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Soluble Niobium Polysulfide Complexes from the Reaction of (t-$BuC_5H_4)_2NbH_3$, $(C_5Me_5)_2NbBH_4$, and $(C_5Me_5)Nb(CO)_4$ with Sulfur

Transition-metal complexes with polysulfide ligands are of considerable interest because of their structural variety and their reactivity. Modern aspects of application include catalysis and materials science.[1] In this regard it is striking that only few soluble niobium polysulfide complexes have been reported although polyselenide chemistry of Nb is already well established.[1,2] With the only exception of $[Nb_2(OMe)_2(S_2)_3(S_5)O]^{2-}$,[3] known molecular niobium sulfides contain mono- or diatomic sulfur ligands together with one or two cyclopentadienyl ligands per Nb atom.[4] Here we report on a promising entry to niobium polysulfide chemistry by means of substituted niobium cyclopentadienides, e.g. Cp'_2NbH_3[5] (Cp′ = η^5-t-BuC_5H_4), $Cp^*_2NbBH_4$[6] (Cp* = η^5-C_5Me_5), or $Cp^*Nb(CO)_4$.[7] In their reactions with elemental sulfur the influence of steric and electronic factors on the nature of the products was studied.

Stirring of a toluene solution (18 h, 20 °C) of Cp'_2NbH_3 (or Cp'_2NbBH_4) with $^5/_8$ S_8 results in the instantaneous evolution of H_2S. After chromatographic workup on SiO_2 (5:1 toluene/ether), a mixture of two apparently very similar products was isolated.[8] Elemental analyses of this mixture were in agreement with a ratio 4:2:8 (or 9) for Cp′/Nb/S, although FD–mass spectra exhibited a considerably lower mass peak. This observation is indicative of a facile loss of Cp′ and sulfur ligands from **1** under thermal conditions.

Red-orange crystals of **1** were isolated by fractional crystallization from 2:1 toluene/pentane. An X-ray diffraction analysis[9] of these crystals shows as the principal result two $Cp'_2Nb(\eta^2$-$S_2)$ moieties linked together by a twisted pentasulfide chain (Figure 1). Inspite of the low quality of the structural solution (some of the Cp′ carbon atoms could not be localized) the core of the molecule could be determined unambiguously. The sulfide chain is one of the few examples in which polysulfide bridges do not form cyclic structures,[1,2] which may be responsible for the kinetic lability of **1**. This is expressed by the high thermal sensitivity in the mass spectrum as well as by the easy formation of niobium polysulfide compounds of higher nuclearity.[10] In this context it must be noted that there is spectroscopic evidence for dismutation reactions in solution for the structurally analogous μ-η^1-Se_5^{2-} ligand in $[Ph_4P]_4[In_2Se_{21}]$.[11] The existence of two different conformations may be explained by packing effects. Rotational isomers could not be detected in solution by ^1H NMR spectroscopy even after cooling a sample to −80 °C. This is in agreement with the generally low activation barrier for the rotation around the MCp bond in metallocenes.[12]

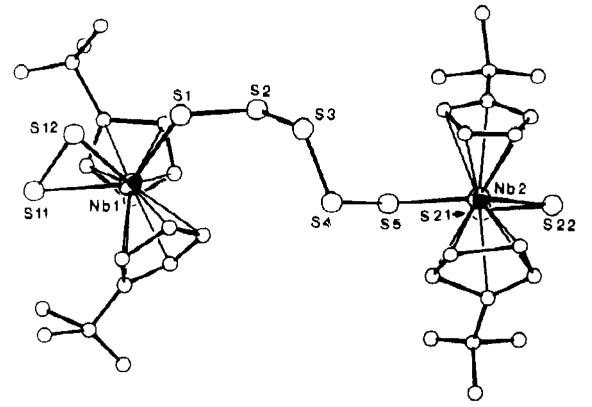
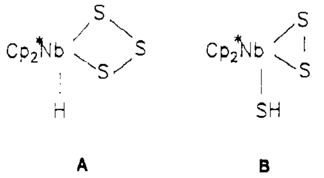


