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Alkyne-Bridged Dicopper(I) Complexes of the Tropocoronand Macrocycles

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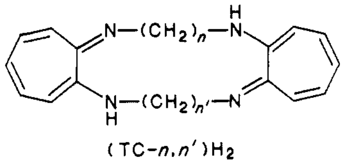
The synthesis, characterization, and chemical properties of alkyne-bridged binuclear copper(I) tropocoronand complexes are described. Two methods, employing labile copper(I) acetonitrile or carbon monoxide intermediates, were used to prepare $[Cu_2(\mu\text{-DEAD})(TC\text{-}6,6)]$ (**1**) and $[Cu_2(\mu\text{-DMAD})(TC\text{-}6,6)]$ (**2**), where DEAD and DMAD are the diethyl and dimethyl esters of acetylenedicarboxylic acid, respectively, and TC-6,6 is the tropocoronand ligand having six methylene groups in the two linker chains connecting the aminotroponeiminate poles of the macrocycle. The diaryl- and dialkyl-substituted alkyne complexes $[Cu_2(\mu\text{-PhC}{\equiv}\text{CPh})(TC\text{-}6,6)]$ (**3**) and $[Cu_2(\mu\text{-CH}_3\text{C}{\equiv}\text{CCH}_3)(TC\text{-}6,6)]$ (**4**) were synthesized directly by a third route in which the "$Cu_2(TC\text{-}6,6)$" unit was generated in the presence of excess alkyne. The novel alkyne-bridged dicopper(I) complexes were characterized by UV–vis, infrared, proton, and carbon-13 NMR spectroscopy and, in the case of **1** and **2**, by X-ray diffraction. The molecular structures reveal the alkyne positioned above and perpendicular to the copper–copper vector. The Cu···Cu distances are 2.806 (1) and 2.788 (1) Å, the average Cu—C bond lengths are 1.946 (5) and 1.942 (7) Å, and the C≡C bond lengths are 1.320 (6) and 1.314 (9) Å for **1** and **2**, respectively. The unit cell parameters of **3** are also reported. These compounds exhibit unusual stability both in the solid state and in solution, being unreactive toward air oxidation (except for **4**), hydrogenation, and nucleophilic attack, and in attempted cycloaddition and cyclopentenone annelation reactions.

Introduction

Large macrocyclic ligands having two metal-binding sites have been introduced into organometallic chemistry.[1] One such class of ligands are the tropocoronands, tetraaza macrocycles having two aminotroponeiminate rings joined by two polymethylene linker chains. Tropocoronands have shown great versatility in binding divalent metal ions to form neutral mononuclear complexes.[2] In one case, a binuclear asymmetrically bridged cupric compound, $[Cu_2(\mu\text{-OAc})(\mu\text{-OMe})(TC\text{-}6,6)]$, was isolated.[3] Following this discovery, we were interested in extending the chemistry of these ligands to low oxidation state metal ions, such as copper(I), with the aim of obtaining binuclear organometallic complexes. One long-term objective is to discover new species and chemical properties characteristic of the bimetallic centers.



$(TC\text{-}n,n')H_2$

n,n' = 3,3; 4,4; 4,5; 5,5; 6,6

This paper describes the synthesis and characterization of a class of compounds representing the first examples of discrete, neutral molecules containing the alkyne-bridged dicopper(I) core, $[Cu_2(\mu\text{-RC}{\equiv}\text{CR})(TC\text{-}6,6)]$, where R = $CO_2CH_2CH_3$ (**1**), CO_2CH_3 (**2**), Ph (**3**), and CH_3 (**4**). Some initial results were described in a preliminary communication.[4]

Experimental Section

General Methods. Tropocoronands were synthesized with overall yields of ~10% by a literature method.[5] *n*-Butyllithium (BuLi) was purchased from Aldrich Chemical Co. and titrated periodically to determine the active alkyllithium content.[6] Alkynes were obtained and used as received from Aldrich, except for 2-butyne, which was purchased from Farchan Laboratories, distilled, and stored over 4-Å molecular sieves before use. Carbon monoxide (CP grade) was supplied by Matheson. Tetrakis(acetonitrile)copper(I) tetrafluoroborate was prepared by a literature method[7] and stored in a nitrogen-filled drybox. Solvents were freshly distilled from solutions of sodium benzophenone ketyl and degassed with nitrogen or argon for 15 min prior to use. All manipulations were carried out on inert gas lines, using standard Schlenk and syringe techniques, or in a drybox. Reaction workup and recrystallization procedures were carried out in the following manner. Crude products were dissolved in toluene (2–3 mL), filtered through a cotton plug into a few small test tubes, layered carefully with pentane, sealed with rubber septa, and kept at −20 °F in the drybox freezer over several days.

Infrared spectra were recorded from KBr pellets on a Beckman Acculab 10 spectrophotometer. NMR spectra were obtained on a Bruker 250, a Bruker 270, or a JEOL FX90Q instrument using benzene-d_6 solutions. Chemical shifts were referenced to TMS. A Perkin-Elmer Lambda 7 UV–vis spectrometer was used to record optical spectra. Elemental analyses were carried out by Spang Microanalytical Laboratory (Eagle Harbor, MI) and Schwarzkopf Microanalytical Laboratory (Woodside, NY).

Preparation of Compounds. Three methods were used to synthesize the $[Cu_2(\mu\text{-alkyne})(TC\text{-}n,n')]$ complexes.

