

Methanolysis of 2-cyanopyridine in the coordination sphere of manganese(II). The structure of $Mn_4L_6Cl_2$ cluster (L= methyl picolinimide)[†]

Lara Rouco ¹, Rosa Pedrido ², M. Isabel Fernández-García ¹, Ana M. González-Noya ² and Marcelino Maneiro ^{1,*}

¹ Departamento de Química Inorgánica, Facultade de Ciencias, Universidade de Santiago de Compostela

² Departamento de Química Inorgánica, Facultade de Química, Universidade de Santiago de Compostela

* Correspondence: marcelino.maneiro@usc.es; Tel.: +34982824106

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Abstract: The reaction of 2-cyanopyridine and Mn(II) in methanol solution led to the formation of a $Mn_4L_6Cl_2$ cluster **1** containing *O*-methyl picolimidate as a ligand (L). The coordination of 2-cyanopyridine to the Mn(II) ion as a chelating bidentate ligand activated the CN triple bond which subsequently suffered a nucleophilic attack by CH₃OH. Complex **1** was characterized by standard techniques including microanalysis, IR spectroscopy, ESI spectrometry, and magnetic susceptibility measurements. The crystal structure of **1** was determined by X-ray diffraction techniques, and the crystallographic studies revealed a planar-diamond array for **1** where the six monoanionic picolinimidates act as chelating ligands through the two nitrogen atoms.

Keywords: manganese; methanolysis; X-ray diffraction; supramolecular chemistry

1. Introduction

Increased reactivities of molecules coordinated in metal complexes have wide applications in chemistry. Manganese(II) complexes containing chelating N,N-donor ligands are important due to their application in catalytic systems [1], antioxidant drugs [2-3], MRI contrast agents [4], antibacterial [5], antifungal [6] and nanomaterials [7]. The activation of ligands containing the nitrile group upon their coordination to a manganese ion has been exploited in addition reactions of nucleophiles such as amines, alcohols and water.

The 2-cyanopyridine as a chelating bidentate ligand can be coordinated to manganese ion from two nitrogen atoms of pyridine ring and carbonitrile group in the presence of non-protonic solvents. Reaction of this chelating ligand with manganese(II) salts in protonic solvents as methanol leads to the formation of complexes which contain *O*-methyl picolimidate. Although this type of process is already known, this communication describes for the first time the synthesis and complete characterization, including X-ray crystal structure, of the resulting $Mn_4L_6Cl_2$ cluster, where L is the *O*-methyl picolimidate ligand.

2. Materials and Methods

$Mn_4L_6Cl_2$ (1): To a CH₃OH/H₂O solution of 2-cyanopyridine (42 mg, 0.4 mmol) was added dropwise a methanol solution (40 mL) of MnCl₂ (40 mg, 0.2 mmol). The mixture turned light green. It was heated for 40 min with stirring and then filtered after cooling to room temperature. Well-shaped colorless crystals of **1** suitable for X-ray diffraction were obtained within 2 months with a 25% yield upon slow evaporation of the solvents. Yield: 0.01 g (20 %). Selected data for **1**: MS(ESI): *m/z* 1108.4

[1+ H⁺]⁺, 1129.5 [1 + Na⁺]⁺. Elemental analysis found: C, 45.1; H, 4.4; N, 14.9 %. C₄₂H₄₈Cl₂Mn₄N₁₂O₆ (MW 1107.6) requires C, 45.6; H, 4.3; N, 15.2 %. IR (cm⁻¹): IR (cm⁻¹): ν(N-H carboxamide) 3237 (m), ν(C-H)_{Ar} 3072 (m), ν(C-H)_{Me} 2981 (w), 2940 (w), ν(C=NH carboxamide) 1659 (s), ν(C=N) 1631 (s), ν[(N=C-O-) + δ(NH)] 1379 (s), δ(O-CH₃) 1206 (m), ν_{as}(C-O-C) 1138 (s), ν_s(C-O-C) 965 (m), ν(Mn-Cl) 303 (m).

