Contribution No. 5573 from the Division of Chemistry and Chemical Engineering,
California Institute of Technology, Pasadena, California 91125

Unusual Structural and Reactivity Types for Copper: Structure of a Macrocyclic Ligand Complex Apparently Containing Copper(I) in a Distorted Square-Planar Coordination Geometry

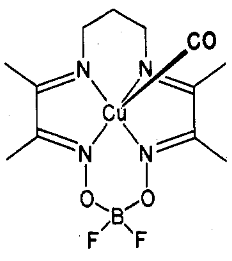
ROBERT R. GAGNÉ,* JUDITH L. ALLISON, and GEORGE C. LISENSKY

Received May 18, 1978

The diamagnetic macrocyclic ligand complex [1,1-difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetraaza-2,14-dioxacyclotetradeca-3,5,10,12-tetraenato]copper(I), Cu(LBF_2), reacts with monodentate ligands including CO to give five-coordinate Cu(I) adducts, e.g., Cu(LBF_2)CO, **1**. The crystal and molecular structure of the four-coordinate complex Cu(LBF_2), **2**, was determined in order to help elucidate the nature of the adduct formation reaction. Complex **2** crystallized in the space group $P2_1/n$ (No. 14) with a = 11.800 (2) Å, b = 9.005 (1) Å, c = 13.704 (1) Å, β = 96.40 (1)°, and Z = 4. An $R(F)$ of 0.054 was obtained using 2882 reflections to 2θ = 140°. The complex contains isolated mononuclear molecules with no significant intermolecular interactions. Each copper atom is bound by the four nitrogens of the macrocyclic ligand in a near-square-planar array, resulting in a highly unusual structural environment for Cu(I). The four nitrogens are, however, tetrahedrally distorted from planarity, with dihedral angles of 23 and 27° for the two sets of planes defined by copper and two adjacent nitrogen atoms. Copper–nitrogen bond lengths average to 1.939 (3) Å. The infrared spectrum of **2** exhibits no bands in the 1500–1700-cm^{-1} region expected for the ligand α-diimine moiety but does not show two bands at 1320 and 1470 cm^{-1} which might be associated with α-diimine stretching modes. The infrared spectra of **1** and **2**, as well as crystallographic, electrochemical, and magnetic data, are used to discuss a reasonable description for the oxidation state of copper in both **1** and **2**.

Introduction

The most frequently encountered copper(I) geometry is tetrahedral (four-coordinate), though linear (two-coordinate) and trigonal-planar (three-coordinate) structures are known.[1] Some Cu(I) cluster and polymeric complexes do exhibit higher coordination numbers, notably five, six, and seven, but only if unusual copper–copper interactions are included.[2] In contrast, we recently reported the preparation and molecular structure of the square-pyramidal macrocyclic ligand complex Cu(LBF_2)CO, **1** (carbonyl[1,1-difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetraaza-2,14-dioxacyclotetradeca-3,5,10,12-tetraenato]copper(I)).[3] This complex apparently contains unprecedented, mononuclear five-coordinate Cu(I).



1

Table I. Crystal Data for Cu(LBF_2), **2**

$C_{11}H_{18}BCuF_2N_4O_2$

fw = 350.6	V = 1447.2 (4) Å^3
space group $P2_1/n$ (No. 14)	Z = 4
a = 11.800 (2) Å	ρ_{calcd} = 1.61 g cm^{-3}
b = 9.005 (1) Å	ρ_{exptl} = 1.62 g cm^{-3}
c = 13.704 (1) Å	μ = 24.9 cm^{-1}
β = 96.40 (1)°	λ(Cu Kα) = 1.541 78 Å

In the carbonyl complex Cu(LBF_2)CO, **1**, copper is bound to an axial carbon from CO (ν_{CO} = 2068 cm^{-1}) and four basal nitrogens. Copper is displaced an extraordinary 0.96 Å out of the mean plane of the four coordinated nitrogens. This displacement is especially notable when compared with metal-atom displacements in other square-pyramidal metal–macrocyclic ligand systems which are often in the range 0.3–0.6 Å. A few cases with extreme displacements are known, e.g., 0.73 Å for Mn(II) in Mn($C_{22}H_{22}N_4$)(N(C_2H_5)$_3$)[4] ([7,16-dihydro-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]-tetraazacyclotetradecinato](triethylamine)manganese(II)) and 0.74 and 0.98 Å for Tl(III) in ClTlTPP[5] and CH_3TlTPP[5] (chloro- and methyl(5,10,15,20-tetraphenylporphinato)thallium(III)), respectively. The large metal-atom displacement in Cu(LBF_2)CO, **1**, results in an unusual square-pyramidal arrangement of ligands. The angles formed by the apical ligand (CO), copper, and the basal-plane nitrogens, C–Cu–N, range from 114.8 (1) to 120.3 (1)°. The expected value would be 100°.[6] In addition, the copper-to-carbon distance found (1.780 (3) Å) might be regarded as being relatively short when the apparent presence of 20 electrons in the copper valence shell is considered. A similar Cu–C bond length (1.765 (14) Å) is found in the only other crystallographically analyzed Cu–CO complex, carbonyl[hydrotris(1-pyrazolyl)borato]-copper(I),[7] even though the central copper is four-coordinate and has an 18-electron valence shell.

In an attempt to better understand the formation and nature of the five-coordinate adduct Cu(LBF_2)CO, **1**, we have determined the molecular structure of its precursor, Cu(LBF_2), **2**. The ligand geometry observed in analogous metal complexes of the present ligand system[8-13] might be predicted to force copper in Cu(LBF_2), **2**, into a square-planar configuration. The complex would thus contain Cu(I) in a highly unfavorable geometry or copper in a higher oxidation state, e.g., Cu(II) or Cu(III) complexed to a reduced macrocyclic ligand. Alternatively, the ligand configuration found in Cu(LBF_2)CO, **1**, might imply the presence of a fifth ligand for Cu(LBF_2), **2**, either from a solvent molecule (analytical results did not suggest any solvent of crystallization) or via solid-state oligomerization. As reported herein, we believe that Cu(LBF_2), **2**, is best described presently as containing Cu(I) in a distorted square-planar geometry.

Results and Discussion

Structure of Cu(LBF_2), 2. Basic crystal data for Cu(LBF_2), **2**, are summarized in Table I; Tables II–IV contain atomic parameters, bond lengths, and bond angles. Figure 1 is a schematic drawing of the molecule depicting the atom labeling scheme.

The complex crystallized in the space group $P2_1/n$ (No. 14) with four molecules in the unit cell, Figure 2. The two nearest-neighbor molecules in the unit cell are related by an inversion center (Figure 2). The copper atoms of these two molecules are 4.55 Å apart. Calculated best planes through the four nitrogens of each of the two molecules shown in Figure

0020-1669/78/1317-3563$01.00/0

Table II. Atomic Parameters for Cu(LBF_2), 2[a]

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	0.18822 (3)	0.50011 (5)	0.05758 (3)	0.0394 (3)	0.0338 (3)	0.0374 (2)	0.0046 (2)	0.0125 (2)	0.0031 (2)
N1	0.0905 (2)	0.6720 (3)	0.0294 (2)	0.030 (1)	0.035 (2)	0.035 (1)	0.002 (1)	0.006 (1)	0.005 (1)
N2	0.1009 (2)	0.4824 (3)	0.1686 (2)	0.037 (1)	0.040 (2)	0.028 (1)	−0.006 (1)	0.008 (1)	0.001 (1)
N3	0.2553 (2)	0.3047 (3)	0.0488 (2)	0.044 (2)	0.031 (2)	0.046 (2)	0.004 (1)	0.008 (1)	0.000 (1)
N4	0.3036 (2)	0.5548 (3)	−0.0261 (2)	0.033 (1)	0.035 (1)	0.037 (1)	0.001 (1)	0.010 (1)	0.001 (1)
O1	0.2912 (2)	0.6762 (2)	−0.0876 (1)	0.044 (1)	0.037 (1)	0.034 (1)	0.004 (1)	0.016 (1)	0.007 (1)
O2	0.1147 (2)	0.7886 (2)	−0.0317 (2)	0.037 (1)	0.042 (1)	0.047 (1)	0.008 (1)	0.012 (1)	0.017 (1)
B	0.2381 (3)	0.8048 (4)	−0.0431 (3)	0.040 (2)	0.032 (2)	0.042 (2)	0.001 (2)	0.013 (2)	0.006 (2)
F1	0.2431 (2)	0.9196 (2)	−0.1094 (1)	0.059 (1)	0.042 (1)	0.058 (1)	0.006 (1)	0.024 (1)	0.020 (1)
F2	0.2973 (2)	0.8385 (2)	0.0475 (1)	0.051 (1)	0.043 (1)	0.045 (1)	0.000 (1)	0.004 (1)	−0.008 (1)
C1	−0.0256 (3)	0.8481 (4)	0.1129 (3)	0.058 (2)	0.053 (2)	0.063 (2)	0.017 (2)	0.020 (2)	0.000 (2)
C2	0.0268 (2)	0.7019 (3)	0.0981 (2)	0.025 (2)	0.042 (2)	0.037 (2)	0.003 (1)	0.005 (1)	−0.002 (1)
C3	0.0167 (2)	0.5745 (4)	0.1638 (2)	0.030 (2)	0.048 (2)	0.029 (2)	−0.004 (2)	0.006 (1)	−0.006 (2)
C4	−0.0856 (3)	0.5575 (4)	0.2179 (2)	0.042 (2)	0.080 (3)	0.051 (2)	−0.002 (2)	0.018 (2)	0.007 (2)
C5	0.0976 (3)	0.3396 (4)	0.2202 (2)	0.062 (2)	0.051 (2)	0.036 (2)	−0.003 (2)	0.012 (2)	0.010 (2)
C6	0.2062 (3)	0.2542 (4)	0.2176 (3)	0.082 (3)	0.053 (2)	0.056 (2)	0.007 (2)	0.013 (2)	0.019 (2)
C7	0.2349 (3)	0.1891 (4)	0.1210 (3)	0.075 (3)	0.039 (2)	0.065 (2)	0.010 (2)	0.017 (2)	0.010 (2)
C8	0.4301 (3)	0.1847 (4)	0.0021 (3)	0.052 (2)	0.045 (2)	0.101 (3)	0.017 (2)	0.013 (2)	−0.008 (2)
C9	0.3433 (3)	0.3060 (3)	0.0007 (2)	0.037 (2)	0.033 (2)	0.048 (2)	0.007 (2)	0.002 (2)	−0.010 (2)
C10	0.3549 (3)	0.4388 (4)	−0.0594 (2)	0.032 (2)	0.043 (2)	0.045 (2)	0.005 (2)	0.010 (1)	−0.008 (2)
C11	0.4166 (3)	0.4437 (4)	−0.1489 (3)	0.057 (2)	0.074 (3)	0.056 (2)	0.016 (2)	0.028 (2)	−0.005 (2)

