Pyridinesilver Tetraoxometallate Complexes: Overview of the Synthesis, Structure, and Properties of Pyridine Complexed AgXO₄ (X = Cl, Mn, Re) Compounds

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Abstract: We reviewed the synthesis, structure, and properties of pyridine complexes of AgXO₄ (X = Cl, Mn, and Re) compounds with various compositions ([AgPy₂]XO₄, [AgPy₂XO₄]0.5Py, [AgPy₄]XO₄, and 4 [AgPy₂XO₄][AgPy₄]XO₄). We also clarified the controversial information about the existence and composition of pyridine complexes of silver permanganate, used widely as mild and selective oxidants in organic chemistry. We discussed in detail the available structural and spectroscopic (IR, Raman, and UV) data and thermal behavior, including the existence and consequence of quasi-intramolecular reactions between the reducing ligand and anions containing oxygen.

Keywords: silver complexes; permanganates; perchlorates; perrhenate; pyridine; structure; spectroscopy; thermal behavior

1. Introduction

Silver permanganate, perchlorate, and perrhenate (AgXO₄, X = Cl, Mn, and Re) are well soluble in pyridine, and various complexes with studied and unknown chemical nature were isolated even in the 19th and the beginning of the 20th century [1–3]. The composition and purity of the complexes strongly depend on the conditions of synthesis, and even small changes in reaction conditions lead to the formation of other (or a mixture of) compounds [4]. In principle, silver can formally form two, three, or four-coordinated pyridine complexes. However, single-crystal studies [5,6] showed that the complexes with 2.4 or 2.5 pyridine/silver atom ratios always contain 2- and 4-coordinated silver atoms.

Considering the wide use of silver permanganate complexes in organic chemistry, as mild and selective oxidants, and that literature sources contain controversial or incorrect information about these compounds, we discuss the chemistry of pyridine complexes of AgXO₄ (X = Cl, Mn, and Re) in detail. We also comprehensively summarized their synthesis, composition, structure, and redox properties, including the occurring quasi-intramolecular redox reactions between the reducing pyridine ligand and oxidizing XO₄⁻ anions and the existence of hydrogen bonds between the acidic C–H and polarized X–O bonds.

The compounds were prepared and their labels are given in Table 1.
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2. Synthesis and Composition of AgPy\_XO\_4 (X = Mn, Cl, and Re) Complexes

2.1. Pyridine Complexes of Silver Permanganate

The first pyridine complexes of silver permanganate were described by Klobb in 1886 [1], when a small amount of pyridine (20% aq.) was dissolved in an equivalent solution of silver sulfate and potassium permanganate. Based on chemical analysis, two complexes were isolated with formulas AgPy\_2MnO\_4 and AgPy\_2.5MnO\_4 with decomposition points of 65 and 103 °C, respectively. Almost one hundred years later, Firouzabadi et al. (1982) [4] reported an easy preparation of a purple crystalline material in high yield (90%), which was believed to be AgPy\_2MnO\_4. They prepared this compound by adding AgNO\_3 dissolved in ten times more water and three equivalent of pyridine to a KMnO\_4 solution. The crystalline precipitate was recrystallized from acetone–benzene and its decomposition point was found to be 104–105 °C. Lee (2001) [7] reproduced the method described previously [4] to check the oxidation property of this material in several organic reactions.

Kotai et al. [8] reproduced the methods described by Klobb [1] and Firouzabadi [4] and found that AgPy\_2MnO\_4 (compound 2a) and 4[AgPy\_2MnO\_4] (compound 4a) (it is equal to the formula AgPy\_2.5MnO\_4) could be isolated as the main products in Klobb’s methods, but a mixture containing 2a, 3a (2a 0.5Py), and 4a formed in Firouzabadi’s experiments. Recrystallization of the reaction product from acetone–benzene depending on the acetone–benzene solvent concentration and recrystallization conditions, led to pure 2a, 3a, or 4a, or mixtures of these with different 2a:3a:4a ratios.

To study the interconversion of compounds 2a–5a, and further characterize these complexes, Sajó et al. (2018) [9] created new methods for the isolation of pure compounds (Figure 1). They isolated bis (pyridine)silver permanganate (2a) in a pure form by reacting [AgPy\_2]NO\_3 with a concentrated sodium permanganate solution and crystallizing it with a high temperature gradient. To prepare pure 4[AgPy\_2MnO\_4] (compound 4a), they added 10 volumes of water to a pyridine solution containing AgMnO\_4 (Py:Ag = 50) [9]. First, silver (I) permanganate was obtained from a saturated solution of AgNO\_3 and 40% aq. NaMnO\_4 in an Ag:NaMnO\_4 ratio of 1:1. The freshly prepared compound 1a (wet) bookmark0 was dissolved in pure pyridine, resulting in a saturated purple solution (the surface of the dried (old form) AgMnO\_4 crystals (decomposed by sunlight with the formation of catalytically active Ag-Mn oxides) can catalyze the oxidation of heterocycles containing nitrogen. Sometimes it resulted in the inflammation of the pyridine on dissolution of “old” dry AgMnO\_4 in dry pyridine). Sajó et al. immediately diluted it with water to reach a pyridine content of 10%, allowing the formation of the pure double salt (4a). Using one volume of benzene as a salting-out solvent, however, they prepared compound [AgPy\_4] MnO\_4 (5a) in a pure state. Another way to prepare compound 5a is to cool

