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Review

Pyridinesilver Tetraoxometallate Complexes: Overview of the Synthesis, Structure, and Properties of Pyridine Complexed $AgXO_4$ (X = Cl, Mn, Re) Compounds

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Abstract: We reviewed the synthesis, structure, and properties of pyridine complexes of $AgXO_4$ (X = Cl, Mn, and Re) compounds with various compositions ($[AgPy_2]$ XO_4, $[AgPy_2XO_4]\cdot 0.5Py$, $[AgPy_4]$ XO_4, and 4 $[AgPy_2XO_4]$ $[AgPy_4]$ XO_4). 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

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1. Introduction

Silver permanganate, perchlorate, and perrhenate ($AgXO_4$, 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 $AgXO_4$ (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 XO_4^- 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.

Table 1. Labels and Ag: Py ratios in pyridine complexes of $AgXO_4$ (X = Mn (a), Cl (b), and Re (c)) complexes.

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
$[AgPy_2MnO_4]\cdot 0.5Py$	**3a**	2.5
$[AgPy_2ClO_4]\cdot 0.5Py$	**3b**	2.5
$AgPy_2ReO_4\cdot 0.5Py$	**3c**	2.5
$4[AgPy_2MnO_4]\cdot[AgPy_4]MnO_4$	**4a**	2.4
$4[AgPy_2ClO_4]\cdot[AgPy_4]ClO_4$	**4b**	2.4
$4AgPy_2ReO_4\cdot AgPy_4ReO_4$	**4c**	2.4
$[AgPy_4]MnO_4$	**5a**	4
$[AgPy_4]ClO_4$	**5b**	4
$[AgPy_4]ReO_4$	**5c**	4

2. Synthesis and Composition of $AgPy_nXO_4$ (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 $AgPy_{2.5}MnO_4$ 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 $4[AgPy_2MnO_4]$ $[AgPy_4]MnO_4$ (compound **4a**) (it is equal to the formula $AgPy_{2.4}MnO_4$) 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 $4[AgPy_2MnO_4]\cdot[AgPy_4]MnO_4$ (**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:MnO_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 down a concentrated solution of $AgMnO_4$ (**1a**) in pyridine to −18 °C overnight. The authors [8] reported a recrystallization route to synthesize pure $[AgPy_2MnO_4]\cdot 0.5Py$ (**3a**). They recrystallized the mixture of $AgPy_2MnO_4$ and $4[AgPy_2MnO_4][AgPy_4]$ MnO_4 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.

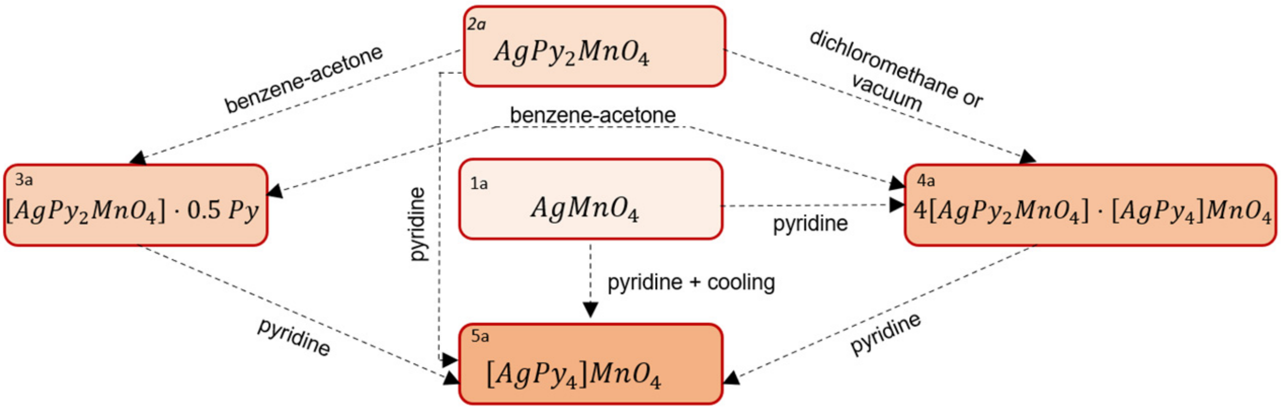

Figure 1. Interconversion scheme of permanganate complexes [9].

