Ni (II) Nitrate Vs. Ni (II) Sulfate: Influence On Coordination With The Pyridoxal-Aminoguanidine (PLAG) Ligand System - A Case Study Of [Ni (PLAG)(NCS)]NO_3· H_2O and PLAG·SO_4·H_2O Crystal Structures

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Abstract:

A new Ni (II) complex with pyridoxal-aminoguanidine (PLAG) as a ligand was synthesized. The ligand is coordinated with the central nickel atom in a neutral form, and the double charge of the central Ni ion comes from the thiocyanate group, which is also coordinated with nickel, that is, from the nitrate anion from the outer sphere. Nitrate salt Ni^{2+} *was used for the synthesis, to which* NH_4NCS *was added for better mixing with the ligand pyridox-aminoguanidine (PLAG) in aqueous solution. On the other hand, the structure of pyridoxal-aminoguanidine ligand with sulfate anion, PLAG·*SO_4*·*H_2O*, is shown. The mentioned ligand was created by crystallization from an aqueous solution of* $NiSO_4$ *salt with a PLAG ligand, with the intention of obtaining a "sulfate" complex of nickel with a PLAG ligand. However, binding with the ligand occurred only through contact with the sulfate group, but the central nickel atom did not enter into coordination. Given that the same synthesis conditions were used in both cases, it is possible that the difficulty in coordinating nickel atoms from the sulfate salt occurred precisely because of the bulkiness of the sulfate group, while the nitrate group is smaller and the Ni complex was successfully synthesized.*

Key words: *Ni (II) complex, Pyridoxal-aminoguanidine (PLAG) ligand, Crystal structures, Synthesis.*

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1. INTRODUCTION

In recent years, many newly synthesized aromatic Schiffs bases have been tested for antimicrobial application due to the often manifested antibacterial and antiviral effects, and some of them have a significant impact on general biological activity, e.g., antitumor agents published by Radanovic et al (2017), Chakraborty et al. (2022), Baharti et al. (2010). Among these are the Schiff bases of aminoguanidine, AG, one of the most powerful inhibitors of carbonyl stress and the occurrence of diabetes complications Ronad et al. (2010) and Edelstein and Brownlee (1992).

Research has shown that Schiff's base AG and pyridoxal, PL, one of the forms of vitamin B6, pyridoxylidene-aminoguanidine, PLAG, is more effective than AG by the issue of treating diabetes complications because it not only prevents lack of vitamin B6, but it also betters controls diabetes nephropathy S. H. Ihm et al. (1999), Chen et al. (2004) and Taguchi et al. (1998). A detailed study of the thermodynamic stability of various Cu (II) complexes with aminoguanidine (AG), and the study of the secondary antioxidant activity of these complexes Miyoshi et al. (2022) greatly clarified the picture of PLAG synthesized products. In the previously mentioned papers, which mention the active role of the PLAG complex in the treatment of nephropathy, it was shown that individually AG (Aminoguandine) and Pyridoxal (PL) have a reduced effect on the inhibition of nephropathy, while in combination, the obtained mixed ligand PLAG shows a significantly better effect.

Aminoguanidine prevents the development of advanced glycation end products and has been widely studied in animals, Miyoshi et al. (2022). Aminoguanidine unfortunately reduces the content of pyridoxal phosphate in the liver. That is why the aminoguanidine pyridoxal Schiff base adduct was developed, which was investigated in the process of healing diabetic nephropathy. The study was conducted on mice using both preparations (PLAG and AG). It was shown that aminoguanidine pyridoxal adduct considerably enhanced urinary albumin excretion by 78.1% compared to diabetic control, and showed a better preventive effect on the progression of renal pathology than aminoguanidine. These findings indicate that the aminoguanidine pyridoxal adduct may be superior to aminoguanidine. It does not only inhibits vitamin B6 deficiency, but is also better at controlling diabetic nephropathy, as this adduct prevents oxidation and glycation.

The vitamin B group, specifically vitamin B, is part of the metabolic processes of all three primarymacronutrients (proteins, carbohydrates, hydrates, and lipids) García-Díez et al. (2022). After confirming that by heating an aqueous solution of PL with amino acids by John, R.A. (1995), pyridoxamine can be obtained, which promotes the non-enzymatic transamination of transition metal complexes due to the complexation effect with Sif bases.

Thus, the synergistic interaction of PL and AG gives one powerful ligand system, which can be coordinated in three forms, which is shown in Figure 1.

