

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 ¹⁵N 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 N³⁴³ (in (CN)₂Cbl), and there is presumably no donation to its carbonyl oxygen in either state, an upfield shift of its ¹⁵N resonance would be expected. Indeed, application of the Taft linear solvation energy relationship to the solvent effect on the ¹⁵N resonance of formamide⁴⁷ 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 ¹⁵N 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 relationship²⁰ to the amide ¹H chemical shifts of *N*-methylacetamide in 10 solvents⁴⁸ 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 ¹⁵N 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 ¹⁵N chemical shifts of (CN)₂Cbl-*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-*e*-COO⁻ do not confirm this interpretation, caution

must be exercised in drawing any conclusions. Attempts to resolve these issues by a complete ¹³C, ¹H, and ¹⁵N assignment of (CN)₂Cbl are currently in progress.

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First Examples of Six-Coordinate Homoleptic Complexes with Monodentate Arenethiolate Ligands. Synthesis and Structural Characterization of [Ph₄P]₂[Nb(SPh)₆], Na(THF)₃Nb(SPh-*p*Me)₆, [(15-crown-5)Na][Ta(SPh)₆], and Nb₂(μ₂-SPh)₄(SPh)₂Cl₂(C₂H₅CN)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 S²⁻ 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 S²⁻-ligands generated by C-S bond cleavage reactions,

- (43) While nitrogen heterocycles are better bases than DMSO (pK_a ~ 0⁴⁰), they are weaker hydrogen bond acceptors (e.g. β = 0.76 for DMSO but 0.64 for pyridine²⁰).
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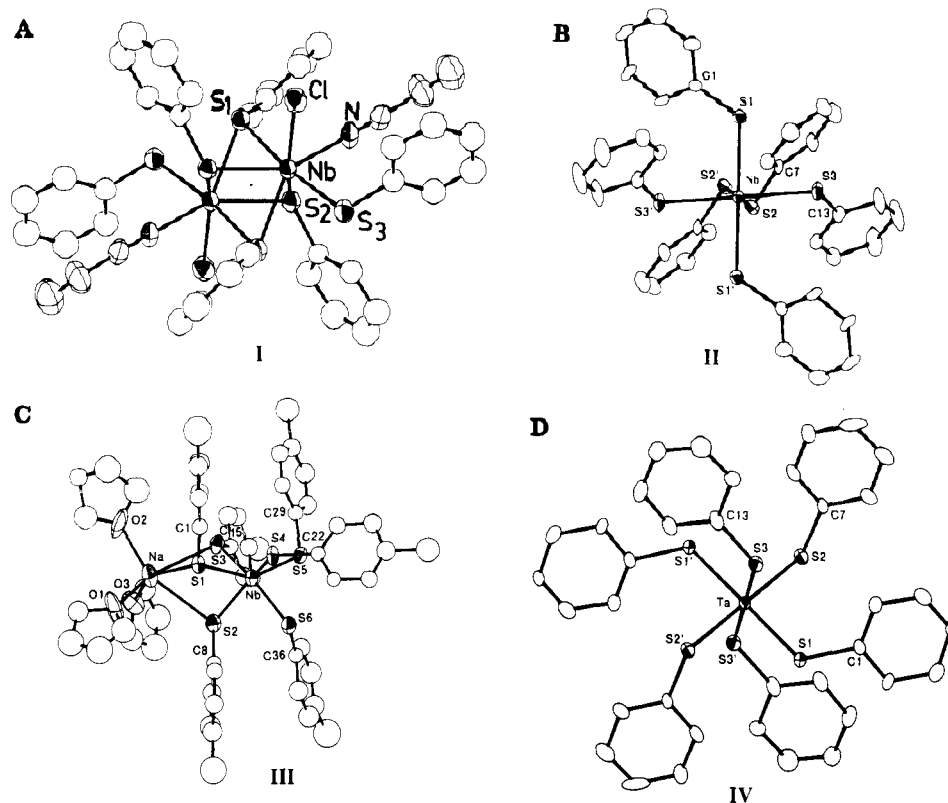


Figure 1. Structures and labeling of $\text{Nb}_2(\mu_2\text{-SPh})_4(\text{SPh})_2\text{Cl}_2(\text{C}_2\text{H}_5\text{CN})_2$ (I), $[\text{Nb}(\text{SPh})_6]^{2-}$ (II), $\text{Na}(\text{THF})_3\text{Nb}(\text{SPh-pMe})_6$ (III), and one of the independent anions, $[\text{Ta}(\text{SPh})_6]^-$, in IV. Thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces.

are included $[\text{M}(\text{norbornane-}exo\text{-}2,3\text{-dithiolate})_3]^{-2a}$, $[\text{M}(\text{ethylene-}1,2\text{-dithiolate})_3]^{-2b}$ ($\text{M} = \text{Nb, Ta}$), $[\text{Nb}(\text{S})(\text{SPh})_4]^{-2d}$ and $\text{Li}_4\text{Nb}_4\text{S}_2(\text{SPh})_{12}$.^{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 to date. 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 $\text{M}(\text{S}_x)_n$ complexes⁶ ($\text{M} = \text{Ni}$, $x = 4$, $n = 2$; $\text{M} = \text{Zn}$, $x = 4$, $n = 2$; $\text{M} = \text{Zn}$, $x = 5$, $n = 2$; $\text{M} = \text{Cd}$, $x = 5$, $n = 2$; $\text{M} = \text{Mn}$, $x = 5$, $n = 2$).

