to effects of hydrogen-bond donation to the amide carbonyl,[38-41] since the tertiary amides of actinomycin D also undergo such a shift.[39] In alumichrome, shifting the solvent from DMSO (an excellent acceptor but not a donor) to trifluoroethanol (an excellent donor) causes a downfield shift of the ^{15}N resonances of four amides whose N–H's are solvent protected but whose carbonyls are exposed, while a single amide whose amide proton is external but whose carbonyl is buried undergoes an upfield shift.[40] Thus, in the current case, where the amide hydrogen bond donor of the tuck-in species sees a decrease in acceptor strength as the acceptor is changed from DMSO (in $(CN)_2Cbi$) to benzimidazole N3[43] (in $(CN)_2Cbl$), and there is presumably no donation to its carbonyl oxygen in either state, an upfield shift of its ^{15}N resonance would be expected. Indeed, application of the Taft linear solvation energy relationship to the solvent effect on the ^{15}N resonance of formamide[47] predicts an upfield shift of ca. 2 ppm on transfer from DMSO to pyridine. However, this calculation ignores the influence of the magnetic anisotropy of the nitrogen heterocycle, which would be expected to deshield the ^{15}N resonance of the hydrogen-bond donor in the tuck-in species due to its edgewise approach.

Hydrogen bonding effects on amide proton chemical shifts are similarly complicated.[45-47] It is now known that formation of intramolecular hydrogen bonds in peptide amides can cause an upfield or downfield shift of the amide proton resonance (relative to the solvated species in water) depending on the H···O internuclear distance.[47] However, application of the Taft linear solvation energy relationship[20] to the amide ^1H chemical shifts of *N*-methylacetamide in 10 solvents[48] predicts a small (0.05–0.2 ppm) upfield shift of the amide proton upon transfer from DMSO to pyridine. Again, however, this treatment ignores the effect of the magnetic anisotropy of the benzimidazole moiety, which would surely deshield the amide proton significantly. The significant decrease in the amide proton chemical shift thermal gradient of the upfield protons of the e amide and the acetamide resonating near 111 ppm upon formation of the tuck-in species is consistent with the formation of an intramolecular hydrogen bond in DMSO solution to either of these amides.[45,49]

The observations summarized in Table II and discussed above are consistent with the possibility that either the e amide or the acetamide whose nitrogen resonates near 111 ppm is the donor in the tuck-in species,[50] while the other amide is involved in a hydrogen-bonded interaction with the f amide in either $(CN)_2Cbl$ or $(CN)_2Cbi$. Alternatively, the chemical shift changes at the f amide could be due entirely to conformational effects upon removal of the nucleotide. In this case, either the e amide or the acetamide whose ^{15}N resonance is near 111 ppm is the hydrogen-bond donor and the chemical shift effects at the other amide are due to its proximity to the benzimidazole in the tuck-in species. The ^{15}N chemical shifts of $(CN)_2Cbl\text{-e-}COO^-$ suggests the former interpretation, since hydrolysis of the e amide appears to cause a loss of the interactions causing the nitrogen chemical shift effects at both the f amide and the acetamide resonating near 111 ppm. This suggests that the e amide is the donor in the tuck-in species and that a hydrogen-bonded interaction between the f amide (as acceptor) and the acetamide resonating near 111 ppm (presumably the g acetamide) in $(CN)_2Cbi$ is prevented from forming in the tuck-in species of $(CN)_2Cbl$. However, since the proton resonances in $(CN)_2Cbl\text{-e-}COO^-$ do not confirm this interpretation, caution must be exercised in drawing any conclusions. Attempts to resolve these issues by a complete ^{13}C, ^1H, and ^{15}N assignment of $(CN)_2Cbl$ are currently in progress.

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(43) While nitrogen heterocycles are better bases than DMSO (pK_a ~ 0[40]), they are weaker hydrogen bond acceptors (e.g. $\beta = 0.76$ for DMSO but 0.64 for pyridine[20]).

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(50) Inspection of models shows that hydrogen-bond formation from benzimidazole N3 to any of the three acetamides is feasible without development of significant strain in the nucleotide loop.

