estimate from the Ham relation (eq 6) rests on the assumption of an effective frequency of the Jahn–Teller coupling mode of ~700 cm^{-1}. Electronic Raman or inelastic neutron scattering experiments seem to be necessary for an unambiguous location of the excited Kramers' doublet, thereby allowing a determination of the effective frequency.

(7) The average energies of the spin-allowed d–d transitions estimated for several d^7 metallocenes, mixed sandwiches, and bis(benzene) compounds are within an order of magnitude agreement with experimental values. Further, the **g** tensor analysis predicts the correct sequence for the energies of these transitions for the various d^7 sandwich compounds.

(8) The observation of four chemically inequivalent sites for Fe(Cp,Bz) in Fe(Cp)$_2$ is in agreement with the expectation from the low-temperature crystal structure of triclinic ferrocene.[31]

Acknowledgment. We thank Professor François Varret and Jean-Pierre Mariot from the University of Le Mans for stimulating discussions. We thank M. Heinzle for secretarial assistance. This work has been supported by the Swiss National Science Foundation (Project No. 2.683-0-80).

Registry No. Fe(Cp,Bz), 51812-05-6; Fe(Cp,hmBz), 70414-92-5; Fe(hmBz)$_2$PF$_6$, 53382-61-9; Fe(pmCp,hmBz), 71713-53-6; Fe(Cp,heBz), 71713-55-8; Fe(Cp,(pm,e)Bz), 71742-81-9.

Coordination Behavior of L-Aspartic Acid: Ternary Nickel(II) Complexes with Imidazoles. Crystal and Molecular Structure of (L-Aspartate)tris(imidazole)nickel(II)

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Abstract: Two ternary compounds of formula Ni(L-asp)B$_3$ (L-asp = L-aspartate ion; B = imidazole and 2-methylimidazole) were prepared and characterized by means of magnetic and spectroscopic measurements. For one of them, the Ni(L-asp)(im)$_3$ complex, the crystal structure was also determined. The compound crystallizes in the monoclinic space group $P2_1$ with four formula units in a cell of dimensions $a = 22.001$ (2) Å, $b = 8.631$ (1) Å, $c = 8.514$ (1) Å, and $\beta = 95.07$ (1)°. X-ray diffraction data were collected with a Philips PW 1100 automated four-circle diffractometer by using Mo Kα radiation. The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedures to a final R factor of 0.0514 for 2051 independent reflections. The structure consists of two crystallographically independent but chemically equivalent Ni(L-asp)(im)$_3$ molecules in which each Ni atom is coordinated in a distorted octahedral geometry by one L-aspartate ion, acting as a tridentate ligand, and by three imidazole molecules. Infrared and ligand field spectroscopies and magnetic measurements all agree with the observed crystal structure.

There is great interest in the coordination ability of aspartic acid to metal ions, from either a biological or simple coordinative point of view. The majority of reports are based on solution studies, in which it was generally suggested that aspartate usually acts as a tridentate ligand,[2] while the few structural results, performed on solid compounds, show changeable behavior depending on the metal ion to which the amino acid is coordinated. In fact, the aspartate ion acts as truly tridentate to the same metal ion only in bis(L-aspartate)cobalt(III) complexes,[3] being tetradentate bridging two zinc(II) ions or three copper(II) ions in zinc(II) aspartate trihydrate[4] or in (L-aspartate)(imidazole)copper(II) dihydrate,[5] respectively.

Our interest in the solid-state complexes of aspartic acid began with a study of its ternary copper(II) complexes with amines[5] in the attempt to rationalize its different coordination behavior and is now extended to the investigation of the spectroscopic, magnetic, and structural properties of two mixed-ligand complexes of the nickel(II) with L-aspartic acid and imidazole or 2-methylimidazole (L-aspH, im, and 2Meim, respectively).

The presence of small biologically important molecules in these complexes, which makes them usable as models for more complicated systems, and the presence of heteroatomic N base moieties and O donors in the coordinative sphere of the nickel(II) ion, a combination of donor atoms present in many naturally occurring mixed-ligand complexes and recognized as enhancing the complex stability,[6] also confer some interest on this work from the biological point of view.

