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The Crystal Structure of (2,3,9,10-tetramethyl-1,4,8,11-tetraaza-1,3,8,10-cyclotetradecatetraene)copper(II) Tetraphenylborate*

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The crystal structure ($P2_1/c$, $a = 1199.7(2)$, $b = 1304.2(4)$, $c = 1639.1(4)$ pm, beta = 102.10(1)° (λ Mo$K\alpha$ = 71.069 pm), Z = 2) of this compound, $[CuC_{14}H_{24}N_4]$ $[B(C_6H_5)_4]_2$, has been determined from diffractometer x-ray data and refined by least-squares to R = 0.055 and Rw = 0.037.

The CuTIM cation, planar except for two methylene groups, is one of the rare cases of planar four-coordinate copper(II), although the apical regions of the coordination sphere are occupied by the centers of phenyl groups from two tetraphenylborate ions. The tetraphenylborate ion has a normal conformation which deviates slightly, but significantly, from S_4 symmetry.

INTRODUCTION

The macrocycle 2,3,9,10-tetramethyl-1,4,8,11-tetraaza-1,3,8,10-cyclotetradecatetraene (TIM) has been of interest as a fairly rigid tetradentate ligand of appropriate size for complexing first-row transition metal ions. The present paper presents the crystal structure of [Cu(TIM)] $[B(C_6H_5)_4]_2$, which is four-coordinate. Structures of three other Cu(TIM) complexes have been reported previously: [Cu(TIM) $(H_2O)_2$] $(NO_3)_2$,[1] six-coordinate, and [Cu(TIM) (NCS)] (PF_6)[2] and [Cu(TIM) (N-methylimidazole)] $(PF_6)_2$,[3] both five-coordinate.

EXPERIMENTAL

The crystals, gold-orange, were prepared by M. J. Maroney and Prof. N. J. Rose[4]. Four different crystals were used for the study. A set of oscillation, Weissenberg, and precession photographs taken with the first crystal showed monoclinic symmetry and the systematic absences h 0 l, l = 2n+1, and 0 k 0, k = 2n+1, indicated the space group $P2_1/c$. Diffractometer measurements of $\pm 2\Theta$ for 12 reflections from the fourth crystal (see below) and density measurement by flotation gave $a = 1199.7(2)$, $b = 1304.2(4)$, and $c = 1639.1(4)$ pm, beta = 102.10(1)° (λ Mo$K\alpha$ = 71.069 pm), Z = 2, d (exp) = 1.36, and d (calc) = 1.27 g cm^{-3}.

Intensities from the second, third, and fourth crystals (0.20 × 0.19 × 0.06, 0.22 × × 0.13 × 0.07, and 0.31 × 0.18 × 0.11 mm) were measured by $\Theta - 2\Theta$ scans (0.5, 2, and 2 deg/min, 20-sec background counts fore and aft) on a Picker FACS-1 diffractometer over the 2Θ ranges 5—35° and 35—45° with Mo$K\alpha$ radiation filtered through

* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

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TABLE I

Fractional Atomic Coordinates (×10[4]) and Equivalent Isotropic Gaussian Amplitudes (×10[3]) of the Non-Hydrogen Atoms

