



Review

Coordination chemistry with pyridine/pyrazine amide ligands. Some noteworthy results

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ARTICLE INFO

Article history:

Received 30 January 2012

Received in revised form 16 March 2012

Accepted 21 March 2012

Available online 7 April 2012

Dedicated to Professor Edward Solomon on his 65th birthday.

Keywords:

Pyridine/pyrazine-2-carboxamide ligands

Pyridine-2,6-dicarboxamide ligands

Coordination complexes

Crystal structures

Redox properties

Notable properties

ABSTRACT

Pyridine-2-carboxamide and pyridine-2,6-dicarboxamide-based chelating ligands form a variety of coordination complexes with a number of metal ions, providing varying coordination geometry and nuclearity. Recent years have seen considerable interest in the designing of this class of ligands and to study their structural properties to serve specific stereochemical requirement of a particular metal-binding site. Notably, this class of ligands has been extensively utilized by Mascharak and co-workers to provide low-molecular-weight representations of metallo-proteins/enzymes such as bleomycins, nitrile hydratase. Moreover, the transition metal complexes of this class of ligands are being used as various exogenous nitric oxide (NO) donors. Using over 60 this class of chelating carboxamide ligands, the stereochemical properties of over 150 discrete coordination complexes, studied by single-crystal X-ray crystallography have been analyzed. Various bonding modes for a given chelating ligand are involved, and are reviewed with reference to ligand structure and the resulting coordination complexes. It is shown that the complexes synthesized have served to address notable issues such as effect of ligand structure/donor atom on metal-centered redox potentials, change of spin-state of iron(III), ligand-radical coordinated metal-complexes, interesting chemical reactivity studies, and catalytic potential. The ligands are introduced systematically as a function of their denticity, making easy access to information on specific type of ligands and coordination complexes thereof. X-ray crystallographically determined

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bond lengths of various donor atoms/groups are collected in a table, thus providing an accessible source for reference purposes. Source material for the review amounts to about 90 references.

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1. Introduction: purpose and scope of the review

The coordination chemistry of bispyridylamides and applications of such complexes in catalysis have been reviewed in 2005 in this journal [1]. There has been an explosion of growth in the coordination chemistry of pyridine/pyrazine amide ligands in both the nonbiological and biological areas. There is thus a scope and this article therefore attempts to highlight some notable results in the coordination chemistry of pyridine/pyrazine amide ligands, in their deprotonated forms. Deprotonated pyridine amide groups usually coordinate *via* the nitrogen atom whereas coordination *via* oxygen is more frequent for neutral ligands [2]. The anionic ligand is a strong σ -donor capable of stabilizing metal ions in high (≥ 3) oxidation states.

The properties of metal–ligand coordination compounds are determined in large measure by the nature of ligands bound to the metal ion. Focus is therefore placed on the design of chelating ligands whose metal-binding sites differ in the nature of the donor atom. The purpose of this article is (i) to update the progress made in the design of pyridine/pyrazine amide ligands and (ii) to highlight some notable results of the coordination chemistry developed, using deprotonated forms of the chelating ligands. A large amount of structural data for coordination complexes of selected transition metal ions with various ligand types has been accumulated, giving rise to an opportunity to look into their structural varieties in a systematic manner. Emphasis has been directed to the structural patterns, redox properties, and reactivity aspects. Importance and relevance of coordination chemistry of pyridine carboxamide ligands in the context of bioinorganic chemistry has been kept outside the scope of this article. However, relevant literature references of such chemistry have been provided for ready reference [3–7].

