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Synthesis and X-ray crystallographic study of $K[Ni(NH_2CH_3CHCOO)_3].3H_2O$

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A complex of formula $K[Ni(NH_2CH_3CHCOO)_3].3H_2O$ has been prepared from nickel(II) chloride in aqueous solution by adding L-alanine and potassium hydroxide. It has been crystallised from DMSO and its structure determined by X-ray crystal structure analysis. The nickel(II) atom adopts distorted octahedral coordination geometry with three bidentate alanine molecules. The complex is anionic and synthesised in the form of the potassium salt. The network crystal structure shows hydrogen bonding between all the chelate molecules, and each $K[Ni(NH_2CH_3CHCOO)_3]$ fragment contains three water molecules as hydrated water. The geometry of the potassium ion is octahedral.

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

Complexes formed by metal cations and organic species are incorporated in many biochemical structures, such as cytochromes of mitochondrial membranes, hemoglobin and chlorophyll, and are known to be of great interest due to their importance as essentially biologically active species,[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] A complex of alanine with nickel(II) was reported[16,17] and described as neutral bis(alaninato)(diaqua)nickel(II), in which two water molecules in a *trans*-position and two bidentate alanine molecules are coordinated to the metal centre. Many attempts were made to replace the two water molecules in this complex by a third alanine molecule, but in vain. Therefore, it was considered worthwhile and of great significant chemical interest to develop a method to prepare the *tris*-moiety. Several trials were made and fortunately a successful route was achieved to produce this compound. This paper describes, for the first time, the synthesis of potassium salt of tris (alaninato) nickel(II), $K[Ni(NH_2CH_3CHCOO)_3]3H_2O$, by using L-alanine, and its characterisation by X-ray crystallography.

The title complex was prepared by the reaction of $NiCl_2.6H_2O$, KOH and L-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 to favour ready binding to the nickel(II) ion. A method for the preparation of *K[tris(alaninato)]Ni(II)* is illustrated, and this method involves a judicious choice of a solvent in order to reduce the polarity of water. DMSO was selected for this purpose. The proposed mechanism for the stepwise formation of the complex is described as follows:

$$NiCl_2.6H_2O + H_2O \rightarrow [Ni(H_2O_6]^{+2}$$

$$[Ni(H_2O)_6]^{+2} + KOH + alanine \rightarrow [Ni\ (alanine)_2(H_2O)_2]$$

$$[Ni\ (alanine)_2(H_2O)_2] + KOH + alanine + DMSO \rightarrow K\ [Ni\ (alanine)_3].3H_2O$$

The formation of the complex $K[Ni(NH_2CH_3CHCOO)_3].3H_2O$ was proved by X-ray crystallography (Fig. 1). It was crystallised from DMSO as blue/pale purple dichroic block-like crystals. The present paper describes the synthesis and structure determination of nickel(II) ion coordinated by three alanine molecules, being to our knowledge the first example of nickel(II) coordinated by three molecules of an amino acid.

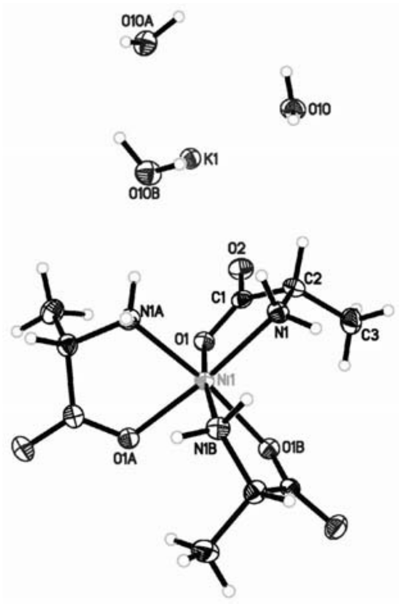

Fig. 1 $K[Ni(NH_2CH_3CHCOO)_3]$ showing the atomic number scheme.

