EXCELLENCIA
INTERNATIONAL MULTI-DISCIPLINARY JOURNAL OF EDUCATION
Volume 02, Issue 10, 2024 ISSN (E): 2994-9521

Synthesis and Investigation of Zinc(Ii) Nitrate Complexes With Thiadiazole–1,3,4 Derivatives

Husenov Kakhramon Shayimovich [1], Navruzova Mashhura Bakhtiyor kizi [2],

Bakhronova Ozoda Zhuraevna [3]

[1] Candidate of Chemical Sciences, Associate Professor of the Department of Chemical Technology, Navoi State University of Mining and Technology, Republic of Uzbekistan, 72 M.Tarobiy str., Navoi, 210100

[2] Intern researcher of the Department of Chemical Technology of Navoi State University of Mining and Technology, Republic of Uzbekistan, Navoi, M.Tarobiy str., 72, 210100

[3] Assistant at the Mining Faculty of Navoi State University of Mining and Technology Republic of Uzbekistan, 72 M.Tarobiy str., Navoi, 210100

Abstract:

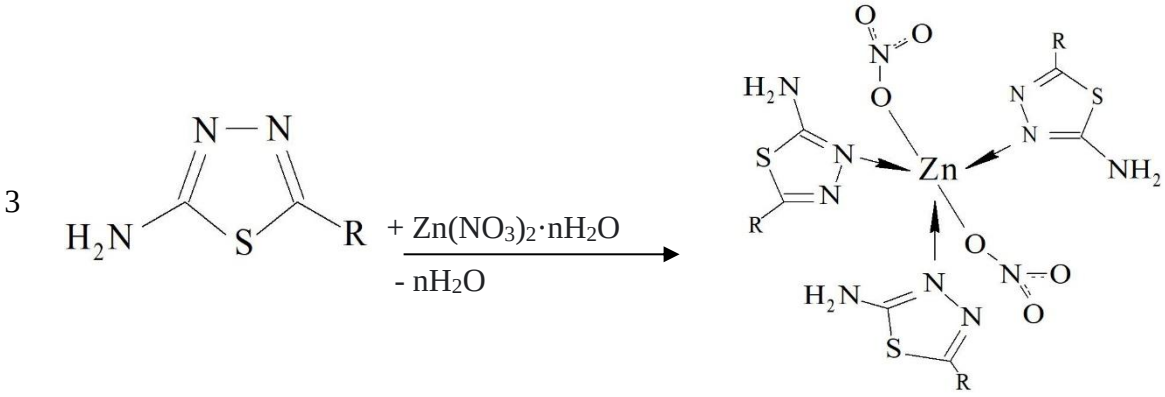
This article presents methods for the synthesis of new complex compounds of zinc(II) with 2-aminothiadiazole-1,3,4 (AT) structure [Zn(AT)3(NO3)2] and 2-amino-5-methylthiadiazole-1,3,4 (AMT) structure [Zn(AMT)3(NO3)2]. The structure of the obtained complexes was established by the methods of elemental and X-ray diffraction analyses. In complexes around the Zn(II) ion, three nitrogen atoms of thiadiazole cycles and two oxygen atoms of two nitrate anions are coordinated in the equatorial plane in axial positions.

Keywords: 2-Aminothiadiazole-1, 3,4, 2-amino-5-methylthiadiazole-1,3,4, X-ray diffraction analysis, polyhedron, trigonal bipyramide.

Introduction. Of particular interest are biologically active heterocyclic compounds that are used in medicine, veterinary medicine, agriculture and other areas of the national economy [1-9]. Among polydentate organic ligands in the chemistry of complex compounds, 2-aminothiadiazole-1,3,4 and its derivatives are of important interest [10-17]. This is due to the presence of several donor atoms in their composition and their widespread use in medical practice, agriculture and industry [18-24].

