RESEARCH ARTICLE

Synthesis and Characterization of Two New Hofmann-Type-Like Compounds From Some Alkali Metal Atoms and Glycine Anhydride

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Abstract: In this study, two new compounds with their closed formula, $C_8H_{10}K_2N_6NiO_4$, and $C_8H_{10}Na_2N_6NiO_4$, were synthesized, the first in crystal form and the second in powder form. Various properties of these compounds were characterized by SC-XRD and FT-IR methods. Theoretical information about the compounds was obtained with the help of the Gaussian 03 program. The molecular formula that best reflects the structural properties of this first 3D compound, which is in crystalline form and has polymeric properties, can be given as $\{K_2(GA)(H_2O)_2[Ni(CN)_4]\}_n$. With a similar thought, it can be suggested that the molecular formula that best reflects the structural properties of the second 3D compound in powder form and with polymeric properties will be $\{Na_2(GA)(H_2O)_2[Ni(CN)_4]\}_n$. The asymmetric unit of the $\{K_2(GA)(H_2O)_2[Ni(\mu_4\text{-}CN)_4]\}_n$ compound is composed of a half Ni(II) ion, one K(I) cation, two cyanide ligands, a half GA ligand molecule, and one bounded water ligand molecule. The structure of the compound, which consists of 3D polymeric chains, is formed by various bonds between the GA molecule, K(I) cations, water ligand molecules, and $Ni(CN)_4$ ions.

1. INTRODUCTION

The entry of Hofmann-type compounds and clathrates into scientific research began with synthesizing a new compound for the first time in 1897 (1). If a chemical complex has at least two components, this compound may be called "clathrate" in the chemical literature (2–4).

The clathrates, which have very different usage areas according to their structural properties, have recently been obtained by many researchers with very different properties and are still being obtained. More detailed information on clathrates can be found in previous studies (5,6).

The general formula of Hofmann-type compounds synthesized in scientific studies by researchers has formula as $M(II)LM'(II)(CN)_4.nG$ and $M(II)LM'(II)(CN)_4$, respectively. The meaning of each term in this formula has been explained broadly in various studies (2,4,7). Our published studies on the Hofmann-type compounds can be seen in the literature (8,9). One published article is about Hofmann-type-like clathrates formed by 4AP and water molecules (H_2O) (10).

A compound desired to be synthesized as the Hofmann type may occur in a form that does not fully comply with the "Hofmann type compounds" formula. Such compounds are called "Hofmann-type-like compounds". Hofmann-type-like compounds are usually formed by adding more ligand

molecules instead of two ligand molecules, attaching the solvent molecule to the transition metal atom, using another ligand alongside the first ligand, or replacing the transition metal atom with another metal atom.

A formula such as MLL'M'(II)(CN)$_4$ can be suggested for the structural formula of Hofmann-type-like compounds formed by chance or planning because of a chemical reaction. In this formula, M denotes any metal atom and L' additional ligand molecule in the reaction medium. Hofmann-type-like compounds can form polymeric layers ranging from 1D to 3D, depending on the type of chemical bonds formed between [M'(CN)$_4$]$^{2-}$ anions and [MLL']$^{2+}$ cations.

The results of replacing the transition metal atom in the Hofmann-type compound with another metal atom or adding a new ligand molecule to the structure of the Hofmann-type compound obtained from the same transition metal atom and the same ligand molecule can be seen by comparing their spectroscopic and crystalline data. If the change in the structure of the compound leads to a positive increase in the stability, volume, gas storage, and some other properties of the obtained crystal structure, further studies can be conducted on this subject. For this reason, we wanted to obtain new Hofmann-type-like compounds in crystal form by using some alkali metal atoms and a different ligand molecule (Glycine anhydride; GA) from the previous ones.

The structure with the closed formula (C$_4$H$_6$N$_2$O$_2$) and in which two oxo groups are bonded instead of two hydrogen atoms in the 2 and 5 position in a piperazine molecule is called "glycine anhydride" (GA). In the GA molecule, both N-H and C=O groups are in a Trans state concerning each other. Various studies and information about this GA molecule can be found in different literature, which is structurally small but interesting and important in terms of various properties (11,12).

This study aims to obtain crystal forms of Hofmann-type-like compounds using a different ligand molecule and two alkali metal atoms. In addition to the chemicals and GA ligand molecules routinely used to achieve the goal, the water molecule, which is abundant in the reaction medium, was also used as a second ligand or guest molecule. Also, the alkaline potassium (K) and sodium (Na) atoms were used instead of the transition metal atom. In this study, two new Hofmann-type-like compounds were obtained, one in crystal form and the other in powder form.

2. EXPERIMENTAL SECTION

2.1. Materials
Starting materials used to obtain the desired compounds: Glycine anhydride (GA, C$_4$H$_6$N$_2$O$_2$, Sigma Aldrich, 99%), potassium tetracyanonickelate(II) monohydrate {K$_2$[Ni(CN)$_4$]·H$_2$O, Fluka, 96%} and sodium tetracyanonickelate(II) trihydrate {Na$_2$[Ni(CN)$_4$]·3H$_2$O, Chempro Tech Co, 96%}. The starting materials used in the synthesis of the obtained compounds were used as they were obtained commercially.

2.2. Syntheses of Hofmann-Type-Like Compounds [M$_2$(GA)Ni(CN)$_4$]·(H$_2$O)n or [M$_2$(GA)(H$_2$O)$_n$Ni(CN)$_4$] [M(I) = K and Na)]
Procedures followed to obtain the first compound: 1 mmol of potassium tetracyanonickelate(II) monohydrate (0.259 g) was dissolved at 65 °C (50 mL), and 1 mmol of GA (0.114 g) was added to this solution. This mixture was stirred for 2 hours at 65 °C, then filtered and crystallized under normal atmospheric conditions. About two months after this study, a transparent, colorless, crystalline compound with a yield of approximately 61%, was obtained.

