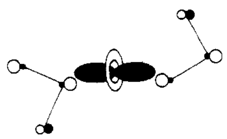
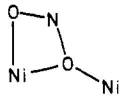


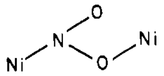
6

which can be largely delocalized toward the NO_2 groups. The $x^2 - y^2$ type magnetic orbital is partially delocalized toward the $(NO_2)^*$ group for the species **1**. This is not true anymore for both the species **2** and the chain. The exchange parameter J experimentally observed may be expressed as the sum of an antiferromagnetic component J_{AF} and a ferromagnetic component J_F. The magniture of J_{AF}, which is here the leading factor, is governed by the overlap integrals $S_{z^2z^2}$ and $S_{x^2-y^2x^2-y^2}$ between magnetic orbitals. $S_{x^2-y^2x^2-y^2}$ is clearly zero for both the dimer and the chain. The relatively weak antiferromagnetic interaction in the dimer with respect to the chain may be simply justified from the schemes **4**, **5**, and **6** by focusing on $S_{z^2z^2}$. Indeed, owing to the weak delocalization of the magnetic orbital shown in **4** toward the chelating NO_2 group, the overlap $S_{z^2z^2}$ is not favored. In the chain, on the contrary, the delocalization on the bridging ligands and the relative orientation of the magnetic orbitals are favorable to give a relatively large $S_{z^2z^2}$ in spite of the Ni–Ni distance.

We are quite conscious that the arguments above are very qualitative and may be even rather rough. However, we believe that we have shown in a simple language the difference between the bridging networks



and



In the former case, the $6a_1$ HOMO of the NO_2^- bridge is not favorably orientated regarding the orientations of the singly occupied orbitals of the Ni(II) ion bound to the two oxygen atoms. In the latter case, in contrast, the $6a_1$ HOMO of the bridge is properly orientated and the antiferromagnetic coupling is more pronounced in spite of the large Ni–Ni distance.

Acknowledgment. This work was technically financially supported by the CNRS, the DGRST, and the DESR.

Supplementary Material Available: Listings of structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

Contribution from the Consiglio Nazionale delle Ricerche, Rome, Italy,
Istituto di Chimica Generale e Inorganica, University of Modena, 41100 Modena, Italy,
and Istituto di Chimica, Facoltà di Medicina-Veterinaria, University of Bari, 70126 Bari, Italy

Thermal, Spectroscopic, Magnetic, and Structural Properties of Mixed-Ligand Complexes of Copper(II) with L-Aspartic Acid and Amines. Crystal and Molecular Structure of (L-Aspartato)(imidazole)copper(II) Dihydrate

L. ANTOLINI,[1a] G. MARCOTRIGIANO,[1b] L. MENABUE,[1a] G. C. PELLACANI,*[1a] and M. SALADINI[1a]

Received November 5, 1981

A blue compound of the type $Cu(\text{L-Asp})\cdot 2H_2O$ (L-Asp = L-aspartate ion) and its mixed complexes with amine $[Cu(\text{L-Asp})B]\cdot xH_2O$ (B = Im (imidazole), mf (morpholine) and $x = 2$; B = 2-MeIm (2-methylimidazole) and $x = 1$; B = py (pyridine), 4-pic (4-methylpyridine) and $x = 0$) were prepared and characterized by means of thermal, spectroscopic, and magnetic measurements. For one of the mixed complexes, $[Cu(\text{L-Asp})(\text{Im})]\cdot 2H_2O$, the crystal structure was also determined by the single-crystal X-ray diffraction method. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with four formula units in a cell of dimensions $a = 16.049$ (2) Å, $b = 9.622$ (1) Å, and $c = 7.465$ (1) Å. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares procedure to a conventional R index of 0.083 for 594 counter data. The structure consists of a polymeric two-dimensional network in which each copper atom is coordinated in a distorted square-pyramidal geometry by three aspartate ions and one imidazole molecule. The aspartate ion acts as a bidentate ligand bridging, in an extended configuration, three metal ions. For $[Cu(\text{L-Asp})B]\cdot xH_2O$ complexes thermal and spectroscopic measurements indicate the presence of distorted square-pyramidal configuration around the copper(II) atoms, similar to that found for the $[Cu(\text{L-Asp})(\text{Im})]\cdot 2H_2O$ complex. Their apparently "anomalous" EPR spectra, suggesting a d_{z^2} ground state, are interpreted as due to the presence of magnetically inequivalent sites. For the $[Cu(\text{L-Asp})(H_2O)_2]$ and $[Cu(\text{L-Asp})(\text{4-pic})]$ complexes a square-pyramidal configuration tetragonally distorted is tentatively suggested on the basis of their physical measurements.

