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Effects of Larger Chelate Rings on the Geometry and Properties of Copper(II) Complexes. Crystal and Molecular Structure and Spectral Properties of Aquo(1,1-difluoro-4,5,12,13-tetramethyl-1-bora-3,6,11,14-tetraaza-2,15-dioxacyclopentadeca-3,5,11,13-tetraenato)copper(II) Perchlorate

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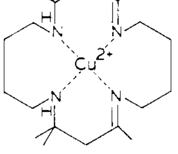
The crystal and molecular structure of aquo(1,1-difluoro-4,5,12,13-tetramethyl-1-bora-3,6,11,14-tetraaza-2,15-dioxacyclopentadeca-3,5,11,13-tetraenato)copper(II) perchlorate, $C_{12}H_{22}BClCuF_2N_4O_7$, has been determined by single-crystal X-ray diffraction methods. The space group is $P2_1/c$ with $a = 9.663$ (2) Å, $b = 13.401$ (2) Å, $c = 15.012$ (3) Å, and $\beta = 95.11$ (2)°. Refinement using 2214 unique reflections with $I > 3\sigma(I)$ gave an unweighted R factor of 0.052 and a weighted R factor of 0.073. The structure is essentially square pyramidal with the aquo ligand at the apex. The nitrogen donors are alternately above and below the best basal plane for the square pyramid by about 0.1 Å, and the aquo ligand is distorted from the ideal apical position, probably due to interaction with an F atom of the BF_2 group within the six-membered ring. The Cu–aquo O distance is 2.250 (3) Å, and the average Cu–N distance is 1.972 (8) Å. The effects of the seven-membered chelate ring on the structure and on other properties of the complex are discussed. Visible spectral data are discussed for the complex cations (2-oximino-11-oximato-3,10-dimethyl-4,9-diazadodeca-3,9-diene)copper(II), $C_{12}H_{21}CuN_4O_2^+$, and (1,1-difluoro-4,5,12,13-tetramethyl-1-bora-3,6,11,14-tetraaza-2,15-dioxacyclopentadeca-3,5,11,13-tetraenato)copper(II), $C_{12}H_{22}BCuF_2N_4O_2^+$, with various axial ligands. These complexes do not follow the usual spectrochemical series. Axial ligands which bind strongly to copper(II) pull it further from the basal nitrogen plane, reducing the crystal field splitting caused by these donors. The perturbed spectrochemical series observed for these complexes is different from that observed for the copper(II) complexes of an analogous 14-membered macrocycle. The differences are attributed to the geometrical distortions resulting from the presence of the seven-membered chelate ring in the 15-membered macrocycles. Spectra of the complex cation (2,3,10,11-tetramethyl-1,4,9,12-tetraazacyclohexadeca-1,3,9,11-tetraene)copper(II), $C_{16}H_{28}CuN_4^{2+}$, are indicative of tetrahedral distortion from square-planar geometry or of square-pryamidal geometry. Current macrocycle nomenclature is extended to cover compounds having heteroatoms which do not serve as donors.

Introduction

It has been suggested[2-4] that copper redox proteins adopt geometries intermediate between those favorable to the +2 oxidation state and those favorable to the +1 oxidation state. The structure of plastocyanin determined by Freeman et al.[5] supports this suggestion. The copper atom in plastocyanin adopts "a highly distorted tetrahedral coordination geometry"[5] which destabilizes copper(II) with respect to copper(I). According to the "entatic state" model for copper redox proteins, this intermediate geometry favors the redox reactions which are essential to the functions of these proteins. Thus, the reduction potential of a blue copper protein is considerably higher than the potential for reduction of copper(II) to copper(I) in aqueous solution.

Macrocyclic ligands which form larger than normal chelate rings may prove useful in modeling copper redox proteins, since they have been shown to produce tetrahedral distortions in copper(II) complexes. In the isomeric pair of complexes **1** and **2**,[6-8] the geometry about the central copper(II) ion is distinctly different. The cis complex, **1**, in which there is a seven-membered ring involving two imino nitrogen donors, has a pseudotetrahedral geometry (36.6° angle between N(1)CuN(2) and N(3)CuN(4) planes). The trans complex, **2**, with seven-membered rings joining secondary amino and imino donor atoms, has only a 10° twist from the square-planar geometry.



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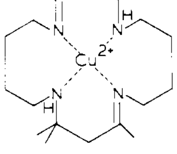
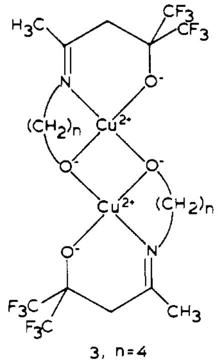


2

The effect of a seven-membered relative to a six-membered ring on the geometry and magnetic properties of an alkoxo-bridged dinuclear copper(II) complex has been shown by the X-ray crystal structural characterization of the nonmacrocyclic complexes bis[μ-(9,9,9-trifluoro-8-trifluoromethyl-6-methyl-5-azanon-5-ene-1,8-diolato(2−)-*O,N,O'*)]-dicopper(II) (**3**) and bis[μ-(8,8,8-trifluor-7-trifluoromethyl-5-methyl-4-azaocta-4-ene-1,7-diolato(2−)-*O,N,O'*)]-dicopper(II) (**4**).[9] In these



3, n=4
4, n=3

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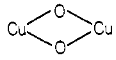
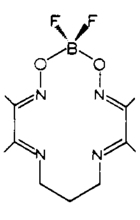
compounds, the complex **3** containing the seven-membered chelate ring had a lower magnetic moment than **4**, due to a greater magnetic exchange interaction, and was perfectly planar about the copper atom and within the



bridging moiety. Surprisingly, in this case, the compound containing the seven-membered chelate ring had a smaller distortion from square-planar coordination geometry than did the compound containing the six-membered ring.

Structural studies by Anderson et al.[10,11] have shown a number of the copper(II) complexes of the macrocyclic ligand 1,1-difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetraaza-2,14-dioxacyclotetradeca-3,5,10,12-tetraene, cyclops (**5**), Me_4F_2-BO_2[14]teteneN$_4$, to have a square-pyramidal geometry about the copper(II) ion. These complexes have been reduced electrochemically to yield neutral copper(I) complexes.[12] The copper(I) complexes of Me_4F_2-BO_2[14]teteneN$_4$ have a four-coordinate distorted tetrahedral geometry[13] or a five-coordinate square-pyramidal geometry[12] similar to that of the copper(II) analogues.



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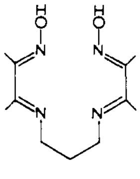

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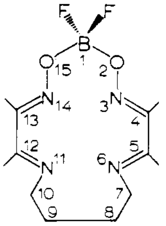
A copper complex of the oxime precursor 4,8-diaza-3,9-dimethylundeca-3,8-diene-2,10-dione dioxime (**6**), PreH, (Me_4-H_2O_2[14]teteneN$_4$), has also been found to have square-pyramidal geometry about the copper(II) ion.[11]

In the present work we report the X-ray crystal and molecular structure of the complex **7**, aquo(1,1-difluoro-4,5,12,13-tetramethyl-1-bora-3,6,11,14-tetraaza-2,15-dioxacyclopentadeca-3,5,11,13-tetraenato)copper(II) perchlorate, [Cu(Me_4F_2-BO_2[15]teteneN$_4$)(H_2O)]ClO_4, which contains a seven-membered chelate ring between two imino donors, and compare this structure to that already reported for the analogous complex **8**, [Cu(Me_4F_2-BO_2[14]teteneN$_4$)(H_2O)]-ClO_4.[11] Structural investigations are presently being carried out on a copper(II) complex of the oxime precursor, **9**, $Me_4(OH)_2$[15]teteneN$_4$, on the novel copper(II) complex **10**, [Cu(Me_4-[16]teteneN$_4$)]$(ClO_4)_2$,[9] and on the copper(I) complex of the ligand Me_4F_2-BO_2[15]teteneN$_4$ in order to further establish the interesting geometrical effects of seven-membered chelate rings in macrocyclic copper(II) complexes.



