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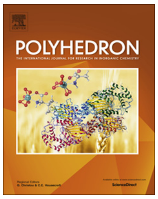

Ir(III) and Ir(III)/Re(I) complexes of a new bis(pyrazolyl-pyridine) bridging ligand containing a naphthalene-2,7-diyl spacer: Structural and photophysical properties

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ABSTRACT

A new bridging ligand has been prepared in which two chelating bidentate pyrazolyl-pyridine termini are connected to a central naphthalene-2,7-diyl core *via* methylene spacer units. This ligand has been used to prepared mononuclear and dinuclear Ir(III) complexes in which $\{Ir(F_2ppy)_2\}$ [F_2ppy = cyclometallating anion of 2-(3,5-difluorophenyl)-pyridine] complex fragments are coordinated to one or both of the pyrazolyl-pyridine termini; in addition a heterodinuclear complex has been prepared containing one $\{Ir(F_2ppy)_2\}$ unit and one $\{Re(CO)_3Cl\}$ unit in the two binding sites. X-ray crystallographic studies show that the bridging naphthyl group lies stacked with a coordinated F_2ppy ligand from a terminal $\{Ir(F_2ppy)_2\}$ unit in every case. Luminescence measurements show that the usual strong Ir(III)-centred blue luminescence is substantially quenched by the presence of a low-lying triplet state on the naphthyl group; in the Ir(III)/Re(I) dyad we observe both weak Ir(III)-based emission as well as lower-energy Re(I)-based emission which overlap; Ir(III) → Re(I) energy-transfer occurs on a timescale of <1 ns as no rise-time for sensitised Re(I)-based emission could be detected, in contrast to other Ir(III)/Re(I) dyads in which the Ir(III) → Re(I) energy-transfer is slower (10–100 ns timescale). We ascribe this to the spatial and energetic intermediacy of the naphthyl group whose triplet energy lies between that of the Ir(III) and Re(I) termini, providing an effective conduit for energy-transfer to occur.

1. Introduction

We have extensively investigated the use of bis(pyrazolyl-pyridine) ligands, in which two *N*,*N*-chelating termini are connected to an aromatic spacer *via* flexible methylene groups, for two distinct purposes. Firstly, they have formed the basis of an extensive family of self-assembled coordination cages which display interesting structures and guest binding properties [1]. Secondly, they have been used as a basis for preparing luminescent heterodinuclear complexes in which a blue-luminescent $\{Ir(ppy)_2(NN)\}^+$ unit [2] is connected to $\{Ln(hfac)_3(NN)\}$ [3,4] or $\{Re(CO)_3Cl(NN)\}$ [5] units in order to investigate phenomena such as inter-component photoinduced energy-transfer and white light emission. The ease with which the basic 3-(2-pyridyl)-1H-pyrazole unit can be functionalised by alkylation at the pyrazolyl N^1 site provides a facile synthetic route into a wide range of such ligands, and has allowed in particular the incorporation of napthyl units as aromatic spacers between the chelating termini [4,6,7]. This has provided a 'stepping stone' for long-distance Ir → Eu photoinduced energy transfer in which the ^{3}napthyl excited state was demonstrated to be an intermediate between the Ir-based and Eu-based excited states [4]; and the luminescence of the naphthyl unit has also provided added functionality to coordination cages by providing photophysically active units surrounding the central cavity which can interact with bound guests [6,7].

In this paper we report the preparation of a new member of this ligand series, L^{27naph}, in which the two pyrazolyl-pyridine units are separated by a naphthalene-2,7-diyl spacer: this is a simple isomer of other naphthyl-containing ligands in this series [4,6,7] but, as we have demonstrated, such structural changes can lead to striking differences in coordination behaviour [1a]. In this contribution we report the ligand synthesis and crystal structure, as well as the preparations, structures and photophysical properties of some homonuclear Ir-based complexes and a heterodinuclear Ir/Re complex.

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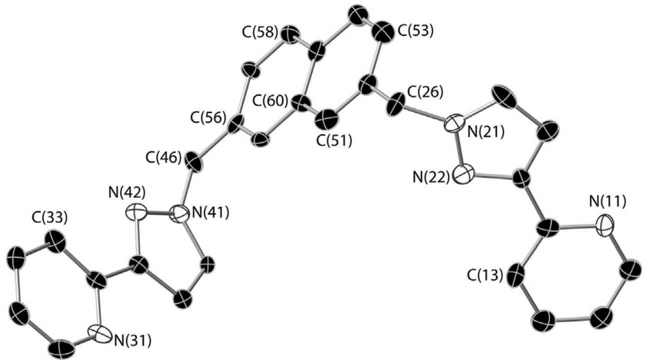
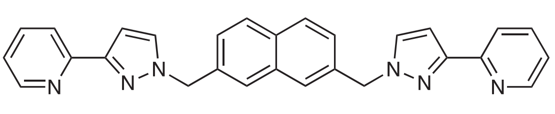


Fig. 1. Structure of L^{27naph} from crystallographic data; thermal ellipsoids are at the 40% probability level.

