

Research Letter

Crystal Structure of [Bis(L-Alaninato)Diaqua] Nickel(II) Dihydrate

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Received 4 December 2008; Accepted 4 February 2009

Recommended by Hakan Arslan

The title complex, $[\text{Ni}(\text{C}_3\text{H}_6\text{O}_2\text{N})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, has been prepared from nickel(II) chloride in aqueous solution by adding L-alanine and potassium hydroxide. It has been crystallized from aqueous solution, and its structure was determined by X-ray structure analysis. The nickel(II) ion adopts distorted octahedral coordination geometry with two bidentate L-alanine molecules and two water molecules. The complex is neutral and dihydrated. The crystal structure shows the hydrogen bonding between water and amide hydrogens within the lattice, and each fragment of the complex contains two water molecules as hydrated water. The L-alaninato ligand skeleton of the compound adopts the most stable trans-III configuration in the solid state. The alternating two five-membered chelate rings are in the stable gauche conformation.

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1. Introduction

Complexes formed by metal cations and organic species are incorporated in many biochemical structures, such as cytochromes of mitochondrial membranes, hemoglobin, and chlorophyll. Transition metal complexes with Schiff-base ligand containing the carboxylate group have been of great interest due to their importance as essentially biologically active [1–3] models for metalloproteins [4] and their various geometry aspects [5]. Metals bound to amino acids are essential for the catalytic function of certain enzymes, and their chemistry has received a great deal of research interest due to their significant interaction with enzymes and with different organic ligands which enables a better understanding of the antitumor/viral activities of this class of compounds and for modeling substrates involved in enzyme inhibition [6, 7]. A number of complexes of amino acids with many transition metal ions have been prepared and thoroughly studied [8–14]. A complex of alanine with nickel(II) was reported [15] and described as a neutral *bis*(alaninato)diaqua nickel(II), and its X-ray crystal structure seems not to have been explicitly studied. Therefore, it was considered worthwhile and of great significant chemical interest to synthesize this complex and to study thoroughly its crystal structure in order to get greater depth into its composition.

Study of the structures of metal-amino acid complexes is a classical problem initiated by the school of Pauling in the 40s, with the nickel-glycine compound. Many authors have worked in this direction with increasing resolution and details. This paper describes the single-crystal structure of [*bis*(L-alaninato)diaqua] Nickel(II) dihydrate.

2. Experimental

2.1. Chemicals and Instrumentation. All chemicals were of reagent grade and used as purchased from commercial source. The single-crystal X-ray diffraction data in this paper were recorded on an instrument Bruker APEX-II 3-circle diffractometer, a CCD area detector with graphite monochromated Mo-K α radiation supported by the National Science Foundation, Major Research Instrumentation (MRI) Program under Grant no. CHE-0521569.

2.2. Preparation Procedures. NiCl₂ · 6H₂O (20 mL, 0.1 M), KOH (20 mL, 1.0 M), and L-alanine (20 mL, 0.2 M) were mixed. The mixture was made basic with pH = 8 and turned from green to pale blue. The flask solution was left at room temperature. After standing for two weeks, pale-blue tablet-shaped crystals were obtained, removed, and dried

under vacuum. The isolated crystals were subjected to X-ray studies.

2.3. *Crystal Structure Determination.* The structure was solved by direct methods and expanded routinely. The model was refined by full-matrix least-squares analysis of F^2 against all reflections. All nonhydrogen atoms were refined with anisotropic thermal displacement parameters. The hydrogens on the water oxygens and amide nitrogens were located from a difference Fourier map and included in their observed positions with thermal parameters tied to that of the atoms to which they are bonded. The hydrogen atoms bonded to carbon were included in calculated positions with thermal parameters tied to that of the carbon to which they are bonded. The crystallographic data and parameters are given in Table 1. The softwares used for direct method, least-squares analysis, molecular drawing, and preparing the crystallographic materials are APEX-II [16], SAINT [17], XPREP [18], SADABS [19], SHELXTL [20], and ORTEPII [21].

3. Results and Discussion

The title complex was prepared by the reaction of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, KOH, and L-alanine. The presence of KOH has two roles: the first is to adjust the pH of the resulting solution from 6 to 8 and the second is to convert the carboxylic group of alanine to carboxylate ion in favor to bind readily with nickel(II) ion.

