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Structural Characterization of the Binuclear Copper(II) Complex {3,3′-Dimethoxy-4,4′-bis(3-methyltriazene-3-oxide)biphenyl}di-copper(II)

DEREK J. HODGSON

Department of Chemistry, University of North Carolina, Chapel Hill, N.C. 27514, U.S.A.

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The crystal and molecular structure of the binuclear copper(II) complex {3,3′-dimethoxy-4,4′-bis(3-methyltriazene-3-oxide)biphenyl}di-copper(II), $Cu_2N_{12}O_8C_{32}H_{36}$, *has been determined from three-dimensional X-ray counter data. The complex crystallizes in the orthorhombic space group* Pcab *with eight binuclear molecules in a cell of dimensions* a = *15.723(6),* b = *34.403(10),* c = *13.785(8) Å. The structure has been refined by least-squares methods to a final value of the weighted R-factor of 0.050 based on 2499 observations. The geometry at the copper centers is tetrahedrally distorted square planar, the geometry being close to* D_{2d}. *The Cu–Cu separation in the binuclear unit is 12.018(1) Å. The biphenyl units are noncoplanar, the torsional angles between the phenyl rings in the two biphenyl moieties being 25.9 and 26.0°. On the basis of magnetic susceptibility measurements, any exchange interaction between the two copper centers is deduced to be very small.*

Introduction

The structural and magnetic properties of dinuclear copper(II) complexes have been of considerable interest to a variety of workers [1–4]. In particular, complexes in which the two metals are separated by several atoms have been studied by many groups [4–6], and in some cases extensive interactions have been found. The synthesis of the title complex and its analogues (see Fig. 1) have been described by Zacharias and coworkers [7]. The advent of such complexes provided us with the opportunity to examine the possibility of interactions over a known, long distance. We here describe the structure of the complex and its magnetic properties.

Experimental

A sample of the complex was generously provided by Dr. P. S. Zacharias. Suitable crystals were obtained by recrystallization from acetone solution. A crystal was placed on an Enraf-Nonius CAD4 diffractometer equipped with a molybdenum tube and a graphite monochromator; the cell constants, obtained in the usual manner [8] by least-squares methods, were determined to be a = 15.723(6), b = 34.403(10), c = 13.785(8) Å; the space group is *Pcab* of the orthorhombic system* and there are eight dinuclear molecules in the cell.

The structure was solved by a combination of direct methods and heavy atom techniques. An empirical absorption correction was applied, the maximum, minimum, and average transmission factors being 0.99, 0.82, and 0.96, respectively. Because of the large number of atoms in the assymmetric unit (54 atoms not including hydrogen, 90 atoms altogether), only the thirty Cu, O, N and C atoms which do not form a part of the biphenyl rings were refined anisotropically, the twenty-four C atoms in the phenyl rings being refined isotropically. Hydrogen atoms were located in difference Fourier maps, but were included in calculated positions where possible using trigonal or tetrahedral geometry at carbon as appropriate and C–H distances of 0.95 Å; isotropic thermal parameters of 4.0 $Å^2$ were assigned to the ring hydrogen atoms, while a value of 6.0 $Å^2$ was assigned to methyl and methoxo hydrogen atoms. No hydrogen atom parameters were varied. The final least-squares cycle involved observations with $I > 3\sigma(I)$, and converged to values of the conventional R-factors (on F) of R_1 = 0.058, R_2 = 0.050**. The positional parameters derived from

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*Space group *Pcab* is a non-standard setting of the conventional setting *Pbca*, No. 61; with equivalent positions x, y, z; ½ + x, $\bar{y}$, ½ − z; $\bar{x}$, ½ − y, ½ + z; ½ − x, ½ + y, $\bar{z}$ plus inversion related positions to those four.

**The conventional agreement factors are defined as $R_1 = \Sigma \| F_o| - |F_c \| / \Sigma |F_o|$ and R_2 (or weighted R-factor) = $[\Sigma w(|F_o| - |F_c|)^2 / \Sigma w(F_o)^2]^{1/2}$

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TABLE I. Positional Parameters in the Complex.

