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Review

Chalcogenide clusters of vanadium, niobium and tantalum

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Contents

Abstract

The synthesis, molecular and crystal structures and chemical transformations of homometal chalcogenide clusters of vanadium, niobium and tantalum are considered. These metals form stable binuclear, trinuclear, tetranuclear, pentanuclear and hexanuclear clusters with monochalcogenido (Q^{2-}) and dichalcogenido ($Q_2{}^{2-}$) bridges. The clusters can be accessed both by cluster assembly reactions in solutions and by high-temperature synthesis. In the latter case a cluster core can be further excised from resulting solids by diverse routes.

Keywords: Vanadium; Niobium; Tantalum; Clusters; Chalcogenides

1. Introduction

Chalcogenide clusters constitute a large and rapidly growing family of inorganic compounds and are a fascinating object for study [1,2]. Chalcogenide bridges such as Q^{2-} and $Q_2{}^{2-}$ are excellent ligands to support the formation of metallocluster cages of various nuclearity and they are able to keep the cluster core undestroyed even when the metal atoms are in their highest formal oxidation states. Hence they may act as electron reservoirs, which is important for superconductivity (the Chevrel phases based on Mo_6Q_8 [3]) and biocatalysis (the Fe_4S_4 clusters in the electrons transfer chains in the living organisms) [4]. Catalytic potential of chalcogenide clusters is spectacularly illustrated by the presence of the unique Fe_7MoS_9 cluster core in nitrogenase [5]. It is to no surprise, therefore, that much effort has been directed to create synthetic analogues of Fe/S, Mo/S and Mo–Fe/S clusters [6] and at present these two metals furnish by far the bigger part of known chalcogenide clus-

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ters. Progress in the chemistry of Group 6 chalcogenide clusters (mainly Mo and, to lesser degree, W) has been regularly updated [7]. However, during the 90s chemistry of chalcogenide clusters of other metals underwent a spectacular development. Last-decade progress in rhenium [8] and platinum metal chalcogenide cluster chemistry [9] has been reviewed. Recent results show that lanthanides are as prone to form clusters with bridging chalcogen atoms as transition elements [10]. The coinage metals (Cu and Ag) hold the record in cluster nuclearity in this field (e.g. the giant Cu_{146} cluster in $[Cu_{146}Se_{73}(PPh_3)_{30}]$) [11]. The progress in our knowledge of Group 5 chalcogenide clusters has been slower, less dramatic, but steady. Starting from mid-60s, both solid state and coordination chemists have done much to make this initially barren soil to bear some fruits, and we think the time is ripe to summarize their and our own efforts in the present review. Binary vanadium chalcogenide complexes (including mononuclear) were reviewed in 2001 [12]. Vanadium chalcogenide chemistry shows many similarities (e.g. structural) with its diagonal neighbor, molybdenum. There is vanadium nitrogenase [13] and an interest in vanadium-based hydrodesulfurization (HDS) catalysts [14]. A big problem here, as well as in the Nb and Ta chalcogenide chemistry, is “the difficulty to develop such a chemistry with a metal having a better affinity for oxygen than for sulfur” [12] (and its heavier congeners). Potential applications of Nb and Ta derivatives are still largely hypothetical, but there has been some interest in the catalytic properties of niobium sulphides [15]. Unsupported niobium trisulfide was found to be a better catalyst for thiophene conversion than molybdenum disulfide. In addition to pure niobium sulfide, nickel-doped catalysts have also attracted some attention. The catalytic activity of an unsupported mixed Ni–Nb sulfide was similar to that observed for Ni/MoS_2. In hydrodenitrogenation (HDN) of pyridine, NbS_3 is slightly more active than MoS_2. In the *n*-pentylamine conversion, the rate of C_5 hydrocarbon formation is much higher on niobium sulfide than on molybdenum sulfide and does not vary when the H_2S partial pressure is increased 10-fold [15]. The phases containing linear chains of metal atoms or condensed clusters often have unusual electrophysical properties, including superconductivity [16a]. An 1D phase $NaNb_2PS_{10}$ is soluble in polar organic solvents and forms unprecedented single wall monodispersed nanotubes [16b].

Some of the molecular clusters discussed in this review combine sufficient volatility with hydrolytical and oxidative stability (almost always a problem in Nb and Ta chemistry!) and are attractive precursors for MOCVD preparation of M/Q films of different composition. A strong feature for Nb and Ta is a very close relationship between the clusters found in the extended solids and in the molecular complexes of these two elements, and cluster core excision from the solids has become a preparative routine, e.g., for making various $Nb_2(Q_2)_2^{4+}$ (Q = S, Se) derivatives. Therefore in this review we have opted not to make a sharp division between 1D, 2D and 3D solids and molecular complexes, containing the same or very similar cluster cores, but rather to emphasize their essential unity [16c,d]. Besides, quite often solid-state structures may serve as inspiration to a synthetic chemist—as in the case of Saito et al.’s preparation of molecular analogues of Chevrel phases [17]. We are also not putting much emphasis on the presence or absence of real M–M bonding in the clusters keeping in mind the ability of bridging chalcogens to preserve the cluster core even in the absence of M–M bonding interactions. We deem it important to make a distinction between a cluster core which in our case is two or more metal atoms bridged by Q_2^{2-} or Q^{2-} units. This leaves metal free coordination sites which can be occupied by various ligands in much the same manner as in the classical Werner-type complexes. In this case we think we are justified to talk about cluster complexes. The emphasis in this review will be on the synthesis, chemical transformations and chemical characterization of the clusters. The spectroscopy has played only a secondary part in the development of the field.

2. Binuclear clusters

2.1. $Nb_2(\mu\text{-}Q_2)(\mu\text{-}X)_2^{4+}$ clusters (Q = Se, Te; X = Br, I)

These clusters are known for all possible combinations Q/X. They are made by high-temperature synthesis from the elements (800 °C) [18]. Later it was shown that $[Nb_2Se_2Br_6]$ can also be made by heating the elements at 400–450 °C with a large excess of bromine. They are all isostructural and crystal structure was determined for $[Nb_2Se_2Br_6]$, $[Nb_2Te_2Br_6]$, $[Nb_2Te_2I_6]$ and $[Nb_2Se_2I_6]$. The Nb–Nb distances were found to be 2.832, 2.875, 2.932 and 2.903 Å, respectively, and correspond to the single bond between two d^1-Nb(IV) centers. Crystal structure of $[Nb_2Se_2Br_6]$ was redetermined in 1994 yielding practically the same Nb–Nb (2.832 Å) and Se–Se (2.303 Å) distances [19]. The most recent addition to this family is $[Nb_2Se_2I_6]$, prepared from the elements (Nb:Se:I = 3:1:7) at 1073 K (attempts to use the stoichiometry Nb:Se:I = 2:2:6 led to $[Nb_2(Se_2)_2I_4]$ as the main product). An interesting feature of this compound is that while in all the other known $[Nb_2Q_2X_6]$ solids the chains exhibit centered rod packing, those in $[Nb_2Se_2I_6]$ are packed in a primitive manner [20]. By relative elongation of the Nb–Nb distances on going from selenide to telluride and from bromide to iodide one can see that the matrix effect of bridging halides is more pronounced than that of bridging Q_2^{2-}. The dichalcogenide ligand Q_2 is coordinated slightly asymmetrically, bending away from the orthogonal position with respect to the Nb–Nb vector by 4–5°. The Se–Se (2.305 Å) and Te–Te (2.670–2.685 Å) distances correspond to single bond values. Two bridging halides complete the cluster core. The latter are further connected into chains by intercluster halide bridges, and the crystallographic formula can be written in the notation of Shäfer and von Schnering as ${}^{1}_{\infty}[Nb_2(\mu\text{-}Q^i_2)_2(\mu\text{-}X^i)_2X^a_2X^a_{4/2})]$ (Fig. 1). Little is known

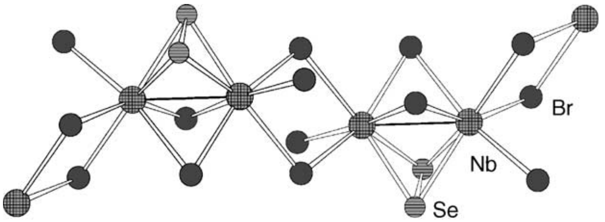

Fig. 1. Fragment of polymeric chain in $[Nb_2Se_2Br_6]$ [19].

about the properties of these clusters. Thermal decomposition of $[Nb_2Te_2I_6]$ in vacuum gives Nb_3Te_4.

Nb and Ta thiochloride and thiobromide with the stoichiometry $NbSX_3$ are made by exchange reactions between NbX_5 and Sb_2S_3, B_2S_3 or $(Me_3Si)_2S$ [21–23]. Their precise structures are unknown, and are unlikely to be the same in all cases, but the vibrational spectra and reactivity seem to favor Nb(V)/S(-II) formulation with Nb = S or Nb–S–Nb fragments.

2.2. $Nb_2(\mu\text{-}Q_2)_2^{4+}$ clusters (Q = S, Se, Te)

Heating the stoichiometric amounts of the elements in a 480–530 °C temperature gradient produces chalcohalides NbQ_2X_2 which in fact contain the binuclear cluster core $Nb_2(\mu\text{-}Q_2)_2^{4+}$ (Q = S, Nb–Nb 2.86–2.92 Å; Q = Se, Nb–Nb 2.93–2.97 Å, which corresponds to single Nb^{IV}–Nb^{IV} bond). This procedure works well when Q = S, Se and X = Br, I. In the case of chlorides, stoichiometric mixtures of $NbCl_4$, Nb and S (or Se) are used. Under favorable circumstances it was possible to obtain single crystals as thin platelets in the cold zone [24]. The only known Te derivative in this family is $[Nb_2(Te_2)_2(Te_2I_6)_2]$, made from the elements in the stoichiometric ratio at 620 °C. It is obtained as blue-black platelets together with an unidentified powdery material, and contains the $Nb_2(Te_2)_2^{4+}$ core (Nb–Nb 3.085(2) Å, Te–Te 2.681(2) Å), coordinated by two unusual $[Te_2I_6]^{2-}$ ligands (Fig. 2) [25]. Later $[Nb_2(Se_2)_2(Te_2I_6)_2]$ was prepared by heating together $[Nb_2(Se_2)_2I_4]$, Te and I_2. It has a similar structure [26]. Niobium selenohalides $Nb_3Se_5X_7$ (X = Cl, Br) are in fact derivatives of $Nb_2(Se_2)_2^{4+}$, too. These cluster units are further bound into chains both by bridging halides and by unique ligands, μ_2-η^3-$[NbSeX_5]^{2-}$, so that the chalcohalides are better formulated as $[Nb_2(Se_2)_2X_{4/2}(NbSeX_5)_{2/2}]$. They were prepared by serendipity either from $[Nb_2(Se_2)_2Cl_4]$ and $[NbCl_4]$ in a 535/525 °C temperature gradient, or from $[Nb_2(Se_2)_2Br_4]$ and $[Nb_2Se_2Br_6]$ (as dark-blue single crystals). Both preparative routes suffer from poor reproducibility [27].

All the $[Nb_2(Q_2)_2X_4]$ chalcohalides have two modifications: low-temperature triclinic (with the exception of $[Nb_2(S_2)_2Cl_4]$) and high-temperature monoclinic (with the exception of $[Nb_2(S_2)_2I_4]$). The structure was determined on single crystals for monoclinic $[Nb_2(S_2)_2Cl_4]$ and for triclinic $[Nb_2(Se_2)_2Cl_4]$ and $[Nb_2(S_2)_2Br_4]$. In both polymorphic modifications the pseudooctahedral units $Nb_2(Q_2)_2^{4+}$ (an octahedron contracted along the Nb–Nb axis) are bound into layers by halide ligands, so that their crystallographic formula may be written as $[Nb_2(\mu_2\text{-}Q^i_2)_2(\mu_2\text{-}X^a)_{8/2}]$ (Fig. 3). In the case of $[Nb_2(S_2)_2Cl_4]$ (Nb–Nb 2.871(4) Å) no asymmetry was found in the orientation of the S_2 ligands with respect to the Nb–Nb bond, while in $[Nb_2(Se_2)_2Cl_4]$ (Nb–Nb 2.973(4) Å) the orientation was found to be slightly asymmetrical. The observed elongation of the Nb–Nb bond length on going from S_2^{2-} to Se_2^{2-} may be attributed to the matrix effect, caused by the bigger size of heavier chalcogen. Due to the localized M–M bonding all $[Nb_2(Q_2)_2X_4]$ are semiconductors and diamagnetics [24]. Their thermal

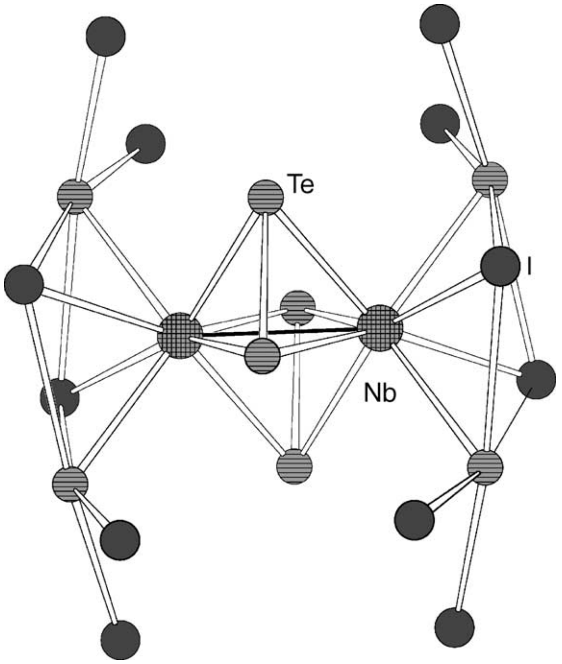

Fig. 2. $[Nb_2(Te_2)_2(Te_2I_6)_2]$ [25].

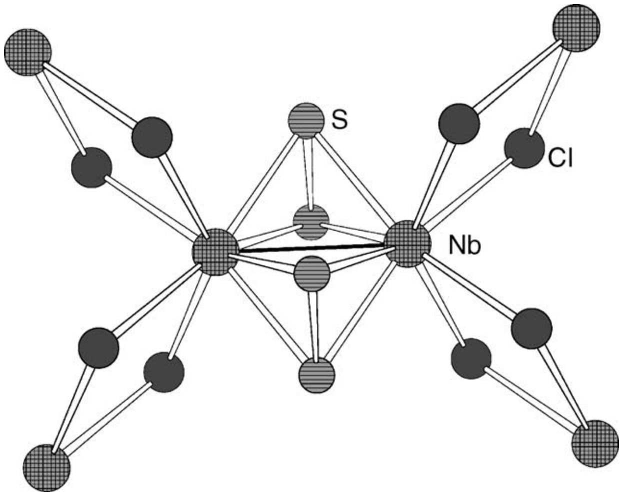

Fig. 3. Fragment of polymeric structure in $[Nb_2(S_2)_2Cl_4]$ [24].

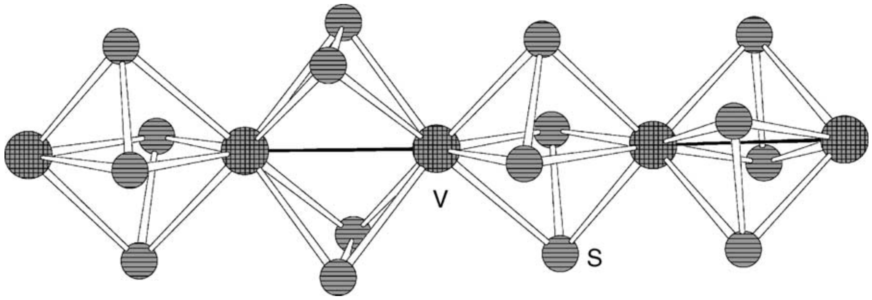

Fig. 4. Fragment of polymeric chain in VS_4 [29].

decomposition leads to NbQ_2, X_2 and volatile $NbQX_3$ (when X = Cl, Br), or simply to NbQ_2 and I_2 in the case of iodides [28].

