Anion Effect and Ligand Preference in the Precipitation of Ni(II) Complex from Methanolic Solution: Case of Tartrate vs Pyrazine

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ABSTRACT

This research aims to incorporate pyrazine in the synthesis of Ni(II)-tartrate-pyrazine metal organic frameworks or Ni(II)-T-P MOF as candidate of porous material. Synthesis of the targeted MOF was conducted at room temperature in a methanolic solution by mixing Ni(II) solution, *L*-tartaric acid (T), and pyrazine (P) solutions sequentially in various molar ratios (Ni(II):T:P = 1:1:0; 1:0:2; 1:2:2; and 1:2:4) using two different Ni(II) salts (chloride and nitrate). Solid products were characterized by infrared spectroscopy, qualitative anion identification test, melting point test, and scanning electron microscopy. The result shows that type of nickel salt affects the precipitation of Ni(II) complex, in which pale blue solids were precipitated out only from the chloride reactions (1:0:2, 1:2:2, and 1:2:4). IR and SEM analyses from the 1:2:2 and 1:2:4 reactions show identical result as also shown by the 1:0:2 reaction, whereas qualitative anion identification test result suggests that the chloride is uncoordinated to the Ni(II). The targeted Ni(II)-T-P is unsuccessfully obtained, instead the product is proposed to be $[Ni(pyrazine)_x(H_2O)_{(6-x)}]Cl_2$. although the tartaric acid was doubled and firstly reacted with the Ni(II), the pyrazine still has higher preference to coordinate to the Ni(II) center than the tartrate ligand.

Keywords: anion, ligand preference, metal organic framework, molar ratio, solvent.

INTRODUCTION

Tartrate based metal complexes has been widely investigated for decades and the current technology of crystallography reveals that most of their transition metal complexes of M(II)-tartrate shows polymeric structures, for example 2D complexes of Co(II) [1], [2], Cu(II) [3-5] or Ni(II) [6], [7] and 3D complexes of Zn(II) [8], Mn(II) [9], [10], or Cd(II) [5], [11], [12]. Some of their transition and lanthanide metal complexes display empty voids with stable framework [9-11]. These polymeric structures are frequently resulted when transition or lanthanide metal ions reacted with tartrate ligand due to this ligand has high flexibility, including chelation ability, and offers many possible coordination modes from their oxygen donor atoms of the carboxylate and the hydroxyl groups. As a result, their coordination polymers display many interesting features such as porosity, magnetism, catalysis, luminescence, etc [4], [8] [13-15].

Particularly the Ni(II)-tartrate complex, this complex form several crystal structures [6], [7] but all of the reported structures have identical coordination environment around the metal center. Scherb (2002) reported that the asymmetric unit of the Ni(II)-tartrate consist of two nickel centres bridged by two tartrate ligands and forms polymeric 2D sheets with a (6, 3)

topology. There are five coordination sites around each Ni(II) centre that occupied by the oxygen of the tartrate, leaving one coordination site which occupied by oxygen of the water [6]. This structure is also identical to that of reported by Khunur & Prananto (2018) with a general formula of $\{[M_2(\mu\text{-}C_4H_4O_6)(\mu^4\text{-}C_4H_4O_6)(H_2O)_2]\cdot 3H_2O\}$, although different synthetic method were used [2]. If the position of water ligand can be replaced by a rigid bridging ligand, crystal structure of the Ni(II)-tartrate can be developed into more stable 3D networks, which may display uniform and bigger voids, thus the compound has better properties as adsorbent or other functional materials.

In order to achieve this, a neutral ligand of pyrazine ($C_4H_4N_2$) is proposed in this work. Pyrazine is as considerably small size with some steric repulsion of the electron cloud around its ring. It is also a rigid bridging ligand since it offers two nitrogen donor atoms in *para* position. Some Ni(II) complexes that uses pyrazine as bridging ligand are frequently reported [16-20]. It is expected that the pyrazine can bridge two neighbouring sheets of Ni(II)-tartrate and forms Ni(II)-tartrate-pyrazine or Ni(II)-T-P MOF, which at the same time, lowering the possibility of interpenetration structure formation that can reduce the empty voids in the crystal packing of the MOF.