Experimental Section

Preparation of (L-Aspartate)tris(imidazole)nickel(II) Complex, Ni(L-Asp)(im)$_3$. By dissolving a mixture of Ni(L-asp)·3H$_2$O (1 mmol) and imidazole (2 mmol) in boiling water and slowly evaporating the solution at 20 °C, we separated blue violet crystals. Anal. Calcd for

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Table I. Summary of Crystal Data Collection[a]

diffractometer	Philips PW 1100
radiation	graphite-monochromated Mo Kα (λ = 0.71069 Å)
temp, °C	18 ± 2
crystal system	monoclinic
space group	$P2_1$ (C_2^2, No. 4)
a, Å	22.001 (2)
b, Å	8.631 (1)
c, Å	8.514 (1)
β, deg	95.07 (1)
V, Å^3	1610.4
mol formula	$C_{13}H_{17}NiN_7O_4$
mol wt	394.04
Z	4
F(000)	816
ρ(calcd), g/cm^3	1.625
ρ(obsd), g/cm^3	1.62 (by flotation in CCl_4–C_2Cl_6 mixture)
reflections measd	$-h_{max} \leqslant h \leqslant h_{max}$ with k and $l \geqslant 0$
scan type	$\theta-2\theta$
θ range, deg	2–24.80
scan speed	2.10°/min
scan width, deg	0.80
background time	10 s at beginning and end of the scan
standards	2 every 120 reflections (no significant changes)
collected reflections	3044, yielding 3013 nonzero independent data
obsd reflections	2051 with $I > 3.0\sigma(I)$ [$\sigma(I)$ = (peak counts + total background counts)$^{1/2}$]
crystal size, mm	~0.23 × 0.19 × 0.16
absorption coefficient, cm^{-1}	11.7
absorption correction	not applied

[a] The unit cell parameters were determined from least-squares refinement of the setting angles of 25 automatically centered reflections from diverse regions of reciprocal space, using the standard control program of the PW 1100 system ("User Manual for PW 1100 Philips"; Eindhoven; The Neverlands).

$C_{13}H_{17}NiN_7O_4$: C, 39.60; H, 4.35; N, 24.89. Found: C, 39.41; H, 4.42; N, 24.92.

Preparation of (L-Aspartate)tris(2-methylimidazole)nickel(II) Complex, Ni(L-Asp)(2Me(im))$_3$. The compound preparation is similar to that of the imidazole complex. The crystals are blue. Anal. Calcd for $C_{16}H_{23}NiN_7O_4$: C, 44.04; H, 5.32; N, 22.49. Found: C, 44.03; H, 5.41; N, 22.63.

Physical Measurements. The electronic spectra of the solid compounds were recorded as mull transmission spectra at room temperature and at liquid nitrogen temperature with a Shimadzu MPS 50L spectrophotometer. The infrared spectra were recorded with a Perkin-Elmer 180 spectrophotometer in Nujol mulls on KBr pellets as support in the 4000–250-cm^{-1} spectral range. The room-temperature magnetic moments were measured by the Gouy method, using $Nien_3S_2O_3$ as calibrant and correcting for diamagnetism with the appropriate Pascal constants.

Crystallographic Data Collection. The crystal selected for X-ray analysis was cleaved from a larger twinned crystal and after sealing in a glass fiber was directly transferred in a random orientation to a Phillips PW 1100 automated four-circle diffractometer. Details specific to the data collection and processing are reported in Table I.

A survey of the complete data set revealed the systematic absences 0*k*0, $k = 2n + 1$; this condition is consistent with the centrosymmetric space group $P2_1/m$ and the noncentrosymmetric space group $P2_1$. The Patterson synthesis[7] and subsequent solution of the structure showed that the true space group was the noncentrosymmetric $P2_1$.

All data were corrected for Lorentz and polarization effects but not for absorption in view of the small crystal size and absorption coefficient. Only the 2051 observed reflections were used in the structure analysis.

Solution and Refinement of the Structure. Neutral atom scattering factors were used,[8a] and anomalous dispersion corrections[8b] were applied to all nonhydrogen atoms. Refinement was by full-matrix least squares with $\sum w(|F_o| - |F_c|)^2$ being minimized; discrepancy indices used below are $R = (\sum ||F_o| - |F_c||)/\sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where *w* is the wieghting factor. Major calculations were performed on a CDC Cyber 7600 computer by using the "SHELX-76" system of programs[9] for Fourier and least-squares calculations and Johnson's ORTEP program[10] for drawing.