Procedures followed to obtain the second compound: 1 mmol of Na$_2$[Ni(CN)$_4$]·3H$_2$O (about 0.209 g) was dissolved at 65 °C (50 mL), and 1 mmol of GA (0.114 g) was added to this solution. As a result of all these chemical reactions, the Hofmann-type-like clathrate or Hofmann-type-like compound was suspended in aqueous media. Then, this mixture was stirred with a magnetic stirrer at 65 °C for one week. Afterward, the whole mixture was filtered, washed three times with distilled water and twice with pure ethyl alcohol, and dried. Despite all efforts, the crystal form of the second compound could not be obtained. Therefore, its powder form was obtained and used in all spectroscopic studies.

Through the utilization of experimental techniques and spectroscopic analyses, researchers were able to ascertain that the crystalline structure of the initial chemical can be represented by the formula K$_2$(GA)(H$_2$O)$_n$Ni(CN)$_4$. For brevity, this compound will be subsequently denoted as "1". Likewise, it was postulated that the chemical composition of the second compound, in its powdered state, may be represented by the formula Na$_2$(GA)(H$_2$O)$_n$Ni(CN)$_4$. The subsequent compound will be henceforth denoted as "2".

2.3. Instrumentation
The experimental values were obtained from Vertex 70 FT-IR Spectrometer for FT-IR, Perkin-Elmer optima 4300 DV ICP-OES for metal amounts, and CHNS-932 (LECO) for other atom

amounts. The amounts of metal and other components in the compounds are given in Table 1.

Crystal data of compound **1** were collected at normal room conditions (296 K) with the aid of a BRUKER D8-QUEST diffractometer. The crystal structure of the compound was resolved by direct methods; SHELXS-2013 (13) was refined by full-matrix least squares methods; SHELXL-2013 (14); data was collected by APEX2 (15); for molecular graphics: Mercury software (16) was used, and analyses were performed with WinGX (17) software. The information obtained on this subject and their details are shown in Table 2 (CCDC number: 2104239).

Table 1: Elemental analysis results of the compounds.

The compound and molecular weight M_r (g)	Found (%) / (Calculated) (%)					
	C	H	N	K	Na	Ni
$K_2(C_4H_6N_2O_2)(H_2O)_2Ni(CN)_4$ $M_r = 391.10$	25.19 (24.57)	2.49 (2.58)	21.88 (21.49)	19.76 (19.99)	- (-)	14.83 (15.01)
$Na_2(C_4H_6N_2O_2)(H_2O)_2Ni(CN)_4$ $M_r = 358.88$	26.31 (26.77)	2.59 (2.81)	23.67 (23.42)	- (-)	12.59 (12.81)	15.93 (16.35)

Table 2: The refinement parameters in compound **1**.

Empirical formula	$C_8H_{10}K_2N_6NiO_4$
Formula weight	391.13
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	9.6592 (18)
b (Å)	6.9310 (12)
c (Å)	12.3958 (19)
$\checkmark$ (°)	116.588 (11)
V (Å³)	742.1 (2)
Z	2
D_c (g cm⁻³)	1.750
θ range (°)	3.4-28.3
Measured refls.	15887
Independent refls.	1852
R_{int}	0.058
S	1.07
R1/wR2	0.038/0.111
$\Delta\rho_{max}/\Delta\rho_{min}$ (eÅ⁻³)	0.53/-0.89

3. RESULTS AND DISCUSSION

3.1. Crystallographic Analysis of 1
The crystal structure studies for compound **1** show that it is a 3D polymeric coordination compound.

The asymmetric unit of compound **1** contains half Ni(II) ion, one K(I) cation, two cyanide ligands, half GA ligand, and one H_2O ligand (see Figure 1).
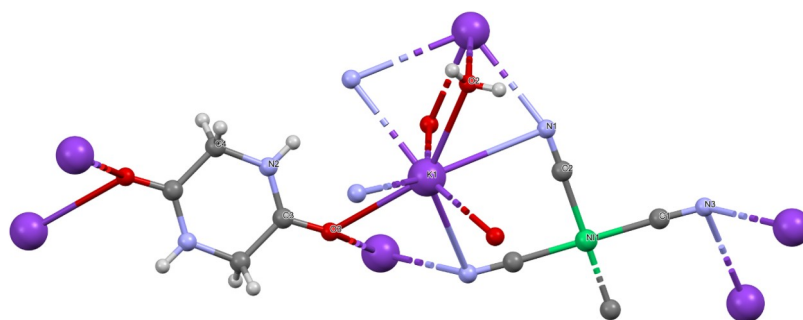

Figure 1: The molecular structure of compound **1** showing the atom numbering scheme.

