Table I. Energy Gaps between the Singlet and Triplet States in Isomeric Dinitroxides 6

| 6 | $\Delta E_{S-T}$/cm$^{-1\,a}$ | $\theta$/K | GS from VB | GS from MO |
|---|---|---|---|---|
| *p,p'* | 10.6 | −2.0 | $S = 1$ | nondisjointed |
| *m,p'* | −3.4 | −2.0 | $S = 0$ | disjointed |
| *m,m'* | −1.8 | −2.1 | $S = 1$ | doubly disjointed |

[a] The energy gap between the two states: $\Delta E_{S-T} = 2J$. +/− signs represent triplet/singlet ground states, respectively.

with a Weiss field and purity factor $F^4$ (eq 1) and refined by a SALS program[5] to give the results summarized in Table I.

$$\chi = F\frac{2Ng^2\mu_B{}^2}{k(T-\theta)[3+\exp(-2J/kT)]} \qquad (1)$$

The measurement of the absolute $\mu_{\text{eff}}$ values and their temperature dependence over wide temperature ranges makes it possible to conclude that, whereas both dipole–dipole and exchange couplings between the two nitroxide radicals in **6** are rather weak, the *p,p'* isomer has a triplet and the *m,p'* and *m,m'* isomers have singlet ground states. The exchange coupling in **2** (X = *p*-N(*t*-Bu)O·) may not be very strong but should be ferromagnetic. The ground states of **4** and **5** are suggested to be singlet. The coupling between the radical molecules in neat solid samples is always weakly antiferromagnetic, as revealed by the small negative $\theta$ values.

*p,p'*-**6** is nondisjointed and is predicted by molecular orbital theory (MO)[2c,d] to have a triplet ground state and the largest magnitude of $\Delta E_{S-T}$; the disjointed *m,p'*-**6** is predicted to have a singlet ground state and a small magnitude of $\Delta E_{S-T}$. The *m,m'* isomer is classified as a "doubly disjointed" system in the sense that the carbons with substantial positive density are separated by three carbons, and therefore the isomer is predicted to have a singlet ground state with the smallest magnitude gap of all. The results in Table I are in line with these predictions. However, formal application of a topology/valence bond theory (VB)[6] would have predicted a ferromagnetic interaction between the *m,m'* spins ($S = (n^* - n)/2 = (9-7)/2 = 1$).[7]

The observed small absolute values of $\Delta E_{S-T}$ are annoying, as semiempirical calculations on sterically unprotected diradicals **1** (X = NHO·, N:) usually give $\Delta E_{S-T}$ on the order of 1 kcal/mol.[8] MM2 calculations give an estimate of the propellar-type torsion of the phenyl rings out of the vinylidene and dimethylvinylidene planes as 40° and 54°, respectively. It has been shown that, in phenyl nitroxides, the electron spins are much more localized in the nitroxide moieties than in the hydrocarbon radicals.[9] These two factors appear to attenuate the topological effect of the radical centers on the mode of the exchange coupling. Studies that would amplify the trend found in this study are necessary on a series of sterically unbiased systems with larger spin polarization on the phenyl rings.[3] Such studies are in progress.[10]

**Acknowledgment**. This work was supported by a Grant-in-Aid for Specially Promoted Research (No. 03102003) from the Ministry of Education, Science and Culture, Japan.

**Supplementary Material Available:** Full experimental description of isomeric dinitroxides **6** including their EPR spectra in solid toluene solutions and figurative presentations of the VB theory predicting the ground-state spin $S = (9-7)/2 = 1$ in *m,m'*-**6** and the MO theory showing singly disjointed *m,p'*-**6** and doubly disjointed *m,m'*-**6** (3 pages). Ordering information is given on any current masthead page.