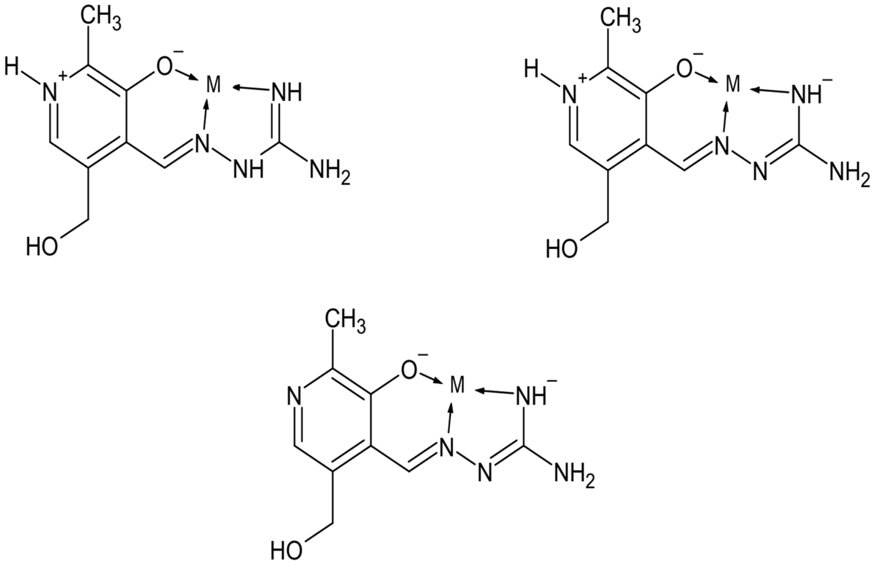
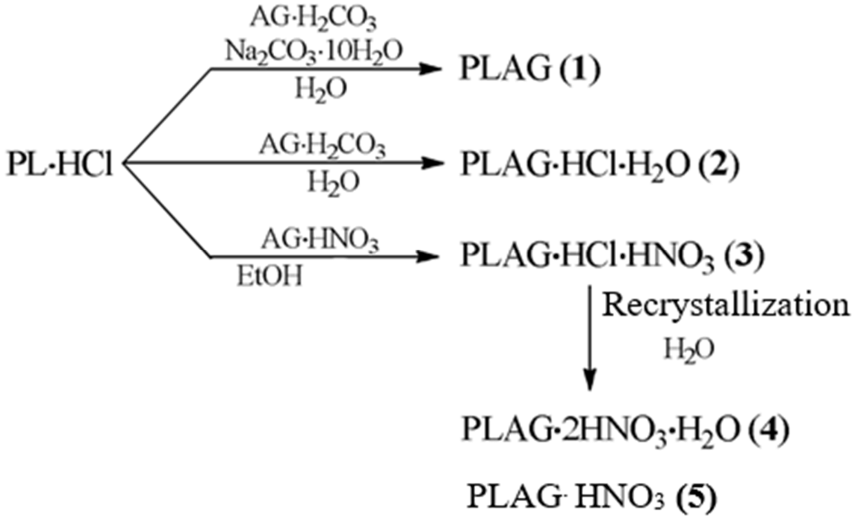


Figure 1. Coordination ligand form

It is possible to synthesize different forms of the PLAG ligand (in this work we used PLAG (1) (Zwitterion ion)). In the Scheme 1 the way of obtaining different forms of PLAG ligand is presented

($PLAG^{\cdot}HCl^{\cdot}H_2O$ (2), $PLAG^{\cdot}HCl^{\cdot}HNO_3$ (3), $PLAG^{\cdot}2HNO_3{}^{\cdot}H_2O$ (4), $PLAG^{\cdot}\ HNO_3$ (5) by Radanovic et al. (2015).



Scheme 1. Synthesis pathway of different forms of the PLAG ligand

In any case, this paper will present the crystal structures of the sulfate form of the PLAG ligand, as well as the Ni (II) complex. Namely, the so-called sulfate form of the PLAG ligand, which has a sulfate group in its composition, was created as a product of an unsuccessful synthesis of the Nickel complex, using Ni SO4 salt and an aqueous solution of the PLAG ligand. Although the synthesis started well, partial coordination and insertion of only the sulfate group from the simple Ni (II) salt occurred. However, using the nitrate salt of nickel and using the same synthetic route, complexation and formation of the PLAG complex Ni(II) occurred. The reason for such a scenario should perhaps be sought in the different dimensions of the sulfate and nitrate groups. The ratios of NO_3^- and SO_4^{2-} anions are already known by Marcus et al. (1988) and are presented in the Table. 1

Table1. Anion ratio NO_3^- / SO_4^{2-}

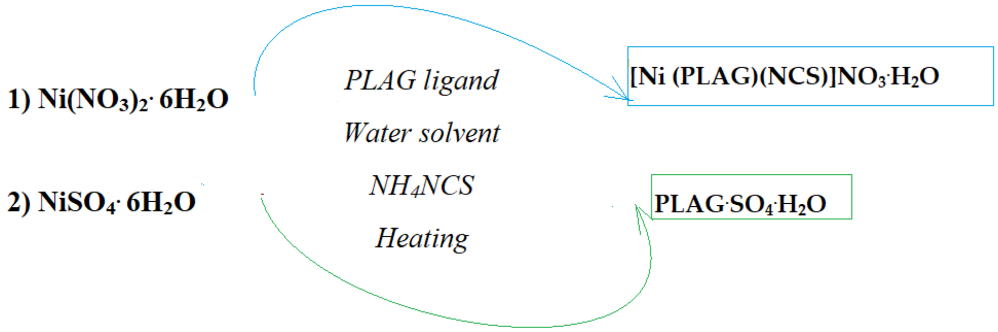
Anion	Ionic radius/nm	Hydrated radius/nm
NO_3^- mean	0.177	0.316
	-	0.265
NO_3^- axial		
NO_3^- equatorial	-	0.345
SO_4^{2-}	0.242	0.392

Of course, the influence of the PLAG ligand system itself should be added to this outcome, which is all presented in this paper. In any case, all factors that affect complexation will be discussed on the Ni complex sample. Nickel complexes are numerous and generally play an important role in many domains. The antibacterial and antitumor properties of the Ni complex are known Alasteir et al. (2023), as well as its antimicrobial effect Das et al. (2021). Nickel complexes can catalyze site-specific oxidative damage to DNA. Such complexes can also be utilized to investigate RNA structure. Ni complexes are interesting for study because in combination with the most diverse ligands, Nickel gave a multitude of complexes that play important roles in living and non-living matter.

