

Nb₂S₄⁴⁺ Complexes with 1,1-Dithioacid Ligands

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The synthesis, structure, and properties of (Et₄N)₄Nb₂S₄(NCS)₈ (**1**), (EtQuin)₄Nb₂S₄(NCS)₈ (**1a**), Nb₂S₄(Et₂NCS₂)₄ (**2**), Nb₂S₄(ROCS₂)₄ (**3**, R = Et, ^tPr, Cy), and Nb₂S₄((^tPrO)₂PS₂)₄ (**4**) are described. Complexes **1** and **1a** have been obtained by fusing together NbS₂Cl₂ and KNCS, dissolving this melt in water, and adding corresponding organic cations. Complex **1a** crystallizes in the P $\bar{1}$ space group with the following unit cell dimensions: *a* = 10.553(2) Å, *b* = 11.773(2) Å, *c* = 13.440(2) Å, α = 97.18(1)°, β = 103.66(1)°, γ = 105.49(1)°, and *Z* = 1. A total of 2060 reflections with *F* > 6σ(*F*) were employed, and the structure solution was refined to the values of conventional indices *R* and *R*_w 0.057 and 0.055, respectively. The anion of **1** has eight-coordinated Nb atoms ligated by η²:η²:μ₂ ligands and eight terminal isothiocyanate ligands. The Nb–Nb distance is 2.913(2) Å. The NCS ligands in **1** and **1a** can be easily replaced with bidentate 1,1-dithioacid ligands to yield the complexes **2–4**. Complex **4** crystallizes in P $\bar{1}$ space group with the following unit cell dimensions: *a* = 8.925(2) Å, *b* = 10.349(1) Å, *c* = 14.161(2) Å, α = 81.57(1)°, β = 107.77(1)°, γ = 98.98(1)°, and *Z* = 1. A total of 1932 reflections with *F* > 4σ(*F*) were employed, and the structure solution was refined to the values of conventional indices *R* and *R*_w 0.030 and 0.028, respectively. Just like **1a**, complex **4** has a Nb₂S₄ core. The Nb–Nb distance is 2.898(1) Å. Each Nb atom, in addition, is coordinated by two chelating dithiophosphate ligands. Mass spectra of **2** and **4** have been studied. Complex **2** is oxidized by Fc⁺ giving paramagnetic cluster cation [**2**]⁺.

Introduction

Formation of metal–metal-bonded dimers is common to d¹ Nb(IV) and Ta(IV) centers. This has been found, e.g., for tetrahalide structures. Much more recently, a new group of dinuclear clusters of Nb (and Ta) having metal–metal bonds along with bridging ligands has been obtained. In this series the metal centers can be bridged by two (μ-S, μ-OMe),¹ three (μ-OMe, μ-Cl; often along with μ-Y₂ (Y = S, Se, Te) ligands),² or even four (μ-Cl, μ-Y₂) atoms.³ Nb₂S₄L₈ clusters with the [Nb₂(μ-S₂)₂]⁴⁺ core, which also belong to the this type of compound, have been known since the 1960s. However, until recently their chemistry was restricted to the synthesis and structure determination of NbS₂Cl₂ (which has the crystallographic formula [Nb₂(μ-S₂)₂Cl_{8/2}]). Analogous bromide and iodide compounds as well as their seleno analogs were also described.^{3a,c,4}

Thio complexes of niobium are of particular interest, keeping in mind the very rich chemistry and versatile electronic properties demonstrated by the thio complexes of the neighboring metals—V and Mo. These thio complexes have a dominant role in some

important enzymes and also are of interest for the design of powerful catalysts for oil hydrodesulfurization. However, the thio complexes of niobium are tangibly less studied than those of other metals (V, Mo, W, Re), even though there is an abundance of compounds in the niobium/chalcogen and niobium/chalcogen/halogen systems. A primary consideration here is an extremely low reactivity of possible starting compounds.

Experimental Section

Syntheses. NbS₂Cl₂ was prepared by the heating of Nb and S₂Cl₂ in a sealed quartz ampule.^{4a} Solvents were purified according to the standard methods. KNCS was dried *in vacuo* (10⁻¹ Torr, 160 °C) for 20 h. Dithiocarbamate and xanthate salts of alkaline metals were recrystallized from ethanol. Potassium cyclohexyl xanthate K₂S₂COC₆H₁₁ was prepared in the standard fashion from CS₂, KOH, and cyclo-C₆H₁₁OH. KS₂P(O^tPr)₂ was prepared by treatment of the corresponding Zn salt with KOH in a water/acetone solution. All other reagents were used as purchased.

A. (Et₄N)₄Nb₂S₄(NCS)₈ (1**).** NbS₂Cl₂ (2.00 g, 8.8 mmol) and dry KNCS (20.0 g) were fused together in a sealed quartz ampule (185 °C, 48 h). After cooling, the resulting melt was taken out of the ampule, ground, and extracted with water (50 mL). The resulting orange solution was filtered and the filtrate diluted with a solution of Et₄NBr (10 g in 50 mL of water). The yellow-orange precipitate was filtered off, washed with H₂O, EtOH, and Et₂O, and dried *in vacuo*. Yield: 45%. Anal. Calcd for C₄₀H₈₀N₁₂Nb₂S₁₂: C, 36.96; H, 6.20; N, 12.23. Found: C, 36.20; H, 5.94; N, 12.58. IR (cm⁻¹): ν(CN) 2086 s, δ(NCS) 472 m, 467 sh. Raman (cm⁻¹): 588 w, 433 w, 333 s, 288 w, 182 w.

B. (EtQuin)₄Nb₂S₄(NCS)₈ (1a**).** This salt can be prepared in the same manner as **1** by adding *N*-ethylquinolinium iodide to the K₄Nb₂S₄(NCS)₈ water solution. The orange material precipitated was dissolved in CH₃CN, and the solution was allowed to stand in Et₂O vapors. Large orange crystals suitable for single-crystal X-ray study were obtained in several hours. Raman (cm⁻¹): 2079 m, 2113 m (ν(CN)); 594 w (ν(S₂)); 333 s (Nb–S).

C. Nb₂S₄(Et₂NCS₂)₄. Complex **1** (0.51 g, 0.4 mmol) was added to a water solution of NaS₂CNEt₂·3H₂O (0.84 g, 3.7 mmol in 20 mL of water), and the mixture was stirred for 12 h. During this time the orange color of solid **1** changed into light-brown. The resulting precipitate was filtered off, washed with MeOH and Et₂O (Caution! **2** is considerably soluble in ether!), and dried *in vacuo*. Yield: 73%. Anal. Calc for

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- (1) (a) Babajan-Kibala, E.; Cotton, F. A. *Inorg. Chim. Acta* **1991**, *182*, 77. (b) Benton, A. J.; Drew, M. G. B.; Hobson, R. G.; Rice, D. A. *J. Chem. Soc., Dalton Trans.* **1981**, 1304. (c) Drew, M. G. B.; Rice, D. A.; Williams, D. M. *J. Chem. Soc., Dalton Trans.* **1985**, 417. (d) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1987**, *26*, 3319.
- (2) (a) Drew, M. G. B.; Rice, D. A.; Williams, D. M. *J. Chem. Soc., Dalton Trans.* **1983**, 2251. (b) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1988**, *27*, 3596. (c) Cotton, F. A.; Babaian-Kibala, E.; Falvello, L. R.; Shang, M. *Inorg. Chem.* **1990**, *29*, 2591.
- (3) (a) Rijnsdorp, J.; De Lange, G. L.; Wiegers, G. A. *J. Solid State Chem.* **1979**, *30*, 365. (b) Franzen, H. F.; Honle, W.; Schnering, H.-G. *Z. Anorg. Allg. Chem.* **1983**, *497*, 13. (c) Meerschaut, A.; Grenouilleau, P.; Brec, R.; Evain, M.; Rouxel, J. *J. Less Common Met.* **1986**, *116*, 229. (d) Drew, M. G. B.; Rice, D. A.; Williams, D. M. *Acta Crystallogr.* **1984**, *C40*, 1547. (e) Drew, M. G. B.; Rice, D. A.; Williams, D. M. *J. Chem. Soc., Dalton Trans.* **1984**, 1087. (f) Cotton, F. A.; Duraj, S. A. *Inorg. Chem.* **1984**, *23*, 3592.
- (4) (a) Beckmann, W.; Schafer, H. Z. *Anorg. Allg. Chem.* **1966**, *347*, 225. (b) Schnering, H.-G.; Beckmann, W. *Z. Anorg. Allg. Chem.* **1966**, *347*, 231.