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# Synthesis and Structural Analysis Using 2-D NMR of Sialyl Lewis X (SLe$^x$) and Lewis X (Le$^x$) Oligosaccharides: Ligands Related to E-Selectin [ELAM-1] Binding

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The sialyl Lewis X (SLe$^x$) determinant (NeuAc-$\alpha$-2,3-Gal-$\beta$-1,4-[Fuc-$\alpha$-1,3]-GlcNAc), compound **1**, is a ligand for E-selectin (endothelial leucocyte adhesion molecule 1, or ELAM-1), a member of the selectin family of cell adhesion molecules.[4-7] Interactions between E-selectin and leucocyte-bound SLe$^x$ or closely related oligosaccharides are thought to be important early events in the inflammation process.[8,9] Binding analysis has shown that the sialic acid (NeuAc) and the fucose (Fuc) moieties are essential for high affinity. The related desialylated trisaccharide Le$^x$ (Gal-$\beta$-1,4-[Fuc-$\alpha$-1,3]-GlcNAc), for example, is not a high-affinity ligand for E-selectin.[4-7] In this communication, we describe the syntheses of SLe$^x$ **1** and the $\beta$-*O*-allyl glycoside of Le$^x$ **2** using a cloned fucosyltransferase and their complete NMR spectral assignments including ROESY and NOESY experiments in order to investigae the conformation of these compounds in solution.

The synthesis of $\beta$-*O*-allyl Le$^x$, compound **2**, starts with the construction of the $\beta$-*O*-allyl-*N*-acetyllactosamine derivative **5** (Scheme I).[10] The glycosyl acceptor, $\beta$-*O*-(2,3,4,6-tetra-*O*-acetyl-$\alpha$-D-galactopyranosyl) trichloroacetimidate **3**[11] was treated with the $\beta$-*O*-allyl glycoside of a selectively protected GlcNAc derivative (compound **4**) using boron trifluoride etherate ($BF_3 \cdot OEt_2$) as a catalyst to give, after deprotection, compound **5**.[12,13]

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(13) See the supplementary material for experimental procedures, full characterization, and spectroscopic data.

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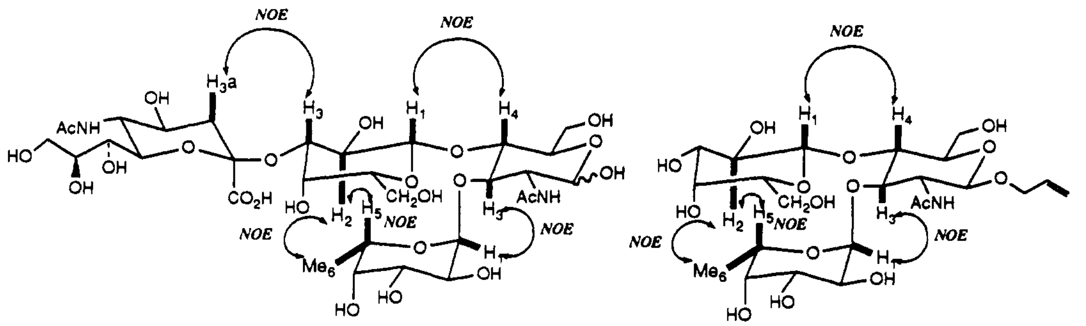
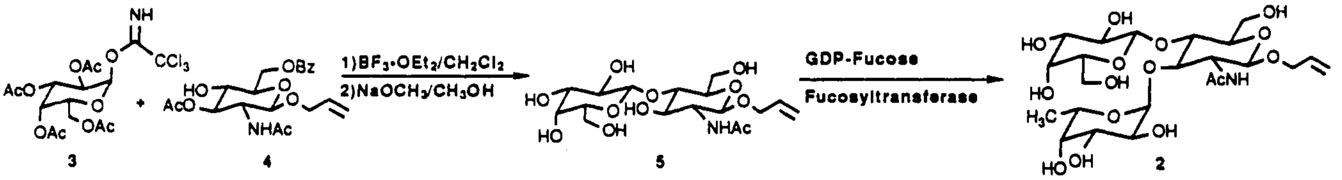