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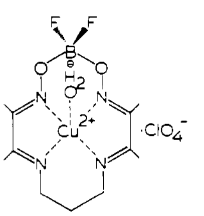

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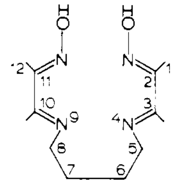

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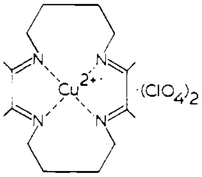

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A study of the copper(II) complexes of Me_4F_2-BO_2[14]-teteneN$_4$ by Addison et al.[14] indicates that the spectrochemical series is not followed when axial ligation occurs. The distance of the copper atom from the basal plane and, thus, the ligand field splitting due to the basal donor atoms are dependent on the binding strength of the axial ligand. The present paper also includes a spectrochemical study of various axial ligands with copper(II) complexes in which the basal donor atoms are likely to be distorted from planarity, including Me_4-H_2O_2-[15]teteneN$_4$, Me_4F_2-BO_2[15]teteneN$_4$, and Me_4-[16]teteneN$_4$. The results are discussed with emphasis on the spectral effects of the distortion of the basal plane.

Experimental Section

General Information. All chemical reagents were obtained commercially and were of high purity. Infrared spectra were recorded on Beckman IR8 or Beckman IR12 spectrophotometers and UV–visible spectra on Unicam SP1800 or Cary 14 spectrophotometers. Microanalyses were carried out by the Center for Trace Characterization, Texas A&M University.

Preparation of Ligands and Complexes. 4,9-Diaza-3,10-dimethyldodeca-3,9-diene-2,11-dione Dioxime (9), $Me_4(OH)_2$[15]teteneN$_4$. This compound was prepared by a method similar to that recently published by Gagne et al.[15] but was developed independently in this laboratory. 1,4-Diaminobutane (4.41 g, 0.05 mL) was added to a refluxing solution of 2,3-butanedione oxime (10.1 g, 0.10 mol) in ethanol (25 mL). After 30 min the solution was allowed to cool to room temperature and then refrigerated (5 °C) overnight. The product was filtered, washed with diethyl ether, and air-dried; yield of product 4.0 g (31%). Anal. Calcd for $C_{12}H_{22}N_4O_2$: C, 56.7; H, 8.72; n, 22.0. Found: C, 57.2; H, 8.73; N, 22.2.

(2-Oximino-11-oximinato-3,10-dimethyl-4,9-diazadodeca-3,9-diene)copper(II) Perchlorate, [Cu(Me_4-OHO[15]teteneN$_4$)]ClO_4. Method I. A hot solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (1.8 g, 5 mmol) in acetone (25 mL) was slowly added to a hot solution of the free ligand **9** (2.8 g, 10 mmol) in acetone (20 mL). The resulting red-brown solution was heated at reflux for 15 min, cooled to room temperature, and then refrigerated (5 °C) for 2 h. The black-green product was filtered and washed with cold acetone and diethyl ether. The product was recrystallized from acetonitrile/ethanol mixed solvent.

Anal. Calcd for $C_{12}H_{21}ClCuN_4O_6$: C, 34.6; H, 5.08; N, 13.5. Found: C, 34.7; H, 5.05; N, 13.7.

Method II. The method used by Addison et al.[14] for the preparation of (2-oximino-10-oximinato-3,9-dimethyl-4,8-diazaundeca-3,8-di-

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ene)copper(II) perchlorate dihydrate was adapted to the preparation of this complex. Copper acetate hydrate (10 g, 50 mmol), sodium acetate (15 g, 175 mmol), 1,4-diaminobutane (4.6 g, 54 mmol), and 2,3-butanedione oxime (11 g, 110 mmol) were refluxed together in methanol (50 mL) for 6 h. The crude product was preciptated by addition of sodium perchlorate (15 g), filtered off, and recrystallized from methanol.

(Isothiocyanato)(2-oximino-11-oximinato-3,10-dimethyl-4,9-diazadodeca-3,9-diene)copper(II), [Cu(Me_4-OHO[15]teteneN$_4$)(NCS)]. A 1.5 molar proportion of NaNCS was added to an acetonitrile solution of [Cu(Me_4-OHO[15]teteneN$_4$)]ClO_4 (9), and diethyl ether was added dropwise until the solution became turbid. Upon refrigeration, deep green needle crystals of the product separated. The product was filtered, washed with diethyl ether, and air-dried. Anal. Calcd for $C_{13}H_{21}CuN_5O_2S$: C, 41.6; H, 5.64; N, 18.7. Found: C, 41.9; H, 5.58; N, 18.7.

Iodo(2-oximino-11-iminato-3,10-dimethyl-4,9-diazadodeca-3,9-diene)copper(II), [Cu(Me_4-OHO[15]teteneN$_4$)I]. The preparation was carried out as for the isothiocyanato adduct but with sodium iodide replacing sodium thiocyanate.

Anal. Calcd for $C_{12}H_{21}CuIN_4O_2$: C, 32.5; H, 4.77; N, 12.6. Found: C, 32.5; H, 4.66; N, 12.5.

Chloro(2-oximino-11-oximinato-3,10-dimethyl-4,9-diazadodeca-3,9-diene)copper(II), [Cu(Me_4-OHO[15]teteneN$_4$)]. A warm solution of the free ligand 9 (2.8 g, 10 mmol) in acetonitrile/acetone mixed solvent (24 mL) was added with stirring to a warm suspension of cuprous chloride (0.50 g, 5 mmol) in acetonitrile (25 mL). An initial golden orange coloration was observed, followed by an increasingly intense green coloration. The solution was filtered after 15 min of reaction, and a few drops of diethyl ether were added. Well-formed, deep green needle crystals of the oxidized product separated upon standing at room temperature. They were washed with diethyl ether and air-dried. Anal. Calcd for $C_{12}H_{21}ClCuN_4O_2$: C, 40.9; H, 6.01; N, 15.9. Found: C, 41.1; H, 5.91; N, 16.0.

(2-Oximino-11-oximinato-3,10-dimethyl-4,9-diazadodeca-3,9-diene)nickel(II) Perchlorate, [Cu(Me_4-OHO[15]teteneN$_4$)]ClO$_4$. A hot solution of $Ni(ClO_4)_2{\cdot}6H_2O$ in acetone was added to a twofold molar excess of the free ligand 9 in hot acetone. The resulting orange-yellow solution was heated for 15 min and then cooled to room temperature. The orange crystalline product was filtered, washed with diethyl ether, and air-dried.

Anal. Calcd for $C_{12}H_{21}ClN_4NiO_6$: C, 35.0; H, 5.14; N, 13.6. Found: C, 35.0; H, 4.97; N, 13.8.

(Dioxane)bis[(1,1-difluoro-4,5,12,13-tetramethyl-1-bora-3,6,11,14-tetraaza-2,15-dioxacyclopentadeca-3,5,11,13-tetraenato)-copper(II) Perchlorate], [Cu$_2$(Me_4F_2-BO$_2$[15]teteneN$_4$)$_2$(dioxane)]-(ClO$_4$)$_2$. This complex was prepared by essentially the same method as that very recently reported by Gagne et al.[15] The Gagne[15] complex is a monodioxane adduct as well, although this is never clearly stated by the authors. The complex is similar to (dioxane)bis[(difluoro-(3,3′-trimethylenedinitrilo)bis(2-butanone oximato)borato)copper(II) perchlorate] reported elsewhere.[12]

Anal. Calcd for $C_{14}H_{24}BClCuF_2N_4O_7$: C, 33.1; H, 4.76; N, 11.0. Found: C, 33.2; H, 4.71; N, 11.2.

Aquo(1,1-difluoro-4,5,12,13-tetramethyl-1-bora-3,6,11,14-tetraaza-2,15-dioxacyclopentadeca-3,5,11,13-tetraenato)copper(II) Perchlorate, [Cu(Me_4F_2-BO$_2$[15]teteneN$_4$)]ClO$_4$. Purple crystals of this complex were obtained as crystals from a solution of the dioxane adduct in dilute acetic acid solution. Crystals used for the X-ray crystal structure determination were recrystallized again from water.