$C_{20}H_{40}N_4Nb_2S_{12}$: C, 26.54; H, 4.64; N, 6.18; Nb, 20.54. Found: C, 26.08; H, 4.43; N, 5.76; Nb, 19.80. IR (cm^{-1}): 2968 s, 2930 s, 2967 s, 1490 vs, 1486 sh, 1454 m, 1447 sh, 1427 vs, 1375 m, 1350 s, 1300 m, 1268 vs, 1208 s, 1142 s, 1093 m, 1073 s, 1007 m, 916 m, 847 s, 773 m, 573 w, 557 m, 490 w. Raman (cm^{-1}): 563 vs, 369 m, 326 s, 295 w, 250 s, 151 s, 128 w, 116 s. 1H NMR (CD_2Cl_2 , ppm, δ): 3.56, 3.65, 3.71, 3.78, 3.87 m ($-CH_2-$) (4H); 1.25, 1.17, 1.09 t ($-CH_3$) (6H).

D. $Nb_2S_4(S_2COEt)_4$ (**3a**). A suspension of **1** (0.20 g, 0.15 mmol) and KS_2COEt (0.42 g, 2.6 mmol) was stirred in a H_2O/CH_2Cl_2 mixture for 12 h to form a clear solution. The bottom organic layer was separated, dried over $CaCl_2$, and evaporated to dryness. The resulting oil was extracted with hot CH_3CN . After the solution was cooled to $+5^\circ C$, an orange microcrystalline substance was obtained. Yield: 0.05 g (33%). Anal. Calc for $C_{12}H_{20}O_4Nb_2S_{12}$: Nb, 23.26. Found: Nb, 23.40. IR (cm^{-1}): 2974 m, 2934 w, 2898 w, 1465 m, 1433 m, 1390 w, 1369 s, 1290 m, 1230 (vs, broad), 1165 m, 1150 sh, 1130 s, 1090 w, 1047 s, 1007 s, 865 m, 813 w, 560 m, 447 m. Raman (cm^{-1}): 564 s, 448 m, 353 m, 327 s, 297 m, 255 s, 128 w.

E. $Nb_2S_4(S_2CO^iPr)_4$ (**3b**). The complex was obtained in a manner similar to the preparation of **3a**. The total yield was 80%. Anal. Calc for $C_{16}H_{28}O_4Nb_2S_{12}$: Nb, 21.78. Found: Nb, 22.38. Raman (cm^{-1}): 569 s, 499 w, 466 m, 393 w, 383 w, 367 w, 343 m, 307 m, 257 m, 247 m, 238 w, 190 w, 158 w. 1H NMR (CD_2Cl_2 , ppm, δ): 1.33, 1.39 (d, 6H); 5.53, 5.47, 5.40, 5.33 (m, 1H).

F. $Nb_2S_4(S_2COC_6H_{11})_4$ (**3c**). **3c** was obtained from **1** and $KS_2COC_6H_{11}$ in the CH_2Cl_2/H_2O mixture in a manner similar to **3a**. After recrystallization from $CHCl_3/CCl_4$ (1:1) the yield was 52%. Anal. Calc for $C_{28}H_{44}O_4Nb_2S_{12}$: C, 33.64; H, 4.41. Found: C, 34.15; H, 3.94. IR (cm^{-1}): 2933 s, 2853 s, 1467 w, 1446 s, 1368 m, 1349 s, 1330 (vw), 1313 w, 1247 vs, 1228 vs, 1195 sh, 1156 s, 1117 s, 1095 w, 1067 s, 1050 s, 1033 m, 1020 sh, 1004 s, 925 s, 872 m, 847 w, 560 m, 480 w.

G. $Nb_2S_4(S_2P(O^iPr)_2)_4$ (**4**). Complex **1** (0.30 g, 0.23 mmol) and $KS_2P(O^iPr)_2$ (0.38 g, 1.5 mmol) were stirred in a CH_2Cl_2/H_2O mixture for 12 h. Then the orange organic layer was separated, dried over $CaCl_2$, and evaporated *in vacuo*. The solid residue was extracted with hot CH_3CN . After cooling of the solution at $+15^\circ C$, long yellow needles of complex **4** were obtained. The yield was 0.08 g (30%). Anal. Calc for $C_{24}H_{36}O_8P_4Nb_2S_{12}$: C, 24.61; H, 4.80. Found: C, 25.17; H, 4.80. IR (cm^{-1}): 2973 s, 2932 m, 2866 w, 1466 s, 1388 s, 1370 s, 1330 w, 1179 s, 1143 m, 1103 s, 1015 s, 987 s, 966 s, 900 sh, 887 s, 780 s, 767 s, 753 sh, 733 sh, 655 s, 634 s, 573 m, 549 s, 537 s, 460 m, 450 w, 430 w, 420 w. Raman (cm^{-1}): 578 vs, 551 s, 539 m, 441 m, 325 m, 306 m, 292 m, 256 w, 222 w.

Measurements. The IR spectra were recorded on an IR-75 spectrometer in KBr pellets. Raman spectra were detected on a Triplate 21 spectrometer with an excitation of the 632.8-nm line of a He-Ne laser. The 1H spectra were recorded on a SXP-4-100 (Bruker) spectrometer at 90.05 MHz at 290 K. Chemical shifts are given for TMS as an internal standard. The FAB⁺ mass spectra were measured on a VAG ZAB VSEQ instrument. Test solutions were prepared by dissolving the samples in CH_2Cl_2 and mixing 1 μL of the resulting solutions with 1 μL of 3-nitrobenzyl alcohol prior to introduction into the spectrometer. ESR spectra were recorded on a Varian E-109 instrument (X-range) at 77–300 K. C, H, and N analysis was performed in the Laboratory of Microanalysis at the Institute of Organic Chemistry (Novosibirsk, Russia). Nb was determined gravimetrically in the form of Nb_2O_5 after mineralization with HNO_3 and calcination at $950^\circ C$.

X-ray Data Collection and Structure Solution. Data collection parameters are summarized in Table 1. The data were collected at room temperature by using standard procedures. The structures were solved by direct methods using the SHELX-86 program^{20a} and refined by the full-matrix least-squares method using the YANX program.^{20b} Hydrogen atoms were introduced in calculated positions and refined isotropically in "ride approximation" with fixed $U = 0.08 \text{ \AA}^2$. All non-hydrogen atoms were refined anisotropically. A final difference Fourier map was featureless, with the largest peaks measuring 1.1 e/ \AA^3 .

Results and Discussion

Syntheses. Although chalcogenides NbS_2X_2 can be easily prepared, the $[Nb_2(S_2)_2]^{4+}$ clusters were left aside in the study of niobium chemistry. First obtained by the heating of a stoichiometrical mixture of the metal, halogen, and chalcogen ($Nb, S_2Cl_2; Nb, S, \text{ and } Br_2; Nb, S, \text{ and } I_2$), they were found to be insoluble in all organic solvents and nonoxidizing mineral acids. Such behavior is in good agreement with their polymeric structure.

