



Review

The chameleon-like coordinating ability of 2,3-di(pyridyl)pyrazine-type ligands

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ABSTRACT

This survey is dedicated to the multifaceted modes of binding of metal ions by polyazine N donors like 2,3-di(2-pyridyl)pyrazine (dpp), 5,6-di(2-pyridyl)quinoxaline (dpq) and 9,10-di(2-pyridyl)benzoquinoxaline (dqbq) and related substituted analogs, covered until the end of 2016. These compounds display the potential coordination of the dipyridinopyrazine block consisting of two pyridine and two pyrazine N donor atoms.

This report illustrates the structural features of the mono-, di- and multinuclear complexes, whenever crystallographic information was available. In the absence of X-ray work, as is the case for tri-, tetra-, and multinuclear systems, the overall organization of the complex systems is that proposed by the authors. Synthetic procedures, physicochemical properties, especially UV–visible spectroscopic and electrochemical behaviour, are given some attention.

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1. Introduction

The compound 2,3-di(2-pyridyl)pyrazine (dpp) is an extraordinary molecule for metal coordination. It acts as a chelating agent in

Abbreviations: BL, bridging ligand; DCM, dichloromethane; DFT, density functional theory; DMF, *N,N*-dimethylformamide; fsTA, femtosecond transient absorption spectra; LLCT, ligand-to-ligand charge-transfer; MeCN, acetonitrile; Meim, 1-methylimidazole; MLCT, metal-to-ligand charge-transfer; NIR, near infrared; OTf, trifluoromethanesulfonate, CF₃SO₃⁻; PHOLED, phosphorescent organic-light emitting diode; THF, tetrahydrofuran.

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mononuclear complexes or as a bis-chelating agent in homo/heterodinuclear ones, involving two or four N atoms, respectively, in the binding to metal centers. Moreover, dpp is also involved, as a bridging moiety, in the formation of three or more linearly or bi/tridimensionally developed oligomers and dendrimers. The formation of discrete or extended coordination compounds include related ligands, such as 2,3-di(2-pyridyl)quinoxaline (dpq) and 2,3-bis(2-pyridyl)benzo[*g*]quinoxaline (dqbq), and substituted derivatives of all three dpp, dpq and dqbq. The formulae of the most frequently used ligands are presented in [Chart 1](#).

Two different modes of bidentate chelation are observed to occur for the pyridylpyrazine fragment in the formation of mononuclear metal derivatives, one involving the two N atoms of

List of ligand abbreviations

bpm	2,2'-bipyrimidine	Hmbtfa	4-methoxybenzoyltrifluoroacetone (IUPAC: 4,4,4-trifluoro-1-(4-methoxyphenyl)-1,3-butanedione)
biq	2,2'-biquinoline	Htta	4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione
bpy	2,2'-bipyridine	ipaH ₂	isophthalic acid (IUPAC: 1,3-benzenedicarboxylic acid)
^t Bu ₃ tpy	4,4',4''-tri- <i>tert</i> -butyl-2,2':6',2''-terpyridine	malH ₂	malonic acid ((IUPAC: propanedioic acid)
cbdc	1,1-cyclobutane dicarboxylate	2,3-Medpp ⁺	2-(<i>N</i> -methylpyridinio-2-yl)-3-(2-pyridyl)pyrazine
Cldpbq	6-chloro-2,3-bis(2-pyridyl)benzo[g]quinoxaline	Medpq	6-methyl-2,3-bis(2-pyridyl)quinoxaline
Cldpq	6-chloro-2,3-bis(2-pyridyl)quinoxaline	Me ₂ dpbq	6,7-dimethyl-2,3-bis(2-pyridyl)benzo[g]quinoxaline
Cl ₂ dpq	6,7-dichloro-2,3-bis(2-pyridyl)quinoxaline	Me ₂ dpq	6,7-dimethyl-2,3-bis(2-pyridyl)quinoxaline
(CN) ₂ dpp	2,3-dicyano-5,6-bis(2-pyridyl)pyrazine	Mephtpy	4'-(4-methylphenyl)-2,2':6',2''-terpyridine
(CN) ₂ dpq	6,7-dicyano-2,3-bis(2-pyridyl)quinoxaline	NO ₂ dpq	6-nitro-2,3-bis(2-pyridyl)quinoxaline
(CN)(ime)dpp	2-ciano-3-ethoxymimidocarbonyl-5,6-bis(2-pyridyl)pyrazine	ppy	phenylpyridine anion
COD	1,5-cyclooctadiene	(2-py)dpp	2,3-bis(2,2'-bipyridin-6-yl)pyrazine
dpbq	2,3-bis(2-pyridyl)benzo[g]quinoxaline	py	pyridine (azabenzene)
dpbqOH	1 <i>H</i> -2-hydroxy-2,3-bis(2-pyridyl)benzo[g]quinoxaline	pym	pyrimidine (1,3-diazabenzene)
dpp	2,3-bis(2-pyridyl)pyrazine	pyz	pyrazine (1,4-diazabenzene)
2,5-dpp	2,5-bis(2-pyridyl)pyrazine	Py ₈ TPyzPz	tetrakis[5,6-di(2-pyridyl)-2,3-pyrazino]porphyrizina to dianion
dpq	2,3-bis(2-pyridyl)quinoxaline	Py ₈ QxPz	tetra-2,3-[6,7-di(2-pyridyl)quinoxalino]porphyrizinato dianion
F ₂ ppy	2-(4,6-difluorophenyl)pyridine	tpq	2,3,5,6-tetrakis(2-pyridyl)pyrazine
Hbtfa	benzoyltrifluoroacetone (IUPAC: 4,4,4-trifluoro-1-phenyl-1,3-butanedione)	tpq	2,3,7,8-tetrakis(2-pyridyl)pyrazino[2,3- <i>g</i>]quinoxaline
Hcbtfa	4-chlorobenzoyltrifluoroacetone (IUPAC: 1-(4-chlorophenyl)-4,4,4-trifluoro-1,3-butanedione)	tpy	2,2':6',2''-terpyridine
Hhfacac	hexafluoroacetylacetone (IUPAC: 1,1,1,5,5,5-hexafluoro-2,4-pentanedione)		