Previously, we reported on the synthesis and crystal structure of a complex of zinc(II) halides with 2-aminothiadiazole-1,3,4 (AT) of the composition $[Zn(AT)_2X_2]$ (where X is Cl, Br, I) [25-27]. In the crystal of the complex around the central halide ion, the resulting complex has a distorted tetrahedral coordination sphere consisting of two coordinated nitrogen atoms of the thiadiazole rings of two L and two halide atoms. In the case when the ligand is 2-amino-5-ethylthiadiazole-1,3,4 (AET), the complex is a distorted tetrahedron, at the vertices of which there are three nitrogen atoms of three ligand molecules and an oxygen atom of a water molecule, nitrate anions are located in the outer sphere of the complex $[Zn(AET)_3(H_2O)](NO_3)_2$ [28].

In contrast to these works, this work is devoted to the results of the synthesis and study of the crystalline and molecular structure of the zinc(II) nitrate complex with 2-amino-5-R-thiadiazole-1,3,4 synthesized according to the equation (Scheme 1).



Scheme 1. ligands: R= – H (I, AT), – CH_3 (II, AMT); complexes: R= – H (III), – CH_3 (IV);

Zinc(II) nitrate forms a five-coordination complex compound with 2-amino-5-R-thiadiazole–1,3,4 (R= –H and -CH_3). The increase in the coordination number in this case is obviously explained by the large repulsion of voluminous nitrate ions located around the central ion from each other. As a result, it becomes possible to coordinate to the central atom of the third molecule of the heterocycle. The resulting complexes of $[Zn(AT)_3(NO_3)_2]$ – III and $[Zn(AMT)_3(NO_3)_2]$ – IV zinc nitrate with aminothiadiazoles of the coordination polyhedron represent a trigonal bipyramide, in the equatorial plane of which there are three nitrogen atoms of three heterocycle molecules; the axial positions of the polyhedron are occupied by oxygen atoms of two nitrates-anions, the coordination sphere in the complexes $[Zn(AT)_3(NO_3)_2]$ – III and $[Zn(AMT)_3(NO_3)_2]$ – IV trigonal bipyramide.

The experimental part.

Synthesis of the $[Zn(AMT)_3(NO_3)_2]$ complex. For the synthesis of this complex, a hot solution of 1,036 g (0.009 mol) of AMT ligand in 50 ml of ethanol was added with gradual stirring, a hot solution of 0.57 g (0.003 mol) of zinc (II) nitrate in 50 ml of ethanol, then heated with a reverse refrigerator for an hour, filtered and left for crystallization. After a day, the fallen beige crystals were filtered and dried in air.

Elemental analysis of compounds on C, H, N was performed on the EA 1108 device of the Carlo Erba company, Zn was determined on the 3030V device of the Perkin Elmer company.

III: pale yellowish crystals, T_m. -195°C, yield 1.36 g (85.0% based on $[ZnL^2_3(NO_3)_2]$.

Found, %:	C 20.65;	H 2.94;	N 28.42;	Zn 12.12.
As for $C_9H_{15}N_{11}S_3O_6Zn$				
calculated, %	C 20.21;	H 2.83;	N 28.81;	Zn 12.22.

The complex is synthesized in a similar way $[ZnL^1{}_3(NO_3)_2]$ (IV) [29-31].

IV: pale yellowish crystalls, Tm. – 183-85 ºC, output 1,24 g (84,0 % based on $[ZnL^1{}_3(NO_3)_2]$.

found, %:	C 14.48;	H 2.13;	N 31.21;	Zn 13.09.
As for $C_6H_9N_{11}S_3O_6Zn$				
calculated, %	C 14.62;	H 1.84;	N 31.27;	Zn 13.27.

Research methodology. The crystallographic parameters for crystal structure III were determined and refined from 15 reflections on an automatic four-circle diffractometer Syntex-P21 at room temperature. It is established that the isolated crystals are triclinic with parameters: *a*=7.563(2), *b*=8.033(3), *c*=14.741(4) Å, α=100.17(2)º, β=91.58(2)º, γ=101.96(2)º, V=860.4(0.9)Å^3, Z=2, d = 1.902 g/cm^3, spatial group *P-1*, *R=0.057*, R_w= 0.057 [12, 27, 29-30].

