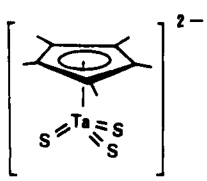
metrical parameters. A striking feature of the structure is the presence of the novel Cp*TaS$_3^{2-}$ unit (**A**) which is the first organometallic species having three terminal sulfides. The known tri(sulfido) complexes are limited to a family of the MS$_3$E^{n-} anions (E = O, S, Se),[8] and for Ta the occurrence of metal–sulfur double bonds itself is very rare indeed.[9-11] The molecule that most closely resembles **A**, both geometrically and electronically, is perhaps the trioxorhenium complex, Cp*ReO$_3$.[12,13]



A

In the crystal structure, four Li cations link two Cp*TaS$_3^{2-}$ units where a crystallographic center of symmetry lies in the middle of the two units. The main frame of **1** may be viewed as a distorted hexagonal prism with metal atoms (Ta and Li) and sulfur atoms occupying alternative vertices. Such a prismatic M$_6$S$_6$ core also has been found in (Ph$_2$PCH$_3$)$_4$Ag$_4$W$_2$S$_8$[14] and [Fe$_6$S$_6$X$_6$]$^{3-}$ (X = Cl, I, SR, OR).[15] Complex **1** extends this limited range of compounds to two more groups of the periodic table and to new types of supporting ligands including the organometallic Cp* group. This suggests that the M$_6$S$_6$ cage structure will be found in many more M$_x$S$_y$ clusters.

The geometry about the two crystallographically independent lithium atoms is basically tetrahedral where each lithium is bonded to three sulfurs and a THF molecule. In the Ta$_2$Li$_4$S$_6$ core, the six unique Li–S bond lengths vary from 2.44 (2) to 2.54 (2) Å. The Ta–S distances range from 2.268 (3) to 2.300 (3) Å with the longest being the Ta–S(3) bond. They may be compared with the terminal Ta–S bond lengths of TaSCl$_3$(PhSCH$_2$CH$_2$SPh) (2.204 (5) Å),[9a] TaS(S$_2$CNEt$_2$)$_3$ (2.181 (1) Å,[9b] and [Et$_4$N]$_4$[Ta$_6$S$_{17}$] (2.145 (5)–2.204 (4) Å).[9c] The somewhat longer Ta–S distances observed for **1** have to be interpreted with caution and should not be attributed entirely to the presence of Li–S interactions, because in going from sulfido to tri(sulfido) systems M=S bonds tend to be elongated due to electronic reasons. As a matter of fact, whereas the Ta=S stretching mode of **1** (Raman, 434 cm^{-1}) is at lower frequency than those of TaSX$_3$L$_2$ (X = Cl, Br) (504–512 cm^{-1}),[9a] it is higher than the A$_1$ mode stretch of TaS$_4^{3-}$ (424 cm^{-1}).[10c] Thus the tantalum–sulfur double bond character remains strong in the dimeric structure.

Our synthetic study of **1** provides a convenient entry into rare Ta sulfides, and the Cp*TaS$_3^{2-}$ unit may serve as a potential building block of a wide range of homo- and heteronuclear sulfide clusters.

Acknowledgment. The support of this work at the University of Hawaii by the National Science Foundation, Grant CHE 85-19289, and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Supplementary Material Available: Complete listings of positional and thermal parameters and bond distances and angles for **1** (44 pages); table of observed and calculated structure factors for **1** (16 pages). Ordering information is given on any current masthead page.

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(7) Crystal data for **1**: crystal size 0.7 × 0.5 × 0.3 mm, monoclinic, space group $C2/c$, a = 24.879 (5) Å, b = 11.501 (2) Å, c = 16.669 (3) Å, β = 99.21 (1)°, V = 4708 (1) Å^3, ρ_{calcd} = 1.61 g cm^{-3}, Z = 4, μ (Mo Kα) = 4.88 cm^{-1}. Of 5782 reflections collected (Nicolet R diffractometer, 25 °C, scan type $\theta/2\theta$, 4° < 2θ < 55°, scan speed 3.0–29.3°/min), 4775 observed reflections $I > 3\sigma(I)$ were used for the structure determination. An empirical correction for absorption was applied to the data. The structure was solved by direct methods and was refined by subsequent full-matrix least squares where hydrogen atoms were not located and the other atoms except for lithiums were treated anisotropically. R = 4.3%, R_G = 4.7%, GOF = 7.96, Δ/σ = 0.21, $\Delta(\rho)_{\max}$ = 0.42 eÅ^{-3}, N_o/N_v = 21.2. All computations used Nicolet SHELXTL PLUS with micro VAX II.