Method 1. Solid $[Cu(NCCH_3)_4](BF_4)$ (95.2 mg, 0.303 mmol) was dissolved in 20 mL of a 1:1 (v/v) MeCN/THF solvent mixture. A solution of $Li_2(TC\text{-}6,6)$ was prepared by treating 61.2 mg (0.151 mmol) of $H_2(TC\text{-}6,6)$ in 10 mL of THF with BuLi (2.0 equiv) at 0 °C and stirring the yellow solution for an additional 10 min.[8] The $Li_2(TC\text{-}6,6)$ solution was then added dropwise, with vigorous stirring and under an inert atmosphere at −78 °C, to the copper(I) salt solution. The resulting yellow-green mixture was stirred an additional 10 min at −78 °C and then treated with neat diethyl acetylenedicarboxylate (DEAD, 25 μL, ~1.0 equiv). Product

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[1] See, for example: (a) Martin, A. E.; Bulkowski, J. E. *J. Organomet. Chem.* **1981**, *217*, C29. (b) Parker, D. *J. Chem. Soc., Chem. Commun.* **1985**, 1129. (c) Lehn, J.-M. *Science (Washington, D.C.)* **1985**, *227*, 849. (d) Bell, M. N.; Blake, A. J.; Schröder, M.; Stephenson, T. A. *J. Chem. Soc., Chem. Commun.* **1986**, 471. (e) Wei, L.; Bell, A.; Warner, S.; Williams, I. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1986**, *108*, 8302.

[2] (a) Imajo, S.; Nakanishi, K.; Roberts, M.; Lippard, S. J.; Nozoe, T. *J. Am. Chem. Soc.* **1983**, *105*, 2071. (b) Davis, W. M.; Zask, A.; Nakanishi, K.; Lippard, S. J. *Inorg. Chem.* **1985**, *24*, 3737. (c) Davis, W. M.; Roberts, M. M.; Zask, A.; Nakanishi, K.; Nozoe, T.; Lippard, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 3864.

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[8] The formation of $Li_2(TC\text{-}6,6)$ is sometimes accompanied by a slight darkening of the yellow solution.

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Table I. $^{13}C\{^1H\}$ NMR Chemical Shifts of Alkyne-Bridged Dicopper(I) Tropocoronands, $[Cu_2(\mu\text{-}RC{\equiv}CR)(TC\text{-}6,6)]$[a]

carbon[b]	H_2(TC-6,6)	1 (R = CO_2Et)	2 (R = CO_2Me)	3 (R = Ph)[c]	4 (R = Me)[d]
11	153.20	164.73	164.94		164.26
12	110.40	112.23	112.29	111.76	111.06
13	133.82	133.74	133.85	133.63	133.49
14	117.66	117.38	117.60	116.57	115.83
31	45.94	51.18	51.72	51.11	51.69
32[e]	31.04	28.05	27.89	27.38	28.07
33[e]	28.66	28.70	28.97	28.56	28.94

[a] Observed at 22.4 MHz, using benzene-d_6 solutions, unless otherwise noted. [b] See Figure 1 for atom-labeling scheme. [c] 67.9 MHz spectrum. A C11 resonance was not observed. [d] Using toluene-d_8. [e] Tentative assignments; may be reversed.

formation was almost instantaneous, judging by the appearance of a deep burgundy color. The cooling bath was removed at this point, and the solution was allowed to warm up to room temperature, after which the solvents were evaporated in vacuo. The red residue was transferred to the drybox for workup and recrystallization. Crystals of $[Cu_2(\mu\text{-DEAD})(TC\text{-}6,6)]$ (1) were harvested and washed with fresh pentane (yield 47.6 mg, 45%). Analytical, ^1H, and ^{13}C NMR data are reported in ref 4. IR (KBr) cm^{-1}): 1717 and 1710 sh (s, C=O), 1647 and 1635 sh (m, C≡C), 1599 (s, C=C), 1517 (s), 1485 (m), 1442 (s), 1408 (s), 1356 (m), 1287 (s), 1250 (s), 1207 (s, C—O), 1112 (w), 1056 (m), 1025 (m), and 749 (s, =C—H).

Compound 2 was prepared similarly in 48% yield, using 1.0 equiv of dimethyl acetylenedicarboxylate (DMAD). Analytical data and UV-vis spectral data are reported in ref 4. IR (KBr, cm^{-1}): 1732 and 1712 (s, C=O), 1648 and 1638 (w, C≡C), 1598 (s, C=C), 1519 (s), 1482 (w), 1447 (s), 1408 (m), 1352 (m), 1292 (m), 1250 (m), 1217 (m, C—O), 1060 (w), and 745 (s, =C—H). ^1H NMR (270 MHz, 295 K, C_6D_6): δ 6.93 (4 H, dd, J = 11.7, 9.5 Hz), 6.58 (4 H, d, J = 10.6 Hz), 6.33 (2 H, t, J = 9.1 Hz), 3.87 and 3.81 (8 H, overlapping m), 3.40 (6 H, s), and a broad signal centered at δ 1.59 (16 H). $^{13}C\{^1H\}$ NMR (22.4 MHz, 296 K, C_6D_6): δ 159.74 and 52.37 for the DMAD C3 and C5 carbons (see Figure 1), respectively, in addition to the values listed in Table I.

Method 2. To a CO-saturated suspension of $[Cu(NCCH_3)_4](BF_4)$ (63.4 mg, 0.202 mmol) in THF at −78 °C was added a 14.4 μM THF solution of Li_2(TC-6,6) (7.0 mL), prepared from 40.8 mg (0.101 mmol) of H_2(TC-6,6) and BuLi (2.0 equiv). The resulting yellow-green mixture was stirred at low temperature for an additional 0.5 h, after which time a yellow-green precipitate[9] had formed. Neat DMAD (15 μL, 1.0 equiv) was addded, the CO atmosphere was replaced with N_2, and the mixture was allowed to warm up to ambient temperature. After a period of 45 min, the resulting burgundy solution was filtered and concentrated under vacuum to yield a red solid. The residue was transferred to the drybox and worked up in the usual manner to give red crystals of $[Cu_2(\mu\text{-DMAD})(TC\text{-}6,6)]$ (2), the spectroscopic properties of which were identical with those of samples prepared by method 1 (yield 38.3 mg, 56%).