For the crystal structure IV, X-ray diffraction analysis was performed on an X taLA B Synergy diffractometer (Rigaku, Japan) installed in the Center for Collective Use of the Institute of Bioorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan. The experiments were carried out using CuK_α radiation (mirror monochromator, 3D scanning). Triclinic crystals: *a*=8.4152(3), *b*=8.43370(16), *c*=12.9394(5) Å, α=84.562(2)º, β=85.949º, γ=67.892(3)º, V=846.37(5)Å^3, Z=2, d = 1.624 g/cm^3, spatial group *P-1*, *R=0.027*, R_w= 0.072 (fig. 1.).

The results obtained and their discussion

The compared distances, angles and deviations in the polyhedra of the complexes are as follows: the zinc atom leaves the equatorial plane of the bipyramide by 0.088 Å(III), 0.071 Å (IV) towards the O(1B) atom (Fig. 1). The zinc-oxygen distances in the axial positions of the bipyramide are not the same: Zn(1)-O(1A) 2.460(8) (III), 2.331(5) Å (IV) and Zn(1)-O(1B) 2.191(6) (III), 2.169(4) (IV) Å [29-30];

A coordination node is formed in the equatorial plane of the bipyramid Zn(1), N(1A), N(1B), N(1C). The angles between the "middle" plane of this coordination node and the "middle" planes of the five-membered heterocycles N(1A), N(2A), C(1A), C(2A), S(1A); N(1B), N(2B), C(1B), C(2B), S(1B) и N(1C), N(2C), C(1C), C(2C), S(1C) contain 19.4º, 11.7º and 7.2º (III); 30.7º, 28.0º and 31.2º (IV) Accordingly, this seems to be explained by a change in the ligand molecule, where the complex (III) was replaced by a methyl group (IV) instead of the hydrogen atom.

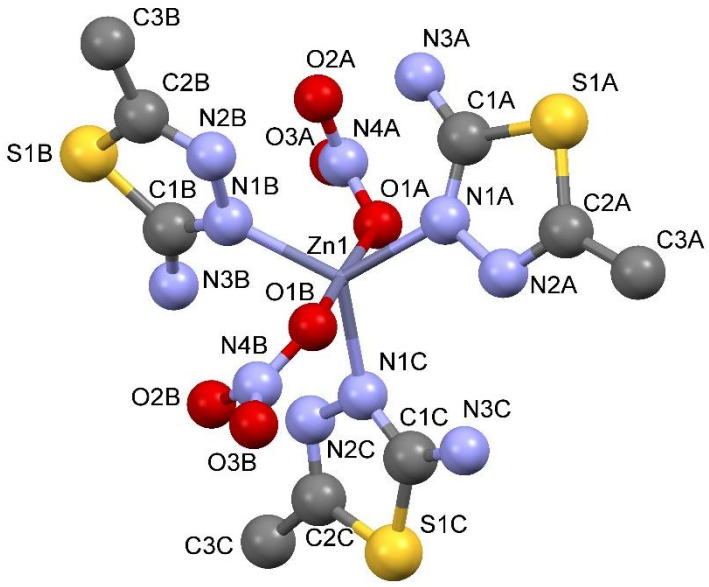


Fig.1. The molecular structure of the complex $[Zn(AMT)_3(NO_3)_2]$.

Bond lengths and valence angles in the three independent ligands of the AMT complex are in good agreement with each other. The C-S distances (1.730(6)-1.741(8) Å) lie within the usual lengths of carbon-sulfur bonds, the N-N distances are in the range 1.374(7)-1.387(7) Å and correspond to standard values for single bonds in a five-membered heterocycle [31-32].

