at 2048 cm^{-1} and a weak ν(C—S) stretch at 760 cm^{-1} in its IR spectrum, characteristic of ionic thiocyanate.[2,25]

The blue and yellow isomers **4** and **5** are readily interconvertible in a fashion very similar to that observed by Busch et al.[28] between [Ni(*ms-trans*-[14]dieneN$_4$)(NCS)$_2$] (also prepared in chloroform as a metastable solid) and [Ni(*ms-trans*-[14]dieneN$_4$)](NCS)$_2$.

Butanediamine–Acetone Reaction. Attempts to prepare the [18]dieneN$_4$ macrocycle by reacting 1,4-butanediamine with acetone were unsuccessful. When 1,4-butanediamine and acetone were reacted at room temperature, the solution turned dark brown after 1 week and only tarry aldol condensation products were isolated. The same reaction at 0 °C also yielded no crystalline products even after 2 weeks of reaction. When copper(II) perchlorate hexahydrate in methanol was added to a reaction mixture 4 days aged at 25 °C, only bis(1,4-butanediamine)copper(II) perchlorate could be isolated.

Reactivity of Macrocyclic Complexes. The [18]diene macrocylic complexes are generally less resistant to acid- and base-catalyzed hydrolysis than are the [16]diene analogues and much less resistant than the [14]diene complexes of nickel(II) and copper(II). The [Cu(*cis*-[18]dieneN$_4$)]$^{2+}$ ion has greater resistance to nucleophilic attack by water than the [Cu(*trans*-[18]dieneN$_4$)]$^{2+}$. Attempts to reduce the imino group double bonds in [Cu(*trans*-[18]dieneN$_4$)](ClO$_4$)$_2$, in [Ni(*trans*-[18]dieneN$_4$)](ClO$_4$)$_2$, or in the free ligand bis(hydroperchlorate) salt[20] by using BH$_4^-$ or H$_2$ with Pd/charcoal catalyst in anhydrous methanol solvent resulted in the breakdown of the macrocycle to 1,4-butanediamine. Reduction of the Cu^{II}(*cis*-[18]diene) complex is presently being investigated.

Conclusions

The preparation of copper(II) and nickel(II) complexes of novel 18-membered macrocycles by the template reaction of 1,4-butanediamine indicates that large-ring macrocycles can be synthesized by reaction of acetone with α,ω-diamine complexes. We are currently working on the extension of this preparative method to larger macrocycles which may exhibit further interesting effects on the coordination geometry of their metal chelates and about copper(II) in particular.

The chemistry of the [18]diene complexes described in this paper involves interesting cases of isomerism. Similarities of these complexes to the well-known [14]diene analogues have been observed, but also significant differences have been noted, the most important of which is the large tetrahedral distortion observed for the Cu^{II}(*cis*-[18]diene) complex.[12] Studies are under way to determine the factors causing tetrahedral distortions in copper(II) macrocyclic complexes.

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Registry No. **3**, 73531-91-6; **4**, 73544-67-9; **5**, 73557-34-3; H$_2$-(*trans*-[18]dieneN$_4$)(ClO$_4$)$_2$, 73531-93-8; 1,4-diaminobutane, 110-60-1; acetone, 67-64-1; [Cu(*cis*-[18]dieneN$_4$)](ClO$_4$)$_2$, 73429-78-4; [Cu-(*trans*-[18]dieneN$_4$)](ClO$_4$)$_2$, 72765-21-0; bis(1,4-butanediamine)-copper(II) diperchlorate, 73429-80-8; [Ni([18]dieneN$_4$)](ClO$_4$)$_2$, 73544-68-0.

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Crystal and Molecular Structures of Complexes of Two Isomeric 18-Membered Tetraaza Macrocylic Ligands Having the Empirical Formula [CuC$_{20}$H$_{40}$N$_4$](ClO$_4$)$_2$. Effects of Chelate Ring Size and Double-Bond Placement on Coordination Geometry about Copper(II)

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Crystal and molecular structures are reported for two isomeric compounds, {[5*S*(*R*),10*R*(*S*)]-2,4,4,11,11,13-hexamethyl-1,5,10,14-tetraazacyclooctadeca-1,13-diene}copper(II) perchlorate, [Cu(*cis*-[18]dieneN$_4$)](ClO$_4$)$_2$, I, and {[5*R*-(*S*),14*R*(*S*)]-2,4,4,11,13,13-hexamethyl-1,5,10,14-tetraazacyclooctadeca-1,10-diene}copper(II) perchlorate, [Cu(*trans*-[18]dieneN$_4$)](ClO$_4$)$_2$, II, having the empirical formula [CuC$_{20}$H$_{40}$N$_4$](ClO$_4$)$_2$. This is the first reported structural characterization of an 18-membered tetraazamacrocyclic ligand complex and only the second structural characterization of cis/trans isomerism in tetraazamacrocyclic complexes. Compound I forms purple monoclinic crystals, space group *C*2/*c* (No. 15): $a = 29.132$ (16), $b = 14.021$ (8), $c = 14.838$ (9) Å; $\beta = 113.89°$; $Z = 8$; $D_{\text{calcd}} = 1.44$, $D_{\text{obsd}} = 1.45$ (2) g/cm^3. The nitrogens coordinate copper(II) in a pseudotetrahedral manner, with a dihedral angle of 36.6° between the N(1)CuN(2) and N(3)CuN(4) planes. Compound II forms orange-red orthorhombic crystals, space group *P*2$_1$2$_1$2 (No. 18): $a = 14.720$ (2), $b = 12.308$ (2), $c = 7.982$ (1) Å; $Z = 2$; $D_{\text{calcd}} = 1.38$, $D_{\text{obsd}} = 1.39$ (2) g/cm^3. The tetrahedral distortion in this complex is rather small, with a dihedral angle between the N(1)CuN(2) and N(1)′CuN(2)′ planes of 11.5°. The extent of tetrahedral distortion about Cu(II) and the amount of strain in the macrocyclic ligand (as determined by deviation of bond angles and torsional angles from ideal values) depend on both the chelate ring size and the C–N double-bond placement. It appears that a variety of tetrahedral distortions about Cu(II) may be obtained if these features of the ligand are modified.

Introduction

The chemistry of 14-membered tetraaza macrocycles has been studied extensively in the recent past.[2-8] These compounds are useful ligands for complexing metal ions and are interesting organic compounds as well. Complexes of tetraaza

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Table I. Crystallographic Data

compd	$[Cu(cis\text{-}[18]\text{-}dieneN_4)](ClO_4)_2$	$[Cu(trans\text{-}[18]\text{-}dieneN_4)](ClO_4)_2$
space group	$C2/c$ (monoclinic)	$P2_12_12$ (orthorhombic)
space group no.	15	18
a, Å	29.081 (4)	14.720 (2)
b, Å	14.013 (3)	12.308 (2)
c, Å	14.862 (2)	7.982 (1)
β, deg	113.95	
V, Å^3	5535 (3)	1446.1 (6)
D_{calcd}, g/cm^3	1.44	1.38
D_{obsd}, g/cm^3	1.45 (2)	1.39 (2)

macrocycles with larger ring sizes would be expected to exhibit interesting steric and geometric properties. It is quite surprising, then, that tetraaza macrocycles with more than 14 atoms in the ring have been reported in only a few instances.[9,10] This may be due in part to the conviction that complex formation by larger ring analogues would be too weak to allow their formation by template condensation. Nontemplate methods have not appeared to offer much hope of providing these macrocycles, since attempts to make the 16-membered macrocycle 2,4,4,10,12,12-hexamethyl-1,5,9,13-tetraazacyclohexadeca-1,9-diene have resulted only in the formation of a tarry product,[11] probably the result of an aldol condensation. Recently, however, we have shown that 18-membered tetraaza macrocyclic complexes may be prepared with relative ease by reacting bis(1,4-diaminobutane)copper(II) perchlorate with acetone at 5 °C.[12] The reaction yields an orange-red and a purple crystalline product, both with the empirical formula $[CuC_{20}H_{40}N_4](ClO_4)_2$. The orange-red compound may also be formed by nontemplate methods[13] which are reported elsewhere.[12]

The crystal and molecular structures of the compounds were undertaken in order to demonstrate their macrocyclic nature and identify the isomerism responsible for their difference in color. The structures also provide interesting information on the steric and geometrical properties of these unique compounds. Single-crystal X-ray analysis of the compound $[NiC_{20}H_{40}N_4](NCS)_2$, prepared by addition of sodium thiocyanate to an aqueous solution of the perchlorate salt formed by template condensation of acetone with bis(1,4-diaminobutane)nickel(II) perchlorate, was also attempted.