Anal. Calcd for $C_{12}H_{22}BClCuF_2N_4O_7$: C, 29.9; H, 4.59; N, 11.6. Found: C, 30.0; H, 4.51; N, 11.6.

Iodo(1,1-difluoro-4,5,12,13-tetramethyl-1-bora-3,6,11,14-tetraaza-2,15-dioxacyclopentadeca-3,5,11,13-tetraenato)copper(II), [Cu-(Me_4F_2-BO$_2$[15]teteneN$_4$)I]. A 1.2 molar proportion of sodium iodide in acetone was added to a warm solution of the preceding perchlorate salt in acetonitrile. The solution was filtered, and the iodo product crystallized upon standing as grass green crystals.

Anal. Calcd for $C_{12}H_{20}BCuF_2IN_4O_2$: C, 29.3; H, 4.10; N, 11.4. Found: C, 29.6; H, 3.89; N, 11.3.

Imidazolyl(1,1-difluoro-4,5,12,13-tetramethyl-1-bora-3,6,11,14-tetraaza-2,15-dioxacyclopentadeca-3,5,11,13-tetraenato)copper(II) Perchlorate, [Cu(Me_4F_2-BO$_2$[15]teteneN$_4$)(imidazole)]ClO$_4$. Turquoise crystals of the product were formed by slow evaporation of an acetonitrile solution of the perchlorate salt after addition of a 1.2 molar proportion of imidazole.

Anal. Calcd for $C_{15}H_{24}BClCuF_2N_6O_6$: C, 33.8; H, 4.54; N, 15.8. Found: C, 33.6; H, 4.41; N, 15.7.

(2,3,10,11-Tetramethyl-1,4,9,11-tetraazacyclohexadeca-1,3,9,11-tetraene)copper(II) Diperchlorate, [Cu(Me_4-[16]teteneN$_4$)](ClO$_4$)$_2$. A 2.1 molar proportion of 2,3-butanedione in dry methanol was added dropwise to a stirred suspension of bis(1,4-diaminobutane)copper(II) perchlorate in dry methanol, kept at less than 20 °C. The reaction mixture was filtered and placed in a tightly stoppered flask at 10 °C for 2 days. The resultant solution was warmed (35 °C) for 10 min with activated charcoal to remove alcohol condensation polymeric byproducts, filtered, and then evaporated down by rotatory evaporation. Addition of sodium perchlorate and subsequent chilling produced a low yield of deep blue crystals of the product. These were washed with cold acetone/diethyl ether and air-dried. The product was recrystallized from water.

Anal. Calcd for $C_{16}H_{28}Cl_2CuN_4O_8$: C, 35.6; H, 5.25; N, 10.4. Found: C, 35.3; H, 5.13; N, 10.2.

X-ray Data Collection. A crystal of [(Me_4F_2-BO$_2$[15]teteneN$_4$)(H_2O)Cu^{II}]ClO$_4$ approximately 0.17 mm × 0.15 mm × 0.18 mm 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 with use of graphite-monochromated Mo Kα ($\lambda = 0.70930$ Å) radiation: $a = 9.633$ (2) Å, $b = 13.401$ (2) Å, $c = 15.012$ (3) Å, $\beta = 95.11$ (2)°. The observed density of 1.65 (1) g cm^{-3} agrees with the calculated value of 1.654 g cm^{-3}. 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

$$\theta_{\lambda\alpha 2} = \theta_{\lambda\alpha 1} + \frac{\lambda\alpha_2 - \lambda\alpha_1}{\lambda\alpha}\,\frac{360}{2\pi}\tan \theta_{\lambda\alpha 1}$$

and A depends on the crystal mosaic spread and on the divergence of the primary beam. A for this structure was 0.70. The scan was extended on each of the peaks by 25% for background determination. Reflections were collected over the range $3° < \theta < 24°$. 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 0.05. Of 3365 unique reflections originally scanned including systematically absent ones, 2214 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.[16] Correction for absorption was not required due to the low absorption coefficient ($\mu = 13.7$ cm^{-1}). Neutral-atom scattering factors[16] were used, and the metal atom was corrected for anomalous dispersion (both real and imaginary). The space group was uniquely determined to be $P2_1/c$ from the systematic absences: $0k0$ with $k = 2n + 1$ and $h0l$ with $l = 2n + 1$.

Structure Solution and Refinement. The copper atom position was determined by Patterson methods with a three-dimensional map. The remaining atom positions were determined by the difference Fourier method. Hydrogen atom positions were not included in the refinement. Full-matrix refinement of these atom positions with anisotropic temperature factors gave an unweighted R index (R_F) of 0.052 and a weighted index (R_{wF}) of 0.073. The esd of an observation of unit weight was 1.993. 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 $w = 1/[\sigma(F_o)]^2 = 4F_o^2/[\sigma(F_o^2)]^2$, where $\sigma(F_o^2) = [[\sigma(I)]^2 + (pI)^2]^{1/2}/Lp$. The function minimized was $\sum w(|F_o| - |F_c|)^2$.[16] The final difference map was featureless (all peaks less than 0.3 e/Å^3).

Results and Discussion

Nomenclature. In general, the systematic names for macrocycles and macrocyclic compounds are too long to be con-

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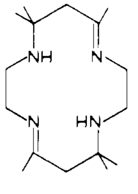
(16) All calculations were performed on a PDP11 computer using programs from the Enraf-Nonius structure determination package (SDP), Enraf-Nonius, Delft, Holland, 1975; revised 1977.

