WEB OF SCIENTIST: INTERNATIONAL SCIENTIFIC RESEARCH JOURNAL
ISSN: 2776-0979, Volume 4, Issue 3, Mar., 2023

ELECTRONIC STRUCTURES AND REACTIVITY OF EIGHT MIXED-LIGAND COMPLEXES OF CALCIUM ACETATE BY A QUANTUM-CHEMICAL METHOD

Jurayeva Umida Boxodir kizi
Turakulov Jakhongir Ulugbekovich
Norbutayeva Kanoat Pulatovna
Kenjaeva Munavvarbonu Abdumannon kizi
Tukhtamurodova Zilola Khamidjon kizi
Jizzakh Polytechnic Institute, jakhongir.turakulov@gmail.com

ABSTRACT

In the present work, the results of calculations of the electronic structure of eight mixed-amide complex compounds of calcium acetate with semi-empirical PM3 methods using the molecular orbital method are carried out, and the energy characteristics of eight new coordination compounds are compared. The calculations were carried out by the semi-empirical PM3 method in the Hyper-Chem.8-07 software package.

Keywords: Coordination compounds, composition, ligands, mixed amide, structure

Previously, the authors of [1-8] synthesized some new coordination compounds, studied their composition, properties, and methods of synthesis.

We have calculated the electronic structure of eight mixed-amide coordination compounds of calcium acetate using the semi-empirical PM3 method in the framework of the self-consistent field model using the molecular orbital method (MO LCAO), which makes it possible to take into account hydrogen bonds in the calculation.

Comparison of the energy characteristics of eight complex compounds shows that the total energy values are close. While the values of bond energies, electron energy, internuclear energy, heat of formation, energies of the upper occupied and lower vacant molecular orbitals differ significantly. The bond lengths and charges on the atoms also differ. An increase in the value of the difference Δ = HOMO-LUMO indicates that complex calcium compounds are more reactive to nucleophilic agents and this increases the stimulating activity of plant growth more than calcium compounds of a different composition.

As is known, polyfunctional ligands containing several donor atoms, when coordinated with the central atom, exhibit competition with respect to each other, the study of this problem and the establishment of the competitive ability of ligands is an urgent task of coordination chemistry. Studying this problem by traditional methods requires a lot of time. Therefore, at present, more and more attention is paid to the use of computational programs in solving such problems. It should be noted that organic molecules and ligands, when coordinated with the central atom, change their properties, and at the same time, the influence of electron pairs of ligands leads to the appearance in coordination compounds of their inherent properties.

Eight mixed-ligand coordination compounds of calcium acetate became the objects of our quantum-chemical studies. The calculations were carried out by the semi-empirical PM3 method in the Hyper-Chem.8-07 software package (table 1).

Using the methods of elemental, derivatographic and X-ray phase analyzes and IR absorption spectra, the composition, individuality and methods of coordination of amide molecules and acetate fragments of the following compounds were established $Ca(CH_3COO)_2 \cdot CH_3CONH_2 \cdot NH_2CONHNO_2$ (1), $Ca(CH_3COO)_2 \cdot HCONH_2 \cdot NC_5H_4CONH_2 \cdot H_2O$ (2), $Ca(CH_3COO)_2 \cdot CS(NH_2)_2 \cdot NC_5H_4CONH_2$ (3), $Ca(CH_3COO)_2 \cdot CH_3CONH_2 \cdot CO(NH_2)_2 \cdot H_2O$ (4), $Ca(CH_3COO)_2 \cdot HCONH_2 \cdot NC_5H_4COOH \cdot H_2O$ (5), $Ca(CH_3COO)_2 \cdot CO(NH_2)_2 \cdot C_6H_5CONH_2 \cdot H_2O$ (6), $Ca(CH_3COO)_2 \cdot CS(NH_2)_2 \cdot C_6H_5CONH_2 \cdot H_2O$ (7) and $Ca(CH_3COO)_2 \cdot NC_5H_4CONH_2 \cdot C_6H_5CONH_2$ (8).

In order to determine the geometry of the coordination sites, we carried out a quantum chemical calculation of several possible structures of the coordination site.

