Synthesis, crystal structure and magnetism of iron(III) and manganese(III) dipicolinates with pyridinemethanols

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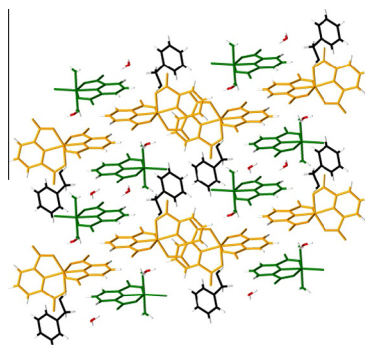[d] *Department of Chemistry, University of SS Cyril and Methodius, SK-917 01 Trnava, Slovakia*

HIGHLIGHTS

- Four novel ionic iron(III) and manganese(III) dipicolinato complexes were prepared.
- The complexes were characterized by single-crystal X-ray structural analysis, FTIR, and magnetic measurements.
- The magnetic properties were interpreted quantitatively using the spin Hamiltonian.

GRAPHICAL ABSTRACT

Four ionic iron(III) and manganese(III) dipicolinato complexes with pyridinemethanol have been prepared and characterized by the single-crystal X-ray structure analysis, infrared spectroscopy and magnetic measurements. The magnetic data were quantitatively interpreted within the spin Hamiltonian approach with consistently included molecular field correction.

ARTICLE INFO

ABSTRACT

Four ionic iron(III) and manganese(III) dipicolinato complexes of the formula (2-pymeH) [$Fe^{III}(dipic)_2$]·[$Fe^{III}(H_2O)_2Cl(dipic)$]·$2H_2O$, (3-pymeH)[$Mn^{III}(dipic)_2$]·$1.5H_2O$, (4-pymeH)[$Fe^{III}(dipic)_2$]·$2H_2O$ and (4-pymeH)[$Mn^{III}(dipic)_2$]·$2H_2O$, where H_2dipic = pyridine-2,6-dicarboxylic acid, 2-pyme = 2-pyridinemethanol, 3-pyme = 3-pyridinemethanol, 4-pyme = 4-pyridinemethanol, have been prepared and characterized by the single-crystal X-ray structure analysis, infrared spectroscopy and magnetic measurements. The magnetic data were fitted to a zero-field splitting model revealing a slight magnetic anisotropy for Mn(III) systems. The molecular field correction was consistently formulated and included in the analysis for both, magnetic susceptibility and magnetization data.

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Introduction

Pyridinecarboxylato complexes have been widely investigated in recent years due to their interesting coordination chemistry, allowing unusual structural features and leading to various physical and chemical properties [1–4]. Pyridinedicarboxylic acids are present in many natural products, such as alkaloids, vitamins, and enzymes, so their metal complexes can be used as models in many research fields [5]. The dicarboxylic acid analogue especially pyridine-2,6-dicarboxylic acid is one of the most suitable ligand systems for modeling potential metallo-pharmaceutical compounds because of the low toxicity, amphophilic nature and diverse biological activities [6–8].

To our best knowledge, there are only few complexes with 2-hydroxymethylpyridinium cation [9–12], 3-hydroxymethylpyridinium cation [13] and 4-hydroxymethylpyridinium cation [14].

The N,O-donoring ligands in complexes with iron(III) and manganese(III) are interesting also for their magnetic properties. While the former ones often show the spin crossover behavior [15–17], the latter are attractive for their potential single molecule magnetism properties [18–20].

As an extension of our research on carboxylato coordination compounds [21], we are reporting here on the synthesis, crystal structure and magnetic properties of four new iron(III) and manganese(III) dipicolinato complexes with the hydroxymethylpyridinium cations.

Experimental

Materials and measurements

All materials and solvents were purchased from commercial sources (Acros or Sigma) and used without further purification. Infrared spectra of the complexes were recorded by ATR techniques in the region of 4000–400 cm^{-1} using Nicolet 5700 FT–IR spectrometer (Thermo Scientific) at the room temperature. Elemental C/H/N analysis was carried out on Thermo Electron Flash EA 1112 analyzer. The magnetic measurements were conducted using a SQUID apparatus (MPMS-XL7, Quantum Design) in the RSO mode of detection. About 20 mg of the sample was encapsulated in a gelatin-made sample holder. The susceptibility has been taken at $B = 0.1$ T, corrected for the underlying diamagnetism and converted to the effective magnetic moment in units of Bohr magneton via the formula $\mu_{eff}/\mu_B = (797.7\ \text{mol}^{1/2}\ \text{K}^{-1/2}\ \text{m}^{-3/2})\sqrt{\chi_{corr}T}$. The magnetization was measured at two temperatures: $T = 2.0$ and $T = 4.6$ K.

