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Živković, J. M., Milovanović, M. R.,& Zarić, S. D.. (2022). Hydrogen Bonds of Coordinated Ethylenediamine and a Water Molecule: Joint Crystallographic and Computational Study of Second Coordination Sphere. in Cryst. Growth Des.

ACS Publication., 22(9), 5198-5205.

https://doi.org/10.1021/acs.cgd.2c00196

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HYDROGEN BONDS OF COORDINATED ETHYLENEDIAMINE AND WATER MOLECULE. JOINT CRYSTALLOGRAPHIC AND COMPUTATIONAL STUDY.

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ABSTRACT

In the study of hydrogen bonds between noncoordinated and metal-coordinated ethylenediamine with water molecule the data in the Cambridge Structural Database (CSD) were analyzed and DFT calculations were performed. For coordinated ethylendiamine in the CSD, the analyzed distributions of d_{OH} distances show a maximum in the range of 2.0 Å -2.1 Å, while angle α shows maximum in the range of 150^0 - 160^0. The DFT calculations were done for octahedral geometries of cobalt(III), copper(II) and nickel(II) complexes and square-planar geometry of palladium(II) complexes. The coordination of ethylenediamine to the metal ions strengthens its hydrogen bond with the water molecule. Namely, the noncoordinated ethylenediamine and water molecule have interaction energy of -2.3 kcal/mol while for coordinated ethylenediamine

interacting energy span from -4.0 kcal/mol to -28.0 kcal/mol, depending on the metal ion and charge of the complex. The hydrogen bond energies have a good correlation with the electrostatic potential on interacting hydrogen atoms.

Introduction

Hydrogen bonds are an important type of interaction that stabilizes crystal packing of small molecules, structures of proteins, and various geometries of coordination compounds. One of the most studied hydrogen bonds is between water molecules.[1-14] It was shown that the most stable geometry of water dimers has an interaction energy of ca. -4.8 kcal/mol.[15] Coordination of water molecule increase pK values[16] and strength of hydrogen bond, due to increased positive electrostatic potential on interacting hydrogen atom.[17] The increased strength of hydrogen bonds due to coordination of water can be observed in the shortening of d_{OH} distances in the analysis of crystal structures from the Cambridge Structural Database (CSD). The peaks in the crystal structures are in the range of 1.8–2.0 Å for hydrogen bonds between two free water molecules and 1.6–1.8 Å for coordinated/free water molecules hydrogen bonds.[15] The calculated interaction energies have shown that even for neutral complexes, hydrogen bonds of a coordinated water molecule (-5.4 kcal/mol to -9.7 kcal/mol) are significantly stronger compared to hydrogen bonds of noncoordinated water molecules (ca. -4.84 kcal/mol).[15,17] For positively charged $[Zn(H_2O)_6]^{2+}$ complex hydrogen bond energy was calculated to be -21.9 kcal/mol.[15]

The N-H···O hydrogen bonds were also very often studied in various systems.[18-25] The amino groups found in DNA and protein chains are very frequent hydrogen bond donors.[21-25] The hydrogen atom of the amino groups forms short range specific, and directional hydrogen bonds, which play a decisive role in the specificity and stability of protein-DNA complexes. An analysis of the geometrical parameters associated with N-H···O in amino acids and peptides show

that the maximum of d_{NO} distribution is between 2.8 Å and 2.9 Å for the charged donor group and between 2.9 Å and 3.0 Å for the uncharged donor group and does not depend on the charge of the acceptor group.[24,25] This analysis also indicates that the NH group has a very strong tendency to point towards the acceptor oxygen atom.[24]

The N-H···O interactions were studied for metal-coordinated ammonia.[18] Similar to a water molecule,[15,17] coordination of ammonia molecule to metal ions significantly strengthens hydrogen bond between ammonia and water molecule. The data obtained in the analysis of crystal structures from the CSD showed that (N)H···O distances in hydrogen bonds of water with coordinated ammonia, in most of crystal structures, are quite short (2.0 - 2.2 Å). These short distances are in agreement with very strong hydrogen bonds calculated by quantum chemical calculations. Namely, the calculated hydrogen bond energy of water molecule with noncoordinated ammonia is -2.3 kcal/mol, while with coordinated ammonia it is in the range of -3.7 to -25.0 kcal/mol, depending on the metal ion and charge of the complex.[18]

Due to many hydrogen bond donors, the coordinated ethylenediamine, $[Co(en)_3]^{3+}$, has been recognized as possible catalyst for enantioselective reactions.[26] One study on over one hundred and fifty crystal structures of $[Co(en)_3]^{3+}$ salts shows extensive hydrogen bonding in the solid state.[27] The $[Co(en)_3]^{3+}$ crystalizes with counter anions and H_2O molecules and it usually engages all twelve N-H units in hydrogen bonds. There is also NMR evidence that most of the interactions existing in solid state remain in solution.[28]

In this work, we studied geometries and energies of hydrogen bonds of noncoordinated and of coordinated ethylenediamine with water molecule using a combination of statistical analysis of crystallographic data from the Cambridge Structural Database (CSD) and accurate quantum chemical calculations.

Methodology

CSD search. The search of crystal structures archived in Cambridge Structural Database (CSD, version 5.41, November 2019 released, May 2020 updated)[29] was performed in order to find crystal structures containing at least one coordinated ethylenediamine molecule (*en*) to a transition metal, and at least one free water molecule interacting with *en* molecule via NH...O hydrogen bond. According to imposed structural criteria of the search, a group of *en* coordinated to any transition metal, interacting with a water molecule (*M-en···H_2O*, **Figure 1**) is defined. The CSD search program ConQuest 2020.1.1.[30] was used to retrieve structures satisfying the following criteria: (a) the crystallographic *R* factor ≤ 0.1, (b) the error-free coordinates according to the criteria used in the CSD, (c) no polymer structures, (d) no structures with the disorder, (e) no structures solved from powder and (f) only X-Ray diffraction solved structures. The geometric criterion was that at least one O···N (**Figure 1a**) distance is less than 4.0 Å. Since we studied interactions where water molecule plays a role of proton acceptor, the following geometrical parameters were considered: the shortest O···H distance (d_{OH}, **Figure 1a**) and the corresponding angle N-H···O (α, **Figure 1b**). In accordance with our recent study[31], all crystal structures containing water molecules with the bond angle (H-O-H) outside the range of 96.4^0 - 112.8^0 were excluded from a further study. In order to elude a misinterpretation of obtained data and to get only hydrogen bonded contacts, the contacts having d_{HH} (**Figure 1a**) shorter than d_{OH} (**Figure 1a**) were excluded from the study.