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First Examples of Six-Coordinate Homoleptic Complexes with Monodentate Arenethiolate Ligands. Synthesis and Structural Characterization of $[Ph_4P]_2[Nb(SPh)_6]$, $Na(THF)_3Nb(SPh\text{-}pMe)_6$, $[(15\text{-crown-5})Na][Ta(SPh)_6]$, and $Nb_2(\mu_2\text{-}SPh)_4(SPh)_2Cl_2(C_2H_5CN)_2$

Recent synthetic and crystallographic studies of early-transition-metal complexes with aliphatic or aromatic thiolate ligands indicate that the chemistry of these M/S compounds (M = Zr,[1] Nb,[2] Ta[2a,3]) may be as extensive as that of the Mo/S and W/S systems. Coordination of aliphatic thiolate ligands to early-transition-metal ions often is followed by C–S bond cleavage that generates the S^{2-} ligand.[2b-d] The latter is incorporated in monomeric or oligomeric complexes in either terminal or bridging coordination modes. The C–S bond cleavage appears to be a heterolytic intramolecular process, facilitated by β-proton elimination.[4] Not unexpectedly, this reaction does not readily occur with benzenethiolate ligands although an example of C–S bond cleavage of benzenethiolate is known.[2c] Among the known thiolate complexes of "mixed"-ligand complexes that contain thiolate ligands, and S^2-ligands generated by C–S bond cleavage reactions,

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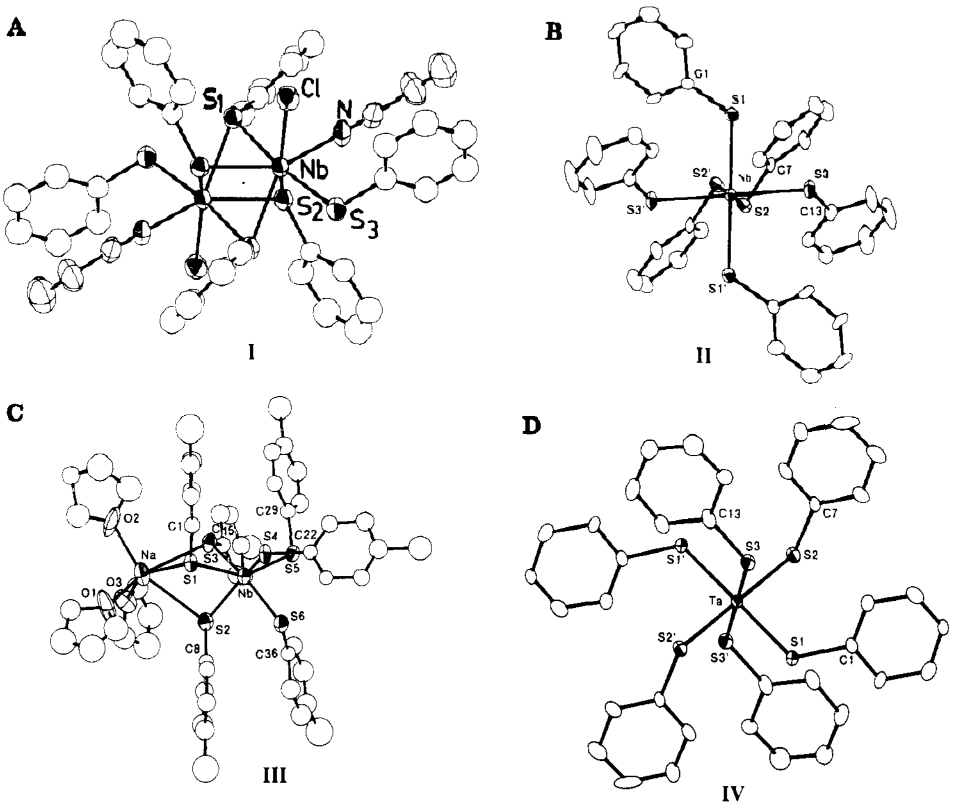

Figure 1. Structures and labeling of $Nb_2(\mu_2\text{-}SPh)_4(SPh)_2Cl_2(C_2H_5CN)_2$ (I), $[Nb(SPh)_6]^{2-}$ (II), $Na(THF)_3Nb(SPh\text{-}pMe)_6$ (III), and one of the independent anions, $[Ta(SPh)_6]^-$, in IV. Thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces.

are included $[M(\text{norbornane-}exo\text{-2,3-dithiolate})_3]^-$,[2a] $[M(\text{ethylene-1,2-dithiolate})_3]^{-}$[2b] (M = Nb, Ta), $[Nb(S)(SPh)_4]^-$,[2d] and $Li_4Nb_4S_2(SPh)_{12}$.[2c] The reductive cleavage of C–S bonds in the industrially important hydrodesulfurization reaction is catalyzed by various metal sulfides.[5] As a result, an understanding of the factors that influence the activation of C–S bonds in coordinated thiolate ligands remains an important goal of our studies in M–S coordination chemistry.

