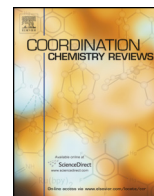




Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Recent advances in coordination chemistry of metal complexes based on nitrogen heteroaromatic alcohols. Synthesis, structures and potential applications

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Abbreviations: AcO, actate; MeCN, acetonitrile; AdCO₂, 1-adamantanecarboxylate; PhCO₂, benzoate; H₂dae, 1,2-bis(5-carboxyl-2-methyl-3-thienyl)perfluorocyclopentane; bba, 2-benzoylbenzoate; L^p, N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)amine; 2Brbz, 2-bromobenzoate; 2Clbz, 2-chlorobenzoate; 2Clnic, 2-chloronicotinate; 4Clsal, 4-chlorosalicylate; C₅H₅⁻, cyclopentadienyl anion; C₆H₄O₂, cyclopentadienyl carboxylate; chp, 3-cyclohexyl-1-propanol; dcn, dicyanate; 5Fsal, 5-fluorosalicilate; 2,6pdmH₂, 2,6-(dihydroxymethyl)pyridine; dmb, 3,3-dimethyl-1-butanol; 2,2MeepH, 2-(2,2-dimethylethanol)pyridine; 3,5(NO₂)₂bz, 3,5-dinitrobenzoate; dp2hmpH, diphenyl(pyridine-2-yl)methanol; 5ehmpH, 5-ethoxycarbonyl-2-(hydroxymethyl)pyridine; hmbimH, 2-(hydroxymethyl)benzimidazole; mmiH, 3,5DMePzMeOH, 1-hydroxymethyl-3,5-dimethylpyrazole, 2-hydroxymethyl-1-methyl-imidazole; 3hmpH₂⁺, 3-(hydroxymethyl)pyridinium cation; 2hepH, 2-(hydroxyethyl)pyridine; 2hmpH, 2-(hydroxymethyl)pyridine; 3hmpH, 3-(hydroxymethyl)pyridine; 4hmpH, 4-(hydroxymethyl)pyridine; 2hppH, 2-(hydroxypropyl)pyridine; ⁱPrO, isopropanolate; PrⁱNH₂, isopropylamine; mef, mefenamate; MeO⁻, methoxy; 2MeSnic, 2-methylthionicotinate; HL, 2-methyl-1-(pyridine-2-yl)propan-2-ol; mal, metoxyaniline; nif, niflumate; 2NO₂bz, 2-nitrobenzoate; 4NO₂bz, 4-nitrobenzoate; nmpdH₂, 2-nitro-2-methyl-1,3-propanediol; piv, pivalate; 2pyc, pyridine-2-carboxylate; HL S, 2,6dpyc, pyridine-2,6-dicarboxylate, 4-(pyridin-2-ylmethyl)tetrahydro-2H-thiopyran-4-ol; PrCO₂, propionate; PhPrCO₂, 3-phenylpropionate; dm2hmpH, 2-(pyridine-2-yl)propan-2-ol; 3paCO₂, 3-pyridylacrylate; sac, saccharinate; Bu2hmpH, 4-tertbutyl-2-(hydroxymethyl)pyridine; Et₃N, triethanolamine; thmeH₃, L^s, N,N,N-tris(3,5-dimethylpyrazol-1-ylmethyl)amine, 1,1,1-tris(hydroxymethyl)ethane; PPh₃, triphenylphosphine; Bu2hmpH, 4-tertbutyl-2-(hydroxymethyl)pyridine; Et₄N⁺, tetraethylammonium cation.

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<http://dx.doi.org/10.1016/j.ccr.2016.01.007>

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ARTICLE INFO

Article history:

Received 15 December 2015
Received in revised form 18 January 2016
Accepted 20 January 2016
Available online xxx

Dedicated to Professor Henryk Kozłowski
on the occasion of his 70th birthday.

Keywords:

N-heteroaromatic alcohol
Coordination mode
Magneto-structural relationship
Single-molecule magnet
Biological activity
Multipodal ligand

ABSTRACT

This review is focused on the use of nitrogen-containing heteroaromatic alcohols as ligands with increasing significance in diverse areas of chemistry. The application of such ligands ranges from structural chemistry, catalysis, and biomimetic modelling to molecular magnetism of polynuclear transition metal clusters as single-molecule magnets (SMMs). The efficiency of these ligands for the assembly of polynuclear complexes is due to their simultaneous N,O-chelating and O-bridging capabilities. For these reasons, to investigate the coordination chemistry of N-donor heteroaromatic alcohols presented in our earlier review, in this study, we paid special attention to (i) general approaches to formulate new SMMs based on 3d and 3d–4f central ions of polynuclear species and their structural and magnetic properties and (ii) synthesis of functional mimetics of metalloenzymes, such as catalase, and complexes with cytotoxic and antimicrobial properties. We also present an interesting group of coordination complexes with new multipodal ligands obtained *in situ* using 1-hydroxymethyl-3,5-dimethylpyrazole as a proligand.