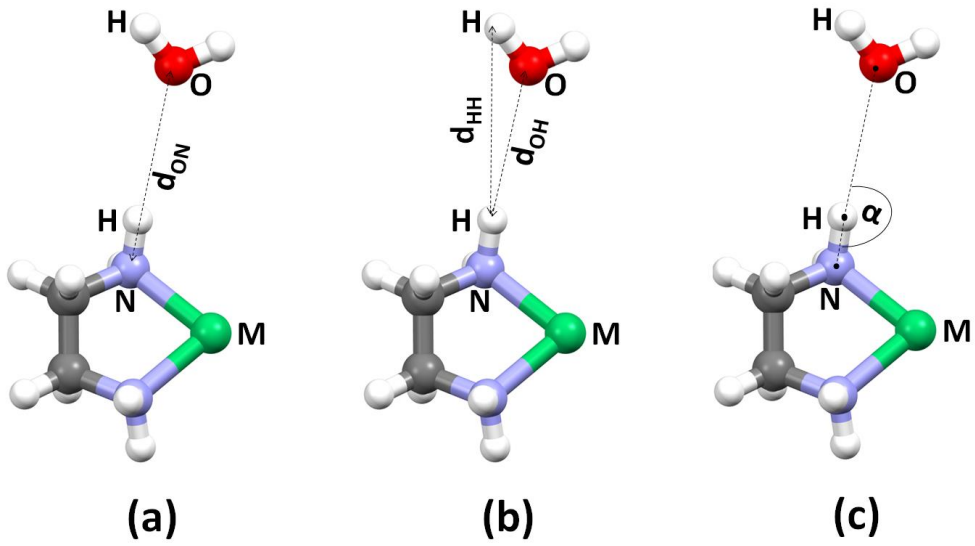


Figure 1. Graphical representation of model structure used in CSD search for a group of ethylenediamine coordinated to any transition metal (***M***), interacting with a water molecule (*M-en···H_2O*). Considered parameters were the following: *(a)* $\boldsymbol{d_{NO}}$ represents shorter O···N distance; *(b)* $\boldsymbol{d_{OH}}$ represents shorter O···H(N) distance; $\boldsymbol{d_{HH}}$ represents the shortest H(O)···H(N) distance; *c)* $\boldsymbol{\alpha}$ represents the angle N-H···O.

Computational methods. All calculations were performed using the M06L-GD3[32] method and def2-TZVPP[33] basis set for all atoms. The BSSE correction was performed using the counterpoise procedure of Boys and Bernardi.[34] This level of theory was chosen since it gives results that are in good agreement with the CCSD(T)/CBS method that is considered as a gold standard in quantum chemistry. Namely, the calculated CCSD(T)/CBS interaction energies for $NH_2CH_2CH_2NH_2/OH_2$, $[Co(H_2O)enCl_3]/OH_2$, $[Co(H_2O)_2enCl_2]^+/OH_2$ and $[Co(H_2O)_4en]^{3+}/OH_2$, were -2.3 kcal/mol, -6.3 kcal/mol, -10.8 kcal/mol and -28.0 kcal/mol, respectively, while the corresponding interaction energies calculated with M06L-GD3/def2-TZVPP were -1.8 kcal/mol, -6.5 kcal/mol, -11.3 kcal/mol and -28.0 kcal/mol, respectively. Since

M06L-GD3/def2-TZVPP underestimates interaction energy for noncoordinated ethylenediamine, here we used CCSD(T)/CBS value.

Single molecules were completely optimized and these geometries were used in interaction energy calculations. Only the most stable isomers of metal complexes (monomers) were taken into consideration The interaction energies were calculated for model systems with rigid monomers, where d_{NO} distance was varied (**Figure 1**). The free water molecule was orientated in a way to avoid repulsive interactions with chlorine atoms where it was possible. In addition, the interaction energies for totally optimized dimer model systems were calculated.

The electrostatic potentials for metal complexes were computed at M06L-GD3/def2-TZVPP level, on surfaces defined as the 0.001 au (electronbohr^{-3}) contours of the electronic densities, as suggested by Bader *et al*.[35] The positive potentials on hydrogen atoms involved in the interaction for rigid monomers were calculated (Vs_r), as well as potential on the interacting site for totally optimized structures (Vs_t). All geometry optimizations, interaction energies calculations, and electrostatic potential calculations were performed using Gaussian09[36] software.

Results and discussion.

CSD search.

As results of the performed CSD search, satisfying criteria given in the Methodology section, 536 contacts for M-*en*$\cdots H_2O$ (**Figure 1**) were obtained. In the distribution of d_{OH} (**Figure 2**), the maximum is at 2.0 Å - 2.1 Å, with a relatively large number of structures with distances shorter than 2.0 Å. The distribution of α (**Figure 3**) revealed the maximum at 150^0 -

160^0. The d_{OH} and α are correlated, i.e. shorter distances correspond to larger angles (**Figure 4),** as typical for classical hydrogen bonds.