Introduction

Copper(II) complexes of aspartic acid have received considerable attention, but most of the studies only treat the solution-state behavior.[2] It has been generally suggested that aspartate acts as a tridentate ligand to the same metal ion, while the possibility of polymerization, as found in solid copper(II) glutamate dihydrate, in which the amino acid, in an extended chain conformation, bridges three metal ions,[3] has never been considered. Some other interesting studies in solution regard the mixed-ligand complexes with imidazole or bipyridyl, which seem to enhance the affinity of copper(II) for the oxygen donor sites of anionic ligands,[4,5] and the ternary complexes containing two optically active amino acids with interacting charged group in their side chains.[2,6]

---

(1) (a) University of Modena. (b) University of Bari.
(2) Evans, C. A.; Guevremont, R.; Rabenstein, D. L. *Met. Ions Biol. Syst.* **1979**, *9*, 41 and references cited therein.
(3) Gramaccioli, C. M.; Marsh, R. E. *Acta Crystallogr.* **1966**, *21*, 594.
(4) Mohan, M. S.; Bancroft, D.; Abbott, E. H. *Inorg. Chem.* **1979**, *18*, 1527.
(5) Sigel, H. *Inorg. Chem.* **1980**, *19*, 1411.
(6) Yamauchi, O.; Odani, A. *J. Am. Chem. Soc.* **1981**, *103*, 391.

0020-1669/82/1321-2263$01.25/0

Despite the abundancy of material for the aspartate in solution, there are only few and unclear reports about the copper(II) aspartate complexes in the solid state.[7-9] In one of them for a $K_2[Cu(Asp)_2]\cdot H_2O$ complex, on the basis of an infrared investigation, the presence of tridentate aspartates in the crystal was suggested[10] although Evans et al.[2] wonder about the role of the water molecule.

As all these studies are defective with respect to the disposal of the ligands around the metal ion and to the coordination geometry of the metal ion, to clarify that we have now isolated in the solid state and investigated by means of spectroscopic, magnetic, thermogravimetric, and calorimetric measurements a copper(II) aspartate complex having a copper(II):aspartate ratio of 1:1 and its mixed-ligand complexes with amines having copper(II):aspartate:amine ratios of 1:1:1. For one of the latter complexes, (L-aspartato)(imidazole)copper(II) dihydrate, the crystal structure has also been determined. For $Cu(Asp)\cdot xH_2O$ ($x = 1$[7] or 3[8]) and $Cu(L\text{-}Asp)(Im)\cdot H_2O$, which are also objects of our study, the visible circular dichroism has been previously reported.[8] Two other ternary complexes of the aspartic acid with 2,2′-bipyridyl and 1,10-phenanthroline have been recently synthesized and characterized.[11]

Further interest in this work derives from its biological implications since we are dealing with ternary complexes containing a heteroatomic N base moiety and O donors, which is the preferred combination of donor atoms dominating in many naturally occurring complexes of low and high molecular weight as it enhances the complex stability.[5] In particular, in (L-aspartato)(imidazole)copper(II) dihydrate the presence of biologically important ligands, which form part of several proteins, makes it a realistic mimic for copper enzymes or copper-nonenzymatic proteins, especially for those containing non- or low-blue copper(II) atoms (blue proteins of type 2Cu).

Experimental Section

All chemicals were of reagent grade and used as received.

Preparation of (L-Aspartato)diaquacopper(II), $[Cu(L\text{-}Asp)(H_2O)_2]$. By mixing copper(II) acetate monohydrate (4 mmol) and L-aspartic acid (4 mmol) in boiling water, a bulky pale blue compound precipitated, which, after stirring at 50 °C for 1 h in water, becomes blue. Anal. Calcd for $C_4H_9CuNO_6$: C, 20.81; H, 3.93; N, 6.07. Found: C, 21.02; H, 4.01; N, 6.06. Mp = 230 °C dec.

Preparation of (L-Aspartato)(imidazole)copper(II) Dihydrate. $[Cu(L\text{-}Asp)(Im)]\cdot 2H_2O$. A concentrated aqueous solution of imidazole (6 mmol) was added drop by drop to a vigorously stirred hot (50 °C) aqueous solution of a slurry of $[Cu(L\text{-}Asp)(H_2O)_2]$ (3 mmol) until its complete dissolution. After concentration of the solution by adding methanol, blue crystals separated. The compound, washed with methanol, was dried in vacuo over NaOH for 24 h. Anal. Calcd for $C_7H_{13}CuN_3O_6$: C, 28.18; H, 4.39; N, 14.07; H_2O, 12.06. Found: C, 28.19; H, 4.17; N, 14.15; H_2O, 12.40. Mp = 220 °C dec.

Preparation of the Other Complexes, $[Cu(L\text{-}Asp)B]\cdot nH_2O$ ($n = 1$ and B = 2-Methylimidazole (2-MeIm) and Morpholine (mf); $n = 0$ and B = 4-Methylpyridine (4-pic) and Pyridine (py)). All the compounds were prepared as reported for the imidazole derivative in water/methanolic (1/10) solution. When the solution was cooled at 4–5 °C or diethyl ether added, blue crystalline compounds separated.

$[Cu(L\text{-}Asp)(2\text{-}MeIm)]\cdot H_2O$. Anal. Calcd for $C_8H_{13}CuN_3O_5$: C, 32.58; H, 4.45; N, 14.26; H_2O, 6.11. Found: C, 32.70; H, 4.45; N, 14.12; H_2O, 6.40. Mp = 210 °C dec.

