

# The chemical identity of '[Ag(py)<sub>2</sub>]MnO<sub>4</sub>' organic solvent soluble oxidizing agent and new synthetic routes for the preparation of [Ag(py)<sub>n</sub>]XO<sub>4</sub> (X= Mn, Cl, Re, n=2-4) complexes

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## Abstract

A widely used oxidizing agent in organic chemistry with an assumed structure of '[Ag(py)<sub>2</sub>]MnO<sub>4</sub>' and its perchlorate and perrhenate analogues are studied. Their synthesis in pure form is challenging. In order to clarify the chemical nature of known compounds and find routes to new derivatives, a systematic study is presented for the synthesis of [Ag(py)<sub>n</sub>]XO<sub>4</sub> (X= Mn, Cl, Re, n=2-4) complexes. Ten complexes including four new derivatives, namely [Ag(py)<sub>2</sub>]MnO<sub>4</sub>, [Ag(py)<sub>4</sub>]MnO<sub>4</sub>·4[Ag(py)<sub>2</sub>]MnO<sub>4</sub>, [Ag(py)<sub>2</sub>]ClO<sub>4</sub>·0.5py, and [Ag(py)<sub>2</sub>]ReO<sub>4</sub> are synthesized and characterized. The chemical identity of '[Ag(py)<sub>2</sub>]MnO<sub>4</sub>' is also clarified. A novel route to prepare [Ag(py)<sub>2</sub>]MnO<sub>4</sub> is developed. The reaction of AgXO<sub>4</sub> salts with neat pyridine followed by various crystallization techniques is used to prepare [Ag(py)<sub>2</sub>]XO<sub>4</sub>, [Ag(py)<sub>4</sub>]XO<sub>4</sub>, [Ag(py)<sub>4</sub>]XO<sub>4</sub>·4[Ag(py)<sub>2</sub>]XO<sub>4</sub> and [Ag(py)<sub>2</sub>]XO<sub>4</sub>·0.5py (X=Cl, Mn), complexes. The solid phase structure of [Ag(py)<sub>2</sub>]MnO<sub>4</sub>·0.5py is determined (a=19.410 Å, b=7.788 Å, c=21.177 Å, β=104.20°, C2/c (15), Z=4(8)). [Ag(py)<sub>2</sub>]<sup>+</sup> cations in the crystal form dimeric units where silver ions are connected by oxygen atoms of two MnO<sub>4</sub><sup>-</sup> anions. The Ag...Ag distance is indicative of argentophilic interaction. The pyridine ring π...π interactions contribute to the stability of the crystal lattice.

Keywords: metal organic permanganates, perchlorates, perrhenates, synthesis, structure, x-ray diffraction

## Introduction

Silver permanganate (AgMnO<sub>4</sub>, **1a**), silver perchlorate (AgClO<sub>4</sub>, **1b**), and silver perrhenate (AgReO<sub>4</sub>, **1c**) readily dissolve in pyridine (py) with the formation of various pyridine complexes. The available information about these complexes in the literature, however, is quite controversial. Considering the silver ion coordination number of two or four, lattice pyridine, and mixed silver coordination number, six series of pyridine complexes can be derived, namely [Ag(py)<sub>2</sub>]XO<sub>4</sub> (**2**), [Ag(py)<sub>2</sub>]XO<sub>4</sub>·xpy (**3**), [Ag(py)<sub>2</sub>]XO<sub>4</sub>·y[Ag(py)<sub>4</sub>]XO<sub>4</sub> (**4**), [Ag(py)<sub>4</sub>]XO<sub>4</sub> (**5**), [Ag(py)<sub>4</sub>]XO<sub>4</sub>·xpy (**6**), and [Ag(py)<sub>2</sub>]XO<sub>4</sub>·y[Ag(py)<sub>4</sub>]XO<sub>4</sub>·xpy (**7**), where X= Mn, Cl, or Re. It is a critical question whether x and y are concrete numbers for these complexes or varied. Out of the possible 18 complexes of these series, only six are known to date. The most frequently synthesized compound is the bis(pyridine)silver(I) permanganate ([Ag(py)<sub>2</sub>]MnO<sub>4</sub>, **2a**). Due to its solubility in polar organic solvents, it is widely used as a mild oxidizing agent in organic synthesis [1-11]. The chemical identity of the compound used in these reactions, however, is doubtful [12,13]. Bis(pyridine)silver(I) perchlorate (**2b**) is known since 1960 [14]. Interestingly, an intermediate complex with the formula of [Ag(py)<sub>4</sub>]ClO<sub>4</sub>·4[Ag(py)<sub>2</sub>]ClO<sub>4</sub> (**4b**) ([Ag(py)<sub>2.4</sub>]ClO<sub>4</sub>) could be isolated during its synthesis [15]. The four py coordinated tetrakis(pyridine)silver(I) perchlorate (**5b**) and perrhenate (**5c**) have been synthesized and characterized earlier [16,17]. Although a complex with the formula of [Ag(py)<sub>2.5</sub>]MnO<sub>4</sub> was described by Klobb [18], its identity with [Ag(py)<sub>2</sub>]MnO<sub>4</sub>·0.5py (**3a**) has not been confirmed yet. No member of

the series of **6** and **7** have been synthesized to date. The controversial and missing literature data of  $[\text{Ag}(\text{py})_n]\text{XO}_4 \cdot x\text{py}$  complexes prompted us to perform a systematic study on the effect of anions and synthesis conditions on the formation of these complexes in the  $\text{AgXO}_4\text{-py-water}$ ,  $\text{AgXO}_4\text{-py-benzene}$ ,  $\text{AgNO}_3\text{-MXO}_4\text{-py-H}_2\text{O}$ , and  $\text{Ag}_2\text{SO}_4\text{-MXO}_4\text{-py-H}_2\text{O}$  systems ( $\text{X}=\text{Cl, Mn, Re}$ ;  $\text{M}=\text{Na, K}$ ;  $n=2-4$ ). In this paper, we present the synthesis of 10 pure silver(I)-py complexes and their identification based on powder x-ray diffraction (PXRD), elemental analysis, and in a selected case on single crystal x-ray diffraction (SXRD).

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## Results and Discussion

### General considerations on the synthesis of permanganate complexes $[\text{Ag}(\text{py})_n]\text{MnO}_4$ ( $n = 2-4$ ) (**2a-5a**)

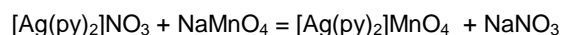
Firouzabadi et al. [10] synthesized a purple material by reacting  $\text{AgNO}_3$  with  $\text{KMnO}_4$  in dilute aq. pyridine and declared that the elemental analysis was in agreement with the formula of the  $[\text{Ag}(\text{py})_2]\text{MnO}_4$  (**2a**) complex. Unfortunately, numerical data of elemental analysis were not provided. Repeating the published method, including the purification step by recrystallization from acetone-benzene, however, resulted in the isolation of  $[\text{Ag}(\text{py})_2]\text{MnO}_4 \cdot 0.5\text{py}$  (**3a**) ( $[\text{Ag}(\text{py})_{2.5}]\text{MnO}_4$ ) [12,13]. The PXRD investigation of the raw product (before recrystallization) (Suppl. Fig.S1) unambiguously indicated that the precipitate contained the compounds described by Klobb with the formulas  $[\text{Ag}(\text{py})_2]\text{MnO}_4$  and  $[\text{Ag}(\text{py})_{2.5}]\text{MnO}_4$  [18]. These two compounds were synthesized by reacting silver sulfate and potassium permanganate. The compound  $[\text{Ag}(\text{py})_{2.5}]\text{MnO}_4$  prepared by the Klobb [18] method, however, was found to be isomorphic with the known complex  $[\text{Ag}(\text{py})_4]\text{ClO}_4 \cdot 4[\text{Ag}(\text{py})_2]\text{ClO}_4$  ( $[\text{Ag}(\text{py})_{2.4}]\text{ClO}_4$ ) (**4b**) [15], indicating the same structure and composition for the cationic part of these two materials. Consequently, the Klobb's formula of  $[\text{Ag}(\text{py})_{2.5}]\text{MnO}_4$  seems to be incorrect. In order to clarify product composition, all previously described experiments were repeated and our results are summarized in Table 1. Product compositions were confirmed by PXRD. As data in Table 1 shows, all products based on previous methods provided mixtures of complexes. Besides Ag:py ratio, other factors like the cooling played key role in the composition of the crystalline precipitates formed. The cooling rate and time were not provided in the original articles [10,18]. In order to isolate pure **2a**, **3a**, and **4a** compounds, novel methods were developed by us.

**Table 1.** The effect of reaction conditions on the composition of the reaction products ( $\text{AgX}:\text{MMnO}_4=1:1$ ;  $\text{M}=\text{K, Na}$ ;  $\text{X}=\text{NO}_3$  or  $1/2\text{SO}_4$ ).

X	M	Ag:Py molar ratio	Pyridine conc., wt.%	Temp. gradient, start °C/end °C	Product
SO <sub>4</sub>	K	1:50	6	25/0	<b>2a:4a=</b> 1:50
SO <sub>4</sub>	K	1:50	6	10/0	<b>2a:4a=</b> 1:2
SO <sub>4</sub>	K	1:100	10.5	25/8	<b>2a:4a=</b> 1:50
SO <sub>4</sub>	K	1:100	10.5	10/8	<b>2a:4a=</b> 1:100
NO <sub>3</sub>	K	1:3	1.25	10/0	<b>2a:3a:4a=</b> 10:1:10
NO <sub>3</sub>	Na	1:6	36.5	10/10	<b>2a:4a =</b> 1:6

### Synthesis of $[\text{Ag}(\text{py})_2]\text{MnO}_4$ (**2a**)

To synthesize **2a**, we prepared bis(pyridine)silver(I) nitrate first by reacting  $\text{AgNO}_3$  with aq. pyridine [19].  $[\text{Ag}(\text{py})_2]\text{NO}_3$  was reacted in the consecutive step with concentrated sodium permanganate solution and the product was crystallized using 25/0, 10/0, and 0/0 °C temperature gradients. Pure **2a** was isolated with 50-58% yields in all cases.



