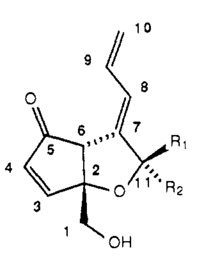
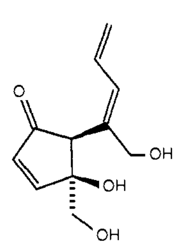
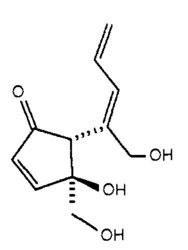




3



4

1 $R_1 = H, R_2 = OH$
2 $R_1 = OH, R_2 = H$
5 $R_1 = H, R_2 = OCH_3$
6 $R_1 = OCH_3, R_2 = H$
7 $R_1, R_2 = O$

octane/ethyl acetate mixtures. Compound **5**, produced along with **6** as an artifact of the chromatography,[4] was crystalline, and its relative stereostructure was established by single-crystal X-ray diffraction analysis.[5]

Compound **5** was central to the structure elucidation of compounds **1** through **4**.[6] An important observation on **5** was that irradiation of the proton at C9 (δ 6.85) gave a 13.4% NOE enhancement for the methine proton at C6 (δ 3.61). Similarly, irradiation of the olefinic proton at C8 (δ 6.30) gave a 9% NOE enhancement to the acetal proton at C11. Acetals **5** and **6** could be interconverted with hemiacetals **1** and **2** upon treatment with acid in aqueous THF. The ^1H NMR and ^{13}C NMR spectra[7] of didemnenones A (**1**) and B (**2**) were very similar to those for **5**. In addition to the similarity of chemical shifts and coupling constants, the same NOE enhancements could be observed. This establishes that **1** and **2** are related as epimers at C11 and not double bond isomers at C7.

Didemnenones C (**3**, 0.007% dry weight) and D (**4**, 0.006% dry weight) were isolated from the methanol extract of *D. voeltzkowi* following solvent partitioning and Sephadex LH-20 (MeOH/$CHCl_3$, 1/1) chromatography. Their ^1H NMR spectra were essentially identical and showed many similarities with the spectra of didemnenones A (**1**) and B (**2**).[8,9] A decisive experiment was the MnO_2 oxidation of didemnenone C (**3**) to give γ-lactone **7** (1751 cm^{-1}). Lactone **7** was also formed on MnO_2 oxidation of **1** and **2**. This oxidation established the relative stereostructure of didemnenone C (**3**). Similar oxidation of didemnenone D (**4**) gave the C11 aldehyde which did not form a γ-lactol, indicating that the C2 hydroxyl and the C6 side chain were trans. The aldehyde from **4** ultimately formed a δ-lactol in protic solvents. Most plausibly, didemnenones C (**3**) and D (**4**) were epimeric at C6 with the relative stereochemistries shown.

Surprisingly, the optical rotation of lactone **7** depended on the source organism. Lactone **7** prepared by the oxidation of didemnenone C (**3**) from *D. voeltzkowi* had a negative rotation at 589, 578, 546, 436, 365, and 302 nm. In contrast, lactone **7** from the oxidation of didemnenones A and B (**1** and **2**) from *T. cyanophorum* had a positive rotation at the same wavelengths. Thus the two different organisms produce related metabolites in enantiomeric series.

Didemnenones C and D exhibit cytotoxicity in an in vitro L1210 murine leukemia cell line with IC_{50}'s of 5.6 μg/mL. Didemnenones A and B showed antibacterial activity against a variety of microorganisms and antifungal activity against the pathogenic marine fungus *Lagenidium callinectes*.

Acknowledgment. This work was partially funded by NSF CHE 8315546 (W.F.); A. P. Sloan Foundation, CA36622, CA01179 (C.I.); and CA24487 and the New York State Sea Grant (J.C.). We thank Uday Raj and the Institute of Marine Resources, University of the South Pacific, for use of their facilities.

Registry No. 1, 110935-52-9; **2**, 111056-70-3; **3**, 110935-53-0; **4**, 111056-71-4; **5**, 110935-54-1; **6**, 111056-72-5; **7**, 110935-55-2.