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 $[AgPy_2]ClO_4$ (**2b**) $AgPy_{2.25}ClO_4$ (later it was proved to be compound **4b** with the formula $AgPy_{2.4}ClO_4$), $[AgPy_4]ClO_4$ (**5b**), and $AgClO_4\cdot H_2O$ (**1b**.H_2O) 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 $AgClO_4$ in pyridine. Line d–e specifies the solubility of $AgClO_4$, whereas line b–c represents the composition of the solid phases. Macy found that $[AgPy_2]ClO_4$ (**2b**) was the most stable solid phase with a melting point between 144 and 147 °C, whereas $AgPy_{2.25}ClO_4$ and $[AgPy_4]ClO_4$ (**5b**) are unstable solid phases, which melt at 68 °C and 95.6 °C, respectively.

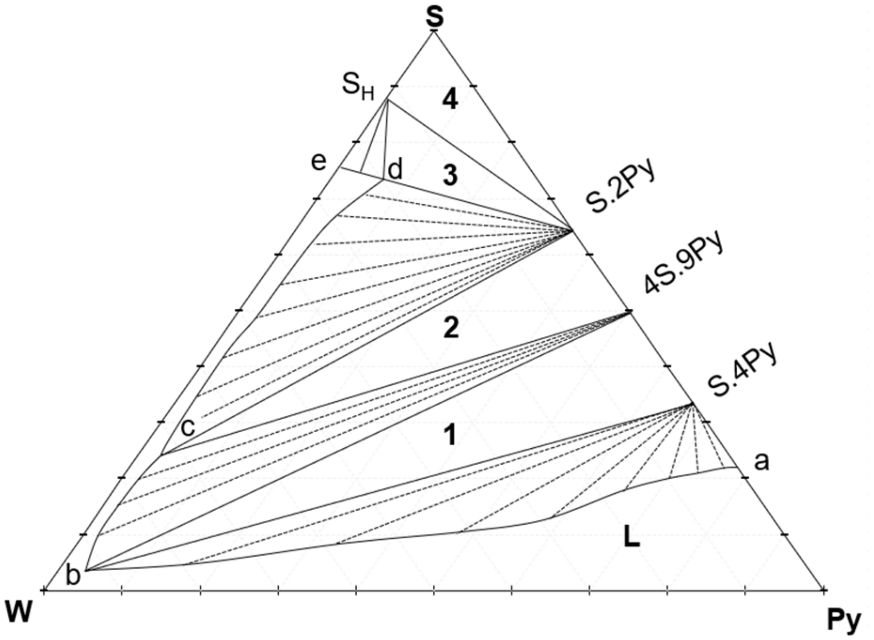

Figure 2. Ternary phase diagram of the $AgClO_4$–pyridine–H_2O system [3] (W—water, Py—pyridine, S—salt ($AgClO_4$)). Areas of invariant equilibria are marked with letters a–e.

The complex $[AgPy_2]ClO_4$ (2**b**) was prepared by Kauffman and Pinnell (1960) [10] in the reaction of $AgNO_3$ with $NaClO_4$ in an aqueous pyridine solution in an Ag^+:ClO_4^-:Py = 1:1.3:6 (molar) and pyridine/H_2O = 5/9 (*v/v*) ratio. Cooling the solution at 10 °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 Ag_2SO_4, pyridine, and $NaClO_4$ (20% aq. pyridine and 0.2 M of aq. $NaClO_4$) at lower temperatures (5–8 °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.

Nilson and Oskarsson (1982) [5] reported the preparation of pure $[AgPy_4]$ ClO_4 by dissolving silver (I) perchlorate in pyridine solution at −18 °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 $[AgPy_2ClO_4]\cdot 0.5Py$ (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.

