Inorg. Chem. **1983**, *22*, 141–145 **141**

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

Coordination Behavior of L-Aspartic Acid: Thermal, Spectroscopic, Magnetic, and Structural Properties of Aqua(L-aspartato)(2,2′-bipyridine)copper(II) Trihydrate

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

Received June 8, 1982

The title compound crystallizes in the orthorhombic space group $P2_12_12_1$ with four formula units in a cell of dimensions $a = 21.978$ (2) Å, $b = 11.275$ (1) Å, and $c = 6.841$ (1) Å. The structure was solved by the heavy-atom method and refined by least-squares calculations to $R = 0.037$ for 1640 independent reflections. The structure consists of a monomeric [Cu(L-asp)(bpy)H_2O] molecule with three water molecules in the lattice. The geometry around Cu(II) is five-coordinated distorted square pyramidal. The organic ligands act as bidentate in the basal plane, with a water molecule occupying the apical position. Thermogravimetric analysis shows the complete loss of water molecules in the 335–400 K temperature range. Infrared and ligand field spectroscopic results and variable-temperature magnetic measurements are interpreted in the light of the known structure.

Introduction

The solution-state behavior of the copper(II)–aspartate complexes has been extensively investigated, as well as that of their ternary complexes with imidazole (im) or 2,2′-bipyridine (bpy),[2] which were suggested to enhance the affinity of copper(II) for the oxygen donor sites of anionic ligands.[3,4]

Although the study of the same systems in the solid state can undoubtedly contribute to clarify the coordination sites of the ligand and the preferred coordination geometry of the metal ion, up to now the only known crystal structure is that of the solid (L-aspartato)(imidazole)copper(II) dihydrate.[5] In this complex the copper(II) atom presents a distorted square-pyramidal geometry and the aspartate ion, in an extended-chain configuration, bridges three metal ions, contradicting what was previously suggested.[2]

In order to examine closely the aspartate behavior and its influence on the coordination geometry of the copper(II) ion, we have now investigated a second copper(II)–aspartate complex, aqua(L-aspartato)(2,2′-bipyridine)copper(II) trihydrate, by means of thermal, spectroscopic, magnetic, and structural measurements. For a similar compound of formula Cu(asp)(bpy)·$2H_2O$ some IR, electronic, ESR, and polarographic data were previously reported.[6]

Experimental Section

Preparation of the Complex [Cu(L-asp)(bpy)H_2O]·$3H_2O$. This compound was prepared by dissolving Cu(asp)·$2H_2O$[5] (5 mmol) and bpy (5 mmol) in hot water (~70 °C), by adding ethanol until the water:ethanol ratio was 1:1, and by allowing the blue solution to stand for some days, yielding blue crystals. Anal. Calcd for $C_{14}H_{21}CuN_3O_8$: C, 39.74; H, 5.01; N, 9.94. Found: C, 39.83; H, 5.07; N, 9.96. Mp: 157–160 °C dec.

Physical Measurements. The electronic spectrum of the solid compound was recorded as a mull transmission spectrum with a Shimadzu MPS 50L spectrophotometer. The infrared spectrum (4000–300 cm^{-1}) obtained in a KBr pellet or as a Nujol mull on a KBr pellet, as support, was recorded with a Perkin-Elmer 180 spectrophotometer. Magnetic susceptibility measurements were obtained on a Newport Instruments magnetic (Gouy) balance employing a Newport Instruments cryostatic cooling system using [HgCo$(SCN)_4$] as calibrant and were corrected for diamagnetism with the appropriate Pascal constants. The EPR spectra of a polycrystalline sample were recorded on a JEOL PE-3X spectrometer at 100 and 295 K by using diphenylpicrylhydrazyl (DPPH, $g = 2.0036$) as the calibrating field marker. TGA and DTA measurements were performed on a Du Pont 990 instrument.

Table I. Summary of Crystal Data Collection

diffractometer	Siemens AED
radiation	Ni-filtered Cu Kα ($\lambda = 1.541\,78$ Å)
temp, °C	20 ± 2
cryst system	orthorhombic
space group	$P2_12_12_1$ (D_2^4, No. 19)
a, Å	21.978 (2)
b, Å	11.275 (1)
c, Å	6.841 (1)
V, Å^3	1695.3
mol formula	$C_{14}H_{21}CuN_3O_8$
mol wt	422.732
Z	4
$F(000)$	875.9
ρ(calcd), g cm^{-3}	1.656
ρ(obsd), g cm^{-3}	1.68 (by flotation in C_4Cl_6)
reflcns measd	$+h, +k, +l$
scan type	ω–2θ
θ range, deg	2–70
lowest speed, deg min^{-1}	2.5
scan width max, deg	1.1
stds	1 every 50 reflcns (no changes)
collected reflcns	1899
obsd reflcns	1640 with $I > 2.0\sigma(I)$ [$\sigma^2(I)$ = (total counts) + (0.01 × intens)^2]
cryst size, mm	~0.26 × 0.22 × 0.19
abs coeff, cm^{-1}	21.0
abs cor	not applied