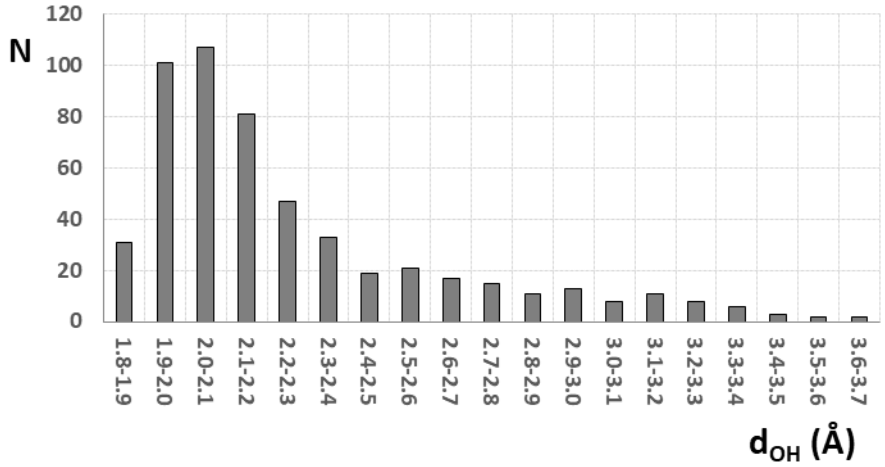


Figure 2. Distribution of distance d_{OH} (**Figure 1a**) in N-H···O (**Figure 1**) hydrogen bond of the ethylenediamine complexes with a water molecule.

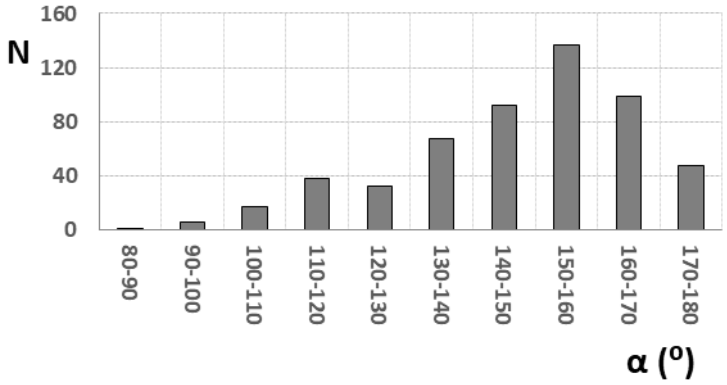


Figure 3. Distribution of the angle α (**Figure 1b**) in N-H···O (**Figure 1**) hydrogen bond of the ethylenediamine complexes with a water molecule.

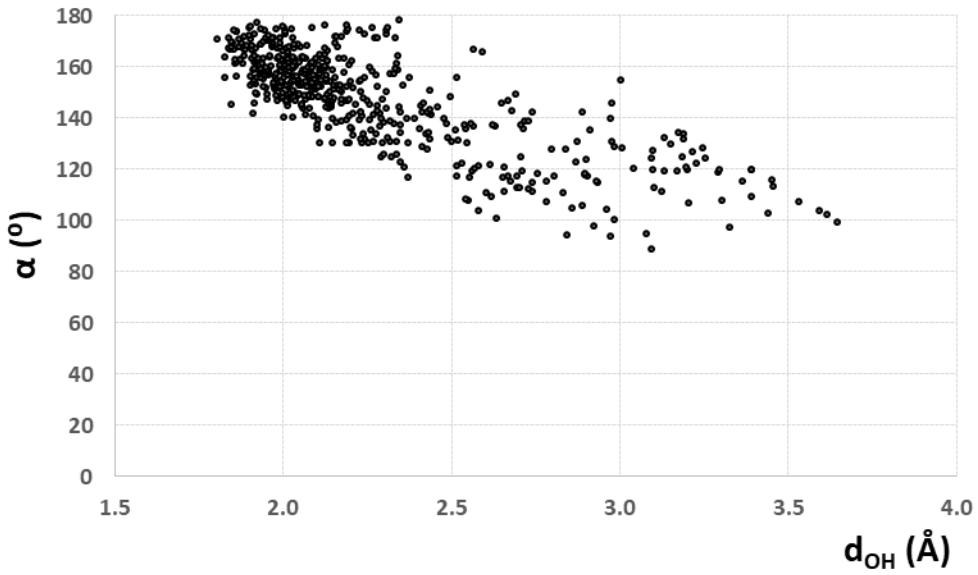


Figure 4. The plot of the distance d_{OH} (**Figure 1a**) and the angle α (**Figure 1b**) of N-H···O hydrogen bond of the ethylenediamine complexes with a water molecule.

Considering the type of transition metal (**Figure 5**) in ethylenediamine complexes that form hydrogen bonds with a water molecule, most complexes contain cobalt, followed with palladium, nickel, and copper, while other metals are much less abundant. The majority of complexes have octahedral geometries.

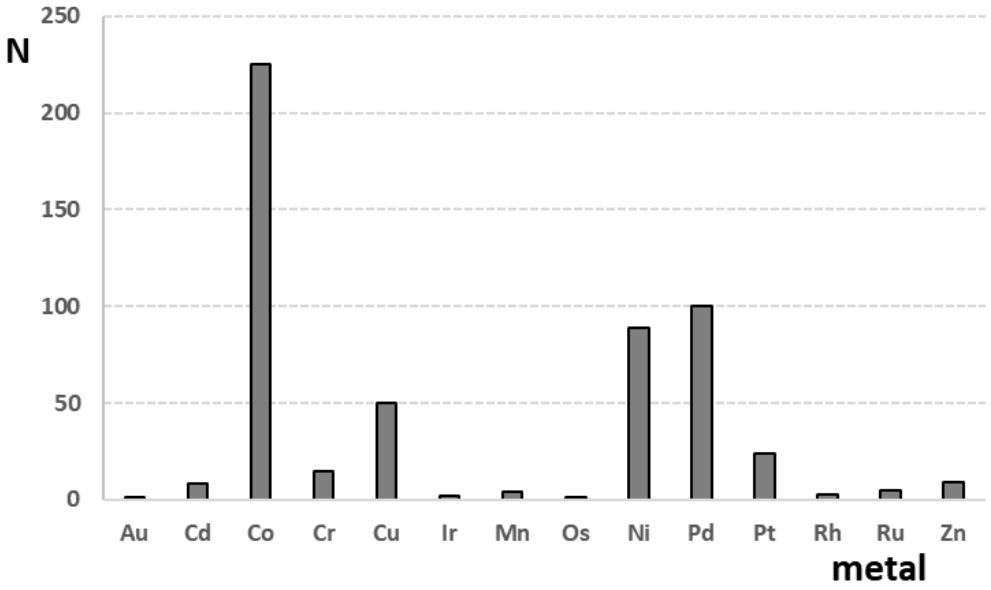


Figure 5. Distribution of metals within the ethylenediamine complexes interacting with water via N-H···O (**Figure 1**) hydrogen bond.

