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# New mononuclear manganese(II) and zinc(II) complexes with a terpyridine ligand: Structural, magnetic and spectroscopic properties

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ABSTRACT

Six mononuclear complexes of the dimethylterpyridine ligand 1,3-bis(6-methylpyridin-2-yl)pyridine, **L**, $C_{17}H_{15}N_3$, of the general formula $ML X_2$ were prepared from different manganese(II) and zinc(II) salts (M = Mn(II), X = $Cl^-$ – **1a**, $Br^-$ – **1b**, $NO_3^-$ – **1c** and $ClO_4^-$ – **1d**; M = Zn(II), X = $Cl^-$ – **2a** and $NO_3^-$ – **2c**). The complexes have been characterized through analytical, spectroscopic (UV–Vis, ESI-MS, and IR) and magnetic measurements. Single crystal X-ray structure analyses of these complexes revealed five-coordinate metal ions in **1a**, **1c**, **2a** and **2c**, whereas **1d** turned out to contain a six-coordinate Mn(II) ion.



## 1. Introduction

Manganese and zinc ions are very important metals in nature. Complexes of manganese are good models for the active sites of many enzymes [1–4] and the manganese ion has been found at the active sites of enzymes like catalase and superoxide dismutase [5]. The crystal structure of an Mn superoxide dismutase shows the Mn(II) ion to be present in a five-coordinate and trigonal bipyramidal form [6], whereas a bimetallic manganese catalase contains the metal ions as octahedral species [7].

Zinc is one of the more abundant metals in the human body, and is vital for the growth, development, and differentiation of all type of organisms. Over 300 enzymes contain zinc ions in their active sites [8]. The zinc(II) ion is redox-inactive and its function in metalloenzymes is ascribed to its Lewis acidity [9].

A great deal of interest has been focused on the coordination chemistry of terpyridines because of the variety of supramolecular structures found [10,11]. These ligands and their complexes can act as anion-responsive fluorophores [12], chemosensors for metal ions and amino acids [13–15] or as sensors for the detection of other compounds, *e.g.* a carbon electrode-modified terpyridine manganese(II) complex provides a sensitive method for the detection of hydrazine and exhibits good catalytic activity for its oxidation [16]. Terpyridine complexes have found applications as therapeutics [17], MRI contrast agents [18], inhibitors of enzymes like mammalian topoisomerases and human thioredoxin reductase [19], and they can exhibit antimicrobial [20] and DNA-cleavage activity [21]. Many zinc complexes of terpyridines display emission properties and can be used as light-emitting diodes (LEDs) emitting a very broad spectrum of colors [22–27].

In view of the successful synthesis of Cu(II) [28] and Co(II) [29] complexes with the terpyridine ligand **L**, 1,3-bis(6-methylpyridin-2-yl)pyridine ($C_{17}H_{15}N_3$) (Fig. 1), we attempted to prepare an analogous series of lanthanide(III) [30], manganese(II), and zinc(II) complexes.

In this paper we present the preparation, crystal structures, spectroscopic and magnetic properties of a series of six mononuclear complexes of Mn(II) and Zn(II) containing the ligand **L**. Variation of the counter anion has been found to provide control of the stoichiometry and coordination number of these complexes.

## 2. Experimental

### 2.1. General procedure

The terpyridine ligand **L** was obtained as a side product of a Stille coupling reaction used to prepare 2-(6-methylpyridin-2-yl)-

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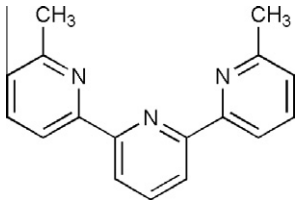