X-ray crystallographic studies. Data for **1** were collected at room temperature on a Bruker Smart CCD-1000 diffractometer. Mo-Kα radiation (λ=0.71073 Å) from a fine-focus sealed tube source (at 100 K). The computing data and reduction were made by BRUKER SAINT [8] software. An empirical absorption correction was applied using SADABS [9]. The structure was solved by SIR-97 [10] and refined by full-matrix least-squares techniques against F² using SHELXL-97 [11]. Positional and anisotropic atomic displacement parameters were refined for all heteroatoms. The hydrogen atoms positions were included in the model by electronic density, and they were refined isotropically [Uiso(H) = 1.2Ueq(Atom)] or were geometrically calculated and refined using a riding model (isotropic thermal parameters 1.2–1.5 times those of their carrier atoms).

3. Results and Discussion

3.1. Synthesis and spectroscopic characterization

The reaction of 2-cyanopyridine and Mn(II) in methanol solution leads to the formation of **1** containing *O*-methyl picolinimidate as the chelate ligand. The methanolysis of the initial 2-cyanopyridine takes place upon coordination with the Mn(II) ion as a chelating bidentate ligand through the two nitrogen atoms of the pyridine ring and the carbonitrile group. As observed previously, the coordination of 2-cyanopyridine to some divalent metal ions activates the CN triple bond and makes it much more amenable toward nucleophilic attack by CH₃OH molecules [12-13]. The proposed stoichiometry for complex **1**, Mn₄L²⁻Cl₂, in which six *O*-methyl picolinimidate ligands are in a monoanionic mode (L²⁻), was confirmed by analytical and spectroscopic data. Moreover, recrystallization from the mother liquors afforded X-ray quality crystals for **1**.

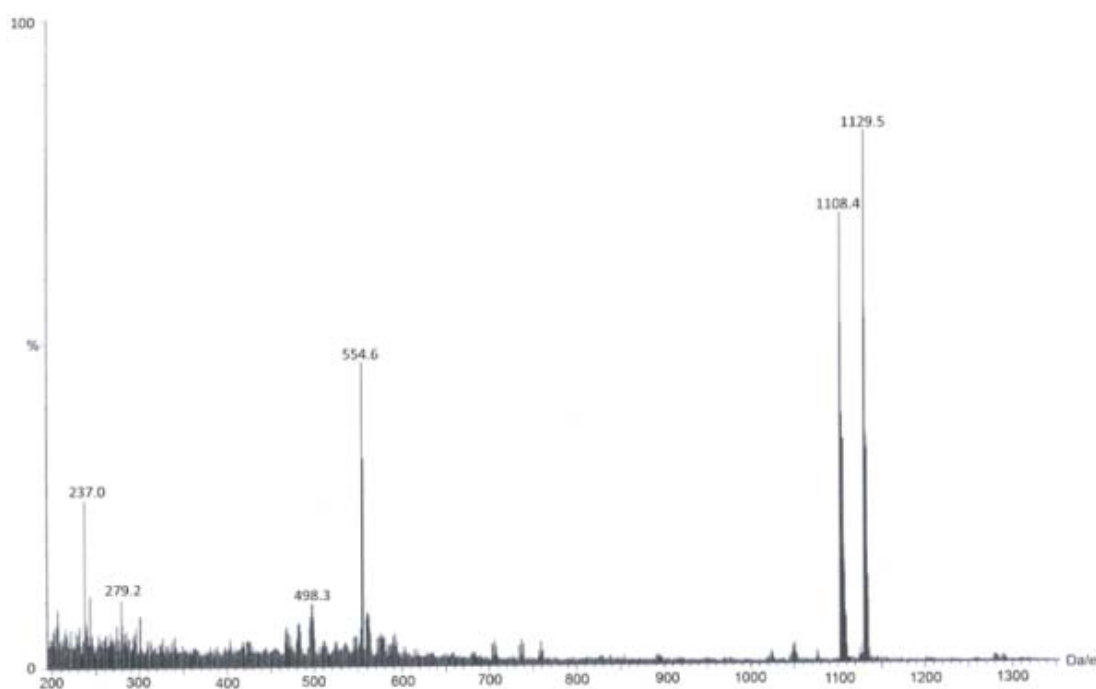


Figure 1. ESI mass spectrum for **1**.

The ESI-MS of the CH₂Cl₂ solution of **1** gives peaks at *m/z* 1108.4 and 1129.5, which corresponds to [**1** + H]⁺ and [**1** + Na]⁺ (positive mode), suggesting the stability of this biomimetic model in solution (Figure 1).

