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Xanthate Complexes of $\{Nb_2S_4\}^{4+}$

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Abstract—Alkyl xanthate complexes $[Nb_2S_4(S_2COR)_4]$ (R = Et (**I**), *iso*-Pr (**II**), *n*-Bu (**III**), and *iso*-Am (**IV**)) are synthesized by the ligand exchange reaction in solutions from $(Et_4N)_4[Nb_2S_4(NCS)_8]$ and the corresponding potassium salts in satisfactory yields. The X-ray diffraction analyses are carried out for the isopropyl xanthate (**II**) and butyl xanthate (**III**) complexes. From the view point of mutual arrangement of chelate cycles, complexes **II** and **III** exist in crystals as ΛΔ isomers. The niobium–niobium distances are 2.8789(4) Å in complex **II** and 2.8856(3) Å in complex **III**. The first example for the formation of short S···S contacts between the disulfide ligands of the $\{Nb_2S_4\}^{4+}$ fragments in the crystal structure of **III** is found (3.146 Å).

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INTRODUCTION

Niobium is characterized by the formation of stable binuclear clusters with the framework $\{Nb_2(\mu_2\text{-}S_2)_2\}^{4+}$. Many diverse derivatives are known: complexes $[Nb_2S_4X_8]^{4-}$ (X = Cl, Br, NCS), aqua complex $[Nb_2S_4(H_2O)_8]^{4+}$, and complexes with bidentate ligands (oxalates, β-diketonates, dithiocarbamates, dithiophosphates, and others) [1]. Thiohalides NbS_2X_2 (X = Cl, Br) described by the crystal chemical formula $^{2}_{\infty}[Nb_2(\mu\text{-}S_2)_2X_{8/2}]$, being 2D layered coordination polymers, are the starting compounds for the synthesis of binuclear complexes [2]. These $[Nb_2S_4(NCS)_8]^{4-}$ complexes are very inert but can be transformed into the $[Nb_2S_4(NCS)_8]^{4-}$ complex, whose isothiocyanate ligands are rather labile, in turn, to be substituted by bidentate ligands such as dithiocarbamate, dithiophosphate, or xanthate, and can be hydrolytically decomposed to form aqua complex $[Nb_2S_4(H_2O)_8]^{4+}$ [3]. The thermolysis of these compounds can be used for the preparation of niobium sulfides under fairly mild conditions [4, 5]. The cluster group $\{Nb_2(\mu_2\text{-}S_2)_2\}^{4+}$ can be interesting for catalytic processes of hydrogenation, alkene and alkyne activation, and hydrodesulfurization [6]. In this work, we report the syntheses and X-ray structure of a series of xanthogenate complexes $[Nb_2S_4(S_2COR)_4]$ (R = Et (**I**), *iso*-Pr (**II**), *n*-Bu (**III**), and *iso*-Am (**IV**)).

EXPERIMENTAL

All experiments were carried out in air. Solvents were purified using standard procedures. The starting reagents were commercial (Reakhim) and used without additional purification. The starting complex $(Et_4N)_4[Nb_2S_4(NCS)_8]$ was synthesized according to a described procedure [3]. IR spectra were recorded on a Scimitar FSC 2000 spectrophotometer (KBr pellets). Elemental analyses were carried out at the Analytical Laboratory of the Nikolaev Institute of Inorganic Chemistry (Siberian Branch, Russian Academy of Sciences).

Synthesis of $[Nb_2S_4(S_2COC_2H_5)_4]$ (I). A suspension of $(Et_4N)_4[Nb_2S_4(NCS)_8]$ (600 mg, 460 μmol) in CH_2Cl_2 (20 mL) was stirred with a solution of $KS_2COC_2H_5$ (800 mg, 5 mmol) in water (20 mL) for 12 h. The dark red organic phase was separated from the aqueous layer, dried above anhydrous $CaCl_2$, and evaporated to dryness. The obtained red oily substance was dissolved in a minimum volume of CH_2Cl_2 and deposited on a chromatographic column (silica gel 100/60, eluent CH_2Cl_2). The single red fraction was collected and evaporated to obtain complex **I**.

For $C_{12}H_{20}S_{12}Nb_2$			
anal. calcd., %:	C, 18.0;	H, 2.5;	S, 48.2.
Found, %:	C, 18.6;	H, 3.4;	S, 48.8.