Table 1. Crystallographic Data for Complexes **1a** and **4**

parameters	1a	4
formula	$C_{52}H_{48}N_{12}Nb_2S_{12}$	$C_{24}H_{36}Nb_2O_8P_4S_{12}$
molar mass, g mol ⁻¹	1411.62	1167.18
cryst size, nm	$0.05 \times 0.05 \times 0.12$	$0.10 \times 0.15 \times 0.20$
cryst system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> , \AA	10.553(2)	8.925(2)
<i>b</i> , \AA	11.773(2)	10.349(1)
<i>c</i> , \AA	13.440(2)	14.161(2)
α , deg	97.18(1)	81.57(1)
β , deg	103.66(1)	107.77(1)
γ , deg	105.49(1)	98.98(1)
<i>Z</i>	1	1
<i>V</i> , \AA^3	1531.8(4)	1223.5(6)
<i>D_x</i> , g cm ⁻³	1.530	1.584
diffractometer	Syntex P2 ₁	CAD-4
radiation (λ , \AA)	Cu K α (1.5418)	Mo K α (0.7107)
($\sin \theta$)/ λ max	0.497	0.539
<i>F</i> _{hkl} tot./used	3343/2060 > 6 σ (<i>F</i>)	2316/1932 > 4 σ (<i>F</i>)
abs coeff, cm ⁻¹	73.6	11.1
abs corr	ψ -scan around 010	none
<i>R_F</i> ^a	0.057	0.030
<i>R_{wF}</i> ^b	0.055	0.028
<i>w</i>	$1/(\sigma(F)^2 + 0.002F^2)$	$1/(\sigma(F)^2 + 0.002F^2)$

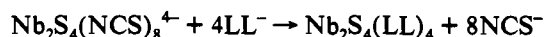
$$^a R_F = \sum |F_o - F_d| / \sum |F_d|. \quad ^b R_{wF} = \sum w^{1/2} |F_o - F_d| / \sum w^{1/2} |F_d|.$$

Our early efforts to involve NbS_2Cl_2 in reaction with typical N-donors (DMSO, DMF, py, Ph_3PO) were not successful. Even upon prolonged heating the starting reagents remained unchanged.

In 1989 the interaction of NbS_2Cl_2 with a KNCS melt was described. It brings about the formation of discrete, soluble $Nb_2S_4(NCS)_8^{4-}$ complexes.⁵ This reaction is completed within 48 h and gives a dark-red flux containing the $K_4Nb_2S_4(NCS)_8$ salt. For the synthesis to be successful, a thorough drying and grinding of the reagents and accurate temperature control (180 – $185^\circ C$) are necessary, otherwise dark-green water-insoluble decomposition products come into existence.

The extraction with water gives a stable orange solution of $K_4Nb_2S_4(NCS)_8$. An addition of Et_4NBr to the solution gives a copious yellow-orange precipitate of $(Et_4N)_4Nb_2S_4(NCS)_8$ (**1**) salt. Complex **1** is an air-stable solid, quite soluble in CH_3CN or $(CH_3)_2CO$, and it was found to be handy for syntheses of various $Nb_2S_4^{4+}$ complexes with a number of 1,1-dithioacid ligands. Unfortunately, **1** does not form single crystals suitable for X-ray diffraction. Although Me_3NH^+ and Rb^+ cations also precipitate $Nb_2S_4(NCS)_8^{4-}$ from water solutions, single crystals of good quality have been produced nevertheless only for the *N*-ethylquinolinium salt $(EtQuin)_4Nb_2S_4(NCS)_8$.

We employed two different methods for the synthesis of 1,1-dithioacid complexes of $Nb_2S_4^{4+}$. The first one is the interaction of solid **1** with water solutions of ligands (NaS_2CNEt_2 , KS_2COR ($R = Et, ^iPr, Cy$), or $KS_2P(O^iPr)_2$), and the other includes the reaction of the same reagents in the two-phase system CH_2Cl_2 /water. In both cases the reactions taking place are described by the following general equation:



In the first case, the initial complex **1**, which is water insoluble, changes into insoluble chelates **2–4**. In the second case, the arising $Nb_2S_4(LL)_4$ complexes transfer completely to the organic layer from the water suspension, thus indicating the completion of the reaction. The evaporation of CH_2Cl_2 solutions gives solids **2–4**, which are readily soluble in CH_2Cl_2 and $CHCl_3$ and only sparingly

- (5) Mishchenko, A. V.; Fedorov, V. Ye.; Kolesov, B. A.; Fedotov, M. A. *Koord. Khim.* **1989**, *15*, 200.
 (6) (a) Fedorov, V. Ye.; Mishchenko, A. V.; Fedin, V. P. *Russ. Chem. Rev.* **1985**, *54*, 694. (b) Lee, S. C.; Holm, R. H. *Agnew. Chem., Int. Ed. Engl.* **1990**, *29*, 840.
 (7) Fiechter, S.; Kuhs, W. F.; Nietsche, R. *Acta Crystallogr.* **1980**, *B36*, 2217.

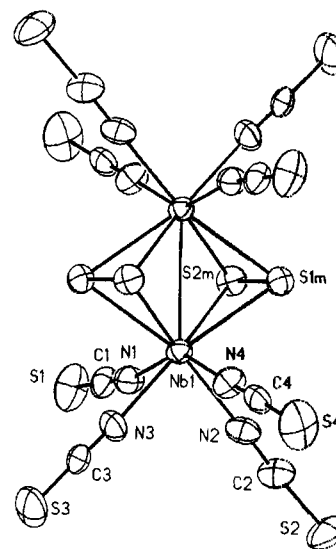
Table 2. Atomic Coordinates and Equivalent Thermal Parameters (Å²) for Non-Hydrogen Atoms in **1a**

atom	X	y	Z	U _{eq} ^a
Nb(1)	0.0561(1)	0.4368(1)	0.0773(1)	0.0403(8)
S(1M)	0.1927(4)	0.6118(3)	0.0183(3)	0.053(2)
S(2M)	0.1191(4)	0.4580(3)	-0.0897(3)	0.057(3)
S(1)	-0.0741(5)	0.0365(4)	-0.1479(3)	0.083(2)
S(2)	0.5017(5)	0.3664(4)	0.2175(4)	0.094(4)
S(3)	-0.1289(5)	0.2616(5)	0.3461(4)	0.103(4)
S(4)	0.2983(6)	0.7382(4)	0.4063(3)	0.096(4)
C(1)	-0.032(1)	0.161(1)	-0.065(1)	0.05(1)
C(2)	0.352(2)	0.382(1)	0.166(1)	0.07(1)
C(3)	-0.067(1)	0.307(1)	0.253(1)	0.05(1)
C(4)	0.214(2)	0.640(1)	0.298(1)	0.06(1)
N(1)	0.003(1)	0.250(1)	-0.0054(8)	0.053(8)
N(2)	0.250(1)	0.399(1)	0.1320(8)	0.059(9)
N(3)	-0.020(1)	0.341(1)	0.1898(8)	0.059(9)
N(4)	0.156(1)	0.571(1)	0.2239(8)	0.056(9)
N(1K)	0.548(1)	1.007(1)	0.1694(8)	0.050(8) ^b
C(1K)	0.567(1)	0.896(1)	0.159(1)	0.039(9)
C(2K)	0.651(2)	0.873(2)	0.099(1)	0.06(1)
C(3K)	0.721(2)	0.964(2)	0.057(1)	0.07(1)
C(4K)	0.699(2)	1.073(2)	0.069(1)	0.07(1)
C(5K)	0.613(2)	1.094(2)	0.127(1)	0.06(1)
C(6K)	0.500(1)	0.809(1)	0.208(1)	0.06(1)
C(7K)	0.521(2)	0.697(2)	0.192(1)	0.06(1)
C(8K)	0.604(2)	0.673(1)	0.130(1)	0.07(1)
C(9K)	0.668(2)	0.759(2)	0.085(1)	0.07(1)
C(10K)	0.455(2)	1.039(2)	0.226(1)	0.07(1)
C(11K)	0.516(2)	1.073(2)	0.342(1)	0.11(2)
N(2K)	-0.216(2)	-0.355(3)	0.506(2)	0.14(2)
C(12K)	-0.191(2)	-0.240(2)	0.471(2)	0.09(2)
C(13K)	-0.143(3)	-0.214(5)	0.389(3)	0.16(3)
C(14K)	-0.094(3)	-0.286(5)	0.341(3)	0.27(6)
C(15K)	-0.118(4)	-0.411(3)	0.368(3)	0.20(4)
C(16K)	-0.178(3)	-0.421(5)	0.444(2)	0.17(4)
C(17K)	-0.231(2)	-0.166(3)	0.531(3)	0.18(3)
C(18K)	-0.221(2)	-0.059(3)	0.524(3)	0.17(3)
C(19K)	-0.165(5)	-0.038(4)	0.426(3)	0.24(5)
C(20K)	-0.125(6)	-0.081(6)	0.368(3)	0.20(4)
C(21K)	-0.283(4)	-0.385(4)	0.587(2)	0.27(4)
C(221)	-0.443(5)	-0.468(4)	0.528(4)	0.08(2)
C(222)	-0.257(6)	-0.257(6)	0.640(4)	0.09(2)
C(223)	-0.234(7)	-0.446(6)	0.526(5)	0.09(2)