No corresponding chalcohalides are known for V and Ta. However, the ${V_2(S_2)_2}^{4+}$ clusters are encountered in a mineral patronite VS_4, whose crystallographic formula can be written as ${}^{1}_{\infty}[V_2(S^{i}_2)_2(S^{a}_2)_{4/2}]$ (chain structure, Fig. 4). The V–V distances alternate between 2.84 Å in the cluster and 3.21 Å between the clusters. Accordingly, it is diamagnetic and a semiconductor [29]. The even more chalcogen-rich selenides Nb_2Se_9 and V_2Se_9 can be regarded as $\{Nb_2(Se_2)_2\}^{4+}\{{Se_5}^{4-}\}$ and $\{V_2(Se_2)_2\}^{4+}\{{Se_5}^{4-}\}$, respectively. The cluster units are separated from each other by unusual ${Se_5}^{4-}$ anions in the chains [30,31]. In the structure of $[Nb(Se_2)_2]_3I$ the ${Nb_2(Se_2)_2}^{4+}$ clusters (Nb–Nb 3.06 Å) are separated from each other in the 1D Nb chain by single Nb^{5+} centers (Nb^{4+}–Nb^{5+} 3.25 Å); some electron delocalization, however, must account for respective lengthening and shortening of the Nb^{4+}–Nb^{4+} and Nb^{4+}–Nb^{5+} distances in the chain. Due to the presence of Nb^{5+} the chains are positively charged and separated by iodide anions [32]. Blue-green $[Nb(S_2)_2]_3I$ may have a similar structure [33]. A strong tendency of V and Nb to form the ${M_2(Q_2)_2}^{4+}$ clusters even dominates the structures of ternary pnicochalcogenides of these elements: in PV_2S_{10}, PNb_2S_{10} and PNb_4S_{21} the clusters are connected into chains or layers by extra ${S_2}^{2-}$, as well as by S^{2-} and thiophosphate ligands. For example, PV_2S_{10} has a 1D-structure, where the ${V_2S_4}^{4+}$ clusters (V–V 2.852 Å, S–S 2.015 Å) are connected into chains by ${S_2}^{2-}$ and ${P_2S_8}^{4-}$ (the latter is the thioanalogue of peroxodiphosphate, d(S–S) = 2.075 Å) so that it could be better represented as ${}^{1}_{\infty}[V_2(S^{i}_2)_2(S^{a}_2)_{2/2}(P_2S_8)_{2/4}]$. It is made by heating the stoichiometric mixture of the elements at 490 °C for 10 days as fiber-like black crystals. Curiously, it possesses a weak paramagnetism, corresponding at room temperature to 0.19 e/V atom [34]. PNb_2S_{10} is built in a similar way, except that the ${P_2S_8}^{4-}$ bridges interconnect all the chains into a 2D layered structure [35]. A trisulphido-bridged thiophosphate, $S_3P\text{-}S_3\text{-}{PS_3}^{4-}$, is found in $P_2Nb_4S_{21}$ (i.e., $[Nb_2(S^{i}_2)_2(S^{a}_2)_{2/2}(P_2S_9)_{2/4}]$) [36]. Two different structures correspond to the stoichiometry PNb_2S_8. In the orthorhombic modification the ${Nb_2(S_2)_2}^{4+}$ units are connected into layers by ${P_2S_6}^{2-}$ (two edge-sharing tetrahedra PS_4) [37], whereas in the tetragonal modification the clusters are engaged into a 3D framework through cyclo-thiotetraphosphate anions, ${P_4S_{12}}^{4-}$, in accordance with the formula ${}^{3}_{\infty}[Nb_2(S_2)_2(P_4S_{12})_{4/4}]$. The latter compound is obtained as red-orange blocks by heating the stoichiometric element mixture for several days at 650 °C [38]. Geometrical parameters of the ${Nb_2S_4}^{4+}$ units are very similar in both cases (Nb–Nb 2.86 Å, S–S 2.01 Å). Anionic chains are present in MNb_2PS_{10} (M = Na–Cs), where the ${Nb_2(S_2)_2}^{4+}$ clusters are joined by ${S_2}^{2-}$ and ${PS_4}^{3-}$ ligands to form the chains. Accordingly, the formula can be written as $M[Nb_2(S^{i}_2)_2(S^{a}_2)_{2/2}(PS_4)_{2/2}]$. They may be regarded as products of reduction of the ${P_2S_8}^{4-}$ in 2D PNb_2S_{10} to give two ${PS_4}^{3-}$ units with the transformation of the parent 2D structure into 1D structure. However, attempts to intercalate PNb_2S_{10} electrochemically were not conclusive [39b]. The Rb compound (Nb–Nb 2.888(2) Å) was prepared by reacting Nb, P and S in an elemental ratio of 2:1:10 in an eutectic mixture of RbCl/LiCl as dark-red needle-shaped crystals [39]. The K salt was prepared similarly using a KCl/LiCl eutectic [39]. The most interesting compound in this family is red Na salt, prepared from P_4S_{10}, Nb and Na_2S_3 at 500 °C. Despite it's 1D chain structure, it is soluble in polar organic solvents such as *N*-methylformamide (NMF) where the polymer chains fold into single walled monodispersed nanotubes (external diameter 10 nm, wall thickness 1.6 nm, lengths from 10 nm to over 1 μm). It is thought that cooperative weak hydrogen bonds to the amide solvent assist in assembling the flexible, charged covalent mineral polymer and stabilize the nanotube wall [16b]. Tantalum, for which the ${Ta_2(S_2)_2}^{4+}$ cluster core is at present unknown, does produce oxydized dimeric units ${Ta_2(S_2)_2}^{6+}$, found in $TaPS_6$ and in $Ta_4P_4S_{29}$. The former compound has a 3D-structure in which the dimers are bound together via tetrahedral thiophosphate anions, ${PS_4}^{3-}$, and its formula can be written as ${}^{3}_{\infty}[Ta_2(S_2)_2(PS_4)_{4/2}]$. This 3D-network has channels which are large enough to accommodate the infinite chain of neutral catena-polysulfur, as found in $Ta_4S_4S_{29}$. It is made as large black needle-like crystals (together with much microcrystalline powder) by heating together elements in the required stoichiometry at 500 °C for 10 days. In both compounds long Ta–Ta distances (3.36–3.38 Å) and the +5 oxidation state exclude metal–metal bonding. The polysulfur chain here is helicoidal (right-hand helix), while in the so-called fibrous sulfur both left-hand and right-hand helices are found [40].

Due to their polymeric structure, the $[Nb_2(Q_2)_2X_4]$ solids are highly inert. Attempts to dissolve orange $[Nb_2(S_2)_2Cl_4]$ by heating in organic solvents (like pyridine, DMF, DMSO) or in conc. HCl failed. However, with KNCS under rather drastic conditions (heating in a melt at 185 °C, or treatment in a vibration mill with stainless steel balls) does produce discrete $[Nb_2(S_2)_2(NCS)_8]^{4-}$ by ligand exchange. Extraction gives the potassium salt, from which by subsequent precipitation by a large cation (Cs^+, Et_4N^+, Bu_4N^+, ethylquinolinium (EtQ^+)) other salts are obtained [41]. For $Cs_4[Nb_2(S_2)(NCS)_8]\cdot 2H_2O$ [42] and $(EtQ)_4[Nb_2(S_2)_2(NCS)_8$ [41] X-ray analysis confirmed N-coordination of the NCS ligand, postulated earlier on the basis of Raman and ^{14}N NMR data [43]. Corresponding Se complex is less stable and can be made only by mechanochemical synthesis from $[Nb_2(Se_2)_2X_4]$ (X = Cl, Br) and KNCS [44], because in the melt chalcogen exchange readily takes place. This was confirmed by FAB-MS data, where peaks corresponding to the whole range of $Nb_2S_xSe_{4-x}$ (x = 0–4) were observed, with x increasing with time [45]. Direct substitution of NCS^- by some bidentate ligands, mainly S,S′-bidentate (dithiocarbamates, dithiophosphates, xanthates, 2-mercaptopyridinate, 2-mercaptopyrimidinate) leads to the formation of neutral $[Nb_2(Q_2)_2(R_2NCS_2)_4]$ (Q = S, Se; R = Et, *i*-Pr, *n*-Bu, *i*-Bu, *i*-Am, cyclo-C_4H_8), $[Nb_2(Q_2)_2((RO)_2PS_2)_4]$ (Q = S, Se; R = Et, *i*-Pr), $[Nb_2(S_2)_2(pyS)_4]$ and $[Nb_2(S_2)_2(pmS)_4]$ [46]. Chalcogen-mixed $[Nb_2S_{1.71}Se_{2.28}(Et_2NCS_2)_4]$, whose Raman spectrum shows the characteristic bands of S–S, S–Se and Se–Se units, is also known [47]. By treatment with Et_3PSe (in the presence of free PEt_3) $[Nb_2(S_2)_2(Et_2NCS_2)_4]$ (Nb–Nb 2.8928(9) Å) was converted into $[Nb_2(Se_2)_2(Et_2NCS_2)_4]$ (Nb–Nb 2.974(2) Å) in a good yield. To explain the catalytic effect of free phosphine, a stepwise elimination-addition mechanism of the substitution was put forward [48]. A complex reaction between $[NbO(Et_2NCS_2)_3]$ and B_2S_3 gives $[Nb_2(S_2)_2(Et_2NCS_2)_4]$ in a very low yield (3%) [49]. The vanadium analogues are available through various synthetic routes: (a) from $[VO(R_2NCS_2)_3]$ or $[VO(ROCS_2)_3]$ and H_2S [50]; (b) from $VS_4{}^{3-}$ and $(R_2NCS_2)_2$ (R = Et, *i*-Bu) [51,52]; (c) from $[(C_6H_6)_2V]$ and CH_3CS_2H to give $[V_2(S_2)_2(CH_3CS_2)_4]$ [53]; (d) from $[VO(Et_2NCS_2)_3]$ and B_2S_3 to give $[V_2(S_2)_2(Et_2NCS_2)_4]$ [54] (Fig. 5); (e) from $[V(S_2)(S)_2(SPh)]^{2-}$ with CS_2. The latter reaction gives anionic $[V_2(S_2)_2(CS_3)_4]^{4-}$, which can be methylated into neutral $[V_2(S_2)_2(CH_3SCS_2)_4]$, which in turn reacts with R_2NH (R = Et, *n*-Bu) to give corresponding dithiocarbamates in good yields [55]. So far the $V_2(S_2)_2{}^{4+}$ clusters could be stabilized only in sulfide environment. The EHMO calculations on $[V_2(S_2)_2(CS_3)_4]^{4-}$ show that V–S interactions are mainly responsible for the stability of the cluster core, assisted but rather weak V–V bond [55]. The only $V_2(Se_2)_2{}^{4+}$ molecular complex is represented by anionic $[V_2Se_{13}]^{2-}$, made from NH_4VO_3, Et_4NCl and $(Me_2OctSi)_2Se$. It has a unique structure, where the cluster core is coordinated by two terminal $Se_2{}^{2-}$ ligands and by a bridging $Se_5{}^{2-}$ zig-zag chain ("basket handle"). Surprisingly, its V–V distance is shorter (2.779(5) Å) than in $V_2(S_2)_2{}^{4+}$ derivatives, contrary to the expectation based on sterical effects and comparison with the data on the $Nb_2(Q_2)_2{}^{4+}$ clusters [56]. The stereochemistry of dithiocarbamates was studied in some detail. Both for V and Nb, when R in the dithiocarbamate is not sterically demanding (Et, *n*-Bu), of two possible isomers caused by different mutual orientation of four chelate rings around the cluster core only the centrosymmetrical *meso*-isomer is found, However, when R is bulkier (*i*-Bu), the non-centrosymmetrical isomer is observed. In the case of other ligands (*i*-$PrOCS_2$, (*i*-$PrO)_2PS_2$, as well as in the acetylacetonate and oxalate, described below) the centrosymmetrical isomer always forms, reflecting the greater relative stability of the latter [46,50]. The Nb dithiocarbamates, $[Nb_2(Q_2)_2(Et_2NCS_2)_4]$ show waves of quasi-reversible one-electron oxidation with $E_{1/2}$ 770 and 638 mV for the sulfido and the selenido cluster, respectively (versus NHE, in CH_2Cl_2). The oxidation can be achieved chemically (by Fc^+ or Ag^+) and solid salts such as $[Nb_2(Q_2)_2(R_2NCS_2)_4]PF_6$ (Q = S, Se; R = Et, *n*-Bu) were isolated and analyzed. The ESR spectra of $[Nb_2(Q_2)_2(Et_2NCS_2)_4]^+$ in CH_2Cl_2 at 300 consist of 19 lines with the intensity ratio 1:2:3:4:5:6:7:8:9:10:9:8:7:6:5:4:3:2:1. This is due to hyperfine interaction of the unpaired electron in this mixed-valence d^0–d^1 with two ^{93}Nb nuclei (I = 9/2, natural abundance 100%). For $[Nb_2(S_2)_2(Et_2NCS_2)_4]^+$ A = 54 G, g = 2.0113; for $[Nb_2(Se_2)_2(Et_2NCS_2)_4]^+$ A = 52.5 G, g = 2.0489. Cooling down to 77 K does not cause electron localization. Our attempts at two-electron oxidation of

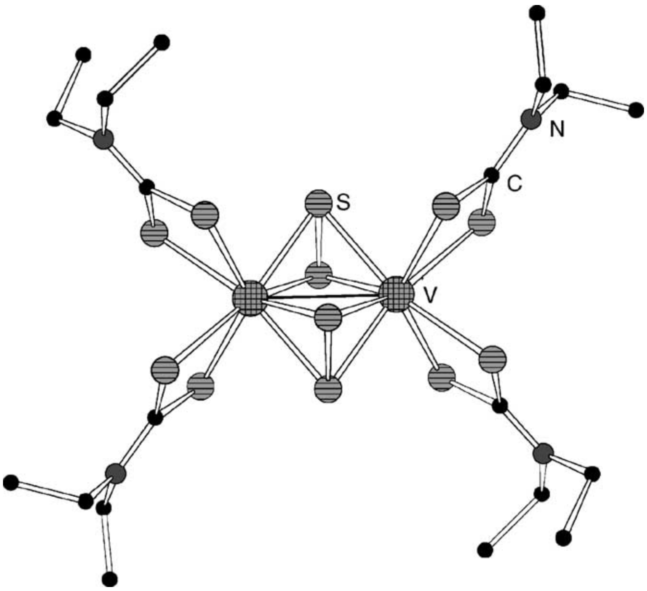

Fig. 5. $[V_2(S_2)_2(Et_2NCS_2)_4]$ [54]. Hydrogen atoms are omitted for clarity.

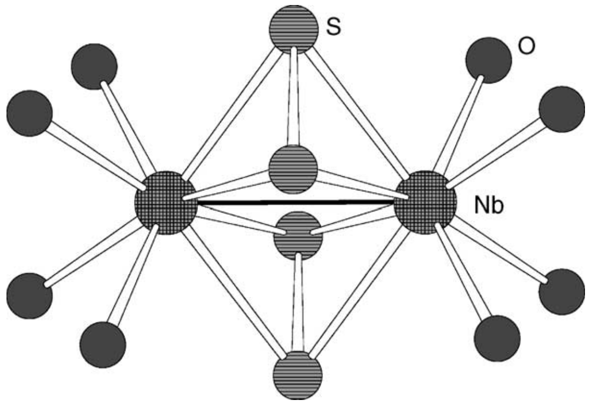

Fig. 6. $[Nb_2(S_2)_2(H_2O)_8]^{4+}$ [42]. Hydrogen atoms are omitted for clarity.