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

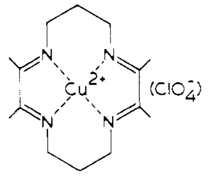
atom	x	y	z	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
Cu	0.15099 (8)	0.12947 (6)	0.39131 (5)	0.00802 (8)	0.00460 (4)	0.00342 (3)	−0.0008 (1)	0.00057 (9)	−0.00075 (8)
Cl	0.2888 (2)	0.3455 (1)	0.2174 (1)	0.0143 (2)	0.0063 (1)	0.00462 (9)	−0.0010 (3)	0.0021 (3)	0.0008 (2)
F1	−0.1596 (4)	0.3482 (3)	0.4899 (3)	0.0111 (5)	0.0062 (3)	0.0049 (2)	0.0007 (6)	0.0037 (5)	−0.0033 (4)
F2	−0.0870 (4)	0.1882 (3)	0.5211 (2)	0.0152 (5)	0.0057 (3)	0.0038 (2)	−0.0035 (6)	0.0043 (5)	0.0007 (4)
O1	0.0698 (4)	0.3131 (3)	0.4852 (3)	0.0090 (5)	0.0046 (3)	0.0037 (2)	−0.0011 (7)	0.0010 (6)	−0.0008 (4)
O2	−0.1125 (4)	0.2478 (3)	0.3736 (3)	0.0094 (5)	0.0046 (3)	0.0038 (2)	0.0004 (7)	0.0004 (6)	−0.0014 (4)
O3	0.1555 (6)	0.0167 (4)	0.5025 (3)	0.0236 (9)	0.0062 (3)	0.0036 (2)	−0.0055 (9)	−0.0002 (8)	0.0024 (5)
O4	0.2249 (8)	0.4334 (5)	0.1778 (4)	0.0353 (13)	0.0083 (4)	0.0051 (3)	0.0092 (13)	−0.0022 (11)	0.0023 (6)
O5	0.3909 (7)	0.3107 (5)	0.1631 (4)	0.0210 (9)	0.0130 (5)	0.0077 (3)	−0.0016 (13)	0.0072 (9)	−0.0082 (7)
O6	0.1888 (7)	0.2715 (5)	0.2254 (5)	0.0174 (8)	0.0103 (5)	0.0128 (5)	−0.0124 (11)	−0.0004 (11)	0.0033 (9)
O7	0.3508 (6)	0.3722 (5)	0.3037 (3)	0.0204 (9)	0.0116 (5)	0.0036 (2)	−0.0031 (11)	0.0014 (8)	0.0018 (6)
N1	0.1735 (5)	0.2497 (4)	0.4639 (3)	0.0078 (6)	0.0050 (3)	0.0025 (2)	−0.0015 (8)	0.0005 (6)	−0.0001 (5)
N2	0.3585 (5)	0.1358 (4)	0.4072 (4)	0.0085 (6)	0.0062 (4)	0.0039 (3)	−0.0006 (9)	0.0003 (7)	−0.0001 (6)
N3	0.1144 (5)	0.0291 (4)	0.2967 (3)	0.0098 (6)	0.0046 (3)	0.0032 (2)	0.0005 (8)	0.0013 (7)	−0.0004 (5)
N4	−0.0379 (5)	0.1693 (4)	0.3436 (3)	0.0080 (6)	0.0040 (3)	0.0028 (2)	−0.0002 (7)	0.0013 (6)	−0.0002 (5)
C1	0.2975 (7)	0.2824 (5)	0.4805 (4)	0.0094 (8)	0.0061 (4)	0.0027 (3)	−0.0046 (10)	−0.0002 (8)	0.0010 (6)
C2	0.3317 (9)	0.3826 (6)	0.5235 (5)	0.0165 (11)	0.0064 (5)	0.0053 (4)	−0.0085 (12)	−0.0015 (11)	−0.0031 (8)
C3	0.4031 (7)	0.2109 (6)	0.4523 (5)	0.0073 (7)	0.0077 (5)	0.0041 (3)	−0.0003 (11)	0.0001 (9)	0.0019 (7)
C4	0.5566 (8)	0.2372 (7)	0.4781 (6)	0.0073 (9)	0.0113 (7)	0.0083 (5)	−0.0052 (13)	−0.0006 (12)	−0.0028 (11)
C5	0.4535 (8)	0.0608 (6)	0.3719 (6)	0.0097 (9)	0.0096 (6)	0.0067 (5)	0.0071 (12)	0.0010 (11)	−0.0036 (9)
C6	0.4132 (8)	0.0513 (6)	0.2686 (5)	0.0145 (10)	0.0078 (6)	0.0055 (4)	0.0021 (13)	0.0065 (11)	−0.0001 (8)
C7	0.3287 (8)	−0.0429 (6)	0.2371 (5)	0.0130 (10)	0.0069 (5)	0.0063 (4)	0.0019 (12)	0.0043 (11)	−0.0025 (8)
C8	0.2004 (7)	−0.0612 (5)	0.2894 (5)	0.0124 (9)	0.0052 (5)	0.0054 (4)	0.0043 (11)	0.0034 (10)	−0.0008 (7)
C9	0.0084 (7)	0.0475 (5)	0.2414 (4)	0.0107 (8)	0.0044 (4)	0.0031 (3)	−0.0011 (9)	0.0039 (8)	−0.0002 (6)
C10	−0.0330 (8)	−0.0084 (6)	0.1553 (4)	0.0149 (10)	0.0071 (5)	0.0030 (3)	−0.0010 (13)	−0.0011 (9)	−0.0041 (7)
C11	−0.0816 (6)	0.1313 (5)	0.2677 (4)	0.0091 (7)	0.0042 (4)	0.0029 (3)	−0.0027 (10)	0.0021 (8)	−0.0001 (6)
C12	−0.2093 (7)	0.1640 (6)	0.2115 (4)	0.0107 (9)	0.0059 (5)	0.0039 (3)	0.0013 (11)	−0.0025 (9)	−0.0004 (7)
B	−0.0729 (8)	0.2728 (6)	0.4698 (5)	0.0091 (9)	0.0054 (5)	0.0033 (3)	−0.003 (1)	0.0017 (9)	0.0004 (7)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta(1,1)h^2 + \beta(2,2)k^2 + \beta(3,3)l^2 + \beta(1,2)hk + \beta(1,3)hl + \beta(2,3)kl)]$. Estimated standard deviations in the least significant digits are shown in parentheses.

venient for common use. This difficulty has been overcome in many cases by assigning short abbreviations which provide chemical information about the macrocycle or complex. Particularly useful in this regard is the abbreviation scheme suggested by Busch et al.[17] which has been widely applied. This scheme provides information about the number of atoms in the macrocyclic ring, the number of double bonds, the number and types of donor heteroatoms, and the number and types of substituents. Thus, **11** is abbreviated as $Me_6[14]$-dieneN_4 and **12** is abbreviated as $[Cl_2(Me_2[14]teteneN_4)Co^{III}](ClO_4)$. While it is obvious that these abbreviations are not completely unambiguous, they provide a great deal more information than trivial names such as cyclam and require very little more space.



11



12

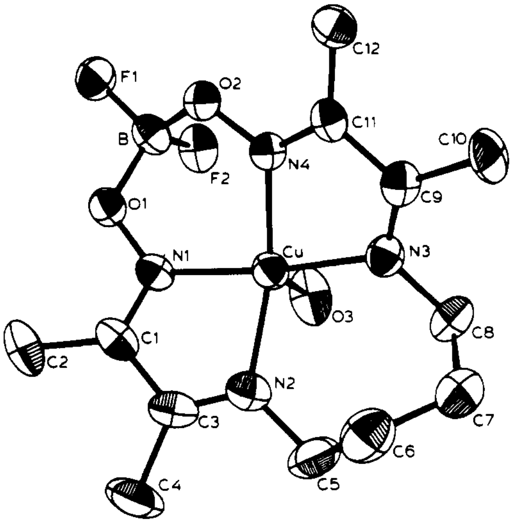
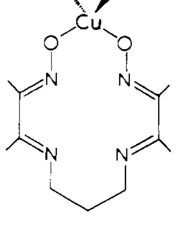


Figure 1. ORTEP[24] drawing of the complex cation $[(Me_4F_2\text{-}BO_2\text{-}[15]teteneN_4)(H_2O)Cu^{II}]^+$ at the 50% probability level.

Unfortunately, the general principles outlined by Bush et al. have not been followed in abbreviating macrocycles containing nondonor heteroatoms such as boron. These have been named by various trivial names such as cyclops[10] or mac[15] or simply referred to as L. As the literature in this area increases, trivial names will become increasingly cumbersome. In this report, therefore, we suggest a modification of the nomenclature of Busch et al.[17] which may be applied to these compounds. This involves inserting the nondonor heteroatoms after the substituents in the abbreviation. Thus, cyclops (**5**) is abbreviated as $Me_4F_2\text{–}BO_2[14]teteneN_4$ and the title compound is abbreviated as $[(Me_4F_2\text{-}BO_2[16]teteneN_4)(H_2O)\text{-}Cu^{II}](ClO_4)$. The slight increase in space which such abbreviations require is justified by the information which the abbreviation supplies. The nomenclature suggested here is also applicable to metallocycles such as compound **13** reported by Gagne et al.[12]



13

Description of the Structure of $[(Me_4F_2\text{-}BO_2[15]teteneN_4)(H_2O)Cu^{II}]ClO_4$. Positional and thermal parameters for

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(17) Goedken, V. L.; Merrell, P. H.; Busch, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 3397.

Table II. Least-Squares Planes through Selected Atoms from $[(Me_2F_2\text{-}BO_2[15]teteneN_4)(H_2O)Cu^{II}]ClO_4$

(a) Deviations from the Planes[a]

plane 1: *N1* (−0.021), *C1* (0.036), *C3* (−0.037), *N2* (0.022) Cu (0.098), O1 (0.087), C5 (0.012), C2 (0.171), C4 (−0.130)
plane 2: *N3* (0.004), *C9* (−0.007), *C11* (0.007), *N4* (−0.004) Cu (0.352), O2 (0.023), C8 (−0.239), C12 (0.005), C10 (−0.060)
plane 3: *N1* (−0.107), *N2* (0.097), *N3* (−0.098), *N4* (0.108) Cu (−0.293), C1 (0.276), C3 (0.292), C9 (0.427), C11 (0.571)
plane 4: *O1* (−0.034), *O2* (0.034), *N1* (0.030), *N4* (−0.030) B (−0.683), Cu (−0.242)

(b) Equations of the Planes[b]

plane	A	B	C	D	χ^2
1	0.0433	0.5039	−0.8627	−4.2308	0.99
2	0.5915	0.6544	−0.4710	−1.4194	0.04
3	0.2607	0.6034	−0.7536	−2.8255	16.38
4	0.3521	0.6165	−0.7043	−2.4799	2.07

(c) Dihedral Angles between Planes

planes	angle, deg	planes	angle, deg
1-2	40.4	2-3	25.3
1-3	15.1	2-4	19.4
1-4	1.0	3-4	6.0

[a] Planes were calculated by using the italicized atoms. All atoms were weighted equally. The number in parentheses is the distance (Å) of the atom from the plane. Esd's of these distances are approximately 0.01 Å. [b] The equation of the plane is of the form $Ax + By + Cz - D = 0$.