Mononuclear, homoleptic, six-coordinate complexes of early-transition-metal ions with monodentate, arenethiolate ligands have not been reported todate. Such complexes are expected to be appropriate for (a) studies of the conditions that lead to C–S bond cleavage and (b) the synthesis of soluble sulfido and polysulfido complexes of Nb and Ta using reactions that already have been proven successful in the synthesis of various other $M(S_x)_n]^{n-}$ complexes[6] (M = Ni, $x = 4$, $n = 2$; M = Zn, $x = 4$, $n = 2$; M = Zn, $x = 5$, $n = 2$; M = Cd, $x = 5$, $n = 2$; M = Mn, $x = 5, 6$, $n = 2$).

In this communication we report on the synthesis and structural characterization of the dimeric, diamagnetic $Nb^{IV}{}_2(\mu_2\text{-}SPh)_4(SPh)_2Cl_2(C_2H_5CN)_2$ (I), the paramagnetic ($S = {}^1/_2$) $(Ph_4P)_2Nb^{IV}(SPh)_6$ (II), the diamagnetic $Na(THF)_3Nb^V(SPh\text{-}pMe)_6$ (III), and $[(15\text{-crown-5})Na][Ta^V(SPh)_6]$ (IV), complexes that contain the monomeric, six-coordinate $M(SAr)_6{}^{n-}$ anions. The reaction of $NbCl_5$ with NaSPh in C_2H_5CN at 90 °C, in a 1:4 molar ratio, affords a deep red solution that upon cooling deposits red crystals of I[7] in 10% yield. A similar reaction, with the reagents in a 1:6 molar ratio and in the presence of 1 equiv of Ph_4PBr, in boiling CH_3CN solution, results in the formation of II[8] that can be isolated from solution in crystalline form in 10% yield by cooling to –20 °C. If Et_4NBr is used in place of Ph_4PBr, a different complex is obtained in modest yield with a ^1H NMR spectrum indicative of the $(Et_4N)_2Nb^{IV}{}_2(SPh)_{10}$ stoichiometry but not fully characterized as yet. The same compound is obtained upon addition of 4 equiv of NaSPh to I. The reaction of $NbCl_5$ with NaSPh-pMe in THF solution, at ambient temperature, proceeds with formation of the $[Nb^V(SPh\text{-}pMe)_6]^-$ anion that can be isolated in crystalline form in 23% yield as the $Na(THF)_3{}^+$ salt, III.[9] At this stage we can only surmise that the $Nb(SR)_6{}^-$ anion is stabilized by coordination to the $Na(THF)_3{}^+$ cation (vida infra) and is not reduced by RS^- to the $Nb^{IV}(SR)_6{}^{2-}$ anion. Such a reduction apparently takes place in the synthesis of II from $NbCl_5$. The reaction of NaSPh with $TaCl_5$ in Et_2O solution, in a 6:1 molar ratio, results in the formation of red solution of the $Na(Et_2O)_3[Ta^V(SPh)_6]$ complex[10] in 70% yield. Addition of 1 equiv of 15-crown-5 ether to this solution affords a red solid. Recrystallization of this material from a CH_3CN/Et_2O mixture gives red crystals of IV[11] in 60% yield. The structures of I–IV have been determined,[12] and selected structural parameters are

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[7] Due to its extreme sensitivity, I did not give entirely satisfactory analysis. Anal. Calcd for $Nb_2Cl_2S_6N_2C_{42}H_{40}$: Nb, 18.22. Found: Nb, 19.11. The observed X-ray powder pattern of the bulk of this compound however was found identical with that calculated on the basis of the single-crystal data. Better analysis could be obtained for the microcrystalline pMe–Ph–S⁻ analogue of I. Anal. Calcd for $Nb_2Cl_2S_6N_2C_{48}H_{52}$: C, 52.13; H, 4.71; S, 17.38. Found: C, 51.85; H, 4.91; S, 17.84.

[8] For reasons discussed previously[7] satisfactory elemental analysis could not be obtained for II. However, the X-ray powder pattern of the bulk of this compound was found identical with that calculated from single-crystal data.

[9] Anal. Calcd for $NbNaS_6O_3C_{54}H_{66}$ (III): Nb, 8.67; Na, 2.15. Found: Nb, 8.65; Na, 2.52. The X-ray powder pattern of the bulk of this compound was found identical with that calculated from single-crystal data.

[10] An incomplete crystal structure determination of this complex verifies the stoichiometry. This structural determination was terminated prior to completion due to extreme disorder problems associated with the ether ligands on the Na^+ ion.