Experimental Section

Preparation of the Complexes. The preparation of the compounds identified above has been described elsewhere.[12] Orange-red crystals of $[Cu(trans\text{-}[18]dieneN_4)](ClO_4)_2$ were grown slowly from a methanol solution. A crystal with the approximate dimensions 0.28 × 0.28 × 0.27 cm^3 was selected for X-ray analysis. Deep purple crystals of $[Cu(cis\text{-}[18]dieneN_4)](ClO_4)_2$ were grown from a methanol–ethanol solution. These crystals had a tabloid shape. The crystals selected for analysis had the approximate dimensions 0.40 × 0.36 × 0.12 cm^3. The preparation of $[NiC_{20}H_{40}N_4)](NCS)_2$ has also been described elsewhere.[12] Crystals were grown by slow evaporation of an aqueous solution.

Data Collection. The crystal of $[Cu(cis\text{-}[18]dieneN_4)](ClO_4)_2$ was mounted on a CAD-4 automated diffractometer. Unit cell dimensions were determined from a least-squares treatment of 25 reflections obtained at medium and high Bragg angles by using graphite-monochromated Mo Kα_1 (λ = 0.709 30 Å) radiation (see Table I). Intensity data were collected by the θ–2θ scan method. Scanning speeds ranged from approximately 20°/min for the most intense reflections to approximately 2°/min for the weakest. The angular scan width was $A + 0.347$ ($\tan \theta_{\lambda\alpha_2}$), where $\theta_{\lambda\alpha_2}$ is determined from the formula

$$\theta_{\lambda\theta_2} = \theta_{\lambda\alpha_1} + \frac{\lambda\alpha_2 - \lambda\alpha_1}{\lambda\alpha_1}\left(\frac{360}{2\pi}\right) \tan \theta_{\lambda\alpha_1}$$

and A depends on the crystal mosaic spread and on the divergence of the primary beam. A for this structure was 0.85. The scan was extended on each side of the peak by 25% for background determination. Reflections were collected over the range $3° < \theta < 22.5°$. Three standard reflections scanned approximately every 200 reflections were used to place the intensity data on a common scale; systematic variation in these standards was not observed. Reflection intensities were calculated from peak and background measurements as $I = S(C - RB)$ where S = scan rate, C = total integrated peak count, B = total background count, and R = the ratio of the scan time for the peak to the scan time for the background. The estimated error was calculated as $\sigma(I) = [S^2(C + R^2B) + pI^2]^{1/2}$. The value of p was varied to test its effect on refinement. The optimum value of p was determined to be 0.05. Of 3790 unique reflections originally scanned including systematically absent ones, 2477 with $I > 3\sigma(I)$ were used in the solution and refinement of the structure. The intensities and $\sigma(I)$ values were corrected for Lorentz and double polarization effects.[14] Neutral atom scattering factors were used, and the metal atom was corrected for anomalous dispersion (both real and imaginary). Corrections for absorption were unnecessary because of the low absorption coefficient, μ = 10.6 cm^{-1}. The space group was determined to be $C2/c$ on the basis of the systematic absences (hkl, $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$) and statistical data (N[z] test) indicating centrosymmetry.[14] Attempts to solve the structure in Cc and in $C2$ were unsuccessful.

The $[Cu(trans\text{-}[18]dieneN_4)](ClO_4)_2$ crystal was mounted on a Syntex P$\bar{1}$ diffractometer. The monochromator and tube mount were in the equatorial (parallel, antiparallel) mode. Data were collected in the bisection position by using a θ–2θ scanning technique. The range was $3° < \theta < 22.5°$. Of the 949 reflections originally collected, 863 with intensities greater than 3σ were used in the refinement. The equations and corrections were the same as those used for $[Cu(cis\text{-}[18]dieneN_4)](ClO_4)_2$ except that $p = 0.08$ on this instrument. The data were not corrected for absorption (μ = 10.2 cm^{-1}). From the systematic absences ($h00$, $h = 2n + 1$, and $0k0$, $k = 2n + 1$) the space group was uniquely determined to be $P2_12_12$.

Structure Solution and Refinement. In each case, Cu atom positions were determined by Patterson methods using three-dimensional maps, and the remaining nonhydrogen atoms positions were determined by difference Fourier methods. These atoms were refined anisotropically. Hydrogen atom positions were calculated from geometric considerations. They were then included as a fixed contribution in the final stages of refinement. The inclusion was justified in each structure by a significant improvement in the R index. Recalculation of the hydrogen positions followed by refinement was continued until no further improvement in the residual was achieved. R values were calculated as $R_F = [\sum||F_o| - |F_c||)/\sum|F_o|$ and $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$. Reflections were weighted as $w = 1/\sigma^2(F_o) = 4F_o{}^2/[\sigma(F_o{}^2)]^2$ where $\sigma(F_o)^2 = [\sigma^2(I) + (pI)^2]^{1/2}Lp$. The function minimized was $\sum w(|F_o| - |F_c|)^2$.[14]

The $[Cu(cis\text{-}[18]dieneN_4)](ClO_4)_2$ structure converged at R_F = 0.084 and R_{wF} = 0.107. These values are rather high because of extremely large thermal motion in the perchlorate anions (see Table VII). The $[Cu(trans\text{-}[18]dieneN_4)](ClO_4)_2$ structure converged at R_F = 0.064 and R_{wF} = 0.090. No disorder was observed in the perchlorate anions of this structure, and the final difference map was featureless. Both enantiomorphs were refined.

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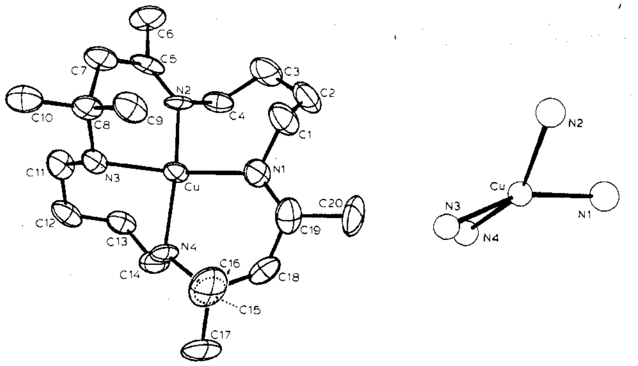

Figure 1. A perspective view of the macrocyclic complex [Cu(*cis*-[18]dieneN$_4$)]$^{2+}$ (left) together with the numbering scheme used in the tables and the pseudotetrahedral distortion about Cu(II) (right). Double bonds are between N(1) and C(19) and between N(2) and C(5).

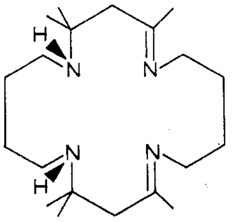

Figure 2. Illustration of the N-meso configuration present in the free *cis*-[18]dieneN$_4$ macrocyclic ligand.

Results

[Cu(*cis*-[18]dieneN$_4$)](ClO$_4$)$_2$. Positional and thermal parameters for all atoms in the structure are given in Table II. As Figure 1 shows, the macrocyclic ligand adopts a geometry about Cu(II) which is intermediate between square-planar and tetrahedral coordination. The N(1)CuN(2) plane and the N(3)CuN(4) plane intersect with a dihedral angle of 36.6°. Since 14-membered tetraaza macrocycles normally adopt a square-planar geometry,[2] it is most reasonable to consider this structure to be a tetrahedrally distorted square-planar complex.