IR, ν, cm^{-1}: 2965m, 2073 m, 1717 br, 1464 m, 1366 m, 1260 s, 1102 s, 1040 s, 860 m, 800 s, 690 m, 560 m, 444 m, 396 m. ^1H NMR, $CDCl_3$, δ, ppm: 1.50 (m, CH_3 with relative intensity 3.0), 4.60 (m, CH_2 with relative intensity 1.9). ^{13}C NMR, $CDCl_3$; δ, ppm: 1.5 (br.s, CH_3), 53.4 (br.s, CH_2), 225.5, 25.7 (s, COS_2).

Synthesis of $[Nb_2S_4(S_2CO\text{-}\textit{iso}\text{-}C_3H_7)_4]$ (II). The crude product was obtained similarly to the previous one using potassium isopropyl xanthate. Red single crystals were obtained by recrystallization from a chloroform–ethanol system.

For $C_{16}H_{28}S_{12}Nb_2$

anal. calcd., %:	C, 22.5;	H, 3.3;	S, 45.0.
Found, %:	C, 24.8;	H, 3.9;	S, 44.4.

IR, ν, cm^{-1}: 2965 s, 1729 m, 1460 m, 1446 m, 1371 m, 1346 m, 1261 s, 1139 m, 1088 s, 1028 s, 898 m, 802 m, 754 m, 555 w, 462 m, 391 w. ^1H NMR, $CDCl_3$, δ, ppm: 1.43 (m, CH_3 with relative intensity 6.2), 5.65 (m, CH with relative intensity 1.0). ^{13}C NMR, $CDCl_3$, δ, ppm: 2.2 (br.s, CH_3), 53.4 (br.s, CH), 224.7, 224.9 (s, COS_2).

Synthesis of $[Nb_2S_4(S_2CO\text{-}\textit{n}\text{-}C_4H_9)_4]$ (III). The crude product was obtained similarly to the previous one using potassium *n*-butyl xanthate. Dark red crystals were obtained by recrystallization from chloroform.

For $C_{20}H_{36}S_{12}Nb_2$

anal. calcd., %:	C, 26.4;	H, 4.0.
Found, %:	C, 26.1;	H, 4.0.

IR, ν, cm^{-1}: 3408 br, 2961 s, 2930 s, 2874 m, 2076 m, 1728 w, 1633 w, 1568 w, 1491 m, 1459 m, 1398 m, 1261 s, 1236 s, 1174 m, 1098 s, 1022 s, 800 s, 660 m, 614 m, 492 w, 398 w. ^1H NMR, $CDCl_3$, δ, ppm: 1.0 (m, CH_3 with relative intensity 3.1), 1.47 (m, CH_2 with relative intensity 2.2), 1.82 (m, CH_2 with relative intensity 1.95), 4.56 (m, CH_2 with relative intensity 2.0). ^{13}C NMR, $CDCl_3$; δ, ppm: 13.0 (br.s, CH_3), 19.5 (br.s, CH_2), 30.7 (br.s, CH_2), 72.9 (br.s, CH_2), 225.6, 225.8 (s, COS_2).

Synthesis of $Nb_2S_4(S_2CO\text{-}\textit{iso}\text{-}C_5H_{11})_4]$ (IV). The crude product was obtained similarly to the previous one using potassium isoamyl xanthate.

For $C_{20}H_{44}S_{12}Nb_2$

anal. calcd., %:	C, 29.8;	H, 4.6;	S, 39.8.
Found, %:	C, 30.1;	H, 5.2;	S, 39.8.

IR, ν, cm^{-1}: 2956 s, 2442 br, 1731 m, 1464 m, 1385 m, 1344 m, 1242 s, 1204 s, 1047 s, 928 m, 801 m, 557 w, 498 w. ^1H NMR, $CDCl_3$, δ, ppm: 0.98 (multiplet CH_3 with relative intensity 6.0), 1.47 (multiplet CH_2 with relative intensity 1.9), 1.74 (multiplet CH with relative intensity 1.0), 4.60 (multiplet CH_2 with relative intensity 1.9). ^{13}C NMR, $CDCl_3$; δ, ppm: 22.9 (br.s, CH_3), 25.5 (br.s, CH), 37.3 (br.s, CH_2), 71.8 (br.s, CH_2), 225.5, 225.7 (s, COS_2).