$[Cu(L\text{-}Asp)(py)]$. Anal. Calcd for $C_9H_{10}CuN_2O_4$: C, 39.47; H, 3.68; N, 10.24. Found: C, 39.36; H, 3.63; N, 10.17. Mp = 210 °C dec.

Table I. Summary of Crystal Data Collection[a] for $[Cu(L\text{-}Asp)(Im)]\cdot 2H_2O$

diffractometer	Philips PW 1100
radiation	graphite-monochromated Mo Kα (λ = 0.71069 Å)
temp, °C	18 ± 2
crystal system	orthorhombic
space group	$P2_12_12_1$ (D_2^4, No. 19)
a, Å	16.049 (2)
b, Å	9.622 (1)
c, Å	7.465 (1)
V, Å^3	1152.73
mol formula	$C_7H_{13}CuN_3O_6$
mol wt	298.67
Z	4
$F(000)$	612
ρ(calcd), g/cm^3	1.72
ρ(obsd), g/cm^3	1.68 by flotation in C_4Cl_6 (hexachlorobutadiene)
reflctns measd	$+h, +k, +l$
scan type	$\theta - 2\theta$
θ range, deg	2–25
scan speed, deg/min	2.1
scan width, deg	1.1
bkgd time, s	10 at beginning and end of the scan
stds	2 every 60 reflctns (no significant changes)
collected reflctns	1223, yielding 1184 nonzero independent data
obsd reflctns	594 with $I > 3\sigma(I)$ [$\sigma(I)$ = (peak counts + total background counts)$^{1/2}$]
crystal size, mm	~0.17 × 0.14 × 0.13
abs coeff, cm^{-1}	18.4
abs corn	not applied

[a] The unit cell parameters were determined from a least-squares refinement of the setting angles of 24 automatically centered reflections from diverse regions of reciprocal space, with use of the standard control program of the PW 1100 system.[12]

$[Cu(L\text{-}Asp)(mf)]\cdot 2H_2O$. Anal. Calcd for $C_8H_{18}CuN_2O_7$: C, 30.22; H, 5.71; N, 8.82; H_2O, 11.34. Found: C, 29.92; H, 5.61; N, 8.78; H_2O, 11.62. Mp = 190 °C dec.

$[Cu(L\text{-}Asp)(4\text{-}pic)]$. Anal. Calcd for $C_{10}H_{12}CuN_2O_4$: C, 41.72; H, 4.21; N, 9.74. Found: C, 41.26; H, 4.30; N, 9.62. Mp = 215 °C dec.

Physical Measurements. The electronic spectra of the solid compounds were recorded as mull transmission spectra with a Shimadzu MPS 50L spectrophotometer. The infrared spectra were recorded with a Perkin-Elmer 180 spectrophotometer in KBr pellets or in Nujol on KBr pellets as support in the 4000–250-cm^{-1} spectral range. The room-temperature magnetic moments were measured with the Gouy method with $Ni(en)_3S_2O_3$ as calibrant and by correcting for diamagnetism with the appropriate Pascal constants. The EPR spectra were recorded on a JEOL PE-3X spectrometer on polycrystalline samples by using diphenylpicrylhydrazyl (DPPH, $g = 2.0036$) as a calibrating field marker. DSC measurements were made with a Perkin-Elmer DSC 1 instrument, and the TG measurements were made on a Du Pont 990 instrument.

X-ray Data Collection. The crystals obtained exhibited extensive twinning or were shown to be badly split when checked by precession and cone-axis photographs. The only crystal of fairly satisfactory quality was obtained from a careful cleavage into four unequal pieces of a twinned crystal. The largest fragment, sealed on a glass fiber, was transferred, in a random orientation, to a Philips PW 1100 automatic four-circle diffractometer.

Details of data collection and processing are given in Table I. The systematic absences (from a survey of the complete data set) $h00$ ($h = 2n + 1$), $0k0$ ($k = 2n + 1$), and $00l$ ($l = 2n + 1$) uniquely determined the space group to be $P2_12_12_1$ (No. 19).

All data were corrected for Lorentz and polarization effects but not for absorption in view of the small absorption coefficient and the small and almost isotropic crystal dimensions; only the 594 observed reflections were used in the structure analysis.

Solution and Refinement of the Structure. Neutral-atom scattering factors were used,[13a] and anomalous dispersion corrections[13b] were

---

(7) Kinoshita, H.; Yoshino, Y. *Sci. Pap. Coll. Gen. Educ., Univ. Tokyo* **1972**, *23*, 99; *Chem. Abstr.* **1974**, *81*, 114013.

(8) Boos, G. A.; Yarkova, E. G.; Zakharov, A. V.; Pribylow, K. P.; Solov'eva, T. F. *Zh. Neorg. Khim.* **1979**, *24*, 2166.

(9) Bunel, S.; Ibarra, C.; Rodriguez, M.; Urbina, A.; Bunton, C. A. *J. Inorg. Nucl. Chem.* **1981**, *43*, 190. The preparations of these complexes are reported in a paper cited as a reference, which appears as a submitted paper.

