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Manganese(II) complexes of 2,3,5,6-tetra-(2-pyridyl)pyrazine – Syntheses, crystal structures, spectroscopic, magnetic and catalytic properties

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ABSTRACT

A systematic studies on complex formation between Mn(II) ions, 2,3,5,6-tetra(2-pyridyl)pyrazine and halide or pseudohalide (N_3^-, NCS^- and $N(CN)_2^-$) ligands have been carried out and the following complexes $[Mn_2(\mu\text{-}Cl)_2Cl_2(tppz)_2]$ (**1**), $[Mn_2Cl_2(\mu\text{-}N_3\text{-}\kappa N1)_2(tppz)_2]$ (**2**), $[MnCl(SCN)(tppz)(H_2O)]\cdot H_2O$ (**3**), $[MnCl(dca)(tppz)(H_2O)_{0.57}(MeOH)_{0.47}]$ (**4**), $[Mn(NO_3)_2(tppz)(H_2O)]$ (**5**), $[Mn(N_3)(NO_3)(tppz)(H_2O)]$ (**6**), $[Mn(SCN)_2(tppz)]$ (**7**) and $[Mn(NO_3)(dca)(tppz)]_n$ (**8**) have been obtained. The compounds were characterized by elemental analysis, IR, EPR, magnetic measurements and X-ray analysis. Two of them (**5** and **6**) have been tested as catalysts in oxidation of alcohol to aldehydes/ketones using oxone ($2KHSO_5\cdot KHSO_4\cdot K_2SO_4$) as an oxidant under biphasic reaction conditions (CH_2Cl_2/H_2O) and tetra-*n*-butylammonium bromide as phase transfer agent under air at room temperature and as catalysts in oxidation of sulfides to sulfoxides with UHP (urea hydrogen peroxide) as oxidant.

1. Introduction

2,3,5,6-Tetra-(2-pyridyl)pyrazine (*tppz*), synthesized by Goodwin and Lions in 1959, was designed as an analogue of terpyridine but with the idea that it also might bridge central ions and form extended chain structures due to six potential donor sites [1]. In metal complexes *tppz* forms seven distinct binding modes illustrated in Scheme 1.

As we can see from scheme 1, *tppz* binds to a metal center in a bidentate α (a) or γ (b), bis-bidentate α (c) or γ (d), tris-bidentate (e), tridentate (f) or bis-tridentate (g) coordination mode, forming both mono- and polynuclear complexes with interesting electronic and magnetic properties.

The rich photophysical and redox properties associated with these complexes make them useful for analytical purposes and probes for biologically relevant molecules such as DNA. Recently, *tppz* has been examined as fluorescence sensors for series of metal ions and off–off–on switching of fluorescence depending on stepwise complex formation with *tppz* has been reported [3].

Studies on *tppz* metal(II) complexes have illustrated the ability of this polydentate organic ligand to mediate magnetic interactions between paramagnetic centers bridged by the central pyrazine moiety and hence separated by more than 6.4 Å [4,5]. The largest antiferromagnetic interaction has been found in the dinuclear complexes $[Cu_2(tppz)(H_2O)_4](ClO_4)_4\cdot 2H_2O$ ($J = -61.1\ cm^{-1}$) and $[Ni_2(tppz)(H_2O)_6](NO_3)_4\cdot 2.5H_2O$ ($J = -76\ cm^{-1}$) [5]. Interestingly, the relatively good efficiency of the *tppz* bridge in transmitting magnetic interactions between paramagnetic centers contrasts with much poorer ability of unsubstituted pyrazine bridges in its metal complexes, where negligible or weak antiferromagnetic interactions were observed (with J values ranging from $-0.14\ cm^{-1}$ in $[Ni(pyz)_2Cl_2]$ to $15.1\ cm^{-1}$ in $Cu(pyz)_2(ReO_4)_2$) [6,7]. In binuclear ruthenium(II) complexes, *tppz* bridges have been found to mediate intermetallic electronic communication through the π symmetry orbitals [8]. In turn, the mononuclear complexes of Co(II) of formula $[Co(tppz)_2]^{2+}$ with *tppz* ligands coordinated in a tridentate coordination mode attract scientific interest due to thermally induced spin crossover behaviour from a high-spin $S_{Co} = 3/2$ at high temperatures to a low-spin $S_{Co} = 1/2$ at lower temperatures [9].

