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[BIS(D-ALANINATO)DIAQUA]NICKEL(II) DIHYDRATE:

PREPARATION AND CRYSTAL STRUCTURE

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ABSTRACT

The title complex of formula $[Ni(NH_2CH_3CHCOO)_2(H_2O)_2].2H_2O$ *has been prepared from nickel(II) chloride in aqueous solution by adding D-alanine and potassium hydroxide. It has been crystallized from aqueous solution and its structure was determined by X-ray structure analysis. The nickel(II) atom adopts distorted octahedral coordination geometry with two bidentate alanine molecules and two water molecules. The complex is neutral and dihydrated. 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.*

KEY WORDS: **Alanine Complex, Crystal Structure, Hydrogen Bonding, Water of Hydration**

RESUMO

O complexo com a fórmula $[Ni(NH_2CH_3CHCOO)_2(H_2O)_2].2H_2O$ *foi preparado a partir de cloreto de níquel(II) em solução aquosa adicionando alanina e hidróxido de potássio. O composto foi cristalizado de solução aquosa e a sua estrutura foi determinada por análise de Raios-X. O níquel(II) tem uma geometria de coordenação octaédrica distorcida com duas moléculas de alanina bidentada e duas moléculas de água. O complexo esta neutro e desidratado. A rede cristalina indica pontes de hidrogênio entre a água e os hidrogênios da amida, e cada fragmento do complexo contém duas moléculas de água hidratada.*

PALAVRAS-CHAVE: **Complexos da Alanina, Estrutura Cristalina, Pontes de Hidrogênio, Água de Hidratação**

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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 (6-7). A number of complexes of amino acids with many transition metal ions have been prepared and thoroughly studied (8-16). Therefore, it was considered worthwhile and of great significant chemical interest to synthesize this complex and to study thoroughly its crystal structure. This paper describes the synthesis of bis(D-alaninato)(diaqua)nickel(II) dihydrate, $[Ni(NH_2CH_3CHCOO)_2(H_2O)_2].2H_2O$ and its characterization by X-ray crystallography.

EXPERIMENTAL

All chemicals were of reagent grade and used as purchased from commercial source. Crystallographic data for the structure reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and allocated deposition number CCDC 716012 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].

Preparation of $[Ni(NH_2CH_3CHCOO)_2(H_2O)_2].2H_2O$

The compound $NiCl_2.6H_2O$ (20 ml, 0.1 M), KOH (20 ml, 1.0 M) and D-alanine (20 ml, 0.2 M) were mixed. The mixture became basic with 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 under vacuo. The isolated crystals were subjected to x-ray studies.

Crystal structure determination

Crystal data for $C_6H_{20}N_2NiO_8$; M_r = 306.95; monoclinic; space group C2; a = 20.188(6) Å; b = 6.4989(19) Å; c = 9.666(3) Å; $\alpha = 90°$; $\beta = 94.482(4)°$; $\gamma = 90°$; V = 1264.3(6) $Å^3$; Z = 4; T = 150(2) K; λ(Mo-Kα) = 0.71073 Å; μ(Mo-Kα) = 1.566 mm^{-1}; d_{calc} = 1.613g.cm^{-3}; 7185 reflections collected; 3064 unique (R_{int} = 0.0223); giving R_1 = 0.0247, wR_2 = 0.0553 for 2821 data with

[$I > 2\sigma(I)$] and $R_1 = 0.0283$, $wR_2 = 0.0575$ for all 3064 data. Absolute structure (Flack) parameter 0.017(15). Residual electron density ($e^-.Å^{-3}$) max/min: 0.311/-0.225. An arbitrary sphere of data were collected on a pale blue prism-like crystal, having approximate dimensions of 0.80 × 0.21 × 0.06 mm, on a Bruker APEX-II diffractometer using a combination of ω- and φ-scans of 0.3°. 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. Water and amide hydrogen atoms were located from a difference Fourier map and included in refined positions with thermal parameters tied to that of the atom to which they are bonded. All other hydrogens were included in calculated positions with thermal parameters tied to that of the carbon to which they are bonded. The correct enantiomorph of the space group and handedness of the molecule were determined both by comparison of intensities of Friedel pairs of reflections and the known handedness of D-alanine. Both techniques agreed and the correct configuration is shown in the Figures.