There are four molecules of the nickel complex and eight water of crystallization in the unit cell of the C-centered, acentric, and monoclinic space group C2. The correct enantiomorph of the space group and handedness of the molecule were determined by comparison of the intensities of Friedel pairs of reflections (Fleck parameter = 0.018(13)) and by the known stereochemistry of the L-alanine ligands. Both techniques agreed, and the correct configuration is shown in the Figure 1.

The title compound is crystallized from aqueous solution as pale-blue prismatic crystals. The structure consists of an $[\text{Ni}(\text{L-alaninato})_2(\text{H}_2\text{O})_2]$ and two water molecules. The nickel ion resides at the center of symmetry of the octahedron and is surrounded by two oxygen atoms of two alanine molecules, two oxygen atoms of two water molecules, and two nitrogen atoms of the same two alanine molecules. The carboxylato oxygens and the amido nitrogens of the two alanine molecules define the equatorial positions, whereas the two oxygen atoms of the two water molecules occupy the axial ones. It is observed that the axial Ni–O bond distances (Table 2) of 2.0706(18) and 2.1006(16) Å are significantly longer than the equatorial Ni–O bonds of 2.0422(17) and 2.0567(17) Å. All the Ni–O distances are in agreement with those found in six coordinate nickel(II) complexes [22]. The average Ni–N bond distance of 2.073(17) Å is in the normal range for Ni–N primary amines of high-spin octahedral nickel(II)

TABLE 1: Crystal data and structure refinement of the title compound.

<i>Empirical formula</i>	$\text{C}_6\text{H}_{20}\text{N}_2\text{NiO}_8$
Formula weight	306.95
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2
Unit cell dimensions	$a = 20.162(4)$ Å
	$b = 6.5089(13)$ Å
	$c = 9.6476(19)$ Å
	$\beta = 94.823(2)^\circ$
Volume	$1261.6(4)$ Å ³
Z	4
Density (calculated)	$1.616 \text{ g} \cdot \text{cm}^{-3}$
Absorption coefficient (μ)	1.570 mm^{-1}
F(000)	648
Crystal size	$0.16 \times 0.10 \times 0.09 \text{ mm}^3$
ω range for data collection	2.03 to 28.28°
	$-26 \leq h \leq 6$
Index ranges	$-8 \leq k \leq 8$
	$-12 \leq l \leq 12$
Reflections collected	7100
Independent reflections	3070 [$R_{\text{int}} = 0.0218$]
Completeness to $\theta = 28.28^\circ$	99.6%
Absorption correction	Numerical
Max. and min. transmission	0.8716 and 0.7873
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3070/3/192
Goodness-of-fit on F^2	1.013
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0232$, $wR_2 = 0.0528$
Absolute structure parameter	0.018(13)
Largest diff. peak and hole	0.400 and $-0.251 \text{ e}^- \cdot \text{Å}^{-3}$

complexes with chelating ligands [23]. The axial angle O–Ni–O is $178.36(9)^\circ$, whereas the equatorial O–Ni–O is $179.33(7)^\circ$ (Table 2) that are close to linearity. The average Ni–O and Ni–N bond lengths are in accordance to that known for nickel(II) distorted octahedral geometry. Therefore, two alanine molecules and two water molecules are directly involved in coordination. The coordination geometry around the nickel(II) ion is a six-coordinated tending toward distorted octahedral, with a metal center not lying exactly within the N_2O_2 plane because the bond angles are not perfect [24, 25]. The two apical positions