Table 1 Calculation of Energy Parameters of Complex Compounds of Calcium Acetate with Amides of Composition $Ca(CH_3COO)_2 \cdot CH_3CONH_2 \cdot H_2NCONHNO_2$ (1), $Ca(CH_3COO)_2 \cdot HCONH_2 \cdot NC_5H_4CONH_2 \cdot H_2O$ (2), $Ca(CH_3COO)_2 \cdot CS(NH_2)_2 \cdot NC_5H_4CONH_2 \cdot H_2O$ (3) and $Ca(CH_3COO)_2 \cdot CH_3CONH_2 \cdot CO(NH_2)_2 \cdot H_2O$ (4)

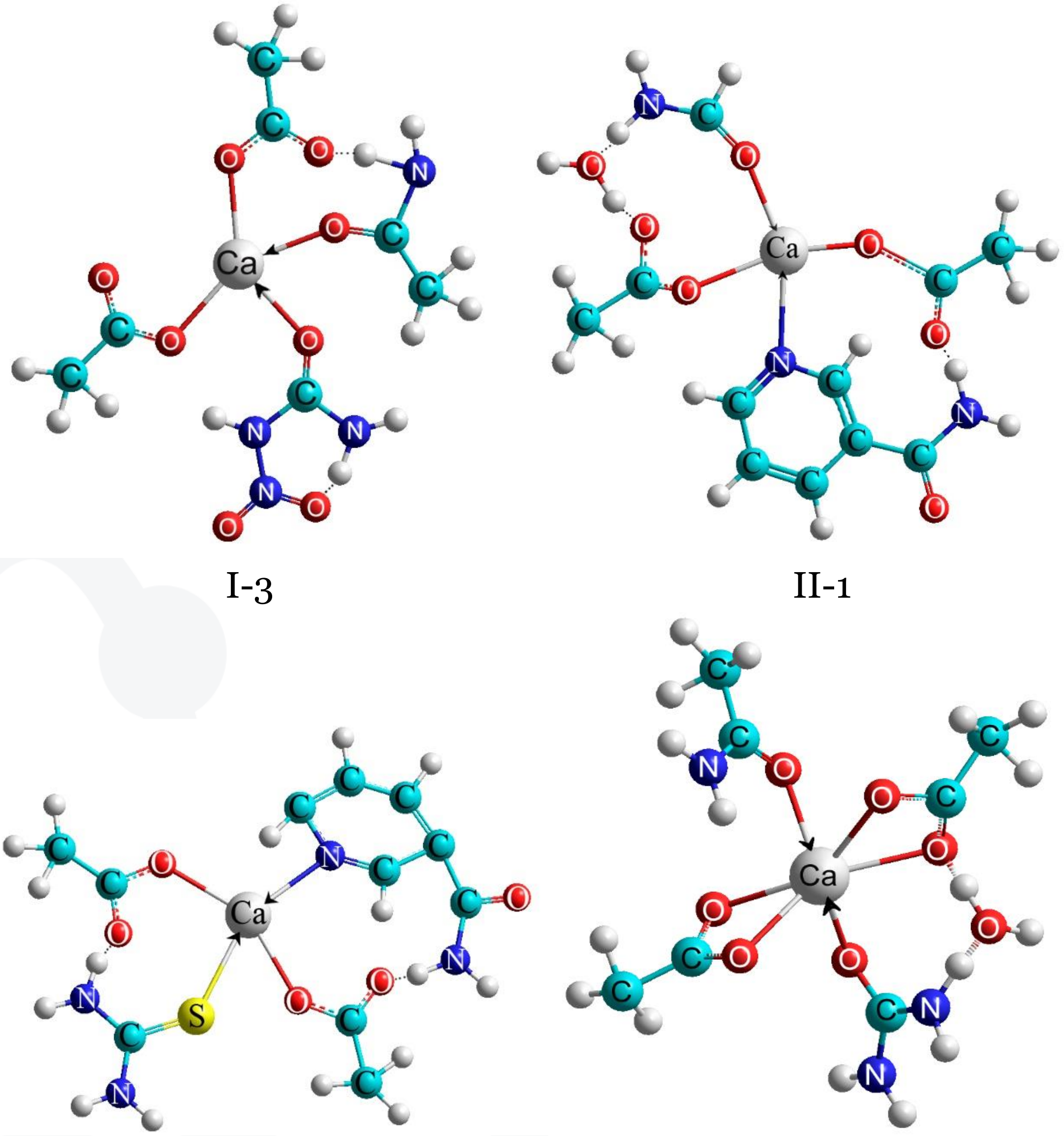
Compounds	**1-3**	**2-1**	**3-2**	**4-5**
Total energy, kcal/mol	-94235,157	-95820,056	-89916,861	-84897,536
Total energy (au)	-150,173	-152,699	-143,292	-135,293
Binding energy, kcal/mol	-3749,235	-4476,657	-4354,601	-3814,438
Energy of isolated atoms, kcal/mol	-90485,922	-91343,399	-85562,260	-81083,099
Electronic energy, kcal/mol	-646020,116	-723869,623	-688114,498	-579991,486
Energy of internuclear interaction, kcal/mol	551784,959	628049,567	598197,636	495093,950
Heat of formation, kcal/mol	-852,505	-912,620	-782,384	-933,961
Gradient	0,009	0,009	0,007	0,008
HOMO	-10,151	-9,655	-8,918	-9,936
LUMO	-0,855	-1,198	-1,560	-0,486
HOMO-LUMO	-9,296	-8,457	-7,358	-9,450