### Synthesis of $[\text{Ag}(\text{py})_2]\text{MnO}_4 \cdot 0.5\text{py}$ (**3a**)

Recrystallizing a mixture of **2a+4a**, prepared by the Firouzabadi's method [10] from 1:1 acetone-benzene (v/v), led to the formation of platelet-like crystal bunches of pure **3a** and some amorphous brown decomposition

product. Since the solvent did not contain pyridine, the decomposition of  $[\text{Ag}(\text{py})_4]^+$  cations seemed to be the source of pyridine to convert **2a** to **3a** (**3a** is richer in pyridine than the compound **2a**). It is in line with this that the recrystallization of pure **4a** from acetone-benzene (1:1, v/v) led to the formation of a mixture of **3a** and **4a** in 1:10 ratio. Interestingly, the recrystallization of pure **2a** gave a 4:1 mixture of **3a** and **2a** under analogous conditions. This suggests that the main source of free pyridine to form **3a** is the py ligand dissociation from **2a**. It may be also concluded that **4a** is more stable in 1:1 acetone-benzene solution than **2a**. Recrystallization of the **2a:4a** (1:1) mixture from pyridine-chloroform (1:5, v/v) solvent mixture resulted in the formation of a completely amorphous decomposition product. It might be explained by the formation and fast decomposition of unstable **5a** ( $[\text{Ag}(\text{py})_4]\text{MnO}_4$ ) due to high pyridine concentration ensured by the solvent mixture. The compound **3a** was grown as a bunch of platelet-like purple monoclinic single crystals.

### Synthesis of $[\text{Ag}(\text{py})_4]\text{MnO}_4 \cdot 4[\text{Ag}(\text{py})_2]\text{MnO}_4$ (**4a**) and $[\text{Ag}(\text{py})_4]\text{MnO}_4$ (**5a**)

**1a** is well soluble in pyridine.<sup>1</sup> The solution contains tetrakis(pyridine)silver(I) and bis(pyridine)silver(I) cations, and their ratio depends on the  $\text{AgMnO}_4$  concentration. In principle, any of the permanganate compounds containing these cations (**2a**, **3a**, **4a** or **5a**) could be precipitated/crystallized from this solution due to equilibria between the pyridine solvent and complex cationic species influenced by temperature and solvent composition. Accordingly, the slow crystallization at room temperature led to pure **4a** with the appearance of **5a** as an intermediate product. Cooling the saturated solution to  $-18\text{ }^\circ\text{C}$ , however, led to **5a**. Since pyridine is a polar and aromatic solvent, it is miscible with water and benzene. Adding these co-solvents to pyridine has great influence on the composition of the crystallized compounds. Addition of water to the pyridine solution of  $\text{AgMnO}_4$  in 1:10 ratio (v/v) ( $\text{Ag:py}$  molar ratio=1:50) led to pure **4a**. Trituration of solid  $\text{AgMnO}_4$  with 1:1 pyridine:water mixture gave a **4a:5a** mixture. Upon adding benzene as co-solvent to the pyridine solution of  $\text{AgMnO}_4$  in 1:1 (v/v) ratio, pure **5a** could be isolated when crystals were in contact with the mother liquor. However, **5a** transformed into **4a** during evaporation of the solvent to dryness. Increasing the benzene amount to 1:10 (v/v), first **5a** then **4a**, and finally **2a:4a** mixture (1:10) could be isolated by the solvent evaporating process. The  $[\text{Ag}(\text{py})_4]\text{MnO}_4$  (**5a**) was found to be a relatively unstable solid, which easily decomposed during its isolation and analysis.

### Studies on interconversion of compounds **1a-5a**

Surprisingly, the behaviour of the neat **2a**, **4a**, and their mixtures was not identical during recrystallization from acetone-benzene. The reason for these differences might be attributed to the different  $\text{Ag/py}$  ratio in the solutions of pure compounds and mixtures. This prompted us to study the effect of various polar solvents like dichloromethane, benzene, and pyridine in the recrystallization process of pure **2a** and **4a**, as well as **2a+4a** mixtures (see Table 2).

**Table 2.** Compounds formed during crystallization of **2a** and **4a** from various solvents

Compound	Solvent	Product
<b>2a</b>	pyridine	<b>4a+5a*</b>
<b>2a</b>	$\text{CH}_2\text{Cl}_2$	<b>2a+4a</b> (3:1)
<b>2a</b>	$\text{C}_6\text{H}_6$ -acetone (1:1, v/v)	<b>3a+4a</b> (4:1)
<b>4a</b>	pyridine	<b>4a+5a*</b>
<b>4a</b>	$\text{CH}_2\text{Cl}_2$	<b>2a+4a</b> (1:9)
<b>4a</b>	$\text{C}_6\text{H}_6$ -acetone (1:1, v/v)	<b>3a+4a</b> (1:10)
<b>4a</b>	$\text{C}_6\text{H}_6$ -acetone (1:1, v/v, heating)	<b>3a+2a</b> (6:1)
<b>4a</b>	$\text{C}_6\text{H}_6$ -acetone (1:1, v/v, trituration)	<b>3a+4a</b> (1:4)
<b>4a</b>	benzene, trituration	<b>3a+4a</b> (3:2)
<b>2a:4a</b> (1:1)	$\text{CH}_2\text{Cl}_2$	<b>3a+2a</b> (30:1)
<b>2a:4a</b> (1:1)	$\text{C}_6\text{H}_6$ -acetone (1:1, v/v)	<b>3a</b>
<b>2a:4a</b> (1:1)	pyridine	<b>2a+4a</b> (1:10)

<sup>1</sup> Freshly prepared wet silver(I) permanganate (**1a**) can easily and safely be dissolved in pure pyridine resulting in a deep purple solution. Using dried or older sample of silver permanganate, however, may result in a violent flame phenomena (silver manganese oxides (Körbl's catalyst) [11] formed on the surface of **1a** which catalyze the ignition and combustion of pyridine). Thus, adding of solid  $\text{AgMnO}_4$  to pyridine has to be done with care.

\*The **4a:5a** ratio could not be determined exactly because **5a** partly decomposed during the powder X-ray measurement done at room temperature.

Recrystallization of either pure **2a** or **4a** from dichloromethane resulted in mixtures of **2a:4a** in 3:1 and 1:9 ratio, respectively, what indicates that **2a** and **4a** can transform into each other in this solvent (**2a** in 25%, **4a** in 10% amount). It must be noted that the analogous perchlorate (**2b**) and perrhenate (**2c**) salts can be recrystallized from dichloromethane without any transformation. Recrystallization of **2a** and **4a** mixture (1:1) from dichloromethane, however, gave **2a:3a** = 1:30 mixture showing that **4a** almost completely transformed into **3a**. Using pyridine as the solvent, the crystallization of an 1:1 mixture of **2a:4a** resulted in the transformation of **2a** into **4a** (1:10 mixed product was formed), while in pyridine-chloroform (1:5, v/v) a mixture of amorphous decomposition products was obtained only. Pure **2a** or **4a** crystallization in pyridine resulted in the formation of **5a**, but due to the decomposition of **5a**, **4a** could be isolated as the final product. Recrystallization of pure **2a** from acetone-benzene (1:1, v/v) resulted in a mixture of **3a** and **4a** (**3a:4a** = 4:1). Pure **4a** behaved similarly, but produced only small amounts of **3a** (**3a:4a** = 1:10). Trituration of solid **4a** with this solvent mixture and with pure benzene resulted in increasing the **3a:4a** ratio to 1:4 and 3:2, respectively. Gentle heating (40 °C) caused the most remarkable effect, the **3a:4a** ratio was changed to 6:1. Results of recrystallization experiments performed with pure **2a**, **4a**, and their mixtures in various solvents are summarized in Table 2. The general interconversion scheme for the compounds **1a-5a** can be seen in Figure 1.

Figure 1. The interconversion scheme for compound **1a-5a**

An unexpected result was observed during the vacuum treatment of the **2a+4a** (1:1) mixture. This treatment resulted in the formation of **4a** instead of **2a**. It is surprising, because the pyridine vapour pressure above the higher coordinated tetrakis(pyridine)silver(I) complex **4a** should be higher than in the case of bis(pyridine)silver(I) compound **2a**, as it was observed in the case of **2b** and **4b**. It is worth to note that **2b** can be prepared from **4b** or **5b** by vacuum treatment [14,20]. This uncommon behaviour of compound **2a** both in solid phase and in solution compared to the behaviour of **2b** and **2c** might be attributed to the appearance of a redox reaction between part of pyridine ligands and permanganate ion [12,13] with the destruction of the cation symmetry and pyridine loss. Note that free pyridine is liberated from **2a**, because only one of the pyridine rings is oxidized [12,13]. The low decomposition point of **2a** (65 °C [18]) compared to **2b** and **2c** (144 °C [14] (perchlorate) and 140 °C (perrhenate), respectively) supports this hypothesis, taking into consideration the low oxidation ability of perchlorate and perrhenate ions towards the pyridine ring. The compound **4a** decomposes almost at the same temperature as **4b** (100 and 95.6 °C [14,21], respectively), which indicates that there is no key role for the anion in the decomposition of **4a** and **4b**. The reason of this might be hidden in the different crystal packing of compounds **2a,b** and **4a,b** [15,20].