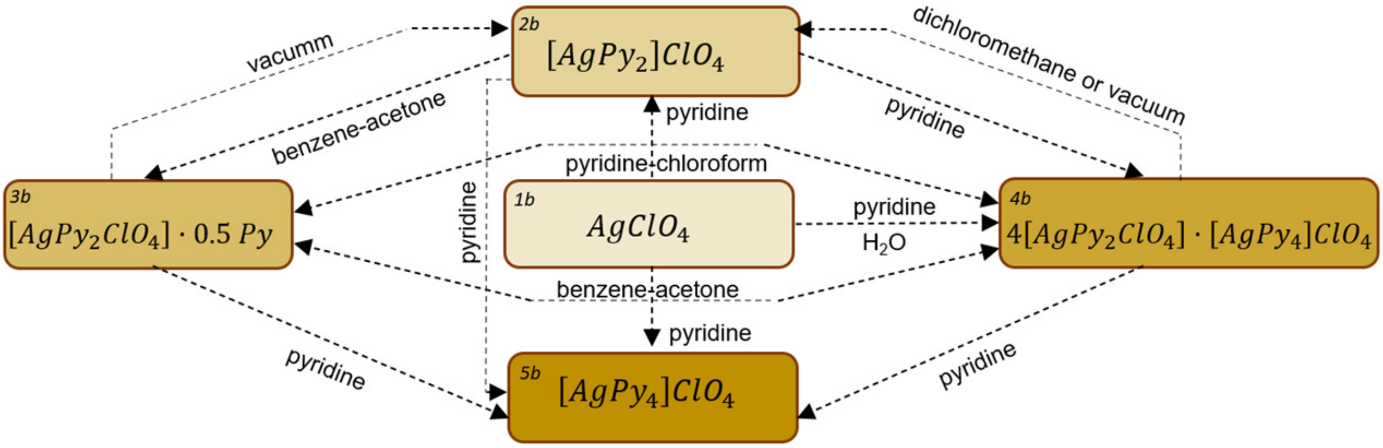

Figure 3. Interconversion scheme of perchlorate complexes [9].

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.

Recently, Sajó et al. (2018) [8] 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_2SO_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 $AgPy_nReO_4$ 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_2O (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_{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 pyridine ring and an oxygen of permanganate ion. Rearrangement via transition states TS_1 and TS_2 due to thermal activation results in a 2-hydroxypyridine derivative (TS_2). They assumed tautomerization and a Dewar benzene-type ring (TS_4) and the transformation of Dewar-C_5H_5NO to HNCO and "C_4H_4". The decomposition of these intermediates result in CO, CO_2, NO, and H_2O as reaction products [16,17].