Introduction of pyrazine into the Ni(II)-tartrate complex may be influenced by several factors, such as synthetic method, type of metal ions salt, solvent, reaction temperature, molar ratio, etc. Any changes in the reaction condition may or may not affect the formation of solid product. In this work, effect of anion from the nickel(II) salt in the precipitation of Ni(II)-T-P MOF is also studied. This factor is predicted to have a role in the formation of the targeted compound. The different anion of Ni(II) salts may bring different solubility in a methanolic solution, hence it may alter the kinetics of the complexation. Although it is not expected, the anion may also involve in the crystal lattice, whether as free ions or as ligands; which eventually may be resulting in different products.

EXPERIMENT
Chemicals and instrumentation

Chemicals used in this work were used as supplied (from SigmaAldrich) without further treatment, namely pyrazine ($C_4N_2H_4$), *L*-tartaric acid ($C_6H_6O_6$), nickel(II) chloride dihydrate ($NiCl_2\cdot 6H_2O$), nickel(II) nitrate hexahydrate ($Ni(NO_3)_2\cdot 6H_2O$), and methanol (CH_3OH).

Instrumentations used for characterization were infrared spectroscopy (IR-Spirit T Shimadzu), scanning electron microscopy (FEI Quanta FEG 650), and digital open-capillary melting point apparatus (InnoTech DMP800). All instrumentations are available and provided by the Brawijaya University.

Synthesis and Characterisation of the Ni(II) Complex

Each Ni(II) solution and ligand solution was firstly prepared in a 3-mL methanol separately (details for each molar ratio are presented in Table 1). Into the Ni(II) solution, tartaric acid solution was added and then stirred for 10 minutes using magnetic stirrer. Next, pyrazine solution was added and the solution was kept stirred for another 10 minutes. For reaction that gives precipitate, the solution was filtered-off using filter paper. The precipitate was then dried in an oven (105 °C) and saved it in a desiccator with silica gel beads as drying agent. For reaction that gives clear solution (no precipitation), the solution was slow evaporated for 21 days in a small-open vial in order to check the possibility of slow formation of the product.

Dry solid products were characterised by: (a) FT-IR using KBr pellet method at frequency of 4000 – 400 cm^{-1}, (b) melting point test using an open capillary tube with increasing rate of 10°C/minutes up to 400 °C, (c) SEM using 10 kV high vacuum in which the sample was put on top of the stub with double sided carbon tape and then sputter coated with gold, and (4) qualitative anion identification test using aqueous AgNO$_3$.

Table 1. Reaction series

| Code | Ni(II):T:P | Type of Ni(II) salt | Amount of chemicals | | |
			Ni(II)	*L*-Tartaric acid	Pyrazine
A1	1:0:2	nitrate	145 mg (0.5 mmol)	---	80 mg (1 mmol)
A2	1:0:2	chloride	118 mg (0.5 mmol)	---	80 mg (1 mmol)
B1	1:2:2	nitrate	145 mg (0.5 mmol)	150 mg (1 mmol)	80 mg (1 mmol)
B2	1:2:4	nitrate	145 mg (0.5 mmol)	150 mg (1 mmol)	160 mg (2 mmol)
C1	1:2:2	chloride	118 mg (0.5 mmol)	150 mg (1 mmol)	80 mg (1 mmol)
C2	1:2:4	chloride	118 mg (0.5 mmol)	150 mg (1 mmol)	160 mg (2 mmol)
D1	1:2:0	nitrate	145 mg (0.5 mmol)	150 mg (1 mmol)	---
D2	1:2:0	chloride	118 mg (0.5 mmol)	150 mg (1 mmol)	---

RESULT AND DISCUSSION
Synthesis of the complex

Series of reactions were conducted and the results are presented in Table 2. The A1, A2, D1, and D2 were reaction using single ligand only, namely pyrazine (A1, A2) and tartaric acid (D1, D2). These reactions were also conducted as comparison for the mixed ligand reactions of B1, B2, C1, and C2. The B and C represents the nitrate salt and the chloride salt, respectively.