^a Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized U(i,j) tensor. ^b Atoms from N(1K) to C(223) belong to the organic cation.

soluble in CH₃CN; from the latter they can be crystallized for purification. By means of these approaches were obtained complexes Nb₂S₄(S₂CNET₂)₄ (**2**), Nb₂S₄(S₂COR)₄ (R = Et (**3a**), ^tPr (**3b**), Cy, (**3c**)), and Nb₂S₄(S₂P(O^tPr)₂)₄ (**4**). All these complexes are air-stable both in the solid state and in solution. They can be chromatographed on silica gel without decomposition, which may be used for purification purposes. To the best of our knowledge, there are no reports about other molecular Nb₂S₄ complexes. Only for Nb₂Se₄⁴⁺ are described two complexes having thioether ligands: Nb₂Se₄Cl₄(tht)₄ (tht = tetrahydrothiophene) and Nb₂Se₄Cl₄(Me₂S)₄. They have been obtained in complex reactions between NbSeCl₃ and the corresponding thioether.^{3d,e} For the closest analog of niobium—tantalum—there is no tendency for formation of Ta₂Y₄⁴⁺ complexes. In the case of vanadium, a variety of 1,1-dithioacid complexes V₂S₄(LL)₄ have been obtained (LL = Et₂NCS₂, Bu₂NCS₂, ^tBu₂NCS₂, MeCS₂, MeSCS₂) as well as anionic V₂S₄(CS₃)₄⁻⁸.

Vibrational Spectra. The infrared spectra of **1–4** have no peculiarities in the region of ligand vibrations when compared to published data for the usual coordination modes. Both **1** and **1a**

**Figure 1.** ORTEP drawing of the Nb₂(μ-S₂)₂(NCS)₈⁴⁻ anion in **1a**. Atoms are represented by their ellipsoids at the 50% probability level.

have characteristic bands of the N-coordinated NCS near 2090 and 470 cm⁻¹. For complex **1a** this coordination mode has been confirmed by X-ray analysis; for other salts (K⁺, Cs⁺, Bu₄N⁺), by the use of ¹⁴N NMR.⁵ Complex **4** also contains dithiophosphate ligands coordinated in a bidentate fashion; this was established by X-ray analysis and is responsible for a rather strong shift of ν_{as}(PS) and ν_s(PS) toward low frequencies. For complex **2** there is also a good agreement between IR data indicative of the bidentate coordination of the ligand and the structure of the material (the crystal structure of **2** has been reported previously¹⁴). For xanthate complexes, the IR data alone do not give sufficient grounds to make conclusions about the coordination mode of the ligands (predominantly due to the problem of mixing C–O and C=S vibrations). But we also have no reasons to reject the bidentate S,S' coordination of the xanthate ligands.

Raman spectra are especially characteristic for the Nb₂S₄⁴⁺ core. Intense ν(S–S) vibrations fall within the narrow range 560–590 cm⁻¹ depending on the type of other ligands (A_g vibration for D_{2h} symmetry of the Nb₂S₄ core). Intense bands at 330–340 cm⁻¹ can be attributed predominantly to the Nb–S vibrations, and ones at 170–180 cm⁻¹ can be Nb–Nb vibrations (A_g type). A detailed study of high-resolution absorption spectra of single crystals of NbS₂X₂ (X = Cl, Br, I) has been reported by Rijnsdorp and Haas.⁹

X-ray Structures. Complex **1a** has an ionic structure; complex **4**, a molecular one. Views of the Nb₂S₄(NCS)₈⁴⁻ anion in **1a** and Nb₂S₄(S₂P(O^tPr)₂)₄ in **4** are shown in Figure 1 and 2, respectively. Atomic coordinates and bond distances and angles are given in Tables 2–5. Both of the complexes have the central [Nb₂(S₂)₂]⁴⁺ core, in which the coordination of disulfur ligands resembles acetylene type η²:η²;μ₂ coordination. A wide range of analogous complexes having the M₂(μ-S₂)₂ cores have been described earlier for transition metals of the 5th, 6th, and 8th groups (Table 6). In addition, there are indications of the possibility of the presence of a Re₂S₄⁶⁺ core in ReS₂Cl₃, which is not, however, structurally characterized.¹¹

- (8) (a) Halbert, T. R.; Hutschings, L. L.; Rhodes, R.; Stiefel, E. I. *J. Am. Chem. Soc.* **1986**, *108*, 6437. (b) Duraj, S. A.; Andras, M. T.; Kibala, P. A. *Inorg. Chem.* **1990**, *29*, 1232. (c) Yang, Y.; Huang, L.; Liu, Q.; Kang, B. *Acta Crystallogr.* **1991**, *C47*, 2085. (d) Sendlinger, S. C.; Nicholson, J. R.; Lobkovsky, E.; Huffman, J. C.; Rehder, D.; Christou, G. *Inorg. Chem.* **1993**, *32*, 204. (e) Tiekink, E. T. R.; Xue Feng Yan; Yang, C. G. *Aust. J. Chem.* **1992**, *45*, 897.

- (9) Rijnsdorp, J.; Haas, C. *J. Phys. Chem. Solids* **1980**, *41*, 375.
 (10) (a) Reynolds, J. D.; Cook, K. D.; *J. Am. Soc. Mass Spectrom.* **1990**, *1*, 149. (b) Hegetschweiler, K.; Caravatti, P.; Fedin, V. P.; Sokolov, M. N. *Helv. Chim. Acta* **1992**, *75*, 1659. (c) Hegetschweiler, K.; Keller, T.; Amrein, W.; Schneider, W. *Inorg. Chem.* **1991**, *30*, 873.
 (11) Ul'ko, N. V.; Kolesnichenko, V. L. *Zh. Neorg. Khim.* **1980**, *25*, 2565.
 (12) Virovets, A. V.; Podbereskaya, N. V.; Sokolov, M. N.; Korobkov, I. V.; Fedin, V. P.; Fedorov, V. Ye. *Zh. Struct. Khim.* **1993**, *34*, 134.
 (13) Virovets, A. V. X-Ray Structural and crystallochemical investigations of compounds containing M₃X₇⁴⁺ and M₃X₄⁴⁺ cluster fragments (M = Mo, W; X = S, Se). Ph.D. Thesis, Institute of Inorganic Chemistry, Novosibirsk, Russia, 1993.

