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Quantum chemical study of structural properties for copper halide complexes with protonated acetamides

Abstract. *The chemistry of copper complexes, which contain organic ligands, is one of the important research areas for modern chemical technology and science. Herein, the copper complexes coordinated with organic ligands are playing an important role in many applications including crop production, animal husbandry, and pharmacology. At this point, the coordination of copper halides with acetamides are good research object for fundamental research. The purpose of the article is to perform quantum chemical calculations, and analysis for the coordination of copper halides (chloride, bromide) with acetamides using HyperChem software and PM3 method. The study helps with the rational design of copper halide complexes with acetamides.*
Keywords: *copper halides, acetamides, quantum chemical calculations, PM3 method, HyperChem.*

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Introduction

The transition metals are chemical elements that are located in the d-block of the periodic table and have the following general structures in their configurations $(n-1)d^{1-10}ns^{1-2}$, where n is the periodic number [1-5]. The transition metals are classified as 3d, 4d, and 5d elements, where copper is a 3d transition metal. Copper has unique properties including good electric conductivity, high density, high strength, high boiling, and melting point strength [5-12]. In addition, multiple coordination of organic ligands with copper metal is forming complexes called "coordination compounds", where coordination bonds are present between organic ligands and copper metal [9-15]. The chemistry of copper halide complexes with the coordination of organic ligands is one of the interesting research areas of scientists.

At the same time, the two-electron donor centers in amide molecules such as carbonyl oxygen, and amine nitrogen provide them with unique chemical and physical properties and become special objects of basic chemical research [12-16]. Moreover, several complex compounds of transition metals coordinated with organic ligands are implemented in organic and inorganic synthesis [14-18]. Herein, the quantum chemical study of copper halide complexes with coordination of organic ligands are important to study by various software such as Gaussian16, HyperChem, Materials Studio, Spartan, and others [15-18]. In addition, the copper halide complexes coordination with the nitrogen and oxygen atoms of acetamide is very important which determine the physical and chemical properties of obtained copper halide complexes [18-22]. In this regard, the quantum chemical parameters such as optimized structures, bond length, bond angles, dihedral angles, molecular electrostatic maps, molecular orbitals for various copper halide complexes coordinated with organic ligands are highly important to study and understand their structural properties in this current research work [19-25].

The article is aimed at determining the physicochemical properties of copper halides (chloride, bromide) coordinated with acetamides via quantum chemical calculations. Consequently, we will

construct various computational models of copper halides coordinating with acetamide as complexes for our computational work. At this stage, copper halides will be coordinated with acetamide via two options such as i) by nitrogen atom of an amine group, and ii) by oxygen of carbonyl group. After that, the quantum chemical properties including optimized structures, bond length, bond angles, charge distributions, molecular orbital distributions, and energies will be studied for copper halides (chloride, bromide) with acetamide structures.

Methods and materials

Calculations were performed using the semi-empirical quantum chemical PM3 method, which is part of the software package MOPAC 7 and HyperChemPro 8.0. The 2D structures of acetamide, protonated acetamide, and copper halides with protonated acetamides were illustrated in Figure 1. The geometry optimizations were performed via HyperchemPro 8.0 software using the PM3 method to obtain optimized structures, bond length, bond angles, charge distributions, molecular orbital distributions, and energies of designed systems.

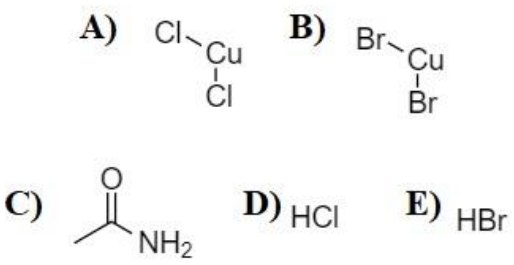

Figure 1. The 2D structures of A) Copper chloride, B) Copper Bromide, C) Acetamide, D) Hydrochloric acid, and E) Hydrobromic acid