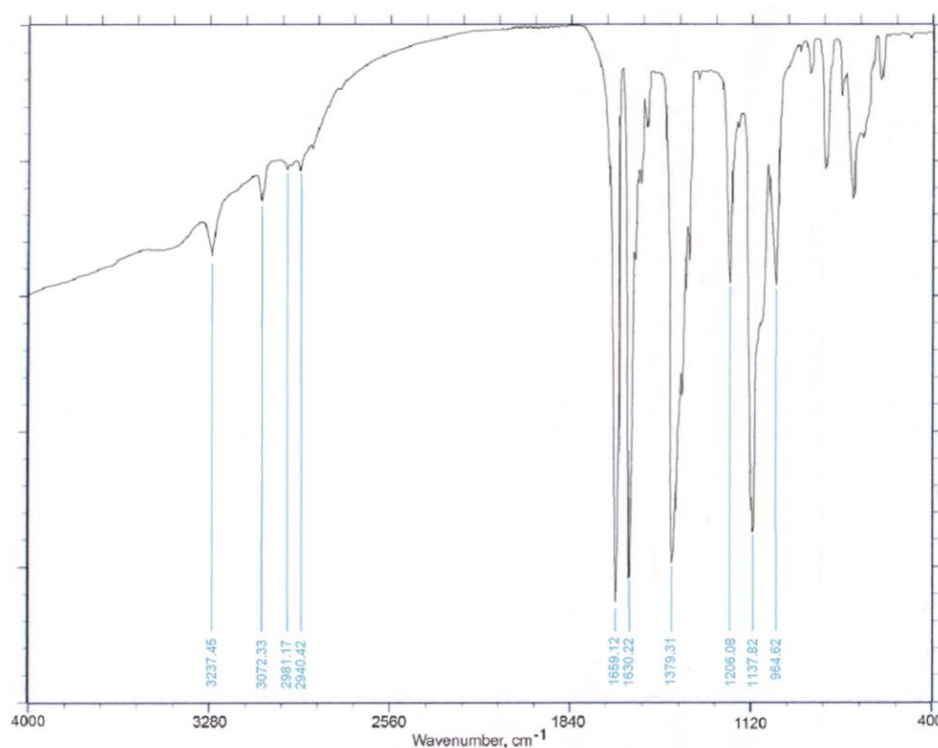


Figure 2. IR spectrum for **1**.

The IR spectrum for **1** also confirms the methanolysis reaction of the 2-cyanopyridine to give the *O*-methyl picolinimidate ligand. Thus, the spectrum (Figure 2) has a sharp band with a medium intensity at 3237 cm⁻¹, characteristic of the N–H vibration of *O*-methyl picolinimidate [14]. The C–H stretching vibrations of the methyl groups of the carboxamide appear at 2981 and 2940 cm⁻¹, while the absence of the $\nu(\text{C}\equiv\text{N})$ band (which should have appeared at about 2240 cm⁻¹) is indicative that the nitrile group has been converted to a carboxamide one. An additional strong band at 1659 cm⁻¹ is also assigned to $\nu(\text{C}=\text{NH})$ of the carboxamide group. The C–H stretching vibrations of the pyridine rings appear at 3072 cm⁻¹. Different medium and strong bands observed in the range 1631–1591 cm⁻¹ are assigned to C=N, C=C and C–C stretching vibrations. The absorption band at 1379 cm⁻¹ is assigned to the $\nu(\text{C}=\text{O})$ stretching vibration which mixes with $\delta(\text{NH})$ of the imino ether group. The $\nu_{\text{as}}(\text{C}=\text{O}-\text{C})$ and $\nu_{\text{s}}(\text{C}=\text{O}-\text{C})$ absorption bands appear at 1138 and 965 cm⁻¹, respectively. The absorption band observed at 1206 cm⁻¹ is assigned to $\delta(\text{O}-\text{CH}_3)$.

3.2. Crystallographic studies

Single crystals of complex **1**, suitable for X-ray diffraction studies, were obtained by slow evaporation of the mother liquors at room temperature. The main crystal data and structure refinement details are collected in Tables 1 and 2. Figure 3 show different views of the structure of **1**, which displays a planar-diamond core of the tetrameric cluster.