In the 3D polymeric structure of compound **1**, the Ni(II) ion is surrounded by four carbon atoms of the four cyanide ligands [Ni1-C1 = 1.867(2) Å and Ni1-C2 = 1.863(3) Å] in a square planar form. The same bond length was 1.865(4) Å in a crystal structure we obtained earlier (9). The K(I) cation is coordinated by four cyanide nitrogen atoms [bond distances ranged between 2.919(3) - 3.238(3) Å], two oxygen atoms [K1-O3 = 2.992(2) Å and K1-O3^{vi} = 2.881(2) Å] from GA molecule and two oxygen atoms [K1-O2 = 2.842(2) Å and K1-O2^{iii} = 2.851(2) Å] from H_2O molecule [(iii) 1-x, 1-y, 2-z; (vi) 1-x, 1/2-y, 3/2-z]. In the studies of other researchers, K-N bond lengths were found to be between 2.704(2) and 2.937(3) Å (18). K-O bond lengths were also found to be between 2.69(1) and 3.17(1) Å in studies with different ligand molecules by other researchers and us (19,20). The Ni(II) ions and K(I) cations are bound to each other with cyanide ligands. In these bonds, the Ni⋯K intervals are between 5.487 Å and 5.852 Å, while the K⋯K intervals are 3.914 Å, 4.404 Å, 8.997 Å and 9.855 Å. In addition, as mentioned before, K(I) cations also formed bonds with the oxygen atoms of GA and H_2O ligands. Combining these ions and ligands with the indicated bonds produces a 3D coordination polymer (see Figure 2). The bond distances, bond angles and hydrogen bond parameters of compound **1** are given in Table 3, respectively. The molecules of compound **1** are also connected by strong hydrogen bonds (Table 4). These strong hydrogen bonds play a major role in creating a supramolecular network.

3.2. Spectral Examination of Compounds
The experimental spectra of compounds **1** and **2** are given in Figure 3 (a - d), as well as their theoretical spectra for comparison. When the FT-IR spectra of the compounds are examined, it is seen that there are a large number of similarities and a small amount of differences in them. The reason for these similarities is that the GA molecule, $Ni(CN)_4$ ion group, and the H_2O molecule are common in the structure of the compounds. The

reason for the differences in the spectra of compounds **1** and **2** is the presence of different alkaline metal (K and Na) atoms in the structure of each compound.

The spectral data of compound **1** were analyzed separately for the vibrations of GA, H_2O molecules, and $[Ni(CN)_4]^{2-}$ anions in its structure. Similar results apply to compound **2**. All spectral data of compounds are given in Tables S1 and S2.

3.2.1. Vibrations of the GA molecule
Peptides are short chains of amino acids, which are very important chemically and biologically, linked by peptide bonds. Peptides can be found structurally in the chain and cyclic forms. As the number of amino acids in a peptide's structure increases, both the structure and chemical function of that peptide increase. If the number of amino acids in the structure of a peptide is more than about fifty, that peptide is known as a "polypeptide", that is, a "protein" (21). Proteins are chemical compounds that are very valuable in terms of the vital behavior of living things. GA is an organic compound and is the smallest cyclic dipeptide consisting of a six-membered ring containing two amide bonds (22).

The GA molecule is among the components that make up several molecules with significant biological activity. In the cyclic ring of the GA molecule, all other atoms are located almost in the same plane, except for the hydrogen atoms bonded to the alpha-carbon atoms. The molecular structure of GA is shown in Figure S1 a. Since there are parts that can easily donate electrons, such as N-H, C=O, and ring structure in the structure of the GA molecule, it can make a very different number of bonds in the chemical reactions it participates in (23). The number of bonds to be made by the GA molecule in a chemical reaction depends on the degree of activity of its parts, such as N-H, C=O, and the ring structure.

Table 3: Selected bond distances and angles (Å, º).

Ni1-C1	1.867(2)	Ni1-C2	1.863(3)
K1-N1^{iii}	3.047(3)	K1-N1	3.238(3)
K1-N3^{vii}	2.919(3)	K1-N3^{i}	3.182(3)
K1-O3^{vi}	2.881(2)	K1-O3	2.992(2)
K1-O2	2.842(2)	K1-O2^{iii}	2.851(2)
C2-Ni1-C1^{i}	89.03(10)	C2-Ni1-C1	90.97(10)
K1-O2-K1^{iii}	86.89(6)	O2-K1-N1	60.20(6)
N1-K1-N1^{iii}	103.03(6)	N3^{i}-K1-N1	80.91(7)
N3^{vii}-K1-N1	140.30(8)	O3-K1-N1	139.96(7)
O2^{iii}-K1-N1	66.45(7)	O2-K1-O3	147.21(6)
Symmetry codes: (i) −x+2, −y+1, −z+2; (iii) −x+1, −y+1, −z+2; (vi) −x+1, y−1/2, −z+3/2; (vii) x−1, −y+1/2, z−1/2.			

Table 4: Hydrogen-bond parameters (Å, °).