The structure (Fig. 1) consists of an $[Ni(alaninato)_3]$ anion, a potassium cation and three water molecules. The nickel(II) is coordinated to three nitrogen and three oxygen atoms associated with the three bidentate alanine ions. Interestingly, coordination of three alanine groups to nickel(II) ion is less common due to the steric hindrance and the high polarity of water, which has been decreased by DMSO. The complex is, then, built up of one potassium cation, one nickel(II) ion, three alanine molecules and three water molecules. The octahedron is made up by three alanine molecules through their carboxylate- and amido-groups. It is observed that the Ni–O bond length is 2.0616 (18)Å and that of Ni–N is 2.102 (2) Å (Table 1).

It is to be noted that these bond lengths are longer than those in the previously reported counterpart $[Ni(alaninato)_2(H_2O)_2]^{16}$ due to bulkiness and strain on the coordination sites of the alaninato- groups. The structure with the atomic numbering scheme of the complex $K[Ni(alaninato)_3].3H_2O$ is shown in Fig. 1. The conventional line drawing of the structure is presented in Fig. 2. The average Ni–O and Ni–N bond length

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Table 1 Selected bond lengths [Å] for the compound

Atom–atom	Distance	Atom–atom	Distance
Ni(1)–O(1)#1	2.0616(18)	Ni(1)–O(1)#2	2.0616(18)
Ni(1)–O(1)	2.0616(18)	Ni(1)–N(1)#1	2.102(2)
Ni(1)–N(1)#2	2.102(2)	Ni(1)–N(1)	2.102(2)
K(1)–O(2)#3	2.759(2)	K(1)–O(2)#4	2.759(2)
K(1)–O(2)	2.759(2)	K(1)–O(10)#3	2.785(2)
K(1)–O(10)	2.785(2)	K(1)–O(10)#4	2.785(2)
K(1)–K(1)#5	4.8842(12)	K(1)–K(1)#6	4.8842(12)

Symmetry transformations used to generate equivalent atoms:
#1 −y + 1,x–y,z #2 −x + y + 1,−x + 1,z #3 −x + y,−x,z
#4 −y,x–y,z #5 x,y,z–1 #6 x,y,z + 1

are in accordance with those known for nickel(II) in distorted octahedral geometry. Therefore, three alanine molecules are directly involved in coordination. The coordination geometry around the nickel(II) ion is six–coordinated tending towards distorted octahedral, a trigonal antiprismatic geometry; or it may be described as a trigonal antiprism, with a metal centre not lying exactly within the N_2O_2 plane because the bond angles (Table 2) are not perfect such as O–Ni–O = 92.42 (7), N–Ni–N = 95.03 (8), O–Ni–N = 81.29 (8), 91.64 (8) and 172.65 (9).

It is seen that there are three water molecules not chemically bonded to Ni(II) and located at the opposite site of the alanine group, with no significant interaction with the metal atom. To keep the compound anionic with one negative charge, one potassium cation is linked to the three water molecules and surrounded by their oxygen atoms. The K….O interatomic distances range from 2.759(2) Å to 2.785(2) Å. The K atom position is supported by an analysis of the hydrogen bonding network and by bond length, in which the K….K distance is observed to be 4.8842(12) Å. Fig. 3 and Table 3 show an extensive hydrogen bond network within the lattice, with the amide hydrogen forming hydrogen bonds to a nearby carboxylate oxygen, and the water molecules forming hydrogen bonds to oxygen of different nearby carboxylate groups. On the other hand, Fig. 4 shows the octahedral geometry of potassium ion and how it is bonded to water and the complex.

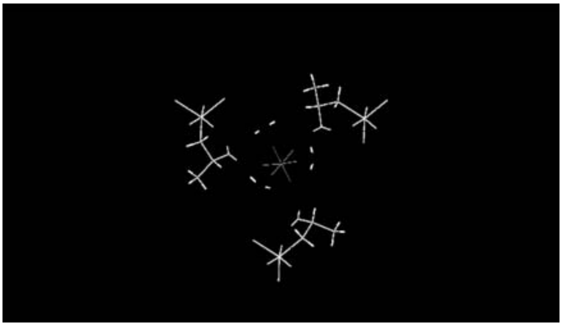

Fig. 2 Conventional line drawing of the structure of *K*[*Ni*(*NH*$_2$ *CH*$_3$*CHCOO*)$_3$].3H_2O.