Crystallographic Data Collection. Lauê symmetry and approximate lattice constants were obtained from rotation and Weissenberg photographs (Cu Kα radiation). Unit cell dimensions were then refined by least-squares methods using 2θ values of 15 high-angle reflections accurately measured on an "on line" single-crystal-automated Siemens AED diffractometer. Details specific to the X-ray data collection and processing are given in Table I. A survey of the complete data set revealed systematic absences compatible only with space group $P2_12_12_1$. All data were corrected for Lorentz and polarization effects but not for absorption in view of the small absorption coefficient and of small and almost isotropic crystal dimensions. Only the observed reflections, placed on an (approximately) absolute scale by means of a Wilson plot, were used in the structure analysis.

Solution and Refinement of the Structure. Neutral-atom scattering factors were used,[7a] and anomalous dispersion corrections were applied[7b] to non-hydrogen 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[8] for Fourier and least-squares calculations and

---

[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] Mohan, M. S.; Bancroft, D.; Abbott, E. H. *Inorg. Chem.* **1979**, *18*, 1527.

[4] Sigel, H. *Inorg. Chem.* **1980**, *19*, 1411 and references cited therein.

[5] Antolini, L.; Marcotrigiano, G.; Menabue, L.; Pellacani, G. C.; Saladini, M. *Inorg. Chem.* **1982**, *21*, 2263.

[6] Kwik, W. L.; Ang, K. P.; Chen, G. *J. Inorg. Nucl. Chem.* **1980**, *42*, 303.

[7] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) pp 99–101; (b) pp 149–150.

0020-1669/83/1322-0141$01.50/0

Table II. Final Positional Parameters

atom	x	y	z
Cu	0.2862 (1)	0.2962 (1)	0.6838 (2)
O(w1)	0.3247 (2)	0.2749 (4)	0.3623 (7)
N(1)	0.2102 (2)	0.2009 (4)	0.6686 (8)
C(1)	0.1544 (2)	0.2441 (5)	0.6554 (10)
C(2)	0.1027 (3)	0.1740 (6)	0.6750 (12)
C(3)	0.1106 (3)	0.0527 (6)	0.7048 (12)
C(4)	0.1690 (3)	0.0066 (5)	0.7136 (12)
C(5)	0.2178 (3)	0.0821 (5)	0.6980 (9)
N(2)	0.3221 (2)	0.1345 (4)	0.7323 (8)
C(6)	0.3814 (3)	0.1080 (6)	0.7437 (11)
C(7)	0.4031 (3)	−0.0064 (6)	0.7337 (12)
C(8)	0.3618 (3)	−0.0972 (6)	0.7123 (12)
C(9)	0.3002 (3)	−0.0729 (5)	0.7025 (11)
C(10)	0.2809 (3)	0.0446 (5)	0.7119 (9)
O(1)	0.2435 (2)	0.4410 (3)	0.6182 (7)
O(2)	0.2536 (2)	0.6361 (4)	0.5911 (7)
C(11)	0.2744 (3)	0.5351 (5)	0.6338 (9)
C(12)	0.3399 (2)	0.5267 (5)	0.7013 (10)
N(3)	0.3514 (2)	0.4048 (4)	0.7769 (8)
C(13)	0.3814 (3)	0.5573 (5)	0.5325 (9)
C(14)	0.4439 (3)	0.6076 (5)	0.5825 (11)
O(3)	0.4543 (2)	0.6419 (4)	0.7528 (7)
O(4)	0.4802 (2)	0.6184 (4)	0.4385 (7)
O(w2)	0.4415 (2)	0.2829 (4)	0.2093 (9)
O(w3)	0.4732 (2)	0.3268 (4)	0.6293 (9)
O(w4)	0.4490 (3)	0.5102 (5)	0.0940 (9)
H(1w1)	0.3003	0.3112	0.2652
H(2w1)	0.3645	0.2909	0.3111
H(1w2)	0.4662	0.2208	0.1444
H(2w2)	0.4513	0.3693	0.1491
H(1w3)	0.5045	0.2644	0.6925
H(2w3)	0.5034	0.3746	0.5713
H(1w4)	0.4515	0.5420	−0.0323
H(2w4)	0.4813	0.5223	0.1007

the ORTEP plotting program[9] for drawing.

