Structural, Spectroscopic, and Magnetic Properties of Diaqua(L-aspartato)nickel(II) Hydrate †

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The crystal structure of the title compound was determined by *X*-ray analysis. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with cell dimensions a = 12.306(2), b = 8.996(2), c = 7.596(1) Å, and Z = 4. The structure was solved by the heavy-atom method and refined by least-squares calculations to a final R value of 0.034. The compound is isostructural with the corresponding zinc(II) salt. The structure consists of polymeric linear chains in which the Ni atom is co-ordinated in a distorted octahedral manner by one aspartate ion, acting as a tridentate ligand, by two water molecules, and by one β-carboxylate O atom of a second aspartate ion. Magnetic and spectroscopic results are also discussed.

The complexes of aspartic acid have received considerable attention because of interest in their biological[1] and co-ordinative properties, but the majority of these studies only concerned the behaviour in solution.[2] Crystal-structure results on solid complexes, which could provide support for structural hypotheses based upon the magnitude of equilibrium constants, are lacking.

Therefore our previous structural investigations performed on two mixed-ligand complexes of nickel(II)[3] and copper(II)[4] with L-aspartate and imidazole have been extended to the simple nickel(II)–L-aspartate(2−) complex $[Ni(L\text{-}aspO)(H_2O)_2]\cdot H_2O$ [previously suggested as isomorphous with the zinc(II) complex].

Experimental

All chemicals were reagent grade and used as received.

Preparation of the Complex, $[Ni(L\text{-}aspO)(H_2O)_2]\cdot H_2O$.—Nickel(II) acetate tetrahydrate (1 mmol) and L-aspartic acid (1 mmol) in the solid state were dissolved in boiling water until a limpid green solution was obtained. After addition of methanol and cooling a greenish microcrystalline compound precipitated. This was filtered off. Slow evaporation for several days at room temperature (20 °C) of the remaining solution yielded turquoise crystals, m.p. 480—485 K (decomp.) (Found: C, 19.8; H, 4.60; N, 5.70. Calc. for $C_4H_{11}NNiO_7$: C, 19.7; H, 4.55; N, 5.75%).

Physical Measurements.—Electronic and i.r. spectra were recorded as described previously.[3] Nitrogen, carbon, and hydrogen analyses were obtained by Mr. G. Pistoni on a C. Erba Model 1106 elemental analyser.

Structure Determination.—A prismatic green crystal with dimensions 0.19 × 0.16 × 0.24 mm was used throughout the determination of lattice constants and data collection. Large and unexpected differences were found between the present cell dimensions and those previously reported[5] for the same complex and for its isomorphous cobalt(II) and zinc(II) trihydrate salts.

Crystal data. $C_4H_{11}NNiO_7$, $M = 243.89$, Orthorhombic, $a = 12.306(2)$, $b = 8.996(2)$, $c = 7.596(1)$ Å, $U = 840.9$ Å^3, D_m(by flotation) = 1.91 g cm^{-3}, $Z = 4$, $D_c = 1.93$ g cm^{-3}, $F(000) = 504$, nickel-filtered Cu-K_α radiation, $\lambda = 1.541\,78$ Å, μ(Cu-K_α) = 32.6 cm^{-1}, space group $P2_12_12_1$ (D_2^4, no. 19), T = 293 K.

Intensity data were collected on an automated Siemens AED on-line four-circle diffractometer with the ω—2θ scan technique up to $\theta \leqslant 70°$. One standard reflection, measured every 50 reflections, showed no significant change during data collection. A total of 949 reflections was measured of which 805, having $I > 2\sigma(I)$, were corrected for Lorentz and polarization effects, but not for absorption, and used in the structure analysis.

The structure was solved by conventional Patterson and Fourier methods and refined first isotropically and then anisotropically by full-matrix least-squares calculations to R = 0.034 and R' = 0.040 $\{w = 1.0/[\sigma^2(F) + 0.0038F^2]\}$. In the later cycles of refinement the water hydrogen atoms were added as fixed contributions at locations previously obtained from difference maps, whereas the hydrogen atoms of the L-aspartate ion were constrained to ride at ideal positions relative to the atoms to which they are bonded (C–H and N–H 1.0 Å). In the final least-squares cycle the shift in all parameters was less than 0.15 of an estimated standard deviation (e.s.d.); no trend in $w\Delta^2$ *vs.* $|F_o|$ or sin θ was observed. A final difference map was featureless, with no peaks higher than 0.30 e Å^{-3}. Additional least-squares cycles with positional parameters inverted, to determine the correct enantiomeric form, led to convergence at $R = 0.037$ and $R' = 0.044$; therefore the previous refinement was judged to give the correct enantiomeric configuration.