In this communication we report on the synthesis and structural characterization of the dimeric, diamagnetic $\text{Nb}^{\text{IV}}_2(\mu_2\text{-SPh})_4(\text{SPh})_2\text{Cl}_2(\text{C}_2\text{H}_5\text{CN})_2$ (I), the paramagnetic ($S = 1/2$) $(\text{Ph}_4\text{P})_2\text{Nb}^{\text{IV}}(\text{SPh})_6$ (II), the diamagnetic $\text{Na}(\text{THF})_3\text{Nb}^{\text{V}}(\text{SPh-pMe})_6$ (III), and $[(15\text{-crown-}5)\text{Na}][\text{Ta}^{\text{V}}(\text{SPh})_6]$ (IV), complexes that contain the monomeric, six-coordinate $\text{M}(\text{SAr})_6^n$ anions. The reaction of NbCl_5 with NaSPh in $\text{C}_2\text{H}_5\text{CN}$ at 90°C , in a 1:4 molar ratio, affords a deep red solution that upon cooling deposits red crystals of I⁷ 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 II⁸ 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 $(\text{Et}_4\text{N})_2\text{Nb}^{\text{IV}}_2(\text{SPh})_{10}$ 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 $[\text{Nb}^{\text{V}}(\text{SPh-pMe})_6]^-$ anion that can be isolated in crystalline form in 23% yield as the $\text{Na}(\text{THF})_3^+\text{Nb}(\text{SR})_6^-$ anion is stabilized by coordination to the $\text{Na}(\text{THF})_3^+$ cation (*vide infra*) and is not reduced by RS^- to the $\text{Nb}^{\text{IV}}(\text{SR})_6^{2-}$ 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 $\text{Na}(\text{Et}_2\text{O})_3[\text{Ta}^{\text{V}}(\text{SPh})_6]$ complex¹⁰ 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 $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$ mixture gives red crystals of IV¹¹ 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 $\text{Nb}_2\text{Cl}_2\text{S}_6\text{N}_2\text{C}_4\text{H}_{10}$: 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 $\text{Nb}_2\text{Cl}_2\text{S}_6\text{N}_2\text{C}_{48}\text{H}_{52}$: C, 52.13; H, 4.71; S, 17.38. Found: C, 51.85; H, 4.91; S, 17.84.

(8) For reasons discussed previously⁷ 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 $\text{NbNaS}_6\text{O}_3\text{C}_{34}\text{H}_{66}$ (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 $\text{TaNaS}_6\text{O}_3\text{C}_{46}\text{H}_{50}$ (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 Nb₂(μ₂-SPh)₄(SPh)₂Cl₂(C₂H₅CN)₂ (I), (Ph₄P)₂Nb(SPh)₆ (II), Na(THF)₃Nb(SPh-pMe)₆ (III), and [(15-crown-5)Na][Ta(SPh)₆] (IV)

	I	II	III	IV
	Distances ^a			
M-S _i ^b	2.546 (4, 5) ^h	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 _{PR} ^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, $\sigma = [\sum_i (x_i - \bar{x})^2 / N(N-1)]^{1/2}$. ^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 MS₆ 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 MS₆ 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 Nb₄(Se₂)-ScBr₁₀(CH₃CN)₄¹⁵ at 2.886 (1) Å and significantly longer than the Nb^{III}-Nb^{III} bond in [Nb₂S₂(SPh)₁₂]⁴⁻ at 2.83 (2) Å^{2c} and the Nb^{IV}-Nb^{IV} bonds in Nb₂Cl₄(OMe)₄(MeOH)₂¹⁶ and Nb₂S₃Br₄-

(THT)₄¹⁷ (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 Nb₂(μ₂-Se₂)₂Cl₄(dms)₄ complex¹⁸ (dms = dimethyl sulfide) at 2.962 (3) Å. The latter contains eight-coordinate Nb^{IV} ions.

The Nb^{IV}-S_b bond in I at 2.541 (3) Å is longer than the Nb^{IV}-S_i bond in II of 2.488 (3) Å. The latter as expected is longer than the Nb^V-S bond in III (2.447 Å). The difference in the Nb-S bond lengths between I and II can be attributed to 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 (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 Ta-S bond of 2.446 (6) Å is found in the two crystallographically independent, centrosymmetric Ta^VS₆ 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 Nb₂(μ₂-SPh)₄(SPh)₂Cl₂(C₂H₅CN)₂ (I), (Ph₄P)₂Nb(SPh)₆ (II), Na(THF)₃Nb(SPh-pMe)₆ (III), and [(15-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.

- (12) Crystal and refinement data: Red crystals of Nb₂(μ₂-SPh)₄(SPh)₂Cl₂(C₂H₅CN)₂ (I) are monoclinic, space group P2₁/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 (Ph₄P)₂Nb(SPh)₆ (II) are monoclinic, space group P2₁/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-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-crown-5)Na][Ta(SPh)₆] (IV) are triclinic, space group P1 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 (2θ_{max} = 35°, *I* > 3σ(*I*)) for I, on 1642 unique reflections (2θ_{max} = 40°, *I* > 3σ(*I*)) for II, on 1766 unique reflections (2θ_{max} = 35°, *I* > 3σ(*I*)) for III, and on 4365 unique reflections (2θ_{max} = 45°, *I* > 3σ(*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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