X-ray diffraction analyses. Single crystals of compounds **II** and **III** suitable for X-ray diffraction analysis were obtained by slow crystallization from chloroform. All measurements were carried out at 150 K using a standard procedure on a Bruker-Nonius X8 Apex automated four-circle diffractometer equipped with a CCD two-coordinate detector (MoK_α, graphite monochromator, $\lambda = 0.71073$ Å). An absorption correction was applied empirically using the SADABS program [7]. The structures were solved by a direct method and refined by full-matrix least squares using the SHELXL program package [8]. Hydrogen atoms were placed in geometrically calculated positions. The crystallographic characteristics and details of diffraction experiments are given in Table 1. Selected bond lengths are listed in Table 2. The atomic coordinates and thermal parameters were deposited with the Cambridge Crystallographic Data Centre (915219 (**II**), 915220 (**III**); deposit@ccdc.cam. ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Alkyl xanthate complexes $[Nb_2S_4(S_2COR)_4]$ (R = Et (**I**), *iso*-Pr (**II**), *n*-Bu (**III**), and *iso*-Am (**IV**)) were synthesized by the ligand exchange reaction in solutions from $(Et_4N)_4[Nb_2S_4(NCS)_8]$ and the corresponding potassium salts in satisfactory yields. The substances are orange powders stable in air and highly soluble in chloroform and dichloromethane. Single crystals suitable for X-ray diffraction analysis were obtained after chromatographic purification for the isopropyl xanthate (**II**) and *n*-butyl xanthate (**III**) complexes. The IR spectra of the complexes contain characteristic bands of stretching vibrations of the xanthate ligands (cm^{-1}): 1040 (**I**), 1028 (**II**), 1022 (**III**), and 1047 (**IV**). The sulfur–sulfur bond stretching vibrations of the coordinated disulfide ligands appear as weak bands at 550–560 cm^{-1}. The characteristic absorption peaks in the IR spectra for the synthesized complexes and their assignment are presented in Table 3.

The structures of complexes **II** and **III** (Fig. 1) are typical of coordination compounds based on the cluster core $\{Nb_2S_4\}^{4+}$. Two disulfide ligands are coordinated to Nb_2 according to the μ_2-η^2:η^2 mode. The coordination environment of each niobium atom is supplemented by two bidentate-chelating alkyl xanthate ligands coordinated through the sulfur atoms. In both complexes, the molecules are localized at the inversion centers arranged in the middle of the Nb–Nb section. The Nb–Nb spacings in compounds **II** and **III** are somewhat elongated compared to the distances observed in the coordination polymer, thiochloride $[Nb_2S_4Cl_{8/2}]_\infty$ (2.873(3) Å [9]). The scatter of Nb–S spacings in the cluster fragment $\{Nb_2(S_2)_2\}$ for two sulfur atoms in thiochloride is substantially lower

Table 1. Crystallographic data and the diffraction experiment and structure refinement parameters for complexes **II** and **III**

Parameter	Value	
	II	**III**
M	854.92	911.03
Crystal system	Triclinic	Triclinic
Space group; Z	$P\bar{1}$; 1	$P\bar{1}$; 1
a, Å	7.5481(2)	6.29940(10)
b, Å	11.0953(4)	10.4370(3)
c, Å	11.2472(6)	13.5966(4)
α, deg	117.728(2)	77.7560(10)
β, deg	107.773(2)	77.2620(10)
γ, deg	93.0170(10)	88.0480(10)
V, Å^3	772.51(5)	852.02(4)
ρ_{calcd}, g/cm^3	1.838	1.776
μ, mm^{-1}	1.576	1.435
F(000)	430	462
Crystal sizes, mm	0.25 × 0.12 × 0.10	0.40 × 0.30 × 0.03
θ Range of data collection, deg	2.13–31.37	2.27–30.99
Reflection index ranges	$-9 \le h \le 10, -13 \le k \le 15, -16 \le l \le 14$	$-5 \le h \le 8, -14 \le k \le 13, -19 \le l \le 16$
Measured/independent reflections	9011/3648	7095/4069
R_{int}	0.0273	0.0237
Reflections with $I \ge 2\sigma(I)$	3169	3620
Number of refined parameters	158	174
Goodness-of-fit (all reflections)	1.032	1.046
R_1 ($I > 2\sigma(I)$)	0.0285	0.0237
wR_2 (all reflections)	0.0633	0.0521
Residual electron density (min/max), e/Å^3	–0.426/0.643	–0.540/0.479

Table 2. Selected bond lengths (Å) in the structures of complexes **II** and **III**