2. RESULTS

2.1. Synthesis of [Ni (PLAG)(NCS)]$NO_3.H_2O$ complex and ligand $PLAG.SO_4.H_2O$

The same conditions were used for the synthesis of the [Ni (PLAG)(NCS)]$NO_3{\cdot}H_2O$ complex and ligand $PLAG{\cdot}SO_4{\cdot}H_2O$. Namely, the same amounts of Ni sulfate and Ni nitrate salts were taken, a two separate syntheses with PLAG ligand in an aqueous solution with heating were performed, and the addition of the same amount of NH_4NCS salt in both beakers for synthesis Scheme 2. Considering the lower solubility of the nickel sulfate salt, it was observed that complete dissolution does not occur, as was the case with the nitrate salt. It was thought that better dissolution would result from the addition of NH_4NCS, which is the sole purpose of adding this component during the synthesis reaction. To obtain the same synthesis conditions and in the case of the nitrate salt, NH_4NCS was added. In any case, since single crystals can only be obtained from completely clear solutions, the sulfate salt solution was filtered to obtain a clear solution that did not become cloudy later on standing in the air. After some time, green single crystals appeared in the nickel nitrate salt, while in the second Erlenmeyer (nickel sulfate salt) yellow single crystals appeared, which indicated that the ligand in question had crystallized. However, after the X-ray analysis, it was seen that coordination of sulfate anions with PLAG ligands did occur.



Scheme 2. Synthesis reaction pathway

The reason why complexation occurs in the first case and the second not, is in the different chemistry of sulfate and nitrate salts of nickel since all other synthesis conditions were the same (the same volume of aqueous solvent was taken, the same heating temperature was used, the same amount of NH_4NCS

was added). Nickel salts (nitrate and sulfate) are hexahydrates. Figure 2 shows the structures of those salts. The connection of nickel with nitrate groups is coordination and nitrate salts are connected to the central nickel by strong bonds. On the other hand, sulfates are in the outer sphere, the bond is ionic, and thus breaking occurs more easily. Ionic bonds are stronger than covalent bonds due to the electronegativity difference between the two elements which is much greater than that of the two elements in the case of a covalent bond. In the case of covalent bond, electrons are shared between the two elements and usually favor one element over the other one depending on the polarity (Zumdahl, S. et al. 2010). This could be the only reason why in the first case the complex is formed, but not in the second.

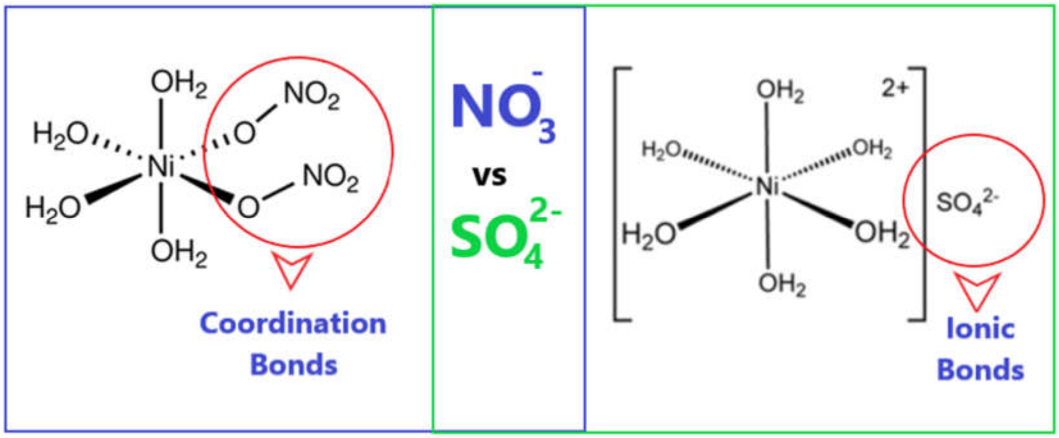


Figure 2. The relationship between nitrate and sulfate salts of nickel (II)

Finally, it is known from the literature that sulfate salts are more difficult to dissolve in water than nitrate salts precisely because of the above reasons [16].

2.2. Crystal Structures

2.2.1. [Ni(PLAG)(NCS)]NO_3.H_2O crystal structure

It is a square planar complex with the ligand PLAG (tridentate ONN) in coordination with the central nickel in a neutral form, while the fourth coordination position is occupied by the NCS^- group (Figure 3). As can be seen from Table 2, the angles around the Ni central atom are almost at right angles. Table 3 give the basic crystallographic data for the [Ni(PLAG)(NCS)]$NO_3 \cdot H_2O$ complex.

In the outer sphere is a nitrate group, connected by hydrogen bonds to nitrates N4 and N5 from the aminoguanidine chain. It is interesting to point out that due to the presence of a direct Ni-Ni bond (3.396(1)) Figure 4, this crystal system can be viewed as a dimmer. Namely due to the existence of a Hydrogen bonding network between the $[Ni(L)(NCS)]^+$ cations, the $[NO_3]^-$ anions, and the water molecule resulting in an infinite 2-D undulating sheet lying approximately parallel to the bc plane (Figure 5) . Anyway, here, hydrogen bonds are present as shown in the Figure 6 (a,b), giving cell packing as viewed done the c axis and showing the overall 3-D hydrogen-bonded network and Cell packing by Mercury program

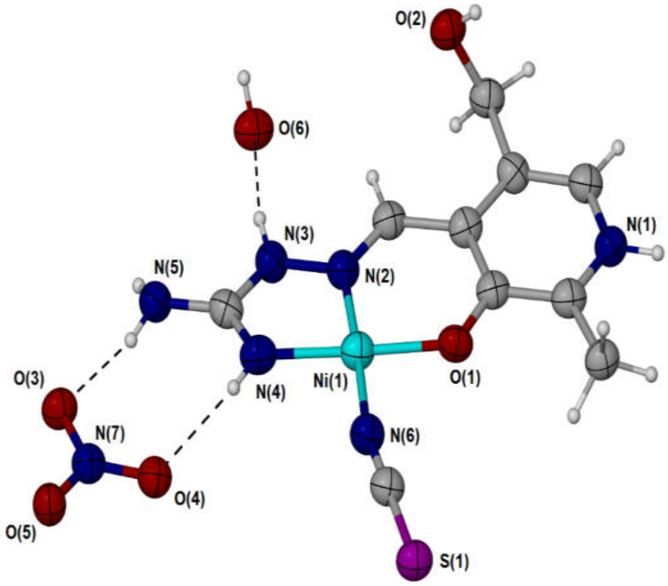


Figure 3. Molecular diagram of $[Ni(PLAG)(NCS)]^{.}[NO_3]^{.}H_2O$ (L = $C_9H_{13}N_5O_2$, PLAG) with non-hydrogen atoms represented as 30% displacement ellipsoids and hydrogen atoms as spheres of arbitrary size.

