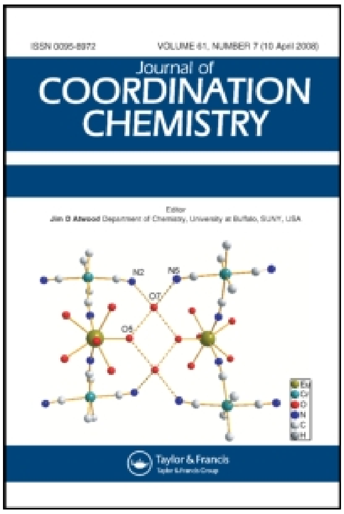

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THE CRYSTAL AND MOLECULAR STRUCTURE OF DECACHLORO -μ-1, 4, 8, 11-TETRATHIACYCLOTETRADEC-ANEDINIOBIUM(V). AN ADDUCT OF $NbCl_5$ WITH AN "INSIDE-OUT" BRIDGING MACROCYCLIC LIGAND

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THE CRYSTAL AND MOLECULAR STRUCTURE OF DECACHLORO -μ-1, 4, 8, 11-TETRATHIACYCLOTETRADECANEDINIOBIUM(V). AN ADDUCT OF $NbCl_5$ WITH AN "INSIDE-OUT" BRIDGING MACROCYCLIC LIGAND[1]

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The crystal and molecular structure of decachloro-μ-1,4,8,11-tetrathiacyclotetradecanediniobium(V) is reported. This is the first example of a complex in which such a macrocycle adopts an inside-out or *exo* configuration. $(NbCl_5)_2$-(S_4-e-pr[14]) crystallizes in space group $P2_1/n$ with two complex molecules and two solvent benzene molecules per unit cell of dimensions a = 7.925(6) Å, b = 19.516(11) Å, c = 10.212(5) Å, and β = 88.62°(5). Full matrix least squares refinement gave final discrepancy factors of R_1 = 0.109 and R_2 = 0.127 for 1061 data having $F^2 > 3\sigma(F^2)$. The molecular structure consists of two $NbCl_5$ units bridged through sulfur by the macrocycle with two of the four sulfur atoms uncoordinated. The macrocyclic ring is substantially disordered. The implications of this structure for bonding in macrocyclic complexes is discussed and the possible significance to kinetic studies of macrocyclic complexes is explored.

INTRODUCTION

Study of transition metal complexes of macrocyclic ligands has been extensively pursued in recent years.[2–5] Structural data on these sytems has not been as completely reported as other aspects of their chemistry and virtually all of such work has involved macrocyclic amine complexes.[6–8] We have recently begun a program to investigate the chemistry of macrocyclic polythiaethers, and report here complete data on the first structurally characterized entirely sulfur-donor macrocyclic complex,[1] decachloro-μ-(1,4,8,11,tetrathiacyclotetradecane)diniobium(V), $(NbCl_5)_2(S_4C_{10}H_{20})$. The obvious inability of the macrocycle to circumscribe the $NbCl_5$ moiety indicated an alternate mode of bonding and this complex turns out to be the first example of a macrocyclic complex in which the macrocycle is in the "inside-out" or "exo-" configuration. The structure of the ligand, 1,4,8,11-tetrathiacyclotetradecane, S_4-ethano-propano[14], S_4-e-pr[14],[1,9] has been determined in our laboratory[10] and likewise shows the same *exo* configuration. The copper complex, $[Cu(S_4$-e-pr[14])]$(ClO_4)_2$, however, shows the *endo* structure,[11a] as found in typical N_4 macrocycles of the cyclam variety, and the nickel(II) complex is similar.[11b] The factors regulating the mode of bonding and the implications of this structure for understanding of substitution reactions are subjects of some interest.