### General considerations on the synthesis of perchlorate complexes $[Ag(py)_n]ClO_4$ ( $n=2-4$ ) (**2b-5b**)

There are three known pyridine-silver(I) perchlorate complexes, namely the bis(pyridine)silver(I) perchlorate (**2b**) [14,20], the tetrakis(pyridine)silver(I) perchlorate (**5b**) [16] and the mixed complex  $[Ag(py)_4]ClO_4 \cdot 4[Ag(py)_2]ClO_4$  (**4b**) [15]. The compound **3b** has not been synthesized earlier, and the complex  $[Ag(py)_{2.25}]ClO_4$  [21] was proven to be identical with the compound **4b**. In order to synthesize perchlorate complexes, we reacted  $AgNO_3$  and  $Ag_2SO_4$  with pyridine and  $NaClO_4$  following procedures discussed above for permanganate complexes. Products formed during the synthesis are summarized in Table 3.

Table 3. The effect of reaction conditions on the composition of the reaction products ( $AgX: NaClO_4 = 1:1$ ,  $X=NO_3$  or  $1/2SO_4$ )

X	Ag:Py molar ratio	Pyridine conc., wt. %	Temp. gradient start °C/end °C	Product
SO <sub>4</sub>	1:100	10.5	25/0	<b>4b</b>
SO <sub>4</sub>	1:50	6	25/25	<b>2b:4b</b> = 1:6
NO <sub>3</sub>	1:3	1.25	10/10	<b>2b:4b</b> = 1:1
NO <sub>3</sub>	1:6	36.5	25/10	<b>2b:3b:4b</b> = 3:1:15

Almost all reaction products of the perchlorate complex synthesis proved to be mixtures of  $[Ag(py)_2]ClO_4$  (**2b**),  $[Ag_2(py)_2]ClO_4 \cdot 0.5py$  (**3b**), and  $[Ag(py)_4]ClO_4 \cdot 4[Ag(py)_2]ClO_4$  (**4b**). Thus, not surprisingly, Kauffman [14] could prepare pure  $[Ag(py)_2]ClO_4$  (**2b**) only in a three step process by reacting silver nitrate with sodium perchlorate in

aq. pyridine in the first step (Ag:ClO<sub>4</sub>:py = 1:1.3:6, py/water ratio = 5/9 (v/v)), recrystallizing the primary product in the second step, and vacuum treating the secondary product in the third step. Dyason confirmed that the intermediate product formed in the second step (recrystallization of the primary product from pyridine-chloroform 1:5, v/v) was the compound [Ag(py)<sub>4</sub>]ClO<sub>4</sub>·4[Ag(py)<sub>2</sub>]ClO<sub>4</sub> (**4b**) [15]. Chen et al. confirmed the importance of vacuum treatment by synthesizing [Ag(py)<sub>2</sub>]ClO<sub>4</sub> (**2b**) by dissolving AgClO<sub>4</sub> (**1b**) in pyridine and evaporating the mixture to dryness [20]. Colourless crystals of [Ag(py)<sub>4</sub>]ClO<sub>4</sub> were also prepared by dissolving AgClO<sub>4</sub> (**1b**) in pyridine and cooling the saturated solution [16]. We repeated the work of Kauffman and our PXRD studies unambiguously confirmed that the primary product of this reaction was a mixture of two known and one newly isolated compounds, namely [Ag(py)<sub>2</sub>]ClO<sub>4</sub> (**2b**), [Ag(py)<sub>4</sub>]ClO<sub>4</sub>·4[Ag(py)<sub>2</sub>]ClO<sub>4</sub> (**4b**), and [Ag(py)<sub>2</sub>]ClO<sub>4</sub>·0.5py (**3b**). The main product was compound **4b**, while **3b** was only a minor component. The molar ratio of **4b**:**2b** was >2:1.

#### Synthesis of compound [Ag(py)<sub>2</sub>]ClO<sub>4</sub>·0.5py (**3b**)

The complex **3b** could be synthesized by triturating a 1:1 mixture of **2b** and **4b** with acetone:benzene (1:1, v/v) mixture. The separated solid phase was found to be pure **3b** while the solid product isolated from the dissolved part was proved to be a mixture of **2b** and **3b**. This result suggested that the free pyridine source for the formation of **3b** was mainly the **4b** content of the **2b**+**4b** mixture. This is, however, in contrast to the formation of the analogous permanganate **3a**, where the pyridine source to form **3a** was mainly the **2a** content of the **2a**+**4a** mixture. Similarly to permanganates, an interchangeability of phases could be observed for perchlorates depending on the solvent, namely the ratio of **2b** and **4b** could be altered in a substantial way. The formed **3b** is stable in contact with the mother liquor only, and slowly decomposes to **2b** on drying in the air. The compound **3b** was formed only in the case of an acetone-benzene solvent mixture. Recrystallization of the 1:1 mixture of **2b**:**4b** from dichloromethane resulted in the enrichment of **2b** (**2b**:**4b** = 2:1), while pyridine or pyridine:chloroform (1:5) mixture led to the enrichment of **4b** (**2b**:**4b** = 1:4 and 1:9, respectively). Recrystallization results are summarized in Table 4.

**Table 4.** Recrystallization experiments on **2b**+**4b** (1:1) mixture with various organic solvents

Solvent	Product	Remark
Pyridine	<b>2b</b> : <b>4b</b> (1:4)	evaporated to dryness
	( <b>5b</b> ) <b>4b</b> *	mother liquor
Pyridine-CHCl <sub>3</sub> (1:5, v/v)	<b>2b</b> : <b>4b</b> (1:9)	evaporated to dryness
Dichloromethane	<b>2b</b> : <b>4b</b> (2:1)	evaporated to dryness
C <sub>6</sub> H <sub>6</sub> -acetone (1:1, v/v)	<b>3b</b>	solid phase, trituration
	<b>2b</b> : <b>3b</b> (1:10)	evaporation of liquid phase/trituration

\*The wet product contacted with the mother liquor was proved to be **5b** which decomposes during the XRD measurement into **4b** on drying.

Compound **5b** could be isolated from a saturated solution of AgClO<sub>4</sub> (**1b**) in pyridine by cooling it to -18 °C. By allowing the solution to evaporate to dryness at room temperature, however, only pure **2b** was obtained. It is interesting to note that the crystalline phase formed during the evaporation was a 1:2 mixture of **4b** and **5b** until it was in contact with the mother liquor. This indicates that both **4b** and **5b** change to **2b** upon standing in air at room temperature, or in vacuum [20]. Diluting the pyridine solution of **1b** with water or benzene and evaporating these diluted solutions to dryness had a strong impact on the identity of isolated products. A 2- and 10-fold dilution with benzene resulted in the formation of **4b**:**5b** (1:3) mixture and pure **5b**, respectively. Evaporation always resulted in the formation of a mixture of **2b**+**4b**. These results are summarized in Table 5, and the interphase relationships between compounds of the AgClO<sub>4</sub>-py-H<sub>2</sub>O system (compounds **1b**-**5b**) are shown in Figure 2.

**Figure 2.** The interconversion scheme for compound **1b**-**5b**

**Table 5.** Transformation of **1b** (AgClO<sub>4</sub>) in pyridine solutions

Pyridine dilution	Temperature (°C)	Products	Remark
Pure pyridine	25/–18	<b>5b</b>	Evaporation
Pure pyridine	25/25	<b>4b:5b</b> (1:2)	In contact with mother liquor
		<b>2b</b>	Evaporation to dryness
H <sub>2</sub> O	25/25	<b>2b:4b</b> (1:100)	10-fold dilution, evaporation to dryness
Benzene	25/25	<b>4b:5b</b> (1:3)	2-fold dilution
		<b>5b</b>	10-fold dilution
		<b>2b:4b</b> (1:5)	10-fold dilution, evaporation to dryness

**General considerations on [Ag(py)<sub>n</sub>]ReO<sub>4</sub> complexes and the synthesis of [Ag(py)<sub>2</sub>]ReO<sub>4</sub>.**

Only one pyridine complex of silver(I) perrhenate, the tetrakis(pyridine)silver(I) perrhenate, [Ag(py)<sub>4</sub>]ReO<sub>4</sub> (**5c**), was known previously. **5c** was isolated from the pyridine solution of silver(I) nitrate and perrhenium acid or ammonium perrhenate on cooling [17]. We attempted the synthesis of novel perrhenate complexes by adopting methods used to prepare analogous permanganates and perchlorates (**2a-5a** and **2b-5b**). However, only one compound, the previously unknown [Ag(py)<sub>2</sub>]ReO<sub>4</sub> (**2c**) could be isolated in pure form. All of our efforts to prepare **3c** and **4c** compounds led to multiphase reaction products with 2.3-3.5 pyridine/AgReO<sub>4</sub> average pyridine content. These results are summarized in Tables 6 and 7.

The recrystallization of **2c** and multiphase products obtained from various solvents did not result in pure **3c** or **4c**. Application of dichloromethane and acetone-benzene (1:1, v/v) solvents yielded compound **2c**, while in the case of pyridine or pyridine containing mixed solvents (py-CHCl<sub>3</sub> 1:5), a higher pyridine containing product mixture was isolated, which transformed back with pyridine loss into **2c** on standing in air (in the dark) for several days. Compound **5c** is very unstable and loses its pyridine content very easily at room temperature. Therefore, it has to be stored and dried for analysis under pyridine vapour atmosphere.

