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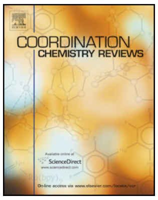

Review

Coordination chemistry and metal-involving reactions of amidoximes: Relevance to the chemistry of oximes and oxime ligands

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Contents

Abbreviations: Alk, alkyl; Me, methyl; Et, ethyl; ^{n}Pr, *n*-propyl; ^{i}Pr, isopropyl; ^{n}Bu, *n*-butyl; ^{t}Bu, tert-butyl; Ar, aryl; Ph, phenyl; Tol, tolyl; Xyl, xylyl, 2,6-dimethylphenyl; Ac, acetyl; Tf, triflyl,trifluoromethylsulfonyl; acac, acetylacetonate; PPN, bis(triphenylphosphine)iminium; dppf, 1,1′-bis(diphenylphosphino)ferrocene; RT, room temperature; ND, no data; THF, tetrahydrofuran; DMF, dimethylformamide; Boc, *tert*-butyloxycarbonyl; Fc, ferrocenyl; XRD, X-ray diffraction; CP MAS, cross-polarization magic angle spinning; HSQC, heteronuclear single quantum coherence; HMBC, heteronuclear multiple bond correlation; ESI-MS, electrospray ionization mass spectrometry; TOSS, total suppression of spinning sidebands; MALDI-MS, matrix-assisted laser desorption ionization mass spectrometry.

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ABSTRACT

Although the versatile chemistry of conventional oximes has been extensively reviewed over the years in both the organic chemistry literature and the coordination chemistry literature, amidoximes, $RC(NH_2)=NOH$, have so far received substantially less attention. Taking into account the increased publication activity on the subject, we systematically review the data on the routes for preparation of amidoxime complexes, the coordination patterns of ligands, and the classification of metal-involving reactions of amidoxime species. This survey includes a comparison of the coordination chemistry and metal-involving reactions of amidoximes with those of conventional ketoximes and aldoximes.

1. Introduction

According to the IUPAC nomenclature [1], amidoximes, $RC(NH_2)=NOH$ (R = Alk, Ar; Fig. 1), are derivatives of carboxamides, which sets them apart from conventional oximes, $RR'C=NOH$ (R′ = Alk, Ar; derivatives of ketones and aldehydes), as a separate class of compounds. Although the oxime and amidoxime structures presented in Fig. 1 are similar, the availability of the NR_2 group exhibiting a strong mesomeric effect in many instances results in a substantial difference in the chemistry of amidoximes and that of conventional oximes.

Although the versatile chemistry of conventional oximes has been extensively reviewed over the years in both the organic chemistry literature (for recent work, see [2,3]) and the coordination chemistry literature [4–13], amidoximes have so far received substantially less attention despite a number of limited-scope reviews specifically focusing on metal-free organic chemistry [14,15], pharmacology [15–18], and amidoxime-based adsorption of heavy metal cationic species [19–21]. Taking into account the increased publication activity on the subject (Fig. 2), and the lack of reviews covering the coordination chemistry of amidoximes and their metal-involving reactions, we believe a comprehensive review of amidoxime coordination chemistry is thus timely.

We aimed to systematically review the data on the routes for preparation of amidoxime complexes, the coordination patterns of ligands, and the classification of metal-involving reactions of amidoxime species. Importantly, our approach included a comparison of the coordination chemistry and metal-involving reactions of amidoximes with those of conventional oximes.

This review is organized as follows. Section 2 provides a brief overview of general synthetic methods leading to metal-free amidoximes and the properties of these species, with an emphasis on acid–base equilibria, which are relevant to ligation of amidoximes to metal centers. Section 3 summarizes the known coordination modes of amidoximes, with particular focus on how the availability of one more donor site (the NR_2 group) affects the coordination patterns known for conventional oximes. Section 4 deals with reactions of ligated amidoxime species, the reactivity of metal-free amidoximes toward ligands, and metal-mediated and metal-catalyzed transformations of amidoximes. We hope that this article will stimulate interest in amidoxime chemistry and prompt further experimental studies and theoretical calculations in this field.

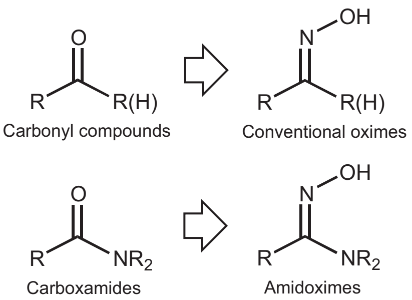


Fig. 1. Structures of conventional oximes and amidoximes and their formal precursors.

2. Synthesis and properties of uncomplexed amidoximes

2.1. Synthesis and commercial availability of amidoximes

One of two general routes to amidoximes includes the treatment of nitriles, RCN **1** (R = Alk, Ar) [22–24], or cyanamides, R′R″NCN (R′/R″ = H, Alk, Ar) [25], with H_2NOH in the presence of a base (typically Na_2CO_3) in MeOH or EtOH on heating (65 or 80 °C, respectively; 6–24 h). This reaction leads to unsubstituted amidoximes, $RC(NH_2)=NOH$ **2** (R = Alk, Ar, NR′R″; Scheme 1), in isolated yields of 60–96%.

Yang et al. [26] recently reported modification of the first method and described one-pot synthesis of $ArC(NH_2)=NOH$ **4** from ArBr **3** via Pd-catalyzed cyanation followed by amidoximation of in situ generated nitrile, ArCN. This reaction was conducted for a series of substituted aryl bromides bearing various substituents

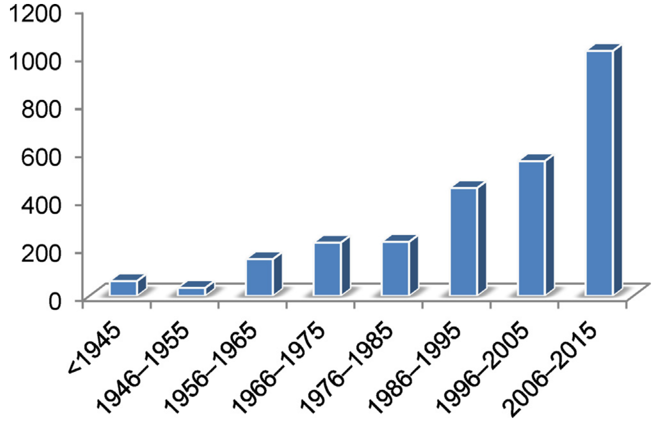
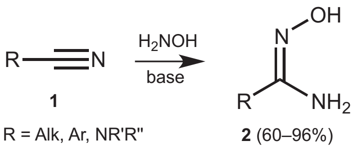


Fig. 2. Number of publications listed in *Chemical Abstracts* mentioning the term "amidoxime" over the years.



Scheme 1. Preparation of unsubstituted amidoximes.