EXPERIMENTAL

Synthesis of Complex

All operations were carried out in a dry-N_2 filled glove box equipped with a circulating system to keep the atmosphere as free of moisture and oxygen as possible. All solvents were thoroughly degassed with high-purity N_2 and stored over sodium ribbon. All chemicals and solvents were reagent grade.

The complex $(NbCl_5)_2(S_4$-e-pr[14]) is prepared as follows. $NbCl_5$, (re-sublimed, Alfa-Inorganics), ~ 100 mg is warmed in ~ 100 ml dry, degassed benzene and dissolves to give an orange solution which is then filtered. S_4-e-pr[14], in excess prepared and purified as described,[9] is dissolved in ~ 15 ml benzene and added all at once to the $NbCl_5$ solution. The reaction mixture immediately turns a deeper red–orange and a very small quantity of fluffy $(NbCl_5)_4(S_4$-e-pr[14]) is filtered off. To the filtrate is added an equal volume of cyclohexane. Subsequent

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cooling to room temperature leads overnight to the deposition of dark, wine–red, opaque crystals of the complex. These are filtered and dried *in vacuo*.

Selection of Crystals

Since all but the smallest of the crystals are opaque, optical examination proved impossible. A number of crystals were mounted in the dry box in sealed .3 mm thin-walled glass capillaries. Rotation photographs taken on the Syntex $P2_1$ four-circle diffractometer showed all crystals to be either twinned or disordered to some degree, with very serious splitting observed in rotation photographs about the *a* axis of the crystal. The crystal chosen for data collection was the best found, but still of poor quality. Dimensions of the crystal were .42 x .30 x .12 mm. The crystal was mounted along a*, the long axis. The linear absorption coefficient μ is 18.1 cm^{-1}. In view of the poor quality of the crystal, an absorption correction was not made. Based on transmission coefficients, we estimate this leads to a maximum error of 10% in F.

X-ray Data Collection

Inspection of axial rotation photographs and the counter intensity data revealed the space group to be $P2_1/n$. Lattice constants were determined by centering on 15 strong reflections, most with 2θ between 10° and 20° using a programmed centering routine, and subsequent least squares refinement of these angles. The results for the monoclinic crystal are $a = 7.925 \pm .006$ Å, $b = 19.516 \pm .011$ Å, $c = 10.212 \pm .005$ Å, $\beta = 88.62° \pm .05°$, $V = 1579.1 \pm 1.7$ Å^3. Air sensitivity of the crystal precluded an accurate determination of the density, but a measurement by flotation in hexane: tetrabromoethane yielded a value of 1.88 gm/cm^3. The calculated density based on 2 molecules per unit cell is 1.86 gm/cm^3.

Intensity data were collected to a value of $2\theta = 50°$ ($\sin\theta/\lambda = 0.579$ Å^{-1}) in the ± hkl quadrants, using monochromatized MoK_α radiation. The monochromator consisted of a highly oriented graphite crystal whose diffraction vector was parallel to the diffraction vector of the sample. The $\theta : 2\theta$ scan technique was used with scan rates varying between 2.02° and 8.37°/min. The scan rate varied with I; however 95% of all peaks were scanned at the slowest rate. Backgrounds were measured at each end of the scan for a total time equal to one-half the scan time.

The scan range extended from 1.2° below $MoK\alpha_1$ to 1.2° above $MoK\alpha_2$. While this is a wider scan than normally taken, we felt that the broadened peaks might be more adequately scanned in this manner. With an axis as long as 19.5 Å, however, one might be concerned that intensities of reflections on or near b* might be affected by overlap. Due to systematic absences along b*, this is no problem for 0k0 reflections. Examination of backgrounds for reflections on or near 0k0 shows some high values. However, backgrounds are generally high, even for arbitrary hkl, and detailed examination of profiles reveals no evidence of overlapping peaks on or near 0k0. The profiles were broad and showed considerable rippling.