The chemical structures of copper chloride, copper bromide, acetamide, hydrochloric acid, and hydrobromic acid were illustrated in Figure 1. Moreover, the designed systems to study the electronic structural properties of copper halide complexes with acetamide were illustrated in Table 1. As can be seen from Table 1, pure acetamide was designed for quantum chemical calculation to understand the structural properties of unprotonated acetamide. Next, acetamide was coordinated with hydrochloric acid to design protonated acetamide with hydrochloric acid. Thirdly, acetamide was coordinated with hydrobromic acid to design protonated acetamide with hydrobromic acid. Fourthly, unprotonated acetamide was coordinated with copper (II) chloride to study the energetic, electronic, and geometrical properties of copper (II) chloride coordinated with unprotonated acetamide. Fifthly, unprotonated acetamide was coordinated with copper (II) bromide to study the energetic, electronic, and geometrical properties of copper (II) bromide coordinated with unprotonated acetamide. After that, protonated acetamide with hydrochloric acid was coordinated with copper (II) chloride to study the energetic, electronic, and geometrical properties of copper (II) chloride coordinated with protonated acetamide with hydrochloric acid. Finally, protonated acetamide with hydrobromic acid was coordinated with copper (II) bromide to study the energetic, electronic, and geometrical properties of copper (II) bromide coordinated with protonated acetamide with hydrobromide acid as can be seen in Table 1.

Table 1

The description of designed systems in our current work

Acetamide	HCl	HBr	$CuCl_2$	$CuBr_2$	Purpose
1	-	-	-	-	Unprotonated Acetamide
1	1	-	-	-	Protonated Acetamide
1	-	1	-	-	Protonated Acetamide
1	-	-	1	-	$CuCl_2$ with unprotonated acetamide
1	-	-	-	1	$CuBr_2$ with unprotonated acetamide
1	1	-	1	-	$CuCl_2$ with protonated acetamide
1	-	1	-	1	$CuBr_2$ with protonated acetamide

Results. *Identification of energetic, electronic, and geometrical parameters of unprotonated and protonated acetamide.* As mentioned above, the structural properties of unprotonated and protonated acetamide were studied in this section by HyperChem software using the PM3 method. As can be seen from Figure 2, the optimized structures of unprotonated and protonated acetamide were illustrated.

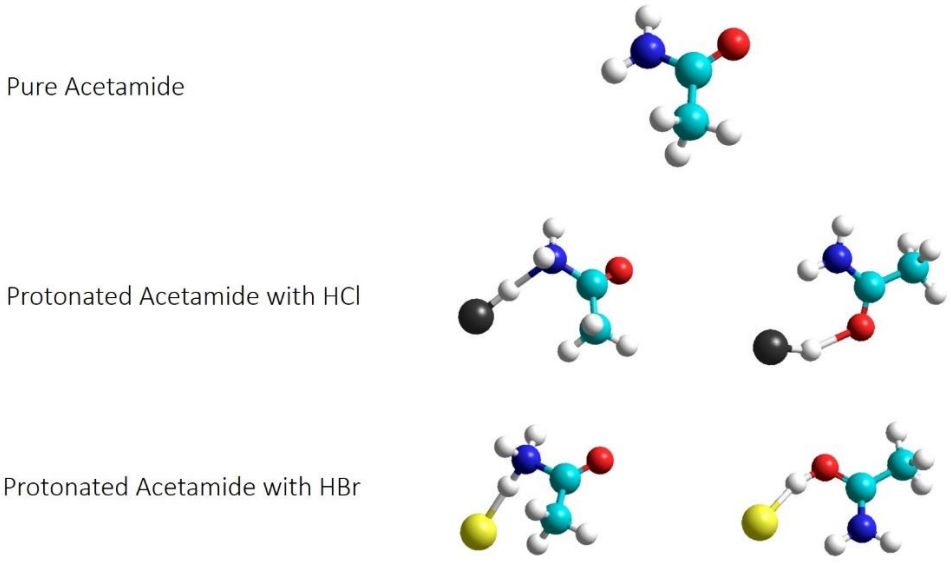

Figure 2. The quantum chemical calculation is based on optimized structures for pure acetamide, protonated acetamide with HCl, and finally protonated acetamide with HBr.
Color keys: nitrogen: blue; gray: hydrogen; violent: carbon; oxygen: red; chloride: black; bromine: yellow.

Moreover, the results of optimization including energies, dipole moments, charges, distances, and angles were illustrated in Table 2. The quantum chemical parameters for acetamide, HCl coordinated with N atom of acetamide, HCl coordinated with O atom of acetamide, HBr coordinated with N atom of acetamide, HBr coordinated with O atom of acetamide were illustrated in Table 2.