A three-dimensional Patterson map revealed interatomic vectors consistent with two crystallographically independent nickel atoms in the unit cell, whose origin was arbitrarily defined by assigning the value $^3/_4$ to the *y* coordinate of the Ni(1) atom. All the remaining nonhydrogen atoms were located by means of subsequent electron density syntheses. Least-squares refinement of positional and individual isotropic thermal parameters led to convergence at $R = 0.070$ and $R_w = 0.079$.

All the hydrogen atoms, located from difference maps, were added to the model as fixed contributors, and the structure was further refined by using anisotropic thermal parameters for the nickel and oxygen atoms. The model converged with $R = 0.0514$ and $R_w = 0.0577$, with changes in parameters in the last cycle being 0.10 or less. A final Fourier difference function was featureless, with no peaks higher than 0.45 e Å^{-3}. Unit weights were used at all stages; no systematic variation of $\sum w(|F_o| - |F_c|)^2$ vs. $|F_o|$, sin θ, or Miller indices was noted. Correction for secondary extinction was not deemed necessary. A least-squares refinement of the structure of opposite polarity, leading to final values of 0.0520 and 0.0583 for R and R_w, respectively, showed that our original choice of chirality was correct.

The final structural parameters of the nonhydrogen atoms are given in Table II. A list of the positional parameters of the hydrogen atoms and a list of $10|F_o|$ and $10|F_c|$ are available as supplementary material.

Analysis. Nitrogen, carbon, and hydrogen were analyzed with a C. Erba Elemental Analyzer Instrument Model 1106 by G. Pistoni.

Results and Discussion

Description of the Structure. A drawing of the structure showing the atom numbering is given in Figure 1 and a drawing of the unit cell contents in Figure 2. Bond distances and angles involving the Ni atoms are listed in Table III. Bond lengths and angles involving the O, N, C, and H atoms are available as supplementary material.

The structure consists of two crystallographically independent but chemically equivalent Ni(L-asp)(im)$_3$ molecules tied in an infinite three-dimensional network by hydrogen-bonding interactions.

In both complex molecules the Ni atom is octahedrally coordinated to four N and two O atoms by three imidazole molecules and one L-aspartate ion, which acts as a tridentate ligand. Individual and mean bond distances and angles within the two coordination polyhedra compare well with those found in other octahedral complexes of Ni(II) involving amino or imidazole N atoms and carboxylate O atoms.[11-21] Nevertheless, a comparison between the corresponding bond distances and angles shows small but significant differences, occurring in the five-membered glycinate rings of the L-aspartate ions. The presently found values of the two N(amino)–Ni–O(α-carboxylate) bond angles (76.3 (3)° and 80.7 (4)°, respectively) correlate well with their average Ni–ligand bond distances (2.132 (9) Å and 2.084 (9) Å, re-