The structure was solved by conventional Patterson and Fourier techniques; least-squares refinement of positional and isotropic thermal parameters for all non-hydrogen atoms led to convergence with $R = 0.097$ and $R_w = 0.110$. All the hydrogen atoms were then added to the model as fixed contributors, those of organic ligands at their calculated positions (C–H and N–H = 1.0 Å) and those of water molecules at locations obtained from difference maps; their isotropic thermal parameters were set 1.0 $Å^2$ greater than those of the atom to which they are bonded. Further refinement of positional and anisotropic thermal parameters for all the non-hydrogen atoms led to final convergence at $R = 0.0374$ and $R_w = 0.0473$, with changes in parameters in the last cycles being 0.1σ or less. A final difference Fourier map was featureless, with no peaks higher than 0.30 e $Å^{-3}$. Unit weights were used at all stages; no trend of $\sum w(|F_o| - |F_c|)^2$ vs. $|F_o|$, sin θ, or Miller indices was observed. During the refinement zero weight was assigned to three strong low-order reflections, which may be affected by secondary extinction. Additional cycles of refinement were carried out with positional parameters inverted to define the correct enantiomeric form. Convergence was reached at $R = 0.0396$ and $R_w = 0.0497$; therefore, the previous refinement was judged to give the correct enantiomeric structure.

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

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

Results and Discussion

Description of the Structure. Bond distances are shown in Figure 1, together with the atom numbering scheme and atomic vibrational ellipsoids. Bond angles involving the copper(II) ion are listed in Table III. Complete bond distances and bond angles are given as supplementary material. A stereoview of unit cell contents is shown in Figure 2.

Table III. Bond Angles (Deg) Involving the Cu(II) Ion

O(w1)-Cu-N(1)	101.3 (2)	N(2)-Cu-O(1)	172.5 (2)
O(w1)-Cu-N(2)	85.5 (2)	N(3)-Cu-O(1)	84.5 (2)
O(w1)-Cu-N(3)	95.9 (2)	Cu-N(1)-C(1)	125.8 (4)
O(w1)-Cu-O(1)	92.5 (2)	Cu-N(1)-C(5)	114.8 (4)
N(1)-Cu-N(2)	81.3 (2)	Cu-N(2)-C(6)	126.3 (4)
N(1)-Cu-N(3)	162.5 (2)	Cu-N(2)-C(10)	113.3 (4)
N(1)-Cu-O(1)	92.0 (2)	Cu-O(1)-C(11)	115.3 (4)
N(2)-Cu-N(3)	102.9 (2)	Cu-N(3)-C(12)	109.6 (3)

The structure consists of a discrete [Cu(L-asp)(bpy)H_2O] molecule with three water molecules in the lattice, which provide crystalline stability by bridging the complex molecules through a network of hydrogen-bond interactions.

Environment of the Copper Atom. The geometry about Cu(II) is five-coordinate distorted square pyramidal. The four atoms of the equatorial plane (the N atoms of the bipyridyl ligand, one α-carboxylate O atom, and the amino nitrogen of the aspartate ion) show deviation from +0.173 to −0.175 Å in the pattern of a tetrahedral distortion of the approximately square-planar base. The copper atom is displaced toward the apical water O atom 0.126 Å from the mean plane through its basal atoms. This is a common feature of the Cu(II) small peptide[10,11] or amino acid[5,12] complexes. The closest approach to the sixth octahedral position about the metal atom is due to the α-carboxylate O(2) atom from a neighboring complex molecule, but at a distance (3.019 (5) Å) too long to be involved in even weak coordination to the copper atom.[13] Equatorial bond distances and angles are similar to those in previously reported structures.[5,11-16] while the rather long Cu–O apical bond length of 2.368 (5) Å compares well with the value of 2.36 Å found in (glycylglycinato)bis(imidazole)copper(II)[16] and of 2.37 Å observed in (L-asp)(im)$Cu^{II}\cdot 2H_2O$.[5] It is interesting to note that in the five-membered glycinate ring of the aspartate ligand the N–Cu–O bond angle (84.5°) correlates well with the mean metal–ligand bond lengths (1.963 (5) Å), on the basis of the relation suggested by Freeman[16] between mean metal–donor bond distances and bond angles in α-amino acid chelate rings. In this correlation, based on the constancy of the N···O distance, whose reported values average 2.66 Å (2.640 (8) Å in our case), the mean metal–donor distance increases linearly from 2.0 to 2.5 Å as the interatomic angle decreases from 84 to 64°.