The subject matter has been broadly divided into two parts. First part deals with the ligand design, the coordination complexes synthesized and their structural characterization, and compilation of their metal–ligand bonding parameters in a systematic manner. Ligand design is organized by ligand denticity, with further subdivision into ligand donor type, the nature of spacers between two chelating units, and the nature of heterocycle ring (pyridine or pyrazine). The sections dealing with specific ligand donor types cut across several structural types. For each subgroup of ligands the following facts will be presented: the types of coordination compounds, molecular structural aspects, and selected properties. Second part deals with specific coordination complexes for discussion because they exemplify important concepts concerning the relationship of ligand structure to properties of the metal complexes. Notable contributions from author's laboratory and by others have been presented. Specifically, attention is placed to highlight (i) the spin-state variation of iron(III) complexes as a function of the nature of axial ligands, (ii) the generality and versatility of deprotonated pyridine amide ligands to highly stabilize trivalent state of iron, cobalt, and ruthenium, (iii) the versatility of a common tridentate pyridine-2,6-dicarboxamide ligand to stabilize bivalent, trivalent, and tetravalent states of nickel, (iv) the *noninnocence* nature of 1,2-phenylenediamine-based tetradentate ligand to stabilize ligand-radical coordinated low-spin iron(III) and tridentate pyridine-2,6-dicarboxamide ligand-radical coordinated low-spin ruthenium(III), (v) base-assisted C–S bond cleavage of –SCH₂CH₂S– spacer and Co–C bond formation with –SCH₂CH₂CH₂S– spacer in the case of cobalt complexes, and

(vi) effect of donor atom type and stereochemistry at the metal center on the trends of $E_{1/2}$ values of Fe^{III}–Fe^{II}, Co^{III}–Co^{II}, Co^{II}–Co^I, Ni^{IV}–Ni^{III}, Ni^{III}–Ni^{II}, and Cu^{II}–Cu^I redox processes.

Although there has been much interest in the variety of bonding possibilities associated with pyridine-2-carboxamide- and pyridine-2,6-dicarboxamide-based chelating ligands, in their neutral and deprotonated form, and the amount of structural, spectral, redox, and reactivity properties of their coordination complexes in general and bioinorganic perspectives in particular reported in the literature, so far there is no general review article on the present theme. Since 1990 an extensive variety of coordination complexes with such ligands, and their structures and properties have been published by our group. Therefore we now undertake an attempt to present an overview of these compounds.

The purpose of this review is to update the progress made (i) in the design of chelating ligands having pyridine-2-carboxamide- and pyridine-2,6-dicarboxamide functionality and (ii) in the development of systematic coordination chemistry thereof, utilizing deprotonated form of such ligands.

Understandably, every reference cannot be cited and selection has had to be severely limited. Priority is given mainly to work related to structural chemistry, redox properties, and reaction chemistry. Only those structures that exist as discrete molecules, as opposed to a polymeric network extending throughout the crystal lattice, will be considered. The present review also does not cover categorically multinuclear (more than three metal centers have been excluded) cluster compounds, neither does it attempt to explore specifically organometallic compounds, extensive supramolecular networks, helical structures, and work of an essentially magnetic and catalytic nature.

This review concentrates on notable chemistry developed, with coverage until end of 2011, and it is hoped that it will make researchers in this area aware of a wider range of available ligands and aid them in selecting appropriate ligands for their specific requirements.

2. The ligands and the complexes

In all the complexes described in this article the metal ion is bound to a large variety of chelating ligands containing at least one pyridine/pyrazine amide moiety. The relevant metric parameters for all the structurally characterized complexes of pyridine/pyrazine-2-carboxamide- and pyridine-2,6-dicarboxamide-based chelating ligands considered in this article, are collected in Table 1.

2.1. One pyridine carboxamide unit (bidentate ligands)

The ligands HL¹–HL⁶ are considered in this section (Fig. 1). The complex [Au^{III}(L¹)Cl₂] (**1**) ($S=0$) is nearly square-planar with the two rings being almost coplanar [8]. The copper(II) geometry in [Cu^{II}(L²)₂] (**2**) ($S=1/2$) is distorted toward tetrahedral. In fact, the dihedral angle between the two Cu^{II}N₂ planes is $\sim 40^\circ$ [9]. Compared to the structurally characterized square-pyramidal structure of [Cu^{II}(L²⁷)(H₂O)] [10] (see below) it is revealed that two L²(–) ligands exert a measurable degree of geometric control over the coordination sphere of **2** (distorted toward tetrahedral). The Cu^{II}–Cu^I redox potentials in *N,N'*-dimethylformamide (DMF) solution were determined by cyclic voltammetry. Upon replacement of the tetradentate ligand L²⁷(2–) by two bidentate ligands

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