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Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni(1)	0.6225 (1)	0.75	0.3216 (2)	1.67 (6)	1.62 (8)	1.29 (5)	0.02 (6)	−0.05 (5)	0.17 (5)
Ni(2)	0.1172 (1)	0.7819 (2)	0.2937 (2)	1.33 (6)	2.09 (9)	1.17 (5)	0.13 (6)	−0.03 (4)	0.02 (6)
O(1)	0.6055 (4)	0.6568 (13)	0.0897 (9)	1.5 (3)	3.2 (5)	1.5 (3)	−0.7 (3)	0.3 (3)	0.1 (3)
O(2)	0.5496 (4)	0.4618 (12)	−0.0111 (10)	2.9 (4)	2.8 (5)	2.9 (4)	0.7 (4)	−0.6 (3)	0.1 (4)
O(3)	0.6180 (4)	0.5211 (12)	0.4019 (10)	1.5 (4)	2.9 (5)	3.0 (4)	−0.1 (4)	−0.7 (3)	1.4 (4)
O(4)	0.5742 (4)	0.3285 (11)	0.5170 (10)	2.3 (4)	3.4 (4)	3.3 (4)	−0.1 (3)	0.1 (3)	1.8 (4)
O(5)	0.0975 (4)	1.0065 (10)	0.3688 (9)	1.3 (3)	1.7 (4)	1.9 (3)	−0.7 (3)	0.1 (3)	−0.1 (3)
O(6)	0.0196 (4)	1.1671 (12)	0.3894 (11)	3.4 (5)	3.2 (5)	3.9 (5)	0.8 (4)	0.6 (4)	−0.1 (4)
O(7)	0.0945 (4)	0.8587 (13)	0.0621 (9)	2.5 (4)	3.4 (5)	1.5 (3)	0.4 (4)	−0.1 (3)	0.3 (3)
O(8)	0.0533 (4)	1.0282 (13)	−0.1112 (11)	2.8 (4)	4.3 (5)	3.1 (4)	1.3 (4)	0.9 (3)	1.6 (4)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(1)	0.5591 (5)	0.5708 (15)	0.0823 (13)	1.8 (2)	N(7)	0.6288 (5)	0.8222 (14)	0.5572 (11)	2.3 (2)
C(2)	0.5120 (5)	0.5977 (15)	0.2058 (14)	2.0 (2)	C(15)	0.6200 (5)	0.7283 (17)	0.6798 (14)	2.2 (3)
N(1)	0.5255 (4)	0.7472 (14)	0.2833 (10)	1.7 (2)	N(8)	0.6299 (5)	0.8071 (17)	0.8153 (13)	3.0 (2)
C(3)	0.5120 (6)	0.4637 (16)	0.3222 (15)	2.3 (2)	C(16)	0.6456 (7)	0.9613 (19)	0.7813 (16)	3.0 (3)
C(4)	0.5729 (6)	0.4369 (16)	0.4237 (14)	2.2 (2)	C(17)	0.6463 (6)	0.9700 (17)	0.6188 (15)	2.6 (3)
C(5)	0.0407 (6)	1.0393 (16)	0.3548 (14)	2.1 (2)	N(9)	0.2082 (4)	0.8463 (12)	0.2747 (11)	1.7 (2)
C(6)	−0.0017 (6)	0.9145 (16)	0.2722 (14)	2.3 (2)	C(18)	0.2555 (5)	0.8131 (16)	0.3788 (14)	2.3 (2)
N(2)	0.0240 (4)	0.7596 (15)	0.3057 (10)	2.1 (2)	N(10)	0.3090 (5)	0.8553 (13)	0.3205 (12)	2.4 (2)
C(7)	−0.0064 (6)	0.9528 (16)	0.0938 (14)	2.3 (3)	C(19)	0.2947 (6)	0.9132 (17)	0.1718 (15)	2.8 (3)
C(8)	0.0520 (6)	0.9481 (16)	0.0097 (14)	2.0 (2)	C(20)	0.2322 (6)	0.9036 (17)	0.1467 (15)	2.7 (3)
N(3)	0.7162 (4)	0.7099 (12)	0.3240 (11)	1.8 (2)	N(11)	0.1335 (5)	0.5505 (15)	0.2245 (11)	2.1 (2)
C(9)	0.7534 (4)	0.6708 (15)	0.4459 (14)	2.1 (2)	C(21)	0.1001 (6)	0.4296 (16)	0.2613 (15)	2.4 (2)
N(4)	0.8083 (5)	0.6324 (14)	0.4078 (12)	2.5 (2)	N(12)	0.1322 (5)	0.3023 (15)	0.2304 (12)	3.3 (2)
C(10)	0.8081 (7)	0.6476 (19)	0.2465 (17)	3.1 (3)	C(22)	0.1849 (7)	0.3417 (20)	0.1734 (17)	3.5 (3)
C(11)	0.7504 (6)	0.6971 (17)	0.1965 (16)	2.9 (3)	C(23)	0.1861 (6)	0.4986 (17)	0.1700 (16)	2.7 (3)
N(5)	0.6317 (5)	0.9723 (15)	0.2334 (11)	1.9 (2)	N(13)	0.1340 (5)	0.7138 (13)	0.5343 (11)	1.9 (2)
C(12)	0.5915 (6)	1.0687 (16)	0.1642 (15)	2.3 (2)	C(24)	0.1158 (6)	0.7911 (20)	0.6527 (13)	2.5 (2)
N(6)	0.6144 (5)	1.2070 (15)	0.1286 (14)	3.3 (2)	N(14)	0.1305 (5)	0.7155 (16)	0.7911 (12)	2.7 (2)
C(13)	0.6747 (8)	1.2050 (20)	0.1815 (18)	3.7 (3)	C(25)	0.1575 (6)	0.5835 (17)	0.7563 (15)	2.5 (3)
C(14)	0.6860 (6)	1.0584 (17)	0.2438 (16)	2.8 (3)	C(26)	0.1599 (6)	0.5828 (17)	0.5973 (15)	2.5 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

