trans-cyclooctene.[19b] However, the presence of two mutually reinforcing chiral ring elements in betweenanenes might conceivably cause enhanced molecular rotations relative to simple *trans*-cycloalkenes. It was therefore of interest to prepare a sample of optically pure [10.10]betweenanene (**10**).[5]

Hydroboration–oxidation of triene (+)-**4c** afforded the diol (+)-**5** ($[\alpha]^{29}_{D}$ +30.3° (*c* 3.00, $CHCl_3$)), which was oxidized to the dialdehyde (+)-**6** ($[\alpha]^{28}_{D}$ +77.1° (*c* 2.62, $CHCl_3$)) in 82% yield with pyridinium chlorochromate.[20] Cyclization with activated titanium by McMurry's method[5,21] gave diene **9**, a 4:1 mixture of trans and cis isomers according to GLC and NMR analysis. Hydrogenation afforded (+)-(*R*)-[10.10]betweenanene (**10**) ($[\alpha]^{29}_{D}$ +46.9° (*c* 1.16, $CHCl_3$), mp 85–88 °C).

The absolute configuration of (+)-**10** follows from the known enantioselectivity of the Sharpless epoxidation and from the CD curves of both **10** and its monocyclic precursor (+)-**4c**. Both showed negative Cotton effects in agreement with the assigned (*R*) configuration.[22] The optical purity of these samples is estimated to be greater than 90% on the basis of the ^{13}C NMR analysis of diol (−)-**8**.

Thus, [10.10]betweenanene (**10**) possesses a molecular rotation ($[\phi]$ = 140°) comparable with simple 1,2-disubstituted *trans*-cycloalkenes.[19] Evidently, the two chiral ring elements are not optically reinforcing at the sodium D line.[23] It seems likely that smaller ring betweenanenes could show enhanced rotations as a consequence of ring strain analogous to *trans*-cyclooctene. We hope to resolve this point in due course.

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Supplementary Material Available: Listing of spectral and physical data for **1**, (±)-**2a**, (±)-**2b**, (±)-**2c**, (+)-**2c**, (*R*)-**3c**, (+)-**4b**, (+)-**4c**, (+)-**5**, (+)-**6**, (±)-**8**, (−)-**8**, (*R*)-**9**, and (+)-**10** (4 pages). Ordering information is given on any current masthead page.

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Ruthenium and Osmium Thiolate Compounds

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Although the chemistry of iron–thiolate[1-3] and iron–sulfide–thiolate[4] compounds is extensive, the analogous chemistry of ruthenium and osmium complexes has not been established.[5]

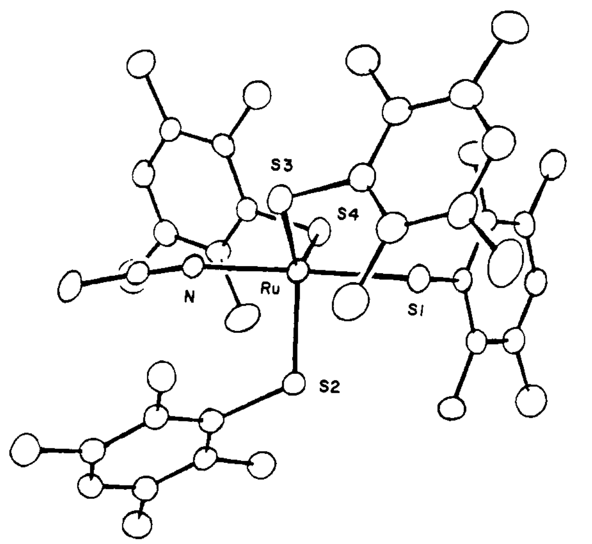

Figure 1. Structure of $Ru(SC_{10}H_{13})_4(CH_3CN)$; selected bond lengths (Å): Ru–S1, 2.383 (1); Ru–S2, 2.196 (2); Ru–S3, 2.219(2); Ru–S4, 2.212 (2); Ru–N 2.096 (5).

Herein we report the synthesis, structure, and properties of the first polythiolate complexes of ruthenium and osmium.

The reaction of $[RuCl_4(CH_3CN)_2](Et_4N)$[12] or $OsCl_3$ with 4 equiv of the lithium salt of 2,3,5,6-tetramethylbenzenethiolate[13] and a 0.5 equiv of 2,3,5,6-tetramethylphenyl disulfide[14] in refluxing methanol–acetonitrile (2:1) solutions for 6 h under nitrogen produces upon cooling 80–95% isolated yields of $Ru(SC_{10}H_{13})_4(CH_3CN)$ (**1**) or $Os(SC_{10}H_{13})_4(CH_3CN)$ (**2**), respectively. Methylene chloride solutions of **1** are red-orange [λ_{max} (ϵ_M) 281 nm (17000), 306 (sh) (13600), 377 (32500)]; solutions of **2** are yellow-green [λ 260 nm (sh) (18300), 334 (23500)].

