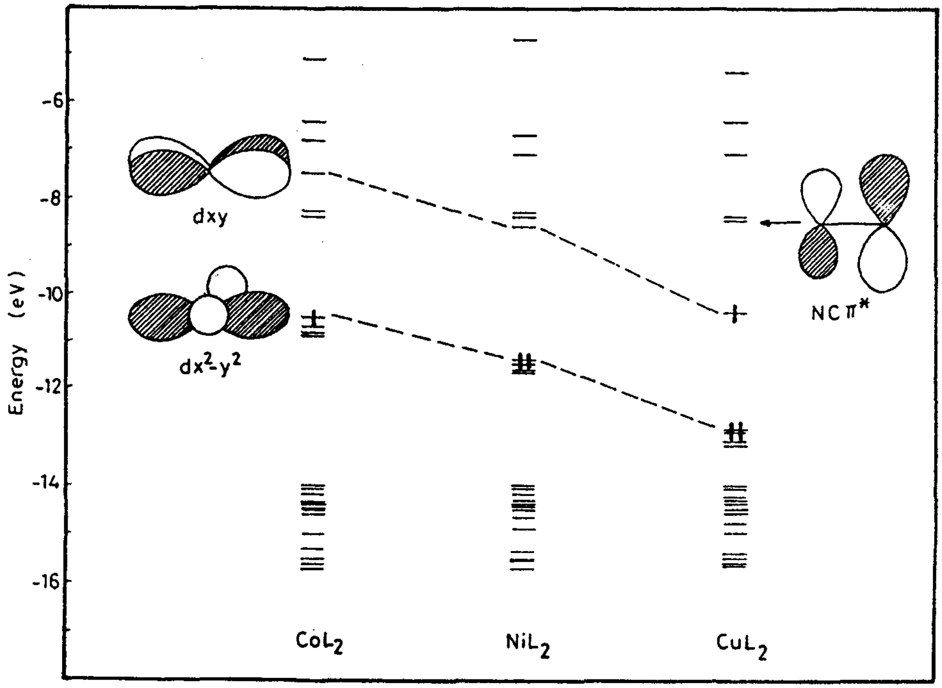

Fig. 2 Calculated electronic structures for metformin-metal complexes

The DTA data (Table 2) show that the initial temperature of decomposition (thermal stability) of the complexes follows the order Co>Ni>Cu. This order was confirmed by the values of calculated binding energy of the optimized structures (Table 2), which indicate that the structure of cobalt complex is by 0.47 and 2.44 eV more stable than that of nickel and copper complexes, respectively. The calculated electronic structures of the complexes (Fig. 2) show that the activation energies (ΔE) correspond to transition of electron from the metal d_{x-y} orbital to the $\pi^*_{C=N}$ orbital ($d_{x-y} \rightarrow \pi^*_{C=N}$). The calculation produced energy gaps of 0.631 and 0.217 eV for cobalt and nickel-complexes, respectively.

These values coincide closely with the experimental ones (0.625 and 0.15 eV) obtained from electrical conductivity [4, 5] data. For the copper-complex, a very low conductivity was found [5]. A high-energy gap is also obtained from the theoretical calculations (1.907 eV). The higher value is attributed to the stabilization of the highest occupied d_{x-y} orbital for copper(II) (Fig. 2).

Considering the calculated charge density on the metal atom (Table 2), it is suggested that there is a back donation from the metal *d*-orbitals to the $\pi^*_{C=N}$ orbital. This back donation will increase the M–N bond order and decrease that of the C=N. Figure 1 shows that the cobalt complex has the highest M–N bond order and the lowest C=N ones. This means that higher back donation is expected for the cobalt complex. However, the charge density on the cobalt atom is lower than that on nickel (Table 2). This could be explained by the stabilization of the $\pi^*_{C=N}$ orbital in the case of the cobalt complex, as shown in Fig. 2.

On the other hand, the optimization of the structures showed that the most stable state is distorted from planarity for cobalt and nickel complexes, whilst the copper complex has a slight distortion with keeping its planarity. Moreover, the calculations show that the two chelate rings are involved in the distortion for cobalt, but only one chelate ring is distorted for nickel.

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Zusammenfassung — Unter Einsatz der ASED-MO-Theorie wurden Strukturen und relative Stabilitäten von Metformin-Metallkomplexen berechnet. Als Funktion von Bindungsordnung, Bindungsenergie und der Art der Ladung des Zentralatoms wurden relative Stabilität und Zersetzungswege discutiert. Elektronenübergänge und deren verbotene Energiebänder wurden ebenfalls untersucht. Die Optimierung der Strukturen zeigte, daß für Co^{II}- und Ni^{II}-Komplexe im stabilsten Zustand eine Deformierung der Planarität auftritt.