mediate III to move toward each other. In isomer V, on the other hand, no such close approach is involved, and the two pairs of carbon atoms are in fact well separated. One might then expect that in the tetra-*C*-methylated system, the cage geometry of V would be strongly favored and those of VI and VII hindered, as a consequence of methyl–methyl repulsions.

Conclusions

The structure reported in this paper, taken together with previously established structures,[1,2,4,12,18] extends our understanding of tetracarbon cobaltacarborane stereochemistry in a significant way: it allows us to consider in some detail the mechanisms of formation and interconversion of the $Co_2C_4B_6$ cage isomers. In general, we appear to have reached a point at which the available structural information in this area can support at least some mechanistic ideas. In other publications we shall attempt to deal with the observed[15] reversible rearrangement of $(CH_3)_4C_4B_8H_8$ isomers, the formation and stereochemistry of $(CH_3)_4C_4B_8H_8^{2-}$ and $(CH_3)_4C_4B_8H_9^-$ ions,[5] the insertion of transition metals into these species to give tetracarbon metallacarboranes of various types,[2] and related problems.

Acknowledgment. This work was supported in part by the Office of Naval Research and by the National Science Foundation, Grant CHE 76-04491.

Registry No. $(C_5H_5)_2Co_2(CH_3)_4C_4B_6H_6$, 67799-31-9.

Supplementary Material Available: Listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Part 5: K.-S. Wong, J. R. Bowser, J. R. Pipal, and R. N. Grimes, *J. Am. Chem. Soc.*, **100**, 5045 (1978).
(2) For a review, see R. N. Grimes, *Acc. Chem. Res.*, **11**, 420 (1978).
(3) (a) K. Wade, *Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976); (b) R. W. Rudolph, *Acc. Chem. Res.*, **9**, 446 (1976); (c) D. M. P. Mingos, *Nature (London), Phys. Sci.*, **236**, 99 (1972).
(4) J. R. Pipal and R. N. Grimes, *J. Am. Chem. Soc.*, **100**, 3083 (1978).
(5) W. M. Maxwell, R. F. Bryan, and R. N. Grimes, *J. Am. Chem. Soc.*, **99**, 4008 (1977).
(6) W. M. Maxwell, R. Weiss, E. Sinn, and R. N. Grimes, *J. Am. Chem. Soc.*, **99**, 4016 (1977).
(7) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(8) D. T. Cromer and J. T. Waber, "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.
(9) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(10) D. T. Cromer and J. A. Ibers, ref 8.
(11) D. P. Freyberg, G. M. Mockler, and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 447 (1976).
(12) D. P. Freyberg, R. Weiss, E. Sinn, and R. N. Grimes, *Inorg. Chem.*, **16**, 1847 (1977).
(13) W. M. Maxwell, V. R. Miller, and R. N. Grimes, *J. Am. Chem. Soc.*, **98**, 4818 (1976).
(14) D. F. Finster and R. N. Grimes, unpublished results.
(15) W. M. Maxwell, V. R. Miller, and R. N. Grimes, *Inorg. Chem.*, **15**, 1343 (1976).
(16) (a) V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 2830 (1973); (b) W. J. Evans, G. B. Dunks, and M. F. Hawthorne, *ibid.*, **95**, 4565 (1973); (c) V. R. Miller and R. N. Grimes, *ibid.*, **97**, 4213 (1975).
(17) Supporting this assignment are the facts that (1) no other known tetracarbon metallacarborane has an ^{11}B resonance lower than $\delta \sim 35$ and (2) no previously characterized tetracarbon metallacarborane has a low-coordinate boron adjacent to more than one metal. Thus, the strikingly different ^{11}B spectrum of VI implies a structural type not previously seen in this class of compounds.
(18) J. R. Pipal, W. M. Maxwell, and R. N. Grimes, *Inorg. Chem.*, **17**, 1447 (1978).

Contribution from the Department of Chemistry,
Colorado State University, Fort Collins, Colorado 80523

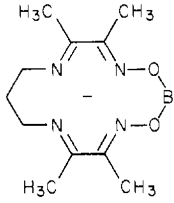
Structural Variations in Macrocyclic Copper(II) Complexes: Crystal and Molecular Structures of $[Cu(cyclops)H_2O](ClO_4)$ and $[Cu(PreH)H_2O](ClO_4)\cdot H_2O$

OREN P. ANDERSON* and ALAN B. PACKARD

Received January 19, 1979

The crystal and molecular structures of $[Cu(cyclops)H_2O](ClO_4)$ (**1**, cyclops = difluoro-3,3′-(trimethylenedinitrilo)bis(2-butanone oximato)borate) and of $[Cu(PreH)H_2O](ClO_4)\cdot H_2O$ (**2**, PreH = 3,3′-(trimethylenedinitrilo)bis(2-butanone oximate)) have been determined from three-dimensional single-crystal X-ray diffraction data, collected by counter techniques. Violet crystals of **1** were monoclinic, space group $P2_1/n$, with four formula units in the unit cell (a = 9.427 (5) Å, b = 15.921 (9) Å, c = 12.808 (8) Å, β = 96.69 (2)°). The structure of **1** was refined to R = 0.070 (R_w = 0.072) for 1333 independent reflections with $F^2 > 3\sigma(F^2)$. Red-violet crystals of **2** were orthorhombic, space group $P2_12_12_1$, with four formula units in the unit cell (a = 6.860 (2) Å, b = 12.436 (5) Å, c = 21.595 (7) Å). The structure of **2** was refined to R = 0.049 (R_w = 0.064) for 1538 independent reflections with $F^2 > 3\sigma(F^2)$. In both cases, the monomeric complex ions exhibited square-pyramidal coordination geometries about the copper(II) ion. In the structure of **2**, the copper(II) ion was only 0.10 Å above the plane of the four coordinating nitrogen atoms of the highly planar nonmacrocyclic ligand, and the Cu–O(H_2O) bond length of 2.355 (7) Å observed was elongated by an amount normal for apically bound water in square-pyramidal copper(II) complexes. Closure of the dioximate ligand of **2** to form the macrocyclic complex **1** resulted in an increase in the apical displacement of the copper(II) ion to the relatively large distance of 0.32 Å above the plane of the coordinating nitrogen atoms. In **1** the macrocyclic ligand was found to be nonplanar, and the bond to the apical water molecule (Cu–O(H_2O) = 2.253 (9) Å) was shortened considerably relative to that in **2**.

Introduction



3

Recent structural and chemical studies have explored some of the unique properties of metal complexes involving macrocyclic ligands such as difluoro-3,3′-(trimethylenedinitrilo)bis(2-butanone oximato)borate (**3**, hereafter referred to as cyclops).[1-5] Our general interest in the structural properties of potentially unusual copper(II) complexes led to the determination of the structure of the cyanato-*N* adduct [Cu(cyclops)NCO].[1] This complex was found to exhibit a very large displacement of the copper(II) ion from the basal plane of the four coordinating nitrogen atoms of the cyclops macrocycle. This large apical displacement of 0.58 Å was coupled with a very short bond between copper(II) and the

0020-1669/79/1318-1940$01.00/0

apical cyanato-*N* ligand (Cu–N = 2.038 (6) Å). Both of these observations were quite unusual, given the normally expected values of approximately 0.2 Å for the metal ion displacement from the basal plane and 0.2–0.6 Å for the elongation of the bond to the apical ligand relative to the bond lengths typically seen when the same ligand occupies a position in the basal plane of a square-pyramidal complex.

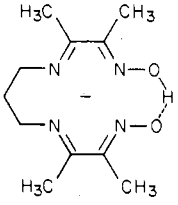
Other workers have also studied the properties of copper complexes of the cyclops macrocycle. Gagné has reported that the four-coordinate copper(I) cyclops complex forms very stable five-coordinate copper(I) complexes with ligands such as carbon monoxide[5] which can accept electron density from the metal. The spectroscopic and electrochemical properties of a series of monomeric copper(II) cyclops complexes involving varying apical substitution have been investigated,[4] and the energies of the d–d bands in the visible spectra of these complexes have been used to assign a "spectrochemical series" for apical ligands L and X^- in complexes such as $[Cu(cyclops)L]^+$ and [Cu(cyclops)X]. The spectrochemical series obtained in this manner was

$$H_2O \ll C(CN)_3^- < py < imidazole < I^-, Br^- < N(CN)_2^- < Cl^- < NCS^- \ll CN^-, NCO^- \quad (1)$$

These earlier authors pointed out that the placement of the neutral ligands such as water, imidazole, and pyridine relative to the halides in this series was highly unusual and demanded (based on a crystal field argument) a large amount of variation in the apical displacement of the copper(II) ion and unusually strong bonds to anionic ligands in the apical position.