	x	y	z	B, Å^2		x	y	z	B, Å^2
H1a	0.001 (3)	0.898 (4)	0.166 (3)	8.5 (1.1)	H11a	0.493 (3)	0.428 (4)	−0.141 (3)	7.7 (1.0)
H1b	0.000 (3)	0.903 (4)	0.076 (3)	8.6 (1.1)	H11b	0.397 (4)	0.521 (4)	−0.189 (3)	9.0 (1.2)
H1c	−0.093 (4)	0.841 (4)	0.120 (3)	9.5 (1.2)	H11c	0.380 (3)	0.391 (4)	−0.195 (3)	7.7 (1.1)
H4a	−0.134 (3)	0.622 (4)	0.203 (3)	7.6 (1.0)	H5a	0.084 (2)	0.359 (3)	0.282 (2)	3.8 (0.7)
H4b	−0.069 (3)	0.534 (4)	0.285 (3)	7.3 (1.0)	H5b	0.038 (3)	0.267 (4)	0.176 (2)	6.5 (0.9)
H4c	−0.122 (3)	0.475 (4)	0.198 (3)	7.6 (1.0)	H6a	0.205 (2)	0.171 (3)	0.266 (2)	4.9 (0.8)
H8a	0.489 (4)	0.212 (5)	−0.020 (3)	10.0 (1.3)	H6b	0.273 (3)	0.321 (4)	0.239 (2)	6.3 (0.9)
H8b	0.467 (4)	0.195 (5)	0.059 (3)	11.0 (1.3)	H7a	0.149 (3)	0.149 (4)	0.105 (2)	7.8 (1.0)
H8c	0.402 (4)	0.102 (5)	−0.007 (3)	11.2 (1.3)	H7b	0.298 (3)	0.126 (4)	0.127 (2)	6.8 (0.9)

[a] The form of the thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)]$ for the anisotropic thermal parameters.

Table III. Bond Distances (Å) for Cu(LBF_2), 2

Cu–N1	1.943 (2)	C1–H1a	0.88 (4)
Cu–N2	1.937 (2)	C1–H1b	0.79 (4)
Cu–N3	1.938 (2)	C1–H1c	0.82 (4)
Cu–N4	1.939 (2)	C4–H4a	0.82 (3)
N1–C2	1.297 (3)	C4–H4b	0.94 (3)
N2–C3	1.290 (3)	C4–H4c	0.89 (3)
N3–C9	1.291 (3)	C8–H8a	0.82 (4)
N4–C10	1.315 (3)	C8–H8b	0.85 (4)
N2–C5	1.470 (3)	C8–H8c	0.82 (4)
N3–C7	1.474 (4)	C11–H11a	0.91 (3)
N1–O2	1.392 (2)	C11–H11b	0.90 (4)
N4–O1	1.378 (3)	C11–H11c	0.87 (4)
C1–C2	1.478 (4)	C5–H5a	0.90 (3)
C2–C3	1.472 (3)	C5–H5b	1.09 (3)
C3–C4	1.493 (4)	C6–H6a	1.00 (3)
C5–C6	1.499 (4)	C6–H6b	1.00 (3)
C6–C7	1.520 (5)	C7–H7a	1.07 (3)
C8–C9	1.496 (4)	C7–H7b	0.94 (3)
C9–C10	1.467 (4)		
C10–C11	1.495 (4)		
B–O1	1.480 (3)		
B–O2	1.489 (3)		
B–F1	1.381 (3)		
B–F2	1.389 (3)		

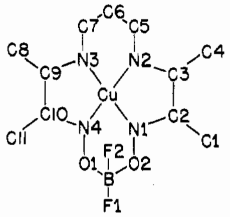


Figure 1. Atomic numbering scheme used for Cu(LBF_2), 2. Hydrogens are labeled in reference to the carbon to which they are bound (e.g., the hydrogens bound to C1 are H1a, H1b, and H1c).

Table IV. Bond Angles (deg) for Cu(LBF_2), 2

N1–Cu–N2	82.3 (1)	C2–C3–C4	120.6 (3)
N2–Cu–N3	103.3 (1)	C2–C3–N2	114.7 (2)
N3–Cu–N4	82.9 (1)	N2–C3–C4	124.8 (3)
N4–Cu–N1	96.9 (1)	N2–C5–C6	111.7 (3)
N1–Cu–N3	161.5 (1)	C5–C6–C7	119.5 (3)
N2–Cu–N4	162.9 (1)	C6–C7–N3	112.4 (3)
Cu–N1–O2	124.3 (2)	C8–C9–C10	119.7 (3)
Cu–N1–C2	113.6 (2)	C8–C9–N3	125.2 (3)
O2–N1–C2	117.0 (2)	N3–C9–C10	115.1 (3)
Cu–N2–C3	112.5 (2)	C9–C10–C11	124.7 (3)
Cu–N2–C5	119.7 (2)	C9–C10–N4	112.2 (3)
C3–N2–C5	121.6 (2)	N4–C10–C11	123.1 (3)
Cu–N3–C7	120.1 (2)	N4–O1–B	113.0 (2)
Cu–N3–C9	112.4 (2)	N1–O2–B	113.9 (2)
C7–N3–C9	123.3 (3)	O1–B–O2	115.5 (2)
Cu–N4–O1	122.0 (2)	F1–B–O1	105.3 (2)
Cu–N4–C10	112.6 (2)	F2–B–O1	110.2 (2)
O1–N4–C10	116.1 (2)	F1–B–O2	104.8 (2)
C1–C2–C3	123.1 (3)	F2–B–O2	109.2 (2)
C1–C2–N1	124.7 (3)	F1–B–F2	111.7 (3)
N1–C2–C3	112.1 (2)		

Table V. Nonbonding Distances for Cu(LBF_2), 2

A. Intramolecular Distances (Å)

N1–N2	2.553 (3)	N3–N4	2.565 (3)
N2–N3	3.040 (3)	N1–N4	2.905 (3)

B. Intermolecular Distances between Atom 1 and Atom 2 (Å)

atom 1–atom 2	dist <4.2 Å	symmetry	
		atom 1	atom 2
Cu–C2	3.619	x, y, z	$\bar{x}, 1-y, \bar{z}$
Cu–N1	3.710	x, y, z	$\bar{x}, 1-y, \bar{z}$
Cu–C3	3.724	x, y, z	$\bar{x}, 1-y, \bar{z}$
Cu–C4	3.869	x, y, z	$\bar{x}, 1-y, \bar{z}$
Cu–C6	3.927	x, y, z	$^1/_2-x, ^1/_2+y, ^1/_2-z$

2 are separated by a distance of 3.62 Å. Several fluorine–hydrogen intermolecular distances less than 3.0 Å were found, which may indicate very long F–H interactions, contributing to crystal packing forces. No other intermolecular interactions