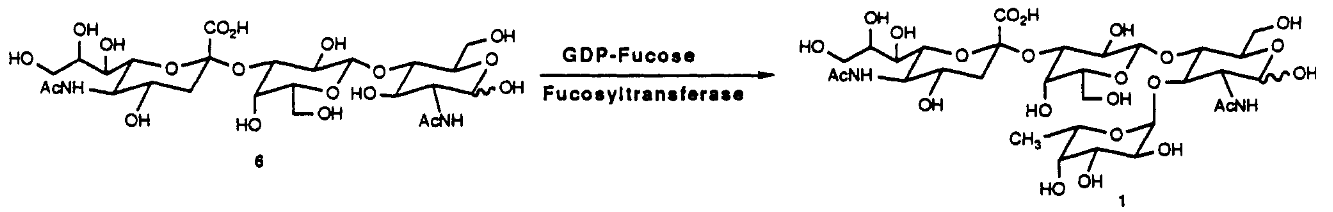
Conformation I (compound 1) Conformation II (compound 2)

**Figure 1.** Results of the ROESY spectrum of SLe$^x$ **1** (left) and ROESY and NOESY spectra of $\beta$-*O*-allyl Le$^x$ **2** (right). Certain protons relevant to the NOE analysis are labeled in the structures. The major conformation for the $\beta$-*O*-allyl glycoside of Le$^x$ (conformation II) is also present in SLe$^x$. (The spectra are available in the supplementary material.) The NOESY spectrum was recorded at 27 °C with a mixing time of 720 ms, and the ROESY spectra was recorded at 26 °C with a mixing time of 200 ms.

**Scheme I**



**Scheme II**



The fucose was introduced by an enzymatic glycosylation reaction using guanosine diphosphate (GDP) fucose and a recently cloned fucosyltransferase to give the target compound **2**.[14] The fucosylation reaction proceeded in greater than 95% yield and worked with a free hydroxyl at either the reducing carbon of the disaccharide or the $\beta$-*O*-allyl glycoside (i.e., compound **5**).

Scheme II describes the construction of SLe$^x$ **1**.[15] The trisaccharide **6** was treated with GDP-fucose using the fucosyltransferase to give SLe$^x$ **1** in greater than 95% yield. Compound **6** is commercially available or can be synthesized from lactosamine or its glycosides by using an $\alpha$-2,3-sialyltransferase and CMP-NeuAc.[16,17]

Proton ($^1$H) and carbon-13 ($^{13}$C) assignments were made for compounds **1** and **2** using a combination of DQF-COSY, TOCSY, homonuclear *J*-resolved, and HMQC, HMBC, and DEPT-135 techniques.[18] Compounds **1** and **2** were then analyzed using ROESY and NOESY NMR experiments in an attempt to study their solution conformations. Figure 1 shows the results of the ROESY experiments on SLe$^x$ and the ROESY and NOESY experiments on Le$^x$. We detected significant NOEs in both the $\beta$-anomer of SLe$^x$ and the $\beta$-*O*-allyl glycoside of Le$^x$ between protons H-5 and H-6 of fucose with the H-2 proton of galactose.[19] These NOEs suggest a folded conformation for both compounds in which the fucose moiety is tucked underneath the galactose (Figure 1, conformations I and II). NOEs between Fuc H-1 and GlcNAc H-3 and between Gal H-1 and GlcNAc H-4 seem to support these solution conformations. An additional NOE was also observed between Fuc H-1 and GlcNAc H-2 in the $\beta$-*O*-allyl glycoside of Le$^x$, suggesting some flexibility around the Fuc-(1→3)-GlcNAc linkage.[20,21] Semiempirical quantum mechanical calculations and NMR analysis of Le$^x$ containing oligosaccharides have shown that II is the major conformation of this trisaccharide, which agrees with our NMR data.[22] Preliminary calculations on SLe$^x$ performed using Biosym's consistent valence force field (CVFF) also indicate that conformation I is a minimum energy structure.[23] *Therefore the major conformation for the $\beta$-O-allyl glycoside of Le$^x$ is also present in the Le$^x$ portion of SLe$^x$, and we believe that this is most likely the active conformation that is involved in binding to E-selectin.* The only significant NOE that was clearly resolved involving the sialic acid group of the $\beta$-anomer of SLe$^x$ and the other sugars was detected between NeuAc H-3a and Gal H-3. No unusual conformations were suggested for the sialic acid moiety when compared to literature studies on other sialic acid containing oligosaccharides.[24,25]