Method 3. A THF solution of Li_2(TC-6,6) (0.118 mmol, prepared from 47.7 mg of H_2(TC-6,6) and 2.0 equiv of BuLi) was added dropwise to a stirred suspension of $[Cu(NCCH_3)_4](BF_4)$ (74.4 mg, 0.237 mmol) and 2-butyne (1 mL, excess) in 10 mL of THF at −78 °C under an inert atmosphere. After an additional 0.5 h of stirring, the yellow-green mixture was allowed to warm up to room temperature, filtered, and concentrated under vacuum. The crude solid was recrystallized as usual in the drybox, providing gold plates of 4 (yield 26 mg, 38%). UV-vis spectrum (benzene): λ 272 nm (ϵ 42 900 cm^{-1} M^{-1}), 284 (46 100), 300 sh (34 300), 395 (31 400), 437 (18 500), 463 (21 500), and a very broad weak feature centered at 751 (2600). IR (KBr, cm^{-1}): 1750 (w, C≡C), 1597 (s, C=C), 1514 (s), 1480 (m), 1435 sh (s), 1404 (s), 1343 (m), 1285 (s), 1242 (s), 1020 (w), 1000 (w), and 736 (s, =C—H). Analytical data, along with ^1H and ^{13}C NMR spectra, are reported in ref 4 and Table I.

Compound 3 was synthesized in 40% yield by the same method, using 2.2 equiv of diphenylacetylene. Anal. Calcd for $C_{40}H_{44}N_4Cu_2$: C, 67.87; H, 6.26; N, 7.91. Found: C, 67.75; H, 6.54; N, 8.18. UV-vis spectrum (benzene): λ 288 nm (ϵ 53 800 cm^{-1} M^{-1}), 392 (39 600), 434 (20 200), and 459 (20 000). IR (KBr, cm^{-1}): 1676 (m, C≡C), 1591 (s, C=C), 1507 (s), 1470 (m), 1430 (s), 1393 (m), 1343 (m), 1265 (s), 1233 (s), 885 (m), 766 (m, =C—H), and 716 and 696 (s, phenyl C-H bend). ^1H NMR (270 MHz, 295 K, C_6D_6): δ 7.30 (4 H, d, J = 7.3 Hz), 7.14–6.95 (10 H, complex m), 6.68 (4 H, d, J = 11.0 Hz), 6.37 (2 H, t, J = 9.1 Hz), 3.84 (4 H, m), 3.56 (4 H, m), broad signal centered at 1.58 (8 H), 1.47 (4 H, br m), and 1.11 (4 H, br m). $^{13}C\{^1H\}$ NMR (67.9 MHz, 295 K, C_6D_6): δ 129.32, 128.74, and 128.63 for the proton-bearing carbons of the phenyl groups (the quaternary phenyl and alkyne carbon resonances were not observed) along with the chemical shift values listed in Table I. Triclinic unit cell parameters listed in Table II and are consistent with the above formulation.

X-ray Structural Work. Table II summarizes the details of data collection, reduction, and refinement; typical procedures in our laboratory are further described in ref 10. All data were collected on an Enraf-Nonius CAD-4F diffractometer with monochromatized Mo Kα (λ = 0.710 69 Å) radiation and $\theta/2\theta$ scans. No attempt was made to collect data for compound 3.

$[Cu_2(\mu\text{-DEAD})(TC\text{-}6,6)]$ (1). A red parallelepiped of dimensions of 0.31 × 0.30 × 0.35 mm was mounted in a glass capillary and found to be monoclinic by study on the diffractometer. The space group was determined to be $P2_1/c$ (C_{2h}^5, No. 14)[11] from the systematic absences and, ultimately, the solution and successful refinement of the structure. The unit cell parameters were refined by using the setting angles of 25 reflections having $2\theta > 38°$. Standard reflections showed no crystal decay over the total time of data collection (6 days). No absorption correction was made. The structure was solved by standard Patterson and difference Fourier techniques and refined by using anisotropic temperature factors for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms, the positions of which were calculated and refined as described below for 2. Carbon atom C34 was found to be disordered over two sites, designated as C34A and C34B, that refined to occupancy factors of 0.55 and 0.45, respectively. Although this model accounted for the electron density in this region, the resulting molecular geometry is distorted. The weighting scheme employed was $w = 1.509/[\sigma^2(F_o) + 0.000625\,F_o^2]$, and the function $\sum w(|F_o| - |F_c|)^2$ was minimized in the least-squares refinement. Calculations were carried out with the program package SHELX-76[12] on a DEC VAX 11/780 computer. Atomic scattering factors for the neutral atoms and anomalous dispersion corrections were taken from ref 13. Final coordinates for the non-hydrogen atoms are given in Table IV, and bond lengths and angles are reported in Table VI. Listings of anisotropic thermal parameters, hydrogen atom positional and thermal parameters, and observed and calculated structure factors are available as supplementary material (Tables S1–S3).