For the complex compound $Ca(CH_3COO)_2 \cdot CH_3CONH_2 \cdot NH_2CONHNO_2$ (I), four tetrahedral structures and four octahedral environments with different ways of coordinating acetate groups and the presence of intramolecular hydrogen bonds have been proposed. Of the eight structures, the structure turned out to be energetically favorable in terms of the heat of formation, where the central calcium atom is surrounded by a tetrahedral site due to the monodentate coordination of acetate fragments and donor-acceptor coordination of acetamide and nitrocarbamide molecules through the oxygen atom of the carbonyl group. Intramolecular hydrogen bonds are carried out at the expense of oxygen atoms of one acetate group and hydrogen of the amine group of acetamide. Another intramolecular bond is manifested by the oxygen and hydrogen atoms of the nitrocarbamide molecule (I-3).

Table 2 Calculation of Energy Parameters of Complex Compounds of Calcium Acetate with Amides of Composition $Ca(CH_3COO)_2 \cdot HCONH_2 \cdot NC_5H_4COOH \cdot H_2O$ (5-6), $Ca(CH_3COO)_2 \cdot CO(NH_2)_2 \cdot C_6H_5CONH_2 \cdot H_2O$ (6-6), $Ca(CH_3COO)_2 \cdot CS(NH_2)_2 \cdot C_6H_5CONH_2 \cdot H_2O$ (7-6) and $Ca(CH_3COO)_2 \cdot NC_5H_4CONH_2 \cdot C_6H_5CONH_2$ (8-6)

Compounds	**5-6**	**6-6**	**7-6**	**8-6**
Total energy, kcal/mol	-90977.3719555	-91781.2137045	-89277.6492478	-106140.4208132
Total energy (au)	-144.981652832	-146.262656041	-142.272972616	-169.145506306
Binding energy, kcal/mol	-4173.1390015	-4545.2557695	-4483.5744808	-5476.1348222
Energy of isolated atoms, kcal/mol	-86804.2329540	-87235.9579350	-84794.0747670	-100664.2859910
Electronic energy, kcal/mol	-637050.0134698	-693690.3242680	-681572.093026	-914903.1533332
Energy of internuclear interaction, kcal/mol	546072.6415143	601909.1105635	592294.4437784	808762.7325200
Heat of formation, kcal/mol	-878.4080015	-869.8877695	-801.3654808	-842.1128222
Gradient	0.0054863	0.0099021	0.0083918	0.0069232
HOMO	-10.218055	-10.084900	-8.743964	-9.956254
LUMO	-2.153327	-1.111696	-1.653750	-1.367209
HOMO-LUMO	-8,064728	-8,9732	-7,090214	-8,58905

For the complex compound $Ca(CH_3COO)_2 \cdot HCONH_2 \cdot NC_5H_4CONH_2 \cdot H_2O$ (II), four tetrahedral environments and four octahedral structures have also been proposed. In terms of the heat of formation, the most energetically favorable structure turned out to be one in which the calcium ion is surrounded by oxygen atoms of formamide and nicotinamide molecules and two oxygen atoms from two acetate groups and exhibits a tetrahedral environment. The water molecule is held due to the presence of two bonds between the oxygen and hydrogen atoms of water with the participation of oxygen and hydrogen atoms of the formamide molecule and the acetate group, the intramolecular hydrogen bond is carried out between the oxygen and hydrogen atoms with the participation of the acetate group and the nicotinamide molecule (II-1).

