Structures of the Macrocyclic Polythiaether 1,4,8,11-Tetrathiacyclotetradecane and Implications for Transition-Metal Chemistry

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Abstract: The crystal structures of two forms of the macrocyclic polythiaether 1,4,8,11-tetrathiacyclotetradecane have been determined. The α form is monoclinic, $P2_1/n$, $a = 15.512$ (4) Å, $b = 8.261$ (3) Å, $c = 5.340$ (2) Å, $\beta = 86.72$ (2)°, $Z = 2$. The β form is monoclinic, $P2_1/a$, $a = 9.421$ (1) Å, $b = 9.111$ (2) Å, $c = 15.688$ (3) Å, $\beta = 88.79$ (1)°, $Z = 4$. The structure of the α form was determined from 1098 diffractometer data with a conventional discrepancy factor of 0.027. The structure of the β form was determined from 1988 diffractometer data with a discrepancy factor of 0.055. The α form contains a centrosymmetric molecule in the exodentate conformation (with the four sulfur atoms at the corners of the rectangular molecule, where lone pairs on the sulfur atoms point out of the macrocyclic cavity) with energetically favorable torsion angles. The β form contains two distinctive centrosymmetric molecules in the exodentate conformation, one of which resembles that found in the α form, and the second of which contains an energetically unfavorable orientation of the ethano group relative to the propano group. This latter molecule, which shows some disorder, is similar in conformation to that previously found when this molecule bridges two $NbCl_5$ moieties. The exodentate conformation appears to dominate in this system and may be responsible for the kinetic observation of second-step control of the rate of complexation of this ligand with copper.

The study of structure and conformation of large molecules has been a topic of interest for a number of years among workers in various areas of chemistry for equally various reasons. Among inorganic chemists, the nature of macrocyclic species with the potential to coordinate metal ions has been an area of detailed study in recent years, especially as relevance of these systems to biochemical problems has been appreciated. Macrocycles subjected to structural studies have included nitrogen donor systems[1-3] contemplated as models for corrin and/or porphyrin systems, oxygen donor systems—the crown ethers[4-7]—often suggested as models for ion-transport agents and natural antibiotics, and a number of mixed donor species of various sorts.[8-11] Recently the synthesis and properties of a family of cyclic polythiaethers[12] and their complexes with a number of transition metals[13] have further extended the scope of macrocyclic chemistry. DeSimone and Glick[14] and Glick et al.[15] have reported structures of 1,4,8,11-tetrathiacyclotetradecane, S_4-ethano-propano[14][16] (S_4-e-pr[14]), with $NbCl_5$ and $Cu(ClO_4)_2$, respectively. Davis, White, and Belford[17] have reported the structure of the Ni(II) complex as the BF_4^- salt. The finding in our laboratory that the macrocycle existed in the unusual exo conformation in the $NbCl_5$ adduct, and in the usual endo conformation in the copper complex, led us to investigate the structure of the free ligand which we report here. In view of the major conformational differences exhibited by this ligand in these various complexes, the origins of this aspect of its chemistry seem worth thorough investigation.

Experimental Section

The synthesis of this compound was carried out as previously described.[12] Crystals were deposited from warm acetone solution upon slow cooling. Examination of the crystals obtained revealed two distinctly different crystal habits. Present in greatest abundance were crystals resembling long rectangular rods, which we will designate as the α form. A much smaller number of crystals were small, almost square plates which we refer to as the β form. Both forms melted at 110-111°C.

Collection of Data. Suitable crystals were sealed in thin-walled glass capillaries and mounted on a Syntex $P2_1$ four-circle diffractometer. Rotation and axial photographs, together with a small set of counter data, were used to determine space groups. Fifteen reflections with 2θ between 15 and 24° for the α crystal and between 16 and 23° for the β crystal were centered using a programmed centering routine. Cell constants and errors were obtained by least-squares refinement of these angles. A summary of data collection and crystal parameters for both crystals is given in Table I.

Intensity data were collected using Mo Kα radiation which had been monochromatized using a highly oriented graphite crystal whose diffraction vector was parallel to the diffraction vector of the sample. The θ-2θ scan technique was used with a scan rate of 2.02°/min. Backgrounds were measured at each end of the scan for a total time equal to one-half the scan time. During data collection, the intensities of three standard reflections were measured every 50 reflections, with no indication of decomposition or crystal movement. The data were reduced to F^2 and $\sigma(F^2)$ by procedures previously described.[18] Standard deviations were assigned as follows:

$$\sigma(I) = [\sigma_{\text{counter}}(I)^2 + (0.04I)^2]^{1/2}$$

where $\sigma_{\text{counter}} = (I + K^2B)^{1/2}$, I = net intensity, B = total background counts, and K = ratio of scan time to background time. Corrections for Lorentz polarization were applied. Extinction and absorption corrections were not applied. Data for which $F^2 \geq 3\sigma(F^2)$ were used in solution and refinement of the structure.

