II, was obtained (60%) by using 6 equiv of $(CO)_9Co_3(\mu_3\text{-}CCO_2H)$ along with a mixed solvent system of toluene and THF.[14] Compounds **I** and **III** produced X-ray quality crystals.[15,16]

Considering published information on the carboxylate exchange reaction,[10] the clean, quantitative reaction described above at room temperature is surprising. We know that there is substantial electronic interaction between the $(CO)_9Co_3C$ fragment and the $(COO)^-$ functional group,[2] and this, along with the substantial steric bulk of the cluster, presumably makes $[(CO)_9Co_3(\mu_3\text{-}CCO_2)]^-$ a much better ligand than acetate.

Structural representations of **I**–**III** (Scheme II) and an ORTEP plot of **III** (Figure 1) show that the three compounds differ only the nature of the axial ligation. For **III** the structural features in the vicinity of Mo_2^{4+} are similar to those in published structures.[6] In this case two cluster carboxylic acids occupy the axial positions of Mo_2^{4+} with a nonbonding Mo–O distance of 2.515 (2) Å and form hydrogen bonds between the axial cluster acid proton and an equatorial carboxylate oxygen O21. The hydrogen bonding elongates the Mo–O21 distance [2.124 (1) Å]. There are no significant structural differences among the six tricobalt clusters surrounding the Mo_2^{4+} core.

The symmetric A_1 stretching mode of the carbonyl ligands on the tricobalt cluster alkylidyne is a sensitive probe of the charge density on the Co_3 unit.[17] In $M^{II}_4[(CO)_9Co_3(\mu_3\text{-}CCO_2]_6$, M = Zn, Co[1-3], the cores behave essentially like a proton to the cluster carboxylates, and the A_1 mode has the same frequency, within experimental error, as in the uncoordinated acid. However, for the title compounds, the A_1 frequencies are at lower energy (2103–2106 cm^{-1}) compared to those (2111 cm^{-1}) in the uncoordinated cluster acid. This reveals an increase in the electron density on the equatorial tricobalt clusters of **I**–**III** compared to the free acid. Although the differences are small, they are real as **III**, which contains both four equatorial carboxylates and two axially coordinated cluster acids, exhibits both A_1 modes (2111 and 2105 cm^{-1}) in a 1:2 ratio.[14]

Although **I** and **III** are soluble in hydrocarbons and ethers, **II** has very poor solubility in the same solvents. This could result from a strong intermolecular axial interaction between the molybdenum of one molecule and a carboxylate oxygen of another, as has been well established in other systems.[6,10] Note that the electron donation from Mo_2^{4+} to the cobalt cluster makes Mo_2^{4+} more electrophilic, which in turn should enhance this interaction.

Another interesting feature of the title compounds is their intense midnight blue color (**I**, 572 nm, ϵ_{mole} = 22 000 cm^{-1} M^{-1}; **III**, 536 nm, ϵ_{mole} = 31 000 cm^{-1} M^{-1}) vs pale yellow color in starting material $Mo_2(O_2CCH_3)_4$ (435 nm, ϵ_{mole} = 100 M^{-1} cm^{-1})[10,18] and purple-brown $(CO)_9Co_3(\mu_3\text{-}CCO_2H)$ (510 nm, ϵ_{mole} = 1300; 370 nm, ϵ_{mole} = 3300).[17,19,20] The ionization potentials of $Mo_2(CH_3CO_2)_4$[21] and $(CO)_9Co_3(\mu_3\text{-}CCH_3)$[20] combined with HOMO–LUMO gaps derived from Fenske–Hall calculations[22] for the same molecules and, separately, direct calculations on $Mo_2(CH_3CO_2)_3[(CO)_9Co_3(\mu_3\text{-}CCO_2)]$ suggest that a $\delta(Mo_2^{4+}) \rightarrow \sigma^*(Co_3)$ transition is responsible for the intense color. That is, in both approaches the ~4-eV gap between the δ and δ^* levels of the Mo_2^{4+} core contains a single empty orbital corresponding to the $\sigma^*(Co_3)$ orbital of the cobalt cluster. Because the extinction coefficient falls in the range of 10^4–10^5 cm^{-1} M^{-1}, this absorption is allowed. The calculations suggest that it can be considered as a type of metal–ligand charge-transfer band but one where the final state now has high metal character due to the presence of the metal cluster substituent.