Quantum-chemical calculations

In order to find the interactions energies of hydrogen bonds in ethylenediamine/water (*en*/O) and coordinated ethylenediamine/water (M-*en*/O) systems, the geometries of monomers (ethylenediamine, ethylenediamine complexes, and water molecule) were firstly optimized. These monomers were used to construct model systems and interaction energies were calculated on model systems with rigid monomers (**Figures 6, 7 – 10, Table 1**). In addition, the interaction energies were calculated when the whole model systems were optimized (**Figures 12 - 15, Table 2**).

Calculations with rigid monomers. The model systems for coordinated ethylenediamine were constructed by taking into account the most frequent metals (**Figure 5**) and their geometries

found in CSD. Hence, the interaction energies of coordinated ethylenediamine and water molecule were calculated for octahedral complexes of cobalt(III), copper(II), and nickel(II) complexes and square-planar complexes of palladium(II).

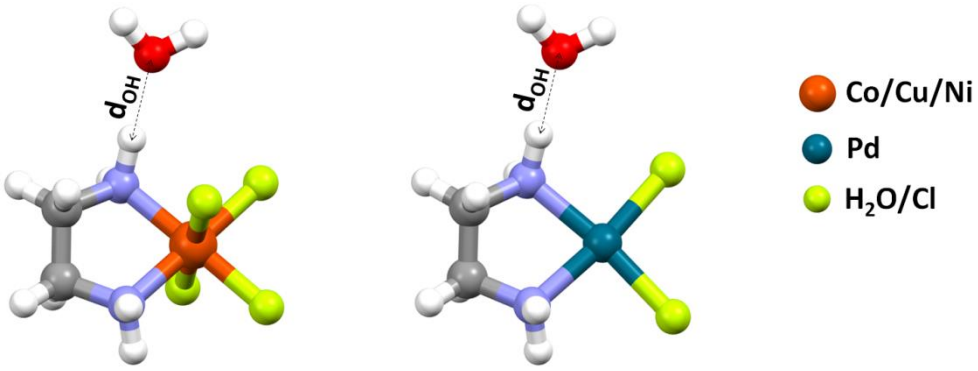
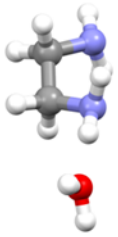
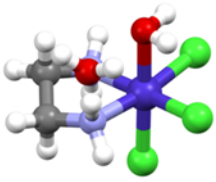


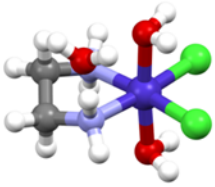
Figure 6. The octahedral and square-planar model systems with coordinated ethylenediamine molecule.



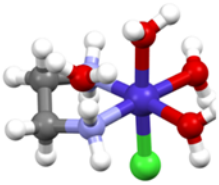
en/OH_2



$[Co(H_2O)enCl_3]/OH_2$



$[Co(H_2O)_2enCl_2]^+/OH_2$



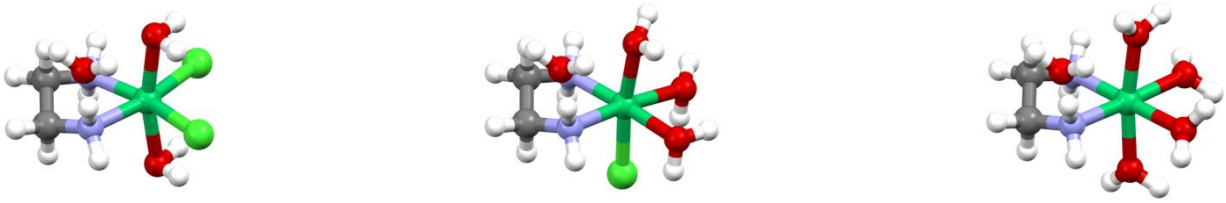
$[Co(H_2O)_3enCl]^{2+}/OH_2$

$[Co(H_2O)_4en]^{3+}/OH_2$

Figure 7. The model systems used to calculate the hydrogen bonds between the hydrogen atom of ethylenediamine and noncoordinated water with rigid monomers for noncoordinated and coordinated ethylenediamine molecule in cobalt(III) complexes.

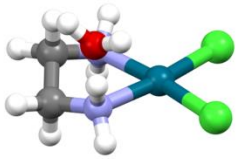
$[Cu(H_2O)_2enCl_2]/OH_2$ $[Cu(H_2O)_4en]^{2+}/OH_2$

Figure 8. The model systems used to calculate the hydrogen bonds between hydrogen atom of ethylenediamine and noncoordinated water with rigid monomers for coordinated ethylenediamine molecule in copper(II) complexes.

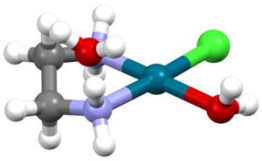


$[Ni(H_2O)_2enCl_2]/OH_2$ $[Ni(H_2O)_3enCl]^{+}/OH_2$ $[Ni(H_2O)_4en]^{2+}/OH_2$

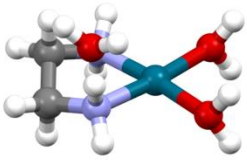
Figure 9. The model systems used to calculate the hydrogen bonds between hydrogen atom of ethylenediamine and noncoordinated water with rigid monomers for coordinated ethylenediamine molecule in nickel(II) complexes.