(10) Kirschner, S. *J. Am. Chem. Soc.* **1956**, *78*, 2372.

(11) Kwik, W. L.; Ang, K. P.; Chen, G. *J. Inorg. Nucl. Chem.* **1980**, *42*, 303.

(12) "User Manual for PW 1100 Philips"; Eindhoven, The Netherlands.

Table II. Atomic Coordinates with Esd's in Parentheses

atom	x	y	z
Cu	0.1656 (2)	0.1583 (3)	0.2598 (6)
O(1)	0.2590 (12)	0.1843 (15)	0.5032 (25)
O(2)	0.2703 (11)	−0.0323 (16)	0.5988 (29)
O(3)	0.5813 (11)	0.2281 (19)	0.6246 (30)
O(4)	0.4981 (14)	0.2935 (27)	0.8367 (30)
W(1)	0.4834 (18)	0.5005 (40)	0.3960 (45)
W(2)	0.0556 (26)	0.2072 (43)	0.8038 (41)
C(1)	0.2874 (16)	0.0934 (24)	0.5981 (35)
C(2)	0.3619 (13)	0.1375 (23)	0.7111 (31)
N(1)	0.3731 (13)	0.0240 (21)	0.8521 (30)
C(3)	0.4395 (15)	0.1606 (33)	0.6036 (36)
C(4)	0.5100 (20)	0.2290 (28)	0.6961 (38)
N(2)	0.2216 (12)	0.3238 (23)	0.1576 (27)
C(5)	0.1901 (19)	0.4474 (34)	0.1204 (46)
N(3)	0.2516 (18)	0.5357 (25)	0.0683 (33)
C(6)	0.3227 (20)	0.4597 (31)	0.0740 (40)
C(7)	0.3056 (16)	0.3312 (33)	0.1259 (35)

Table III. Interatomic Distances (Å) and Angles (Deg) for $[Cu(L\text{-}Asp)(Im)]\cdot 2H_2O$[a]

Cu–O(1)	2.37 (2)	C(2)–C(3)	1.50 (3)
Cu–O(2′)	1.99 (2)	C(3)–C(4)	1.48 (4)
Cu–N(1′)	1.98 (2)	C(4)–O(3)	1.26 (3)
Cu–O(3″)	1.94 (2)	C(4)–O(4)	1.23 (3)
Cu–N(2)	1.98 (2)	N(2)–C(5)	1.32 (4)
Cu···O(4″)	2.82 (2)	N(2)–C(7)	1.37 (3)
C(1)–O(1)	1.22 (3)	C(5)–N(3)	1.36 (4)
C(1)–O(2)	1.24 (3)	N(3)–C(6)	1.36 (4)
C(1)–C(2)	1.52 (3)	C(6)–C(7)	1.32 (4)
C(2)–N(1)	1.53 (3)		

O(1)–Cu–O(2′)	101.6 (8)	C(5)–N(2)–Cu	129 (2)
O(1)–Cu–N(1′)	91.4 (7)	C(7)–N(2)–Cu	124 (2)
O(1)–Cu–O(3″)	92.3 (7)	C(4″)–O(4″)···Cu	74 (2)
O(1)–Cu–N(2)	85.6 (7)	O(1)–C(1)–O(2)	128 (2)
O(1)–Cu···O(4″)	141.4 (9)	O(1)–C(1)–C(2)	115 (2)
O(2′)–Cu–N(1′)	80.4 (7)	O(2)–C(1)–C(2)	116 (2)
O(2′)–Cu–O(3″)	166.0 (9)	C(1)–C(2)–C(3)	113 (2)
O(2′)–Cu–N(2)	91.3 (7)	C(1)–C(2)–N(1)	106 (2)
O(2′)–Cu···O(4″)	116.0 (8)	N(1)–C(2)–C(3)	112 (2)
N(1′)–Cu–O(3″)	97.2 (7)	C(2)–C(3)–C(4)	117 (2)
N(1′)–Cu–N(2)	170.5 (9)	C(3)–C(4)–O(3)	120 (3)
N(1′)–Cu···O(4″)	86.3 (8)	C(3)–C(4)–O(4)	120 (3)
O(3″)–Cu–N(2)	92.0 (7)	O(3)–C(4)–O(4)	120 (3)
O(3″)–Cu···O(4″)	50.0 (9)	N(2)–C(5)–N(3)	110 (3)
N(2)–Cu···O(4″)	101.6 (8)	C(5)–N(3)–C(6)	105 (2)
C(1)–O(1)–Cu	127 (1)	N(3)–C(6)–C(7)	110 (3)
C(1′)–O(2′)–Cu	119 (1)	C(6)–C(7)–N(2)	108 (3)
C(2′)–N(1′)–Cu	111 (1)	C(7)–N(2)–C(5)	107 (2)
C(4″)–O(3″)–Cu	116 (1)		

[a] Superscript primes refer to the following transformations of the coordinates: ′, $1/2 - x, -y, z - 1/2$; ″, $x - 1/2, 1/2 - y, 1 - z$.