The N–H bonds project from the side of the mean plane of the coordination sphere, such that the free macrocyclic ligand would have the N-meso configuration (Figure 2). The six-membered chelate rings have conformations intermediate between boat and half-chair forms. The four-carbon bridges and their associated nitrogen atoms form crescent-shaped chelate rings. These rings curve away from the mean plane of the coordination sphere in one direction, while the six-membered rings curve away in the opposite direction. The overall effect is a saddle shape which is skewed by tetrahedral distortion.

Approach to the metal ion on one side (the bottom side in Figure 1) is sterically hindered by carbon atoms of the seven-membered chelate rings (principally C(4) and C(13)). Approach from the other side is moderately hindered by methyl carbons.

A stereoview of the unit cell is provided in Figure 3. There are no features that require special comment. Table III contains bond distances and bond angles of interest. Torsion angles for the complex are given in Figure 4; their significance is discussed elsewhere.

[Cu(*trans*-[18]dieneN$_4$)](ClO$_4$)$_2$. Positional and thermal parameters for the atoms in this structure are given in Table IV. The geometry about Cu(II) is much closer to square planar, the dihedral angle between the N(1)CuN(2) and N(1)′CuN(2)′ planes being only 11.5°. Table V compares the mean planes through the nitrogen atoms for the cis and trans structures and the positions of the copper atoms with respect to these planes. The copper atom is on a special position and the two sides of the macrocyclic complex are related by a twofold rotation axis (see Figure 5).

The macrocyclic complex has the N-racemic configuration of the macrocyclic ligand. The N–H bonds thus project toward the same side of the mean plane of the coordination sphere. This complex also resembles a saddle, with carbon atoms from the two seven-membered chelate rings projecting downward and carbon atoms from the two six-membered chelate rings projecting upward. The metal ion is thus inside a cavity ~1.3 Å deep on each side.

This complex seems generally to have fewer steric problems than the cis complex. The six-membered rings form very definite half-boats, and the seven-membered rings have the same general shape as observed for the cis complex. Table VI contains bond distances and bond angles for this complex. A stereoview of the unit cell is provided in Figure 6. Torsion angles are given in Figure 7. It should be noted that the data/parameter ratio for this structure is low (5). This may result in a certain amount of inaccuracy in the structure.

Discussion

Bond Length and Angle Strain. The cis macrocycle adopts a rather contorted conformation in order to minimize angular, torsional, and bond length strain within the molecule and in the coordination sphere. The distorted tetrahedral geometry about copper(II) is the most apparent feature, but the large variation in the "bite angles" of the chelate rings is also of interest. The two six-membered rings have bite angles, N(1)CuN(4) and N(2)CuN(3) of 97.5° and 90.7°, respectively, compared to a 92° bite angle in the six-membered rings of the