Data Collection

A fragment of a pale blue, prism-like crystal of $C_6H_{20}N_2NiO_8$ having approximate dimensions of 0.80 × 0.21 × 0.06 mm was mounted on a Kapton loop using Paratone N hydrocarbon oil. All measurements were made on a Bruker APEX-II (17) CCD area detector with graphite monochromated Mo-Kα radiation.

Cell constants and an orientation matrix, obtained from a least-squares refinement using the measured positions of 3363 centered reflections with $I > 10\sigma(I)$ in the range $3.30 < \theta < 28.14°$ corresponded to a Monoclinic cell with dimensions:

$a = 20.188(6)$ Å	$\alpha = 90°$
$b = 6.4989(19)$ Å	$\beta = 94.482(4)°$
$c = 9.666(3)$ Å	$\gamma = 90°$
$V = 1264.3(6)$ Å^3	

For $Z = 4$ and F.W. = 306.95, the calculated density is 1.613 g.cm^{-3}.

Analysis of the systematic absences allowed the space group to be uniquely determined to be:

C2

The data were collected at a temperature of 150(2) K. Frames corresponding to an arbitrary sphere of data were collected using ω-scans of 0.3° counted for a total of 10 seconds per frame.The crystal data of the complex are shown in Tables 1,2 and 3.

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

Empirical formula	$C_6H_{20}N_2NiO_8$	
Formula weight	306.95	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	C2	
Unit cell dimensions	a = 20.188(6) Å	α = 90°
	b = 6.4989(19) Å	β = 94.482(4)°
	c = 9.666(3) Å	γ = 90°
Volume	1264.3(6) $Å^3$	
Z	4	
Density (calculated)	1.613 $g.cm^{-3}$	
Absorption coefficient (μ)	1.566 mm^{-1}	
F(000)	648	
Crystal size	0.80 × 0.21 × 0.06 mm^3	
ω range for data collection	2.02 to 28.27°	
Index ranges	$-26 \leq h \leq 6$, $-8 \leq k \leq 8$, $-12 \leq l \leq 12$	
Reflections collected	7185	
Independent reflections	3064 [R_{int} = 0.0223]	
Completeness to θ = 28.27°	99.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9119 and 0.3672	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3064 / 3 / 192	
Goodness-of-fit on F^2	1.028	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0247, wR_2 = 0.0553	
R indices (all data)	R_1 = 0.0283, wR_2 = 0.0575	
Absolute structure parameter	0.017(15)	
Largest diff. peak and hole	0.311 and -0.225 $e^-.Å^{-3}$	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for the compound. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

x	y	z	U(eq)	
Ni(1)	0.74664(1)	0.74526(11)	0.24736(3)	0.013(1)
O(1)	0.77203(7)	1.0241(3)	0.33744(15)	0.016(1)
O(2)	0.85325(6)	1.2549(5)	0.36350(14)	0.018(1)