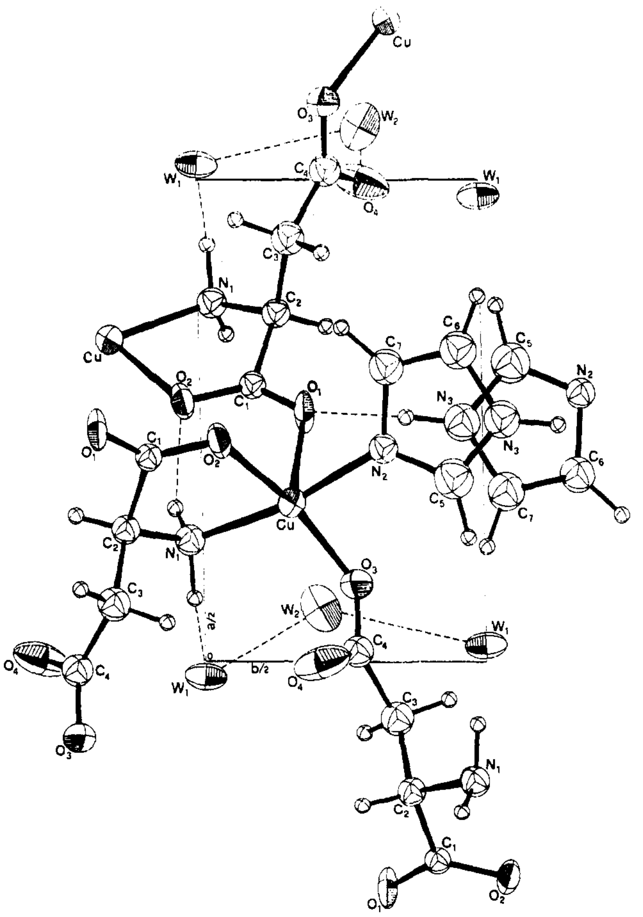


Figure 1. ORTEP view of a fourth of the unit cell of $[Cu(L\text{-}Asp)(Im)]\cdot 2H_2O$ showing the labeling scheme and thermal motion ellipsoids at the 40% level, except for H and water O atoms which are drawn arbitrarily small for clarity. Hydrogen bonds are shown as dashed lines.

applied to 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 weighting factor. Major calculations were performed on a CDC Cyber 7600 computer by using the "SHELX-76" system of programs[14] for Fourier and least-squares calculations and the ORTEP plotting program[15] for drawing.

The structure was solved by conventional Patterson and Fourier techniques; unit weight least-squares refinement of positional and isotropic thermal parameters for all nonhydrogen atoms resulted in convergence at $R = 0.113$ and $R_w = 0.125$. Hydrogen atoms were then added to the model as fixed contributors at their calculated positions (based upon appropriate sp^2 or sp^3 geometry and bond lengths of 1.0 Å) with an isotropic thermal parameter arbitrarily assessed at 5.0 Å. Further refinement, allowing the copper and oxygen atoms to vibrate anisotropically, led to final convergence at $R = 0.083$ and $R_w = 0.090$ ($w = 1/\sigma^2(F)$), with changes in parameters in the last cycle being 0.1σ or less. The weighting scheme showed no systematic dependence of $\sum w\Delta^2$ on $|F_o|$ or sin θ. A final difference density map was featureless, with no peaks higher than 1.0 e $Å^{-3}$. Correction for secondary extinction was not deemed necessary. Because of the poor agreement factor, no tests were made for the chirality of the crystal.

The least-squares refinement produced unusually large thermal motion parameters for the two water oxygen atoms; doubt, owing to the chemical analysis results and to the density measurements, increased with regard to the exact H_2O composition of the cell. In order to examine the possibility of partial occupancy of the water sites, we performed a series of refinements of their occupation probabilities or of the thermal parameters of the oxygen atoms with various fixed fractional values of their occupancy factors. Nevertheless, in no case were the R and R_w factors lower than in the case of full occupancy of the water sites, to which all X-ray results presented therein refer.

The final atomic coordinates are given in Table II. The final structure factors, thermal parameters, and calculated hydrogen atom positions are available as supplementary material.

Analysis. Nitrogen, carbon and hydrogen were analysed with a C. Erba elemental analyzer instrument, model 1106, by Mr. G. Pistoni.

Results and Discussion

Description of the Structure. Interatomic distances and angles (with esd's) are listed in Table III, with atoms numbered as in Figure 1.

Lists of selected least-squares planes (and atomic deviations therefrom) and of hydrogen-bonding distances and angles are given in supplementary material.

The structure consists of a polymeric two-dimensional network in which each copper atom is coordinated in a dis-

---

(13) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) pp 99–101; (b) pp 149–151.

(14) Sheldrick, G. M. "SHELX-76 Program for Crystal Structure Determination"; University Chemical Laboratory: Cambridge, England, 1976.

