Acta. Chim. Asiana., 2022, 5(1), 166 –172
e-ISSN/p-ISSN 2550-0503/2550-049x
Available online at: www.aca.unram.ac.id

RESEARCH PAPER

Crystallization of Mn(II) and Cd(II) Complexes in A Water-Methanol System: Tartrate vs. Nicotinamide Ligand Selectivity

Yuniar P. Prananto[a]*, Rafi D. Wibisono[a], Sasti G. Fadhilah[a], Rachmat T. Tjahjanto[a], Darjito[a], and Firsta L. Salsabila[a]

a] Department of Chemistry, Faculty of Science, Brawijaya University, Indonesia
Jl. Veteran 01 Malang, East Java
E-mail: prananto@ub.ac.id

DOI: 10.29303/aca.v5i1.114

Article info:

Received 27/03/2022

Revised 11/04/2022

Accepted 11/04/2022

Available online 230/04/2022

Abstract: Ligand selectivity of tartrate vs. nicotinamide in a water-methanol system has been observed in the crystallization of Mn(II) and Cd(II) complexes. These complexes were crystallized at room temperature by a layered solution technique using a water-methanol mixture solvent in a M(II):tartrate: nicotinamide (M = Mn, Cd) molar ratio of 1:1:2. Complexes of M(II)-nicotinamide and M(II)-tartrate were also prepared for data comparison. Analysis of the crystals by infrared spectroscopy, powder-X-ray diffraction, and qualitative anion test showed that in the presence of both tartrate and nicotinamide, the Mn(II) forms a neutral Mn(II)-tartrate hydrate complex, whereas the Cd(II) forms ionic Cd(II)-nicotinamide chloride complex. In the case of Mn(II) complex, tartrate tends to coordinate as ligand than the nicotinamide, although the molar ratio of nicotinamide was doubled than that of tartrate ligand. In contrast, the neutral nicotinamide ligand is more predominant in coordinating in the Cd(II) complex than the anionic tartrate. The tartrate-nicotinamide ligand selectivity in the crystallization of Mn(II) and Cd(II) complexes is likely due to the use of tartrate salt as a precursor and the choice of solvent mixture. In addition, powder-XRD analysis confirms no indication of M(II)-tartrate and M(II)-nicotinamide that co-crystallized together at the same time by both metal ions.

Keywords: ligand preference, tartrate, niacinamide, metal complex, layered solution.

Citation: Prananto, Y. P., Wibisono, R. D., Fadhilah, S. G., Tjahjanto, R., Darjito, & Salsabila, F. L. (2022). Crystallization of Mn(II) and Cd(II) Complexes in A Water-Methanol System: Tartrate vs. Nicotinamide Ligand Selectivity. *Acta Chimica Asiana*, 5(1). 166-172. https://doi.org/10.29303/aca.v5i1.114

INTRODUCTION

Tartrate ligand has been widely explored due to its versatility in constructing functional metal complexes, including coordination polymers or metal-organic frameworks. Specifically, Mn(II)-tartrate and Cd(II)–tartrate complexes, which were made by many methods, were reported to form 3D networks with small voids [1–4]. To improve its function as porous material (*e.g.* adsorbents, catalysts, etc.), the void can be enlarged by adding rigid neutral ligand (L) as pillars. The addition of a rigid pillar in the framework is expected not only to enlarge the void of the M(II)-tartrate-L complexes but also to gain better thermal stability [5, 6]. Thermal stability is needed due to, in some cases, porous material should be able to survive the high temperature during the drying or regeneration of the material. In other words, the targeted M(II)-tartrate-L complexes are expected to have bigger voids and better thermal stability by adding a neutral ligand.

Nicotinamide ($C_6H_6N_2O$), also known as niacinamide, is one of many options for such a neutral ligand. It has three possible coordination sites through pyridyl (N), carbonyl (O), and amide (N) groups (Figure 1). It may also act as terminal [5] or bridging ligands [7] and has many coordination modes, including chelation. Some metal complexes containing nicotinamide and dicarboxylate ligand have been successfully made, in which some of them show antibacterial activity. The dicarboxylate were succinate [8], saccharinate [9], fumarate [10], 2,2'-iminodiacetate, 2,2'-oxydiacetate, 2,2'-thiodiacetate [11], etc. The pyridyl and carbonyl groups of nicotinamides are expected to bring their semi-rigid properties to support the thermal stability of the framework.