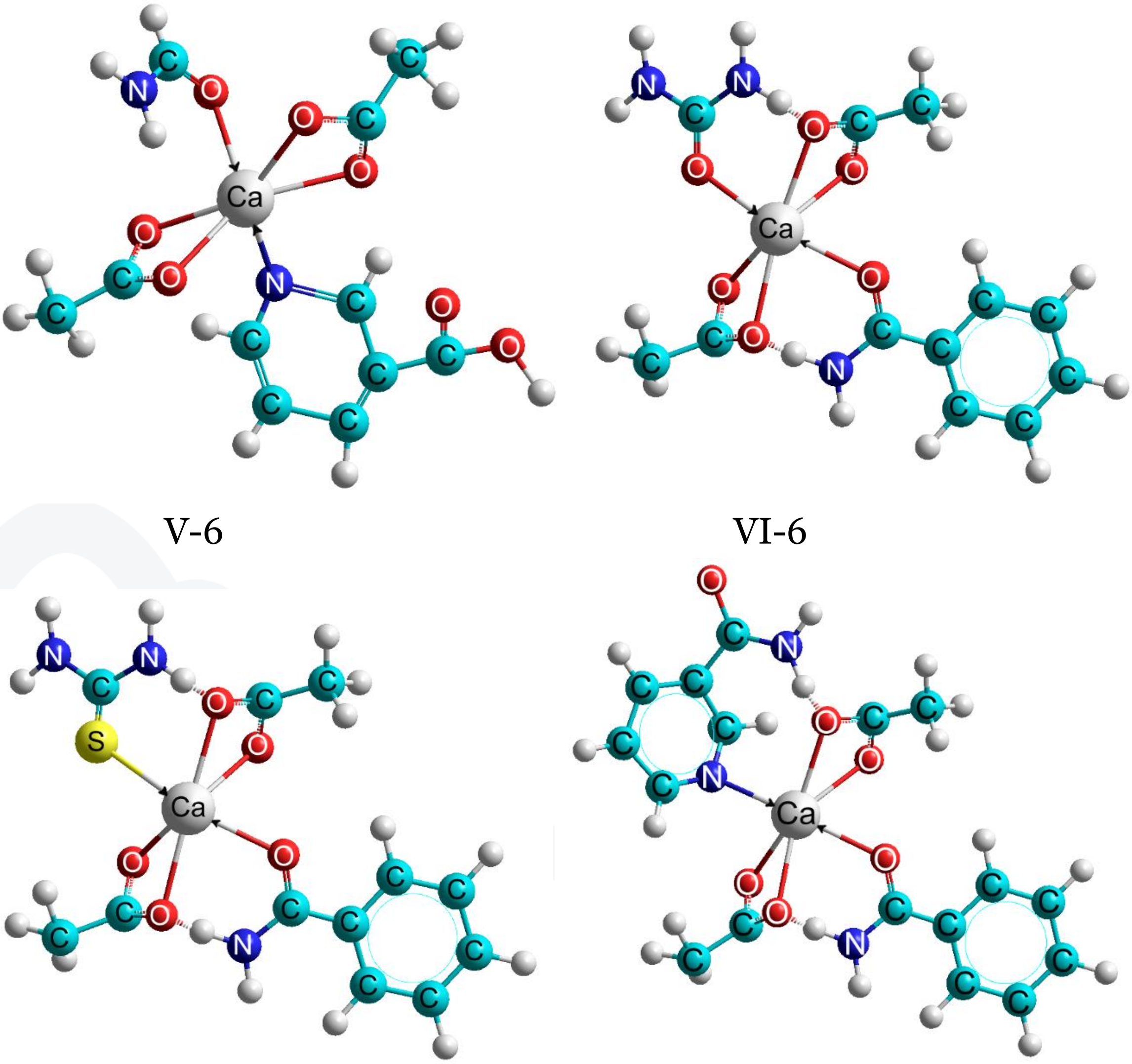


I-3 II-1

III-2 IV-5

Fig. 2. Spatial models of molecules of compositions
$Ca(CH_3COO)_2{\cdot}CH_3CONH_2{\cdot}H_2NCONHNO_2$ *(I-3)*, $Ca(CH_3COO)_2{\cdot}HCONH_2{\cdot}NC_5H_4CONH_2{\cdot}H_2O$ *(II-1)*, $Ca(CH_3COO)_2{\cdot}CS(NH_2)_2{\cdot}NC_5H_4CONH_2$ *(III-2) and* $Ca(CH_3COO)_2{\cdot}CH_3CONH_2{\cdot}CO(NH_2)_2{\cdot}H_2O$ *(IV-5).*

For the complex compound $Ca(CH_3COO)_2{\cdot}CS(NH_2)_2{\cdot}NC_5H_4CONH_2$ (III), four tetrahedral and four octahedral environments have been proposed. According to the value of the heat of formation, the most energetically favorable structure turned out to be the structure where the central calcium atom is surrounded by a tetrahedral site, i.e. sulfur atoms of thiocarbamide, nitrogen of the pyridine ring, nicotinamide molecule and two atoms of monodentate, acetate fragments. There are two intramolecular bonds involving oxygen atoms, two acetate groups, and molecules of thiocarbamide and nicotinamide (III-2).



V-6 VI-6

VII-6 VIII-6

Fig.3. Spatial model of molecules of coordination compounds of compositions $Ca(CH_3COO)_2{\cdot}HCONH_2{\cdot}NC_5H_4COOH$ *(V-6).* $Ca(CH_3COO)_2{\cdot}CO(NH_2)_2{\cdot}C_6H_5CONH_2$ *(VI-6).* $Ca(CH_3COO)_2{\cdot}CS(NH_2)_2{\cdot}C_6H_5CONH_2$ *(VII-6).* $Ca(CH_3COO)_2{\cdot}NC_5H_4CONH_2{\cdot}C_6H_5CONH_2$ *(VIII-6).*

For the complex compound $Ca(CH_3COO)_2{\cdot}CH_3CONH_2{\cdot}CO(NH_2)_2{\cdot}H_2O$ (IV), four tetrahedral and four octahedral environments have been proposed. According to the value of the heat of formation, the structure turned out to be the most energetically favorable, where the central calcium atom is surrounded by an octahedral