| Compound | Label | Py:Ag Ratio |
|----------|-------|-------------|
| AgMnO\_4 | 1a    | -           |
| AgClO\_4 | 1b    | -           |
| AgReO\_4 | 1c    | -           |
| AgPy\_2MnO\_4 | 2a | 2           |
| [AgPy\_2]ClO\_4 | 2b | 2           |
| [AgPy\_2]ReO\_4 | 2c | 2           |
| [AgPy\_2MnO\_4] 0.5Py | 3a | 2.5         |
| [AgPy\_2ClO\_4] 0.5Py | 3b | 2.5         |
| AgPy\_2ReO\_4 0.5Py | 3c | 2.5         |

4[AgPy\_2MnO\_4] 4[AgPy\_2]MnO\_4 | 4a | 2.4         |
| 4[AgPy\_2ClO\_4] 4[AgPy\_2]ClO\_4 | 4b | 2.4         |
| 4AgPy\_2ReO\_4 4AgPy\_2ReO\_4 | 4c | 2.4         |
| [AgPy\_4]MnO\_4 | 5a | 4           |
| [AgPy\_4]ClO\_4 | 5b | 4           |
| [AgPy\_4]ReO\_4 | 5c | 4           |

2.2. Synthesis and Composition of AgPy\_XO\_4 (X = Mn, Cl, and Re) Complexes
down a concentrated solution of AgMnO₄ (1a) in pyridine to −18 °C overnight. The authors [8] reported a recrystallization route to synthesize pure [AgPy₂MnO₄]·0.5Py (3a). They recrystallized the mixture of AgPy₂MnO₄ and 4[AgPy₂MnO₄][AgPy₄] MnO₄ in various ratios from a 1:1 (v/v) acetone–benzene mixture. This led to the formation of a large quantity of platelet-like purple monoclinic single crystals, and some amount of amorphous brown decomposition product.

Figure 1. Interconversion scheme of permanganate complexes [8].

Compound 5a, containing the highest amount of pyridine (Py/Ag = 4), decomposes into the double salt-type compound (4a) (Py/Ag = 2.4), which contains less pyridine, or into its mixture with 2a (Py/Ag = 2) by controlled evaporation of the solvent. The removal of pyridine from compound 4a in a vacuum, however, did not give the expected compound 2a. Surprisingly, compound 2a decomposed into compound 4a in vacuum or by recrystallization from dichloromethane. It means that compound 2a decomposes in a vacuum or on dissolution with liberation of free pyridine, which recombines with the silver and permanganate ions into 4a.

2.2. Pyridine Complexes of Silver Perchlorate

Macy (1925) [3] constructed the silver perchlorate-pyridine-water ternary phase diagram at 25 °C. Four compounds, including three pyridine complexes, namely [AgPy₂]ClO₄ (2b) AgPy₂₂₅ClO₄ (later it was proved to be compound 4b with the formula AgPy₂₄ClO₄), [AgPy₄]ClO₄ (5b), and AgClO₄·H₂O (1b·H₂O) were described in the system as shown in Figure 2. The author claimed that these materials could be isolated under different temperatures from a saturated solution of silver perchlorate in pyridine. The important features regarding the solubility curve are presented in Figure 2.