Particularly in this work, the molar ratio of the neutral ligand (nicotinamide) is doubled to increase the possibility of gaining a mixed ligand complex since the tartrate ligand easily forms a negative charge and coordinates to the metal center (Figure 1). In addition, the tartrate ligand can be supplied from several compounds, in which KNa-tartrate was used in this work.

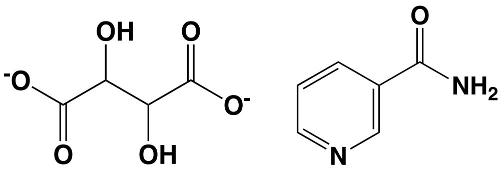

Figure 1. Structure of tartrate ion (left) and nicotinamide (right)

MATERIALS AND METHODS

All chemicals, including solvents, were used as received, namely nicotinamide, $MnCl_2.4H_2O$, $CdCl_2.4H_2O$, KNa-tartrate, methanol, and aquadest.

In total, six reactions were conducted (Table 1), in which reactions 1, 2, 4, and 5 were done only with one ligand, whereas reactions 3 and 6 were done using two ligands, KNa-tartrate, and nicotinamide. Codes 1 to 3 represent the Mn(II) reactions, whereas codes 4 to 6 correspond to Cd(II) reactions. A 1.26 mmol of $MCl_2.4H_2O$ was used, and the amount of ligand(s) used in each reaction corresponded to that of the molar ratio of each code.

As illustrated in Figure 2, a layered solution technique was used in this work, involving solutions 1, 2, and 3. Buffer solution (or solution 2) was prepared by mixing both solvents in a 1:1 ratio. A 5 mL of solvent (either H_2O or CH_3OH) was used for solutions 1 and 3 in each reaction code. The reactions were stood at room temperature for 21 days in a closed vial. The precipitation resulting from any reaction was separated by filter paper and washed with water. The solid was then air-dried for a day and kept in the desiccator (with silica gel beads) for several days until the solid was fully dried.

Table 1. Details of reaction series

Code	Code - Molar ratio	Solution 1	Solution 3
1	Mn(II):T:Nic = 1:0:2	$MnCl_2$ in H_2O	Nic in MeOH
2	Mn(II):T:Nic = 1:1:0	KNaT in H_2O	$MnCl_2$ in MeOH
3	Mn(II):T:Nic = 1:1:2	KNaT in H_2O	$MnCl_2$ + Nic in MeOH
4	Cd(II):T:Nic = 1:0:2	$CdCl_2$ in H_2O	Nic in MeOH
5	Cd(II):T:Nic = 1:1:0	KNaT in H_2O	$CdCl_2$ in MeOH
6	Cd(II):T:Nic = 1:1:2	KNaT + Nic in H_2O	$CdCl_2$ in MeOH

Note: T = tartrate; Nic = nicotinamide; MeOH = methanol; KNaT = KNa-tartrate

Characterisation of the crystals were done by IRSpirit–T Shimadzu (ATR, 4000-500 cm^{-1}), PANalytical X'pert3 Powder-XRD (2 = 10-70°, Cu-Kα = 1.541874 Å), and InnoTech DMP800 melting point apparatus (25–400°C, rate = 10°C). The infrared spectroscopy and melting point test were conducted at Fundamental Chemistry Laboratory of Chemistry Department, Brawijaya University, whereas powder-XRD analyses were performed in the Central Laboratory of Life Science, Brawijaya University, Malang.

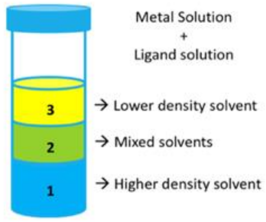

Figure 2. Illustration of the layered solution technique

RESULTS AND DISCUSSION

Synthesis of the Complex

After 21 days, all reactions were examined. For the Mn(II) series, reaction code 1 gives a clear solution, and reaction codes 2 and 3 result in colorless block crystals. Meanwhile, for the Cd(II) series, all reactions (codes 4, 5, and 6) give a white powder. The yields obtained from each reaction varied, as detailed in Table 2. Since reaction codes 2, 4, and 5 use only one type of ligand, it is most likely that the solid products were Mn(II)-tartrate, Cd(II)-nicotinamide, and Cd(II)-tartrate complexes, respectively. These compounds were then characterized and used as a reference for solid products produced from reactions that use both KNaT and nicotinamide (codes 3 and 6).

