

Tropocoronands: a versatile macrocyclic ligand system for mononuclear and binuclear metal complexes

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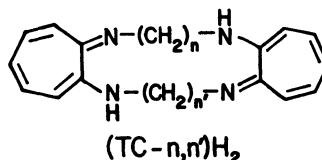
Abstract - Synthetic, structural, and spectroscopic investigations of a series of mononuclear nickel(II) and copper(II) tropocoronand complexes are presented. By varying the length of the chains linking the two halves of the tropocoronand macrocycle it was possible to alter the stereochemistry at the metal center. Specifically, a square-planar to distorted tetrahedral structural transition occurs as the number of methylene groups in the connecting chains increases. The distortion is smooth in the case of copper(II) but discontinuous in the nickel(II) series owing to the additional electronic barrier associated with a change in ground-state spin multiplicity. Binuclear species have also been obtained, including an asymmetrically bridged dicopper(II) complex as well as novel alkyne-bridged dicopper(I) compounds. The linker chain length has also been found to modulate the structural characteristics and chemical properties of a new series of binuclear copper(I) and rhodium(I) carbonyl complexes. The $[\text{Rh}_2(\text{CO})_4(\text{TC}-5,5)]$ compound exists as a resolvable pair of conformational isomers with the metal atoms on either the same or on opposite faces of the macrocycle. X-ray structural data along with the results from proton and carbon-13 NMR experiments are summarized.

INTRODUCTION

Tropocoronands are derived from aminotropeimines, a class of chelating bidentate nitrogen donor ligands with a rich history in transition metal coordination chemistry.¹ Bis(aminotropeiminato)metal complexes of Ni^{2+} , Cu^{2+} , Co^{2+} , Cr^{2+} , Mn^{2+} , and Fe^{2+} are known, with both square planar and tetrahedral metal geometries.² In the case of Ni^{2+} chelates, equilibrium mixtures of the two limiting structures have been characterized by magnetic studies and temperature dependent NMR experiments for a range of N,N' -disubstituted aminotropeimines.³

With bulkier R substituents, the tetrahedral arrangement predominates and is accompanied by a change in ground electronic spin state from $S = 0$ in square planar complexes to $S = 1$ in tetrahedral stereochemistry. The macrocycle framework of the tropocoronands is created by linking two cycloheptatriene units with two linear hydrocarbon chains, each tethered to nitrogen atoms at its ends.⁴

The tropocoronands retain the strong metal-complexing ability of the parent aminotropeimines. Upon complexation with divalent metal ions, the two enamine protons are displaced, leading to neutral mononuclear complexes. As expected, the electroneutrality conveys very good solubility in moderately nonpolar solvents such as toluene, benzene, and chlorinated and ethereal solvents. The synthetic route to the ligands allows for the incorporation of a variety of α,ω -diaminoalkyls, ethers, and sulfides as the linker chains.⁵ In the present article we discuss how variations in the length of the linker chains not only modifies the size of the macrocyclic cavity but also dictates, to a predictable extent, the metal stereochemistry. We also describe reactions of the tropocoronands to form new binuclear copper(I) and rhodium(I) complexes. These latter results considerably expand our earlier efforts⁶ to delineate the chemistry of metal ions in binucleating macrocycles.



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

MONONUCLEAR COMPLEXES

I. Nickel(II) tropocoronands

Addition of an ethanolic solution of nickelous acetate dihydrate to a yellow methylene chloride solution of the tropocoronand ($n,n' = 3,3; 4,4; 4,5; 5,5; 2,0,2; 6,6$) yields, upon workup,

black crystals of the mononuclear nickel(II) complexes.^{4,7} The molecular structures of six nickel(II) tropocoronands Ni(TC-3,3), Ni(TC-4,4), Ni(TC-4,5), Ni(TC-5,5), Ni(TC-2,0,2), and Ni(TC-6,6) were determined by X-ray diffractometry, and magnetic susceptibility measurements were made on solid samples of each complex except for Ni(TC-2,0,2). Varying the length of the linker chains has a pronounced effect on the metal stereochemistry, causing a discontinuous distortion from planar toward tetrahedral geometry with increasing values of n and n' . This distortion is measured by the twist angle, θ , the dihedral angle between the two sets of planes defined by nickel and the two aminotroponoiminate nitrogen atoms. As revealed in Table 1, the geometry about nickel is planar (Fig. 1) or distorted square-planar, with θ values under 30° , for $(n+n') < 9$, but changes abruptly for complexes where $(n+n') > 10$. In these latter compounds, $\theta > 70^\circ$, and the structures are best described as having distorted tetrahedral geometries (Fig. 2).