Table 2

Parameters of optimization for unprotonated and protonated acetamide

Parameters	Acetamide	Acetamide+HCl by N	Acetamide+HBr by N	Acetamide+HCl by O	Acetamide+HBr by O
-E (total), kcal/mol	-17769.1	-25446.40	-26288.3	-25448.1	-26285.00
μ, D	3.78	3.78	7.591	5.067	10.79
q (O)	-0.321	-0.321	-0.261	-0.431	-0.260
q (N)	-0.014	-0.014	0.366	0.006	0.181
q (C)	0.219 -0.142	0.219 -0.142	0.203 -0.166	0.238 -0.129	0.193 -0.123
r (C=O), nm	1.2164	1.2164	1.2073	1.2369	1.2921
r (C-C), nm	1.5011	1.5011	1.4927	1.5031	1.5008
r (C-N), nm	1.4516	1.4516	1.5152	1.3874	1.3526
r (O-HX, X is Cl or Br), nm	-	-	-	1.7447	1.0371
r (N-HX, X is Cl or Br), nm	-	1.7505	1.1172	-	-
Angle, O-C-N	117.4859	117.4859	115.5702	117.2532	122.1379
Angle, O-C-C	125.5723	125.5723	128.3617	123.7668	117.0125
Angle, O or N - H-X (X is Cl or Br)	-	170.1912	163.9789	152.7383	161.5919

Identification of energetic, electronic, and geometrical parameters of unprotonated and protonated acetamide coordinated with copper (II) halides. As mentioned above, the quantum chemical calculation results including energies, dipole moments, charges, bond length, and bond angles for copper halide coordination with unprotonated and protonated acetamide were discussed in this part. Herein, the quantum chemical parameters for copper chloride coordinated with hydrochloric acid by nitrogen and oxygen atoms, copper bromide coordinated with hydrobromic acid by nitrogen and oxygen atoms are discussed in detail. The optimized structures for the copper halide (chloride or bromide) coordinated with pure acetamide, copper chloride coordinated with protonated acetamide with HCl, and finally, copper bromide coordinated with protonated acetamide with HBr were illustrated in Figure 3.

The quantum chemical properties for copper halide (chloride or bromide) coordinated with pure acetamide was illustrated in Table 3. The quantum chemical properties for copper chloride coordinated with protonated acetamide with HCl, and finally, copper bromide coordinated with protonated acetamide with HBr were illustrated in Table 4.

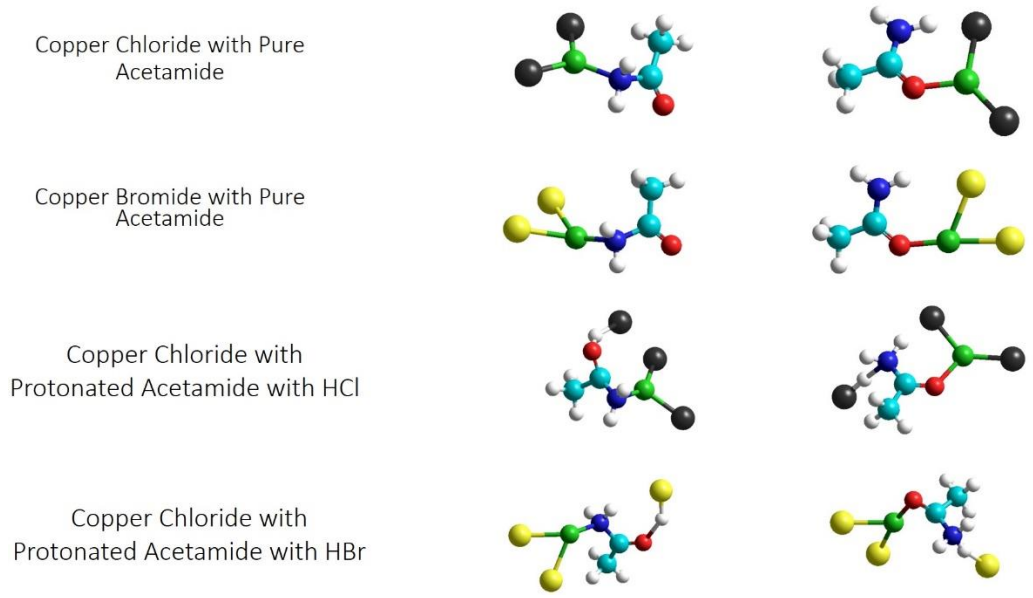

Figure 3. The quantum chemical calculation is based on optimized structures for copper halide (chloride or bromide) coordinated with pure acetamide, copper chloride coordinated with protonated acetamide with HCl, and finally, copper bromide coordinated with protonated acetamide with HBr. Color keys: nitrogen: blue; gray: hydrogen; violent: carbon; oxygen: red; chloride: black; bromine: yellow.