Bond	*d*, Å	Bond	*d*, Å
II		**III**	
Nb(1)–Nb(1)'	2.8789(4)	Nb(1)–Nb(1)'	2.8856(3)
Nb(1)–S(1)'	2.5064(7)	Nb(1)–S(1)	2.4970(5)
Nb(1)–S(1)	2.5108(7)	Nb(1)–S(1)'	2.4986(5)
Nb(1)–S(2)'	2.4812(7)	Nb(1)–S(2)'	2.5011(5)
Nb(1)–S(2)	2.4962(7)	Nb(1)–S(2)	2.5021(5)
Nb(1)–S(11)	2.5906(7)	Nb(1)–S(3)	2.5832(5)
Nb(1)–S(12)	2.6217(7)	Nb(1)–S(4)	2.6009(5)
Nb(1)–S(21)	2.5907(7)	Nb(1)–S(5)	2.5997(5)
Nb(1)–S(22)	2.5968(7)	Nb(1)–S(6)	2.6007(5)
S(1)–S(2)	2.0362(9)	S(1)–S(2)	2.0305(7)

(2.484(5)–2.487(6) Å) than those for compounds **II** and **III** (Table 2). This is most likely due to the coordination of the bidentate-chelating sulfur-containing ligands in compounds **II** and **III** instead of the bridging chlorine atoms in the polymer, because a similar phenomenon is observed in structures of the dithiocarbamate and dithiophosphate complexes [3, 6, 10].

In spite of a seeming complexity in the representation of the geometry of isomers for the coordination number 8, there is a distinct method for relating any coordination polyhedron with eight vertices to three basic polyhedra: cube, square antiprism, and trigonal dodecahedron. A characteristic of antiprism distortion is the angle α between the 4-fold inversion axis and the metal–ligand bond. The dodecahedron is characterized by two angles: φ_a and φ_b. Since the real polyhedron around niobium in compounds **II** and **III** can be considered to an equal extent as a strongly distorted dodecahedron and an antiprism, we introduced additional angular characteristics (Fig. 2). The resulting angular parameters of the $\{NbS_4(LL)_2\}$ node are presented in Table 4. These data show that the coordination polyhedron NbS_8 is a unique "hybrid" of a dodecahedron and a square antiprism.

Geometric isomers are formed upon the coordination of four bidentate ligands to the $\{Nb_2S_4\}^{4+}$ group. If the disulfide ligands are approximated as monodentate ones (at the center of the sulfur–sulfur bond), a distorted octahedron appears around each niobium atom. The Δ- and lambda isomers related to different orientations of the chelate cycles exist for the distorted octahedron. As a whole, three isomers, ΔΔ, ΛΔ, and ΛΛ, are possible in $[Nb_2S_4(LL)_4]$ (LL is the bidentate ligand), whereas the ΛΔ and ΛΛ isomers have no symmetry centers and are pairs of enantiomers. Complexes **II** and **III** are present in crystals as ΛΔ isomers, and their geometric centers are localized at the inversion centers. The mutual molecular packing in crystal is provided, most likely, by the sulfur–sulfur contacts and the densest packing of the alkyl radicals. Structure **III** contains short intermolecular contacts S···S 3.146 Å between the atoms of the disulfide ligands of the adjacent molecules (Fig. 3). Taking into account that the S_2^{2-} ligand is isoelectronic to halogen molecules, the formation of these contacts resembles the formation of shortened contacts in the structures of solid halogens and interhaloid compounds (for example, in the Cl_2 structure, the shortest intermolecular contacts are 3.32 Å) [11]. No similar phenomena

Table 3. Assignment of absorption bands in the IR spectra of complexes **I–IV**

Compounds	ν(C–O)	ν(C=S)	ν(C–S)	ν(Nb–S)
$[Nb_2(S_2)_2(C_2H_5OCS_2)_4]$ (**I**)	1102	1260	1040	560
$[Nb_2(S_2)_2(C_3H_7OCS_2)_4]$ (**II**)	1088	1261	1028	555
$[Nb_2(S_2)_2(C_4H_9OCS_2)_4]$ (**III**)	1098	1261	1022	555
$[Nb_2(S_2)_2(C_5H_{11}OCS_2)_4]$ (**IV**)	1047	1242	1047	557