Atom	*X*	*Y*	*Z*
Cu(1)	0.11900(8)	0.12416(3)	0.15737(8)
Cu(2)	0.14361(9)	0.47077(3)	0.05260(9)
O1A	0.0539(4)	0.0838(2)	0.0948(4)
O1B	0.1813(4)	0.0897(2)	0.2418(4)
O2A	0.2186(5)	0.5048(2)	−0.0192(5)
O2B	0.0735(4)	0.5118(2)	0.0979(5)
O3A	0.2458(4)	0.1794(2)	0.0695(4)
O3B	0.0006(4)	0.1918(2)	0.2093(5)
O4A	0.0428(4)	0.4044(2)	−0.0362(5)
O4B	0.2427(4)	0.4124(2)	0.1793(4)
N1A	0.0929(5)	0.1508(2)	0.0364(5)
N2A	0.0409(5)	0.1316(2)	−0.0207(5)
N3A	0.0231(5)	0.0975(2)	0.0112(6)
N4A	0.1961(5)	0.4332(2)	−0.0326(5)
N5A	0.2561(5)	0.4468(2)	−0.0882(5)
N6A	0.2647(5)	0.4842(2)	−0.0803(6)
N1B	0.1491(4)	0.1607(2)	0.2582(5)
N2B	0.2024(5)	0.1473(2)	0.3255(5)
N3B	0.2138(5)	0.1103(2)	0.3132(5)
N4B	0.0895(5)	0.4443(2)	0.1600(5)
N5B	0.0279(5)	0.4636(2)	0.2023(5)
N6B	0.0233(5)	0.4984(2)	0.1664(6)
C13A	−0.0257(7)	0.0706(3)	−0.0473(8)
C14A	0.3223(8)	0.5045(3)	−0.1434(9)
C15A	0.3295(6)	0.1921(3)	0.0851(8)
C16A	−0.0429(7)	0.3922(3)	−0.0428(9)
C13B	0.2666(8)	0.0901(3)	0.3843(8)
C14B	−0.0346(7)	0.5254(3)	0.2111(8)
C15B	−0.0794(6)	0.2072(3)	0.1820(9)
C16B	0.3259(7)	0.3973(3)	0.1898(7)
C1A	0.1089(6)	0.1896(2)	0.0082(6)
C2A	0.1885(6)	0.2048(2)	0.0321(6)
C3A	0.2046(5)	0.2446(3)	0.0191(6)
C4A	0.1428(6)	0.2688(2)	−0.0208(6)
C5A	0.0666(6)	0.2527(3)	−0.0513(7)
C6A	0.0499(6)	0.2130(3)	−0.0355(7)
C7A	0.1584(6)	0.3116(2)	−0.0290(6)
C8A	0.0906(6)	0.3369(3)	−0.0306(6)
C9A	0.1052(5)	0.3775(3)	−0.0342(6)
C10A	0.1870(6)	0.3921(2)	−0.0366(6)
C11A	0.2549(6)	0.3668(2)	−0.0394(6)
C12A	0.2410(6)	0.3264(3)	−0.0351(7)
C1B	0.1401(5)	0.2019(2)	0.2618(6)
C2B	0.0635(5)	0.2173(2)	0.2308(6)
C3B	0.0552(6)	0.2578(3)	0.2217(6)
C4B	0.1213(5)	0.2828(2)	0.2473(6)
C5B	0.1969(5)	0.2668(2)	0.2807(6)
C6B	0.2056(5)	0.2265(3)	0.2872(6)
C7B	0.1123(6)	0.3259(2)	0.2323(6)
C8B	0.1827(6)	0.3485(3)	0.2157(6)
C9B	0.1744(6)	0.3884(3)	0.1961(6)
C10B	0.0944(6)	0.4053(2)	0.1906(6)
C11B	0.0246(6)	0.3834(3)	0.2095(7)
C12B	0.0326(6)	0.3432(3)	0.2331(7)

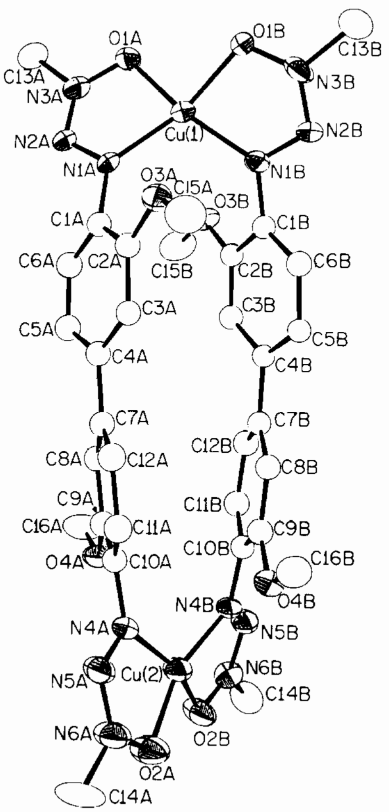

Fig. 1. View of the dinuclear complex, (3,3′-dimethoxy-4,4′-bis(3-methyltriazene-3-oxide)biphenyl)di-copper(II). Hydrogen atoms are omitted for clarity.