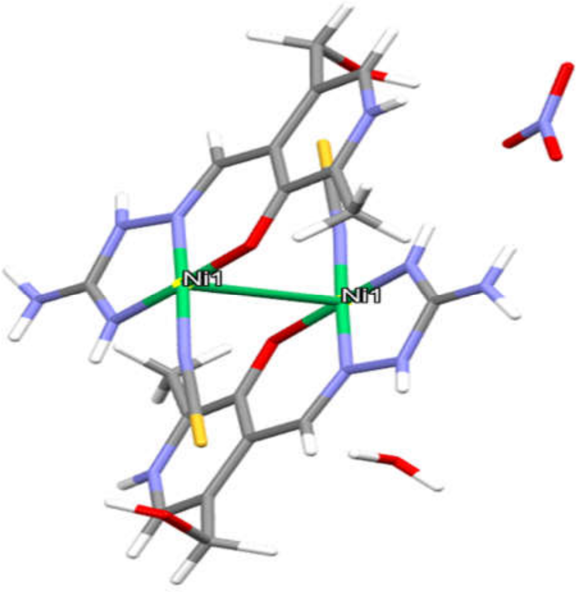


Figure 4. Dimer structure of Ni complex.

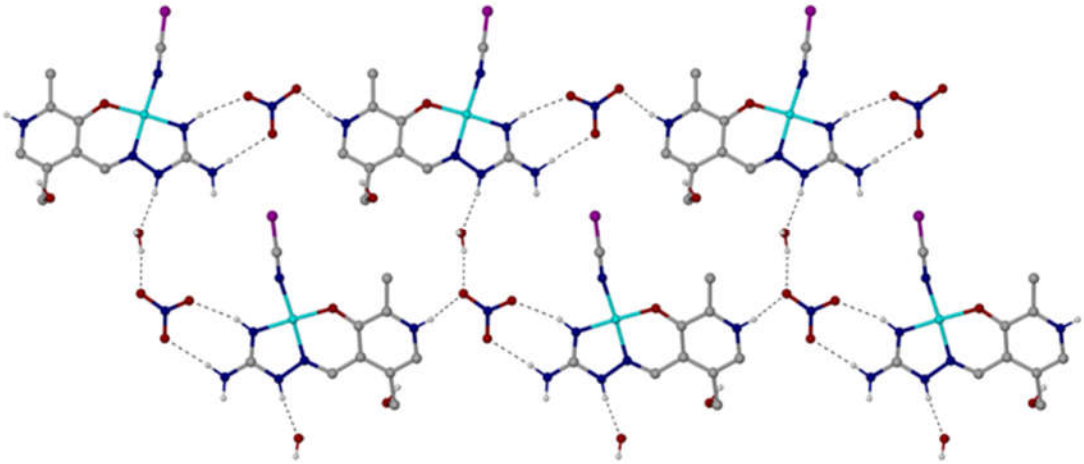


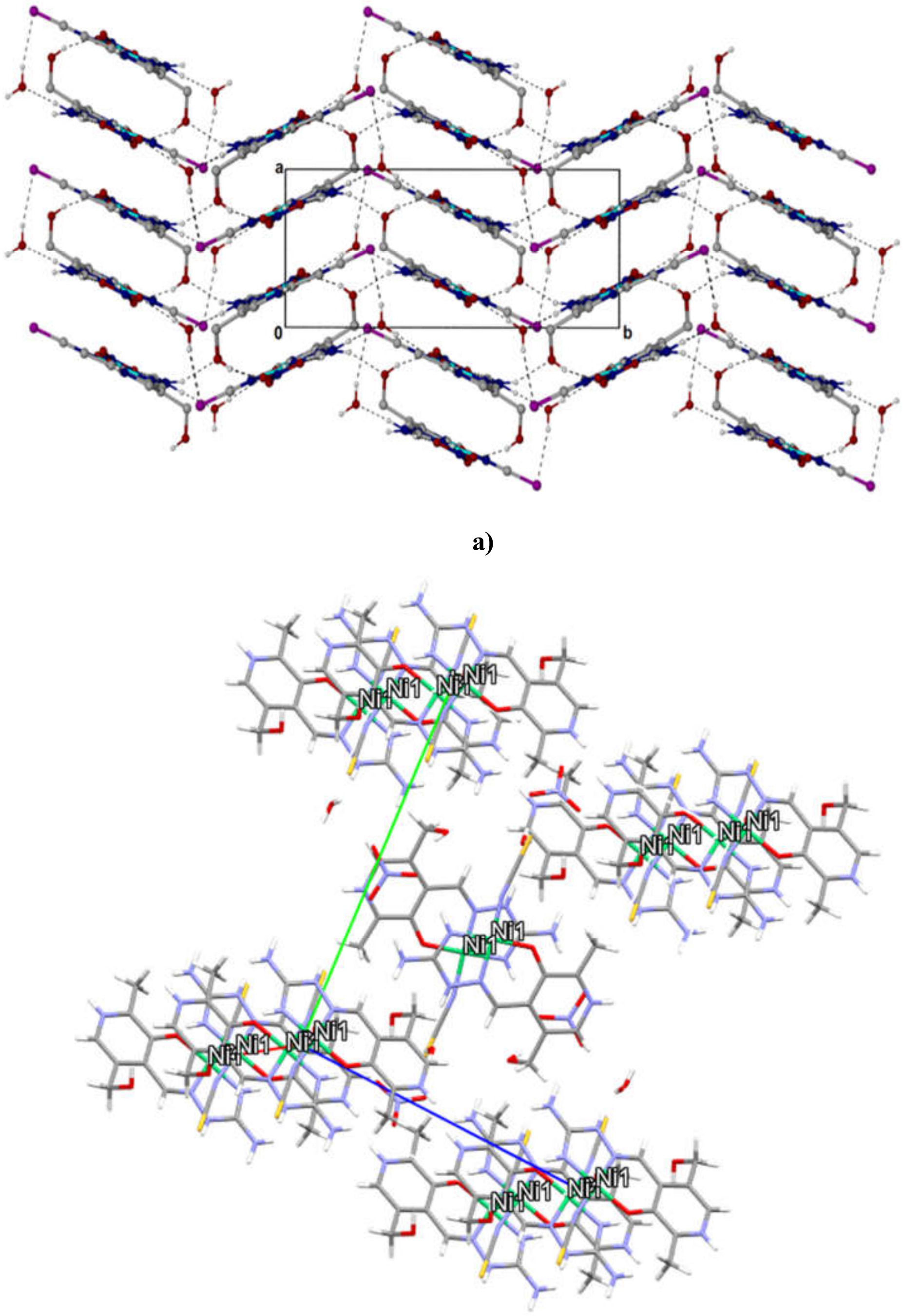
Figure 5. Hydrogen bonding network between the $[Ni(PLAG)(NCS)]^+$ cations, the $[NO_3]^-$ anions and the water molecule resulting in an infinite 2-D undulating sheet lying approximately parallel to the *bc* plane.