**Table 6.** Synthesis of pyridine complexes of silver(I) perrhenate from silver salts and NaReO<sub>4</sub>.

Ag-salt	Ag:Py molar ratio	Pyridine conc., wt. %	Temp. gradient, start °C/end °C	Product
Ag <sub>2</sub> SO <sub>4</sub>	1:50	6	25/25	<b>2c</b>
Ag <sub>2</sub> SO <sub>4</sub>	1:100	10.5	25/25	Multiphase
AgNO <sub>3</sub>	1:3	1.25	10/10	<b>2c</b>
AgNO <sub>3</sub>	1:6	36.5	25/10	Multiphase

**Table 7.** Recrystallization experiments on [Ag(py)<sub>2</sub>]ReO<sub>4</sub> (**2c**) with various solvents

Solvent	Product	Remark
Pyridine	Multiphase	Changes to <b>2c</b> on standing
Pyridine-CHCl <sub>3</sub> (1:5, v/v)	Multiphase	Changes to <b>2c</b> on standing
Dichloromethane	<b>2c</b>	Evaporation to dryness
Acetone-benzene (1:1, v/v)	<b>2c</b>	Evaporation to dryness

Comparing synthetic results of perchlorate, permanganate, and perrhenate complexes, it can be concluded that the nature of anion plays a key role in the composition of isolated pyridine-silver(I) complexes. Compounds

belonging to one cationic series with different anions could be prepared only under different experimental conditions. All permanganate and perchlorate complexes (**2a**, **b-5a**, **b**) were isolated in pure form, but in the case of perrhenate, only **2c** and **5c** compounds could be synthesized in pure form. Our efforts to isolate pure **3c** and **4c** were unsuccessful, although a mixture of compounds in which the average pyridine content is higher than the pyridine content of **2c** and lower than pyridine content of **5c** could be synthesized.

### Crystal and molecular structure of compound 3a

Attempts to grow single crystals of pure, isolated compounds with appropriate size and quality were successful in case of compounds **3a** and **2b**, only. The structure of **2b** at 150 K has already been published [20]. There is no phase transition of **2b** in the temperature range of 150 to 298 K proved by the unchanged cell parameters, slightly extended by the increase of the temperature only. The main crystallographic parameters of the silver complexes are summarized in Table 8.

Table 8. Crystallographic parameters of the isolated  $[Ag(py)_n]XO_4$  (X=M, Cl, Re, n=2-4) compounds\*

Compounds	Parameters
<b>2a</b>	PXRD, purple, monoclinic, a=22.875, b=12.666, c=20.225, $\beta=62.361$ , $Cc$ (No. 15), Z=16, V=5191.2 Å <sup>3</sup> , T=298 K, D <sub>x</sub> =1.970
<b>2b</b>	PXRD, colourless, orthorhombic, a=20.138, b=12.694, c=10.125, $Pnn2$ (34) or $Pnmm$ (No.58), Z=8, V=2588.3 Å <sup>3</sup> , D <sub>x</sub> =1.876, T=298 K. SXR D, colourless, orthorhombic, a=20.133, b=10.128, c=12.704, $Pbcn$ (No. 60), T=298 K SXR D [20], colourless, orthorhombic, a=19.958, b=10.0034, c=12.3082, $Pbcn$ (no. 60), Z=8, V=2457.3 Å <sup>3</sup> , D <sub>x</sub> =1.976, T=150 K.
<b>2c</b>	PXRD, colourless, triclinic, a=7.140, b=8.616, c=10.827, $\alpha=102.20$ , $\beta=96.25$ , $\gamma=105.58$ , Z=2, V=645.85 Å <sup>3</sup> , D <sub>x</sub> =2.655, T=298 K
<b>3a</b>	SXR D, purple, monoclinic plates, a=19.410, b=7.788, c=21.177, $\beta=104.20$ , $C2/c$ (15), Z=4(8), V=3103 Å <sup>3</sup> , D <sub>x</sub> =1.817, T=298 K.
<b>3b</b>	PXRD, colourless, monoclinic, a=19.52, b=7.83, c=21.02, $\beta=104.05$ , $C2/c$ (15), Z=4(8), V=3116 Å <sup>3</sup> , D <sub>x</sub> =1.726.
<b>4a</b>	PXRD, purple, tetragonal, a=22.01 Å, c=7.6075 Å, I-4 (No. 82), Z=10(1), V=3685.4 Å <sup>3</sup> , D <sub>x</sub> =1.877, T=298 K.
<b>4b</b>	SXR D [15], colourless, tetragonal, a=21.95, c=7.684, I-4 (No. 82), V=3702.2 Å <sup>3</sup> , D <sub>x</sub> =1.78, T=295 K.
<b>5a</b>	PXRD, purple, monoclinic, a=15.24, b=13.89, c=5.31, $\beta=84.13$ , Z=2, $P2_1$ (No. 4), V=1117 Å <sup>3</sup> , T=298 K.
<b>5b</b>	SXR D [16], colourless, tetragonal, a=12.874, b=6.748, I-4 (82), Z=2, V=1118.4 Å <sup>3</sup> , D <sub>x</sub> =1.55, T=260 K.

\*The compound 5c decomposed during the long-term room temperature PXRD measurement

The purple, platelet shape single crystals of compound **3a** were grown from acetone-benzene (1:1) by slow evaporation of the solvents at room temperature. **3a** crystallizes in the monoclinic crystal system, space group C2/c. A crystal of **3a** with the size of 0.40 x 0.30 x 0.07 mm was measured at room temperature using MoK $\alpha$  radiation. The atomic positions were determined by direct methods, hydrogen atoms were placed into calculated positions [22]. Crystal data and details of the structure determination and refinement are listed in Table 9, while intermolecular interactions of **3a** are presented in Table 10.

There is one  $[Ag(py)_2]MnO_4 \cdot 0.5py$  in the asymmetric unit, Z'=0.5 (Figure 3). The permanganate anion is disordered over two positions in 66 : 34 ratio. The Kitaigorodskii packing coefficient (calculated with the main disordered positions of  $MnO_4^-$ ) is 67.4% [23]. The space available for the guest pyridine is 604.5 Å<sup>3</sup> in the unit cell, which is 19.5% of the total unit cell volume of 3103.4 Å<sup>3</sup>. There is no additional residual solvent accessible void in the crystal lattice

Figure 3 ORTEP presentation of the molecular structure and atomic numbering scheme of compound **3a**. The asymmetric unit contains  $[\text{Ag}(\text{py})_2]\text{MnO}_4$  and the half of the pyridine, arranged by a twofold axis,  $Z'=0.5$ . The displacement ellipsoids are drawn at the 30% probability level.

Two  $[\text{Ag}(\text{py})_2]^+$  cations and two  $\text{MnO}_4^-$  anions form a dimeric complex molecule,  $[\text{Ag}(\text{py})_2]_2(\text{MnO}_4)_2$ , where silver ions are connected by oxygen atoms of two  $\text{MnO}_4^-$  anions (Figure 4). In the central centrosymmetric square of Ag-O-Ag-O, the Ag...Ag distance is 3.4213(9) Å, while the Ag...O distances are 2.548(14) Å and 2.745(9) Å (Figure 4a).

Figure 4. The dimer of  $[\text{Ag}(\text{py})_2]_2(\text{MnO}_4)_2$ . a) The Ag...O distances are indicated. b) The  $\text{C}_\alpha\text{-H}(\text{pyridine ligand})\cdots\text{O}(\text{permanganate})$  interactions which support the complex stability are shown.

$\text{C}_\alpha\text{-H}(\text{pyridine ligand})\cdots\text{O}(\text{permanganate})$  interactions support the complex formation (Table 10, Figure 4b).  $\pi\cdots\pi$  interactions contribute to the stability of the crystal lattice (Figure 5). The distance between the aromatic rings containing N1 and N2 is 3.740(5) Å, while the distance between the aromatic rings containing N2 and N2, respectively, is 3.782(5) Å. The stoichiometric ratio of the dimer  $[\text{Ag}(\text{py})_2]_2(\text{MnO}_4)_2$  and the solvent pyridine is 1 : 1. The neighbouring dimers are connected by the weak C12-H12...O3 intermolecular interaction (Table 10). The packing arrangement in the crystal of **3a** viewing from the b crystallographic axis is shown in Figure 6.

Figure 5. The  $\pi\cdots\pi$  interactions formed between pyridine ligands. The distances of the ring centroids are indicated.

Figure 6. The packing arrangement of complex molecules **3a** (capped sticks) and the solvent pyridine (ball and stick representation) viewed from the b crystallographic axis.

Table 9. Crystal data and details of the structure determination and refinement of **3a**.

Empirical formula	$2(\text{C}_{10}\text{H}_{10}\text{N}_2\text{Ag})\cdot 2(\text{MnO}_4)\cdot (\text{C}_5\text{H}_5\text{N})$
Formula weight	849.12
Temperature	293(2) K
Radiation and wavelength	Mo-K $\alpha$ , $\lambda = 0.710730$ Å
Crystal system	monoclinic
Space group	$C2/c$
Unit cell dimensions	$a = 19.410(1)$ Å
	$b = 7.788(1)$ Å
	$c = 21.177(1)$ Å
	$\beta = 104.20(1)^\circ$
Volume	$3103.4(5)\text{Å}^3$
Z, Z'	4, 0.5
Density (calculated)	$1.817 \text{ Mg/m}^3$
Absorption coefficient, $\mu$	$2.091 \text{ mm}^{-1}$
$F(000)$	1672
Crystal colour and description	purple, plates
Crystal size	0.40 x 0.30 x 0.07 mm
Absorption correction	psi-scan
Max. and min. transmission	0.6931 0.8647
$\theta$ -range for data collection	$2.16 \leq \theta \leq 23.96^\circ$
Index ranges	$-21 \leq h \leq 22; 0 \leq k \leq 8; -24 \leq l \leq 0$



Reflections collected	2569
Completeness to 2 $\theta$	1.000
Independent reflections	2423 [ $R(\text{int}) = 0.0092$ ]
Reflections $> 2\sigma(I)$	1303
Refinement method	full-matrix least-squares on $F^2$
Data / restraints / parameters	2423 / 531 / 238
Goodness-of-fit on $F^2$	0.793
Final $R$ indices [ $> 2\sigma(I)$ ]	$R1 = 0.0451$ , $wR2 = 0.1143$
$R$ indices (all data)	$R1 = 0.1038$ , $wR2 = 0.1317$
Max. and mean shift/esd	0.011; 0.001
Largest diff. peak and hole	0.849; $-0.713 \text{ e.}\text{\AA}^{-3}$

Table 10. Intermolecular interactions in **3a**.