TABLE II. Principal Bond Lengths (Å) in the Binuclear Complex.

Atoms	Distance	Atoms	Distance
Cu(1)–O(1)A	1.928(5)	Cu(2)–O(2)A	1.934(5)
Cu(1)–O(1)B	1.928(5)	Cu(2)–O(2)B	1.897(5)
Cu(1)–N(1)A	1.947(5)	Cu(2)–N(4)A	1.931(6)
Cu(1)–N(1)B	1.933(5)	Cu(2)–N(4)B	1.934(6)
N(1)A–C(1)A	1.411(8)	N(1)B–C(1)B	1.425(7)
N(1)A–N(2)A	1.313(7)	N(1)B–N(2)B	1.332(7)
N(2)A–N(3)A	1.285(7)	N(2)B–N(3)B	1.296(7)
N(3)A–O(1)A	1.336(7)	N(3)B–O(1)B	1.316(7)
N(3)A–C(13)A	1.448(8)	N(3)B–C(13)B	1.461(9)
N(4)A–C(10)A	1.424(8)	N(4)B–C(10)B	1.409(8)
N(4)A–N(5)A	1.303(7)	N(4)B–N(5)B	1.311(7)
N(5)A–N(6)A	1.298(7)	N(5)B–N(6)B	1.298(7)
N(6)A–O(2)A	1.318(7)	N(6)B–O(2)B	1.314(7)
N(6)A–C(14)A	1.439(9)	N(6)B–C(14)B	1.439(9)

the final cycle, along with e.s.d.s as estimated from the inverse matrix, are listed in Table I. Hydrogen atom coordinates and anisotropic thermal parameters are available as supplementary material [9].

TABLE III. Principal Bond Angles (deg.) in the Binuclear Complex.

Atoms	Angle	Atoms	Angle
O(1)A–Cu(1)–O(1)B	95.6(2)	O(2)A–Cu(2)–O(2)B	94.1(2)
O(1)A–Cu(1)–N(1)A	81.0(2)	O(2)A–Cu(2)–N(4)A	80.4(2)
O(1)A–Cu(1)–N(1)B	156.9(2)	O(2)A–Cu(2)–N(4)B	160.8(2)
O(1)B–Cu(1)–N(1)A	156.0(2)	O(2)B–Cu(2)–N(4)A	161.1(2)
O(1)B–Cu(1)–N(1)B	80.9(2)	O(2)B–Cu(2)–N(4)B	80.9(2)
N(1)A–Cu(1)–N(1)B	111.2(2)	N(4)A–Cu(2)–N(4)B	109.8(2)
Cu(1)–O(1)A–N(3)A	109.0(4)	Cu(2)–O(2)A–N(6)A	109.7(5)
Cu(1)–O(1)B–N(3)B	108.5(4)	Cu(2)–O(2)B–N(6)B	109.0(4)
Cu(1)–N(1)A–N(2)A	114.1(4)	Cu(2)–N(4)A–N(5)A	115.3(4)
Cu(1)–N(1)A–C(1)A	130.0(5)	Cu(2)–N(4)A–C(10)A	130.3(5)
N(2)A–N(1)A–C(1)A	114.9(6)	N(5)A–N(4)A–C(10)A	114.0(6)
Cu(1)–N(1)B–N(2)B	115.5(4)	Cu(2)–N(4)B–N(5)B	115.3(4)
Cu(1)–N(1)B–C(1)B	130.4(5)	Cu(2)–N(4)B–C(10)B	130.8(5)
N(2)B–N(1)B–C(1)B	112.4(6)	N(5)B–N(4)B–C(10)B	112.9(6)
N(1)A–N(2)A–N(3)A	113.0(6)	N(4)A–N(5)A–N(6)A	112.4(7)
N(1)B–N(2)B–N(3)B	109.6(6)	N(4)B–N(5)B–N(6)B	109.8(6)
N(2)A–N(3)A–O(1)A	122.5(6)	N(5)A–N(6)A–O(2)A	122.0(7)
N(2)A–N(3)A–C(13)A	120.6(7)	N(5)A–N(6)A–C(14)A	119.8(8)
O(1)A–N(3)A–C(13)A	116.6(6)	O(2)A–N(6)A–C(14)A	118.1(7)
N(2)B–N(3)B–O(1)B	124.9(6)	N(5)B–N(6)B–O(2)B	124.3(6)
N(2)B–N(3)B–C(13)B	117.3(7)	N(5)B–N(6)B–C(14)B	117.9(7)
O(1)B–N(3)B–C(13)B	117.8(6)	O(2)B–N(6)B–C(14)B	117.6(7)