Table 2. Bond lengths [Å] and angles [deg] for Ni complex.

Bond lengths [Å]		Bond angles [deg]	
Ni(1)-O(1)	1.824(5)	O(1)-Ni(1)-N(2)	94.2(2)
Ni(1)-N(2)	1.849(5)	O(1)-Ni(1)-N(4)	177.7 (2)
Ni(1)-N(4)	1.846(7)	O(1)-Ni(1)-N(6)	88.6(2)
Ni(1)-N(6)	1.871(5)	N(2)-Ni(1)-N(6)	177. 7(2)
		N(4)-Ni(1)-N(2)	83.5(2)
		N(4)-Ni(1)-N(6)	93.8(3)

2.2.2. PLAG. SO_4. H_2O crystal structure

Basic crystallographic data for the crystal structure of the PLAG·SO_4·H_2O ligand is given in Table 4, while Figure 6 shows the appearance of the crystal structure. Figure 7 presents a molecular diagram of [C9H15N4O2][SO4].H2O with non-hydrogen atoms represented by 50% displacement ellipsoids and hydrogen atoms as spheres of arbitrary size, while Figure 8 and 9 show cell contents as viewed down the b axis and showing the 3- D network formed through stacking of the 2-D layers along the axis, connected by additional O-H...O hydrogen bonds.



a)

b)

Figure 6. a) Cell packing as viewed done the *c* axis and showing the overall 3-D hydrogen bonded network, b) Cell packing by Mercury program.

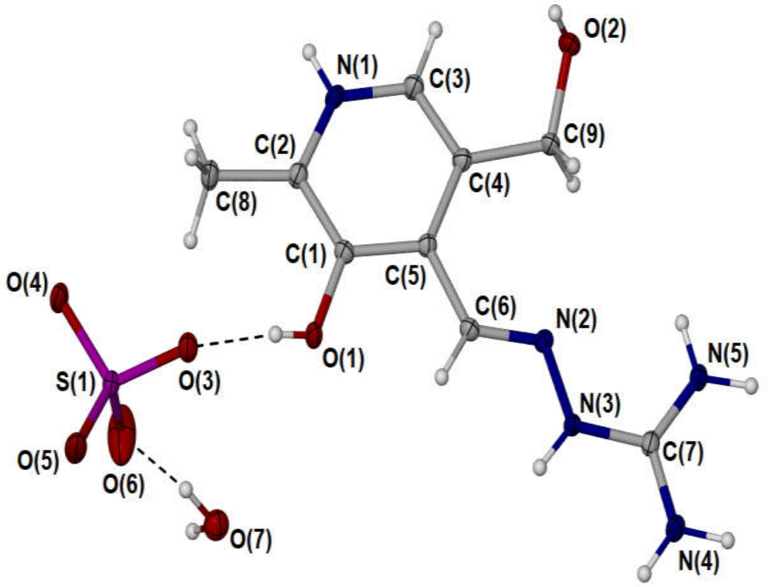


Figure 7. Molecular diagram of [$C_9H_{15}N_4O_2$][SO_4].H_2O; (PLAG·SO_4·H_2O) with non-hydrogen atoms represented by 50% displacement ellipsoids and hydrogen atoms as spheres of arbitrary size.