During data collection, the intensities of three standard reflections, measured every fifty reflections, all remained within ± 2% of their mean values. The data were reduced to F^2 and $\sigma(F^2)$ by previously described procedures.[12] Standard deviations were assigned as follows:

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

where $\sigma_{counter} = (I + K^2B)^{1/2}$, I = net intensity, B = total background counts, K is the ratio of scan time to background counting time and P is an instrument instability factor. Corrections for Lorentz polarization were applied. Those data for which $F^2 \geqslant 3\sigma(F^2)$ were used in solution and refinement. These totaled 1061 independent reflections of the 3071 collected. This low percentage of 35% observed reflections should be considered in terms of the poor quality of the crystal and the relatively high backgrounds noted above. Of the "unobserved" data, 70% had apparent net intensities greater than zero.

Solution and Refinement

A three-dimensional Patterson synthesis revealed the position of the niobium atom. All chlorine and sulfur atoms were revealed on a subsequent Fourier map. Two cycles of full matrix least squares refinement of these atoms reduced R_1 to .217, R_2 to .269 ($R_1 = \Sigma| |F_o| - |F_c| |/\Sigma| F_o{}^2 |$; $R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o{}^2]^{1/2}$). All of the carbon atoms were then located, although the C(5) peak was small and was not included in the refinement until the thermal parameters of the other carbons had been refined isotropically. Inclusion of C(5) isotropically refined, yielded $R_1 = .112$ and $R_2 = .136$. The thermal parameters were 7. and 16. for C(4) and C(5), respectively, and it was apparent that disorder concentrated in the vicinity of C(4) and

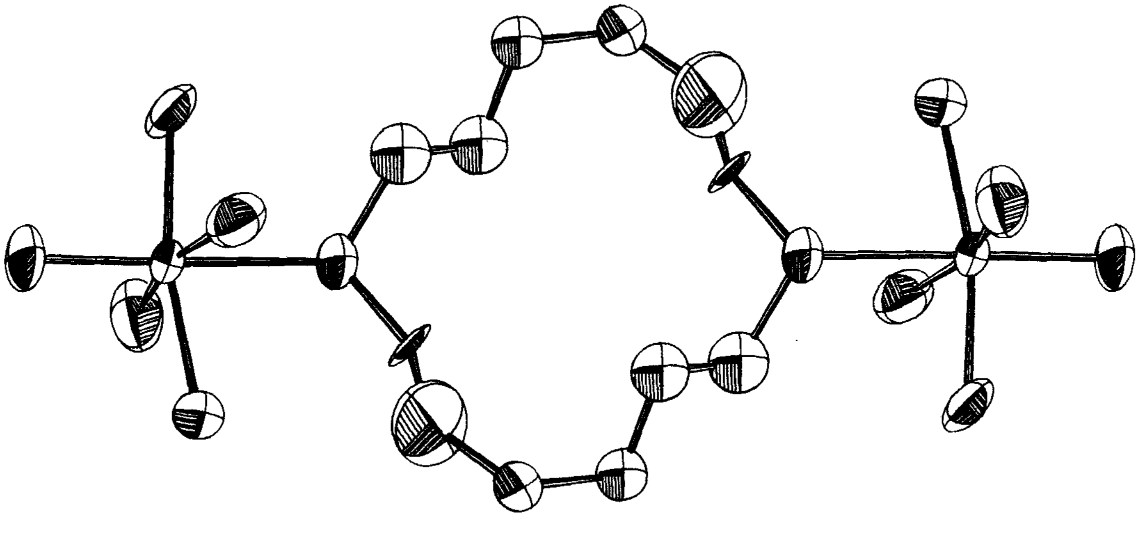

FIGURE 1 Molecular structure of decachloro-μ-1,4,8,11-tetrathiacyclotetradecanediniobium(V).