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(19) The $\alpha$-anomer of SLe$^x$ also had NOEs similar to those observed for the $\beta$-anomer. We plan to report our NMR work on the $\beta$- and $\alpha$-*O*-allyl glycoside of SLe$^x$ after biological testing of these compounds has been completed.

(20) All of the observed NOEs can be explained purely on the basis of intramolecular distances, but the possibility of aggregation of the oligosaccharides is not excluded.

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We are continuing our studies on the synthesis and structural analysis of E-selectin related oligosaccharides and will report on our results in due course.

**Acknowledgment**. This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Materials Sciences, by the Division of Energy Biosciences of the U. S. Department of Energy (DE-AC03-76SF0098), and the National Institutes of Health (Awards No. R29 GM43037-02 to M.B. and No. GM14279 to J.B.L. and B.W.). M.B. thanks the American Cancer Society for a Junior Faculty Award and Eli Lilly for a Young Investigator Grant. J.B.L. is an assistant investigator of the Howard Hughes Medical Institute.

**Supplementary Material Available:** Details of the experimental procedures for the synthesis of the *β*-*O*-allyl glycosides and compounds **1** and **2** and spectral data for **1** and **2** (28 pages). Ordering information is given on any current masthead page.

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# On the Interface of Metal–Metal Multiple Bond Compounds and Organometallic Clusters: Synthesis and Structure of $Mo_2\{\mu\text{-}[(CO)_9Co_3(\mu_3\text{-}CCO_2)]\}_4[(CO)_9Co_3(\mu_3\text{-}CCO_2H)]_2$ and Related Compounds

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The octahedral array of organometallic clusters in $M^{II}{}_4$-$[(CO)_9Co_3(\mu_3\text{-}CCO_2)]_6$, M = Zn, Co,[1-3] is defined by the tetrahedral $M^{II}{}_4$ core (Scheme Ia). In order to explore the consequences of a square planar geometry (Scheme Ib), we have now investigated metal–metal quadruply bonded compounds[4-6] as cores for coordinating organometallic cluster carboxylate ligands.[7] Although some related chemistry is known,[5,8] hybrid compounds having both quadruply bonded and trimetal alkylidyne subunits are not. Another development is the assembly of metal–metal multiple bond compounds into low-dimensional materials with both parallel and perpendicular multiple bond arrays using designed tetradentate ligands.[9-11] Here we report that $Mo_2(O_2CCH_3)_4$ reacts with the cluster acid $(CO)_9Co_3(\mu_3\text{-}CO_2H)$ to form three related high nuclearity clusters of clusters with the general formula $Mo_2\{\mu_2\text{-}[(CO)_9Co_3(\mu_3\text{-}CCO_2)]\}_m(CH_3CO_2)_{4-m}[(CO)_9Co_3(\mu_3\text{-}CCO_2H)]_n$ ($m = 3$, $n = 0$, **I**; $m = 4$, $n = 0$, **II**; $m = 4$, $n = 2$, **III**).