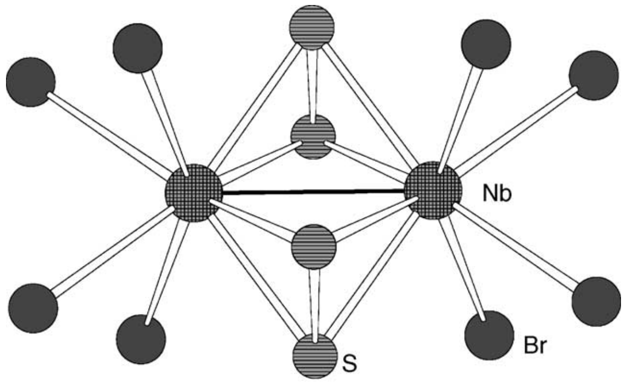

Fig. 7. $[Nb_2(S_2)_2Br_8]^{4-}$ [60].

$[Nb_2(S_2)_2(Et_2NCS_2)_4]$ gave untractable solids [46]. However, in 1997 a Nb(V) complex $[Nb_2(S_2)_2(C_3S_5)_4]^{2-}$ was prepared from $NbCl_5$ and $[Zn(C_3S_5)_2]^{2-}$. It has a unique $Nb_2(S_2)_2{}^{6+}$ core without Nb–Nb bonding, which can be compared to $Ta_2(S_2)_2{}^{6+}$, discussed above [57].

$[Nb_2(S_2)_2(Et_2NCS_2)_4]$ reacts with $[PdCl_2(PhCN)_2]$ to give a new trinuclear Pd(II) dithiocarbamate, $[Pd_3(Et_2NCS_2)_4Cl_2]$. This reaction can be regarded as a transfer of a soft ligand from a hard (Nb(IV)) to a soft (Pd(II)) metal center, and it may have some synthetic potential [58].

By acid hydrolysis of $[Nb_2(S_2)_2(NCS)_8]^{4-}$ another key compound in the $Nb_2(S_2)_2{}^{4+}$ chemistry, the aqua complex $[Nb_2(S_2)_2(H_2O)_8]^{4+}$ can be prepared. Its isolation was achieved in the form of *p*-toluensolufonate, $[Nb_2(S_2)_2(H_2O)_8](pts)_4{\cdot}4H_2O$, for which crystal structure was determined (Fig. 6) [42]. This unambiguously characterized Nb aqua complex is surprisingly stable and its solution in 4 M HCl could be kept for 3 years in air without appreciable decomposition. A supramolecular adduct with cucurbit[6]uril ($C_{36}H_{36}N_{24}O_{12}$, cuc) of the composition $\{[Nb_2(S_2)_2(H_2O)_8](cuc)\}Cl_4{\cdot}15H_2O$ was also prepared and structurally characterized. In it the cucurbituril molecule is bound to the cluster only via hydrogen bonds between its carbonyl groups and coordinated water molecules [59]. Kinetics of H_2O/NCS^- exchange:

$$[Nb_2(S_2)_2(H_2O)_8]^{4+} + NCS^- = [Nb_2(S_2)_2(H_2O)_7(NCS)]^{3+} + H_2O$$

was found to be much slower (by five orders of magnitude) than for another d^1-aqua complex—mononuclear $[Ti(H_2O)_6]^{3+}$. Marked $[H^+]$-dependence indicates participation of the conjugate base $[Nb_2(S_2)_2(H_2O)_7(OH)]^{3+}$ in the substitution. The equilibrium constant found for this reaction is 370(72) M^{-1} [42]. The aqua ligands can easily be substituted by a variety of other ligands. From concentrated HCl and HBr corresponding halogeno complexes $[Nb_2(S_2)_2X_8]^{4-}$ were isolated as Cs salts, $Cs_5[Nb_2(S_2)_2X_8]X$ (X = Cl, Br) (Fig. 7), as well as $(H_3O)_5[Nb_2(S_2)_2Cl_8]Cl$ [60]. The presence of $[Nb_2(S_2)_2X_8]^{4-}$ in these solids was proved by X-ray analysis. Though no corresponding selenides are known, mixed ligand, neutral complexes $[Nb_2(Se_2)_2Cl_4(dms)_4]$ or $[Nb_2(Se_2)_2Cl_4(tht)_4]$ (dms = dimethylsulfide, tht = tetrahydrothiophene) were prepared by complicated reactions of $NbSeCl_3$ (of unknown structure, see above) with corresponding ligand in low yields [61,62]. A large series of β-diketonates was obtained from the aqua complex and β-diketon: $[Nb_2(S_2)_2(acac)_4]$ (acac = $CH_3C(O)CHC(O)CH_3$), $[Nb_2(S_2)_2(tfa)_4]$ (tfa = $CF_3C(O)CHC(O)CH_3$), $[Nb_2(S_2)_2(dpm)_4]$ (dpm = *t*-BuC(O)CHC(O)*t*-Bu), $[Nb_2(S_2)_2(dfhd)_4]$ (dfhd = $C_3F_7C(O)CHC(O)CF_3$), $[Nb_2(S_2)_2(chf)_4]$ (chf = $CF_3C(O)CHC(O)C_6F_{11}$; C_6F_{11}-perfluorcyclohexyl), $[Nb_2(S_2)_2(ptfa)_4]$ (ptfa = *t*-BuC(O)CHC(O)CF_3), $[Nb_2(S_2)_2(btfa)_4]$ (btfa = PhC(O)CHC(O)CF_3), $[Nb_2(S_2)_2(tta)_4]$ (tta = $CF_3C(O)CHC(O)C_4H_3S$; C_4H_3S 2-thienyl) [63]. Crystal structures were determined for $[Nb_2(S_2)_2(acac)_4]$ (Nb–Nb 2.9039(9) Å, Fig. 8) and $[Nb_2(S_2)_2(tfa)_4]$ (Nb–Nb 2.879(1) Å) [48,63]. In the latter, four isomers differing by mutual orientation of CH_3 and CF_3 groups were found in the same crystal. Fluorinated *beta*-diketonates have appreciable volatility: the trifluo-

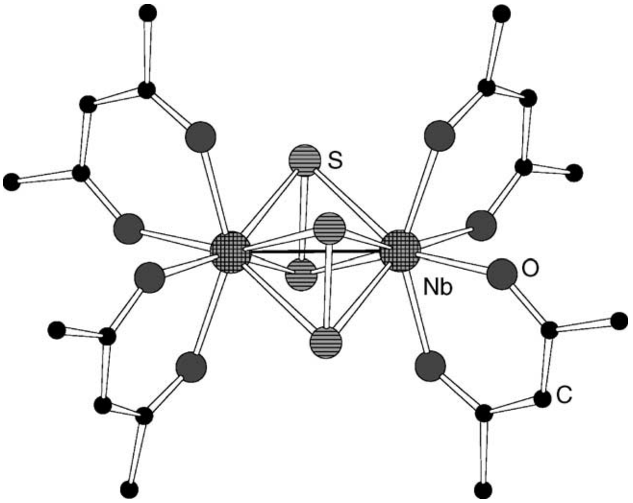

Fig. 8. $[Nb_2(S_2)_2(acac)_4]$ [48]. Hydrogen atoms are omitted for clarity.

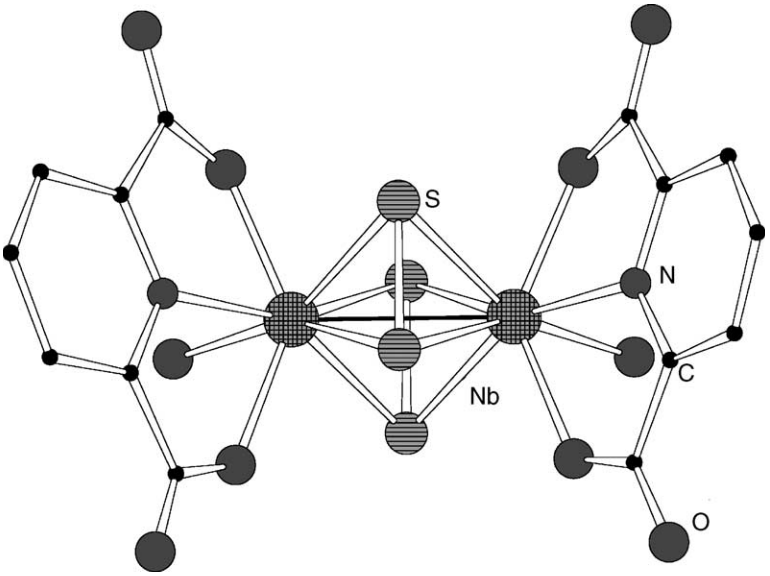

Fig. 9. $[Nb_2(S_2)_2(dipic)_2(H_2O)_2]$ [68]. Hydrogen atoms are omitted for clarity.

racetylaconate, $[Nb_2(S_2)_2(tfa)_4]$ can be sublimed in vacuo (10^{-3} Torr, 220 °C) in 80% yield. The temperature dependence of vapor pressure, measured for $[Nb_2(S_2)_2(acac)_4]$ by Knudsen method, is expressed with the following equation: $\log P$ (Torr) $= 12.0–6040/T$ within 360–450 K [64].

Treatment of the aqua complex with oxalate gives $[Nb_2(S_2)_2(C_2O_4)_4]^{4-}$. Isolated as solids and structurally characterized were K^+, mixed Na^+/NH_4^+, NH_4^+, and Cs^+ salts. No reversible oxidation of $[Nb_2(S_2)_2(C_2O_4)_4]^{4-}$ was observed in CV experiments [65–67]. Bidentate ligands 8-oxyquinoline (Hoxine) and salicylaldoxim (Hsal) give neutral complexes $[Nb_2(S_2)_2(oxine)_4]$ and $[Nb_2(S_2)_2(Sal)_4]$, which are only sparingly soluble in common organic solvents and were characterized by elemental analysis and mass-spectroscopy (occurrence of the expected molecular peaks) [65]. A tridentate ligand, 2,6-pyridinedicarboxylate (H_2dipic), gives $[Nb_2(S_2)_2(dipic)_2(H_2O)_2]\cdot 3H_2O$, whose crystal structure was determined (Nb–Nb 2.88 Å, Fig. 9) [68]. It is possible that the unsoluble complex with another tridentate ligand, $[Nb_2(S_2)_2(ida)_2(H_2O)_2]$ (H_2ida $= NH(COOH)_2$), has the same ligand arrangement [42]. A sparingly soluble complex with ethylediaminetetraacetate, $[Nb_2(S_2)_2(H_2edta)_2]$, was also prepared. Its structure is probably similar to that of $[Tc_2(\mu\text{-}O)_2(H_2edta)_2]$, where each tetradentate ligand H_2edta^{2-} has two uncoordinated carboxylic groups [42]. An attempt to prepare a complex with nitrilotriacetate unexpectedly gave a Nb(V) binuclear hydroxo complex, isolated and structurally characterized as $K_2[Nb_2(O)_2(\mu\text{-}OH)_2(nta)_2]\cdot 4H_2O$. This reaction proceeds via $[Nb_2(S_2)(S)(nta)_2]^{4-}$ as intermediate, followed by hydrolysis and Nb^{IV} to Nb^{V} oxidation [69]. Interatomic distances in molecular complexes with $Nb_2(Q_2)_2{}^{4+}$ cores (Q = S, Se) are summarized in Table 1.

2.3. $Nb_2(\mu\text{-}Q_2)(\mu\text{-}Q)^{4+}$ clusters (Q = S, Se, Te)

These clusters are structurally very closely related to the above treated chalcogen-rich $Nb_2(S_2)_2{}^{4+}$ clusters. Removal of one sulfur atom does not change the oxidation state of Nb (+4), therefore the single metal–metal bond is preserved and the Nb–Nb distances are not appreciably affected. To this family belong $[Nb_2(\mu\text{-}S_2)(\mu\text{-}S)X_4(tht)_4]$ (X = Cl, Nb–Nb 2.844 Å; Br, Nb–Nb 2.820 Å) [70], and a unique S/Te cluster, $[Nb_2(Te_2)(S)(Et_2NCS_2)_4]$ (Fig. 10). It was made by ligand exchange reaction from $[Nb_2(S_2)_2(Et_2NCS_2)_4]$ and Et_3PTe [48]. The distances in the $Nb_2(Te_2)(S)^{4+}$ core are following: Nb–Nb 2.920 Å, Nb–Te 2.84–2.85 Å, Te–Te 2.648(1) Å, Nb-(μ_2-S) 2.376(7) Å. Whereas in the structures of $[Nb_2(S_2)(S)X_4(tht)_4]$ the bridging μ-S ligand forms a plane with two Nb atoms and the midpoint of the S_2 group, in $[Nb_2(Te_2)(S)(Et_2NCS_2)_4]$ the plane is defined by two Nb, μ-S and one of the Te atoms [48]. $[Nb_4Se_3Br_{10}(CH_3CN)_4]$ (Fig. 11), prepared from $[NbBr_4(CH_3CN)_2]$ and Sb_2Se_3 in CH_3CN (50°, 7 d), has a well-defined $Nb_2(\mu\text{-}Se_2)(\mu\text{-}Se)^{4+}$ core (Nb–Nb 2.886 Å). The other two niobium atoms are in fact Nb^{III} which do not participate in M–M bonding (Nb^{III}–Nb^{IV} 3.1 Å). Accordingly, the cluster is ESR-silent from −195.8 to 20.0° and is diamagnetic [71]. It is highly probable, that Nb thiocloride and thiobromide $Nb_2S_3X_4$ of unknown structure, made from NbX_5 and Sb_2S_3 at 50 °C in CS_2, are in fact ${}^{2}_{\infty}[Nb_2(\mu\text{-}S^{i}_{2})(\mu\text{-}S^{i})X_{4/4}]$. Accordingly, they react with monodentate ligands (L) such as tht, dms, CH_3CN to give the expected $[Nb_2(S_2)(S)X_4L_4]$, and with bidentate 1,2-bisphenylthioethane (bpte), to give $[Nb_2(S_2)(S)X_4(bpte)_2]$ [72]. In addition, $[Nb_2(S_2)(S)Br_4(tht)_4]$ is obtained, together with $[NbSBr_3(tht)_2]$, from $NbSBr_3$ and the ligand [70]. In the structure of triclinic niobium trisulfide, NbS_3, Nb atoms are arranged into chains by bridging by one $S_2{}^{2-}$ (S–S 2.05 Å) and one S^{2-} ion.