The coordination numbers are six and five for Mn1 and Mn2, respectively. The metal coordination geometry is described as distorted octahedral for Mn1 and distorted trigonal bipyramidal for Mn2 [15]. Analysis of the shape determining angles for Mn2, using the approach of Reedijk and coworkers [16], yielded $\tau [(\alpha-\beta)/60]$, being with α and β being the two greatest valence angles of the coordination

center] having a value of 0.9 for Mn2 ($\tau = 0.0$ and 1.0 for square-pyramidal and trigonal bipyramidal geometries respectively).

Table 1. Crystal data and structure refinement parameters for **1**.

| Compound | 2 |
|---|---|
| Empirical formula | C ₂₁ H ₂₄ ClMn ₂ N ₆ O ₃ |
| Formula weight | 553.79 |
| Temperature [K] | 293(2) |
| Wavelength [Å] | 0.71069 |
| Crystal system | Monoclinic |
| Space group | P2 ₁ /n |
| <i>a</i> [Å] | 11.953(5) |
| <i>b</i> [Å] | 11.256(5) |
| <i>c</i> [Å] | 17.889(5) |
| α [°] | 90 |
| β [°] | 99.051(5) |
| γ [°] | 90 |
| Volume [Å ³] | 2376.9(16) |
| Z | 4 |
| D _{calcd.} [g cm ⁻³] | 1.548 |
| μ [mm ⁻¹] | 1.21 |
| F(000) | 1132 |
| $\theta_{\min/\max}$ [°] | 1.92/24.73 |
| Goodness-of-fit on F ² | 1.067 |
| Total data | 4038 |
| Unique data | 4038 |
| Data/restraints/parameters | 4038/0/299 |
| Final R indices [<i>I</i> > 2 σ (<i>I</i>)] | <i>R</i> ₁ = 0.0894; <i>wR</i> ₂ = 0.2658 |
| R indices (all data) | <i>R</i> ₁ = 0.1223; <i>wR</i> ₂ = 0.2812 |

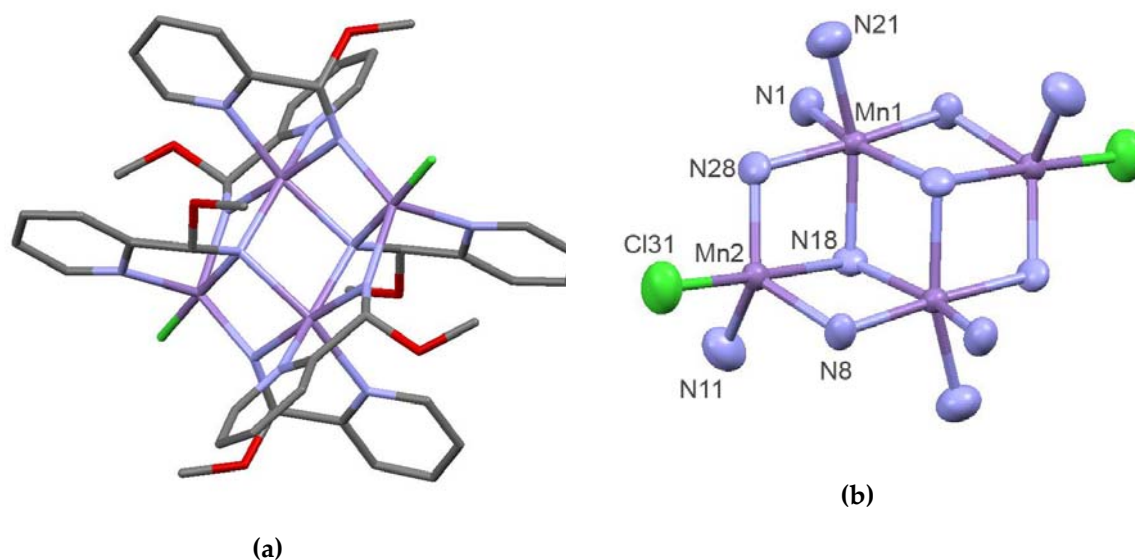


Figure 3. (a) Stick diagram of planar-diamond cluster **2**. (b) Planar-diamond cluster core showing the atomic numbering scheme.