D-H···A	D-H	H···A	D···A	D-H···A
N2—H2···N1[iii]	0.86	2.16	2.962 (3)	154
O2—H2A···O3[viii]	0.83 (2)	2.05 (2)	2.860 (3)	167
O2—H2B···N3[ix]	0.81 (2)	2.36 (3)	3.080 (3)	149
Symmetry codes:	(iii) −x+1, −y+1, −z+2; (viii) x, −y+1/2, z+1/2; (ix) −x+2, y−1/2, −z+5/2.			
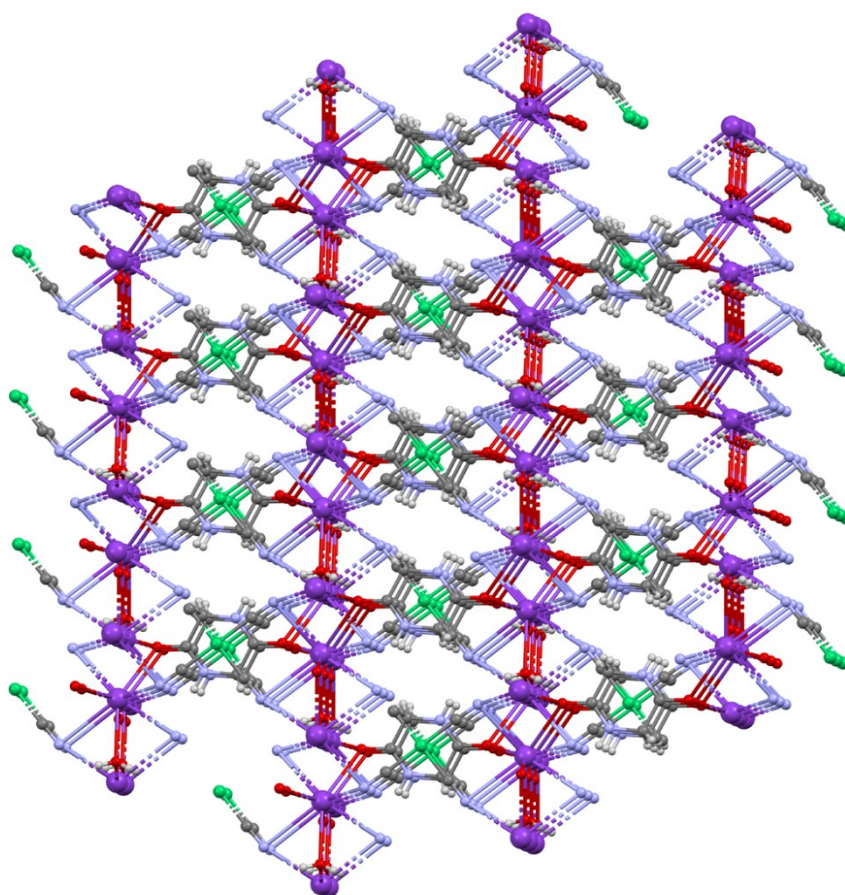
Figure 2: 3D supramolecular network in compound **1**.

The GA molecule has a flexible structure because its six-membered ring structure can change from the boat form to the planar form or vice versa with an energy difference of only a few kcal/mol. The GA molecule, which has a planar ring structure in its solid state, has C_{2h} symmetry. Since there are 14 atoms in the GA molecule's structure, it has a total of 36 vibration modes. Of these vibration modes, 12 of the 23 in-plane vibrations have Raman-active and A_g symmetry, while the other 11 have IR active and B_u symmetry. While 6 of the remaining 13 out-of-plane vibrations have Raman active and B_g symmetry, the other 7 have IR active and A_u symmetry (21,24).

When Figure S1 (a) is examined, it is understood that when the GA molecule forms a compound under normal conditions, it will only form bonds from its own oxygen atoms. Because the oxygen atoms in the structure of the GA molecule have the largest (-) charge values compared to other atoms. The SC-XRD examination of compound 1 shows that the GA molecule only makes bonds from oxygen atoms to other atoms in compound **1** (see Figure 1).

In the literature review on the GA molecule, it is seen that it makes zero bonds (guests) (25), two bonds (24), and four and more bonds (23) in some of its compounds. The number of bonds that any ligand molecule makes in a compound will cause changes in some vibration modes according to its free state because the bonds formed in a

compound will change the bond constant and bond length of the functional group forming that bond.

When Table S3 is examined, it is seen that the ν(NH) vibration of the GA molecule in compounds **1** and **2** shifts towards the low wavenumber region by 8 and 12 cm^{-1} values, respectively. The reason for this shift is the very weak interactions of the NH group's hydrogens with the cyanide group's carbon atoms.

Similarly, it is seen that the peak originating from Fermi resonance in the GA molecule in compounds **1** and **2** shifts towards the wavenumber region as high as 34 and 36 cm^{-1}, respectively. The reason for this shift is that the groups participating in forming the Fermi resonance are affected by the formation of the compound.

The amount of shift to high wavenumber in the combination bands occurring in the wavenumber range of approximately 3000 and 3100 cm^{-1} in the compounds is considerably higher than the other modes. It can be thought that this is due to the sum of the changes in the modes participating in the combination event.

Particularly, there appears to be a large shift in the modes of ν(CH) vibration of the GA molecule in compounds **1** and **2** to the higher wavenumber. The reason for this shift is that the CH groups' hydrogen interacts with the cyanide group's carbon atoms. These interactions make the stretching movements of the CH group difficult.

It is seen that the largest value of shifts in the vibration modes of the GA molecule in compounds occurs in the stretching vibrations of the carbonyl group (C=O). This shift is because the oxygen of the C=O group interacts with the alkali metal atoms and the hydrogen atoms of the other ligand molecules, such as water. These interactions make the stretching and bending movements of the C=O group more difficult. The reality of this situation is clearly seen in the values in the last row of Table S1.

It can be said that some minor shifts in the vibration frequencies of the GA ligand-constituting compounds are due to some changes in the environmental conditions of GA due to the formation of compounds. The vibration wavenumbers of the GA, which are most affected by environmental conditions or compound formation, and their shifts are marked in bold in Table S1 (with Δ sign).

In general, in vibration spectroscopy, the new vibration value that emerges as a result of the interaction of the stretching vibration of any functional group of a molecule and the overtone of

the bending vibration of that group is called "Fermi resonance vibration". Fermi resonance can also occur due to hydrogen bonds formed by any group with other atoms around it. From the examination of Table S3, the vibrational mode at 3331 cm^{-1} in the solid state IR spectrum of the GA molecule belongs to its free ν(NH) mode. The vibration peak at 3195 cm^{-1} is the Fermi resonance vibration, which arises from the interaction of the ν(NH) mode and the overtone of the δ(NH) bending mode (26)

In the IR spectra of the compounds, there is a peak at 535 and 547 cm^{-1}. While this peak is actually an IR inactive peak of the free GA molecule or $[Ni(CN)_4]^{2-}$ ion, it can be thought that it belongs to a peak that becomes IR active as a result of its contribution to the formation of compounds. Perhaps this vibration mode may have been composed of the sum of the vibration modes of some peaks with lower wavenumbers, or it may have been composed of the overtones of the vibration modes of those peaks with lower wavenumbers.