(15) Johnson, C. K. "ORTEP", Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

Table IV. Ideal and Observed Dihedral Angles (Deg) for CuL$_5$ Polyhedra

complex	shape-determining δ' angles[a] (e_3, e_1, e_2)	δ angles (a_2, a_5, and remaining angles)
ideal trigonal bipyramid[b]	53.1	101.5, 101.5, 101.5
	53.1, 53.1	101.5, 101.5, 101.5
[Cu(L-Asp)(Im)].2H$_2$O	17.3	80.2, 84.3, 119.7
	63.1, 76.7	110.2, 115.2, 109.4
ideal tetragonal pyramid[b]	0.0	75.7, 75.7, 119.8
	75.7, 75.7	119.8, 119.8, 119.8

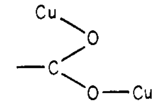
[a] e_n and a_n refer to pairs of adjacent triangular faces which form equatorial or axial edges, respectively. [b] The ratio Cu–L$_{eq}$ to Cu–L$_{ax}$ bond lengths for the idealized models is set at unity and a L$_{ax}$–Cu–L$_{eq}$ (basal) angle of 102° is assumed for the C_{4v} model.

torted square-pyramidal geometry by three L-aspartate ions and by one imidazole molecule; in addition there are two water molecules which provide crystalline stability through a network of hydrogen-bonding interactions.

The four donor atoms which form the N$_2$O$_2$ basis of the coordination polyhedron are the β-carboxylate O(3) atom, the unprotonated imidazole N(3) atom, the α-carboxylate O(2), and the amino N(1) atoms of a second L-asparte ion, which, acting as a bidentate ligand, forms a five-membered glycine-like ring. The α-carboxylate O(1) atom of a third L-aspartate ion occupies the apical positions of the square pyramid. The closest approach to the sixth octahedral position about the copper(II) ion is due to the β-carboxylate O(4) atom, but at a distance (2.82 (2) Å) and with interatomic angles (O(3)–Cu···O(4) = 50.0 (9)° and O(1)–Cu···O(4) = 141.4(9)°) which may be associated with an only weak axial nonbonding interaction.[16] The Cu(II) ion lies 0.086 Å above the mean plane of the four equatorially bonded atoms, whose deviations from the plane (from 0.153 to –0.159 Å) indicate a tetrahedral distortion of their basic square-planar geometry. As a consequence, there is a relevant distortion of the square-pyramidal geometry toward the trigonal-bipyramidal coordination; the results of a detailed analysis of the geometry, according to the Muetterties and Guggenberger criterion,[17] reported in Table IV, show a distortion from the ideal square pyramid slightly larger than those observed in the copper(II) glycil-L-tyrosine[18] and (L-methionylglycinato)copper(II)[19] complexes.

The Cu–N and Cu–O equatorial bond distances are in good agreement with those in other structural reports,[2,20,21] while the rather long Cu–O apical bond length of 2.37 (2) Å is consistent with the value of 2.36 Å found in (glycylglycinato)bis(imidazole)copper(II)[22] and of 2.30 Å observed in copper(II) glutamate dihydrate.[23]

The present mixed complex is the first example of aspartate ion acting as a bidentate ligand and bridging, in an extended configuration, three metal ions. The crystal structures of zinc(II) aspartate trihydrate[23,24] and of three isomers of bis(L-aspartato)cobalt(III) ion[25] show that the ligand is tridentate, as is strongly suggested also for other metal complexes by stability constant determinations or spectroscopic investigations.[2] It is therefore the binding of the imidazole molecule to the copper ion which probably produces the present unusual arrangement of the aspartate ion, which shows exactly the same kind of coordination exhibited by the glutamate ion in the copper(II) glutamate dihydrate.[3] In both complexes the α-carboxylate group bridges two Cu atoms in a configuration of the following, already reported,[19,26,27] syn–anti type:



and one β-carboxylate O atom is bonded, in apical position, to a third Cu atom. Analogously, in both complexes the nonbonded β-carboxylate O atom, in both cases involved in hydrogen-bonding interaction, completes a severely distorted octahedral geometry about the copper atom. The most significant difference between the complexes appears to be the presently found relevant distortion of the square-pyramidal geometry about the copper atom, undoubtly due to the replacement of the water by an imidazole molecule in the copper coordination sphere. We attribute the distortion to a strong, nearly linear hydrogen bond between the N-bonded imidazole H atom and the apical β-carboxylate O atom rather than to steric hindrance effects of the planar imidazole molecule. It is interesting to note that the carbon skeleton of the aspartate ion retains the planar arrangement found in the free L-aspartic[28] and DL-aspartic acid.[29] Bond distances and bond angles of the anion are consistent with the values reported for the free acids[28,29] and their metal complexes.[23-26]

The internal geometry of the imidazole ligand is in good agreement with that found in imidazole at –150 °C[30] and those reported for the neutral ligand in other metal complexes.[2,20,21]

A list of the hydrogen-bonding interactions which occur in the crystal is given in the supplementary material; those involving the water molecules were judged probable only on the basis of the interatomic distances.