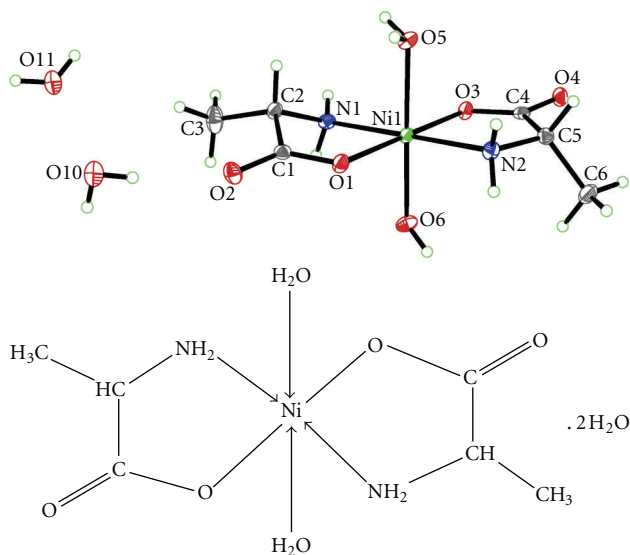


FIGURE 1: The chemical diagram and the crystal structure of the title compound showing the atomic numbering scheme.

TABLE 2: Important bond lengths [\AA] and angles [$^\circ$] of the title compound.

Bond distance					
Ni(1)–O(3)	2.0422(17)	Ni(1)–O(1)	2.0567(17)		
Ni(1)–N(1)	2.0703(17)	Ni(1)–O(6)	2.0706(18)		
Ni(1)–N(2)	2.0758(16)	Ni(1)–O(5)	2.1006(16)		
Bond angles					
O(3)–Ni(1)–O(1)	179.33(7)	O(3)–Ni(1)–N(1)	99.35(8)		
O(1)–Ni(1)–N(1)	80.30(8)	O(3)–Ni(1)–O(6)	90.09(7)		
O(1)–Ni(1)–O(6)	89.33(6)	N(1)–Ni(1)–O(6)	88.07(7)		
O(3)–Ni(1)–N(2)	82.32(9)	O(1)–Ni(1)–N(2)	98.03(9)		
N(1)–Ni(1)–N(2)	178.29(15)	O(6)–Ni(1)–N(2)	92.29(7)		
O(3)–Ni(1)–O(5)	88.27(7)	O(1)–Ni(1)–O(5)	92.31(7)		
N(1)–Ni(1)–O(5)	92.22(7)	O(6)–Ni(1)–O(5)	178.36(9)		
N(2)–Ni(1)–O(5)	87.46(7)	C(1)–O(1)–Ni(1)	115.63(13)		

are occupied by water molecules, and the equatorial plane is occupied by the chelating alanine ligands. Distortions about nickel atom are observed, in which slightly different bond distances to the coordinating water molecules; essentially identical bond distances to the nitrogens and slightly different bond distances to the chelating oxygens O1 and O3. The enforced distortion about the equatorial plane due to the formation of the two five-membered chelate rings is seen. The two ligands adopt an envelope and a planar geometry, with respect to the mean equatorial plane about the nickel (Table 3).

It is seen that there are two water molecules not chemically bonded to Ni(II) and located at the opposite site

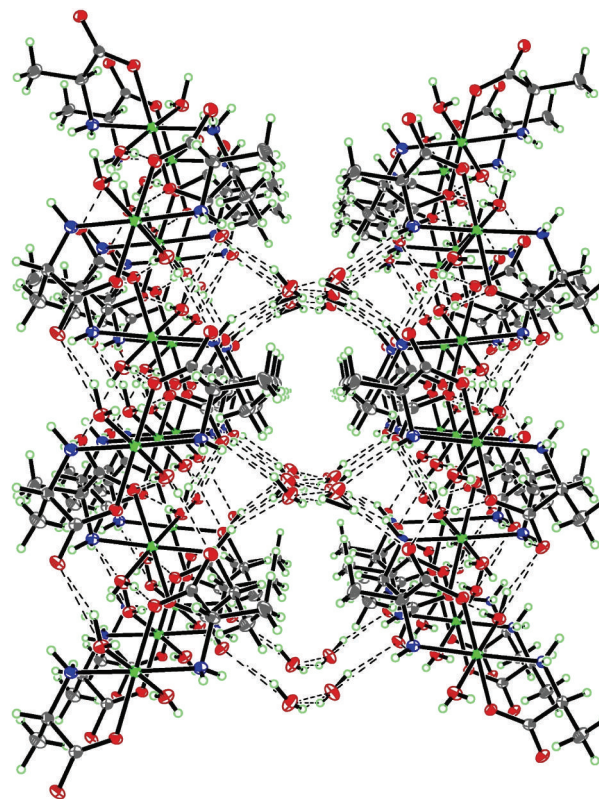


FIGURE 2: Hydrogen bonding network of the title compound.