A search in CCDC (Cambridge Crystallographic Data Centre, Version 5.33) database reveals only three Mn(II) complexes of *tppz*, namely $[Mn_2(\mu\text{-}Cl)_2Cl_2(tppz)_2]$ [10], $[MnI(tppz)(H_2O)_2]I\cdot H_2O$[11] and $[Mn(dca)(NO_3)(tppz)(H_2O)]$ [12]. This prompt us to systematic studies on complex formation between Mn(II) ions, *tppz* and halide or pseudohalide (N_3^-, NCS^- and $N(CN)_2^-$) ligands. Here, we present

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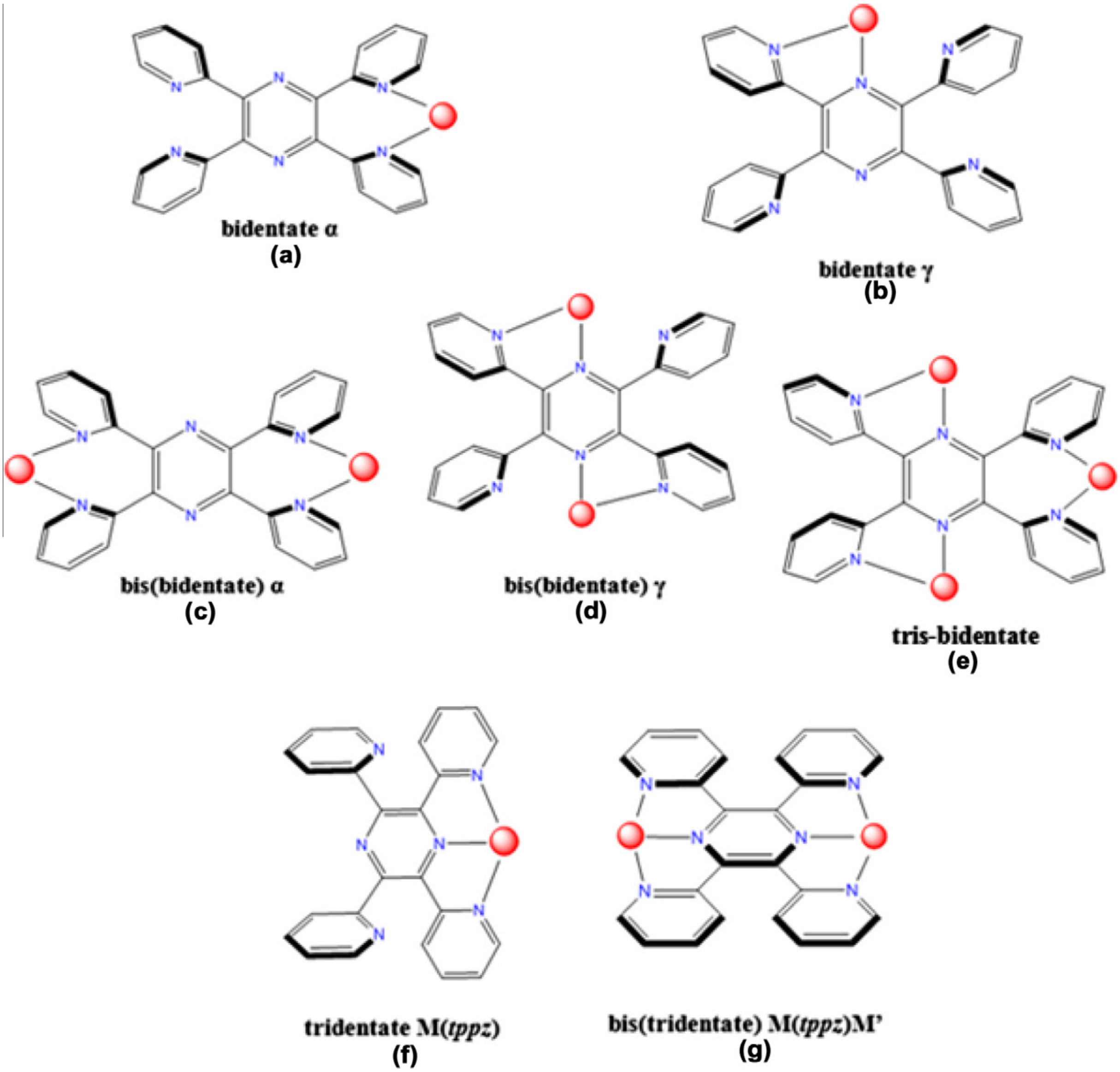
bidentate α
(a)
bidentate γ
(b)
bis(bidentate) α
(c)
bis(bidentate) γ
(d)
tris-bidentate
(e)
tridentate M(*tppz*)
(f)
bis(tridentate) M(*tppz*)M'
(g)

