3D METAL COMPLEXES WITH PHENOXYACETIC ACID DERIVATIVES: SYNTHESIS AND CRYSTAL STRUCTURES

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Abstract: Phenoxyacetic acid derivatives occupy an important place in coordination chemistry because they combine a chemically active carboxyl group with an aromatic aryloxy fragment that influences steric environment, electron density, supramolecular packing, and solid-state stability. In complexes of 3d-series metal ions, these ligands behave as structurally flexible O-donor systems and can coordinate in monodentate, chelating, or bridging modes. This determines whether the final products crystallize as hydrated mononuclear compounds, binuclear units, or extended coordination polymers. Published structural studies show that Co(II) and Ni(II) complexes of chlorophenoxyacetic acids often form octahedral environments with coordinated water molecules, whereas Cu(II) more readily gives square-planar or bridged motifs depending on synthesis conditions. Complexes based on 2,4-dichlorophenoxyacetic acid and 4-chlorophenoxyacetic acid demonstrate that the same ligand family can produce 0D, 1D, 2D, and 3D architectures, especially when auxiliary N-donor ligands or hydrothermal conditions are used. The scientific value of these compounds is not limited to structural chemistry. They are relevant for crystal engineering, modeling herbicide–metal interactions, studying the effect of coordination on biological and physicochemical behavior, and designing functional materials with tunable packing and intermolecular contacts.

Key words: 3d metals, phenoxyacetic acid derivatives, coordination compounds, crystal structure, carboxylate coordination, single-crystal X-ray diffraction, analysis, supramolecular architecture.

Introduction

Complex compounds of **3d metals** with oxygen-containing organic ligands remain one of the most productive directions of modern inorganic chemistry because the geometry, nuclearity, and physical properties of such compounds are highly sensitive to small changes in ligand structure and synthesis conditions. **Phenoxyacetic acid derivatives** are especially informative in this respect. Their coordination behavior is governed by deprotonation of the carboxyl group, while the aryloxy fragment affects hydrophobicity, intermolecular packing, and the distribution of substituent effects across the aromatic ring. Chlorinated representatives such as **2,4-**

dichlorophenoxyacetic acid and **4-chlorophenoxyacetic acid** are of particular interest because their donor properties and steric profile allow the formation of multiple coordination modes with Mn, Co, Ni, Cu, and Zn ions. This gives a convenient platform for studying the regularities of structure formation in metal carboxylates and for understanding how the central ion controls coordination number, ligand arrangement, and crystal packing [1].

The relevance of this topic is strengthened by its practical dimension. Phenoxyacetic acid derivatives are not abstract ligands. Many of them are connected with agrochemical systems and with real processes of metal binding in soil, plants, and technical media. When they coordinate with 3d metal ions, their physicochemical behavior changes substantially. Solubility, thermal stability, hydration state, magnetic response, and supramolecular organization may all be altered. This makes the study of their synthesis and crystal structures important not only for academic coordination chemistry, but also for environmental chemistry, crystal engineering, and the targeted design of metal-organic systems with predictable properties [3].

Literature Review

Classical crystallographic work laid the foundation for this field by showing that phenoxyalkanoate ligands do not impose a single coordination pattern. Early studies by **G. Smith, E. J. O'Reilly, C. H. L. Kennard, K. Stadnicka, and B. Oleksyn** demonstrated that phenoxyacetic and chlorophenoxyacetic systems can generate both discrete aqua complexes and strongly bridged copper carboxylates. The structural series reported in **Inorganica Chimica Acta** established that the carboxylate fragment is the decisive coordination center, while the aromatic substituent and hydration state influence molecular symmetry and packing. These works were important because they moved the discussion from simple composition to real crystal architecture and showed that ligand identity alone does not determine structure. The same ligand family can yield markedly different motifs in the presence of different metal ions or under different crystallization regimes [1], [2].