$[Pd en Cl_2]/OH_2$



$[Pd(H_2O) en Cl]^+/OH_2$



$[Pd(H_2O)_2 en]^{2+}/OH_2$

Figure 10. The model systems used to calculate the hydrogen bonds between hydrogen atom of ethylenediamine and noncoordinated water with rigid monomers for coordinated ethylenediamine molecule in palladium(II) complexes.

Table 1. The d_{OH} distances (Å), CCSD(T)/CBS interaction energy (ΔE (kcal/mol)) between noncoordinated ethylenediamine and noncoordinated water molecule and M06L-GD3/def2-TZVPP interaction energies (ΔE (kcal/mol)) between coordinated ethylenediamine and noncoordinated water molecule, and positive electrostatic potential on hydrogen atom involved in the interaction (Vs_r (kcal/mol)) for the model systems with rigid monomers presented in **Figures 7-10**.

Charge	***Complex***	d_{OH} **(Å)**	**ΔE (kcal/mol)**	Vs_r **(kcal/mol)**
neutral	$NH_2CH_2CH_2NH_2/OH_2$	2.15	-2.3	20
	$[Co(H_2O)enCl_3]/OH_2$	1.95	-6.7	49
	$[Cu(H_2O)_2enCl_2]/OH_2$	2.02	-4.0	38
	$[Ni(H_2O)_2enCl_2]/OH_2$	1.99	-5.4	44
	$[Pd(en)Cl_2]/OH_2$	1.92	-6.7	46
singly positive	$[Co(H_2O)_2enCl_2]^+/OH_2$	1.90	-11.8	135
	$[Cu(H_2O)_3enCl]^+/OH_2$	/	/	/
	$[Ni(H_2O)_3enCl]^+/OH_2$	2.02	-8.5	112
	$[Pd(H_2O)enCl]^+/OH_2$	1.90	-11.1	134
doubly positive	$[Co(H_2O)_3enCl]^{2+}/OH_2$	1.84	-19.9	214
	$[Cu(H_2O)_4en]^{2+}/OH_2$	1.92	-15.7	189
	$[Ni(H_2O)_4en]^{2+}/OH_2$	1.94	-15.6	191
	$[Pd(H_2O)_2en]^{2+}/OH_2$	1.78	-18.0	215
triply positive	$[Co(H_2O)_4en]^{3+}/OH_2$	1.71	-28.0	305

The complexes of cobalt(III), copper(II) and nickel(II) are

octahedral while the complexes of palladium(II) are square-planar. The interaction energy for $[Cu(H_2O)_3enCl]^+/OH_2$ was not calculated due to dissociation of water molecule during optimization of $[Cu(H_2O)_3enCl]^+$ (**Figure S1**).

The interaction energy between noncoordinated ethylenediamine and water molecule is -2.3 kcal/mol. The ethylenediamine in neutral metal complexes has several times stronger interaction energy than noncoordinated ethylenediamine. Namely, the interaction energies between coordinated ethylenediamine and free water molecule for neutral octahedral cobalt(III), copper(II), nickel(II) and square-planar palladium(II) complexes are -6.7 kcal/mol, -4.0 kcal/mol, -5.4 kcal/mol and -6.7 kcal/mol, respectively (**Table 1**). The stronger interactions are a consequence of increased positive potential (Vs_r) on the interacting hydrogen atoms when ethylenediamine is coordinated (**Table 1**).

For singly charged octahedral cobalt(II), nickel(II), and square-planar palladium(II) complexes interaction energies are stronger, as it can be anticipated. The corresponding interaction for singly charged copper(II) complex was not calculated since the optimization of the complex resulted in five coordinated complexes, due to dissociation of ligand (**Figure S1**). The interaction energies for octahedral cobalt(III) and square-planar palladium(II) complexes are -11.8 kcal/mol and -11.1 kcal/mol, respectively, while for octahedral nickel(II) complex energy is somewhat weaker, -8.5 kcal/mol.

The doubly charged octahedral complexes have even stronger interactions than singly charged complexes (**Table 1**). The strongest interaction is for octahedral cobalt(III) complex, -19.9 kcal/mol, followed with square-planar palladium(II) complex with -18.0 kcal/mol. The octahedral copper(II) and nickel(II) complexes have weaker interactions, -15.7 kcal/mol, and

-15.6 kcal/mol, respectively. This result is in accordance with Vs_r value, the higher value leads to the stronger interaction (**Table 1**).

The triply charged complex was only possible for cobalt(III) complex and the interaction for this complex is the strongest, -28.0 kcal/mol which is accompanied by the highest Vs_r value (**Table 1**).

The differences in the interaction energies among metal complexes are a consequence of an oxidation state of the metal atom and the coordination number of the complex. One can notice that interactions of Co(III) and Pd(II), for each charge of a complex, are always stronger than interactions of the corresponding Cu(II) and Ni(II) complexes. Relatively strong interactions of Co(III) complexes are a consequence of a high oxidation state of the metal, which can give a more positive charge to the ligands, leading to more positive potential on the interacting hydrogen atom (**Table 1**). Strong interactions of Pd(II) complexes are consequence of the coordination number; in Pd(II) complexes coordination number is four, and because of a smaller number of ligands, each ligand can get a more positive charge from the metal leading to more positive potential on the interacting hydrogen (**Table 1**). A similar influence of coordination number to the strength of the hydrogen bonds was observed for hydrogen bonds of the coordinated water molecule, where interactions were stronger for tetrahedral than for octahedral complexes.[15]

With the increasing charge of the complex, together with increasing strength of hydrogen bonds, d_{OH} distances are shortened (**Table 1**). For each metal, distances are shorter from neutral to single charged and shorter even more for double charged complexes. The only exception single charged is Ni(II) complex for which d_{OH} distance is somewhat longer than for the neutral complex. This is a consequence of the geometries of the neutral and single charged complexes

(**Figures 9** and **S2**). In the neutral complex, two chlorine atoms are in the equatorial plane causing hydrogen atoms of coordinated water to be oriented towards them. There is also some attraction of noncoordinated water forming a hydrogen bond with the chlorine atoms. The electrostatic potential maps, presented in **Figure S3**, illustrate the strong influence of chlorine atoms on the electrostatic potential and on the intermolecular and intermolecular interactions in these systems. On the other hand, in the single charged complex, there are no chlorine atoms in the cis-position to coordinated water; hence hydrogen atoms have different orientations. This position of hydrogen atoms is causing repulsion with noncoordinated water (**Figure S2**). The repulsion, together with the lack of attraction to a chlorine atom, are causing longer d_{OH} distance in single charged Ni(II) complex, despite the larger positive Vs_r potential on the interacting (N)H atom (**Table 1**). We want to point out that the isomers of the complexes used in these calculations are the most stable isomers obtained by optimization.