	X	Y	Z	*U*eq		X	Y	Z	*U*eq
					B	2350(6)	4967(10)	2649(5)	36(6)
Cu	10000(—)	5000(—)	5000(—)	49(2)	C(11)	2447(7)	4911(8)	1676(5)	42(6)
					C(12)	3473(8)	4672(6)	1457(6)	58(8)
N(1)	9244(5)	3710(5)	4628(4)	53(5)	C(13)	3611(8)	4642(7)	619(7)	86(9)
					C(14)	2712(10)	4842(8)	—17(5)	67(7)
N(2)	8503(5)	5544(5)	4512(5)	52(5)	C(15)	1699(7)	5087(9)	168(6)	55(7)
					C(16)	1576(6)	5104(8)	992(6)	43(6)
C(1)	8223(7)	3786(8)	4246(5)	57(7)	C(21)	970(6)	4892(10)	2647(4)	39(6)
					C(22)	216(11)	5738(7)	2481(6)	56(8)
C(2)	7776(6)	4872(9)	4183(5)	53(6)	C(23)	—968(9)	5634(9)	2325(6)	51(9)
					C(24)	—1463(7)	4709(9)	2316(6)	51(8)
C(3)	8227(6)	6630(6)	4522(5)	55(7)	C(25)	—775(11)	3867(7)	2488(6)	56(8)
					C(26)	407(9)	3962(8)	2642(6)	50(8)
C(4A)*	9184(9)	7266(11)	4474(9)	80(12)	C(31)	3078(7)	4034(8)	3194(6)	38(8)
					C(32)	3111(7)	3052(9)	2883(5)	48(7)
C(4B)*	8875(19)	7197(20)	5265(15)	56(12)	C(33)	3716(8)	2246(7)	3296(7)	57(8)
					C(34)	4334(7)	2418(9)	4109(7)	54(8)
C(5)	9808(8)	2722(6)	4722(5)	90(9)	C(35)	4329(7)	3366(9)	4459(5)	55(7)
					C(36)	3706(7)	4147(6)	4011(6)	49(7)
C(6)	7472(6)	2927(6)	3874(5)	83(7)	C(41)	2859(8)	6074(7)	3063(6)	36(8)
					C(42)	3800(9)	6550(9)	2845(5)	51(7)
C(7)	6560(6)	5075(8)	3762(4)	89(7)	C(43)	4249(8)	7461(10)	3204(8)	68(10)
					C(44)	3765(11)	7953(9)	3776(8)	65(10)
					C(45)	2879(10)	7526(9)	4029(6)	63(8)
					C(46)	2453(6)	6579(9)	3687(6)	51(7)

* Population parameters are 0.67(5) for C(4A) and 0.33(5) for C(4B)

0.001-inch niobium foil. Because the second crystal was too small and the third deteriorated too much after the first shell, only the fourth contributed to the outer shell of the final intensities (3396 symmetry-independent reflections) as merged and averaged after scaling on six standard reflections, monitored each 50 to 100 reflections (average instability constants for the three crystals: 0.3, 0.8, and 0.9%). Corrections were made for deterioration linear in exposure (12%) and coincidence loss, but not for absorption (mu = 0.5 mm^{-1}), since the maximum and minimum transmission factors, roughly estimated, ranged only from 0.97 to 0.90.

Space group $P2_1/c$ requires that the two copper atoms in the cell lie at centers of symmetry. They were placed at 0,1/2,1/2 and 0,0,0, whereupon successive structure--factor and density-map calculations revealed the positions of all the non-hydrogen atoms except C(4) (see Figure 1). Difference maps after several cycles of least-squares refinement showed C(4) to be disordered in the same manner as in $[Cu(TIM)(H_2O)_2](NO_3)_2$,[1] and after further cycles revealed all but the C(4) hydrogen atoms. Two cycles were run to adjust the hydrogen positions and isotropic *U*'s (excepting the C(4) H's) and the populations of the disorder components A and B of C(4).

The final least-squares cycles (all were on F), including both the real and imaginary components of anomalous dispersion and weights equal to the reciprocals of the Fo variances (estimated from the counting statistics and the instability constants), adjusted the non-hydrogen positions and anisotropic *U*'s, and the scale factor. In the final cycle, the mean and maximum shift/error were 0.10 and 0.82, R and Rw were 0.055 and 0.037, the goodness-of-fit was 1.21, and 1640 of the 3396 reflections were excluded because F_c and F_0 were both less than 3sigma(F_0).* Most of the calculations were made with programs of the system XRAY-76.[5]

The non-H coordinates and *U*eq's are given in Table I in terms of the atom--numbering shown in Figure 1.