Solution and Refinement of Structures. α Form. The structure was solved by the iterative application of the Sayre relationship for centrosymmetric crystals. Normalized structure factors were ordered in decreasing magnitude, and the 145 reflections with $E \geq 1.3$ were used. Of the 16 sets of phases generated, the correct set of signs had a consistency index of 0.967 and required three cycles to correctly phase the reflections. The E map computed from the 145 phased reflections clearly showed the two sulfur atoms in the asymmetric unit. One cycle of least-squares refinement and subsequent Fourier synthesis revealed the five carbon atoms. Least-squares refinement of positional and isotropic thermal parameters yielded $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.138$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2} = 0.185$. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$ with the weighting factor $w = 1/(\sigma F_o)^2$. Full-matrix least-squares refinement with anisotropic thermal parameters reduced R_1 to 0.070 and R_2 to 0.107. A difference Fourier map revealed the positions of the ten hydrogen atoms in agreement with the calculated positions. Inclusion of all hydrogen atoms with $B = 5.0$ reduced R_1 to 0.047 and R_2 to 0.062. Refinement of hydrogen positional parameters reduced R_1 to 0.030 and R_2 to 0.037. Refinement of isotropic thermal parameters on all hydrogen atoms yielded final discrepancy factors $R_1 = 0.027$ and $R_2 = 0.033$ and an error of fit of 1.26. A total of 104 parameters were refined. Table II is a list of atomic coordinates and thermal parameters.

β Form. This structure was also solved by Sayre's method. The

Table I. Physical Constants and Experimental Data

	α Crystal	β Crystal
Space group	$P2_1/n$[a]	$P2_1/a$[b]
Molecules/unit cell	2	4
a, Å	15.512 (4)	9.421 (1)
b, Å	8.261 (3)	9.111 (2)
c, Å	5.340 (2)	15.688 (3)
β, deg	86.72 (2)	88.79 (1)
V Å^3	683.2 (4)	1346.4 (5)
Crystal size, mm	0.51 × 0.30 × 0.32	0.30 × 0.24 × 0.08
Density (calcd), g/cm^3	1.303	1.322
Density (obsd), g/cm^3	1.32	1.32
2θ scan range, deg	$K\alpha_1$ −1.0 to $K\alpha_2$ +1.0	$K\alpha_1$ −1.0 to $K\alpha_2$ +1.0
Max dev of standards during data collection, %	±1.0	±1.5
Crystal mounted along (*h*,*k*,*l*)	(−1,0,2)	(1,1,−1)
Data collected	1098	1988
No. of data with $F^2 > 3\sigma(F^2)$	799	1157
2θ (max), deg	45	45

[a] The transformation to the conventional space group $P2_1/c$ would correspond to $c' = -(a + c) = 18.62$ Å, $b' = -b$, and $\beta' = 160.7°$. This choice of unit cell would obviously be rather cumbersome. [b] The transformation to the conventional space group $P2_1/c$ would correspond to $c' = -a$, $a' = c$, and $\beta' = (180° - \beta) = 91.21°$.

268 reflections with normalized *E*'s greater than 1.2 were used. The correct set of signs had a consistency index of 0.901 and required three iterations to correctly phase the reflections. The *E* map computed from these reflections revealed four sulfur atoms, two from each of two-half molecules in the asymmetric unit. The ten carbon atoms were located from a Fourier map phased upon these positions and yielded R_1 of 0.126 and R_2 of 0.162. Refinement of anisotropic thermal parameters reduced R_1 to 0.078 and R_2 to 0.101. At this point, examination of the difference map indicated the presence of disorder in this crystal. One of the independent molecules, which we will call β_1, appeared nearly identical with that found in the α crystal. The other, which we will call β_2, appeared disordered about C(6) and C(7). The disorder could not be accommodated within a meaningful model and was therefore not treated in any more detail. Addition of the 20 hydrogen atoms reduced R_1 to 0.055 and R_2 to 0.061, with refinement of positional parameters only on H atoms. These final values, obtained with 187 adjustable parameters, resulted in an error of fit of 2.01. Table III is a list of atomic coordinates and thermal parameters. A listing of calculated and observed structure factors for both the α and β forms is available.[19]

Results. Description of the Structures

In the two different crystalline forms, α and β, of 1,4,8,11-tetrathiacyclotetradecane, there are present three independent molecules, one in the α crystal and two in the β crystal. Each of these molecules possesses the crystallographically required inversion center ($\bar{1}$, C_i symmetry). All three of these molecules are found to exist in the exodentate conformation, with the lone pairs of the four sulfur atoms pointing outward at the corners of approximately rectangular molecules and with the sulfur atoms bridged alternately by two carbon (ethano) and three carbon (propano) moieties.