site due to the coordination of the monodentate coordination of the molecules of acetamide, urea and four oxygen atoms in the trans position of two acetate groups with bidentate cyclic coordination. The water molecule is held by the formation of hydrogen bonds involving the oxygen and hydrogen atoms of water, the carbamide amide group and one acetate fragment (IV -5).

For the complex compound $Ca(CH_3COO)_2 \cdot HCONH_2 \cdot NC_5H_4COOH$ (V), four tetrahedral structures and four octahedral environments with different ways of coordinating acetate groups and the presence of intramolecular hydrogen bonds have been proposed. Of the eight structures, the structure turned out to be energetically favorable in terms of the heat of formation, where the central calcium atom is surrounded by an octahedral site due to the bidentate coordination of acetate fragments and the donor-acceptor coordination of formamide and nicotinic acid molecules through the oxygen atoms of the carbonyl groups. There are no intramolecular hydrogen bonds (V-6).

For the complex compound $Ca(CH_3COO)_2 \cdot CO(NH_2)_2 \cdot C_6H_5CONH_2$ (VI), four tetrahedral environments and four octahedral structures have also been proposed. According to the value of the heat of formation, the structure turned out to be the most energetically favorable, where the calcium ion is surrounded by oxygen atoms of urea and benzamide molecules and four oxygen atoms from two acetate groups and exhibits an octahedral environment. Intramolecular hydrogen bonding is carried out between oxygen and hydrogen atoms with the participation of acetate and amine groups, acetic acid anions and carbamide and benzamide molecules (VI-6).

