

Metal Co-Ordination Compounds with Carbonyl Oximes

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Abstract - This review classifies and summarizes the past 10–15 years of advancements in the field of metal-involving (i.e., metal-mediated and metal-catalyzed) reactions of oximes. These reactions are diverse in nature and have been employed for syntheses of oxime-based metal complexes and cage-compounds, oxime functionalizations, and the preparation of new classes of organic species, in particular, a wide variety of heterocyclic systems spanning small 3-membered ring systems to macroheterocycles. This consideration gives a general outlook of reaction routes, mechanisms, and driving forces and underlines the potential of metal-involving conversions of oxime species for application in various fields of chemistry and draws attention to the emerging putative targets.

Keywords: oxime-based metal complexes, cage-compounds, oxime functionalizations

1. Introduction

The most widely studied carbonyl oxime is 3- hydroxyiminobutane-2-one. It exists in two forms and as shown in Fig. 2.8 and Fig. 2.9. The isomer is unsuitable to yield metal chelates¹. In sharp contrast to vicinal dioximes, carbonyl oximes are poor coordinating agents for Ni(II). The amorphous greyish co-ordination compounds that they yield are usually unstable.²⁻³

They have the stoichiometry, $\text{Ni(L) (LH) (OH)}^{3-4}$ where LH stands for ligands for ligand possess the composition, Cu(L) (OH) . An attempted synthesis of Pd(II) co-ordination compounds of 3-hydroxyiminobutane-2-one has been unsuccessful⁴.

Co(II) ion undergoes rapid oxidation in presence of carbonyl oximes and crystalline co-ordination compounds of the type CoL_3 are isolated having pseudo octahedral⁵⁻⁶ structure (Fig. 2.9), octahedral blue Fe(II) co-ordination compounds $\text{FeL}_2(\text{H}_2\text{O})_2$ and $\text{FeL}_2(\text{PY})_2$ are readily obtained⁷⁻⁸. The hydrates and anhydrous co-ordination compounds are paramagnetic (μ_{eff} 3.4) at room temperature) and the observed moments are somewhat less than the spin only value⁹⁻¹⁰.

Isonitrosoacetylacetone (abbreviated as Hinaa) is a well known example of ligand of the type in Fig. 2.10 which is a poor co-ordinating agent for Ni(II) is reported to yield the co-ordination compound, Cu(L) (OH) . Crystalline, quadri-coordinated, planar Pd(II) coordination compound, Pd(inna)_2 (Fig. 2.11 is readily obtained either by the action of the ligand with Pd(II) salts¹¹ or by nitrosation of Pd(acac)_2 with nitric oxide.

The Co(II) tris chelates of ligand (Fig. 2.12) possess octahedral structure (Fig. 2.11, n=3) as evidenced from spectroscopic data¹²⁻¹³.



Fig.2.8

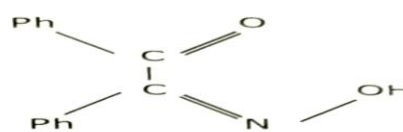


Fig.2.9

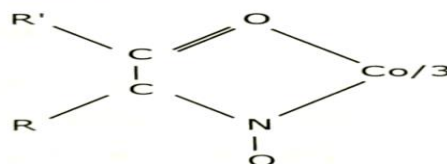


Fig.2.10

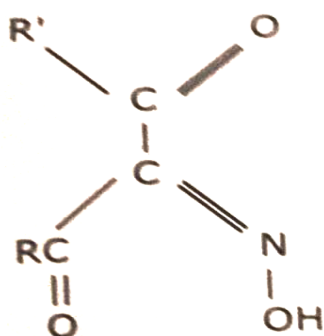


Fig.2.11

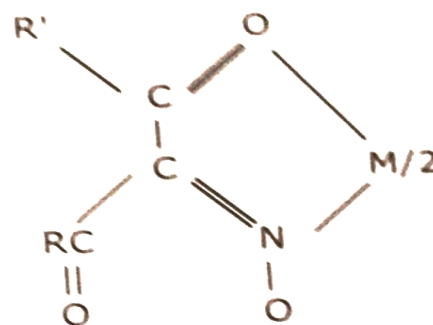


Fig.2.12

Fe(II) yields two types of diamagnetic coordination compounds¹⁴ with Hinaa, $MFe(inna)_3$ ($M = Na, Ca/2$ etc.) in which the co-ordination compounds anion is octahedral (Fig. 2.12) and $Fe(inna)_2(PY)_2$ in which the PY molecules are presumed to occupy axial position of the $Fe(inna)_2$ plane.

We attempted to classify and summarize the past 10–15 years of advancements in the field of metal-involving reactions of oximes. These reactions are diverse in nature and have been employed for syntheses of oxime-based metal complexes and cage-compounds, oxime functionalizations, and the preparation of new classes of organic species, in particular, a wide variety of heterocyclic systems spanning small 3-membered ring systems to macroheterocycles.

In all studied reactions, metal centers play diverse roles in the promotion of the oxime reactions. In nonredox chemistry, the coordination of substrates having multiple bonds (e.g., C=C, C=C, C≡N) to positively charged metal centers leads to their electrophilic activation and facilitates nucleophilic attack by oximes. In contrast, metal-bound oximes are easily deprotonated, as an effect of the metal centers, and are subject to attack by various electrophiles. In some cases, a metal center plays the dual role of activating both the oxime and substrate, thus providing their coupling. Importantly, that coordination of an oxime could lead to C–H, C–Hal, or C–N activation of remote groups, thus inducing oxime side-chain functionalization.

When a redox step is involved, metals provide consequent oxidative addition–reductive elimination reactions, which are quite useful for modern organometallic catalysis, and stimulate reductive splitting of the N–O bond, oxidation, or reduction of the oxime N atom, accompanied by splitting of the C=N bond.

In the vast majority of cases, the reported oxime reactions are catalyzed or mediated by group 8–13 metals, with dominant contributions by copper, palladium (or their combination), rhodium, and iron species. Reactions of oximes involving boron, cobalt, nickel, zinc, ruthenium, iridium, and platinum centers are also known but are less abundant. The promotion of oxime transformations by the early transition metals is either little explored or even unknown for group 3–5 d metals.

Despite the broad spectrum of the reported oxime reactions, these transformations were typically performed with conventional ketoximes and aldoximes, whereas reactions with functionalized oximes featuring heteroatomic substituents at the oxime moiety, viz., amidoximes, nitrooximes (nitrolic acids), oxyoximes, cyanooximes, sulfonyloximes, and chlorooximes, are almost unexplored. Future achievements in metal-involving oxime chemistry could be sought with the early transition metals and the utilization of less common (but easily available) oximes in addition to the commonly used ketoximes and aldoximes. We hope that this survey will stimulate additional interest in the area of organometallic and metal-involving organic chemistry of oximes.

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