The fact that water, which is normally a ligand of moderate ligand field, was found to occupy an extreme position at the low end of series 1 suggested that it would be interesting to determine the structure of the $[Cu(cyclops)H_2O]^+$ complex ion, in order to see whether the $Cu–O(H_2O)$ bond was actually weak, as the above series suggests, and whether the copper(II) ion was indeed much closer to the plane of the coordinating nitrogen atoms of cyclops in the aquo complex than in the cyanato-*N* complex discussed previously, as Addison and Wicholas' interpretation[4] of the spectrochemical series above would demand.

At the same time, it seemed advisable to explore the degree to which the macrocycle itself influences the structures of these complexes. The cyclops macrocycle affords a particularly convenient means of addressing this question, since one can also synthesize complexes of the noncyclized dioximate precursor of cyclops, 3,3′-(trimethylenedinitrilo)bis(2-butanone oximate) (**4**, hereafter referred to as PreH). Thus, by the



4

study of the structure of the $[Cu(PreH)H_2O]^+$ complex ion, it should be possible to ascertain the magnitude of the structural changes, particularly those involving metal displacement out of the basal plane and the bond between copper and the apical ligand, which accompany closure of **4** to form the cyclops macrocycle **3**. Therefore, this report concerns the crystal and molecular structures of the compounds aquo(difluoro-3,3′-(trimethylenedinitrilo)bis(2-butanone oximato)borato)copper(II) perchlorate (**1**, $[Cu(cyclops)H_2O]ClO_4$) and aquo(3,3′-(trimethylenedinitrilo)bis(2-butanone oximato))copper(II) perchlorate monohydrate (**2**, $[Cu(PreH)H_2O](ClO_4)\cdot H_2O$).

Experimental Section

Synthesis. (a) Aquo(3,3′-(trimethylenedinitrilo)bis(2-butanone oximato))copper(II) Perchlorate Monohydrate, $[Cu(PreH)H_2O](ClO_4)\cdot H_2O$ (2). The compound was prepared by the method described by previous workers.[4] Copper(II) acetate monohydrate (Mallinckrodt A.R., 10 g, 50 mmol), sodium acetate (15 g, 175 mmol), 1,3-propanediamine (4.6 mL, 55 mmol), and 2,3-butanedione monoxime (Aldrich, 11 g, 110 mmol) were maintained at reflux temperature in methanol (50 mL) for approximately 17 h. The crude product precipitated on addition of sodium perchlorate (15 g) and was separated by filtration. The product was recrystallized from water and dried in air to yield red-violet prisms, which slowly dehydrated when exposed to the atmosphere.

(b) Aquo(difluoro-3,3′-(trimethylenedinitrilo)bis(2-butanone oximato)borato)copper(II) Perchlorate, $[Cu(cyclops)H_2O](ClO_4)$ (1). The following procedure is a modification of that described by earlier workers.[4] **2** (8.8 g, 20 mmol) was added to 60 mL of boron trifluoride etherate ($BF_3\cdot OEt_2$) and the mixture was stirred and heated in a boiling water bath for 1 h. The resulting red-violet mixture was cooled to room temperature and was poured slowly onto a mixture of 800 g of crushed ice and 200 g of sodium acetate. The ether was removed with a rotary evaporator, and the product was precipitated by addition of 20 g of sodium perchlorate. The crude product was recrystallized from 10% acetic acid to give 6.1 g (65% yield) of violet crystals.

Crystal data: (a) for **1**, $[Cu(C_{11}H_{20}N_4O_3BF_2)](ClO_4)$, mol wt 468.11, monoclinic, $a = 9.427$ (5) Å, $b = 15.921$ (9) Å, $c = 12.808$ (8) Å, $\beta = 96.69$ (2)°, $V = 1909.2$ Å^3, $\rho_{obsd} = 1.64$ g cm^{-3} (by neutral buoyancy in 1,2-dibromoethane/chloroform), $\rho_{calcd} = 1.63$ g cm^{-3}, $Z = 4$, $F(000) = 956$, space group $P2_1/n$; Mo Kα radiation, $\lambda_1 = 0.70930$ Å, λ_2 0.71359 Å, μ(Mo Kα) = 13.9 cm^{-1}; (b) for **2**, $[Cu(C_{11}H_{21}N_4O_3)](ClO_4)\cdot H_2O$, mol wt 438.32, orthorhombic, $a = 6.860$ (2) Å, $b = 12.436$ (5) Å, $c = 21.595$ (7) Å, $V = 1842.3$ Å^3, $\rho_{obsd} = 1.61$ g cm^{-3} (by neutral buoyancy in 1,2-dibromoethane/chloroform), $\rho_{calcd} = 1.58$ g cm^{-3}, $Z = 4$, $F(000) = 908$, space group $P2_12_12_1$, MoKα radiation, λ_1 0.70930 Å, λ_2 0.71359 Å, μ(Mo Kα) = 14.2 cm^{-1}.

Data Collection and Reduction. (a) For 1, $[Cu(cyclops)H_2O](ClO_4)$. Preliminary Weissenberg and precession photographs revealed only Laue symmetry $2/m$, consistent with the monoclinic crystal system. These photographs exhibited the systematic absences $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, which are consistent only with the monoclinic space group $P2_1/n$, a nonstandard setting of $P2_1/c$ (No. 14).[7]

The small, violet crystal chosen for data collection was mounted on the Enraf-Nonius CAD-3 diffractometer, with the *c* axis approximately coincident with the diffractometer ϕ axis. After accurate centering of the crystal, the orientation matrix for data collection and the unit cell parameters reported above were obtained from least-squares calculations[8] on the automatically determined[9] 2θ, χ, and ϕ settings of 25 reflections (at 20 (±1) °C) with 2θ values in the range 20–24°.

The intensities of 3332 reflections (not all were unique) with $4.5° < \theta < 25°$ in the quadrant characterized by indices $\pm h$, $+k$, and $+l$ were measured by θ–2θ scans, employing Zr-filtered Mo Kα radiation. The total scan range was 1.0° for all reflections, with a constant scan rate of 10° min^{-1}. The weakest reflections were scanned a maximum of four times, while fewer scans were employed for stronger reflections. Background was counted at both ends of the scan, for a total time equal to the scan time. The takeoff angle was 3.5°, and Zr attenuators were inserted if necessary to avoid coincidence losses when the counting rate at the reflection maximum was greater than 2500 counts s^{-1}.

The intensity of one of three reference reflections ($\bar{2}46$, $\bar{1}74$, and 240) was measured every 25 reflections. During the course of data collection, these intensities were observed to decrease in a linear manner by approximately 15%. The data were corrected for this smooth decrease in intensity during the data reduction treatment. Lorentz and polarization corrections were applied to the observed data. The uncertainty parameter, *g*, in the formula used for the calculation of the standard deviation in the intensity[10,11] was taken as 0.04. No absorption correction was performed on the data, due to the low absorption coefficient (μ = 13.9 cm^{-1} for Mo Kα radiation) for this compound. The crystal used for data collection measured 0.14 × 0.10 × 0.25 mm, with the longest dimension oriented approximately along the diffractometer ϕ axis. Reflections for which $F^2 > 3\sigma(F^2)$ were taken to be observed, and 1333 unique reflections met this criterion.

Only these "observed" reflections were used in the solution and refinement of the structure.