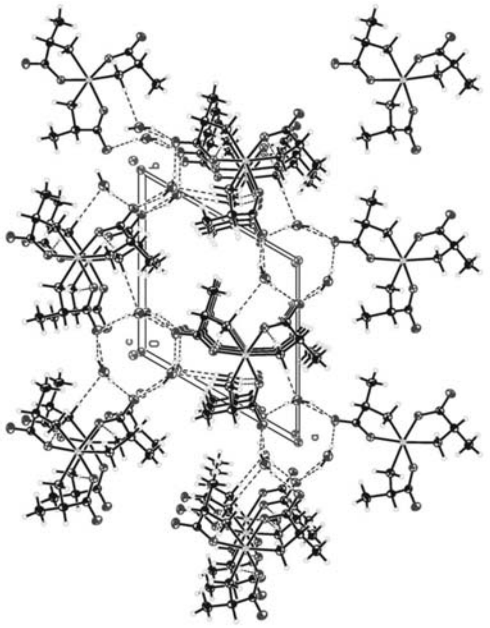

Fig. 3 View of hydrogen bonding network between all the chelate molecules.

There are one molecule of nickel and three waters of crystallisation in the unit cell, trigonal space group P3. The complex crystallises with the Ni occupying a position on the three-fold axis at [0.6667, 0.3333, z] and the K on the three-fold axis located at [0, 0, z]. The nickel has distorted octahedral geometry, tending towards a trigonal antiprismatic geometry or it may be trigonal antiprismatic, with the water oxygens occupying the same face. The alaninato-ligands are disposed such that the amide nitrogens all coordinate the Ni in a facial fashion.

The IR spectrum of the complex shows strong absorption maxima in the range 1000–850 cm^{-1} confirming the presence of an M–O bond[18] while the absorption maxima at 1612 cm^{-1} is indicative of the C=O group. The two strong peaks at 1499 and 1459 cm^{-1} are attributed to the COO_{as} and COO_{sym} stretching frequencies, respectively.[19] No band is seen in the range 3700–3500 cm^{-1} suggesting the removal of the hydrogen of the carboxylate group of alanine *i.e* converting

Table 2 Selected bond angles [°] for the compound.

Atom–atom–atom	Angle	Atom–atom–atom	Angle
O(1)#1–Ni(1)–O(1)#2	92.42(7)	O(1)#1–Ni(1)–O(1)	92.42(7)
O(1)#2–Ni(1)–O(1)	92.42(7)	O(1)#1–Ni(1)–N(1)#1	81.29(8)
O(1)#2–Ni(1)–N(1)#1	172.65(9)	O(1)–Ni(1)–N(1)#1	91.64(8)
O(1)#1–Ni(1)–N(1)#2	91.64(8)	O(1)#2–Ni(1)–N(1)#2	81.29(8)
O(1)–Ni(1)–N(1)#2	172.65(9)	N(1)#1–Ni(1)–N(1)#2	95.03(8)
O(1)#1–Ni(1)–N(1)	172.65(9)	O(1)#2–Ni(1)–N(1)	91.64(8)
O(1)–Ni(1)–N(1)	81.29(8)	N(1)#1–Ni(1)–N(1)	95.03(8)
N(1)#2–Ni(1)–N(1)	95.03(8)	O(2)#3–K(1)–O(2)#4	98.53(5)
O(2)#3–K(1)–O(2)	98.53(5)	O(2)#4–K(1)–O(2)	98.53(5)

Symmetry transformations used to generate equivalent atoms:
#1 −y + 1,x–y,z #2 −x + y + 1,−x + 1,z #3 −x + y,−x,z
#4 −y,x–y,z #5 x,y,z–1 #6 x,y,z + 1

Table 3 Hydrogen bonds for the compound [Å and°]