Table 3

Parameters of optimization for copper halide coordination with unprotonated acetamide

Parameters	$CuCl_2$+Acetamide by N	$CuCl_2$+Acetamide by O	$CuBr_2$+Acetamide by N	$CuBr_2$+Acetamide by O
-E (total), kcal/mol	-59697.8	-59686.6	-61394.3	-61376.2
μ, D	5.48	5.266	6.668	10.14
q (O)	-0.273	-0.200	-0.270	-0.239
q (N)	0.547	-0.019	0.450	0.120
q (C)	0.165	0.181	0.178	0.203
q (Cu)	-0.341	-0.146	-0.161	0.044
r (C=O), nm	1.2108	1.295	1.2099	1.277
r (C-C), nm	1.4954	1.5039	1.4965	1.5045

r (C-N), nm	1.5246	1.3555	1.5177	1.3674
r (Cu-X (X is Cl or Br)), nm	2.1408 2.1704	2.2124 2.1275	2.4238 2.4223	2.4427 2.3980
r (N-Cu), nm	1.9112	-	1.9232	-
r (O-Cu), nm	-	1.8946	-	1.9097
Angle, O-C-N	115.5974	122.9816	116.0607	123.4406
Angle, O-C-C	126.5563	116.0873	126.5579	117.3119
Angle, C-N or O-Cu	124.0378	127.9239	125.5949	133.106
Angle, X-Cu-N or O	125.5848 113.9035	103.5923 125.4748	136.8242 139.2161	117.5904 175.1818

Table 4

Parameters of optimization for copper halide coordination with protonated acetamide

Parameters	$CuCl_2$+Acetamide+ HCl by O	$CuCl_2$+Acetamide+ HCl by N	$CuBr_2$+Acetamide+ HCl by O	$CuBr_2$+Acetamide +HCl by N
-E (total), kcal/mol	-67362.4	-67357.2	-69903.4	-69902.3
μ, D	6.275	4.766	5.541	7.465
q (O)	-0.300	-0.169	-0.303	-0.134
q (N)	0.692	0.103	0.451	0.426
q (C)	-0.024	0.224	-0.159	0.098
q (Cu)	-0.389	-0.154	-0.157	-0.127
r (C=O), nm	1.4023	1.2777	1.2175	1.3342
r (C-C), nm	1.5288	1.5026	1.4954	1.5265
r (C-N), nm	1.4764	1.3898	1.5124	1.545
r (Cu-X (X is Cl or Br)), nm	2.16 2.1403	2.2085 2.1257	2.4332 2.4129	2.351 2.3678
r (N-Cu), nm	1.8948	-	1.9248	-
r (O-Cu), nm	-	1.9003	-	1.8789
Angle, O-C-N	112.3214	123.1026	116.9329	117.4859

Angle, O-C-C	110.1739	117.1607	125.3114	125.5723
Angle, C-N or O-Cu	75.9901	127.835	122.4702	151.2548
Angle, X-Cu-N or O	144.2997 108.4462	126.0109 103.2195	119.6481 137.2847	141.4844 112.5839

Discussion

The unprotonated and protonated acetamides, and then the copper halides (chloride, and bromide) coordination with unprotonated and protonated acetamides were studied in this research work via HyperChem software package using the PM3 method. As a result, coordination of copper halides with unprotonated and protonated acetamides was leading to important structural change in comparison with pure unprotonated and protonated acetamides. In this regard, quantum chemical parameters including energies, dipole moments, charges, bond length, and bond angles were illustrated in Table 2-3, and Figure 2-3.