A more detailed structural interpretation was later developed in studies on **2,4-dichlorophenoxyacetic acid** complexes of Co, Ni, and Cu. In the work of **Drzewiecka-Antonik, Ferenc, Wolska, Klepka and co-authors**, XAFS and DFT data were used together with synthesis and structural analysis. That study showed that **Co(2,4-D)2·6H2O** and **Ni(2,4-D)2·4H2O** possess octahedral environments in which two carboxylate groups and four water molecules complete the coordination sphere. By contrast, **Cu(2,4-D)2·4H2O** displays a square-planar arrangement built by two monodentate carboxylate ligands and two water molecules. An especially important result was the observation that recrystallization of the nickel compound produced a

binuclear "Chinese lantern" structure with bridging carboxylate groups. This is a strong illustration of the fact that crystal structure in this class is governed not only by the metal ion, but also by solvent history and recrystallization pathway [3].

Research on **4-chlorophenoxyacetic acid** broadened the picture further. **Long Li, Kaisheng Diao, Yuqiu Ding, and Xianhong Yin** described several complexes in which the same ligand yielded different dimensionalities and intermolecular assemblies. In one series, complexes such as **[CoL2(H2O)4]** and **[CuL2(H2O)2]** were characterized by single-crystal X-ray diffraction and shown to form **0D molecular units**, while hydrogen bonding and weak contacts generated higher-order supramolecular organization. In a hydrothermal series, the same ligand produced **1D, 2D, and 0D architectures** depending on the metal ion and auxiliary ligands. In the manganese system **[MnL2(4,4′-bipy)]**, each carboxylate bridge linked adjacent Mn centers into **infinite Mn–O–C–O rods**, which then assembled into a three-dimensional supramolecular framework [6].

Uzbek researchers have also contributed to the structural and theoretical development of this area. **Alimnazarov, Ashurov, Eshimbetov, Turaev, and Ibragimov** analyzed the **electronic structure of diaquabis (p-chlorophenoxyacetato) copper (II)** by DFT and reported a low-lying LUMO with a dominant metal d-orbital contribution above 60%, which is important for understanding reactivity and electronic redistribution in Cu-based aryloxyacetate complexes. Related Uzbek studies by **Ruzmetov**, **Razzoqova**, **Ibragimov**, and co-authors on other carboxylate and N,O-donor coordination systems have demonstrated the value of combining **single-crystal X-ray diffraction** with **Hirshfeld surface analysis**, a methodology that is directly relevant for future work on phenoxyacetic acid derivatives because it links molecular coordination to packing contacts and crystal stability [10].

Analysis and Results

A comparative reading of the available structural data shows a clear regularity. In complexes of phenoxyacetic acid derivatives, the **carboxylate group** is the principal coordination center, while the phenoxy oxygen usually does not dominate as the primary donor in the final crystal structure. The structural outcome is largely determined by five factors: the preferred geometry of the 3d metal ion, the degree of ligand deprotonation, the number of coordinated water molecules, the presence of auxiliary N-donor ligands, and the crystallization medium. When hydration dominates and no strong co-ligand competes for coordination sites, **Co(II)** and **Ni(II)** frequently form hydrated octahedral complexes. When Jahn–Teller-active **Cu(II)** is involved, lower-symmetry environments and bridged motifs become more probable. When bipyridyl ligands are introduced, dimensionality increases and polymeric or rod-like architectures become accessible [6].

This behavior can be illustrated by several concrete cases. In the **2,4-D** system, the Co and Ni compounds crystallize as hydrated species with regular octahedral coordination, while the Cu compound adopts a square-planar arrangement. The difference is not accidental. It reflects the distinct stereochemical preferences of the metal ions and the stronger structural flexibility of Cu(II). In the recrystallized Ni compound, the structure changes from a hydrated mononuclear environment to a **binuclear carboxylate-bridged "Chinese lantern" motif**, proving that even when elemental composition is similar, the structural type may change sharply under modified crystallization conditions [3]. In the **4-chlorophenoxyacetic acid** series, one set of compounds remains discrete at the molecular level, whereas hydrothermal synthesis and the addition of aromatic N-donor bridges convert the system into chain or network structures. This confirms that ligand substitution alone is not enough to predict the structure. The whole **reaction environment** must be treated as a structure-forming factor [4].