Table 1
Interatomic distances in molecular complexes with $Nb_2(Q_2)_2^{4+}$ cores (Q = S, Se)

Compound	Nb–Nb (Å)	Nb-(μ_2-Q) (Å)	Q-Q (Å)	References
$Cs_4[Nb_2(S_2)_2(NCS)_8]\cdot 2H_2O$	2.858(2)–2.867(2)	2.495(3)–2.524(3)	1.984(9)–2.010(6)	[42]
$(EtQuin)_4[Nb_2(S_2)_2(NCS)_8]$	2.913(2)	2.508(3)–2.513(3)	2.012(3)	[41]
$[Nb_2(S_2)_2(H_2O)_8](pts)_4\cdot 4H_2O$	2.891(1)	2.484(2)–2.515(2)	2.020(2)–2.024(2)	[42]
$Cs_5[Nb_2(S_2)_2Cl_8]Cl$	2.924(3)	2.503(3)	2.020(8)	[60]
$(H_3O)_5[Nb_2(S_2)_2Cl_8]Cl$	2.902(2)	2.495(2)	2.000(4)	[60]
$Cs_5[Nb_2(S_2)_2Br_8]Br$	2.914(3)	2.504(3)	2.022(8)	[60]
$(NH_4)_3Na_2[Nb_2(S_2)_2(ox)_4]Cl$	2.879(2)–2.880(2)	2.493(3)–2.513(3)	2.022(4)–2.031(4)	[65]
$K_4[Nb_2(S_2)_2(ox)_4]\cdot 6H_2O$	2.879(1)	2.500(1)–2.513(1)	2.024(2)	[66]
$Cs_4[Nb_2(S_2)_2(ox)_4]\cdot 5H_2O$	2.890(2); 2.901(1)	2.497(2)–2.519(2)	2.028(2)–2.030(3)	[67]
$(NH_4)_6[Nb_2(S_2)_2(ox)_4](ox)$	2.855(2); 2.857(1)	2.497(3)–2.507(2)	2.030(3)–2.032(3)	[66]
$[Nb_2(S_2)_2(acac)_4]$	2.9039(9)	2.498(1)–2.535(1)	2.033(2)	[48]
$[Nb_2(S_2)_2(tfa)_4]$	2.879(1)	2.487(3)–2.525(2)	2.008(4)	[63]
$[Nb_2(S_2)_2(dipic)_2(H_2O)_2]$	2.879(2)–2.880(2)	2.483(4)–2.525(4)	1.999(6)–2.045(6)	[68]
$[Nb_2(S_2)_2(Et_2NCS_2)_4]$	2.8928(9)	2.492(1)–2.520(1)	2.033(2)	[48]
$[Nb_2(S_2)_2(n\text{-}Bu_2NCS_2)_4]$	2.8838(5)	2.496(1)–2.510(1)	2.026(2)	[46]
$[Nb_2(S_2)_2(i\text{-}Bu_2NCS_2)_4]$	2.875(1)	2.489(2)–2.516(2)	2.030(3)	[46]
$[Nb_2(S_2)_2((i\text{-}PrO)_2PS_2)_4]$	2.898(1)	2.488(2)–2.504(2)	2.011(3)	[41]
$[Nb_2(Se_2)_2(Te_2I_6)_2]^*$	2.926(2)	2.602(2)–2.614(2)	2.310(2)–2.311(2)	[26]
$[Nb_2(Se_2)_2(Me_2S)_4Cl_4]^*$	2.962(3)	2.625(3)–2.640(2)	2.289(3)	[61]
$[Nb_2(Se_2)_2(Et_2NCS_2)_4]$	2.974(2)	2.625(2)–2.649(2)	2.303(2)	[48]
$[Nb_2(Se_2)_2(n\text{-}Bu_2NCS_2)_4]$	2.961(2)	2.633(1)–2.652(1)	2.288(1)	[46]

Thus it can be described as $Nb^{4+}(S_2^{2-})(S^{2-})$. The Nb–Nb distances are not equivalent: Nb_2 units (Nb–Nb 3.04 Å) are separated from each other at a nonbonding distance of 3.69 Å and thus NbS_3 can be regarded as having the cluster core $Nb_2(\mu\text{-}S_2)(\mu\text{-}S)^{4+}$ [73].

2.4. $M_2(\mu\text{-}Q)_2^{4+}$ clusters

The $Nb_2(S)_2^{4+}$ clusters can easily be derived from $Nb_2(S_2)_2^{4+}$ and $Nb_2(S_2)(S)^{4+}$ by sulfur abstraction from the S_2 ligands with phosphines. For example, PPh_3 reacts with $[Nb_2(S_2)(S)Cl_4(tht)_4]$ (50 °C, 3 months!) [72]. From $[Nb_2(S_2)_2(acac)_4]$ and PEt_3 or PEt_3Te green $[Nb_2(S)_2(acac)_4]$ can be prepared in high yield (Nb–Nb 2.880(5) Å, Nb–S 2.37–2.39 Å) (Fig. 12) [48]. Similarly, the orange aqua complex, $[Nb_2(S_2)_2(H_2O)_8]^{4+}$ reacts with PPh_3 or PR_3^{3-} ($R = C_6H_4SO_3$) in 4M Hpts to give green $[Nb_2(S)_2(H_2O)_8]^{4+}$, which undergoes NCS^- for H_2O substitution some two orders of magnitude faster, than the disulfido-bridged cluster [42]. Although poly-

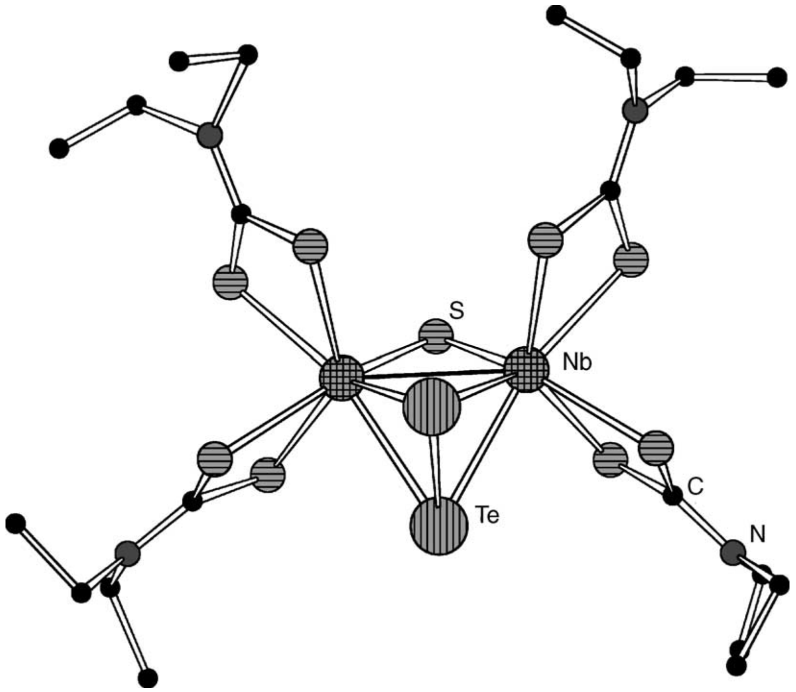

Fig. 10. $[Nb_2(Te_2)(S)(Et_2NCS_2)_4]$ [48]. Hydrogen atoms are omitted for clarity.

meric $[Nb_2(S_2)_2X_4]$ (X = Cl, Br) were unreactive toward aliphatic phosphines, the selenide $[Nb_2(Se_2)_2Cl_4]$ did give with PBu_3 (slow reaction, 1 week at room temperature) $[Nb_2(Se)_2Cl_4(PBu_3)_4]$. If the reaction with PBu_3 were done in the presence of pyridine or dppe, $[Nb_2(Se)_2Cl_4(py)_4]$ and $[Nb_2(Se)_2Cl_4(dppe)_2]$ were the products [46]. In all cases the change from two dichalcogenido bridges to two monochalcogenido bridges drastically decreases the oxidative and hydrolytic stability of the clusters, and the $Nb_2(Q)_2{}^{4+}$ clusters need to be handled under drastically air-free conditions. These may be caused by sterical reasons since the metal coordination number becomes six instead of eight and the attack at metal is facilitated. Another straightforward way to the $Nb_2(S)_2{}^{4+}$ clusters is metathesis of $[NbCl_4(CH_3CN)_2]$ with Sb_2S_3 or $(Me_3Si)_2S$ in the presence of such ligands as CH_3CN, THF or tht. The products are, accordingly, $[Nb_2(S)_2Cl_4(CH_3CN)_4]$, $[Nb_2(S)_2Cl_4(THF)_4]$, and $[Nb_2(S)_2Cl_4(tht)_4]$ [74,75]. A Ta(IV) cluster of this type, $[Ta_2(S)_2Cl_4(PMe_2Ph)_4]$ is obtained from $TaCl_5$, PhSSPh and Na/Hg, followed by addition of PMe_2Ph, in a 26% yield. Obviously here the C–S bond is broken and S atoms become the bridges in the cluster core. Closely related $[Ta_2(S)_2Cl_4(PMe_3)_4]$ is also known (Ta–Ta 2.865(1) Å, Ta–S 2.36 Å). It is made in a more straightforward way by reducing a mixture of $TaCl_5$ and Li_2S with Na/Hg in the presence of PMe_3 in 20% yield. The same reaction with $NbCl_5$ gives orange-brown $[Nb_2(S)_2Cl_4(PMe_3)_4]$ (Nb–Nb 2.869(1) Å, Nb–S 2.36 Å) in a 30% yield [76]. The ability of C–S bonds to cleave with the subsequent sulfur transfer to the metal in the presence of low-valence Nb and Ta compounds, together with a careful analysis of M–M and M-μ-Y (Y = Cl, S) distances have led to reformulate M(III) species $[M_2(\mu\text{-}Cl)_2Cl_4(dms)_4]$ (M = Nb, Ta) and $[Ta_2(\mu\text{-}Cl)_2Cl_4(EtSCH_2CH_2SEt)_2]$ as M(IV) $[M_2(\mu\text{-}S)_2Cl_4(dms)_4]$ (M = Nb, Ta) and $[Ta_2(\mu\text{-}S)_2Cl_4(EtSCH_2CH_2SEt)_2]$ [77]. Recently prepared $[(MeCp)_4Ta_2(\mu\text{-}S)_2]$ formally also belongs to this family, but its $Ta_2(S)_2{}^{4+}$ core has drastically elongated Ta–Ta (3.211 Å) and Ta–S (2.40–2.42 Å) distances [78]. Two vanadium atoms, bridged by two μ-Q units, are encountered in $[V_2(\mu\text{-}Q)_2(N(SiMe_3)_2)_2]$, made from $[V(N(SiMe_3)_2)_2Cl(THF)]$ and S_8, and from $[V(N(SiMe_3)_2)_2Br(THF)]$ and $LiSeC(SiMe_3)_3$, respectively. In these reactions oxidation of V(III) into V(IV) takes place. Here bulky silazanido ligands reduce coordination number at V to four [79,80]. The affinity of V(IV) for oxygen is very well known and is manifested in the formation of vanadyl, VO^{2+}. Accordingly, such complexes as $[V_2O_2(\mu\text{-}S)_2(Et_2NCS_2)_2]^{2-}$ (V–V 2.78–2.81 Å) [81], $[V_2O_2(Se)_2(Se_4)_2]^{2-}$ (V–V 2.90–2.96 Å) and $[V_2O_2(\mu\text{-}Se)_2(Se_2)(Se_4)]^{2-}$ (V–V 2.958(7) Å) [82] are in fact built from two VO^{2+} bridged by two monochalconide ligands and coordinated to bidentate $Et_2NCS_2{}^{2-}$, $Se_4{}^{2-}$ or $Se_2{}^{2-}$. A general way to make the dithiocarbamate complexes $[V_2O_2(\mu\text{-}S)_2(R_2NCS_2)_2]^{2-}$ is to treat $(NH_4)_3VS_4$ with PPh_3 in the presence of dithiocarbamate. In this manner black diethyldithiocarbamato, dimethyldithiocarbamato and piperidyldithiocarbamato complexes were obtained in moderate-to-high yields, sometimes together with some $[V(R_2NCS_2)_3]$. Magnetic measurements on dithiocarbamates indicate a strong paramagnetic coupling between two V(IV) centers with J about $-240\,cm^{-1}$, probably via direct metal–metal (d_{xy}-d_{xy}) exchange route [83]. Binuclear $[V_2(O)(S)_4(edt)]^{3-}$ (V–V 2.977(1) Å) is better regarded as a complex of VO^{2+} with bidentate edt^{2-} and $VS_4{}^{3-}$ in the coordination sphere [84].

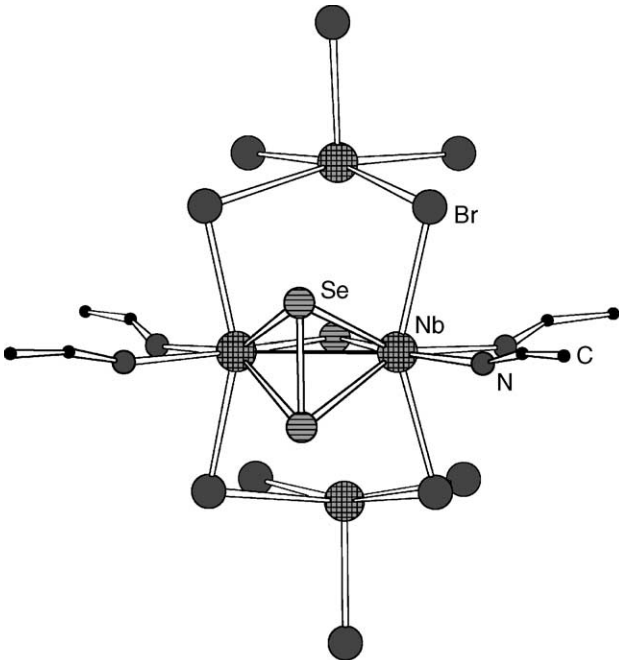

Fig. 11. $[Nb_4Se_3Br_{10}(CH_3CN)_4]$ [71]. Hydrogen atoms are omitted for clarity.

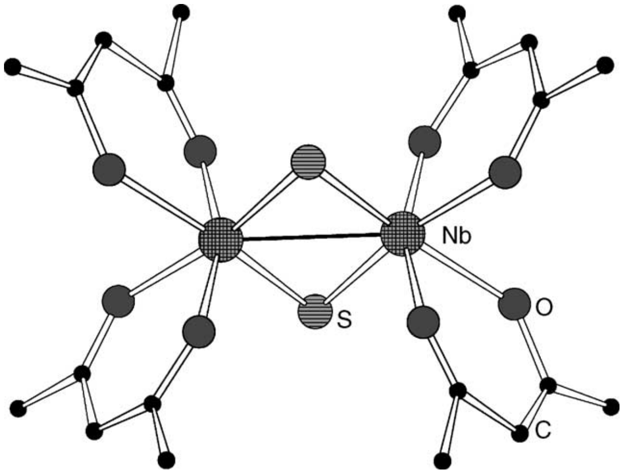

Fig. 12. $[Nb_2(S)_2(acac)_4]$ [48]. Hydrogen atoms are omitted for clarity.