Herein, we can obviously note that the highest negative charge belongs to the oxygen atom of the acetamide compound when coordinated with copper halides. The results imply that the charge of oxygen is around -0.273 when copper chloride is coordinated with unprotonated acetamide, and then the charge of oxygen is around -0.300 when copper chloride is coordinated with protonated acetamide. In addition, the charges of nitrogen, in this case, were reaching the highest value around +0.692 for coordination of copper chloride with protonated acetamide, and +0.451 for coordination of copper bromide with protonated acetamide by oxygen atom. It could mean that the proton of acetamide could connect with the oxygen atom of the carbonyl group of acetamide.

Basically, the quantities of total energy obtained by quantum chemical method. The following conclusion can be drawn from the comparison, that is, all the total energy of the calculated models and their qualitative composition depending on the construction and the calculation of the chosen research method.

Conclusion

To sum up, the quantum chemical calculations were performed for the pure acetamide, protonated acetamide with HCl, protonated acetamide with HBr, copper halide (chloride or bromide) coordinated with pure acetamide, copper chloride coordinated with protonated acetamide with HCl, and finally, copper bromide coordinated with protonated acetamide with HBr. The quantum chemical parameters such as energies, dipole moments, charges, bond length, and bond angles were illustrated and discussed in detail.

As a result, we can conclude that the highest charge of oxygen and nitrogen atoms was obtained when copper halides are coordinated by oxygen atoms of protonated acetamide compound. Moreover, we can see that this could mean a proton could connect with the oxygen atom of acetamide.

These quantum chemical calculations results are very important in the future to the rational design of the complexes of copper halides which are coordinated with organic ligands such as unprotonated and protonated acetamides. Copper halide complexes have a wide range of applications including crop production, animal husbandry, and pharmacology.

References

1. Hassan F.E.H., Zaoui A., Sekkal W. Structural properties of copper halides //Materials Science and Engineering: B. – 2001. – Vol. 87(1). – P. 40-47.

2. Ferhat M., Zaoui A., Certier M., Dufour J.P., Khelifa B. Electronic structure of the copper halides CuCl, CuBr and CuI. //Materials Science and Engineering: B. – 1996. – Vol. 39(2). – P. 95-100.

3. Li G., Shi Z., Liu X., Dai Z., Feng S. Low-dimensional hybrid copper halides with novel D6R Cu6I6 cores //Inorganic chemistry. – 2004. – Vol. 43(22). – P. 6884-6886.

4. Sekkal W., Zaoui A. Monte Carlo study of transport properties in copper halides //Physica B: Condensed Matter. – 2002. – Vol. 315(1-3). – P. 201-209.

5. Popov L.D., Shcherbakov I.N., Levchenkov S.I., Tupolova Y.P., Kogan V.A., Lukov V.V. Binuclear copper (II) and oxovanadium (IV) complexes with 2, 6-diformyl-4-tert-butylphenol-bis-(1′-phthalazinylhydrazone). Synthesis, properties and quantum chemical study //*Journal of Coordination Chemistry*. – 2008. – Vol. 61(3). – P. 392-409.

6. Seo J.H., Lee S.K., Lee I. Quantum chemical calculations of equilibrium copper (I) isotope fractionations in ore-forming fluids //*Chemical Geology*. – 2007. – Vol. 243(3-4). – P. 225-237.

7. Bower J.K., Cypcar A.D., Henriquez B., Stieber S.C.E., Zhang S. C (sp3)–H fluorination with a copper (II)/(III) redox couple //*Journal of the American Chemical Society*. – 2020. – Vol. 142(18). – P. 8514-8521.

8. Olshin P.K., Myasnikova O.S., Kashina M.V., Gorbunov A.O., Bogachev N.A., Kompanets V.O., Mereshchenko A.S. The electronic spectra and the structures of the individual copper (II) chloride and bromide complexes in acetonitrile according to steady-state absorption spectroscopy and DFT/TD-DFT calculations //*Chemical Physics*. – 2018. – Vol. 503. – P. 14-19.

9. Ignaczak A., Gomes J.A.N.F. Quantum calculations on the adsorption of halide ions on the noble metals //*Journal of Electroanalytical Chemistry*. – 1997. – Vol. 420(1-2). – P. 71-78.