O(3)	0.72239(7)	0.4674(2)	0.15836(15)	0.016(1)
O(4)	0.64087(7)	0.2403(5)	0.11909(14)	0.020(1)
O(5)	0.70662(8)	0.8869(3)	0.06409(16)	0.018(1)
O(6)	0.78539(9)	0.5982(3)	0.42583(19)	0.019(1)
N(1)	0.84249(9)	0.7728(4)	0.1885(2)	0.016(1)
N(2)	0.65052(8)	0.7264(5)	0.30809(19)	0.016(1)
C(1)	0.82682(10)	1.0997(4)	0.3067(2)	0.014(1)
C(2)	0.85997(10)	0.9947(3)	0.1878(2)	0.017(1)
C(3)	0.93413(11)	1.0309(4)	0.1906(3)	0.030(1)
C(4)	0.66387(11)	0.4027(4)	0.1738(2)	0.015(1)
C(5)	0.61846(11)	0.5285(4)	0.2595(2)	0.017(1)
C(6)	0.59699(12)	0.4027(4)	0.3811(2)	0.025(1)
O(10)	0.53355(9)	-0.0195(3)	0.13225(19)	0.032(1)
O(11)	0.53810(9)	0.0212(4)	0.6317(2)	0.032(1)
H(5OA)	0.6961(12)	1.009(4)	0.083(3)	0.021
H(5OB)	0.7314(11)	0.914(4)	-0.002(3)	0.021
H(6OA)	0.8020(14)	0.515(5)	0.416(3)	0.022
H(6OB)	0.7639(12)	0.592(4)	0.496(3)	0.022
H(1NA)	0.8673(11)	0.718(4)	0.254(2)	0.019
H(1NB)	0.8491(11)	0.732(7)	0.120(2)	0.019
H(2NA)	0.6233(11)	0.836(4)	0.269(2)	0.019
H(2NB)	0.6482(10)	0.746(6)	0.393(2)	0.019
H(2A)	0.8395	1.0541	0.0991	0.020
H(3A)	0.9522	0.9537	0.1150	0.045
H(3B)	0.9555	0.9843	0.2796	0.045
H(3C)	0.9427	1.1780	0.1789	0.045
H(5A)	0.5777	0.5635	0.1987	0.021
H(6A)	0.5665	0.4842	0.4331	0.037
H(6B)	0.6362	0.3654	0.4422	0.037
H(6C)	0.5744	0.2773	0.3462	0.037
H(10A)	0.5123(13)	-0.012(5)	0.197(2)	0.038
H(10B)	0.5567(13)	0.081(4)	0.117(3)	0.038
H(11A)	0.5167(13)	0.006(5)	0.569(2)	0.039
H(11B)	0.5624(13)	-0.067(4)	0.635(3)	0.039

Table 3. Anisotropic displacement parameters (Å)^2 for the compound. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni(1)	0.0147(1)	0.0112(1)	0.0128(1)	-0.0003(1)	0.0038(1)	-0.0014(1)
O(1)	0.0166(8)	0.0145(9)	0.0162(8)	-0.0028(7)	0.0037(6)	-0.0024(6)
O(2)	0.0190(7)	0.0145(8)	0.0215(7)	-0.0061(11)	0.0034(5)	-0.0032(11)
O(3)	0.0170(8)	0.0135(9)	0.0170(8)	-0.0018(7)	0.0057(6)	-0.0024(6)
O(4)	0.0203(7)	0.0181(8)	0.0227(7)	-0.0018(12)	0.0037(6)	-0.0045(12)
O(5)	0.0228(9)	0.0149(9)	0.0152(8)	0.0020(7)	0.0054(6)	0.0020(7)
O(6)	0.0235(9)	0.0177(10)	0.0150(8)	0.0022(7)	0.0065(7)	0.0043(7)
N(1)	0.0189(9)	0.0152(16)	0.0147(9)	-0.0004(10)	0.0039(7)	-0.0002(9)
N(2)	0.0177(8)	0.0151(13)	0.0159(8)	-0.0014(11)	0.0062(7)	-0.0002(10)
C(1)	0.0163(11)	0.0126(11)	0.0132(10)	0.0019(8)	0.0004(9)	0.0018(8)
C(2)	0.0182(11)	0.0157(11)	0.0166(11)	-0.0012(8)	0.0050(9)	-0.0020(8)
C(3)	0.0235(13)	0.0286(13)	0.0395(15)	-0.0109(12)	0.0140(11)	-0.0086(10)
C(4)	0.0173(11)	0.0164(12)	0.0122(10)	0.0018(9)	-0.0012(8)	0.0007(9)
C(5)	0.0152(11)	0.0174(11)	0.0194(11)	-0.0020(9)	0.0005(9)	-0.0001(8)
C(6)	0.0289(13)	0.0249(12)	0.0210(11)	-0.0026(10)	0.0099(10)	-0.0093(10)
O(10)	0.0295(11)	0.0323(12)	0.0340(11)	0.0010(9)	0.0105(8)	-0.0099(8)
O(11)	0.0272(11)	0.0300(12)	0.0392(12)	-0.0014(10)	0.0005(8)	0.0103(8)

Data Reduction

Data were integrated by the program SAINT (18) to a maximum θ-value of 28.27°. The data were corrected for Lorentz and polarization effects. Data were analyzed for agreement and possible absorption using XPREP (19). An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS (20). (Tmax = 0.9119, Tmin = 0.3672). Of the 7185 reflections that were collected, 3064 were unique (R_{int} = 0.0223); equivalent reflections were merged. No decay correction was applied.