2.5. $[V_2(\mu\text{-}Q_2)(\mu\text{-}Q)_2]^{2+}$ and $[V_2(\mu\text{-}Q_2)_2(\mu\text{-}Q)]^{2+}$ cores

In $[(RCp)_2V_2S_4]$ two V(IV) atoms (R = *i*-Pr, V–V 2.610(1) Å) are bound by a μ-η^1-S_2 bridge and two μ-S bridges [85]. This cluster type is very rare and has not been observed for Nb or Ta. It is made either by sulfur abstraction from $[(RCp)_2V_2S_5]$ [85], or by reacting $[(RCp)V(CO)_4]$ with elemental sulfur [86]. The corresponding selenide (Cp = Cp*) is made in a similar way [86]. One of the bridging chalcogens (Q) can be replaced by oxygen, giving $[(RCp)_2V_2(Q_2)(Q)(O)]$ (Q = S, Se, Te). These oxo-chaclogenido clusters are formed as side-products from reactions between vanadium carbonyls and chalcogen. As can be predicted from relative stabilities of $S^{2-}/Se_2{}^{2-}$ versus $S_2{}^{2-}/Se^{2-}$, $[(Cp^*)_2V_2(Se_2)(S)_2]$ has the diselenide bridge and two single sulfide bridges [87]. The chalcogen-richest binuclear cluster is found in $[(RCp)_2V_2Q_5]$ (Q = S, Se), where two V(IV) centers are bound by three different types of bridging ligands: a μ-Q bridge, a μ-η^2-Q_2 bridge and a μ-η^1-Q_2 bridge (R = CH_3, *i*-Pr). The V–V distance in $[(MeCp)_2V_2S_5]$ is 2.658(1) Å [88]. The derivatives of MeCp are best made by mild thermolysis of $[(MeCp)_2V(Q_5)]$ in refluxing THF [88,89], the Cp* derivatives—by thermal or photochemical reactions of $[Cp^*V(CO)_4]$ with elemental chalcogen [86]. Thermolysis of $[Cp_2V(S_5)]$ or reaction of $[CpV(CO)_4]$ with S_8 gives poorly characterized $Cp_2V_2S_4$ and $Cp_2V_2S_5$ which presumably have the same composition as their alkylsubstituted analogs [90]. $Cp_2Nb_2S_5$, made from $[CpNb(CO)_3(THF)]$ and S_8 may belong to the same family. Reaction of $[CpNb(CO)_3(THF)]$ with H_2S or CH_3SH gives doubly and triply-bridged compounds $[(CpNb(CO)_2)_2\text{-}\mu\text{-}(S)_2]$ and $[(CpNb(CO)_2)_2\text{-}\mu\text{-}(S)_3]$ [91].

The synthetic potential of the $[Cp_2V_2(Q_2)_2(Q)]$ clusters was thoroughly explored by Herberhold et al. It is possible (i) to abstract stepwise one or two Q atoms of the two Q_2 bridges, making $[Cp_2V_2(Q_2)_2]$ and $[Cp_2V_2(Q)_3]$ clusters; (ii) to add (again stepwise) chalcogens to $[Cp_2V_2(Q_2)(Q)_2]$ and $[Cp_2V_2(Q)_3]$; (iii) to substitute chalcogens in the $[Cp_2V_2(Q_2)_2(Q)]$ clusters. By combining these three approaches it was possible to isolate or at least to detect (combination of mass-spectroscopy and ^{51}V NMR proved to be a very powerful tool for this) all possible mixed S/Se clusters in the $[Cp^*_2V_2Q_5]$, $[Cp^*_2V_2Q_4]$ and $[Cp^*_2V_2Q_3]$ families. The chalcogen abstraction was effected by PBu_3, chalcogen addition—by Na_2Q_x (Q = S; $x = 2$; Q = Se; $x = 5$) and exchange—by reacting with H_2S or H_2Se. The reactions were often remarkably clean and efficient: $[Cp^*_2V_2(Se_2)(S)_2]$ reacts with PBu_3 to give $[Cp^*_2V_2(Se)(S)_2]$ without any indication for sulfur elimination; and $[Cp^*_2V_2(S)_3]$ reacts with Na_2Se_5 to give mainly one isomer of $[Cp^*_2V_2SeS_3]$—with μ_2-S-Se ligand. However, reaction of $[Cp^*_2V_2(Se_2)_2(Se)]$ with H_2S in THF gives all possible mixed $[Cp^*_2V_2S_xSe_{5-x}]$ ($x = 1$–5) species. The oxocomplexes $[Cp^*_2V_2(Q_2)(Q)(O)]$ seem to be much less flexible and form neither chalcogen-richer $[Cp^*_2V_2(Q_2)_2(O)]$ nor chalcogen-poorer $[Cp^*_2V_2(Q)_2\ (O)]$ derivatives. Dark-green $[Cp^*_2V_2(Te_2)(Te)(O)]$ was made by treatment of kinetically labile $[Cp^*V(CO)_3(Me_2S)]$ with Te. It gives with H_2S $[Cp^*_2V_2(Te_2)(S)_2]$ and $[Cp^*_2V_2(Te_2)(S)(O)]$, and by photolysis in the presence of S_8 looses Te completely to give mainly $[Cp^*_2V_2(S_2)(S)(O)]$ together with some $[Cp^*_2V_2(S_2)_2(O)]$ [87].

3. Trinuclear clusters

3.1. Clusters with linear M_3 units

Such clusters are found in the structure of $Nb_6Se_{20}Br_6$, where trinuclear clusters $Nb_3(\mu\text{-}Se_2)_4{}^{5+}$ are linked into zig-zag chains by other $Se_2{}^{2-}$ and Br^-. Thus the central Nb atom in the core is surrounded only by four inner diselenido-bridges, and the periferic niobium atoms are linked to other trinuclear cluster unit via one μ-$Se_2{}^{2-}$, one μ-Br and have another terminal bromide so that the structure is represented by the formula $[Nb_3(\mu\text{-}Se^i_2)_4(\mu\text{-}Se^a_2)_{2/2}Br^a_{2/2}Br^a_2]$ (Fig. 13). The Nb–Nb distances in the cluster are 3.085 Å (only two electrons are available for M–M bonding between three metal centers giving formal bond order of 0.5), while the intercluster Nb–Nb distances in the chain are non-bonding, ca. 3.9 Å. As the metal–metal bonding is strongly localized, the compound is a dielectric [92]. No molecular derivatives of $Nb_3(\mu\text{-}Q_2)_4{}^{5+}$ have been reported.

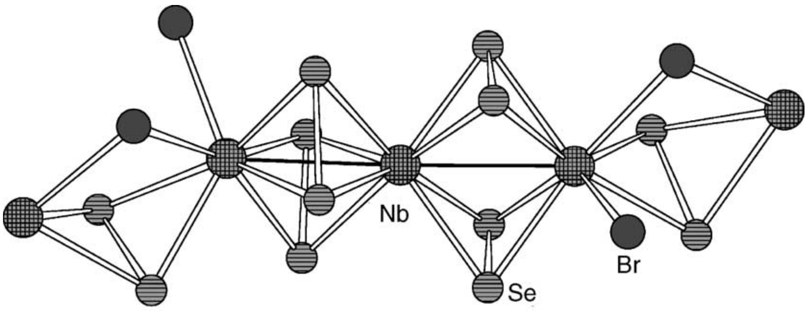

Fig. 13. Fragment of polymeric chain in $[Nb_3(\mu\text{-}Se^i_2)_4(\mu\text{-}Se^a_2)_{2/2}Br^a_{2/2}Br^a_2]$ [92].

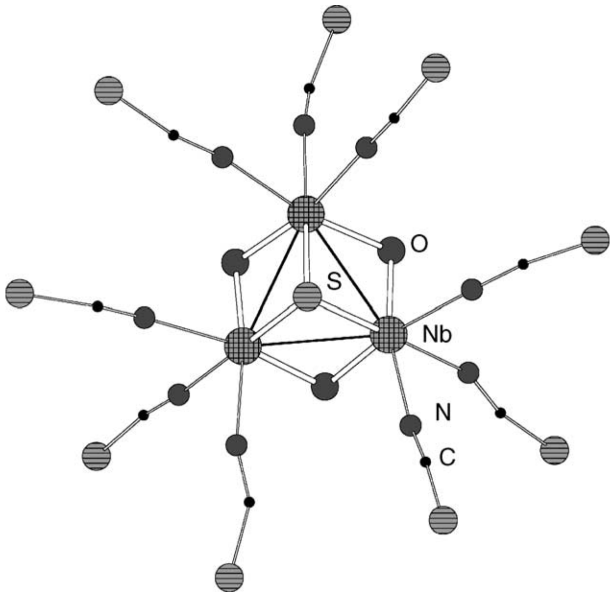

Fig. 14. $[Nb_3SO_3(NCS)_9]^{6-}$ [95].

Linear trinuclear Nb_3 groups can also be discerned in the structure of $Nb(Te_2)_2$. They are connected with ditellurido bridges which simultaneously act both as inter and intracluster links to give a 3D-structure. Again, the Nb–Nb distances in the group (3.07–3.25 Å) are much shorter than those between the clusters (arranged into chains running along *c* axis). However, the Nb–Nb bonding is again electron-deficient (bond order 0.75) [93].

3.2. Triangular clusters

The only cluster in this group having the incomplete cuboidal core $V_3S_4^{3+}$ was isolated from a complicated reaction mixture of $Na_2S_2(CH_2)_2$ (Na_2edt), Et_4NBr, VCl_3 and sulfur as black $(Et_4N)_3[V_3S_4(edt)_3]\cdot 2CH_3CN$. The yield was 20%. Its structure shows a triangular arrangement of vanadium atoms (V–V 2.89–2.92 Å) and the core possesses idealized C_{3v} symmetry. The coordination polyhedron around V, neglecting V–V bonds, is close to a trigonal bipyramid. The structure shows no trends to justify a trapped-valence assignment ($V^{III}V^{IV}V^{IV}$). The cluster can be oxidized and reduced reversibly in a CV experiment, showing the following waves: 3-/4- − 1.51 V (rev.), 2-/3- − 0.63 V (rev.) and 1-/2- 0.00 V (irrev.) (CH_3CN, versus NHE) [94]. No Nb or Ta analogues are known, though Nb in black $(Me_4N)_3(NH_4)_3[Nb_3SO_3(NCS)_9]$ a $Nb_3(\mu_3\text{-}S)(\mu\text{-}O)_3^{3+}$ core is present (Nb–Nb 2.763(3) Å). It was prepared by aquation of $[Nb_2Cl_6(THT)_3]$ in HCl with subsequent treatment with NH_4NCS in a 60% yield. Without counting the Nb–Nb bonds the metal has an octahedral coordination (Fig. 14) [95]. These clusters are electron-deficient since only four electrons are available for the bonding in the M_3 triangle.

Closely related chalcogen-rich cluster core $M_3(\mu_3\text{-}Q)(\mu\text{-}Q_2)_3$ is known only for vanadium. Reaction of $[V(SPh)_2(bpy)_2]PF_6$ with sulfur in acetonitrile gives $[V_3S_7(bpy)_3]PF_6$ in a 35–40% yield. In this V^{III} derivative, the V–V distances are 2.75–2.77 Å, and six electrons are available to give three single V–V bonds (Fig. 15). The calculations show that indeed the HOMO and LUMO are almost pure M–M bonding and antibonding orbitals, respectively. The cluster is diamagnetic both in the solid state and in solutions. Cyclic voltammetry shows one-electron reversible oxidation at −0.47 V versus Fc^+/Fc couple in acetonitrile [96]. The oxidized $V_3S_7^{2+}$ core is found in the black $(Et_4N)[V_3S_7(Me_2NCS_2)_3]$ which forms from $(NH_4)_3VS_4$, CuCl, PhSNa, Nadtc and Et_4NCl in DMF in only 3% yield. The cluster is very stable and the solutions are not air sensitive. It is paramagnetic, $\mu_{eff} = 1, 76$ B.M. at 300 K. An IR band of 442 cm^{-1} was assigned to μ_3-S, and that of 554 cm^{-1} to S–S of the disulfido bridge, while $V\text{–}S_{dtc}$ appears at only 354 cm^{-1}. The three vanadium atoms are identical and no separate oxidation states can be ascribed to them, the V–V bond is 2.74–2.75 Å. Cyclic voltammetry shows a reversible reduction at –1.09 V and a reversible oxidation at 0.04 V [97]. The presence of Cu(I) is in fact not necessary for the V_3S_7 cluster core assembly. Ammonium thiovanadate reacts with $(HOCH_2CH_2)_2NCS_2Na$ and Et_4NCl in CH_3OH to give a black $(Et_4N)[V_3S_7((HOCH_2CH_2)_2NCS_2)_3]$ in a 19% yield. The yield increases when a stream of H_2S is passed through the reaction mixture and a thiol is added. Thus $(Et_4N)[V_3S_7(Et_2NCS_2)_3]$ forms from $(NH_4)_3VS_4$, Nadtc, Et_4NCl and dithiothreitol ($C_4H_{10}O_2S_2$) under these conditions. It has also been structurally characterized. The CV behavior of all the three dithiocarbamates is very similar [98].

The black air-sensitive compound $(Et_4N)[V_3(\mu\text{-}O)_2(\mu\text{-}S)_2(O)(Et_2NCS_2)_3]$ can only formally be treated here since in this all-V(IV) derivative two vanadium atoms are close enough (2.715(3) Å) to form a single metal–metal bond and they are in fact spin-coupled. The third V atom is a typical V(IV) and forms a typical tetragonal pyramidal VO^{2+} unit, and in fact its ESR spectrum resembles that of $[VO(edt)_2]^{2-}$. The compound was made from VCl_3, Li_2S, Et_4NBr and Nadtc$\cdot 3H_2O$ (1:2:1:1 molar ratio) in acetonitrile [99].

Niobium and tantalum do not resemble vanadium very much in the type of trinuclear chalcogenide clusters which they form, though it may be due to very different synthetic methodologies employed by the groups working in the area. An unusual Nb cluster is obtained from $[(EtMe_4C_5)_2Nb_2(B_2H_6)_2]$ and S_8 in decane at 170 °C in a 26% yield. An equilateral triangle Nb_3 (Nb–Nb 3.15 Å) in $[(\eta^5\text{-}EtMe_4C_5)_3Nb_3(S_3BSH)(\mu_3\text{-}S)_3(\mu\text{-}S)_3]$ is capped by a $[BS_3(SH)]^{4-}$ anion in a symmetrical way (Nb–S 2.55 Å) (Fig. 16). There are only 2e to fill M–M bonding orbitals. The S–H group shows a weak band in the IR spectrum at 2560 cm^{-1}. If the same reaction is done in xylene at 144 °C, the same product forms along with a more sulfur-rich cluster $[(EtMe_4C_5)_3Nb_3S_8]$ of unknown structure [100]. A very similar cluster is known also for Ta except the capping

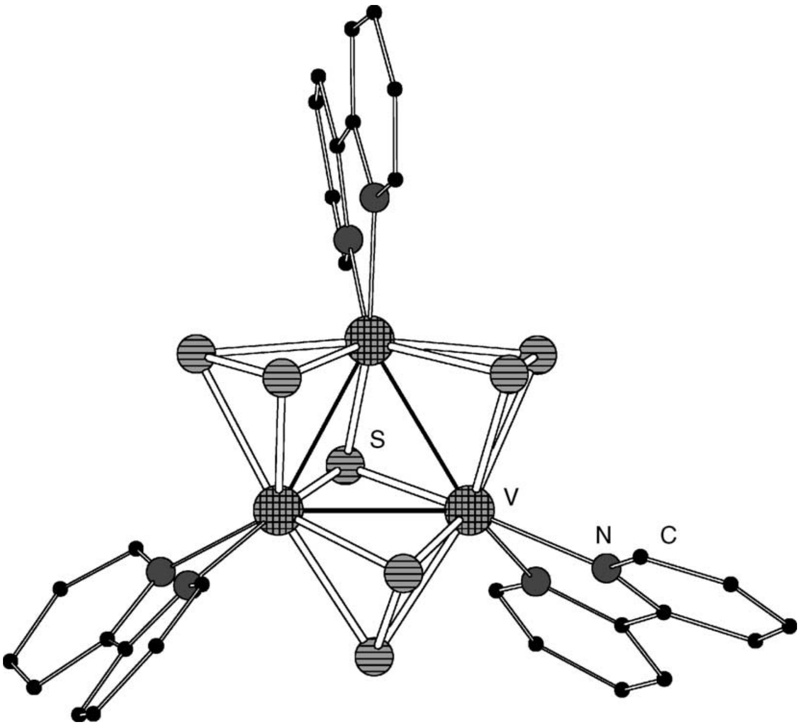

Fig. 15. $[V_3S_7(bpy)_3]^+$ [96]. Hydrogen atoms are omitted for clarity.

ligand here is anion $[BS_3(SH)]^{4-}$. It was prepared from a mononuclear complex $[Cp^*Ta(S)(SCPh_3)_2]$ and $NaBH_4$ in a 70% yield. ^{11}B NMR shows a sharp resonance at −21.3 ppm. The Ta–S (thioborate) distance is 2.54 Å and the Ta–S (bridging sulfide) is shorter, 2.36 Å [101]. Treatment of $[Cp^*TaCl_4]$ with Li_2S (THF, 0 °C) gives another Ta triangular cluster, isolated as $Li_2(THF)_2[Cp^*{}_3Ta_3S_6]$ [102].

