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Structure of the 14-Membered Macrocyclic Tetrathia Ether Complex of Copper(II). Evidence for Undistorted Geometries in Blue Copper Protein Models

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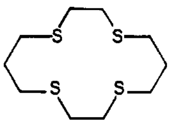
The crystal structure of Cu(14-ane-S_4)$(ClO_4)_2$ is reported where 14-ane-S_4 represents the saturated 14-membered cyclic tetrathia ether ligand, 1,4,8,11-tetrathiacyclotetradecane. The copper atom is centered in the plane of the four sulfur atoms with elongated bonds to two trans perchlorate groups completing the tetragonal coordination. Average bond lengths are Cu–S = 2.303 (1) Å and Cu–O = 2.652 (4) Å. The direct comparison of the crystal and solution spectra of Cu(14-ane-S_4)$(ClO_4)_2$ indicates that this complex maintains the same regular coordination geometry in the solution state. Moreover, the spectral and redox properties of the thia ether complex, similar to those exhibited by the blue copper proteins, indicate that coordinative distortion is not a primary factor in generating the distinctive properties which have been the hallmark of this class of proteins.

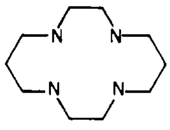
Introduction

Interest in macrocyclic complexes of transition metals has been stimulated both by their interesting kinetic and thermodynamic properties and by the apparent similarities of these species to systems of biological interest.[1] Most investigations reported to date have dealt with either the tetramine or polyether (crown ether) macrocycles. Recently, however, we have shown that the cyclic tetrathia ethers[2,3] represent an excellent series of ligands for the systematic investigation of the dependence of kinetic parameters on ligand ring size, presumably reflecting the influence of ligand structure upon bond formation and rupture processes.[4]

Of even greater interest is the very recent discovery that the copper(II) thia ether complexes exhibit unusual spectral and redox properties similar to those found in the blue copper proteins.[5-7] Since the blue copper protein phenomena have frequently been ascribed to the presence of tetrahedral or five-coordinate copper(II),[8-10] a rigorous determination of the structural features inherent in the copper(II) thia ether complexes was deemed a matter of the utmost importance.

In this paper we wish to report on the crystal structure of the diperchlorate salt of the most stable tetrathia ether–copper(II) complex involving the 14-membered macrocycle, 1,4,8,11-tetrathiacyclotetradecane (TTP or 14-ane-S_4). We will also compare this structure with that of the cyclic tetramine 1,4,8,11-tetraazacyclotetradecane (cyclam or 14-ane-N_4).


TTP
(14-ane-S_4)


cyclam
(14-ane-N_4)

Experimental Section

After recrystallization from a methanol–water mixture, a suitable crystal (0.11 × 19 × 23 mm) of Cu(14-ane-S_4)$(ClO_4)_2$ was mounted on a glass fiber with shellac. Initial x-ray examination by rotation and axial photographs on a Syntex $P2_1$ diffractometer yielded approximate lattice constants and showed the crystal to be of monoclinic symmetry. Least-squares refinement of 15 reflections with 2θ between 10 and 25°, which were centered with Mo Kα radiation (λ 0.71069 Å) diffracted from a highly oriented graphite monochromator in the parallel orientation with a takeoff angle of 4°, was used to determine precise lattice constants and orientation parameters. The crystal data are $a = 7.904$ (3) Å, $b = 8.830$ (4) Å, $c = 16.840$ (6) Å, $\beta = 126.33$