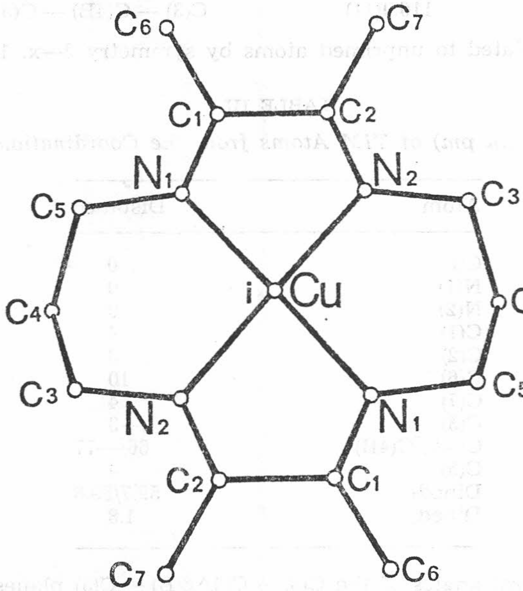

Figure 1. Numbering for the macrocycle of $[Cu(TIM)](BPh_4)_2$

DISCUSSION

The bond lengths and angles (Table II) are essentially the same as for other TIM complexes.[1-3,6-9] Except for C(4) the macrocycle, including the copper

* Tables of hydrogen atom parameters, anisotropic *U*'s, and structure factors are available in the Ph. D. dissertation of A. E. Elia.

ion, is essentially planar (Table III), as is the case for all six-coordinate TIM complexes, but for none of the five-coordinate CuTIM complexes, in which the metal ion is displaced from the coordination plane toward the apical ligand atom and the macrocycle is bent (»domed«) away from the apical atom.

TABLE II

Bond Lengths (in pm) and Bond Angles (in Degrees) of the Cation. Standard Deviations are Given in Parentheses

Cu — N(1)	194.8(6)	C(1) — C(2)	151.0(15)
Cu — N(2)	194.0(6)	C(1) — C(6)	148.6(12)
N(1) — C(1)	125.7(10)	C(2) — C(7)	150.0(10)
N(1) — C(5)	144.8(10)	C(4A) — C(3)	143.3(15)
N(2) — C(2)	127.5(11)	C(4A) — C(5')	159.1(15)
N(2) — C(3)	145.5(10)	C(4B) — C(3)	149.7(24)
		C(4B) — C(5')	157.9(25)
N(1) — Cu — N(2)	81.8(2)	N(1) — Cu — N(2')	98.2(2)
Cu — N(1) — C(1)	115.4(6)	Cu — N(2) — C(2)	114.5(6)
Cu — N(1) — C(5)	124.0(5)	Cu — N(2) — C(3)	123.0(4)
N(1) — C(5) — C(4A')	109.7(7)	N(2) — C(3) — C(4A)	112.1(8)
N(1) — C(5) — C(4B')	112.7(11)	N(2) — C(3) — C(4B)	114.1(10)
N(1) — C(1) — C(6)	126.1(8)	N(2) — C(2) — C(7)	125.9(10)
N(1) — C(1) — C(2)	113.8(8)	N(2) — C(2) — C(1)	114.5(7)
C(1) — C(2) — C(7)	119.6(8)	C(2) — C(1) — C(6)	120.2(7)
C(3) — C(4A) — C(5')	116.0(11)	C(3) — C(4B) — C(5')	113.0(17)

Primed atoms are related to unprimed atoms by symmetry 2—x, 1—y, 1—z

TABLE III

Distances (in pm) of TIM Atoms from the Coordination Plane

Atom	Distance
Cu	0
N(1)	0
N(2)	0
C(1)	4
C(2)	3
C(6)	10
C(7)	4
C(3)	—3
C(4A)/C(4B)	66/—77
C(5)	4
$Dihed_1$	59.7/59.3
$Dihed_2$	1.8

$Dihed_1$ are the dihedral angles of the C(3) — C(4A&B) — C(5) planes with the coordination plane, in degrees.
$Dihed_2$ is the dihedral angle of the C(1) — C(2) — C(6) — C(7) plane with the coordination plane, in degres.