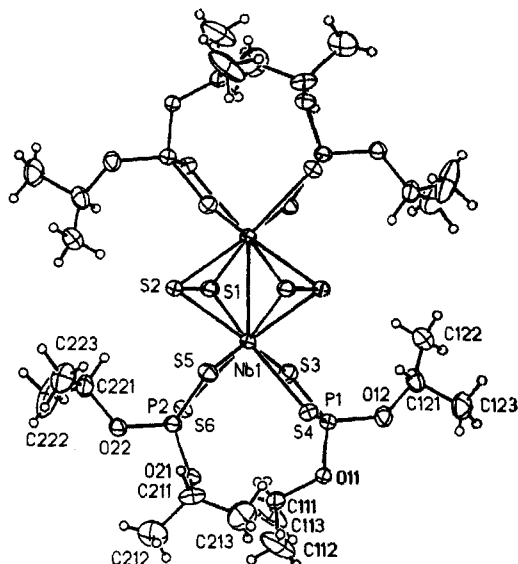


Figure 2. ORTEP drawing of $\text{Nb}_2(\mu\text{-S}_2)_2(\text{S}_2\text{P}(\text{O}^i\text{Pr})_2)_4$ in **4**. Atoms are represented by their ellipsoids at the 50% probability level.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Thermal Parameters ($\text{\AA}^2 \times 10^3$) for Non-Hydrogen Atoms in **4**

atom	X	y	Z	U_{eq}^a
Nb(1)	562(1)	200(1)	1048(1)	28(1)
S(1)	-2014(2)	-1076(2)	217(1)	36(1)
S(2)	-1942(2)	880(2)	-149(1)	37(1)
S(3)	690(2)	-2088(2)	2123(1)	35(1)
S(4)	3330(2)	375(2)	2435(1)	35(1)
P(1)	2858(2)	-1473(2)	2971(1)	32(1)
O(11)	3001(5)	-1686(4)	4113(3)	36(2)
C(111)	1948(10)	-1128(9)	4532(6)	46(4)
C(112)	2963(22)	-236(22)	5271(15)	106(9)
C(113)	1064(22)	-2257(16)	4993(13)	116(10)
O(12)	4127(5)	-2395(4)	3032(3)	42(2)
C(121)	4939(10)	-2371(8)	2274(6)	47(4)
C(122)	4143(15)	-3467(12)	1637(9)	71(6)
C(123)	6636(11)	-2532(14)	2811(9)	67(5)
S(5)	1123(2)	2733(2)	1211(1)	37(1)
S(6)	-856(2)	580(2)	2373(1)	34(1)
P(2)	136(2)	2425(2)	2330(1)	33(1)
O(21)	1343(5)	2675(4)	3360(3)	37(2)
C(211)	2386(10)	3927(8)	3514(6)	52(4)
C(212)	1832(19)	4664(11)	4156(9)	76(6)
C(213)	4052(14)	3616(15)	3956(11)	89(6)
O(22)	-1038(5)	3465(4)	2221(3)	38(2)
C(221)	-2398(9)	3634(8)	1356(6)	47(4)
C(222)	-3845(15)	3208(18)	1658(16)	113(9)
C(223)	-2294(15)	5018(10)	933(9)	71(5)

^a Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized $U(i,j)$ tensor.

The cluster anion in **1a** and the whole molecule in **4** have crystallographic point symmetry C_2 (close to idealized C_{2h}). The same symmetry occurs in other $\text{M}_2\text{Y}_4\text{L}_8$ complexes (where L is a unidentate ligand) and in the majority of $\text{M}_2\text{Y}_4(\text{LL})_4$ complexes (where LL is a η^2 bidentate ligand) (Table 6). However, in the last case, as it has been supposed,^{6c} the C_2 point symmetry (close to idealized D_2) can take place, as in $\text{V}_2\text{S}_4(\text{S}_2\text{CN}^i\text{Bu}_2)_4$,^{8a} with the metal-metal bond lying along the 2-fold axis. An equilibrium between C_2 and C_2 isomers can exist in solution. Data from Table 6 show that Nb-Nb bond distances in **1a** and **4** are somewhat longer than those in polymeric NbS_2Cl_2 ^{4b} and in molecular complex **2**. The Nb-S (for S_2) distances change to a smaller extent. Similar trends take place for other M_2Y_4 complexes: the variation of terminal ligands brings about marked changes in M-M bond lengths (up to 0.07 Å); corresponding M-S distances vary within 0.02 Å. The variation of M-M bond distances as a function of the terminal ligands has been studied earlier for triangular clusters having $\text{M}_3(\mu_3\text{-Y})(\mu\text{-Y})_3^{4+}$ and $\text{M}_3(\mu_3\text{-Y})(\mu\text{-Y})_3^{4+}$ cores (M_3Y_4 and M_3Y_7 types, respectively; $\text{M} = \text{Mo}, \text{W}$; $\text{Y} = \text{S}, \text{Se}$). It was shown that for the M_3Y_4 type the variations of M-M distances are more pronounced than for the M_3Y_7 type.¹³ On the other hand, there are some calculations pointing to the fact that M_3Y_4 clusters have weaker M-M bonds than those in M_3Y_7 .¹⁴ Drawing the analogy to dinuclear M_2Y_4 clusters, we can suppose that M-M bonding in clusters of the latter type is not strong, the bond order being significantly less than 1. This hypothesis gains some support from the comparison of the M-M distances: only for Nb_2S_4 are they close to those in niobium metal (2.858 Å). In the other cases corresponding values in the free metals are sufficiently shorter than in the complexes (2.622, 2.725, 2.741, and 2.402 Å for V, Mo, W, and Fe, respectively¹⁵). As one can see from Table 6, two Fe(IV) complexes have the

Table 4. Main Bond Lengths (Å) and Angles (deg) for **1a**

Bond Lengths			
Nb(1)-Nb(1a)	2.913(2)	S(1M)-S(2M)	2.012(3)
Nb(1)-S(1M)	2.513(3)	Nb(1)-S(2M)	2.510(3)
Nb(1)-S(1Ma)	2.508(3)	Nb(1)-S(2Ma)	2.509(3)
Nb(1)-N(1)	2.20(1)	Nb(1)-N(2)	2.19(1)
Nb(1)-N(3)	2.17(1)	Nb(1)-N(2)	2.20(1)
S(1)-C(1)	1.62(2)	S(2)-C(2)	1.63(2)
S(3)-C(3)	1.62(2)	S(4)-C(4)	1.63(2)
C(1)-N(1)	1.14(1)	C(2)-N(2)	1.15(2)
C(3)-N(3)	1.15(1)	C(4)-N(4)	1.13(1)
Valence Angles			
S(1M)-Nb(1)-S(2M)	47.2(1)	S(1M)-Nb(1)-N(1)	122.5(3)
S(2M)-Nb(1)-N(1)	76.4(3)	S(1M)-Nb(1)-N(2)	86.0(3)
S(2M)-Nb(1)-N(2)	86.2(3)	S(1M)-Nb(1)-N(3)	155.5(3)
S(2M)-Nb(1)-N(3)	156.1(3)	S(1M)-Nb(1)-N(4)	77.5(3)
S(2M)-Nb(1)-N(4)	123.5(3)	N(1)-Nb(1)-N(2)	78.9(4)
N(1)-Nb(1)-N(3)	79.7(4)	N(2)-Nb(1)-N(3)	88.9(4)
N(1)-Nb(1)-N(4)	147.9(4)	N(2)-Nb(1)-N(4)	77.9(4)
N(3)-Nb(1)-N(4)	78.0(4)	Nb(1)-S(1M)-Nb(1a)	70.9(1)
Nb(1)-S(2M)-Nb(1a)	71.0(1)	Nb(1)-S(1M)-S(2M)	66.3(1)
Nb(1)-S(2M)-S(1M)	66.4(1)		