α Molecule. The structural features of this molecule have been determined most precisely of any of the molecules studied. All atoms, including hydrogens, were found and refined. Figure 1 shows in detail the molecular structure and Figure 2 illustrates the packing within the crystal. Bond lengths and angles appear in Table IV. All aspects of this structure appear completely regular. The C–S distances average to 1.808 Å, similar to those found in the copper(II) complex[15] of this molecule and reasonable for a C–S distance in a saturated molecule.[20] The C–C distances average to 1.509 Å, a bit shorter than the expected 1.54 Å for single-bonded carbon. This has been observed before in crown ethers[7] and in sulfur substituted crown compounds,[11] although in the latter case, refinement apparently was without hydrogen atoms. The same behavior has also been observed in the C–C distances of cyclen,[21] a 12-membered N_4 macrocycle. We found that the C–C distances shortened

Table II. Atomic Coordinates and Thermal Parameters–α form of 1,4,8,11-Tetrathiacyclotetradecane[a, b]

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
S(1)	0.0692 (0)	0.8188 (1)	0.8895 (1)	H(3)	0.1562 (16)	0.5013 (32)	0.8227 (59)
S(2)	0.1836 (0)	0.2367 (1)	0.4522 (1)	H(4)	0.0735 (17)	0.4891 (30)	0.6672 (48)
C(1)	0.1316 (2)	0.7162 (3)	0.6400 (5)	H(5)	0.1634 (16)	0.4928 (32)	0.2928 (57)
C(2)	0.1317 (2)	0.5331 (3)	0.6637 (5)	H(6)	0.2444 (19)	0.4840 (32)	0.4617 (53)
C(3)	0.1844 (2)	0.4548 (3)	0.4514 (6)	H(7)	0.0383 (14)	0.2283 (27)	0.5381 (49)
C(4)	0.0724 (2)	0.1868 (3)	0.4072 (5)	H(8)	0.0719 (14)	0.0673 (36)	0.4181 (46)
C(5)	0.0401 (2)	0.2462 (3)	0.1633 (5)	H(9)	0.0758 (16)	0.2001 (30)	0.0312 (52)
H(1)	0.1855 (17)	0.7546 (29)	0.6507 (50)	H(10)	0.0433 (13)	0.3609 (31)	0.1470 (42)
H(2)	0.1104 (14)	0.7464 (26)	0.4688 (49)				

Atom	β_{11} (or *B*)	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	0.0058 (0)	0.0174 (1)	0.0399 (3)	−0.0005 (0)	−0.0045 (1)	−0.0063 (2)
S(2)	0.0041 (0)	0.0188 (1)	0.0586 (4)	0.0016 (0)	−0.0021 (1)	−0.0056 (2)
C(1)	0.0042 (1)	0.0162 (5)	0.0408 (12)	−0.0011 (2)	−0.0025 (3)	0.0011 (6)
C(2)	0.0049 (1)	0.0150 (4)	0.0367 (12)	−0.0011 (2)	−0.0006 (3)	0.0006 (6)
C(3)	0.0041 (1)	0.0188 (5)	0.0439 (13)	−0.0015 (2)	0.0003 (3)	−0.0003 (7)
C(4)	0.0050 (1)	0.0137 (5)	0.0377 (11)	−0.0007 (2)	−0.0017 (3)	0.0009 (6)
C(5)	0.0050 (1)	0.0153 (5)	0.0322 (11)	−0.0002 (2)	−0.0000 (3)	−0.0010 (6)
H(1)	2.8 (6)					
H(2)	1.9 (5)					
H(3)	3.7 (6)					
H(4)	3.2 (6)					
H(5)	3.2 (6)					
H(6)	4.3 (7)					
H(7)	1.8 (5)					
H(8)	2.9 (6)					
H(9)	2.8 (6)					
H(10)	1.8 (5)					

[a] Throughout this paper, standard deviations from the full variance-covariance matrix are given in parentheses for the least significant digit(s). [b] The form of the anisotropic temperature factor reported in Tables II and III is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Table III. Atomic Coordinates and Thermal Parameters–β Form of 1,4,8,11-Tetrathiacyclotetradecane[a]