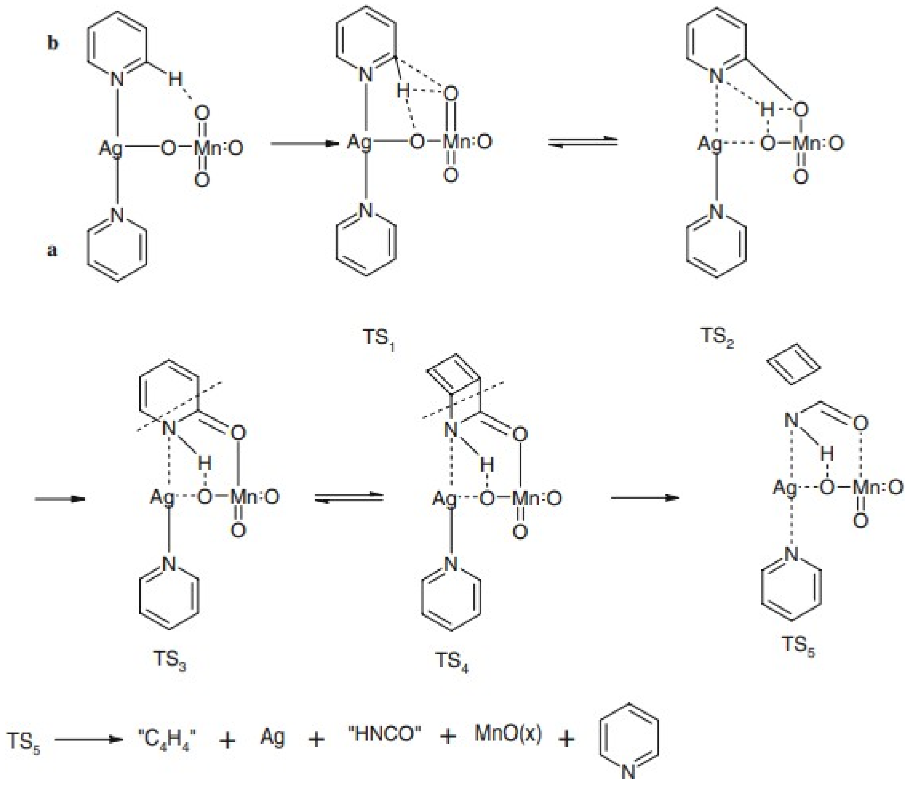

Figure 4. Proposed mechanism for the thermal decomposition of $AgPy_2MnO_4$ [16]. a -non-hydrogen bound pyridine ring: b-hydrogen bound pyridine ring.

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_3O_4, and Mn_2O_3. Based on the decomposition temperatures of $MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO$ [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_2O, 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 $AgClO_4$ [19]. The unreacted $AgClO_4$ decomposed into AgCl and O_2, which suggests the presence of a complex decomposition process with simultaneous pyridine ligand loss with $AgClO_4$ formation, and a redox reaction between pyridine and $AgClO_4$ in the solid phase.

The thermal decomposition of **4b** was also investigated under an oxidizing atmosphere [13]. The presence of O_2 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.

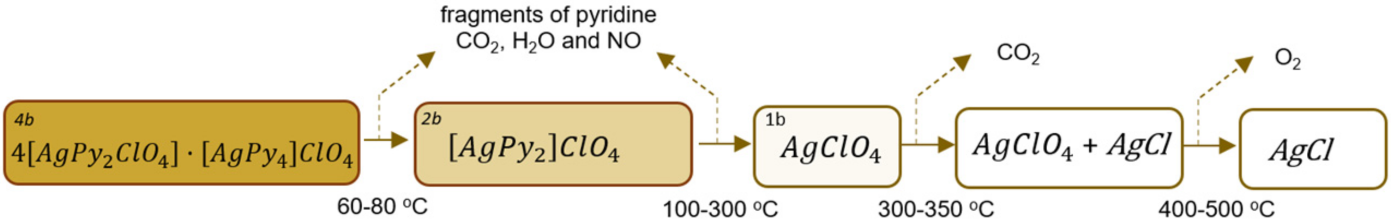

Figure 5. Proposed mechanism for the thermal decomposition of **4b** in argon [13].

3.3. Pyridine Complexes of $AgReO_4$

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 $AgXO_4$ Compounds (X = Mn, Cl, and Re)

The crystallographic parameters of pyridine complexes of $AgXO_4$ are summarized in Table 2.

Holló et al. [13] and Dyason et al. [11] crystallized compound **4b** in a tetragonal system containing one $[AgPy_2ClO_4]$ and one-quarter of $[AgPy_4]ClO_4$ 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** ($[AgPy_2MnO_4]\cdot 0.5Py$) 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 $[4AgPy_2MnO_4].[AgPy_4]MnO_4$ (Ag··· Ag = 4.822 Å) [11,13].

The compound $[AgPy_2]ClO_4$ (**2b**) crystallizes in an orthorhombic crystal system [20]. The argentophilic interaction in this compound (Ag··· Ag = 2.9997) provides a closer contact between $[AgPy_2]^+$ 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-XO_4 (X = Mn, Cl, and Re) compounds.

