



SYNTHESIS AND CRYSTAL STRUCTURE OF [BIS(DL-ALANINATO)DIAQUA]NICKEL(II) DIHYDRATE

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Abstract

The complex of formula $[\text{Ni}(\text{NH}_2\text{CH}_2\text{CHCOO})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ has been prepared from nickel(II) chloride in aqueous solution by adding DL-alanine and potassium hydroxide. It has been crystallized from aqueous solution and its structure was determined by X-ray structure analysis, i.r. and uv-visible spectroscopy. The molecular structure shows that the complex is a chelate with two N,O-coordinating bidentate alanine ligands and two water molecules. The complex is neutral and dihydrated. The molecular symmetry is C_2 . The coordination polyhedron is an octahedron with *trans* arrangement of the aqua ligands. The oxygen atom of the carboxylato group is deprotonated. The network crystal structure shows hydrogen bonding between water and amide hydrogens within the lattice, and each fragment of the complex contains two water molecules as hydrated water. The methyl group on the chelate rings is *anti* with respect to the N_2O_2 plane. The complex has an inversion center at the nickel(II) ion.

Keywords: alanine complex; crystal structure; hydrogen bonding; water of hydration

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Resumen

Se ha preparado el complejo de fórmula $[\text{Ni}(\text{NH}_2\text{CH}_3\text{CHCOO})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ a partir de soluciones acuosas de cloruro de níquel(II) por agregado de DL-alanina e hidróxido de potasio. El complejo fue cristalizado desde una solución acuosa y su estructura se determinó por difracción de Rayos X y espectroscopías ir y uv-visible. La estructura molecular muestra que el complejo es un quelato con dos ligandos bidentados N,O coordinados de alanina y dos moléculas de agua. El complejo es neutro y dihidratado. La simetría molecular es C_2 . La coordinación del poliedro es un octaedro con arreglo *trans* de los acuoligandos. El átomo de oxígeno del grupo carboxilato está desprotonado. La estructura cristalina muestra la presencia de enlace hidrógeno entre el agua y los hidrógenos de la amida dentro de la red, y cada fragmento del complejo contiene dos moléculas de agua de hidratación. El grupo metilo en los anillos del quelato es *anti* respecto al plano N_2O_2 . El complejo posee un centro de inversión en el ión níquel(II).

Palabras clave: complejos de alanina; estructura cristalina; enlace de hidrógeno; agua de hidratación

Introduction

Still the complexes of amino acids continue to be an active field of study because they are incorporated in many biochemical structures, such as cytochromes of mitochondrial membranes, hemoglobin and chlorophyll and 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 [8-15]. The crystal and molecular structure of DL-nickel alaninato tetrahydrate and a hydrated complex of DL-alanine with cadmium chloride were reported [16,17]. We have recently reported the crystal structures of D- and L-alanine complexes with Ni(II) [18,19], and in continuation to this work it was considered worthwhile and of great significant chemical interest to synthesize the DL-alanine complex with nickel(II) and to study thoroughly its crystal structure in order to get greater depth into its composition.

This paper describes the synthesis of bis(DL-alaninato)(diaqua)nickel(II), $[\text{Ni}(\text{NH}_2\text{CH}_3\text{CHCOO})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ and its characterization.

Materials and methods

All chemicals were of reagent grade and used as purchased from commercial source. The ir spectra were recorded in KBr with an FTIR 1600 FT spectrophotometer in the $4000 - 400 \text{ cm}^{-1}$ region. Uv.-visible spectra were measured and recorded with a Hewlett-Packard UV-Vis spectrophotometer.

Preparation of $[\text{Ni}(\text{NH}_2\text{CH}_3\text{CHCOO})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (20 ml, 0.1 M), KOH (20 ml, 1.0 M) and DL-alanine (20 ml, 0.2 M) were mixed. The mixture became basic with $\text{pH}=8$ and turned from green to pale blue. The flask solution was left at room temperature. After standing for two weeks blue/pale tablet-shaped crystals were obtained, removed and dried *in vacuo*. The isolated crystals were subjected to x-ray studies.

