



The Crystal Structure of the Macrocyclic Hexathioether 1,4,7,11,14,17-Hexathiacycloeicosane: Implications for Metal Complexation

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(Received: 6 August 1998; in final form: 2 June 1999)

Abstract. Several metal complexes of the twenty-membered ring hexathioether macrocycle, 1,4,7,11,14,17-hexathiacycloeicosane (20S6), have now been prepared and crystallographically characterized. In order to examine structural changes in the ligand which may occur under complexation, we undertook an analysis of the structure of the 20S6 ligand by single crystal X-ray diffraction. The compound crystallizes in the monoclinic space group C_2/c with the unit cell dimensions: $a = 22.481(1)$ Å, $b = 5.433(2)$ Å, $c = 17.9259(9)$ Å, and $\beta = 117.711(4)^\circ$. The conformation adopted by this ligand is such that four of the sulfur atoms are *exodentate*, but two sulfur atoms are *syn endodentate*, unusual for a macrocycle of this type. All twelve of the C—S—C—C torsional bond angles in 20S6 are *gauche* as expected, and the ligand conformation may account for the complexation properties observed for this hexathioether macrocycle.

Key words: Crown thioethers, macrocycles, crystal structures, hexathioethers

1. Introduction

The past ten years has witnessed a marked increase in research activity for the study of the coordination chemistry of crown thioether ligands, largely due to the improvement in yields of these macrocyclic materials. Research interest in this area has steadily increased, and several review articles describing the transition metal chemistry of 1,4,7-trithiacyclononane and related ligands have appeared [1–4]. These macrocyclic polythioethers have been found to be effective polydentate ligands for complexing a variety of transition metals, and numerous complexes have been characterized [5–7].

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In our research into the complexation of mesocyclic and macrocyclic polythioethers, we have been interested in studying the effect of ring size versus complex formation, complex stability, and complex structure for various transition-metal and heavy-metal ions [8–9]. As part of this study, we have synthesized trithioethers and hexathioethers which incorporate varying size chelate rings and functional groups. One particular ligand of focus is the 20-membered ring hexathioether, 1,4,7,11,14,17-hexathiacycloeicosane (20S6). An initial report by Riley described a ligand-bridged Rh(I) binuclear complex containing 20S6 [10]. Our group has now reported four crystal structures involving homoleptic complexes of this ligand, and a fifth crystal structure of its Ni(II) complex has also recently been reported by Lucas [6,7,11,12]. Although three possible stereoisomers can theoretically be formed in homoleptic octahedral complexes of this ligand, only one of these has been ever been observed by either NMR or X-ray crystallography. Using molecular mechanics and crystallographic studies, Hay and co-workers have quantified the selectivity of alkali metal ions by large crown ether ligands [13]. Similarly, the importance of free ligand conformation in thioethers has been convincingly demonstrated by Gellman and co-workers [14]. Ligand pre-organization is an important factor in the stabilities and structures found in metal complexes formed by macrocyclic thioethers [15]. To further understand the basis for its transition metal chemistry and the observed high stereoisomer selectivity, we undertook a crystallographic study of the 20S6 ligand and have determined its solid-state conformation using single crystal X-ray diffraction.

2. Experimental

2.1. MATERIALS

The 20S6 ligand was prepared by the cesium dithiolate method as previously reported [16].

2.2. X-RAY CRYSTALLOGRAPHIC DETERMINATION OF 20S6

A crystal of 20S6, suitable for X-ray diffraction studies, was grown by the diffusion of hexane into a chloroform solution. A clear prism of 20S6 was mounted on a Rigaku AFCSR diffractometer equipped with graphite monochromated Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) and a 12 KW rotating anode generator. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $68.40^\circ < 2\theta < 77.07^\circ$. Based upon the systematic absences of $hkl : h+k = 2n$ and $h0l : l = 2n$, packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $C2/c$ (No. 15).