**Table 2**. Observation result of the reaction series

Code	Molar ratios of Ni(II):T:P	Type of Ni(II) salt	Observation result	Yield (mg)
A1	1:0:2	nitrate	clear blue-greenish solution	-
A2	1:0:2	chloride	pale blue powder	56
B1	1:2:2	nitrate	clear blue-greenish solution	-
B2	1:2:4	nitrate	clear blue-greenish solution	-
C1	1:2:2	chloride	pale blue powder	83
C2	1:2:4	chloride	pale blue powder	92
D1	1:2:0	nitrate	clear light green solution	-
D2	1:2:0	chloride	clear light green solution	-

From all reactions, only reactions A2, C1, and C2 gives precipitate, in which all precipitates were in the form of pale blue fine powder. For other reactions, direct mix of the metal and ligand solutions at room temperature did not yield any precipitate, including the reactions between nickel(II) salts with the tartaric acid (D1 and D2). To these solutions, slow evaporation at room temperature for another two weeks were performed, which only resulting in a clear solution with slightly darker colour than that of before the slow evaporation due to increasing of nickel(II) ions concentration. At this point, the reactions were stopped for further observation. Based on reactions A2, C1, and C2, only reaction involving chloride salts gives

precipitate, which indicate that the anion has a role in the precipitation of the Ni(II) complex. To confirm this and to identify the precipitated compound, the dry powder was then characterized using FTIR, qualitative anion identification test, melting point test, and SEM. In addition, the more pyrazine added into the reaction, the higher yield obtained, in which the C2 reaction (1:2:4) gives higher yield than the C1 reaction (1:2:2). This is reasonable since the presence of more pyrazine may lead to a fulfilment of stoichiometric reaction, based on the octahedral geometry that frequently observed in the Ni(II) complex. Moreover, it also in accordance to the Le chatelier principle, in which if concentration of the one or more reactant is increased, the complexation equilibrium will preferably go to the product formation.

Characterization of the Complex

Infrared analysis was performed to identify the organic functional groups that contained in the compound, which eventually used for background information on the presence of the pyrazine and/or tartrate ligands. The result of FTIR analyses (4000–400 cm^{-1}) are presented in Figure 1. Infrared spectra of the free ligands are also included as reference.
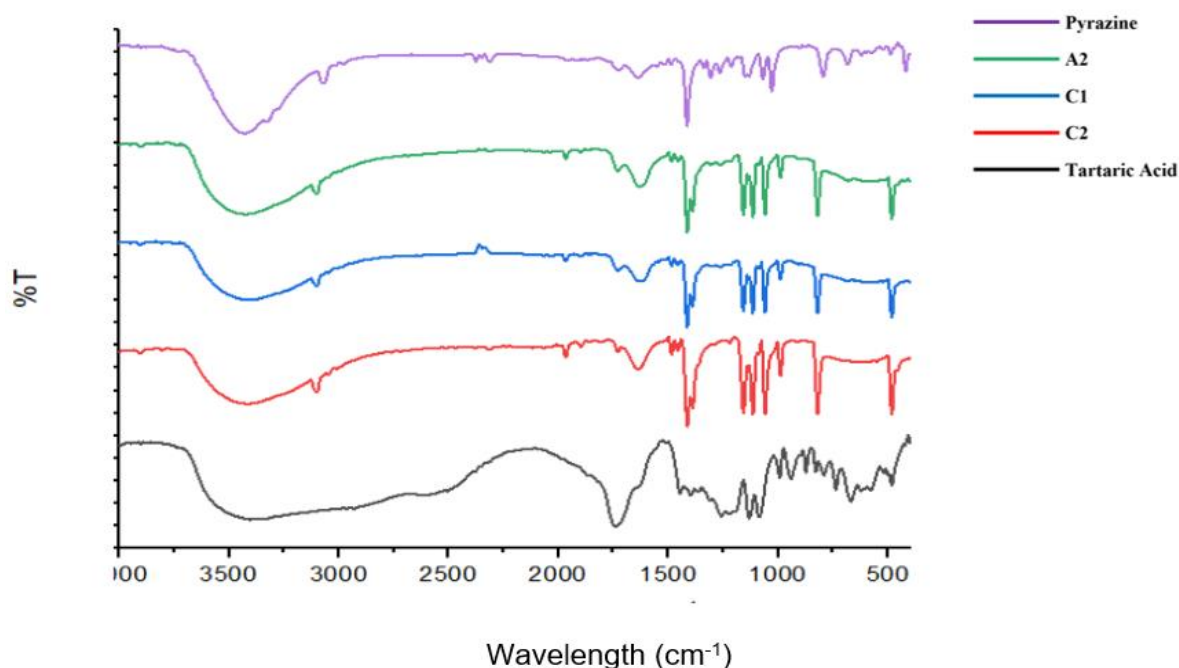
Figure 1. Infrared spectra of free ligands (pyrazine and tartaric acid) and the dry powder obtained from reactions A2, C1, and C2.