C(5) was preventing further improvement in the refinement. As discussed below, C(4) and C(5) were treated anisotropically and all other carbon atoms were treated isotropically. Two final cycles of refinement with 115 parameters yielded final values of R_1 = .109 and R_2 = .127. The error of fit was 3.47. A difference Fourier map revealed ripples of 2–3 e/Å^3 in the immediate vicinity of the Nb atom. No other significant peaks were found, although the noise level of the final difference map is above average.

TABLE I[a]
Atomic coordinates

	x	y	z
Nb	.0490(4)	.1916(1)	–.0089(3)
Cl(1)	.0122(14)	.1990(5)	.2160(9)
Cl(2)	.3184(12)	.2347(5)	.0011(10)
Cl(3)	.1171(14)	.0795(4)	–.0133(11)
Cl(4)	–.2383(14)	.1780(5)	.0330(12)
Cl(5)	.0669(16)	.2124(5)	–.2333(10)
S(1)	–.0491(14)	.3246(3)	.0072(10)
S(2)	–.0560(20)	.5466(5)	.3387(12)
C(1)	.054(4)	.464(2)	.301(4)
C(2)	–.043(4)	.436(2)	.176(4)
C(3)	.052(4)	.373(2)	.144(4)
C(4)	.067(9)	.374(2)	–.136(4)
C(5)	–.057(9)	.393(3)	–.228(6)
C(6)	.007(4)	.038(2)	.364(4)
C(7)	–.005(4)	.071(2)	.488(4)
C(8)	.009(4)	.036(2)	.619(4)

[a] Standard deviation from the full variance-covariance matrix is given in parentheses for the least significant digit(s).

The refinement of the data reported here is obviously less than satisfactory but not unexpected in view of obvious poor quality of the crystal. Nevertheless, in order to detect any systematic errors in our data, as well as to gain insight into possible causes of poor refinement, a number of statistical checks were carried out on various subsets of the data. Data were grouped according to increasing F_{obsd}, increasing 2θ, increasing $(\sin\theta)/\lambda$, and various parity combinations of h, k, l. The results of these checks indicate a notably poorer fit for high-angle data as judged by the error-of-fit. A minor adjustment in the assignment of standard deviations, increasing the value of "P" from . 04 to . 08 reduced the error-of-fit to 2.50. There was, however, *no* improvement in R or in any of the unsatisfactory bond distances. In view of this, we retained the original σ's. Throughout all of our consideration of possible causes for poor refinement we have found nothing which leads us to conclude that our problems are due to anything more than a poor crystal.

Table I lists atomic coordinates and Table II lists thermal parameters.

DESCRIPTION OF THE STRUCTURE

The three-dimensional x-ray analysis of the crystals of the decachloro-μ-1,4,8,11 tetrathiacyclotetradecanedinobium (V) complex indicate that the ligand has assumed a most unusual *exo-* conformation (I). This is in contrast to the usual *endo*

TABLE II[a]
Thermal parameters

	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Nb	244(7)	15(1)	94(4)	−1(3)	−28(4)	6(2)
Cl(1)	564(38)	29(3)	80(12)	42(9)	72(17)	18(6)
Cl(2)	192(23)	51(4)	153(15)	−10(8)	−40(15)	21(7)
Cl(3)	500(37)	16(3)	192(17)	21(7)	31(21)	3(6)
Cl(4)	372(30)	30(4)	273(21)	−5(8)	−115(20)	−8(7)
Cl(5)	592(39)	28(4)	105(13)	14(9)	−88(18)	−1(5)
S(1)	385(29)	18(3)	129(14)	14(8)	−14(16)	−1(6)
S(2)	649(7)	24(3)	133(15)	9(9)	−88(22)	−1(5)
C(1)	4.8(8)					
C(2)	6.0(9)					
C(3)	6.6(10)					
C(4)	1642(336)	16(12)	34(49)	63(49)	−37(99)	15(20)
C(5)	1105(274)	76(30)	213(102)	−129(72)	161(139)	−21(46)
C(6)	6.4(10)					
C(7)	6.4(9)					
C(8)	6.3(10)					

[a] Standard deviation from the full variance-covariance matrix is given in parentheses for the least significant digit(s). 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.