Empirical Formula	Label	Space Group	Unit Cell Dimensions, (Å or °)	Z	D ($g{\cdot}cm^{-3}$)	T (K)	V $(Å)^3$	Reference
$Agpy_2MnO_4$	**2a**	Cc	a = 22.875 b = 12.266 c = 20.225 β = 62.361	16	1.970	298	5191.2	[9]
$[Agpy_2]ClO_4$	**2b**	Pnn2/Pnnm	a = 20.138 b = 12.694 c = 10.125	8	1.876	298	2588.3	[9]
$[Agpy_2]ClO_4$	**2b**	Pbcn	a = 19.958 (2) b = 10.0034 (13) c = 12.3082 (16)	8	1.976	150	2457.3 (5)	[20]
$[Agpy_2]ReO_4$	**2c**	-	a = 7.140 b = 8.616 c = 10.827 α = 102.20 β = 96.25 γ = 105.58	2	2.655	298	645.85	[9]
$4[Agpy_2MnO_4]\cdot[Agpy_4]MnO_4$	**4a**	I_4^-	a = 22.01 c = 7.6075	10 (1)	1.877	298	3685.4	[9]
$4[Agpy_2MnO_4]\cdot[Agpy_4]MnO_4$	**4a**	I_4^-	a = 21.982 (3) b = 21.982 (3) c = 7.5974 (15)	2	1.885	293	3671.13	[6]
$4[Agpy_2ClO_4]\cdot[Agpy_4]ClO_4$	**4b**	I_4^-	a = 21.95 (1) c = 7.6843 (3)	-	1.78	295	3702 (2)	[11]
$4[Agpy_2ClO_4]\cdot[Agpy_4]ClO_4$	**4b**	I_4^-	-	-	-	-	-	[13]
$[Agpy_2MnO_4]\cdot0.5Py$	**3a**	C_2/c	a = 19.410 (1) b = 7.788 (1) c = 21.177 (1) α = 90.00 β = 104.20 (1) γ = 90.00	4	1.817	293	3103.4 (5)	[9]
$[Ag(py)_4]MnO_4$	**5a**	P_21	a = 15.24 b = 13.89 c = 5.31 β = 84.13°	2	-	298	1117	[9]
$[Ag(py)_4]ClO_4$	**5b**	I_4^-, I_4/m	a = 12.874 (1) c = 6.748 (4)	2	1.55	260	1118.4	[5]

Nilsson and Oskarsson (1982) [4] described the crystal system of $[AgPy_4]ClO_4$ (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.

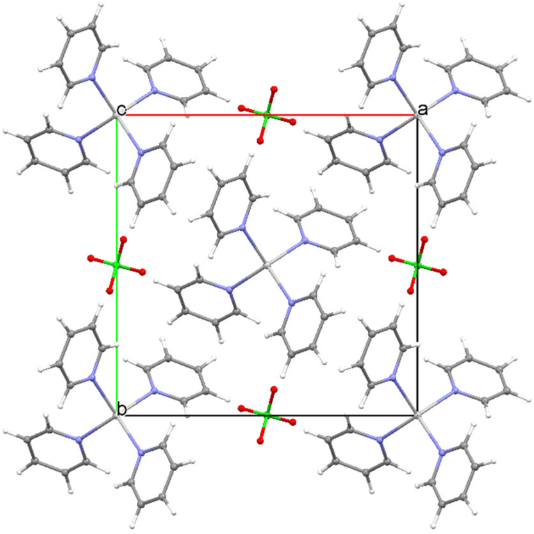

Figure 6. Structure and packing in compound **5b** [9].

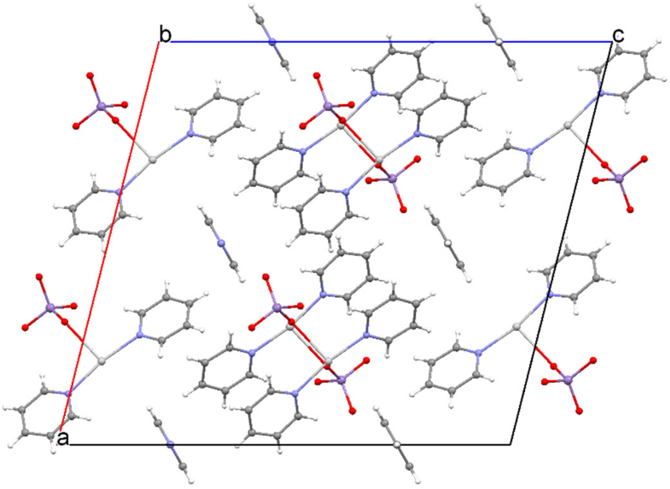

Figure 7. Structure and packing of compounds **3a** and **3b** [9].