Typical absorption band of pyrazine in the C1 and C2 spectra are observed in the wavenumbers of 820 cm^{-1} (v_{C-N} bend, sharp), 900-1200 cm^{-1} (v_{C-N}, sharp; v_{C-C}, sharp), 1350-1420 cm^{-1} ($v_{C=C}$, sharp), around 1630 cm^{-1} ($v_{C=N}$, medium-broad) and around 3000 cm^{-1} (v_{C-H}, medium). In addition, there is a broad band around 3300-3500 that suggest the presence of hydroxyl groups, which probably due to the presence of water as ligand or as lattice solvent. The spectra of C1 and C2 compounds are closely identical to that of A2. Compound A2 is most likely to be complex of Ni(II)-pyrazine since the reaction did not involve any tartaric acid, whereas the C1 and C2 using both pyrazine and tartaric acid in their reaction in different molar ratio. This infrared information, along with an absence of sharp peak around 1700 cm^{-1} that

correspond to the carbonyl groups of tartrate ligand, suggest that the targeted Ni(II)-T-P was unsuccessfully obtained. Instead, the C1 and C2 compounds are only Ni(II)-pyrazine complex.
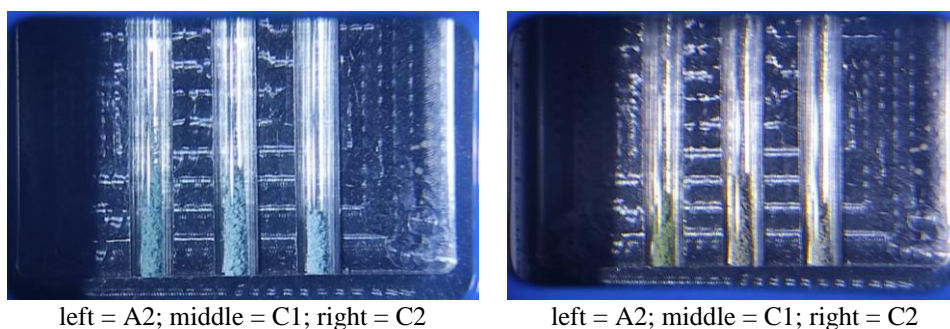
Although spectra of free pyrazine, A1, C1, and C2 compounds are identical, in term of frequency of the adsorption, there is a change in the peak profile that suggest the interactions of pyrazine ligand and the Ni(II) metal centre. The peak intensities around 1600 and around 900-1200 cm^{-1} in the C1 and C2 increases significantly, which indicates that the M–L coordination bonds occurred between the nitrogen atoms of pyrazine and the Ni(II) centre. The Ni–N$_{pyrazine}$ band itself is probably observed in the region below 400 cm^{-1}, as commonly observed in other Ni(II) complex with N-donor based ligand, which is out of the infrared instrument range used in this work. Based on the infrared analysis itself, the number of pyrazine in the complex, as well as the coordination geometry of the complex remains unsure.

Furthermore, since only the chloride reaction gave precipitation and the powder product is more likely to be Ni(II)-pyrazine, the role of chloride needs to be determined. In the complex, the chloride may act as free ions or as ligands. This is important to predict the chemical formula and to proposed the predicted structure of the complex. In order to determine the chloride role, anion qualitative test was conducted using aqueous silver(I) nitrate. In a separate test tube, 5 mg of each A2, C1, and C2 was dissolved in a 5-mL water, resulting in clear blueish solution. After adding the solution with 5 mL AgNO$_3$ 0.5M, white precipitate of AgCl formed immediately in all test tubes. This result shows that the chloride is likely act as free ions in the complex. Since the chloride is located in the lattice as free ions, the remaining coordination sites around the Ni(II) centre may be occupied by water ligand, which is also indicated by the broad band in the infrared spectra. Therefore, it is predicted that compound C1 and C2 are [Ni(pyrazine)$_x$(H$_2$O)$_{(6-x)}$]Cl$_2$ complexes. Nevertheless, the possibility of other formula and complex structure, such as complex with tetrahedral structure or even polymeric structures, remain open since the exact structure of the complex has not been confirmed by the single crystal XRD analysis.