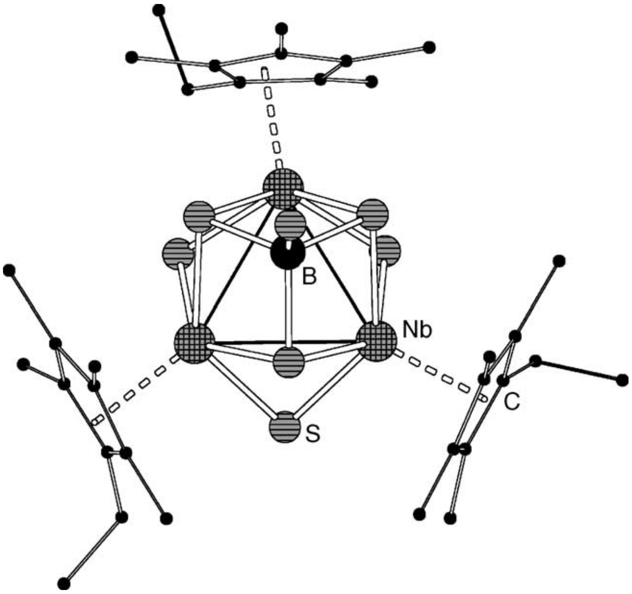

Fig. 16. $[(\eta^5\text{-}EtMe_4C_5)_3Nb_3(S_3BSH)(\mu_3\text{-}S)_3(\mu\text{-}S)_3]$ [100]. Hydrogen atoms are omitted for clarity.

There are also less symmetrical triangular cores which contain bridging disulfido or trisulfido ligands, often obtained as a part of complicated reaction products mixtures. The corresponding $[CpMCl_4]$ (M = Nb, Ta) react with $(Me_3Si)_2Q$ (Q = S, Se) to form black $[Cp_3Nb_3Se_5Cl_2]$ (Fig. 17), red $[Cp_3Ta_3S_7Cl_2]$ (Fig. 18), brown $[Cp_4Ta_4S_{13}]$, and black $[Cp_8Ta_6S_{10}][TaSCl_5]_2$ [103]. The Nb cluster has a bent chain of three Nb atoms bridged by Se and Se_2. The central Nb aton is Nb(V) and the two periferic—Nb(IV). The trinuclear Ta^V cluster shows a triangle of three Ta atoms bridged by μ_2-S, μ_3-S and μ_2-S_2 bridges. Long Ta–Ta distances of 3.24–3.60 Å indicate no M–M bonding, in agreement with the oxidation state formalism [103]. The group $Nb_3{}^{15+}$ gives even more chalcogen-rich cores. Ther-

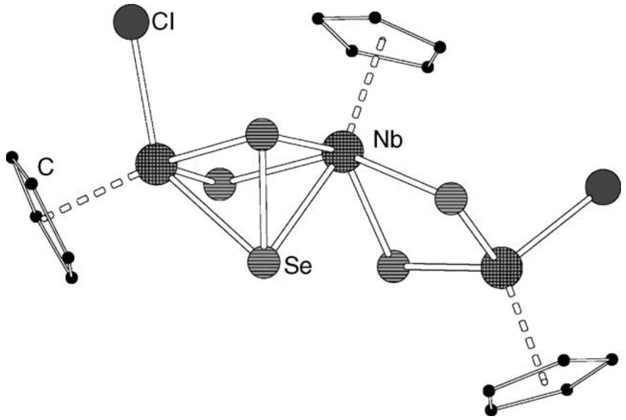

Fig. 17. $[Cp_3Nb_3Se_5Cl_2]$ [103]. Hydrogen atoms are omitted for clarity.

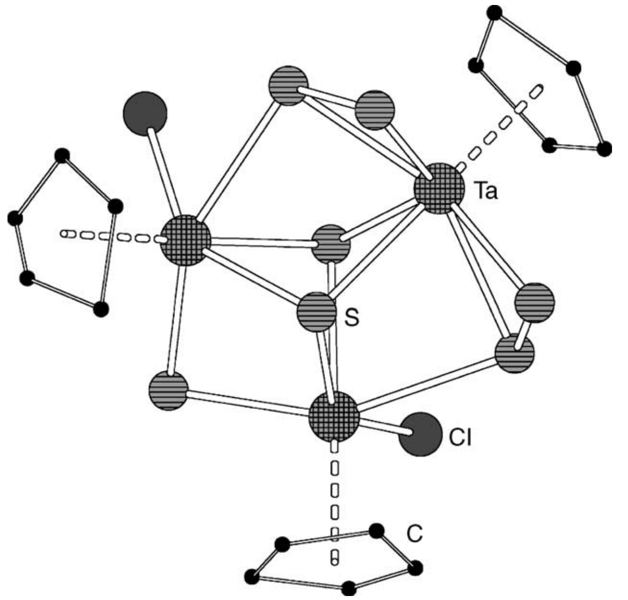

Fig. 18. $[Cp_3Ta_3S_7Cl_2]$ [103]. Hydrogen atoms are omitted for clarity.

molysis of a polysulfide mixture of $[(t\text{-BuCp})_4Nb_2(S_n)]$ ($n = 8, 9$) in toluene (1 h, 100 °C) gives a mixture of products: red-orange structurally characterized as $[(t\text{-BuCp})_3Nb_3S_{12}]$ (Fig. 19), $[(t\text{-BuCp})_3Nb_3(O)S_{10}]$ (Fig. 20), and $[(t\text{-BuCp})_4Nb_4S_{13}]$ of unknown structure. The first cluster has a $Nb_3(\mu_3\text{-}S)(\mu_3\text{-}S_2)(\mu\text{-}S_2)_2(\mu\text{-}S_3)(S_2)^{3+}$ core with three different types of Nb atoms, and its ^1H NMR spectrum indicates three different t-BuCp rings. The Nb–Nb distances range from 3.61 to 4.08 Å. The structure of $[(t\text{-BuCp})_3Nb_3(O)S_{10}]$ is similar, with μ_3-O instead of μ_3-S (Nb–O 2.07–2.12 Å) and a $\mu_3\text{-}S_2$ ligand instead of S_3. The Nb atoms here are not equivalent and they remain so in solution, as can be seen from ^1H NMR. The Nb–Nb distances are 3.33–3.74 Å [104].

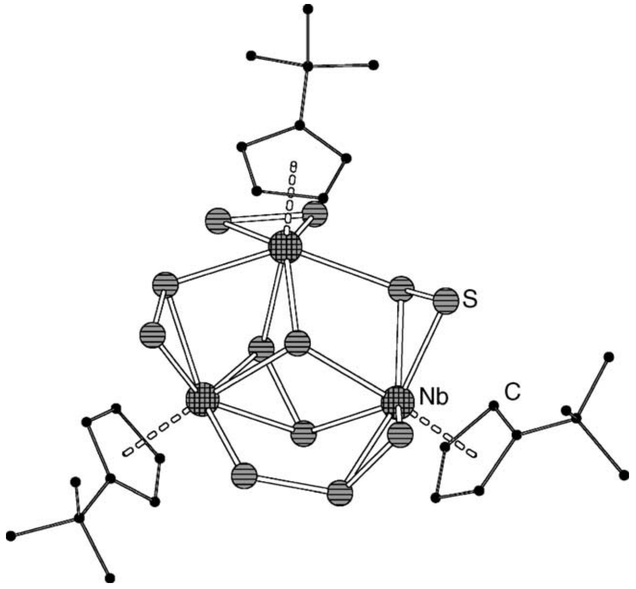

Fig. 19. $[(t\text{-BuCp})_3Nb_3S_{12}]$ [104]. Hydrogen atoms are omitted for clarity.

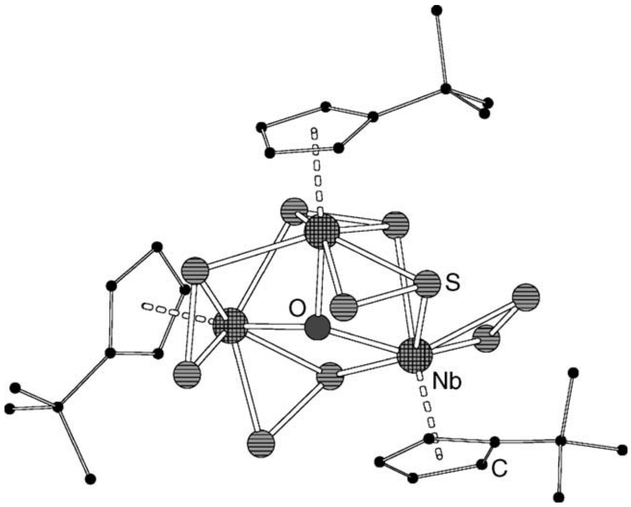

Fig. 20. $[(t\text{-BuCp})_3Nb_3(O)S_{10}]$ [104]. Hydrogen atoms are omitted for clarity.

Though the Nb_3X_8 halides ($X = Cl$, Br, I) have long been known, only recently a closely related family of chalcohalides M_3QX_7 was uncovered, starting with the preparation of Nb_3SBr_7 from Nb, S and Br_2 at 550 °C [105]. Very soon the whole family Nb_3QX_7 ($Q = S$, Se, Te; $X = Cl$, Br, I) was prepared [106]. Both in the pure halides and in the chalcohalides of this type the metal cluster unit belongs to the common M_3X_{13} type and can be formulated with the notation of Schäfer and Schnering as $[M_3(\mu_3\text{-}X^i)(\mu\text{-}X^i)_3(\mu_3\text{-}X^a)_3(\mu\text{-}X^a)_6]$ (Fig. 21). It is the $\mu_3\text{-}X^i$ capping position which the chalcogen enters. In the case of halides there are seven electrons per cluster, resulting in an unpaired electron and paramagnetism. In the chalcohalides there are only 6 electrons and they are diamagnetic. The extra electron is located on a weakly M–M bonding orbital and its removal does not produce much impact on M–M bonding in the cluster. Despite the non-existence of reliable proofs for Ta_3X_8, the corresponding chalcohalides Ta_3SeI_7, Ta_3TeI_7 and Ta_3SBr_7 have been prepared. They have however rather narrow existence limits, and Ta_3SBr_7 decomposes into Ta_6Br_{15}, $TaBr_5$ and TaS_2 already above 575 °C [107].

The 7e clusters in the M_3QX_7 family are also known. The X-ray analysis of $Cs[Nb_3SBr_7]$, prepared from $NbBr_5$, Nb, S and CsBr, shows that the extra electron here is used for intercluster binding in such a way that the Nb_3 clusters (Nb–Nb 2.90 Å) are linked by two additional Nb–Nb bonds (Nb–Nb 3.11 Å) to form infinite chains. Electrical conductivity measurements in this direction show semiconductor behavior between room temperature and 50 K [108]. It is interesting that in the formally isoelectronic compounds Nb_3Q_4 ($Q = S$, Se, Te) the intracluster M–M bonding is very weak (3.37 Å in Nb_3S_4) and is almost completely replaced by intercluster bonding leading to the formation of

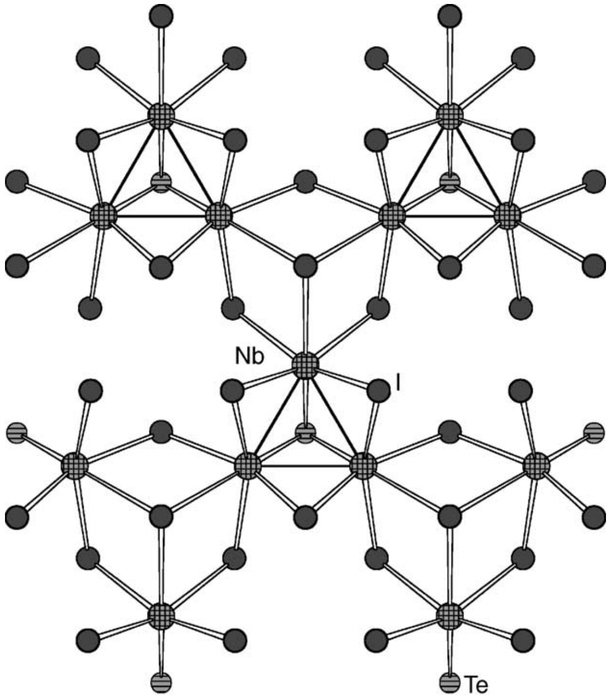

Fig. 21. Fragment of polymeric structure in Nb_3TeI_7 [106].

zig-zag metal chains running perpendicular to the M_3 plane, with short Nb–Nb distances 2.881 Å (Q = S), 2. 885 Å (Q = Se) and 2.973 Å (Q = Te) [109]. A mixed calcogenide halide bridged cluster core $Nb_3(\mu_3\text{-}S)(\mu_3\text{-}I)(\mu\text{-}I)_3^{4+}$ is encountered in a layered compound $Nb_7S_2I_{19}$, that is present as $[Nb_3SI_7]_2(NbI_5)$. Each Nb is octahedrally coordinated by one S and five I atoms. The sulfur atom and one of the iodine atoms cap the triangle (Nb–Nb 2.776(5) Å). The 2D network forms through intercluster bridging iodine atoms, forming nearly hexagonal channels along the c axis. There isolated NbI_5 molecules reside. This inclusion compound was made by heating the elements in a molar ratio 7Nb:2S:19I in a quartz ampoule at 1100 K for 2 days. Another triangular cluster compound, Nb_3IS_7 formed under these conditions as an impurity. Two-probe electrical resistivity measurements indicated $\rho(300\,K) > 10^4\,\Omega\,cm$ [110]. Recently Ta_4SI_{11} was prepared by heating the elements at 430 °C for 2 weeks. Most probably it has the $Ta_3(\mu_3\text{-}S)(\mu\text{-}I)_3^{4+}$ cluster core (6e), linked into layers via bridging I^- and single Ta^{4+} centers. It is paramagnetic with $\mu_{eff.} = 1.53$ BM, the single Ta(IV) being responsible for paramagnetism. Ta_3SI_7 is also briefly mentioned in the same work [111]. In the compound $[Nb_3O(Te_4)(Te_2)_2I_6]I$ (Fig. 22) the metal core is arranged in a form of an isosceles triangle with the Nb–Nb distances 3.013(2) Å, 3.048(2) Å and 3.861(2) Å. The core is capped by a μ_3-O atom. Each of the two short sides of the triangle is bridged by one Te_2 group, while a similar planar Te_4 group ($Te–Te_{av.}$ 2.797 Å) is bonded in a $\mu\text{-}\eta^2{:}\eta^2$ fashion to the longer side. The bonding is rationalized in terms of the formalism $[(Nb^{3+})(Nb^{4+})_2(O^{2-})(Te_4^{2+})(Te_2^{2-})_2(I^-)_6]^+$, thus leaving four electrons to form two localized Nb–Nb bonds.