There are four invariant equilibriums (1–4) and an unsaturated solution (L). The amount of water in the system can directly affect the solubility of AgClO₄ in pyridine. Line d–e specifies the solubility of AgClO₄, whereas line b–c represents the composition of the solid phases. Macy found that [AgPy₂]ClO₄ (2b) was the most stable solid phase with a melting point between 144 and 147 °C, whereas AgPy₂₂₅ClO₄ and [AgPy₄]ClO₄ (5b) are unstable solid phases, which melt at 68 °C and 95.6 °C, respectively.
The complex \([\text{AgPy}_2]\text{ClO}_4\) (2b) was prepared by Kauffman and Pinnell (1960) \([10]\) in the reaction of \(\text{AgNO}_3\) with \(\text{NaClO}_4\) in an aqueous pyridine solution in an \(\text{Ag}^+:\text{ClO}_4^-:\text{Py} = 1:1.3:6\) (molar) and pyridine/\(\text{H}_2\text{O} = 5/9\) (\(v/v\)) ratio. Cooling the solution at \(10\,^\circ\text{C}\) produced a white precipitate, which was recrystallized from a chloroform–pyridine mixture (5:1 (\(v/v\))). Dyason et al. (1985) \([11]\) determined the composition of this product and found it to be compound 4b instead of 2b. However, vacuum treatment of compound 4b produced pure compound 2b. Chen et al. (2007) \([12]\) emphasized that different stoichiometry of silver (I) pyridine adducts could be obtained depending on preparation conditions and also reinforced the importance of a vacuum system to form compound 2b during the drying process \([10,11]\). Hollo et al. (2019) \([13]\) reported that a mixture containing compound 4 and compound 5 could be easily prepared from an aqueous solution of \(\text{Ag}_2\text{SO}_4\), pyridine, and \(\text{NaClO}_4\) (20% aq. pyridine and 0.2 M of aq. \(\text{NaClO}_4\)) at lower temperatures (5–8 \(^\circ\text{C}\)). If the container is left open, [AgPy\(_4\)] ClO\(_4\) (compound 5b) completely transforms into [AgPy\(_{2.4}\)] ClO\(_4\) (compound 4b) at lower temperatures, while at room temperature or vacuum, compound 2b was the final product.

Nilsson and Oskarsson (1982) \([5]\) reported the preparation of pure [AgPy\(_4\)] ClO\(_4\) by dissolving silver (I) perchlorate in pyridine solution at \(-18\,^\circ\text{C}\). It slowly loses pyridine at room temperature and transforms into 2b. Dyason et al. and Bowmaker et al. also proved that compound 4b is also converted to compound 2b \([11,12]\).

Sajó et al. (2018) \([9]\) reproduced the method described by Kauffman and Pinnell \([10]\). They found that the raw product consists of a mixture of compounds 2a and 4a. A new compound was also identified as [AgPy\(_2\text{ClO}_4\)] 0.5Py (compound 3b), which formed when a mixture of compounds 2b and 4b were triturated (1:1 mixture) with an acetone:benzene solution (1:1, \(v/v\)). They mentioned that the free pyridine to form 3b from 2b or 4b came from the decomposition of compound 4b. Compound 3b is stable only in the presence of the mother liquor, but decomposes to [AgPy\(_2\)] ClO\(_4\) when it is kept in air.

The interconversions of compound 1b–5b can be seen in Figure 3.
low temperature. However, since that time, no detailed information regarding its structure and properties has been available in the literature. Recently, Sajó et al. (2018) synthesized the previously unknown [AgPy\(_2\)]ReO\(_4\) (2c) in a pure form, and studied its properties. This complex was formed from a mixture of Ag\(_2\)SO\(_4\), 0.2 M aq. NaReO\(_4\), and 10% aq. pyridine. A white precipitate was obtained after the reaction mixture was cooled to 0 °C. Another way to produce the same compound was to dissolve silver (I) perrhenate (1c) in pyridine, and completely remove the solvent by vacuum treatment at room temperature. Efforts to isolate complexes (3c) and (4c) have been unsuccessful until now. The existence of two AgPy\(_n\)ReO\(_4\) compounds with 3 and 5 pyridines was mentioned without any characterization by Woolf [15].

### 3. Thermal Analysis of Pyridine Complexes of AgXO\(_4\) Compounds (X = Mn, Cl, and Re)

#### 3.1. Pyridine Complexes of AgMnO\(_4\)

Pyridine complexes of silver permanganate decompose in exothermic reactions on slow heating. Fast heating causes explosion-like decomposition with flames. Decomposition points of compounds 2a and 4a are 65 and 103 °C, respectively [1,2].

Kotai et al. performed thermogravimetric and mass spectrometry analysis on compound 3a obtained by the recrystallization of a mixture of compound 2a and 4a from acetone–benzene [8], under an Ar atmosphere. A small amount of benzene was evolved at the beginning of thermal decomposition, with a maximum rate at 73 °C. They attributed the presence of benzene to the presence of a pyridine solvate substituent in the lattice. They also reported the thermal behaviors of compounds 2a and [AgPy\(_{2.25}\)]MnO\(_4\) (it was later proved to be a pyridine-deficient compound 4a [6]) under an inert atmosphere. Both complexes started to decompose at 50 °C with a maximum mass loss achieved at 78. They observed unusual phenomena, such as the lack of oxygen evolution and the appearance of free pyridine (m/z = 79) and pyridine oxidation products, such as CO\(_2\) (m/z = 44), CO (m/z = 28), H\(_2\)O (m/z = 18), and NO (m/z = 30). They attributed the presence of the pyridine ring oxidation products to the partial oxidation of the pyridine ligands by the permanganate ion (the experiments were done in an inert atmosphere). This quasi-intramolecular redox reaction took place in the solid phase between the permanganate anion and the coordinated pyridine, even below the temperature of the pyridine loss of the AgPy\(_2\)\(^+\) cation (T\(_{\text{dec}}\) > 147 °C) of other compounds containing an [AgPy\(_2\)]\(^+\)-cation with thermally stable and non-reactive anions [10,14]. The mechanism proposed is shown in Figure 4. The decomposition center is the hydrogen bond between the α-CH of the

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**Figure 3.** Interconversion scheme of perchlorate complexes [8].