3.2.2. Vibrations of the H_2O in compounds
The presence of overlapping ν_{as}(OH) and ν_s(OH) modes in certain water compounds leads to the formation of a significantly broad vibration band in their vibration spectra, spanning a wavenumber range of around 3500 to 3200 cm^{-1}. A distinct and intense stretching vibration peak is observed at around 3600 cm^{-1} wavenumber when free water molecules are present within a chemical product. Nevertheless, it is worth noting that certain water compounds, including bound water molecules, exhibit distinct vibration modes that manifest at frequencies lower than the stretching vibration frequency observed in free water molecules. We have experimentally obtained these vibration modes at wavenumbers ν_{as}(OH) 3470 cm^{-1}, ν_s(OH) 3257 cm^{-1}, and δ(OH) 1641 cm^{-1}.

The presence of the NH group, C=O group, and even water molecules as ligands or guests in a chemical compound makes it very difficult to explain 1700-1550 cm^{-1}—all these vibration peaks specified overlap with each other in the same region. As a result of this overlap, each vibration peak does not appear on its own but as a single highly enlarged peak (27,28).

As seen in the experimental FT-IR spectra of compounds **1** and **2** in Figure 3 (a) and 3 (c), ν_{as}(OH) and ν_s(OH) stretching vibrations of the bonded water molecules have appeared at wavenumbers as individual peaks, 3565; 3456 cm^{-1} and 3576; 3472 cm^{-1}, respectively. According to these values obtained, the vibration modes ν_{as}(OH) and ν_s(OH) in compound **1** shifted to higher wavenumbers of 95 and 199 cm^{-1} compared to

their values in the free water molecule. In compound **2**, the shift values of $v_{as}(OH)$ and $v_s(OH)$ vibration modes to this high wavenumber were realized as 106 and 215 cm⁻¹.

When the broad peak located in the wavenumber range of approximately 1760 to 1550 cm⁻¹ in the FT-IR spectrum of compound **1** is examined more closely, it is seen that it has another peak at 1646 cm⁻¹ wavenumber in addition to the peak at 1669

cm⁻¹ wavenumber. This new peak can be attributed to the bending vibration of the water molecule [δ(OH)]. The same peak appeared in the FT-IR spectrum of compound **2** at 1653 cm⁻¹. According to these data, due to the participation of the water molecule in the formation of the compound, the δ(OH) vibration mode shifted to the wavenumber region as high as (5 and 12) cm⁻¹ in compounds **1** and **2**, respectively.
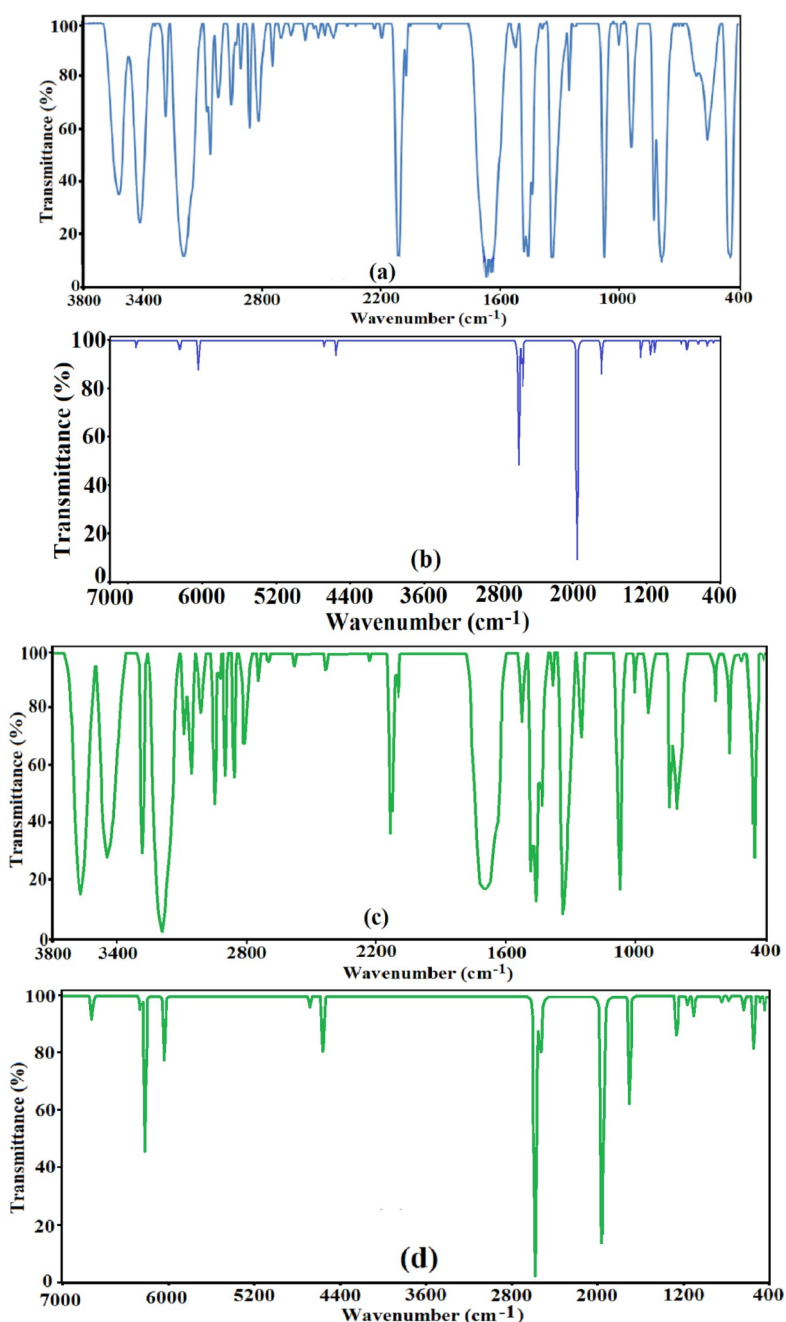

Figure 3: FT-IR spectra of compound **1** are experimental (a), theoretical (b), and FT-IR spectra of compound **2** are experimental (c), theoretical (d).