To support physical characterization of the obtained complex, melting points of C1 and C2 were also measured in an open capillary tube from room temperature to 400 °C. Both complexes did not undergo phase change from solid to liquid (melt), instead the colour only change from pale blue to grey gradually until reaching temperature of 400 °C, which probably due to decomposition of the complex. However, complex A2 shows different result, in which the complex turn into pale green when it reaches 400 °C. This result indicates that the A2 may have different geometry, different crystal packing, or different number of coordinated pyrazine in their structure. This thermal behaviour difference is probably due to the fact that C1 and C2 complexes were precipitated out from solutions that contains tartaric acid. Although the acid did not able to coordinate as ligand, its presence in the solution alters the acidity of the solution and the formation of the complex, which eventually affecting the property of the complex. Further analysis using DTA–TGA is suggested to investigate this and to study the thermal properties of the obtained complexes in a more detail.

In addition, surface morphology of the complexes is also studied using SEM and the images of the complexes are presented in Figure 3. Using 5,000x magnification, it is reveal that the complex has a rough and uneven surface. When the surface examined in a more detail (magnify by 10,000x), the powder seems to build up from tiny irregular shape particles or aggregates. The particle size varies from 100 to 200 nm (compound A2) or from 300 to 500 nm (compound C1 and C2). The different in particle size is might be due to the presence of tartaric acid in the solutions of C1 and C2 during the precipitation.

J. Pure App. Chem. Res., 2022, 11 (2), 128-135

25 July 2022

| left = A2; middle = C1; right = C2 | left = A2; middle = C1; right = C2 |

Figure 2. Screen capture of melting point determination of the complexes at room temperature (left) and after it reaches 400 °C (right)

A2; 100x	A2; 5,000 x	A2; 10,000x
C1; 100x	C1; 5,000 x	C1; 10,000x
C2; 100x	C2; 5,000 x	C2; 10,000x
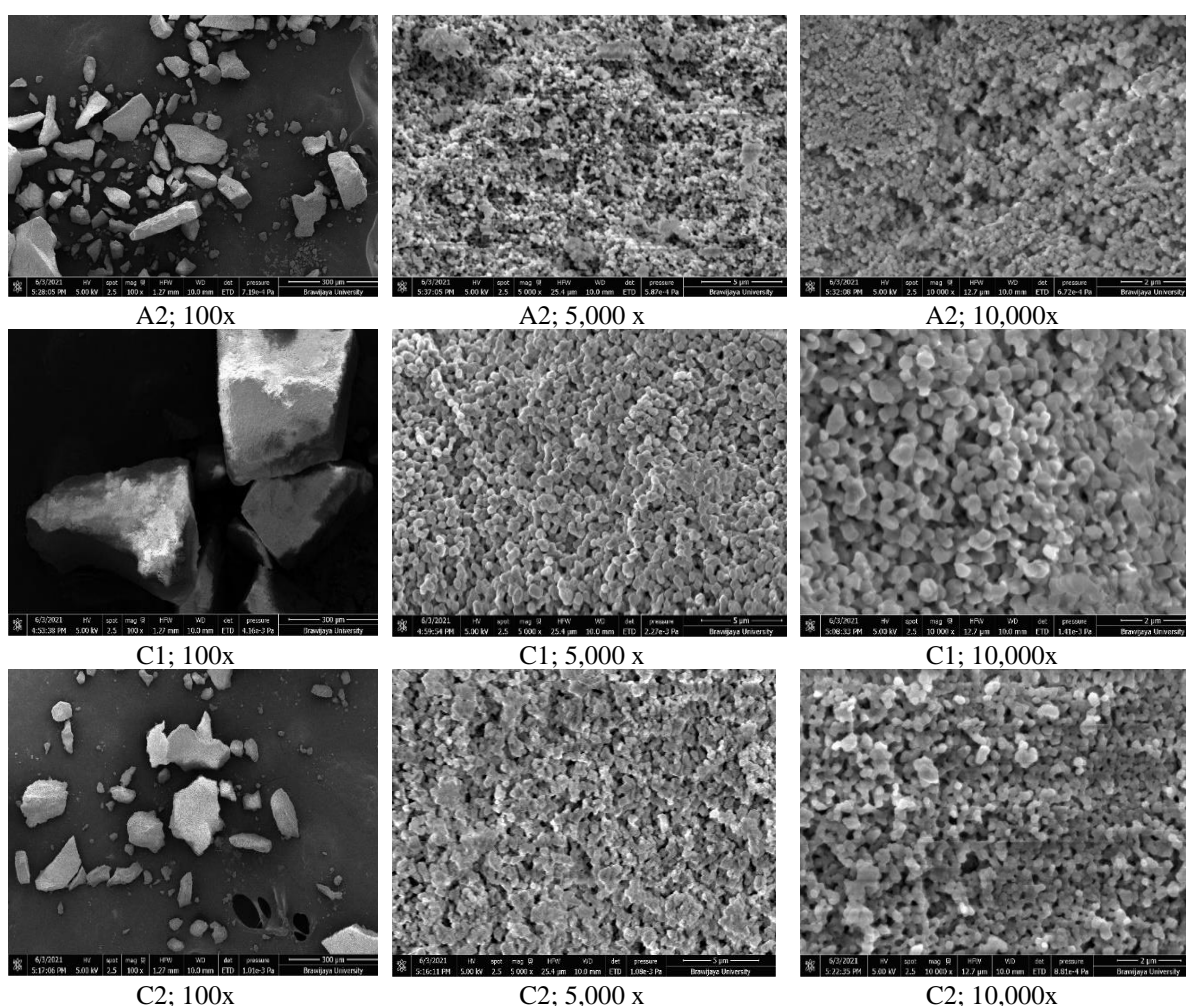
Figure 3. Surface morphology of the complexes, magnify by 100x (left); 5,000x (middle) and 10,000x (right)