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Supplementary Material Available: Tables of crystal structure analysis data which include atomic coordinates for all atoms and anisotropic thermal parameters for non-hydrogen atoms (14 pages); table of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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(13) Data for **III**: FT-IR (KBr) $(CO)_9Co_3^-$ 2111 m(sh), 2105 s, 2042 vs (br), COOH 1646 s, COO$^-$ 1449 m, 1362 m.

(14) Data for **II**: FT-IR (KBr) $(CO)_9Co_3^-$ 2104 s, 2075 s(sh), 2042 vs, 2022 s, 2013 s, COO$^-$ 1453 m, 1375 m(br). Anal. Calcd for $Mo_2Co_{12}C_{44}O_{44}$: Co, 33.18; Mo, 9.00; C, 24.79. Found: Co, 33.34; Mo, 8.31; C, 23.03.

(15) Crystal data for $Mo_2Co_9C_{42}O_{35}H_{11}$ (**I**): space group *Pmma*; a = 42.738 (16), b = 15.110 (3), c = 8.988 (3) Å; V = 5804 Å^3, d(calcd) = 2.06 g/cm^3, d(obsd) = 2.04 g/cm^3; M_r = 1797.8; Z = 4, μ = 19.3 cm^{-1}. Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal monochromated Mo Kα X-radiation source. Although the structure remains unsolved because of a space group ambiguity, the cell and density data confirm the formula.

(16) Crystal data for $Mo_2Co_{18}C_{66}O_{66}H_2$ (**III**): space group triclinic $P\bar{1}$; a = 12.976 (2), b = 14.347 (5), c = 15.584 (5) Å; α = 89.38 (2), β = 66.07 (2), γ = 68.90 (1)°; V = 2442.7 Å^3, d(calcd) = 2.11 g/cm^3, d(obsd) = 2.20 g/cm^3; M_r = 3103.4; Z = 1, μ = 33.1 cm^{-1}. Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal monochromated Mo Kα X-radiation source. Crystallographic computations were carried out on a VAXstation 3200 computer using the SDP/VAX software. The structure was solved by a combination of direct methods and difference Fourier syntheses. Full-matrix least-squares refinements were employed. $R(R_W)$ = 0.043(0.053) (685 variables refined including the hydrogen atom parameters) for 11 825 reflections $[F_o > 3.0\sigma(F_o)]$ of 13 329 independent reflections collected over the 2θ range $3.0° \leq 2\theta \leq 58.7°$.

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Conformational Studies of Sialyl Lewis X in Aqueous Solution

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The tetrasaccharide sialyl Lewis X (sialyl Le^x, Figure 1) NeuAcα(2→3)Galβ(1→4)[Fucα(1→3)]GlcNAc has recently been demonstrated to be the ligand of endothelial leukocyte adhesion molecule-1 (ELAM-1).[1] This discovery has led to the development of effective methods for the synthesis of sialyl Le^x and its derivatives as potential antiinflammatory agents. Both chemical[2,3] and enzymatic[4] methods are available for the synthesis of sialyl Le^x and its analogs. In order to further understand the structure–function relation of sialyl Le^x and to develop sialyl Le^x mimetics, we report our conformational study of sialyl Le^x based on two-dimensional NMR techniques in combination with MM2 molecular mechanics calculations.

It has been indicated in the early work of Lemieux[5] that polysaccharides are capable of adopting ordered conformations which place sugar unit and functional groups at regular and predictable

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‡ On sabbatical leave from National Taiwan University.