Table III. Bond Distances and Bond Angles for $[(Me_4F_2\text{-}BO_2[15]teteneN_4)(H_2O)Cu^{II}]ClO_4$

A. Bond Distances, Å

Cu-N1	1.947 (4)	Cu-N3	1.966 (4)
Cu-N2	2.000 (4)	Cu-N4	1.974 (4)
Cu-O3	2.249 (4)		
F1-B	1.364 (7)	F2-B	1.384 (6)
B-O1	1.480 (6)	B-O2	1.498 (6)
O1-N1	1.373 (5)	O2-N4	1.374 (5)
N1-C1	1.279 (6)	N4-C11	1.285 (6)
C1-C2	1.513 (7)	C11-C12	1.497 (7)
C1-C3	1.489 (7)	C11-C9	1.494 (7)
C3-C4	1.540 (7)	C9-C10	1.516 (7)
C3-N2	1.266 (7)	C9-N3	1.284 (6)
N2-C5	1.491 (7)	N3-C8	1.477 (6)
C5-C6	1.571 (8)	C8-C7	1.545 (8)
C6-C7	1.553 (8)		
Cl-O4	1.434 (4)	Cl-O6	1.398 (5)
Cl-O5	1.414 (5)	Cl-O7	1.424 (4)

B. Bond Angles, Deg

N1-Cu-N2	80.6 (2)	N2-Cu-N4	156.4 (2)
N1-Cu-N3	167.2 (2)	N2-Cu-O3	89.3 (2)
N1-Cu-N4	91.9 (2)	N3-Cu-N4	79.8 (2)
N1-Cu-O3	98.5 (2)	N3-Cu-O3	93.8 (2)
N2-Cu-N3	103.3 (2)	N4-Cu-O3	114.0 (2)
O1-N1-Cu	126.5 (3)	O2-N4-Cu	125.7 (3)
C1-N1-Cu	116.6 (4)	C11-N4-Cu	115.8 (3)
C3-N2-Cu	112.8 (4)	C9-N3-Cu	114.6 (3)
C5-N2-Cu	124.8 (4)	C8-N3-Cu	123.2 (3)
F1-B-O1	106.1 (4)	F1-B-O2	105.6 (4)
F2-B-O1	110.4 (4)	F2-B-O2	108.9 (4)
F1-B-F2	113.0 (4)	O1-B-O2	112.8 (4)
B-O1-N1	115.3 (4)	B-O2-N4	113.0 (4)
O1-N1-C1	115.7 (4)	O2-N4-C11	117.0 (4)
N1-C1-C2	123.5 (5)	N4-C11-C12	125.0 (4)
N1-C1-C3	112.2 (5)	N4-C11-C9	112.3 (4)
C2-C1-C3	124.2 (5)	C12-C11-C9	122.7 (4)
C1-C3-C4	116.7 (5)	C11-C9-C10	118.8 (4)
C1-C3-N2	116.9 (4)	C11-C9-N3	115.1 (4)
C3-N2-C5	122.3 (5)	C9-N3-C8	122.1 (4)
N2-C5-C6	107.4 (4)	N3-C8-C7	112.9 (4)
C5-C6-C7	116.3 (5)	C8-C7-C6	113.5 (5)
O4-Cl-O5	109.2 (3)	O5-Cl-O6	109.8 (3)
O4-Cl-O6	110.1 (3)	O5-Cl-O7	110.5 (3)
O4-Cl-O7	107.5 (3)	O6-Cl-O7	109.8 (3)

C. Close Contacts Indicative of H Bonding, Å

O3-F2[a]	2.839 (5)	Cu-O3-F2[a]	124.6 (2)
O3-O4[b]	2.741 (6)	Cu-O3-O4[b]	122.4 (2)
		F2[a]-O3-O4[b]	113.0 (2)

[a] F2 at 0.0870, −0.1882, 0.4789. [b] O4 at 0.2249, 0.0666, 0.6778.

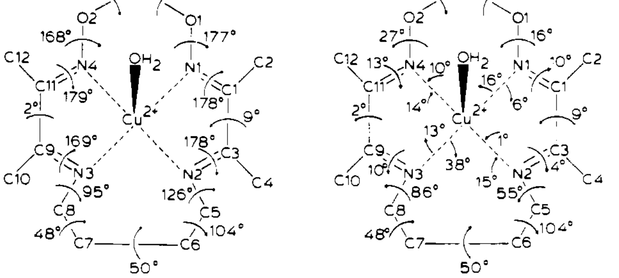

Figure 2. Torsional angles about bonds in the complex cation $[(Me_4F_2\text{-}BO_2[15]teteneN_4)(H_2O)Cu^{II}]^+$.

atoms in the structure are displayed in Table I. The structure of the macrocyclic complex is indicated in Figure 1. The complex is essentially square pyramidal, with water at the apex and macrocyclic nitrogen donors at the base. In contrast to the analogous complex $[(Me_4F_2\text{-}BO_2[14]teteneN_4)(H_2O)\text{-}Cu^{II}]ClO_4^-$, the nitrogen donors do not form a true plane. This can be appreciated in the least-squares plane for the four nitrogen atoms (Table II). These atoms extend alternately above and below the least-squares plane by about 0.1 Å. If the apical coordination is lost (as is the case upon reduction to Cu(I) in acetone or DMF[15]), the geometry would be tetrahedrally distorted square planar. This will favor the reduction to Cu(I), since Cu(I) favors a tetrahedrally distorted coordination in these complexes, as demonstrated by the 27° dihedral angle between N–Cu–N planes in the complex $[(Me_4F_2\text{-}BO_2[14]teteneN_4)Cu^I]$.[13] Indeed, Gagne et al.[15] report that the reduction of the copper(II) complex of **7** is more facile than that of complex **8** although they did not report exact values for the reduction potentials. Bond distances and bond angles for the complex and the counterion are listed in Table III. The closest perchlorate oxygen (O6) is 3.4 Å from the copper ion, indicating that perchlorate is not bound to copper. The Cu–O distance is approximately the same as that observed in **8**,[11] but the average Cu–N distance is somewhat longer (1.972 (8) Å) than the average Cu–N distance in **8** (1.94 (2) Å).[20] The displacement of copper from the mean nitrogen plane was, however, approximately the same (0.29 Å) as that in **8** where the displacement was 0.32 Å. The remaining bond distances were typical and do not require comment.