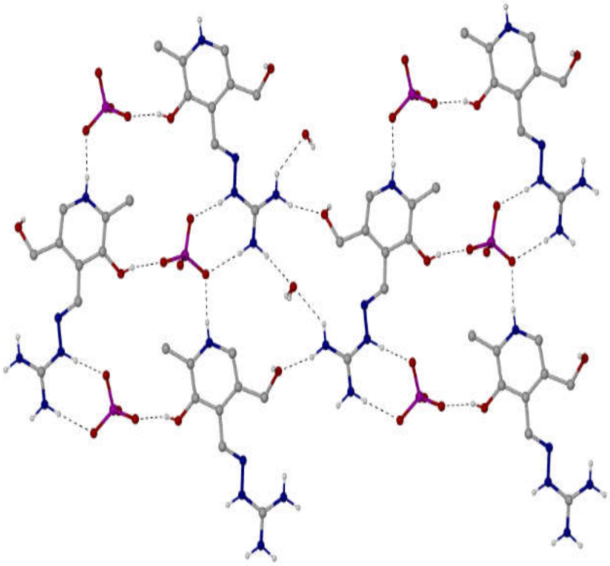


Figure 8. Part of the hydrogen bonded network showing an infinite 2-D sheet of parallel [$C_9H_{15}N_4O_2$][SO_4]·H_2O moieties connected through N-H…O and O-H…O hydrogen bonds.

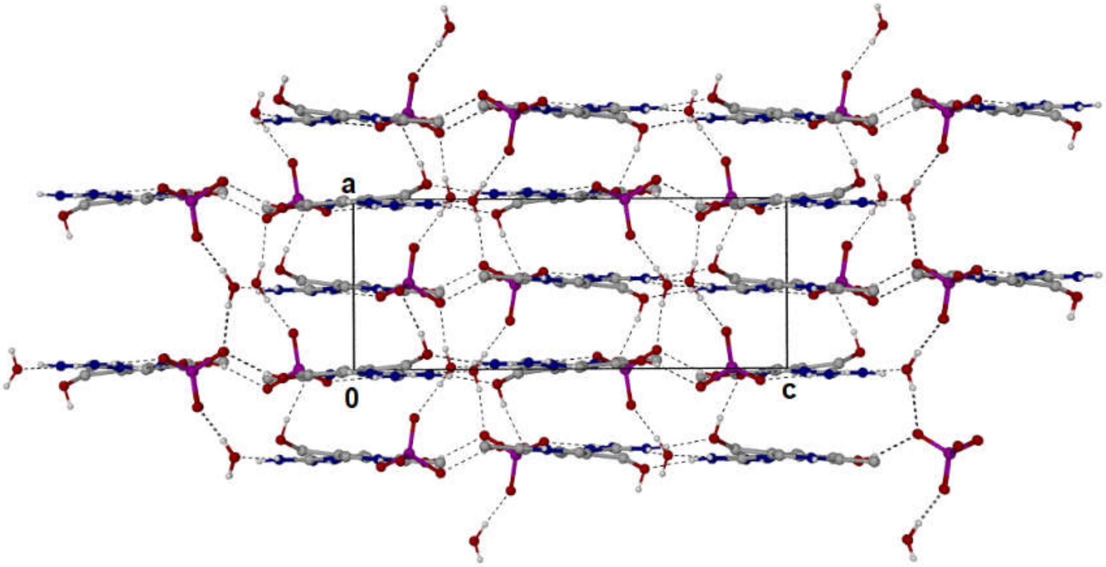


Figure 9. Cell contents as viewed down the *b* axis and showing the 3-D network formed through stacking of the 2-D layers along the a xis, connected by additional O-H…O hydrogen bonds.

3. DISCUSSION

The key thing for which we wanted to compile this paper and presentation of facts was to prove that the size of the anion has a decisive influence on the coordination, and therefore also on the formation of complexes.The size ratio of nitrate and sulfate anions has already been presented by Zumdahl, S. Book (2010) . It is logical to assume that when it comes to a larger anion that should enter into coordination, the AG chain of the ligand PLAG would have to bend less, that is, or more if the anion is smaller. Starting from the assumption of inertia, everybody wants to keep their previous position. Therefore, it turns out to be contradictory that it is easier for a larger anion to enter the coordination because the ratio of angles and bonds of the coordinated and non-coordinated ligand will not change significantly. That's why when you look at the angles of the AG chain of the ligand and complex (Table 3), there are not so big deviations. However, here is teeny NCS^- anion in coordination.

Table 3. Values of significant angles for the ligand and complex

	Pyridine angle	AG chain (N3)	AG chain C angle
Ligand	C3N1C2 124.22(17)	N2N3C7 118.99(16)	N3C7N5 120.19
Complex	C3N1C1 124.1(16)	N2N3C9 113.5(5)	N3C9N4 114.3

The initial goal was to prove that the nitrate and sulfate anions in themselves have competition when it comes to the coordination process. It must be concluded that it still depends more on the ability of the mentioned anions to dissolve in the solvent. Namely, if complete dissolution is possible, then the possibility of coordination increases. The generally known rule of dissolution is laid out in 5 rules:

- **Rule 1** : Compounds of NH_4^+ and group 1A metal ions are soluble.
- **Rule 2** : Compounds of NO_3^-, ClO_4^-, ClO_3^- and $C_2H_3O_2^-$ are soluble.
- **Rule 3** : Compounds of Cl^-, Br^- and I^- are soluble except those of Ag^+, Cu^+, Tl^+, Hg_2^{2+} and Pb^{2+}.
- **Rule 4** : Compounds of SO_4^{2-} are soluble except those of Ca^{2+}, Sr^{2+}, Ba^{2+} and Pb^{2+}.
- **Rule 5** : Most other ionic compounds are insoluble.