Crystal structure determination

Crystal data for the complex are tabulated in Table I. Data were corrected for absorption and polarization effects and analyzed for space group 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 non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded (1.5 Å for methyl, 1.2 for all others). The softwares used for direct method, least-squares analysis, molecular drawing and preparing the crystallographic materials are APEX-II, SAINT, XPREP, SADABS, SHELXTL and ORTEPII.

Table 1. Crystal data and structure refinement for the compound.

Empirical formula	$C_6H_{20}N_2NiO_8$
Formula weight	306.95
Temperature	220(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$Pna2_1$
Unit cell dimensions	$a = 9.6006(12)$ Å $\alpha = 90^\circ$ $b = 6.4536(8)$ Å $\beta = 90^\circ$ $c = 20.653(3)$ Å $\gamma = 90^\circ$
Volume	1279.6(3) Å ³
Z	4
Density (calculated)	1.593 g.cm ⁻³
Absorption coefficient (μ)	1.548 mm ⁻¹
F(000)	648
Crystal size	0.27 × 0.16 × 0.06 mm ³
ω range for data collection	3.31 to 26.51°
Index ranges	-12 ≤ h ≤ 2, -8 ≤ k ≤ 8, -25 ≤ l ≤ 25
Reflections collected	11664
Independent reflections	2630 [$R_{int} = 0.0210$]
Completeness to $\theta = 26.51^\circ$	99.9 %
Absorption correction	Numerical
Max. and min. transmission	0.9129 and 0.6800
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2630 / 35 / 188
Goodness-of-fit on F^2	1.069
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0231$, $wR_2 = 0.0567$
R indices (all data)	$R_1 = 0.0256$, $wR_2 = 0.0586$
Absolute structure parameter	0.473(19)
Largest diff. peak and hole	0.365 and -0.282 e ⁻ .Å ⁻³

Results and discussion

The complex was prepared by the reaction of $NiCl_2 \cdot 6H_2O$, KOH and DL-alanine. The presence of KOH has two roles; 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. The formation of the complex $[Ni(NH_2CH_2CHCOO)_2(H_2O)_2] \cdot 2H_2O$ was proved by X-ray crystallography (Figure 1). It is crystallized from aqueous solution as pale blue crystals. The

present paper describes the synthesis and structure determination of nickel(II) ion coordinated by two alanine molecules and two water molecules.