(b) For 2, [Cu(PreH)H_2O](ClO_4)·H_2O. The general procedure was the same as described above, and only variations in this scheme will be reported here. Weissenberg and precession photographs revealed Laue symmetry *mmm*, and the observed systematic absences ($h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$) required the choice of space group $P2_12_12_1$ (No. 19).[7]

The red-violet crystal chosen for data collection was sealed in a thin-walled capillary tube with a small amount of mother liquor (to prevent dehydration and the resultant shattering of the crystal) and was mounted on the diffractometer with the *a* axis approximately coincident with the diffractometer ϕ axis. The angular coordinates of 26 reflections with $18° < 2\theta < 22°$ were used to calculate the orientation matrix and the cell parameters reported above.

The intensities of 1828 reflections in the octant $+h$, $+k$, $+l$ were sampled, and 1538 reflections were taken to be observed by the criterion mentioned in (a) of this section. The control reflections (312, 0,0,10, and 060) showed no significant changes in intensity during the course of data collection. No absorption correction was applied. The crystal measured 0.35 × 0.30 × 0.35 mm.

Solution and Refinement of the Structure. (a) For 1, [Cu(cyclops)H_2O](ClO_4). The position of the copper atom was assigned from the Patterson map, and initial positions for all other nonhydrogen atoms were then obtained from Fourier syntheses for which the atoms in known positions provided phase information. Scattering factors for copper(II), chlorine, fluorine, oxygen, nitrogen, carbon, boron, and spherical bonded hydrogen[12] atoms were taken from ref 13, as were correction terms $\Delta f'$ and $\Delta f''$ for anomalous dispersion due to copper and chlorine.

On the first cycle of refinement, employing isotropic thermal parameters for all atoms, the value of the thermal parameter for C4 underwent a large increase. Examination of a difference Fourier map of this region of the molecule (calculated with C4 removed) revealed two partially occupied sites for the atom C4. Interpolation of the peak intensities (in e Å^{-3}) suggested relative population parameters of 0.52 and 0.48 for C4 and C4′, respectively. No adjustment of these population parameters was done during subsequent refinement.

Due to the limited amount of observed data available, only a limited number of atoms could be allowed to have anisotropic thermal parameters if the data/parameter ratio was to remain acceptably high. Further refinement attributed anisotropic thermal parameters to Cu(II), N1–N4, O(H_2O), C4/C4′, and all atoms of the perchlorate anion. Refinement in this fashion gave a total of 173 parameters, for a data/parameter ratio of 7.7. The thermal parameters for the oxygen atoms of the perchlorate anion were quite large, but since no indication of resolution of partially occupied sites appeared in a difference Fourier synthesis, treatment of this motion was restricted to the use of anisotropic thermal parameters as described above.

Hydrogen atoms were included in the model when they were clearly visible in a difference Fourier map on the basis of refined atomic positions. These hydrogen atoms were placed in fixed, idealized positions 0.95 Å from carbon and given isotropic thermal parameters 1 Å^2 larger than that for the atom to which they were attached.

Full-matrix least-squares refinement continued until all shifts in parameters were less than 10% of the estimated standard deviation for that parameter (except for the disordered C4/C4′ positions, where shifts were still as great as 25%).

The final R $(=[\sum||F_o| - |F_c||/\sum|F_o|])$ value was 0.070 (unobserved reflections not included), while the final R_w $(=[\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2})$ value was 0.072. The NUCLS refinement program minimizes $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factor amplitudes, respectively, and w is the weight for each reflection $(=4F_o^2/\sigma^2(F_o^2))$. The error in an observation of unit weight was 1.86. These relatively high residual indices are due to the large thermal motions of the perchlorate group and to the fact that many atoms have only been assigned isotropic thermal parameters in the final model. No extinction correction was carried out, and a final difference Fourier map revealed no peaks higher than 0.43 e Å^{-3}.

Final atomic positional parameters for 1 are listed in Table I, while the final values of isotropic and anisotropic thermal parameters for 1 are listed in Table II.

Table I. Atomic Coordinates (Fractional)[a] for [Cu(cyclops)H_2O]ClO_4

atom	x	y	z
Cu	0.44698 (15)	0.15035 (9)	0.11561 (11)
Cl	0.2720 (5)	0.2814 (3)	0.3440 (3)
F1	0.8087 (7)	0.0334 (5)	0.3256 (5)
F2	0.7087 (7)	0.0181 (4)	0.1556 (5)
O(H_2O)	0.4977 (9)	0.0902 (6)	−0.0349 (6)
O1	0.5680 (9)	0.0441 (5)	0.2919 (6)
O2	0.7367 (8)	0.1510 (6)	0.2352 (6)
O3	0.2666 (14)	0.3486 (10)	0.4132 (12)
O4	0.3169 (18)	0.2158 (12)	0.4074 (15)
O5	0.3736 (13)	0.2955 (10)	0.2756 (9)
O6	0.1429 (13)	0.2656 (14)	0.2976 (12)
N1	0.4515 (10)	0.0636 (6)	0.2234 (7)
N2	0.2437 (10)	0.1229 (6)	0.1025 (8)
N3	0.4345 (10)	0.2596 (6)	0.0485 (7)
N4	0.6349 (9)	0.1901 (6)	0.1647 (7)
C1	0.3261 (14)	0.0379 (8)	0.2429 (10)
C2	0.2135 (15)	0.0695 (10)	0.1691 (11)
C3	0.1404 (18)	0.1629 (11)	0.0254 (14)
C4	0.1992 (26)	0.2086 (22)	−0.0512 (21)
C4′	0.1764 (36)	0.2639 (18)	0.0159 (30)
C5	0.3057 (17)	0.2863 (10)	−0.0210 (12)
C6	0.5461 (13)	0.3028 (8)	0.0648 (9)
C7	0.6637 (12)	0.2663 (8)	0.1359 (9)
C8	0.3111 (16)	−0.0149 (11)	0.3386 (13)
C9	0.0592 (20)	0.0387 (13)	0.1729 (14)
C10	0.5670 (15)	0.3891 (10)	0.0194 (11)
C11	0.8038 (15)	0.3106 (9)	0.1704 (10)
B1	0.7037 (16)	0.0601 (11)	0.2485 (13)

[a] Estimated standard deviations are given in parentheses.

(b) For 2, [Cu(PreH)H_2O](ClO_4)·H_2O. Only instances where the procedure for solution and refinement differed from that described in (a) of this section will be reported here. The oxygen atoms of the perchlorate anion again showed a large degree of thermal motion on refinement, but since no partially occupied sites were suggested by a difference Fourier map, the only compensation for this motion was anisotropic refinement of these atoms. All other atoms, including C4, refined normally. In this case the amount of data available allowed all atoms to be assigned anisotropic thermal parameters, and the final data/parameter ratio was 6.8 on this basis. Full-matrix least-squares refinement continued until all parameter shifts were less than 15% of the esd for that parameter. The R value at this point was 0.049 (unobserved reflections not included), while the value of R_w was 0.064. The error in an observation of unit weight was 2.05. At this point all atomic coordinates (x, y, z) were changed to ($\bar{x}$, $\bar{y}$, $\bar{z}$) and the resulting parameters were also refined to convergence. Since the normal residual indices at the conclusion of this second refinement were significantly higher ($R = 0.060$, $R_w = 0.075$) than those reported above from the refinement of the originally chosen atomic coordinates, the final coordinates and anisotropic thermal parameters obtained from the first refinement of the structure are reported in Tables III and IV, respectively. In a final difference Fourier map based on this model, all peaks were less than 0.5 e Å^{-3} in height, except for a weak peak (0.65 e Å^{-3}) near O5 of the perchlorate anion.

Results and Discussion

Crystals of 1 consist of discrete complex cations [Cu(cyclops)H_2O]$^+$ and isolated perchlorate anions. Figure 1 displays the structure found for this complex cation, while Figure 2 shows the manner in which the cations and anions are arranged within the cell. Ionic forces and hydrogen bonding involving the coordinated water molecule (see below) are responsible for the observed packing in this crystalline material. Table V lists bond lengths and angles for 1 derived from the atomic coordinates of Table I, while Table VI contains calculated results relating to the planarity of various parts of the complex cation.