Bipyridyl Ligand. The bond lengths and bond angles within the bidentate bpy ligand compare well with those reported in similar Cu(II) complexes.[12,13,15,17-19] The planar individual pyridine rings are twisted about the 2,2′ bond by 13.4°; this value is slightly larger than those, up to 11°, previously observed for this coordinated ligand.[17-19]

L-Aspartate Ligand. The bond distances and angles within the L-aspartate ion are consistent with the values reported for the free acids[20,21] and their metal complexes.[5,22-24] Rather

---

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

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

(10) Freeman, H. C. "The Biochemistry of Copper"; Peisach, J., Aisen, P., Blumberg, W. E., Eds.; Academic Press: New York, 1966.

(11) Simmons, C. J.; Lundeen, M.; Seff, K. *Inorg. Chem.* **1978**, *17*, 1429.

(12) Nardin, G.; Randaccio, L.; Bonomo, R. P.; Rizzarelli, E. *J. Chem. Soc., Dalton Trans.* **1980**, 369.

(13) Fitzgerald, W.; Hathaway, B. J. *J. Chem. Soc., Dalton Trans.* **1981**, 567.

(14) Freeman, H. C. *Adv. Protein Chem.* **1967**, *22*, 257 and references cited therein.

(15) Harrison, D.; Kennedy, D.; Hathaway, B. J. *Inorg. Nucl. Chem. Lett.* **1981**, *17*, 87 and references cited therein.

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

(17) Stephens, F. S. *J. Chem. Soc. A* **1969**, 2081.

(18) Belicchi Ferrari, M.; Gasparri Fava, G.; Pelizzi, C. *J. Chem. Soc., Chem. Commun.* **1977**, 8.

(19) Tyagi, S.; Hathaway, B. J. *J. Chem. Soc., Dalton Trans.* **1981**, 2029.