Complex neutral-atom scattering factors[6] were employed throughout; major calculations were carried out on a CDC Cyber 7 600 computer, using the SHELX 76 program package.[7]

Final fractional co-ordinates of the non-hydrogen atoms are given in Table 1.

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† *Supplementary data available* (No. SUP 23429, 9 pp.): thermal parameters, H-atom co-ordinates, H-bonding parameters, least-squares planes, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Final fractional co-ordinates with standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni	0.079 1(1)	0.063 9(1)	0.125 2(1)	C(4)	0.062 0(4)	0.397 8(6)	0.116 2(9)
O(1)	0.210 0(3)	0.129 0(5)	0.280 2(5)	O(3)	0.018 3(3)	0.274 9(4)	0.152 3(6)
O(2)	0.349 0(3)	0.286 0(5)	0.274 7(6)	O(4)	0.021 3(4)	0.520 7(4)	0.163 0(6)
C(1)	0.269 9(5)	0.223 3(7)	0.204 0(8)	W(1)	0.136 4(3)	−0.153 8(4)	0.111 5(6)
C(2)	0.240 1(5)	0.265 4(7)	0.015 5(8)	W(2)	−0.043 2(4)	0.011 7(5)	−0.049 9(7)
N	0.182 3(4)	0.139 4(6)	0.066 3(7)	W(3)	0.093 6(4)	0.219 4(5)	0.584 8(6)
C(3)	0.169 1(5)	0.405 8(6)	0.017 8(8)				

Table 2. Bond distances (Å) and angles (°)

Ni-O(1)	2.080(4)	C(2)-C(3)	1.536(8)
Ni-N	2.047(5)	C(3)-C(4)	1.517(8)
Ni-O(3)	2.050(4)	C(4)-O(3)	1.260(6)
Ni-O(4′)	2.065(4)	C(4)-O(4)	1.265(6)
Ni-W(1)	2.084(4)	W(1)-H(1W1)	1.00
Ni-W(2)	2.063(5)	W(1)-H(2W1)	0.81
O(1)-C(1)	1.265(7)	W(2)-H(1W2)	0.91
O(2)-C(1)	1.246(7)	W(2)-H(2W2)	0.87
C(1)-C(2)	1.526(8)	W(3)-H(1W3)	1.04
C(2)-N	1.475(8)	W(3)-H(2W3)	0.85

O(1)-Ni-N	80.1(2)	Ni-O(3)-C(4)	129.4(3)
O(1)-Ni-O(3)	88.0(2)	Ni-O(4′)-C(4′)	128.3(3)
O(1)-Ni-W(1)	91.8(2)	O(1)-C(1)-O(2)	124.2(6)
O(1)-Ni-W(2)	174.0(2)	O(1)-C(1)-C(2)	117.1(5)
O(1)-Ni-O(4′)	94.3(2)	O(2)-C(1)-C(2)	118.7(5)
N-Ni-O(3)	89.5(2)	C(1)-C(2)-N	108.7(5)
N-Ni-W(1)	93.8(2)	C(1)-C(2)-C(3)	109.3(5)
N-Ni-W(2)	94.0(2)	N-C(2)-C(3)	111.2(5)
N-Ni-O(4′)	170.8(2)	C(2)-C(3)-C(4)	117.4(5)
O(3)-Ni-W(1)	176.6(2)	C(3)-C(4)-O(3)	121.3(5)
O(3)-Ni-W(2)	90.5(2)	C(3)-C(4)-O(4)	116.2(5)
O(3)-Ni-O(4′)	83.0(2)	O(3)-C(4)-O(4)	122.5(5)
W(1)-Ni-W(2)	90.0(2)		
W(1)-Ni-O(4′)	93.7(2)	H(1W1)-W(1)-H(2W1)	131
W(2)-Ni-O(4′)	91.3(2)	H(1W2)-W(2)-H(2W2)	106
Ni-O(1)-C(1)	112.4(4)	H(1W3)-W(3)-H(2W3)	101
Ni-N-C(2)	104.8(4)		

Primes correspond to the symmetry operation $-x, y - \frac{1}{2}, \frac{1}{2} - z$.

Results and Discussion

Description of the Structure.—Bond distances and angles are listed in Table 2, with atoms labelled as in the Figure.

The structural results confirm that the L-aspartatonickel(II) trihydrate [or, better, diaqua(L-aspartato)nickel(II) hydrate] is isostructural with the corresponding cobalt(II)[5] and zinc(II)[5,8] complexes, as suggested by their isomorphism.[5]

The structure consists of polymeric linear chains, which parallel the *a* cell axis; the metal ion shows a distorted octahedral co-ordination, with bonds to the N(amino), O(α-carboxylate), and O(β-carboxylate) of one L-aspartate ion acting as a tridentate ligand, to a β-carboxylate O atom of a second L-aspartate, and to two water molecules. The chains are linked by an extensive hydrogen-bonding network, to which the ' free ' water molecule contributes.