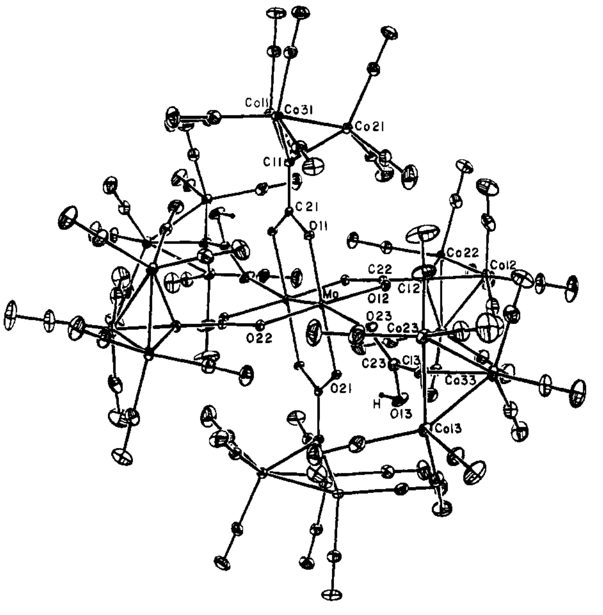
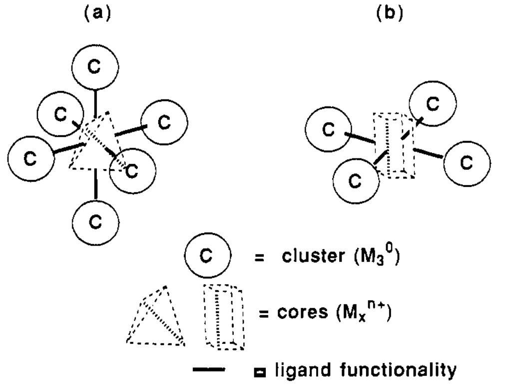
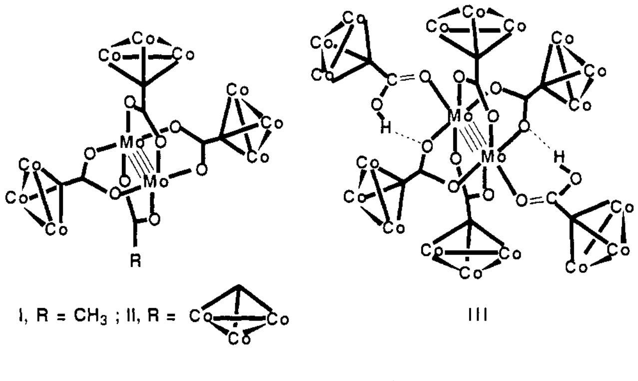


**Figure 1**. ORTEP plot (30% thermal ellipsoids) and selected bond distances (Å) and angles (deg) for **III**: Mo–Mo′ 2.1126 (3), Mo–O11 2.089 (1), Mo–O12 2.104 (1), Mo–O21 2.124 (1), Mo–O22 2.089 (1), $(Co\text{–}Co)_{eq,av}$ 2.47 (1), $(Co\text{–}Co)_{ax,av}$ 2.475 (3); $(Mo\text{–}Mo\text{–}O)_{eq,av}$ 92 (1), O11–C21–O21 120.7 (2), O12–C22–O22 122.2 (2).

**Scheme I**



**Scheme II**



$Mo_2(CH_3CO_2)_4$ reacts with 2 equiv of $(CO)_9Co_3(\mu_3\text{-}CCO_2H)$ in THF at room temperature to give a deep midnight blue solution. On immediate cooling, a toluene extract gave needle-like blue-black crystals (73%) that were characterized as the solvated tricluster-substituted species $\mathbf{I}\cdot C_6H_5CH_3$.[12] Crystallization at room temperature for days yielded both barlike crystals (~15%) and large pseudorhombohedral crystals (1–2 mm in size, ~40%). The latter crystals were selected and characterized as the tetracluster-substituted, cluster acid adduct **III**.[13] Another compound,

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