The data were collected at a temperature of $23 \pm 1^\circ\text{C}$ using the $\omega - \theta$ scan technique to a maximum 2θ value of 120.2° . Omega scans of several intense

reflections, made prior to data collection, had an average width at half-height of 0.26° with a take-off angle of 6.0° . Scans of $(1.00 + 0.30 \tan \theta)^\circ$ were made at a speed of $16.0^\circ/\text{min}$ (in ω). The weak reflections [$I < 10.0\sigma(I)$] were rescanned (maximum of 2 rescans), and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background time was 2 : 1. The diameter of the incident beam collimator was 0.5 mm, and the crystal to detector distance was 600.0 mm.

Of the 1663 reflections which were collected, 1614 were unique ($R_{\text{int}} = 0.039$). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied). The linear absorption coefficient for Cu $K\alpha$ is 63.5 cm^{-1} . An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.75 to 1.00. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 0.81176×10^{-5}).

The structure was solved by direct methods [17]. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1096 observed reflections [$I > 3.00\sigma(I)$] and 116 variable parameters and converged with agreement factors of $R = 0.052$ and $R_w = 0.070$.

3. Results and Discussion

A structural perspective view of the 20S6 molecule is shown in Figure 1. A summary of the crystallographic data for the molecule is listed in Table I while the final atomic parameters are listed in Table II. Geometrical parameters for the macrocycle are compiled in Table III. Note that the molecule lies on a crystallographic two-fold rotation axis, imposing C_2 symmetry on the macrocycle in this crystal structure. The solid state conformation adopted by the free 20S6 ligand is such that four of the six sulfur atoms (S4 and S7) are *exodentate* (pointing out of the cavity of the ring), but two of the sulfur atoms (S1) are *syn endodentate*. That is, two of the sulfur atoms point toward the cavity of the ring *and* are on the same side of the ring. The C—S bond distances range from 1.802(6) Å to 1.822(6) Å. Although this is a smaller range of values than observed in other crown thioether structures, nevertheless the values correspond closely to previous ones [14, 15]. The C—C bond lengths range from 1.495(7) Å to 1.521(7) Å, again a smaller range, but consistent with related thioether structures.

X-ray crystal structures have been carried out on a number of other crown thioethers including 1,4,7,10-tetrathiacyclododecane (12S4) [15], 1,4,8,11-tetrathiacyclotetradecane (14S4) [18], 1,4,7,10,13-pentathiacyclopentadecane (15S5) [15], 1,4,7,10,13,16-hexathiacyclooctadecane (18S6) [15], 1,4,7,11,14,17-hexathiacycloeicosan-9,19-dione(diketo-20S6) [19], 1,4,7,12,15,18-hexathia-

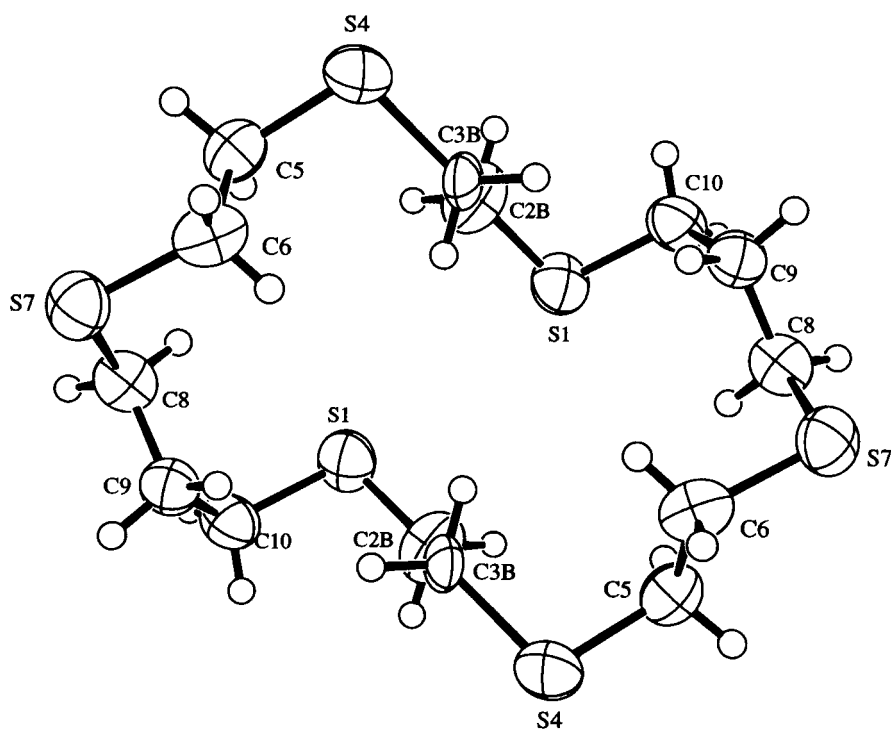


Figure 1. Ortep perspective of 20S6.