Crystals of 2 also consist of discrete complex cations [Cu(PreH)H_2O]$^+$, together with the perchlorate anions and the molecules of lattice solvent. Figure 3 shows the structure of the [Cu(PreH)H_2O]$^+$ cation, and Figure 4 shows how one of the symmetry elements within the cell relates the cell contents. In addition to ionic forces, hydrogen bonding (see below) involving the coordinated water molecule is important

Table II. Anisotropic Thermal Parameters[a] for [Cu(cyclops)H$_2$O]ClO$_4$

atom	10^3U_{11}[b]	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Cu	43.8 (8)	53.2 (9)	50.0 (9)	−3.0 (10)	4.2 (6)	0.3 (1)
Cl	72 (3)	96 (4)	75 (3)	11 (2)	9 (2)	−8 (3)
F1	73 (2)					
F2	64 (2)					
H_2O	89 (7)	72 (6)	64 (6)	−26 (5)	35 (5)	−32 (6)
O1	60 (2)					
O2	56 (2)					
O3	143 (12)	178 (14)	210 (14)	−20 (11)	99 (10)	−104 (13)
O4	186 (16)	214 (18)	241 (18)	39 (14)	37 (13)	114 (16)
O5	142 (11)	232 (16)	95 (9)	13 (11)	76 (8)	−1 (10)
O6	70 (9)	414 (27)	167 (13)	−19 (13)	−26 (9)	−76 (16)
N1	47 (6)	49 (7)	60 (7)	−6 (5)	13 (5)	−14 (6)
N2	55 (7)	57 (8)	75 (8)	17 (5)	−13 (6)	0 (6)
N3	56 (6)	63 (7)	41 (6)	11 (7)	−2 (5)	−7 (6)
N4	42 (6)	50 (6)	44 (6)	9 (5)	−1 (3)	1 (7)
C1	62 (4)					
C2	74 (4)					
C3	99 (5)					
C4	47 (16)	106 (26)	63 (19)	8 (18)	−34 (15)	15 (19)
C4′	100 (27)	28 (18)	131 (32)	19 (17)	0 (23)	13 (19)
C5	79 (4)					
C6	50 (3)					
C7	47 (3)					
C8	100 (6)					
C9	134 (7)					
C10	87 (5)					
C11	76 (4)					
B1	64 (4)					

[a] Estimated standard deviations are given in parentheses. The form of the anisotropic thermal ellipsoid is given by $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)]$. [b] When only the value of U_{11} is given, that atom has been refined isotropically, and the value of U_{iso} is reported.

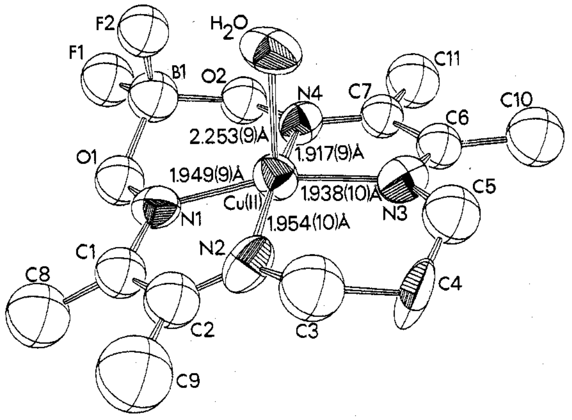


Figure 1. A view of the complex ion of **1**, [Cu(cyclops)H$_2$O]$^+$. Hydrogen atoms have been omitted, and thermal ellipsoids are drawn at the 50% probability level. Unshaded atoms correspond to those which were refined with isotropic motion only.

Table III. Atomic Coordinates (Fractional)[a] for [Cu(PreH)H$_2$O]ClO$_4$·H$_2$O

atom	x	y	z
Cu(II)	0.07593 (15)	0.07862 (8)	0.02599 (4)
Cl	0.2996 (4)	0.7711 (2)	0.1674 (1)
$H_2O(1)$	0.2607 (9)	−0.0793 (6)	0.0125 (3)
$H_2O(2)$	−0.2076 (14)	0.6390 (8)	0.1109 (4)
O1	0.4041 (9)	0.2054 (4)	−0.0189 (2)
O2	0.3818 (9)	0.1821 (5)	0.0955 (3)
O3	0.3392 (45)	0.7607 (12)	0.1098 (5)
O4	0.3302 (19)	0.8725 (8)	0.1896 (5)
O5	0.4108 (40)	0.7049 (16)	0.1982 (8)
O6	0.1486 (29)	0.7230 (20)	0.1909 (9)
N1	0.2381 (10)	0.1532 (5)	−0.0345 (3)
N2	−0.0795 (11)	0.0468 (5)	−0.0486 (3)
N3	−0.0968 (13)	0.0175 (6)	0.0892 (3)
N4	0.2189 (11)	0.1250 (6)	0.0991 (3)
C1	0.1898 (13)	0.1406 (7)	−0.0905 (3)
C2	−0.0019 (13)	0.0826 (7)	−0.0989 (4)
C3	−0.2599 (15)	−0.0134 (9)	−0.0441 (5)
C4	−0.2589 (13)	−0.0916 (8)	0.0085 (4)
C5	−0.2730 (14)	−0.0437 (9)	0.0739 (5)
C6	−0.0386 (13)	0.0358 (7)	0.1442 (4)
C7	0.1421 (14)	0.0968 (7)	0.1516 (3)
C8	0.3076 (21)	0.1825 (10)	−0.1454 (4)
C9	−0.0793 (17)	0.0691 (8)	−0.1611 (4)
C10	−0.1428 (18)	−0.0051 (9)	0.2020 (5)
C11	0.2399 (20)	0.1259 (9)	0.2126 (4)

[a] Estimated standard deviations are given in parentheses.

to the packing within the lattice, and hydrogen bonding from coordinated water to lattice solvent and an oxygen atom of a perchlorate anion is depicted in Figure 4. Table VII lists the bond lengths and angles calculated for **2**, and Table VIII presents the results of tests of the planarity of various portions of the [Cu(PreH)H$_2$O]$^+$ cation.

In the structure of **2**, the coordination geometry about the copper(II) ion is square pyramidal. The basal plane of this square pyramid contains the four coplanar nitrogen atoms of the quadridentate PreH ligand, with observed Cu–N bond lengths (1.950 (6), 1.972 (7), 1.960 (8), and 1.945 (7) Å for Cu(II) to N1–N4, respectively) which suggest that the Cu–N(oxime) bond lengths are slightly shorter than the Cu–N(imine) bond lengths. Small differences of this type have been observed in recently determined structures of related complexes such as [Cu(PreH)](ClO$_4$)·$^1/_2$CH$_3$OH,[14] [Cu(PnAO-H)(ReO$_4$)][15] (where PnAO-H corresponds to PreH saturated at C2 and C6 by addition of methyl groups), and the cobalt(III) complex [Co(PreH)(CH$_3$)$_2$].[16] The Cu–N bond lengths in the two copper(II) complexes cited above are quite similar in magnitude to those reported here for the [Cu(PreH)H$_2$O]$^+$ complex cation.

The copper(II) ion in [Cu(PreH)H$_2$O]$^+$ is found to be displaced only 0.10 Å above the plane of the four coordinating nitrogen atoms, in the direction of the water molecule which occupies the apical position in the coordination sphere about the metal. This value for the metal atom's apical displacement is certainly lower than expected[6] and may be compared with observed values of 0.13 Å in the case of the [Cu(PreH)]$^+$ methanol hemisolvate[14] and 0.24 Å in the case of the partially saturated perrhenate dioximate complex.[15] In the present case,

