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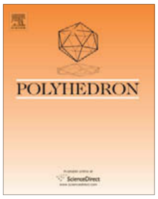

The Re(I) coordination chemistry of a series of pyrido[2,3-*b*]pyrazine-derived ligands: Syntheses, characterisation and crystal structures

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ABSTRACT

Reaction of 2,3-diaminopyridine with one equivalent of a functionalised vicinal diketone, in ethanol, yields a series of ligands based upon the pyrido[2,3-*b*]pyrazine core. The ligands were characterised by ^{1}H, ^{13}C–{^{1}H} NMR, MS and UV–Vis spectroscopy. Reaction of the ligands with one equivalent of {ReBr(CO)$_5$} gave a series of **Re-L^n** complexes based upon the general formula *fac*-{ReBr(CO)$_3$(L)} (where L = pyrido[2,3-*b*]pyrazine-derived ligands, **L^1**–**L^6**). Solution IR studies confirmed the retention of the facially capped, tri-carbonyl coordination geometry at rhenium, and ^{1}H NMR studies confirmed coordination of the ligand to Re(I). EI HR MS data were obtained for each complex confirming the proposed formulation and stoichiometry. Single crystal X-ray structures were obtained for three of the complexes (**Re-L^1**, **Re-L^2**, **Re-L^6**), with each demonstrating that the ligands coordinate to Re(I) in a bidentate manner, via a four-membered chelate ring, which was unsymmetrical in the former two cases. The electronic absorption spectra of the complexes showed absorption into the visible region ca. 375–500 nm, (the complexes are orange-red in appearance). Following irradiation at 350–450 nm, the complexes display a solid-state broad emission peaking between 600–700 nm. The complexes were not sufficiently luminescent in solution to allow further investigation into the origin of this emission band, although with reference to related 1,8-naphthyridine complexes of Re(I) it is likely to incorporate significant ^{3}MLCT character.

1. Introduction

The coordination chemistry of Re(I) with di-imine type ligands has attracted significant effort since the discovery by Wrighton in 1974 of luminescence originating from a triplet metal(rhenium)-to-ligand(1,10-phenanthroline) charge transfer (^{3}MLCT) transition [1]. This has encouraged numerous studies focusing on the syntheses of poly-pyridine complexes of Re(I), their incorporation into supramolecular architectures and their photophysical properties [2]. Importantly, the luminescent characteristics of the generic molecular form *fac*-{Re(CO)$_3$(**L^x**)(**L^y**)}$^+$ (where **L^x** = di-imine; **L^y** = monodentate ligand) can be tuned via consideration of the electronic characteristics of the coordinated ligands [2c–d,3]. Consequently, since the ^{3}MLCT excited state is localised on the sole di-imine ligand, this has allowed the rational design of responsive systems that can report the presence of an analyte [4] or the local solvent environment [5].

More specifically, the precise physical molecular requirements of the complex depend upon the chosen application. For example, the use of Re(I) complexes in the fluorescence microscopy of cells [6] obviously requires species with good kinetic stability in aqueous solutions with an ionic background. In contrast, materials applications involving di-imine complexes of Re(I), such as photovoltaics [7], potentially allow rarer ligand systems to be exploited: for example, the use of 1,8-naphthyridine (when coordinated in a bidentate fashion 1,8-naphthyridine induces a four-membered chelate ring) with Ru(II) has shown improved photovoltaic efficiencies when compared to the Grätzel prototype which incorporates 2,2-bipyridine [8]. Related recent reports have also demonstrated that 1,8-naphthyridine derivatives can also coordinate to Re(I) in a bidentate fashion, giving rise to emission from a ^{3}MLCT excited state [9], whilst methylation at the 2,7-positions appears to moderately improve stability in non-polar solvents [9]. A closely related class of heterocyclic ligands are the pyrido[2,3-*b*]pyrazines [10], which could potentially allow an analogous coordinating mode to the related 1,8-naphthyridine systems. Pyrido[2,3-*b*]pyrazines have been the subject of many investigations in their own right particularly due to their biological importance [11], including anti-tumour activity [12]. Such species can be conveniently synthesised via the condensation of 2,3-diaminopyridines with a variety of functionalised dione reagents. In contrast, the coordination chemistry of pyrido[2,3-*b*]pyrazines is extremely limited. Examples appear to be limited to pyrido[2,3-*b*]pyrazine itself: complexes with Sn(II) are known [13] where ligation occurred in a bidentate fashion; and bidentate coordination to Ru(II) (in an analogous manner to 1,8-naphthyridine) has also been

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reported [14]. The coordination chemistry of substituted pyrido[2,3]pyrazines is confined to dipyridophenazine analogues [15] which induce coordination via the bipyridine-like chelating units to both Os(II) and Re(I). Monodentate coordination of a 2,3-dipyrrolyl derivative has been reported with Ni(II) and exploited in the design of colorimetric chemosensing of fluoride [16], and a bridging motif within a Rh(II) dimer has recently been highlighted [17].

Therefore the aim of this work was to synthesise a range of functionalised ligands based upon the pyrido[2,3-*b*]pyrazine core and investigate their coordination chemistry with Re(I) together with their spectroscopic properties.