Structure Solution and Refinement

The structure was solved by direct methods (21) and expanded using Fourier techniques (22). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions but were not refined. The final cycle of full-matrix least-squares refinement (23) was based on 3064 reflections (all data) and 192 variable parameters and converged (largest parameter shift was 0.002 times its esd) with conventional unweighted and weighted agreement factors of:

$$R_1 = \Sigma||Fo| - |Fc|| / \Sigma|Fo| = 0.0247 \text{ for 2821 data with } I > 2\sigma(I)$$

$$wR_2 = [(\Sigma w (|Fo|^2 - |Fc|^2)^2 / \Sigma w |Fo|^2)]^{1/2} = 0.0553$$

The standard deviation of an observation of unit weight (24) was 1.029. The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.311 and -0.225 $e^-.Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber (25). Anomalous dispersion effects were included in Fcalc; the values for Δf' and Δf" were those of Creagh and McAuley (26). The values for the mass attenuation coefficients are those of Creagh and Hubbel (27). All calculations were performed using the SHELXTL (17-22) crystallographic software package of Bruker Analytical X-ray Systems Inc. The drawing of the structures were made as ORTEP diagrams (28).

RESULTS AND DISCUSSION

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The title complex was prepared by the reaction of $NiCl_2.6H_2O$, KOH and D-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 $[Ni(NH_2CH_3CHCOO)_2(H_2O)_2].2H_2O$ was proved by X-ray crystallography (Fig.1). It is crystallized from aquous solution as pale blue prismatic crystals. The present paper describes the synthesis and structure determination of nickel(II) ion coordinated by two D-alanine molecules and two water molecules, being to our knowledge the first time the x-ray crystal structure of this complex is described.

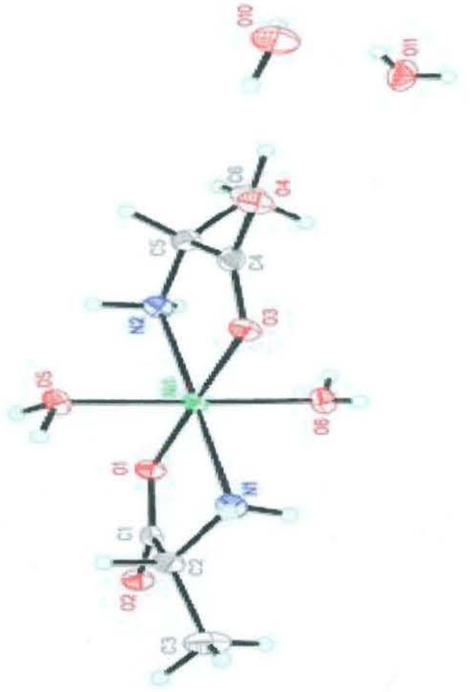

Figure 1.Illustration of the compound showing the atomic numbering scheme

The Structure (Fig.1) consists of an $[Ni(D\text{-}alaninato)_2(H_2O)_2]$ 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 D-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 D-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 D-alanine molecules and two coordinated and two hydrated water molecules. The octahedra is made up by two D-alanine molecules through their carboxylato and amido groups and two water molecules. It is observed that the axial Ni – O bond distances (Table 4) of 2.0712(19) Å and 2.1011(17) Å are significantly longer than the equatorial Ni-O bonds of 2.0433(18) Å and 2.0579(18) Å. All the Ni-O distances are in agreement with those found in six coordinate nickel(II) complexes (29). The Ni-N bond lengths are 2.0669(19) and 2.0744(18) Å that are longer than the equatorial N-O, and shorter than the axial counterparts. The average Ni – O and Ni – N bond length are in accordance to that known for nickel(II) distorted octahedral geometry. Therefore, two D-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 N_2O_2 plane because the bond angles (Tables 5, 6) are not perfect.