An X-ray crystallographic study of $Ru(SC_{10}H_{13})_4(CH_3CN)$,[15] Figure 1, shows the five ligands to be coordinated to the ruthenium in a trigonal bipyramidal[16] arrangement with the acetonitrile

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(5) Molecular ruthenium and osmium compounds possessing predominately metal–sulfur interactions have been limited to complexes of the bidentate ligands SacSac,[6] 1,1-dithiolate,[7] and 1,2-dithiolene.[8] Complexes of the type $[Ru(NH_3)_5(L)]^{n+}$, where L is a range of sulfur donors including thiolate, have been well characterized.[9] Polymeric $Ru(SR)_2$ and $Ru(SR)_3$ have been mentioned.[10,11]
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(14) In the absence of the disulfide, $Ru(SC_{10}H_{13})_4(CH_3CN)$ is acquired in about 45% yield under the same conditions.
(15) $Ru(SC_{10}H_{13})_4(CH_3CN)$ crystallizes from ethanol in the monoclinic space group $P2_1/c$ with a = 18.706 (3) Å, b = 11.637 (2) Å, c = 19.223 (4) Å, β = 93.02 (1)°, V = 4179 (2) Å^3, Z = 4. Diffraction data were collected at room temperature on an Enraf-Nonius CAD4 automated diffractometer. The structure was solved by using normal Patterson and difference Fourier methods. The hydrogens whose positions were located or calculated were used in the structure factor calculations but were not refined. Final least-squares refinement gave R = 0.037 and R_w = 0.050 for 3751 reflections with $|F_o| > 3\sigma(|F_o|)$.

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occupying an axial position. The Ru–S_{ax} bond length of 2.383 (1) Å is substantially longer than the average of the Ru–S_{eq} bond length of 2.207 (10) Å, which is the situation predicted for this diamagnetic low-spin d^4 complex.[17] The Ru–N bond is 2.096 (5) Å in length. The unit cell parameters of $Os(SC_{10}H_{13})_4(CH_3CN)$[18] show it to be isomorphous and presumably isostructural with compound **1**. These compounds are the first examples of five-coordinate ruthenium and osmium complexes in the +4 oxidation state.[19]

In an effort to synthesize ruthenium and osmium compounds with still lower coordination numbers [e.g., $M(SR)_4$, M = Ru, Os], we carried out similar reactions using the more sterically hindered thiolate 2,4,6-triisopropylbenzenethiolate;[21] however, the compounds obtained were $Ru(SC_{15}H_{23})_4(CH_3CN)$ (**3**) and $Os(SC_{15}H_{23})_4(CH_3CN)$ (**4**). As determined by X-ray crystallographic techniques, the arrangement and conformation of the ligands in $Ru(SC_{15}H_{23})_4(CH_3CN)$[22,23] are very similar to those of **1**; the bond distances of the $[RuS_4N]$ core of **1** and **3** are alike, within experimental error.[23] No bonding interactions are apparent between the hydrogens on the orthosubstituents of the ligands and the ruthenium atom. The ruthenium and osmium derivatives of the 2,4,6-triisopropylbenzenethiolate ligands (**3** and **4**) are isomorphous.[24]

In spite of the high oxidation state of the metal and reducing capacity of the thiolate ligands, all four compounds (**1–4**) are thermally and air stable in solution and in the solid state. Other evidence that supports the ability of these thiolate ligands[25] to stabilize high oxidation states of ruthenium and osmium complexes comes from electrochemical measurements. Each of these compounds is the central member of the electron-tranfer series represented by eq 1. The differences between the corresponding

$$[M(SR)_4(L)]^+ \rightleftharpoons [M(SR)_4(L)] \rightleftharpoons [M(SR)_4(L)]^- \quad (1)$$

redox couples[26] of the ruthenium and osmium complexes are small (0.1–0.2 V); a similar situation has been observed for other ruthenium and osmium compounds with sulfur donor ligands.[27]

The new metal–thiolate compounds described in this communication should be good reagents for the syntheses of ruthenium- and osmium–sulfur cluster compounds. Work is continuing.

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Registry No. 1, 85479-95-4; **2**, 85479-96-5; **3**, 85506-85-0; **4**, 85479-97-6; $[RuCl_4(CH_3CN)_2](Et_4N)$, 74077-58-0; 2,3,5,6-tetramethylphenyl disulfide, 63157-79-9; 2,4,6-triisopropylphenyl disulfide, 20875-34-7.

Supplementary Material Available: Table of fractional atomic coordinates and thermal parameters and an ORTEP of $Ru(SC_{15}H_{23})_4(CH_3CN)$ (6 pages). Ordering information is given on any current masthead page.