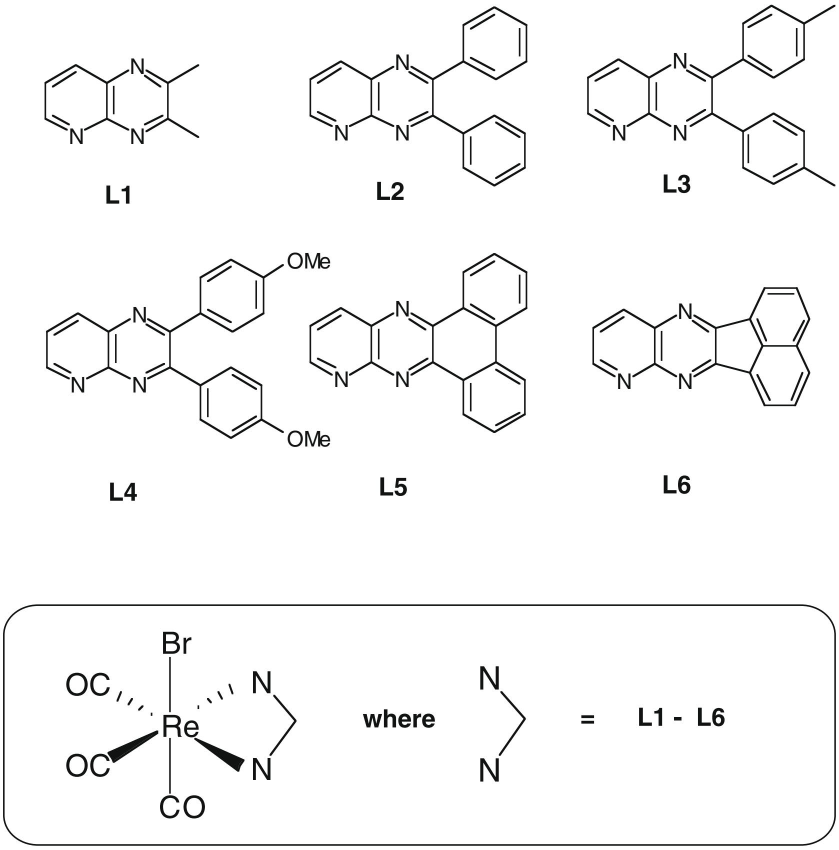
2. Results and discussion

2.1. Synthesis and characterisation of the ligands and corresponding Re(I) complexes

Although most of the ligands included here have been synthesised previously (**L^1** [18], **L^2** [19], **L^3** [20], **L^4** [21], **L^5** [22]) these reports do not uniformly include data such as ^{1}H and ^{13}C–{^{1}H} NMR, mass spectrometry or UV–Vis absorption spectroscopy, which we include herein for clarity and convenience (however, note that due to solubility limitations it was not possible to obtain ^{13}C–{^{1}H} NMR spectra for **L^5** and **L^6**). Our general synthetic methodology for the ligands **L^1–L^6** involved reacting 2,3-diaminopyridine with one equivalent of an appropriate vicinal diketone in ethanol, with a small aliquot of acetic acid. Purification was achieved by the use of activated charcoal and occasionally column chromatography (typically silica using CH_2Cl_2 to MeOH solvent gradient from 10:0 to 9:1) was required to remove unreacted diketone from the crude material. In all cases, using this general approach, gave the pure ligands in excellent yields (78–97%).

The corresponding rhenium complexes (Scheme 1), *fac*-{ReBr(CO)$_3$(**L^n**)} were synthesised by reacting one equivalent of pentacarbonylbromorhenium with the ligand, in toluene, except in the case of **L^5** where the product did not appear to be stable under such condition: chloroform was used as an alternative [9]. The reaction mixtures typically turned red-brown in appearance within an hour, but were left for 12–24 h to allow reaction completion. The complexes were isolated as air stable powders, which were typically orange-to-brown in appearance. The complexes were characterised by ^{1}H NMR, ^{13}C–{^{1}H} NMR (where sufficiently soluble), IR and UV–Vis spectroscopies, ES LR MS and EI HR MS, and for selected examples via single crystal X-ray diffraction.

The solution state (chloroform) IR studies showed that each complex possessed three carbonyl stretching frequencies ν(CO) between 2040 and 1900 cm^{-1}, consistent with an approximate local *Cs* symmetry at Re(I). ^{1}H NMR spectra were obtained for each complex confirming the presence of the ligand in all cases. Since the pyrido[2,3-*b*]pyrazine core induces asymmetry (each proton environment is chemically unique) in the ligands it was not possible to determine the binding mode of the ligand in terms of chelating bidentate or monodentate. However, each of the spectra showed a single set of proton resonances that were shifted in comparison to the free ligands. As an example, the aromatic proton resonances of **L^1** showed a general downfield shift upon coordination to Re(I). The two unique methyl resonances also showed very minor, but observable downfield shifts of 0.03–0.05 ppm. ^{13}C–{^{1}H} NMR spectra were obtained for those complexes with sufficient solubility, but only allowed ligand-based resonances to be observed: carbonyl resonances were not. For each of the complexes low resolution electrospray mass spectra were easily obtained and showed



Scheme 1. The ligands **L^1–L^6** and the Re(I) complexes synthesised in this study.