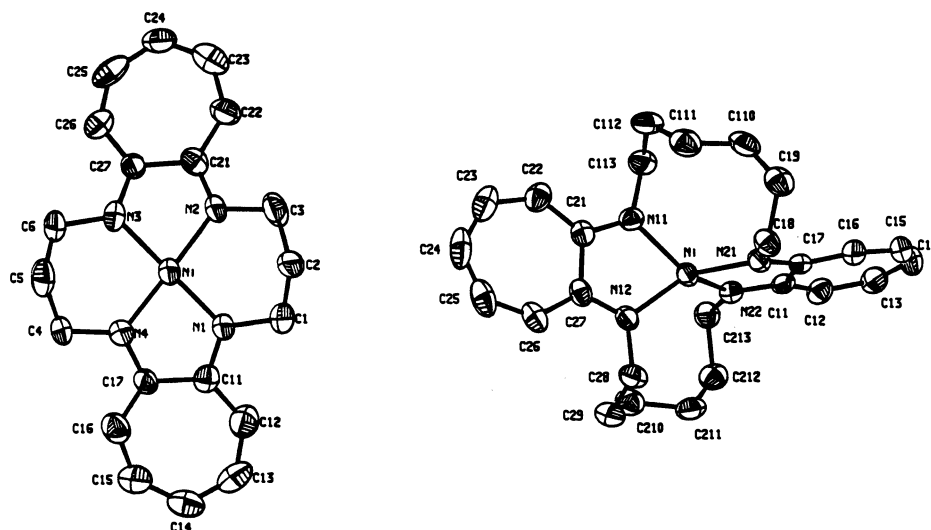


Fig. 1. The structure of [Ni(TC-3,3)]. Fig. 2. The structure of [Ni(TC-6,6)].

The observed change in metal stereochemistry with $(n+n')$ in the nickel(II) tropocoronands is the result of two opposing forces. Firstly, unfavorable steric interactions, including close non-bonding van der Waals contacts, angle bending and torsional strain, occur as the number of methylene groups in the connecting hydrocarbon chain increases. From molecular mechanics (MM-2) calculations we find that these steric interactions become severe when the coordination geometry is constrained to be square-planar as $(n+n')$ increases. Relief of steric strain occurs as the geometry is relaxed toward tetrahedral stereochemistry. Thus expansion of the metal coordination sphere and a steady increase in the intramolecular distance of the C_α and C_ω carbon atoms, the terminal methylene groups in the linker chain (e.g., C1 and C3 in Fig. 1), are manifest in the structures of the series of nickel tropocoronands (see Table 1). The second factor involved in the nickel(II) system is the change in ground-state spin multiplicity in going from a square-planar ($S = 0$) to a tetrahedral ($S = 1$) geometry. The higher energy state with unpaired electronic spins is accessible only when both linker chains contain at least five methylene groups.

TABLE 1. Geometric and magnetic properties of the nickel(II) tropocoronands

Compound	θ , deg	av. M-N distance, Å ^a	C_α - C_ω distance, Å	μ_{eff} , μ_B^b
Ni(TC-3,3)	8.31	1.861(7)	2.54	
Ni(TC-4,4)	28.9	1.883(4)	2.95	
Ni(TC-4,5)	27.1	1.891(22)	2.95, 3.09	
Ni(TC-5,5)	70.1	1.949(2)	4.09	3.18 (1.46)
Ni(TC-2,0,2)	74.5	1.946(16)	4.10	c
Ni(TC-6,6)	85.2	1.951(2)	4.44	3.11 (1.56)

^aStandard deviations are presented in parentheses. ^bValue of μ_{eff} above 80 K; numbers in parentheses are values observed at 8 K. ^cNot determined.