cyclodocosane (22S6) [16], 1,5,9-trithiacyclododecane (12S3) [20], and 1,5,9-trithiacyclodecan-3-ol(hydroxy-12S3) [16]. Note that except for 22S6, all of these macrocycles adopt conformations such that the C—C—S—C dihedral angles are *gauche* (two of the dihedrals in 22S6 are *anti*). In addition, except for 12S3, hydroxy-12S3, and 18S6, the sulfur atoms of the macrocycles are directed out of the cavities of the respective rings, exodentate (two sulfur atoms in 12S3, hydroxy-12S3, and 18S6 are *anti endodentate*). The crystal structure of 20S6, presented here, is the first example of a macrocyclic crown thioether adopting a conformation with *syn endodentate* sulfur atoms. This conformation may have important consequences in chelation of metal ions. In our previous work with 20S6, we have already noted unusual chromatographic behavior displayed by this ligand [16]. Also, we would like to highlight the fact that metal complexes of 20S6 show significant enhanced solubility over complexes involving other crown hexathioethers such as 18S6 [7]. Furthermore, the 20S6 ligand complexes Pt(II) and Pd(II) to form a different linkage isomer than the one observed in the 18S6 complexes of the two ions [1, 11].

Exodentate conformations completely disfavor chelation by these macrocyclic polythioethers. In order to form an encircling chelate complex, the macrocycle will need to undergo a significant conformational change from its exodentate

Table I. Crystallographic Data for 20S6

Empirical formula	C ₁₄ H ₂₈ S ₆
FW, amu	194.37
Crystal habit, color	Colorless prism
Lattice	Monoclinic
Space group	C2/c (No. 15)
a, Å	22.481 (1)
b, Å	5.433 (2)
c, Å	17.9259 (9)
β, deg	117.711 (4)
V, Å ³	1938.4(6)
Z	8
ρ _{calcd} , g cm ⁻³	1.332
μ, cm ⁻¹	63.46
F ₀₀₀	832
R ^a	0.052
R _w ^b	0.070
GoF	2.21
Max. peak in final diff. map, e-/Å ³	0.22
Min. peak in final diff. map, e-/Å ³	-0.23

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}.$$

conformation to a higher-energy endodentate form. Any 'preorganization' of the sulfur atoms towards *syn endodentate* dispositions should serve to favor chelation. Accordingly, the chelation of nickel(II) is significantly enhanced in 6,6,13,13-tetramethyl-1,4,8,11-tetrathiacyclotetradecane (14S4-Me₄) over 6,6-dimethyl-1,4,8,11-tetrathiacyclotetradecane (14S4-Me₂) or 14S4 itself [15]. Steric effects of the methyl substituents serve to predispose the sulfur donor atoms toward *endodentate* conformation in the free ligands. Two of the six sulfur atoms of 20S6 adopt a *syn endodentate* conformation, unlike conformations of other macrocyclic hexathioethers (like 18S6) which show two *anti endodentate* sulfurs. As was also seen in the structure of 18S6, all twelve C—S—C—C torsional angles in the 20S6 structure are *gauche*, and all S—C—C—S torsional angles are *anti*, consistent with previous behavior for crown thioethers [15]. Every reported crystal structure of homoleptic metal complexes involving 20S6 also have exclusive *gauche* C—S—C—C torsional angles [5, 6, 12]. We have previously proposed that stereoisomer selectivity in octahedral 20S6 complexes is due to the dual requirements of *gauche* C—S—C—C torsional angles and the ease in which the two six-membered chelate rings of the 20S6 can readily adopt preferred chair conformations. Octahedral metal complexes of this ligand, like those of 18S6 which form only a single *meso* stereoisomer, also show exclusive formation of a single stereoisomer, a consequence