Figure 1. Structure of $(t$-$BuC_5H_4)_4Nb_2S_9$. Bond distances (Å): Nb(1)–S(1), 2.523 (6); Nb(1)–S(11), 2.462 (5); Nb(1)–S(12), 2.543 (8); Nb(2)–S(5), 2.524 (6); Nb(2)–S(21), 2.455 (6); Nb(2)–S(22), 2.514 (6); S(1)–S(2), 2.054 (9); S(2)–S(3), 2.111 (9); S(3)–S(4), 2.027 (9); S(4)–S(5), 2.056 (9); S(11)–S(12), 2.054 (9); S(21)–S(22), 2.01 (1). Bond angles (deg): S(1)–Nb(1)–S(12), 67.9 (2); S(11)–Nb(1)–S(12), 48.4 (2); S(5)–Nb(2)–S(21), 69.3 (2); S(21)–Nb(2)–S(22), 47.7 (2); $Cp(1)_{cent}$–Nb(1)–$Cp(2)_{cent}$, 128.7 (1); $Cp(3)_{cent}$–Nb(2)–$Cp(4)_{cent}$, 131.4 (1).

Variation of the substituents at the Cp ligands exerts a drastic influence on the nature of the products as shown in the reaction of $Cp^*_2NbBH_4$ with $^1/_2$ S_8 (THF, 20 °C, 60 min). After chromatographic workup on SiO_2 (toluene), two red orange compounds **2** and **3** were isolated. For complex **3**[13] (23% yield) the composition $Cp^*_2NbS_3H$ follows unambiguously from analytical and mass spectroscopic data. However, spectroscopic data and reactivity arguments do not yet allow one to differentiate between the two isomeric forms **A** and **B**. The presence of a ^1H NMR signal at δ = −1.64 may be indicative of a hydrogen atom directly attached to the metal center, but it may be also representative of an SH proton. An argument supporting structure **2A** is the absence of any ν_{SH} absorption at about 2400 cm⁻¹ in the IR



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[8] Compound **1** was analyzed correctly for C, H, and S. ^1H NMR (toluene-d_8, 24 °C): δ 6.19 (m, 4 H), 5.90 (m, 4 H), 5.59 (m, 4 H), 5.26 (m, 4 H), 1.17 (s, 36 H). IR (KBr): ν(S–S) 542 (m), 461 cm⁻¹ (w). FDMS (m/z): 588 (mass accounts for $Cp'_2Nb_2S_5$). The second yet unidentified component in the mixture exhibits ^1H NMR data quite close to those of **1**. The yield is ca. 80% with respect to composition **1**.

[9] Crystal data for $C_{36}H_{52}Nb_2S_9$ (**1**): $P2_1/c$, a = 15.553 (1) Å, b = 10.339 (1) Å, c = 31.984 (3) Å, β = 92.9 (1)°, V = 5136.47 Å³, Z = 4, μ(Cu) = 7.26 cm⁻¹, D(calcd) = 1.24 g·cm⁻³; crystal, 90 × 150 × 180 μm; Enraf-Nonius CAD4 ($2 \leq \theta \leq 47°$), 5865 observed data ($I > 2\sigma(I)$, 4592 independent data, R(int) = 0.06. The metal atoms were located by using MULTAN. The other atoms were derived from difference Fourier syntheses. Of the 36 C atoms, 9 tended to drift from their positions. Fixing them resulted in acceptable bond angles and distances. Disorder problems could be excluded. R = 0.162 (Nb and S anisotropic).

[10] Warming solutions of **1** gives rise to the formation of (among others) the highly asymmetric cluster $Cp'_3Nb_3S_{12}$, which is distinguished by five different sets of S_n^{2-} ligands, n ranging from 1 to 3: Brunner, H.; Meier, W.; Wachter, J.; Nuber, B.; Ziegler, M. L. *J. Organomet. Chem.*, in press.

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[13] Compounds **2–4** all give correct elemental analyses (C, H, S.) ^1H NMR ($CDCl_3$, 24 °C): **2**, δ 1.78 (s, 30), −1.64 (s, 1); **3**, δ 1.83 (s); **4**, δ 2.20 (s, 30), 2.03 (s, 15). IR (KBr; cm⁻¹): **2**, ν(S–S) 543 s, ν(Nb–S) 354 (s), 323 (s); **3**, ν(S–S) 528 (m).