**Fig. 1.** The ligand **L** ($C_{17}H_{15}N_3$).

6-(trimethylstannyl)pyridine [31]. The salts were used as supplied from Aldrich without further purification. NMR spectra were run on a Varian Gemini 300 MHz spectrometer and were calibrated against the residual protonated solvent signals ($CD_3CN$: $\delta$ 1.94) and shifts are given in ppm. Mass spectra for acetonitrile solutions $\sim 10^{-4}$ M were determined using a Waters Micromass ZQ spectrometer. Magnetization measurements in the temperature range 1.8–300 K were carried out on powdered samples of the complexes, at a magnetic field of 0.5 T, using a Quantum Design SQUID Magnetometer (type MPMS-XL5). Corrections for diamagnetism of the constituting atoms were calculated using Pascal's constants [32], the value of $60 \times 10^{-6}$ cm$^3$ mol$^{-1}$ being used as the temperature-independent paramagnetism of the copper(II) ion. Microanalyses were obtained using a Perkin Elmer 2400 CHN microanalyzer. IR spectra in the 4000–400 region were measured in KBr pellets, obtained with a Perkin–Elmer 580 spectrophotometer and are reported in cm$^{-1}$. All absorption spectra were recorded with a Shimadzu UVPC 2001 spectrophotometer, between 200 and 450 nm, in $10 \times 10$ mm quartz cells using $5 \times 10^{-5}$ M solutions with respect to the metal ion. Excitation and emission spectra were measured at room temperature on a Hitachi 7000 spectrofluorimeter with excitation and emission slits at 2.5 nm. Luminescence quantum yields were determined using as standards tryptophan ($f = 0.14$, in water; pH 7.2) and anthracene ($f = 0.27$ in ethanol) [33]. The refractive indices were equal to 1.346, 1.361 and 1.338 for $CH_3CN$, ethanol and water, respectively. The quantum yields of **1a**, **1b** and **1c** were measured taking tryptophan as a reference, while the quantum yields of **1d**, **2a** and **2c** were measured relative to anthracene.

### 2.2. Preparation of the complexes: general procedures

All complexes were prepared under similar conditions. A mixture of the appropriate metal salts (78 μmol) and the ligand **L** (20.4 mg, 78.2 μmol) in $CH_3CN$:$CH_2Cl_2$ 1:1 (10 mL) was stirred at room temperature for 48 h under normal atmosphere. The complexes were isolated by evaporation of the solvent and recrystallisation of the residue from a minimum volume of $CH_3NO_2$ by the gradual addition of ether to obtain complexes as yellow (**1**) or white (**2**) solids.

#### 2.2.1. [Mn**L**$Cl_2$] (**1a**)

Yield: 69.3% (20.3 mg) ESI-MS: *m*/*z* (%) = 433 (100) [Mn**L**Cl($CH_3CN$)$_2$]$^+$, 351 (70) [Mn**L**Cl]$^+$, 158 (10) [Mn**L**]$^{2+}$. IR (KBr, cm$^{-1}$): $\nu$(C–H)$_{ar}$ = 3069, 3037, $\nu_{as}(CH_3)$ = 2924, $\nu_s(CH_3)$ = 2852, $\gamma$(C–H)$_{py}$ overtones = 2013–1664, $\nu$(C=C)$_{py}$ = 1597, 1568, 1474, 1453, $\delta(CH_3)$ = 1395, $\nu$(C=N)$_{py}$ = 1377, 1251, $\rho$(C–H)$_{py}$ = 1197, 1180, 1141, $\gamma$(C–H)$_{py}$ = 1039, 1016, 790, 650. *Anal.* Calc. for [Mn($C_{17}H_{15}N_3$)$Cl_2$] (387.16): C, 52.74; H, 3.91; N, 10.85. Found: C, 53.93; H, 3.67; N, 11.07%.

