discussion of this phenomena is given in the references of footnote 7).

The ^{13}C chemical shifts for *N*-phenyltriphenylphosphinimine (7) indicate that there may be some contribution of **7c** to the total electron distribution in this compound. Thus the para carbon of the phenyl group adjacent to nitrogen (carbon-4) is shielded by 4.5 ppm in **7** compared to *N*-anilinotriphenylphosphonium bromide (**8**). The similarity of the chemical shifts for the methylene carbons in formyltriphenylphosphazene (**9**) and its phosphonium salt, **10**, suggests that **9c** does not contribute appreciably toward the electronic structure of **9**. It is also interesting that there is a large difference in ${}^{3}J_{^{31}P-^{13}C}$ for the methylene carbon in **9** compared to ${}^{3}J_{^{31}P-^{13}C}$ for carbon-2 in **7**. Part of this difference is assuredly due to the substitution of an additional nitrogen atom in **9**. This is analogous to the large values of ${}^{3}J_{C-C}$ and ${}^{3}J_{C-H}$ when one of the coupled carbons is adjacent to a nitrogen, in pyridine for example.[11] It is also found that the methylene protons are nonequivalent in **9** which implies that the P=N and N=CH$_2$ groups lie solely in a cisoid or transoid configuration. Framework molecular models clearly show the transoid geometry to be less sterically hindered. Thus part of the difference in ${}^{3}J_{^{31}P-^{13}C}$ in **7** and **9** results from the fact that the coupling in **9** is transoid, while that in **7** is an average of cis and transoid.

Acknowledgment. We wish to thank the National Institutes of Health for partial financial support of this project.

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(9) A referee has suggested that estimations of the percent *s* character in the C–H bond by J_{C-H} using the Muller-Pritchard relationship for **2** and **3** indicate that the hybridization of carbon-1 in **2** and **3** is not substantially changing. This is contrary, however, to the X-ray data for **3.** This relationship, also, is of dubious merit for compounds other than hydrocarbons; see, for example, ref 8 for a full discussion.
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(11) Reference 8, p 378; Y. Takeuchi and N. Dennis, *J. Am. Chem. Soc.*, **96,** 3657 (1974).

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Crystal and Molecular Structure of $(NbCl_5)_2(C_{10}H_{20}S_4)$. An Adduct of $NbCl_5$ with an "Inside Out" Bridging Macrocyclic Ligand

Sir:

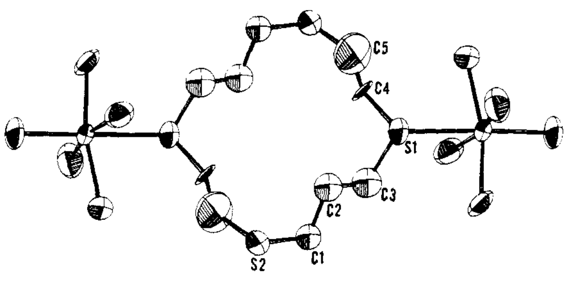
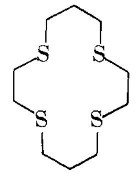
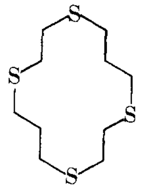


Figure 1.

Numerous structural studies of macrocyclic amine complexes[1-3] have appeared in recent years. We now wish to report the first structure of a transition metal complex containing a four-sulfur macrocyclic ligand (I). Following Ochrymowycz,[4] we shorten the full name 1,4,8,11-tetrathiacyclotetradecane to S$_4$-ethano-propano[14], or S$_4$-e-pr-[14], thus denoting a 14-membered ring containing four sulfur atoms separated by alternating ethano and propano fragments.[5] Reaction of NbCl$_5$ with (I) in benzene yields dark, wine-red crystals of (NbCl$_5$)$_2$(S$_4$-e-pr[14]) which slowly deposit over a period of hours.[6] Unlike any other macrocycle for which structural data are available, the ligand exists in the complex as II, an "inside out" conformation.