Another important result concerns **crystal packing**. In these complexes, the final crystal structure is stabilized not only by metal–oxygen bonds but also by **O–H···O**, **C–H···Cl**, and sometimes **π–π** contacts. Such interactions influence crystal density, hydration stability, and the persistence of a given polymorphic form. The DFT study of the p-chlorophenoxyacetate copper complex by Uzbek authors adds an electronic argument to this structural picture. A low-lying LUMO with strong copper d-character means that the metal center remains electronically active and may strongly affect redox behavior, spectroscopic response, and intermolecular interactions in the crystal. This is one reason why purely geometric analysis is no longer sufficient. Electronic structure must be discussed together with coordination geometry [5], [7].

Discussion

The scientific meaning of these results goes beyond structural description. Complexes of 3d metals with phenoxyacetic acid derivatives are model systems for understanding how **ligand substitution, hydration, and co-ligation** control the transition from molecular compounds to supramolecular and polymeric frameworks. This makes them useful for **crystal engineering**. A researcher who knows how a carboxylate ligand behaves with Co, Ni, Cu, or Mn under conventional and hydrothermal conditions can deliberately direct synthesis toward a desired topology. For practical chemistry, that is valuable because structure determines thermal stability, solubility, and the distribution of intermolecular contacts, all of which influence handling and application [3].

The applied significance of this field is also visible in environmental and biological contexts. Phenoxyacetic herbicides can interact with metal ions in natural media, and this may reduce metal uptake by plants. In wheat treated with phenoxyacetic herbicides, the reported decrease reached about **50% for Mn**, **20% for Cu**, and **13% for Zn** compared with untreated systems. This indicates that metal binding by such ligands is not only a laboratory phenomenon. It can affect real migration processes in agrochemical environments [11]. In another direction, **aqua(aryloxyacetato)copper(II)** complexes were shown to inhibit oxygen evolution in spinach chloroplasts and were associated with changes at the donor side of photosystem II. That result does not mean every complex of this class is directly applicable in biology, but it does show that coordination changes can substantially alter biological activity and mechanism [12].

At the same time, the field has clear methodological and practical problems. The first is **structural variability caused by hydration**. A compound isolated from aqueous medium may differ from the recrystallized form even when the ligand and metal are unchanged. The second is **phase purity**. Powder products can contain mixtures of hydrates and coordination isomers, while the single crystal chosen for X-ray analysis may represent only one stable fraction. The third problem is the **gap between solid-state and solution-state behavior**. A crystal structure gives precise information about one form of matter, but catalytic, biological, or environmental behavior may depend on partially dissociated or solvent-reorganized species. The fourth issue is **ecological caution**. Since many phenoxyacetic derivatives are connected with herbicidal chemistry, the design of new metal complexes in this family must be accompanied by toxicity, stability, and mobility assessment rather than by structural description alone [12].

The most realistic way to develop this direction is methodological integration. Future studies should combine **single-crystal X-ray diffraction** with **IR spectroscopy**, **thermal analysis**, **XAFS**, **DFT**, and **Hirshfeld surface analysis**. X-ray diffraction establishes the coordination framework. IR spectroscopy helps identify carboxylate binding behavior. Thermal methods clarify hydration and decomposition stages. XAFS is valuable when single crystals are not ideal. DFT explains electron distribution and frontier orbitals. Hirshfeld analysis quantifies the intermolecular contacts that make one packing arrangement more stable than another. Uzbek structural chemistry has already shown the usefulness of this combined approach in related carboxylate systems, and extending it systematically to phenoxyacetic acid derivatives of Mn, Co, Ni, and Cu would produce more robust and practically relevant results [10].

Conclusion

The available evidence shows that **3d metal complexes with phenoxyacetic acid derivatives** form a structurally rich and chemically meaningful class of coordination compounds. Their central закономерность is clear: the same ligand family can generate hydrated mononuclear species, binuclear bridged units, and extended coordination polymers depending on metal-ion preferences, solvent, hydration, recrystallization conditions, and the presence of auxiliary ligands. The strongest results in this area come from studies that do not stop at empirical synthesis but connect **coordination mode, crystal structure, supramolecular contacts, and electronic structure**. That is the line along which the field can be advanced most effectively in future work [10].