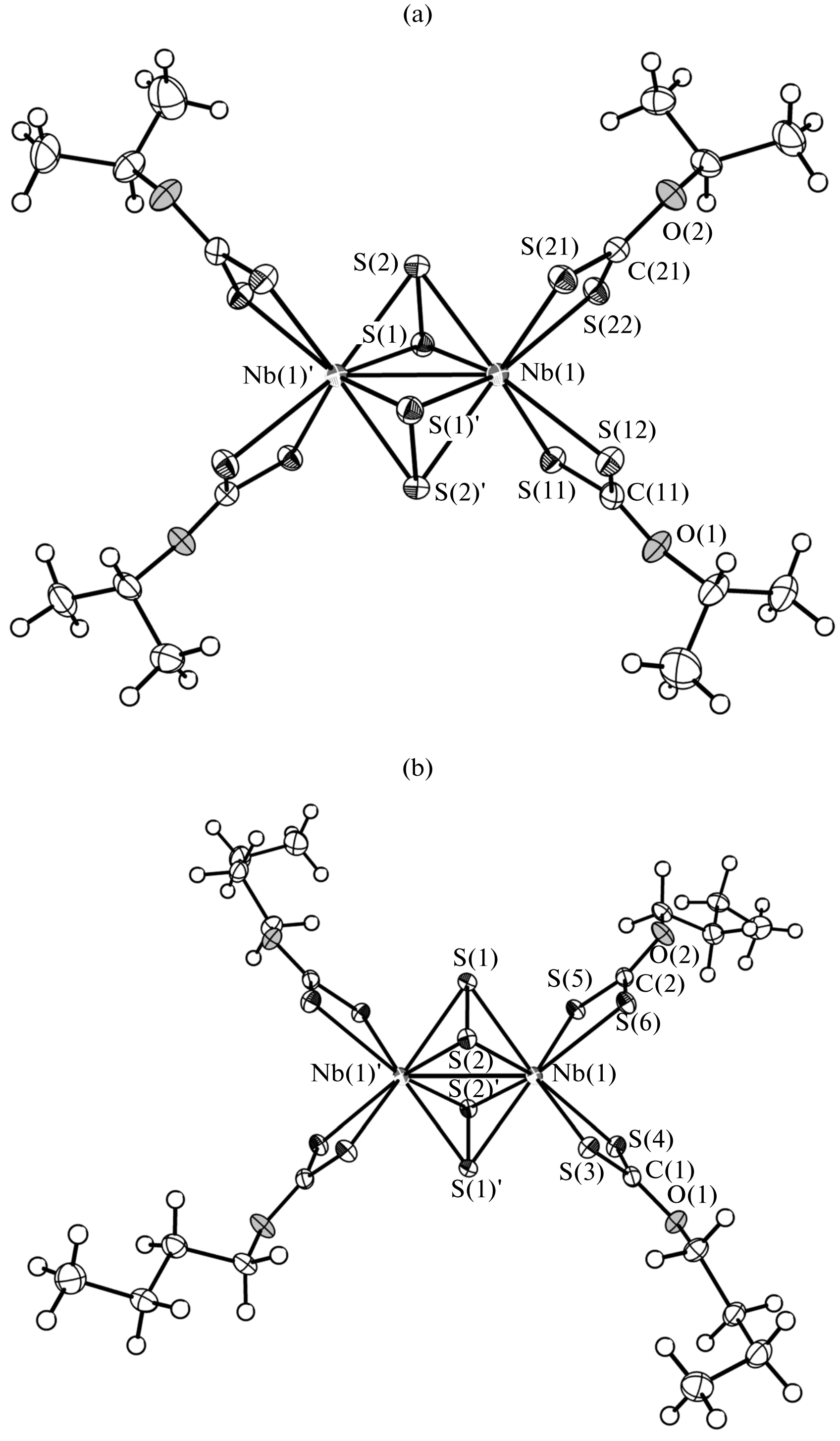

Fig. 1. Structures of complexes (a) **I** and (b) **III** (ellipsoids of atomic replacements with 50% probability).

were observed earlier in other complexes with the $\{Nb_2S_4\}^{4+}$ core in which the disulfide ligands are nearly symmetrically coordinated. On the contrary, intermolecular contacts of this type are characteristic of the $\{Mo_3S_7\}^{4+}$ derivatives containing asymmetrically coordinated ligands μ_2-η^2:η^2. Asymmetric coor-