For the complex compound $Ca(CH_3COO)_2 \cdot CS(NH_2)_2 \cdot C_6H_5CONH_2$ (VII), four tetrahedral and four octahedral environments have been proposed. According to the value of the heat of formation, the most energetically favorable structure turned out to be the structure where the central calcium atom is surrounded by an octahedral site, i.e. sulfur atoms of thiocarbamide, oxygen of the carbonyl group, a benzamide molecule and four atoms of bidentate, acetate fragments. There are two intramolecular bonds involving oxygen atoms, two acetate groups, an amine group hydrogen atom, and thiocarbamide and nicotinamide molecules (VII-6).

For the complex compound $Ca(CH_3COO)_2 \cdot C_6H_5CONH_2 \cdot NC_5H_4CONH_2$ (VIII), four tetrahedral and four octahedral environments have been proposed. According to the value of the heat of formation, the structure turned out to be the most energetically favorable, where the central calcium atom is surrounded by an octahedral site due to the monodentate coordination of the benzamide molecule and due to the coordination of nicotinamide with the participation of the nitrogen heteroatom of the pyridine ring, and four oxygen atoms in the cis position of two acetate groups with bidentate cyclic coordination . Intramolecular hydrogen bonding is carried out between oxygen and hydrogen atoms with the participation of acetate groups and molecules of benzamide and nicotinamide (VIII-6).

The electronic structure of the structure and the reactivity of eight mixed-ligand complexes of calcium acetate were analyzed by the quantum-chemical method. The values of the heat of formation, electron energy, nuclear repulsion, ionization potential, HOMO and LUMO energies were determined. The features of the environment of the central atom depending on the nature of the donor atoms are revealed.

REFERENCES:

1. Turakulov J. U. Synthesis, properties and application of new coordination compounds of calcium acetate with some amides, benzoic and nicotinic acids. diss. according to chem //Sciences.(PhD)-Tashkent. – 2019.
2. Ulugbekovich, Turakulov Jakhongir. "Complex compounds of calcium acetate with nitrocarbamide." *Austrian Journal of Technical and Natural Sciences* 7-8 (2018): 67-72.
3. Туракулов Ж. У. и др. Термическое исследование смешанноацетамидных комплексных соединений ацетата кальция //Химия и химическая технология. – 2015. – №. 2. – С. 22-26.
4. Гулбаев Я. И., Туракулов Ж. У., Азизов Т. А. РЕНТГЕНОФАЗОВОЕ И ИК-СПЕКТРОСКОПИЧЕСКОЕ ИССЛЕДОВАНИЕ ОДНОРОДНЫХ И СМЕШАННОЛИГАНДНЫХ КОМПЛЕКСНЫХ СОЕДИНЕНИЙ АЦЕТАТА КАЛЬЦИЯ //Universum: химия и биология. – 2022. – №. 6-2 (96). – С. 60-63.
5. Туракулов Ж. У., Азизов Т. А. Синтез и исследование координационных соединений ацетата кальция с ацетамидом //Universum: химия и биология. – 2018. – №. 9 (51). – С. 18-24.
6. Туракулов Ж. У. и др. Однородные координаационные соединения ацетата магния с карбамидом и тиокарбамидом //Химия и химическая технология. – 2016. – Т. 52. – №. 2. – С. 17-21.
7. Lobar S., Taxir A., Mavluda I. ACETAMIDE AND NICOTINIC ACID OF MONOTYPE LIGAND COORDINATION COMPOUNDS OF ZINC NITRATE //Universum: химия и биология. – 2021. – №. 5-2 (83). – С. 74-77.
8. Turakulov Jakhongir Ulugbekovich, Tukhtamurodova Zilola Khamidjon kizi, Norbutayeva Kanoat Pulatovna, Ismailov Akmal Aslanbekovich, & Tojiboyeva Feruzakhon Mamajonovna. (2023). Coordination Compounds Of Calcium Acetate With Some Ligands. *Texas Journal of Engineering and Technology*, *18*, 12–18. Retrieved from https://zienjournals.com/index.php/tjet/article/view/3571.