10. Shcherbakov I.N., Popov L.D., Levchenkov S.I., Morozov A.N., Kogan V.A., Vikrishchuk A.D. Specificity of complex formation of benzoin (phthalazin-1-yl) hydrazone with copper (II) and nickel (II): Physicochemical study and quantum-chemical simulation //*Russian Journal of General Chemistry*. – 2009. – Vol. 79(4). – P. 826-832.

11. Lan Z., Meng J., Zheng K., Castelli I.E. Exploring the Intrinsic Point Defects in Cesium Copper Halides //*The Journal of Physical Chemistry C*. – 2021. – Vol. 125(2). – P. 1592-1598.

12. Remy-Speckmann I., Bredow T., Lerch M. Two new quaternary copper bismuth sulfide halides: CuBi2S3Cl and CuBi2S3Br as candidates for copper ion conductivity. *Zeitschrift für Physikalische Chemie*. – 2021. – Vol. 236 – P. 727-740.

13. Kepp K.P. Halide binding and inhibition of laccase copper clusters: the role of reorganization energy //*Inorganic Chemistry*. – 2015. – Vol. 54(2). – P. 476-483.

14. Li X. Metalophilic interaction in gold halide: Quantum chemical study of AuX (X= F at) //*Journal of Computational Chemistry*. – 2014. – Vol. *35*(12). – P. 923-931.

15. Hargittai M., Schwerdtfeger P., Réffy B., Brown R. The Molecular Structure of Different Species of Cuprous Chloride from Gas-Phase Electron Diffraction and Quantum Chemical Calculations //*Chemistry–A European Journal*. – 2003. – Vol. 9(1). – P. 327-333.

16. Shamsieva A.V., Kolesnikov I.E., Strelnik I.D., Gerasimova T.P., Kalinichev A.A., Katsyuba S.A., Sinyashin O.G. Fresh look on the nature of dual-band emission of octahedral copper-iodide clusters—promising ratiometric luminescent thermometers //*The Journal of Physical Chemistry C*. – 2019. – Vol. 123(42). – P. 25863-25870.

17. Ignaczak A., Gomes J.N. Interaction of halide ions with copper: the DFT approach //*Chemical physics letters*. – 1996. – Vol. *257*(5-6). – P. 609-615.

18. Gerengi H., Mielniczek M., Gece G., Solomon M.M. Experimental and quantum chemical evaluation of 8-hydroxyquinoline as a corrosion inhibitor for copper in 0.1 M HCl //*Industrial & Engineering Chemistry Research*. – 2016. – Vol. 55(36). – P. 9614-9624.

19. Shamsieva A.V., Musina E.I., Gerasimova T.P., Strelnik I.D., Strelnik A.G., Kolesnikov I.E., Sinyashin O.G. Triple-bridged helical binuclear copper (I) complexes: Head-to-head and head-to-tail isomerism and the solid-state luminescence //*Dalton Transactions*. – 2020. – Vol. 49(34). – P. 11997-12008.

20. Bi C., Wang S., Li Q., Kershaw S.V., Tian J., Rogach A.L. Thermally stable copper (II)-doped cesium lead halide perovskite quantum dots with strong blue emission //*The journal of physical chemistry letters*. – 2019. – Vol. 10(5). – P. 943-952.

21. Huang G., Xia Y. Catalyst-Controlled C–C σ Bond Cleavages in Metal Halide-Catalyzed Cycloisomerization of 3-Acylcyclopropenes via a Formal 1, 1-Halometalation Mechanism: Insights from Quantum Chemical Calculations //*ACS Catalysis*. – 2015. – Vol. 5(2). – P. 859-868.

22. Huang H.Y., Padin J., Yang R.T. Anion and cation effects on olefin adsorption on silver and copper halides: Ab initio effective core potential study of π-complexation //*The Journal of Physical Chemistry B*. – 1999. – Vol. 103(16). – P. 3206-3212.

23. Kuznetsov A., Reinhold J., Lorenz W. Quantum chemical studies of the chemisorption of water and of unhydrated and hydrated halide ions on mercury //*Journal of electroanalytical chemistry and interfacial electrochemistry*. – 1984. – Vol. 164(1). – P. 167-175.

24. Brewer G.J. Copper in medicine. Current opinion in chemical biology. – 2003. – Vol. 7(2). – P. 207-212.

25. Puig S., Thiele D.J. Molecular mechanisms of copper uptake and distribution. Current opinion in chemical biology. – 2002. – Vol. 6(2). – P. 171-180.