Table IV. Anisotropic Thermal Parameters[a] for $[Cu(PreH)H_2O]ClO_4 \cdot H_2O$

atom	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Cu	39.9 (5)	54.3 (6)	32.9 (4)	−9.2 (5)	0.9 (5)	0.1 (4)
Cl	74 (2)	54 (1)	48 (1)	−1 (1)	−2 (1)	6 (1)
$H_2O(1)$	64 (4)	63 (4)	63 (4)	15 (4)	1 (3)	2 (3)
$H_2O(2)$	107 (7)	123 (7)	82 (5)	−11 (6)	−4 (6)	−38 (5)
O1	48 (3)	55 (3)	49 (3)	−18 (3)	0 (3)	−2 (3)
O2	49 (4)	62 (4)	45 (3)	−15 (3)	−2 (3)	−7 (3)
O3	606 (42)	146 (12)	89 (7)	−115 (21)	58 (16)	−11 (7)
O4	158 (10)	90 (6)	131 (8)	−21 (7)	6 (8)	−37 (6)
O5	374 (28)	214 (18)	175 (14)	165 (20)	−45 (19)	30 (12)
O6	200 (17)	299 (25)	258 (20)	−140 (20)	121 (17)	−70 (18)
N1	39 (4)	42 (4)	35 (3)	−3 (3)	7 (3)	−7 (3)
N2	36 (3)	38 (3)	45 (3)	−2 (3)	4 (3)	−5 (3)
N3	51 (4)	48 (4)	44 (4)	−3 (4)	8 (4)	2 (3)
N4	52 (5)	46 (4)	37 (3)	−2 (4)	−5 (3)	−3 (3)
C1	45 (5)	38 (5)	39 (4)	−5 (4)	4 (4)	3 (4)
C2	60 (5)	39 (4)	39 (4)	7 (5)	−9 (4)	3 (4)
C3	44 (5)	68 (6)	76 (7)	−4 (5)	−13 (5)	−12 (5)
C4	44 (5)	56 (5)	69 (6)	−5 (4)	11 (4)	−6 (5)
C5	40 (5)	79 (7)	79 (7)	−11 (5)	12 (5)	−2 (5)
C6	42 (5)	46 (5)	43 (5)	8 (4)	12 (4)	−1 (4)
C7	65 (6)	43 (5)	33 (4)	7 (4)	4 (4)	5 (4)
C8	102 (9)	97 (8)	41 (5)	−26 (8)	9 (6)	−4 (5)
C9	76 (6)	71 (6)	43 (4)	−15 (7)	−16 (5)	−16 (4)
C10	83 (8)	85 (8)	65 (6)	−2 (6)	30 (6)	9 (6)
C11	108 (10)	76 (7)	38 (4)	−17 (7)	−7 (6)	−12 (4)

[a] Estimated standard deviations are in parentheses. The form of the anisotropic thermal ellipsoid is given by $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)]$.

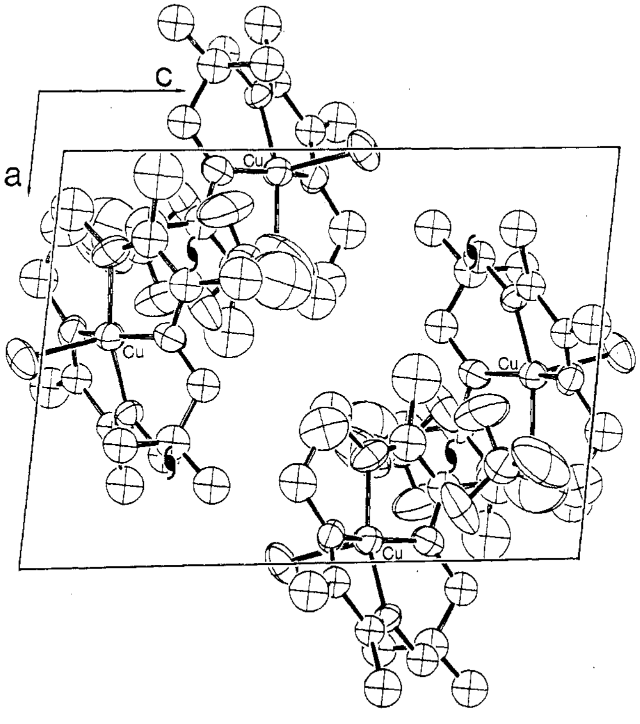


Figure 2. A view of the unit cell contents for compound **1**, $[Cu(cyclops)H_2O](ClO_4)$, looking down the *b* axis. The twofold crystallographic screw axes which relate complex ions within the cell are shown.

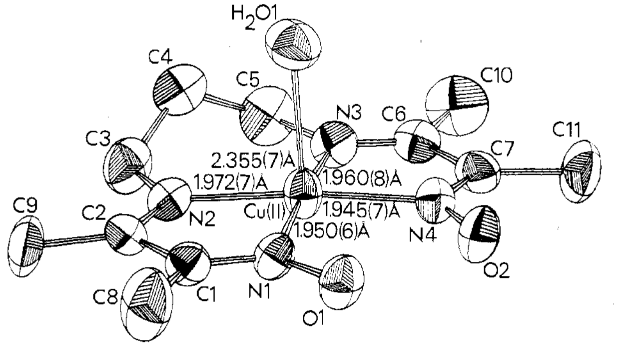


Figure 3. A view of the complex ion of **2**, $[Cu(PreH)H_2O]^+$. Hydrogen atoms have been omitted, and thermal ellipsoids are drawn at the 50% probability level.

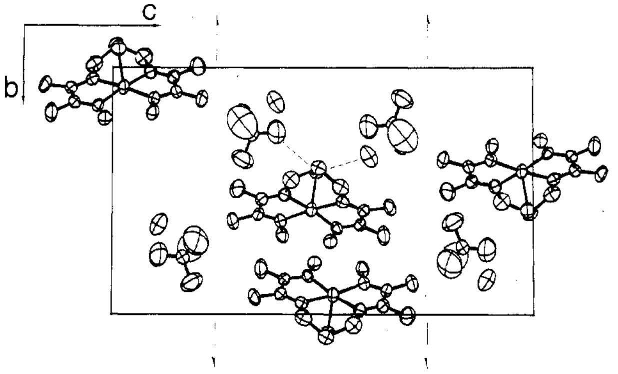


Figure 4. A view of the unit cell contents for compound **2**, $[Cu(PreH)H_2O](ClO_4) \cdot H_2O$, looking down the *a* axis. The twofold crystallographic screw axes relating the complex ions are shown.

the close approach of the metal ion to the basal plane (the N1–N4 plane) of the square pyramid leads to a flattening of the quadridentate PreH ligand into a nearly planar conformation (ignoring C4) more like the ligand conformation found in the six-coordinate Co(III) species.[16] In addition to this unexpectedly high degree of planarity, the methylene carbon C4 in the saturated portion of the ligand is found to be on the same side of the basal plane as the copper(II) ion and the apical water molecule, instead of the opposite side, as was the case in the earlier studies.[14,15] Despite these rather large changes in the ligand conformation, the bond lengths within the ligand are very similar to those reported previously.[14-16] As also was the case in these earlier studies, the ligand is "closed" by formation of a strong hydrogen bond involving the remaining oxime hydrogen atom and the two oxime oxygen atoms, with the distance O1–O2 observed here being 2.49 Å.

At 2.355 (7) Å, the bond between the copper(II) ion and the water molecule which occupies the apical position in the coordination sphere is elongated by an amount typical for

Table V. Bond Lengths and Angles[a] for [Cu(cyclops)H_2O]ClO_4

(a) Bond Lengths (Å)

Cu-O[b]	2.253 (9)	C1–C2	1.43 (2)
Cu-N1	1.949 (9)	C1–C8	1.51 (2)
Cu-N2	1.954 (10)	C2–C9	1.54 (2)
Cu-N3	1.938 (10)	C3–C4	1.39 (4)
Cu-N4	1.917 (9)	C3–C4′	1.65 (3)
N1-O1	1.36 (1)	C4–C5	1.61 (3)
N1-C1	1.30 (2)	C4′–C5	1.40 (4)
N2-C2	1.26 (2)	C6–C7	1.47 (2)
N2-C3	1.45 (2)	C6–C10	1.51 (2)
N3-C5	1.48 (2)	C7–C11	1.52 (2)
N3-C6	1.25 (2)	B1–F1	1.38 (2)
N4-O2	1.39 (1)	B1–F2	1.37 (2)
N4-C7	1.31 (2)	Cl–O3	1.39 (2)
O1-B1	1.48 (2)	Cl–O4	1.36 (2)
O2-B1	1.49 (2)	Cl–O5	1.39 (1)
		Cl–O6	1.32 (1)

(b) Bond Angles (deg)

