The First Example of a Niobium–Sulphide–Thiolate Cluster: Metal–Metal Bonding and μ_4-Sulphide Groups in Tetranuclear $[Nb_4S_2(SPh)_{12}]^{4-}$

Jeffrey L. Seela, John C. Huffman, and George Christou*

Department of Chemistry and the Molecular Structure Center, Indiana University, Bloomington, IN 47405, U.S.A.

Reaction of $Nb_2Cl_6(Me_2S)_3$ with of excess of LiSPh·THF (THF = tetrahydrofuran) leads to formation of $Li_4[Nb_4S_2(SPh)_{12}]$·4THF: the crystal structure shows the tetra-anion to contain a metal–metal bonded Nb_4 square with a μ_4-S^{2-} atom both above and below the metal plane.

Continuing interest in early transition metal sulphide compounds stems from their relevance to a variety of areas, including heterogeneous catalysis,[1] development of novel electrode materials,[2] and the occurrence of M–S linkages within biological systems.[3] Most effort to date has been concentrated on Mo (and W) chemistry,[4] but some recent interest in Zr/S/SR[5] and V/S/SR[6] chemistry has been reported. Our own interest in the latter has now been extended to niobium and we have investigated the reaction of the double-bonded complex $Nb_2Cl_6(Me_2S)_3$[7] with PhS^-, seeking a metathesis reaction to yield a dinuclear Nb/SPh species which might, on reaction with elemental S or S^{2-}, lead to higher nuclearity Nb/S/SPh clusters. We herein report that this reaction instead leads *directly* to a tetranuclear sulphide-bridged species, and describe the structure of the interesting $[Nb_4S_2(SPh)_{12}]^{4-}$ cluster.

A solution of $Nb_2Cl_6(Me_2S)_3$ (3.4 mmol) in toluene (75 ml) was added over 10 min to a stirred slurry of LiSPh·THF (THF = tetrahydrofuran) (21.3 mmol) in toluene (125 ml). The white solid slowly dissolved to yield an intensely coloured red-brown solution. After an additional 2 h stirring, the reaction mixture was filtered, and hexanes (200 ml) added to precipitate a dark brown powder. The product was collected by filtration, washed copiously with hexanes, and dried *in*

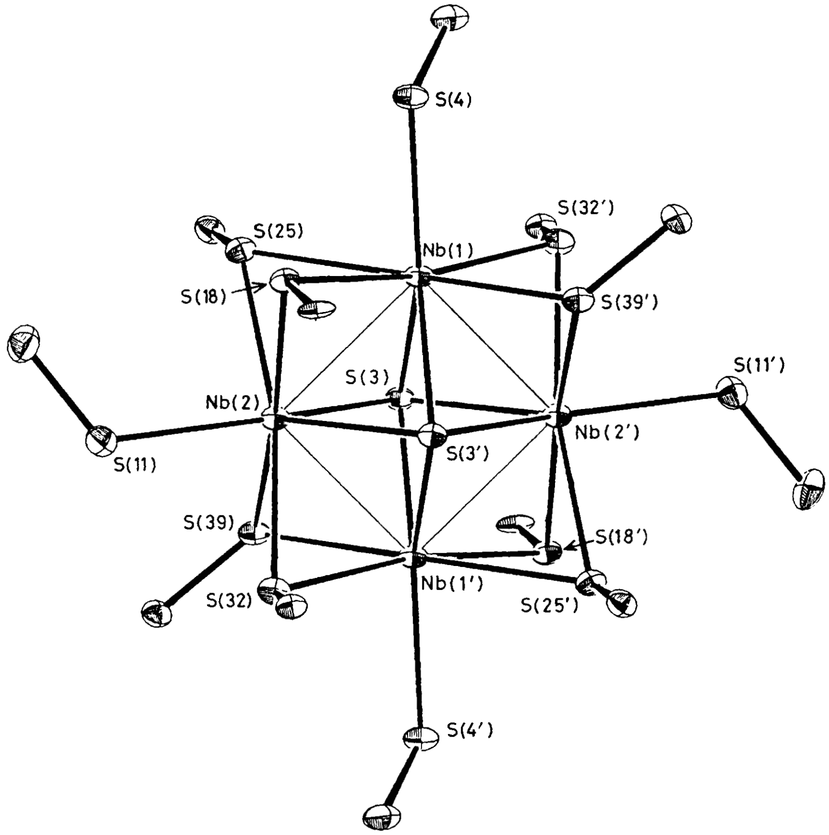

Figure 1. ORTEP projection at the 20% probability level of the anion of complex (**1**). Primed and unprimed numbers are related by the inversion centre. Selected distances (Å) and angles (°): Nb(1)–Nb(2), 2.8261(22); Nb(1)–Nb(2'), 2.8291(22); Nb(1)–S(3), 2.462(4); Nb(1)–S(3'), 2.516(4); Nb(2)–S(3), 2.513(4); Nb(2)–S(3'), 2.515(4); Nb(1)–S(4), 2.534(5); Nb(2)–S(11), 2.650(4); Nb(1)–S(18,25,32',39'), 2.641(4), 2.598(4), 2.624(4), 2.659(4); Nb(2)–S(18,25,32,39), 2.571(4), 2.665(4), 2.557(4), 2.626(4); Nb(2)–Nb(1)–Nb(2'), 90.90(7); Nb(1)–Nb(2)–Nb(1'), 89.10(7); S(3)–Nb(1)–S(3'), 74.32(13); S(3)–Nb(2)–S(3'), 73.45(13).

vacuo. The yield of $Li_4[Nb_4S_2(SPh)_{12}]\cdot 4THF$ (**1**) was 55—60%. Crystals suitable for structural studies were obtained by layering a toluene solution with hexanes. Slow diffusion of the layers yielded black needle-shaped crystals.