Some theoretical calculations with the Gaussian program and source searches have been made about the bonds between the oxygen atoms of the GA and H_2O ligand molecules of the K and Na metal atoms in compounds **1** and **2**. According to these studies, it has been observed that some of the wavenumbers of the Na-O stretching mode occur at values greater than 400 cm^{-1}, while all of the wavenumbers of the K-O stretching mode occur at wavenumbers less than 400 cm^{-1} (29). Since the working range of the FT-IR spectrometer used is in the range of 4000-400 cm^{-1} wavenumber, information about the K-O bonds in compound **1** could not be obtained.

An examination of Figure 3 (c) shows that the wavenumber of the stretching vibration [v(Na-O=C)] of the bond of the sodium atom in compound **2** with an oxygen atom of the GA molecule is 472 cm^{-1}. Similarly, it is seen that the wavenumber of the stretching vibration [v(Na-OH$_2$)] of the bond between the sodium atom in compound **2** and the oxygen atom of the water molecule is 412 cm^{-1} (29).

3.2.3. Vibrations of the $[Ni(CN)_4]^{2-}$ group in compounds

If there is a cyanide group in the structure of a chemical compound, there is usually a very sharp v(CN) band in the vibration spectrum of that chemical compound in the range of 2200-2000 cm^{-1} (30).

The determination of the $[Ni(CN)_4]^{2-}$ ion in the compounds **1** and **2** was based on the work of McCullough et al. for the $Na_2[Ni(CN)_4]\cdot 3H_2O$ compound (31). Comparisons of $[Ni(CN)_4]^{2-}$ ions in both compound **1** and compound **2** with the vibration modes of $[Ni(CN)_4]^{2-}$ ions in $K_2[Ni(CN)_4]\cdot H_2O$ and $Na_2[Ni(CN)_4]\cdot 3H_2O$ compounds are given in Table S2, respectively.

In the FT-IR spectrum of the $K_2[Ni(CN)_4]\cdot H_2O$, the E_u mode is at 2122 cm^{-1}. This vibration was observed at 2127 cm^{-1} in **1**. Similarly, the v(C≡N), E_u stretching vibration mode of $Na_2[Ni(CN)_4]\cdot 3H_2O$ is observed at 2130 cm^{-1}. This vibration was observed at 2139 cm^{-1} in **2**.

In general, it consists of ^{13}C atoms, about 1.11% of all carbon atoms of a substance. Therefore, the contribution of ^{13}C atoms in a substance to any event is very low. In the FT-IR spectra of compounds **1** and **2**, due to the replacement of the normal carbon atom of the cyanide group with a ^{13}C isotope carbon atom, a very weak intensity v(^{13}C≡N) vibration band appeared at 2086 and 2092 cm^{-1} wavenumbers, respectively.

In the FT-IR spectrum of $K_2[Ni(CN)_4]\cdot H_2O$, the v_9(Ni–CN), E_u mode, is observed at 544 cm^{-1}. This

vibration was observed at 591 cm^{-1} in **1**. Similarly, in the FT-IR spectrum of $Na_2[Ni(CN)_4]\cdot 3H_2O$, the v_9(Ni–CN), E_u mode, is observed at 550 cm^{-1}. This vibration was observed at 596 cm^{-1} in **2**.

When the experimental and theoretical FT-IR spectra of the compounds are examined together, it can be thought that they are very different from each other. However, they support each other scientifically. The reasons why the experimental and theoretical FT-IR spectra appear different can be explained as follows. In the theoretical calculation, a compound is considered as gaseous and only as much as its empirical formula. As a result, the theoretical FT-IR spectrum of the compound has a plain appearance. Experimentally, the compound is in a crystalline form, solid state, and an almost infinite number of them interact.

For this reason, many atomic and intermolecular interactions are also active in the experimental FT-IR spectra. As a result, the experimental FT-IR spectrum of the compound has a more complex appearance. Another factor is the emergence of combination and overtone bands at high wavenumbers of vibration modes occurring at small wavenumbers while taking the experimental spectrum.

2.3. Computational Studies

Considering the similarity of the experimental data of compound **2**, which was obtained in powder form, to compound **1**, which was in crystal form, it was desired to obtain its 3D structure. For this purpose, Na atoms were taken instead of K atoms in the crystal structure of **1** in the Gaussian 03 program (32), and their bond lengths were optimized. In order to compare the experimental and theoretical results of both compounds studied, theoretical calculations were made by taking only the parts of them, indicating their empirical formula. The operation numbers assigned by the Gaussian 03 program to the atoms of GA and atoms of compounds **1** and **2** are given in Figure 4.

To compare with the experimental spectra of compounds **1** and **2**, their theoretical spectra were calculated with the Gaussian 03 program using the LanL2MB basis set by the DFT method. They are scaled with a recommended coefficient of 0.958 for the calculation method used. The theoretical spectra obtained for the compounds are given in Figure 3 (b) and (d), respectively.