Table 2. Result of reaction series after 21 days

Code	Metal ions	MCl_2 (mmol)	Result (yield)
1	Mn(II)	1.26	colorless solution
2	Mn(II)	1.26	block colorless crystals (268 mg)
3	Mn(II)	1.26	block colorless crystals (115 mg)
4	Cd(II)	1.26	white powder (305 mg)
5	Cd(II)	1.26	white powder (277 mg)
6	Cd(II)	1.26	white powder (415 mg)

Characterization of the Complex

Infrared analyses of all dry solids obtained from reaction codes 2 to 6 are presented in Figure 3. Infrared spectra of the free ligands (KNaT and nicotinamide) were also included for comparison. The formation of M(II)-tartrate-nicotinamide complex can be determined by identifying the presence of characteristic peaks that correspond to both ligands, namely $–NH_2$, C=O groups for nicotinamide and C=O, C–OH, COO^- groups for tartrate. If the complex only shows some part of the functional groups while other groups are absence, then it is most likely that the complex is M(II)-tartrate or M(II)-nicotinamide only. To support this, infrared spectra of complexes 3 and 6 were compared not only to that of the free ligand (KNa-tartrate and nicotinamide), but also compared to related complexes. Particularly, the infrared spectra of complex 3 was compared to that of complex 2, which is made from a reaction of Mn(II) and KNaT, whereas Mn(II)-nicotinamide (complex 1) was not yielded using a similar technique. Meanwhile, the infrared spectra of complex 6 was compared to that of complex 4, which is Cd(II)-nicotinamide, and complex 5, which is Cd(II)-tartrate.

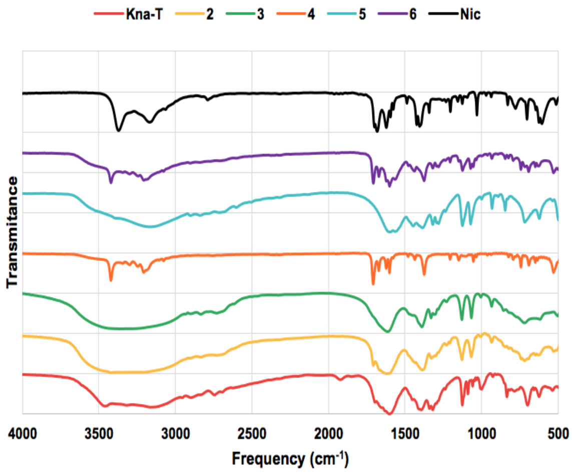

Figure 3. Infrared spectra of complexes 2 to 6, compared to free ligands (KNa-T = KNa-tartrate; Nic = nicotinamide)

Assignment of the functional group of each complex by infrared analyses shows that complexes of 2, 3, and 5 have identical infrared spectrum profiles to that of KNa-T, which contain characteristic tartrate ligand, namely 1300–1200 cm^{-1} (ν_{as} C–OH) and 1100-1000 cm^{-1} (ν_s C–OH), 1700–1600 cm^{-1} (ν_s & ν_{as} COO^-). In addition, ν_s C–H groups were also observed in the area of 3000-2900 cm^{-1}. The presence of water, either as ligand or lattice molecule and hydroxyl groups of the tartrate, is confirmed by the broadband around 3400–3100 cm^{-1}, along with an intense broad peak observed close to 1400 cm^{-1} that corresponds to O–H (in-plane bending). Particularly for complex 3, the amide groups of the nicotinamide were absence. In other words, complexes of 2, 3, and 5 were all M(II)-tartrate hydrate. These spectra are also following previously reported M(II)-tartrate [2, 4].

Meanwhile, for complexes 4 and 6, infrared analyses of those compounds confirm that they have identical infrared spectrum profiles to that of nicotinamide free ligand, namely $–NH_2$ and C=O groups, which were observed as two sharp peaks (3368 and 3061 cm^{-1}) and one very sharp peak (1681 cm^{-1}), respectively. The –NH_2 and C=O peak of the metal complexes were shifted to higher wavenumbers. In detail, the characteristic peaks observed in Figure 2 are presented in Table 3.

Based on infrared data and analyses (Figure 2 and Table 3), functional groups identification of all complexes indicates that the complex of M(II)-tartrate-nicotinamide was not achieved. Instead, complexes 3 and 6 are most likely only has only one type of ligand (tartrate only or nicotinamide only). Hence the products were Mn(II)-tartrate hydrate and Cd(II)-nicotinamide, respectively.