Magnetic data reveal that the first three complexes are diamagnetic in the solid state. The Ni(TC-5,5) and (TC-6,6) compounds, by contrast, are paramagnetic. Temperature dependent magnetic studies of these latter complexes revealed appreciable spin-orbit coupling, a behavior characteristic of pseudotetrahedral nickel(II) complexes having 3T_1 ground terms.⁸

The proton and carbon-13 NMR spectra of the nickel(II) tropocoronands indicate that the magnetic features exhibited in the solid state are maintained in solution. Both Ni(TC-3,3) and Ni(TC-4,4) exhibit resonances within the normal range observed for diamagnetic compounds. The remaining three symmetric ($n=n'$) compounds, on the other hand, show isotropically-shifted spectra with narrow line widths. The temperature dependence of the NMR spectra was markedly different for the two groups. The spectrum of the diamagnetic compound, Ni(TC-4,4), was essentially invariant over a 100°C temperature range whereas the contact shifts displayed by Ni(TC-6,6) diminished significantly with increasing temperature. These results are consistent with the fact that the longer linker chains permit access to both tetrahedral and planar conformations, which are in equilibrium with one another in solution.⁵ This dynamic equilibrium⁹ may also explain why enantiomerically pure crystals of Ni(TC-5,5) and Ni(TC-2,0,2), both of which crystallize in optically active space groups, failed to produce CD spectra upon dissolution. The chirality imparted by the helical twist of the hydrocarbon chains (Fig. 2) cannot be detected in solution where, owing to the accessibility of the planar intermediate, only racemic mixtures occur. The chirality of the molecules is manifest, however, by the observation of distinct resonances for the diastereotopic, and therefore magnetically nonequivalent, protons of the methylene groups attached directly to nitrogen in the Ni(TC-6,6) spectrum.

II. Copper(II) tropocoronands

Unlike the nickel(II) system, where an electronic barrier must be overcome in converting from square-planar to tetrahedral geometry, the d^9 copper(II) ion experiences no such change in spin state. The series of copper(II) tropocoronands therefore provides an especially attractive system for delineating changes in metal coordination geometry as a function of ligand size.¹⁰ The metal complexes Cu(TC-3,3), Cu(TC-4,4), Cu(TC-4,5), and Cu(TC-5,5) were prepared by the same procedure used to synthesize the corresponding nickel complexes. This route failed, however, to provide the desired mononuclear cupric complex of Ni(TC-6,6). Instead, a binuclear species was isolated (see next section). Table 2 lists the crystallographically determined values for the twist angle, θ , along with metal-nitrogen and C α -C ω distances for three copper(II) tropocoronands. As anticipated, the metal geometry converts smoothly from square-planar ($\theta = 0.0^\circ$) to pseudotetrahedral ($\theta = 61.3^\circ$) with an intermediate value of $\theta = 36.6^\circ$ obtained for the Cu(TC-4,4) structure. Interestingly, the Cu-N bonds do not change much (1.94 to 1.96 Å) across the series although the C α -C ω interatomic distance lengthens as in the nickel(II) case.

TABLE 2. Structural features of copper(II) tropocoronand complexes.^a

Compound	θ , deg	M-N, Å	C α -C ω , Å
Cu(TC-3,3)	0.0	1.939(6)	2.60
Cu(TC-4,4)	36.6	1.938(7)	3.06
Cu(TC-5,5)	61.3	1.96(1)	4.00

^aSee footnotes to Table 1.

Magnetic susceptibility measurements reveal that all four copper(II) tropocoronands obey the Curie-Weiss law, with effective magnetic moments in the range of 1.77 - 1.80 μ_B . Some aspects of the optical and ESR spectroscopic properties of these complexes are worth mentioning. A strong correlation exists between the wavelength, λ_{\max} , of the lowest energy d-d transitions and the parameter θ for the four compounds. In particular, a steady decrease in energy is observed with increasing tetrahedral distortion. In the ESR spectrum, the A_{\parallel} hyperfine coupling constants decrease with increasing θ , and a semiquantitative analysis revealed that a decrease in the Fermi contact parameter was largely responsible for the attenuation of A_{\parallel} .¹⁰