3.3.1. Mulliken atomic charge values of the compounds

The Mulliken electronic charge values of each atom in the GA molecule and compounds **1-2** were calculated and displayed with the GaussView program (33). The results obtained are shown as 3D graphs in Figure S1.

The differences between the charge values of the two oxygen atoms of the free GA molecule and the charge values of the same two oxygen atoms of the GA molecule bonded in compounds **1** and **2** were calculated as 0.287e and 0.293e for compound **1**. Similarly, these differences were calculated as 0.200e and 0.249e for compound **2**.
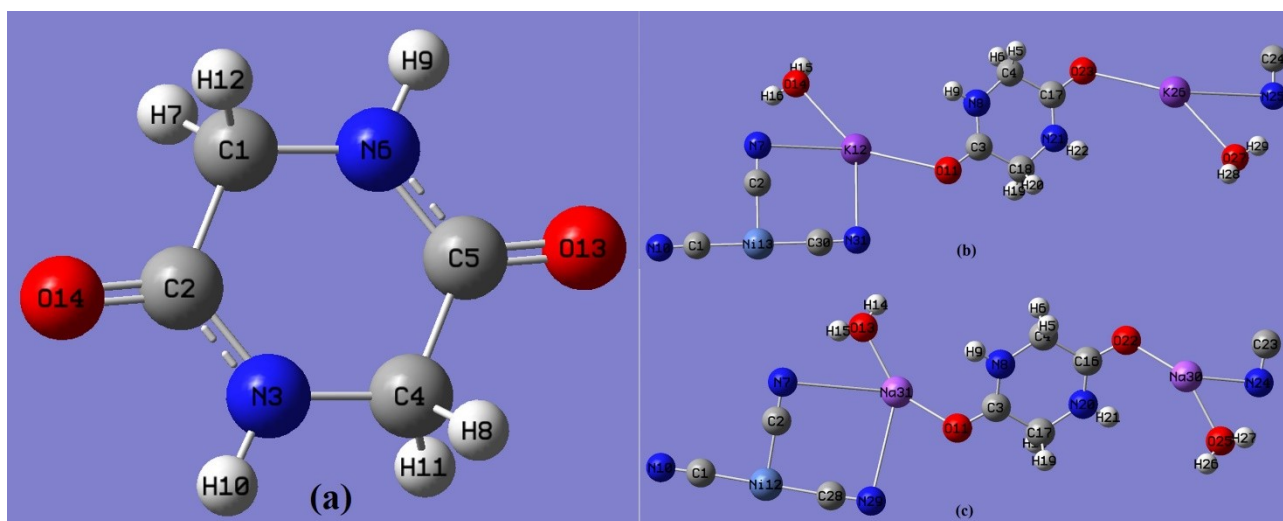

Figure 4: The numbering scheme is given by the Gaussian 03 program for the GA molecule (a), compounds **1** (b) and **2** (c).

It can be seen from the examination of Figure S1 that there are some charge changes in the other non-bonded atoms of the free GA molecule if it forms a compound. For example, the differences between the charge values of the two nitrogen atoms of the free GA molecule and the charge values of the same two nitrogen atoms of the GA molecule non-bonded in compounds **1** and **2** were calculated as 0.069e and 0.067e for compound **1**. As can be seen in Figure S1, these differences were calculated as 0.066e and 0.063e for compound **2**.

The two examples clearly show that the electrical charge values of bonding and non-bonding atoms in a molecule can change as a compound is formed. However, the change in the electric charge of the bonding atoms is always greater than the change in the electric charge of the non-bonding atoms.

3.3.2. Energy levels of compounds 1 and 2

As seen in Figure 5, the localization regions of the HOMO and LUMO states in both compounds overlap with almost the same parts of the compounds. Theoretical calculations with the Gaussian 03 program showed that a total of 129 molecular orbitals were found for compound **1**, of which 84 are occupied orbitals, and the remaining 45 are vacant orbitals. The HOMO and LUMO energy values are -0.13616 au (-3.705 eV) and -0.07847 au (-2.135 eV) in atomic units and electron volt units, respectively.

Similarly, 121 molecular orbitals were found for compound **2**, 76 of which are occupied and the remaining 45 are vacant. The HOMO and LUMO energy values are -0.16430 au (-4.471 eV) and -0.07365 au (-2.004 eV) in atomic units and electronvolt units, respectively.

In the HOMO and LUMO calculations for both compounds, the fact that compound **1** has more molecular orbitals than compound **2** is due to the fact that the K atom has more electrons in electronic arrangement than the Na atom.

The formulas for the electrochemical properties of a compound are given below.

$$\Delta E = A - I \text{ (Energy gap value) (Eq. 1)}$$
$$\chi = (I + A) / 2 = -\mu \text{ (Electronegativity, Negative chemical potential (Eq. 2)}$$
$$\eta = (I - A) / 2 \text{ (Chemical hardness) (Eq. 3)}$$
$$S = 1 / 2\eta \text{ (Chemical softness) (Eq. 4)}$$
$$\omega = \mu^2 / 2\eta \text{ (Electrophilicity index) (Eq. 5)}$$

Considering the theoretical values of the compounds in Table 5; **1** has a lower kinetic stability and a higher chemical activity than **2** since $\Delta E_1 < \Delta E_2$.