Table I. Atomic Parameters[a] for $Cu(14\text{-ane-}S_4)(ClO_4)_2$

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.0	0.0	0.0	113 (3)	83 (1)	23 (1)	−8 (2)	28 (1)	7 (1)
S1	0.1293 (2)	−0.1306 (2)	0.1432 (1)	132 (4)	71 (2)	25 (1)	1 (2)	30 (1)	6 (1)
S2	0.3380 (2)	0.0395 (1)	0.0489 (1)	118 (4)	59 (2)	26 (1)	−1 (2)	32 (1)	−1 (1)
C1	−0.2863 (8)	−0.1964 (6)	0.0345 (4)	147 (16)	75 (8)	30 (3)	−18 (9)	31 (6)	5 (4)
C2	−0.1074 (8)	−0.1475 (6)	0.1388 (4)	158 (16)	108 (9)	33 (3)	−20 (10)	48 (6)	1 (4)
C3	0.2934 (9)	0.0065 (6)	0.2403 (4)	196 (17)	110 (9)	28 (3)	−51 (11)	40 (6)	−12 (5)
C4	0.4930 (9)	0.0344 (6)	0.2466 (4)	157 (16)	114 (9)	28 (3)	−32 (10)	24 (6)	4 (4)
C5	0.4699 (8)	0.1362 (6)	0.1669 (4)	168 (15)	101 (9)	26 (3)	−62 (9)	36 (6)	−19 (4)
Cl	−0.1248 (2)	0.3536 (1)	0.0787 (1)	161 (4)	77 (2)	31 (1)	3 (2)	42 (2)	−2 (1)
O1	0.0190 (7)	0.2756 (5)	0.0667 (3)	309 (15)	136 (7)	84 (3)	29 (8)	13 (6)	−9 (4)
O2	−0.3054 (7)	0.3986 (5)	−0.0148 (3)	243 (14)	219 (9)	45 (3)	39 (10)	34 (5)	36 (4)
O3	−0.1864 (6)	0.2502 (5)	0.1235 (3)	290 (14)	135 (7)	54 (3)	−48 (8)	85 (6)	58 (4)
O4	−0.0215 (7)	0.4806 (4)	0.1420 (3)	376 (17)	106 (7)	65 (3)	−61 (9)	90 (6)	35 (4)

[a] Standard deviations from the full variance-covariance matrix are given in parentheses for the least significant digit(s) in all tables. The form of the anisotropic temperature factor is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The β's are multiplied by 10^4.

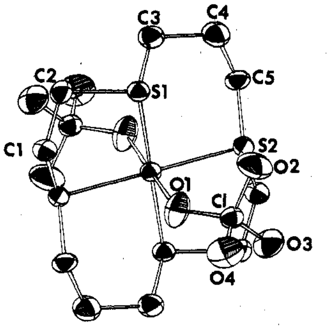


Figure 1. Molecular structure and atomic labeling of $Cu(14\text{-ane-}S_4)(ClO_4)_2$ with thermal ellipsoids.

(2)°, d(flotation) = 1.90 g cm^{-3}, d(calcd) = 1.87 g cm^{-3}, $Z = 2$, and $\mu_a = 19.35$ cm^{-1}. Examination of counter intensities showed systematic absences of $l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$, uniquely consistent with the space group $P2_1/c$.

Intensity data for $(\sin\theta)/\lambda < 0.595$ were collected by the θ–2θ scan technique with a scan range from 2θ(Mo Kα_1) − 1.0° to 2θ(Mo Kα_2) + 1.0° and a scan rate of 2.02°/min. Backgrounds were measured at each end of the scan for a total of half the scan time. Three standard reflections, measured after every 97 reflections, were statistically constant. Standard deviations[12] were assigned to the intensities according to the formula $\sigma(I) = [\sigma_{\text{counter}}^2 + 0.03I^2]^2$, where $\sigma_{\text{counter}} = (I + 4B)^{1/2}$, I is the net intensity, and B is the total background counts. Extinction and absorption corrections were not applied. The maximum error introduced by absorption between the shortest path and largest path in a worst-case approximation is less than 7% on F. Of the 1378 data examined, 968 had observed net intensities greater than $3\sigma(I)$ and were used in the solution and refinement of the structure.