The structure† of the anion of (**1**) is shown in Figure 1. The complex has an inversion centre yielding two independent Nb–Nb distances which are identical within the 3σ criterion [Nb(1)–Nb(2), 2.8261(22); Nb(1)–Nb(2'), 2.8291(22) Å]. This defines the Nb_4 unit as being planar and a square, a rare structural unit in the established chemistry of this metal. Each edge is bridged by two μ-SPh groups and there is one terminal SPh group on each Nb. Two μ_4-S^{2-} atoms, one above and one below the Nb_4 plane, complete seven-co-ordination for each metal atom and yield a $[Nb_4S_{14}]$ core with near D_{4h} symmetry. The Li^+ ions are disposed about the anion in the following manner: Li(51) is four-co-ordinate and bound to sulphur atoms S(11), S(18), and S(25) [bond lengths 2.41(3), 2.598(26) and 2.482(26) Å, respectively], and to a terminal THF molecule [Li(51)–O(50), 1.92(3) Å]; Li(57) is three-co-ordinate and is bound to sulphur atoms S(4) and S(32') [bond lengths 2.433(24) and 2.50(3) Å, respectively], and to a terminal THF molecule [Li(57)–O(56), 1.82(3) Å]; the symmetry-related Li^+ ions are bonded similarly. The complete, tightly ion-paired assembly thus has the appearance of a neutral molecule and rationalizes the otherwise surprisingly high solubility of this tetra-anionic unit in toluene. It is also soluble in polar solvents such as MeCN, in which one would expect the ion-pairing to be disrupted.

$$2\,Nb_2Cl_6(Me_2S)_3 + 16\,LiSPh \rightarrow Li_4Nb_4S_2(SPh)_{12} + 12\,LiCl + 6\,Me_2S + Ph\text{–}Ph + PhSSPh \quad (1)$$

The formation of (**1**) from a reaction mixture originally devoid of sulphide suggests that C–S bond cleavage within PhS^- groups has occurred, as summarized in equation (1); we see no visual evidence of an intermediate likely to correspond to a non-sulphido Nb/SPh species. Sulphur abstraction by Nb from NCS^- has recently been reported[8] in the formation of $[Nb_3(\mu_3\text{-}S)O_3(NCS)_9]^{6-}$.

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† *Crystal data:* $C_{88}H_{92}Li_4Nb_4O_4S_{14}$ (**1**), M_r = 2061.94, monoclinic, space group $P2_1/c$, Z = 2, a = 14.298(8), b = 16.425(9), c = 22.139(13) Å, β = 103.92(2)°, U = 5046.64 Å^3, T = −155 °C, crystal dimensions 0.30 × 0.35 × 0.35 mm; data collected in the range $6 \leq 2\theta \leq 45°$; the structure was solved by direct methods (MULTAN) and refined by full-matrix least-squares. All non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms of the phenyl and THF rings were included in fixed, idealized positions. Seven additional peaks were located in a difference Fourier. These were assigned to carbon atoms of seriously disordered toluene or hexane solvates, and were included in the final refinement cycles with isotropic thermal parameters. 4682 unique reflections with $F > 3.00\sigma(F)$, were refined to R 8.72 and R_w 8.34%. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Charge considerations indicate the oxidation state niobium(III), making available eight d electrons for Nb–Nb bonding and leading to a bond order assignment of one. The observed Nb–Nb bond lengths (*ca.* 2.83 Å) are consistent with this description, being in the range found for other Nb complexes with single Nb–Nb bonds; *e.g.*, $Nb_2Cl_4(OMe)_4(MeOH)_2$ [2.781(1) Å],[9] $Nb_2S_3Br_4(THT)_4$ (THT = tetrahydrothiophene) [2.8371(7) Å],[10] $Nb_2S_2Cl_4(MeCN)_4$ [2.862(2), 2.872(3) Å],[11] and $Nb_4(Se_2)SeBr_{10}(MeCN)_4$ [2.886(1) Å].[11] Some oxo-capped trinuclear Nb systems have Nb–Nb bond orders of 2/3 and distances in a similar range [2.763(3)—2.885(7) Å][8,12] but Nb–Nb double bonds are noticeably shorter, in the range 2.611(3)—2.764(1) Å.[8,13,14] The implied pairing of all available d electrons in (**1**) within metal–metal bonding orbitals is confirmed by the observed diamagnetism of this complex; an M.O. calculation is planned to characterize better the electronic makeup of this unusual species.

Initial studies show that complex (**1**) is rather robust. Treatment with an excess of PhSSPh in hot toluene solutions leads to recovery of starting material, and no sign of any oxidative attack by the disulphide molecule to yield higher oxidation state Nb/S/SPh species. This is surprising, given the usual ease of oxidation of Nb^{III}.[8,9] Similarly, attempts to effect higher aggregation by abstraction of a μ_4-S with Ph_3P in hot toluene solutions have also failed.

The coupling of dinuclear multiply bonded metal complexes as a route to tetranuclear metal–metal bonded systems is becoming relatively common with metals such as Mo,[15,16] but the present work represents the first such observation for Nb. In addition, the Nb_4 square of (**1**) represents two thirds of the Nb_6 octahedron found in NbO and other compounds such as Nb_6I_{11} and $[Nb_6X_{12}]^{n+}$ (X = halide),[17] and suitable choice of thiol, Nb oxidation state, and general reaction conditions may allow access to the corresponding Nb_6 sulphide species.

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