Discussion

As predicted by Zacharias and coworkers [7], the complex consists of binuclear units which are well separated from each other. A view of a single dimer is shown in Fig. 1, and the principal bond lengths and angles are listed in Tables II and III. Bond lengths and angles involving the biphenyl moieties are available as supplementary material.

The geometry at the two copper(II) centers is best described as tetrahedrally distorted square planar, the actual geometry being close to D_{2d}. Thus, at Cu(1) the *trans* atoms N(1)A and O(1)B lie 0.343(7) and 0.397(6) Å, respectively, above the least-squares plane through the four ligating atoms while atoms N(1)B and O(1)A sit 0.346(7) and 0.394(6) Å, respectively, below this plane; the copper atom, Cu(I), is nearly in the plane, lying 0.009(1) Å below it. The situation at Cu(2) is substantially similar, although here the deviations from planarity are smaller, ranging from 0.268(7) to 0.308(7) Å. The four independent Cu–N distances are in the range 1.931(6) to 1.947(5) Å with an average value of 1.936(7) Å, while the Cu–O bond lengths range from 1.897(5) to 1.934(5) Å with an average of 1.922(17) Å. These distances can be compared with those of 2.005(10) and 1.991(9) Å in the closely related cobalt(II) complex bis(1-methyl-3-*o*-chlorophenyltriazene-1-oxide)cobalt(II) [10]; in both cases, the M–N average distance is approximately 0.014 Å longer than the M–O distance. The Cu(1)–Cu(2) separation in the dinuclear complex is 12.018(1) Å.

The N–N bond lengths in the triazene portions of the ligands are unequal, the N(2)–N(3) distances, as expected, indicating more double bond character than the N(1)–N(2) lengths. The biphenyl moieties of the ligands each consist of two non-coplanar six-membered rings. Thus, the greatest deviation of any atom from its six-membered least-squares plane is 0.031(9) Å, the average deviation being only 0.014(9) Å. The torsional angle between the two phenyl planes is 25.9° in the A ligand and 26.0° in the B ligand. These values can be compared with those of approximately zero and 42° reported for biphenyl itself in the solid state and the gas phase, respectively [11–13], those of 33–40° for 4,4′-disubstituted biphenyls in the solid state [13, 14], and values in the range of 0–31 °C reported [15, 16] for a variety of complexes of 2,2′-bipyridine. A consequence of this twisting is that the coordination 'planes' at Cu(1) and Cu(2) are not coplanar, but are inclined at an angle of 70.3°. The phenyl rings attached to N(1)A and N(1)B [*i.e.*, associated closely with Cu(1)] are twisted by 39.8° and 63.7° from the least-squares plane through the ligating atoms at Cu(1). The senses of these rotations are opposite, so that the *o*-methoxy groups are directed on opposite sides of the copper center; this is in contrast to the disposition of the *o*-chloro groups in bis-(1-methyl-3-*o*-chlorophenyltriazene-1-oxide)cobalt-(II), in which the two Cl atoms are in *cis* positions in the *pseudo*-octahedral environment around cobalt. At Cu(2), the analogous twists are 68.2° and 44.4° at N(4)A and N(4)B, respectively.

The X-band room temperature EPR spectrum of a polycrystalline sample shows a single, sharp resonance at $g = 2.12$; there is no sign in this spectrum of any $\Delta Ms = \pm 2$ transition at half-field, which would be indicative of a singlet-triplet transition (*i.e.*, non-zero J value). Moreover, the resonance is very sharp, less than 100 G, which may be indicative of exchange narrowing. The magnetic susceptibility of a polycrystalline sample, examined by the Faraday method over the temperature range 2.0–240 K, shows no significant deviation from the behavior predicted by the Curie-Weiss law. Hence, the only possible conclusion is that any interaction between the two copper centers must be very small, and within the limits of this experiment $|2J|$, the singlet–triplet splitting, is indistinguishable from zero.

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