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A New Class of Endoglycosidase Inhibitors. Studies on Endocellulases

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Although the study of glycosidases dates back to the time of Liebig and Wohler, relatively little is known about the mechanisms and structures of these important enzymes.[1,2] In fact lysozyme remains the only glycosidase for which detailed structural information is available.[2] Recent interest in the naturally occurring exoglycosidase inhibitors **1** and **2** (Chart I) has led to the rational design of other monosaccharide analogues.[3-6] Unfortunately **1** and **2** have no effect on endoglycosidases like lysozyme, chitinase, and cellulase, which bind and cleave randomly at the interior of polysaccharides. It was intriguing to speculate whether oligosaccharides containing a strategically positioned azasugar residue might inhibit endoglycosidases.[7] Here we describe an unusual new reaction of organomercurials leading to the synthesis of oligosaccharides **3**–**5** (Chart I) which competitively inhibit β-1,4-endoglucanases from the cellulolytic bacterium *Thermomonospora fusca*.

The NaBH$_4$-O$_2$-DMF reductive oxygenation of mercurial **6** to alcohol **9**, a key step in our published syntheses of **1** and **2**,[8,9] also afforded an unusual byproduct **11** (Scheme I, 5% yield) in which the C4-benzyl ether was selectively removed with concomitant

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Scheme I

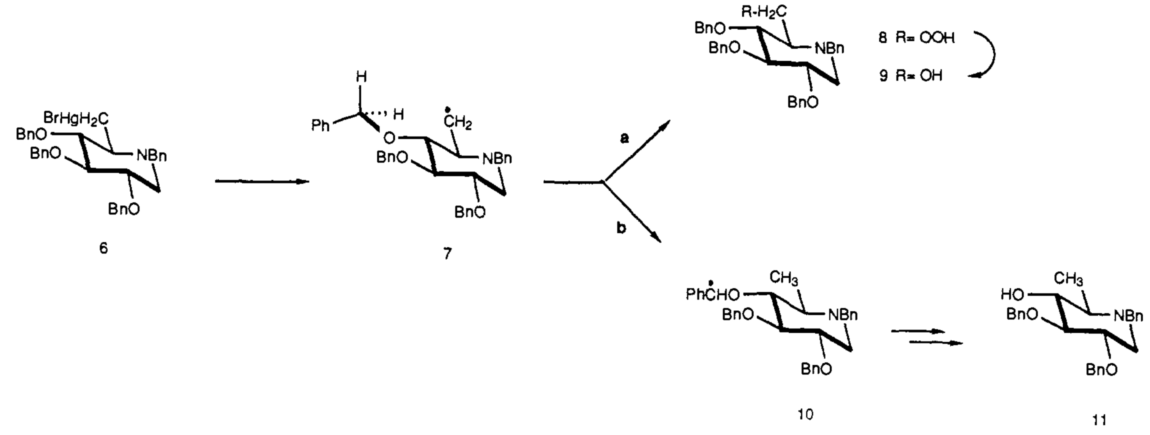
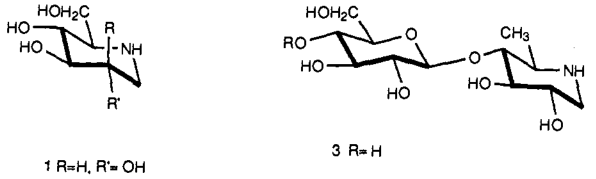


Chart I



1 R=H, R'= OH

2 R=OH, R'= H

3 R= H

4 R= beta-1,4-glucopyranosyl

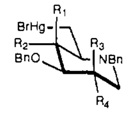
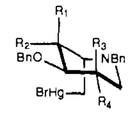
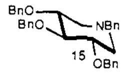
5 R= beta-1,4-cellobiosyl

reduction at C6. Formation of **11**, an ideal candidate for the abovementioned glycoside construction, could best be rationalized by partitioning of the putative[10] radical intermediate **7** between O_2 capture (a, Scheme I, leading to **8** and **9**) and 1,5-hydrogen rearrangement to **10**. Oxygenation of **10** (b, Scheme I) in the presence of $NaBH_4$ thus furnished **11** via its benzaldehyde hemiacetal.[11] By simply changing the flow of oxidant in the reaction from a vigorous flux of pure O_2 to a slow stream of air (0.04 mL/s) the yield of **11** was improved to 68% in gram-scale reactions.[12]

Examination of several other organomercurials revealed the scope of this remarkable reaction (Table I). Like **6**, D-manno and D-galacto derivatives **12** and **13** with equatorial CH_2HgBr groups also underwent reductive oxygenation with significant amounts of 1,5-H rearrangement. The 5-*epi*-D-mannose analogue **16** which exists predominantly in the alternate chair conformation (equatorial CH_2HgBr) behaved similarly. However the chemistry of axial mercurial **14** exhibited two unexpected features. First, reductive oxygenation afforded only normal C6-hydroxylation and no rearrangement product whatsoever, apparently for steric reasons.[13] Second, a heretofore unobserved dealkylation product **15** was detected (10%) whose structure was confirmed through unambiguous synthesis.[14] Compound **15** likely forms by an unusual Grob fragmentation[15] of the initial hydroperoxide and then reduction of the resultant iminium ion. Consistent with this hypothesis, reaction of **14** with $NaBD_4$–DMF–air led to **15**-d_1.[16]