#### 2.2.2. [Mn**L**$Br_2$] (**1b**)

Yield: 76.1% (20.8 mg) ESI-MS: *m*/*z* (%) = 396 (20) [Mn**L**Br]$^+$, 288 (50) [Mn**L**$_2$]$^{2+}$, 284 (90) [Na**L**]$^+$, 262 (80) [H**L**]$^+$, 167 (40) [Mn**L**($H_2O$)]$^{2+}$, 158 (100) [Mn**L**]$^{2+}$. IR (KBr, cm$^{-1}$): $\nu$(C–H)$_{ar}$ = 3066, 3035, $\nu_{as}(CH_3)$ = 2920, $\nu_s(CH_3)$ = 2852, $\gamma$(C–H)$_{py}$ overtones = 2013–1636, $\nu$(C=C)$_{py}$ = 1596, 1567, 1477, 1452, $\delta(CH_3)$ = 1394, $\nu$(C=N)$_{py}$ = 1375, 1249, $\rho$(C–H)$_{py}$ = 1196, 1180, 1140, $\gamma$(C–H)$_{py}$ = 1036, 1017, 788, 650. *Anal.* Calc. for [Mn($C_{17}H_{15}N_3$)$Br_2$] (476.07): C, 42.89; H, 3.18; N, 8.83. Found: C, 42.63; H, 3.37; N, 8.72%.

#### 2.2.3. [Mn**L**$(NO_3)_2$] (**1c**)

Yield: 67.3% (20.2 mg) ESI-MS: *m*/*z* (%) = 378 (10) [Mn**L**($NO_3$)]$^+$, 289 (30) [Mn**L**$_2$]$^{2+}$, 262 (100) [H**L**]$^+$, 176 (10) [Mn**L**($H_2O$)$_2$]$^{2+}$, 167 (50) [Mn**L**($H_2O$)]$^{2+}$, 158 (100) [Mn**L**]$^{2+}$. IR (KBr, cm$^{-1}$): $\nu$(C–H)$_{ar}$ = 3099, 3069, 3045, $\nu_{as}(CH_3)$ = 2928, $\nu_s(CH_3)$ = 2852, $\gamma$(C–H)$_{py}$ overtones = 1915–1684, $\nu$(C=C)$_{py}$ = 1598, 1571, 1479, 1453, $\nu_{as}(NO_2)$ = 1423, $\nu_s(NO_2)$ = 1330, $\nu$(C=N)$_{py}$ = 1289, 1251, $\rho$(C–H)$_{py}$ = 1188, 1178, 1137, $\nu$(NO) = 1004, $\gamma$(C–H)$_{py}$ = 1027, 788, 650. *Anal.* Calc. for [Mn($C_{17}H_{15}N_3$)($NO_3$)$_2$] (440.28): C, 46.38; H, 3.43; N, 15.91. Found: C, 46.29; H, 3.37; N, 15.74%.

#### 2.2.4. [Mn**L**$(ClO_4)_2(H_2O)$] (**1d**)

Yield: 73.6% (28.7 mg) ESI-MS: *m*/*z* (%) = 415 (20) [Mn**L**$ClO_4$]$^+$, 288 (10) [Mn**L**$_2$]$^{2+}$, 284 (100) [Na**L**]$^+$, 262 (20) [H**L**]$^+$, 167 (20) [Mn**L**($H_2O$)]$^{2+}$, 158 (70) [Mn**L**]$^{2+}$. IR (KBr, cm$^{-1}$): b $\nu$(O–H)$_{H2O}$ = 3397, $\nu$(C–H)$_{ar}$ = 3092, 3067, 3040, $\nu_{as}(CH_3)$ = 2925, $\nu_s(CH_3)$ = 2854, $\gamma_{(C-H)py}$ and $\delta$(OClO) overtones = 1985–1699, $\nu$(C=C)py = 1609, 1579, 1476, 1452, $\delta(CH_3)$ = 1409, $\nu$(C=N)$_{py}$ = 1401, 1249, $\rho$(C–H)$_{py}$ = 1193, 1179, 1135, $\delta$(OClO) = 1120, 1105, 1073, $\gamma$(C–H)$_{py}$ = 1035, 1009, 788, 650 $\nu$(ClO) = 615. *Anal.* Calc. for [Mn($C_{17}H_{15}N_3$)($ClO_4$)$_2$($H_2O$)] (533.18): C, 38.30; H, 3.21; N, 7.88. Found: C, 38.51; H, 3.46; N, 7.94%.