Table 4. Bond lengths [Å] for the compound.

atom-atom	distance	atom-atom	distance
Ni(1)-O(3)	2.0433(18)	Ni(1)-O(1)	2.0579(18)
Ni(1)-N(1)	2.0669(19)	Ni(1)-O(6)	2.0712(19)
Ni(1)-N(2)	2.0744(18)	Ni(1)-O(5)	2.1011(17)
O(1)-C(1)	1.267(3)	O(2)-C(1)	1.248(4)
O(3)-C(4)	1.274(3)	O(4)-C(4)	1.253(4)
O(5)-H(5OA)	0.84(3)	O(5)-H(5OB)	0.86(3)
O(6)-H(6OA)	0.65(3)	O(6)-H(6OB)	0.84(3)
N(1)-C(2)	1.485(4)	N(1)-H(1NA)	0.85(2)
N(1)-H(1NB)	0.73(3)	N(2)-C(5)	1.499(4)
N(2)-H(2NA)	0.96(2)	N(2)-H(2NB)	0.84(2)
C(1)-C(2)	1.534(3)	C(2)-C(3)	1.514(3)
C(2)-H(2A)	1.0000	C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800	C(3)-H(3C)	0.9800
C(4)-C(5)	1.521(3)	C(5)-C(6)	1.522(3)
C(5)-H(5A)	1.0000	C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800	C(6)-H(6C)	0.9800
O(10)-H(10A)	0.791(19)	O(10)-H(10B)	0.82(2)
O(11)-H(11A)	0.720(18)	O(11)-H(11B)	0.75(2)

Symmetry transformations used to generate equivalent atoms:

Table 5. Bond angles [°] for the compound.

atom-atom-atom	angle	atom-atom-atom	angle
O(3)-Ni(1)-O(1)	179.42(7)	O(3)-Ni(1)-N(1)	99.16(9)
O(1)-Ni(1)-N(1)	80.36(9)	O(3)-Ni(1)-O(6)	90.31(8)
O(1)-Ni(1)-O(6)	89.34(7)	N(1)-Ni(1)-O(6)	88.18(8)
O(3)-Ni(1)-N(2)	82.43(10)	O(1)-Ni(1)-N(2)	98.04(10)
N(1)-Ni(1)-N(2)	178.36(16)	O(6)-Ni(1)-N(2)	92.17(8)
O(3)-Ni(1)-O(5)	88.20(7)	O(1)-Ni(1)-O(5)	92.15(7)
N(1)-Ni(1)-O(5)	92.11(8)	O(6)-Ni(1)-O(5)	178.51(10)
N(2)-Ni(1)-O(5)	87.58(8)	C(1)-O(1)-Ni(1)	115.81(14)
C(4)-O(3)-Ni(1)	115.87(14)	Ni(1)-O(5)-H(5OA)	108.4(17)
Ni(1)-O(5)-H(5OB)	120.4(17)	H(5OA)-O(5)-H(5OB)	98(2)
Ni(1)-O(6)-H(6OA)	115(3)	Ni(1)-O(6)-H(6OB)	120.8(18)
H(6OA)-O(6)-H(6OB)	113(3)	C(2)-N(1)-Ni(1)	108.25(16)
C(2)-N(1)-H(1NA)	106.5(17)	Ni(1)-N(1)-H(1NA)	105.7(15)
C(2)-N(1)-H(1NB)	107(3)	Ni(1)-N(1)-H(1NB)	117.1(19)
H(1NA)-N(1)-H(1NB)	112(3)	C(5)-N(2)-Ni(1)	110.66(16)

Table 5. (cont.)

C(5)-N(2)-H(2NA)	107.1(15)	Ni(1)-N(2)-H(2NA)	111.2(14)
C(5)-N(2)-H(2NB)	113(3)	Ni(1)-N(2)-H(2NB)	113.2(15)
H(2NA)-N(2)-H(2NB)	101(3)	O(2)-C(1)-O(1)	124.1(2)
O(2)-C(1)-C(2)	119.48(19)	O(1)-C(1)-C(2)	116.33(19)
N(1)-C(2)-C(3)	112.7(2)	N(1)-C(2)-C(1)	108.10(17)
C(3)-C(2)-C(1)	114.00(19)	N(1)-C(2)-H(2A)	107.2
C(3)-C(2)-H(2A)	107.2	C(1)-C(2)-H(2A)	107.2
C(2)-C(3)-H(3A)	109.5	C(2)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5	C(2)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5	H(3B)-C(3)-H(3C)	109.5
O(4)-C(4)-O(3)	123.0(2)	O(4)-C(4)-C(5)	117.60(19)
O(3)-C(4)-C(5)	119.4(2)	N(2)-C(5)-C(4)	111.59(17)
N(2)-C(5)-C(6)	111.19(17)	C(4)-C(5)-C(6)	110.58(19)
N(2)-C(5)-H(5A)	107.8	C(4)-C(5)-H(5A)	107.8
C(6)-C(5)-H(5A)	107.8	C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5	H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5	H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5	H(10A)-O(10)-H(10B)	116(3)
H(11A)-O(11)-H(11B)	106(3)		