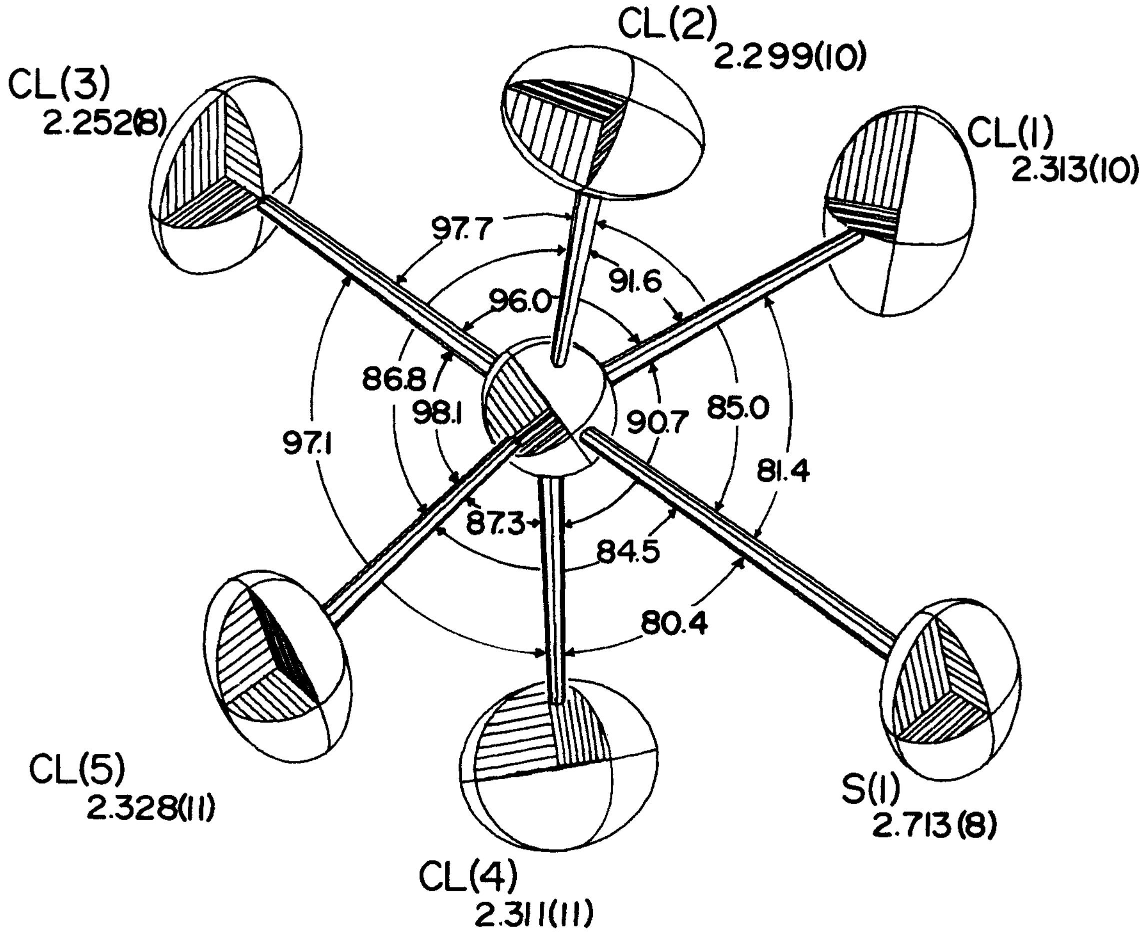

FIGURE 2 $NbCl_5S$ cluster showing details of coordination about the niobium.

conformation (II) found in the Cu(II) and Ni(II) complex. (II) functions as a typical tetradentate macrocycle while (I) functions as a monodentate bridging group. Figure 1 shows the $(NbCl_5)_2$ (S_4-e-pr[14]) molecule. The molecule is symmetric about a crystallographic center of inversion at the center of the macrocycle, one-half of the molecule thus constituting the asymmetric unit along with one-half of a solvent benzene molecule. The two $NbCl_5$ groups are bridged by the macrocycle. Two of the four sulfur atoms are uncoordinated.