There are no unusual bond lengths within the co-ordination polyhedron, and the deviations of bond angles from ideal geometry are in a range commonly reported for octahedral nickel(II) complexes with multidentate ligands.[3,9–11] The largest distortion occurs at the five-membered ' glycinate-type ' chelate ring with a N(amino)-Ni-O(α-carboxylate) angle of 80.1(2)°.

The internal geometry of the L-aspartate ion compares well with those observed in the corresponding and isostructural zinc(II) salt[8] and in mononuclear nickel(II)[3] and cobalt(III)[11–13] complexes.

The principal difference between the conformations of the isostructural zinc(II) and nickel(II) aspartate trihydrate salts involves the co-ordination by the bridging β-carboxylate group: the deviations of the Ni atoms from the plane of the bonded β-carboxylate group are 0.276 Å (chelate ring) and 0.759 Å (side chain), respectively; the corresponding values for the zinc(II) salt[8] are 0.262 and —1.358 Å, a considerably larger deviation of opposite sign. Another remarkable difference involves the nature and disposition of the eight hydrogen-bonding interactions affecting both the complexes. Unlike the zinc(II) salt, both the amino H atoms of the nickel(II) complex participate in hydrogen-bonding interactions; also the β-carboxylate O(4) atom of the zinc(II) salt is engaged in three hydrogen-bonding interactions, whereas there is only one in the nickel(II) complex.

Physical Properties.—The low- and room-temperature ligand-field spectra, very similar to one another, show three strong absorptions and one weak. The *Dq* and *B* values (Table 3), calculated for these bands according to the averaged-environment rule, are in the range expected for octahedrally co-ordinated nickel(II) ions with a ligand set of one N and five O atoms.[14]

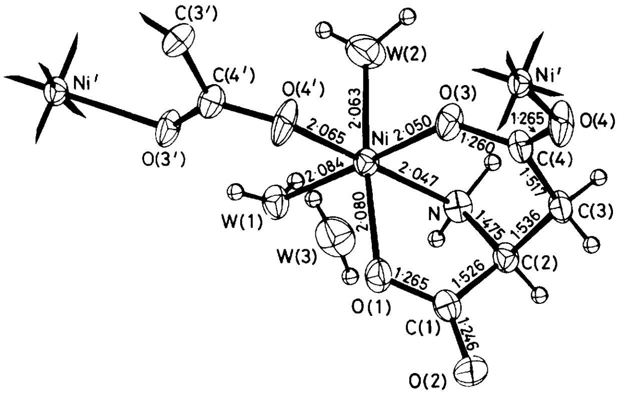

Figure. ORTEP view of the complex showing the atom numbering, the bond distances (Å), and the thermal motion ellipsoids (60%) for the non-hydrogen atoms. The hydrogen atoms are represented as spheres of radius 0.1 Å

Table 3. Electronic and i.r. spectra (cm^{-1}), ligand-field parameters (cm^{-1}), and magnetic moment (B.M.) * of [Ni(L-aspO)(H$_2$O)$_2$]·H$_2$O

$^3A_{2g} \rightarrow {}^3T_{2g}$	9 660	ν(NH$_2$)	3 290
$\rightarrow {}^1E_g$	13 330vw	δ(NH$_2$)	3 204
$\rightarrow {}^3T_{1g}(F)$	15 870	ν_{asym}(OCO)	1 582, 1 545
$\rightarrow {}^3T_{1g}(P)$	26 320	ν_{sym}(OCO)	1 428, 1 412
Dq	966	$\mu_{eff.}$ (120—307 K)	3.16
B	880		

* 1 B.M. ≈ 9.274 × 10^{-24} J T^{-1}.

A plot of $1/\chi_M$ *vs.* T shows that the Curie–Weiss law is perfectly obeyed in the 120—307 K temperature range with Curie and Weiss constants of $C = 1.248$ c.g.s. units and $\theta = -0.4$ K. All these facts exclude the presence of any type of interaction between the nickel(II) ions, although the aspartate ion acts as a bridging ligand.

In Table 3 we have also reported the more relevant i.r. bands assigned on the basis of our previous investigations.[3,4] In particular, in the 1 650—1 400 cm^{-1} region, characteristic of carboxylate-group vibrations,[15-17] multiple bands are present in agreement with the different types of co-ordination in which both the carboxylate groups are involved.

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