Atom	x	y	z	Atom	x	y	z
S(1)	0.5933 (2)	0.5336 (2)	0.2875 (1)	H(4)	0.4311	0.5560	0.4391
S(2)	0.1444 (2)	0.6674 (2)	0.5130 (1)	H(5)	0.1388	0.5826	0.3655
S(3)	0.1624 (2)	0.8628 (2)	−0.0080 (1)	H(6)	0.2086	0.4719	0.4349
S(4)	0.0150 (2)	0.4073 (2)	0.2159 (1)	H(7)	0.7197	0.5494	0.4389
C(1)	0.4085 (8)	0.5146 (8)	0.3159 (5)	H(8)	0.8393	0.5172	0.3644
C(2)	0.3627 (7)	0.5956 (9)	0.3971 (4)	H(9)	0.7163	0.2997	0.3395
C(3)	0.2066 (7)	0.5773 (9)	0.4162 (5)	H(10)	0.5995	0.3499	0.4122
C(4)	0.7743 (10)	0.4682 (10)	0.4068 (6)	H(11)	−0.1574	0.3753	0.0695
C(5)	0.6764 (10)	0.3900 (11)	0.3724 (6)	H(12)	−0.2167	0.2677	0.1455
C(6)	−0.1441 (9)	0.2735 (11)	0.0969 (5)	H(13)	0.0385	0.1906	0.1500
C(7)	−0.0019 (9)	0.2873 (10)	0.1261 (5)	H(14)	0.0709	0.3251	0.0836
C(8)	−0.0202 (8)	0.5884 (8)	0.1774 (5)	H(15)	−0.0163	0.6678	0.2229
C(9)	0.0856 (8)	0.6439 (8)	0.1083 (5)	H(16)	−0.1157	0.6009	0.1482
C(10)	0.0447 (7)	0.7916 (8)	0.0745 (5)	H(17)	0.1057	0.5680	0.0625
H(1)	0.4088	0.4100	0.3392	H(18)	0.1773	0.6598	0.1401
H(2)	0.3369	0.5177	0.2690	H(19)	−0.0525	0.7960	0.0494
H(3)	0.3980	0.6975	0.3789	H(20)	0.0468	0.8716	0.1213

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	0.0145 (3)	0.0176 (3)	0.0041 (1)	0.0010 (3)	0.0008 (1)	0.0010 (2)
S(2)	0.0128 (3)	0.0141 (3)	0.0058 (1)	0.0046 (3)	0.0009 (1)	0.0010 (2)
S(3)	0.0121 (3)	0.0115 (3)	0.0057 (1)	−0.0027 (2)	−0.0002 (1)	0.0005 (1)
S(4)	0.0155 (3)	0.0158 (3)	0.0038 (1)	−0.0010 (3)	0.0008 (1)	0.0003 (2)
C(1)	0.0145 (12)	0.0151 (14)	0.0048 (4)	0.0014 (10)	−0.0003 (6)	−0.0007 (6)
C(2)	0.0110 (10)	0.0164 (13)	0.0043 (4)	−0.0004 (9)	0.0001 (5)	0.0001 (6)
C(3)	0.0124 (10)	0.0160 (13)	0.0063 (4)	0.0026 (10)	0.0002 (5)	−0.0011 (6)
C(4)	0.0344 (15)	0.0294 (19)	0.0101 (6)	−0.0174 (14)	0.0130 (8)	−0.0090 (8)
C(5)	0.0196 (14)	0.0305 (22)	0.0085 (5)	−0.0120 (15)	0.0054 (7)	−0.0071 (9)
C(6)	0.0148 (13)	0.0320 (20)	0.0041 (4)	−0.0025 (13)	0.0011 (6)	0.0026 (7)
C(7)	0.0169 (13)	0.0222 (16)	0.0059 (4)	−0.0014 (12)	0.0016 (6)	0.0014 (7)
C(8)	0.0138 (11)	0.0133 (11)	0.0046 (4)	−0.0006 (9)	0.0005 (5)	0.0004 (6)
C(9)	0.0117 (10)	0.0134 (11)	0.0054 (4)	0.0009 (10)	0.0012 (5)	0.0007 (6)
C(10)	0.0126 (11)	0.0123 (11)	0.0050 (4)	0.0005 (9)	0.0002 (5)	0.0001 (6)

[a] Atomic B's for hydrogen atoms = 5.0.

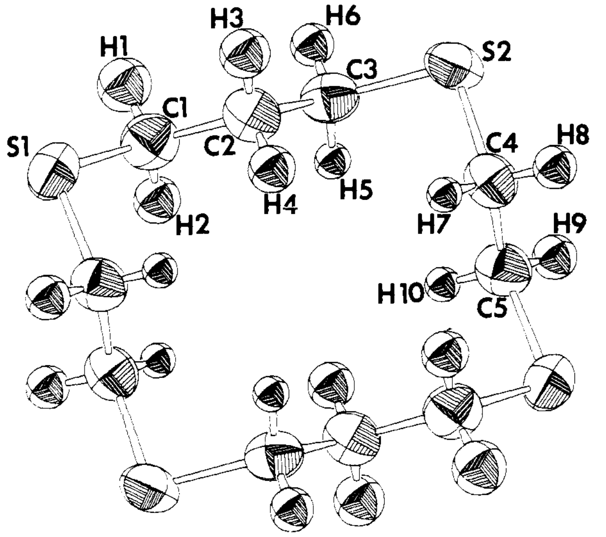


Figure 1. Molecular structure of the α molecule of S_4-ethano-propano[14].