The Heavy Atom Cluster

The $NbCl_5S$ unit is shown in Figure 2 with pertinent bond angles and distances. $NbCl_5$ in the gas phase exists as a trigonal bipyramidal molecule with average NbCl distances of 2.29 Å.[13] In the solid state[14] and in CCl_4 solution[15], the $NbCl_5$ molecule exists as a dimer, Nb_2Cl_{10}, with two distorted octahedra sharing a common edge. The crystal structure of Nb_2Cl_{10} shows bridging Nb–Cl distances are 2.55 Å, terminal equatorial Nb–Cl distances are 2.25 Å, and terminal apical Nb–Cl distances are 2.30 Å. In Figure 2 we see that the $NbCl_5S$ cluster has assumed a geometry most akin to a square pyramid. The Nb–Cl(3) distance of 2.252 Å is ~.06 Å shorter than the average of the other 4 Nb–Cl distances, 2.312 Å, as might be expected for the atom opposite the more weakly bound sulfur.

The Nb-S distance of 2.71 Å is quite long and might be taken to reflect the weakly complexed nature of the molecule. A more typical Nb–S distance might be ~ 2.5 Å, although other long distances have been observed. Donohue and Bierstadt[16] report Nb–S distances of 2.59 and 2.60 Å in formally Nb(IV) species. Chen *et al.*[17] report a Nb–S distance of 2.736 Å in $Nb_{14}S_5$ in which the sulfur atom in question is bound to a cluster of Nb atoms in a bicapped trigonal prismatic geometry. Both of these systems are quite different than that reported here.

The Nb atom is ~ . 3 Å out of the plane formed by the four "equatorial" Cl atoms with Cl(3)-Nb–Cl_{eq} angles averaging 97.2°. Despite the lack of resolution among the lighter atoms, this part of the molecule seems fairly well defined.

The Macrocyclic Ligand

The disorder in the crystal resides primarily in the

TABLE III[a]
Interatomic distances and angles

Atoms[b]	Distance(Å)	Atoms[b]	Angles (deg)
Nb–Cl(1)	2.314(10)	Cl(1)–Nb–Cl(2)	91.6(4)
Nb–Cl(2)	2.299(10)	Cl(1)–Nb–Cl(3)	96.0(4)
Nb–Cl(3)	2.252(8)	Cl(1)–Nb–Cl(4)	90.7(4)
Nb–Cl(4)	2.311(11)	Cl(1)–Nb–S(1)	81.4(3)
Nb–Cl(5)	2.328(11)	Cl(2)–Nb–Cl(3)	97.7(4)
Nb–S(1)	2.713(8)	Cl(2)–Nb–Cl(5)	86.8(4)
S(1)–C(3)	1.88(4)	Cl(2)–Nb–S(1)	85.0(3)
S(1)–C(4)	1.96(5)	Cl(3)–Nb–Cl(4)	97.1(4)
S(2)–C(1)	1.87(3)	Cl(3)–Nb–Cl(5)	86.8(4)
S(2)–C(5)*	1.85(6)	Cl(4)–Nb–Cl(5)	87.3(5)
C(1)–C(2)	1.60(4)	Cl(4)–Nb–S(1)	80.4(3)
C(2)–C(3)	1.46(5)	Cl(5)–Nb–S(1)	84.5(3)
C(4)–C(5)	1.42(8)	C(5)*–S(2)–C(1)	101.5(25)
C(6)–C(7)	1.42(5)	S(2)–C(1)–C(2)	103.5(23)
C(7)–C(8)	1.49(5)	C(1)–C(2)–C(3)	102.6(30)
C(6)–C(8)*	1.46(5)	C(2)–C(3)–S(1)	111.2(27)
		C(3)–S(1)–C(4)	95.9(19)
		S(1)–C(4)–C(5)	107.6(57)
		C(4)–C(5)–S(2)*	103.9(51)
		C(6)–C(7)–C(8)	126.4(34)
		C(7)–C(6)–C(8)*	110.0(36)
		C(7)–C(8)–C(6)*	123.6(35)