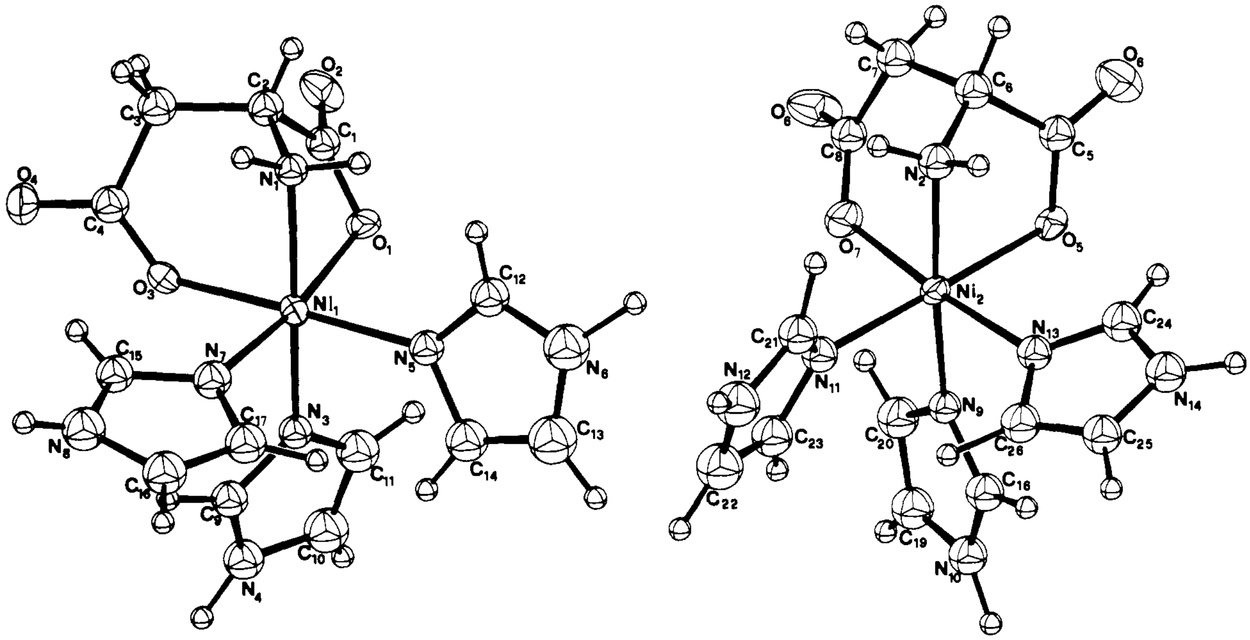

Figure 1. ORTEP drawing of the Ni(L-asp)(im)$_3$ molecules showing the atom numbering and thermal motion ellipsoids (50%) for nonhydrogen atoms. The hydrogen atoms are represented as spheres of radius 0.1 Å.

spectively) on the basis of the relation suggested by Freeman[11,22] between the metal–ligand bond lengths and bond angles for the metal atoms in α-amino acid complexes. According to this correlation, based on the constancy of the N···O distance, whose reported values average 2.66 Å[11] (in our case they are 2.63 (2) and 2.70 (2) Å, respectively), the mean metal–donor distance increases linearly from 2.0 to 2.5 Å as the interatomic angle decreases from 84° to 64°. The readily apparent distortions from the ideal octahedral geometry about the Ni atoms are of the same extent as those commonly observed for Ni(II) complexes containing multidentate ligands;[11,13,22,23] the deviations of the Ni atoms from the four-donor coordination planes, reported as supplementary material, range, as absolute values, from 0.025 to 0.125 Å.