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
N(1)–H(1Y)...O(1)#6	0.97(3)	2.09(3)	3.053(3)	169(3)
N(1)–H(1Z)...O(10)#7	0.93(4)	2.40(4)	3.329(3)	179(3)
O(10)–H(10Y)...O(2)#6	0.97(4)	1.99(4)	2.919(3)	160(3)
O(10)–H(10Z)...O(2)#8	0.83(4)	2.04(4)	2.867(3)	170(3)
O(10)–H(10Z)...O(1)#8	0.83(4)	2.59(4)	3.222(3)	134(3)

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

COOH to COO$^-$ ion. These results are in good agreement with the X-ray structural studies.

In conclusion, this paper describes the synthesis and crystallographic characterisation of the first anionic nickel(II), tris(alanine) complex, namely, *K*[*Ni*(*alaninato*)$_3$].3H_2O produced from DMSO solution, which seems not to have been done before. The compound is of good significant interest, and the method of preparation is ingenious and could be applied to other metals such as iron, copper and zinc, and amino acids. 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 three bidentate alanine ligands bonding through N and O. The oxygen of the carboxylate groups of alanine is deprotonated by removal of its hydrogen with the hydroxyl group of KOH producing water molecules. The crystal structure contains molecules of water, between all chelate molecules, many hydrogen bonds exist which leads to chains of molecules. The K also has a distorted octahedral geometry and forms strong electrostatic contacts to three symmetrically disposed water oxygens and the carboxylate oxygen of the Ni tris–alaninato anion. It cannot be claimed that the use of L-alanine has any implication for the arrangement of the three ligands around the nickel.

Experimental

All chemicals were of reagent grade and used as purchased from commercial sources. The type of alanine used was L-alanine. The IR spectra were recorded in KBr with an FTIR 1600 FT spectrophotometer in the 4000–850 cm^{-1} region.

Preparation of $K[Ni(NH_2CH_3CHCOO)_3].3H_2O$

$NiCl_2.6H_2O$ (20 mL, 0.1 M), KOH (20 mL, 1.0 M) and alanine (20 mL, 0.3 M) were mixed. The mixture became basic with pH = 8 and turned from green to blue. 10 mL of this mixture was added to 10 mL of DMSO solvent in a small flask. The flask solution was left at room temperature. After standing for two weeks blue/pale purple dichronic block–like crystals were obtained, removed and dried under vacuo. The isolated crystals were subjected to X-ray studies. Yield = 30%. IR (cm^{-1}):1499 (COO$_{as}$), 1459 (COO$_{sym}$). Crystal data for the compound: Empirical formula = $C_9H_{24}KN_3NiO_9$; M_r = 416.12; trigonal; space group P3; a = 10.132(2) Å; b = 10.132(2) Å; c = 4.8842(12) Å; α = 90°; β = 90°; γ = 120°; V = 434.27(17) Å^3; Z = 1; T = 220(2) K; λ(Mo-Kα) = 0.71073 Å; μ(Mo-Kα) = 1.402 mm^{-1}. The crystallographic data of the compound are available from the author Awni Khatib.

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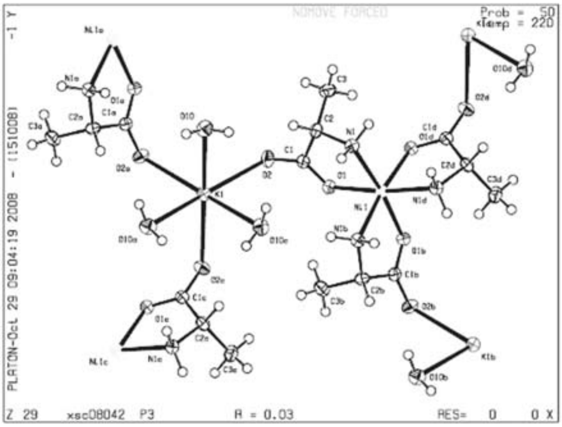

Fig. 4 View of the octahedral geometry of potassium ion in the complex.

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