Symmetry transformations used to generate equivalent atoms:

Table 6. Torsion angles [°] for the compound.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
O(3)-Ni(1)-O(1)-C(1)	44(7)	N(1)-Ni(1)-O(1)-C(1)	8.07(16)
O(6)-Ni(1)-O(1)-C(1)	96.34(16)	N(2)-Ni(1)-O(1)-C(1)	-171.56(16)
O(5)-Ni(1)-O(1)-C(1)	-83.70(15)	O(1)-Ni(1)-O(3)-C(4)	145(7)
N(1)-Ni(1)-O(3)-C(4)	-179.17(16)	O(6)-Ni(1)-O(3)-C(4)	92.62(15)
N(2)-Ni(1)-O(3)-C(4)	0.47(16)	O(5)-Ni(1)-O(3)-C(4)	-87.33(16)
O(3)-Ni(1)-N(1)-C(2)	155.89(15)	O(1)-Ni(1)-N(1)-C(2)	-24.45(14)
O(6)-Ni(1)-N(1)-C(2)	-114.09(15)	N(2)-Ni(1)-N(1)-C(2)	-12(3)
O(5)-Ni(1)-N(1)-C(2)	67.38(16)	O(3)-Ni(1)-N(2)-C(5)	1.41(15)
O(1)-Ni(1)-N(2)-C(5)	-178.26(15)	N(1)-Ni(1)-N(2)-C(5)	169(3)
O(6)-Ni(1)-N(2)-C(5)	-88.62(16)	O(5)-Ni(1)-N(2)-C(5)	89.91(16)
Ni(1)-O(1)-C(1)-O(2)	-171.7(2)	Ni(1)-O(1)-C(1)-C(2)	10.8(2)
Ni(1)-N(1)-C(2)-C(3)	162.11(15)	Ni(1)-N(1)-C(2)-C(1)	35.2(2)
O(2)-C(1)-C(2)-N(1)	151.0(2)	O(1)-C(1)-C(2)-N(1)	-31.3(3)
O(2)-C(1)-C(2)-C(3)	24.9(3)	O(1)-C(1)-C(2)-C(3)	-157.5(2)
Ni(1)-O(3)-C(4)-O(4)	176.2(2)	Ni(1)-O(3)-C(4)-C(5)	-2.3(2)
Ni(1)-N(2)-C(5)-C(4)	-2.8(2)	Ni(1)-N(2)-C(5)-C(6)	121.18(17)
O(4)-C(4)-C(5)-N(2)	-175.1(2)	O(3)-C(4)-C(5)-N(2)	3.5(3)
O(4)-C(4)-C(5)-C(6)	60.5(3)	O(3)-C(4)-C(5)-C(6)	-120.8(2)

Symmetry transformations used to generate equivalent atoms:

It is observed that there are two water molecules not chemically bonded to Ni(II) and located at the opposite site of D-alanine group, 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 carboxylato groups. Also, the hydrogen bonds are seen between the hydrogen of the amide nitrogen and the oxygen atoms of the hydrated water molecules and carboxylato groups (Table 7). The hydrogen bonding network structure of the compound is shown in Figure 2. These results are in good agreement with the X-ray structural studies, and in consistence with the previous investigations of amino acids complexses with metal ions (30-37).