Both angle strain and torsional strain are evident within the seven-membered ring. Angle strain is spread throughout the ring, with most angles somewhat larger than the expected tetrahedral (sp^3) or planar (sp^2) geometries (Table III). Torsional strain is very apparent (Figure 2), especially about the N2–C5, C5–C6, and C7–C8 bonds. Strain is concentrated in particular at the imino nitrogens. This results in considerable torsion about the N3–C9 double bond (11°) and about the C1–C3 bond between conjugated double bonds. Strain within the boron-containing six-membered ring is comparable to that observed in **8**.[11]

The six-membered ring adopts a boat configuration, with N1, O1, O2, and N4 nicely coplanar (Table II). The seven-membered ring curves downward, away from the coordinated water. This probably occurs to prevent unfavorable interactions between the ring and the coordinated water. In **8**, where

Table IV. IR Spectral Data

compd	selected band maxima, cm^{-1}	
	ν(C=N) conjugated	other
$[Ni(Me_4\text{-}OHO[15]teteneN_4)]ClO_4$	1624 (w), 1523 (m)	~1090 vs, br [ν_3 of ClO_4^-]
$[Cu(Me_4\text{-}OHO[15]teteneN_4)I]$	1637 (w), 1541 (m)	
$[Cu(Me_4\text{-}OHO[15]teteneN_4)Cl]$	1604 (w), 1512 (m)	
$[Cu(Me_4\text{-}OHO[15]teteneN_4)(NCS)]$	1608 (w), 1516 (m)	2073 (s) [ν(C≡N)], obscured [ν(C–S)]
$[Cu(Me_4F_2\text{-}BO_2[15]teteneN_4)(H_2O)]ClO_4$	1640 (m), 1591 (m)	3566, 3422 [ν(O–H) of coordinated H_2O]
$[Cu(Me_4F_2\text{-}BO_2[15]teteneN_4)I]$	1640 (w), 1570 (m)	
$[Cu(Me_4F_2\text{-}BO_2[15]teteneN_4)(CN)]$	1635 (w), 1534 (m)	2122 (sh), 2111 (m) [ν(C≡N) of CN^-]
$[Cu(Me_4F_2\text{-}BO_2[15]teteneN_4)(NCS)]$	1642 (m), 1577 (m)	2096 (s), 2071 (s) [ν(C≡N) of NCS^-]
$[Cu(Me_4\text{-}[14]teteneN_4)](ClO_4)_2$	1616 (s)	~1100 vs, br [$\nu_3(ClO_4^-)$]
$[Cu(Me_4\text{-}[16]teteneN_4)](ClO_4)_2$	1599 (s)	~1100 vs, br [$\nu_3(ClO_4^-)$]

Table V. Optical Absorption Spectra

compd	medium	λ, nm	ε, M^{-1} cm^{-1}
$[Cu(Me_4\text{-}OHO[15]teteneN_4)]ClO_4$	CH_3CN	512 (sh)	201
	H_2O	536	120
$[Cu(Me_4\text{-}OHO[15]teteneN_4)(py)]ClO_4$	CH_3NO_2[a]	550	229
$[Cu(Me_4\text{-}OHO[15]teteneN_4)(imidazole)]ClO_4$	CH_3NO_2[a]	588	194
$[Cu(Me_4\text{-}OHO[15]teteneN_4)(2\text{-}methylimidazole)]ClO_4$	CH_3NO_2[a]	602	190
$[Cu(Me_4\text{-}OHO[15]teteneN_4)N_3]$	CH_3CN[b]	564	162
$[Cu(Me_4\text{-}OHO[15]teteneN_4)I]$	CH_3CN[b]	572	196
$[Cu(Me_4\text{-}OHO[15]teteneN_4)Br]$	CH_3CN[b]	578	176
$[Cu(Me_4\text{-}OHO[15]teteneN_4)Cl]$	reflectance, solid	644	
	CH_3CN	636	182
$[Cu(Me_4\text{-}OHO[15]teteneN_4)(NCS)]$	CH_3CN	582	176
$[Cu(Me_4F_2\text{-}BO_2[15]teteneN_4)H_2O]ClO_4$	reflectance, solid	586	
	H_2O	582	100
	CH_3NO_2	513	125
	CH_3CN	589	138
$[Cu(Me_4F_2\text{-}BO_2[15]teteneN_4)(py)]ClO_4$	CH_3NO_2[a]	633	131
$[Cu(Me_4F_2\text{-}BO_2[15]teteneN_4)(imidazole)]ClO_4$	CH_3NO_2[a]	650	144
$[Cu(Me_4F_2\text{-}BO_2[15]teteneN_4)(2\text{-}methylimidazole)]ClO_4$	CH_3NO_2[a]	672	163
$[Cu(Me_4F_2\text{-}BO_2[15]teteneN_4)(2,6\text{-}lutidine)]ClO_4$	CH_3NO_2[a]	606	136
$[Cu(Me_4F_2\text{-}BO_2[15]teteneN_4)(CN)]$	CH_3CN[b]	606	142
$[Cu(Me_4F_2\text{-}BO_2[15]teteneN_4)N_3]$	CH_3CN[b]	615	113
$[Cu(Me_4F_2\text{-}BO_2[15]teteneN_4)I]$	CH_3CN[b]	653	143
$[Cu(Me_4F_2\text{-}BO_2[15]teteneN_4)Br]$	CH_3CN[b]	628	123
$[Cu(Me_4F_2\text{-}CO_2[15]teteneN_4)Cl]$	CH_3CN[b]	595	135
$[Cu(Me_4F_2\text{-}BO_2[15]teteneN_4)(NCS)]$	CH_3CN	670	151
$[Cu(Me_4\text{-}[16]teteneN_4)](ClO_4)_2$	CH_3NO_2	606	125
	CH_3CN	670	129
$[Cu(Me_4\text{-}[16]teteneN_4)(H_2O)](ClO_4)_2$	reflectance, solid	655	
$[Cu(Me_4\text{-}[14]teteneN_4)](ClO_4)_2$	reflectance, solid	518	
	CH_3NO_2	516	80

[a] 0.1 M in the axial donor ligand. [b] With a large excess of the anion added as the sodium salt; sh = shoulder.

the ring is smaller, the ring is disordered with the central ring carbon occurring sometimes on the same side as H_2O and sometimes on the opposite side.[11] The coordinated water is significantly displaced from the true apex of the square pyramid, probably due to interaction with F2. In this case, if B was on the opposite side from H_2O there would be unfavorable steric interactions between F1 and carbons 1 and 12.

One of the hydrogens of the aquo ligand forms a hydrogen bond with a perchlorate anion, and the other forms a hydrogen bond with the fluorine atom of a second complex cation, as indicated in Table III. These bonds may contribute to displacement of O3 from a truly apical position. A stereoview of the unit cell is provided in Figure 3.

Infrared Spectra. Important IR bands are shown in Table IV. The complexes of ligands **7** and **9** all show two sharp bands in the 1500–1640-cm^{-1} region of the IR spectrum attributed to vibration of the conjugated imino groupings. In the IR spectra of the tetene complexes $[Cu(Me_4\text{-}[16]teteneN_4)](ClO_4)_2$ and $[Cu(Me_4\text{-}[14]teteneN_4)](ClO_4)_2$ strong bands at 1500 and 1616 cm^{-1}, respectively, are assigned to similar vibrations. The tetene complexes show no appreciable splitting in the ν_3 band at ~1100 cm^{-1} or the ν_4 band at 620 cm^{-1} for the ClO_4^- ion. Thus there is no evidence for ClO_4^- coordination. In the complexes of **5**, the ν(B–F) bands and the $\nu_3(ClO_4^-)$ bands are in a similar region of the spectrum so that splitting is hard to ascertain. No evidence of ClO_4^- coordination is apparent from the IR spectra of the appropriate complexes of ligand **6**.

The cyanide adduct $[Cu(Me_4F_2\text{-}BO_2[15]teteneN_4)(CN)]$ shows a medium band at 2111 cm^{-1} with a shoulder at 2122 cm^{-1}. This band is in a position close to that observed by Curtis and Curtis[18] in the complex cation $[Cu(teta)(CN)]^+$ but occurs at a somewhat lower energy than that observed by Addison et al.[14] for the complex $[Cu(Me_4F_2\text{-}BO_2[14]teteneN_4)(CN)]$. The band is within the range expected for terminal cyanide binding to copper(II).[19]

The thiocyanate adduct $[Cu(Me_4F_2\text{-}BO_2[15]teteneN_4)(NCS)]$ shows a strong band at 2073 cm^{-1} attributed to ν(C≡N) of N-coordinated thiocyanate, but the region around 800 cm^{-1}, in which the ν(C—S) band is expected, is obscured by other bands of the macrocyclic ligand. The ν(C≡N) band for the complex $[Cu(Me_4F_2\text{-}BO_2[15]teteneN_4)(NCS)]$ is also in the region expected for N-bound thiocyanate, but it is for

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(20) The esd's given are the root mean squares of the esd's for the individual bond distances.