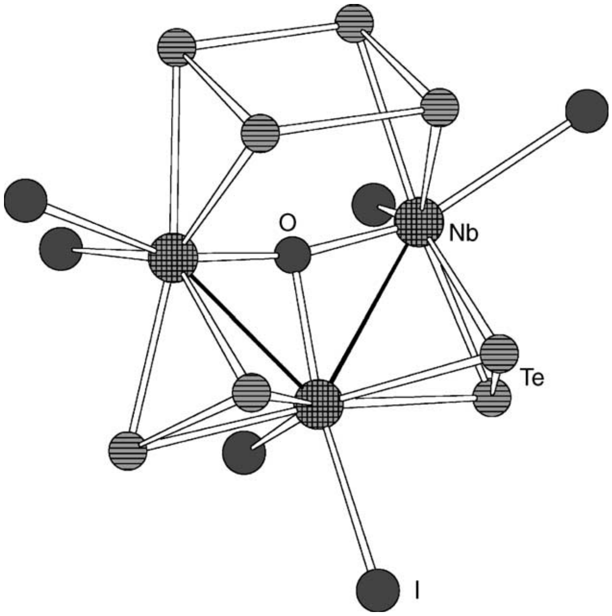

Fig. 22. $[Nb_3O(Te_4)(Te_2)_2I_6]^+$ [112].

The compound was obtained in a moderate yield from Nb, $NbOI_3$, Te and I_2 (2:1:8:2 molar ratio). It can also be made in a low yield directly from the elements (3Nb, 11Te, $2I_2$, 680 °C) [112].

4. Tetranuclear clusters

4.1. Linear M_4 clusters

In the selenobromides $M_4Se_{16}Br_2$ (M = Nb, Ta) there are tetranuclear units $\{M_4(\mu\text{-}Se_2)_6\}$ which result from condensation of $\{M_2(\mu\text{-}Se_2)_2\}$ clusters. The M–M distances within them are about 3.1 Å. These clusters are further connected by outer bridging Se_2^{2-} groups into infinite chains. However inside the chain they remain well separated from each other (M–M 3.7 Å). The chains are positively charged and Br^- between the chains balances the charge. The formula can thus be written as $[M_4(\mu\text{-}Se_2)_6(\mu\text{-}Se_2)_{4/2}]Br_2$ [113].

4.2. Tetrahedral clusters with the cuboidal M_4 $(\mu_3\text{-}Q)_4$ core

A tetrahedral M_4 core is present in cuboidal clusters M_4Q_4 and they are in fact well known for V, Nb and, to a less extent, for Ta. Vanadium forms a dithiocarbamate $(Et_4N)[V_4S_4(C_4H_8NCS_2)_6]$ in a 67% yield from $(NH_4)_3VS_4$, ammonium pyrrolidinedithiocarbamate $NH_4C_4H_8NCS_2$ and PPh_3, in the presence of Et_3N in acetonitrile at room temperature. V–S distances vary 2.27–2.33 Å and V–V distances in this $V_4S_4^{5+}$ core indicate M–M bonding (2.77–3.00 Å), with the involvement of only seven electrons [114]. The cyclopentadienyl derivatives have been long known and can be accessed by var-

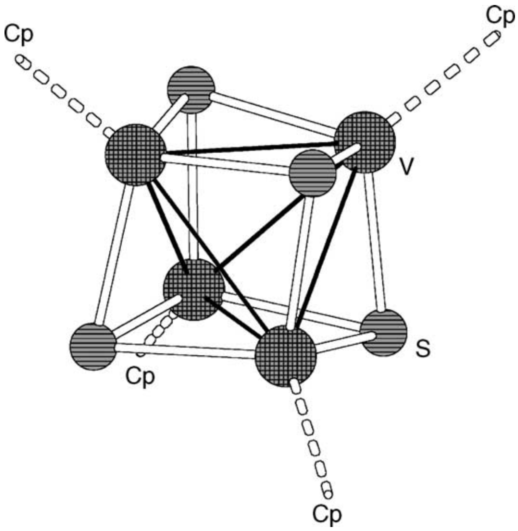

Fig. 23. $[Cp_4V_4S_4]$ [116]. Hydrogen atoms are omitted for clarity.

ious routes. The oxidative sulfurisation of $[(MeC_5H_4)_2V]$ with ^{t}BuSH under reflux in heptane gives relatively air stable $[(MeC_4H_5)_4V_4S_4]$, with some amount of pentanuclear $[(MeC_5H_4)_5V_5S_6]$ [115]. The unsubstituted less soluble $[Cp_4V_4S_4]$ (Fig. 23) is made from vanadocene and $CH_3C(S)SH$ (yield 47%, reaction takes 4 days) [116]. This cluster can also be made from Cp_2V and H_2S in THF at room temperature [117]. Another approach involves a condensation of two V_2 units. Desulfurisation of S_2 bridged $[(MeC_5H_4)_2V_2(\mu\text{-}\eta^1\text{-}S_2)(S)_2]$ with PBu_3 gives a mixture of $[(MeC_4H_5)_4V_4S_4]$ and $[(MeC_5H_4)_5V_5S_6]$ [118]. The cube $[Cp_4V_4S_4]$ is made from corresponding $[Cp_2V_2S_4]$ and PBu_3. Reaction of $[Cp_2V]$ with $[(CH_3C_5H_4)_2V_2S_4]$ gives mixed species $[(C_5H_5)_x(MeC_4H_5)_{4-x}V_4S_4]$, which have been characterized by ^{1}H NMR and mass-spectroscopy [118]. Similarly, selenium-rich $[Cp_2V_2Se_5]$ reacts with PBu_3 to give $[Cp_4V_4Se_4]$ (72%, 2h in CH_2Cl_2) [119]. The MeCp analogue is obtained in a 46% yield from $[(CH_3C_5H_4)_2V_2Se_4]$ and PBu_3 in CH_2Cl_2 [119]. The tellurides $[(RCp)_4V_4Te_4]$ (R = H, Me) are obtained by heating $[(RCp)_2V_2(CO)_4(\mu\text{-}Te)_2]$ in toluene at 50–60 °C in almost quantitative yields (R = H, Me) [119]. These cuboidal clusters have 8e available for M–M bonding and are paramagnetic, in agreement with the orbital population pattern $a_1^2 + e^4 + 1t_2^2$. $[(MeC_4H_5)_4V_4S_4]$ gives the molecular peak in the mass-spectrum, with subsequent loss of all the Cp ligands, when the "naked" $V_4S_4^+$ ion appears. X-ray analysis of this cluster shows a regular tetrahedron with V–V bonds 2.87–2.88 Å, and V–S of 2.29–2.30 Å [115,120]. The cube $[(C_5H_5)_4V_4S_4]$ has a very similar structure [116]. Although cyclic voltammetry experiments show that $[(MeC_4H_5)_4V_4S_4]$ loses reversibly four electrons in four consecutive 1e oxidation steps, only the first oxidation gives a product stable enough to be isolated. It was obtained as $[(MeC_4H_5)_4V_4S_4]BF_4$ by oxidation with Ph_3CBF_4. The V–V and V–S distances in this cation are somewhat shorter than in the neutral molecule, 2.86 and 2.30 Å, respectively [118b].

Unlike the V_4Q_4 clusters, the $Nb_4(\mu_3\text{-}Q)_4^{4+}$ core is found only in solid state, in chalcohalides $Nb_4Q_4X_4$ (Q = S, Se; X = Br, I). They are prepared by high-temperature synthesis from the elements. Only selenoiodide $Nb_4Se_4I_4$ could be obtained pure by heating the elements in a sealed quartz ampoule in a 880/850 °C temperature gradient. It is built from the cuboidal units $Nb_4Se_4^{4+}$ and I atoms in such a way that a cubic NaCl type lattice is formed. Each Nb atom is connected to three I's and each I is triply bridging. The Nb–I distance is 3.01 Å and Nb–Nb 2.96 Å—appreciably longer than in the isoelectronic V_4S_4 cubes. $Nb_4S_4Br_4$, $Nb_4Se_4Br_4$ and $Nb_4S_4I_4$ are also known but could not be prepared pure [121]. Cuboidal clusters $M_4Q_4^{5+}$ are present in ternary chalcogenides $GaNb_4Q_8$ (Q = S, Se) and $GaTa_4Se_8$. As they are more electron-deficient than the $Nb_4Se_4^{4+}$, the Nb–Nb bonds in the tetrahedron are expectedly longer: 3.026 Å. Nb can substitute for Mo and solid solutions $GaNb_{4-x}Mo_xS_8$ were prepared. The magnetic properties of these compounds were studied. They indicate a semimetal behavior [122].

Incorporation an oxygen atom into the M_4 tetrahedron is also known in the case of Nb and Ta. Both cluster anions $[M_4(\mu_4\text{-}O)Te_4(CN)_{12}]^{6-}$ are known and made by heating MTe_4 with KCN at 440–460 °C (M = Nb) or 340–360 °C (M = Ta). They are relatively air-stable and have been structurally characterized. The Nb–Nb distances in $K_6[Nb_4(O)Te_4(CN)_{12}]\cdot KOH\cdot K_2CO_3\cdot 8H_2O$ are 3.19–3.21 Å, the Ta–Ta distances in $K_6[Nb_4(O)Te_4(CN)_{12}]\cdot KOH\cdot 4H_2O$ are 3.19–3.26 Å. There are only 4e available for M–M bonding, which occupy weakly M–M bonding doubly degenerated HOMO, in accordance with the observed diamagnetism of the complexes. The Nb cluster undergoes a quasi reversible oxidation at 309 mV followed by irreversible oxidation at 900 mV in 0.1 M Na_2SO_4 solution, whereas for the Ta cluster only irreversible oxidation takes place at 642 mV (versus NHE) [123,124].

The tetrahedral arrangement of Ta atoms is also found in $[Cp_4Ta_4S_{13}]$, where the Ta atoms are bridged by four μ_2-S_2, two μ_3-S and one μ_4-S ligands. The quadruply bridging sulfide forms rather long bonds with Ta ranging from 2.62 to 2.67 Å. No Ta–Ta bonding exist in this Ta(V) compound (Fig. 24). $[({}^{t}BuC_5H_4)_4Nb_4S_{13}]$ may have the same structure [104].

Opening up the M_4 tetrahedron gives square planar units, represented here by a $Nb_4(\mu_4\text{-}S)_2^{8+}$ core. The first cluster of this type to be prepared was black $Li_4[Nb_4(S)_2(SPh)_{12}]$, made from $[Nb_2Cl_6(Me_2S)_3]$ and LiSPh (taken in a large excess) in toluene in a 55–60% yield. In this diamagnetic cluster four Nb(III) atoms have 8e—exactly to satisfy the requirement for four single metal–metal bonds. The Nb–Nb distances are 2.83 Å (Fig. 25). This cluster is rather robust and cannot be oxidized with PhSSPh, nor does it react with PPh_3 in a hot toluene [125]. Orange $[Nb_4(S)_2(SPh)_8(PMe_2R)_4]$ (R = Me, Ph) were prepared

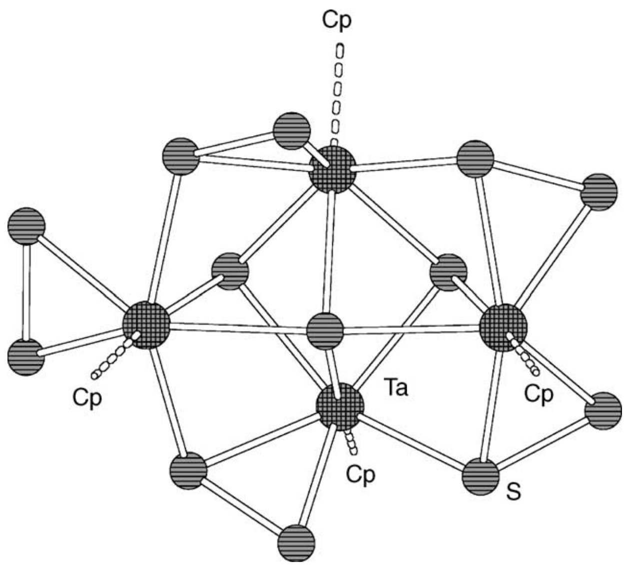

Fig. 24. $[Cp_4Ta_4S_{13}]$ [104]. Hydrogen atoms are omitted for clarity.

by reducing $NbCl_5$ with Na/Hg, adding PhSSPh and then the phosphine, in about 20% yields. The Nb–Nb bonds are here somewhat shorter, 2.81–2.82 Å (in both clusters) and the Nb–P bonds are unusually long (2.67–2.70 Å) [126].

Reduction of a mixture of $TaCl_5$ and Li_2S with Na/Hg gives a green solution, which turns dark orange. Addition of PMe_3 gives a binuclear Ta(IV) complex $[Ta_2(\mu\text{-}S)_2Cl_4(PMe_3)_4]$ (20%), together with 2% of green tetranuclear $[Ta_4S_4Cl_8(PMe_3)_6]$. In the latter Ta(IV) cluster only for electrons are available for M–M bonding, and this is realized within a zig-zag chain Ta(1)–Ta(2)–Ta(2)–Ta(1) with Ta(1)–Ta(2) distance of 3.09 Å and the central Ta(2)–Ta(2) bond of 2.90 Å (Fig. 26) [127].

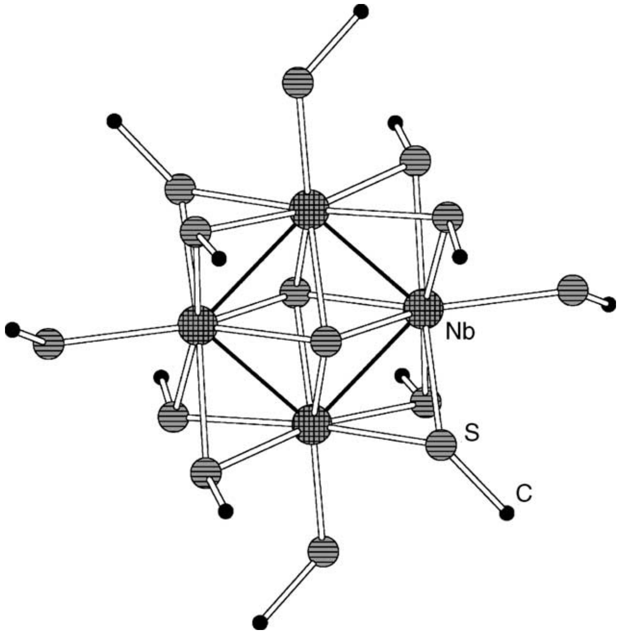

Fig. 25. $[Nb_4(S)_2(SPh)_{12}]^{4-}$ [125]. Hydrogen atoms are omitted for clarity. Only carbon atoms attached to S atoms are shown.

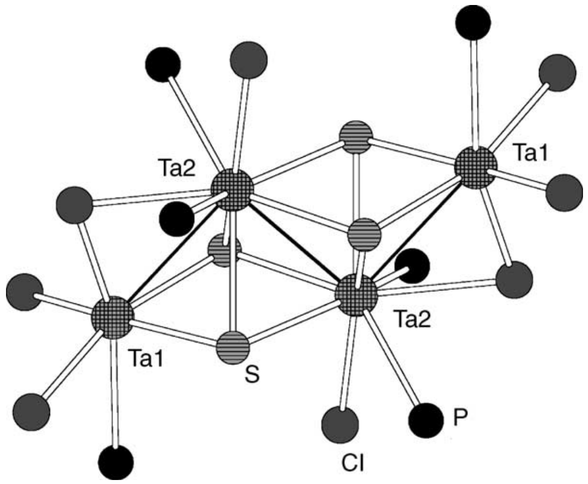

Fig. 26. $[Ta_4S_4Cl_8(PMe_3)_6]$ [127]. Hydrogen and carbon atoms are omitted for clarity.