Scheme 1.

synthesis, X-ray studies as well as spectroscopic and magnetic properties of manganese(II) complexes [Mn_2(-Cl)$_2Cl_2$(tppz)$_2$] (**1**), [Mn_2Cl_2(μ-N_3-κN1)$_2$(tppz)$_2$] (**2**), [MnCl(SCN)(tppz)(H_2O)]·H_2O (**3**), [MnCl(dca)(tppz)(H_2O)$_{0.57}$(MeOH)$_{0.47}$] (**4**), [Mn(NO_3)$_2$(tppz)(H_2O)] (**5**), [Mn(N_3)(NO_3)(tppz)(H_2O)] (**6**), [Mn(SCN)$_2$(tppz)] (**7**) and [Mn(NO_3)(dca)(tppz)]$_n$ (**8**). The molecular structure of **1** have been previously determined by Kwang [10], but the compound presented here has different conformation of the side pyridine rings and different crystal packing as compared to the literature-known one. Because the structural differences affect the magnetic properties, the contemporary structural data of **1** was included into study.

Two of these compounds (**5** and **6**) have been tested as catalysts in oxidation of alcohol to aldehydes/ketones using oxone ($2KHSO_5$·$KHSO_4$·K_2SO_4) as an oxidant under biphasic reaction conditions (CH_2Cl_2/H_2O) and tetra-*n*-butylammonium bromide as phase transfer agent under air at room temperature and as catalysts in oxidation of sulfides to sulfoxides with UHP (urea hydrogen peroxide) as oxidant. Selective oxidation of alcohols and sulfides, respectively to aldehydes/ketones and sulfoxides is a prominent reaction in laboratory and industrial synthetic chemistry [13]. In view of their importance as intermediates in organic synthesis, several methods are available to effect this conversion, and continuous attention is drawn to newer and more selective methods of oxidation [14]. Recently, some metal complexes with N-donor ligands were used as catalysts in these reactions [15].

2. Experimental

tppz and the other reagents used to the syntheses were commercially available (POCh and Aldrich) and were used without further purification. IR spectra were recorded on a Nicolet Magna 560 spectrometer in the spectral range 4000–400 cm^{-1} with the samples in the form of KBr pellets.

2.1. Preparation of [Mn_2(μ-Cl)$_2Cl_2$(tppz)$_2$] (**1**) and [Mn(NO_3)$_2$(tppz)(H_2O)] (**5**)

tppz was dissolved in a mixture of methanol/acetonitrile (30/60 ml) and slowly added to methanolic solution of $MnCl_2$·$4H_2O$ or Mn(NO_3)·$4H_2O$, and stirred at room temperature for 12 h. The