D-H...A	D-H [Å]	H...A [Å]	D...A [Å]	D-H...A [°]	Symmetry operation
C12-H12 ...O3	0.93	2.40	3.040(15)	126	$x, 1-y,$ $1/2+z$
C15-H15 ...O4	0.93	2.77	3.679(15)	166	
C21-H21 ...O3	0.93	2.60	3.503(15)	163	

CCDC-201884 (3a) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Table 11 contains the Ag...Ag, Ag-N and the pyridine  $\alpha$ -CH...O(F)-X (X= central atom of the anion) distances of some pyridinesilver complexes. These distances indicate the strength of interactions between neighboring silver atoms and the possibilities of reaction between the most reactive C-H group of pyridine and the anion. Argentophilic interactions must be considered to be present in all molecular and crystal structures where two or more low-coordinated silver cations with a  $[\text{Kr}]4d^{10}$  electronic configuration appear in pairs or groups with sub van der Waals contacts between the metal atoms (shorter than 3.44) [26]. The weak forces such as p-p stacking established between the ligands can influence the mode and strength of aggregation and thus determine the Ag-Ag distance between the neighboring fragments. The argentophilic interaction in **3a** seems to be weaker ( $\text{Ag}\dots\text{Ag} = 3.421 \text{ \AA}$ ) than in non-solvated bis(pyridine)silver(I) compounds ( $\sim 3 \text{ \AA}$  in the case of complexes with  $\text{BF}_4^-$ ,  $\text{PF}_6^-$  and  $\text{ClO}_4^-$  anions). Compared to these and **3a**, the Ag...Ag distance is much longer in the hydrated nitrate compound (4.703 Å) and in **4b** containing both  $[\text{Ag}(\text{py})_2]^+$  and  $[\text{Ag}(\text{py})_4]^+$  cations with perchlorate anion (4.843 Å). There is no argentophilic interaction between  $[\text{Ag}(\text{py})_4]^+$  cations of **4b** and **5b**.

Table 11. Comparison of Ag...Ag and pyridine ring  $\alpha$ -CH...O(F)-X distances

Compound/space group	Ag-Ag	Ag-N	$\alpha$ -CH.. O-X / F-X	Ref.
[Ag(py) <sub>2</sub> ]MnO <sub>4</sub> ·0.5py ( <b>3a</b> ), C2/c	3.421	2.166	2.602	this work
		2.174	2.770	
[Ag(py) <sub>2</sub> ]ClO <sub>4</sub> ( <b>2b</b> ), Pbcn	2.9997	2.126	2.672, 2.581	[20]
		2.133	2.700, 2.566	
[Ag(py) <sub>2</sub> ]BF <sub>4</sub> , Pbcn	3.0001	2.123	2.784,	[20]

		2.127	2.526 2.579, 2.489	
[Ag(py) <sub>2</sub> ]ClO <sub>4</sub> in <b>4b</b> , I-4	4.843	2.149	2.645, 2.753 2.781	[15]
		2.157		
		2.294		
[Ag(py) <sub>4</sub> ]ClO <sub>4</sub> in <b>5b</b> , I-4	no argento- philic bond	2.322	2.712, 3.237	[16]
[Ag(py) <sub>2</sub> ]NO <sub>3</sub> ·H <sub>2</sub> O, I2/a	4.703	2.180	2.691, 2.883 2.624	[24]
[Ag(py) <sub>2</sub> ]PF <sub>6</sub> , P42/m	2.964	2.128	2.723	[20]
		2.133		
		2.143		

The Ag-N distances in compound **3a** are close to those of other bis(pyridine)silver(I) compounds, indicating only small dependence from the counter anion and presence of solvate molecule. The distance between the most reactive ring CH and permanganate oxygen is very similar in the listed compounds, so differences between the reactivity and stability of these compounds might be attributed to the strong oxidizing nature of permanganate compared to perchlorate or nitrate.

## Conclusions

A series of [Ag(py)<sub>n</sub>]XO<sub>4</sub> compounds have been isolated from AgXO<sub>4</sub>-pyridine-water, AgXO<sub>4</sub>-pyridine-benzene, AgNO<sub>3</sub>-MXO<sub>4</sub>-py-H<sub>2</sub>O, and Ag<sub>2</sub>SO<sub>4</sub>-MXO<sub>4</sub>-py-H<sub>2</sub>O systems (M=Na, K; X=Cl, Mn, Re; n=2-4), and reaction conditions for synthesizing pure compounds have been presented. 10 pyridine-silver(I) complexes belonging to the [Ag(py)<sub>2</sub>]XO<sub>4</sub>, [Ag(py)<sub>2</sub>]XO<sub>4</sub>·0.5py, [Ag(py)<sub>4</sub>]XO<sub>4</sub>·4[Ag(py)<sub>2</sub>]XO<sub>4</sub>, and [Ag(py)<sub>4</sub>]XO<sub>4</sub> series have been synthesized using metathesis reactions and selective precipitation. Interconversion of these complexes during recrystallization experiments have been discussed. Co-crystallization of several complexes is pointed out. It is observed that the formation and isolation of these compounds are strongly influenced by conditions of the synthetic procedure and crystallization parameters, namely starting material, solvent, and crystallization temperature and gradient.

The crystal lattice parameters of three permanganate [Ag(py)<sub>2</sub>]MnO<sub>4</sub>, [Ag(py)<sub>4</sub>]MnO<sub>4</sub>·4[Ag(py)<sub>2</sub>]MnO<sub>4</sub>, and [Ag(py)<sub>4</sub>]MnO<sub>4</sub>, one perrhenate, [Ag(py)<sub>2</sub>]ReO<sub>4</sub>, and two perchlorate, [Ag(py)<sub>2</sub>]ClO<sub>4</sub> and [Ag(py)<sub>2</sub>]ClO<sub>4</sub>·0.5py compounds have been determined using PXRD. The crystal and molecular structure of [Ag(py)<sub>2</sub>]MnO<sub>4</sub>·0.5py based on SXR measurement is analysed.

During the synthetic work it was learned that methods described previously in the literature for synthesizing [Ag(py)<sub>2</sub>]MnO<sub>4</sub> from the AgNO<sub>3</sub>-KMnO<sub>4</sub>-py-H<sub>2</sub>O or Ag<sub>2</sub>SO<sub>4</sub>-KMnO<sub>4</sub>-py-H<sub>2</sub>O systems resulted in mixtures of compounds. Therefore, in the light of the present study we reveal that the compound used in previous synthetic reactions [1-11] as an oxidizing agent was not pure [Ag(py)<sub>2</sub>]MnO<sub>4</sub> as stated, but a mixture of various complexes. The chemical activity and usefulness of pure complexes in oxidizing reactions will be clarified in future research.

## Experimental Section

### Synthetic procedures

*Caution.* Perchlorate, permanganate, and nitrate salts of metal organic complexes are potentially explosive and should be handled with great care. Reagent grade silver(I) nitrate, sodium sulfate, sodium perrhenate, pyridine, sodium perchlorate, sodium permanganate and potassium permanganate were supplied by Deuton-X Ltd., Hungary.

### Preparation of AgXO<sub>4</sub> (X=Mn (**1a**), Cl (**1b**) and Re (**1c**)) salts

#### Silver(I) permanganate (**1a**)

Silver nitrate (1.036 g, 6.10 mmol) was dissolved in ca. 5 ml of water then this solution was added to a 3.3 ml solution of 40% aq. NaMnO<sub>4</sub> (d = 1.391) (30% excess to the stoichiometric amount). The purple precipitate was separated by filtration, washed 3 times with a copious amount of water, and finally dried in a desiccator over CaCl<sub>2</sub>. The yield was 0.87 g, 63.0%. Elem. anal. (ICP, uncorrected): found: Ag-47.70%, Mn-25.81%; calcd. for AgMnO<sub>4</sub>: Ag-47.55%, Mn-25.98%.

#### Silver(I) perchlorate (1b)

Silver nitrate (10 mmol, 1.72 g) was dissolved in 17 ml of water then mixed with 5.8 g (20 mmol, excess) of sodium carbonate decahydrate in 10 ml H<sub>2</sub>O. The yellowish white precipitate was washed successively 6 times with water then the precipitate was suspended in a minimal amount of water and dissolved in 20% aq. HClO<sub>4</sub>. The solution was filtered and evaporated to dryness in an oven at 150 °C. The yield was 1.58 g, 76.2%. The compound is very hygroscopic, absorbs water during weighing. Phase identity was confirmed by XRD.

#### Silver(I) perrhenate (1c)

The procedure given for the synthesis of silver permanganate was followed using sodium perrhenate instead of KMnO<sub>4</sub>. A white precipitate was formed with 1.63 g (74.5%) yield. Elem. anal.: Ag-29.45%; Re-51.71%; Calcd.: Ag-29.64%; Re-51.18%.