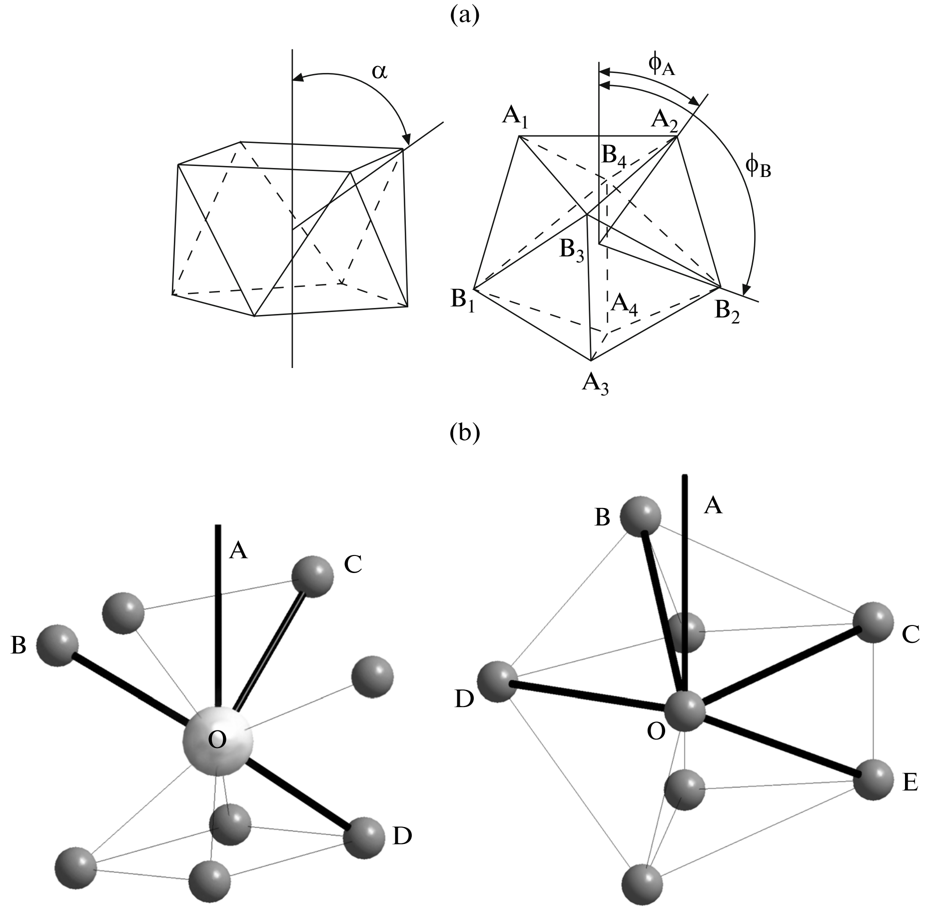

Fig. 2. Angular parameters of (a) square antiprism and trigonal dodecahedron and (b) the $\{NbS_4(LL)^2\}$ node: A–O–B = $\alpha(LL^2)$, A–O–C = $\alpha(LL^1)$, A–O–D = $\alpha(\mu)$, and A–O–B = $\varphi_a(LL)$, A–O–C = $\varphi_a(\mu)$, A–O–D = $\varphi_b(LL)$, A–O–E = $\varphi_b(\mu)$s, respectively.

dination induces a noticeable polarization of the disulfide ligand favoring the formation of short intermolecular contacts [12].

Since the reaction conditions have no prerequisites for the formation of the lambdadelta isomer only, it seems reasonable to conclude that a pair of noncen-

Table 4. Characteristics of the coordination polyhedra around the niobium atoms in structures **II** and **III**

Compound	$\alpha(LL^1)$	$\alpha(LL^2)$	$\alpha(\mu)$	$\varphi_a(LL)$	$\varphi_a(\mu)$	$\varphi_b(LL)$	$\varphi_b(\mu)$
	deg						
II	66	44	55	15	71	99	117
III	67	44	55	14	70	99	115
Antiprism	57	57	57				
Dodecahedron				36	36	108	108