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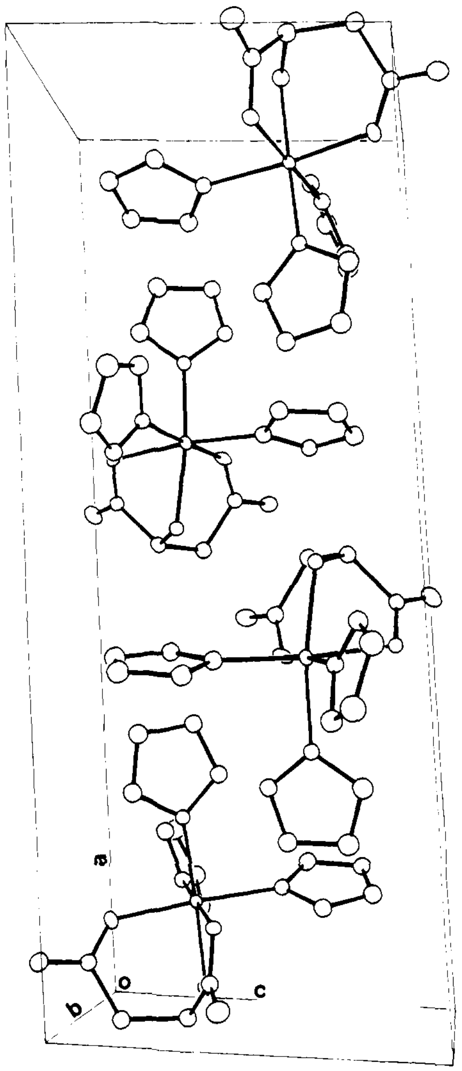

Figure 2. Perspective view of the crystal packing in a unit cell of Ni(L-asp)(im)$_3$. The hydrogen atoms have been omitted for clarity.

There are no surprising features in the internal geometries of the L-aspartate ions, which are facially coordinated to the Ni atoms through their amino N, and α-carboxylate and β-carboxylate O atoms. The same coordination to the metal occurs in the (L-aspartato)zinc(II) trihydrate[4] and its isomorphous Co(II) and Ni(II) trihydrate salts,[4a] in three isomers of the bis(L-aspartato)cobalt(III) ion,[3] and in the [*N*-(2-pyridylmethyl)-L-aspartato](L-phenylalaninato)cobalt(III) trihydrate,[24] whereas in the mixed complex (L-aspartato)(imidazole)copper(II) dihydrate,[5] the L-aspartate group is bonded in an extended configuration to three different Cu atoms, and each Cu atom links three L-aspartate ions. In our case, it is interesting to note that the most significant difference between the internal geometries of the two independent L-aspartate ions occurs again at the five-membered chelate rings with torsion angles at the C–C bonds of 13.7° and 31.7°, respectively. This latter value is slightly outside the 0–30° range observed for other α-amino acid–metal complexes.[11,24] In both anions the individual and mean C–O distances for the coordinated O atoms appear significantly longer[11] than those for the uncoordinated O atoms; their values average 1.26 (1) and 1.24 (1) Å, respectively.