REFERENCES

1 Smith G., O'Reilly E. J., Kennard C. H. L., Stadnicka K., Oleksyn B. Metal-phenoxyalkanoic acid interactions. Part I. Crystal and molecular structures of diaquabis(p-chlorophenoxyacetato)zinc(II) and related phenoxyacetate complexes // Inorganica Chimica Acta. 1981. Vol. 47. P. 111–120.

2 Smith G., O'Reilly E. J., Kennard C. H. L., Stadnicka K., Oleksyn B. Metal-phenoxyalkanoic acid interactions. Part 3. Crystal and molecular structures of tetra-μ-(2,4-dichlorophenoxyacetato)bis[aquacopper(II)] dihydrate and tetra-μ-(2,4,5-trichlorophenoxyacetato)bis[pyridinecopper(II)] // Inorganica Chimica Acta. 1981. Vol. 49. P. 53–61.

3 Drzewiecka-Antonik A., Ferenc W., Wolska A., Klepka M. T., Cristóvão B., Sarzyński J., Rejmak P., Osypiuk D. The Co(II), Ni(II) and Cu(II) complexes with herbicide 2,4-dichlorophenoxyacetic acid – Synthesis and structural studies // Chemical Physics Letters. 2017. Vol. 667. P. 192–198.

4 Li L., Diao K., Ding Y., Yin X. Hydrothermal synthesis, crystal structure of five novel complexes based on 4-chlorophenyloxyacetic acid // Molecular Crystals and Liquid Crystals. 2013. Vol. 575. No. 1. P. 173–187.

5 Li L., Diao K., Ding Y., Yin X. Synthesis and structure of three novel complexes based on 4-chlorophenyloxyacetic acid // Molecular Crystals and Liquid Crystals. 2014. Vol. 588. No. 1. P. 63–73.

6 Li L., Diao K., Ding Y. Pb(II) and Mn(II) supermolecular polymers of bipy and 4-chlorophenyloxyacetate anions: Syntheses, structure and fluorescence properties // South African Journal of Chemistry. 2012. Vol. 65. P. 265–270.

7 Alimnazarov B. Kh., Ashurov J. M., Eshimbetov A. G., Turaev Kh. Kh., Ibragimov B. T. Electronic structure of diaquabis(p-chlorophenoxyacetato)copper(II) complex by DFT method // ISJ Theoretical & Applied Science. 2021. No. 10(102). P. 964–968.

8 Ruzmetov A., Ibragimov A., Ashurov J., Boltaeva Z., Ibragimov B., Usmanov S. Synthesis, crystal structure and Hirshfeld surface analysis of hexaaquanickel(II) bis(4-hydroxybenzoate) dihydrate // Acta Crystallographica Section E: Crystallographic Communications. 2022. Vol. 78. P. 660–664.

9 Ruzmetov A. Kh., Ibragimov A. B., Yakubov Y. Yu., Akitsu T., Shimonishi D., Xia C., Hossain A. M. S. Synthesis, crystal structure and Hirshfeld surface analysis of binuclear Cu(II) complexes from o/p-hydroxybenzoic acid with ethanol and water solution of monoethanolamine // Polyhedron. 2023. Vol. 242. Art. 116491.

10 Razzoqova S., Ibragimov A., Torambetov B., Kadirova S., Holczbauer T., Ashurov J., Ibragimov B. Synthesis, structure and Hirshfeld surface analysis of a coordination compound of cadmium acetate with 2-aminobenzoxazole // Acta Crystallographica Section E: Crystallographic Communications. 2023. Vol. 79. P. 862–866.

11 Kobyłecka J., Skiba E. The effect of phenoxyacetic herbicides on the uptake of copper, zinc and manganese by Triticum aestivum L. // Polish Journal of Environmental Studies. 2008. Vol. 17. No. 6. P. 895–901.

12 Král’ová K., Šeršeň F., Bláhová M. Effects of Cu(II) complexes on photosynthesis in spinach chloroplasts. Aqua(aryloxyacetato)copper(II) complexes // General Physiology and Biophysics. 1994. Vol. 13. P. 483–491.