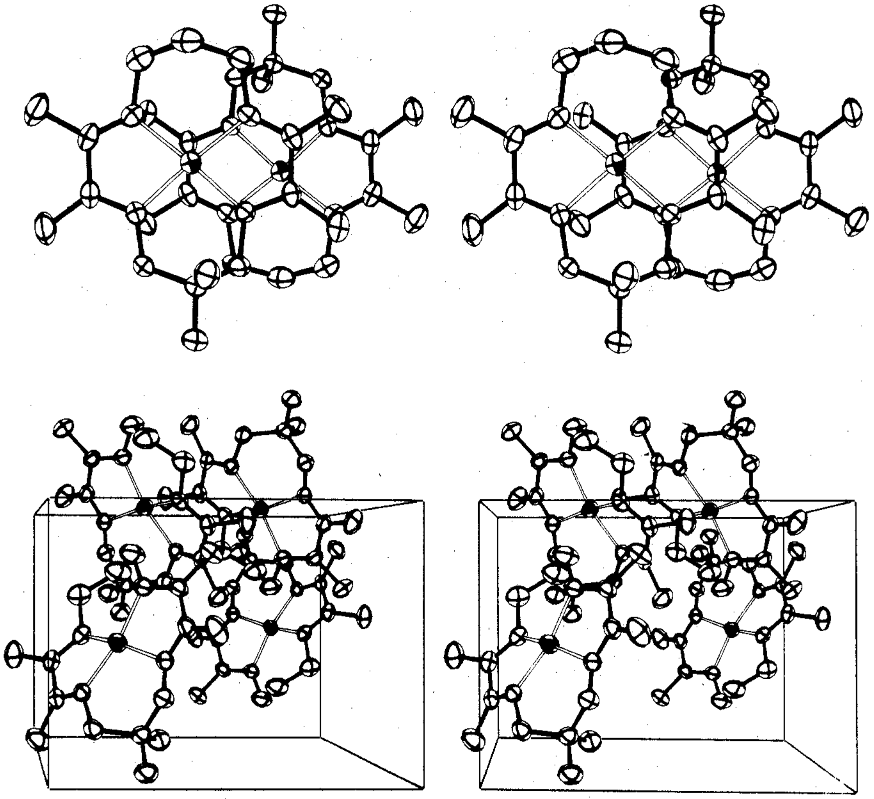


Figure 2. The upper stereopair shows two parallel molecules of $Cu(LBF_2)$, **2**, related in the crystal lattice by a center of symmetry. The molecules are viewed normal to the best planes determined by the four coordinated nitrogens. Note that the axial coordination sites of copper are occupied by the noncoordinating C2–C3 bond (upper view). The other axial coordination site is vacant, as in the lower view which shows the contents of a unit cell. The origin of the unit cell is the upper left front corner; *a* goes across, *b* down, and *c* back. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted.

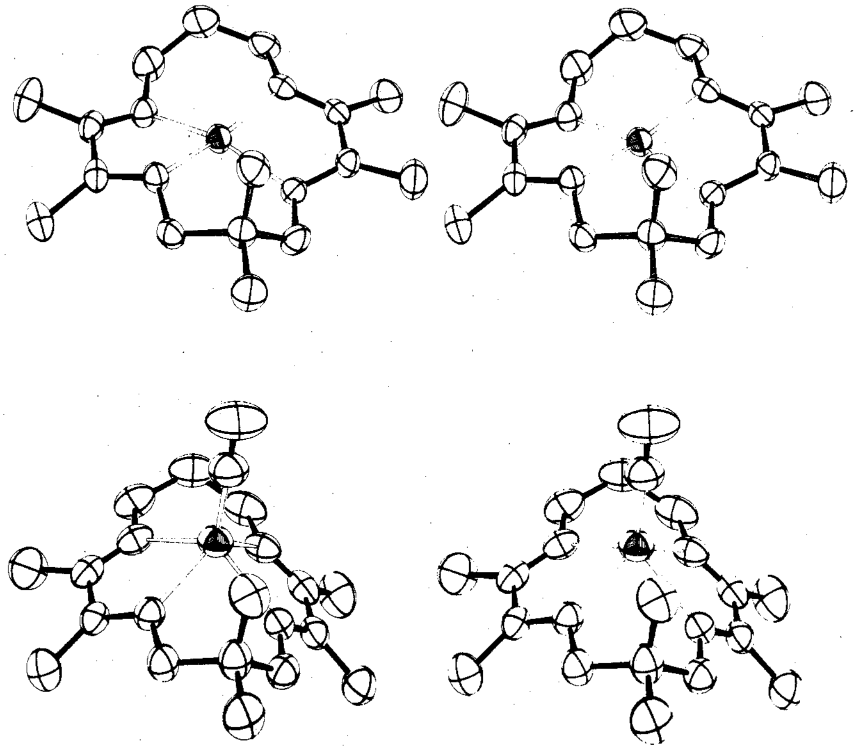


Figure 3. The upper stereopair shows the four-coordinate $Cu(LBF_2)$, **2**, in a tetrahedrally distorted square-planar geometry. For comparison, a stereoview of $Cu(LBF_2)CO$, **1**, is presented with the ligand in a similar orientation. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted.

appear to be important to the crystal structure.

Copper atoms in individual molecules of $Cu(LBF_2)$, **2**, are bonded to the four macrocyclic ligand nitrogen atoms with essentially equal Cu–N bond lengths averaging to 1.939 (3) Å.[14] No other atoms are within 3.6 Å of copper (Table V). As seen in the stereoview of a single molecule (Figure 3), the coordination geometry is best described as a distorted square plane. A perfect square would have 90° cis N–Cu–N bond

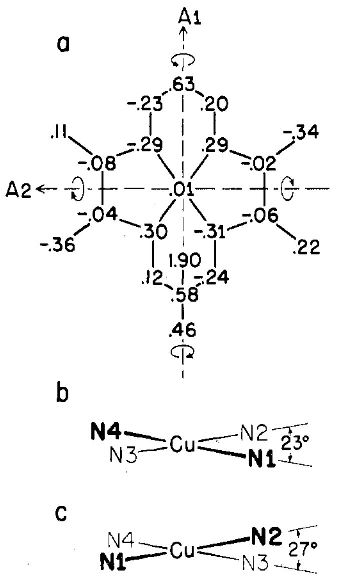


Figure 4. (a) Deviations from best plane for copper and the four nitrogens (Table VI) given in Å for the nonhydrogen atoms of Cu(LBF$_2$), **2**. Atomic positions correspond to those in Figure 1, i.e., with the BF$_2$ in the lower part of the figure. The positions of the four nitrogens indicate a tetrahedral distortion of the basic square plane about copper. The angular distortion is illustrated by viewing the copper and four nitrogens down A1 (b) and A2 (c). The angles given are those between the planes formed by two nitrogens and the copper: (b) N1–Cu–N4 and N2–Cu–N3. (c) N1–Cu–N2 and N3–Cu–N4. For a square-planar complex these angles would be 0° and for a tetrahedral complex, 90°.

angles; the observed values range from 82.3 (1) to 103.3 (1)°. Correspondingly, the trans N–Cu–N angles, theoretically 180°, are 161.5 (1) and 162.9 (1)°. The four nitrogen–nitrogen nonbonding distances, Table V, range from 2.553 (3) to 3.040 (3) Å, distances which would be equal in a square-planar complex.

The macrocyclic ligand is in a *boat* conformation with boron of the BF$_2$ bridge and C6 of the propylene bridge both bent in the same direction away from the mean-square plane of the copper and four nitrogens (Figure 4). Copper sits 0.01 Å out of this best plane and toward the same side as C6 and B. Table VI lists this and several other best plane calculations. Dihedral angles of 23 and 27° are found between the planes Cu, N1, N4 vs. Cu, N2, N3 and Cu, N1, N2 vs. Cu, N3, N4, respectively (Figure 4 and Table VI). These angles are closer to expected square-planar values, 0°, than to corresponding tetrahedral angles, 90°. The resulting distortion from planarity is reflected by substantial deviations from the best plane calculated for copper and the full ligand, even if the obvious out-of-plane atoms, C6, B, F1, and F2, are deleted (Table VI). Significant planar distortion is also indicated by ligand bond torsion angles listed in Table VII when compared with theoretical square-planar angles.

Comparisons to Related Structures. Structures have now been obtained for four-, five-, and six-coordinate complexes containing LBF$_2^-$ and LH$^-$ (LH$^-$ is the ligand in Figure 1 with a single hydrogen atom in place of the BF$_2$ group). Several distinctive ligand configurations are revealed in these structures. *Boat* conformations, in which B and C6 of LBF$_2^-$ are bent in the same direction away from the mean macrocycle plane, have been found in Cu(LBF$_2$)CO, **1**, Cu(LBF$_2$), **2**, and Cu(LBF$_2$)NCO, **3**.[17] In contrast, *chair* conformations with C6 and B on opposite sides of the mean macrocycle plane were found in the six-coordinate complexes Rh(L′BF$_2$)(SeC$_6$H$_5$)$_2$, **4**,[8,15] and Rh(L′BF$_2$)(CH$_3$)I, **5**.[9,15]

Whether a ligand is in a *boat* or a *chair* conformation may indicate overall distortion from planarity in the macrocycle.