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Table I. ^1H and ^{13}C NMR Data of Sialyl Lewis X β-OMe

	NeuAc		Gal		GlcNAc		Fuc		OMe	
	H	C	H	C	H	C	H	C	H	C
1		173.5	4.52	101.2	4.49	100.6	5.09	98.3	3.50	56.3
2		99.3	3.52	68.9	3.89	55.5	3.68	67.3		
3	1.79 2.76	39.4	4.10	75.3	3.83	74.6	3.90	68.8		
4	3.69	68.0	3.93	66.9	3.93	73.0	3.78	71.5		
5	3.86	51.3	3.58	74.5	3.58	74.9	4.83	66.3		
6	3.65	72.6	3.69	61.1	4.03 3.88	59.3	1.16	14.9		
7	3.59	67.7								
8	3.90	71.4								
9	3.64 3.87	62.2								
CH_3	2.03	21.7			2.01	21.9				
C=O		174.7				173.8				

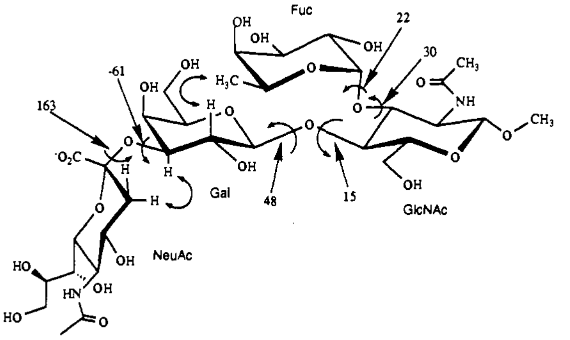

Figure 1. Solution structure of sialyl Le^x determined by 2D NMR spectroscopy and MM2 calculations. ϕ and ψ are torsion angles, and double arrows indicate NOEs.

spacial dispositions as a result of exo anomeric effect. NMR studies and hard sphere energy calculations have been used in the conformational analysis of human ABH and Lewis group determinants[5,6] and several other oligosaccharides.[7,8] It has been shown[8] that in sialic acid-containing oligosaccharides, the aglycon attached to the sialic acid residue preferred to adopt an antiperiplanar-like orientation to the anomeric carboxylate group, thus enabling an interresidual interaction to stabilize the conformation. Wormald et al. have also reported that the Lewis X determinant shows a relatively rigid conformation in aqueous media.[9]

In the ^1H NMR spectrum of sialyl Le^x β-OCH_3, the majority of the ring protons fall within a narrow chemical shift range of 3.5–4.0 ppm. The complete assignment of ^1H and ^{13}C resonances, based on DQF-COSY, TOCSY, HMQC, and HMBC NMR techniques,[7] is listed in Table I. The signals for all anomeric hydrogens, C-6 methyl hydrogens of fucose, C-3 methylene hydrogens of NeuAc, and especially H-2 of Gal residues were well resolved. Total correlation spectroscopy was therefore used to relay spin–spin information from these hydrogens within a pyranose ring to establish the assignment. Furthermore, since those well-resolved hydrogens are located around the fucoside and the sialoside linkages, these ^1H signals could be used for clear identification of the NOEs in rotating frame.

Similar to what has been observed in LNFP III,[9] the NOESY spectrum of sialyl Le^x shows very weak intraresidue and interresidue NOEs, indicating a correlation time of approximately $1/\omega_0$. Thus, ROESY was used to obtain conformational information. To reduce the coherent transfer (HOHAHA) in ROESY spectra, the carrier frequency, field strength of the rotating frame spin lock irradiation, and the mixing time were carefully adjusted.[10] In such a ROESY spectrum, a number of interresidue ROEs as well as intraresidue ROEs are observed. The conformationally important ROEs other than those intraresidue ones are between NeuAcH-3_{ax} and GalH-3 and between FucH-6 and GalH-2. Variations of the spin lock mixing time from 90 to 490 ms to cause the disappearance of the cross peak from coherence transfer confirm the proximity of these protons.