The crystallographic symmetry required the independent copper ion to be at the origin. Successive Fourier syntheses yielded the positions of the nonhydrogen atoms. After isotropic least-squares refinement, the positions of the hydrogen atoms were calculated with assumed C–H distances of 0.97 Å and verified on a difference Fourier synthesis. Full-matrix least-squares refinement of all nonhydrogen positional coordinates and anisotropic thermal parameters with isotropic hydrogen atoms included as fixed contributions yielded the discrepancy factors

Table II. Distances (Å) and Angles (deg) in $Cu(14\text{-ane-}S_4)(ClO_4)_2$

	Distances		
Cu–S1	2.308 (1)	C1–C2	1.528 (5)
Cu–S2	2.297 (1)	C3–C4	1.551 (6)
Cu–O1	2.652 (4)	C4–C5	1.550 (6)
S1–C2	1.831 (5)	Cl–O1	1.441 (4)
S1–C3	1.828 (5)	Cl–O2	1.421 (4)
S2–C5	1.829 (5)	Cl–O3	1.443 (4)
S2–C1′	1.825 (5)[a]	Cl–O4	1.428 (4)
	Angles		
S1′–Cu–S2	89.9 (4)	S2–C2–C1	107.7 (3)
S1–Cu–S2	90.1 (4)	S2–C5–C4	112.0 (4)
S1–Cu–O1	97.7 (2)	S1–C3–C4	109.3 (4)
S2–Cu–O1	87.0 (2)	C3–C4–C5	114.9 (5)
Cu–S1′–C1	100.8 (2)	O1–Cl–O2	109.8 (3)
Cu–S2–C2	99.1 (2)	O1–Cl–O3	108.2 (2)
Cu–S1–C3	104.2 (2)	O1–Cl–O4	109.1 (3)
Cu–S2–C3	104.7 (2)	O2–Cl–O3	109.5 (3)
Cu–O1–C1	130.3 (2)	O2–Cl–O4	110.9 (3)
S1′–C1–C2	107.9 (3)	O3–Cl–O4	109.3 (2)

[a] The primed atoms are related to unprimed atoms by the inversion center at the origin.

$$R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.032$$
$$R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.038$$

and an error of fit of 1.77. The highest residual electron density in the final difference map was 0.58 e/Å^3. The atomic parameters are given in Table I.

Results and Discussion

The molecular structure of $Cu(14\text{-ane-}S_4)(ClO_4)_2$ and the packing arrangement are shown in Figures 1 and 2, respec-

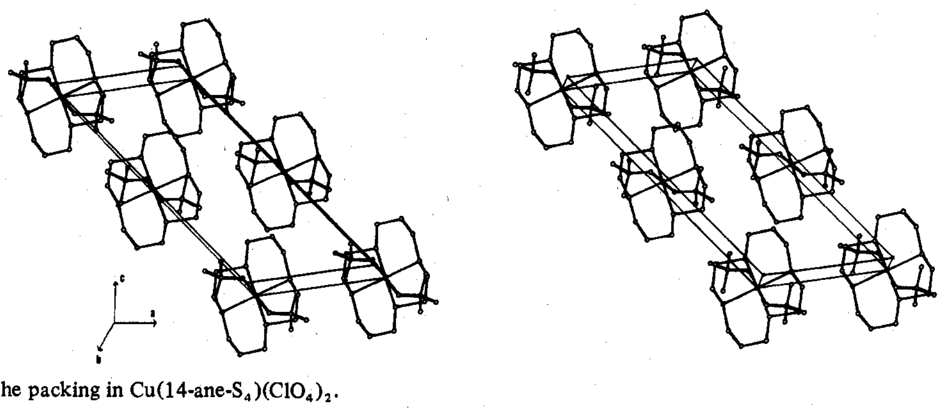


Figure 2. View of the packing in $Cu(14\text{-ane-}S_4)(ClO_4)_2$.