Based on characterization of compounds C1 and C2 by FTIR and qualitative anion identification test, it is confirmed that introduction of pyrazine into the Ni(II)-tartrate complex was unsuccessful. The precipitated product is more likely to be complexes of Ni(II)-pyrazine chloride or $[Ni(pyrazine)_x(H_2O)_{(6-x)}]Cl_2$. Based on stoichiometry, the tartaric acid needs equal

133

moles with the nickel(II) salt to form Ni(II)-tartrate complexes. In this study, although the molar ratio of tartaric acid to nickel(II) salt was doubled (2 times higher) and the Ni(II) was firstly reacted with the *L*-tartaric acid, the pyrazine still has higher preference than the tartrate ligand to coordinate to the Ni(II) centre and form precipitated product from the methanolic solution.

To the best of our knowledge, it is rarely reported by the Ni(II)-tartrate complexes. However, it should be noted that this ligand preference is only occurred when methanol solvent and chloride salt were used. If one of them is absence, precipitation of Ni(II) complex may not or even did not occurred, as shown by reactions B1 and B2, or reported by other papers [17-21]. Although the use of nitrate salt in this study did not result in precipitated product, investigation on the use of other Ni(II) salts is needed to comprehensively study the effect of anions in the formation of targeted Ni(II)-T-P complex. Since each anion of the salt has its own characteristic in terms of size, charge, acidity, reactivity, etc; the use of different anion of Ni(II) salts may resulting in Ni(II) complexes with plenty of possibilities.

This finding also highlights that ligand preference of tartrate vs pyrazine in the precipitation of the Ni(II) complex is govern by both solvent (methanol) and anion of the nickel salt (chloride). As summarised by Payehghadr & Hashemi (2017), the property of the solvent hold a crucial role in stabilization of the precipitated complex [21]. Further investigation on this ligand preference in different system is needed and still ongoing. Since the synthesis of MOF are influenced by many factors, the use of other type of anion, metal ion, or solvent may resulting in different result and/or compound of interest, thus the possibility of obtaining the targeted Ni(II)-T-P MOF in many different ways remains open. Characterisation by single crystal XRD will also be helpful to confirm the structure of the complex.

CONCLUSION

The targeted Ni(II)-T-P MOF is unsuccessfully obtained, instead the product is proposed to be $[Ni(pyrazine)_x(H_2O)_{(6-x)}]Cl_2$. The use of different type of the Ni(II) salt affects the precipitation of the Ni(II) complex from methanolic solution, in which the chloride salt gives precipitated product whereas the nitrate salts only give clear solution. Moreover, in the case of chloride, pyrazine has higher preference than that of tartrate ligand, although the amount of tartaric acid was doubled and was firstly reacted with the Ni(II) solution. The use of other types of anion, metal ion, or solvent may be resulting in different result, and further research on this issue is still ongoing.

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