Table 3. Infrared data of complexes 2 to 6.

2	3	4	5	6	Interpretation
1:1:0	1:1:2	1:0:2	1:1:0	1:1:2	
3400-3100	3400-3100	-	3400-3100	-	*v*(O–H) of water and hydroxyl (broad)
-	-	3419, 3205	-	3419, 3204	*v*(N–H) of primary amine
2928	2928	3075	2900	3075	*v*(C–H)
1700-1600	1700-1600	1707	1650-1550	1706	*v*(C=O)
1328, 1298	1329, 1301	-	1318, 1280	-	*v*(C–OH) asymmetric
1128, 1066	1128, 1066	-	1124, 1071	-	*v*(C–OH) symmetric

Note: 2 and 3 = Mn(II) complexes; 4, 5, 6 = Cd(II) complexes

To support this result, powder-XRD analyses was performed to all complexes, and the result is presented in Figure 4. In accordance to infrared analyses, the X-ray diffraction pattern of complexes 2 and 3 are identical, which confirms that the nicotinamide is absence in complex 3, and instead, Mn(II)-tartrate was precipitated out from the reaction. Similarly, the X-ray diffraction pattern of complexes 4 and 6 are also identical, which confirms that the tartrate is absence in complex 6, and instead, Cd(II)-nicotinamide was yielded from the reaction. To be noticed, the diffraction pattern of complex 3 and 6 shows that there was no indication of a mixture of M(II)-tartrate and M(II)-nicotinamide in the sample that co-crystallized together by both metal ions.

Meanwhile, for complex 5, since it is a reaction between Cd(II) salt and the KNaT in 1:1 ratio, the product is indeed a complex of Cd(II)-tartrate. Although the infrared spectra of complex 5 is identical to that of complex 2 and 3, the crystal system and crystal packing of complex 5 are different to that of complex 2 and 3, which is confirmed by the different powder diffraction pattern (peaks positioned at 2theta angles). Moreover, complex 5 shows less intensity and less number of peaks than that of complex 2 and 3, which indicates a lower level of crystallinity. This is also supported by the fact that complex 5 forms fine powder, while complex 2 and 3 forms block colorless crystals.

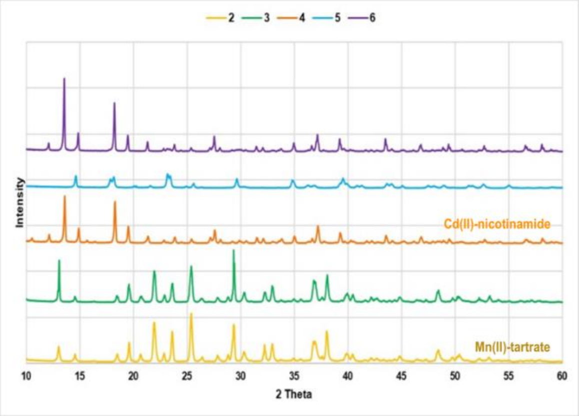

Figure 4. Powder diffraction pattern of complexes 2, 3, 4, 5, and 6 (from bottom to top, respectively)

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Since the solid product of reactions 4 and 6 turned out to be Cd(II)-nicotinamide complex, further analysis was done to assign whether the complex is in a neutral form or anionic form. In a neutral form, the chloride will act as a coordinated ligand, whereas in an ionic form, the chloride will occupy the crystal lattice as free ions. The complex was then diluted in water and tested with an aqueous silver nitrate solution. Both solutions give a significant amount of white precipitate of silver chloride. Therefore, complexes 4 and 6 were confirmed to be ionic complexes. Melting point test was also conducted as additional information in which complexes 2 and 3 decomposes around 320-330 °C, whereas complex 5 melts at 220 °C. Complexes 4 and 6 decomposes around 300-310 °C.

To sum up, based on IR and powder-XRD analyses, the targeted M(II)-tartrate-nicotinamide complex was not successfully obtained. Instead, Mn(II)-tartrate and Cd(II)-nicotinamide chloride complexes were formed from the respective reactions (Table 4).