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, interatomic distances, interatomic angles, perspective drawing for **5**, and chiroptical data for **7** (5 pages). Ordering information is given on any current masthead page.

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(4) The crude extract was dissolved in MeOH, mixed with silica gel, and evaporated to dryness prior to chromatography.

(5) Compound **5** crystallized in the monoclinic space group $P2_1$ with $a = 7.662$ (1) Å, $b = 7.709$ (1) Å, $c = 9.808$ (1) Å, and $\beta = 104.308$ (13)°, and one molecule of composition $C_{12}H_{14}O_4$ forming the asymmetric unit. The structure was solved with direct methods and refined to a conventional crystallographic residual of 0.042. Additional details can be found in the paragraph entitled Supplementary Material at the end of this paper.

(6) Spectral data for **5**: HREIMS, *m/z* 222.0877 ($C_{12}H_{14}O_4$ requires 222.0892); UV (MeOH) λ_{max} 236 (ϵ = 21000); IR ($CHCl_3$) 3690, 3550, 1720, 1215, 1075, 1020 cm^{-1}; $[\alpha]_D$ = +371.8° (*c* 0.86 g/100 mL, $CHCl_3$); ^{13}C NMR (acetone-d_6) δ 65.3 (t, C1), 94.7 (s, C2), 163.7 (d, C3), 128.4 (d, C4), 203.5 (s, C5), 52.9 (d, C6), 138.8 (s, C7), 135.2 (d, C8), 134.4 (d, C9), 120.2 (t, C10), 108.6 (d, C11), 54.2 (q, C12); ^1H NMR ($CDCl_3$) δ 3.90 (dd, 11.0, 3.0, C1), 3.71 (dd, 11.0, 7.0, C1), 7.57 (d, 5.5, C3), 6.17 (d, 5.5, C4), 3.61 (d, 2.0, C6), 6.30 (dd, 10.5, 2.0, C8), 6.85 (ddd, 17.0, 10.5, 10.5, C9), 5.39 (d, 17.0, C10), 5.36 (d, 10.5, C10), 5.33 (s, C11), 3.34 (s, C12, 3H), 2.03 (dd, 7.0, 3.0, exch.).

(7) All attempts to separate didemnenones A (**1**) and B (**2**) were unsuccessful. The spectral data for the approximately 1:1 mixture are the following: HREIMS, *m/z* 208.0747 ($C_{11}H_{12}O_4$ requires 208.0736), 190.0616, 177.0549; UV (CH_3CN) λ_{max} 238 (ϵ = 13000), irreversibly base shifted to 243 nm; IR (Nujol) 3100–3500, 1710, 1272, 1255, 1203, 1083, 1045, 1005, 995 cm^{-1}; $[\alpha]_D$ = +576.1° (*c* 0.49 g/100 mL, DMSO); ^{13}C NMR (MeOH-d_4), δ 203.5 (s), 203.1 (s), 164.5 (d), 163.1 (d), 139.8 (s), 139.0 (s), 134.3 (d), 134.1 (d), 133.8 (d), 132.8 (d), 126.5 (d), 126.1 (d), 119.8 (t), 119.6 (t), 100.7 (d), 98.6 (d), 92.9 (s), 89.3 (s), 63.9 (t, 2C), 52.5 (d), 52.4 (d); ^1H NMR (MeOH-d_4) δ 7.62 (d, 5.5, 1 H), 7.55 (d, 5.5, 1 H), 6.90 (ddd, 17.0, 10.8, 9.8, 2 H), 6.28 (br d, 10.8 2 H), 6.21 (d, 5.5, 1H), 6.12 (d, 5.5, 1 H), 5.73 (s, 1 H), 5.51 (br s, 1 H), 5.35 (d, 17.0, 2 H), 5.28 (d, 9.8, 2 H), 3.81–3.62 (m, 6 H).