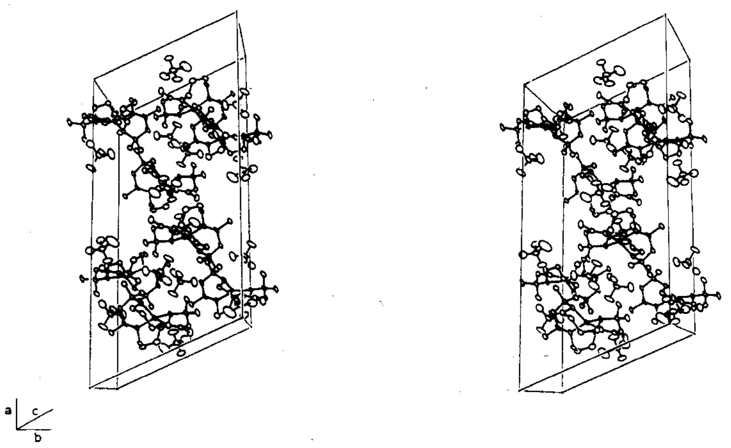

Figure 3. Stereo diagram of one unit cell of [Cu(*cis*-[18]dieneN$_4$)](ClO$_4$)$_2$ showing the packing of the complex cations and perchlorate anions.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations in [Cu(*cis*-[18]dieneN$_4$)](ClO$_4$)$_2$[a]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Cu	0.13944 (4)	0.22464 (9)	0.10851 (7)	0.00136 (1)	0.00276 (6)	0.00260 (5)	0.00013 (6)	0.00266 (4)	0.0001 (1)
Cl(1)	0.4476 (1)	0.2474 (2)	0.4770 (3)	0.00152 (4)	0.0062 (2)	0.0115 (2)	0.0009 (2)	0.0048 (1)	0.0058 (3)
Cl(2)	0.7393 (1)	0.0148 (2)	0.4648 (2)	0.00267 (4)	0.0051 (2)	0.0070 (1)	−0.0003 (2)	0.0064 (1)	0.0018 (3)
O(11)	0.4026 (3)	0.2879 (8)	0.4434 (9)	0.0018 (1)	0.0124 (9)	0.0202 (9)	0.0010 (6)	0.0069 (5)	0.0107 (15)
O(12)	0.4860 (4)	0.3102 (10)	0.4999 (9)	0.0017 (2)	0.0175 (11)	0.0149 (9)	−0.0028 (7)	0.0038 (6)	0.0040 (17)
O(13)	0.4528 (4)	0.1814 (9)	0.5482 (9)	0.0040 (2)	0.0140 (8)	0.0200 (8)	0.0056 (8)	0.0104 (6)	0.0246 (12)
O(14)	0.4496 (6)	0.1953 (11)	0.3934 (12)	0.0094 (4)	0.0134 (12)	0.0320 (13)	−0.0065 (11)	0.0262 (9)	−0.0147 (21)
O(21)	0.7078 (3)	0.0140 (8)	0.5159 (6)	0.0045 (1)	0.0102 (8)	0.0193 (5)	−0.0023 (6)	0.0161 (3)	0.0012 (11)
O(22)	0.2828 (4)	0.0220 (8)	0.6310 (7)	0.0053 (2)	0.0111 (8)	0.0085 (6)	−0.0068 (8)	0.0070 (6)	−0.0071 (12)
O(23)	0.7559 (3)	0.1078 (7)	0.4598 (6)	0.0038 (1)	0.0063 (6)	0.0102 (5)	−0.0040 (5)	0.0096 (3)	−0.0028 (9)
O(24)	0.2200 (4)	0.0442 (11)	0.4897 (8)	0.0051 (2)	0.0198 (12)	0.0158 (7)	0.0113 (9)	0.0123 (6)	0.0204 (16)
N(1)	0.1050 (3)	0.3413 (6)	0.0369 (6)	0.0017 (1)	0.0031 (5)	0.0044 (4)	0.0000 (4)	0.0032 (3)	0.0017 (8)
N(2)	0.1340 (3)	0.2635 (6)	0.2324 (5)	0.0013 (1)	0.0036 (5)	0.0020 (3)	−0.0009 (4)	0.0019 (3)	−0.0027 (7)
N(3)	0.1997 (3)	0.1435 (6)	0.1847 (5)	0.0015 (1)	0.0023 (4)	0.0035 (4)	0.0001 (4)	0.0029 (3)	0.0009 (7)
N(4)	0.1227 (3)	0.1390 (6)	−0.0102 (5)	0.0013 (1)	0.0040 (5)	0.0019 (4)	−0.0005 (4)	0.0021 (3)	−0.0006 (7)
C(1)	0.1140 (4)	0.4304 (8)	0.0964 (8)	0.0021 (2)	0.0029 (6)	0.0073 (7)	−0.0001 (6)	0.0041 (5)	0.0003 (12)
C(2)	0.0712 (5)	0.4502 (8)	0.1276 (9)	0.0019 (2)	0.0037 (7)	0.0086 (8)	0.0016 (6)	0.0029 (6)	−0.0024 (13)
C(3)	0.0747 (4)	0.3953 (9)	0.2186 (8)	0.0019 (2)	0.0066 (8)	0.0073 (7)	0.0017 (7)	0.0043 (5)	−0.0039 (13)
C(4)	0.0819 (4)	0.2886 (8)	0.2169 (7)	0.0013 (1)	0.0053 (7)	0.0042 (5)	−0.0006 (5)	0.0034 (4)	−0.0029 (10)
C(5)	0.1670 (4)	0.2594 (7)	0.3178 (6)	0.0020 (1)	0.0039 (6)	0.0041 (4)	−0.0011 (5)	0.0050 (3)	−0.0034 (9)
C(6)	0.1587 (4)	0.2759 (10)	0.4124 (7)	0.0019 (2)	0.0096 (10)	0.0035 (5)	0.0000 (7)	0.0034 (4)	−0.0036 (12)
C(7)	0.2210 (4)	0.2353 (8)	0.3426 (7)	0.0019 (1)	0.0049 (7)	0.0034 (4)	−0.0003 (6)	0.0038 (4)	−0.0016 (10)
C(8)	0.2379 (4)	0.2083 (7)	0.2589 (6)	0.0014 (1)	0.0042 (6)	0.0033 (4)	−0.0002 (5)	0.0029 (3)	−0.0005 (9)
C(9)	0.2432 (4)	0.2980 (8)	0.2049 (8)	0.0017 (2)	0.0033 (6)	0.0057 (6)	−0.0009 (5)	0.0036 (4)	−0.0003 (10)
C(10)	0.2888 (4)	0.1619 (8)	0.3052 (7)	0.0015 (2)	0.0056 (7)	0.0044 (6)	−0.0008 (6)	0.0027 (4)	−0.0020 (11)
C(11)	0.1886 (4)	0.0523 (7)	0.2275 (7)	0.0018 (2)	0.0028 (6)	0.0053 (5)	−0.0000 (5)	0.0034 (4)	0.0025 (10)
C(12)	0.1530 (4)	−0.0105 (7)	0.1515 (7)	0.0020 (2)	0.0024 (6)	0.0062 (5)	−0.0006 (5)	0.0050 (4)	−0.0006 (10)
C(13)	0.0990 (4)	0.0306 (8)	0.0980 (7)	0.0016 (1)	0.0033 (6)	0.0050 (5)	−0.0011 (5)	0.0034 (4)	−0.0014 (10)
C(14)	0.0861 (4)	0.0662 (8)	−0.0050 (7)	0.0017 (2)	0.0047 (7)	0.0039 (6)	−0.0006 (6)	0.0018 (5)	−0.0021 (11)
C(15)	0.1054 (4)	0.1889 (9)	−0.1092 (7)	0.0015 (1)	0.0071 (8)	0.0033 (5)	0.0014 (6)	0.0031 (4)	0.0011 (11)
C(16)	0.1512 (4)	0.2408 (11)	−0.1093 (8)	0.0023 (2)	0.0101 (11)	0.0060 (6)	0.0018 (8)	0.0054 (4)	0.0057 (14)
C(17)	0.0859 (5)	0.1183 (11)	−0.1946 (8)	0.0027 (2)	0.0105 (11)	0.0034 (5)	0.0016 (8)	0.0041 (5)	−0.0023 (13)
C(18)	0.0639 (4)	0.2579 (9)	−0.1201 (7)	0.0014 (2)	0.0067 (8)	0.0028 (5)	−0.0002 (6)	0.0016 (4)	0.0019 (11)
C(19)	0.0763 (4)	0.3457 (8)	−0.0548 (8)	0.0015 (2)	0.0053 (7)	0.0064 (6)	0.0015 (6)	0.0039 (4)	0.0046 (11)
C(20)	0.0507 (5)	0.4373 (10)	−0.1088 (9)	0.0033 (3)	0.0060 (9)	0.0066 (7)	0.0039 (9)	0.0040 (7)	0.0085 (14)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
H(1)	0.1173 (0)	0.4823 (0)	0.0585 (0)	H(21)	0.2191 (0)	0.0188 (0)	0.2607 (0)
H(2)	0.1446 (0)	0.4231 (0)	0.1537 (0)	H(22)	0.1502 (0)	−0.0689 (0)	0.1812 (0)
H(3)	0.0405 (0)	0.4336 (0)	0.0746 (0)	H(23)	0.1656 (0)	−0.0224 (0)	0.1028 (0)
H(4)	0.0712 (0)	0.5165 (0)	0.1410 (0)	H(24)	0.0955 (0)	0.0825 (0)	0.1356 (0)
H(5)	0.0445 (0)	0.4062 (0)	0.2275 (0)	H(25)	0.0756 (0)	−0.0181 (0)	0.0948 (0)
H(6)	0.1024 (0)	0.4201 (0)	0.2738 (0)	H(26)	0.0532 (0)	0.0926 (0)	−0.0299 (0)
H(7)	0.0594 (0)	0.2643 (0)	0.1547 (0)	H(27)	0.0865 (0)	0.0130 (0)	−0.0450 (0)
H(8)	0.0744 (0)	0.2597 (0)	0.2674 (0)	H(28)	0.1631 (0)	0.2836 (0)	−0.0561 (0)
H(9)	0.1243 (0)	0.2906 (0)	0.3958 (0)	H(29)	0.1767 (0)	0.1948 (0)	−0.1026 (0)
H(10)	0.1674 (0)	0.2194 (0)	0.4519 (0)	H(30)	0.1421 (0)	0.2734 (0)	−0.1697 (0)
H(11)	0.1792 (0)	0.3270 (0)	0.4486 (0)	H(31)	0.0572 (0)	0.0857 (0)	−0.1940 (0)
H(12)	0.2294 (0)	0.1826 (0)	0.3870 (0)	H(32)	0.0768 (0)	0.1513 (0)	−0.2549 (0)
H(13)	0.2403 (0)	0.2891 (0)	0.3753 (0)	H(33)	0.1113 (0)	0.0726 (0)	−0.1878 (0)
H(14)	0.2115 (0)	0.3287 (0)	0.1750 (0)	H(34)	0.0390 (0)	0.2231 (0)	−0.1074 (0)
H(15)	0.2668 (0)	0.3402 (0)	0.2504 (0)	H(35)	0.0504 (0)	0.2793 (0)	−0.1859 (0)
H(16)	0.2547 (0)	0.2805 (0)	0.1556 (0)	H(36)	0.0611 (0)	0.4875 (0)	−0.0630 (0)
H(17)	0.2866 (0)	0.1060 (0)	0.3392 (0)	H(37)	0.0620 (0)	0.4476 (0)	−0.1596 (0)
H(18)	0.2998 (0)	0.1456 (0)	0.2550 (0)	H(38)	0.0162 (0)	0.4277 (0)	−0.1342 (0)
H(19)	0.3119 (0)	0.2053 (0)	0.3498 (0)	H(39)	0.2116 (0)	0.1210 (0)	0.1467 (0)
H(20)	0.1745 (0)	0.0687 (0)	0.2736 (0)	H(40)	0.1489 (0)	0.1136 (0)	−0.0076 (0)

[a] The form of the anisotropic thermal parameter is $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$. $B =$ 5.0000 (0) Å^2 for all H atoms.

nonmacrocyclic analogue *trans*-bis(2-methyl-2-amino-4-iminopentane)copper(II) nitrate.[15] The magnitude of the N(1)CuN(4) angle is interesting when it is noted that the larger seven-membered rings have bite angles of only 90.1 and 93.3°, respectively. The geometry about the metal ion is indicative of considerable strain within the molecule.