Thermal, Magnetic, and Spectral Properties. The thermal studies performed on the hydrate compounds show very broad peaks, corresponding to a complete loss of their water molecules, in very large and differing temperature ranges. In particular, the [Cu(L-Asp)B]·xH$_2$O (B = 2-MeIm, mf) complexes such as the structurally known [Cu(L-Asp)(Im)]·2H$_2$O complex in a temperature range of 25–130 °C, continuously lose water molecules, confirming that in these complexes the water molecules are only involved in hydrogen-bonding interactions in the crystal packing, while the presence of coordinated water molecules in [Cu(L-Asp)(H$_2$O)$_2$] is strongly suggested since the thermal extrusion of both the water molecules appears in a temperature range of 160–220 °C accompanied by a decomposition of the complex.

A similar structure to that found for the [Cu(L-Asp)(Im)$_2$]·2H$_2$O complex may be proposed for all the mixed complexes, except the 4-pic one, since their magnetic and spectroscopic properties (Table V) are very similar to one another and similar to those of the imidazole complex. In fact their room-temperature solid electronic spectra exhibit a broad

---

(16) Brown, D. S.; Lee, J. D.; Melsom, B. G. A.; Hathaway, B. J.; Procter, I. M.; Tomlinson, A. A. G. *Chem. Commun.* **1967**, 369.

(17) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748.

(18) Mosset, A.; Bonnet, J. J. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2807.

(19) Dehand, J.; Jordanov, J.; Keck, F.; Mosset, A.; Bonnet, J. J.; Galy, J. *Inorg. Chem.* **1979**, *18*, 1543 and references cited therein.

(20) Freeman, H. C. "Inorganic Biochemistry"; Eichhorn, G. L.; Ed.; Elsevier: Amsterdam, 1973; Vol. 1, pp 121–166 and references cited therein.

(21) Hathaway, B. J. *Coord. Chem. Rev.* **1981**, *35*, 211 and references cited therein.

(22) Bell, J. D.; Freeman, H. C.; Wood, A. M.; Driver, R.; Walker, W. R. *J. Chem. Soc. D* **1969**, 1441.

(23) Doyne, T.; Pepinsky, R.; Watanabe, T. *Acta Crystallogr.* **1957**, *10*, 438.

(24) Kryger, L.; Rasmussen, S. E. *Acta Chem. Scand.* **1973**, *27*, 2674.

(25) Oonishi, I.; Sato, S.; Saito, Y. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1318.

(26) Freeman, H. C. *Adv. Protein Chem.* **1967**, *22*, 257.

(27) Amirthalingam, V.; Muralidharan, K. V. *Acta Crystallogr., Sect. B* **1976**, *B32*, 3153.

(28) Derissen, J. L.; Endeman, H. J.; Peerdeman, A. F. *Acta Crystallogr., Sect. B* **1968**, *B24*, 1349.

(29) Rao, S. T. *Acta Crystallogr., Sect. B* **1973**, *B29*, 1718.

(30) Martinez-Carrera, S. *Acta Crystallogr.* **1966**, *20*, 783.

Table V. Room-Temperature Electronic and Infrared (cm^{-1}) Spectra, Magnetic Moments, and Powder EPR Spectra of the Solid Compounds

	d–d band $\times 10^{-3}$	$\nu(NH_2)$	$\nu(COO^-)$		μ_{eff}, μ_B	$g_\parallel$, $g_\perp$
			asym	sym		
L-AspH		3020 br s[a]	1690 vs, 1600 vs	1418 vs, 1245 vs		
L-AspD		2270 br s[b]	1680 vs, 1600 vs	1420 vs		
$[Cu(L\text{-}Asp)(H_2O)_2]$	14.4	3250 s, 3160 s	1615 vs, br, 1595 sh	1410 s, 1400 s, 1378 vs	1.85	2.249, 2.076
[Cu(L-Asp)(4-pic)]	14.4	3270 s, 3135 s	1620 vs, 1592 vs, br	1408 sh, 1395 vs	1.87	2.147[c]
$[Cu(L\text{-}Asp)(Im)]\cdot 2H_2O$	15.4	3360 s, 3250 m	1618 vs, br, 1590 sh	1405 sh, 1390 sh, 1368 vs	1.83	2.053, 2.175
$[Cu(L\text{-}Asp)(2\text{-}MeIm)]\cdot H_2O$	14.9	3365 s, 3215 vs	1610 sh, 1595 vs, br	1408 vs, 1392 vs	1.82	2.060, 2.184
$[Cu(L\text{-}Asp)(mf)]\cdot 2H_2O$	15.3	3360 s, 3200 vs	1610 vs, br, 1592 vs	1405 sh, 1390 sh, 1370 vs	1.80	2.179, 2.050
[Cu(L-Asp)(py)]	15.3	3355 s, 3210 vs	1610 vs, br 1590 sh	1412 s, 1400 vs, br	1.85	2.257,[d] 2.126,[e] 2.059[f]

[a] $\nu(NH_3^+)$. [b] $\nu(ND_3^+)$. [c] g_{iso}. [d] g_3. [e] g_2. [f] g_1.

maximum at 14860–15380 cm^{-1}. As the d–d band position is determined by the ligand field contribution from the four donor atoms which define the square plane around the Cu, our results are in agreement with the presence of mixed O and N donor groups.[19]

Table V also reports only absorptions assigned to the most significant ligand functions of L-aspartate. Although the presence of extensive hydrogen bonding makes it difficult to rationalize frequency shifts upon metal coordination, there are two aspects worthy of note: (a) the disappearance of the $\nu(NH_3^+)$ band in the free L-aspartic acid associated with the zwitterionic structure, coupled with the appearance of two absorptions in the mixed complexes in the 3190–3360-cm^{-1} region assigned to N–H stretching modes; (b) the presence in the mixed complexes of multiple bands in the region characteristic of the asymmetric and symmetric modes of the carboxylate groups.[31,32] This indicates that both the carboxylate groups of the L-aspartate ion are coordinated to the copper atoms, even if it is not possible to distinguish between the bidentate syn–anti coordination of the C(1)O(1)O(2) group and the monodentate coordination of the C(4)O(3)O(4) group.