Table III. Comparison of Torsion Angles (deg) in Some 14-Membered Saturated Macrocyclic Complexes

	Strain-free value	Cu(14-ane-S_4)-$(ClO_4)_2$	Ni(14-ane-S_4)-$(BF_4)_2$[13]	Cu(14-ane-N_4)-$(ClO_4)_2$[16]	Co(14-ane-N_4)-$(ClO_4)_2$[16]
C5′–X2′–C1–C2	180	−158	−157	−170	−171
X2′–C1–C2–X1	60	67	61	55	53
C1–C2–X1–C3	180	−153	−157	−171	−171
C2–X1–C3–C4	180	180	180	180	180
X1–C3–C4–C5	−60	−77	−75	−69	−68
C3–C4–C5–X2	60	75	75	70	69
C4–C5–X2–C1′	180	−170	180	180	178

tively. Distances and angles are given in Table II. The molecule is a discrete monomer in which the tetradentate macrocycle, 14-ane-S_4, is in the endodentate conformation and occupies the four equatorial coordination sites about the copper(II) ion. The two perchlorate ions are coordinated in the axial positions at a distance of 2.652 (4) Å completing the typical Jahn–Teller distorted coordination sphere of the copper(II) ion. The molecule has crystallographically required symmetry of $\bar{1}$ (C_i), and thus the copper(II) ion and the four sulfurs are precisely coplanar.

We find that the structure of Cu(14-ane-S_4)$(ClO_4)_2$ is typical of tetragonal Cu(II) complexes. As seen in Table II, the Cu–S bond lengths are equivalent at 2.297 (1) and 2.308 (1) Å while the S–Cu–S bond angles are equivalent at 90.1 (4) and 89.9 (4) Å. This implies that there is no distortion in the equatorial plane of the coordination sphere from D_{4h} symmetry.

Previous authors have suggested that the unique spectral and redox properties of the blue copper proteins result from the imposition of a highly distorted coordination sphere upon the Cu(II) ion.[8–10] Both flattened tetrahedral and trigonal-bipyramidal geometries have been suggested, with the latter generally given preference.

The solution spectra and redox properties of complexes of Cu(II) with 14-ane-S_4 and related polythia ethers have been shown to be comparable to those of blue copper proteins.[5,6] Moreover, the single-crystal spectrum of Cu(14-ane-S_4)-$(ClO_4)_2$ is essentially identical with the corresponding solution spectrum for this complex.[5] From this we conclude that *distortions from tetragonal geometry are not requisite for the generation of the spectral and redox properties* which typify blue copper proteins.

Of secondary interest is the comparison of the steric requirements of tetrathia and tetraaza macrocycles. In earlier work, the 14-ane-S_4 ligand has been shown to exist either in the endodentate conformation[13] found in this study or in an exodentate conformation in which the sulfur atoms are at the corners of a rectangular array. This latter conformation is found in $(NbCl_5)_2$(TTP)[14] and the free 14-ane-S_4 molecule.[15] The 14-ane-N_4 ligand has been shown either to occupy equatorial coordination sites[16–19] about an octahedral metal or to fold and occupy cis coordination sites[20] about an octahedral metal. In the equatorial conformation, metals have been found to sit in the center of a 14-ane-N_4 ligand with M–N distances ranging from 1.90 to 2.15 Å.[17–19] This is in contradistinction to the narrow range of M–N distances observed in metalloporphyrins.[21] The Cu–S distance of 2.303 Å in Cu(14-ane-S_4)$(ClO_4)_2$, when contrasted with the Ni–S distance of 2.178 Å in Ni(14-ane-S_4)$(BF_4)_2$,[13] shows considerable dimensional flexibility in the 14-ane-S_4 endodentate conformation.

Stereochemical measures of strain in macrocyclic complexes include the M–X distances, the X–M–X angles, and the torsional angles within the macrocycle. The S–M–S bond angles subtended at the metal ion in Cu(14-ane-S_4)$(ClO_4)_2$ are essentially 90.0 (1)°, as are those in Ni(14-ane-S_4)-$(BF_4)_2$.[13] By contrast, angles of approximately 86 and 94° are found in Cu(14-ane-N_4)$(ClO_4)_2$[16] and in other complexes of 14-ane-N_4 and other saturated tetraazo macrocycles.[17–19] These angles relieve strain in the five-membered rings in the nitrogen macrocycles; the larger radius of the sulfur atom apparently allows the formation of unstrained five-membered rings without distortion of the X–M–X angle in the sulfur macrocycles. In Cu(14-ane-S_4)$(ClO_4)_2$, the Cu–S bond distance of 2.303 (1) Å is 0.49 Å greater than the average C–S distance, whereas in Cu(14-ane-N_4)$(ClO_4)_2$, the difference is 0.54 Å.[16] If we assume that the C–X distances are "normal", then the Cu–S bond is somewhat shortened vis a vis the Cu–N distance.