Within the six-membered chelate rings the mean of the Cu–N(sp^2)–C(sp^2) angles about N(1) and N(2) is 126.5° compared to the trigonal angles of 120°. The angles about the central carbon atoms C(7) and C(18) have a mean value of 119°. The opening of the angles about the sp^2 nitrogen atoms and the central methylene carbon atoms of analogous six-membered rings has been observed in a number of macrocyclic cations and has been attributed to the accumulated strain in the six-membered ring. Distortions (mean) in analogous positions in some related diene macrocycles are 131 and 119° in *rac*-(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(II) perchlorate,[16,17] [Ni(*rac*-*trans*-[14]diene)](ClO$_4$)$_2$, 125 and 115° in dicyano(5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene)cobalt(III) perchlorate,[17,18] *trans*-[Co(*ms*-*cis*-

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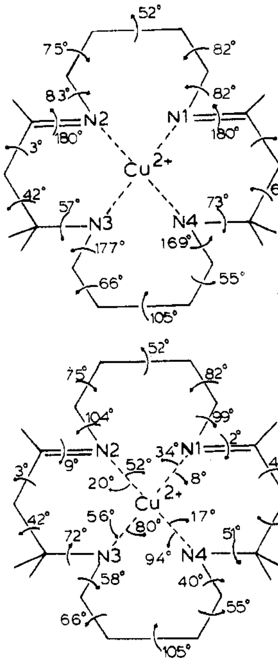

Figure 4. Magnitude and sense of torsion angles in [Cu(*cis*-[18]-dieneN$_4$)]$^{2+}$.

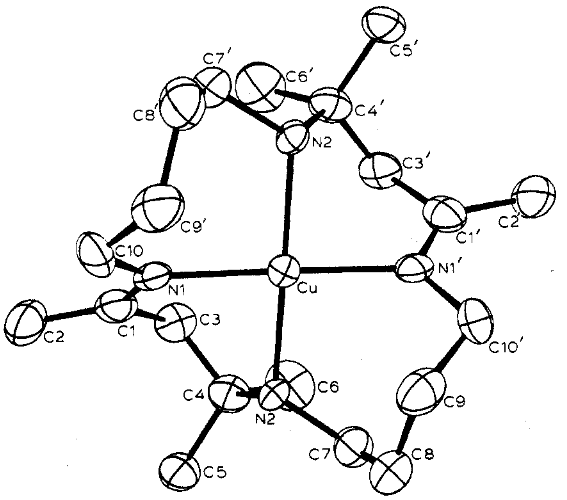

Figure 5. ORTEP[36] diagram of the macrocyclic complex [Cu(*trans*-[18]dieneN$_4$)]$^{2+}$. Thermal ellipsoids at the 50% probability level. Double bonds are between N(1) and C(1) and between N(1)′ and C(1)′.

[14]diene)(CN)$_2$](ClO$_4$)$_2$, 136 and 123.5° in *trans*-bis(isothiocyanato)(*N*-*rac*-*N*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)cobalt(III) thiocyanate monohydrate,[19] [Co(*trans*-*N*-*rac*-Me$_2$[14]diene)(NCS)$_2$]CNS·H$_2$O, and 129° and 119° in *rac*-(5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene)nickel(II) perchlorate, [Ni(*rac*-*cis*-[14]diene])(ClO$_4$)$_2$.[17,20] Within the seven-membered chelate rings a number of the angles at sp^3 carbon atoms are widened to about 115°, and the C(11)–C(12) bond is rather short at 1.474 (9) Å.

The conformation of the cis macrocycle and of the six- and seven-membered rings is best understood by a study of the torsion angles. The torsion angles of the macrocycle are given in Figure 4a and those within the six- and seven-membered chelate rings in Figure 4b. Strain-free torsion angles correspond to a potential energy minimum and depend on the hybridization of the two atoms involved as follows:[17] minima for sp^3–sp^3 60 or 180°, for sp^3–sp^2 30, 90, or 150°, and for sp^2–sp^2 0 or 180°. Considerable deviation from these idealized torsion angles are observed throughout the macrocycle. For example, the torsion angles of 105° about C(13)–C(12) and 40° about N(4)–C(14) are quite notable.

Table III. Bond Distances and Angles in [Cu(*cis*-[18]dieneN$_4$)](ClO$_4$)$_2$

	A. Bond Distances (Å)		
Cu–N(1)	1.986 (5)	Cu–N(2)	1.988 (4)
Cu–N(3)	2.010 (5)	Cu–N(4)	2.024 (5)
N(1)–C(1)	1.491 (8)	N(3)–C(8)	1.509 (8)
N(1)–C(19)	1.277 (8)	N(3)–C(11)	1.520 (7)
N(2)–C(4)	1.479 (8)	N(4)–C(14)	1.499 (8)
N(2)–C(5)	1.244 (8)	N(4)–C(15)	1.518 (8)
C(1)–C(2)	1.520 (10)	C(11)–C(12)	1.474 (9)
C(2)–C(3)	1.523 (11)	C(12)–C(13)	1.554 (9)
C(3)–C(4)	1.512 (10)	C(13)–C(14)	1.505 (9)
C(5)–C(6)	1.536 (8)	C(15)–C(16)	1.519 (10)
C(5)–C(7)	1.500 (9)	C(15)–C(17)	1.525 (10)
C(7)–C(8)	1.559 (8)	C(15)–C(18)	1.502 (10)
C(8)–C(9)	1.533 (9)	C(18)–C(19)	1.518 (10)
C(8)–C(10)	1.504 (9)	C(19)–C(20)	1.537 (10)
Cl(1)–O(11)	1.326 (6)	Cl(2)–O(21)	1.409 (5)
Cl(1)–O(12)	1.353 (7)	Cl(2)–O(22)	1.401 (6)
Cl(1)–O(13)	1.366 (6)	Cl(2)–O(23)	1.403 (5)
Cl(1)–O(14)	1.462 (10)	Cl(2)–O(24)	1.375 (6)
	B. Bond Angles (Deg)		
N(1)–Cu–N(2)	93.3 (2)	N(2)–Cu–N(3)	90.7 (2)
N(1)–Cu–N(3)	154.6 (2)	N(2)–Cu–N(4)	152.7 (2)
N(1)–Cu–N(4)	97.5 (2)	N(3)–Cu–N(4)	90.1 (2)
Cu–N(1)–C(1)	116.3 (4)	Cu–N(3)–C(8)	106.6 (4)
Cu–N(1)–C(19)	125.5 (5)	Cu–N(3)–C(11)	115.2 (4)
Cu–N(2)–C(4)	112.5 (4)	Cu–N(4)–C(14)	106.4 (3)
Cu–N(2)–C(5)	127.8 (4)	Cu–N(4)–C(15)	116.1 (4)
N(1)–C(1)–C(2)	111.5 (6)	N(2)–C(4)–C(3)	111.9 (5)
N(1)–C(19)–C(18)	121.7 (6)	N(2)–C(5)–C(6)	125.7 (6)
N(1)–C(19)–C(20)	124.5 (7)	N(2)–C(5)–C(7)	124.0 (5)
N(3)–C(8)–C(7)	110.6 (5)	N(4)–C(14)–C(13)	112.9 (5)
N(3)–C(8)–C(9)	108.2 (5)	N(4)–C(15)–C(16)	106.0 (5)
N(3)–C(8)–C(10)	111.7 (5)	N(5)–C(15)–C(17)	111.9 (6)
N(3)–C(11)–C(12)	112.6 (5)	N(4)–C(15)–C(18)	109.7 (5)
C(1)–N(1)–C(19)	125.5 (5)	C(5)–N(2)–C(5)	119.2 (5)
C(9)–N(3)–C(11)	114.8 (5)	C(15)–N(4)–C(15)	113.7 (5)
C(1)–C(2)–C(3)	114.3 (6)	C(11)–C(12)–C(13)	114.8 (5)
C(2)–C(3)–C(4)	116.4 (6)	C(12)–C(13)–C(14)	115.3 (5)
C(6)–C(5)–C(7)	110.3 (6)	C(16)–C(15)–C(17)	109.8 (6)
C(5)–C(7)–C(8)	119.8 (6)	C(16)–C(15)–C(18)	111.0 (6)
C(7)–C(8)–C(9)	110.5 (5)	C(17)–C(15)–C(18)	108.5 (6)
C(7)–C(8)–C(10)	108.1 (5)	C(15)–C(18)–C(19)	118.7 (6)
C(9)–C(8)–C(10)	107.7 (5)	C(18)–C(19)–C(20)	113.8 (7)

It is apparent that in order to minimize strain within the molecule the macrocyclic ligand has adopted a rather contorted conformation and the coordination geometry about the copper(II) atom has distorted considerably from a regular square-planar arrangement. The ligand in [Cu(*trans*-[18]-dieneN$_4$)]$^{2+}$ adopts a less contorted conformation than that observed in the cis complex. Relatively little distortion from a square-planar coordination geometry is observed in the trans complex. The "bite angle" is not surprising considering the presence of the adjacent larger seven-membered rings, the bite angles of which are 95.4°. The angle at the C(3) methylene carbon atom of the six-membered rings in this trans complex is opened less than that observed at the analogous atoms of the cis complex (114.2° for trans; 119.3° mean for cis).

