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The pentadentate ligands 2PyN2Q and N4Py, and their Cu(II) and Zn(II) complexes: A synthetic, spectroscopic and crystallographic structural study

Warrick K.C. Lo [a,*], C. John McAdam [a], Allan G. Blackman [b], James D. Crowley [a], David A. McMorran [a,*]

[a] Department of Chemistry, University of Otago, P.O. Box 56, Dunedin 9054, New Zealand
[b] School of Applied Sciences, Auckland University of Technology, Private Bag 92006, Auckland 1142, New Zealand

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ABSTRACT

The synthesis and characterization of the new ligand *N*,*N*-bis(2-quinolylmethyl)-*N*-bis(2-pyridyl)methylamine (2PyN2Q), a derivative of *N*,*N*-bis(2-pyridylmethyl)-*N*-bis(2-pyridyl)methylamine (N4Py) is reported. Purification of both N4Py and 2PyN2Q on Dowex cation exchange columns as their hydrochloride salts allowed the isolation of the byproducts N3Py and 2PyNQ, respectively. The X-ray crystal structure of $[H_2N4Py](PF_6)_2$ shows that the two more basic picolyl nitrogens are protonated. X-ray structural analyses of the copper(II) complexes $[Cu(N4Py)(NO_3)](NO_3)$ (**1**) and $[Cu(2PyN2Q)(NO_3)](NO_3)$ (**2**) show that the binding of the nitrate ligand is influenced by the steric bulk of the quinoline rings while electrochemical studies show that the poorer basicity of the quinolinyl donors makes **2** more easily reduced than **1**. X-ray structural analyses of the zinc(II) complexes $[Zn(N4Py)(OH_2)](CF_3SO_3)_2{\cdot}H_2O$ (**3a**$\cdot H_2O$), $[Zn(N4Py)(CH_3OH)](ClO_4)_2{\cdot}CH_3OH$ (**4**$\cdot CH_3OH$) and $[Zn(2PyN2Q)(NCCH_3)](ClO_4)_2{\cdot}CH_3CN$ (**6**$\cdot CH_3CN$) again show that the quinoline rings have a significant influence on the way in which the monodentate ligand can bind to the zinc center. The X-ray crystal structure of $[Zn(2PyNQ)_2](ClO_4)_2$ (**7**) is also reported. In **7** the zinc(II) ion is bonded to two pyridyl donors and one amine donor from each of two ligands and the quinolinyl donors are not bound.

1. Introduction

Ligands containing multiple pyridyl donors are now a key part of many areas of modern coordination chemistry. The subtle interplay of electronic and structural properties of these ligands, combined with the ease of their synthesis, means that a wide variety of ligands have been prepared and studied [1–3].

The pentadentate ligand *N*,*N*-bis(2-pyridylmethyl)-*N*-bis(2-pyridyl)methylamine (N4Py, Fig. 1) has been shown to be of considerable use in the construction of various transition metal complexes. Comprising two pairs of pyridyl donors and one amine donor, it is essentially preorganized for the generation of octahedral complexes where the remaining monodentate ligand is *trans* to the amine donor and *cis* to the four pyridyl donors. As such, N4Py complexes have been the subject of significant study as models for biologically interesting non-heme systems [4]. The majority of these works have focused on the ability of the N4Py scaffold to stabilize Fe(IV)-oxo species [5–8], which have been shown to act as oxidants for a variety of biological [9,10] and non-biological [8,11–14] substrates. The oxidizing properties of Mn systems [15–22] and, to a lesser extent, Ru [23,24], Co [25] and Cu [26] systems have also been reported.

It has been clearly shown that the electronic and structural properties of different pentadentate N5 ligands can have a marked effect on the catalytic properties of Fe(IV)=O complexes derivatives [27,28], and there have been several reports of complexes containing derivatives of the basic N4Py skeleton (Fig. 1). For example, in a recent study, the ligand N3PyS (species **A** in Fig. 1), where one pyridyl donor was replaced by a thiolate, has been used to prepare $[Fe(NO)(N3PyS)]^+$ as a model for NO-bound cysteine dioxygenase [29]. This complex was found to have enhanced photochemical properties compared to the related N4Py complex. Manganese complexes containing an N4Py derivative in which one pyridyl donor is replaced by a deprotonated amide (species **B** in Fig. 1) have also been reported to display enhanced oxidation properties compared to the N4Py complexes themselves [30]. N4Py derivatives that maintain the same donor set have also been reported. Appending amide groups and/or phenyl rings to the

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* Corresponding authors. Tel.: +64 3 479 7934.
E-mail addresses: warrick.lo@otago.ac.nz (W.K.C. Lo), davidm@chemistry.otago.ac.nz (D.A. McMorran).