Table 5. Main Bond Lengths (Å) and Angles (deg) for **4**

Bond Lengths			
Nb(1)-Nb(1a)	2.898(1)	S(1)-S(2)	2.011(3)
Nb(1)-S(1)	2.504(2)	Nb(1)-S(2)	2.488(2)
Nb(1)-S(1a)	2.507(2)	Nb(1)-S(2a)	2.488(2)
Nb(1)-S(3)	2.619(2)	Nb(1)-S(4)	2.645(2)
Nb(1)-S(5)	2.622(2)	Nb(1)-S(6)	2.664(2)
S(3)-P(1)	2.003(2)	S(4)-P(1)	1.982(2)
S(5)-P(2)	2.001(3)	S(6)-P(2)	1.976(2)
Valence Angles			
S(1)-Nb(1)-S(2)	47.5(1)	S(1)-Nb(1)-S(3)	77.1(1)
S(2)-Nb(1)-S(3)	122.5(1)	S(1)-Nb(1)-S(4)	151.2(1)
S(2)-Nb(1)-S(4)	159.3(1)	S(1)-Nb(1)-S(5)	127.5(1)
S(2)-Nb(1)-S(5)	81.3(1)	S(1)-Nb(1)-S(6)	85.8(1)
S(2)-Nb(1)-S(6)	82.0(1)	S(3)-Nb(1)-S(4)	74.1(1)
S(5)-Nb(1)-S(6)	74.6(1)	S(3)-Nb(1)-S(5)	141.8(1)
S(4)-Nb(1)-S(5)	78.1(1)	S(3)-Nb(1)-S(6)	79.6(1)
S(4)-Nb(1)-S(6)	89.8(1)	Nb(1)-S(1)-Nb(1a)	70.7(1)
Nb(1)-S(2)-Nb(1a)	71.3(1)	Nb(1)-S(1)-S(2)	65.8(1)
Nb(1)-S(2)-S(1)	66.7(1)		

Y_2)⁴⁺ cores (M_3Y_4 and M_3Y_7 types, respectively; $\text{M} = \text{Mo}, \text{W}$; $\text{Y} = \text{S}, \text{Se}$). It was shown that for the M_3Y_4 type the variations of M-M distances are more pronounced than for the M_3Y_7 type.¹³ On the other hand, there are some calculations pointing to the fact that M_3Y_4 clusters have weaker M-M bonds than those in M_3Y_7 .¹⁴ Drawing the analogy to dinuclear M_2Y_4 clusters, we can suppose that M-M bonding in clusters of the latter type is not strong, the bond order being significantly less than 1. This hypothesis gains some support from the comparison of the M-M distances: only for Nb_2S_4 are they close to those in niobium metal (2.858 Å). In the other cases corresponding values in the free metals are sufficiently shorter than in the complexes (2.622, 2.725, 2.741, and 2.402 Å for V, Mo, W, and Fe, respectively¹⁵). As one can see from Table 6, two Fe(IV) complexes have the

- (14) (a) Chen Zhida; Lu Jiaxi; Liu Chunwan; Zhang Gianer. *Polyhedron* **1991**, *10*, 2799. (b) Sztterenber, L. *Polyhedron* **1990**, *9*, 2585.
- (15) Barret, Ch. S.; Massalsky, T. B. *Structure of metals*; Metallurgija: Moscow, 1984; Vol. 2.
- (16) Allman, R.; Baumann, I.; Kutoglu, A.; Rosch, H.; Hellner, E. *Naturwissenschaften* **1964**, *51*, 263.
- (17) (a) Kocaba, T. O.; Young, Ch. G.; Tiekink, E. T. R. *Inorg. Chim. Acta* **1990**, *174*, 143. (b) Marcoll, J.; Rabenau, A.; Mootz, D.; Wunderlich, H. *Rev. Chim. Miner.* **1974**, *11*, 607. (c) Volkov, S. V.; Mikhailov, Yu. N.; Kolesnichenko, V. L.; Kanishcheva, A. S.; Timoshchenko, N. I. *J. Coord. Chem.* **1988**, *A17*, 367. (d) Muller, A.; Nolte, W. O.; Krebs, B. *Inorg. Chem.* **1980**, *19*, 2835. (e) Fenske, D.; Czeska, B.; Schumacher, C.; Schmidt, R. E.; Dehnicke, K. Z. *Angew. Chem.* **1985**, *520*, 7. (f) Fedin, V. P.; Geras'ko O. A.; Fedorov, V. Ye.; Slovohtov, Yu. L.; Struchkov, Yu. T. *Izv. Sib. Otd. Acad. Nauk SSSR, Ser. Khim.* **1988**, *19*, 64. (g) Virovets, A. V.; Slovohtov, Yu. L.; Struchkov, Yu. T.; Fedorov, V. Ye.; Mironov, Yu. V.; Fedin, V. P. *Koord. Khim.* **1990**, *19*, 198.

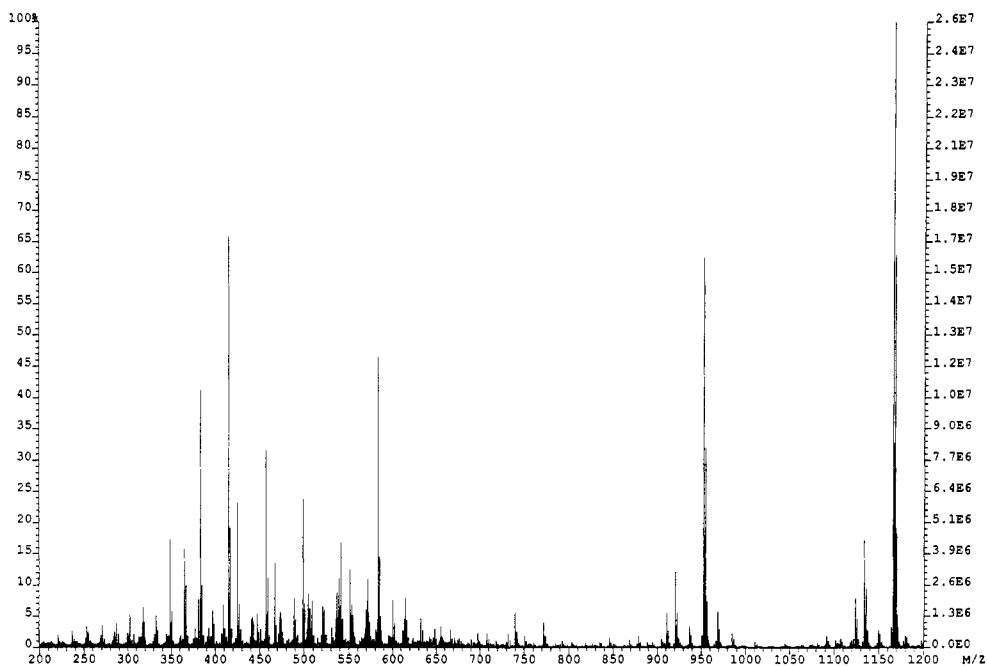


Figure 3. FAB mass spectrum of **2**.



Figure 4. FAB mass spectrum of **4**.

shortest M–S₂ bonds. The Fe–Fe distances are practically nonbonding, on the contrary. With the S–S distances in the disulfur ligands, they practically do not vary in the compounds under consideration.

The metal atoms in **1a** and **4**, as well as in the other compounds listed in Table 6 (excepting those of Fe), have coordination number 8 in a distorted square antiprismatic environment. Bond distances and angles in the isothiocyanate ligands and the heterocyclic cation (for **1a**) and the dithiophosphate ligands (for **4**) have their usual values.