The angles at the central methylene carbon atoms of the seven-membered rings C(8) and C(9) are opened out to 116.3 and 116.2°, respectively. The torsion angles of the complex are given in Figure 7.

The [Cu(*trans*-[18]dieneN$_4$)](ClO$_4$)$_2$ complex adopts a less distorted conformation than that of the cis isomer, indicative of a smaller amount of overall strain within the molecule.

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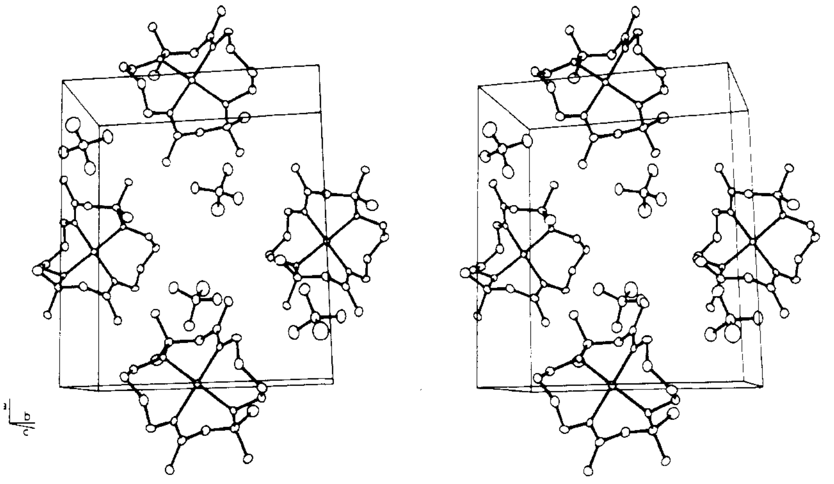

Figure 6. Stereo diagram of one unit cell of the macrocyclic complex $[Cu(\textit{trans}\text{-}[18]dieneN_4)]^{2+}$.

Table IV. Positional and Thermal Parameters and Their Estimated Standard Deviation in $[Cu(\textit{trans}\text{-}[18]dieneN_4)](ClO_4)_2$[a]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Cu	0.0000 (0)	−0.5000 (0)	−0.1388 (3)	0.00244 (8)	0.0033 (1)	0.0108 (3)	0.0002 (3)	0.0000 (0)	0.0000 (0)
Cl	−0.1946 (3)	−0.0537 (3)	−0.1998 (5)	0.0064 (2)	0.0059 (2)	0.0148 (6)	0.0002 (4)	−0.0004 (7)	0.0009 (8)
O(1)	−0.2827 (8)	−0.0892 (9)	−0.147 (2)	0.0076 (7)	0.0089 (9)	0.037 (3)	−0.001 (1)	0.015 (3)	0.000 (4)
O(2)	−0.2018 (8)	0.0427 (8)	−0.296 (2)	0.0085 (7)	0.0062 (7)	0.029 (2)	−0.000 (1)	−0.001 (3)	0.008 (2)
O(3)	−0.1550 (9)	−0.1389 (9)	−0.298 (2)	0.0094 (8)	0.0084 (9)	0.022 (2)	0.001 (2)	0.008 (2)	−0.003 (3)
O(4)	−0.1457 (11)	−0.0354 (11)	−0.052 (2)	0.0151 (11)	0.0161 (15)	0.020 (2)	−0.001 (2)	−0.014 (3)	−0.003 (3)
N(1)	−0.1122 (7)	−0.4120 (7)	−0.127 (1)	0.0031 (5)	0.0026 (6)	0.015 (2)	−0.0013 (10)	−0.001 (2)	0.002 (2)
N(2)	−0.0865 (6)	−0.6301 (7)	−0.160 (1)	0.0028 (4)	0.0029 (6)	0.009 (2)	0.0006 (9)	−0.000 (2)	0.002 (2)
C(1)	−0.1726 (9)	−0.430 (1)	−0.241 (2)	0.0036 (7)	0.0049 (9)	0.017 (3)	−0.001 (2)	−0.002 (2)	0.006 (3)
C(2)	−0.2617 (11)	−0.382 (1)	−0.246 (2)	0.0044 (8)	0.0053 (10)	0.025 (4)	0.001 (2)	−0.005 (3)	0.000 (3)
C(3)	−0.1445 (8)	−0.508 (1)	−0.379 (1)	0.0043 (6)	0.0059 (8)	0.011 (2)	−0.001 (2)	−0.005 (2)	0.000 (4)
C(4)	−0.1390 (9)	−0.624 (1)	−0.324 (2)	0.0038 (7)	0.0056 (9)	0.012 (3)	−0.002 (1)	−0.002 (2)	−0.003 (3)
C(5)	−0.2346 (9)	−0.673 (1)	−0.299 (2)	0.0034 (6)	0.0055 (9)	0.017 (3)	−0.002 (1)	−0.004 (2)	−0.001 (3)
C(6)	−0.0876 (11)	−0.687 (1)	−0.465 (2)	0.0063 (9)	0.0107 (14)	0.017 (3)	−0.001 (2)	−0.001 (3)	−0.006 (4)
C(7)	−0.0490 (9)	−0.738 (1)	−0.124 (2)	0.0037 (6)	0.0043 (8)	0.020 (3)	0.000 (1)	0.001 (3)	−0.002 (3)
C(8)	−0.0224 (9)	−0.749 (1)	0.062 (2)	0.0042 (8)	0.0060 (9)	0.023 (3)	0.001 (1)	0.001 (3)	0.009 (3)
C(9)	0.0494 (10)	−0.672 (1)	0.124 (2)	0.0054 (7)	0.0051 (9)	0.014 (2)	−0.000 (2)	−0.004 (3)	0.003 (3)
C(10)	−0.1316 (9)	−0.340 (1)	0.016 (2)	0.0026 (6)	0.0065 (9)	0.018 (3)	0.000 (1)	0.005 (2)	−0.003 (3)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
H(1)	−0.2703 (0)	−0.3350 (0)	−0.1538 (0)	H(11)	−0.1194 (0)	−0.6802 (0)	−0.5657 (0)
H(2)	−0.3062 (0)	−0.4390 (0)	−0.2414 (0)	H(12)	−0.0940 (0)	−0.7909 (0)	−0.1529 (0)
H(3)	−0.2695 (0)	−0.3431 (0)	−0.3477 (0)	H(13)	0.0028 (0)	−0.7488 (0)	−0.1941 (0)
H(4)	−0.1888 (0)	−0.5037 (0)	−0.4663 (0)	H(14)	−0.0750 (0)	−0.7379 (0)	0.1295 (0)
H(5)	−0.0872 (0)	−0.4880 (0)	−0.4214 (0)	H(15)	−0.0006 (0)	−0.8214 (0)	0.0807 (0)
H(6)	−0.2279 (0)	−0.7475 (0)	−0.2634 (0)	H(16)	0.0229 (0)	−0.6026 (0)	0.1321 (0)
H(7)	−0.2669 (0)	−0.6714 (0)	−0.4007 (0)	H(17)	0.0692 (0)	−0.6962 (0)	0.2302 (0)
H(8)	−0.2657 (0)	−0.6341 (0)	−0.2150 (0)	H(18)	−0.1800 (0)	−0.3681 (0)	0.0809 (0)
H(9)	−0.0823 (0)	−0.7607 (0)	−0.4329 (0)	H(19)	−0.1490 (0)	−0.2691 (0)	−0.0248 (0)
H(10)	−0.0284 (0)	−0.6559 (0)	−0.4750 (0)	H(20)	−0.1231 (0)	−0.6223 (0)	−0.0792 (0)

[a] The form of the anisotropic thermal parameter is $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$. $B = 4.0000\ (0)$ Å^2 for all H atoms.