BINUCLEAR COMPOUNDS

I. [Cu₂(μ -OAc)(μ -OMe)(TC-6,6)]

Reaction of Cu(OAc)₂·H₂O with H₂(TC-6,6) in methylene chloride/methanol failed to give mononuclear Cu(TC-6,6); instead, binuclear [Cu₂(μ -OAc)(μ -OMe)(TC-6,6)] was isolated.¹¹ MM-2 calculations revealed that expansion of the metal coordination sphere and the lengthening of the interatomic C α -C ω distance that accompanies the change in metal geometry for Cu(TC- n,n')

complexes are insufficient to relieve the steric strain progressively built up with increasing ($n+n'$). In a model calculation for Ni(TC-6,6), relaxing the $C\alpha-C\omega$ distance to 6.9 Å from the observed value of 4.44 Å resulted in additional release of strain energy. The propensity of the hexamethylene linker chain to adopt an extended conformation, combined with the general reluctance of the cupric ion to adopt a tetrahedral geometry, precluded formation of Cu-(TC-6,6) under the conditions employed. It is, however, possible to prepare this complex under carefully controlled aprotic conditions.¹²

The binuclear compound $[Cu_2(\mu-OAc)(\mu-OMe)(TC-6,6)]$ provides a basis for studying the structural features and magnetic properties of asymmetrically-bridged dicopper(II) centers.¹¹ In particular, any relationship between the magnitude and sign of the magnetic exchange coupling constant and the structural parameters found for this and related systems is of value. Dicopper(II) compounds with various bridging groups have been used to model the physical and chemical properties of binuclear copper centers in biology.¹³

Salient features of the structure, illustrated in Fig. 3, include the saddle-shaped conformation of the tropocoronand ligand with the $\{Cu_2(\mu-OAc)(\mu-OMe)\}^{2+}$ moiety situated above the cavity, a tetrahedral twist of 31.4° at the metal centers, and a $Cu\cdots Cu$ distance of 3.100(3) Å. The average $C\alpha-C\omega$ distance was found to be 4.962 Å. A crystallographically imposed mirror plane relates the two aminotroponeiminate halves of the molecule and contains the two carbon atoms of the bridging acetate and both the non-hydrogen atoms of the μ -methoxide ligand.

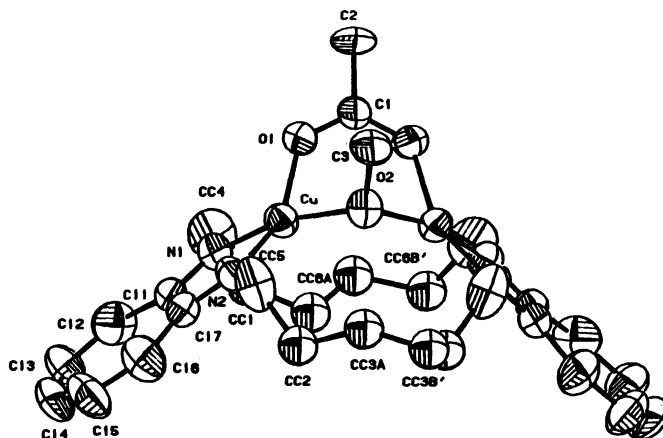


Fig. 3. The structure of $[Cu_2(\mu-OAc)(\mu-OMe)(TC-6,6)]$.

Values of $J = -35.4(1) \text{ cm}^{-1}$ and $g = 2.012$, where the spin-exchange Hamiltonian is defined as $H' = -2JS_1 \cdot S_2$, were obtained from temperature-dependent molar susceptibility data. At least three other examples of structurally and magnetically characterized compounds with the $\{Cu_2(\mu-OAc)(\mu-OR)\}^{2+}$ fragment showed either ferromagnetic or antiferromagnetic behavior.¹⁴⁻¹⁶ A careful examination of all four molecules provided no obvious relationship between the coupling constants and any one or combination of structural parameters. A frozen-solution ESR spectrum displayed features typical of moderately antiferromagnetically coupled, bridged dicopper(II) species including a low-field $\Delta M = \pm 2$ transition at ca 1500 G and $\Delta M = \pm 1$ transitions between 2 and 4 kG.