from ~1.54 Å only upon inclusion of hydrogen atoms into the refinement. Collins et al. have discussed this point.[22] The C–S–C angles average to 102.9°, less than the tetrahedral angle of 109.5° as expected. Carbon hydrogen distances average 0.96 (3) Å, this after two cycles of refinement with isotropic thermal parameters which are quite reasonable for hydrogen atoms. The thermal ellipsoids for all carbon and sulfur atoms show no irregularities. Torsion angles about the bonds and displacements of the carbon atoms from the plane containing the four sulfur atoms are shown graphically in Figures 3 and 4.

β_1 Molecule. One of the independent molecules found in the β crystal has essentially the same structure and conformation as the α molecule just described. However, because of the substantially poorer refinement of the overall structure, the parameters describing the β_1 molecule are not nearly so accurate or precise. Bond lengths and angles are to be found in Table IV. Figure 5 shows the detailed molecular structure of β_1 and β_2 and Figure 6 the packing of molecules in the crystal. One sees immediately that the C(7)–C(6) bond length in the ethano fragment is notably bad. This is the part of the molecule which has proven most troublesome in the previously reported niobium complex and in the β_2 molecule discussed below. We find here no evidence for disorder, however, and the possibility exists that some of the problem may be due to difficulty with the β_2 molecule in the same crystal. Also one must consider that no refinement of hydrogen positions or thermal parameters was attempted here. The only other suspect distance, a long C–S distance of 1.877 Å, also involves C(6) and leads one to surmise that it is the position of C(6) which is the problem. Angles agree fairly well with those of the α molecule, and torsion angles and displacements from the S_4 plane confirm the conformational similarity.

β_2 Molecule. The other independent molecule in the unit cell of the β crystal has a conformation substantially different from the α and β_1 molecules (see Figure 5). Unfortunately, there appears to be severe disorder within the ethano fragment, and we have not been able to adequately account for this disorder in our refinement of the structure. Therefore, some distances are quite poor, and this disorder has possibly also affected refinement of the β_1 molecule. The disorder observed in the ethano fragment appears to be of the same sort found in the $(NbCl_5)_2(S_4\text{-e-pr}[14])$ molecule, but even more severe. Both the β_2 molecule and the S_4-e-

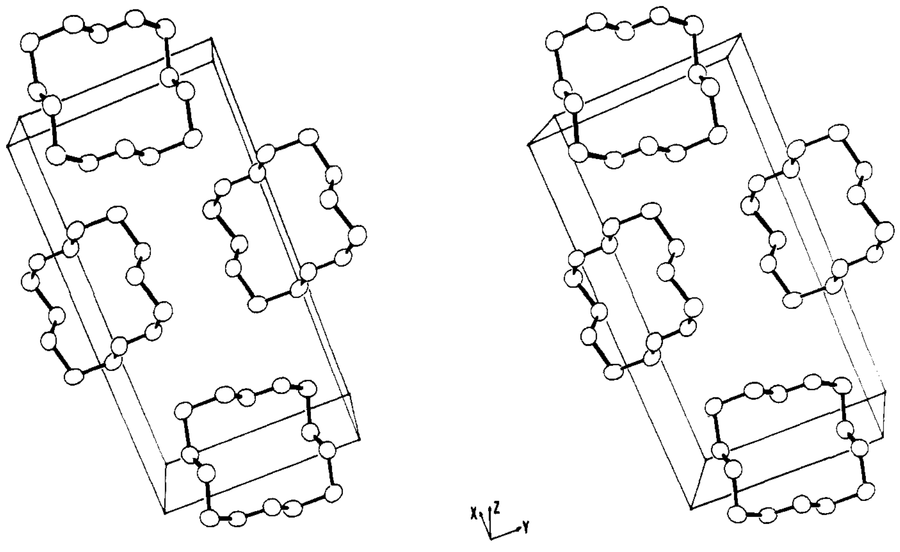


Figure 2. Stereoscopic view of the unit cell contents of the α form of S_4-ethano-propano[14].