Each manganese atom is coordinated to three or four different *O*-methyl picolinimidate ligands, depending on whether the ion is trigonal bipyramidal or octahedral. In the case of Mn1, which has an octahedral geometry, two chelating (L^2)⁻ are bound via the pyridyl nitrogen donor (Mn1–N1 = 2.123(9) Å and Mn1–N21 = 2.143(10)) and the imine nitrogen atoms (Mn1–N8 = 2.051(8) Å and Mn1–N28 = 2.048 Å), two additional monodentate (L^2)⁻ ligands are also bound through their imine nitrogen atoms (Mn1–N18 = 2.141(8) and 2.120(7) Å). For Mn2, three (L^2)⁻ are bound; one of them behaves as the chelating ligand through the pyridyl and the imine nitrogen atoms (Mn2–N11 = 2.081(11) Å and Mn2–N18 = 2.353(8) Å), while two (L^2)⁻ act as monodentates via the imine nitrogen atoms (Mn2–N28 = 1.939(8) and Mn2–N8 = 1.971(8)). The fifth coordination position for Mn2 is completed with a chloride ion. Accordingly, each one of the six *O*-methyl picolinimidate ligands chelates a manganese ion but also bridges two manganese centers via the imine nitrogen atom.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

| | | | |
|---------------------|-----------|----------------------|-----------|
| Mn(1)–N(28) | 2.048(8) | Mn(1)–Mn(2)#1 | 3.206(2) |
| Mn(1)–N(8) | 2.051(8) | Mn(2)–N(28)#1 | 1.939(8) |
| Mn(1)–N(18)#1 | 2.120(7) | Mn(2)–N(8) | 1.971(8) |
| Mn(1)–N(1) | 2.123(9) | Mn(2)–N(11) | 2.081(11) |
| Mn(1)–N(18) | 2.141(8) | Mn(2)–Cl(31) | 2.305(4) |
| Mn(1)–N(21) | 2.143(10) | Mn(2)–N(18) | 2.353(8) |
| Mn(1)–Mn(2) | 3.203(2) | Mn(2)–Mn(1)#1 | 3.206(2) |
| N(28)–Mn(1)–N(8) | 175.2(3) | N(28)#1–Mn(2)–N(8) | 124.9(4) |
| N(28)–Mn(1)–N(18)#1 | 80.3(3) | N(28)#1–Mn(2)–N(11) | 118.5(4) |
| N(8)–Mn(1)–N(18)#1 | 102.2(3) | N(8)–Mn(2)–N(11) | 101.3(4) |
| N(28)–Mn(1)–N(1) | 98.5(3) | N(28)#1–Mn(2)–Cl(31) | 101.6(2) |
| N(8)–Mn(1)–N(1) | 77.1(3) | N(8)–Mn(2)–Cl(31) | 102.9(2) |
| N(18)#1–Mn(1)–N(1) | 98.9(3) | N(11)–Mn(2)–Cl(31) | 105.2(3) |
| N(28)–Mn(1)–N(18) | 102.7(3) | N(28)#1–Mn(2)–N(18) | 76.8(3) |
| N(8)–Mn(1)–N(18) | 81.9(3) | N(8)–Mn(2)–N(18) | 78.4(3) |
| N(18)#1–Mn(1)–N(18) | 78.2(3) | N(11)–Mn(2)–N(18) | 75.4(4) |
| N(1)–Mn(1)–N(18) | 157.7(3) | Cl(31)–Mn(2)–N(18) | 178.4(2) |
| N(28)–Mn(1)–N(21) | 77.9(4) | | |
| N(8)–Mn(1)–N(21) | 100.4(4) | | |
| N(18)#1–Mn(1)–N(21) | 155.7(4) | | |
| N(1)–Mn(1)–N(21) | 94.8(4) | | |
| N(18)–Mn(1)–N(21) | 96.2(4) | | |

4. Conclusions

Methanolysis of 2-cyanopyridine in the coordination sphere of manganese(II) led to the formation of a manganese complex which contains *O*-methyl picolinimidate (L^-). The structure of this bidentate ligand favors the stabilization of a high-nuclearity cluster as $Mn_4L_6Cl_2$. Characterization of the resulting planar-diamond cluster shows that the six *O*-methyl picolinimidate ligands are in a monoanionic mode.

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Conflicts of Interest: The authors declare no conflict of interest.

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