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Протондалған ацетамидтері бар мыс галогендік кешендерінің құрылымдық қасиеттерін кванттық химиялық жолмен зерттеу

Аңдатпа. Құрамында органикалық лигандтары бар мыс кешендерінің химиясы қазіргі заманғы химиялық технология мен ғылым үшін маңызды зерттеу бағыттарының бірі болып табылады. Бұл жерде органикалық лигандтармен үйлестірілген мыс кешендері өсімдік шаруашылығында, мал шаруашылығында, фармакологияда және көптеген қосымшаларда маңызды рөл атқарады. Осы кезде мыс галогенидтерін ацетамидтермен үйлестіру іргелі зерттеулер үшін жақсы зерттеу объектілері болып табылады. Ағымдағы жұмыстың мақсаты – HyperChem бағдарламалық құралын және PM3 әдісін қолдана отырып, кванттық химиялық есептеулер мен мыс галогенидтерін (хлорид, бромид) ацетамидтермен үйлестіру үшін талдау жасау. Мақала ацетамидтермен мыс галогенді кешендерін ұтымды жобалауға көмектеседі.

Түйін сөздер: мыс галогениді, ацетамид, кванттық-химиялық есептеулер, PM3 әдісі, HyperChem.

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Квантово-химическое исследование структурных свойств комплексов галогенидов меди с протонированными ацетамидами

Аннотация. Химия комплексов меди, содержащих органические лиганды, является одним из важных направлений современной химической технологии и науки. Здесь комплексы меди, скоординированные с органическими лигандами, играют важную роль во многих приложениях, включая растениеводство, животноводство и фармакологию. На данный момент координация галогенидов меди с ацетамидами является хорошим объектом для фундаментальных исследований. Целью данной статьи являются выполнение квантово-химических расчетов и анализ координации галогенидов меди (хлорид, бромид) с ацетамидами с использованием программного обеспечения HyperChem и метода PM3. Настоящая работа поможет рационально сконструировать комплексы галогенидов меди с ацетамидами.

Ключевые слова: галогениды меди; ацетамиды; квантово-химические расчеты; PM3 метод; HyperChem.

References

1. Hassan F.E.H., Zaoui A., Sekkal W. Structural properties of copper halides, Materials Science and Engineering: B, 87(1), 40-47 (2001).

2. Ferhat M., Zaoui A., Certier M., Dufour J.P., Khelifa B. Electronic structure of the copper halides CuCl, CuBr and CuI., Materials Science and Engineering: B. 39(2), 95-100 (1996).

3. Li G., Shi Z., Liu X., Dai Z., Feng S. Low-dimensional hybrid copper halides with novel D6R Cu6I6 cores, Inorganic chemistry, 43(22), 6884-6886 (2004).

4. Sekkal W., Zaoui A. Monte Carlo study of transport properties in copper halides, Physica B: Condensed Matter, 315(1-3), 201-209 (2002).

5. Popov L.D., Shcherbakov I.N., Levchenkov S.I., Tupolova Y.P., Kogan V.A., Lukov V.V. Binuclear copper (II) and oxovanadium (IV) complexes with 2, 6-diformyl-4-tert-butylphenol-bis-(1′-phthalazinylhydrazone). Synthesis, properties and quantum chemical study, *Journal of Coordination Chemistry*. 61(3), 392-409 (2008).

6. Seo J.H., Lee S.K., Lee I. Quantum chemical calculations of equilibrium copper (I) isotope fractionations in ore-forming fluids, *Chemical Geology*, 243(3-4), 225-237 (2007).

7. Bower J.K., Cypcar A.D., Henriquez B., Stieber S.C.E., Zhang S. C (sp3)–H fluorination with a copper (II)/(III) redox couple, *Journal of the American Chemical Society*, 142(18), 8514-8521 (2020).

8. Olshin P.K., Myasnikova O.S., Kashina M.V., Gorbunov A.O., Bogachev N.A., Kompanets V.O., Mereshchenko A.S. The electronic spectra and the structures of the individual copper (II) chloride and bromide complexes in acetonitrile according to steady-state absorption spectroscopy and DFT/TD-DFT calculations, *Chemical Physics*, 503, 14-19 (2018).

