

Coordination Chemistry of Orotic acid

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ABSTRACT: Our research group have been working on transition metal complexes and their activity in the biology field, especially antimicrobial and anticancer properties. Novel pseudohalide ligands with orotic acid and its metal salt Ni(II) have been synthesized¹ and evaluated for their antimicrobial activities by disc diffusion method. The complexes have been characterized by IR, SEM, Raman, P-Xrd and UV-Visible spectroscopic techniques. The Diaquabis(imidazole)orotatoNickel(II), [Ni(HOr)(H₂O)₂(Imd)₂](1), Diazidobis(orotato)nickel(II), [Ni(HOr)₂(N₃)₂](2), Diisocyanatobis(orotato)nickel(II), [Ni(HOr)₂(NCO)₂] and Dithiocyanatobis(orotato)nickel(II), [Ni(HOr)₂(NCS)₂] have been synthesized¹ and characterized by means of elemental analysis, IR, UV-Vis studies. The Ni(II) ions in [M(C₅H₂N₂O₄)(H₂O)₂(C₃H₄N₂)₂] the complex has a distorted octahedral coordination geometry comprised of one deprotonated pyrimidine N atom and the adjacent carboxylate O atom of the orotate ligand, two tertiary imidazole N atoms and two aqua ligands.

KEYWORDS: Antimicrobial activity, Complex, Ligand, Orotic acid.

I. IMPORTANCE OF OROTIC ACID

Orotic acid (Vitamin B13, uracil carboxylic acid) plays a key role in the biosynthesis of pyrimidine bases of nucleic acids². Some metal compounds of the acid itself and derivatives have successful applications in curing syndromes related with metal ion deficiencies³ and promising applications as therapeutic agents for cancer⁴.

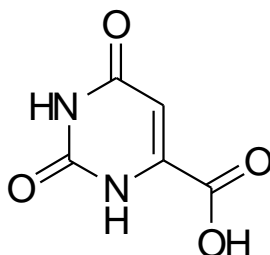


FIG 1 : OROTIC ACID

II. RELATED LITERATURE WORK

The Biocoordination-Chemistry:

The biocoordination chemistry of vitamin B13 therefore demands a better understanding regarding its interactions with metal ions. The orotic acid molecule (H₃Or) has a multidentate nature. The most potential coordination sites in the pH range of 3 to 9 are the carboxylic oxygen and the adjacent pyrimidine nitrogen atom (N1), for the formation of a stable chelate ring. In very alkaline solutions, deprotonation occurs from (N1) and coordination through the other sites becomes available as well due to the existence of different tautomeric forms⁵⁻⁷ and the references therein. The literature lists several reports on mononuclear and polynuclear orotate complexes.

Bioconversion reactions of orotic acid occur in the presence of enzymes. Their activation and normal functioning require metal ions. For this reason a number of papers devoted to the interaction of metal ions with orotic acid and its derivatives have appeared in publications.^{8,9} Attention has been devoted mainly to the interrelation between the chemistry of the metal ions and their role in the life of organisms.

It also exhibits bacteriostatic and cytostatic properties. Besides the biological relevance, the orotic acid and its anions H₂Or₂, HOr₂₂ and Or₃₂ are interesting multidentate ligands as they can coordinate through the two pyrimidine nitrogen atoms, the two carbonyl oxygens and the, oxygens from the carboxyl group. The equilibrium composition of the reactant mixture and thus the solution pH are critical factors which determine the mode of coordination. Between pH 3 and 9, orotic acid exists mainly as readily-coordinating monodeprotonated

H_2Or_2 . It is preferred in ketonic form at low and neutral pH so it coordinates monoanionic from the $-\text{COOH}$ group. At higher pH values, enolic form is preferred and makes the deprotonated heterocyclic ring N atoms available for bidentate coordination¹⁰. The tautomerism between the ketonic and enolic forms allows multifaceted coordinations¹¹ and thus makes the acid an interesting ligand.

Recent interest has focused on the proposed biological carrier function of orotic acid and the corresponding anionic species for metal ions, which is held responsible for the obviously successful application of metal orotates in curing syndromes associated with a deficiency of a variety of metals such as calcium, magnesium, zinc or iron^{12,13}. In the literature review we have mentioned calcium and magnesium structural, spectral and biological chemistry of orotate metal complexes.

So far many complexes containing orotate anions have been prepared and structurally studied^{14,15,16,17,18-28}. In previous works, others have prepared and structurally characterized a series of cobalt(II), nickel(II), copper(II) and zinc(II) complexes containing the orotate anion and 2-methylimidazole ligand²⁹. We have been preparing similar complexes but the ligands are different. We have chosen bridging ligands, pseudohalides for our thesis work.