Mass Spectrometry. The FAB⁺ mass spectra of **2** and **4** are shown in Figures 3 and 4. Both spectra are dominated by the peaks of the molecular ions Nb₂S₄L₄⁺. The detection of these species as monocationic ions indicates an oxidation reaction and the formation of a mixed-valent Nb(IV)/Nb(V) complex. This is understandable if one considers that the 3-nitrobenzyl alcohol matrix reacts as an oxidizing agent under FAB conditions.^{10a} Assignments of the major daughter ions are presented in Table 7. These ions were readily identified by their characteristic isotope patterns caused by the ³²S/³⁴S ratio of 22.5. Since the fragmentation reactions occur mainly in the matrix, the observed fragmentation products are a useful indicator for the elucidation of the possible reactivity of these complexes in solution.^{10b} Four different types of fragmentation reactions were observed: (i) elimination of one or two sulfur atoms; (ii) dissociation of one or two ligand molecules; (iii) formation of mononuclear complexes; (iv) fragmentation reactions within the ligand itself (only observed for **4**). Some of these reactions are

- (18) (a) Ogino, H.; Tobita, H.; Inomata, S.; Shimai, M. *J. Chem. Soc., Chem. Commun.* **1988**, 586. (b) Brunner, H.; Merz, A.; Pfauntsch, J.; Serhadli, O.; Wachter, J.; Ziegler, M. L. *Inorg. Chem.* **1988**, *27*, 2055.
- (19) (a) Zardon, M.; Gunthard, H. H. *J. Chem. Phys.* **1966**, *44*, 2010. (b) Gajnullin, I. F.; Garif'janov, N. S.; Kozyrev, B. M. *Dokl. Acad. Nauk SSSR* **1968**, *180*, 858.
- (20) (a) Sheldrick, G. M. In *Crystallographic Computing*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: London, 1985; Vol. 3. (b) Gerr, R. G.; Yanovskii, A. I.; Struchkov, Yu. T. *Kristallografija* **1983**, *28*, 1029.

Table 6. Geometrical Characteristics (Å) of Complexes Containing the $M_2(\mu, \eta^2-S_2)_2$ Fragment

compd	$d(M-M)$	$d(M-S(S_2))$: mean, range	$d(S-S)$	ref
M = Group 5 Transition Metal				
$[V_2(S_2)_2]$ (patronite)	2.83	2.40, 2.38–2.41	2.03	16
$V_2(S_2)_2(S_2CN^tBu)_4$	2.851	2.405, 2.402–2.413	1.997	8a
$V_2(S_2)_2(S_2CMe)_4$	2.800(2)	2.392, 2.366–2.412(3)	1.997(3)	8b
$V_2(S_2)_2(S_2CNEt_2)_4$	2.883(4)	2.409, 2.373–2.450(4)	1.985(4)	8c
$(Me_3NBz)_2[V_2(S_2)_2(CS_3)_4]$	2.841(6), 2.872(6)	2.415, 2.393–2.433(3)	2.012(3), 2.014(3)	8d
$V_2(S_2)_2(S_2CNEt_2)_4 \cdot 2CHBr_3$	2.900	2.413, 2.386–2.446(6)	2.00(1)	8e
$[Nb_2(S_2)_2Cl_8/2]$	2.871(4)	2.485, 2.484–2.486(6)	2.00(1)	3a
$Nb_2(S_2)_2(S_2CNEt_2)_4$	2.890(2)	2.494, 2.469–2.541(4)	2.282(5) ^a	12
$Nb_2(S_2)_2(S_2P(O^iPr)_2)_4$	2.898(1)	2.497, 2.488–2.504(2)	2.011(3)	c
$(C_{11}H_{13}N)_4[Nb_2(S_2)_2(NCS)_8]$	2.913(2)	2.510, 2.508–2.513(3)	2.012(5)	c
M = Group 6 Transition Metal				
$[Mo_2S_4(S_2CNEt_2)_4](BF_4)_2 \cdot 2CHBr_3$	2.808(1)	2.436, 2.426–2.444(2)	1.999(2)	17a
$[Mo_2(S_2)_2Cl_4Cl_4/2]$	2.833(2)	2.432, 2.404–2.458(2)	1.980(3)	17b
$[Mo_2(S_2)_2Br_6(SeBr_2)_2]$	2.801(3)	2.427, 2.413–2.437(6)	2.026(8)	17c
$(NH_4)_2[Mo_2(\mu-S_2)_2(S_2)_4] \cdot 2H_2O$	2.827(2)	2.444, 2.382–2.507(4)	2.043(5)	17d
$(Ph_3MeP)_2[Mo_2(S_2)_2Cl_8] \cdot 2CH_2Cl_2$	2.858	2.425, 2.422–2.430	1.981	17e
$(Ph_3EtP)_2[Mo_2(S_2)_2Cl_8] \cdot CH_2Cl_2$	2.856	2.423, 2.421–2.425	1.974	17f
$(Ph_3MeP)_2[Mo_2(S_2)_2Br_8] \cdot 3CH_2Br_2$	2.854	2.417, 2.402–2.424	1.984	17e
$(Et_4N)_2[W_2(S_2)_2Br_8]$	2.835(1)	2.428, 2.416–2.437(2)	2.004(2)	17g
$[W_2(S_2)_2Br_6(SeBr_2)_2]$	2.792(2)	2.43, 2.41–2.43(1)	1.99(1)	17c
M = Group 8 Transition Metal				
$[Cp_2^*Fe_2(S_2)_2](PF_6)_2$ ($Cp^* = \eta^5-C_5Me_5$)	2.856	2.282, 2.276–2.288	1.983	18a
$[Cp_2^*Fe_2(S_2)_2]I_2 \cdot 2CH_2Cl_2$	2.883(3)	2.275, 2.272–2.282(4)	2.014(5) ^b	18b

^a May be so long due to total disorder of the molecule. ^b This values taken from the paper's Table 2. Different values of bond lengths may be calculated from cell constants and atomic coordinates taken from the paper. ^c Present work.

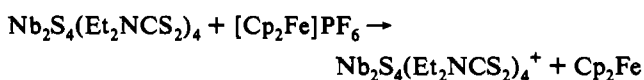
Table 7. FAB MS Data for $Nb_2(S_2)_2(dtc)_4$ and $Nb_2(S_2)_2(S_2P(iPrO)_2)_4$: Relative Intensities (%) of the Major Nb-Containing Ions^a

	$Nb_2(S_2)_2(dtc)_4$	$Nb_2(S_2)_2(S_2P(iPrO)_2)_4$
$Nb_2(S_2)_2L_4^+$	100	100
$Nb_2(S_2)_2L_4^+ - CH_2=CHCH_3$		8
$Nb_2(S_2)(S)L_4^+$	7	17
$Nb_2(S_2)L_4^+$	4	
$Nb_2(S_2)L_3^+$	40	62
$Nb_2(S_2)L_3^+ - CH_2=CHCH_3$		6
$Nb_2(S_2)(S)L_3^+$	10	12
$Nb_2(S_2)L_2^+$	7	4
$Nb_2(S_2)(S)L_2^+$	4	
$NbS_2L_2^+$	10	47
$NbSL_2^+$	14	12
$NbS_2L_2^+ - CH_2=CHCH_3$		17
$NbS_2L_2^+ - 2CH_2=CHCH_3$		24
$NbS_2L_2^+ - 3CH_2=CHCH_3$		31
$NbS_2L_2^+ - 4CH_2=CHCH_3$		67
$NbSL_2^+ - 4CH_2=CHCH_3$		41