Table III. Bond Distances (Å) and Angles (deg) Involving Ni Atoms

Ni(1)-O(1)	2.134 (8)	Ni(2)-O(5)	2.099 (9)
Ni(1)-O(3)	2.096 (10)	Ni(2)-O(7)	2.098 (8)
Ni(1)-N(1)	2.129 (9)	Ni(2)-N(2)	2.070 (10)
Ni(1)-N(3)	2.090 (10)	Ni(2)-N(9)	2.098 (10)
Ni(1)-N(5)	2.076 (9)	Ni(2)-N(11)	2.121 (13)
Ni(1)-N(7)	2.094 (10)	Ni(2)-N(13)	2.132 (10)
O(1)-Ni(1)-O(3)	86.4 (4)	O(5)-Ni(2)-O(7)	87.5 (4)
O(1)-Ni(1)-N(1)	76.3 (3)	O(5)-Ni(2)-N(2)	80.7 (4)
O(1)-Ni(1)-N(3)	92.2 (2)	O(5)-Ni(2)-N(9)	90.2 (4)
O(1)-Ni(1)-N(5)	91.6 (4)	O(5)-Ni(2)-N(11)	177.1 (4)
O(1)-Ni(1)-N(7)	172.0 (4)	O(5)-Ni(2)-N(13)	89.1 (4)
O(3)-Ni(1)-N(1)	87.9 (4)	O(7)-Ni(2)-N(2)	85.5 (4)
O(3)-Ni(1)-N(3)	85.2 (4)	O(7)-Ni(2)-N(9)	89.6 (4)
O(3)-Ni(1)-N(5)	176.2 (5)	O(7)-Ni(2)-N(11)	93.9 (4)
O(3)-Ni(1)-N(7)	88.2 (4)	O(7)-Ni(2)-N(13)	175.4 (4)
N(1)-Ni(1)-N(3)	166.9 (4)	N(2)-Ni(2)-N(9)	169.8 (5)
N(1)-Ni(1)-N(5)	94.8 (4)	N(2)-Ni(2)-N(11)	96.8 (5)
N(1)-Ni(1)-N(7)	97.5 (4)	N(2)-Ni(2)-N(13)	90.9 (4)
N(3)-Ni(1)-N(5)	91.7 (4)	N(9)-Ni(2)-N(11)	92.4 (4)
N(3)-Ni(1)-N(7)	93.3 (5)	N(9)-Ni(2)-N(13)	93.5 (4)
N(5)-Ni(1)-N(7)	94.1 (4)	N(11)-Ni(2)-N(13)	89.3 (4)
Ni(1)-O(1)-C(1)	110.0 (7)	Ni(2)-O(5)-C(5)	113.8 (8)
Ni(1)-O(3)-C(4)	130.8 (8)	Ni(2)-O(7)-C(8)	129.2 (8)
Ni(1)-N(1)-C(2)	103.9 (7)	Ni(2)-N(2)-C(6)	105.8 (8)
Ni(1)-N(3)-C(9)	126.7 (9)	Ni(2)-N(9)-C(18)	125.8 (8)
Ni(1)-N(3)-C(11)	127.8 (8)	Ni(2)-N(9)-C(20)	127.3 (8)
Ni(1)-N(5)-C(12)	131.5 (9)	Ni(2)-N(11)-C(21)	124.2 (9)
Ni(1)-N(5)-C(14)	125.2 (9)	Ni(2)-N(11)-C(23)	125.1 (10)
Ni(1)-N(7)-C(15)	124.9 (9)	Ni(2)-N(13)-C(24)	124.4 (9)
Ni(1)-N(7)-C(17)	127.9 (9)	Ni(2)-N(13)-C(26)	129.9 (9)

Table IV. Hydrogen Bonding Distances (Å) and Angles (deg)[a]

atoms	H···O	N···O	N–H	N–H···O
N(1)-H(1N1)···O(4[b])	2.01	2.98 (1)	0.94	149
N(1)-H(2N1)···O(2[c])	2.41	3.29 (2)	1.01	145
N(2)-H(1N2)···O(8[d])	2.11	3.02 (1)	0.93	166
N(2)-H(2N2)···O(6[e])	1.97	2.96 (1)	1.00	169
N(4)-H(N4)···O(5[f])	1.90	2.90 (1)	1.01	169
N(6)-H(N6)···O(2[g])	1.62	2.83 (2)	1.18	160
N(8)-H(N8)···O(1[h])	1.89	2.77 (1)	0.91	162
N(10)-H(N10)···O(4[b])	1.81	2.82 (1)	1.01	177
N(12)-H(N12)···O(5[i])	2.09	2.94 (2)	0.88	163
N(14)-H(N14)···O(7[h])	1.79	2.79 (1)	1.02	166

[a] Superscripts refer to the following transformations of the reference coordinates: [b] $1-x, {}^1/_2+y, 1-z$. [c] $1-x, {}^1/_2+y, -z$. [d] $-x, y-{}^1/_2, -z$. [e] $-x, y-{}^1/_2, -z$. [f] $1-x, y-{}^1/_2, 1-z$. [g] $x, y+1, z$. [h] $x, y, z+1$. [i] $x, y-1, z$.