(16) The bond angles (deg) that define the geometry of the $[RuS_4N]$ core are S1–Ru–N = 178.3 (1), S1–Ru–S2 = 86.36 (6), S1–Ru–S3 = 92.98 (6), S1–Ru–S4 = 89.37 (6), S2–Ru–S3 = 115.89 (7), S3–Ru–S4 = 122.55 (7), S2–Ru–S4 = 121.54 (7).

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(18) Unit cell parameters for $Os(SC_{10}H_{13})_4(CH_3CN)$ are as follows: monoclinic space group $P2_1/c$ with a = 18.687 (8) Å, b = 11.647 (6) Å, c = 19.225 (5) Å, β = 92.86 (3)°, V = 4179 (3) Å^3, Z = 4.

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(22) $Ru(SC_{15}H_{23})_4(CH_3CN)$ crystallizes from ethanol in the monoclinic space group $P2_1/n$ with a = 13.844 (3) Å, b = 21.583 (4) Å, c = 22.043 (3) Å, β = 93.90 (2)°, V = 6571 (5) Å^3, Z = 4. Final least-squares refinement gave R = 0.047 and R_w = 0.071 for 5760 reflections with $|F_o| > 3\,\sigma(|F_o|)$.

(23) Bond lengths (Å) and bond angles (deg) of the $[RuS_4N]$ core are Ru–S1 = 2.372 (1), Ru–S2 = 2.207 (1), Ru–S3 = 2.210 (1), Ru–S4 = 2.210 (1), Ru–N = 2.108 (4), S1–Ru–N = 178.1 (1), S1–Ru–S2 = 87.32 (5), S1–Ru–S3 = 93.88 (5), S1–Ru–S4 = 86.96 (4), S2–Ru–S3 = 114.23 (5), S3–Ru–S4 = 121.48 (5), S2–Ru–S4 = 124.25 (5).

(24) Unit cell parameters for $Os(SC_{15}H_{23})_4(CH_3CN)$: monoclinic space group $P2_1/n$ with a = 13.865 (3) Å, b = 21.614 (6) Å, c = 22.034 (6) Å, β = 93.97 (1)°, V = 6587 (5) Å^3, Z = 4.

(25) One of these ligands has been used to prepare a stable iron(III) tetrathiolate complex, $[Fe(SC_{10}H_{13})_4](Et_4N)$.[3]

(26) Polarographic data for the ruthenium and osmium thiolate compounds, $[M(SR)_4(L)]^z$, were obtained in DMF with 0.10 M $(Bu_4N)BF_4$ as the supporting electrolyte and the SCE as the reference electrode. The half-wave potential and slope (in parentheses and as determined by the plot of E vs. log $[(i_d - i)/i]$) for the z = +1/0 and z = 0/–1 couples, respectively, are as follows: +0.68 (57 mV) and –0.85 V (60 mV) for $Ru(SC_{10}H_{13})_4(CH_3CN)$; +0.69 (66 mV) and –0.89 V (61 mV) for $Ru(SC_{15}C_{23})_4(CH_3CN)$; +0.78 (75 mV) and –1.09 V (61 mV) for $Os(SC_{10}H_{13})_4(CH_3CN)$; +0.75 (62 mV) and –1.09 V (60 mV) for $Os(SC_{15}H_{23})_4(CH_3CN)$.

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Detection of Hydrogen Bonding in Peptides by the $^{13}C\{^1H\}$ Nuclear Overhauser Effect

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It is well-known that various conformations of peptides and proteins such as α-helix, β-turn, and β-pleated sheets are stabilized by intra- and/or intermolecular hydrogen bonds formed between peptide NH and C=O groups. Several nuclear magnetic resonance (NMR) methods[1] have been employed extensively to characterize such interactions. However, the previous methods, in additon to possibly introducing perturbations into the molecular system,[2] cannot be used to identify a unique hydrogen-bonded pair, i.e., N-H···O=C, simultaneously. Here we present an independent NMR technique that, without disturbing the molecular system, can detect such a hydrogen bonded pair.

The present NMR method is demonstrated on the well-defined model system of valinomycin. It is a cyclic dodecadepsipeptide with a tetramer sequence of L·Val-D·Hyiv-D·Val-L·Lac repeated three times. Various solution conformational models of this molecule in its uncomplexed form have been described.[3,4] The most dominant conformation in nonpolar solvents contains two intramolecular hydrogen bonds, one between the D·Val NH and the L·Lac C=O group and the other between the L·Val NH and the D·Hyiv C=O group, giving a total of six such hydrogen bonds, making the molecule appear like a bracelet.[4] The hydrogen bonding scheme is depicted in Scheme I.

It can be seen from the scheme that each peptide C=O carbon is ^2J coupled to the NH proton of the adjacent amino acid residue (indicated by the broken arrows). In two recent reports[5,6] we made use of this coupling in assigning the ^{13}C and ^1H NMR spectra

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