Also the fact that the mixed complexes have all similar anomalous EPR spectra strongly suggests that they must have similar structures, too. In fact, although they have "normal" room-temperature magnetic moments typical of "magnetically dilute" complexes,[33] they present EPR spectra of axial reversed type ($g_\perp > g_\parallel$), suggesting a d_{z^2} ground state,[33,34] inconsistent with the structure of the $[Cu(L\text{-}Asp)(Im)]\cdot 2H_2O$ complex. Five-coordinate copper(II) complexes having geometries intermediate between the two limiting square-pyramidal and trigonal bipyramidal, which is our case, seem to be characterized by strong rhombic distortions.[35] An analysis based on the known crystal structure of the $[Cu(L\text{-}Asp)(Im)]\cdot 2H_2O$ complex may suggest a reasonable explanation of the observed EPR spectra. In some cases EPR spectra inconsistent with the coordination geometry of the copper(II) ion were explained as due to the presence of inequivalent sites within the unit cell in an antiferrodistortive arrangement.[34,36] In our case the contemporaneous presence of a distortion from square-pyramidal geometry and of inequivalent sites may be considered as responsible for the "anomalous" EPR spectra.

The other two complexes, $[Cu(L\text{-}Asp)(H_2O)_2]$ and [Cu(L-Asp)(4-pic), show very similar physical behavior, presenting a broad d–d band at 14390 cm^{-1}, two strong IR bands at 3250, 3130 and 3270, 3135 cm^{-1}, respectively, assignable to $\nu(NH_2)$, at energies considerably lower than those found for the mixed complexes discussed above, and multiple bands around 1600 and 1400 cm^{-1}, indicating that in these complexes, too, both the carboxylate groups of the L-aspartate ion are involved in the metal coordination. These facts, enhanced by the EPR spectrum of the $[Cu(L\text{-}Asp)(H_2O)_2]$ complex, which is of the axial type (Table V), enable us to suggest tentatively for these complexes a square-pyramidal configuration tetragonally distorted rather than distorted toward a trigonal-bipyramidal configuration.

In particular, for the $[Cu(L\text{-}Asp)(H_2O)_2]$ complex two ill-resolved maxima assignable to the coordinated water molecules are clearly observed at 3410 s ($\nu(OH)_{asym}$) and 3330 mw ($\nu(OH)_{sym}$).[37]

Acknowledgment. The authors are grateful to Dr. W. Porzio of the Istituto di Chimica delle Macromolecole del CNR for the X-ray data collection, the Centro di Calcolo Elettronico del'Università di Modena for the computing support, and the Centro Strumenti dell'Università di Modena for the recording of the infrared spectra.

Registry No. $[Cu(L\text{-}Asp)(Im)]\cdot 2H_2O$, 80907-70-6; $Cu(L\text{-}Asp)(H_2O)_2$, 80925-53-7; Cu(L-Asp)(2-MeIm), 80925-55-9; Cu(L-Asp)(mf), 80925-57-1; Cu(L-Asp)(py), 80925-59-3; Cu(L-Asp)(4-pic), 80925-61-7.

Supplementary Material Available: Listings of thermal parameters, calculated hydrogen atom positions, hydrogen-bonding distances and angles, selected least-squares planes, and final structure factors (10 pages). Ordering information is given on any current masthead page.

---

(31) Battaglia, L. P.; Bonamartini Corradi, A.; Marcotrigiano, G.; Menabue, L.; Pellacani, G. C. *J. Am. Chem. Soc.* **1980**, *102*, 2663.

(32) (a) Catterick, J.; Thornton, P. *Adv. Inorg. Chem. Radiochem.* **1977**, *20*, 291. (b) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227 and references cited therein.

(33) Hathaway, B. J.; Billing, D. E. *Coord. Chem. Rev.* **1970**, *5*, 143.

(34) Bertini, I.; Gatteschi, D.; Scozzafava, A. *Coord. Chem. Rev.* **1979**, *29*, 67 and references cited therein.

(35) Bencini, A.; Bertini, I.; Gatteschi, D.; Scozzafava, A. *Inorg. Chem.* **1978**, *17*, 3194 and references cited therein.

(36) Estes, W. E.; Gavel, D. P.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1978**, *17*, 1415 and references cited therein.

(37) Vallarino, L. M.; Goedken, V. L.; Quagliano, J. V. *Inorg. Chem.* **1973**, *12*, 102.