Table VI

Best Plane Calculations for Cu(LBF$_2$), 2

plane	atoms in plane	equation of plane[a] *A*	*B*	*C*	*D*
1	Cu, N1, N2, N3, N4	0.5967	0.3965	0.6977	3.595
2	Cu, 20 non-H atoms	0.5939	0.3363	0.7309	3.453
3	all except H, C6, B, F1, F2	0.6023	0.3961	0.6931	3.560

plane	atoms in plane[b]	equation of plane[a] *A*	*B*	*C*	*D*
4	Cu, N1, N4	0.4212	0.4912	0.7624	3.708
5	Cu, N2, N3	0.7334	0.2939	0.6130	3.368
6	Cu, N1, N2	0.6112	0.5735	0.5455	4.314
7	Cu, N3, N4	0.5535	0.1983	0.8089	2.708

Deviations from Plane (Å)

plane	Cu	N1	N2	N3	N4	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	B	O1	O2	F1	F2
1	0.01	−0.31	0.29	−0.29	0.30	0.22	−0.06	−0.02	−0.34	0.20	0.63	−0.23	0.11	−0.08	−0.04	−0.36	0.58	0.12	−0.24	0.46	1.90
2	−0.10	−0.52	0.24	−0.30	0.12	−0.04	−0.25	−0.11	−0.39	0.25	0.73	−0.14	0.14	−0.11	−0.17	−0.54	0.26	−0.16	−0.55	0.05	1.60
3	0.05	−0.27	0.31	−0.24	0.35	0.25	−0.03	0.00	−0.32	0.22	0.67	−0.19	0.17	−0.02	0.02	−0.28	0.64	0.18	−0.20	0.52	1.95

[a] Equation of plane in the form $Ax + By + Cz = D$. [b] Dihedral angles: planes 4–5, 23°; planes 6–7, 27°

Table VII. Torsion Angles (deg)[a]

A-B-C-D	"planar" values[b]	Rh-($L'BF_2$)-(CH_3)I, 5[15,16]	Cu-(LBF_2)	Cu-(LBF_2)-CO
O2-N1-C2-C3	180	−177	−174	175
N1-C2-C3-N2	0	3	26	−1
C2-C3-N2-C5	180	−177	−172	−174
C3-N2-C5-C6	−150	−155	−179	174
N2-C5-C6-C7	−60	−69	−69	−63
C5-C6-C7-N3	60	71	66	63
C6-C7-N3-C9	150	151	131	180
C7-N3-C9-C10	180	176	−173	174
N3-C9-C10-N4	0	−4	25	7
C9-C10-N4-O1	180	176	−168	−175
C10-N4-O1-B	±150[c]	157	−177	173
N4-O1-B-O2	±60[c]	62	−71	−64
O1-B-O2-N1	∓60[d]	−60	62	65
B-O2-N1-C2	∓150[d]	−156	130	−179

[a] The torsion angle is the angle defined by A-BC and BC-D when viewing the atoms A-B-C-D down the B-C axis from B to C. Clockwise rotation from A to D is regarded as positive. [b] "Planar" values are based on a theoretical planar ligand; planar except for C6 and B.[c,d] [c] Sign of angle is positive for B on the opposite side of the mean molecular plane from C6 and negative for B and C6 on the same side. [d] Sign of angle is negative for B on the opposite side of the mean molecular plane from C6 and positive for B and C6 on the same side.

In turn the macrocyclic ligand configuration may be influenced by the preferred metal coordination geometry. Six-coordinate $Rh(L'BF_2)(CH_3)I$, **5**, which has a *chair* conformation, is one example of a planar, unstrained system. The macrocyclic ligand itself is essentially square planar; no special strain is indicated when its torsion angles are compared with theoretical planar angles (Table VII). In contrast, when the macrocycle is distorted from planarity due to the influence of the preferred metal coordination geometry, the ligand assumes a *boat* conformation.

In both five-coordinate copper complexes, $Cu(LBF_2)CO$, **1**, and $Cu(LBF_2)NCO$, **3**, the metal is far above the mean plane of the four coordinated nitrogens. A distorted *dome* macrocyclic ligand configuration results. Projections of the two conjugated sections of the macrocycle, i.e., atoms N1–C2–C3–N2 and atoms N3–C9–C10–N4, point (from C to N) toward copper. The four methyl substituents are forced downward, away from copper. There is significant deviation from planar torsion angles, notably in the $(CH_2)_3$ and $O–BF_2–O$ bridges, for the *dome* configuration as shown for $Cu(LBF_2)CO$, **1**, Table VII. Note that the molecule adopts a *boat* conformation which apparently serves to minimize macrocyclic ligand strain due to distortion from planarity.

No undistorted, four-coordinate, square-planar complexes of LBF_2^- have been structurally characterized. One might expect that the macrocyclic ligand in such complexes would not be strained by the metal coordination geometry but would be similar to that found in six-coordinate $Rh(L'BF_2)(CH_3)I$, **5**, i.e., a strain-free, *chair* conformation. Four- and six-coordinate complexes of LH^-, $[Cu(LH)]_2(ClO_4)_2·CH_3OH$, **6**,[10] $Co(LH)(CH_3)_2$, **7**,[11] Rh(LH), **8**,[12] and $[Co(LH)(CH_3)H_2O]ClO_4$, **9**,[13] have been structurally characterized. The LH^- ligands of these complexes do not exhibit either *boat* or *chair* conformations due to the lack of the bridging BF_2 group found in LBF_2^-.

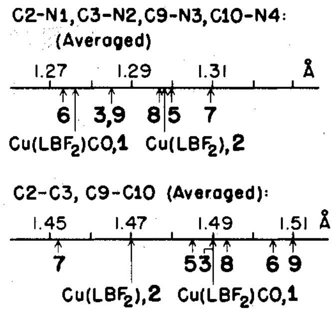


Figure 5. Line graph of pertinent LBF_2^- and LH^- bond lengths for a variety of metal complexes.

The macrocyclic ligand in $Cu(LBF_2)$, **2**, exists in a *boat* conformation and is obviously strained. One can imagine twisting a perfectly square-planar molecule, about either A1 or A2 shown in Figure 4, to achieve the tetrahedral distortion of four nitrogens. Deviations from planarity in the rest of the ligand (Figure 4) are a reflection of the tetrahedral distortion. That the tetrahedral twist results in strain when compared to a theoretical planar molecule may be indicated by the torsion angles listed in Table VII. Significant distortions are found for the $(CH_2)_3$ and $O–BF_2–O$ bridges in $Cu(LBF_2)$, **2**. As in the *domed*, five-coordinate molecule, $Cu(LBF_2)CO$, **1**, these distortions do not suffice to indicate severe macrocyclic ligand strain. Unlike the *dome* configuration of $Cu(LBF_2)CO$, **1**, the ligand of $Cu(LBF_2)$, **2**, exhibits twisting about the C2–C3 and C9–C10 bonds (25 and 26°, respectively). This twisting evidences appreciable bonding strain if any π delocalization is acknowledged for the N1–C2–C3–N2 and N3–C9–C10–N4 fragments.

The foregoing geometrical analysis of ligand strain raises the question of a proper bonding description for the macrocyclic ligand in $Cu(LBF_2)$, **2**, as well as in the previously reported five-coordinate complex $Cu(LBF_2)CO$, **1**. Is the LBF_2^- ligand in **1** and **2** adequately described by the line drawing for **1**, which has carbon–nitrogen double bonds for C2–N1, C3–N2, C9–N3, and C10–N4? Or are both complexes better regarded as containing Cu(II) or even Cu(III) bound in a one- or two-electron-reduced ligand system? Macrocyclic ligand structural parameters are helpful in addressing these questions. The structures obtained for $Cu(LBF_2)$, **2**, and for $Cu(LBF_2)CO$, **1**, permit a careful comparison of pertinent ligand bond lengths with those

Table VIII. Comparisons of $M(LBF_2)$ and M(LH) Structural Parameters

complex	complex geometry	ligand geometry	averaged bond lengths,[a] Å C2-N1[b]	C3-N2[c]	C2-C3[d]	R[e]
$Cu(LBF_2)CO$, 1[3]	square-pyramidal	*dome,boat*	1.279 (6)	1.273 (6)	1.490 (6)	0.055
$Cu(LBF_2)$, 2[f]	square-planar	square-planar, *boat*	1.306 (13)	1.291 (1)	1.470 (4)	0.054
$Cu(LBF_2)NCO$, 3[17]	square-pyramidal	*dome,boat*	1.293 (9)	1.277 (2)	1.490 (12)	0.045
$Rh(L'BF_2)(CH_3)I$, 5[9,15]	octahedral	square-planar, *chair*	1.303 (3)	1.297 (21)	1.485 (16)	0.031
$[Cu(LH)]_2(ClO_4)_2·CH_3OH$, 6[10]	tetragonal	square-planar	1.278 (7)	1.269 (10)	1.505 (8)	0.060
$Co(LH)(CH_3)_2$, 7[11]	octahedral	square-planar	1.312 (13)	1.307 (8)	1.452 (1)	0.034
Rh(LH), 8[12]	square-planar	square-planar	1.303 (4)	1.293[g]	1.493 (5)	not reported
$[Co(LH)(CH_3)H_2O]ClO_4$, 9[13]	octahedral	square-planar	1.29 (4)	1.28 (3)	1.51 (0)	0.112

[a] All atom designations refer to a ligand numbered as in Figure 1; standard deviations of the mean bond length values, as defined in ref 14, are given in parentheses. [b] The C2-N1 bond length values are averages of the C2-N1 and C10-N4 bond lengths. [c] The C3-N2 bond length values are averages of the C3-N2 and C9-N3 bond lengths. [d] The C2-C3 bond length values are averages of the C2-C3 and C9-C10 bond lengths. [e] $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [f] This work. [g] Only one value available; therefore no mean standard deviation is given.

