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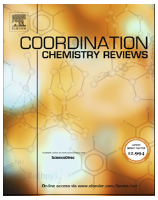

Review

Tridentate pyridine–pyrrolide chelate ligands: An under-appreciated ligand set with an immensely promising coordination chemistry

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ABSTRACT

This review covers all aspects of the chemistry of metal complexes of tridentate κ^3-N pyridine–pyrrolide ligands, from the syntheses of the ligands to what is known about the metal complexes – their structural and physical properties, and their reactivities, including use in catalytic processes. Applications of the complexes range from the switching elements in molecular devices, to luminophores in electroluminescent devices and photosensitisers in light-driven catalyses, to anticancer therapeutics and to efficient catalysts for organic transformations. The general properties of the ligands and metal complexes are deduced from the available literature, and areas of κ^3-N pyridine–pyrrolide metal complex chemistry ripe for development are pinpointed.

Contents

Abbreviations: CT, charge transfer; CV, cyclic voltammetry; DFT, density functional theory; EL, electroluminescence/electroluminescent; Fc$^{+/0}$, ferrocenium/ferrocene; Py, pyridine; Pyr, pyrrole/pyrrolide; RMS, root mean squared; SC-XRD, single crystal X-ray diffraction; SCE, saturated calomel electrode.

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1. Introduction

We provide a first and comprehensive review of tridentate pyridine–pyrrolide ligands with cores $\mathbf{B}^{-}$–$\mathbf{E}^{2-}$ (Fig. 1), their preparations and properties, and their coordination chemistry, with an emphasis on the uses or potential uses of their coordination complexes, all in order to raise awareness of these under-appreciated ligands and complexes.

1.1. An obvious analogy between 2,2′:6′,2″-terpyridine and tridentate pyridylpyrrolide anions

At the cutting edge of contemporary ligand design are pincer ligands. Innovation in pincer ligands has provided a veritable cornucopia of novel metal complexes, which have bolstered many advances, for example, in molecular sensing [1–4], as potential therapeutic agents [1,2,5–7] and, most of all, in catalysis [1,2,8–12] including in cutting-edge molecular devices for (light-driven) energy conversion and storage [1,2,13–16]. The term “pincer ligand” is of course just an affectatious modernism; it is an *avant-garde 'nom de guerre'* for the coordination chemists’ commonplace meridional ligand.

2,2′:6′,2″-Terpyridine (tpy or terpy) is the prototypal meridional metal-binding κ^3-N-ligand, **A** in Fig. 1 [17–39]. The coordination chemistry of terpyridine is rich and varied, extending as it does throughout the Periodic Table from the *s*-block metal cations, through the variable oxidation state transition metal ions to the *p*-block metal cations, and on to the lanthanide and actinide ions [17]. Numerous terpyridyl metal complexes have been discovered that exhibit diverse and very useful photophysical, redox, magnetic, catalytic and medicinal properties [17–39]. Given the diversity and usefulness of simple monometallic terpyridyl complexes, it is not surprising that the terpyridyl ligand has been regularly exploited to construct metal-containing supramolecular assemblies or macromolecular polymers, with those containing bis(terpyridyl)metal photo and/or redox centres being of particular interest [21,22,24,28,31,33,40,41]. The reader is referred to the many excellent and comprehensive reviews for further information on this now voluminous body of ever-expanding research [17–39].

The focus of this review is ligands formed by replacement of one or more the pyridine rings in terpyridine (**A**) by the pyrrolide anion to afford three-ring, pyridine-pyrrolide ligands $\mathbf{B}^{-}$–$\mathbf{E}^{2-}$. In comparison with terpyridine, the coordination chemistry of the pyridine–pyrrolide ligands $\mathbf{B}^{-}$–$\mathbf{E}^{2-}$ is sparse. Why: is there a reason

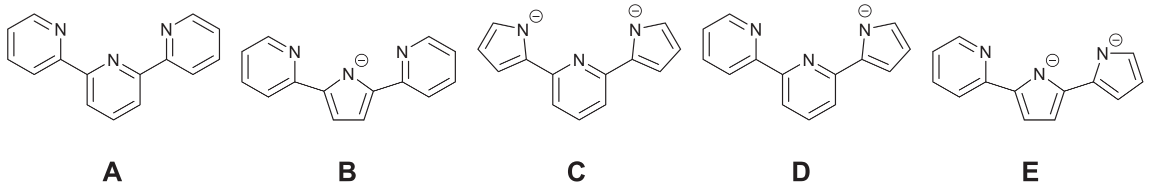

Fig. 1. Drawings of the three ring, 18 π-electron, meridional ligands with pyridine and pyrrolide donors; namely commonplace 2,2′:6′,2″-terpyridine (**A**), 2,5-di(2-pyridyl)pyrrolide anion (**B**), 2,6-di-(2-pyrrolide)pyridine dianion (**C**), and the asymmetric ligands, 2-(2,2′-bipyridin-6-yl)pyrrolide anion (**D**) and 5-(2-pyridyl)-2,2′-bipyrrolide dianion (**E**) (not shown is the 2,2′:5′,2″-terpyrrolide trianion as a genuine metal complex of this is yet to be reported).

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