H_2O-Cu-N1	108.4 (4)	N2-C2-C1	118.5 (13)
H_2O-Cu-N2	97.8 (4)	N2-C2-C9	121.6 (13)
H_2O-Cu-N3	90.6 (4)	C1-C2-C9	119.9 (14)
H_2O-Cu-N4	98.1 (4)	N2-C3-C4	114.8 (16)
N1-Cu-N2	81.0 (4)	N2-C3-C4′	110.5 (16)
N1-Cu-N3	160.9 (4)	C3-C4-C5	121.4 (20)
N1-Cu-N4	93.3 (4)	C3-C4′-C5	117.8 (23)
N2-Cu-N3	98.9 (4)	N3-C5-C4	111.6 (14)
N2-Cu-N4	164.1 (4)	N3-C5-C4′	114.1 (18)
N3-Cu-N4	81.7 (4)	N3-C6-C7	116.4 (11)
Cu-N1-O1	124.6 (7)	N3-C6-C10	125.3 (11)
Cu-N1-C1	114.4 (8)	C7-C6-C10	118.3 (11)
Cu-N2-C2	112.9 (9)	N4-C7-C6	112.0 (10)
Cu-N2-C3	122.3 (10)	N4-C7-C11	123.5 (10)
Cu-N3-C5	121.8 (8)	C6-C7-C11	124.4 (11)
Cu-N3-C6	114.3 (8)	O1-B1-O2	114.3 (12)
Cu-N4-O2	127.5 (7)	O1-B1-F1	104.9 (11)
Cu-N4-C7	115.4 (7)	O1-B1-F2	111.2 (11)
N1-O1-B1	112.8 (9)	O2-B1-F1	103.8 (11)
N4-O2-B1	111.9 (9)	O2-B1-F2	110.2 (12)
O1-N1-C1	119.2 (9)	F1-B1-F2	112.1 (12)
C2-N2-C3	124.8 (12)	O3-Cl-O4	104.0 (10)
C5-N3-C6	123.8 (11)	O3-Cl-O5	110.8 (9)
O2-N4-C7	116.8 (9)	O3-Cl-O6	109.5 (10)
N1-C1-C2	112.6 (12)	O4-Cl-O5	108.1 (10)
N1-C1-C8	120.3 (11)	O4-Cl-O6	109.3 (12)
C2-C1-C8	127.0 (13)	O5-Cl-O6	114.6 (9)

[a] Estimated standard deviations are given in parentheses. [b] O is from the H_2O.

square-pyramidal copper(II) coordination and falls well within the expected range of 2.22–2.89 Å for Cu^{II}–O(aquo) bond lengths for bonds of this type.[6] In particular, it is very similar to the bond length of 2.339 (9) Å observed for the apical Cu–O(aquo) bond in aquotetraamminecopper(II) sulfate[17] and to the value of 2.372 Å observed in the structure of diaquo(glycyl-L-tyrosinato)copper(II) dihydrate.[18] The coordinated water molecule is not directly over the copper(II) ion, as is clear from a comparison of the O(aquo)–Cu^{II}–N angles of 90.4 (2) and 91.3 (2)° for N1 and N2 with the angles of 95.0 (3) and 94.4 (3)° for N3 and N4. This small degree of distortion may be necessitated by the formation of hydrogen bonds between the coordinated water molecule and the lattice solvent molecule ($H_2O(1)$–$H_2O(2)$ = 2.77 (1) Å, Cu^{II}–$H_2O(1)$–$H_2O(2)$ = 112.6 (3)°) and between the coordinated water molecule and the perchlorate ion ($H_2O(1)$–O3 = 2.94 (2) Å, Cu^{II}–$H_2O(1)$–O3 = 125.0 (5)°). The only other possibly significant chemical interaction found in this structure involves a very long contact of 2.9 Å between oxime oxygen O1 of one complex ion and the copper(II) atom of another complex ion related by the crystallographic twofold screw axis parallel to *a*. This "contact" occurs in a direction that would correspond to the sixth coordination site in a very distorted octahedral environment, but since the distance involved is characteristic of a van der Waals contact between the two elements,[19] it cannot represent an interaction of any chemical importance.

Table VI. Least-Squares Planes[a] for [Cu(cyclops)H_2O]ClO_4

(a) Deviations from the Planes

plane 1 ($n = 4$): N1 (0.000), N2 (0.110), N3 (0.000), N4 (0.008), Cu (0.321), O1 (−0.192), O2 (−0.072), C1 (−0.334), C2 (−0.185), C3 (0.246), C4 (0.795), C4′ (−0.451), C5 (0.102), C6 (−0.228), C7 (−0.291), B1 (0.505)

plane 2 ($n = 4$): N1 (0.000), N2 (−0.129), C1 (0.000), C2 (0.000), Cu (−0.288), O1 (−0.109), C8 (−0.080), C9 (0.142), C3 (−0.197)

plane 3 ($n = 4$): N2 (−0.055), N3 (0.000), C3 (0.000), C5 (0.000), Cu (0.316), C2 (−0.371), C4 (0.589), C4′ (−0.647), C6 (−0.132)

plane 4 ($n = 4$): N3 (0.000), N4 (0.102), C6 (0.000), C7 (0.000), Cu (0.102), O2 (0.060), C5 (0.005), C10 (−0.031), C11 (−0.080)

plane 5 ($n = 4$): O1 (0.000), O2 (0.000), N1 (0.000), N4 (−0.134), Cu (0.052), C1 (−0.352), C7 (−0.563), B1 (0.704)

(b) Equations of the Planes[b]

plane	*A*	*B*	*C*	*D*
1	2.898	−8.898	−10.255	1.549
2	1.426	−12.724	7.626	1.869
3	3.636	−8.652	−10.060	1.154
4	4.236	−6.952	−10.585	0.478
5	3.541	−10.353	−8.961	1.062

(c) Dihedral Angles (deg) between the Planes

planes	angle	planes	angle
1-2	19.8	2-4	29.5
1-3	4.8	2-5	16.1
1-4	10.8	3-4	7.4
1-5	9.1	3-5	7.9
2-3	22.1	4-5	14.7

[a] In section (a), numbers in parentheses refer to the distance (Å) of the given atom from the calculated plane. The first *n* atoms in each case determine the given plane. [b] In the form $Ax + By + Cz = D$.

The high degree of thermal motion observed for the oxygen atoms of the perchlorate anion leads to calculated bond lengths and angles that are highly uncertain and, in some cases, apparently rather far from the ideal values. The values reported must, however, be regarded as satisfactory in light of the well-known propensity of the perchlorate anion for rotational disorder and, in fact, are very similar to the bond parameters observed for the perchlorate anion in the structure of [Cu(PreH)](ClO_4)·$^1/_2CH_3OH$[14] cited above.

Thus, the five-coordinate copper(II) complex of the nonmacrocyclic PreH ligand with water as the apical ligand exhibits a nearly planar quadridentate ligand, a metal atom position very close to the basal coordination plane, and a bond to the apical aquo ligand of normal length and, presumably, strength. This situation undergoes significant changes in all respects as the ligand is closed by the $-BF_2$ moiety to form the macrocyclic complex ion [Cu(cyclops)H_2O]$^+$ of **1**.