Table IX. Infrared Spectra of LBF_2^- Complexes[a]

possible assign	$Cu(LBF_2)$, 2	$[Cu(LBF_2)]_2(ClO_4)_2 \cdot C_4H_8O_2$, 10	$Cu(LBF_2)I_3$, 11	$Cu(LBF_2)CO$, 1
$\nu_{C=N}$asym[12,19]		1660 w	1645 w	1640 w
$\nu_{C=N}$sym[12,19]		1590 w	1580 m	1560 m
δ_{CH_3} asym[20,21]	(1430) w	1440 w	1440 w	1430 w
δ_{CH_3} sym[20,21]	1380 w	1390 w	1390 w	1380 w
CH_3	1365 w	(1370) w	1370 w	1360 w
ν_{B-O}[12,22]	1190 m	1180 m	1180 m	1185 m
ν_{N-O}[12,20-22]	1150 s	(1150)[b] s	1130 s	1135 s
or ν_{B-F}[12]	1075 m	(1060)[b] m	1100 m, 1065 m	1090 m, 1075 m, 1045 m
ν_{B-F}[12,22]	995 s	1030 s	1030 s	1015 s
HCC[21]	(945) m	940 s	950 s	960 s
ν_{B-O}[12,22]	795 w	810 m	805 m	790 m
ClO_4^- [23]		630 m, 1115 vs, 1130 vs		
other	1470 m	880 m (dioxane)	690 w	2070 vs (CO)
	1320 s			680 w
	1280 w			
	910 w			
	870 w			

[a] KBr pellet in region 600–2500 cm^{-1}. Shoulders given in parentheses. w = weak, m = medium, s = strong, vs = very strong. [b] Obscured by perchlorate bands.

previously reported for several other complexes containing LBF_2^- or LH^- (Table VIII and Figure 5). In all structurally characterized complexes the ligands are essentially symmetric about a plane containing A1 and perpendicular to A2, Figure 4. Averaged bond lengths are presented in Table VIII and Figure 5, and the following discussion is restricted to the pertinent bonds of only half of the molecule.

Reduction of the macroyclic ligand system might be expected to manifest itself by lengthening of either or both of the formally double carbon–nitrogen bonds, C2–N1 and C3–N2. Additionally, partial reduction of the conjugated fragment, N1–C2–C3–N2, could lead to C2–C3 bond shortening. In fact both of these parameters appear to be rather insensitive to changes in metal geometry and oxidation state. The C2–N1 and C3–N2 bonds range from 1.269 (10) Å (C3–N2 in $[Cu(LH)]_2(ClO_4)_2 \cdot CH_3OH$, **6**) to 1.312 (13) Å (C2–N1 in $Co(LH)(CH_3)_2$, **7**), a variation of 0.043 Å which is small when compared to typical bond differences in C–N single and double bonds (1.47 vs. 1.28 Å, a difference of 0.19 Å[18]). Similarly, the C2–C3 bond varies from 1.452 (1) Å (in $Co(LH)(CH_3)_2$, **7**) to 1.51 (0) Å (in $[Co(LH)(CH_3)H_2O]ClO_4$, **9**), a range of 0.058 Å, again small compared to the difference between typical C–C single and double bonds (1.54 vs. 1.34 Å, a difference of 0.20 Å[18]). Of greater significance, however, is a direct comparison of bond parameters in $Cu(LBF_2)CO$, **1**, and in $Cu(LBF_2)$, **2**, with related complexes.

The tetrahedrally distorted, square-planar complex $Cu(LBF_2)$, **2**, has no good structural analogue. The macrocyclic ligand exists in the *boat* conformation as in $Cu(LBF_2)CO$, **1**, and in $Cu(LBF_2)NCO$, **3**, but the latter are five-coordinate. Copper is essentially in the mean nitrogen plane in $Cu(LBF_2)$, **2**, and the macrocyclic ligand is probably better compared to the ligands in square-planar or six-coordinate octahedral complexes. The only noncopper complex with a BF_2 bridge is $Rh(L'BF_2)(CH_3)I$, **5**, which has a square-planar, *chair* macrocyclic conformation. The C2–C3 bond lengths in $Cu(LBF_2)$, **2**, and in $Rh(L'BF_2)(CH_3)I$, **5**, differ by only 0.015 Å and the C2–N1 and C3–N2 bonds by 0.003 and 0.006 Å, respectively. Similar results are obtained on comparing $Cu(LBF_2)$, **2**, with most other complexes in Table VIII. All comparisons reveal little ligand bond-length variation. A better perspective for macrocyclic ligand parameters is obtained from Figure 5 which depicts a line graph for averaged C2–C3 and C2–N1 bond lengths for all structurally characterized LBF_2^- or LH^- complexes. Note the overall small variations and the relative location of $Cu(LBF_2)$, **2**. All of the pertinent macrocycle bond lengths in $Cu(LBF_2)$, **2**, are within the range observed for similar Co(III), Rh(I), Rh(III), and Cu(II) complexes and none of the latter contain LBF_2^- or LH^- which appear to be reduced. It does seem that in $Cu(LBF_2)$, **2**, C2–C3 is slightly toward the short end and C2–N1 and C3–N2 are slightly toward the long end of the bond-length ranges represented in Figure 5. In view of the very different macrocyclic ligand configurations involved in comparing $Cu(LBF_2)$, **2** (distorted square-planar, *boat*), with any of the other complexes in Table VIII (square-planar or *dome,boat* or *chair*), it is difficult to definitively attribute small bond-length variations to any single factor. Nonetheless, the C2–C3, C2–N1, and C3–N2 bond lengths in $Cu(LBF_2)$, **2**, might indicate π delocalization of electron density from the copper into the π system of the ligand (Figure 6) with configuration **a** as the major contributing structure.

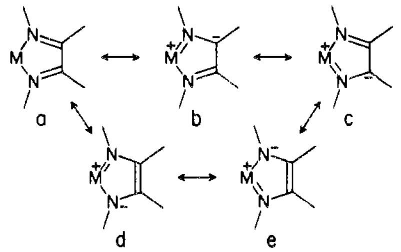


Figure 6. Proposed π delocalization in $Cu(LBF_2)$, **2**, which can also be regarded as metal-to-ligand back-bonding.

A π-delocalization scheme as represented in Figure 6 also helps to explain electronic and infrared spectral observations. The complex $Cu(LBF_2)$, **2**, is deep blue (677 nm, ε 10 300 M^{-1} cm^{-1} at 25 °C).[3] The visible band can be explained by a metal-to-ligand charge-transfer transition, an assignment made more realistic by structural evidence of π delocalization.

In the $Cu(LBF_2)$, **2**, infrared spectrum, there are no bands in the 1500–1700-cm^{-1} region and, therefore, there are no bands which would normally be assigned to imine stretching modes, $\nu_{C=N}$. The absence of $\nu_{C=N}$ suggested the possibility of fully reduced C2–N1 and C3–N2 bonds, but that has been made unlikely on the basis of the structural data. When the infrared spectral data for several LBF_2^- metal complexes (Table IX) are examined, a strong similarity of all spectra is found. The sole exception is the spectrum of $Cu(LBF_2)$, **2**, which has no bands from 1500 to 1700 cm^{-1} and has three additional bands from 1250 to 1500 cm^{-1}. The two bands at 1320 and 1470 cm^{-1} might be associated with the α-diimine stretching modes, although these values are unusually low.[24]

Because of metal back-bonding into macrocyclic ligand π* orbitals, alternatively regarded as the π delocalization depicted in Figure 6, the imine bonds in $Cu(LBF_2)$, **2**, would be expected to be weaker than in the free ligand or than in metals in higher oxidation states, and have α-diimine stretching modes shifted to lower energies. Note that Cu(LBF_2), **2**, which exhibits no usual α-diimine bands, reacts with CO to give the *domed*, five-coordinate Cu(LBF_2)CO, **1**. The latter complex no longer absorbs at 677 nm and has bands in the infrared at 1640 and 1560 cm^{-1} (Table IX).