Table IV. Interatomic Distances (A) and Angles (Deg) in 1,4,8,11-Tetrathiacyclotetradecane

Molecule	Atoms[a]	Distance	Atoms[a]	Angle
α	S(1)–C(1)	1.812 (3)	C(5)'–S(1)–C(1)	102.2 (1)
	S(1)–C(5)'	1.817 (3)	C(3)–S(2)–C(4)	103.6 (1)
	S(2)–C(3)	1.802 (3)	S(1)–C(1)–C(2)	114.1 (2)
	S(2)–C(4)	1.803 (3)	C(1)–C(2)–C(3)	111.6 (2)
	C(1)–C(2)	1.518 (3)	C(2)–C(3)–S(2)	115.1 (2)
	C(2)–C(3)	1.505 (3)	S(2)–C(4)–C(5)	114.1 (2)
	C(4)–C(5)	1.504 (4)	C(4)–C(5)–S(1)'	113.4 (2)
	C–H[b]	0.96 (3)		
β_1	S(3)–C(10)	1.807 (7)	C(6)'–S(3)–C(10)	103.3 (3)
	S(3)–C(6)'	1.877 (9)	C(8)–S(4)–C(7)	106.1 (4)
	S(4)–C(8)	1.790 (7)	S(3)–C(10)–C(9)	114.6 (5)
	S(4)–C(7)	1.792 (9)	C(10)–C(9)–C(8)	112.1 (6)
	C(10)–C(9)	1.500 (9)	C(9)–C(8)–S(4)	114.7 (5)
	C(9)–C(8)	1.542 (9)	S(4)–C(7)–C(6)	113.9 (6)
	C(7)–C(6)	1.431 (10)	C(7)–C(6)–S(3)'	113.4 (7)
β_2	S(1)–C(1)	1.796 (8)	C(5)'–S(1)–C(1)	99.2 (3)
	S(1)–C(5)'	2.035 (10)	C(3)–S(2)–C(4)	97.5 (3)
	S(2)–C(3)	1.812 (8)	S(1)–C(1)–C(2)	114.6 (5)
	S(2)–C(4)	1.933 (10)	C(1)–C(2)–C(3)	111.8 (6)
	C(1)–C(2)	1.526 (9)	C(2)–C(3)–S(2)	114.5 (5)
	C(2)–C(3)	1.504 (9)	S(2)–C(4)–C(5)	102.4 (7)
	C(4)–C(5)	1.292 (10)	C(4)–C(5)–S(1)'	101.9 (8)

[a] The primes represent the symmetry related atoms corresponding to inversion centers at (0, ½, ½) in α, (½, ½, 0) in β_1, and (½, ½, ½) in β_2. [b] Average of ten C–H distances.

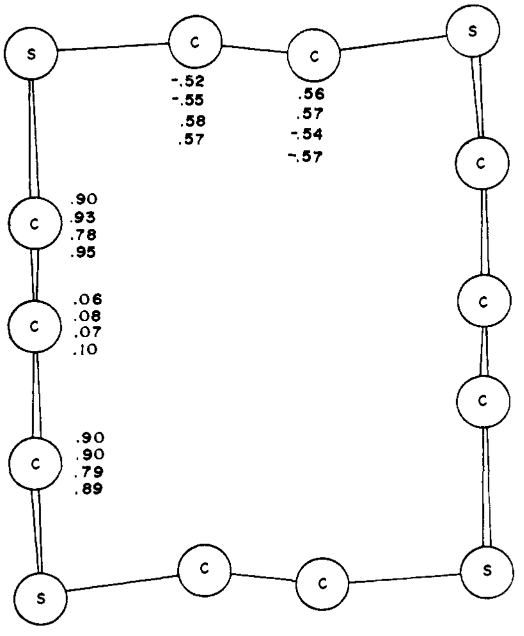


Figure 3. Displacements (in Å) of the carbon atoms from the plane of the four sulfur atoms. For each carbon atom, the four numbers correspond vertically to α, β_1, β_2, and $(NbCl_5)_2(S_4\text{-e-pr}[14])$ molecules.

pr[14] ligand in the $NbCl_5$ complex have the same conformation, as can be seen from the torsion angles in Figure 4. During the latter stages of the refinement, before addition of hydrogen atoms, a significant (~1.6 e/Å^3) unexplained peak in the difference Fourier map was located at a position roughly midway between C(4) and C(5), but displaced toward the outside of the ring. One would expect that if a static disorder were present, both C(4) and C(5) might be found to have alternate positions of roughly equal occupancy. However, no other peak was ever located. Placement of ~0.5 carbon atom at the position of this spurious peak, with simultaneous reduction in the weights of C(4) and C(5), did slightly improve the fit, reducing R_1 from 0.078 to 0.069 at that point. However, since we cannot impute any chemical sense to the model, we have chosen not to proceed further with it. In all likelihood, the disorder in this molecule, like that in the $NbCl_5$ complex, is a random[23] one. Owing to this unfortunate problem, a comparison of angles with the β_1 molecule is difficult. A comparison of dihedral angles indicates that the simplest way to describe the difference between β_1 and β_2 molecules is that the (sense of the) pucker in the ethano fragment is reversed. More discussion of this point follows in the next section.