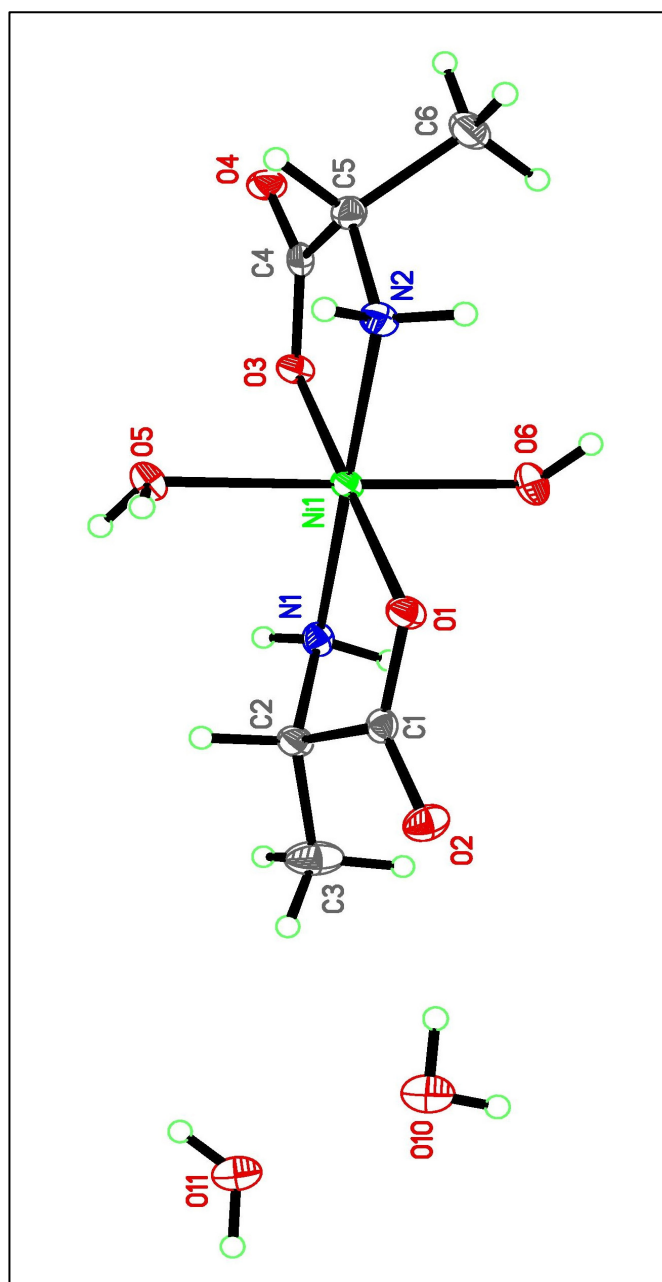


Figure 1. Drawing of the DL-alanine compound showing the atomic numbering scheme.

The structure (Figure1) consists of an $[\text{Ni}(\text{DL-alaninato})_2(\text{H}_2\text{O})_2]$ and two water molecules. The nickel atom 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. The complex is, then, built up of one

nickel(II) ion, two alanine molecules and two coordinated and two hydrated water molecules. The octahedron is made up by two alanine molecules coordinated to nickel(II) through their carboxylate and amido groups and two water molecules. It is observed that the axial Ni – O bond distances (Table 2) of 2.0915(18) Å and 2.0978(18) Å are significantly longer than the equatorial Ni-O bonds of 2.048(2) Å and 2.0535(19) Å. All the Ni-O distances are in agreement with those found in six coordinate nickel(II) complexes. The Ni-N bond lengths of 2.068(2) and 2.073(2) are in the normal range for Ni-N of high-spin octahedral nickel(II) complexes with chelating ligands [20-23]. Accordingly, the axial angle O-Ni-O is 179.76(11) where as the equatorial O-Ni-O is 179.48(14). The perpendicular O-Ni-O bond angles are 88.06(8), 91.93(8), 91.86(8) and 88.15(8). The equatorial N-Ni-N bond angle is 179.60(11). The perpendicular N-Ni-O bond angles are 88.02(9) , 87.46(9), 92.22(9) and 92.31(9). The equatorial O-Ni-N bond angles are 99.17(10), 98.44(10), 81.06(9) and 81.34(9). The drawing structure with the atomic numbering scheme of the complex is shown in Figure 1. The average Ni – O and Ni – N bond length 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 towards distorted octahedral, with a metal center not lying exactly within the N₂O₂ plane because the bond angles (Tables 3) are not perfect, with the average deviation of the twelve octahedral bond angles [24]. It is interesting to note that the displacement of Ni(II) atom in the compound is significantly different, though out-of-plane coordination in six-coordinate Ni(II) complexes with N₂O₂ atoms in plane is frequently observed [25].

It is seen that there are two water molecules not chemically bonded to Ni(II) and located at the opposite sites of alanine groups, and has 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. 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). There are many hydrogen bonds responsible of the packing, and the values of these interactions are shown in Table 4. The hydrogen bonding unit cell diagram and the hydrogen bond table showing the packing mechanism are valuable contribution to the work. 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. It is to be noted that the observed H-bonds lie in the range 2.7 to 2.8 and the Ni-O(w) bond length is 2.1 that agree with the reported octahedral *trans*-diaqua complexes [26-29]. A number of investigations on hydrogen bonding of metal-bound water have been reported, addressing the effect of hydrogen bonds on the acidity or nucleophile of such complexes [30-32]. An examination of hydrogen bonding of some metal-bound water complexes reveals that the strength of hydrogen bonding in these compounds is directly related to the bond lengths of the metal-bound water, the coordination number of the metal atom and the displacement from the N₄ or N₂O₂ plane [29].

The nickel alaninato complex crystallizes as pale blue tablet-shaped crystals from a water solution. There are four molecules of the complex and eight waters of crystallization in the unit cell of the primitive, acentric, orthorhombic space group Pna2₁. Refinement of the Flack parameter gave a value of 0.48 indicating a racemic twin. The structure was refined with a racemic twin component, giving a twin component of 0.473(19). The nickel is coordinated in an octahedral fashion by two alaninato ligands and two water molecules. The water molecules occupy positions *trans* to each other. The alaninato ligands are disordered between the planar and envelope five-membered rings that were observed in each of the pure D or L-alaninato species. Each component in the disorder was modeled with 50% occupancy. Separate refinement of the occupancy gave a value close to this also (within experimental error).