Delocalization of electron density into the macrocyclic ligand π system may best explain the ligand structural parameters and complex spectral properties discussed above. Structural parameters alone cannot serve to definitely preclude the possibility of a formal one- or two-electron reduction of the macrocyclic ligand in Cu(LBF_2), **2**. Even a one-electron reduction would affect at least three bonds in the ligand (C2–C3, C2–N1, C3–N2), but delocalization through the copper or even crystallographic disorder could average the observed effect to six bonds, two C–C and four C–N bonds. No precedent in LBF_2^- or LH^- complex chemistry is available to adequately define the structural nature of a reduced ligand.

It would appear that the best structural description of Cu(LBF_2), **2**, is, at present, copper(I) in an uncommon, tetrahedrally distorted, square-planar coordination geometry with substantial back-bonding into macrocyclic ligand π^* orbitals. Since Cu(LBF_2), **2**, yields comparable solution and solid-state electronic absorption spectra, it is likely that the solid-state structure is a good representation of the species in solution as well.

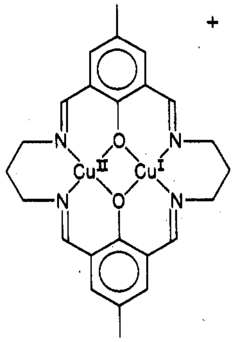
Structurally, the five-coordinate carbonyl Cu(LBF_2)CO, **1**, is probably most closely mirrored by the Cu(II) complex Cu(LBF_2)NCO, **3**. Both complexes are five-coordinate and square pyramidal with LBF_2^- in a *dome,boat* conformation. Copper is displaced 0.96 Å out of the mean nitrogen plane in Cu(LBF_2)CO, **1**, but only 0.58 Å in Cu(LBF_2)NCO, **3**, leading to longer Cu–N bond lengths in the former (2.13 (4) Å for **1**, 2.00 (1) Å for **3**). There are no significant differences in pertinent macrocyclic ligand bond parameters (Table VIII). Figure 5 graphically illustrates that Cu(LBF_2)CO, **1**, has C2–C3 and C2–N1, C3–N2 bond lengths which can be described as average for all known LBF_2^- and LH^- complexes. In addition, as noted earlier, Cu(LBF_2)CO, **1**, has peaks in its infrared spectrum (Table IX) that can be assigned as normal imine stretching modes. There is no direct LBF_2^- structural evidence to support the suggested description of Cu(LBF_2)CO, **1**, as containing Cu(II) or Cu(III) complexed to a reduced macrocyclic ligand system.

Oxidation State of Copper. An accurate oxidation state description for copper in both Cu(LBF_2), **2**, and Cu(LBF_2)CO, **1**, is more than a mere formalism or question of semantics. These complexes represent new structural and reactivity types for copper and merit more precise description. Furthermore, the role of the macrocyclic ligand in promoting unusual complex structures and reactivities poses more general questions regarding other transition-metal complexes.

While it is beyond the scope of this paper to present a detailed bonding description for Cu(LBF_2), **2**, or for Cu(LBF_2)CO, **1**, it may be useful to summarize certain pertinent observations regarding their copper oxidation states. That these complexes are presently best described as containing Cu(I) is suggested by the following points. (1) Cu(LBF_2), **2**, was obtained from acetone by the one-electron electrochemical reduction, at −0.7 V vs. NHE, of the Cu(II) complex $[Cu(LBF_2)]_2(ClO_4)_2\cdot C_4H_8O_2$, **10**.[3] In dimethylformamide the reversible wave of the Cu(II) complex, **10**, is found at $E_{1/2}$ = −0.452 V vs. NHE, with further reduction occurring below −1.5 V. The corresponding Zn(II) complex, $[Zn(LBF_2)]_2(ClO_4)_2\cdot CH_3OH$, **12**, is electrochemically inactive in the region +0.20 to −0.95 V but yields reduction waves below −0.95 V. The reduction processes in the zinc complex are presumably due to LBF_2^- reduction. (2) Cu(LBF_2), **2**, and Cu(LBF_2)CO, **1**, are diamagnetic by magnetic susceptibility and give no EPR signals. (3) There is no obvious structural evidence of macrocyclic ligand reduction in either Cu(LBF_2), **2**, or Cu(LBF_2)CO, **1**, as discussed earlier. (4) The four-coordinate complex Cu(LBF_2), **2**, is not planar as would be expected for Cu(II) or Cu(III) and as has been demonstrated to be possible for $L'BF_2^-$ in Rh($L'BF_2$)(CH_3)I, **5**. Rather, the four coordinated nitrogens exhibit a distortion toward tetrahedrality, suggestive of Cu(I). (5) Cu(LBF_2), **2**, binds both CO, a good π acceptor, and 1-methylimidazole, a good σ donor, but the former is bound more strongly ($K_c = 4.7 \times 10^4$ M^{-1}, eq 1) than the latter (K_c = 16 M^{-1}).[3] These equilibrium

$$Cu(LBF_2) + B \overset{K_c}{\rightleftharpoons} Cu(LBF_2)B \qquad (1)$$

constants and the charge-transfer band (677 nm, ϵ 10 300 M^{-1} cm^{-1}) suggest an electron-rich copper atom. (6) The binding of CO to the four-coordinate, presumably Cu(I) species to give a five-coordinate carbonyl complex is not a unique reaction. The mixed-valence Cu^{II}Cu^{I} complex, **13**, also binds CO to give what is probably a five-coordinate analogue of Cu(LBF_2)CO, **1**. Complex **13** was obtained via one-electron reduction of the corresponding Cu^{II}Cu^{II} species and has an intervalence transition in the near-infrared which strongly implicates the Cu(I) assignment.[26] (7) From a reactivity viewpoint the most important observation may be that Cu(LBF_2), **2**, *reacts like Cu(I)*. Certain Cu(II) complexes have recently been shown to be oxidized to Cu(III) by dioxygen.[27] However, no complexes characterized by spectral or physical properties to be Cu(II) or Cu(III) have been reported to bind CO. In contrast, Cu(LBF_2), **2**, reacts rapidly with both CO and O_2.



13

While it is presently convenient to regard both Cu(LBF_2), **2**, and Cu(LBF_2)CO, **1**, as formally containing Cu(I), the nature of the bonding in both complexes is not apparent. We are presently engaged in ESCA studies of these and related complexes to better define the metal oxidation states. Further physical measurements will provide information on the factors conducive to the formation of five-coordinate complexes. These data along with theoretical bonding calculations may lead to acceptable bonding descriptions for these unusual copper complexes.

Conclusions

The macrocyclic ligand anion LBF_2^- is capable of producing unusual structural and reactivity types for copper, including square-planar and five-coordinate complexes apparently containing Cu(I). Most four-coordinate Cu(I) complexes enjoy a tetrahedral geometry in bonding. In contrast Cu(LBF_2), **2**, is a distorted square-planar structure and manifests its unusual structure by an unusual reactivity, the capacity to bind a fifth ligand such as CO. We are continuing our investigation of a wide variety of copper–macrocyclic ligand complexes in order to delineate the structural and electronic factors which promote these new reactions.

Experimental Section

All operations requiring an inert atmosphere were performed in a Vacuum Atmospheres Dri-Lab containing He. Electronic absorption spectroscopy (EAS) was performed on a Cary-14 automatic recording spectrometer, infrared spectra were obtained via KBr pellets on a Beckman IR-12 spectrometer, and nuclear magnetic resonance measurements were made using Me_4Si as an internal standard on a Varian EM-390 90-MHz spectrometer.

Tetrabutylammonium perchlorate (TBAP) was dried exhaustively in vacuo before use. Spectroquality dimethylformamide (DMF) was dried and vacuum distilled before use as a solvent for polarographic measurements. All other solvents were reagent grade.

Electrochemistry. The apparatus used for sampled dc polarography and cyclic voltammetry was a Princeton Applied Research Model 174A polarographic analyzer coupled with an X-Y recorder. A cell with two compartments separated by a medium-porosity sintered glass frit was used for all measurements. The working compartment was filled with DMF, which was 0.1 M in TBAP, 0.5 mM in sample, and 1 mM in ferrocene. The dropping mercury working and platinum auxiliary electrodes were placed in the working half of the cell. The other compartment contained 0.1 M TBAP in DMF and the reference electrode, which was a silver wire in 0.01 M $AgNO_3$ and 0.1 M TBAP acetonitrile solution. The acetonitrile solution was separated from the DMF solution by a fine frit. The sampled dc polarographic measurements were done using a drop time of 5 s and a scan rate of either 0.5 or 1 mV/s. Cyclic voltammetric scan rates were 50 mV/s. The polarographically determined half-wave potentials, $E_{1/2}$, of the samples were related to the normal hydrogen electrode (NHE) by the use of a solvent-independent redox couple of ferrocene, its Fe(II)/Fe(III) couple.[28] The formal reduction potential, $E^f = (E_{p_a} + E_{p_c})/2$, of this couple was determined by cyclic voltammetry. The expression used was $E_{1/2}(\mathrm{Ag/Ag^+}) - E^f(\mathrm{Fe(II)/Fe(III)}) + 0.400\ \mathrm{V} = E_{1/2}(\mathrm{NHE})$.