Discussion

The most distinctive structural parameters in these compounds are the conformational parameters. Figures 3 and 4 summarize these parameters for the three molecules reported here and for the niobium complex reported previously. The displacements in the propano groups are comparable for all four different molecules studied, while the ethano group reflects the difference between β_1 and β_2. In α and β_1, the displacement pattern of carbon atoms from the S_4 plane is ++−−+, whereas in β_2 and the niobium complex, the pattern is ++++−.

A more fundamental set of conformational parameters are the torsion angles. The torsion or dihedral angles are most conveniently defined as follows. In a molecular frag-

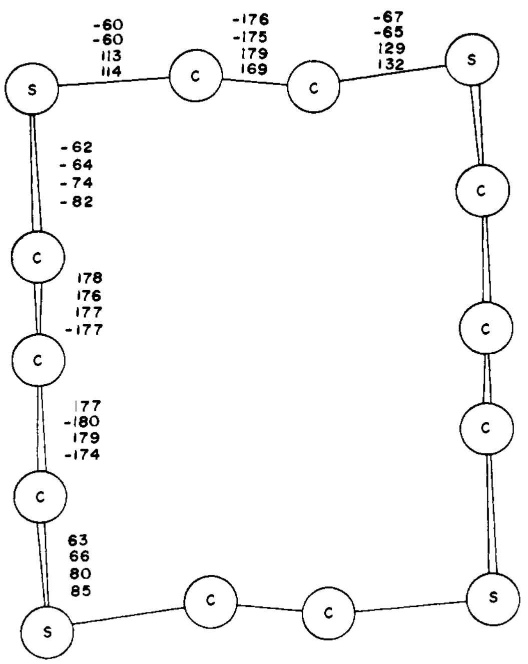
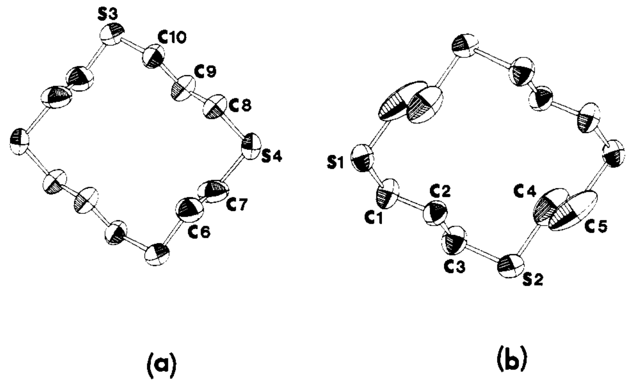


Figure 4. Torsion angles about C-C and C-S bonds. For each bond, the four numbers correspond vertically to α, β_1, β_2, and $(NbCl_5)_2(S_4$-e-pr[14]) molecules.



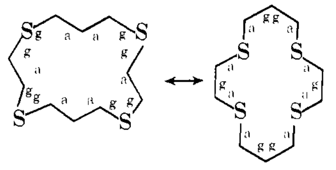
(a) (b)

Figure 5. Molecular structure of (a) the β_1 molecule and (b) the β_2 molecule of S_4-ethano-propano[14].

ment -A-B-C-D-, the torsion angle about the B-C bond is the same as the dihedral angle between the planes defined by -A-B-C- and -B-C-D-. Optimally, these torsion angles should be 180° (anti) or 60° (gauche). For all four compounds, the torsion angles within the propano group approximate these optimal values, although the deviations from ideality are as much as 25° in the β_2 and niobium complexed molecules, whereas in α and β_1, they are all less than 6°. In the ethano groups of the α and β_1 molecules, these angles are within 7° of the ideal values. However, the torsion angles about the S-C bonds of the ethano fragment have values of 113 and 129°, and 114 and 132° in the β_2 and niobium complexed molecules, respectively. Torsion angles of 120° are energetically less favorable then those of 60 or 180° by about 3 kcal/mol[24] and indicate a considerable amount of torsional strain in these conformers.

Examination of the thermal ellipsoids found in these four compounds is instructive. In the α and β_1 molecules, where optimal torsion angles are adequately approximated, all thermal ellipsoids are well formed and of reasonable size. In the β_2 molecule and niobium complex, thermal ellipsoids of the ethano carbon atoms are extremely distorted in shape and indicative of some possible disorder or a high amount of anisotropic vibration. Based on our unsuccessful attempts, both here and in a previously reported structure,[14] to account for this apparent disorder in terms of a chemically meaningful model, we conclude that we most likely have a random disorder, perhaps coupled with high thermal motion. We suggest that in the β_2 molecule and the niobium complex, where the torsion angles approach those of the eclipsed configuration, a very broad, shallow, local minimum in potential energy is encountered, while in the α and β_1 molecules, the potential energy profile with respect to torsion angles exhibits a narrow deep minimum near the optimal values of these angles.