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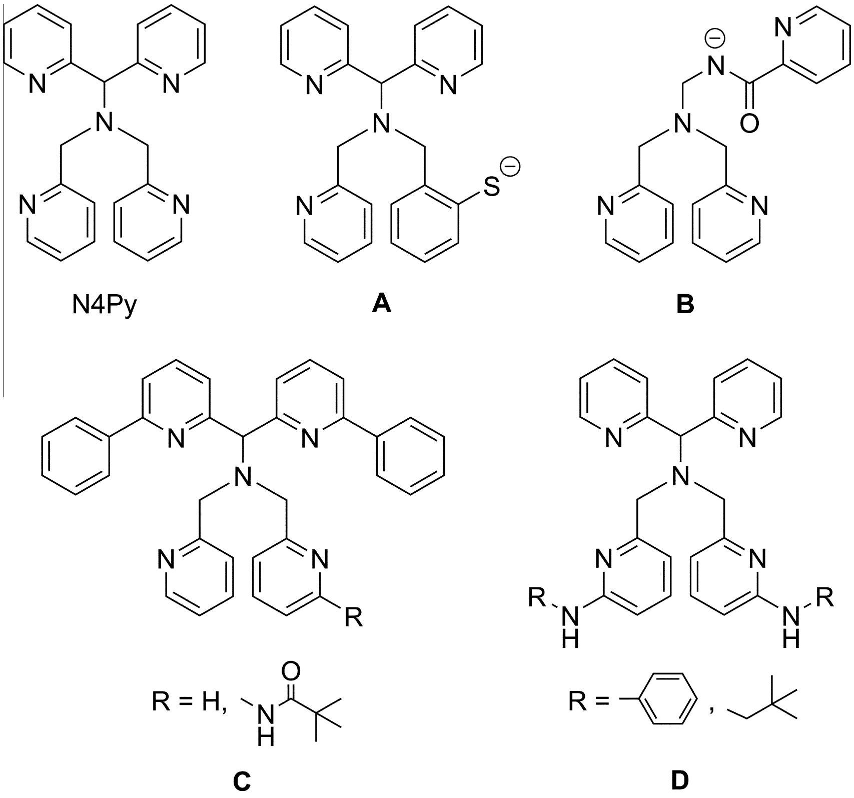

Fig. 1. Ligand N4Py and some of its derivatives reported in the literature.

pyridyl donors (species **C** in Fig. 1) has been shown to modify the reactivity of Fe(IV)=O complexes [31]. N4Py derivatives have also been reported where neopentyl amine or aniline groups were appended to the two picolyl rings (species **D** in Fig. 1) in such a way that their NH protons pointed towards the coordination site for the monodentate ligand, facilitating the complexes' reactivity towards dioxygen [32].

We have been interested in the potential use of cobalt N4Py complexes as catalysts in photocatalytic hydrogen production. A recent preliminary report shows that such complexes can indeed act as photocatalysts for such reaction [33]. As was the case for the iron and manganese systems, the reactivity occurs at the coordination site for the monodentate ligand, and we have systematically prepared and characterized a series of cobalt N4Py complexes $[Co(N4Py)(L)]^{n+}$ with differing monodentate ligands to ascertain how these affect the oxidative ability of the complex [34]. We have also become interested in how variations to the N4Py skeleton itself might influence the properties of these complexes [35]. To this end, we now report the new ligand *N*,*N*-bis(2-quinolylmethyl)-*N*-bis(2-pyridyl)methylamine (2PyN2Q, Fig. 2), where two of the pyridyl donors have been replaced by more sterically imposing quinolinyl donors. We supposed that the presence of these extra rings adjacent to the monodentate ligand might affect the nature of the binding or indeed the types of ligands that can be bound [36,37]. We report here the synthesis and characterization of 2PyN2Q and also a new modification of the standard synthetic procedure for N4Py: both ligands were converted to their hydrochloride salts and then purified by cation exchange chromatography. The ligands, and their Cu(II) and Zn(II) complexes, were characterized by NMR spectroscopy, high resolution electrospray ionization mass spectrometry (HRESI-MS) and elemental analyses. These complexes show, as we expected, that subtle electronic differences result from the modification of the pentadentate ligand. X-ray crystallography further confirms that the quinoline rings modify the steric environment of the monodentate ligand. We also report a Zn(II) complex of the new ligand *N*-(2-quinolylmethyl)-*N*-bis(2-pyridyl)methylamine (2PyNQ, Fig. 2), a byproduct in the synthesis of 2PyN2Q, which highlights the difference in basicities between the pyridyl and quinolinyl donors in the ligand, and the X-ray crystal structure of the diprotonated form of N4Py.

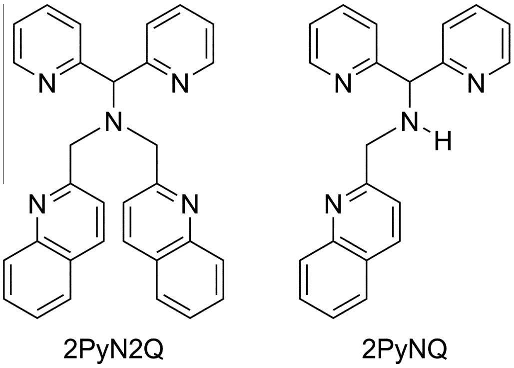

Fig. 2. The quinoline-based ligands featured in this work.

2. Experimental

2.1. General methods

All regents were laboratory reagent grade or better and used as received. Di(pyridin-2-yl)methanone oxime and di(pyridin-2-yl)methanamine were synthesized according to literature procedures [38]. All NMR spectra were recorded at 298 K. One-dimensional (^{1}H and ^{13}C) and two-dimensional (gCOSY, TOCSY,