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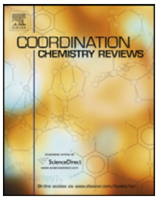

Review

Advances in the coordination chemistry of nitrogen ligand complexes of coinage metals

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This article is dedicated to my mentor Professor John P. Fackler, Jr. on the occasion of his 75th birthday. His guidance has enlightened my life and will continue to do so.

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ABSTRACT

Coinage metals nitrogen chemistry has not been studied extensively until recently. The focus of this review is the base- and halide-free complexes of the monoanionic nitrogen ligands. This review describes how minor ligand modifications can result in a drastic change in the metal–metal interactions in multinuclear compounds. Crystal structures of these complexes show individual complexes, dimers, supramolecular columnar packing or more complex supramolecular aggregates. Bulky substituents on the ligands can prevent intermolecular metal–metal interactions or the formation of supramolecular architectures. The nuclearity and metal–metal interactions in these complexes are controlled by ligand steric and electronic factors and solvent of crystallization. Many classes of nitrogen ligand coordination compounds have given rise to advances in several fundamental and applied research aspects. Recent potential applications of nitrogen ligand complexes are highlighted particularly for those complexes included in this review.

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1. Introduction

Studies involving coinage metal complexes of nitrogen donor ligands range from classical coordination chemistry to the developing field of bioinorganic chemistry. Many classes of these coordination compounds that exhibit various structures have been reported, which has given rise to advances in several fundamental and applied research aspects. There are wide applications for these materials in medicine [1], light emitting diodes fabrication [2], lubricant additives [3], catalysis [4], chemical vapor deposition [5], liquid crystals [6] and ionic liquids [7]. The applications of coinage metal nitrogen complexes represent a major step forward in this area of research.

The interest in metal amide complexes, particularly those of copper, is due to their potential applications in electrophosphorescence devices (EL) [8] and homogenous catalysis [9]. Amide chemistry, specifically the dialkylamides and disilylamides, was reviewed in 1976 by Bradley and Chisholm [10]. An overview of the current state of the tripodal amide complexes in main group and transition metal chemistry has been presented by Gade [11]. Bailey highlighted the synthesis of useful metal amides and imides with applications in organic synthesis in *Science of Synthesis* [12]. Another book *Metal Amide Chemistry*, which appeared recently by Lappert et al., describes the synthesis, structure, reactions and applications of metal amides and related compounds which are stable at ambient temperatures and particularly those which are mono-, di-, or oligonuclear [13].

Pyrazole ligands have been utilized in various applications ranging from anion-recognizing materials to liquid crystals. Copper pyrazolates, for example, form a multinuclear copper cavity with centered anions [14]. Triangular copper(II) pyrazolate complexes can accommodate μ^3-bridging halides; the controlled interchange of these anions brings about an orderly transition from antiferromagnetic to ferromagnetic exchange among the copper centers [15]. In addition, trinuclear copper complexes with trigonal symmetry are of pursuit in terms of both industrial applications and in understanding the mechanism of action of copper-containing enzymes [16]. Metallomesogens, liquid crystals containing metal ions, from substituted gold pyrazolates with long alkyl chains have attracted much attention in expectation of their unique properties [17,18].

Several aspects of the structural chemistry of metal pyrazolates have been investigated such as the use of *ab-initio* X-ray powder diffraction (XRPD) methods to determine the structure of polymeric metal pyrazolate complexes [19], the polydentate ligands containing pyrazole as main donor groups and of their metal complexes [20], the interesting coordination modes from pyrazolate ligands [21], the role of the pyrazolate ligands in building polynuclear transition metal systems [22], various bonding modes for pyrazole-based ligands and the resulting coordination complexes [23], and the structural diversity and the metal coordination modes adopted by pyrazoles and pyrazolides-flexible synthons [24].

Triazoles have been investigated for pharmaceutical purposes. Triazole metal interactions play a major role in the biological actions of triazole containing drugs. The industrial applications of metal-triazole compounds include anti-corrosion coatings, photographic materials, dyes and additives for oils and greases [25]. Specifically azole complexes with silver are of special interest due to their potential applications in photography and silver plating. The first silver azole complex was reported in 1893 [26]. A comprehensive review of metal complexes with triazolates and polyazolates was published by More and Robinson [27]. Haasnoot reviewed the mononuclear, oligonuclear and polynuclear metal coordination compounds with triazole derivatives [28].

The interest in amidinate and guanidinate complexes stems from their diverse applications in many areas of chemistry including organocatalysis [29]. The utilization of bulky guanidinates for the stabilization of low oxidation state metallacycles was reviewed recently by Jones [30]. Edelmann reviewed the nitrogen-silated benzamidines as versatile building blocks in main group and coordination chemistry [31], and the coordination chemistry of amidinate and guanidinate ligands [32]. Amidine ligands coordination chemistry [33] and the neutral guanidines and monoanionic and dianionic guanidinates coordination chemistry have been reviewed by Bailey and Pace [34]. Bicyclic-guanidines were reviewed by Coles in light of the recent advances in the synthesis of new derivatives and the potential for cross-stimulation of different areas [35].

Tris(pyrazolyl)hydroborates (TpRR′) containing alkyl or aryl substituents at the pyrazolate positions are of special interest because of their coordination chemistry and are ideal for bioinorganic model building [36]. The methylated pyrazolylborate complex is of significance since it forms a carbonyl complex with stretching frequency even closer to that of carboxyhemocyanin than the unmethylated analogue. Dinuclear copper complexes of tris(pyrazolyl)borate ligands have been studied as models for the enzyme oxyhaemocyanin [37]. The coordination chemistry of scorpionate has also made an incredible increase in the number of potentially useful ligand derivatives through deliberate syntheses of water-soluble coordinated ligands. Such derivatives

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