Table 4. Characterization result of each solid product based on IR and powder-XRD analyses

Code	**Metal ions**	**Ligand(s)**	**Conclusion**
1	Mn(II)	Nic	Colorless solution
2	Mn(II)	KNaT	Mn(II)-tartrate hydrate
3	Mn(II)	KNaT + Nic	Mn(II)-tartrate hydrate
4	Cd(II)	Nic	Cd(II)-nicotinamide chloride
5	Cd(II)	KNaT	Cd(II)-tartrate hydrate
6	Cd(II)	KNaT + Nic	Cd(II)-nicotinamide chloride

Tartrate vs Nicotinamide Ligand Selectivity

Analyses of complexes 3 and 6 by IR and powder-XRD reveal that in a presence of both tartrate and nicotinamide mixture, Mn(II) reaction resulting in Mn(II)-tartrate hydrate complex, whereas Cd(II) resulting in Cd(II)-niacinamide chloride complex. Powder-XRD analysis also confirms that there was no indication of M(II)-tartrate and M(II)-nicotinamide that co-crystallized at the same time by both metal ions. In the case of Mn(II) complex, tartrate tends to coordinate as ligand than the nicotinamide, although the molar ratio of nicotinamide was doubled than that of tartrate ligand to increase the possibility of gaining nicotinamide as ligand. In contrast, the neutral nicotinamide ligand is more predominant in coordinating in the Cd(II) complex than the anionic tartrate.

The tartrate's negative charge enhances the tartrate ion's dominance over the nicotinamide neutral molecule in the complexation of Mn(II) in a water-methanol mixture system. In the Cd(II) complex, the positive charge of the metal ion is balanced by the presence of two chloride ions from the initial cadmium salt.

The tartrate-nicotinamide ligand selectivity in the crystallization of Mn(II) and Cd(II) complexes is likely due to the use of tartrate salt as a precursor. Additional reactions were conducted to confirm this. When the tartrate salts were replaced by the *L*-tartaric acid, some different results were observed: (1) reaction between Mn(II) or Cd(II) with *L*-tartaric acid gives a clear solution (no precipitation); (2) reaction between Mn(II) with *L*-tartaric acid and nicotinamide also resulting in clear solution (no precipitation); (3) reaction between Cd(II) with *L*-tartaric acid and nicotinamide forms white powder of Cd(II)-nicotinamide chloride complex. Therefore, the use of tartrate salt is crucial in this tartrate vs nicotinamide selectivity.

Furthermore, another factor may also take a role in the tartrate vs nicotinamide selectivity during crystallization of Mn(II) and Cd(II) complexes, which is the choice of solvent. A mixture of water-methanol results in a polar solvent, in which the solubility of precipitated Mn(II) and Cd(II) complexes in this mixture turns out to be considerably low. If other types of solvent were used, for example, dimethylformamide or dimethylsulfoxide, different results might be obtained. In general, the solvent may affect crystallization in terms of the solubility of the reactants and products. The solvent also governs the chemical species distribution in the solution. Some solvent molecules may also involve a ligand or lie in the crystal lattice to stabilize the crystal packing.

Mn(II)-tartrate hydrate obtained in this work may adopt one of several previously known octahedral geometry structures around the metal center [1–3], while Cd(II)-nicotinamide chloride may adopt either octahedral or tetrahedral geometries [4]. The true form of the crystal structure can be determined by single-crystal XRD analysis.

CONCLUSION

This work has not successfully obtained the targeted M(II)-tartrate-nicotinamide complexes. Based on infrared spectroscopy and powder-XRD analyses, as well as qualitative anion test, the products were Mn(II)-tartrate hydrate (complex 3) and Cd(II)-nicotinamide chloride (complex 6). In addition, powder-XRD analysis confirms no indication of M(II)-tartrate and M(II)-nicotinamide that co-crystallized together at the same time by both metal ions. Nevertheless, ligand selectivity of tartrate vs. nicotinamide in a water-methanol system has been observed. The crystallization of Mn(II) and Cd(II) complexes in this work is probably due to tartrate salt as a precursor and the choice of solvent mixture.

ACKNOWLEDGEMENTS

This project was funded using the DPP-SPP 2020 Scheme provided by the Faculty of Mathematics and Natural Sciences, Brawijaya University. Authors are gratefully thanks the Chemistry's MOF group member for teamwork discussion and the Department of Chemistry, Brawijaya University for laboratory and facilities supports. Authors also acknowledge the XRD facility (PANalytical X'Pert3 Powder) at Central Laboratory of Life S Brawijaya University (LSIH-UB).

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