(8) Spectral data for **3**: HREIMS obsd 210.0893, calcd for $C_{11}H_{14}O_4$ 210.0888; UV (MeOH) λ_{max} 231 nm (ϵ 16000); $[\alpha]_D$ −25.3° (*c* 0.08 g/100 mL, MeOH); IR ($CHCl_3$) 3600–3000, 1704 cm^{-1}; ^1H NMR (MeOH-d_4) δ 3.59 (d, 10.5, 1 H), 3.69 (d, 10.5, 1 H), 3.88 (s, 1 H), 3.96 (d, 12.6, 1 H), 4.24 (d, 12.6, 1 H), 5.21 (d, 10.6, 1 H), 5.31 (d, 16.5, 1 H), 6.25 (d, 6, 1 H), 6.38 (d, 11.2, 1 H), 6.65 (ddd, 10.6, 11.2, 16.5, 1 H), 7.51 (d, 6, 1 H); ^{13}C NMR (MeOH-d_4) δ 53.0 (d), 65.3 (t), 66.6 (t), 82.2 (s), 119.8 (t), 133.5 (d), 133.7 (d), 135.0 (d), 136.1 (s), 166.4 (d), 210.0 (s).

(9) Spectral data for **4**: HREIMS *m/z* obsd 210.090, calcd for $C_{11}H_{14}O_4$, 210.0888; UV (MeOH) 231 nm (ϵ 20000); $[\alpha]_D$ −12.6° (*c* 0.15 g/100 mL, MeOH); IR ($CHCl_3$) 3600–3200, 1708 cm^{-1}; ^1H NMR (MeOH-d_4) δ 7.58 (d, 6, 1 H), 6.41 (m, 10, 11, 16.4, 1 H), 6.26 (d, 11, 1 H), 6.15 (d, 6, 1 H), 5.27 (d, 16.4, 1 H), 5.16 (d, 10, 1 H), 4.20 (d, 13.8, 1 H), 4.05 (d, 13.8, 1 H), 3.31 (s, overlapped signals, 3 H); ^{13}C NMR (MeOH-d_4) δ 208.6, 165.7, 136.7, 134.5, 134.3, 132.6, 119.5, 83.7, 65.8, 65.3, 58.7.

X-ray Absorption Study of Octafluorodirhenate(III): EXAFS Structures and Resonance Raman Spectroscopy of Octahalodirhenates

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The structure, bonding, spectroscopy, and photophysics of transition-metal complexes containing quadruple metal–metal bonds are subjects of intense and general interest.[1,2] For both historic and fundamental reasons, the octahalodirhenate(III) ions have become the paradigms of this field.[1] Extensive spectroscopic and photophysical studies exist for the entire $Re_2X_8^{2-}$ series (X = F, Cl, Br, and I).[1-11] However, while excellent structural data

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exist for X = Cl and Br,[3,4] the structures of $Re_2F_8^{2-}$ and $Re_2I_8^{2-}$ have not been determined. These structures are essential for complete understanding of the bonding and the physical and chemical behavior in these systems. Toward this end, we report structural features of $Re_2F_8^{2-}$ determined by extended X-ray absorption fine structure (EXAFS) spectroscopy. We also report X-ray absorption near-edge spectra (XANES); resonance Raman (RR) spectra have been determined previously by others[5,7,11] and subsequently by us.[6] We find that in $Re_2F_8^{2-}$ the Re–Re distance is 2.20 Å and the Re–F distance is 1.95 Å. Both of these distances are unexpected considering the corresponding stretching frequencies in the RR spectra.[5,7]