the vicinal 2-pyridyl rings (“py-py” coordination, Fig. 1 left) and one showing the use of one pyridine N atom and one pyrazine N atom (“py-pyz” coordination, Fig. 1 right). The N donor ligand is also able, to act as a bis-bidentate chelating agent, to generate homo- or heterodinuclear metal derivatives. In these species the coordination is exclusively of type “py-pyz”, as occurs also for tri-, tetra- and multinuclear compounds. The formation of mono-, di- or multinuclear species is primarily a function of the type and oxidation state of the metal center and also depends on the reaction conditions used in the synthetic procedures. Noteworthy, for the first time the “py-py” and “py-pyz” modes of coordination can be seen in direct comparison.

The aim of the present work is to illustrate the various forms of coordination, which may occasionally imply consideration of synthetic aspects and physicochemical properties of the non-metalated and metalated species. Whenever possible, the role played by the metal ion(s) in the type of selected chelation was considered, together with the relevant stereochemical aspects. The potential technological applications of the materials studied will only be given limited attention. Numerous pertinent reviews are available [1–9], for selected examples of reviews and recent articles]. We tried our best to present a review of the topic as completed as possible and we apologize for eventual, unwanted, omission in the reported material.

Lists of the mono-, di- and multinuclear complexes of the pyridylpyrazine-type ligands described here, detailing the mode of coordination, are given in Tables 1–3 reported in the corresponding sections.

2. Historical remarks

The interest in this type of ligand started in late 1950s as an example of polydentate *N*-heterocycles prepared to extend the library of available pyridine-based Schiff bases [10]. In this pioneering paper, attention was mainly devoted to the coordination ability of 2,3,5,6-tetrakis-(2-pyridyl)pyrazine, dictated by the

impossibility of having all the rings simultaneously coplanar. Fe(II), Co(II), and Cu(II) complexes were prepared, but the nature of non-polymeric species was inferred only from their crystalline aspect, while no experimental support was given for the suggested tricoordination of the ligand. To simplify the ligand, 2,3-bis(2-pyridyl)pyrazine, dpp, and the corresponding Fe(II), Co(II) and Cu(II) complexes were prepared. The authors concluded that the coordinating behaviour of dpp resembled that of 2,2'-bipyridine, but only on the basis of elemental analyses. In the same paper, 2,3-bis(2-pyridyl)quinoxaline, dpq, complexes with Fe(II) and Cu(II) and 2,3-bis(2-pyridyl)-5,6-dihydropyrazine (no complex of it) were prepared. Ten years later, the same ligands were given further attention, but interest was focused on chromogenic properties of Fe(II) and Cu(I) complexes and no characterization was given at all [11].

Renewed interest in dpp complexation ability in the 1980s followed the recognition of the photoinduced redox properties of tris-(2,2'-bipyridine)ruthenium(II) and the quest for other polyaza ligands to prepare similar Ru(II) photoactive compounds [12]. Ruthenium complexes containing dpp ligand and bipyridyl, e.g. [Ru(bpy)₂(dpp)]²⁺ and [(bpy)₂Ru(dpp)Ru(bpy)₂]⁴⁺ were synthesized as perchlorate salts. The monometallic complex was prepared by refluxing equimolar amounts of *cis*-[Ru(bpy)₂C1₂] and dpp, whereas two equivalents of the ruthenium precursor were necessary to obtain the bimetallic complex. Dpp and dpq were considered important bridging ligands, as well as 2,2'-bipyrimidine (bpym), to investigate intramolecular energy transfer reactions in polynuclear complexes [13]. Nothing was said about the monometallic complex coordination, while for the bimetallic one the “py-pyz” coordination was supposed.

3. Mononuclear metal complexes of pyridylpyrazine-type ligands

The prevalent mononuclear compounds reported in Table 1 are those of Pd(II) and Pt(II) and will be discussed first, followed by

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