[11] Calcd for $TaNaS_6O_5C_{46}H_{50}$ (IV): Ta, 16.77; Na, 2.13. Found: Ta, 16.31; Na, 2.50. The X-ray powder pattern of the bulk of this compound was found identical with that calculated from single-crystal data.

Table I. Summary of Interatomic Distances (Å) and Angles (deg) in $Nb_2(\mu_2\text{-}SPh)_4(SPh)_2Cl_2(C_2H_5CN)_2$ (I), $(Ph_4P)_2Nb(SPh)_6$ (II), $Na(THF)_3Nb(SPh\text{-}pMe)_6$ (III), and $[(15\text{-crown-}5)Na][Ta(SPh)_6]$ (IV)

	I	II	III	IV
		Distances[a]		
$M–S_i$[b]	2.546 (4, 5)[b]	2.488 (3, 5)[c]	2.49 (3, 1),[c] 2.405 (3, 9)[d]	2.445 (6, 9)[e]
range	2.538 (3)–2.546 (2)	2.476 (3)–2.500 (3)	2.392 (7)–2.506 (7)	2.431 (5)–2.456 (6)
$C–S_i$	1.78 (1)	1.76 (3, 1)[c]	1.76 (6, 2)	1.77 (6, 2)
range	1.769 (10)–1.791 (10)	1.75 (1)–1.77 (1)	1.71 (2)–1.79 (2)	1.75 (2)–1.78 (2)
		Angles[a]		
$S_i–M–S_j$[b]	71.4	90 (3, 1.5)[c]	78 (3, 1),[f] 86 (3, 4)[g]	90 (6, 2)[e]
range	70.0 (1), 72.8 (1)	87.8 (1)–94.2 (1)	77.2 (2)–92.1 (2)	84.6 (2)–94.9 (2)
$M–S_i–C_{Ph}$[b]	118.1	119.2 (3, 7)[c]	115.3 (6, 9)	116.8 (6, 9)
range	117.7 (3), 118.6 (3)	118.8 (5)–119.9 (6)	114.2 (8)–116.3 (9)	114.1 (7)–119.8 (8)

[a] Mean values of crystallographically independent, chemically equivalent structural parameters. The first number in parentheses represents the number of chemically equivalent bond lengths or angles averaged out; the second number represents the larger of the individual standard deviations or the standard deviation from the mean, $\sigma = [\sum_i = 1^N(x_i - \bar{x})^2/N(N-1)]^{1/2}$. [b] Distances and cis angles involving the bridging S atoms; other structural parameters in the centrosymmetric anion in I include Nb–Nb = 2.890 (3) Å, Nb–S(3) = 2.423 (3) Å, Nb–N = 2.223 (10) Å, and Nb–Cl = 2.433 (3) Å. [c] *i* cycles through 1 and 3. [d] *i* cycles through 4 and 6. [e] Distances and angles cycle through 1 and 3 for each of the two crystallographically independent centrosymmetric anions in the unit cell. [f] *i* and *i* cycle through 1 and 3. [g] *i* and *i* cycle through 4 and 6.

shown in Table I. The coordination geometries around the metal ions are irregular seven-coordinate in I (Figure 1A), octahedral in II (Figure 1B), nearly trigonal prismatic in III (Figure 1C), and octahedral in IV (Figure 1D). Earlier studies of six-coordinate dithiolene complexes of Zr(IV), Nb(V), and Ta(V) have shown that the majority of these complexes prefer trigonal-prismatic coordination.[13] This preference was attributed to optimum overlap between ligand p orbitals and the metal vacant d orbitals.[13f,14] In contrast the MS_6 core geometry in the tris(alkanedithiolate) complexes of Nb(V) and Ta(V) with bidentate chelating ligands[2a,b] appears to vary and it has been suggested that the trigonal twist of the MS_6 polyhedron depends on small perturbations due to either crystal-packing forces or electronic factors.[2a] This conclusion finds some support in this work. The $Nb^{IV}–Nb^{IV}$ distance in I of 2.890 (3) Å is comparable to the Nb–Nb bond in $Nb_4(Se_2)SeBr_{10}(CH_3CN)_4]$[15] at 2.886 (1) Å and significantly longer than the $Nb^{III}–Nb^{III}$ bond in $[Nb_4S_2(SPh)_{12}]^{4-}$ at 2.83 (2) Å[2c] and the $Nb^{IV}–Nb^{IV}$ bonds in $Nb_2Cl_4(OMe)_4(MeOH)_2$[16] and $Nb_2S_3Br_4(THT)_4$[17] (THT = tetrahydrothiophene) at 2.781 (1) and 2.8371 (7) Å, respectively. The $Nb^{IV}–Nb^{IV}$ distance in I is shorter than that in the $Nb_2(\mu_2\text{-}Se_2)_2Cl_4(dms)_4$ complex[18] (dms = dimethyl sulfide) at 2.962 (3) Å. The latter contains eight-coordinate Nb^{IV} ions.