$[Cu_2(\mu\text{-DMAD})(TC\text{-}6,6)]$ (2). A dark red crystal of dimensions 0.20 × 0.20 × 0.15 mm was mounted in a capillary and studied

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Table II. Experimental Details of the X-ray Diffraction Studies of [Cu_2(μ-DEAD)(TC-6,6) (1), [Cu_2(μ-DMAD)(TC-6,6)] (2) and [Cu_2(μ-PhC≡CPh)(TC-6,6)] (3)

	1	2	3
formula	$C_{34}H_{44}N_4O_4Cu_2$	$C_{32}H_{40}N_4O_4Cu_2$	$C_{40}H_{44}N_2Cu_2$
a, Å	11.979 (2)	10.950 (1)	10.661 (2)
b, Å	16.691 (1)	16.093 (2)	19.705 (5)
c, Å	16.233 (4)	17.505 (5)	8.914 (1)
α, deg			93.93 (2)
β, deg	94.57 (2)		97.15 (1)
γ, deg			83.04 (2)
V, $Å^3$	3235	3085	1842
fw	699.8	671.8	707.91
Z	4	4	2
ρ_{calcd}, g cm^{-3}	1.432	1.446	1.276
ρ_{obsd}, g cm^{-3}[a]	1.426 (7)	1.449 (2)	
space group	$P2_1/c$	$Pna2_1$	$P\bar{1}$
linear abs coeff, cm^{-1}[b]	14.1	14.8	
no. of reflcns collected	6529	3538	
no. of unique obsd data	3507[c]	2286[d]	
no. of parameters refined	400	251	
max param shift in final refinement cycle	0.004σ	0.001σ	
max electron density on final diff Fourier map	0.35 e $Å^{-3}$	0.5 e $Å^{-3}$	
R_1[e]	0.036	0.033	
R_2[f]	0.047	0.041	

[a] By neutral buoyancy in aqueous KI. [b] No absorption corrections were applied. [c] $F_o \geqslant 4\sigma(F_o)$. [d] $F_o \geqslant 6\sigma(F_o)$. [e] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [f] $R_2 = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$.

Table III. Spectral Properties of [Cu_2(μ-RC≡CR)(TC-6,6)] Compounds as a Function of Alkyne Substituent R

compd	R	vis spectrum MLCT bands, nm[a]	^{1}H NMR spectrum α-CH_2, δ[b]
1 or 2	$CO_2CH_2CH_3$ or CO_2CH_3	430, 452[c]	3.96, 3.85[d]
3	Ph	434, 459	3.84, 3.56
4	Me	437, 463	3.84, 3.42

[a] In benzene solution. [b] In benzene-d_6 or, for 4, toluene-d_8. [c] Values are for compound 2. [d] Values are for compound 1.

on the diffractometer. The systematic absences were consistent with either space group *Pna*2_1 (C_{2v}^9, No. 33)[11] or *Pnma* (D_{2h}^{16}, No. 62).[11] The structure was solved in the former, acentric space group, in which the molecular symmetry is not required to be C_m or C_i. Refinement was carried out as described for 1, with hydrogen atoms placed at fixed C–H distances of 0.95 Å and constrained to "ride" on the respective carbon atoms. The enantiomeric description in the polar space group was confirmed by comparison of agreement factors for the two possible choices, the correct enantiomorph having a lower value for the weighted *R* factor. Weights were assigned as $w = 1.0244/[\sigma^2(F_o) + 0.000625\,F_o^2]$. The final positional parameters for non-hydrogen atoms may be found in Table V. Table VI contains a listing of the bond lengths and angles. Tables S4–S6 list, respectively, anisotropic thermal parameters, hydrogen atom parameters, and structure factors.

Results and Discussion

Syntheses. Three methods were employed to synthesize the [Cu_2(μ-RC≡CR)(TC-*n,n′*)] complexes. The first made use of a highly reactive intermediate believed to be the binuclear acetonitrile adduct, [$Cu_2$$(MeCN)_2$(TC-*n,n′*)], similar to [$Cu_2L(MeCN)_2]^{2+}$, where L is a difuranyl tetraimino macrocycle.[14] This intermediate could not be isolated, owing to its apparent thermal instability. Yellow powder prepared at −78 °C quickly turned dark brown upon warming to ambient temperature under a vacuum. Nevertheless, the yellow color characteristic of this intermediate persisted at low temperature in acetonitrile/THF solvent mixtures until such time as the electron-deficient alkyne was introduced. Reaction was accompanied by a dramatic color change to burgundy, from which solutions the products were isolated. This method avoids potential unwanted side reactions between Li_2(TC-*n,n′*) and the ester functionalities of the alkynes DEAD and DMAD.

Method 2 eliminates acetonitrile as a cosolvent. In this method, dissolved carbon monoxide occupies the third coordination site of copper in the reactive intermediate. The CO ligands in this adduct, which was isolated and found in a separate study to be the compound [$Cu_2(CO)_2$(TC-*n,n′*)],[9] may be displaced by electron-deficient alkynes, DEAD or DMAD, to form the alkyne-bridged complexes. The CO complexes exhibited greater thermal stability than their putative MeCN analogues, and this desirable property may be responsible for the greater yields obtained by method 2. It should be mentioned that addition of Li_2(TC-*n,n′*) to [$Cu(NCCH_3)_4](BF_4)$ in THF gave rise only to the mononuclear Cu(II) complexes [Cu(TC-*n,n′*)], which presumably form by disproportionation. Thus, carbon monoxide, an excess of acetonitrile, or another suitable ligand is needed to stabilize dicopper(I) tropocoronand species.

Method 3 was devised to obtain the binuclear macrocyclic copper(I) complexes with bridging diphenylacetylene or 2-butyne. In the case of the former alkyne, method 1 failed to give the desired products; only the free macrocycle was recovered. With 2-butyne, method 2 gave a mixture of products including the (μ-alkyne)dicopper(I) compound and mononuclear cupric species. Since no side reactions involving the phenyl or methyl groups were expected to occur, "direct" formation of complexes 3 and 4 was attempted by generating the dicopper(I) tropocoronand unit in the presence of excess alkyne. Indeed, the reactions work well, giving moderate yields of the desired alkyne-bridged species.