Table V. Mean Planes through Coordinated Nitrogen Atoms of $[Cu(\textit{cis}\text{-}[18]dieneN_4)](ClO_4)_2$ and $[Cu(\textit{trans}\text{-}[18]dieneN_4)](ClO_4$ $[Cu(\textit{trans}\text{-}[18]dieneN_4)](ClO_4)_2$ Including Distances of Copper Atoms from These Planes

$[Cu(\textit{cis}\text{-}[18]dieneN_4)](ClO_4)_2$

plane: $A = 0.000, B = 0.000, C = -1.000, D = 1.144$[a]

distances: N(1) = −0.133 (11) Å, N(2) = 0.133 (10) Å, N(1)′ = −0.133 (11) Å, N(2)′ = 0.133 (10) Å, Cu = −0.036 Å

$[Cu(\textit{trans}\text{-}[18]dieneN_4)](ClO_4)_2$

plane: $A = 0.814, B = 0.526, C = -0.246, D = 4.783$[a]

distances: N(1) = −0.158 (9) Å, N(2) = −0.034 (8) Å, N(3) = 0.714 (8) Å, N(4) = −0.839 (8) Å, Cu = 0.004 (1) Å

[a] Equation of the plane is of the form $Ax + By + Cz + D = 0$, where *A*, *B*, *C*, and *D* are constants and *x*, *y*, and *z* are orthogonalized coordinates.

Tetrahedral Distortion. Tetrahedral distortion has been observed in a number of copper(II) complexes.[21–29] This distortion normally occurs because steric interactions prevent the adoption of a square-planar geometry, as in the essentially tetrahedral isosparteine complex of Streib et al.[21] or the bis(*N*-*tert*-butylsalicylaldiminato)copper(II) complex of Cheeseman et al.[22] In some of the complexes studied, however,

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Table VI. Bond Distances and Angles in $[Cu(trans\text{-}[18]dieneN_4)](ClO_4)_2$

A. Bond Distances (Å)

Cu–N(1)	1.977 (8)	Cu–N(2)	2.053 (8)
N(1)–C(1)	1.292 (14)	N(2)–C(4)	1.522 (14)
N(1)–C(10)	1.471 (14)	N(2)–C(7)	1.470 (12)
C(1)–C(2)	1.436 (16)	C(4)–C(6)	1.561 (17)
C(1)–C(3)	1.522 (16)	C(7)–C(8)	1.542 (18)
C(3)–C(4)	1.496 (16)	C(8)–C(9)	1.501 (16)
C(4)–C(5)	1.543 (14)	C(9)–C(10)	1.494 (17)
Cl–O(1)	1.432 (10)	Cl–O(3)	1.431 (9)
Cl–O(2)	1.416 (9)	Cl–O(4)	1.403 (11)

B. Bond Angles (Deg)

N(1)–Cu–N(2)	85.0 (3)	N(1)–Cu–N(1)′	174.4 (6)
N(1)–Cu–N(2)	95.4 (3)	N(2)–Cu–N(2)′	170.5 (5)
Cu–N(2)–C(4)	110.4 (6)	Cu–N(1)–C(1)	116.7 (8)
Cu–N(2)–C(7)	117.2 (6)	Cu–N(1)–C(10)	122.0 (7)
N(2)–C(4)–C(6)	110.4 (9)	N(1)–C(1)–C(2)	125.5 (1.1)
C(2)–N(4)–C(5)	109.6 (9)	N(1)–C(1)–C(3)	115.4 (1.0)
N(2)–C(4)–C(3)	108.9 (8)	C(1)–C(3)–C(4)	114.2 (9)
C(6)–C(4)–C(3)	106.9 (1.0)	C(2)–C(1)–C(3)	119.1 (1.0)
C(5)–C(4)–C(3)	111.0 (9)		
C(6)–C(4)–C(5)	110.0 (9)	N(1)′–C(10)′–C(9)	110.5 (9)
N(2)–C(7)–C(8)	111.1 (9)	C(10)′–C(9)–C(8)	116.2 (1.0)
C(7)–C(8)–C(9)	116.3 (1.0)	O(2)–Cl–O(3)	110.5 (6)
O(1)–Cl–O(2)	110.3 (7)	O(2)–Cl–O(4)	111.0 (7)
O(1)–Cl–O(3)	107.8 (6)	O(3)–Cl–O(4)	111.6 (7)
O(1)–Cl–O(3)	105.5 (8)		

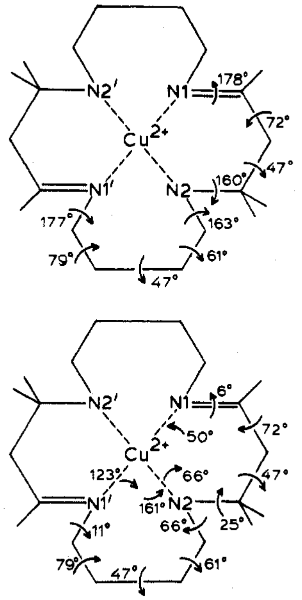

Figure 7. Magnitude and sense of torsion angles in $[Cu(trans\text{-}[18]dieneN_4)]^{2+}$.

the distortion apparently results from a different cause. The complexes *N,N′*-(2,2′-biphenyl)bis(salicylaldiminato)copper(II)[23] (**1**) and bis(2-hydroxyacetophenone)(trimethylenediimino)copper(II)[24] (**2**) have dihedral angles between the O–Cu–N planes of 34.4 and 37°, respectively. The reason for the distortion in **2** is not obvious; in **1**, however, the distortion almost certainly occurs because the ligand could not adopt square-planar geometry without excessive bond and angle strain in the six- and seven-membered chelate rings.

The remarkable difference in copper(II) geometries in the cis and trans macrocyclic complexes seems to result from the difference in the placement of double bonds. It is interesting to note that Schiff bases **1** and **2** both have double-bond placement similar to that in the cis macrocyclic complex. Of even greater interest is the 20° dihedral angle between the N–Cu–N planes in (3,4:9,10-dibenzo-1,5,8,12-tetraazacyclohexadecane-1,11-dienato)copper(II),[30] **3**, the only other

Table VII. General Temperature Factor Expressions for $[Cu(cis\text{-}[18]dieneN_4)](ClO_4)_2$