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

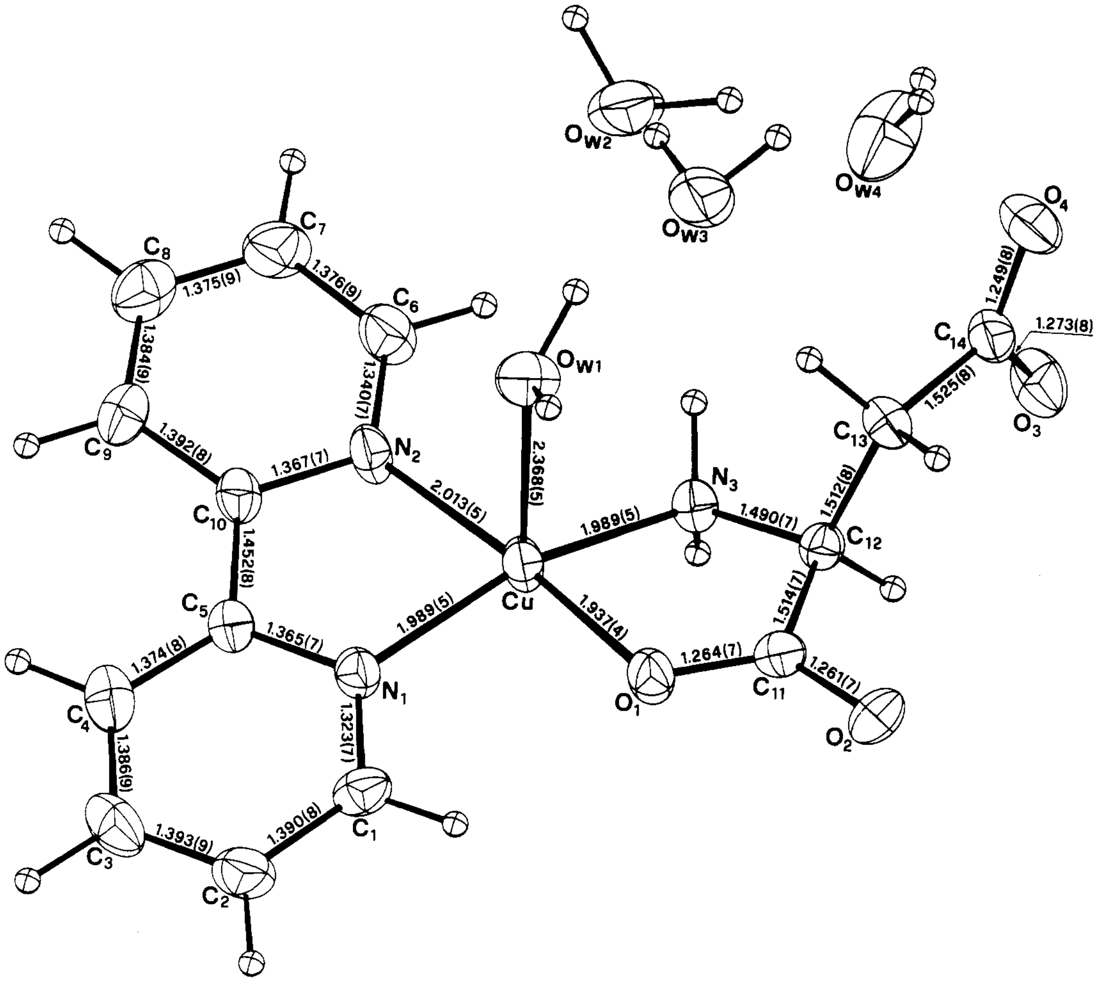

Figure 1. ORTEP view of the $[Cu(L\text{-}asp)(bpy)H_2O]\cdot 3H_2O$ showing the atom numbering, bond distances (Å, with esd's in parentheses), and atomic vibrational ellipsoids (50%). The hydrogen atoms are shown as spheres of arbitrary radius.

surprising appears the bonding mode of the ligand, which forms only a glycinato-copper(II) ring, with three uncoordinated carboxylate O atoms involved only in hydrogen-bond interactions. Previous structural investigations have shown that the aspartate ion acts as a tridentate ligand toward octahedral metal ions,[20,23,24] whereas in the only Cu(II) derivative of known structure, $(L\text{-}asp)(im)Cu^{II}\cdot 2H_2O$,[5] the ligand is bound in an extended configuration to three different metal ions. With respect to this ternary complex, in which the metal atom exhibits a similar tetrahedrally distorted square-pyramidal geometry, the replacement of an apical α-carboxylate O atom by a water molecule in the copper coordination sphere appears particularly significant.

Hydrogen Bonding. The strong, nearly linear hydrogen-bond interactions, which involve the amino group and uncoordinated carboxylate O atoms of the aspartate ion and all the water molecules, are listed in Table IV. These interactions, which are the major contributors to the crystal-packing forces, seem to play an important role in the coordination ability of the aspartate ligand toward the copper(II) ion.

Thermogravimetric, Magnetic, and Spectroscopic Results (Table V). The thermogravimetric studies performed on the compound show a very broad peak in the 335–400 K temperature range, in which both uncoordinated and coordinated water molecules are lost.

Table IV. Hydrogen-Bonding Distances (Å) and Angles (Deg) for $[Cu(L\text{-}asp)(bpy)H_2O]\cdot 3H_2O$

atoms[a]						
1	2	3	1–2	2···3	1···3	∠1–2···3
N(3)	H(2N3)	O(w3)	1.00	1.99	2.99	177
O(w1)	H(1w1)	$O(2^{i})$	0.95	1.78	2.72	172
O(w1)	H(2w1)	O(w2)	0.96	1.83	2.77	166
O(w2)	H(1w2)	$O(4^{ii})$	0.99	1.77	2.72	170
O(w2)	H(2w2)	O(w4)	1.08	1.64	2.69	164
O(w3)	H(1w3)	$O(3^{iii})$	1.07	1.69	2.74	165
O(w4)	H(1w4)	$O(4^{iv})$	0.94	1.85	2.77	165

[a] Superscripts refer to the following transformations of the reference coordinates: (i) $1/2 - x, 1 - y, z - 1/2$; (ii) $1 - x, y - 1/2, 1/2 - z$; (iii) $1 - x, y - 1/2, 3/2 - z$; (iv) $x, y, z - 1$.

Table V. Magnetic, Electronic, and Infrared Results

$\mu_{eff}(305\ K)$, μ_B[a]	1.92
$\mu_{eff}(116\ K)$, μ_B[a]	1.81
$g_{\parallel}$	2.240
$g_{\perp}$	2.062
g_0	2.121
E(d–d), cm^{-1}	16 390
$\nu(OCO)_{asym}$, cm^{-1}	1622 vs 1602 vs
$\nu(OCO)_{sym}$, cm^{-1}	1405 s 1388 vs

[a] $1\ \mu_B = 9.2732 \times 10^{-24}$ A m².

Magnetic susceptibility measurements of a polycrystalline sample between 116 and 305 K obey the Curie–Weiss law, $\chi = C(T - \Theta)$, with Curie and Weiss constants of $C = 0.500$

---

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

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

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

(24) Battagalia, L. P.; Bonamartini Corradi, A.; Antolini, L.; Marcotrigiano, G.; Menabue, L.; Pellacani, G. C. *J. Am. Chem. Soc.* **1982**, *104*, 2407.