2.3. Pyridine Complexes of Silver Perrhenate

This group of complexes has not been extensively studied so far. Wilke-Dörfurt and Gunzert (1933) [14] performed the first attempt to prepare it. [AgPy\(_4\)]ReO\(_4\) (5c) formed when they combined silver nitrate, pyridine, and perrhenic acid in a ratio of 1:10:1 at the low temperature. However, since that time, no detailed information regarding its structure and properties has been available in the literature.

The mechanism proposed is shown in Figure 4. The decomposition center is the hydrogen bond between the α-CH of the...
pyridine ring and an oxygen of permanganate ion. Rearrangement via transition states \( \text{TS}_1 \) and \( \text{TS}_2 \) due to thermal activation results in a 2-hydroxy pyridine derivative (\( \text{TS}_2 \)). They assumed tautomerization and a Dewar benzene-type ring (\( \text{TS}_4 \)) and the transformation of Dewar-C\(_5\)H\(_5\)NO to HNCO and “C\(_4\)H\(_4\)”.

The decomposition of these intermediates result in CO, CO\(_2\), NO, and H\(_2\)O as reaction products [16,17].

\[
\text{TS}_1 \rightarrow \text{TS}_2 \quad \text{TS}_3 \rightarrow \text{TS}_4 \quad \text{TS}_5 \rightarrow \text{C}_4\text{H}_4^* + \text{Ag} + \text{HNCO}^* + \text{MnO} \quad \text{TS}_6
\]

**Figure 4.** Proposed mechanism for the thermal decomposition of AgPy\(_2\)MnO\(_4\) [16]. a -non-hydrogen bound pyridine ring; b-hydrogen bound pyridine ring.

The thermal analysis of 4a was studied in detail by Kovács et al. [6] under an inert (He) and an oxidizing atmosphere. They observed a strongly exothermic reaction during the decomposition process even under an inert atmosphere. It indicates that the O\(_2\) present in the gas phase does not play a key role in starting the decomposition reaction. Thermal decomposition occurred mainly in one step at 85 °C. Metallic silver and manganese oxides formed as solid decomposition products. An intermediate that formed at 300 °C contained metallic silver, MnO, Mn\(_3\)O\(_4\), and Mn\(_2\)O\(_3\). Based on the decomposition temperatures of MnO\(_2\) \(\rightarrow\) Mn\(_2\)O\(_3\) \(\rightarrow\) Mn\(_3\)O\(_4\) \(\rightarrow\) MnO [18] reactions, which are 542, 918, and 1027 °C, respectively, they concluded that these oxide phases could form only in a redox reaction and not in the thermal decomposition of the intermediate manganese oxide phases.

### 3.2. Pyridine Complexes of AgClO\(_4\)

The thermal properties of 4b were investigated by Holló et al. (2019) [13]. The authors studied the decomposition of the compound under an argon and an air atmosphere. They observed that in the inert atmosphere, the compound started to decompose above 45 °C. The first decomposition intermediate was proved to be stable and was isolated at 85 °C as [AgPy\(_2\)]ClO\(_4\) (2b). Compound 2b was found to be stable up to 105 °C. Decomposition continued with the formation of pyridine and pyridine oxidation products (NO, H\(_2\)O, and CO\(_2\)). The authors also investigated in detail the decomposition products prepared at 350 °C and 500 °C. The first decomposition product consist of mainly AgClO\(_4\) and AgCl. The final residue was AgCl. The \(m/z = 44\) (CO\(_2\)) sign in the third decomposition peak around 320 °C was attributed to the oxidation of carbon residues that is formed from
pyridine degradation by AgClO₄ [19]. The unreacted AgClO₄ decomposed into AgCl and O₂, which suggests the presence of a complex decomposition process with simultaneous pyridine ligand loss with AgClO₄ formation, and a redox reaction between pyridine and AgClO₄ in the solid phase.