In general, all nitrate salts dissolve, while the dissolution of sulfates depends on the nature of the cationic part of the salt. In our case it is Ni (II). Starting from the fact that in the experimental part, it was stated that $NiSO_4$ was not completely dissolved, while nitrate $NiNO_3$ was, guidelines were given as to what can be expected in coordination. Finally, the NCS^- anion was added to the synthesis as an anion that would promote the formation of the complex. It turned out in the end that NCS group is in coordination with nitrate Ni, while with sulfate Nickel it is not. The conclusion is that this happened precisely because the nickel nitrate salt was completely dissolved in the water. This is a real consequence of the different sizes of the mentioned anions and not the possibility of coordination as a consequence. It turns out that for the AG chain and the pyridine ring to bend as much as needed, it was only necessary that the anion was previously dissolved, that is, hydrated. Thus, we come to the conclusion that in this case water as a solvent carries anions to the prediction site, and as a trace of this, the appearance of hydrogen bonds later. Therefore, the basis for the assumed structure, that is, the coordination of the participants in the process of synthesis of the complex, is more the ability of solubility, than the size of the same. Therefore, when creating various complex compounds, it is very important to pay attention to the choice of solvents and the solubility model of the salts used during synthesis. Finally, this also applies to the solubility of the ligand. The concept of solubility is related to the breaking of primary bonds so that cations or anions become "free" and thus are ready for coordination bonding. In conclusion, it follows that during coordination synthesis it is much more important to achieve the best possible solubility, than to choose the appropriate sizes of the cationic or anionic part of simple salts, to achieve success in coordination, that is, to successful synthesis of a complex compound.

Taking into account the size of the nitrate and sulfate anion, it is noticeable that the nitrate anion is smaller, which certainly enables it to have a better and easier possibility of coordination. When there is a larger crowd of ions, atoms or even molecules that can potentially enter into coordination with some central metal, smaller voluminous particles have the greatest chance for this, for the simple reason that it is easier for them to secure a place for themselves in the coordination sphere, because of their smaller size, it is easier move and come to a convenient place for coordination. This should always be kept in mind during synthesis because it can help a lot in how to get a single crystal, for example. Knowing these simple predictions, one can target the combination of various salts (anionic residues) which, depending on the solvent used, can affect easier complexation and ultimately obtain single crystals for X-ray analysis in order to use the best method for solving structures, to set accurate molecular and structural formula of the newly synthesized complex compound.

However, in the case of the reported complex, the nitrate anion did not coordinate directly with the central metal. In coordination with the Ni central ion is a thiocyanate group (NCS-). During the synthesis, NH4NCS was added to increase the solubility of the nickel nitrate salt mixture and the PLAG ligand, which is otherwise very difficult to completely dissolve in water. It is interesting that the water molecules in this case did not enter into coordination, but they are only in the outer sphere. In the outer sphere is the nitrate anion too, which together with the mentioned thiocyanate group NCS - gives the double negative charge needed to Nickel.

The question now arises as to why the NCS group was coordinated and not NO3-?. The answer may lie in the geometry of the groups themselves, and thus their voluminousness. NCS group is linear, while NO3 is trigonal. It is easier to occupy a suitable place for coordination if it is a linear structure, because it is better and easier to access the coordination sphere. In the case of the reported Ni complex, a square-planar structure of 3 ligand's atoms (ONN) of PLAG and nitrogen from the thiocyanate group was achieved. The square planar nickel environment is quite regular, with angles close to and around 90 degrees. Therefore, the inclusion of the NCS group in the coordination sphere precisely because of its smaller size is indirect evidence that size determines many possibilities in terms of solubility, coordination, and ultimately the formed structure.

4. MATERIALS AND METHODS

4.1. Ligand syntheses (Pyridoxilidene Aminoguanidine, PLAG)

0.68 g (5 mmol) of $AG \cdot H_2CO_3$ are dissolved in 10 cm^3 of H_2O with heating, and a warm solution of 1.0 g (5 mmol) of $PL \cdot HCl$ in 5 cm^3 of H_2O is added to this solution. 0.71 g (2.5 mmol) of $Na_2CO_3 \cdot 10H_2O$, previously dissolved in 10 cm3 of H_2O, is added to this mixture and everything is gently heated for a few minutes, and then left at room temperature. After 20 hours, the yellow crystals are filtered off and washed with EtOH and Et_2O. Yield: 1.05 g (90 %).

4.2. Ligand synthesis ($PLAG.SO_4.H_2O$)

An amount (0.5 mmol) of PLAG ligand was dissolved in water. The same amount (0.5 mmol) of $NiSO_4$ was added to that solution. Dissolution is carried out by strong heating and the addition of 0.07 mmol NH_4NCS. The solution initially turned a slightly green color that quickly disappeared, and it was visible that the components of the solution were not completely dissolved. The color of the solution was between pale green and yellow. Since a precipitate was separated in the solution, filtration was performed, and the precipitate was removed. The clear yellow-pale green solution was allowed to crystallize. After a few days, dark yellow single crystals are separated.

4.3. Ni Complex Synthesis $[Ni(PLAG)(NCS)]NO_3 . H_2O$

The amount (0.5 mmol) of PLAG ligand was dissolved in water. The same amount (0.5 mmol) of $Ni (NO_3)_2 \cdot 6H_2O$ was added to that solution. The dissolution is carried out with strong heating and adding 0.07 mmol NH_4NCS. When the components of the solution arecompletely dissolved, the heating stops. The green, clear, and still warm solution was allowed to crystallize. After 12 hours dark green single crystals are separated.

4.4. X-ray Analysis

4.4.1. Ni complex

A representative orange thin needle crystal with approximate dimensions 0.1x0.02x0.01 mm was selected and mounted on a nylon cryoloop. XRD diffraction data were collected at 100 K at the MX1 beamline of the Australian Synchrotron with radiation ʌ = 0.71074 Å. Data including an empirical (multi-scan) absorption correction were collected and processed using the CrysAlisPro software by Kabsch, W. (2010). The crystal structure was solved and refined by standard methods using the SHELX software suite in conjunction with the Olex2 graphical interface by SHELX, G. M. Sheldrick (2015) and Dolomanov (2009). Non-hydrogen atoms were refined with anisotropic displacement ellipsoids and hydrogen atoms attached to carbon were put in the calculated positions using a riding model. Most of the positions of hydrogen atoms attached to oxygen and nitrogen were apparent in the difference Fourier map and were refined with restrained geometries d(O-H) = 0.86(2)Å or d(N-H) = 0.88(2)Å (DFIX) and Uiso(H) = 1.5×Ueq(O/N). The hydrogen atom attached to N(1) was placed in a calculated position and was not refined.