9. Ignaczak A., Gomes J.A.N.F. Quantum calculations on the adsorption of halide ions on the noble metals, *Journal of Electroanalytical Chemistry*, 420(1-2), 71-78 (1997).

10. Shcherbakov I.N., Popov L.D., Levchenkov S.I., Morozov A.N., Kogan V.A., Vikrishchuk A.D. Specificity of complex formation of benzoin (phthalazin-1-yl) hydrazone with copper (II) and nickel (II): Physicochemical study and quantum-chemical simulation, *Russian Journal of General Chemistry*, 79(4), 826-832 (2009).

11. Lan Z., Meng J., Zheng K., Castelli I.E. Exploring the Intrinsic Point Defects in Cesium Copper Halides, *The Journal of Physical Chemistry C*, 125(2), 1592-1598 (2021).

12. Remy-Speckmann I., Bredow T., Lerch M. Two new quaternary copper bismuth sulfide halides: CuBi2S3Cl and CuBi2S3Br as candidates for copper ion conductivity, *Zeitschrift für Physikalische Chemie*, 236, 727-740 (2021).

13. Kepp K.P. Halide binding and inhibition of laccase copper clusters: the role of reorganization energy, *Inorganic Chemistry*, 54(2), 476-483 (2015).

14. Li X. Metalophilic interaction in gold halide: Quantum chemical study of AuX (X= F at), *Journal of Computational Chemistry*, *35*(12), 923-931 (2014).

15. Hargittai M., Schwerdtfeger P., Réffy B., Brown R. The Molecular Structure of Different Species of Cuprous Chloride from Gas-Phase Electron Diffraction and Quantum Chemical Calculations, *Chemistry–A European Journal*, 9(1), 327-333 (2003).

16. Shamsieva A.V., Kolesnikov I.E., Strelnik I.D., Gerasimova T.P., Kalinichev A.A., Katsyuba S.A., Sinyashin O.G. Fresh look on the nature of dual-band emission of octahedral copper-iodide clusters—promising ratiometric luminescent thermometers, *The Journal of Physical Chemistry C*, 123(42), 25863-25870 (2019).

17. Ignaczak A., Gomes J.N. Interaction of halide ions with copper: the DFT approach, *Chemical physics letters*, *257*(5-6), 609-615 (1996).

18. Gerengi H., Mielniczek M., Gece G., Solomon M.M. Experimental and quantum chemical evaluation of 8-hydroxyquinoline as a corrosion inhibitor for copper in 0.1 M HCl, *Industrial & Engineering Chemistry Research*, 55(36), 9614-9624 (2016).

19. Shamsieva A.V., Musina E.I., Gerasimova T.P., Strelnik I.D., Strelnik A.G., Kolesnikov I.E., Sinyashin O.G. Triple-bridged helical binuclear copper (I) complexes: Head-to-head and head-to-tail isomerism and the solid-state luminescence, *Dalton Transactions*, 49(34), 11997-12008 (2020).

20. Bi C., Wang S., Li Q., Kershaw S.V., Tian J., Rogach A.L. Thermally stable copper (II)-doped cesium lead halide perovskite quantum dots with strong blue emission, *The journal of physical chemistry letters*, 10(5), 943-952 (2019).

21. Huang G., Xia Y. Catalyst-Controlled C–C σ Bond Cleavages in Metal Halide-Catalyzed Cycloisomerization of 3-Acylcyclopropenes via a Formal 1, 1-Halometalation Mechanism: Insights from Quantum Chemical Calculations, *ACS Catalysis*, 5(2), 859-868 (2015).

22. Huang H.Y., Padin J., Yang R.T. Anion and cation effects on olefin adsorption on silver and copper halides: Ab initio effective core potential study of π-complexation, *The Journal of Physical Chemistry B*, 103(16), 3206-3212 (1999).

23. Kuznetsov A., Reinhold J., Lorenz W. Quantum chemical studies of the chemisorption of water and of unhydrated and hydrated halide ions on mercury, *Journal of electroanalytical chemistry and interfacial electrochemistry*, 164(1), 167-175 (1984).

24. Brewer G.J. Copper in medicine. Current opinion in chemical biology, 7(2), 207-212 (2003).

25. Puig S., Thiele D.J. Molecular mechanisms of copper uptake and distribution. Current opinion in chemical biology, 6(2), 171-180 **(**2002).

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