Structures. Two views of the molecular structure of 2 are shown in Figures 1 and (in stereo) 2. The DMAD molecule lies perpendicular to the Cu–Cu vector with an average Cu–C distance of 1.943 (8) Å. This value is substantially shorter than the mean Cu–C distance of 2.060 (4) Å recently reported for a copper(I) triflate complex of

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Table IV. Final Positional Parameters for $[Cu_2(DEAD)(TC\text{-}6,6)]$ (1)[a]

ATOM	X	Y	Z
Cu1	0.20609(4)	−0.01277(3)	0.16910(3)
Cu2	0.36218(4)	−0.01690(3)	0.30765(3)
O1	0.1960(3)	−0.22461(18)	0.2611(2)
O2	0.4046(3)	−0.1310(2)	0.0870(2)
O3	0.1182(3)	−0.13593(17)	0.3418(2)
O4	0.4813(3)	−0.16995(19)	0.20885(17)
N1	0.0551(3)	0.02540(19)	0.1632(2)
N2	0.2154(3)	0.05095(19)	0.07229(19)
N3	0.3368(3)	0.03498(19)	0.4092(2)
N4	0.5069(3)	0.03140(19)	0.3238(2)
C1	0.2500(3)	−0.0900(2)	0.2548(2)
C2	0.3336(3)	−0.0798(2)	0.2076(2)
C3	0.1867(3)	−0.1576(3)	0.2851(3)
C4	0.4085(3)	−0.1288(2)	0.1605(3)
C5	0.0520(5)	−0.1980(3)	0.3781(4)
C6	0.5573(4)	−0.2231(3)	0.1700(3)
C7	−0.0621(5)	−0.1982(4)	0.3429(4)
C8	0.6713(5)	−0.2092(4)	0.2025(5)
C11	0.0251(4)	0.0673(2)	0.0947(3)
C12	−0.0868(4)	0.0883(3)	0.0720(3)
C13	−0.1375(4)	0.1301(3)	0.0053(3)
C14	−0.0910(5)	0.1694(3)	−0.0569(3)
C15	0.0203(5)	0.1731(3)	−0.0684(3)
C16	0.1126(5)	0.1381(3)	−0.0242(3)
C17	0.1211(4)	0.0858(2)	0.0448(3)
C21	0.4243(4)	0.0764(2)	0.4422(3)
C22	0.4226(5)	0.1154(3)	0.5198(3)
C23	0.5031(6)	0.1597(3)	0.5653(3)
C24	0.6083(6)	0.1830(3)	0.5492(4)
C25	0.6601(5)	0.1630(3)	0.4811(4)
C26	0.6237(4)	0.1162(3)	0.4137(3)
C27	0.5226(4)	0.0749(2)	0.3927(3)
C31	−0.0279(4)	0.0058(3)	0.2206(3)
C32	−0.0606(6)	0.0748(5)	0.2741(4)
C33	−0.0283(8)	0.0732(6)	0.3598(5)
C34A	0.1028(8)	0.1130(6)	0.3504(6)
C34B	0.0232(11)	0.0557(8)	0.4193(9)
C35	0.1585(5)	0.1025(5)	0.4271(5)
C36	0.2323(4)	0.0299(3)	0.4495(3)
C41	0.3169(4)	0.0625(3)	0.0293(3)
C42	0.3796(4)	0.1395(3)	0.0569(3)
C43	0.4485(4)	0.1302(3)	0.1402(3)
C44	0.5535(4)	0.0832(4)	0.1328(3)
C45	0.6310(4)	0.0789(4)	0.2129(3)
C46	0.6008(4)	0.0151(3)	0.2746(3)

[a] Numbers in parentheses are errors in the last significant digit(s). See Figure 1 for atom labeling scheme.

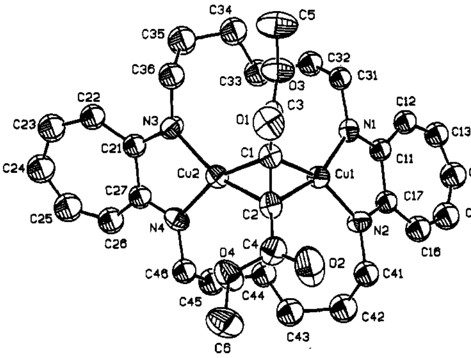

Figure 1. The structure of $[Cu_2(\mu\text{-DMAD})(TC\text{-}6,6)]$ (2), showing the 50% probability thermal ellipsoids and atom labeling scheme.

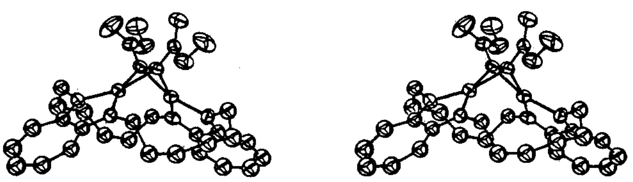

Figure 2. A stereoview of the molecule 2.

Table V. Final Positional Parameters for $[Cu_2(DMAD)(TC\text{-}6,6)]$ (2)[a]