In most of the other known structures of copper complexes that might be expected to show planar four-coordination, the packing arrangement allows one or two atoms from adjacent molecules to interact with the copper(II) ion to increase its coordination number to five or six.[10] In the present case, however,

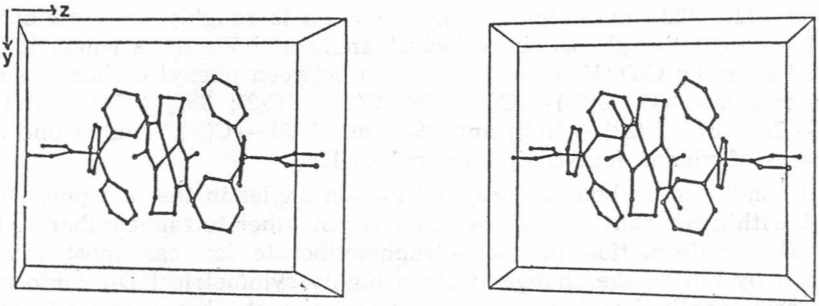

Figure 2. Stereo view of half of the contents of the unit cell

phenyl groups from adjacent tetraphenylborate ions are situated above and below the macrocycle plane, with a dihedral angle of 20° between the phenyl ring plane and the macrocycle mean plane and with the phenyl center 408 pm from the Cu atom and C(21) 426, C(22) 430, C(23) 437, C(24) 440, C(25)

TABLE IV

Bond Lengths (in pm) and Bond Angles (in Degrees) of the Anion

B — C(11)	162.6(12)	B — C(31)	164.8(15)
B — C(21)	165.8(11)	B — C(41)	165.6(16)
C(11) — C(12)	138.8(13)	C(31) — C(32)	138.1(16)
C(12) — C(13)	141.8(16)	C(32) — C(33)	137.3(14)
C(13) — C(14)	135.9(13)	C(33) — C(34)	140.0(14)
C(14) — C(15)	135.2(15)	C(34) — C(35)	136.3(16)
C(15) — C(16)	138.9(14)	C(35) — C(36)	138.0(13)
C(16) — C(11)	138.6(11)	C(36) — C(31)	140.0(13)
C(21) — C(22)	141.7(16)	C(41) — C(42)	139.9(15)
C(22) — C(23)	139.6(17)	C(42) — C(43)	138.3(16)
C(23) — C(24)	134.4(16)	C(43) — C(44)	136.3(19)
C(24) — C(25)	136.8(15)	C(44) — C(45)	134.0(18)
C(25) — C(26)	139.3(17)	C(45) — C(46)	140.7(16)
C(26) — C(21)	138.7(16)	C(46) — C(41)	138.9(15)
C(11) — B — C(21)	105.8(5)	B — C(11) — C(12)	120.9(7)
C(11) — B — C(31)	111.1(8)	B — C(11) — C(16)	126.1(8)
C(11) — B — C(41)	110.2(8)	B — C(21) — C(22)	123.4(10)
C(21) — B — C(31)	111.9(8)	B — C(21) — C(26)	122.4(10)
C(21) — B — C(41)	109.6(8)	B — C(31) — C(32)	122.5(8)
C(31) — B — C(41)	108.3(6)	B — C(31) — C(36)	124.0(9)
		B — C(41) — C(42)	122.1(9)
		B — C(41) — C(46)	124.0(9)
C(16) — C(11) — C(12)	113.1(7)	C(36) — C(31) — C(32)	113.5(8)
C(11) — C(12) — C(13)	123.1(7)	C(31) — C(32) — C(33)	125.5(8)
C(12) — C(13) — C(14)	120.2(9)	C(32) — C(33) — C(34)	117.8(9)
C(13) — C(14) — C(15)	118.7(9)	C(33) — C(34) — C(35)	119.8(9)
C(14) — C(15) — C(16)	120.4(7)	C(34) — C(35) — C(36)	119.7(8)
C(15) — C(16) — C(11)	124.6(8)	C(35) — C(36) — C(31)	123.6(9)
C(26) — C(21) — C(22)	112.9(8)	C(46) — C(41) — C(42)	113.8(9)
C(21) — C(22) — C(23)	122.9(9)	C(41) — C(42) — C(43)	122.4(10)
C(22) — C(23) — C(24)	121.3(10)	C(42) — C(43) — C(44)	120.9(11)
C(23) — C(24) — C(25)	118.2(9)	C(43) — C(44) — C(45)	119.8(11)
C(24) — C(25) — C(26)	120.9(9)	C(44) — C(45) — C(46)	119.2(11)
C(25) — C(26) — C(21)	123.7(9)	C(45) — C(46) — C(41)	123.7(9)