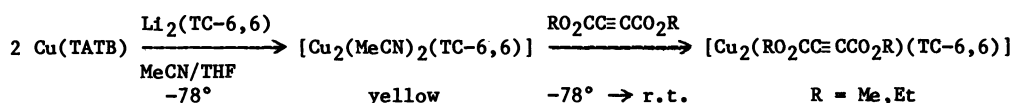
II. $[Cu_2(\mu-RC\equiv CR)(TC-n,n')]$

Having demonstrated the ability of $H_2(TC-6,6)$ to form binuclear cupric complexes, we were interested to explore the chemistry of dicopper(I) analogs.¹⁷ Binuclear cuprous species are few in number and only recently have several well-characterized compounds been reported.¹⁸ We were especially interested to learn whether these complexes would bind small molecules such as CO, H_2 , CO_2 , alkynes, and olefins. We also sought examples of well-documented transformations, either stoichiometric or catalytic, mediated by bimetallic species.

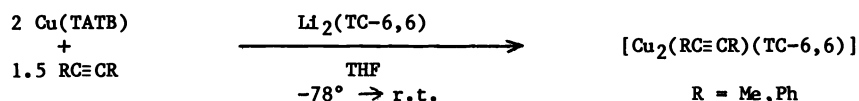
Two methods employed to synthesize alkyne-bridged dicopper(I) tropocoronand complexes from $[Cu(NCCH_3)_4](BF_4)$, Cu(TATB), are outlined in Scheme 1 on the next page. The first involves generation of an intermediate acetonitrile adduct, formulated as $[Cu_2(CH_3CN)_2(TC-6,6)]$, to which is added 1.0 equiv of a dialkylacetylene dicarboxylate. Reaction of the alkyne is accompanied by a dramatic change in the color of the reaction mixture from yellow to burgundy. This sequence was adopted to establish the utility of the acetonitrile adduct and to prevent the possible reaction of the lithium amide with the alkyne ester functionalities. In the second method, employed for the 2-butyne and diphenylacetylene copper complexes, $Li_2(TC-6,6)$ was added to a cooled mixture of the Cu(TATB) and a slight excess of alkyne in tetrahydrofuran solvent. The resulting product mixtures were recrystallized from toluene/pentane to afford analytically pure crystals.

Scheme 1

Method 1.



Method 2.



The alkyne-bridged dicopper(I) tropocoronands are the first examples of discrete, neutral molecules containing the $\{\text{Cu}_2(\mu\text{-RC}\equiv\text{CR})\}^{2+}$ moiety. Previously, only terminally coordinated alkynes and oligomeric acetylide species were known.¹⁹ Symmetrically disubstituted alkynes, $\text{RC}\equiv\text{CR}$, with R = CO_2Me , CO_2Et , Ph, and CH_3 , bridge the two d^{10} metal ions forming unusually stable compounds. All four compounds are unreactive to air in the solid state and, in the case of the diester-substituted alkyne complexes, in solution as well. These neutral compounds are very soluble in most nonpolar aprotic solvents and are easily recrystallized from toluene/pentane solvent mixtures.

The X-ray crystal structure of $[\text{Cu}_2(\mu\text{-EtO}_2\text{CC}\equiv\text{CCO}_2\text{Et})(\text{TC-6,6})]$ (Fig. 4) is comprised of symmetrical molecules in which the alkyne is perpendicular to the $\text{Cu}\cdots\text{Cu}$ vector with an average Cu-C bond distance of 1.948 Å. The copper atoms each have 16 valence electrons if the alkyne

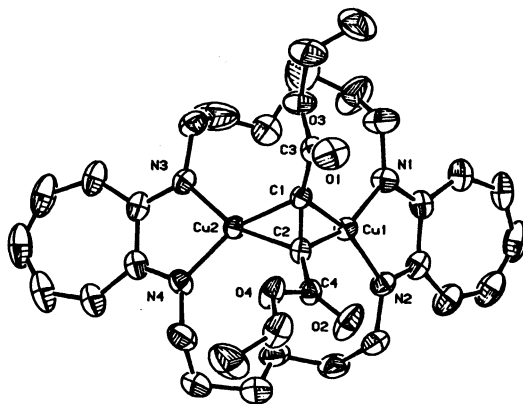


Fig. 4. The structure of $[\text{Cu}_2(\mu\text{-EtO}_2\text{CC}\equiv\text{CCO}_2\text{Et})(\text{TC-6,6})]$.