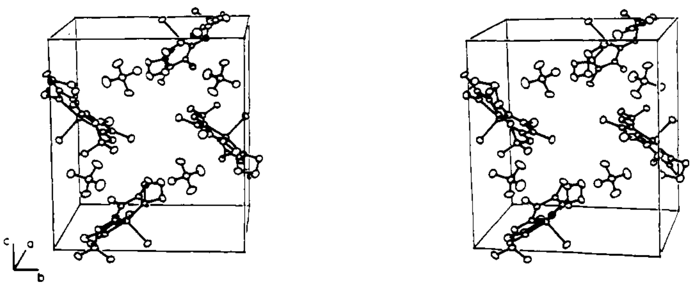

Figure 3. Stereoview of the unit cell for the complex [(Me$_4$F$_2$-BO$_2$[15]teteneN$_4$)(H$_2$O)Cu^{II}]ClO$_4$.

some reason split. The ν(C—S) region is once again obscured by other ligand bands.

Electronic Spectra. The optical absorption spectra of the [Cu(Me$_4$-OHO[15]teteneN$_4$)]$^+$ and [Cu(Me$_4$F$_2$-BO$_2$[15]teteneN$_4$)]$^+$ species are quite solvent sensitive, which is to be expected for cases in which axial ligation occurs. Addison et al.[14] found a similar effect for the [Cu(Me$_4$F$_2$-BO$_2$[15]teteneN$_4$)]$^+$ species in a variety of solvents. In nitromethane solution, the d–d band envelope for [Cu(Me$_4$F$_2$-BO$_2$[15]teteneN$_4$)]$^+$ peaks at 513 nm and shifts to longer wavelength when donor solvents are used (Table V). Larger shifts are observed for 1:1 adducts of the types [Cu(Me$_4$F$_2$-BO$_2$[15]teteneN$_4$)L]ClO$_4$ and [Cu(Me$_4$F$_2$-BO$_2$[15]teteneN$_4$)X], where L is a neutral donor and X$^-$ is a donor anion. The lowest d–d band maxima are observed at 672 nm for the species with L = 2-methylimidazole and at 670 nm for the species with X$^-$ = NCS$^-$.

The complex cation [(Cu(Me$_4$-OHO[15]teteneN$_4$)]$^+$ also interacts with donor solvents and anions, but the shifts in the d–d band maxima are generally less than those observed for [Cu(Me$_4$F$_2$-BO$_2$[15]teteneN$_4$)]$^+$.

Addison et al.[14] derived a "spectrochemical series for the axial ligands" in the adducts of [Cu(Me$_4$F$_2$-BO$_2$[14]teteneN$_4$)]$^+$. Their order was given as $\mathrm{H_2O} \ll \mathrm{C(CN)_3^-} <$ pyridine < imidazole < $\mathrm{I^-} < \mathrm{Br^-} < \mathrm{N(CN)_2^-} < \mathrm{Cl^-} < \mathrm{NCS^-} < \mathrm{CN^-} \sim \mathrm{NCO^-}$. This series is an arrangement of the ligands in order of the wavelengths (nm) of the spectral maxima of the adducts they form and not in the order of the energies (Δ values) of these band maxima as is the usual convention for the spectrochemical series[21-23] to which they refer. For purposes of clear comparison to the usual spectrochemical series, that of Addison et al.[14] sould thus be stated as $\mathrm{NCO^-} \sim \mathrm{CN^-} \ll \mathrm{NCS^-} < \mathrm{Cl^-} < \mathrm{N(CN)_2^-} < \mathrm{Br^-} \sim \mathrm{I^-} <$ imidazole < pyridine < $\mathrm{C(CN)_3^-} \ll \mathrm{H_2O}$.

Similar "observed spectrochemical series" can readily be determined from the data in Table V for the adducts of [Cu[Me$_4$F$_2$-BO$_2$[15]teteneN$_4$)]$^+$ and [Cu(Me$_4$-OHO[15]teteneN$_4$)], respectively. The series for the [Cu(Me$_4$F$_2$-BO$_2$[15]teteneN$_4$)]$^+$ adducts is 2-methylimidazole $\sim \mathrm{NCS^-} \ll \mathrm{I^-} \approx$ imidazole $\ll$ pyridine < $\mathrm{Br^-} < \mathrm{N_3^-} <$ 2,6-lutidine $\sim \mathrm{CN^-} < \mathrm{Cl^-} < \mathrm{CH_3CN} \sim \mathrm{H_2O}$. Within this series the halide ions are in the normal order with respect to one another, but the CN$^-$ and NCS$^-$ ions are in quite abnormal positions. The neutral donors are also in unusual positions with pyridine < Br$^-$ rather than the usual[21-23] $\mathrm{Br^-} < \mathrm{Cl^-} \ll$ pyridine. The spectrochemical series for the [Cu(Me$_4$-OHO[15]teteneN$_4$)]$^+$ adducts is $\mathrm{Cl^-} \ll$ 2-methylimidazole < imidazole < $\mathrm{NCS^-} \sim \mathrm{Br^-} \sim \mathrm{I^-} < \mathrm{N_3^-} \ll$ pyridine < $\mathrm{H_2O} \ll \mathrm{CH_3CN}$. According to this series the halides are in the reverse order to that of the usual spectrochemical series[21-23] but in the same order as that observed by Addison et al.[14] in the adducts of [Cu(Me$_4$-OHO[14]teteneN$_4$)]$^+$. The NCS$^-$ ion and CH$_3$CN are well out of the normal order in the spectrochemical series in the adducts of [Cu(Me$_4$-OHO[15]teteneN$_4$)]$^+$.

The simple crystal field arguments of Addison et al.[14] go partway toward explaining the unusual order in the observed spectrochemical series for these complexes. It must be noted, however, that in the series of Addison et al.[14] the neutral donors are at higher field whereas in both of our series they are placed at lower field. The model used by Addison et al. considers the effect of the axial ligand pulling the copper ion out from a basal N$_4$ plane by a varying distance ρ, which is apparently related to the binding strength of the axial ligand. We suggest that in our two series of complexes the presence of seven-membered rings between imino donors of the ligand gives rise to considerable steric strain which may cause the basal N$_4$ plane to be twisted. A twist of this kind is in fact observed in the solid state as shown by the X-ray crystallographic data previously discussed. It is hoped that the degree to which the twist of the basal plane is affected by changing the axial donor will be understood better following further X-ray crystallographic investigations.

The two complexes [Cu(Me$_4$-[14]teteneN$_4$)](ClO$_4$)$_2$ and [Cu(Me$_4$-[16]teteneN$_3$](ClO$_4$)$_2$ have widely differing visible spectra in CH$_3$NO$_2$. The lack of splitting in the ν(Cl–O) vibration of the perchlorate ion in both these complexes implies that perchlorate is not acting as a donor atom. The solid-state reflectance spectra are very similar to those observed in CH$_3$NO$_2$ solution, so that it appears that the shift in the d–d band observed in CH$_3$NO$_2$ solution must be due to a geometry change about the central copper(II) ion. It appears likely that the red [Cu(Me$_4$-[14]teteneN$_4$)](ClO$_4$)$_2$ complex has an essentially square-planar geometry to relieve torsional strain in the seven-membered chelate rings of the coordinated macrocycle in either of two ways: (i) by pushing the copper(II) ion out from the basal N$_4$ plane so that it is positioned at the apex of a square pyramid or (ii) by twisting the basal plane so that the geometry becomes intermediate between square planar and tetrahedral. The latter kind of distortion has been observed in the blue-purple complex [Cu(*cis*-[18]dieneN$_4$)](ClO$_4$)$_2$ (**2**), which incorporates a seven-membered chelate ring containing two imino donors.[7,8]

The difference in the d–d band envelope maximum is 516–606 nm for the complexes [Cu(Me$_4$-[14]teteneN$_4$)](ClO$_4$)$_2$ and [Cu(Me$_4$-[16]teteneN$_4$)](ClO$_4$)$_2$ and parallels the difference of 488–578 nm for the isomeric complexes **1** and **2**, the band maxima are at higher wavelength for **1** and **2** than for the corresponding tetene complexes which have four imino donor atoms in contrast to two imino and two secondary amino donors for **1** and **2**.

The crystal structure of [Cu(Me$_4$-[16]teteneN$_4$)](ClO$_4$)$_2$ is being investigated in order to determine the nature of and degree of distortion from square-planar geometry about the central copper(II) ion.