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1. Introduction

Recently, special attention in the field of coordination chemistry has been continuously focused on nitrogen heteroaromatic alcohols as a class of commercially available ligands possessing versatility in coordination ability. A wide variety of interesting architectures of complexes based on N,O-donor alcohols results from many variants of their donating capabilities for example: (i) in neutral form: N-monodentate (κN) [1], N,O-chelating ($\kappa^2 N,O$) [2]; and (ii) as deprotonated chelating ($\kappa^2 N,O$) [2] and bridging ($\kappa N:\kappa O$ [3], $\kappa^2 N,O:\kappa O$ [4] and $\kappa^2 N,O:\kappa O:\kappa O$ [5]) or (iii) simultaneously $\kappa^2 N,O:\kappa O$ and $\kappa^2 N,O:\kappa O:\kappa O$ bridging [6]. As a consequence of their special features, N-heteroaromatic alcohols are widely used (i) as a core building material of polynuclear metal complexes (SMMs) [4], (ii) in the preparation of coordination compounds with a broad spectrum of biological activities comprising anticancer [7], antimicrobial [8] and antioxidant [9,10] functions, (iii) as a new catalyst with multipodal ligands based on 1-hydroxymethyl-3,5-dimethylpyrazole [11–16], and (iv) as coordination compounds for modelling the structure or function of biomolecules [17,18].

Accordingly, this review aims to systematize the current information in this field and provide some perspectives for possible applications of this important class of coordination compounds. This work examines N-donor heteroaromatic alcohol coordination chemistry [19] and covers original papers mostly published over the period of 2005–2015 with the inclusion of several prominent earlier publications.

2. Versatility of nitrogen heteroaromatic alcohols as ligands in coordination compounds

Simple pyridine alcohols are commercially available substances that can act as ligands in coordination compound formation and build up interesting architectures because they possess two potential donor atoms: (i) a pyridine N-atom, which usually coordinates to the metal centre, and (ii) hydroxide O-atom, which often acquires a bridging function [20]. The hydroxo group may be deprotonated to yield the alkoxo group, which is known to be a good bridging species with the ability to offer a pathway for magnetic exchange. In addition, a pyridine nitrogen atom can accept a proton to yield a pyridinium cation [21,22]; this is a rare but not unprecedented species observed in the system of simple pyridine-based alcohols [23,24]. Surprisingly, such simple molecules have not been employed widely as ligands in coordination chemistry, and only a portion of these activities are observed in Mn, Co, Cu, Ni and Fe chemistry [25].

2.1. Coordination modes of 2-substituted pyridines depending on alcoholic arm length

Despite the simplicity of the construction of 2-(hydroxymethyl)pyridine (2hmpH) *i.e.*, only two donor atoms it can take different chemical forms and coordination modes in its metal complexes, which is confirmed by the number of examples of coordination compounds characterized in Table 1.

The monodentate κN fashion of 2hmpH *via* the pyridine nitrogen atom is observed only in a small group of Pt^{II} and Pd^{II} analogues of transplatin: **1** [1], **2** [7], **3** [26], **4** [27], **5** [7], and **6** [27] (Table 1). All of those complexes form monomeric units with coordination spheres in a distorted square-planar arrangement. Because of these complexes' biological activities, they will be described more specifically in Section 4. The neutral form of 2hmpH usually occurs in bidentate $\kappa^2 N,O$ mode, forming N,O-chelate five-membered rings, as in the following newest complexes: **7** [20], **8** [28], **9**, **10** [2], **11** [29], **12** [30], **13** [31], **14** [9], **15** [8], **16** [10], **17** [32], and **18** [33] (Table 1). Most of them were obtained by a simple reaction of metal salt with 2hmpH in aqueous or alcoholic solution. There are two complexes of 2hmpH: **19** [34] and **20** [25] (Table 1), in which heteroaromatic alcohol behaves as a bridging $\kappa N:\kappa O$ ligand. Deprotonation of the hydroxyl group enhances the basicity and complexing properties of pyridine-based alcohols. The proton transfer reaction can be caused by the addition of basic compounds, or it occurs unintentionally as a result of specific reaction conditions. A bidentate chelating $\kappa^2 N,O$ fashion of 2hmp is also rarely found in the literature: **21** [2], **22** [26], **23** [35], and **24** [36] (Table 1).

The alkoxide arm of 2hmp usually causes the formation of multinuclear clusters owing to its bridging properties, and it supports ferromagnetic coupling between the metal atoms. Therefore, this feature is often used to design SMMs and high-spin molecules. The following coordination modes of 2hmp were observed (Table 1): (i) $\kappa^2 N,O:\kappa O$ bridging mode in complexes **25** [6], **26** [37], and **27** [38]; (ii) $\kappa^2 N,O:\kappa O:\kappa O$ bridging mode in **28** [39], **29** [5], **30** [32], **31** [37], and **32** [38] and (iii) simultaneously $\kappa^2 N,O:\kappa O$ and $\kappa^2 N,O:\kappa O:\kappa O$ bridging in **33**, **34** [6], and **35** [40]. This class of compounds will be discussed in detail in the next section.

Coordination chemistry of 2-(hydroxyethyl)pyridine (2hepH) and 2-(hydroxypropyl)pyridine (2hppH) is not as broadly explored as the chemistry of 2hmpH. This is probably caused by the fact that 7-membered chelate rings are less stable than 6-membered and 5-membered rings [41,42] (Table 2). According to Table 2, several compounds with a neutral form of 2hepH were noted. Among them, the complexes with monodentate κN behaviour **36** [7] and **37** [7] are observed. 2HepH also exhibits bidentate $\kappa^2 N,O$ fashion in complexes with (i) CN = 5: **38** [20] and **39** [43]; (ii) CN = 6: **40** [9], **41** [44], **42** [45] and **43** [46] and (iii) CN = 8: **44** [29]. All of these

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