X-ray Data Collection and Reduction. Crystals of $Cu(LBF_2)$, **2**, were grown from a slowly evaporating acetone solution under helium. Preliminary oscillation and Weissenberg photographs indicated space group Pn, $P2/n$, or $P2_1/n$.

A purple crystal of dimensions 0.10 mm × 0.12 mm × 0.44 mm was mounted on a $P\bar{1}$ Syntex four-circle diffractometer.[29] Fifteen manually centered reflections were used to find the cell parameters for the data collection. The final cell parameters given in Table I, and used in the crystal structure refinement, were found by a least-squares fit to 46 reflections. Intensity data were collected out to $2\theta = 140°$, using $\theta-2\theta$ scans from 1° below the Cu $K\alpha_1$ value to 1° above the Cu $K\alpha_2$ value (ranging from 2.02 to 2.78° in scan width) at a rate of 2°/min with an equal time spent counting background. Several check reflections measured after every 25 reflections to monitor crystal and instrument stability showed no significant changes.

The measured intensities were reduced to structure factor amplitudes by applying Lorentz and polarization corrections. The standard deviations of the intensities were calculated from the formula

$$\sigma^2(I) = S + (B1 + B2) + (dS)^2$$

where S, $B1$, and $B2$ are the scan and two background counts and d was taken[30] as 0.02. Because of a small absorption coefficient, 24.9 cm^{-1}, no absorption correction was made. After systematic absences were deleted and equivalent reflections were averaged, the number of unique data was 2882 (2652 > 0). Examination of the intensity statistics showed a centrosymmetric structure, thus eliminating the possibility of Pn as a space group. The more common of the two remaining possible space groups, $P2_1/n$, was chosen and later verified by the successful completion of the structure.

Solution and Refinement of the Structure. Scattering factors for C, B, F, N, and O were taken from ref 31; the H scattering factors were from ref 32; and the neutral-atom Cu scattering factors and the real part of the anomalous dispersion correction were taken from ref 33 and 34, respectively. The function minimized in the least-squares refinement was $\sum w(k^2F_o^2 - F_c^2)^2$ where the weight $w = 1/\sigma^2(F_o^2)$, F_o and F_c are the observed and calculated structure factors, and k is the scale factor for F_o.

The positions of the copper and four nitrogen atoms were located from a three-dimensional Patterson map.[35] These positions were used to phase a Fourier map which revealed the positions of all but two nonhydrogen atoms. Use of full-matrix least squares and difference map techniques brought $R(F) = \sum||kF_o| - |F_c||/\sum|kF_o| = 0.125$, with isotropic temperature factors on all nonhydrogen atoms. Since several of the large intensity reflections seemed to suffer from extinction, a secondary extinction parameter g of the form $F_c = F_o(1 + gI)$, where I is the intensity after data reduction, was introduced. The final refined value of g was 8.6×10^{-6}. With anisotropic temperature factors on all nonhydrogen atoms, this lowered $R(F)$ to 0.072. The 18 hydrogen atoms were then located by difference Fourier methods and their positional parameters refined in a second matrix. In the two final cycles of least-squares refinement, the isotropic temperature factors of the hydrogen atoms were also allowed to vary. Most of the hydrogen temperature factors converged, although that of H8c shifted on the order of the estimated deviation during the last cycle. The final $R(F)$ equaled 0.054 for the 2652 reflections with magnitudes greater than zero, and the final goodness of fit $\sum w(k^2F_o^2 - F_c^2)^2/(n-p)k^4$ equaled 1.43, $n = 2882$ is the number of observations and $p = 263$ is the number of parameters. The highest peak in the final difference Fourier map was 0.7 e Å^{-3} and was not located in a chemically significant position (approximately equidistant from C5, C6, and C7). Final parameters are given in Table II. Bond lengths and angles are found in Tables III and IV.

Preparation and Further Characterization of the Complexes. The infrared spectra of the first four of the complexes below are reported in Table IX.

$Cu(LBF_2)$, 2, [1,1-difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetraaza-2,14-dioxacyclotetradeca-3,5,10,12-tetraenato]copper(I), was prepared as described elsewhere.[3] The solid-state visible spectrum was determined from a mineral oil suspension supported on filter paper. The observed peak at 695 nm corresponds to the peak at 677 nm reported previously in acetone solution.[3] The proton nuclear magnetic resonance spectrum in fully deuterated dimethyl sulfoxide shows singlets at δ 1.95 and 2.00 accounting for 12 hydrogen atoms, a multiplet at δ 2.27 which integrates as two hydrogen atoms and a triplet at δ 3.63 integrating as four hydrogen atoms.

$Cu(LBF_2)CO$, 1, carbonyl[1,1-difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetraaza-2,14-dioxacyclotetradeca-3,5,10,12-tetraenato]copper(I), was prepared as described elsewhere.[3] The proton NMR was determined on a sample of $Cu(LBF_2)$, **2**, in deuterated dimethyl sulfoxide solution which had been saturated with CO. Although the color did change from a very dark blue-brown to a pale greenish yellow, indicating formation of $Cu(LBF_2)CO$, **1**, the NMR spectrum was identical with that of $Cu(LBF_2)$, **2**, in dimethyl sulfoxide.

$[Cu(LBF_2)]_2(ClO_4)_2 \cdot C_4H_8O_2$, 10, bis[(1,1-difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetraaza-2,14-dioxacyclotetradeca-3,5,10,12-tetraenato)copper(II)] diperchlorate–dioxane, was prepared as previously reported.[3] The electrochemical behavior of this complex was measured in DMF. Reduction waves (vs. NHE) occur at $E_{1/2} = -0.452$ V ($n = 1$) and at $E_{1/2} \simeq -1.65$ V (irreversible).

$Cu(LBF_2)I_3$, 11, [1,1-Difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetraaza-2,14-dioxacyclotetradeca-3,5,10,12-tetraenato]copper(II) Triiodide. $[Cu(LBF_2)]_2(ClO_4)_2 \cdot C_4H_8O_2$, **10**, and excess KI were stirred in pyridine. After a black solid was filtered off, evaporation of the filtrate yielded a brown powder which was dissolved in a minimum of boiling acetone, the solution was filtered while hot, and the powder was recovered by filtration after the solution had cooled. Anal. Calcd for $C_{11}H_{18}B_1Cu_1F_2I_3N_4O_2$: C, 18.07; H, 2.48; Cu, 8.69; N, 7.66. Found: C, 18.75; H, 2.55; Cu, 8.7; N, 7.10.

$[Zn(LBF_2)]_2(ClO_4)_2 \cdot CH_3OH$, 12, Bis[(1,1-difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetraaza-2,14-dioxacyclotetradeca-3,5,10,12-tetraenato)zinc(II)] Diperchlorate–Methanol. $[Cu(LBF_2)]_2(ClO_4)_2 \cdot C_4H_8O_2$, **10**, and zinc amalgam were stirred in acetone in the absence of oxygen. The solution turns from purple to clear, forming a copper mirror on the walls of the flask. The amalgam and a small amount of dark brown precipitate were filtered off and discarded. The white product is recovered by solution evaporation and can be recrystallized in small yield by dissolving in a minimum of boiling methanol, filtering hot, and recovering by filtration after the solution has cooled. Anal. Calcd for $C_{23}H_{40}B_2Cl_2F_4N_8O_{11}Zn_2$: C, 29.52; H, 4.31: N, 11.97; Zn, 13.97. Found: C, 29.55; H, 4.50; N, 12.10; Zn, 13.9. The complex is diamagnetic (25 °C, Faraday method). Its infrared spectrum is similar to that of the copper(II) complex, **10**, with additional bands due to the methanol. Electrochemical behavior of the zinc complex was measured in DMF. Reduction waves (vs. NHE) occur at $E_{1/2} = -1.015$ V ($n = 2$) and at approximately −1.26 and −1.51 V (irreversible).

Acknowledgment. We sincerely appreciate assistance from Charlotte Ma, Richard Marsh, and Sten Samson and helpful discussions with Harry Gray. This work was supported, in part, by the National Science Foundation, the National Institutes of Health, the International Copper Research Association, and the Biomedical Research Support Program (Grant No. RR07003).

Registry No. **1**, 61128-83-4; **2**, 61114-07-6; **11**, 67814-42-0; $Cu(LBF_2)(ClO_4)$, 64783-10-4; $Zn(LBF_2)(ClO_4)$, 67761-33-5.