Synthesis of (2-pymeH)[Fe^{III}(dipic)$_2$]·[Fe^{III}(H$_2$O)$_2$Cl(dipic)]·2H$_2$O (1)

A solution of pyridine-2,6-dicarboxylic acid (0.167 g, 1 mmol) and 2-hydroxymethylpyridine (100 mm^3, 1 mmol) in mixture of water and methanol (10 cm^3, 1:1) was refluxed at 100 °C for 20 min. To this mixture solid FeCl$_3$·6H$_2$O (0.135 g, 0.5 mmol) was added and it was refluxed for 1 h. Green crystals suitable for the X-ray diffraction analysis were grown in a few days. Anal. Calc. for C$_{27}$H$_{25}$N$_4$O$_{17}$ClFe$_2$: C, 39.33; H, 3.06; N, 6.79%. Found: C, 39.78; H, 3.18; N, 6.87%.

Synthesis of (3-pymeH)[Mn^{III}(dipic)$_2$]·1.5H$_2$O (2)

An aqueous solution of KMnO$_4$ (10 cm^3, 0.1 mmol) was added under continuous stirring to a methanol solution (10 cm^3) of pyridine–2,6–dicarboxylic acid (0.167 g, 1 mmol) and MnCl$_2$·4H$_2$O·(0.079 g, 0.4 mmol). To the resulting dark-red solution 3-hydroxymethylpyridine (100 mm^3, 1 mmol) was added and the final solution was treated under reflux at 100 °C for 1 h. The reaction mixture was gradually cooled down to the room temperature, and then it was filtered from little precipitate. The dark-red filtrate was allowed to stand at refrigerator and the dark violet crystals suitable for the X-ray diffraction analysis were obtained in one day. Anal. Calc. for C$_{20}$H$_{17}$N$_3$O$_{10.5}$Mn: C, 45.99; H, 3.28; N, 8.05%. Found: C, 46.08; H, 3.33; N, 8.18%.

Synthesis of (4-pymeH)[Fe^{III}(dipic)$_2$]·2H$_2$O (3)

The reaction procedure was analogous to 1 except that 4-pyme (0.109 g, 1 mmol) was used instead of 2-pyme. Green crystals suitable for the X-ray diffraction analysis were obtained in a few days. Anal. Calc. for C$_{20}$H$_{18}$N$_3$O$_{11}$Fe: C, 45.14; H, 3.41; N, 7.90%. Found: C, 45.10; H, 3.49; N, 7.82%.

Synthesis of (4-pymeH)[Mn^{III}(dipic)$_2$]·2H$_2$O (4)

The reaction procedure was the same as for 2 except that 4-pyme (0.109 g, 1 mmol) was used instead of 3-pyme. The dark-violet crystals suitable for the X-ray diffraction analysis were obtained in few days. Anal. Calc. for C$_{20}$H$_{18}$N$_3$O$_{11}$Mn: C, 45.21; H, 3.41; N, 7.91%. Found: C, 45.01; H, 3.40; N, 7.88%.

Single crystal X-ray diffraction measurements

Intensity data for 1–3 were collected by Bruker–Nonius KappaCCD diffractometer with graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å). Absorption correction were applied using the program SADABS [22]. Data reductions were performed with EvalCCD [23]. Intensity data for 4 were collected using Siemens P4 diffractometer with graphite monochromated Mo Kα radiation [24]. The diffraction intensities were corrected for Lorentz and polarization effects with XSCANS. Absorption correction was applied using the program XEMP [25]. The structures were solved by direct methods using the program SIR-2011 [26] and refined by the full-matrix least-squares method on all F^2 data using the program SHELXL-2013 [27]. Geometrical analysis was performed using SHELXL-2013. The structures were drawn by ORTEP-3 [28] and MERCURY (Version 3.1) [29] software. The single crystal suite WINGX was used an integrated system for all crystallographic programs and software for preparing the material for publication [30].

All non-hydrogen atoms of the title compound were refined anisotropically as independent atoms. Hydrogen atoms were mostly localized on a difference Fourier map, however, to ensure the uniformity of the treatment of the crystal, all hydrogen atoms were recalculated into idealized positions and assigned temperature factors H$_{iso}$(H) = 1.2U_{eq} (aromatic carbon and amide nitrogen) with d(C—H) = 0.95 (at 150 K) and 0.93 Å (at 293 K) for hydrogen atoms in aromatic rings, d(N—H) = 0.88 Å (at 150 K) and 0.86 Å (at 293 K) for hydrogen atoms in pyridine nitrogen or of 1.5U_{eq} for the O—H groups with d(O—H) = 0.84 Å (at 150 K) and 0.82 Å (at 293 K) for hydrogen atoms in hydroxyl groups and molecules of water. Crystal data and conditions of data collection and refinement are reported in Table 1.

Results and discussion

Description of crystal structures

The molecular structures of 1–3 are displayed in Fig. 1, selected bond lengths and angles are given in Tables 2 and 3, hydrogen bond parameters are given in Table 4. All prepared compounds consist of the complex anion [M^{III}(dipic)$_2$]$^-$ (M = Fe, Mn), hydroxy-methylpy-