Analysis of intra- and intermolecular contacts in the studied structure showed that there are two types of hydrogen bonds in the complex molecule, intramolecular (IntraMHB) and intermolecular (InterMHB) [11]. Comparing IntraMHB between molecules, an interesting fact is observed, in molecule III, each NH_2 group of the thiadiazole ring participates in the formation of IntraMHB N-N⋯N with uncoordinated nitrogen atoms of the neighboring polyhedron molecule, and in molecule IV, in two cases, such IntraMHB as N–N⋯N are formed, and in the other case IntraMHB – N–N⋯O with an oxygen atom of the nitrate anion. These values also come true when the "middle" plane of the coordination polyhedron of the central atom Zn, N(1A), N(1B), N1(C) and the "middle" planes of the five-membered heterocycles are 7.2-19.4º in molecule III and 28.0-31.2º in molecule IV, respectively [30-33]. The deviation of the exocyclic nitrogen atoms of the amino groups from the "average" planes of the aminothiadiazole heterocycles is in the range of 0.003–0.057 Å and -0.014–0.023 Å in molecules III and IV, respectively.

In both cases, when packing a molecule in crystals, InterMHB are formed – nitrogen atoms of the NH_2 group form bonds with oxygen atoms of the nitrate ion and an uncoordinated nitrogen atom of neighboring molecules.

Conclusion. Thus, new zinc complexes were synthesized: 2-aminothiadiazole-1,3,4 (AT), with the structure $[Zn(AT)_3(NO_3)_2]$ and 2-amino-5-methylthiadiazole-1,3,4 (AMT), with the structure $[Zn(AMT)_3(NO_3)_2]$. As a result of XRD studies, it was found that during the complexation of ligands, they are coordinated through an endocyclic nitrogen atom, which is in the α position relative to the amino group.

The polyhedron of the central atoms is a trigonal bipyramide, in the coordination sphere of which there are three nitrogen atoms in the equatorial plane and two oxygen atoms of nitrate anions in an axial position.

References.

1. Ana C.M. O. Lima, Ana L.R.Silva, Jorge M. Goncalves, Maria D.M.C. Ribeiro da Silva Thermodynamic study on the relative stability of 2-amino-1,3,4-thiadiazole and two alkyl-substituted aminothiadiazoles // Journal of the Thermal Analysis and Calorimetry. - 2024. https://doi.org/10.1007/s10973-024-13498-6
2. Luís M.T. Frija, Armando J.L. Pombeiro, Maximilian N. Kopylovich Coordination chemistry of thiazoles, isothiazoles and thiadiazoles // Coordination Chemistry Reviews. – 2015. – V. 308. – №2. – P. 32-55. (https://doi.org/10.1016/j.ccr.2015.10.003)
3. Umirov F.E., Nomozova G.R., Kodirov S.M. Solubility diagrams of the calcium chlorate-4-amino-1,2,4-triazole-water system // Universum: technical sciences: electron. scientific magazine 2021. 3(84). URL: - P.74-78. https://7universum.com/ru/tech/archive/item/11433.
4. Umirov F.E., Khudoiberdiev F.I., Tukhtaev S.T., Murodova S.D. Preparation of defoliants based on 4-amino-1,2,4-triazole with sodium and magnesium chlorates // Bulletin of Science and Education. – 2018. - T.2. - No. 3(39). - pp. 14-16.
5. Umirov F.E. Preparation of a defoliant based on chlorates of organic compounds // Monograph. – 2019. – Bukhara. – ed. "Durdona." – 139 p.