ATOM	X	Y	Z
Cu1	0.39631(7)	0.45501(4)	0.2094
Cu2	0.47737(7)	0.48642(5)	0.06122(8)
N1	0.5118(5)	0.4467(3)	0.2910(3)
N2	0.3292(5)	0.3564(3)	0.2520(3)
C11	0.4942(6)	0.3804(4)	0.3354(4)
C12	0.5702(6)	0.3643(4)	0.3997(4)
C13	0.5688(7)	0.2993(5)	0.4524(5)
C14	0.4963(7)	0.2317(5)	0.4590(5)
C15	0.3971(7)	0.2156(5)	0.4160(5)
C16	0.3470(7)	0.2574(5)	0.3535(4)
C17	0.3880(6)	0.3278(4)	0.3131(4)
N3	0.6315(5)	0.5260(4)	0.0253(3)
N4	0.4980(5)	0.4028(3)	−0.0164(4)
C27	0.6008(6)	0.4111(4)	−0.0561(4)
C26	0.6362(7)	0.3514(5)	−0.1109(4)
C25	0.7268(7)	0.3539(6)	−0.1673(5)
C24	0.8059(7)	0.4157(5)	−0.1860(6)
C23	0.8265(7)	0.4891(5)	−0.1472(5)
C22	0.7695(7)	0.5193(5)	−0.0817(4)
C21	0.6720(6)	0.4861(4)	−0.0366(4)
C6	0.0711(7)	0.4727(6)	−0.0214(6)
O4	0.1903(5)	0.4769(4)	0.0133(3)
O2	0.1064(6)	0.4951(5)	0.1265(4)
C4	0.1948(8)	0.4900(5)	0.0883(5)
C2	0.3221(6)	0.4941(4)	0.1155(4)
C1	0.3990(6)	0.5504(4)	0.1410(4)
C3	0.4021(7)	0.6414(4)	0.1571(4)
O1	0.3228(5)	0.6875(3)	0.1384(3)
O3	0.5023(5)	0.6623(3)	0.1931(3)
C5	0.5196(7)	0.7504(4)	0.2073(6)
C31	0.6110(6)	0.5055(4)	0.3072(4)
C32	0.7357(7)	0.4753(5)	0.2832(5)
C33	0.7589(8)	0.4847(5)	0.1960(5)
C34	0.8046(8)	0.5718(5)	0.1769(4)
C35	0.8101(7)	0.5909(5)	0.0925(5)
C36	0.6913(6)	0.6023(4)	0.0510(4)
C41	0.2130(6)	0.3173(4)	0.2298(4)
C42	0.2237(8)	0.2371(5)	0.1842(5)
C43	0.2670(7)	0.2440(5)	0.1023(5)
C44	0.4030(6)	0.2507(5)	0.0905(4)
C45	0.4398(7)	0.2535(5)	0.0067(5)
C46	0.4114(6)	0.3360(4)	−0.0339(4)

[a] Numbers in parentheses are errors in the last significant digit(s). See Figure 1 for atom labeling scheme.

1,2:5,6:9,10-tribenzocyclododeca-1,5,9-triene-3,7,11-triyne (5), in which copper(I) is bonded to three alkyne units situated in a plane and to a very weakly associated axial triflate oxygen atom.[15] The Cu–C bond lengths in 1 and 2 are comparable to the average value of 1.951 (14) Å reported[16] for the corresponding bonds in the compound $[Cu(PhCO_2)(Ph_2C_2)]_2$ (6), however. The copper atoms in 1 and 2 also have a planar geometry with angles about the metal atoms summing up to 360°. The average Cu–N distance is 1.912 (6) Å, and the N–Cu–N bite angles average to a value of 84.3 (3)°. These values are smaller compared to the corresponding metal–nitrogen bond length and bite angle of 1.968 (3) Å and 96.8 (2)°, respectively, observed for the complex $[Cu(NH(py)_2)(C_2H_2)](BF_4)$ (7), where $NH(py)_2$ is di-2-pyridylamine.[17] The alkyne multiple C–C bond length is 1.314 (9) Å, substantially longer than the values of 1.222 (10), 1.227 (22), and 1.188 (11) Å found in 5, 6, and 7, respectively. This larger distance is consistent with the bridging alkyne unit serving as a four-electron donor, contributing two electrons to each 16-valence electron copper center. In fact, a comparable value for the multiple C–C bond length in compounds of the type $Co_2(CO)_6(\mu\text{-RC}{\equiv}\text{CR})$[18,19]

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(16) Pasquali, M.; Leoni, P.; Floriani, C.; Gaetani-Manfredotti, A. *Inorg. Chem.* 1982, *21*, 4324.

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(18) Baert, F.; Guelzim, A.; Coppens, P. *Acta Crystallogr., Sect. B: Struct. Sci.* 1984, *B40*, 590.

(19) For an extensive list of alkyne-bridged binuclear complexes, see: Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* 1982, *104*, 3858.

Table VI. Interatomic Distance (Å) and Angles (deg) for [Cu_2(DEAD)(TC-6,6)] (1) and [Cu_2(DMAD)(TC-6,6)] (2)[a]