I



II

Since structure I is found in the complex Cu(S$_4$-e-pr[14])(ClO$_4$)$_2$,[7] it is likely that interaction with the metal ion aids in an interconversion to II. The entire process requires considerable conformational reorganization as can be seen from examination of a molecular model, and likely proceeds in a stepwise fashion through several energetic barriers. The structure of S$_4$-e-pr[14] in solution is uncertain, and the interconversion may be substantially aided by a pseudo-rotation process.[8] In the complex, the ring is not completely inside-out, presumably due to repulsions among the eight hydrogen atoms directed toward the center of the ring. This can be seen in the disordered structure looking down the *a* axis of the crystal (Figure 1) where the carbon atoms in the ethano bridges are twisted out of the "plane" of the ring.

The complex, (NbCl$_5$)$_2$(S$_4$-e-pr[14]), crystallizes in the space group $P2_1/n$ with unit cell contents of two complex molecules and two molecules of solvent benzene. The cell constants are a = 7.925 ± 0.006 Å, b = 19.516 ± 0.012 Å, c = 10.212 ± 0.005 Å, and β = 88.62 ± 0.05°. Intensity data were collected on a Syntex P2$_1$ diffractometer using graphite-monochomatized Mo Kα radiation to a 2θ of 50°. Due to the disorder, revealed clearly in rotation photographs of over 12 crystals, the scan range was set to ±1.2°, slightly wider than normal, to ensure that the entire broadened peak was scanned. Since the crystals are nearly opaque, the disorder at this point could not be distinguished from twinning. Of the 3071 reflections, the intensities of 1062 were $>3\sigma(I)$ above background and were used in the refinement. The structure was solved by Patterson and Fourier synthesis and refined by full-matrix least-squares procedures to values of 0.109 and 0.127 for R and R_w, respectively. The relatively high values of the discrepancy factors reflect the disordering. However, the great majority of the uncertainty associated with this structure is concentrated in the ring, where bond lengths and angles are less well defined. Inclusion of anisotropy for all carbon atoms offered little improvement in R (<0.003) and no improvement in bond lengths, over isotropically refined carbon, although intuitively one would expect anisotropic parameters to approximate reality a bit more closely. We have chosen to keep the total number of parameters to a minimum, 115, and only C-4 and C-5, the disordered carbon atoms and the heavier atoms have been treated anisotropically. Application of a disorder model in which C-4 and C-5 were each treated as two half atoms ~0.5 Å apart proved ineffective, implying a random disorder in that part of the molecule.

The centrosymmetric molecule is composed of two $NbCl_5$ groups bridged through sulfur by the "inside-out" macrocycle. Two of the four sulfur atoms are uncoordinated. The niobium atoms are six-coordinate, in a geometry suggesting a square pyramidal $NbCl_5$ bonded at the sixth position to sulfur, with Nb–S of 2.71 ± 0.01 Å.[9] The distance to the Cl opposite to S is ~0.05 Å shorter than the other four Nb–Cl distances which average to 2.31 ± 0.01 Å.[10] The apical-Cl–Nb-equatorial-Cl angles average to 97.2 ± 0.4°.

As seen in Figure 1, the principal disorder involves C(4) and C(5). The C(4) thermal ellipsoid is small and severely flattened, while that of C(5) is abnormally large and elongated in the direction of the position expected for C(5) if the interconversion to II were complete. It is likely that transannular H–H repulsions preclude this configuration[11] and that disorder is the mechanism for relieving this situation.

Consistent with this presumption is the fact that the S(1)–C(4) distance of 1.96 Å is ~0.10 Å longer than the average value of 1.86 Å found for the other three C–S distances; the angles of 108 and 104°, subtended at C(4) and C(5), respectively, are not chemically unreasonable.