Table V. Magnetism, Electronic and Infrared Spectra (cm^{-1}), and Ligand Field Parameters (cm^{-1}) of the Solid-State Complexes

	Ni(L-asp)-(im)$_3$	Ni(L-asp)-(2Meim)$_3$
μ_{eff}	3.16	3.02
$^3A_{2g} \rightarrow {}^3T_{2g}$	10700	10150
$\rightarrow {}^1E_g$	13250 vw	13120 vw
$\rightarrow {}^3T_{1g}(F)$	16950	16530
$\rightarrow {}^3T_{1g}(P)$	27550	27030
D_q	1070	1015
B	825	875
$\nu(NH)$	3320 ms	3340 ms
$\nu(NH_2)$	3262 s	3270 s
	3180 s	3180 sb
$\delta(NH_2)$	1624 vs	1620 vs
$\nu(OCO)_{asym}$	1580 vsb	1590 vsb
	1560 sh	1560 vs
$\nu(OCO)_{sym}$	1412 vs	1420 vs
	1390 vs	1392 vs

The dimensions of the imidazole ligands, which are planar within the experimental uncertainties, compare well with those reported for the neutral ligand in other metal complexes[5,11,15-19] and for the free imidazole at −150 °C.[25] The displacements of the Ni atoms away from the planes of their bonded imidazole molecules range from 0.065 to 0.427 Å. There is no regularity in the rotations of the imidazole rings about the Ni–N bond, which appear determined by packing and hydrogen bonding requirements.

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The network of intermolecular hydrogen bond interactions (Table IV), on which the crystal packing depends, involves all the N-bonded H atoms and all but one (O(3)) carboxylate O atom. The loss of the crystallographic equivalence and the conformational differences between the two independent complex molecules are probably due to the different arrangements of the hydrogen bonding.

Magnetisms and Ligand Field and Infrared Spectra (Table V). The magnetic moments of the complexes are in the range expected for spin-free d^8 systems.

The room-temperature ligand field spectra, very similar to one another, show three strong absorptions and one weak absorption, characteristic of regular octahedral nickel(II) complexes. Although the presence of distortions from the ideal octahedral geometry about the Ni atoms is demonstrated by the structural results, the spectra retain the simple form found in O_h symmetry also at 77K. The absence of clearly visible splitting of the orbital triplets $^3T_{1g}$ and $^3T_{2g}$ (in O_h symmetry) may be due either to the fact that our complexes have cis configurations for which lower splitting is expected than for trans configurations[26] or to the presence of two independent Ni(L-asp)(im)$_3$ molecules in the crystal lattice.

However, band shapes and positions (assigned on the basis of O_h symmetry) and the Dq (ligand field parameter) and B (Racah parameter) values, calculated according to the averaged environment rule, are in the range found for octahedrally coordinated nickel(II) ions with a ligand set of four N and two O atoms.[27-30]

The infrared spectra of the complexes also give expected band shapes and positions, especially in the 3400–3100- and 1650–1350-cm^{-1} spectral regions. In the first region, characteristic of NH and NH$_2$ stretching vibrations, three well-resolved bands appear. The NH$_2$ group of the L-aspartate ion, in addition to metal coordination, is also involved in strong intermolecular hydrogen bonding in the crystal, while the NH group of the imidazole molecules is only involved in the last type of the interaction, the first band appearing at 3340–3320 cm^{-1}, in agreement with literature data,[31] and previous results on copper(II)–L-aspartate complexes[5] may be tentatively associated to the NH stretching frequency of the imidazoles. Steric hindrance in 2-methylimidazole is greater than in imidazole and justifies a higher energy band and a lower ligand field strength in the first compound than in the second.

In the 1650–1350-cm^{-1} spectral region, in which appear the asymmetric and symmetric modes of the carboxylate groups,[32-34] multiple bands are present, in agreement with the coordination of both the carboxylate groups to the nickel(II) ion.

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Registry No. Ni(L-asp)(im)$_3$, 80878-92-8; Ni(L-asp)(2-Me(im))$_3$, 80878-93-9; Ni(L-asp)(H$_2$O)$_3$, 30054-73-0.

Supplementary Material Available: A list of the bond lengths and angles of the Ni, O, N, C, and H atoms, a list of positional parameters of the hydrogen atoms, and a list of the observed and calculated structure factors for Ni(L-asp)(im)$_3$ (18 pages). Ordering information is given on any current masthead page.

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