To synthesize azaoligosaccharides **3**–**5**, alcohol **11** was coupled with samples of peracetylated D-glucopyranose, cellobiose, and cellotriose, respectively,[17] using the trichloroacetimidate method (NaH, CCl_3CN, CH_2Cl_2; then **11**, BF_3–Et_2O).[18] Quantitative deacetylation (KOH, CH_3OH) then debenzylation (H_2, Pd/C, EtOH–HCl) of the coupled products afforded **3**–**5** (overall yields 50%, 38%, 40%, respectively, from **11**).

Table I

	PRODUCTS	
Mercurial	C4-OH (viz 11)	C6-OH (viz 9)
		
6 $R_1, R_3 = H$ $R_2, R_4 = OBn$	68%	15%
12 $R_1, R_4 = H$ $R_2, R_3 = OBn$	50%	33%
13 $R_2, R_3 = H$ $R_1, R_4 = OBn$	24%	27%
		
14 $R_1, R_3 = H$ $R_2, R_4 = OBn$	---  15 10%	40%
16 $R_1, R_4 = H$ $R_2, R_3 = OBn$	20%	30%

T. fusca is an aerobic, thermophilic, cellulolytic soil bacterium from which five different endocellulases (E_1–E_5) have been isolated.[19] Azadisaccharide **3** is active only against cellulase E_1 (which inter alia degrades small β-glucans); however, **4** and **5** retard the digestion of crystalline carboxymethylcellulose by the E_1, E_2, and E_5 enzymes. Compounds **3**–**5** are not hydrolyzed as substrates since controls show no reducing sugars are released. Kinetic measurements on E_1 (pH 6.5, 55 °C) in the presence of **4** or **5** using *p*-nitrophenylcellobioside as substrate ($K_M = 1$ mM) result in Lineweaver–Burk plots indicating mixed competitive inhibition by these small substrate analogues. Additional plots of $1/V$ vs [I] give K_I values (**4**, 47 μM; **5**, 63 μM) that confirm the potent inhibitory effect of introducing an azasugar into the cellulose framework. Irreversible enzyme inactivators based on this design should prove useful in mapping the endocellulase active site. Further applications to the study of polygalacturonases in plants and chitinases in insects are also in progress.

Acknowledgment. We thank the National Institutes of Health (GM 35712) and the donors of the Petroleum Research Fund,

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[11] Besides benzyl alcohol, traces of the benzoate ester of **11** were also detected, presumably by fragmentation of the hydroperoxide of **10**. Basic workup thus led to optimal yields of **11**.

[12] Rigorous exclusion of air ($NaBH_4$–DMF–Ar) gave a complex mixture of unidentifiable products.

[13] In the transition state leading to a resonance-stabilized benzyl radical, Dreiding models reveal an unfavorable 1,6-H,H contact between one of the C4-benzylic hydrogens and the axial C3-H in **14**. No significant steric interactions are evident in rearrangement transition states for the equatorially oriented organomercurial-derived radicals **6**, **12**, **13**, and **16**.

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Supplementary Material Available: Physical and spectral data for **3**, **4**, **5**, and **11** plus graphs showing kinetic data on enzyme assays (4 pages). Ordering information is given on any current masthead page.

Magnetic Phase Transitions in Manganese(II) Pentafluorobenzoate Adducts with Nitronyl Nitroxides

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Magnetic phase transitions of molecular materials are currently of large interest, particularly those leading to a permanent magnetic moment. Several different approaches are used in order to obtain three-dimensional order, and among them one particularly interesting is that of assembling in lattice spins with largely different moments, such as $S = 5/2$ and $S = 1/2$, in order to take advantage of the large moments which result either from a parallel or an antiparallel orientation of the individual spins. According to this procedure ferrimagnetic chains have been obtained,[2-6] and eventually three-dimensional ordered ferromagnets have been reported.[3-6]

We have followed an approach which uses metal ion hexafluoroacetylacetonates, $M(hfac)_2$, coupled to nitronyl nitroxides, NITR (NITR = 2-R-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy-3-oxide, R = methyl, ethyl, propyl, and phenyl), to synthesize one-dimensional ferri- and ferromagnetic chains,[6,7] but, although comparatively strong intrachain interactions are developed, the transitions to three-dimensional magnetic order occur at relatively low temperature due to the fact that the chains are fairly well shielded from each other. In particular we have found that compounds of formula $Mn(hfac)_2NITR$ order ferromagnetically at ca. 8 K.[6]

In order to increase the transition temperature we decided to use metal salts which are more suitable to give intermolecular interactions, and our choice fell on carboxylates which are well known to yield complex magnetic structures.