#### Attempts for the synthesis of [Ag(py)<sub>2</sub>]XO<sub>4</sub> (X=Mn (2a), Cl (2b), Re (2c) and [Ag(py)<sub>2</sub>]XO<sub>4</sub>·0.5py (X=Mn (3a), Cl (3b), Re (3c) compounds

##### Bis(pyridine)silver(I) permanganate (2a) and its hemipyridine solvate (3a)

a) Ag<sub>2</sub>SO<sub>4</sub> (0.4 g, 1.28 mmol) was dissolved in 100 ml of water and a freshly prepared mixture of 12 cm<sup>3</sup> of 0.2 M KMnO<sub>4</sub> and 15 cm<sup>3</sup> of 10% aq. pyridine was added to this solution. A fine fibrous crystalline mass was obtained immediately, and rapid cooling of the solution to +10 °C yielded a further crop of product. The combined yield was 0.68 g. The product contained more than one compound.

b) 2.0 g Ag<sub>2</sub>SO<sub>4</sub> was dissolved in a mixture of 500 ml of water and 90 ml of 10% aq. pyridine, the mixture was stirred until complete dissolution of the silver salt and cooled to +10 °C, and a cooled (+10 °C) solution of 60 ml of 0.2 M KMnO<sub>4</sub> was added. The reaction mixture was cooled to 0 °C and filtered. The purple crystals obtained were dried in the dark over pyridine containing CaCl<sub>2</sub>. The yield was 4.4 g as a mixture of products.

c) Bis(pyridine)silver(I) nitrate (0.6 gram, 1.8 mmol) was dissolved in 9 ml of water then 1.8 mmol of sodium permanganate (40% aq. soln., d = 1.391, 0.46 ml) was added at room temperature. The mixture was cooled to 0 °C. The experiment was repeated with mixing the reactants at +10 °C and 0 °C as well. The mixture formed by mixing the reactants at 0 °C was kept at this temperature for 15 min to complete the crystallization process. The yields were varied between 0.35-0.41 g (50.6-58.4%) of **2a** depending on the mixing and the cooling temperatures. Elem. anal.: Ag-28.00%, Mn-14.17%, C-30.98%, H-2.73%, N-7.11%. Calcd.: Ag-28.05%, Mn-14.29%, C-31.17%; H-2.60%, N-7.27%. IR (ATR): aromatic C-H bands: 3103, 3070, 3039 and 3002 cm<sup>-1</sup>; pyridine ring vibrations (numbering of pyridine ring vibrations given by [25]: 1602 (8a), 1486 (19a), 1448 (19b), 1220 (9a), 1154 (15), 1074 (18a), 1042 (12), 1015 (1), 891(5), 745 (4), 700 (11), 640 (6a), 412 (16b) cm<sup>-1</sup>; permanganate bands: ν<sub>as</sub>(MnO) 919 (very strong, triplet) and ν<sub>s</sub>(MnO): 830 cm<sup>-1</sup> (weak, singlet).

d) A mixture of products (**2a** and **4a**, ~1:1) formed in the reaction described by Firuzabadi [8] was recrystallized from acetone-benzene (1:1, v/v) at room temperature. The crystals of **3a** were removed from the mother liquor and analyzed (CHN, ICP, single crystal X-ray diffraction and IR spectroscopy). Elem. anal.: Ag-25.44%, Mn-12.96%, C-35.34%, H-2.95%, N-8.25%. Calcd.: Ag-25.75%, Mn-13.21%, C-35.04%; H-2.65%, N-8.17%. IR (ATR): aromatic C-H bands: 3102, 3067, 3038 and 3000 cm<sup>-1</sup>; pyridine ring vibrations: 1600 (8a), 1485 (19a), 1447 (19b), 1219 (9a), 1152 (15), 1070 (18a), 1041 (12), 1014 (1), 880(5), 750 (4), 697 (11), 636 (6a), 414 (16b) cm<sup>-1</sup>; permanganate bands: ν<sub>as</sub>(MnO) 920-910 (very strong, triplet) and ν<sub>s</sub>(MnO): 831 cm<sup>-1</sup> (weak, singlet).

##### Bis(pyridine)silver(I) perchlorate (2b) and its hemipyridine solvate (3b)

a) An equivalent amount of silver nitrate (10 mmol) dissolved in ten times of its weight distilled water was added to a mixture of pyridine (30 mmol) and a saturated solution of sodium perchlorate (10 mmol) in distilled water at 10 °C. The white crystalline precipitate formed was washed with cold distilled water and then with dry benzene and Et<sub>2</sub>O for several times and dried over anhydrous calcium chloride. Yield was 3.61 g. The product was a mixture of **2b** and **4b**. The mixture was triturated with 1:1 acetone-benzene mixture at room temperature, and the solid formed (**3b**) was filtered off. Yield: 1.0 g (25 %). Elem. anal.: Ag-26.55%, C-36.11%, H-3.23%, N-8.51%. Calcd: Ag-26.67%, C-37.04%, H-3.09%, N-8.64%; IR (ATR): aromatic C-H bands: 3109, 3071 and 3045 cm<sup>-1</sup>; pyridine ring vibrations (numbering of pyridine ring vibrations given by [25]: 1603 (8a), 1488 (19a), 1447 (19b), 1222 (9a), 1155

(15), 1074 (18a), 1041 (12), 1015 (1), 750 (4), 692 (11), 638 (6a), 413 (16b)  $\text{cm}^{-1}$ ; perchlorate bands:  $\nu_{\text{as}}(\text{ClO})$  1067-1057 (very strong, multiplet) and  $\nu_{\text{s}}(\text{ClO})$ : 930  $\text{cm}^{-1}$  (weak, singlet).

b) Silver(I) perchlorate (1.00 g, 5 mmol) was allowed to stir in 5 ml of pyridine overnight. After completing the reaction, the solvent was removed completely at room temperature in vacuum. The residue was proved by PXRD to be pure  $[\text{Ag}(\text{py})_2]\text{ClO}_4$  (**2b**). The yield was 99.8%. Ag-29.57%, C-26.5%, H-2.81%, N-7.63%. Calcd.: Ag-29.54%, C-27.3%, H-2.74%, N-7.67%. IR (ATR): aromatic C-H bands: 3113, 3080, 3049 and 3008  $\text{cm}^{-1}$ ; pyridine ring vibrations: 1607 (8a), 1491(19a), 1452 (19b), 1224 (9a), 1156 (15), 1046 (12), 1017 (1), 751 (4), 641 (6a), 414 (16b)  $\text{cm}^{-1}$ ; perchlorate bands:  $\nu_{\text{as}}(\text{ClO})$  1132 (very strong, singlet/shoulder) and  $\nu_{\text{s}}(\text{ClO})$ : 945  $\text{cm}^{-1}$  (weak, singlet).

#### **Bis(pyridine)silver(I) perrhenate (2c) and its hemipyridine solvate (3c)**

a) The method (a) used to prepare the analogous permanganate complex was followed, using 0.2 M aq.  $\text{NaReO}_4$  solution. On cooling the reaction mixture to 0 °C a white precipitate appeared, which was filtered off. The yield was 0.75 g for **2c**, 56.8% of the theoretical value. The white crystals were dried in the dark over pyridine containing  $\text{CaCl}_2$ . Ag-20.85%, Re-36.01%, C-23.11%, H-2.01%, N-5.32%. Calcd.: Ag-20.93%, Re-36.07%, C-23.26%, H-1.94%, N-5.43%. IR (ATR): aromatic C-H bands: 3043-3000  $\text{cm}^{-1}$ ; pyridine ring vibrations (numbering of pyridine ring vibrations given by [25]: 1601 (8a), 1483 (19a), 1450 (19b), 1223 (9a), 1149 (15), 1065 (18a), 1043 (12), 1015 (1), 875(5), 748 (4), 708 (11), 639 (6a), 425 (16b)  $\text{cm}^{-1}$ ; perrhenate bands:  $\nu_{\text{as}}(\text{ReO})$  952,959 (very strong) and  $\nu_{\text{s}}(\text{ReO})$ : 933  $\text{cm}^{-1}$  (weak, singlet).

b) The procedure (b) used to prepare the analogous permanganate complex was followed but using a saturated solution of sodium perrhenate. A multiphase white crystalline precipitate (4.77 g) was obtained.

c) Silver(I) perrhenate (1.00 g, 2.8 mmol) was stirred in 5 ml of pyridine overnight. After completing the reaction, the solvent was removed at room temperature. This solid was proved to be pure  $[\text{Ag}(\text{py})_2]\text{ReO}_4$ . Recrystallization of **2c** from acetone: benzene (1:1) and dichloromethane at room temperature resulted in the formation of white crystals of the starting **2c**. The expected **3c** did not form at all.

#### **Attempts to synthesize $[\text{Ag}(\text{py})_4]\text{XO}_4 \cdot 4[\text{Ag}(\text{py})_2]\text{XO}_4$ (X=Mn (4a), Cl (4b), and Re (4c) compounds.**

##### **Tetrakis(pyridine)silver(I)permanganate-co-tetrakis[bis(pyridine)silver(I) permanganate] (4a)**

a) Silver nitrate (1.72 g, 10 mmol) dissolved in 17 ml of distilled water was added to a mixture of pyridine (30 mmol) and a saturated solution of potassium permanganate (1.60 g, 10 mmol) in distilled water (40 ml) at 10 °C. The purple crystalline precipitate formed was washed with cold distilled water several times, dried in air in the dark and then dried under vacuum for 24 h. A mixture of  $[\text{Ag}(\text{py})_4]\text{MnO}_4 \cdot 4[\text{Ag}(\text{py})_2]\text{MnO}_4$  and  $[\text{Ag}(\text{py})_2]\text{MnO}_4$  was formed (2.5 g).

b) 1.72 g (10 mmol) of silver nitrate was dissolved in 7 ml of water, then a mixture of 5 ml of pyridine (60 mmol) and 2.6 ml of 40% aq. solution of the sodium permanganate ( $d = 1.391$ ) was added to it with continuous stirring. The mixture was cooled to +10 °C in an ice bath, the purple precipitate was collected by filtration, washed thoroughly with water, then dried in air. Yield was 3.85 g, based on PXRD analysis. The primary product was  $[\text{Ag}(\text{py})_4]\text{MnO}_4 \cdot 4[\text{Ag}(\text{py})_2]\text{MnO}_4$ , and only a small amount of  $[\text{Ag}(\text{py})_2]\text{MnO}_4$  was present as a contaminant.

c)  $\text{Ag}_2\text{SO}_4$  (0.4 g, 1.28 mmol) was dissolved in 100 ml of water and a freshly prepared mixture of 12 ml of 0.2 M  $\text{KMnO}_4$  and 100 ml of 20% aq. pyridine was added to this solution. A fine fibrous crystalline mass was obtained immediately, and rapid cooling of the solution to +8 °C resulted in further precipitation of the product. The yield was 0.496 g, and the product was proved to be impure (a mixture of **2a** and **4a**).