formally donates $2e^-$ to each metal center. Reduction in the bond order of the alkyne is evidenced by an elongated (1.320(6) Å) C-C separation. Each metal atom has a trigonal coordination geometry with a small aminotroponimine bite angle of 84° . The conformation of the tropocoronand ligand is essentially the same as that found for the binuclear cupric species (Fig. 3) and is saddle-shaped. The bridging alkyne unit produces a short 2.806(1) Å metal-metal distance, however. The average $\text{C}_\alpha\text{-Cu}$ distance of 4.879 Å is longer than that found for the $\text{Ni}(\text{TC-6,6})$ but slightly less than in $[\text{Cu}_2(\mu\text{-OAc})(\mu\text{-OMe})(\text{TC-6,6})]$. Binuclear alkyne-bridged compounds can also be prepared from the ligands $\text{H}_2(\text{TC-5,5})$ and $\text{H}_2(\text{TC-7,7})$. A structural study of $[\text{Cu}_2(\mu\text{-PhC}\equiv\text{CPh})(\text{TC-5,5})]$ reveals a very short M-M distance of 2.67 Å, as expected from the shorter linker chains.

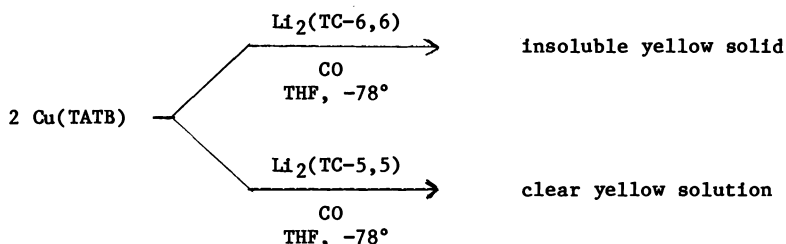
The identity of the R group has a marked effect on the spectroscopic properties of the alkyne-bridged dicopper(I) tropocoronand complexes, which vary in color from yellow to red. Well resolved ^1H and ^{13}C NMR spectra have also been obtained. Resonances for the eight methylene protons adjacent to the four nitrogen atoms, which appear as simple triplets in the NMR of the free ligand, are nonequivalent in the rigid binuclear complexes. Protons within the cavity of the macrocycle and closer to the metal centers resonate at a frequency different from those situated outside the ring. Following the pattern found in the optical spectra, the chemical shift values of these multiplets change with R in a manner which is consistent with the electron-withdrawing properties of the substituents. The highly symmetric nature of the complexes is reflected in their simple, well-resolved ^{13}C NMR spectra. Seven resonances are observed

for the macrocycle, four from the seven-membered ring and three from the connecting chain carbon atoms. The acetylenic carbon resonances were never detected for any of the complexes, possibly because of long relaxation times and/or quadrupolar broadening.

III. $[\text{Cu}_2(\text{CO})_2(\text{TC}-n,n')]$

Examples of stable copper carbonyl complexes are rare.²⁰ Investigations of the chemistry of the copper(I) tropocoronands revealed that CO is readily incorporated to form fairly stable adducts. Scheme 2 depicts a reaction sequence that produced two such complexes. At present,

Scheme 2



the reason for the dramatic difference in solubility between the TC-6,6 and TC-5,5 derivatives is unknown. From their infrared spectra, which both have a terminal CO stretch at 2070 cm^{-1} , the two products appear to be very similar in structure. A striking difference in solubility is also observed for $[\text{Cu}_2(\text{MeCN})_2(\text{TC}-6,6)]$ (yellow solid in THF) and $[\text{Cu}_2(\text{MeCN})_2(\text{TC}-5,5)]$ (yellow solution).¹²