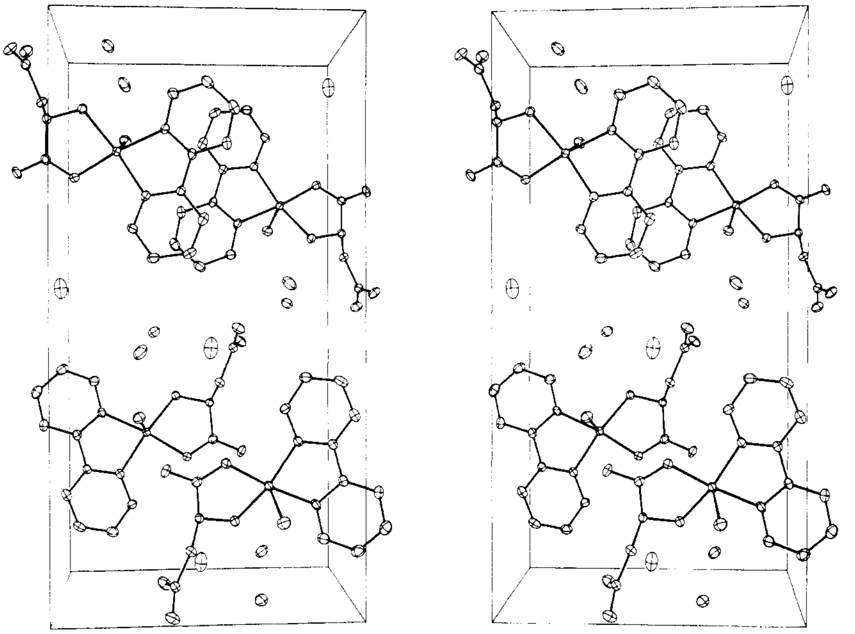

Figure 2. Stereoview of the unit cell contents down the *c* axis (the *b* axis is horizontal). H atoms are omitted for clarity.

cgsu and $\Theta = -25 \pm 1$ K, respectively. The molar susceptibilities were corrected for both diamagnetism (-223.25×10^{-6} cgsu mol^{-1}) and temperature-independent paramagnetism (60×10^{-6} cgsu mol^{-1}). The decreasing of the effective magnetic moment from 1.92 μ_B at 305 K to 1.81 μ_B at 116 K and the negative Weiss constant may indicate the presence of a weak antiferromagnetic interaction, which can be attributed to lattice effects throughout the crystallites.[25-27]

The EPR parameters of the complex are similar to those of synthetic copper(II) peptides[28-30] or to those of the ternary complexes having a similar square-pyramidal environment.[11]

Also, its room-temperature solid electronic spectrum, which shows an absorption maximum at 16 390 cm^{-1}, is comparable with those reported in most square-pyramidal copper(II) complexes.[5,11,30-32] The d–d band maximum in this complex at greater energy than that found for [Cu(L-asp)(im)]·2H$_2$O (15 400 cm^{-1})[5] agrees with the presence of different chromophores (N_3O_2 and N_2O_3 in the former and in the latter, respectively). Furthermore, the gyromagnetic ratio, *g* (calculated as $(g_\parallel + 2g_\perp)/3$), and the wavelength of the maximum d–d transition of our complex fit well on Yokoi's approximate straight-line graph,[30] obtained by correlating these physical properties for some copper–amino acidate complexes (six of them having square-pyramidal structure); considering that in the copper(II) complexes *g* values decrease and d–d transition energies increase as the planar ligand field becomes stronger or the axial ligand field becomes weaker.[29,30,33]

In the infrared spectrum of the complex the more relevant bands of the L-aspartate ion show the predictable frequency shifts being involved in the metal coordination. In particular, the splitting of the bands due to asymmetric and symmetric modes of the carboxylate group may be explained, only in the light of the known crystal structure, as due to the presence of two carboxylate groups, only one of them being involved in the metal coordination. The lack of different spectroscopic behavior in this spectral range between this complex and the previously reported L-aspartate complexes[5,24,34] in which both the carboxylate groups are involved, although in different ways in the metal coordination, may depend on the low symmetry of the free ion COO$^-$.[31] The inadequacy of this technique to reveal not only different ways of coordination but also different ligand conformations is suggested by the absence of relevant differences in the IR spectra (4000–350 cm^{-1}) of the four L-aspartate complexes examined.