III. PROMISING LIGAND (H_3Or) CHEMISTRY WITH METALS

Transition metal complexes of orotic acid and its mixed ligand derivatives continue to attract attention because of orotic acid's multidentate functionality and its considerable role in bioinorganic chemistry³⁰. Metal orotates are also widely applied in medicine³¹. In addition, platinum, palladium and nickel orotates with wide variety of substituents have been screened as therapeutic agents for cancer³² as we mentioned in the introduction chapter. Furthermore, zinc(II) and cobalt(II) orotate complexes have shown antimicrobial activity³³. Orotic acid, besides being biologically important, is also an interesting organic building block in coordination chemistry³⁴⁻³⁶. The deprotonated orotates are a widely used ligand for the construction of coordination compounds due to their versatile bridging modes, such as monodentate, bidentate, tridentate bridging and mixed chelating bridging^{35-44,45}. Great interest has been focused on design and syntheses of novel metal-organic hybrid coordination compounds in recent decades, of which multi nuclear clusters show unique catalysis and magnetism^{46,47} and polymeric complexes can afford the intriguing topological network as well as many potential applications in many areas such as optical, separation and gas storage⁴⁸⁻⁵⁰. One of the key challenges in purposeful construction of the new hybrid frameworks depends particularly on appropriate organic ligands or building blocks, of which the cluster cores and multidentate bridging ligands are fine candidates in most cases⁵¹. In addition to a unique role in bio inorganic and pharmaceutical chemistry⁵², On the other hand, it contains potentially hydrogen-bond acceptor and hydrogen donor, and can play differently hydrogen-bonding interactions in supra molecular systems⁵³. In terms of coordination manners, orotic acid exhibits interesting behaviors, in which it employs its carbonyl oxygen or nitrogen atom to link metal ions and the carboxylate oxygen atoms remain free^{54,55}. In terms of valences, orotic acid can act as mono or bi-valence anions to connect metal cations in general, as well as a neutral free ligand to locate in the lattices of the supramolecules sometimes⁵⁴.

The literature lists many reports on the coordinating preferences of the orotate moiety in metal complexes. It was found that in solutions with neutral or slightly acidic pH, Cu(II), Zn(II), Co(II), Mn(II), Fe(III), Cr(III), VO(II), Cd(II), Hg(II) and Ag(I) are coordinated through the carboxylate group, while Ni(II), Co(II) and Cu(II) are coordinated through the carboxylate end and the adjacent N1⁵⁶⁻⁶⁰. Bidentate binding through N1 and the carboxylate group was observed by several crystal structure determinations⁶¹⁻⁶⁵. In the complexes $[\text{Co}(\text{HOr})(\text{OH})(\text{H}_2\text{O})(\text{NH}_3)]_n$ and $[\text{Ni}(\text{HOr})(\text{OH})(\text{H}_2\text{O})_2(\text{NH}_3)]_n$ the orotate anion bridges the metal ions through the carboxylate and the N1 and O2 atoms, forming one-dimensional polymeric chains⁶⁶. A recent reinvestigation of nickel(II) orotate pentahydrate $[\text{Ni}(\text{HOr})(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$ by modern diffraction, spectroscopic and theoretical methods revealed novel structural features⁶⁷. In the present study, we have synthesized and characterized the analogous hexahydrate salt of nickel(II).

The crystal structures of mononuclear Ni^{68,69}, Mg⁷⁰, Co⁷¹, Zn⁷² complexes have been described where orotate dianions (HOr)₂K act as bidentate ligands. In polymeric complexes, (HOr)₂K acts as a polydentate ligand and bridges the metal ions forming 1D-polymeric chains with Ca⁷³, Cd⁷⁴, Mn, Cu⁷⁵, Ni^{76,77} or 2D-layer structures in mixed metal complexes where the layers are interconnected with hydrogen bonds to form the final network structures⁷⁸. Relatively little information is available regarding the compounds with orotate monoanion, (H_2Or)K. Crystal studies with Mg⁷⁹, Zn⁸⁰ and Ni⁸¹ have showed that aquated metal cations interact with the (H_2Or)K counter ions through hydrogen bonds. In these isotopic compounds, the orotate monoanion does not enter the inner coordination sphere of the metal.

Magnesium orotate complexes:

Both vitamin B₁₃ and magnesium orotate have beneficial effects in prophylaxis and treatment of heart diseases⁸². Moreover, complexes of orotic acid and diaminocyclohexane ligands (DACH) with platinum(II) and palladium(II) ions have been investigated as potential anticancer agents⁸³.

Calcium orotate complexes :

An orientation is given concerning the clinical effects of calcium orotate (called Ca orotate for short). Because calcium orotate is free from side effects, It is superior to conventional calcium salts, which have certain problems when applied in osteoporosis with concomitant arteriosclerosis of the abdominal aorta. Calcium orotate, on the other hand, protects the body from arteriosclerosis. Calcium, for this reason, is of value as a food supplement when used in the form of calcium orotate, which can penetrate the cell membranes as a complex form, compensating for defective calcium transit into the cells. In addition, calcium orotate has a special affinity for cartilage and other bradotrophic tissue, where it is metabolized.

Not only is the basic principle of action quite simple, but the long time therapeutic effects are of considerable interest. A new dimension of therapy now appears with the improvements in osteochondrosis and disk degeneration treatment. Far better than the present therapeutic possibilities. Much the same observations seem to apply to osteoporosis. Parallel investigations point to the important pathogenetic significance of a defective calcium transport through the cell membrane. This is the case, for example, in hypertensions--especially essential hypertension--in fatty liver, in disturbances of the ductile of the heart, and in contractile and metabolic insufficiency of the hypertrophic myocardium. In respect to all of these indications, calcium seems to bring about the most promising therapeutic results, when combined with the carrier orotic acid for better transmembrane transport, in the form of calcium orotate.

Lead orotate complexes :

There has been a resurgence of interest in the coordination chemistry of lead(II) in recent years, not only owing to their biological activities⁸⁴, but also because lead(II) possesses a large radius, a variable stereochemical activity, and a flexible coordination environment, which provides unique opportunities for the construction of novel network of topologies⁸⁵. There are two kinds of classifications in lead(II) complexes, holodirected and hemidirected configurations depending on mainly the coordination number^{85c, 86}. It is showing luminiscent property.

IV. CONCLUSIONS

This review mainly focus on complexes of orotic acid with different metals and their spectroscopical studies and biological importance in various human diseases. The bioactivity of these synthesized compounds is a complex phenomenon related to different factors and the metal complexes are more active than the free ligands. These active compounds may serve as a starting point for further studies on metal complexes acting as drugs.

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