Orange crystals of $[\text{Cu}_2(\text{CO})_2(\text{TC}-5,5)]$, grown from toluene/pentane solutions, are stable in the air over months but their solutions decompose quickly with the formation of an insoluble precipitate upon exposure to oxygen. The structure obtained in an X-ray diffraction study is shown in Fig. 5. Two copper(I) atoms, coordinated in a trigonal fashion, are 4.13 Å apart. Unlike the alkyne-bridged structures, the copper ions each bind a molecule of CO, situated on opposite sides of the macrocycle. An attempt to prepare a CO-bridged complex, analogous to $[\text{Cu}_2(\text{tmen})_2(\mu\text{-CO})(\mu\text{-PhCO}_2)]^+$,^{18g} where tmen = N,N,N',N'-tetramethylethylenediamine, by irradiation of a 2-methyltetrahydrofuran solution of the complex with a Pyrex-filtered medium-pressure mercury lamp, failed as revealed by FTIR studies over the temperature range $113 < T < 300 \text{ K}$. Heating the compound either as a solid or in THF solution results in loss of CO and formation of the mononuclear complex, $[\text{Cu}(\text{TC}-5,5)]$. It is interesting to note that these binuclear copper(I) tropocoronands give bridging alkyne and terminal CO derivatives whereas the dicopper(I) benzoates^{18g,19b} afford terminal alkynes and bridging CO's. In the presence of $\text{RO}_2\text{CC}\equiv\text{CCO}_2\text{R}$, the copper carbonyl tropocoronands, including the insoluble "6,6" adduct, release CO to form the alkyne-bridged complexes. The substitution reaction with 2-butyne, however, produces mononuclear cupric species along with the alkyne-bridged compound.

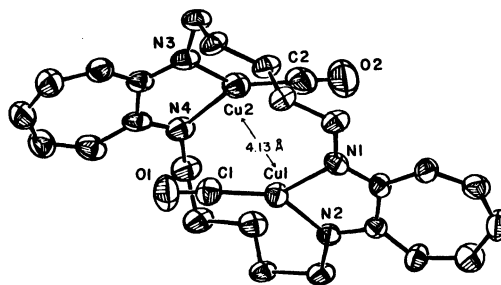


Fig. 5. The structure of $[\text{Cu}_2(\text{CO})_2(\text{TC}-5,5)]$.

Proton NMR studies of $[\text{Cu}_2(\text{CO})_2(\text{TC}-5,5)]$ in benzene- d_6 reveal the existence of a small amount of a second compound, possibly the stereoisomer where the metal atoms are on the same side of the macrocyclic ring. This kind of stereoisomerism has been found to occur for the rhodium(I) complexes described in the following section.

IV. $[\text{Rh}_2(\text{CO})_4(\text{TC}-n,n')]$

Bimetallic carbonyl complexes with a greater thermal stability than displayed by the copper(I) compounds were obtained in studies with rhodium(I). Soluble complexes were obtained upon reaction of $[\text{Rh}_2(\text{CO})_4\text{Cl}_2]$ with either $\text{Li}_2(\text{TC}-6,6)$ or $\text{Li}_2(\text{TC}-5,5)$ under a CO atmosphere.¹² The ^{13}C NMR spectra of the product mixtures revealed a more complex pattern than in any of the previous reactions with the tropocoronands. Instead of the usual seven carbon-13 NMR resonances, fourteen were observed. At first, it was unclear whether the product was less symmet-

ric or whether a mixture of two compounds was present. The infrared spectra showed CO stretching frequencies that differed little from those of the starting rhodium dimer, suggesting the occurrence of a square-planar rhodium(I) dicarbonyl fragment. The products obtained from the reaction of $\text{Li}_2(\text{TC}-5,5)$ were more soluble than those obtained from the reaction of $\text{Li}_2(\text{TC}-6,6)$, following the now familiar pattern of solubility differences between complexes of these pairs of tropocoronand ligands. By taking advantage of differences in solubility of the TC-5,5 derivatives in toluene, it was possible to separate and purify two isomers, designated syn and anti (see below), of $[\text{Rh}_2(\text{CO})_4(\text{TC}-5,5)]$.