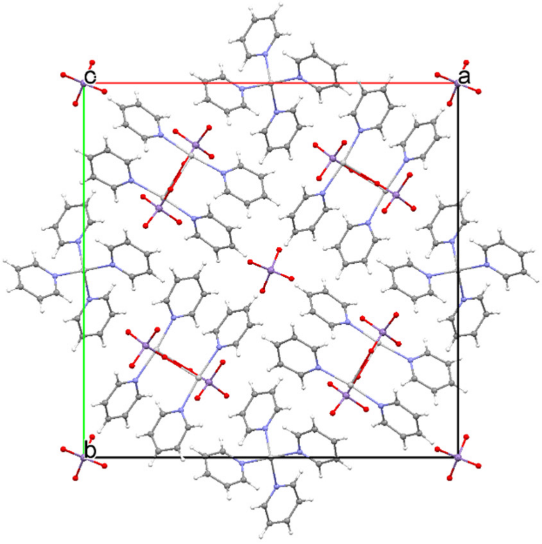

Figure 8. Structure and packing of compounds **4a** and **4b** [9].

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 $[Ag(py)_{2.4}]MnO_4$.

Compounds/Pace Group.	**Label**	**Ag-Ag (Å)**	**Ag-N (Å)**	**α-CH. . . O-X/F-X (Å)**	**Reference**
$4[Agpy_2]ClO_4{\cdot}[Agpy_4]ClO_4$, I-4	**4b**	4.843	2.740 2.15	2.645 2.645	[13]
$4[Agpy_2]ClO_4{\cdot}[Agpy_4]ClO_4$, I-4	**4b**	4.843	2.16 2.30	2.753 2.781	[11]
$4[Agpy_2]MnO_4{\cdot}[Agpy_4]$ MnO_4, I-4	**4a**	4.822	2.601	3.121	[6]
$[Agpy_2MnO_4]{\cdot}0.5Py$ C_2/c	**3a**	3.421	2.166 2.174	2.602 2.770	[9]
$[Agpy_2]ClO_4$, Pbcn	**2b**	2.999	2.126 2.133	2.672 2.581 2.700 2.566	[20]
$[Agpy_4]ClO_4$, I-4	**2b**	6.748	2.322	2.712 3.237	[5]

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 ν (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 ν_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 ν (AgN) of $[AgPy_4]^+$ [12,13]. The coordinated perchlorate ion (C_1 site) and non-coordinated (S_4 site) perchlorate ions were distinguished spectroscopically. The symmetric deformations modes of perchlorates ν_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_4 site [12]. The asymmetric Cl–O stretching bands ν_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–π^* 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^- (($^1A_1$-$^1T_2(t_1$-$4t_2)$); (ii) 258.4 nm regarding the components of pyridine (($^1A_1$-$^1B_2$(n–π^*)) and MnO_4^- ($^1A_1$-$^1T_2(3t_2$-2e)) transitions; (iii) and 521.9 and 710.1 nm assigned to the components of MnO_4^-, ($^1A_1$-$^1T_2(t_1$-2e)) and (($^1A_1$-$^1T_1(t_1$-2e)), respectively.

6. Organic Oxidation Reactions with Pyridine-Silver Permanganate Complexes

A large number of studies report the use of $AgPy_2MnO_4$ 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-dibenzoylnaphthalene 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 α,ω-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-methyltetrangomycin, 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 = Cl, Mn) and 2 or 4 pyridines (X = 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 = Cl, Mn, and Re, Py/Ag = 2, 2.4, 2.5, and 4) compounds have not been prepared and characterized yet (X = Re and Py/Ag = 2.4 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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