TABLE 3: Deviation from the mean plane.

Deviation (\AA)	s.u.	Atom	Deviation (\AA)	s.u.	Atom
* 0.0000	(0.0000)	Ni1	* 0.0000	(0.0000)	Ni1
* 0.0000	(0.0000)	O1	* 0.0000	(0.0000)	O3
* 0.0000	(0.0000)	N1	* 0.0000	(0.0000)	N2
–0.1711	(0.0028)	C1	–0.0050	(0.0029)	C4
–0.5880	(0.0033)	C2	0.0376	(0.0034)	C5

* Atom defining mean plane.

of alanine group, and have no significant interaction with the metal atom. A hydrogen bonding is observed between the hydrogen atoms of coordinated and hydrated waters with the oxygen atoms of the carboxylate groups, there are many hydrogen bonds responsible of the packing, and the values of these interactions are shown in Table 4. Also, the hydrogen bonds are seen between the hydrogen of the amide nitrogen and the oxygen atoms of the hydrated water molecules and carboxylate groups (Figure 2). The hydrogen atoms on the water molecules and the amide nitrogens were all located from a difference Fourier map. All are involved in an extensive three-dimensional network of hydrogen bonds within the lattice.

TABLE 4: Hydrogen bonds of the title compound [\AA and $^\circ$].

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
O(5)–H(5OA)...O(4)#1	0.92(3)	1.85(3)	2.724(4)	158(2)
O(5)–H(5OB)...O(3)#2	0.77(2)	1.97(2)	2.732(2)	175(3)
O(6)–H(6OA)...O(2)#3	0.60(3)	2.11(3)	2.712(3)	171(3)
O(6)–H(6OB)...O(1)#4	0.81(2)	2.11(3)	2.687(2)	169(3)
N(1)–H(1NA)...O(10)#3	0.88(2)	2.44(2)	3.274(3)	159(2)
N(1)–H(1NB)...O(4)#2	0.75(3)	2.31(2)	3.022(2)	159(4)
N(2)–H(2NA)...O(11)#5	0.92(2)	2.36(2)	3.227(3)	157(2)
N(2)–H(2NB)...O(2)#4	0.90(2)	2.28(2)	3.183(2)	173(3)
O(10)–H(10A)...O(2)	0.777(18)	2.043(19)	2.803(3)	166(3)
O(10)–H(10B)...O(10)#6	0.745(17)	2.158(18)	2.860(3)	157(3)
O(11)–H(11A)...O(11)#7	0.745(17)	2.170(19)	2.843(3)	151(3)
O(11)–H(11B)...O(4)#8	0.784(19)	1.994(19)	2.750(3)	162(3)

Symmetry transformations used to generate equivalent atoms: #1 $x, y - 1, z$; #2 $-x + 3/2, y - 1/2, -z$; #3 $x, y + 1, z$; #4 $-x + 3/2, y + 1/2, -z + 1$; #5 $x - 1/2, y + 1/2, z$; #6 $-x + 2, y, -z + 1$; #7 $-x + 2, y, -z$; #8 $x + 1/2, y - 3/2, z$.

4. Conclusions

This communication describes the crystallographic characterization of a complex of nickel(II) with L-alanine. The method illustrated for the preparation of this complex must be extended to other metal ions such as iron, copper, and zinc. In fact, nickel(II) was chosen for our synthesis because it forms well-defined crystals that can be studied by X-ray crystallography. The complex is a chelate with two bidentate alanine ligands bonding through N and O and two water molecules. The oxygen of the carboxylate groups of alanine is deprotonated by removal of its hydrogen with the hydroxyl group of KOH producing water molecule.

Supplementary Material. Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and allocated deposition no. CCDC 718341 for the title compound and can be obtained free of charge on application to CCDC 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (internat.) 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

The authors would like to thank Mohammad Zhou, the university web master for computer assistance. Also, A. Khatib wishes to thank the CIES and Fulbright for a Sabbatical at the University of California.

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