The thermal decomposition of 4b was also investigated under an oxidizing atmosphere [13]. The presence of O₂ in the gas phase accelerated the decomposition reaction and provided the required activation energy (~60 kJ mol⁻¹) [19] for that decomposition. Another essential feature reported is the low mass of the residue obtained at 400 °C, which was less than the total amount of Ag in the initial compound. This suggests that AgCl partly evaporated in the decomposition process [13]. The proposed reaction route is shown in Figure 5.

![Figure 5. Proposed mechanism for the thermal decomposition of 4b in argon [13].](image)

### 3.3. Pyridine Complexes of AgReO₄

No available literature data about thermal decomposition of the pyridine complexes of silver perrhenate. Our preliminary studies on the thermal decomposition of 2C showed the lack of the redox reactions between the pyridine ligand and perrhenate ion.

### 4. Crystallographic Structure of Pyridine Complexes of AgXO₄ Compounds (X = Mn, Cl, and Re)

The crystallographic parameters of pyridine complexes of AgXO₄ are summarized in Table 2.

Holló et al. [13] and Dyason et al. [11] crystallized compound 4b in a tetragonal system containing one [AgPy₂ClO₄] and one-quarter of [AgPy₄]ClO₄ units in the asymmetric unit. The permanganate analog of this compound (compound 4a) [6] is isostructural with compound 4b. The Cα–H···O permanganate distance (3.121 Å) is longer (consequently bond strength is weaker) than the Cα–H···O perchlorate distance in the perchlorate (compound 4b, 2.645 Å), as presented in Table 2.

Compound 3a ([AgPy₂MnO₄]-0.5Py) crystallizes as platelets [9] belonging to the monoclinic crystal system. The shortest argentophilic interaction between the neighboring fragments in the unit cell (Ag···Ag = 3.421 Å) is stronger than what was found in [4AgPy₂MnO₄] [AgPy₄]MnO₄ (Ag···Ag = 4.822 Å) [11,13].

The compound [AgPy₂]ClO₄ (2b) crystallizes in an orthorhombic crystal system [20]. The argentophilic interaction in this compound (Ag···Ag = 2.9997) provides a closer contact between [AgPy₂]⁺ ions than in compounds 3a, 4a, or 4b. The two coordinated pyridine ligands seem to be coplanar and the Ag-N bond distances were reported as 2.126 (4) and 2.133 (4) Å. The linear N-Ag-N bond angles are 173.83 (17°).
Table 2. Crystallographic parameters of Ag-Py-XO₄ (X = Mn, Cl, and Re) compounds.

| Empirical Formula | Label | Space Group | Unit Cell Dimensions, (Å or °) | Z | D (g cm⁻³) | T (K) | V (Å³) | Reference |
|-------------------|-------|-------------|--------------------------------|---|------------|-------|--------|-----------|
| Agpy₂MnO₄         | 2a    | Cc          | \(a = 22.875\) \(\text{b = 12.266}\) \(\text{c = 20.225}\) \(\beta = 62.361\) | 16 | 1.970      | 298   | 5191.2 | [9]       |
| [Agpy₂]ClO₄       | 2b    | Pnn2/Pnnm   | \(a = 20.138\) \(\text{b = 12.694}\) \(\text{c = 10.125}\) | 8  | 1.876      | 298   | 2588.3 | [9]       |
| [Agpy₂]ClO₄       | 2b    | Pbcn        | \(a = 7.140\) \(\text{b = 8.616}\) \(\text{c = 10.827}\) \(\alpha = 102.20\) \(\beta = 96.25\) \(\gamma = 105.58\) | 2  | 2.655      | 298   | 645.85 | [9]       |
| 4[Agpy₂MnO₄]·[Agpy₄]MnO₄ | 4a   | \(I_4\) | \(a = 22.01\) \(\text{c = 7.6075}\) | 10 (1) | 1.877 | 298 | 3685.4 | [9]        |
| 4[Agpy₂MnO₄]·[Agpy₄]MnO₄ | 4a   | \(I_4\) | \(a = 21.982\) \(\text{b = 21.982}\) \(\text{c = 7.5974}\) | 2  | 1.885 | 293 | 3671.13 | [6]        |
| 4[Agpy₂ClO₄]·[Agpy₄]ClO₄ | 4b   | \(I_4\) | \(a = 21.95\) \(\text{c = 7.6843}\) | -  | 1.78  | 295 | 3702 (2) | [11]       |
| 4[Agpy₂ClO₄]·[Agpy₄]ClO₄ | 4b   | \(I_4\) | - | - | - | - | - | [13] |
| [Agpy₂MnO₄]·0.5Py | 3a    | C₂/c        | \(a = 19.410\) \(\text{b = 7.788}\) \(\text{c = 21.177}\) \(\alpha = 90.00\) \(\beta = 104.20\) \(\gamma = 90.00\) | 4  | 1.817 | 293 | 3103.4 (5) | [9] |
| [Ag(py)₄]MnO₄     | 5a    | P₂₁         | \(a = 15.24\) \(\text{b = 13.89}\) \(\text{c = 5.31}\) \(\beta = 84.13°\) | 2  | -     | 298 | 1117   | [9]       |
| [Ag(py)₄]ClO₄     | 5b    | \(I_4\) \(I_4/m\) | \(a = 12.874\) \(\text{c = 6.748}\) | 2  | 1.55  | 260 | 1118.4 | [5]       |