The tetra-*n*-butylammonium salts of $Re_2F_8^{2-}$ and $Re_2Cl_8^{2-}$ were synthesized by published procedures[7,8] and recrystallized from methylene chloride/hexane and methanol/6 M aqueous HCl, respectively. The electronic,[5,7,9] IR,[5,10] and resonance Raman[5,7,11] spectra of both salts were in excellent agreement with literature data. Resonance Raman spectra were obtained by using instrumentation and procedures described elsewhere.[12] Samples for X-ray absorption spectroscopy (XAS) were prepared as naphthalene discs with a Re concentration giving an absorption difference of approximately 1 over the Re L_3 edge. Sample temperature was 80–90 K. The principal inflection point over the edge of $Re_2Cl_8^{2-}$ was defined as 10 534 eV. Fourier filtering was performed over the region 3–17 Å^{-1} by using square windows. Fits of the filtered data were performed over the region 4–16 Å^{-1} by using the theoretical parameters of Teo and Lee.[13] The distances, scale factors, σ's (rms distance deviations), and ΔE_0's for both the Re and Cl shells were allowed to float for the fit of the EXAFS of $Re_2Cl_8^{2-}$. A similar fit was performed for $Re_2F_8^{2-}$ as well as one in which the scale factor, σ, and ΔE_0 were held fixed at the values obtained from the fit of $Re_2Cl_8^{2-}$. The distances obtained from the two approaches agreed within 0.01 Å.

Figure 1 shows the Re L_3 XANES spectra of $Re_2F_8^{2-}$ and $Re_2Cl_8^{2-}$ together with moduli of the Fourier transforms of the EXAFS and the fit for the fluoride. The EXAFS data are quite satisfactorily fit by a fluoride shell at 1.95 Å and a rhenium shell at 2.20 Å from each Re. The EXAFS data on $Re_2Cl_8^{2-}$ (not shown) yield a Re–Re distance of 2.22 Å and a Re–Cl distance of 2.36 Å, compared to the crystallographic distances of 2.222 (2) Å and 2.32 (1) Å (3). The error in the Re–X distance in $Re_2Cl_8^{2-}$ determined by EXAFS is unusually large because, due to fortuitous conditions of phase shift and distance, the Fourier transformed peaks corresponding to the Re–Re and Re–Cl distances are almost superimposed in position. It is clear from Figure 1 that the contributions of the F and Re shells are well resolved so that the error in the bonded Re–F distance should be within the expected ±0.02 Å. The experimental Re–F distance is ca. 0.1 Å shorter than predicted from the other Re–X distances and the covalent radii of the halides, suggesting significant metal–halide π interaction in the fluoride complex. In neither $Re_2F_8^{2-}$ nor $Re_2Cl_8^{2-}$ were the nonbonded Re–X distances observed in the EXAFS, despite the atomic proximity, the large number of atoms, and the absence of static disorder for these shells. The failure to observe these distances is unfortunate because it precludes determination of the Re–Re–X angle. The absence of a significant contribution to the EXAFS from these shells implies that the motions of these atoms are uncorrelated with those of their nonbonded neighbors, leading to large anharmonic Debye–Waller factors in the nonbonded coordinates even at 77 K.