If one contrasts the exodentate conformation of the α and β_1 molecules I, with the endodentate conformation II found in the Cu(II) and Ni(II) complexes, it can be seen that these two conformations are related by a process approximating "pseudo-rotation",[25] in which each anti interaction is rotated into a gauche interaction, and each gauche interaction is rotated into an anti interaction. In 4*n* ring systems this would correspond simply to moving the sulfur atoms



I II

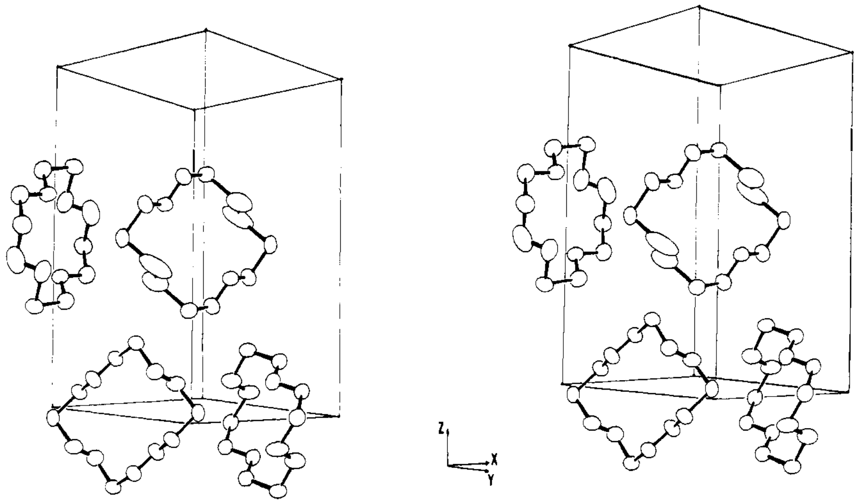


Figure 6. Stereoscopic view of the unit cell contents of the β form of S_4-ethano-propano[14].

around a ring of approximately constant shape, but in $4n + 2$ rings this completely alters the shape of the ring. There are six gauche and eight anti interactions in the endodentate conformation, and eight gauche and six anti interactions in the exodentate conformation. The torsional strain criterion slightly favors the endodentate conformer since it has fewer gauche interactions, but clearly in the exo configurations we find here, this relatively small energy difference is overcome by some other factors. The most obvious is the destabilizing effect due to mutual repulsion of the sulfur lone pairs. However, in complexes where a metal ion occupies the macrocyclic cavity, and donation of lone-pair electron density to the metal occurs, the endodentate conformation is stabilized. It is interesting to note that even in the mixed oxygen-sulfur polyethers, with ring sizes of 12, 15, and 18, the sulfur atoms are always found with lone pairs directed out of the macrocyclic cavity.[11]

The endo and exo conformations, although connected by a complex kinetic process, involve relatively small energy differences. The conformational interconversion between molecules of the β_1 and β_2 types involves little molecular reorganization, but rather more substantial net energy differences due to the presence of the higher energy eclipsed interactions. Even these, however, might be overcome by thermal energy supplied during, say a recrystallization from hot solvent.

The implications of the exodentate conformation found here should be of interest to inorganic chemists, both from a structural and a kinetic standpoint. Structurally, one must be prepared to find coordination to exodentate macrocycles when the ligands coordinated to the metal are not readily displaced by the macrocycle. The covalent halides, of which $NbCl_5$, $MoCl_5$, and WCl_6 are examples, appear to fall into this category. The insoluble precipitates obtained by Travis and Busch[13c] during the preparation of Rh(III) chloride complexes of S_4-e-pr[14] are very likely other examples of this behavior. These were reported to occur when the reaction was carried out in cool or warm, as opposed to boiling ethanol. When the metal ion is simply too large to fit into the cavity, either folding to the endodentate cis configuration or exodentate coordination may occur. A third possibility is for the metal to coordinate to the planar endodentate ligand, but to reside out of the plane of the ring. The mode of coordination in all cases will, we feel, be substantially dependent on the other ligands to which the metal ion is coordinated.

Perhaps most interesting among the implications of this structure are those bearing on complex stabilities and kinetic behavior. Steric hindrance arising from conformational effects in the exo conformers should be minimal with respect to first-bond formation. Second-bond formation, however, must be preceded by a major conformational reorganization, and a reduction in rate is to be expected as this process occurs. Further coordination would obviously be little affected by this factor and might more directly reflect ring size and other minor conformational processes. Recent studies[26] of the macrocyclic effect in copper complexes of cyclic tetrathiaethers support second-bond formation as the rate-determining step, and this is attributed to the added steric constraints involved.

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Supplementary Material Available: a listing of calculated and observed structure factors for the α and β forms (10 pages). Ordering information is given on any current masthead page.

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