2. Results and discussion

2.1. Synthesis and structural properties



L^{27naph}

The new ligand L^{27naph} was prepared by reaction of 3-(2-pyridyl)-1H-pyrazole with 2,7-bis(bromomethyl)naphthalene under basic conditions and purified by chromatography on silica gel; its identify was confirmed by ^1H NMR and mass spectrometric analyses. Recrystallisation from chloroform afforded X-ray quality single crystals; the crystal structure is shown in Fig. 1 (see Table 1 for summary of crystallographic data). Individual bond distances and angles are unremarkable. The pyridyl and pyrazolyl groups within each potentially chelating unit are mutually transoid. The mean planes of the pyrazolyl-pyridine units are substantially twisted away from the mean plane of the central naphthyl group, with torsion angles about N(41)–C(46) and N(21)–C(26) being 85.3° and 71.5° respectively.

Reaction of L^{27naph} with the chloride-bridged dimer $[\{Ir(F_2ppy)_2(\mu-Cl)\}_2]$ in CH_2Cl_2/MeOH afforded a mixture of mononuclear $[Ir(F_2ppy)_2(L^{27naph})]X$ and dinuclear $[\{Ir(F_2ppy)_2)\}_2(\mu-L^{27naph})]X_2$ (where 'X' denotes a nitrate or hexafluorophosphate anion, according to the method used for workup and purification). We abbreviate these hereafter as **Ir·L** and **Ir·L·Ir** respectively. The relative proportions of these products depend on the ratio of components with a higher metal complex:ligand ratio generating more of the dinuclear product. Electrospray mass spectrometry and ^1H NMR spectroscopy were in accord with the formulation of the complexes. Dinuclear **Ir·L·Ir** contains a mixture of two diastereiosomers associated with the chirality of the two metal centres, such that many of the expected ^1H NMR resonances are split into

Table 1
Crystal parameters, data collection and refinement details for the structures in this paper.

Compound	L^{27naph}	$[Ir(F_2ppy)_2(L^{27naph})]\ (NO_3)\cdot 2MeCN\cdot H_2O$	$H[Ir(F_2ppy)_2(L^{27naph})K(NO_3)_3(H_2O)]$
Abbreviation	**L**	**Ir·L**	**Ir·L·K**
Formula	$C_{28}H_{22}N_6$	$C_{54}H_{42}F_4IrN_{11}O_4$	$C_{50}H_{34}F_4IrKN_{11}O_{10}$
Molecular weight	442.51	1177.18	1256.18
T (K)	100(2)	100(2)	1100(2)
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$C2/c$	$I2/a$
a (Å)	4.9279(14)	41.4653(17)	17.5169(7)
b (Å)	11.578(4)	15.8612(6)	16.6681(7)
c (Å)	38.138(12)	15.7425(6)	40.477(2)
α (°)	90	90	90
β (°)	90	1100.806(2)	99.688(4)
γ (°)	90	90	90
V (Å)^3	2176.0(12)	10170.1(7)	11649.7(9)
Z	4	8	8
ρ (g cm^{-3})	1.351	1.538	1.432
Crystal size, mm^3	0.25 × 0.16 × 0.11	0.25 × 0.24 × 0.21	0.26 × 0.24 × 0.16
μ (mm^{-1})	0.083	2.698	2.437
Data, restraints, parameters	2763/0/309	8977/84/690	10343/1876/909
Final R_1, wR_2[a]	0.079, 0.167	0.065, 0.183	0.082, 0.215

Compound	$[\{Ir(F_2ppy)_2)\}_2(\mu-L^{27naph})](PF_6)_2\cdot 6MeCN$	$[\{(F_2ppy)_2Ir\}(L^{27naph})\ \{Re(CO)_3Cl\}](NO_3)\cdot MeCN\cdot 0.64H_2O$
Abbreviation	**Ir·L·Ir**	**Ir·L·Re**
Formula	$C_{84}H_{64}F_{20}Ir_2N_{16}P_2$	$C_{55}H_{38.28}ClF_4IrN_{10}O_{6.64}Re$
Molecular weight	2123.85	1435.32
T (K)	110(2)	110(2)
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	13.6101(9)	12.0080(4)
b (Å)	17.2667(11)	15.1430(5)
c (Å)	18.3547(13)	15.9523(5)
α (°)	103.115(3)	64.392(2)
β (°)	91.695(3)	77.127(2)
γ (°)	99.224(3)	89.872(2)
V (Å)^3	4136.8(5)	2535.41(15)
Z	2	2
ρ (g cm^{-3})	1.705	1.880
Crystal size, mm^3	0.41 × 0.39 × 0.38	0.42 × 0.26 × 0.19
μ (mm^{-1})	3.354	5.139
Data, restraints, parameters	18878/67/1101	11413/38/741
Final R_1, wR_2[a]	0.038, 0.123	0.0372, 0.121

[a] The value of R_1 is based on 'observed' data with $I > 2\sigma(I)$; the value of wR_2 is based on all data.