The existence of this structure would seem to indicate that consideration of alternate bonding modes in complexes of macrocyclic ligands would often be in order, especially in flexible saturated systems and where large rings are involved.

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(8) The structure of S_4-e-pr[14] is under study in our laboratory.
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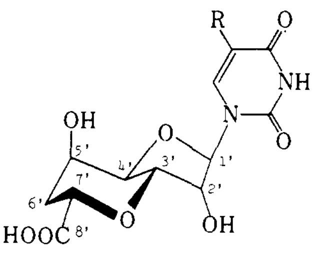
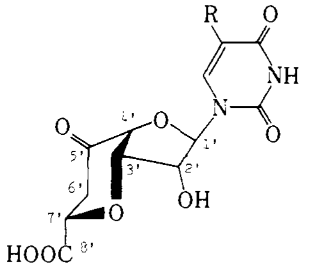
Isolation and Structure of Octosyl Acids. Anhydrooctose Uronic Acid Nucleosides

Sir:

In continuing our studies of the biosynthesis of the polyoxins,[1] nucleoside peptide antibiotics, we have observed considerable amounts of nucleoside-like substances in the acidic fraction from the culture filtrates of *Streptomyces cacaoi* var. *asoensis.*[2] The passed solution from Dowex 50W (all the polyoxins were adsorbed) was adsorbed on Amberlite IR-4B (Cl^-) and eluted with 5% NaCl. Further purification by DEAE-cellulose (Et_3N-carbonate) followed by Avicel-cellulose (BuOH-AcOH-H_2O) afforded four crystalline compounds. They were found to be 5-carboxyuracil, and three unusual pyrimidine nucleosides designated as octosyl acids A (**1**), B (**2**), and C (**3**), which have been assigned the following structures: 1-β-(3,7-anhydro-6-deoxy-D-*glycero*-D-*allo*-octofuranosyluronic acid)-5-carboxyuracil (**1**), 1-β-(3,7-anhydro-6-deoxy-D-*glycero*-D-*allo*-octofuranosyluronic acid)-5-hydroxymethyluracil (**2**), and 1-β-(3,7-anhydro-6-deoxy-D-*glycero*-L-*lyxo*-octofuranos-5-urosyluronic acid)-5-carboxyuracil (**3**). Yield: 5-carboxyuracil, 10 mg; **1**, 300 mg; **2**, 8 mg; **3**, 130 mg from 3 l. of the culture filtrate. These assignments were made on the basis of chemical and spectroscopic evidence, including high resolution mass spectra, as described below.



1 R= COOH
2 R= CH_2OH
6 R= H



3 R= COOH
8 R= H

Octosyl acid A (**1**), $C_{13}H_{14}N_2O_{10} \cdot H_2O$, mp 290–295° dec, $[\alpha]^{20}D$ +13.3° (c 0.425, N NaOH), is a tribasic acid with $pK_a' = 3.0, 4.3$, and 9.4. Uv absorption (λ_{max} 220 nm (9900), 276 (10,700) in H_2O and 0.1 N HCl; λ_{max} 272 nm (7000) in 0.1 N NaOH) is consistent with 1-substituted 5-carboxyuracil.[1] Mass spectra of the TMS and TMS-d_9 derivatives[3] showed $M^+ = 718$ (5TMS), with a base composition of $C_{11}H_{19}N_2O_4Si_2$, and sugar moiety $C_{17}H_{35}O_6Si_3$. 5-Carboxyuracil was obtained by perchloric acid hydrolysis (60% $HClO_4$, 95°, 1 hr). Esterification with 5% HCl in MeOH followed by benzoylation afforded the dimethyl ester tribenzoate (**4**), mp 283–287°, base + 2H = 274, sugar = 425. Presence of a benzoyl group on the 5-methoxycarbonyluracil base[4] was shown by treatment of **4** with 50% AcOH to give the dibenzoate (**5**), $M^+ = 594$, sugar =