Table 7. Hydrogen bonds for the compound [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(5)-H(5OA)...O(4)#1	0.84(3)	1.92(3)	2.726(4)	159(2)
O(5)-H(5OB)...O(3)#2	0.86(3)	1.87(3)	2.726(2)	174(2)
O(6)-H(6OA)...O(2)#3	0.65(3)	2.07(3)	2.711(4)	175(3)
O(6)-H(6OB)...O(1)#4	0.84(3)	1.87(3)	2.688(2)	166(3)
N(1)-H(1NA)...O(11)#5	0.85(2)	2.49(2)	3.294(3)	159(2)
N(1)-H(1NB)...O(4)#2	0.73(3)	2.34(2)	3.026(3)	157(4)
N(2)-H(2NA)...O(10)#1	0.96(2)	2.35(2)	3.250(3)	155(2)
N(2)-H(2NB)...O(2)#4	0.84(2)	2.36(2)	3.187(2)	172(4)
O(10)-H(10A)...O(11)#6	0.791(19)	2.02(2)	2.808(2)	176(3)
O(10)-H(10B)...O(4)	0.82(2)	1.99(2)	2.758(3)	155(3)
O(11)-H(11A)...O(11)#6	0.720(18)	2.162(19)	2.870(4)	168(3)
O(11)-H(11B)...O(2)#7	0.75(2)	2.06(2)	2.792(3)	164(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+3/2,y+1/2,-z+1   #6 -x+1,y,-z+1

#7 -x+3/2,y-3/2,-z+1

The complex crystallizes as pale blue prismatic crystals from a water solution. There are four molecules of the nickel complex and eight waters of crystallization in the unit cell of the C-centered, acentric, monoclinic space group C2. The correct handedness of the molecule and enantiomorph of the space group were determined by comparison of the known handedness of the D-alanine molecule and by comparison of intensities of Friedel pairs of reflections [Flack parameter = 0.017(15), a value of zero indicates the correct handedness, a value of one the inversion isomer]. Both techniques agree and the correct enantiomer is depicted in the Figures.