4.4.2. Ligand PLAG.SO_4.H_2O

A representative yellow-orange prismatic crystal with dimensions 0.340x0.072x0.035 mm was selected and mounted on a nylon cryoloop. XDR diffraction data were collected at 123 K using CuKa radiation (l = 1.54184 Å) on a Rigaku Synergy S diffractometer fitted with a HYPIX 6000 hybrid photon counting detector. Data including an empirical (multi-scan) absorption correction were collected and processed using the CrysAlisPro software.[17] The crystal structure was solved and refined by standard methods using the SHELX software suite in conjunction with the Olex2 graphical interface. [18,19] Non-hydrogen atoms were refined with anisotropic displacement ellipsoids and hydrogen atoms attached to carbon were put in the calculated positions using a riding model. The positions of hydrogen atoms attached to oxygen and nitrogen were apparent in the difference Fourier map and were freely refined. For the final refinement cycles, the data were treated as a racemic twin (TWIN/BASF).

Table 4. Crystal data and structure refinement for the Ni complex.

Identification code CCDC	2349239
Empirical formula	C10 H15 N7 Ni O6 S
Formula weight	420.05
Temperature	100.15 K
Wavelength	0.71074 A
Crystal system, space group	Monoclinic, P 1 21/n 1
Unit cell dimensions	a = 6.9500(14) A alpha = 90 deg.
	b = 17.080(3) A beta = 103.68(3) deg.
	c = 13.930(3) A gamma = 90 deg.
Volume	1606.7(6) A^3
Z, Calculated density	4, 1.737 Mg/m^3
Absorption coefficient	1.384 mm^-1
F(000)	864
Crystal size	0.1 x 0.02 x 0.01 mm

Theta range for data collection	1.920 to 27.495 deg.
Limiting indices	-9<=h<=9, -21<=k<=21, -18<=l<=17
Reflections collected / unique	36941 / 3516 [R(int) = 0.0987]
Completeness to theta	67.684 99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	Values not reported by XDS
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3516 / 7 / 249
Goodness-of-fit on F^2	1.074
Final R indices [I>2sigma(I)]	R1 = 0.0778, wR2 = 0.2112
R indices (all data)	R1 = 0.1338, wR2 = 0.2909
Extinction coefficient	0.019(5)
Largest diff. peak and hole	0.774 and -0.968 e.A^-3

Table 5. Crystal data and structure refinement for the ligand PLAG$^{\cdot}$SO$_4$$^{\cdot}H_2$O.

Identification code CCDC	2374572
Empirical formula	C9 H17 N5 O7 S
Formula weight	339.33
Temperature	123(2) K
Wavelength	1.54184 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 6.681 A alpha = 90 deg.
	b = 12.08990(10) A beta = 90 deg.
	c = 17.01250(10) A gamma = 90 deg.
Volume	1374.144(14) A^3
Z, Calculated density	4, 1.640 Mg/m^3
Absorption coefficient	2.557 mm^-1
F(000)	712
Crystal size	0.340 x 0.072 x 0.035 mm
Theta range for data collection	4.487 to 80.416 deg.
Limiting indices	-8<=h<=8, -15<=k<=13, -21<=l<=21
Reflections collected / unique	50995 / 2999 [R(int) = 0.0522]
Completeness to theta	67.684 100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.58162
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2999 / 0 / 242
Goodness-of-fit on F^2	1.057
Final R indices [I>2sigma(I)]	R1 = 0.0267, wR2 = 0.0705
R indices (all data)	R1 = 0.0269, wR2 = 0.0706
Absolute structure parameter	0.48(2)
Extinction coefficient	0.0014(2)
Largest diff. peak and hole	0.307 and -0.327 e.A^-3

5. CONCLUSION

A comparative analysis of the possibility of complexation of nitrate and sulfate salts of Nickel (II) with Pyridoxal-aminoguanidine ligands (PLAG) was carried out under the same conditions. It was shown that in the case of the nitrate salt, complexation of the central nickel atom with ligands occurred, while in the case when the nickel sulfate salt was used, only the implementation of the sulfate group in the ligand chain occurred. It was concluded that the probable reason for this outcome is not the difference in the size of the nitrate and sulfate anions, but the possibility of their dissolution is the main cause of the different possibilities in the process of formation of the complex as a product. In this way, for the synthesis of complexes to be as successful as possible, it is necessary to search for combinations of simple salts and ligands that are more soluble in used solvents. What's more, if necessary, it is also possible to increase their solubility by adding some other substance to the complexation reaction. Finally, it is known that single crystals of complexcompounds are formed only from very clear solutions, a fact that is another confirmation of the above. On the other hand, the presence of the central nickel ion can have an impact too, because by nature of its existence in this case it is a Lewis acid. Small, highly charged metal ions, such as Cu^{2+} or Ru^{3+}, and Ni^{2+} have the greatest tendency to act as Lewis acids, and consequently, have the greatest tendency to form complex ions. Given that in our case, nickel is the central atom in both complexes, we cannot fully see its role. Also, other factors can influence the favoring of complexation, such as ligand flexibility, and metal-ligand interactions and others, which were discussed and the conclusion was reached that there are many factors that influence the final outcome. All in all, this kind of theoretical analysis and prediction are welcome for setting expected results and developing logical assumptions based on postulates, theories, and rules.

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