First, the metal atom in the macrocyclic complex is found 0.32 Å above the best least-squares plane through the four coordinating nitrogen atoms. This represents a shift of 0.22 Å of the copper(II) atom on closure of the macrocycle and is achieved despite the fact that the Cu–N bond lengths are not found to be significantly altered in the macrocyclic complex when compared with the corresponding bond lengths in the nonmacrocyclic case. These Cu–N bond lengths (see Figure 1) do not show any significant difference between Cu–N(oxime) and Cu–N(imine) bond lengths, and this is in agreement with the fact that no difference was seen between these classes of bonds in the structure of the [Cu(cyclops)NCO] complex.[1]

Instead, this large change in the apical displacement of the copper(II) ion on closure of the macrocycle is accompanied

Table VII. Bond Lengths and Angles[a] for $[\mathrm{Cu(PreH)H_2O}]\mathrm{ClO_4{\cdot}H_2O}$

(a) Bond Lengths (Å)

Cu-O[b]	2.355 (7)	C1-C2	1.51 (1)
Cu-N1	1.950 (6)	C1-C8	1.53 (1)
Cu-N2	1.972 (7)	C2-C9	1.46 (1)
Cu-N3	1.960 (8)	C3-C4	1.50 (1)
Cu-N4	1.945 (7)	C4-C5	1.54 (1)
N1-O1	1.35 (1)	C6-C7	1.46 (1)
N1-C1	1.26 (1)	C6-C10	1.53 (1)
N2-C2	1.29 (1)	C7-C11	1.52 (1)
N2-C3	1.45 (1)	Cl-O3	1.28 (1)
N3-C5	1.47 (1)	Cl-O4	1.37 (1)
N3-C6	1.27 (1)	Cl-O5	1.30 (2)
N4-O2	1.33 (1)	Cl-O6	1.30 (2)
N4-C7	1.30 (1)		

(b) Bond Angles (deg)

O[b]-Cu-N1	90.4 (2)	O2-N4-C7	122.5 (7)
O[b]-Cu-N2	91.3 (2)	N1-C1-C2	113.7 (7)
O[b]-Cu-N3	95.0 (3)	N1-C1-C8	124.2 (8)
O[b]-Cu-N4	94.4 (3)	C2-C1-C8	122.1 (7)
N1-Cu-N2	81.7 (3)	N2-C2-C1	115.0 (7)
N1-Cu-N3	174.4 (3)	N2-C2-C9	126.0 (8)
N1-Cu-N4	96.6 (3)	C1-C2-C9	118.9 (8)
N2-Cu-N3	99.5 (3)	N2-C3-C4	112.5 (8)
N2-Cu-N4	174.1 (3)	C3-C4-C5	116.5 (8)
N3-Cu-N4	81.6 (3)	N3-C5-C4	110.9 (8)
Cu-N1-O1	122.8 (4)	N3-C6-C7	117.5 (8)
Cu-N1-C1	115.6 (6)	N3-C6-C10	123.8 (8)
Cu-N2-C2	113.3 (6)	C7-C6-C10	118.7 (7)
Cu-N2-C3	120.7 (5)	N4-C7-C6	112.8 (7)
Cu-N3-C5	122.9 (6)	N4-C7-C11	120.9 (9)
Cu-N3-C6	113.0 (6)	C6-C7-C11	126.3 (8)
Cu-N4-O2	122.4 (5)	O3-Cl-O4	113.7 (9)
Cu-N4-C7	115.1 (6)	O3-Cl-O5	107.9 (14)
O1-N1-C1	121.2 (7)	O3-Cl-O6	120.1 (15)
C2-N2-C3	125.9 (7)	O4-Cl-O5	108.4 (10)
C5-N3-C6	124.1 (8)	O4-Cl-O6	114.3 (12)
		O5-Cl-O6	88.7 (15)

[a] Estimated standard deviations are given in parentheses. [b] O is from $\mathrm{H_2O(1)}$.

Table VIII. Least-Squares Planes[a] for $[\mathrm{Cu(PreH)H_2O}]\mathrm{ClO_4{\cdot}H_2O}$

(a) Deviations from the Planes

plane 1 ($n = 4$): N1 (0.006), N2 (−0.003), N3 (0.001), N4 (−0.001), Cu (0.096), O1 (0.032), O2 (−0.005), C1 (0.062), C2 (−0.009), C3 (−0.032), C4 (0.701), C5 (0.032), C6 (−0.077), C7 (−0.076)

plane 2 ($n = 4$): N1 (−0.046), N2 (0.021), C1 (0.011), C2 (−0.015), Cu (0.097), O1 (−0.059), C8 (0.055), C9 (−0.038), C3 (0.036)

plane 3 ($n = 4$): N2 (0.008), N3 (−0.003), C3 (−0.007), C5 (0.045), Cu (0.085), C2 (0.001), C4 (0.725), C6 (−0.093)

plane 4 ($n = 4$): N3 (0.000), N4 (0.000), C6 (−0.004), C7 (0.001), Cu (0.001), O2 (−0.015), C5 (0.016), C10 (0.031), C11 (0.024)

plane 5 ($n = 4$): O1 (0.001), O2 (−0.001), N1 (−0.027), N4 (0.006), Cu (0.082), C1 (0.012), C7 (−0.053)

(b) Equations of the Planes[b]

planes	*A*	*B*	*C*	*D*
1	3.626	−10.507	−1.754	0.692
2	3.447	−10.711	−1.591	0.719
3	3.562	−10.571	−1.881	0.695
4	3.611	−10.570	−0.370	0.567
5	3.622	−10.526	−1.456	0.672

(c) Dihedral Angles (deg) between the Planes

planes	angle	planes	angle
1–2	1.8	2–4	3.6
1–3	0.7	2–5	1.7
1–4	3.7	3–4	4.0
1–5	0.8	3–5	1.2
2–3	1.4	4–5	2.9

[a] In section (a), numbers in parentheses refer to the distance (Å) of the given atom from the calculated plane. The first *n* atoms in each case determine the given plane. [b] In the form $Ax + By + Cz = D$.

by distinct alterations in the conformation of the ligand molecule. The nonmacrocyclic ligand was nearly planar, while the macrocyclic ligand is far from planar. The unsaturated portions of the ligand (the four-atom portions N1–C1–C2–N2 and N3–C6–C7–N4) fold down (away from the apical position) to the extent that the dihedral angles between the planes through these unsaturated portions of the molecule and the N1–N4 basal plane of four nitrogen atoms become 20 and 11°, respectively. The same planes in the nonmacrocyclic case gave dihedral angles of 2 and 4°. This "folding" of the ligand upon closure changes the size of the macrocyclic cavity into which the metal must try to fit, and the N1–N4 nonbonding distance in **1** is found to be 2.81 (1) Å, a distance 0.10 Å shorter than the corresponding distance in **2**. It is tempting to consider this shrinkage of the macrocyclic cavity as the determining factor in the extrusion of the metal ion so far out of the basal plane in **1** as compared with **2**, but Gagñe's recent report[20] that the d^{10} copper(I) ion is able to occupy a position in the best plane through the four nitrogen atoms of [Cu(cyclops)] indicates that there may still be enough room for the copper(II) ion to fit into the basal plane in the absence of significant apical ligand bonding. The flexibility of the cyclops macrocyclic ligand is underscored by the two overall conformations present. If one examines the "boat" vs. "chair" configuration of atoms B1, N1, N2, N3, N4, and C4, one finds that both the "boat" and "chair" forms are present in the crystals of **1** by virtue of the observation of two positions of almost equal population for the atom C4 (C4 and C4′ in the atom list). This indicates that the energy difference between these two conformers is rather small, in agreement with the fact that the "boat" configuration was observed in the highly distorted [Cu(cyclops)NCO] complex,[1] while "chair" configurations were observed in a pair of closely related six-coordinate rhodium(III) complexes.[3,21] Individual bond lengths and angles within the macrocyclic ligand of **1** are in good agreement with the corresponding values from the structure of [Cu(cyclops)NCO].

The final consequence of the closure of the macrocyclic ligand is the strengthening of the bond between the copper(II) ion and the apical aquo ligand species. At 2.253 (9) Å, the $\mathrm{Cu{-}O(H_2O)}$ bond length observed for **1** is 0.102 Å shorter than the corresponding bond in the nonmacrocyclic **2**. This represents a strong bond between copper(II) and an apical water ligand, since it is very close to the short end of the range of bond lengths characteristic of water bound in this position (see above). It is still, however, significantly longer than the range of 1.92–2.16 Å characteristic of water bound to copper(II) in a basal position.[6] In addition to making this rather strong bond to the metal ion, the coordinated water molecule also forms hydrogen bonds to O3 of the perchlorate anion ($\mathrm{H_2O{-}O3}$ = 2.87 (2) Å, $\mathrm{Cu{-}OH_2{-}O3}$ = 109.6°) and F2 of another complex cation related by the inversion center ($\mathrm{H_2O{-}F2'}$ = 2.91 (1) Å, $\mathrm{Cu{-}OH_2{-}F2'}$ = 120.8°), which presumably accounts for the fact that the $\mathrm{H_2O{-}Cu^{II}{-}N}$ angles of **1** clearly show that the Cu–O bond is not perpendicular to the basal plane of the nitrogen atoms. No other chemically significant contacts involving the copper(II) ion were found within a distance of 3.5 Å.