The interaction energies have a good correlation with the positive potentials Vs_r calculated for rigid monomers (**Table 1, Figure 11**). The higher positive Vs_r value at the hydrogen atom involved in interaction leads to stronger interaction energy (ΔE). The correlation coefficient (R) between ΔE and Vs_r is 0.963.

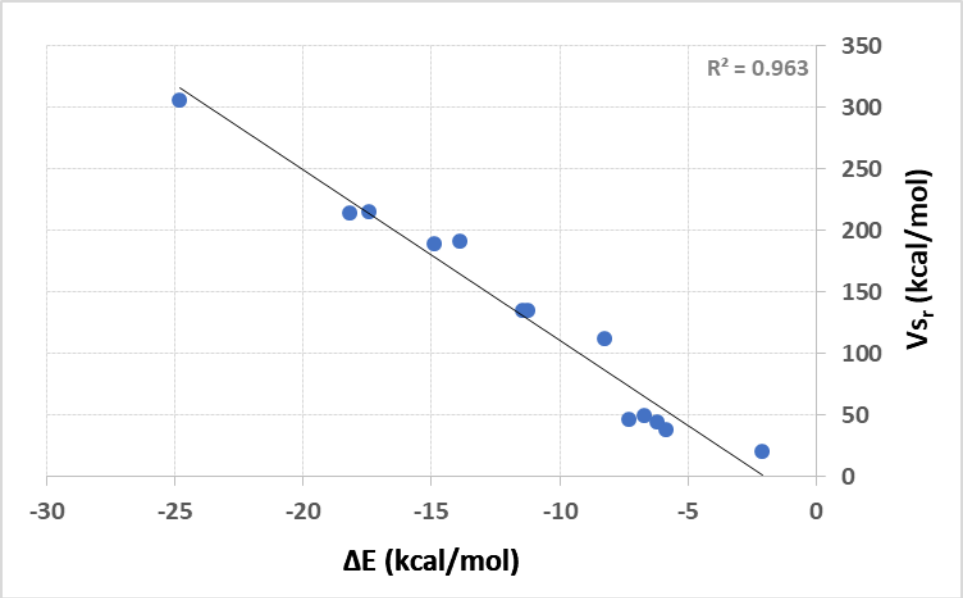
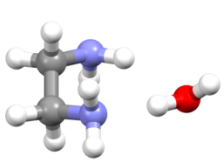


Figure 11. The plot of Δ*E* against Vs_r for interacting ethylenediamine hydrogen atoms in the model systems with rigid monomers (**Table 1**, **Figures 7-10**). The Vs_r value is for electrostatic potential value on interacting hydrogen atom before the interaction. The correlation coefficient (R^2) value is 0.963.

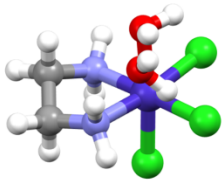
The ethylenediamine/water hydrogen bond (-2.3 kcal/mol, **Table 1**) is the same strength as the ammonia/water hydrogen bond (-2.3 kcal/mol)[18] and more than 50% weaker than the water/water hydrogen bond (-4.84 kcal/mol).[15] The interaction energies for coordinated ethylenediamine, for neutral complexes, are in the range from -4.0 kcal/mol to -6.7 kcal/mol. This is somewhat stronger than coordinated ammonia (-3.7 kcal/mol to -6.1 kcal/mol)[18] and somewhat weaker than interactions of coordinated water (-5.4 kcal/mol to -9.2 kcal/mol).[15] For singly charged complexes, interaction energies for coordinated ethylenediamine span from -8.5 kcal/mol to -11.3 kcal/mol, similar to coordinated ammonia (-5.0 kcal/mol to -14.0 kcal/mol),[18] while the interactions of coordinated water are strongest (-12.2 kcal/mol to -15.8 kcal/mol).[15] Results are similar for doubly charged complexes, as well.[15]

The trend in interaction energies for coordinated ligands, water, ammonia, and ethylenediamine, is in accordance with electrostatic potential calculated at interacting hydrogen atoms prior to interaction. Namely, interactions for coordinated water are the highest due to the highest value of electrostatic potential.[17] However, interaction energies of coordinated-ethylenediamine/water and coordinate-water/water differ less than interaction energies between noncoordinated ethylenediamine/water and noncoordinated water/water interactions.

Calculations with optimized systems. The whole model systems without any constraints were optimized and energies of interactions between noncoordinated water and complex in optimized systems were calculated. The optimized systems are shown in **Figures 12-15**. The calculated interaction energies for optimized model systems are stronger than corresponding interaction in model systems with rigid monomers. The stronger interactions in optimized systems are a consequence of additional attractive interactions of a free water molecule. The most pronounced example is the interaction of noncoordinated ethylenediamine (**Figure 12**). Namely, the interaction energy is quite strong, -7.2 kcal/mol, because of the additional hydrogen bonds.