The d–d band maximum shifts considerably from [Cu(Me$_4$-[16]teteneN$_4$)]$^+$ in the presence of neutral and mo-

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noanionic donor atoms, indicating that axial ligation occurs in these complexes.

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Registry No. [Cu(7)(H_2O)]ClO_4, 75625-54-6; [Cu_2(7)$_2$(dioxane)](ClO_4)$_2$, 75625-56-8; Cu(7)I, 75625-57-9; [Cu(7)(imidazole)]ClO_4, 75625-59-1; Cu(7)(CN), 75625-60-4; Cu(7)(NCS), 75625-61-5; [Cu(7)(py)]ClO_4, 75625-63-7; [Cu(7)(2-methylimidazole)]ClO_4, 75625-65-9; [Cu(7)(2,6-lutidine)]ClO_4, 75625-67-1; Cu(7)N_3, 75625-68-2; Cu(7)Br, 75625-69-3; Cu(7)Cl, 75625-70-6; **9**, 71170-91-7; **10**, 75625-72-8; [Cu(Me_4-OHO[15]teteneN$_4$)]ClO_4, 75625-74-0; Cu(Me_4-OHO[15]teteneN$_4$)(NCS), 75625-75-1; Cu(Me_4-OHO[15]teteneN$_4$)I, 75625-76-2; Cu(Me_4-OHO[15]teteneN$_4$)Cl, 75625-77-3; [Ni(Me_4-OHO[15]teteneN$_4$)]ClO_4, 75400-11-2; [Cu(Me_4-[14]teteneN$_4$)](ClO_4)$_2$, 71170-98-4; [Cu(Me_4-OHO[15]teteneN$_4$)(py)]ClO_4, 75640-36-7; [Cu(Me_4-OHO[15]teteneN$_4$)(imidazole)]ClO_4, 75625-79-5; [Cu(Me_4-OHO[15]teteneN$_4$)(2-methylimidazole)]ClO_4, 75625-81-9; Cu(Me_4-OHO[15]teteneN$_4$)N_3, 75625-82-0; Cu(Me_4-OHO[15]teteneN$_4$)Br, 75625-83-1; [Cu(Me_4-[16]teteneN$_4$)(H_2O)](ClO_4)$_2$, 75625-85-3; 1,4-diaminobutane, 110-60-1; 2,3-butanedione oxime, 95-45-4; 2,3-butanedione, 431-03-8; bis(1,4-diaminobutane)copper(II) perchlorate, 73429-80-8.

Supplementary Material Available: A table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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Studies of Metal-Acetylene Complexes. 8. Syntheses and Molecular Structures of Two Platinum Complexes Containing Bulky Phosphine Ligands

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Single-crystal, three-dimensional structure determinations have been completed on two new platinum acetylene complexes of formula $PtL_2(CF_3C{\equiv}CCF_3)$, where L = $P(C_6H_{11})(C_6H_5)_2$ (**1**) and $P(C_6H_{11})_2(C_6H_5)$ (**2**). Crystals of **2** are monoclinic, space group *Cc*, with $Z = 4$ in a cell of dimensions $a = 22.829$ (5) Å, $b = 9.757$ (2) Å, $c = 19.509$ (4) Å, and $\beta = 111.21$ (1)°; those of **1** are also monoclinic, space group *C*2, with $Z = 2$ and cell dimensions $a = 16.321$ (3) Å, $b = 10.870$ (2) Å, $c = 11.282$ (2) Å, and $\beta = 110.54$ (1)°. Intensity data collected on an automated four-circle diffractometer was used for full-matrix least-squares refinement on *F*, which converged for **1** at $R = 0.036$ and 3761 observations and for **2** at $R = 0.049$ and 3979 observations. In each complex the coordination at the Pt atom is essentially planar, and the same C≡C bond distance was observed (**1**, 1.294 (14); **2**, 1.294 (16) Å). The deviation from linearity of the acetylene upon coordination was 43.5 (5)° in **1**, while values of 40 (1) and 47 (1)° were found in **2**. This variation in the dicyclohexylphenylphosphine complex has been attributed to predominantly steric interactions with the bulky phosphine ligands.

Introduction

Upon coordination to a transition metal an alkyne ligand adopts a cis-bent geometry. The magnitude of the deviation from linearity is referred to as the bend-back angle. A number of bis(triphenylphosphine)(alkyne)platinum(0) complexes have undergone crystallographic analysis, and the results indicate that a bend-back angle of about 40° is normal.[1] For example, a mean value of 39.9 (5)° was found in the complex bis(triphenylphosphine)(hexafluorobut-2-yne)platinum(0).[1] Bis(tricyclohexylphosphine)(hexafluorobut-2-yne)platinum(0) was the subject of the first reported study of an alkyne complex of platinum(0) containing a phosphine ligand other than triphenylphosphine, PPh_3.[2] The mean bend-back angle in the tricyclohexylphosphine, PCy_3, complex is 45.5 (8)°. Whether the significant increase in bend-back angle is due to an electronic or a steric effect, or a combination of both, was uncertain.[2] In an attempt to answer this question, we decided to prepare and examine the complexes containing the phosphines cyclohexyldiphenylphosphine, $PCyPh_2$, and dicyclohexylphenylphosphine, PCy_2Ph, which presumably possess intermediate basicity and steric bulk. Published approaches were not successful for these syntheses, and we report herein a successful synthetic procedure and the results of our structural investigations.

Experimental Section

All reactions were carried out under a dry nitrogen atmosphere by employing standard inert-atmosphere techniques. Microanalyses were performed by Spang Inc., Ann Arbor, Mich.

$PCyPh_2$ and PCy_2Ph were prepared by Grignard reactions on $PClPh_2$ and PCl_2Ph, respectively.[3] $Pt(1,5\text{-}C_8H_{12})_2$ was synthesized as a solution in toluene by the method reported by Stone et al.[4]

Preparation of Complexes. $PtL_2(F_3CC{\equiv}CCF_3)$. The complexes with L = $PCyPh_2$ and PCy_2Ph were prepared by the following method. The appropriate ligand (4 g) was added to a toluene solution of $Pt(1,5\text{-}C_8H_{12})_2$ (1 g), and hexafluorobut-2-yne (3 g) was bubbled in slowly. After the solution was stirred under a hexafluorobut-2-yne atmosphere for 12 h, the solvent was removed on a rotary evaporator. Addition of dichloromethane (15 mL) and methanol (150 mL), followed by cooling, resulted in a white crystalline precipitate.

$Pt(PCyPh_2)_2(F_3CC{\equiv}CCF_3)$: yield, 2.1 g; mp 200–201 °C dec. Anal. Calcd for $C_{40}H_{42}F_6P_2Pt$: C, 53.75; H, 4.74. Found: C, 52.23; H, 4.76.

$Pt(PCy_2Ph)_2(F_3CC{\equiv}CCF_3)\cdot CCl_2H_2$: yield, 2.2 g, mp 206–207 °C dec. Anal. Calcd for $C_{41}H_{56}Cl_2F_6P_2Pt$: C, 49.70; H, 5.65. Found: C, 50.23; H, 5.65.

Structure Determination. Clear, colorless, prismatic crystals of bis(cyclohexyldiphenylphosphine)(hexafluorobut-2-yne)platinum(0) were obtained by recrystallization from dichloromethane/methanol mixtures. An extensive preliminary photographic investigation, employing Weissenberg and precession techniques, showed the crystals to be monoclinic with Laue symmetry 2/*m*. The systematic absence observed, *hkl* for $h + k$ odd, is consistent with the space groups *Cm*, *C*2, or *C*2/*m*. The observed density indicates that the unit cell contains two molecules. Thus space group *C*2/*m* was eliminated since it would impose site symmetry 2/*m* upon the molecule, which it cannot possess. In view of the nature of the complex, symmetry 2 was thought to be more favorable than symmetry *m*, and the space group *C*2 (C_2^3, No. 5)[5] was chosen. This was later confirmed by the Bijvoet method.[6] The crystal data are summarized in Table I.

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