d) The above-mentioned synthesis has been modified. First, the pyridine was added to the silver sulphate solution until complete dissolution of the silver salt, then the mixture was cooled to +10 °C, and a cooled (+10 °C) solution of  $\text{KMnO}_4$  was added. A light purple fine precipitate was formed immediately. The whole mixture was cooled to 0 °C and filtered. The purple crystals (0.68 g, a mixture of **2a** and **4a**) were dried in the dark over pyridine containing  $\text{CaCl}_2$ .

e) Freshly prepared silver(I) permanganate (1 g, 4.5 mmol), was allowed to stir in 18 ml of pyridine overnight. After completing the reaction, the solvent was removed at room temperature. When the purple mass was kept in equilibrium with the mother liquor, the isolated product was pure **4a**. The yield was 0.85 g (47 %). The evaporation of the mixture to dryness resulted in a mixture of  $[\text{Ag}(\text{py})_4]\text{MnO}_4 \cdot 4[\text{Ag}(\text{py})_2]\text{MnO}_4$  and  $[\text{Ag}(\text{py})_4]\text{MnO}_4$ .

f) Freshly prepared wet silver(I) permanganate (2,27 g) was dissolved in pure pyridine, then the saturated purple solution formed was immediately diluted with water to reach a pyridine content of 50 or 10%. A thixotropic mass and a precipitate were immediately formed, respectively. The product formed at 10-fold dilution ( $\text{H}_2\text{O}$ ) was proved to be pure **4a** (elem. anal.: Ag-25.81%, Mn-13.25%, C-33.09%, H-2.98%, N-8.00%, calcd.: Ag-25.92%, Mn-13.20, C-34.56 %, H-2,88%, N-8.07%). IR (ATR): aromatic C-H bands: 2999 and 3039  $\text{cm}^{-1}$ ; pyridine ring vibrations (numbering of pyridine ring vibrations given by [25]: 1592(8a), 1485 (19a), 1448 (19b), 1214 (9a), 1154 (15), 1071 (18a), 40,1033 (12), 1012 (1), 891(5), 756 (4), 707 (11), 413 (16b)  $\text{cm}^{-1}$ ; permanganate bands:  $\nu_{\text{as}}(\text{MnO})$  909, 917

(very strong) and  $\nu_s(\text{MnO})$ :  $826\text{ cm}^{-1}$  (weak, singlet). The yield was 2.3g (55%). At two-fold dilution with water a mixture of **4a** and **2a** was formed.

#### **Tetrakis(pyridine)silver(I)perchlorate-co-tetrakis[bis(pyridine)silver(I) perchlorate] (4b)**

a) The procedure (a) used to prepare the analogous permanganate complex was followed but using a solution of sodium perchlorate. On cooling the mixture to  $+10\text{ }^\circ\text{C}$  in an ice bath, a white precipitate (2.77 g) was isolated with **4b** as the main component.

b) The procedure (c) used to prepare the analogous permanganate complex was followed but using 0.2 M sodium perchlorate. The mixture was left at  $0\text{ }^\circ\text{C}$  for half an hour for crystallization. A colourless crystalline mass appeared, what was filtered. Yield was 0.432 g (84.7%). Ag-27.31%, C-36.01%, H-3.15%, N-8.31%. Calcd.: Ag-27.20%, C-36.26%, H-3.02%, N-8.46%. IR (ATR): aromatic C-H bands:  $3095, 3063$  and  $3043\text{ cm}^{-1}$ ; pyridine ring vibrations:  $1592(8a), 1482(19a), 1440(19b), 1215(9a), 1155(15), 1079(18a), 1034(12), 1002(1), 885(5), 751(4), 700(11), 407(16b)\text{ cm}^{-1}$ ; perchlorate bands:  $\nu_{\text{as}}(\text{ClO})$   $1064$  (very strong) and  $\nu_s(\text{ClO})$ :  $944\text{ cm}^{-1}$  (weak, singlet).

#### **Attempts on preparation of tetrakis(pyridine)silver(I)perrhenate-co-tetrakis[bis(pyridine)silver(I) perrhenate] (4c)**

a) 0.86 g (5 mmol) of silver nitrate was dissolved in 3.5 ml of water, then a mixture of 2.5 ml of pyridine and 5 mmol (1.35 g) sodium perrhenate in 2.5 ml of water was added slowly with continuous stirring. A white precipitate formed immediately; then the mixture was cooled to  $+10\text{ }^\circ\text{C}$  in an ice bath. The white precipitate was collected by filtration, washed thoroughly with water, then dried in air. The yield of multiphase product was 2.37g.

b)  $\text{Ag}_2\text{SO}_4$  (0.4 g, 1.28 mmol) was dissolved in 100 ml of water and 100 ml of a 20% aq. pyridine solution was added to this solution with stirring until complete dissolution of the silver salt. The solution was then cooled to  $+10\text{ }^\circ\text{C}$ , and 12 ml of a cold ( $+10\text{ }^\circ\text{C}$ ) solution of 0.2 M  $\text{NaReO}_4$  was added. A fluffy white precipitate formed immediately, which dissolved in seconds, then during cooling the mixture to  $0\text{ }^\circ\text{C}$  a white cotton like precipitate was deposited. The white crystalline mass was isolated by filtration and dried over pyridine containing CaO in a desiccator placed in a refrigerator. The yield of multiphase product was 0.85 g.

#### **[Ag(py)<sub>4</sub>]MnO<sub>4</sub> (5a), [Ag(py)<sub>4</sub>]ClO<sub>4</sub> (5b)**

Silver(I) permanganate (2.27 g) was dissolved in pyridine then 2-fold excess of benzene was added. The mixture was left to crystallize, when purple crystals of **5a** were formed (1.5 g, 27.6%). The crystals were dried in a fridge at  $-18\text{ }^\circ\text{C}$  with using a desiccator contains pyridine and CaO. Elem. anal. Ag-16.97%, Mn-14.45%, C-35.91%, H-3.00%, N-8.35%. Calcd.: Ag-16.59%, Mn-14.56%, C-36.87%, H-3.07%, N-8.60%. IR (ATR): aromatic C-H bands:  $3056-2999\text{ cm}^{-1}$  (wide multiplet); pyridine ring vibrations (numbering of pyridine ring vibrations given by [25]:  $1591(8a), 1483(19a), 1440(19b), 1214(9a), 1152(15), 1033(12), 1003(1), 885(5), 750(4), 697(11), 618(6a), 411(16b)\text{ cm}^{-1}$ ; permanganate bands:  $\nu_{\text{as}}(\text{MnO})$   $884, 897$  (very strong) and  $\nu_s(\text{MnO})$ :  $825\text{ cm}^{-1}$  (weak, singlet).

Silver(I) perchlorate (2.08 g) was dissolved until saturation in pyridine at room temperature, then the mixture was cooled to  $-18\text{ }^\circ\text{C}$  and left to crystallize **5b**. The yield was 0.78 g, 14.9 %. Elem. anal. Ag-18.01%, C-36.23%, H-3.01%, N-8.15%. Calcd.: Ag-17.10%, C-38.00%, H-3.17%, N-8.87%. IR (ATR): aromatic C-H bands:  $3062\text{ cm}^{-1}$  (wide multiplet); pyridine ring vibrations:  $1592(8a), 1481(19a), 1440(19b), 1215(9a), 1155(15), 1035(12), 1003(1), 885(5), 751(4), 700(11), 618(6a), 408(16b)\text{ cm}^{-1}$ ; perchlorate bands:  $\nu_{\text{as}}(\text{ClO})$   $1064, 1078$  (very strong) and  $\nu_s(\text{ClO})$ :  $944\text{ cm}^{-1}$  (weak, singlet).

#### **[Ag(py)<sub>2</sub>]NO<sub>3</sub>**

30 mmol of  $\text{AgNO}_3$  (5.16 g) was dissolved in 50 ml of water, and 9 ml of pyridine was added at room temperature. A white crystalline precipitate was deposited after several minutes and was separated by filtration on a glass filter. The precipitate was washed with a minimum amount of water, benzene, and diethyl ether. The yield was 4.16 g (42.2%). Its solubility in water is 4.65 g/100 g at room temperature.

#### **Instrumental methods**

The Ag, Mn and Re content of the compounds were determined by atomic emission spectroscopy using a Spectro Genesis ICP-OES (SPECTRO Analytical Instruments GmbH, Kleve, Germany) simultaneous spectrometer with axial plasma observation. Multielement standard solutions for ICP (Merck Chemicals GmbH, Darmstadt, Germany) were used for calibration. The carbon, hydrogen and nitrogen content were measured by elemental analysis (Fisons model CHN 1018S). FT-IR spectra of solid samples were recorded in the attenuated total reflection (ATR) mode on a Bruker Tensor 27 Platinum ATR FT-IR spectrometer at  $2\text{ cm}^{-1}$  resolution between  $4000$  and  $400\text{ cm}^{-1}$ .

The components of mixtures were identified by powder X-ray diffractometry. X-ray powder diffraction measurements were performed using a Philips PW-1050 Bragg-Brentano parafocusing goniometer. It was equipped with a Cu tube operated at 40 kV and 35 mA tube power, a secondary beam graphite monochromator, and a proportional counter. Scans were recorded in step mode. Evaluation of the diffraction patterns was obtained by full profile fitting techniques.