	1	2		1	2
Cu1 —— Cu2	2.806(1)	2.788(1)	C1 - C2	1.320(6)	1.314(9)
Cu1 - C1	1.937(4)	1.946(7)	Cu2 - C1	1.961(4)	1.935(7)
Cu1 - C2	1.955(4)	1.938(7)	Cu2 - C2	1.939(4)	1.952(7)
Cu1 - N1	1.912(3)	1.912(5)	Cu2 - N3	1.907(3)	1.910(6)
Cu1 - N2	1.907(3)	1.901(5)	Cu2 - N4	1.910(3)	1.926(6)
C1 - C3	1.467(6)	1.493(9)	C2 - C4	1.473(6)	1.48(1)
C3 - O1	1.192(5)	1.188(9)	C4 - O2	1.189(5)	1.18(1)
C3 - O3	1.331(5)	1.310(9)	C4 - O4	1.318(5)	1.33(1)
C5 - O3	1.457(6)	1.452(8)	C6 - O4	1.451(6)	1.44(1)
C5 - C7	1.438(8)		C6 - C8	1.442(8)	
N1 - C11	1.337(5)	1.335(9)	N3 - C21	1.331(5)	1.335(9)
N1 - C31	1.453(6)	1.469(9)	N3 - C36	1.460(6)	1.464(9)
N2 - C17	1.317(5)	1.331(9)	N4 - C27	1.333(5)	1.330(9)
N2 - C41	1.462(6)	1.471(9)	N4 - C46	1.457(6)	1.466(9)
C11 - C17	1.490(6)	1.49(1)	C21 - C27	1.478(6)	1.48(1)
C11 - C12	1.405(6)	1.42(1)	C21 - C22	1.418(6)	1.43(1)
C12 - C13	1.385(7)	1.39(1)	C22 - C23	1.381(8)	1.39(1)
C13 - C14	1.360(8)	1.35(1)	C23 - C24	1.36(1)	1.38(1)
C14 - C15	1.363(9)	1.35(1)	C24 - C25	1.352(1)	1.36(1)
C15 - C16	1.396(8)	1.40(1)	C25 - C26	1.385(8)	1.40(1)
C16 - C17	1.416(6)	1.41(1)	C26 - C27	1.411(6)	1.41(1)
C31 - C32	1.512(9)	1.51(1)	C41 - C42	1.537(7)	1.52(1)
C32 - C33	1.41(1)	1.56(1)	C42 - C43	1.533(7)	1.51(1)
C33 - C34A	1.72(1)	1.52(1)	C43 - C44	1.495(7)	1.51(1)
C33 - C34B	1.14(2)		C44 - C45	1.535(7)	1.52(1)
C34A - C35	1.37(1)	1.51(2)	C45 - C46	1.525(8)	1.54(1)
C34B - C35	1.79(1)				
C35 - C36	1.526(9)	1.50(1)			
N2 - Cu1 - N1	83.7(2)	84.5(2)	N4 - Cu2 - N3	84.0(2)	84.1(2)
N2 - Cu1 - C2	119.1(2)	116.2(3)	N4 - Cu2 - C2	116.1(2)	119.4(3)
N1 - Cu1 - C1	117.3(2)	120.3(3)	N3 - Cu2 - C1	120.6(2)	116.9(3)
C1 - Cu1 - C2	39.6(2)	39.5(3)	C2 - Cu2 - C1	39.6(2)	39.5(3)
C2 - C1 - C3	136.9(4)	139.0(7)	C1 - C2 - C4	138.7(4)	138.2(4)
O3 - C3 - C1	112.7(3)	111.2(6)	O2 - C4 - C2	124.1(4)	126.2(8)
O1 - C3 - O3	124.1(4)	125.8(6)	O2 - C4 - O4	123.4(4)	122.7(8)
C3 - O3 - C5	118.1(4)	116.3(6)	C4 - O4 - C6	117.9(3)	117.1(6)
C7 - C5 - O3	111.8(5)		C8 - C6 - O4	110.5(4)	
C11 - N1 - C31	119.8(4)	120.7(6)	C21 - N3 - C36	121.7(3)	120.3(6)
C11 - N1 - Cu1	113.9(3)	113.3(4)	C21 - N3 - Cu2	114.2(3)	113.7(5)
C31 - N1 - Cu1	125.9(3)	126.0(4)	C36 - N3 - Cu2	124.2(3)	125.0(4)
C17 - N2 - C41	120.3(3)	118.9(6)	C27 - N4 - C46	119.8(3)	120.9(6)
C17 - N2 - Cu1	114.8(3)	114.6(4)	C27 - N4 - Cu2	114.2(3)	113.4(5)
C41 - N2 - Cu1	124.9(3)	125.9(4)	C46 - N4 - Cu2	125.3(3)	125.7(4)
N1 - C11 - C12	122.4(4)	121.5(6)	N3 - C21 - C22	121.9(4)	121.1(6)
N1 - C11 - C17	113.1(4)	114.5(6)	N3 - C21 - C27	114.1(3)	113.9(6)
C12 - C11 - C17	124.5(4)	124.1(6)	C22 - C21 - C27	123.9(4)	124.9(7)
C13 - C12 - C11	132.8(5)	130.8(7)	C23 - C22 - C21	131.4(5)	131.1(7)
C14 - C13 - C12	130.0(5)	131.8(8)	C24 - C23 - C22	131.8(5)	129.1(8)
C13 - C14 - C15	125.9(5)	125.6(8)	C23 - C24 - C25	125.3(6)	127.7(9)
C14 - C15 - C16	130.9(5)	131.4(8)	C24 - C25 - C26	130.4(6)	130.0(8)
C15 - C16 - C17	131.8(5)	131.0(7)	C25 - C26 - C27	132.5(5)	130.8(7)
N2 - C17 - C16	123.0(4)	121.8(6)	N4 - C27 - C26	121.9(4)	121.2(6)
N2 - C17 - C11	113.7(3)	113.1(6)	N4 - C27 - C21	113.5(4)	114.1(6)
C16 - C17 - C11	123.2(4)	125.0(7)	C26 - C27 - C21	124.5(4)	124.6(6)
N1 - C31 - C32	114.7(5)	114.1(6)	N2 - C41 - C42	112.2(4)	115.7(6)
C33 - C32 - C31	119.1(7)	112.9(6)	C43 - C42 - C41	112.8(4)	117.3(7)
C32 - C33 - C34A	94.8(7)	110.9(6)	C44 - C43 - C42	112.3(4)	116.4(7)
C34B - C33 - C32	157.0(10)		C43 - C44 - C45	114.3(5)	113.3(6)
C35 - C34A - C33	104.5(7)		C46 - C45 - C44	115.4(4)	114.6(6)
C33 - C34B - C35	112.0(10)	114.4(7)	N4 - C46 - C45	117.6(4)	113.9(6)
C34A - C35 - C36	123.1(7)	117.6(7)			
C36 - C35 - C34B	100.0(6)				
N3 - C36 - C35	110.4(4)	115.7(6)			

[a] Numbers in parentheses are errors in the last significant digit(s). See Figure 1 for atom labeling scheme.

is 1.349 (10) Å, where the bridging alkyne binds in a manner analogous to that in 1 and 2. This overall arrangement results in short metal-metal distances of 2.806 (1) and 2.788 (1) Å in 1 and 2, respectively.