An MM2 calculation based on the ROE distance constraints obtained from NMR as initial values was then carried out[11] to obtain stable conformations for comparison. The six glycosidic torsion angles, designated by ϕ and ψ and defined by the four atoms H1–C1–O1–Cx′ and by C1–O1–Cx′–Hx′, respectively, for sialyl Le^x were determined after energy minimization. The results are consistent with those observed in the ROESY spectrum. The close agreement between the conformation corresponding to the computed energy minimum with the NMR-derived conformation indicates the existence of a predominantly single conformer for sialyl Le^x. Interestingly, the torsion angle between NeuNAc and Gal obtained from MM2 is +163°. The corresponding value for several other sialosides[8] were in the range of −160 ± 10°. The MM2 calculations gave slightly higher energy (0.6 kcal/mol) for conformers with negative torsion angles.

The very close packing (stacking) of the fucose and galactose residues is somewhat unusual. The experimental results are in good agreement with the results of Bush,[12] who reported a single conformer for the blood group trisaccharide derivative Fucα-(1→2)[GalNAcα1→3]Galβ-OMe, and those of Dwek,[9] who reported a single conformer for Lewis X. The interactions between the Gal and Fuc residues provide a very rigid structure with a well-defined hydrophilic surface on the top and hydrophobic surface in the bottom and a close proximity between the 2-OH of Fuc and the C=O of GlcNAc. With the availability of this three-dimensional geometry, we have begun to study the structure–function relation of sialyl Le^x via modification of the surface

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OH groups and to develop a new generation of sialyl Le^x analogs and mimetics which may have better and more desirable biological activities.

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The Dimerization of RC_{60} Radicals†

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Since the discovery, isolation, and characterization of C_{60} and other fullerenes,[1,2] it has become evident that these compounds have a rich and multifaceted chemistry. There are already reports of the alkylation,[3] halogenation,[4] and epoxidation[5] of C_{60} and reports of the addition of $C(C_6H_5)_2$ across its double bonds,[6] in addition to the preparation of organometallic derivatives.[7] In none of these studies, however, has there been any suggestion of concatenation of fullerene molecules, i.e., "necklace" formation of $R(C_{60})_nR$. In the present communication we report the existence of the prototype of such derivatives: dimers of the alkyl–C_{60} radical adducts, which were recently detected by electron spin resonance spectroscopy (ESR).[8]

Alkyl radicals add rapidly and multiply to C_{60} to give products R_nC_{60}, which have been identified by mass spectrometry and, for odd n, by ESR spectroscopy.[8,9] With a few notable exceptions (R = H, F, CH_3), a number of monoalkyl radical adducts have been identified unequivocally by the proton and ^{13}C hyperfine structure of their ESR spectra.

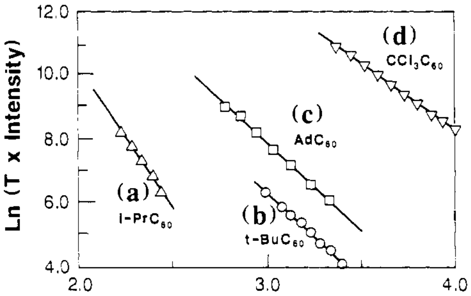

Figure 1. Graphs of ln (T × intensity) versus $1000/T$ for the spectrum of (a) isopropyl–C_{60}, (b) *tert*-butyl–C_{60}, (c) 1-adamantyl–C_{60}, and (d) CCl_3–C_{60} radicals.