The IR spectrum of the complex shows strong absorption maxima at 545 cm⁻¹ confirming the presence of Ni –O bond [33,34]. Also the spectrum exhibits a strong broad band at 1610 cm⁻¹

indicative of COO_{as} stretching mode, while a peak corresponding to COO_s vibration appeared at 1366 cm⁻¹ [34-36]. The difference is 244 cm⁻¹ characteristic of a unidentate carboxylato group. The carboxylic group of alanine was changed to carboxylate group using KOH. Therefore, the C=O group disappeared. It was transformed in COO⁻ group and that is the reason of the presence of asymmetric and symmetric COO⁻ stretching bands. These modes usually appeared at ca. 1600-1500 and 1400-1300 cm⁻¹ depending on the type of coordination of the group (chelate, monodentate or bridge). Strong broad band at 3100 cm⁻¹ is indicative of extensive hydrogen bonding involving the -NH₂ and OH₂ hydrogen atoms. These results are in good agreement with the X-ray structural studies, and in consistence with the previous investigations of amino acids complexes with metal ions such as Pd(II), V(III), Cu(II), Al(III), Gd(III), Pr(III), Co(III), Ni(II) and Zn(II) [37-54]. The electronic absorption spectrum of the crystals was measured at room temperature in the region 200-1000 nm. The result measured is drawn in Figure 3. In the case of Ni(II) octahedral complexes, the lowest electronic transition corresponds to ³T_{2g}(F)→³A_{2g} and falls in the near infrared region. The second higher transition corresponding to ³T_{1g}(F) →³A_{2g} lies in the red region [55]. The uv-visible absorption spectrum of the complex shows three absorption maxima at 363, 606 and 998 nm attributed to transitions from ³A_{2g}(F) to ³T_{1g}(P), ³T_{1g}(F) and ³T_{2g}(F), respectively.

Table 2. Selected bond distances [Å] for the compound.

atom-atom	bond distances	atom-atom	bond distances
Ni(1)-O(1)	2.048(2)	Ni(1)-O(3)	2.0535(19)
Ni(1)-N(1)	2.068(2)	Ni(1)-N(2)	2.073(2)
Ni(1)-O(6)	2.0915(18)	Ni(1)-O(5)	2.0978(18)

Table 3. Bond angles [°] for the compound.

atom-atom-atom	angle	atom-atom-atom	angle
O(1)-Ni(1)-O(3)	179.48(14)	O(1)-Ni(1)-N(1)	81.34(9)
O(3)-Ni(1)-N(1)	99.17(10)	O(1)-Ni(1)-N(2)	98.44(10)
O(3)-Ni(1)-N(2)	81.06(9)	N(1)-Ni(1)-N(2)	179.60(11)
O(1)-Ni(1)-O(6)	88.06(8)	O(3)-Ni(1)-O(6)	91.86(8)
N(1)-Ni(1)-O(6)	88.02(9)	N(2)-Ni(1)-O(6)	92.31(9)
O(1)-Ni(1)-O(5)	91.93(8)	O(3)-Ni(1)-O(5)	88.15(8)
N(1)-Ni(1)-O(5)	92.22(9)	N(2)-Ni(1)-O(5)	87.46(9)
O(6)-Ni(1)-O(5)	179.76(11)	C(1)-O(1)-Ni(1)	116.00(17)
C(4)-O(3)-Ni(1)	116.02(18)	Ni(1)-O(5)-H(5Y)	122(2)
Ni(1)-O(5)-H(5Z)	116(2)	H(5Y)-O(5)-H(5Z)	95(3)
Ni(1)-O(6)-H(6Y)	105(2)	Ni(1)-O(6)-H(6Z)	122(2)

Finally, this work describes the synthesis and crystal structure of [Bis(DL-alaninato) diaqua]nickel(II) dihydrate. Although Jianmin [56] reported studies on crystals of amino acid complexes concerning the crystalline structure and the electronic spectrum of $[\text{Ni}(\text{DL-ala})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, the present paper improves the structural determination, and discusses the electronic solution and the vibrational (FTIR) spectra of the nickel complex. It is observed that there are slight differences that are within the standard deviation of the measured value for this complex and its L- and D- counterparts [18,19]. The differences between the three complexes are small and not statistically significant.