6. Худойбердиев Ф.И. и др. Агрохимическая эффективность дефолиантов на основе хлоратов магния и натрия //ВЕСТНИК. – 2019. – С. 133.
7. Khudoiberdiev, F. I., Murodova, S. D., Takhirova, N. B., & Khusenov, K. Sh. (2018). Study of the process of obtaining defoliants. *Science and education: preserving the past, creating the future* (pp. 13-16).
8. Umarov B.B., Khusenov K.Sh., Ishankhodzhaeva M.M., Parpiev N.A., Gaybullaev Kh.S. New hexadentate ligands based on salicylaldehyde dihydrazones // Zhurnal organicheskoi khimii. – 1996. – T.32. – № 1. – C. 93–95.
9. Khusenov K.Sh. Complex compounds of some 3d metals with derivatives of 1,3,4-thiadiazoles and salicylaldimines // Abstract of the dissertation for the degree of candidate of chemical sciences. - Tashkent. – 1998. – 22 p.
10. Mori A., Sekiguchi A., Masui K. at. all. Facile Synthesis of 2,5-Diarylthiazoles via Palladium-Catalyzed Tandem C-H Substitutions. Design of Tunable Light Emission and Liquid Crystalline Characteristics // J. Am. Chem. Soc. 2003, 125, 1700-1701. (doi: 10.1021/ja0289189.)
11. Umarov B. B. et al. Synthesis and study of crystal structure of the product of combined condensation of 2-amino-5-ethyl-1, 3, 4-thiadiazole with salycilic aldehyde and acetylacetone //Russian journal of organic chemistry. – 1999. – T. 35. – №. 4. – C. 599-602.
12. Khusenov K.Sh. and others. Crystal and molecular structure of the complex of zinc (II) nitrate with 2-amino-1,3,4-thiadiazole // "Journal of Inorganic Chemistry". - 2000. - T.43. - № 12. - S. 1976-1981.
13. Khusenov K.Sh., Aliev T.B., Bakhronova O.Zh. Synthesis and structure of zinc (II) complexes with 2-aminothiadiazole derivatives-1, 3, 4 // International Journal of Advanced Technology and Natural Sciences. - 2023. - T.4. - No. 1. - P. 45-58.
14. Yue Wu, Yongshu Xie, Qiong Zhang at. all. Quantitative Photoswitching in Bis(dithiazole)ethene Enables Modulation of Light for Encoding Optical Signals // Angew. Chem. Int. Ed. – 2014. – V. 53. – Issue 8. – P. 2090-2094. (https://doi.org/10.1002/anie.201309915)
15. Bo-Yeon Kim, Hong-Seok Kim, Aasif Helal. A fluorescent chemosensor for sequential recognition of gallium and hydrogen sulfate ions based on a new phenylthiazole derivative // Sensors and Actuators B: Chemical. – 2015. – V. 206. – P. 430-434. (https://doi.org/10.1016/j.snb.2014.09.071)
16. Thorsten Bach, Stefan Heuser. Synthesis of 2-(*o*-hydroxyaryl)-4-arylthiazoles by regioselective Pd(0)-catalyzed cross-coupling // Tetrahedron Letters. – 2000. – V. 41, Issue 11. – P. 1707-1710. (https://doi.org/10.1016/S0040-4039(00)00018-6)
17. Shaik Karamthulla, Suman Pal, Md. Nasim Khan and Lokman H. Choudhury. "On-water" synthesis of novel trisubstituted 1,3-thiazoles *via* microwave-assisted catalyst-free domino reactions // RSC Advances. – Issue 71. – 2014. . – DOI (https://doi.org/10.1039/C4RA06239F)
18. Khusenov, K. Sh., Umarov, B. B., Bakhronova, O. J., & Aliev, T. B. (2022). Studying the structure of some intermediate metal ion complexes based on 2-Aminothiadiazole-1, 3, 4 derivatives. Chemistry and Medicine: From Theory to Practice (pp. 40-44).
19. Atmaram U.A., Roopan S.M. Biological activity of oxadiazole and thiadiazole derivatives. // Appl. Microbiol. Biotechnol. – 2022. V.106. - P.3489–3505.
20. Szeliga M. Thiadiazole derivatives as anticancer agents. // Pharmacol. Rep. – 2022. – V.72. P. 1079–1100.