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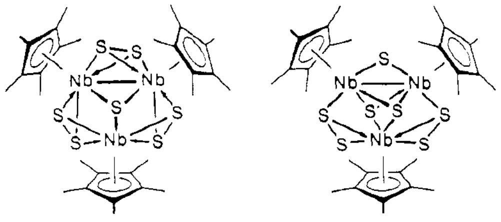
spectrum.[14] On the other hand, it seems unlikely that Nb–H bonds formed during the reaction can be resistive toward the attack of still more excess sulfur.[15]

Only weak hints for the nature of the major product **3**[13] could be obtained thus far. The fact that no hydride resonance was detected in the ^1H NMR spectrum suggests together with analytical data a binuclear complex of formula $Cp^*_4Nb_2S_5$. The diamagnetism of **3** along with IR spectroscopic data requires the presence of $Nb(\eta^2\text{-}S_2)$ moieties as in **1** and a S^{2-} bridge. It is still unclear if there is any relation between **2** and **3**. In this regard it must be pointed out that complexes with terminal SH ligands are able to react with sulfur to give polysulfide complexes.[15,16]

A completely different chemistry is observed when $Cp^*Nb(CO)_4$ is irradiated in the presence of $^1/_2$ S_8 (THF, 3 h). The diamagnetic brown-green $Cp^*_3Nb_3S_7$ (**4**)[13] was isolated in about 30% yield after chromatography (SiO_2, toluene). Suitable single crystals could not be obtained because of the pertinacious tendency of the material to give amorphous aggregates in any solvent. The only structural information available arises from the ^1H NMR spectrum, which indicates two different Nb centers by a 2:1 ratio for the methyl resonances. These are invariable up to 100 °C. Among several possible isomeric forms structural proposal **C** seems reasonable on the basis of a Nb_3S tetrahedron with laterally coordinated S_2 ligands and only one Nb–Nb bond. All Nb atoms in this mixed valence compound (formal charges +III and +IV) thus attain a closed valence shell. A similar M_3S_7 core geometry has already been established for $[Mo_3S(\mu\text{-}S_2)_3(S_2)_3]^{2-}$.[17] A second proposal (**D**) can be derived from the structure of $Cp_3Ta_3S_7Cl_2$[18] by hypothetical reductive halogen elimination and concomitant formation of a metal–metal bond. Interestingly, $Cp^*V(CO)_4$ gives in comparable reactions with S_8 only dinuclear products, e.g. $Cp^*_2V_2S_5$ and $Cp^*_2V_2S_4$.[19]



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In conclusion promising entries to a novel niobium polysulfide complex chemistry have been developed. The high content of S–S bonds, e.g. in **1**, may involve a high reactivity potential, as already demonstrated by preliminary studies.[10] It also raises the question of the mechanism of formation of such compounds. Thus, more detailed investigations on the influence of the substituents as the Cp ligand as well as on the nature of the ligands attached to the CpNb fragment will be necessary.

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Supplementary Material Available: Complete tables of crystal data, atomic coordinates, and anisotropic thermal parameters (4 pages). Ordering information is given on any current masthead page.

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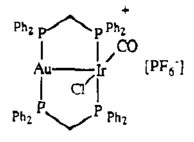
Structure and Photoluminescence of a Heterodinuclear d^{10}–d^8 Complex, $[AuIr(CO)Cl(\mu\text{-}Ph_2PCH_2PPh_2)_2][PF_6]$

Recently, there has been considerable interest in the metal–metal interaction, electronic absorption spectra, and photoluminescence of dinuclear, homometallic complexes with either d^8–d^8 [1] or d^{10}–d^{10} [2] electronic configurations. As yet, there do not appear to be any observations of photoluminescence from heterodinuclear species or from complexes containing a d^{10}–d^8 pair. Here we present preliminary information on the structure and spectroscopy of such a species, $[AuIr(CO)Cl(\mu\text{-dpm})_2][PF_6]$ (**1**; dpm = bis(diphenylphosphino)methane). On the basis of our work on the heterotrinuclear complex **2**,[3] we suspected that **1** should also show photoluminescence.



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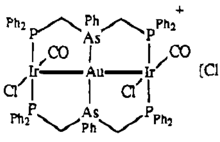

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$[AuIr(CO)Cl(\mu\text{-dpm})_2][PF_6]$ was obtained as orange crystals by the method of Shaw and co-workers.[4] The structure of the cation, as determined by X-ray crystallography,[5] is shown in Figure 1. The complex consists of a planar $Ir(CO)ClP_2$ unit connected to a linear AuP_2 moiety through the two dpm bridges. Interatomic

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