atom	*U*(1,1)	*U*(2,2)	*U*(3,3)	*U*(1,2)	*U*(1,3)	*U*(2,3)
Cu	0.0486 (5)	0.0274 (6)	0.0243 (4)	0.0012 (6)	0.0243 (3)	0.0005 (5)
Cl(1)	0.054 (2)	0.062 (2)	0.107 (1)	0.008 (1)	0.044 (1)	0.028 (2)
O(11)	0.066 (5)	0.124 (9)	0.189 (9)	0.009 (6)	0.063 (5)	0.052 (7)
O(12)	0.061 (6)	0.17 (1)	0.140 (8)	−0.26 (7)	0.035 (5)	0.019 (8)
O(13)	0.145 (8)	0.139 (8)	0.187 (8)	0.053 (7)	0.095 (5)	0.119 (6)
O(14)	0.34 (1)	0.13 (1)	0.30 (1)	−0.06 (1)	0.239 (8)	−0.07 (1)
Cl(2)	0.096 (2)	0.051 (2)	0.065 (1)	−0.003 (2)	0.059 (1)	0.009 (1)
O(21)	0.161 (5)	0.102 (8)	0.180 (5)	−0.022 (5)	0.147 (3)	0.006 (5)
O(22)	0.191 (9)	0.111 (8)	0.079 (6)	−0.065 (7)	0.064 ( )	−0.034 (6)
O(23)	0.137 (5)	0.063 (5)	0.095 (4)	−0.038 (5)	0.088 (3)	−0.014 (4)
O(24)	0.184 (8)	0.20 (1)	0.148 (7)	0.107 (8)	0.112 (5)	0.098 (8)
N(1)	0.061 (5)	0.030 (5)	0.041 (4)	0.000 (4)	0.030 (3)	0.008 (4)
N(2)	0.048 (4)	0.036 (5)	0.019 (3)	−0.008 (4)	0.018 (3)	−0.013 (4)
N(3)	0.053 (4)	0.023 (4)	0.033 (3)	0.001 (4)	0.026 (3)	0.004 (3)
N(4)	0.046 (4)	0.039 (5)	0.018 (3)	−0.005 (4)	0.019 (3)	−0.003 (4)
C(1)	0.076 (6)	0.029 (6)	0.069 (6)	−0.001 (6)	0.038 (4)	0.001 (6)
C(2)	0.069 (7)	0.037 (7)	0.080 (8)	0.015 (6)	0.027 (5)	−0.012 (6)
C(3)	0.068 (6)	0.066 (8)	0.069 (6)	0.016 (6)	0.039 (4)	−0.019 (6)
C(4)	0.048 (5)	0.052 (7)	0.039 (4)	−0.006 (5)	0.031 (3)	−0.014 (5)
C(5)	0.072 (5)	0.039 (6)	0.038 (4)	−0.011 (5)	0.046 (3)	−0.016 (4)
C(6)	0.067 (6)	0.10 (1)	0.032 (4)	0.000 (7)	0.031 (4)	−0.017 (6)
C(7)	0.067 (5)	0.049 (7)	0.032 (4)	−0.003 (5)	0.035 (3)	−0.008 (5)
C(8)	0.050 (5)	0.042 (6)	0.031 (4)	−0.002 (5)	0.027 (3)	−0.002 (4)
C(9)	0.062 (6)	0.033 (6)	0.053 (5)	−0.008 (5)	0.033 (4)	−0.001 (5)
C(10)	0.054 (6)	0.056 (7)	0.042 (5)	−0.008 (6)	0.025 (4)	−0.010 (5)
C(11)	0.065 (6)	0.028 (6)	0.049 (5)	−0.000 (5)	0.031 (4)	0.012 (5)
C(12)	0.073 (6)	0.024 (6)	0.058 (5)	−0.005 (5)	0.046 (4)	−0.003 (5)
C(13)	0.056 (5)	0.032 (6)	0.047 (5)	−0.011 (5)	0.031 (4)	−0.007 (5)
C(14)	0.063 (6)	0.047 (7)	0.036 (5)	−0.005 (6)	0.017 (4)	−0.010 (5)
C(15)	0.055 (5)	0.071 (8)	0.030 (4)	0.013 (6)	0.028 (3)	0.005 (5)
C(16)	0.081 (6)	0.10 (1)	0.056 (5)	0.017 (7)	0.049 (4)	0.028 (7)
C(17)	0.098 (8)	0.10 (1)	0.032 (5)	0.015 (8)	0.037 (4)	−0.011 (6)
C(18)	0.051 (6)	0.067 (8)	0.027 (5)	−0.002 (6)	0.015 (4)	0.009 (5)
C(19)	0.053 (6)	0.053 (7)	0.060 (6)	0.015 (5)	0.036 (4)	0.022 (5)
C(20)	0.12 (1)	0.060 (9)	0.062 (7)	0.037 (8)	0.036 (6)	0.041 (7)

structurally characterized macrocyclic compound having the –CH=N$(CH_2)_4$N=CH– group. That [Cu(*cis*-[18]diene-N_4)]$(ClO_4)_2$ exhibits a tetrahedral distortion nearly twice as large as that of **3** may be attributed to the interaction between methylene hydrogens on C(1) and C(4) in the tetramethylene bridge and methyl hydrogens on C(6) and C(20). The second tetramethylene bridge (not present in **3**) may also contribute to the tetrahedral distortion. A small tetrahedral distortion has also been observed in 6,8,8,13,13,15-hexamethyl-1,2,4,5,9,12-hexaazacyclopentadec-5,14-diene-3-spirocyclohexane,[31] but the details of this structure have not yet been reported. The distortion in this complex is apparently due to the presence of the spirocyclohexane group.

The less distorted geometry of the trans complex is more favorable for coordination of copper(II), as illustrated by the greater yield of the red trans complex during the template condensation. Once the compounds are formed, however, the distorted geometry of the cis complex appears to protect it to some extent from hydrolysis at the double bond. Hydrolysis of these bonds in the trans complex can be assisted by coordination of water to copper(II) above and below the plane of the macrocycle, where they have easy access to the double bonds. Coordination of water to copper(II) in the cis complex is sterically inhibited.

Tetrahedrally distorted complexes of Cu(II) have been of interest as models for copper proteins such as the blue copper proteins.[32–34] In the cis compound reported here, the reduction of copper(II) to copper(I) should be aided by the tetrahedral distortion in the copper(II) complex. By analogy to the geometry in the macrocyclic complex (1,1-difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetraaza-2,14-dioxacyclotetradeca-3,5,10,12-tetraenato)copper(I),[35] which is intermediate between tetrahedral and square planar, it is likely that the geometry in Cu(I) complexes of the macrocycles described here will be distorted toward square-planar configurations. Furthermore, the combination of two imine and two amine donors should not heavily favor either oxidation state of copper. This situation is ideal for modeling oxidases, which must cycle between copper(II) and copper(I). The redox reaction of such enzymes is made more favorable by means of coordination goemetries which favor neither oxidation state but rather adopt intermediate geometries. The cis macrocyclic complex shows promise of providing intermediate geometries similar to those observed in the enzymes.

Macrocyclic complexes have additional promise as copper oxidase models because large variations in chelate ring size, double-bond placement, and side chains may be achieved by straightforward synthetic methods involving only a few steps. Oxidation and reduction of the ligands can provide further variation. By these methods it should be possible to tailor ligands to achieve tetrahedral distortions of varying magnitude for use in model studies. Further investigations of this nature are presently being undertaken in this laboratory.

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Registry No. I, 73429-78-4; II, 72765-21-0.

Supplementary Material Available: Tables of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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Synthesis and Molecular Structure of (η^3-C_3H_5)Fe$(CO)_3$AuP$(C_6H_5)_3$ and the Molecular Structure of (η^3-C_3H_5)Fe$(CO)_3$Br. Two Compounds with Distinctly Different Coordination Geometries

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The compound (η^3-C_3H_5)Fe$(CO)_3$AuP$(C_6H_5)_3$ has been synthesized and its molecular structure solved by X-ray diffraction techniques, space group *C*2/*c* with a = 30.76 (2) Å, b = 11.60 (1) Å, c = 13.54 (2) Å, β = 110.38 (1)°, and Z = 8. The molecular structure of (η^3-C_3H_5)Fe$(CO)_3$Br was also determined, space group *Pnma* with a = 11.497 (7) Å, b = 7.962 (4) Å, c = 9.556 (4) Å, and Z = 4. The coordination geometries of the two compounds are distinctly different. The bromide derivative has a conventional pseudooctahedral geometry while the gold derivative has an unusual geometry which may be described best as a trigonal-bipyramidal (η^3-C_3H_5Fe)$(CO)_3$ moiety with a AuP$(C_6H_5)_3$ ligand located on an edge between two equatorial CO ligands. The resulting Au–Fe–CO angles are acute 70.9 (2) and 72.0 (2)°. The unusual structure may be due to the reversed polarity of the iron–gold bond as compared to the iron–bromide bond. Spectral evidence suggests that there is a high negative charge on the iron atom of the gold derivative.

Introduction

The η^3-allyliron tricarbonyl halides and pseudohalides are known to exist in two conformational isomers in solution. The geometry of each isomer is approximately octahedral with the allyl ligand occupying two cis positions. In the endo isomer, **1**, the allyl points away from the halide, while in the exo isomer, **2**, it points toward the halide.

The existence of the two isomers was first hypothesized by Nesmeyanov and co-workers[1] and was confirmed by Faller and

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