21. Rabie A.M., Eltayb W.A. Potent dual polymerase/exonuclease inhibitory activities of antioxidant aminothiadiazoles against the COVID-19 omicron virus: a promising in silico/in vitro repositioning research study. // Mol Biotechnol. – 2023. V. 66. – P. 592–611.
22. Khusenov K.Sh., Aliev T.B., Bakhronova O.Zh. Crystal and molecular structure, Hirschfeld surface analysis of zinc(II) bromide complex with 2-aminothiadiazole-1, 3, 4 // International Journal of Advanced Technology and Natural Sciences. - 2022. - V.3. - №4. - P. 25-35.
23. Bentiss, F., Lagrenée, M., Vezin, H., Wignacourt, J. P., & Holt, E. M. (2004). Syntheses and crystal structures of two mononuclear Zn (II) complexes with the 2, 5-bis (2-pyridyl)-1, 3, 4-thiadiazole ligand. *Polyhedron*, *23*(11), 1903-1907.
24. Ali, K. O., Mohamad, H. A., Gerber, T., & Hosten, E. (2022). Zinc (II) Complex Containing Oxazole Ring: Synthesis, Crystal Structure, Characterization, DFT Calculations, and Hirshfeld Surface Analysis. *Acta Chimica Slovenica*, *69*(4).
25. Khusenov K.Sh., Umarov B.B., Ishankhodzhaeva M.M., Parpiev N.A., Talipov S.A., Ibragimov B.T. Crystal structure of 2-amino-l,3,4-thiadiazole and its Zn(II) complex // Russian Journal of Coordination Chemistry. – 1997. – T.23. – № 8. – C. 555–559.
26. Ishankhodzhaeva M.M., Khusenov K.Sh., Umarov B.B., Parpiev N.A., Aleksandrov G.G. Crystal structure of a complex of Zinc iodide with 2-amino-l,3,4-thiadiazole // Russian Journal of Inorganic Chemistry. – 1998. – № 43(11). – C. 1709–1711.
27. Ishankhodzhaeva M.M., Umarov B.B., Khusenov K.Sh., Parpiev N.A. Effect of the nature of acidoligand on the geometric structure of zinc (II)-2-amino-1,3,4-thiadiazole complexes // Zhurnal obshchei khimii. - 1998. - T.68. - №8. - C. 1368-1373.
28. Ishankhodzhaeva M.M., Umarov B.B., Kadyrova Sh.A., Parpiev N.A., Makhkamov K.K., Talipov S.A. Crystal and molecular structure of 2-amino-5-ethyl-1,3,4-thiadiazole and its complex with zinc(II) nitrate // Journal of General Chemistry. - 2000. – V. 70. - № 7. - pp. 1187-1193.
29. Khusenov K.Sh., Umarov B.B., Ishankhodzhaeva M.M., Parpiev N.A., Talipov S.A., Ibragimov B.T. Crystal and molecular structure of a complex of zinc(II) nitrate with 2-amino-l,3,4-thiadiazole // Russian Journal of Inorganic Chemistry. – 1998. – № 43(12). – C. 1976–1981.
30. Khusenov K.Sh., Umarov B.B., Turgunov K.K., Aliev T.B., Ibragimov B.T. Synthesis and structure of the complex of zinc(II) nitrate with 2-amino-5-methylthiadiazole-1,3,4 // Reports of the Academy of Sciences of the Republic of Uzbekistan. - 2023. - № 1. - P. 72-80.
31. Ganiev, B. S., Khusenov, K. S., & Umarov, B. B. Crystal Structure and Analysis Hirshfeld Surface of the Zinc (II) Bromide Complex with 2-Aminothiadiazole-1, 3, 4//Available at SSRN 4384289.
32. Khusenov, K. Sh., Aliev, T. B., & Bakhronova, O. Zh. (2022). Crystal and molecular structure, Hirschfeld surface analysis of zinc(II) bromide complex with 2-aminothiadiazole-1, 3, 4. *International Journal of Advanced Technology and Natural Sciences*, *3*(4), 25-35.
33. Khusenov, K. S., Umarov, B. B., Turgunov, K. K., Bakhranova, O. Z., Aliev, T. B., & Ibragimov, B. T. (2024). Zinc (II) complexes with thiadiazole derivatives-1, 3, 4. *Žurnal neorganičeskoj himii*, *69*(2), 193-202.