The individual compounds displayed greatly simplified NMR spectra, assigned to the anti and syn forms of $[\text{Rh}_2(\text{CO})_4(\text{TC}-5,5)]$. Specifically, in the spectrum of only one of the isomers there appeared a complex but symmetrical multiplet centered at δ 2.69 which integrated to two protons. This region of the spectrum is ordinarily too far downfield for saturated methylene protons and is normally associated with protons alpha to carbonyl or unsaturated functionalities. In a transition metal complex possessing high symmetry, the only protons that could possibly give rise to such an anomalous resonance would be those two positioned within the macrocyclic cavity, and hence closest to the metal ions. These resonances were therefore assigned to the two protons attached to the central methylene carbon atoms in the middle of the two linker chains of syn- $[\text{Rh}_2(\text{CO})_4(\text{TC}-5,5)]$ (Fig. 7). The anomalous downfield resonance appears to be characteristic of binuclear tropocoronand complexes possessing five carbon atoms in the linker chains and having the metal ions located on the same face of the macrocycle. Support for this hypothesis comes from the proton NMR spectrum of $[\text{Cu}_2(\mu\text{-PhC}\equiv\text{CPh})-(\text{TC}-5,5)]$, in which a complex multiplet at δ 2.42 corresponding to two protons is observed.¹²

The foregoing analysis was eventually confirmed when suitable crystals of the anti and syn isomers of $[\text{Rh}_2(\text{CO})_4(\text{TC}-5,5)]$ were obtained and the structures solved by X-ray diffraction methods. Figures 6 and 7 display the structures of the two compounds, both of which are comprised of two square-planar rhodium(I) atoms each bound to two nitrogens of the aminotropone-iminate group and two carbon monoxide molecules. The metal atoms of the anti isomer are situated on opposite faces of the tropocoronand at a distance 5.89 Å from one another whereas, in the syn isomer, the metals are only 4.39 Å apart. Two other structurally characterized dirhodium tetracarbonyl macrocyclic compounds are known, one employing a porphyrin derivative that has the metals on opposite sides of the ligand plane,²¹ and the other using an imine-enaminate tetraaza macrocycle that holds the metals in a syn relationship.²² The present work, however, reveals that molecular isomerism can be induced in a single bimetallic macrocyclic system by the stereochemical consequences of ligand conformation.

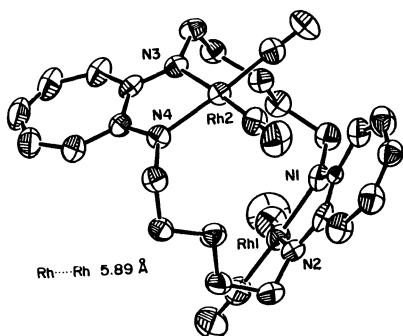


Fig. 6. The structure of anti- $[\text{Rh}_2(\text{CO})_4(\text{TC}-5,5)]$.

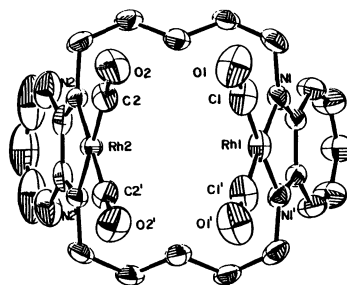


Fig. 7. The structure of syn- $[\text{Rh}_2(\text{CO})_4(\text{TC}-5,5)]$.

The separated isomers, originally present in approximately 1:1 ratio, retain their configurational integrity in solution at ambient temperature. Experiments are currently underway to determine whether it is possible to interconvert the two isomers and to discover any differences in their behavior. Presently, we know that both compounds are resistant to air oxidation even in solution. A mixture of isomers also showed good thermal stability when heated to 200 °C in the solid state, displaying only a moderate decrease in the intensity of the infrared CO absorption band.

CONCLUDING REMARKS

A rich variety of compounds has been derived from the complexation of transition metal ions with the tropocoronand macrocycles. Both mono- and binuclear metal complexes are now avail-

able with physical, stereochemical, and spectroscopic properties that are dictated, to a large extent, by the identity of the tropocoronand ligand employed. The number and scope of small molecules bound to the bimetallic centers and the chemical properties and reactivity of the known metal complexes are the subjects of current investigations. The ability to control the metal stereochemistry and size of the substrate binding cavity by judicious choice of the length and composition of the linker chains should help in our continuing efforts to identify unusual chemical reactivity in these systems.

Acknowledgement

This work was supported by grants from the National Science Foundation (NSF-CHE-8542205) and the National Institute of General Medical Sciences (GM-32134).

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