#### 2.2.5. [Zn**L**$Cl_2$] (**2a**)

Yield: 75.4% (23.3 mg) ESI-MS: *m*/*z* (%) = 360 (70) [Zn**L**Cl]$^+$, 293 (5) [Zn**L**$_2$]$^{2+}$, 262 (50) [H**L**]$^+$, 163 (15) [Zn**L**]$^{2+}$. $^1$H NMR (300 MHz, $CD_3CN$) $\delta$ (ppm): 8.47 (d, 2H, *J* = 7.5 Hz), 8.38 (t, 1H, *J* = 6.9 Hz), 8.23 (d, 2H, *J* = 8.1 Hz), 8.04 (t, 2H, *J* = 7.8 Hz), 7.56 (d, 2H, *J* = 7.5 Hz), 3.07 (s, 6H, $CH_3$). IR (KBr, cm$^{-1}$): $\nu$(C–H)$_{ar}$ = 3075, 3042, $\nu_{as}(CH_3)$ = 2924, $\nu_s(CH_3)$ = 2840, $\gamma$(C–H)$_{py}$ overtones = 1983–1637, $\nu$(C=C)$_{py}$ = 1599, 1571, 1478, 1456, $\delta(CH_3)$ = 1399, $\nu$(C=N)$_{py}$ = 1387, 1251, $\rho$(C–H)$_{py}$ = 1194, 1177, 1142, $\gamma$(C–H)$_{py}$ = 1041, 1025, 789, 650. *Anal.* Calc. for [Zn($C_{17}H_{15}N_3$)$Cl_2$] (397.59): C, 51.35; H, 3.80; N, 10.57. Found: C, 51.53; H, 3.66; N, 10.42%.

#### 2.2.6. [Zn**L**$(NO_3)_2$] (**2c**)

Yield: 74.9% (24.8 mg) ESI-MS: *m*/*z* (%) = 387 (20) [Zn**L**($NO_3$)]$^+$, 293 (5) [Zn**L**$_2$]$^{2+}$, 262 (100) [H**L**]$^+$, 163 (15) [Zn**L**]$^{2+}$. $^1$H NMR (300 MHz, $CD_3CN$) $\delta$ (ppm): 8.52 (d, 2H, *J* = 7.1 Hz), 8.44 (t, 1H, *J* = 6.6 Hz), 8.33 (d, 2H, *J* = 8.1 Hz), 8.11 (t, 2H, *J* = 7.8 Hz), 7.62 (d, 2H, *J* = 7.5 Hz), 2.86 (s, 6H, $CH_3$). IR (KBr, cm$^{-1}$): $\nu$(C–H)$_{ar}$ = 3094, 3074, 3051, $\nu_{as}(CH_3)$ = 2930, $\nu_s(CH_3)$ = 2854, $\gamma$(C–H)$_{py}$ overtones = 2093–1684, $\nu$(C=C)$_{py}$ = 1600, 1574, 1480, 1457, $\nu_{as}(NO_2)$ = 1426, $\nu_s(NO_2)$ = 1332, $\nu$(C=N)$_{py}$ = 1291, 1252, $\rho$(C–H)$_{py}$ = 1189, 1177, 1141, $\nu$(NO) = 1008, $\gamma$(C–H)$_{py}$ = 1033, 789, 650. *Anal.* Calc. for [Zn($C_{17}H_{15}N_3$)($NO_3$)$_2$] (450.71): C, 45.30; H, 3.35; N, 15.54. Found: C, 45.45; H, 3.50; N, 15.37%.

### 2.3. X-ray structure determination

Diffraction data were collected at room temperature by the $\omega$-scan technique up to $2\theta = 60°$, on an Oxford Diffraction Xcalibur four-circle diffractometer with an Eos CCD-detector with graphite-monochromatized Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å) for **1a**, **1c**, **1d** and **2c** and on an Oxford Diffraction SuperNova four-circle diffractometer with an Atlas CCD-detector, equipped with a Nova microfocus Cu K$\alpha$ radiation source ($\lambda = 1.5418$ Å) for **2a**. The data were corrected for Lorentz-polarization as well as for absorption