Supplementary Material Available: A listing of structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

References and Notes

(1) F. H. Jardine, *Adv. Inorg. Chem. Radiochem.*, **17**, 115 (1975); W. S. McDonald, *Mol. Struct. Diffr. Methods*, **4**, 319 (1976); D. M. Johns and C. A. McAuliffe, *Inorg. Chem. Transition Elem.*, **5**, 275 (1977).
(2) See, for example, D. T. Cromer, A. C. Larson, and R. B. Roof, Jr., *Acta Crystallogr.*, **19**, 192 (1965); S. L. Lawton, W. J. Rohrbaugh, and G. T. Kokotailo, *Inorg. Chem.*, **11**, 612 (1972); M. R. Churchill, S. A. Bezman, J. A. Osborn, and J. Wormald, *Inorg. Chem.*, **11**, 1818 (1972); G. Van Koten and J. G. Noltes, *J. Organomet. Chem.*, **102**, 551 (1975); F. J. Hollander and D. Coucouvanis, *J. Am. Chem. Soc.*, **99**, 6268 (1977).
(3) R. R. Gagnê, J. L. Allison, R. S. Gall, and C. A. Koval, *J. Am. Chem. Soc.*, **99**, 7170 (1977).
(4) M. C. Weiss, B. Bursten, S.-M. Peng, and V. L. Goedken, *J. Am. Chem. Soc.*, **98**, 8021 (1976).
(5) K. Henrick, R. W. Matthews, and P. A. Tasker, *Inorg. Chem.*, **16**, 3293 (1977).
(6) L. Sacconi, *Coord. Chem. Rev.*, **8**, 351 (1972).
(7) M. R. Churchill, B. G. DeBoer, F. J. Rotella, O. M. Abu Salah and M. I. Bruce, *Inorg. Chem.*, **14**, 2051 (1975).
(8) J. P. Collman, R. K. Rothrock, J. P. Sen, T. D. Tullius, and K. O, Hodgson, *Inorg. Chem.*, **15**, 2947 (1976).
(9) J. P. Collman, P. A. Christian, S. Current, P. Denisevich, T. R. Halbert, E. R. Schmittou, and K. O. Hodgson, *Inorg. Chem.*, **15**, 223 (1976).
(10) J. A. Bertrand, J. H. Smith, and D. G. Van Derveer, *Inorg. Chem.*, **16**, 1484 (1977).
(11) M. Calligaris, *J. Chem. Soc., Dalton Trans.*, 1628 (1974).
(12) D. W. Murphy, Ph.D. Dissertation, Stanford University, 1972.
(13) S. Brückner, M. Calligaris, G. Nardin, and L. Randaccio, *Inorg. Chim. Acta*, **13**, 278 (1969).
(14) The standard deviation of the mean value, $\bar{X}$, is calculated by the formula $[\sum_{i=1}^{N}(X_i - \bar{X})^2/(N - 1)]^{1/2}$.
(15) The macrocyclic ligand, $L'BF_2^-$, is 1,1-difluoro-4,12-dimethyl-5,11-diethyl-1-bora-3,6,10,13-tetraaza-2,14-dioxacyclotetradeca-3,5,10,12-tetraenato.
(16) The torsion angles for $Rh(L'BF_2)(CH_3)I$ were calculated using atomic parameters from ref 9.
(17) O. P. Anderson and J. C. Marshall, private communication.
(18) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure", McGraw-Hill, New York, N.Y., 1968, p 22.
(19) S. C. Jackels, K. Farmery, E. K. Barefield, N. J. Rose, and D. H. Busch, *Inorg. Chem.*, **11**, 2893 (1972); J. C. Dabrowiak and D. H. Busch, *Inorg. Chem.*, **14**, 1881 (1975); A. M. Tait, F. V. Lovecchio, and D. H. Busch, *Inorg. Chem.*, **16**, 2206 (1977).
(20) N. Yamazaki and Y. Mohokabe, *Bull. Chem. Soc. Jpn.*, **44**, 63 (1971); Y. Yamano, I. Masuda, and K. Shinra, *ibid.*, **44**, 1581 (1971).
(21) A. Bigotto, G. Costa, V. Galasso, and G. De Alti, *Spectrochim. Acta, Part A*, **26**, 1939 (1970).
(22) G. N. Schrauzer, *Chem. Ber.*, **95**, 1438 (1962); D. R. Boston and N. J. Rose, *J. Am. Chem. Soc.*, **90**, 6859 (1968).
(23) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).
(24) In the case of tris(biacetylbis(methylimine))iron(II) iodide,[25a] there is no infrared band, even at very low energy, which can be reasonably assigned to $\nu_{C=N}$. In this case it was suggested that the metal–diimine five-membered ring might have predominant configurations like (d) and (e) of Figure 6. The Co(III) and Ni(II) complexes of the macrocyclic ligand 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (TIM) exhibit the expected α-diimine stretching modes while the Fe(II) complexes show only very weak bands in the 1600-cm^{-1} region.[25b] Clearly α-diimine stretching modes in some complexes, including these Fe(II) species, are not well behaved and may warrant further study.
(25) (a) P. E. Figgins and D. H. Busch, *J. Phys. Chem.*, **65**, 2236 (1961); (b) S. C. Jackels, K. Farmery, E. K. Barefield, N. J. Rose, and D. H. Busch, *Inorg. Chem.*, **11**, 2893 (1972); D. A. Baldwin, R. M. Pfeiffer, D. W. Reichgott, and N. J. Rose, *J. Am. Chem. Soc.*, **95**, 5152 (1973).
(26) R. R. Gagnê, C. A. Koval, and T. J. Smith, *J. Am. Chem. Soc.*, **99**, 8367 (1977).
(27) G. L. Burce, E. B. Paniago, and D. W. Magerum, *J. Chem. Soc., Chem. Commun.*, 261 (1975); G. L. Burce, Ph.D. Thesis, Purdue University, 1975.
(28) D. Baner and M. Breant, *Electroanal. Chem.*, **8**, 300 (1975).
(29) The X-ray diffractometer was modernized with funds from NSF Instrument Grant No. CHE 76-05471.
(30) S. W. Peterson and H. A. Levy, *Acta Crystallogr.*, **10**, 70 (1957).
(31) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962.
(32) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(33) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(34) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(35) Except for C. K. Johnson's ORTEP program, all computer programs used were from the CRYM system of crystallographic computer programs.

Contribution from the School of Chemistry, Georgia Institute of Technology,
Atlanta, Georgia 30332

Preparation, Properties, and Crystal Structure of Dichloro(1,3-dibenzoyl-2-azapropenato)(ethanol)iron(III)

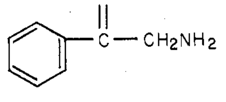
J. A. BERTRAND,* ETSUKO FUJITA, P. GARY ELLER, and D. G. VANDERVEER

Received June 21, 1978

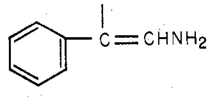
The compound dichloro(1,3-dibenzoyl-2-azapropenato)(ethanol)iron(III), $Fe(C_{16}H_{12}NO_2)Cl_2(C_2H_5OH)$, has been prepared, and its structure has been determined crystallographically. The compound was prepared by the reaction of iron(II) chloride with α-aminoacetophenone in the presence of air. The structure consists of octahedral iron(III) coordinated by two chlorides, an ethanol, and a tridentate ligand derived from two molecules of α-aminoacetophenone by oxidation and condensation. The two five-membered rings of the ligand are virtually identical. The compound crystallizes in monoclinic space group $C2/c$ with eight formula units in a unit cell of dimensions $a = 29.606$ (8) Å, $b = 6.689$ (1) Å, $c = 20.627$ (6) Å, $\beta = 114.70$ (2)°, $\rho_{calcd} = 1.51$ g/cm^3, and $\rho_{obsd} = 1.51$ g/cm^3. The structure was solved by Patterson methods, and least-squares refinement converged at final values of $R = 0.066$ and $R_w = 0.045$ for 1729 reflections with $I \geq 2\sigma(I)$.

Introduction

As part of a continuing investigation of transition-metal complexes of amino alcohols and related compounds, we became interested in the possibility of utilizing α-aminoacetophenone, I, as a ligand. Although it is not an amino alcohol, there is the possibility of an enol form, II. The reaction of α-aminoacetophenone hydrochloride with most metal chlorides produced only salts of the tetrachlorometalate ions, and attempts to neutralize the hydrochloride to carry out reactions of the amine led to organic condensation products. The reaction of iron(II) chloride with the hydrochloride under nitrogen gave the tetrachloroferrate(II) ion, but the same reaction in air produced an iron(III) complex with an unusual ligand; the ligand is an anion formed from α-aminoacetophenone by condensation and oxidation. In this paper we report the preparation, properties, and crystal structure of this



I



II

0020-1669/78/1317-3571$01.00/0 © 1978 American Chemical Society