We found that manganese(II) pentafluorobenzoate dihydrate, $Mn(F_5benz)_2{\cdot}2H_2O$, reacts with NITR[8] radicals (R = methyl and ethyl) to yield blue-violet microcrystalline compounds, as shown by powder diffractograms, of formula $[Mn(F_5benz)_2]_2NITR$,[9] which resisted all our attempts to grow crystals suitable for X-ray analysis but showed interesting magnetic phase transitions at ca. 24 and 20.5 K for R = methyl and ethyl, respectively.

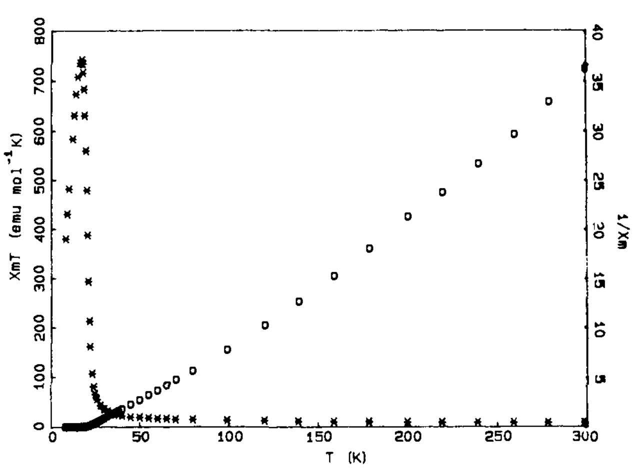


Figure 1. χT (*) and χ^{-1} (O) values for $[Mn(F_5Benz)_2]_2NITEt$ in an external field of 100 Oe.

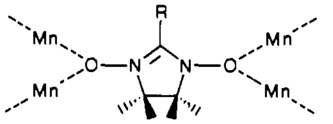
The electronic spectra of $[Mn(F_5benz)_2]_2NITR$ show an intense absorption at 18 500 cm^{-1} typical of the n $\rightarrow$ π^* transition of the radicals,[10] confirming that they do not undergo redox reactions.

The IR spectra suggest that the pentafluorobenzoates are not monodentate, but we cannot distinguish the chelate and bridging structures because the differences of the frequencies in the two types of coordination are too small.[11]

The temperature dependence of the inverse molar susceptibility of $[Mn(F_5benz)_2]_2NITEt$, shown in Figure 1, is loosely reminiscent of that of a bulk ferromagnet, with θ ca. 25 K, but the continuous variation of the slope of χ^{-1} vs T indicates that the Curie–Weiss law is not followed and suggests the presence of short range order typical of low-dimensional magnetic materials. The behavior of $[Mn(F_5benz)_2]_2NITMe$ is similar.

The room temperature value of $\chi T = 8.28$ emu mol^{-1} K is lower than that expected for two spins 5/2 and one spin 1/2, all with isotropic g equal to the free electron value, completely uncorrelated (9.15 emu mol^{-1} K) indicating the presence of antiferromagnetic coupling between the spins of manganese(II) and that of radical, as has been previously observed in a few manganese(II)–nitroxide complexes.[12-14] χT increases slowly on lowering temperature indicating that the Mn_2NITR moieties are not isolated.

A possibility to reconcile the stoichiometry of the complex and the magnetic properties is that of a structural pattern as shown below, in which each radical is bound to four different manganese ions, each of them being shared by two different radicals.



Antiferromagnetic coupling between manganese and radicals keeps all the metal spins parallel to each other, yielding a large uncompensated moment at low temperature. With these blocks

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(1) (a) University of Florence, Italy. (b) Università Paris-Sud, France. (c) Centre d'Etudes Nucleaires Grenoble, France.

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(9) The compounds were synthesized suspending 0.25 mmol of $Mn(F_5Benz)_2{\cdot}2H_2O$ in 40 mL of hot toluene and adding 0.25 mmol of the radical. After stirring for 10 min at 50–60 °C the suspension turned from pink to violet color. The fine microcrystalline precipitate was filtered and dried under vacuum. Anal. Calcd for $[Mn(F_5Benz)_2]_2NITEt$: Mn, 9.75; C, 38.98; H, 1.49; H, 2.46. Found: Mn, 9.98; C, 38.14; H, 1.61; N, 2.39. Anal. Calcd for $[Mn(F_5Benz)_2]_2NITMe$: Mn, 9.87; C, 38.40; H, 1.33; N, 2.49. Found: Mn, 10.02; C, 38.38; H, 1.65; N, 2.58.

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