[a] Number in parentheses represents the estimated standard deviation of the least significant digit.

[b] *Refers to symmetry atoms related by inversion about (0, 1/2, 0).

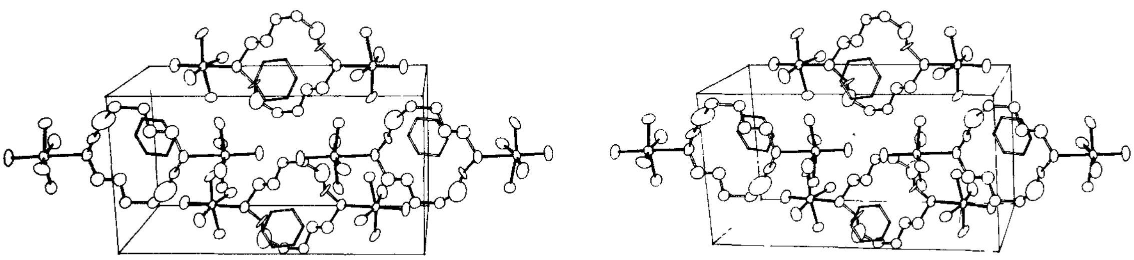

FIGURE 3 Stereoscopic view of the contents of the unit cell, viewed approximately down the *a* crystallographic axis.

ethano bridge, or the two carbon fragment consisting of C(4) and C(5). (See Table III, for bond lengths and angles.) The reasons for this particular disorder are not readily apparent, especially when one considers the structures found by x-ray investigation of the uncomplexed macrocycle itself.[10] One finds that the macrocycle crystallizes in two crystal habits, each with different space group and unit cell constants, each also unsolvated. Both crystal forms contain molecules in the *exo* configuration. One crystal form, which we designate α is readily refined to an R_1 value of 0.027. The other crystal form, designated β, contains two independent molecules, one of which (β_2) is disordered in precisely the manner found in the Nb complex. This structure refines to an R_1 of 0.055. We find in the β_2 molecule that the disorder again resides in the ethano fragment, producing a long C-S bond and a short C-C bond. In the case of the niobium complexes, a possible additional problem is the presumed twinning of the crystal. Nevertheless, since the macrocycle *can* exist in an ordered conformation and since an uncomplexed molecule shows the same disorder as the complexed molecule, the disorder is not due to complexation. A fuller discussion of this phenomenon has been given.[10] Transannular H-H interactions which were thought a likely source of the inability of C(5) to "snap into" its expected position, do not seem to be of great significance in this case. In fact, a calculation of expected H-H distances within the cavity of the macrocycle show that the minimum distance of approach is likely to be ~2.7 Å. This results from the C(5) protons and C(2) protons. One would not expect H–H interactions to be significant beyond about 2.4 Å.

All carbon atoms, with the exception of C(4) and C(5) were refined isotropically. The addition of 30 extra parameters does not seem justified considering the quality of the data and the insignificant ($< .003$) improvement in the R-factors which resulted. In addition, no significant improvement in bond lengths and angles result. C(4) and C(5) were treated anisotropically, however, in order to partially account for the disorder about these atoms. The values of the C(4) and C(5) anisotropic thermal parameters correspond to physically unreasonable values along a. In the case of C(4), β_{11} is 42Å^2 corresponding to a root mean square amplitude of vibration of 0.72Å. These clearly imply disorder concentrated along the *a*-axis of the unit cell. Application of a disdisorder model, treating C(4) and C(5) as two half atoms ~. 5Å apart proved ineffective, and would tend to imply a random disorder about an equilibrium position, rather than two alternate conformations, throughout the crystal.