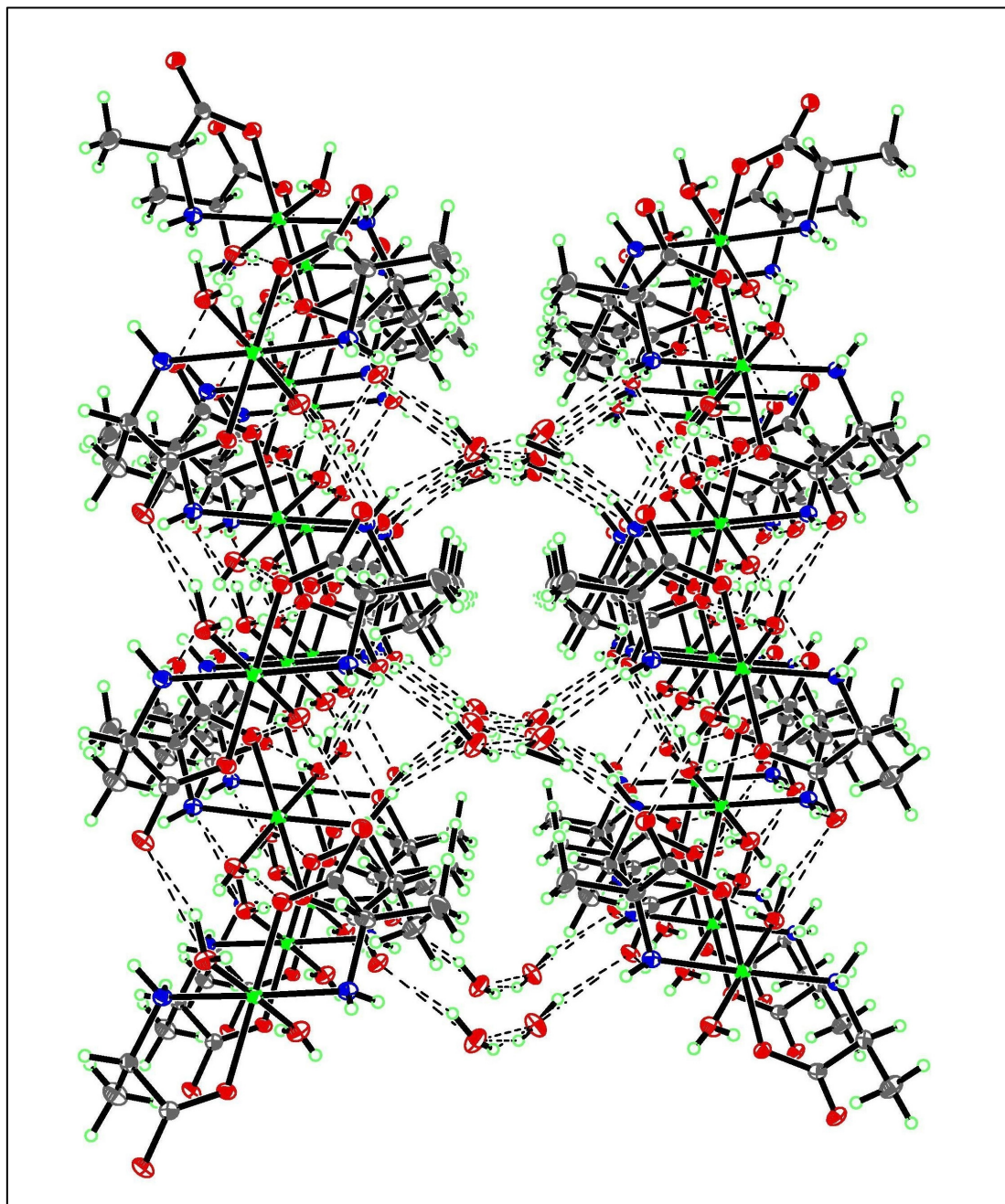
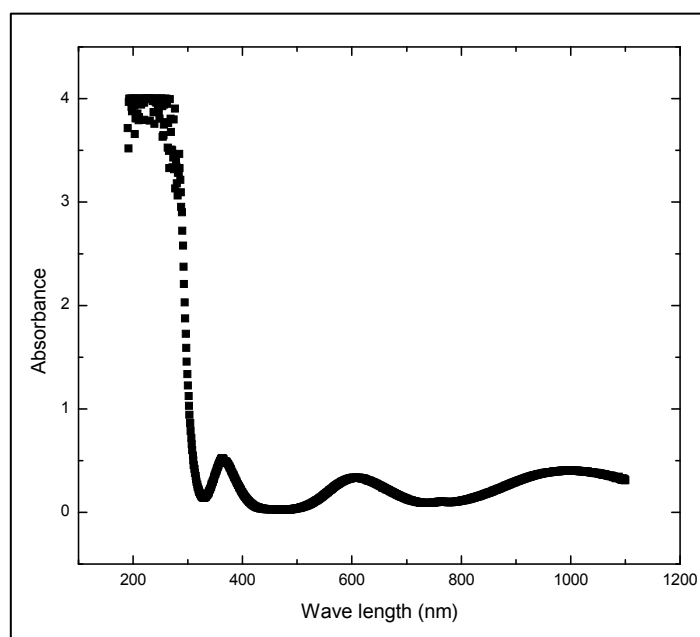