The most significant source of ring strain is the torsional angles about the ring. These torsion angles are defined as follows: in a molecular fragment –A–B–C–D, the torsion angle about the B–C bond is the dihedral angle between the planes defined by –A–B–C– and –B–C–D–. The strain-free values of these angles are 180° (anti) or 60° (gauche). In Table III the values of these angles are compared for Cu(14-ane-S_4)-$(ClO_4)_2$, Cu(14-ane-N_4)$(ClO_4)_2$,[16] Co(14-ane-N_4)$(ClO_4)_2$,[16] and Ni(14-ane-S_4)$(BF_4)_2$.[13] It can be seen that the two 14-ane-N_4 structures are in good agreement with one another and are relatively strain free. The values for the 14-ane-N_4 structures differ from ideality by only 6° (average) with a maximum deviation of 10°. Examination of the same angles for Cu(14-ane-S_4)$(ClO_4)_2$ and Ni(14-ane-S_4)$(BF_4)_2$[13] shows good agreement between the two compounds but considerably larger disparity between the experimental values and the strain-free values. The deviations from the strain-free values average 13° and run as high as 27°. There is, therefore, significantly more ring strain in the complexation of 14-ane-S_4 than of 14-ane-N_4. Thus it is apparent that essentially all strain in the Cu(14-ane-S_4) complex is accommodated by the ligand, leaving the Cu(II) coordination sphere undistorted from a regular tetragonal coordinative geometry.

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Registry No. Cu(14-ane-S_4)$(ClO_4)_2$, 58384-13-7.

Supplementary Material Available: listing of structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

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(12) (a) Local versions of the following programs were used: (i) SYNCOR, W. Schmonsees' program for data reduction; (ii) FORDAP, A. Zalkins' Fourier program; (iii) ORFLS and ORFFE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function and error program; (iv) ORTEP, C. K. Johnson's program for drawing crystal models. (b) Scattering factors, including anomalous dispersion corrections for Cu,

were taken from "International Tables for X-Ray Crystallography", Vol. IV, J. A. Ibers and W. C. Hamilton, Ed., Kynoch Press, Birmingham, England, 1974.

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Structural Characterization of *N*,*N*′-Ethylenebis(1,1,1-trifluoroacetylacetone iminato)nickel(II)

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The crystal and molecular structure of *N*,*N*′-ethylenebis(1,1,1-trifluoroacetylacetone iminato)nickel(II), Ni[en(tfacac)$_2$], $NiC_{12}H_{12}N_2O_2F_6$, has been determined from three-dimensional counter x-ray data. The material crystallizes in the monoclinic space group $P2_1/c$ with four formula units in a cell of dimensions a = 11.044 (8) Å, b = 17.116 (11) Å, c = 7.769 (5) Å, and β = 98.04 (4)°. Least-squares refinement of the structure has led to a final R factor (on F) of 0.047 using 1396 independent intensities. The structure consists of stacks of nearly parallel macrocycles, the Ni–Ni separation in the chain being 4.024 (3) Å. The coordination around each nickel(II) center is square planar, the average Ni–O and Ni–N bond lengths being 1.844 (4) and 1.860 (5) Å, respectively. The macrocyclic ligands are distinctly nonplanar, the principal distortion from planarity being a folding along an O–Ni–N vector. The ligand, which is the 2:1 condensation product of 1,1,1-trifluoro-2,4-pentanedione (tfacac) with ethylenediamine, has the CF_3 groups attached to the carbon atoms which are most distant from the imine linkage; i.e., the condensation took place at the 4 position of the tfacac ligand. The reported EPR spectrum of the analogous copper(II) complex doped in this host lattice is readily explained in the light of the observed structure.