Packing of the Molecule

Figure 3 shows a stereoscopic view of the unit cell contents viewed nearly down the *a*-axis of the unit cell. The cell contents of 2 complex molecules and two solvent benzene molecules are arranged in a layered manner, with molecules in each layer being related by an n-glide. The benzene molecules are situated directly above the center of the macrocyclic ring 1/2 unit cell or ~ 4Å away along the a-axis.

DISCUSSION

Several points of interest emerge from a consideration of this structure. Perhaps the most interesting feature is the unusual conformation of the ligand. To our knowledge this is the first reported transition metal complex wherein such a structure has been observed. Rings of the cyclam type often pucker seriously to achieve *cis* coordination on binding to large metal ions, but this is a much less dramatic, although energetically more demanding, conformational change than occurs here. In addition, the *exo* conformation found here itself appears not to be the most energetically favorable. Structural studies of S_4-e-pr[14][10] itself reveal two different conformers, differing only in their torsion angles within the ethano fragment. The conformer found here is associated, we believe, with higher energy. The dominant process determining the precise configuration is very likely the *exo-endo* interconversion, and the energy barrier to a "pseudorotation" process which converts between *endo* and *exo* conformers depends almost entirely on torsional strain between vicinal hydrogens, with only negligible contributions from non-bonded repulsions and bond angle strain. This barrier is apparently quite small in a ring of this size, allowing rapid interconversion between conformers in solution at room temperature. An analysis considering vicinal interactions only reveals that the *exo* conformer has two more *gauche* interactions than the *endo* conformer and should, therefore, be energetically slightly less favorable; however, the difference should not be great. Transannular distances found in this molecule preclude the contribution to any significant degree of anything but vicinal interactions. Such a simplified analysis is obviously inadequate, and a satisfactory explanation of the energetics must await detailed analysis of the structures of the uncomplexed macrocycles.

One may speculate on the implications of this structure for the chemical reactivity of macrocycles. If one considers the *endo* complexes of first row transition metals, it seems very likely that the initial attack of the metal involves the more accessible *exo* conformer of the ligand. Rearrangement to the *endo* form probably must occur before the second sulfur atom coordinates. This could lead to substantially different kinetics than in macrocycles in which no *exo* conformers are possible. Evidence bearing on this point[19] has been obtained for Cu(II) complexes of S_4 and N_4 macrocycles, but owing to the weaker donor strength of S toward copper, resulting in a higher dissociation equilibrium constant, one does not know the relative contribution of these two effects to the observed decrease in reaction rates. Studies with other metals would be desirable.

Another interesting point involves specificity in the metal-ligand interaction. It is often assumed that specificity in macrocyclic coordination is inherent in the size of the macrocycle. This, however, is only true for molecules in the *endo* form. A macrocycle which can adopt the *exo* conformation will probably display none of the size specificity associated with *endo* coordination.

Finally, from the standpoint of Nb-S chemistry, it is apparent that this class of sulfur ligands behave, as rather weak donors, being unable to displace Cl from the Nb coordination sphere. The bridging mode is thus forced upon the macrocycle. Nevertheless, the properties of this complex indicate that it is not inherently an unstable one. Given this set of conditions, it might be that complexes of coordination number higher than six could be prepared using this type of ligand. Since $(NbCl_5)_2$ contains 6 coordinate niobium, it is likely that formation of this complex proceeds through a 7-coordinate intermediate since there is no evidence of dissociation of the $(NbCl_5)_2$ dimer.

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and error program; (4) ORTEP, C. K. Johnson's program for drawing crystal models.
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