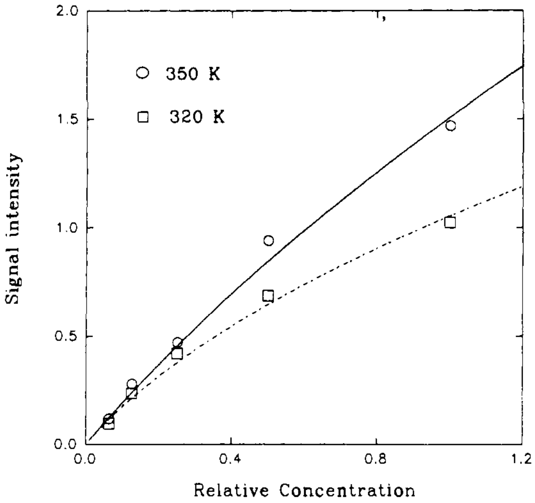

Figure 2. Intensity, in arbitrary units, of the ESR spectrum of *tert*-butyl–C_{60} at 320 and 350 K as a function of relative concentration. The curves are a least-squares fit based on an $R_2 \rightleftharpoons 2R$ equilibrium.[14]

Table I. Isotropic *g* Factors, Proton Hyperfine Interactions (G), and Enthalpies of Dimerization (kcal/mol) of RC_{60} Radicals

R	*g* factor	HFI	$-\Delta H$	temp/K
$(CH_3)_2CH$	2.002 23	6H = 0.15 1H = 0.48	35.5	420–450^a
$(CH_3)_3C$	2.002 25	9H = 0.17	22.1	300–400^{b,c}
1-$C_{10}H_{15}$^{d}	2.002 24	6H = 0.05 3H = 0.26	21.5	300–400^{b,c}
CCl_3	2.003 41		17.1	250–310^e
CBr_3	2.009 10		17.0	300–375^f

^{a}UV photolysis of RBr in *tert*-butylbenzene.[11] ^{b}UV photolysis of RBr in benzene. ^{c}UV photolysis of di-*tert*-butyl peroxide + RH in benzene. ^{d}1-Adamantyl. ^{e}UV photolysis of CCl_4 containing dissolved C_{60}. ^{f}UV photolysis of CBr_4 dissolved in toluene/C_{60}.

A remarkable feature of the ESR spectra of the RC_{60} adducts was the dramatic increase in intensity of the spectrum with increasing temperature, in contrast to the usual decrease in intensity associated with the Curie law. With $(CH_3)_3CC_{60}$ in benzene, for example,[10-12] the spectral intensity increased by 1 order of magnitude as the temperature was raised from 300 to 350 K, and it decreased again as the temperature was lowered, disappearing at ca. 280 K. This cycle could be repeated several times without significant radical decay, although prolonged heating at 400 K

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† Du Pont No. 6223; NRCC No. 34192.

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(11) In a typical experiment, 10 μL of *tert*-butyl bromide was added to 175 μL of a saturated (ca. 0.002 M) solution of C_{60} in benzene or *tert*-butylbenzene in a 4 mm i.d. Suprasil tube, using a glove box continuously flushed with dry N_2 or Ar. The samples were then irradiated in the cavity of the ESR spectrometer with the focused light of a 1000-W high-pressure Hg/Xe lamp (NRCC) or a 500-W Cermax xenon illuminator (Du Pont). The lamp outputs were filtered through an aqueous $CoSO_4/NiSO_4$ filter. The ESR spectrometers were either a Varian Associates E-102 (NRCC) or a Bruker ESP-300 (Du Pont), both being equipped with the usual devices for readout of the temperature, microwave frequency, and magnetic field.

(12) Excellent spectra were also obtained by irradiation of pivalaldehyde (10 μL), pivalaldehyde (10 μL) and di-*tert*-butyl peroxide (10 μL), or di-*tert*-butyl ketone (10 μL) in saturated benzene solutions of C_{60} (175 μL, ca. 0.002 M). Thermal methods consisted of heating at 330 K either *tert*-butyl peroxypivalate (Lupersol 11) or azoisobutane and C_{60} in benzene in a 1:1 molar ratio.

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