Nilsson and Oskarsson (1982) [4] described the crystal system of [AgPy₄]ClO₄ (compound 5b) as tetragonal. The structure of this compound is shown in Figure 6, where pyridine molecules are in almost parallel planar dispositions. The structure and packing of compounds 3a, 3b, and 4a, 4b can be seen in Figures 7 and 8, respectively.
ligands seem to be coplanar and the Ag-N bond distances were reported as 2.126 (4) and 2.133 (4) Å. The linear N-Ag-N bond angles are 173.83 (17°).

Nilsson and Oskarsson (1982) [4] described the crystal system of [AgPy4]ClO4 (compound 5b) as tetragonal. The structure of this compound is shown in Figure 6, where pyridine molecules are in almost parallel planar dispositions. The structure and packing of compounds 3a, 3b, and 4a, 4b can be seen in Figures 7 and 8, respectively.

Figure 6. Structure and packing in compound 5b [8].

Figure 7. Structure and packing of compounds 3a and 3b [9].

The [Agpy2]+ units in compounds 2b, 3a, 3b, 4a, and 4b show weak Ag…O coordination with anions, and π–π stacking between the neighboring pyridine rings, whereas the [Agpy4]+ units in 3a, 3b, and 4b do not show these kinds of interactions.

The lattice parameters of the known AgXO4 complexes with pyridine were studied by Sajó et al. [9]. The single crystal study results are summarized in Table 3.

| Compounds/Pack Group | Label | Ag-Ag (Å) | Ag-N (Å) | α-CH..O-X/F-X (Å) | Reference |
|----------------------|-------|-----------|-----------|--------------------|-----------|
| [Ag(py)2]MnO4·[Agpy4]MnO4, I-4 | 4b | 4.843 | 2.740 | 2.15 | 2.645 | 2.645 | [13] |
| [Ag(py)2]ClO4·[Agpy4]ClO4, I-4 | 4b | 4.843 | 2.16 | 2.30 | 2.753 | 2.781 | [11] |
| [Agpy2MnO4]·0.5Py C2/c | 3a | 3.421 | 2.166 | 2.174 | 2.602 | 2.770 | [9] |
| [Agpy2]ClO4, Pbcn | 2b | 2.999 | 2.126 | 2.133 | 2.672 | 2.581 | 2.700 | 2.566 | [20] |
| [Agpy4]ClO4, I-4 | 2b | 6.748 | 2.322 | 2.712 | 3.237 | [5] |

Spectroscopic Properties of Pyridine Complexes of AgXO4 Compounds (X = Mn, Cl, and Re)

5.1. Infrared and Raman Spectra

Sajó et al. assigned and evaluated, in detail, the IR and Raman band frequencies of the known pyridine complexes of AgXO4 (X = Mn, Cl, Re) compounds [9]. Kovács et al. assigned Ag–N vibrations, arising from the di- and tetracoordinated [AgPyn]+ cations in compound 4a (2019) [6]. The far-IR spectra revealed the symmetric and the antisymmetric ν(AgN) modes of the [Agpy2]+ ion at 246 and 166 cm⁻¹, respectively. Possibly, the deviation along with the ideal (linear) N–Ag–N angle of [Agpy2]+ ion was sufficient to activate the νs (AgN) mode in the IR spectrum [9,12]. Similar spectral characteristics were found in the case of compound 4b [12,13]. The far-IR and Raman spectrum of compound 4b...
The [Agpy$_2$]$^+$ units in compounds 2b, 3a, 3b, 4a, and 4b show weak Ag . . . O coordination with anions, and π–π stacking between the neighboring pyridine rings, whereas the [Agpy$_4$]$^+$ units in 3a, 3b, and 4b do not show these kinds of interactions.

The lattice parameters of the known AgXO$_4$ complexes with pyridine were studied by Sajó et al. [9]. The single crystal study results are summarized in Table 3.