Single crystal diffraction intensity data were collected on an Enraf-Nonius CAD4 diffractometer (carbon monochromator; Mo-K $\alpha$  radiation,  $\lambda = 0.710730\text{\AA}$ ) at 293(2) K in the range  $2.16 \leq \theta \leq 23.96$  [22]. A crystal of **3a** was mounted on a glass fiber. Cell parameters were determined by least-squares using 25 ( $10.03 \leq \theta \leq 13.32^\circ$ ) reflections. A total of 2569 reflections were collected of which 2423 were unique [ $R(\text{int}) = 0.0092$ ,  $R(\sigma) = 0.0526$ ]; intensities of 1303 reflections were greater than  $2\sigma(I)$ . Completeness to  $\theta = 1.000$ . A psi-scan absorption correction was applied to the data (the minimum and maximum transmission factors were 0.6931 and 0.8647). The crystal structure was solved by direct methods [22]. Anisotropic full-matrix least-squares refinement [22] on  $F^2$  for all non-hydrogen atoms yielded  $R1 = 0.0451$  and  $wR2 = 0.1143$  for 1332 [ $I > 2\sigma(I)$ ] and  $R1 = 0.1038$  and  $wR2 = 0.1317$  for all (2423) intensity data, (number of parameters = 238, goodness-of-fit = 0.793, the maximum and mean shift/esd is 0.011 and 0.001). The maximum and minimum residual electron density in the final difference map was 0.849 and  $-0.713\text{e}\cdot\text{\AA}^{-3}$ . The weighting scheme applied was  $w = 1/[\sigma^2(F_o^2) + (0.10000.0000P)^2 + 0.0000P]$  where  $P = (F_o^2 + 2F_c^2)/3$ . Hydrogen atomic positions were calculated from assumed geometries. Hydrogen atoms were included in structure factor calculations but they were not refined. The isotropic displacement parameters of the hydrogen atoms were approximated from the U(eq) value of the atom they were bonded to.

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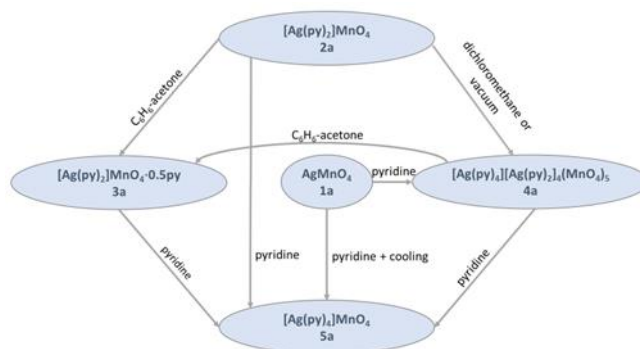


Figure 1.

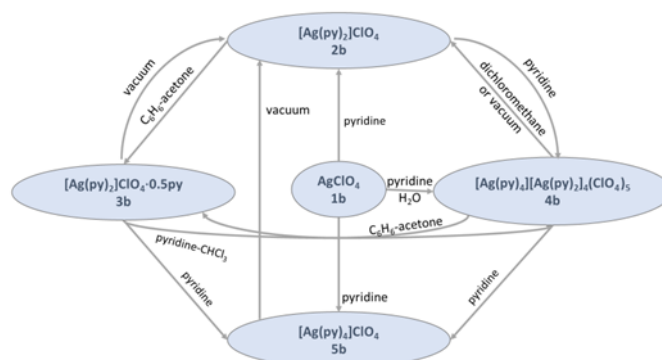


Figure 2.

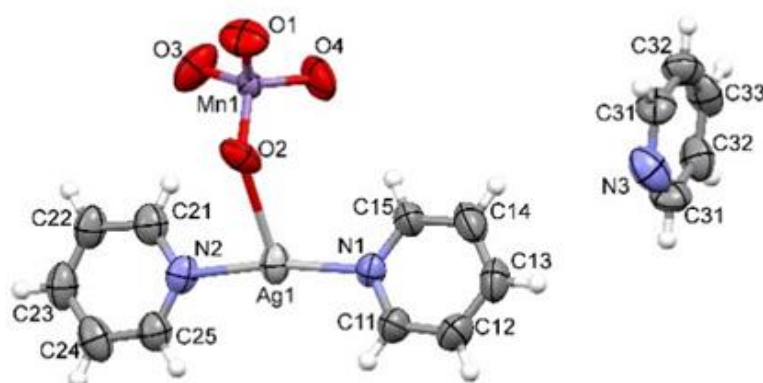


Figure 3.

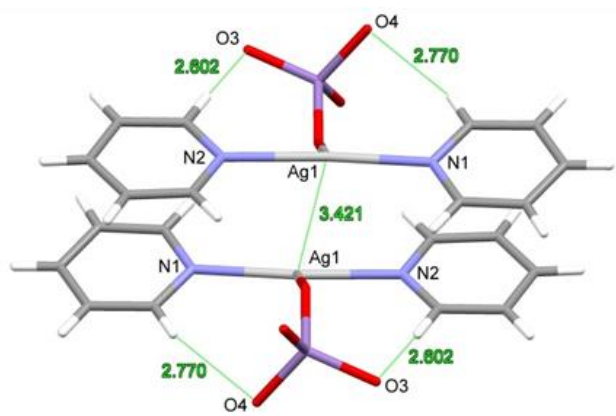
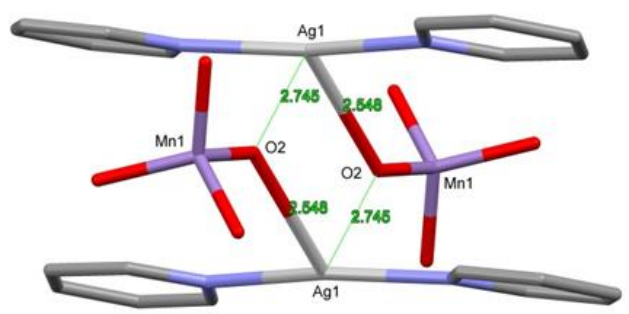


Figure 4.

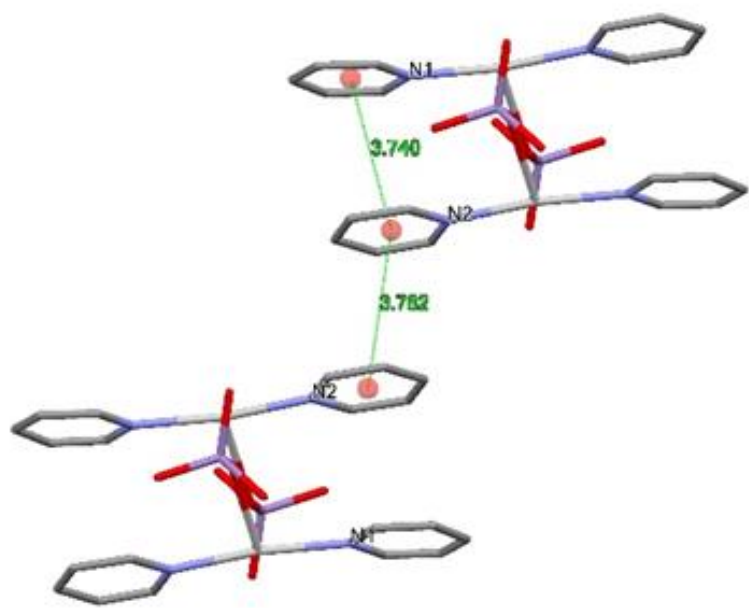




Figure 5.

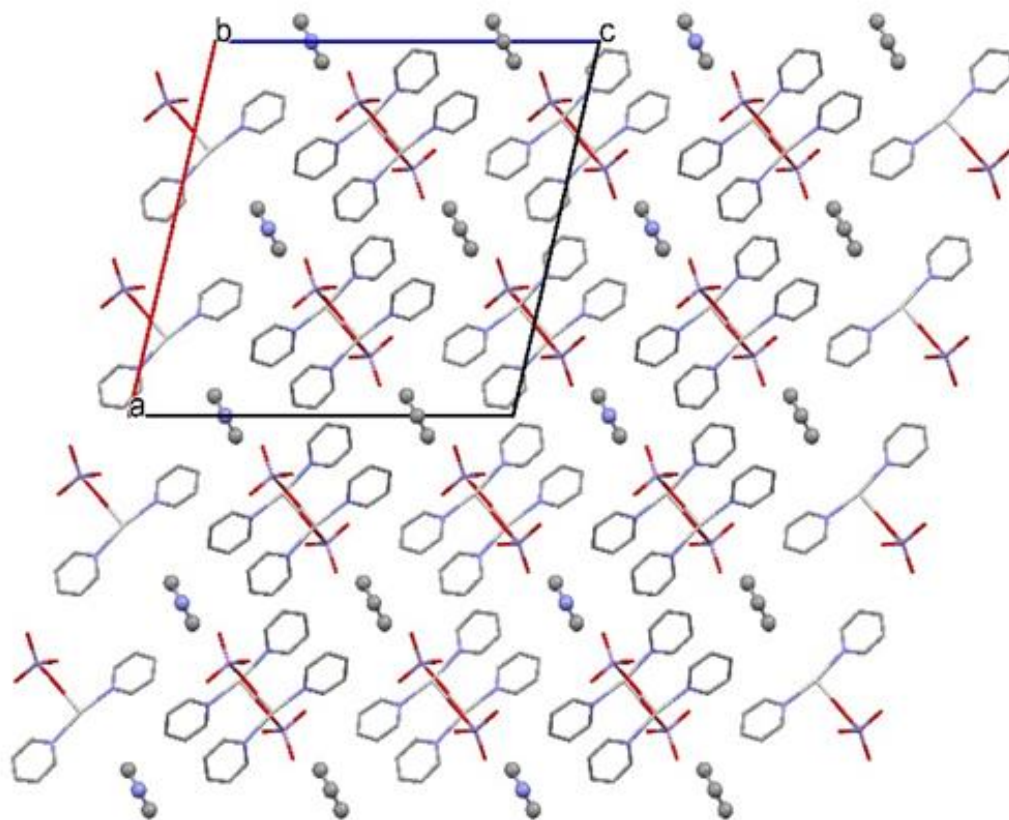


Figure 6.