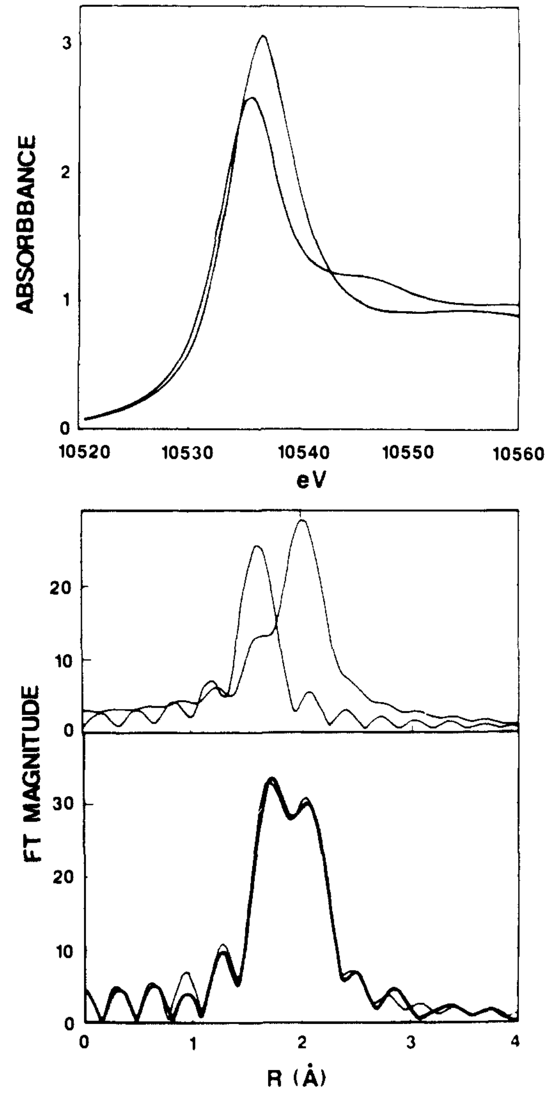

Figure 1. Re L_3 XANES spectra of $Re_2F_8^{2-}$ and $Re_2Cl_8^{2-}$ (top; the more intense XANES spectrum is that of $Re_2F_8^{2-}$) and moduli of the Fourier transforms of the $Re_2F_8^{2-}$ EXAFS (bottom). The upper half of the bottom panel shows the theoretical contributions of the Re and F shells separately. The lower half shows the modulus of the Fourier transform of the experimental EXAFS (dark line) and the theoretical fit (light line).

The Re L_3 XANES spectra exhibit an intense white line which is due to the lowest energy parity allowed electronic transition from the Re 2p core orbital. In these complexes the terminal orbital of this transition is the actual molecular LUMO, namely the δ^* orbital. The white line in the $Re_2F_8^{2-}$ XANES is considerably more intense than that of $Re_2Cl_8^{2-}$. This is a predictable effect of the identity of the halide upon the transition dipole of the (Re 2p) $\rightarrow$ δ^* transition, namely that the fluoride ion is more electronegative, closer, and a better π bonder than chloride, resulting in greater polarity of the δ^{*1} excited electronic configuration of the fluoride complex.

Comparison of the structural and vibrational results on the $Re_2X_8^{2-}$ series is informative. One of us[14,15] has recently devised empirical relationships between force constants and bond distances based on modern structural and vibrational data. These new relationships differ significantly from earlier correlations such as Badger's rule[16,17] and are applicable to all bonding situations except

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Table I. Structural and Vibrational Parameters of Octahalodirhenate(III) Ions

complex	bond dist, Å	stretching freq,[d] cm^{-1}	emprcl force const,[e] mdyne/Å	diatomic force const,[f] mdyne/Å
$Re_2F_8^{2-}$ (M-M)	2.20[a]	318	4.56	5.55
$Re_2F_8^{2-}$ (M-X)	1.95[a]	623	3.68	4.35
$Re_2Cl_8^{2-}$ (M-M)	2.22[b]	274	4.32	4.12
$Re_2Cl_8^{2-}$ (M-X)	2.32[b]	361	2.95	2.73
$Re_2Br_8^{2-}$ (M-M)	2.23[c]	276	4.19	4.18
$Re_2Br_8^{2-}$ (M-X)	2.47[c]	211	1.93	2.10

[a] Present work. [b] Reference 3. [c] Reference 4. [d] Frequencies and assignments from ref 5. [e] Calculated from the following equations and appropriate interpolations:[14,15] first row (Li-Ne), $D = 1.04 + 0.607 \exp(-F/9.28)$; second row (Na-Ar), $D = 1.80 + 0.732 \exp(-F/2.66)$; third row (K-Kr), $D = 1.81 + 1.22 \exp(-F/2.37)$; fifth row (Cs-Rn), $D = 2.01 + 1.31 \exp(-F/2.36)$; Re-F, $D = 1.53 + 0.907 \exp(-F/4.778)$; Re-Cl, $D = 1.90 + 0.948 \exp(-F/3.60)$. ($D$ = bond distance, Å; F = force constant, mdyne/Å). [f] Calculated from the following equation (ν in cm^{-1}, μ in atomic mass units): $F = \nu^2\mu(5.9 \times 10^{-7})$, where $\mu = 93.1$ for the Re-Re stretch and μ = (halide mass) for the Re-X stretch.

van der Waals. From these relationships it is possible to estimate the Re-Re and Re-X force constants from the EXAFS or crystallographic bond distances. It is also possible to calculate these force constants from the symmetric Re-Re and Re-X stretching frequencies in the RR spectra. To the extent that these stretching vibrations are unmixed with one another and with the remaining symmetric coordinate of $Re_2X_8^{2-}$ (the Re-Re-X angle bend), it is appropriate to calculate the force constants from the stretching frequencies by using the diatomic approximation. Indeed, the precision of the empirical correlations, 0.1-0.5 mdyne/Å,[14,15] is such that gross disagreement between the empirical and diatomic force constants can be taken as evidence that the frequencies used to calculate the latter actually represent mixed modes or as evidence of incorrect assignments.