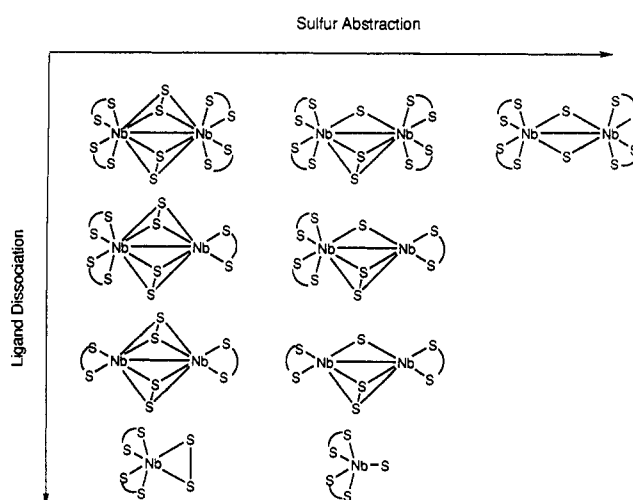
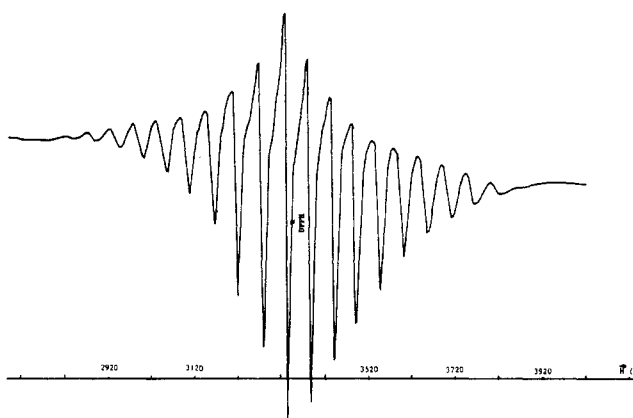
^a $dtc = S_2CNEt_2$.

well established, e.g. the conversion of disulfur bridges to the corresponding monosulfur bridges or the elimination of propene from the coordinated dithiophosphate diisopropyl ester. Possible structures are presented in Figure 5. Both ligand dissociation and sulfur abstraction as well have been observed in FAB MS of a variety of complexes containing the $Mo_3S(S_2)_3^{4+}$ core.^{10c} However, the formation of species of lower nuclearity has not been described in the previous studies. The significant amounts of mononuclear $NbSL_2^+$ and $NbS_2L_2^+$ indicate therefore a somewhat lower stability for the $Nb_2S_4^{4+}$ core.

ESR Spectra. The mixing of the solutions of **2** and $[Cp_2Fe]PF_6$ in CH_2Cl_2 immediately brings about a deep-violet color. Ferrocene was obtained from such solutions in more than 80% yield. We suppose that a one-electron oxidation of **2** takes place according to the following equation:



The ESR spectrum of the solution consists of 19 lines with an intensity ratio 1:2:3:4:5:6:7:8:9:10:9:8:7:6:5:4:3:2:1, A_{Nb} being 54 G and $g = 2.0113$ (Figure 6). This picture arises from the

Figure 5. Main fragmentation processes in FAB MS of **2** and **4**.Figure 6. ESR spectrum of the $Nb_2S_4(S_2CNEt_2)_4^+$ cation at 300 K.

hyperfine interaction between the unpaired electron and two equivalent niobium nuclei with $I = 9/2$. Temperature lowering does not result in localization of the electron on one of the niobium atoms (Figure 7). The changes observed on cooling are due to slowing down of the molecular motion, and eventually, when the

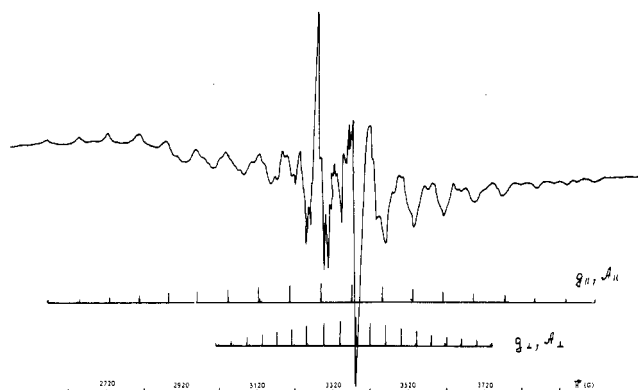


Figure 7. ESR spectrum of the Nb₂S₄(S₂CNET₂)₄⁺ cation at 77 K.

solution freezes, the anisotropy of Zeeman and hyperfine interactions is manifested.

The ESR spectra at 300 and 77 K are described with the following spin Hamiltonian: $H = \hat{g}\vec{H}\hat{S} + \sum_{i=1}^2 A_{\text{Nb}}^i \hat{S} \hat{I}_{\text{Nb}}^i + \sum_{j=1}^4 A_{\text{F}}^j \hat{S} \hat{I}_{\text{F}}^j$ with $g_{\parallel} = 2.0451$, $g_{\perp} = 1.9945$, $A_{\parallel}^1 = A_{\parallel}^2 = 80$ G, $A_{\perp}^1 = A_{\perp}^2 = 41$ G and further splitting on the four fluorine nuclei (from PF₆⁻) for g_{\parallel} and A_{\parallel}^i with $A = 15$ G. The presence of the unpaired d-electron, which is responsible for the observed paramagnetism of the cation radical, residing on two niobium atoms, points to the formally mixed-valence Nb(IV)/Nb(V) oxidation state. Most of the mixed-valence niobium complexes known so far contain Nb(III)/Nb(IV) and even Nb(II)/Nb(III) combinations, but almost all of those are in fact triangular or octahedral clusters.²¹ Similar one-electron oxidation (performed by Ag(I) or Hg(II) is known only for fulvalene-nitrene complexes of Nb(IV), with stable paramagnetic cations [$\eta^5\text{-C}_3\text{H}_4\text{C}_5\text{H}_4$](C₃H₅)₂Nb($\mu\text{-NC}_6\text{H}_4\text{R}$)₂)⁺ being formed (R = H, A

= 49.0 G; R = OMe, A = 49.5 G).²² In our case, however, the hyperfine interaction constants are substantially less than half of the characteristic value known for 4d¹ Nb(IV) ions both in octahedral and distorted tetrahedral environments.¹⁹ In addition, the values of the *g*-factors are significantly different from that for the pure d¹ state ($g > 2$). The differences observed can be explained as the result of the contribution of the p-orbitals of the bridging sulfur atoms to the wave function of the odd electron, the absence of the electron localization on cooling indicating that the delocalization to the sulfur atoms remains significant in the ground state. This conclusion is in good agreement with the calculations performed for the V₂S₄(CS₃)₄⁴⁻ anion, which has a HOMO of $\pi^*\text{-S}_2$ character with the metal contribution as small as 13%. The metal-metal interaction appears to be rather weak and is associated with deeper orbitals.^{8d} To the best of our knowledge no calculations were made for Nb₂S₄ clusters. A qualitative MO diagram of this fragment (*D*_{2h} symmetry) is given in ref 9. Anyway, one should not apply the scheme obtained for V to Nb in a straightforward manner. On the contrary, the results of valence-band X-ray electron spectroscopy of NbS₂Cl₂ indicate that the HOMO corresponds mainly to the Nb-Nb bond.²³ This can be considered as the manifestation of the general trend of strengthening of the metal-metal bond in the 3d-4d-5d series. Therefore, we have some grounds to suppose that the HOMO in the complexes 1-4 has a predominantly metallic character with a minor contribution of the π^* -orbitals of the S₂ ligands.

Supplementary Material Available: Tables of hydrogen atom coordinates and thermal parameters, bond lengths, bond angles, and anisotropic displacement coefficients for **1a** and **4** (13 pages). Ordering information is given on any current masthead page.

(21) Young, Ch. G. *Coord. Chem. Rev.* **1989**, *96*, 89.

(22) Lemenovskii, D. A.; Fedin, V. P.; Slovohotov, Yu. L.; Struchkov, Yu. T. *J. Organomet. Chem.* **1982**, *228*, 153.

(23) Kostikova, G. P.; Gorbachev, A. N.; Shchukarev, A. B.; Korol'kov, D. V. *Zh. Vses. Khim. O-va im. Mend.* **1987**, *32*, 107.