Conclusions

Upon comparison of the structural results performed on the cobalt(II),[23] nickel(II),[24,34] zinc(II),[22,35] and copper(II)[5] (see also present work) complexes, the aspartate configuration seems strictly dependent on the metal ion and/or its coordination geometry. In fact the aspartate ion appears tridentate facially coordinated toward the metal ion such as Co(II), Ni(II), and Zn(II), which have an octahedral geometry, while only with the copper(II) ion, which has square-pyramidal geometry, is it present in an extended configuration.

Furthermore, on the basis of the examination of only two complexes, and considering the mutual influence of both ligands present in a ternary complex, it seems likely that the preferred square-pyramidal geometry of the copper(II) ion may be associated with the aspartate coordination. In fact, with coordination through the amino and carboxylato groups, forming stable five-membered chelate rings with the copper(II) ion, it favors five-coordination since the strong ligand field of the in-plane donor atoms weakens the axial interactions.[36] The presence of square-pyramidal geometry around the copper(II) ion is of great interest as it parallels that found in many copper(II)–peptide complexes.[10,14,37,38] This geometry appears

---

(25) Melnik, M. *J. Inorg. Nucl. Chem.* **1979**, *41*, 779.
(26) Nelson, H. G. *Inorg. Chim. Acta* **1979**, *32*, L51.
(27) Young, D. A.; Chadwick, S. S.; Hyde, K. E. *Inorg. Chim. Acta* **1980**, *55*, 57.
(28) Boas, J. F.; Pilbrow, J. R.; Hatzell, C. R.; Smith, T. D. *J. Chem. Soc. A* **1969**, 572.
(29) Bryce, G. F. *J. Chem. Phys.* **1966**, *70*, 3549.
(30) Yokoi, H.; Sai, M.; Isobe, T.; Oshawa, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2189 and references cited therein.
(31) Dehand, J.; Jordanov, J.; Keck, F.; Mosset, A.; Bonnet, J. J.; Galy, J. *Inorg. Chem.* **1979**, *18*, 1543.
(32) Estes, W. E.; Webster, A. C., III; Wasson, J. R.; Hatfield, W. E. *Inorg. Chem.* **1978**, *17*, 3664.
(33) Belford, G. J. *J. Chem. Phys.* **1957**, *26*, 1165.
(34) Antolini, L.; Marcotrigiano, G.; Menabue, L.; Pellacani, G. C. *J. Chem. Soc., Dalton Trans.*, in press.
(35) Doyne, T.; Pepinsky, R.; Watanabe, T. *Acta Crystallogr.* **1957**, *10*, 438.
(36) Chow, S. T.; McAuliffe, C. A. *Prog. Inorg. Chem.* **1975**, *19*, 51 and references cited therein.
(37) Freeman, H. C. In "Inorganic Biochemistry"; Eichorn, G. L., Ed.; Elsevier: Amsterdam, 1973; Vol. I, pp 121–166.
(38) Lim, M. C.; Sinn, E.; Martin, R. B. *Inorg. Chem.* **1976**, *15*, 807.

Inorg. Chem. **1983**, *22*, 145–147

very important in copper(II)–protein–substrate interactions.[37]

Acknowledgment. The authors are grateful to the Centro di Calcolo Elettronico dell'Universitā di Modena for computing support and the Centro Strumenti dell'Universitā di Modena for recording the infrared spectra.

Registry No. [Cu(L-asp)(bpy)H_2O]·$3H_2O$, 83333-56-6.

Supplementary Material Available: Listings of thermal parameters, calculated hydrogen atom positions, complete bond distances and bond angles, selected least-squares planes, and observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

Contribution from the Division of Chemistry,
National Research Council of Canada, Ottawa, Canada K1A 0R6

EPR Spectrum of $Mn_2(CO)_9^-$ in a Single Crystal of $Mn_2(CO)_{10}$[1]

T. LIONEL, J. R. MORTON, and K. F. PRESTON*

Received April 29, 1982

γ-Irradiated single crystals of $Mn_2(CO)_{10}$ exhibit EPR spectra at 85 K characteristic of anisotropic interactions of a single unpaired electron with the magnetic field and with two ^{55}Mn ($I = {}^5/_2$) nuclei. The two ^{55}Mn hyperfine tensors have identical components within experimental error but are inclined at approximately 120° (or 60°) to each other. A plausible carrier is $Mn_2(CO)_9^-$, having a single carbonyl bridge and a $^2B_2$ (in C_{2v} symmetry) ground state.

Introduction

In this laboratory we recently initiated an investigation by EPR spectroscopy of transition-metal-centered free radicals trapped in single crystals.[2–6] The method provides structural information and is capable in principle of yielding an LCAO description of the semioccupied orbital (SOMO) of the species under investigation. To date[2–6] we have confined our attention to mononuclear species trapped as impurities (defects) in convenient host matrices. We hope eventually to be able to describe the SOMO in polynuclear (cluster) species, although this will be a formidable task indeed.