Table 3. The main crystallographic parameters of [Ag(py)$_2$]MnO$_4$, [Ag(py)$_2$]ClO$_4$, [Ag(py)$_2$]ReO$_4$, and [Ag(py)$_2$]$_2$MnO$_4$.

| Compounds/Pace Group          | Label | Ag-Ag (Å) | Ag-N (Å) | α-CH...O-X/F-X (Å) | Reference |
|------------------------------|-------|-----------|----------|-------------------|-----------|
| [Agpy$_2$]ClO$_4$ [Agpy$_4$]ClO$_4$, I-4 | 4b    | 4.843     | 2.740    | 2.645             | [13]      |
|                              |       |           | 2.15     |                   |           |
|                              |       |           |          | 2.645             |           |
| [Agpy$_2$]ClO$_4$ [Agpy$_4$]ClO$_4$, I-4 | 4b    | 4.843     | 2.16     | 2.753             | [11]      |
|                              |       |           | 2.30     |                   |           |
|                              |       |           |          | 2.781             |           |
| [Agpy$_2$]MnO$_4$[Agpy$_4$]MnO$_4$, I-4 | 4a    | 4.822     | 2.601    | 3.121             | [6]       |
| [Agpy$_2$]MnO$_4$.0.5Py C$_2$/c | 3a    | 3.421     | 2.166    | 2.602             | [9]       |
|                              |       |           | 2.174    |                   |           |
|                              |       |           |          | 2.770             |           |
| [Agpy$_2$]ClO$_4$, Pbcn      | 2b    | 2.999     | 2.126    | 2.672             | [20]      |
|                              |       |           | 2.133    |                   |           |
|                              |       |           |          | 2.581             |           |
|                              |       |           |          | 2.700             |           |
|                              |       |           |          | 2.566             |           |
| [Agpy$_4$]ClO$_4$, I-4       | 2b    | 6.748     | 2.322    | 2.712             | [5]       |
|                              |       |           |          | 3.237             |           |

5. Spectroscopic Properties of Pyridine Complexes of AgXO$_4$ Compounds (X = Mn, Cl, and Re)

5.1. Infrared and Raman Spectra

Sajó et al. assigned and evaluated, in detail, the IR and Raman band frequencies of the known pyridine complexes of AgXO$_4$ (X = Mn, Cl, Re) compounds [9]. Kovács et al. assigned Ag–N vibrations, arising from the di- and tetracoordinated [AgPy$_n$]$^+$ cations in compound 4a (2019) [6]. The far-IR spectra revealed the symmetric and the antisymmetric $\nu$ (AgN) modes of the [Agpy$_2$]$^+$ ion at 246 and 166 cm$^{-1}$, respectively. Possibly, the deviation along with the ideal (linear) N–Ag–N angle of [Agpy$_2$]$^+$ ion was sufficient to activate the $\nu_s$ (AgN) mode in the IR spectrum [9,12]. Similar spectral characteristics were found in the case of compound 4b [12,13]. The far-IR and Raman spectrum of compound 4b showed three Ag-N modes, which correspond to the asymmetric and symmetric Ag-N modes of [AgPy$_2$]+ and $\nu$ (AgN) of [AgPy$_4$]$^+$ [12,13]. The coordinated perchlorate ion (C$_1$ site) and non-coordinated (S$_1$ site) perchlorate ions were distinguished spectroscopically. The symmetric deformations modes of perchlorates $\nu_2$ (E) appeared as a singlet band (459 cm$^{-1}$) in IR spectra and as a doublet in Raman analysis (460 and 417 cm$^{-1}$) in which the higher wave number was correlated to coordinate perchlorate ions (C$_1$ site) and the lower to perchlorates in the S$_1$ site [12]. The asymmetric Cl–O stretching bands $\nu_3$ (F$_2$) resulted in two weak and two very intensive bands in the IR spectra [13].

5.2. UV-Vis Spectra

There are not many studies reporting on the spectral characteristics of pyridine complexes of AgXO$_4$ (X = Cl, Mn, Re) compounds [17]. Holló et al. [13] reported the diffuse reflection UV-Vis of compound 4b and confirmed that [AgPy$_2$]$^+$ and [AgPy$_4$]$^+$ cations are present in the lattice of this compound. However, they assigned a band system containing pyridine n–π* and Ag$^+$-Py electronic charge transfer from metal to ligand (MLCT) [9,21,22]. The bands with band maxima at 218.9 and 295.2 nm are the CT band, and the maximum at 251.5 nm is a pyridine ring (1A$_{1g}$–1B$_{2u}$ (π–π*) transition.
Kovács et al. [6] reported the diffuse reflection UV-Vis spectroscopic data for compound 4b and found the presence of the same band system as mentioned above (pyridine \(n-\pi^*\) and Ag\(^+\)-Py MLCT), and also the permanganate transitions \(t_1-4t_2, 3t_2-2e\). The authors reported three different groups of band maxima, namely (i) 219.9 nm assigned to combined bands of Ag-Py (CT) and MnO\(_4^-\) \((t_1^1A_1^1T_2(t_1-4t_2))\); (ii) 258.4 nm regarding the components of pyridine \((t_1^1A_1^1B_2(n-\pi^*))\) and MnO\(_4^-\) \((t_1^1A_1^1T_2(3t_2-2e))\) transitions; (iii) and 521.9 and 710.1 nm assigned to the components of MnO\(_4^-\), \((t_1^1A_1^1T_2(t_1-2e))\) and \((t_1^1A_1^1T_1(t_1-2e))\), respectively.