Table II. Final atomic parameters for 20S6

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
S(1)	0.43977(7)	-0.5022(3)	0.2982(1)	5.34(6)
C(2A) ^a	0.5025(7)	-0.252(3)	0.352(1)	4.7(7)
C(2B)	0.5091(7)	-0.408(3)	0.388(1)	5.9(7)
C(3A)	0.5394(7)	-0.277(3)	0.446(1)	6.3(6)
C(3B)	0.5178(6)	-0.128(3)	0.395(1)	3.8(6)
S(4)	0.59369(7)	-0.0244(3)	0.4944(1)	5.69(7)
C(5)	0.3397(2)	-0.068(1)	0.0338(3)	5.0(2)
C(6)	0.3421(3)	xxx0.109(1)	0.0990(3)	5.0(2)
S(7)	0.27102(7)	xxx0.0733(3)	0.1207(1)	5.06(6)
C(8)	0.2939(3)	-0.209(1)	0.1817(3)	5.0(2)
C(9)	0.3366(3)	-0.172(1)	0.2743(3)	5.0(2)
C(10)	0.3719(3)	-0.408(1)	0.3186(3)	5.2(2)

^a There is disorder in the two carbons bridging the sulfurs on each side of the ring [i.e., S(1)—C(2)—C(3)—S(4)]. This disorder seems to cause some of the bond distances to be unrealistic; e.g., S—C bonds of 1.77 or 1.87 Å. Even though the Howells Phillips Rodgers test clearly showed the data to match a centrosymmetric space group, we removed the crystallographic twofold relating the two halves (i.e., refined the structure in the space group *Cc*) [21]. The same disorder was still present and the bond distances were worse. Although there are ‘bad’ bond lengths, the general conformation of the ring is apparent. Note that a similar disorder (with corresponding ‘bad’ bond lengths) is seen in both the crystal structures of 18S6 and our reported Pd(II) complex with 20S6 [11, 14].

Table III. Selected bond lengths (Å) and bond angles (deg) for 20S6

Bond distances					
S(7)-C(6)	1.822(6)	S(1)-C(2B)	1.72(2)	C(5)-C(6)	1.495(7)
S(7)-C(8)	1.815(5)	S(4)-C(5)	1.802(6)	C(9)-C(10)	1.521(8)
S(1)-C(10)	1.802(6)	S(4)-C(3A)	1.77(1)	C(9)-C(8)	1.496(6)
S(1)-C(2A)	1.87(1)	S(4)-C(3B)	1.89(1)	C(2B)-C(3B)	1.53(3)
C(2A)-C(3A)	1.50(2)				
Bond angles					
C(6)-S(7)-C(8)	100.9(2)	C(10)-S(1)-C(2A)	101.2(4)	C(10)-S(1)-C(2B)	101.9(6)
C(5)-S(4)-C(3A)	103.6(4)	C(5)-S(5)-C(3B)	101.6(4)	S(4)-C(5)-C(6)	113.7(4)
S(7)-C(6)-C(5)	112.4(4)	C(10)-C(9)-C(8)	112.1(4)	S(1)-C(10)-C(9)	114.8(4)
S(7)-C(8)-C(9)	114.2(4)				

of the conformation adopted by 20S6. Its unusual *syn endodontate* conformation allows for both of these conformational requirements to be met without substantial ligand reorganization.

4. Conclusions

The solid state structure of the macrocyclic hexathioether 20S6 shows four *exo-dentate* sulfur atoms and two *endodontate* sulfur atoms. Both *endodontate* sulfurs adopt an unusual *syn* conformation, and all C—S—C—C dihedral angles adopt a *gauche* conformation as observed in all reported crystal structures of transition metal complexes involving this crown thioether. The complexation properties of 20S6, such as stereoisomer selectivity, are dominated by the conformation adopted by the free ligand.

Supplementary Data

Supplementary Data to this article relating to the crystal structure of 20S6 are deposited with the British Library as Supplementary Publication No. X (15 pages).

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