The effects, then, of closing the macrocycle in going from **2** to **1** are as follows: (a) the copper(II) atom is displaced by more than 0.2 Å from the basal plane; (b) the macrocycle "flexes" and becomes distinctly nonplanar during this distortion process, in order to maintain effective bonding to the metal ion and to keep the Cu–N bond lengths approximately the same; (c) the bond between the copper(II) ion and the water molecule in the apical position becomes shorter and stronger as a result of the out-of-plane displacement of the metal ion.

It is clear that the position of the aquo complex at the extreme lower end of the observed spectrochemical series[4] is not due to a weak interaction between the coordinated water molecule and the copper(II) ion. The bond to the water molecule in the apical position is, in fact, quite strong, and the combined effect of the apical displacement of the metal ion and the strong apical bond must be to compress the energy separation between the $d_{x^2-y^2}$ and the d_{z^2} metal orbitals. Addison and Wicholas[4] predicted that this would be the case and also predicted that in a series of complexes [Cu(cyclops)L]$^+$ and [Cu(cyclops)X], where X$^-$ and L are a variety of apically bound ligands, a wide range of metal atom apical displacements would be seen, with the displacement becoming greater for ligands higher in their observed spectrochemical series.

The two structures presently available in this series, that of **1** and that of [Cu(cyclops)NCO],[1] confirm this second prediction also. The out-of-plane displacement in **1** is only 0.32 Å, whereas in the cyanato-*N* adduct the corresponding value was 0.58 Å and the bond to the apical ligand was found to be exceptionally strong. Since these two compounds represent the extreme ends of the spectrochemical series seen, other macrocyclic cyclops complexes should exhibit apical metal atom displacements and apical bond strengths intermediate in value. It will be of interest to investigate the structures of such complexes and to seek to confirm the final prediction made by Addison and Wicholas that anionic apical ligands in this system should be found to interact much more strongly with the copper(II) ions than would normally be expected. The fact that the iodo ligand lies higher in the observed spectrochemical series than does water certainly seems to support this view, and we expect to see a very strong interaction with the iodo ligand in our forthcoming study of the structure of [Cu(cyclops)I].

Acknowledgment. This work was supported, in part, by the Biomedical Research Support Grant program, administered through Colorado State University. Computing funds for this work were provided by Colorado State University and the Colorado State University Computing Center.

Registry No. **1**, 70178-69-7; **2**, 70178-67-5.

Supplementary Material Available: Table IX, calculated atomic fractional coordinates for hydrogen atoms of [Cu(PreH)H$_2$O](ClO$_4$)·H$_2$O; Table X, calculated fractional atomic coordinates for hydrogen atoms of [Cu(cyclops)H$_2$O](ClO$_4$); Table XI, a listing of structure factor amplitudes (×10) for [Cu(PreH)H$_2$O](ClO$_4$)·H$_2$O; Table XII, a listing of structure factor amplitudes (×10) for [Cu(cyclops)H$_2$O](ClO$_4$) (38 pages). Ordering information is given on any current masthead page.

References and Notes

(1) O. P. Anderson and J. C. Marshall, *Inorg. Chem.*, **17**, 1258 (1978).

(2) J. P. Collman and M. R. MacLaury, *J. Am. Chem. Soc.*, **96**, 3019 (1974).

(3) J. P. Collman, R. K. Rothrock, J. P. Sen, T. D. Tullius, and K. O. Hodgson, *Inorg. Chem.*, **15**, 2974 (1976).

(4) A. W. Addison, M. Carpenter, L. K-M. Lau, and M. Wicholas, *Inorg. Chem.*, **17**, 1545 (1978).

(5) R. R. Gagñe, J. L. Allison, R. S. Gall, and C. A. Kovall, *J. Am. Chem. Soc.*, **99**, 7170 (1977).

(6) B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).

(7) "International Tables for X-Ray Crystallography", Vol. I, Kynoch Press, Birmingham, England, 1969.

(8) The following programs were used in these structure determinations: Zalkin's FORDAP Fourier program; Ibers' NUCLS, a group/nongroup least-squares version of the Busing–Levy ORFLS program; Ibers' CELREF for least-squares refinement of cell parameters; ORFFE, Busing and Levy's function and error program; ORTEP, Johnson's thermal ellipsoid plot program; and HYDRA, Ibers' program to predict hydrogen atom positions. The program for data reduction and *Lp* correction was locally written for the CDC CYBER 171/172 computers at Colorado State University.

(9) The settings were determined by using the automated routines incorporated in the Enraf-Nonius diffractometer package.

(10) O. P. Anderson, A. B. Packard, and M. Wicholas, *Inorg. Chem.*, **15**, 1613 (1976).

(11) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(12) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(13) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.

(14) J. A. Bertrand, J. H. Smith, and D. G. Van Derveer, *Inorg. Chem.*, **16**, 1484 (1977).

(15) I. B. Liss and E. O. Schlemper, *Inorg. Chem.*, **14**, 3035 (1975).

(16) M. Calligaris, *J. Chem. Soc., Dalton Trans.*, 1628 (1974).

(17) B. Morosin, *Acta Crystallogr., Sect. B*, **25**, 19 (1969).

(18) P. A. Mossett and J.-J. Bonnett, *Acta Crystallogr., Sect. B*, **33**, 2807 (1977).

(19) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

(20) R. R. Gagne, J. L. Allison, and G. C. Lisensky, *Inorg. Chem.*, **17**, 3563 (1978).

(21) J. P. Collman, P. A. Christian, S. Current, P. Denisevich, T. R. Halbert, E. R. Schmitton, and K. O. Hodgson, *Inorg. Chem.*, **15**, 223 (1976).

Contribution from the Departments of Chemistry, Delft University of Technology, 2600 GA Delft, The Netherlands,
and the State University, 3508 TB Utrecht, The Netherlands,
and from the Institute for Materials Research, National Bureau of Standards, Washington, DC 20234

Crystal Structure of (Benzotriazolato)thallium(I) and Its Relation with the Mechanism of Corrosion Inhibition by Benzotriazole

J. REEDIJK,*[1a] G. ROELOFSEN,[1b] A. R. SIEDLE,[1c] and A. L. SPEK[1b]

Received February 12, 1979

The crystal and molecular structure of (benzotriazolato)thallium(I) is described. The structure has been determined by using three-dimensional X-ray diffraction data collected by counter methods. Crystal symmetry is consistent with the monoclinic space group $C2/c$. The unit cell parameters are a = 26.605 (3) Å, b = 4.057 (1) Å, c = 12.173 (2) Å, β = 93.74 (1)°, and Z = 8; d_{calcd} = 3.268 g/cm^3 and μ(Mo Kα) 246.8 cm^{-1}. The structure was solved by Patterson and subsequent Fourier techniques. Full-matrix least-squares refinement converged to R_F = 0.022 and R_{wF} = 0.024 for 1297 reflections. The structure consists of sheets of Tl(I) ions separated by benzotriazole anions. Each Tl ion is coordinated by three N atoms of the ligand at distances of 2.725–2.792 Å and by three neighboring N atoms at 3.271–3.326 Å in a distorted trigonal-prismatic geometry. Tl–Tl distances in the sheet are 3.592, 3.679, and 4.057 Å. The Tl ions are arranged in zigzag chains in the metallic layers. The layers are completely separated by the benzotriazole anions, which are packed very closely together and are directed with all N atoms to the Tl layer. The structure of the layers is similar to that predicted for the protective layer formed when metal surfaces (i.e., copper) are treated with the corrosion inhibitor benzotriazole.

Introduction

It is well-known that the heterocyclic ligand benzotriazole (abbreviated BTAH) is a useful inhibitor for staining and tarnishing of many metals, and it is frequently used for corrosion inhibition on copper and its alloys.[2-4] Copper surfaces can be treated simply by immersion in a hot aqueous solution of BTAH or by treating with BTAH-impregnated wrapping paper.[2,5]

Although several investigations have been carried out on the nature of the protective layer,[2-6] the structure and even