The $\overline{Nb^{IV}–S_b}$ bond in I at 2.541 (3) Å is longer than the $\overline{Nb^{IV}–S_t}$ bond in II of 2.488 (3) Å. The latter as expected is longer than the $\overline{Nb^{V}–S}$ bond in III (2.447 Å). The difference in the Nb–S bond lengths between I and II can be attributed the difference in coordination number of the Nb^{IV} ion in the two complexes (7 in I and 6 in II). The $Nb^V–S$ bonds in III are found in two groups, those weakened by the Na–S interactions ($\overline{Na–S}$ = 3.00 (12) Å) above one of the trigonal faces of the prism at 2.488 Å and those associated with the opposite face at 2.405 Å (Figure 1C). A $\overline{Ta–S}$ bond of 2.446 (6) Å is found in the two crystallographically independent, centrosymmetric Ta^VS_6 units in IV. The reactivity of these, exceedingly oxygen- and moisture-sensitive, complexes presently is under investigation.

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Supplementary Material Available: Text describing crystallographic procedures and Tables S1–S4, listing positional parameters, thermal parameters, and selected distances and angles of $Nb_2(\mu_2\text{-}SPh)_4(SPh)_2Cl_2(C_2H_5CN)_2$ (I), $(Ph_4P)_2Nb(SPh)_6$ (II), $Na(THF)_3Nb(SPh\text{-}pMe)_6$ (III), and $[(15\text{-crown-}5)Na][Ta(SPh)_6]$ (IV) (34 pages); Tables S5–S8, listing structure factors for I–IV (40 pages). Ordering information is given on any current masthead page.

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(12) Crystal and refinement data: Red crystals of $Nb_2(\mu_2\text{-}SPh)_4(SPh_2Cl_2\text{-}(C_2H_5CN)_2$ (I) are monoclinic, space group $P2_1/n$ with a = 10.335 (5) Å, b = 12.764 (7) Å, c = 17.021 (8) Å, β = 100.43 (4)°, and Z = 2. Brown crystals of $(Ph_4P)_2Nb(SPh)_6$ (II) are monoclinic, space group $P2_1/n$ with a = 12.811 (6) Å, b = 21.603 (8) Å, c = 13.284 (8) Å, β = 100.27 (4)°, and Z = 4. Purple crystals of $Na(THF)_3Nb(SPh\text{-}pMe)_6$ (III) are monoclinic, space group $C2/c$, with a = 29.024 (10) Å, b = 12.357 (6) Å, c = 32.250 (14) Å, β = 100.57 (3)°, and Z = 8. Red black crystals of $[(15\text{-crown-}5)Na][Ta(SPh)_6]$ (IV) are triclinic, space group $P\bar{1}$ with a = 14.271 (3) Å, b = 14.431 (4) Å, c = 16.730 (5) Å, α = 65.45 (2)°, β = 67.69 (2)°, γ = 60.35 (2)°, and Z = 2. Single-crystal X-ray diffraction data for all crystals were collected on a Nicolet R3m diffractometer using Mo Kα radiation. The solutions of all structures were carried out by a combination of heavy-atom Patterson techniques, direct methods, and Fourier techniques. The refinement of the structures by full-matrix least-squares methods was based on 1060 unique reflections ($2\theta_{max}$ = 35°, $I > 3\sigma(I)$) for I, on 1642 unique reflections ($2\theta_{max}$ = 40°, $I > 3\sigma(I)$) for II, on 1766 unique reflections ($2\theta_{max}$ = 35°, $I > 3\sigma(I)$) for III, and on 4365 unique reflections ($2\theta_{max}$ = 45°, $I > 3\sigma(I)$) for IV. Anisotropic temperature factors were used for all non-hydrogen atoms in I–III with the exception of phenyl ring carbon atoms in all three structures and the THF carbon atoms in III. In IV anisotropic temperature factors were assigned to all non-hydrogen atoms in the anion and to the sodium atom. All other atoms, with the exception of the H atoms, were assigned isotropic temperature factors. At the current stage of refinement on 154 parameters for I, 301 parameters for II, 332 parameters for III, and 400 parameters for IV, with all atoms present in the asymmetric units, R_w = 0.035, 0.047, 0.059, and 0.070, respectively for I–IV.

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