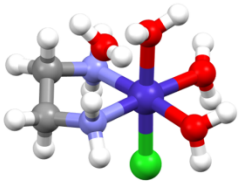


en/OH_2



$[Co(H_2O)enCl_3]/OH_2$

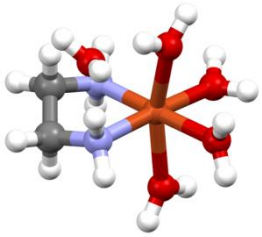
$[Co(H_2O)_2enCl_2]^+/OH_2$



$[Co(H_2O)_3enCl]^{2+}/OH_2$

$[Co(H_2O)_4en]^{3+}/OH_2$

Figure 12. The totally optimized model systems used to calculate hydrogen bond between hydrogen atom of ethylenediamine and noncoordinated water for noncoordinated and coordinated ethylenediamine molecule in cobalt(III) complexes.



$[Cu(H_2O)_4en]^{2+}/OH_2$

Figure 13. The totally optimized model systems used to calculate hydrogen bond between hydrogen atom of ethylenediamine and noncoordinated water for coordinated ethylenediamine molecule in copper(II) complexes.

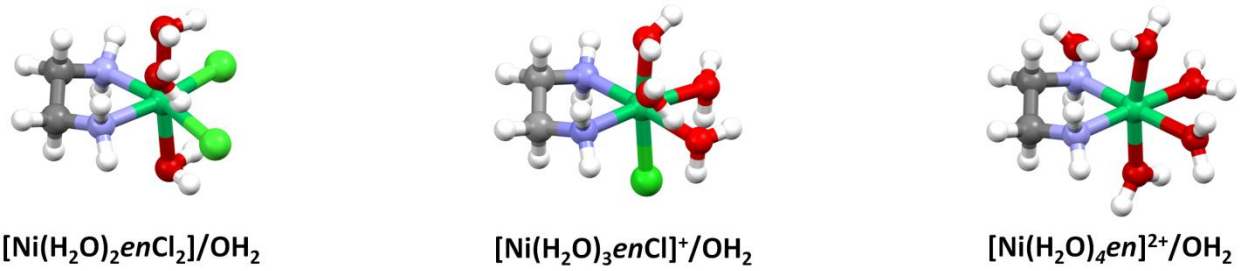


Figure 14. The totally optimized model systems used to calculate hydrogen bond between hydrogen atom of ethylenediamine and noncoordinated water for coordinated ethylenediamine molecule in nickel(II) complexes.

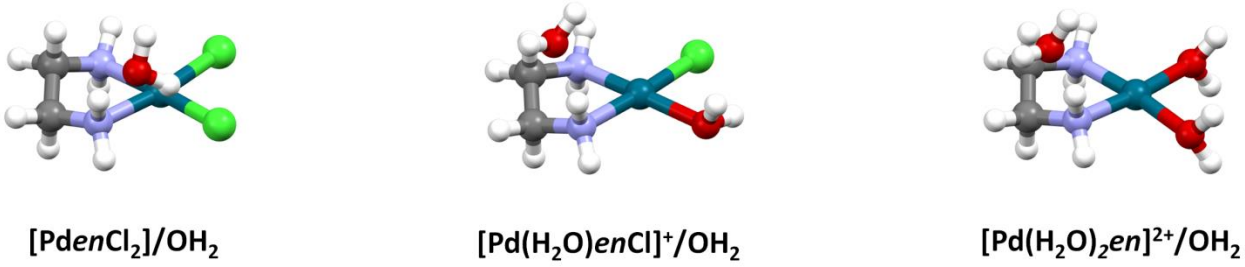


Figure 15. The totally optimized model systems used to calculate hydrogen bond between hydrogen atom of ethylenediamine and noncoordinated water for coordinated ethylenediamine molecule in palladium(II) complexes.

The optimization of the system with neutral copper(II) complex, $[Cu(H_2O)_2enCl_2]/OH_2$, led to a pentacoordinated complex where one water molecule is detached from the complex (**Figure S1**). The neutral octahedral cobalt(III), nickel(II) and square-planar palladium(II) complexes have interaction energies -18.8 kcal/mol, -18.3 kcal/mol and -13.6 kcal/mol, respectively (**Table 2**). The singly positive charged octahedral cobalt(III) complex has stronger interaction energy than neutral complex -22.3 kcal/mol (**Table 2**). However, for singly charged nickel(II) and palladium(II) complexes, interaction energies are slightly weaker (-17.5 kcal/mol

and -12.6 kcal/mol) than for neutral complexes (**Table 2**). This is a consequence of the difference in the interactions for neutral and charged complexes.

Table 2. The d_{OH} distances (Å), CCSD(T)/CBS interaction energy (ΔE (kcal/mol)) between noncoordinated ethylenediamine and noncoordnated water molecule and M06L-GD3/def2-TZVPP interaction energies (ΔE (kcal/mol) between coordinated ethylenediamine and noncoordinated water molecule, and positive electrostatic potential on hydrogen atom involved in the interaction (Vs_t (kcal/mol)) for optimized systems presented in **Figures 12-15**.

Charge	***Complex***	d_{OH} **(Å)**	ΔE **(kcal/mol)**	Vs_t **(kcal/mol)**
neutral	$NH_2CH_2CH_2NH_2/OH_2$	2.21	-7.2	-8
	$[Co(H_2O)enCl_3]/OH_2$	2.02	-18.8	29
	$[Cu(H_2O)_2enCl_2]/OH_2$	/	/	/
	$[Ni(H_2O)_2enCl_2]/OH_2$	2.25	-18.3	57
	$[Pd(en)Cl_2]/OH_2$	1.89	-13.6	35
singly positive	$[Co(H_2O)_2enCl_2]^+/OH_2$	2.16	-22.3	43
	$[Cu(H_2O)_3enCl]^+/OH_2$	/	/	/
	$[Ni(H_2O)_3enCl]^+/OH_2$	2.36	-17.5	135
	$[Pd(H_2O)enCl]^+/OH_2$	1.86	-12.6	117
doubly positive	$[Co(H_2O)_3enCl]^{2+}/OH_2$	2.07	-28.1	194
	$[Cu(H_2O)_4en]^{2+}/OH_2$	2.07	-22.0	165
	$[Ni(H_2O)_4en]^{2+}/OH_2$	2.17	-23.2	163
	$[Pd(H_2O)_2en]^{2+}/OH_2$	2.10	-19.7	171
triply positive	$[Co(H_2O)_4en]^{3+}/OH_2$	2.15	-39.8	242

The complexes of Co, Cu, and Ni are in octahedral geometry while the complexes of Pd are in square-planar geometry. The interaction energies for $[Cu(H_2O)_2enCl_2]/OH_2$ and $[Cu(H_2O)_3enCl]^+/OH_2$ were not calculated due to dissociation of water molecule during optimization of $[Cu(H_2O)_2enCl_2]$ and $[Cu(H_2O)_3enCl]^+$, respectively (**Figure S1**).

