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Review

Phenolic pyrazoles: Versatile polynucleating ligands

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ABSTRACT

The proximity of the donor atoms in phenolic pyrazoles and the ability to function in neutral and in singly and doubly deprotonated forms allows them to form a diverse range of metal complexes. The complexes in this review are classified on the basis of the nuclearity and the number of phenolic pyrazole units present in structures that have been determined by X-ray crystallography. Mononuclear complexes can contain one, two, or three phenolic pyrazoles or polydentate ligands where two phenolic pyrazoles are linked by an organic spacer. Six different coordination modes of the phenolic pyrazole have been identified in single crystal X-ray structure determinations with the ligand providing between one and four lone pairs from its oxygen and nitrogen atoms. Dinuclear complexes feature metals bridged by a phenolate or a pyrazolate unit, by other ligands, or by polydentate systems containing linked phenolic pyrazoles. Polynuclear complexes with up to 21 metal atoms have been reported.

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1. Introduction and background

Phenols carrying a pyrazole substituent *ortho* to the hydroxyl group (Fig. 1a) are proligands with structural and electronic properties very similar to the much more widely studied [1,2] phenolic oximes (Fig. 1b). Both have:

- functional groups, the oxime OH and the pyrazole NH, which are positioned to operate as H-bond donors to the phenolate oxygen atoms of neighbouring ligands. This enhances the stability of their complexes with metal cations (see Fig. 1), forming pseudomacrocyclic structures [1], and
- two ionisable hydrogen atoms which can readily be lost to form dianionic ligands that are well suited to the formation of polynuclear complexes [3] containing subunits such as those shown in Fig. 1.

For these reasons it is timely to review the coordination chemistry of phenolic pyrazole ligands to establish how similar it is to that of the analogous oximes. The number of publications has increased significantly in the last decade and many of them describe unusual polynuclear complexes. In this article we aim to classify structural types and establish the diversity of complexes which can be formed.

A search of complexes of phenolic pyrazoles in the Cambridge Crystallographic Database [4] identified the six different modes of coordination, A–F, shown in Fig. 2 which involve complexation of increasing numbers of metal ions. Mode A has a monodentate *neutral* ligand, modes B and C a *monoanionic* form of the ligand attached to one or two metal ions, and modes D–F a *dianionic* form of the ligand attached to two or three metal ions. The bonding modes are also represented using Harris notation [5].

In this review the structures of the metal complexes contained in the Cambridge Crystallographic Data Centre (CCDC) are discussed in the order of increasing nuclearity (metal cluster sizes). Appendix A provides a compilation of the structures of the phenolic pyrazole ligands present in these complexes and Appendix B lists the molecular composition of all the metal complexes (**1**–**62**), together with their CCDC codes and the modes of coordination (A–F) of the ligands present.

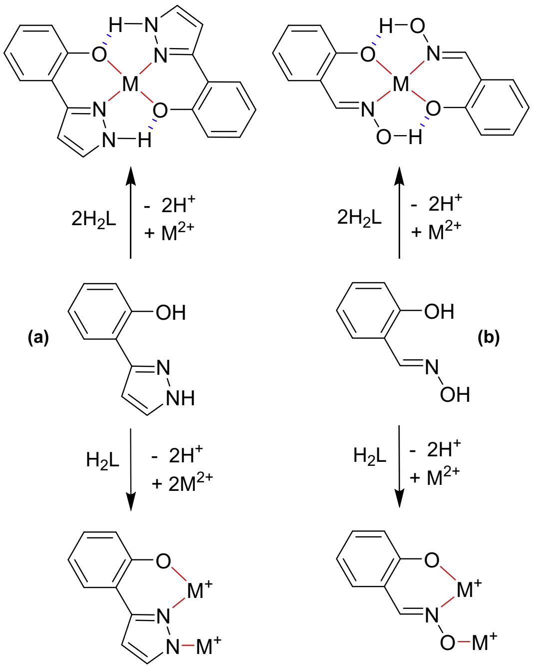

Fig. 1. The structural features of phenolic pyrazole (a) and phenolic oxime (b) proligands which favour the formation of pseudomacrocyclic (top) and polynuclear (bottom) metal complexes.

2. Mononuclear complexes

2.1. Single phenolic pyrazole

Oxorhenium(V) complexes have been studied as catalysts for alkene epoxidation [6]. The complexes are formed from reactions of one equivalent of the proligand with one equivalent of [ReOX$_3$(EPh$_3$)$_2$] (**1**–**10**) (X = Cl$^-$, Br$^-$, E = P, As) to give the mono-substituted complexes [ReOX$_2$(L)(EPh$_3$)] (L = L^1–L^8) shown in Fig. 3 [6,7].

Every complex has a distorted octahedral geometry, where a mono-deprotonated phenolic pyrazole functions as a bidentate ligand coordinating to the rhenium centre as in Mode B. In each case, the terminal oxo group (=O) is *trans* to the phenolate oxygen atom, and the halide ions are *cis* to each other and *trans* to the E donor atoms or the nitrogen donor of the pyrazole ring. The bond lengths and angles are similar across the series of complexes, but deviate from an orthogonal arrangement for a regular octahedral complex. These deviations are most apparent for the bite angle of the phenolato pyrazoles which fall in the range 79.12(8)° to 80.19(8)°, and the very short Re=O bond which leads to elongated adjacent Re—X bonds (due to the increased electron density along this axis) [6]. Selected bond lengths and angles for (**1**) are presented in Table 1 [7].

The two reported complexes of ruthenium(IV) with a single phenolato pyrazole have the distorted trigonal bipyramidal structures shown in Fig. 4 [8]. [Ru(η^3:η^3-C$_{10}$H$_{16}$)Cl$_2$(H$_2$L^1)] (**11**) is

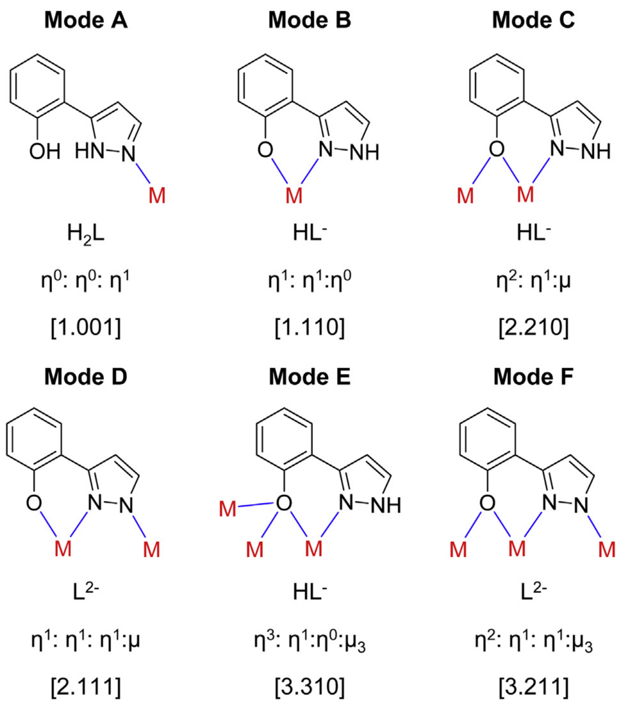

Fig. 2. Summary of the six different coordination modes of phenolic pyrazoles. [M.xxx] represents the coordination mode in Harris notation [5] in which "M" defines the number of metal bound to each ligand and the subsequent three digits indicate how many metal atoms are bonded to the phenol oxygen and to the pyrazole N^2 and N^1 atoms respectively.