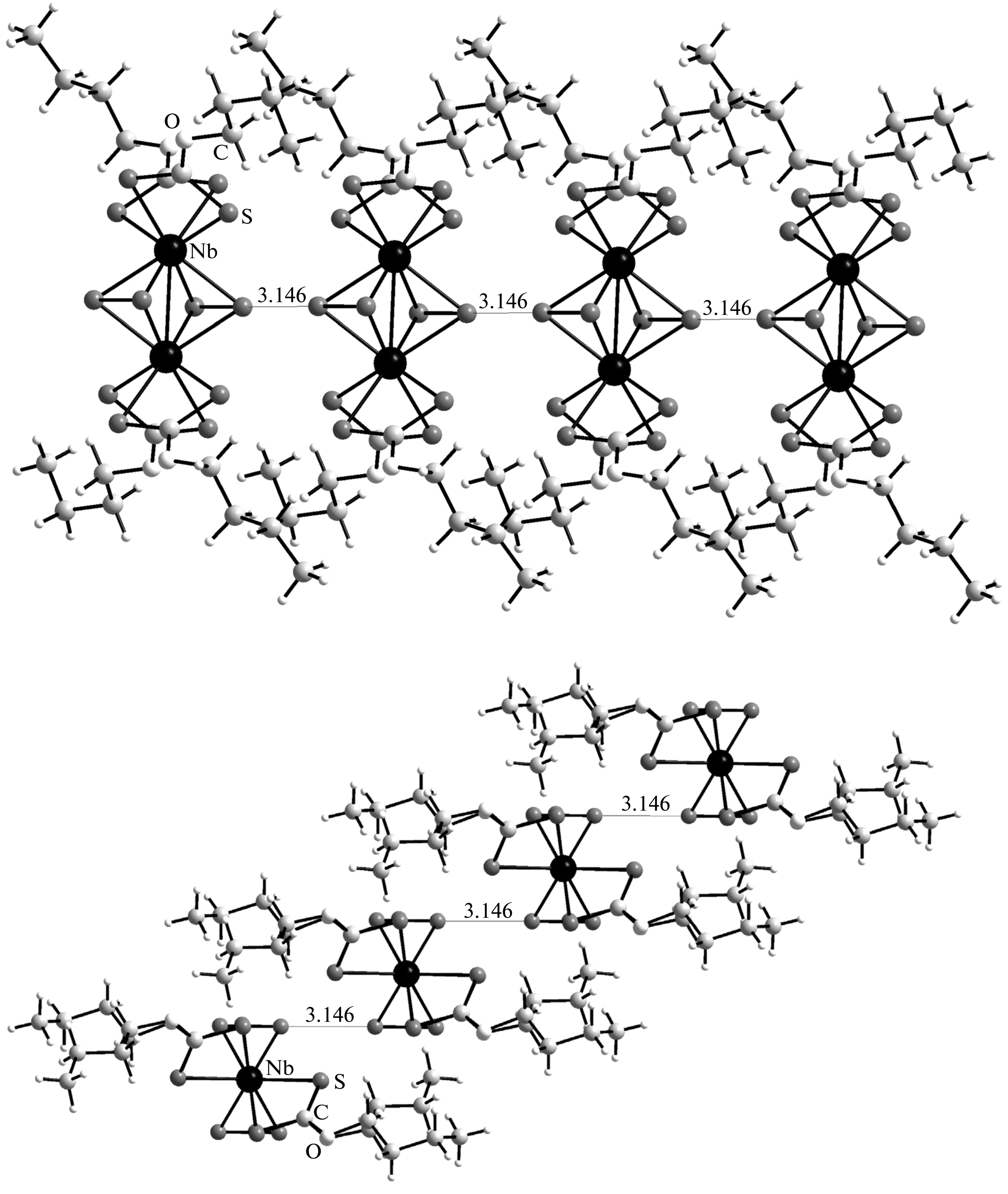

Fig. 3. Short intermolecular S–S contacts in crystal structure **III**.

trosymmetric isomers remain in the mother liquor upon crystallization and they can be detected by the NMR method. The ^{1}H NMR spectra of all complexes exhibit complicated multiplets caused by the superposition of the signals from the diastereomers. Two signals from the carbon atom of the CS_2 group of the centrosymmetric and noncentrosymmetric isomers remote from each other at a distance of 0.2 ppm can be distinguished in the ^{13}C NMR spectra. The difference in chemical shifts can be explained by the interaction of the electron density of the S–S bridges with closely arranged atoms. The carboxyl carbon atoms, being the nearest ones, are the most sensitive, whereas the signals from atoms lying farther in the chain give unresolved broad singlets. The signals from traces of the corresponding alcohols formed upon the hydrolysis of the ligands are observed as impurities in the ^{1}H NMR spectra. Thus, both isomers are formed in all cases.

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