Some thermochemical properties of the compounds calculated using the HOMO and LUMO values are given in Table 6. These thermochemical properties give important information about compounds and their interactions with other compounds.
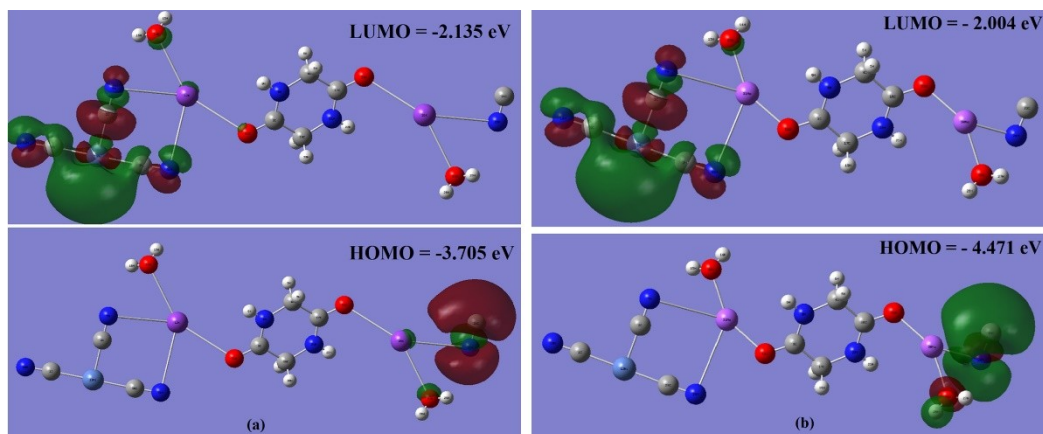
Figure 5: The HOMO and LUMO states in compounds **1** (a) and **2** (b).

Table 5: The chemical efficiency values of compounds in (au) and (eV) units.

Chemical efficiency values	Compounds			
	1		**2**	
HOMO (−I)	−0.13616	−3.705	−0.16430	−4.471
LUMO (−A)	−0.07847	−2.135	−0.07365	−2.004
ΔE	0.05770	1.57	0.09066	2.467
χ	0.10731	2.920	0.11899	3.238
μ	−0.10731	−2.920	−0.11899	−3.238
η	0.02885	0.785	0.04535	1.234
S (au)$^{-1}$; (eV)$^{-1}$	0.02352	0.640	0.01488	0.405
ω	0.20054	5.457	0.15603	4.246

Table 6: Thermochemical data of compounds 1 and 2.

Data		Values			
		1		**2**	
E_{Total} (Kcal/Mol)	Electronic	0.000		0.000	
	Translational	0.889	148.802	0.889	148.803
	Rotational	0.889		0.889	
	Vibrational	147.147		147.025	
Heat Capacity at constant volume C_v (Cal/Mol-Kelvin)	Electronic	0.000		0.000	
	Translational	2.981	63.077	2.981	56.284
	Rotational	2.981		2.981	
	Vibrational	57.115		50.322	
Total entropy S (Cal/Mol-Kelvin)	Electronic	0.000		0.000	
	Translational	43.774	170.561	43.520	146.503
	Rotational	37.224		36.244	
	Vibrational	89.562		66.739	
Zero point Vibrational Energy E_{v0} (Joules/Mol); (Kcal/Mol)		567268.7 135.58048		577074.1 137.92401	
Rotational constants (GHz)	A	0.57634		0.81293	
	B	0.03859		0.05316	
	C	0.03651		0.05036	

3.3.3. Analyses of natural bond orbitals of compounds 1 and 2
The compounds' natural bond orbitals (NBOs) were calculated in the NBO 3.1 program using the LanL2MB basis set by the DFT method. As a result of this study, it was found that there are 129 molecular orbitals for compound **1** and 121 molecular orbitals for compound **2**. It has been observed that there are 387 charge transitions between 129 molecular orbitals in compound **1** and 467 charge transitions between 121 molecular orbitals in compound **2**. Some of these charge transitions in both compounds were taken from the highest value to the lowest value according to their

second-order perturbation energies and are listed in Tables S3 and S4 for illustrative purposes.

The three strongest bonds in compound **1**, according to their $[E^{(2)}]$ values, LP (1) C30 → σ* (C1 - Ni13), LP (1) C30 → π* (C30 - N31) and σ* (C2 -Ni13) → σ * (C1 - Ni13) it is seen that it consists of charge transitions between molecular orbitals. Similarly, the three strongest bonds in compound **2**, according to their $[E^{(2)}]$ values, σ* (C16 - O22) → π* (C16 - O22), LP (1) C28 → σ* (C1 -Ni12) and π* (C3 - O11) → σ* (C3 - O11) it is seen that it consists of charge transitions between molecular orbitals. However, considering their $[E^{(2)}]$ values, it can be said that the first three bonds in compound **2** are stronger than the first three bonds in compound **1**.

4. CONCLUSION

In this study, the first obtained structures in single crystal form and the second obtained in powder form were investigated. In addition, theoretical calculations were made with the Gaussian 03 program to determine some other properties of the compounds. The results obtained from the IR spectral, crystallographic, and theoretical calculation data of these compounds indicate that they are structurally consistent with each other.

The K(I) ions in compound **1** are coordinated by the four nitrogen atoms of the cyanide groups, the oxygen atoms of the GA and H_2O molecules, and other potassium atoms. Similarly, it can be assumed that the sodium atom in compound **2** is coordinated by the oxygen atoms of the GA and H_2O molecules, the nitrogen atoms of the cyanide groups, and other sodium atoms. Again, the Ni(II) ions in compounds **1** and **2** are coordinated by the four carbon atoms of the cyanide groups.

According to the experimental and theoretical results of the compounds, these compounds appear to be new examples of "Hofmann-type-like compounds". In future studies, the ability of newly obtained Hofmann-type-like compounds to store various types of molecules can be investigated, and these abilities can be compared with the similar abilities of Hofmann-type compounds.

5. CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

6. ACKNOWLEDGMENTS

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