The conformation of the macrocycle is saddle-shaped (Figure 2) and similar to that found for the binuclear cupric species [Cu_2(OAc)(OMe)(TC-6,6)].[3] The molecular structure of 1 is virtually identical with that of 2, as expected, with the only difference being the slightly larger value for the metal–metal separation in 1.[20] The disorder found for carbon C34 in one of the hexamethylene linker chains of compound 1 is not uncommon. A similar disorder in the hydrocarbon chains was encountered in the structure of $[Cu_2(OAc)(OMe)(TC\text{-}6,6)]$.[3] The molecular geometries of compounds 3 and 4 are presumed to be similar to those of 1 and 2, on the basis of their spectroscopic properties and chemical composition. Further geometrical information is summarized in Table VI.

Spectroscopic Properties. The (μ-alkyne)dicopper(I) tropocoronands have characteristic solid-state and solution spectra that show an interesting dependence on the nature of the alkyne substituent R. Table III lists the positions (λ_{max}) of some absorption bands in the UV–vis spectra of the binuclear complexes. These absorptions are tentatively assigned as highly allowed ($\epsilon \sim 20\,000$ cm^{-1} M^{-1}) metal-to-ligand charge-transfer (MLCT) bands from Cu(I) to the aminotroponeiminate group and are responsible for the deep burgundy-red color of the compounds. The fact that these optical transitions do not arise from copper(I)-to-alkyne MLCT transitions is underscored by the observation that compounds 5 and 6 are yellow. The band energies of 1–4 shift according to the electron-releasing or electron-withdrawing properties of the substituent R (Table III). Thus, the least energetic absorption bands occur for the most electron-rich 2-butyne adduct, while the electron-withdrawing ester substituents of compounds 1 and 2 stabilize the copper(I) electron-donating orbital, resulting in blue shifts for the MLCT bands.

Compounds 1–4 have sharp well-behaved NMR spectra, consistent with diamagnetism. Apart from resonances arising from the coordinated alkynes, the ^{1}H NMR spectra of these molecules differ from that of the free ligand in that resonances for the α-CH_2 protons, those adjacent to the nitrogen atoms, are split into two multiplets of equal intensity (4 H each). These protons appear as a broad triplet in the free ligand, and their nonequivalence in binuclear compounds 1–4 reflects the more rigid conformation of the metal-bound macrocycle. Protons within the macrocyclic cavity are closer to the copper ions and thus experience a different magnetic environment than those outside the large ring. These α-CH_2 protons are sensitive to the electron density at the metal centers as modulated by the alkyne substituents. Table III reveals that their chemical shifts move to higher field as the electron-releasing ability of the R group increases.

Table I lists the ^{13}C NMR chemical shifts of the tropocoronand carbon atoms in the free ligand and the binuclear complexes. The spectra are well-resolved and consistent with the symmetrical structures of the compounds. Seven resonances are observed for the ligand, four from the tropone rings and three from the hexamethylene linker chains. The alkyne carbons were never observed. Assignments were made on the basis of reference spectra and/or use of well-defined additivity parameters for predicting ^{13}C NMR chemical shifts.[21]

Stability. The bridging alkyne ligands provide a very stable environment for the binuclear copper(I) tropocoronands. All compounds mentioned are stable to air as solids and, in the case of 1 and 2, in solution as well. Benzene solutions of the 2-butyne adduct 4 slowly decompose in the air. A broad weak band in the visible spectrum (λ_{max} = 750 nm) increases its intensity over a few hours, indicating the possible formation of an oxidized complex.

The compounds are generally unreactive. For example, attempts to hydrogenate the C–C multiple bond under very mild conditions (23 °C, 1 atm of H_2) produce no hydrogenated products for 1–4. By contrast, $[Cu_2(PhCO_2)_2(PhC{\equiv}CPh)_2]$, containing terminally bound alkynes, reacts readily with H_2 at atmospheric pressure and room temperature to form 1,2-diphenylethane.[16] The possibility that the complexes may undergo cycloaddition reactions was explored in a study with the hindered alkene norbornylene in toluene at 75 °C. No [2 + 2] adducts were detected from this reaction. No reaction was observed when the same experiment was carried out under a CO atmosphere in an attempt to prepare a cyclopentenone derivative.[22] Finally, the stability of the bimetallic alkyne-bridged complexes was confirmed by the failure of 3 to react with phenyllithium, although one may argue that steric factors could have been important here. Only diphenylacetylene was detected upon quenching the reaction mixture with aqueous acid.

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Registry No. 1, 98876-42-7; 2, 98901-06-5; 3, 98901-08-7; 4, 98901-07-6; $Li_2(TC\text{-}6,6)$, 98876-43-8; $H_2(TC\text{-}6,6)$, 84927-37-7; $[Cu(NCCH_3)_4](BF_4)$, 15418-29-8.

Supplementary Material Available: Tables S1 and S4, heavy-atom thermal parameters and Tables S2 and S5, hydrogen atom positional and thermal parameters for compounds 1 and 2, respectively (4 pages); Tables S3 and S6, observed and calculated structure factors for compounds 1 and 2, respectively (25 pages). Ordering information is given on any current masthead page.

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[20] It is possible to achieve an even shorter metal–metal separation by utilizing the $H_2(TC\text{-}5,5)$ ligand. In an X-ray structural study of the compound $[Cu_2(\mu\text{-}PhC{\equiv}CPh)(TC\text{-}5,5)]$, the Cu···Cu distance was found to be 2.67 Å (Villacorta, G. M.; Whang, E.; Lippard, S. J., unpublished results).

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