Figure 2. Hydrogen bonding network of the DL-alanine compound.

Table 4. Hydrogen bonds for the compound [\AA and $^\circ$]

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
O(5)-H(5Y)...O(1)#1	0.824(15)	1.891(16)	2.714(2)	176(3)
O(5)-H(5Z)...O(4)#2	0.844(16)	1.916(19)	2.711(3)	156(3)
O(6)-H(6Y)...O(2)#3	0.851(16)	1.871(17)	2.718(3)	173(4)
O(6)-H(6Z)...O(3)#4	0.831(15)	1.900(16)	2.729(3)	175(3)
N(1)-H(1Y)...O(2)#1	0.861(17)	2.271(19)	3.111(3)	165(2)
N(1)-H(1Z)...O(7)	0.873(17)	2.519(19)	3.317(4)	152(3)
N(2)-H(2Y)...O(4)#4	0.870(17)	2.257(18)	3.108(3)	166(3)
N(2)-H(2Z)...O(8)#5	0.864(17)	2.57(2)	3.386(4)	159(3)
O(7)-H(7Z)...O(2)#3	0.839(16)	1.960(17)	2.793(4)	172(4)
O(7)-H(7Y)...O(8)#4	0.825(16)	2.001(17)	2.824(4)	175(4)
O(8)-H(8Y)...O(4)#6	0.851(16)	2.01(2)	2.820(4)	160(4)
O(8)-H(8Z)...O(7)	0.852(16)	1.993(19)	2.826(4)	166(4)

**Figure 3.** Uv-visible spectrum of DL-alanine complex.

Conclusions

This paper includes material that in principle is worth and describes the synthesis and structure determination of DL-alanine complexed to nickel(II). In fact, nickel(II) was chosen for our

synthesis because it forms well-defined crystals that can be studied by x-ray crystallography. The crystal structure of the compound shows that the metal atom is ligated by two N atoms and two O atoms from the two alanine ligands at the equatorial positions, and two aqua ligands at the axial positions, resulting in a distorted octahedral geometry. The axial Ni-O distances are slightly longer than that of the equatorial Ni-O. The axial Ni-O linkage is bent slightly off from the perpendicular axis to the NiN₂O₂ plane. The oxygen atoms of the carboxylate groups of DL-alanine are deprotonated by removal of its hydrogen with the hydroxyl group of KOH producing water molecule. The crystal structure contains molecules of water of hydration, and many hydrogen bonds exist. The approximate symmetry of Ni(II) ion is the D₂ group.

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Supplementary material

Crystallographic data for the structure reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and allocated deposition number CCDC 718340 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. The crystal data are available from author Awni Khatib on request.

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