429, and C(26) 422 pm. Note that the Cu atom is roughly centered over the phenyl group, although, as the dihedral angle and Figure 2 show, it is not centered over the CuTIM. Closest distances between phenyl carbon atoms and TIM atoms are 335, C(25) — C(1); 338, C(24) — C(2); 351, C(25) -- N(1); 362, C(25) — C(6); 377, C(23) — N(2); and 388 pm, C(25) — C(2'). This is one of the rare cases of planar four-coordinate copper(II).

All bond lengths, bond angles, and torsion angles in the tetraphenylborate ion fall within the range of values reported for other tetraphenylborate structures. The conformation of the tetraphenylborate ion can most easily be described by noting the changes from a highly symmetrical D_{2d} conformation that is occasionally found. In this conformation, each phenyl group is perpendicular to a diagonal mirror, which relates atoms C(j2) and C(j3) to atoms C(j6) and C(j5) and contains the C(j1) — C(j4) axis, and »faces« another ring across the other mirror, ring 3 facing ring 1 and ring 4 facing ring 2; the S_4 axis bisects angles C(21) — B — C(41) and C(11) — B — C(31). To obtain the conformation found in the present structure, rotate each phenyl group about its C(j1) — C(j4) axis by 60° until ring 2 faces ring 1, 1 faces 4, 4 faces 3, and 3 faces 2; then rotate ring 2 back by 2°, 1 back by 10°, 4 ahead by 3°, and 3 back by 11°; and tip ring 2 toward ring 1 by 7° by rotation about an axis normal to the S_4 axis and to B — C(21) and passing through C(21). Rings 1, 3, and 4 are also tipped, but by statistically insignificant angles (about 0.5°). All four rings show the usual variations in bond angles: C(j6) — C(j1) — C(j2) = = 113°; C(j1) — C(j2) — C(j3) (and C(j1) — C(j6) — C(j5) = 124°; others 120°.

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Kristalna struktura (2,3,9,10-tetrametil-1,4,8,11-tetraaza-1,3,8,10-ciklotetradekatetraen) bakar(II)-tetrafenilborata

A. E. Elia, E. C. Lingafelter i V. Schomaker

Određena je kristalna struktura kompleksa $[CuC_{14}H_{24}N_4]$ $[B(C_6H_5)_4]_2$ koji sadržava makrociklički tetradentatni ligand 2,3,9,10-tetrametil-1,4,8,11-tetraaza-1,3,8,10-

-ciklotetradekatetraen (TIM). Spoj kristalizira u monoklinskom sustavu, prostorna grupa $P2_1/c$ s $a = 1199{,}7(2)$, $b = 1304{,}2(4)$, $c = 1639{,}1(4)$ pm, $\beta = 102{,}10(1)\,^{\circ}$, $Z = 2$. Struktura je utočnjena metodom najmanjih kvadrata do $R = 0{,}055$ i $R_w = 0{,}037$.

Kation CuTIM, planaran osim za dvije metilenske skupine liganda, jedan je od rijetkih slučajeva bakra(II) s planarnom koordinacijom četiri, iako se u aksijalnim područjima koordinacijske sfere nalaze centri fenilnih skupina tetrafenilboratnog aniona. Tetrafenilboratni anion ima normalnu konformaciju, premda malo, ali značajno, odstupa od simetrije S_4.