In two very interesting papers[7,8] Krusic and collaborators discussed the EPR spectra of various iron-cluster carbonyl radicals such as $HFe_2(CO)_8$, $Fe_3(CO)_{12}^-$, and $Fe_4(CO)_{13}^-$. Understandably, they did not attempt a description of the SOMO in these radicals with only isotropic parameters at their disposal. In related work, Peake,[9,10] Kawamura,[11] and coworkers have used anisotropic parameters derived from frozen-solution spectra to obtain a description of the SOMO in certain paramagnetic clusters. Analyses of powder spectra of such complexity are not necessarily unique, however, and their interpretation should be accepted with caution. Clearly, data are needed from single-crystal EPR studies of such species.[12] In this area, our recent success[13] at coupling a two-circle goniometer with a computer constitutes a real advance as it releases the EPR spectroscopist from his dependence on the crystallographer.

Table I. ^{55}Mn Hyperfine Interactions (G^2) and g^2 Tensors in Irradiated $Mn_2(CO)_{10}$

tensor in *lmn* axis system[a]				direction cosines[a] for principal values		
				501	1005	1180
	l	*m*	*n*			
a_{Mn}^2 =	870	±223	0	∓0.517	0.856	0.000
	±223	636	0	0.856	±0.517	0.000
	0	0	1180	0.000	0.000	1.000
tensor in *lmn* axis system				direction cosines for principal values		
				3.990	4.0010	3.9989
	l	*m*	*n*			
g^2 =	3.9940	0	0	1.000	0.000	0.000
	0	4.0010	0	0.000	1.000	0.000
	0	0	3.9989	0.000	0.000	1.000

[a] Upper signs Mn(1); lower signs Mn(2). Almost certainly, *l* is the *b* axis of the monoclinic crystal.

Our first attempt to apply this technique to a study of binuclear transition-metal free radicals is described herein.

Experimental Section

Dimanganese decacarbonyl was obtained from Strem Chemicals Inc., Newburyport, MA. Single crystals were grown by sublimation from 50 °C onto a cold finger held at room temperature. Suitable single crystals were irradiated in vacuo for several hours at 77 K in a 2000-Ci ^{60}Co γ cell and then, under liquid nitrogen, mounted on a two-circle goniometer[13] with use of isopentane as an adhesive. The goniometer was then placed in the cavity of the EPR spectrometer and the spectrum examined at 85 K for various orientations of the crystal in the magnetic field.

Crystallography

Dimanganese decacarbonyl, $Mn_2(CO)_{10}$, crystallizes in the monoclinic system with space group *I*2/*a* and four molecules

---

(1) NRCC No. 20395.

(2) C. Couture, J. R. Morton, K. F. Preston, and S. J. Strach, *J. Magn. Reson.*, **41**, 88 (1980).

(3) M. P. Boyer, Y. Le Page, J. R. Morton, K. F. Preston, and M. J. Vuolle, *Can. J. Spectrosc.*, **26**, 181 (1981).

(4) T. Lionel, J. R. Morton, and K. F. Preston, *J. Chem. Phys.*, **76**, 234 (1982).

(5) T. Lionel, J. R. Morton, and K. F. Preston, *Chem. Phys. Lett.*, **81**, 17 (1981).

(6) T. Lionel, J. R. Morton, and K. F. Preston, *J. Phys. Chem.*, **86**, 367 (1982).

(7) P. J. Krusic, J. San Filippo, B. Hutchinson, R. L. Hance, and L. M. Daniels, *J. Am. Chem. Soc.*, **103**, 2129 (1981).

(8) P. J. Krusic, *J. Am. Chem. Soc.*, **103**, 231 (1981).

(9) B. M. Peake, P. H. Rieger, B. H. Robinson, and J. Simpson, *J. Am. Chem. Soc.*, **102**, 156 (1980).

(10) B. M. Peake, P. H. Rieger, B. H. Robinson, and J. Simpson, *Inorg. Chem.*, **20**, 2450 (1981).

(11) S. Hayashida, T. Kawamura, and T. Yonegawa, *Chem. Lett.*, 985 (1981).

(12) C. E. Strouse and L. F. Dahl, *Discuss. Faraday Soc.*, **47**, 93 (1969).

(13) J. R. Morton, K. F. Preston, and S. J. Strach, *Rev. Sci. Instrum.*, **52**, 1358 (1981).

0020-1669/83/1322-0145$01.50/0 Published 1983 by the American Chemical Society