Table I summarizes the bond distance data, the assigned vibrational frequencies, and the empirical and diatomic force constants of the $Re_2X_8^{2-}$ series (X = F, Cl, Br). The RR data are from solid-state and solution studies by earlier workers[5,7,11] confirmed by results from our laboratories.[6] The RR assignments are from the earlier studies.[5,7] The empirical and diatomic force constants correspond well for the chloride and bromide complexes, supporting the previous assignments and suggesting relatively little mixing of internal coordinates in these systems. In the fluoride complex, however, the agreement between the empirical and diatomic force constants is poor for both the Re-Re stretch and the Re-F stretch. The strong enhancement in $\delta\delta^*$ resonance and the overtone progressions of the 318-cm^{-1} vibration of $Re_2F_8^{2-}$ [5] leave no doubt that the assignment of this peak as primarily the Re-Re stretching mode is correct. Accordingly, the poor agreement between the diatomic and empirical force constants is probably due to mixing of the Re-Re coordinate with the Re-Re-F deformation which should appear near 200 cm^{-1} in the fluoride and could thereby be responsible for an apparently high Re-Re frequency.

The assignment of the Re-F stretching mode is more difficult to establish. The earlier assignment[5,7] of the Re-F stretch is to the weak peak at 623 cm^{-1}; however, other weak features may be equally valid candidates. A specific possibility is the peak at 502 cm^{-1} which was previously assigned as a combination. Its frequency is 3 cm^{-1} too high to be the harmonic frequency of the assigned combination (318 + 181 cm^{-1}), while all of the other combination frequencies are (as expected) lower than the harmonic sums. The frequency calculated for the Re-F stretch based upon the empirically estimated force constant of the Re-F bond (Table I) is 572 cm^{-1}, almost equidistant from 623 cm^{-1} and 502 cm^{-1}, and therefore the empirical rules are not very informative as to this assignment. It is clear, however, that coordinate mixing is a factor in this motion as well as in the Re-Re stretch. It is reasonable to suggest that the 181-cm^{-1} peak represents the Re-Re-F deformation. Quantitative formal vibrational analysis of these systems as well as analysis of their RR intensities and concomitant vibrational dynamics is required to resolve these questions and is proceeding in these laboratories.

Acknowledgment. This work was performed at Los Alamos National Laboratory and Stanford Synchrotron Radiation Laboratory under the auspices of the U.S. Department of Energy and at The University of Texas at Austin under NSF Grant CHE84-03836 (W.H.W.). We thank Professor R. A. Scott for the XFPAK data analysis software and Professor F. Albert Cotton for helpful discussions.

Registry No. $Re_2F_8^{2-}$, 72931-84-1; $Re_2Cl_8^{2-}$, 19584-24-8.

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Organic Reactions in Liquid Crystalline Solvents. 6. Regiochemical Control of Bimolecular Chemical Reactivity in Smectic and Cholesteric Liquid Crystals

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There has been considerable recent interest in the potential ability of liquid crystalline solvents to affect bimolecular chemical reactivity as a result of controlling the orientation of reactants or exerting special effects on transition-state dynamics.[2-6] The studies that have been carried out, along with various others directed toward probing the effects of these media on unimolecular solute reactivity and conformational mobility,[7-12] have led to the general view that the molecular ordering present in nematic and cholesteric liquid crystals is not sufficiently rigid to alter the reactivity of dissolved solutes significantly; most "successful" studies have employed smectic phases, which are considerably more rigidly ordered than simple nematics or cholesterics.[13] We now

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