The doubly positive charged octahedral cobalt(III), copper(II), and nickel(II) complexes have similar interaction energies of -28.1 kcal/mol, -22.0 kcal/mol, and -23.2 kcal/mol, while square-planar palladium(II) complex has the weakest interaction of -19.7 kcal/mol (**Table 2**). As

one can anticipate the strongest interaction is for cobalt(III) complex (-39.8 kcal/mol) and it corresponds to the highest value of electrostatic potential (Vs_r) (**Table 2**).

The weakest interactions for palladium(II) complexes for neutral and charged complexes are due to the lack of possibility for additional interactions with axially coordinated water molecule (**Figure 15**), since only Pd(II) complexes are square-planar complexes.

In optimized model systems, the obtained d_{OH} distances (**Table 2**) are for some cases shorter than for the corresponding model system with rigid monomers, however, there are also cases where d_{OH} distances are longer. The shorter distances were obtained in the systems where the hydrogen bond of noncoordinated water with coordinated ethylenediamine (NH···O) is the most important interaction. In optimized systems where water molecule forms significant interactions with other ligands (**Figures 12-15**), d_{OH} distances are longer.

Although interaction energies for totally optimized complexes are greater than for rigid monomers, the Vs_t values at the interacting sites are less positive than Vs_r values except for neutral and singly charged nickel(II) complexes. Additionally, Vs_t values have much a poorer correlation with interaction energies (R^2=0.465, **Figure S4**) indicating that not only the hydrogen bond of ethylenediamine hydrogen with water oxygen but also additional interactions are important in these optimized water-complex systems.

The calculated d_{OH} distances for rigid systems are in the range of 1.7 - 2.2 Å while for totally optimized systems, d_{OH} distances are in the range 1.9 – 2.3 Å (except for singly positive nickel(II) where d_{OH} distance is larger, 3.0 Å). These calculated values are in good correlation with the distribution of d_{OH} distance from crystal structures (**Figure 2**) where the majority of structures have d_{OH} distance from 1.9 to 2.2 Å.

Conclusions

The data from the CSD search reviled 536 contacts of the coordinated ethylenediamine complexes that interact with water molecule via NH···O hydrogen bond. In the distribution of d_{OH} distance with α angle one can notice that with shorter d_{OH} distance α angle becomes larger, which is typical for hydrogen bonds. The maxima of distributions d_{OH} and α are 2.0-2.1 Å and 150-160^0, respectively. The most abundant metals and geometries are octahedral cobalt, copper and nickel complexes and square-planar palladium complex.

The coordination of ethylenediamine to the metal ions strengthens its hydrogen with a water molecule. The interaction energies for neutral metal complexes are in the range of -4.0 kcal/mol to -6.7 kcal/mol. For singly charged metal complexes, interaction energy is higher and spans from -8.5 to -11.8 kcal/mol. The interaction energies for doubly charged metal complexes are from -15.6 kcal/mol to -19.9 kcal/mol while triply charged Co complex has the strongest interaction from -28.0 kcal/mol. The hydrogen bond energies have a good correlation with the electrostatic potential on interacting hydrogen atom. Totally optimized model systems have even stronger interaction energies, starting from -13.6 kcal/mol for neutral square-planar palladium(II) complex to -39.8 kcal/mol for triply charged cobalt(III) complex. The strong interactions are the consequence of additional interactions that exist in the optimized systems. In accordance with that, the interaction energies for totally optimized model systems do not correspond well with electrostatic potentials at the interacting sites. The ethylenediamine/water hydrogen bond (-2.3 kcal/mol) has the same strength as ammonia/water hydrogen bond (-2.3 kcal/mol)[18] and more than 50% weaker than water/water hydrogen bond (-4.8 kcal/mol).[15] However, coordination of ethylenediamine reduces the difference between interaction energies of coordinated-ethylenediamine/water, coordinated-ammonia/water, and coordinated-water/water systems. This

brings the conclusion that coordination of ligand is more important for hydrogen bond strength than nature of the ligand.

ASSOCIATED CONTENT

Supporting Information.

Additional graphics and coordinates for optimized geometries

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no conflicts of interest.

ACKNOWLEDGMENT

This work was supported by the Serbian Ministry of Education. Science and Technological Development (Contract numbers: 451-03-9/2021-14/200168 and 451-03-9/2021-14/200288).

The high-performance computing resources were provided by the IT Research Computing Group at Texas A&M University at Qatar which is funded by the Qatar Foundation for Education. Science and Community Development.

ABBREVIATIONS

CSD, Cambridge Structural Database; CCSD(T), Coupled-Cluster with Single, Double and Perturbative Triple Excitations; CBS, Complete Basis Set; BSSE, Basis Set Superposition Error.

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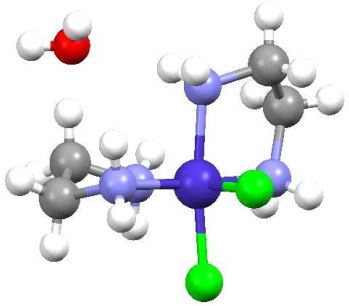
SYNOPSIS

Analysis of interactions between noncoordinated and coordinated ethylenediamine show that they are involved in many hydrogen bond interactions. The noncoordinated ethylenediamine and water molecule has interaction energy of -2.1 kcal/mol while for coordinated ethylenediamine interacting energy spans from -5.8 kcal/mol to -24.8 kcal/mol, depending on the metal ion and charge of the complex.

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