6. Organic Oxidation Reactions with Pyridine-Silver Permanganate Complexes

A large number of studies report the use of AgPy\(_2\)MnO\(_4\) as an oxidative medium in organic reactions. However, in almost all publications, Firouzabadi’s procedure \([4]\) was used to synthesize compound 2a. Thus, the reaction products were probably mixtures of compounds 2a, 3a, and 4a. The first approach was made by Firouzabadi et al. \([4,23]\), and later, Lee \([7]\) used compound 2 in various oxidation reactions. The conversion of polycyclic aromatic hydrocarbons (e.g., anthracene, phenanthrene) \([4,23]\) in dichloromethane resulted in diketones with high yield. The oxidation of diphenylacetylene resulted in 95% benzyl, and in the case of phenylacetylene (nonterminal alkyne), coupling reactions took place with the formation of 1,4-diphenyl-1,3-butadiyne. The conversion of benzocyclobutadiene resulted in 2,3-dibenzylnaphthalene accompanied by carbon–carbon bond cleavage.

Compound 2a (or its mixtures with 3a and 4a) converted primary and secondary alcohols into aldehydes and ketones, respectively, e.g., piperonol into piperonal (81%) and benzyl alcohol into benzaldehyde (100%). Coupling reactions were performed with 4-chloroaniline and 4-nitroaniline \([4,23]\). Besedin et al. (2000) \([24]\) studied nucleophilic substitution of 6,8-dimethylpyrimido[4,5-c]pyridazine-5,7(6H,8H)-dione by reacting it with \(\alpha,\omega\)-diamines, as a result of which, polycyclic heterocycles formed. Gulevskaya et al. \([25]\) reported the oxidative substitution of the pyridazine ring at C-H sites with a secondary amine in the presence of compound 2a (or its mixture with 3a and 4a). The complete reaction was performed at 20 °C for 168 h and the final product was 6,8-dimethyl-3-ethylpyrrolo[1,2,2,3]pyridazino[6,5-d]pyrimidine7,9(6H,8H)-dione with a yield of 42%.

Compound 2a (or its mixture with 3a and 4a) was used by Kesenheimer and Growth (2006) \([26]\) in the synthesis of a natural antibiotic (-)-8-O-methyltetramongycin, in a multi-step process. The oxidation of tetrahydrobenz[a]anthracene into tetrahydrobenz[a]anthra quinone in this reaction had a yield of 65%.

Banerji et al. (2012) \([27]\) reported the oxidation of sulfides into sulfoxides in aqueous acetic acid solutions and achieved a yield of 80% over the conversion of dimethyl sulfide into dimethyl sulfoxide.

Kovács et al. \([6]\) studied the oxidation abilities of 2a, 3a, and 4a in the conversion of benzyl alcohol to benzaldehyde and benzoic acid in various solvents. A higher yield of benzaldehyde was achieved in chloroform as a solvent medium.

7. Conclusions

We comprehensively reviewed the synthesis, structure, and properties of four series of pyridine complexes of AgXO\(_4\) with 2, 2.4, 2.5, and 4 pyridines \((X = \text{Cl, Mn})\) and 2 or 4 pyridines \((X = \text{Re})\) per AgXO\(_4\) unit. The controversial pieces of information about the existence and composition of pyridine complexes of silver permanganate, used widely as mild and selective oxidants in organic chemistry, was evaluated and clarified in detail. We discussed the available structural and spectroscopic (IR, Raman, and UV) data and thermal behavior, including the existence and consequence of quasi-intramolecular reactions between the reducing ligand and anions containing oxygen. The present review clearly shows that two members of the pyridine complexes of AgXO\(_4\) \((X = \text{Cl, Mn, and Re, Py}/\text{Ag} = 2, 2.4, 2.5, \text{and} 4)\) compounds have not been prepared and characterized yet \((X = \text{Re and Py}/\text{Ag} = 2.4 \text{and} 2.5)\). For the members of AgXO\(_4\)-pyridine complexes with unknown crystal structures and thermal properties, structure elucidation and thermal studies are planned.
Clariﬁcation of the phase relations and the chemical nature of AgMnO₄ pyridine complexes provide new and prosperous perspectives for studying AgMnO₄-pyridine complexes in organic reactions, in which only a mixture of these compounds was used earlier.

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