Introduction

Transition metal complexes of Schiff base ligands are always of interest since they exhibit a marked tendency to oligimerize, thus leading to novel structural types, and also display a wide variety of magnetic properties. Many of the reported structural investigations of these complexes are discussed in some detail in a recent review.[1] Although the tetradentate Schiff base complexes of several metals and particularly of copper(II) have been well studied, there is a paucity of data concerning the nickel(II) analogues, and to our knowledge only one structural analysis of such a complex has been reported.[2]

N,*N*′-Ethylenebis(1,1,1-trifluoroacetylacetone iminato)nickel(II), Ni[en(tfacac)$_2$], is a significant example of such complexes. The Schiff base ligand is expected to be similar to en(acac)$_2$, but its exact structure is uncertain since there are three different possible stereochemistries for the 2:1 condensation product of 1,1,1-trifluoro-2,4-pentanedione (tfacac) with en; these arise because the two oxygen atoms of each tfacac moiety are distinguishable, and each condensation might occur at either the 2 or the 4 position. On the basis of the NMR spectra of the pure ligand[3] it has been suggested that the ligand is symmetric and that condensation probably occurred at the 2 position in each case.

The structure of this chelated complex is also of magnetic interest since it was observed by Lancione and Allen[4] that Cu[en(tfacac)$_2$] doped in the nickel lattice yields only one magnetic site in contrast to the unfluorinated analogue,[5] Cu[en(acac)$_2$] doped in Ni[en(acac)$_2$], which exhibited two. From this it is clear that in the former case the molecules either are constrained by space group symmetry or are fortuitously arranged such that all coordination planes are parallel. Thus, since this complex promised to be revealing from several viewpoints, we have undertaken a complete three-dimensional structural analysis of Ni[en(tfacac)$_2$].

Experimental Section

Single crystals of Ni[en(tfacac)$_2$] suitable for x-ray analysis were generously provided by Drs. H. C. Allen and R. L. Lancione. After examination by precession and Weissenberg photography the crystals were assigned to the monoclinic system. Systematic absences were observed for $0k0$ with k odd and $h0l$ with l odd which uniquely determines the space group as $P2_1/c$ (C_{2h}^5). The cell constants obtained by least-squares methods[6] are a = 11.044 (8) Å, b = 17.116 (11) Å, c = 7.769 (5) Å, and β = 98.04 (4)°; these observations were made at 20 °C with the wavelength assumed as λ(Cu kα_1) = 1.5405 Å. The density of 1.79 g/cm^3 calculated for four molecules in a unit cell is in good agreement with the value of 1.78 (2) g/cm^3 observed by flotation in aqueous $ZnBr_2$. Hence, with four formula units per cell, no crystallographic symmetry need be imposed on the molecules.

Intensity data were collected from a parallelepiped-shaped crystal of dimensions 0.077 × 0.009 × 0.010 cm. The crystal was mounted along the long axis, which is parallel to the crystallographic c axis. The crystal mosaicity was examined in the usual way[7] and found to be acceptable. The data were collected in a manner described elsewhere,[8] using an automatic Picker four-circle diffractometer employing nickel-prefiltered copper radiation. The takeoff angle was 1.5°, the scan rate was 1.0°/min, and the scan range was from 0.6° below the calculated Kα_1 position to 0.6° above the calculated Kα_2 peak position; backgrounds were counted for 10 s on each end of the scan. A unique data set of 2297 reflections having 2θ(Cu) ≤ 128° was gathered; of these reflections, 1396 had intensities greater than 3 times their estimated standard deviations.

The data were processed in the usual manner.[7,8] An absorption correction was applied; the linear absorption coefficient for this compound and Cu Kα radiation is 26.5 cm^{-1}. The transmission coefficients for the data crystal ranged between 0.70 and 0.90.[9]