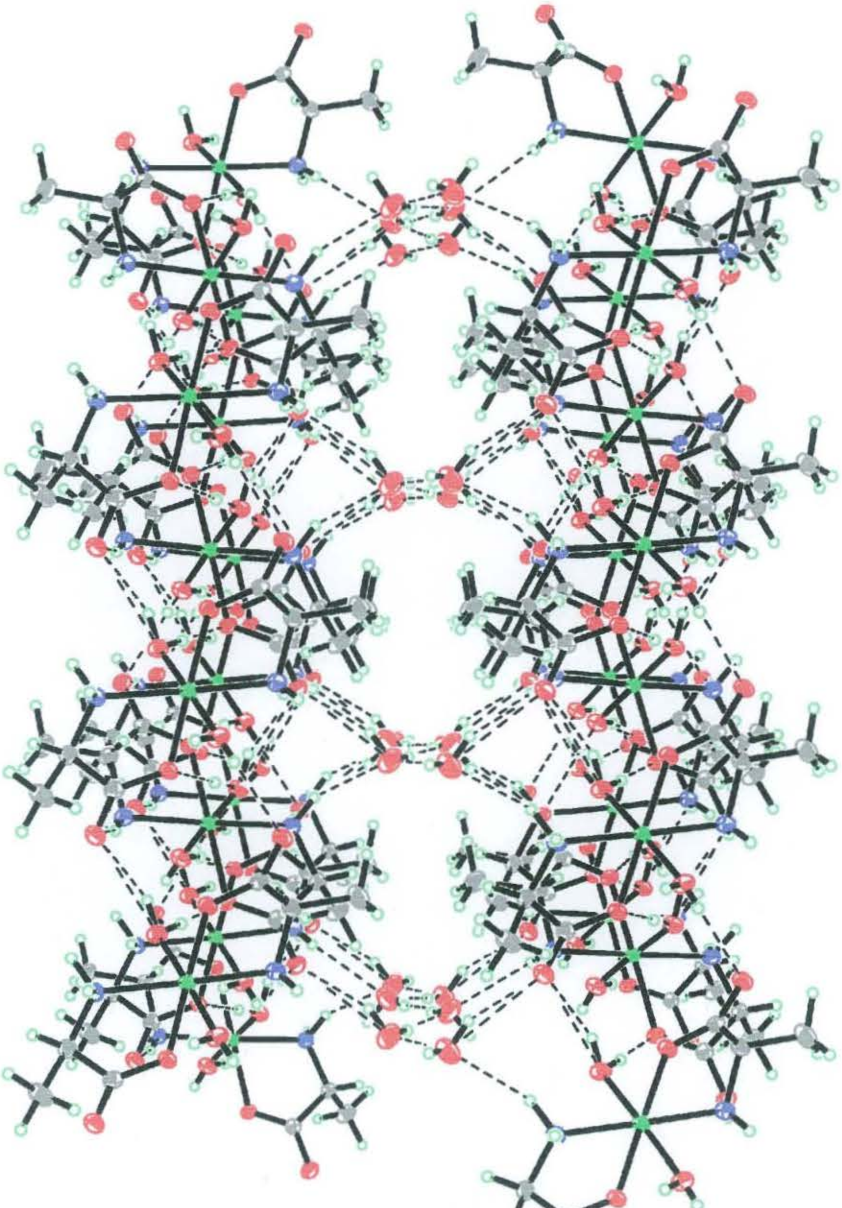

Figure 2 Hydrogen bonding network of D-alanine complex

The nickel is coordinated in a distorted octahedral geometry by the nitrogen and a carboxylate oxygen of each of two D-alanine moieties and two water molecules. The water molecules occupy the apical positions of the coordination sphere. The coordinating nitrogen atoms occupy positions *trans* to each other, as do the carboxylate oxygens [N1-Ni-N2 angle = 178.36(16)° and O1-Ni-O3 angle = 179.42(7)°]. The octahedral coordination geometry is necessarily distorted to accommodate the bonding and formation of two five-membered rings [N1-Ni-O1 and N2-Ni-O3 angles = 80.36(9) and 82.43(10)°, respectively]. The two coordinated waters have slightly different bonding contacts to the nickel center [Ni-O5 distance = 2.1011(17) and Ni-O6 distance = 2.0712(19) Å; the difference of 0.0299 Å is larger than the calculated statistically significant difference $(3.(\{(\sigma d_1)^2 + (\sigma d_2)^2\} = 0.0076$ Å)]. The D-alanine coordinating oxygens display a very small statistical difference in their respective bond distances while the nitrogens are not statistically different in distance. One of the D-alanine ligands has adopted an envelope geometry while the other has a largely planar geometry. Evidence for this is found in the deviations that the carbon atoms of the D-alanine chain exhibit from the Ni-O-N mean plane each ligand (Table 8).

Table 8. Deviations from the mean plane in Å.

	Deviation (Å)	s.u.	atom		Deviation (Å)	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
	-0.1602	(0.0031)	C1		-0.2636	(0.0055)	C3
	-0.5838	(0.0037)	C2		-0.0095	(0.0031)	C4

* *atom included in mean plane calculation*

The complex and the waters of crystallization form an extended three-dimensional network of hydrogen-bonded molecules. All of the located hydrogens (water and amide) are involved in a hydrogen-bond resulting in ten unique H-bonds within the lattice. The bond distances and angles within the molecules are otherwise typical for such interactions.

CONCLUSION

This paper describes the synthesis and crystallographic study of a complex of nickel(II), bis(D-alaninato)(diaqua), namely, $Ni(NH_2CH_3CHCOO)_2(H_2O)_2].2H_2O$ produced from aquous solution, which seems not to have been investigated before. The method illustrated for the preparation of this complex may be extended to other metal ions. In fact nickel(II) was chosen for our synthesis because it forms well-defined crystals that can be studies by x-ray crystallography. The complex is a chelate with two bidentate D-alanine ligands bonding through N and O and two water molecules. The oxygen of the carboxylato groups of D-alanine is deprotonated by removal of its hydrogen with the hydroxyl group of KOH producing water molecule. The crystal structure contains molecules of water, and many hydrogen bonds exist.

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23. Least-Squares:

Function minimized: $\Sigma w\,(|Fo|^2 - |Fc|^2)^2$

24. Standard deviation of an observation of unit weight:

$$[\Sigma w(|Fo|^2 - |Fc|^2)^2/(N_o - N_v)]^{1/2}$$

where: N_o = number of observations N_v = number of variables

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