Carrying out the reaction between VCl_3, Li_2S, Et_4NBr and Na_2edt in CH_3CN in a reagent ratio different from that used to obtain the trinuclear cluster $[V_3S_4(edt)_3]^{3-}$ [94], yields a tetranuclear vanadium cluster $[V_4S_2(SCH_2CH_2S)_6]^{2-}$. In this cluster four vanadium atoms are bonded to two μ_3-S bridges. The V–V distances range from 2.77 to 3.30 Å. The resulting V_4S_{14} fragment is very close to a discrete portion of the Li_xVS_2 phase and displays similar redox chemistry. The cluster can be oxidized at 0.00 V and reduced in two consecutive one-electron steps at −0.41 and −0.97 V (versus SCE) [128].

Single crystal structure determination of V_5S_8 revealed the presence of rhombic vanadium clusters in the structure with hinge V–V bond of 2.88 Å, periferic bonds of 3.04 Å and strong intercluster bonding (V–V 2.92 Å). Lowering temperature down to 100 K causes 1.5 to 1.9% decrease of the V–V distances in the clusters. Each V atom has octahedral coordination by six sulfur atoms [129].

5. Pentanuclear clusters

These are represented only by cyclopentadienyl derivatives of the V_5S_6 core. The compound $[(CH_3C_5H_4)_5V_5S_6]$ can be prepared in low yields either from $[(CH_3C_5H_4)_2V]$ and $CH_3C(S)SH$ or from $[(CH_3C_5H_4)_2V_2S_4]$ and PBu_3, the second (major) product always being the cuboidal $[(MeC_4H_5)_4V_4S_4]$. The V_5 core is trigonal-bipyramidal and each triangular face is capped by a μ_3-S atom. Two types of V–V and V–S distances are observed: $V_{ax} - S$ 2.22–2.23 Å, $V_{eq} - S$ 2.38–2.41 Å, $V_{ax} - V_{eq}$ 3.05–3.08 Å and $V_{eq} - V_{eq}$ 3.19–3.22 Å (Fig. 27). Treatment of a toluene solution of the pentanuclear cluster with TCNQ precipitates dark green crystals of $[(CH_3C_5H_4)_5V_5S_6](TCNQ)_2$ [118a].

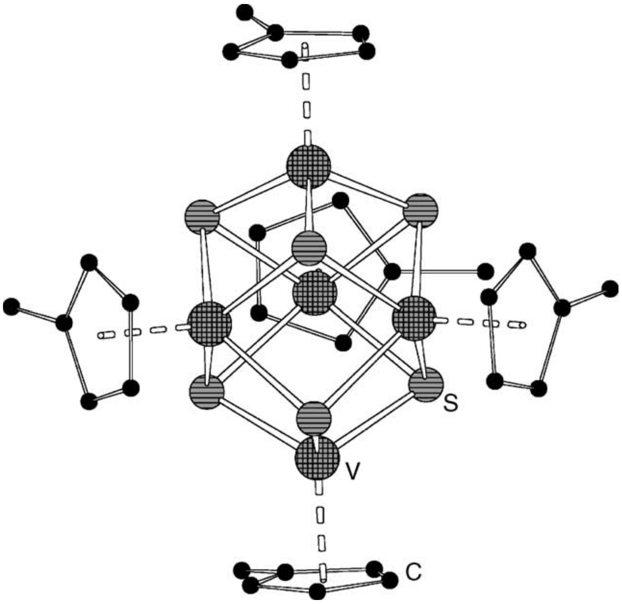

Fig. 27. $[(CH_3C_5H_4)_5V_5S_6]$ [118]. Hydrogen atoms and V–V bonds are omitted for clarity.

6. Hexanuclear clusters

Molecular octahedral clusters are represented only by the octahedral V_6 core with an interstitial oxygen atom inside, $[V_6(\mu_3\text{-}Se)_8(\mu_6\text{-}O)(PMe_3)_6]$ (Fig. 28). This was prepared from $[(\eta^5\text{-}C_5H_5)VCl_2(PMe_3)_2]$ and $(Me_3Si)_2Se$. The V–V distances range from 2.79 to 2.84 Å, V–Se 2.52 Å. The cluster is all-V^{IV} but diamagnetic [130]. High-temperature reactions of Nb_6I_{11} or of Nb_3I_8 plus niobium with sulfur in a sealed niobium container afford Nb_6SI_9 in high yields. It takes up hydrogen to form $Nb_6(H)SI_9$, with the hydrogen atom probably inside the Nb_6 octahedron. Both clusters are isostructural (Nb_6I_8 type), and can be described as 3D polymeric $[(Nb_6I_6)S_{2/2}I_{6/2}]$, with Nb–Nb 2.92 Å. The octahedra in Nb_6I_9S are tetragonally compressed, whereas in the hydride a more regular arrangement is observed. The product Nb_6I_9S is a 1D semi-conductor, with room temperature conductivity of 30 Ω^{-1} cm^{-1} [131].

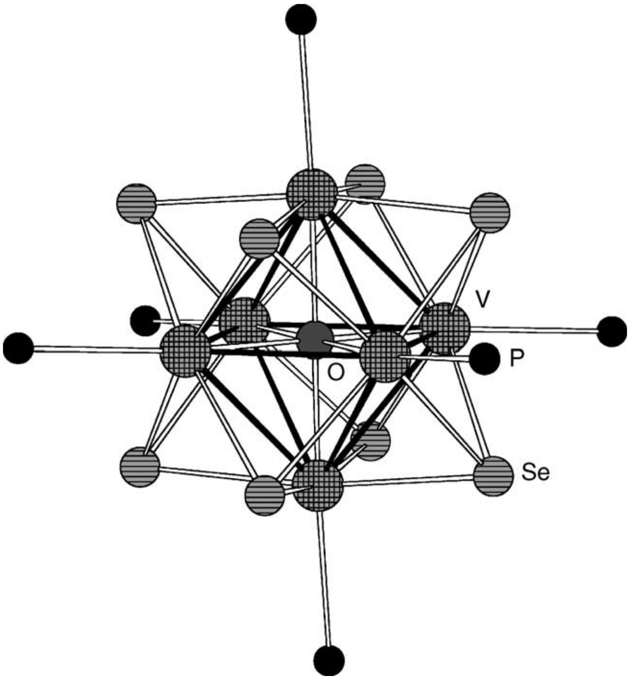

Fig. 28. $[V_6Se_8(\mu_6\text{-}O)(PMe_3)_6]$ [130]. Hydrogen and carbon atoms are omitted for clarity.

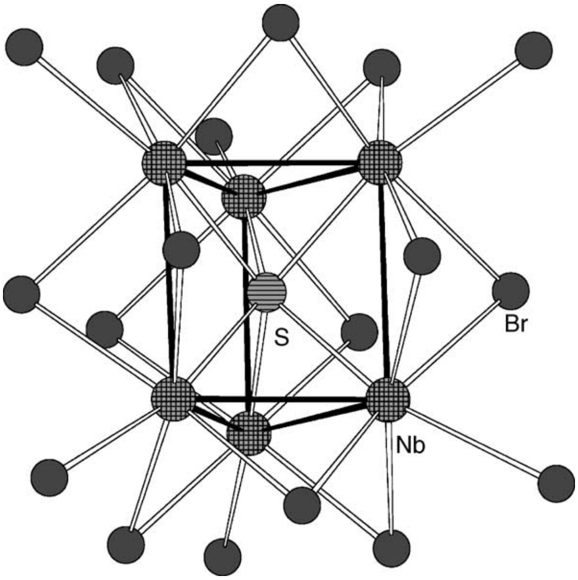

Fig. 29. $[Nb_6SBr_{18}]^{4-}$ [132].

A prismatic Nb_6 cluster having a μ_6-S as an interstitial atom is found in $Rb_3[Nb_6SBr_{17}]$. It was made by heating together RbBr, Nb, $NbBr_5$ and S at 800 °C for 5 days. Here the $[Nb_6SBr_{18}]^{4-}$ units (Fig. 29) are linked through two bromine atoms to form chains. Six bromine atoms lie above the six edges of the triangular faces of the prism (Nb–Br 2.57–2.61 Å), and further six μ_2-Br lie above the rectangular faces (Nb–Br 2.68–2.79 Å). The S atom is located almost exactly in the center of the prism (Nb–S 2.37 Å). The Nb–Nb distances along the edges of the rectangles (3.28 Å) are longer than along the edges of the triangles (2.95–2.98 Å). MO calculations on a $[Nb_6SBr_{18}]^{4-}$ unit show that the fourteen electrons available to the cluster for Nb–Nb bonds fill both the Nb–Nb bonding orbitals, which form the triangles, and those which are assigned to the edges of the rectangles. Indeed, small positive overlap populations are found between the niobium atoms of the edges of the rectangles [132].

An interesting hexanuclear vanadium cluster was obtained by treatment of $(Et_4N)Na[VS(edt)_2]$ with wet Et_3NHCl. Black, diamagnetic, extremely air-sensitive $(Et_4N)_3[V_6S_4(edt)_6(O)_2]$ was isolated from this reaction in a 5–10% yield, It has an open V_6 core, which can be rationalized in terms of a planar V_4 core with two μ_3-S above and below, and two VO^{2+} groups attached to the core via sulfido bridges and sulfur atoms of some edt^{2-} ligands. The V–V interactions can be traced along a zig-zag chain of all the six vanadium atoms. Their lengths vary from 2.758 Å for the central pair of V atoms to 2.82–2.86 Å for the peripheral bonds. All the other V . . . V distances are of the order of 3.3 Å. The cluster is ESR silent, and shows reversible redox behavior with reduction wave at −1.82 V and two oxidation waves at −1.01 and −0.56 V (CH_3CN, versus SCE). Apparently the vanadyl group is not involved in the redox changes [133].

Acknowledgements

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References

[1] E.I. Stiefel, K. Matsumoto (Eds.), Transition Metal Sulfur Chemistry, ACS Symp. Ser., 1996, p. 653.

[2] M.H. Chisholm (Ed.), Early Transition Metal Clusters with π-Donor Ligands, VCH Publishers, New York, 1995.

[3] M.B. Maple, Ø. Fisher (Eds.), Topics in Current Physics, Superconductivity in Ternary Compounds 2: Superconductivity and Magnetism, vol. 34, Springer-Verlag, Heidelberg, 1982.

[4] (a) R.H. Holm, S. Ciurli, J.A. Weigel, Prog. Inorg. Chem. 38 (1990) 1;
(b) R.H. Holm, Adv. Inorg. Chem. 38 (1992) 1.

[5] R.R. Eady, G.J. Leigh, J. Chem. Soc.l, Dalton Trans. (1994) 2739.

[6] S.M. Malinak, D. Coucouvanis, Prog. Inorg. Chem. 49 (2001) 599.

[7] (a) T. Shibahara, Adv. Inorg. Chem. 37 (1991) 143;
(b) T. Shibahara, Coord. Chem. Rev. 123 (1993) 73;
(c) X. Wu, P. Chen, Sh. Du, N. Zhu, J. Lu, J. Cluster Sci. 5 (1994) 265;
(d) T. Saito, H. Imoto, Bull. Chem. Soc. Jpn. 69 (1996) 2403;
(e) T. Saito, Adv. Inorg. Chem. 44 (1996) 45;
(f) R. Hernandez-Molina, A.G. Sykes, J. Chem. Soc., Dalton Trans. (1999) 3137;
(g) R. Hernandez-Molina, M.N. Sokolov, A.G. Sykes, Acc. Chem. Res. 34 (2001) 223;
(h) Q.-F. Zhang, W.-H. Leung, X. Xin, Coord. Chem. Rev. 224 (2002) 35;
(i) R. Llusar, S. Uriel, Eur. J. Inorg. Chem. 1271 (2003);
(j) M.N. Sokolov, V.P. Fedin, A.G. Sykes, Comprehensive coordination chemistry II. 4 (2003) 761.

[8] (a) T. Saito, J. Chem. Soc., Dalton Trans. (1999) 97;
(b) J.C.P. Gabriel, K. Boubekeur, S. Uriel, P. Batail, Chem. Rev. 101 (2001) 2037;
(c) V.E. Fedorov, N.G. Naumov, Yu.V. Mironov, A.V. Virovets, S.B. Artemkina, K.A. Brylev, S.S. Yarovoi, S.S. Yarovoi, O.A. Efremova, U.H. Paek, J. Struct. Chem. 43 (2002) 669;
(c) H.D. Selby, B.K. Roland, Zh. Zheng, Acc. Chem. Res. 36 (2003) 933.

[9] M. Hidai, S. Kuwata, Y. Mizobe, Acc. Chem. Res. 33 (2000) 46.

[10] (a) W.J. Evans, G.W. Rabe, M.A. Ansari, J.W. Ziller, Angew. Chem. Int. Ed. Engl. 33 (1994) 2110;
(b) M. Fitzgerald, Th.J. Emge, J.G. Brennan, Inorg. Chem. 41 (2002) 3528.

[11] H. Krautscheid, D. Fenske, G. Baum, M. Semmelmann, Angew. Chem. Int. Ed. 32 (1993) 1303.

[12] C. Simonnet-Jegat, F. Secheresse, Chem. Rev. 101 (2001) 2601.

[13] B.J. Hales, E.E. Case, J.E. Morningstar, M.F. Dzeda, L.A. Mauterer, Biochemistry 25 (1986) 7251.

[14] N.S. Dean, S.L. Bartley, W.E. Streib, E.B. Lobkowsky, G. Christou, Inorg. Chem. 34 (1995) 1608.

[15] (a) I. Nowak, M. Ziolek, Chem. Rev. 99 (1999) 3603;
(b) Ch. Geantet, J. Alfonso, M. Breysse, N. Allali, M. Danot, Catal. Today 28 (1996) 23;
(c) N. Allali, E. Prouzet, A. Michalowicz, V. Gaborir, A. Nadiri, M. Danot, J. Appl. Catal. A 159 (1997) 333;
(d) N. Allali, A. Leblanc, M. Danot, Ch. Geantet, M. Vrinat, M. Breysse, Catal. Today 27 (1996) 137.

[16] T. Hughbanks, in: Th. P. Fehlner (Ed.), Inorganometallic Chemistry, Plenum Press, New York, 1992, p. 316;
(b) F. Camerel, J.-Ch.P. Gabriel, P. Batail, P. Davidson, B. Romaire, M. Schmutz, Th. Gulick-Krzywicki, Bourgaux, Nano Lett. 2 (2002) 403;
(c) W. Bensch, P. Durichen, C. Nather, Solid State Sci. 1 (1999) 85;
(d) J. Rouxel, Acc. Chem. Res. 25 (1992) 328.

[17] T. Saito, N. Yamamoto, T. Yamagata, H. Imoto, J. Am. Chem. Soc. 110 (1988) 1646.

[18] H.F. Franzen, W. Hönle, H.-G.v. Schnering, Z. Anorg. Allg. Chem. 497 (1983) 13.

[19] A. Meerschaut, P. Grenouilleu, L. Guemas, Eur. J. Solid State Chem. 31 (1994) 1029.

[20] P.J. Schmidt, G. Thiele, Z. Anorg. Allg. Chem. 625 (1999) 1056.

[21] C.W.A. Fowles, R.J. Hobson, D.A. Rice, J. Chem. Soc., Chem. Commun. (1976) 552.

[22] A.O. Baghlaf, A. Thompson, J. Less-Comm. Metals 53 (1977) 291.

[23] Yu.V. Mironov, V.P. Fedin, P.P. Semyannikov, V.E. Fedorov, Zh. Neorgan. Khim. 33 (1987) 2290.

[24] J. Rijnsdorp, G.J. De Lange, G.A. Wiegers, J. Solid State Chem. 30 (1979) 365.

[25] A. Leist, W. Tremel, Angew. Chem. Int. Ed. Engl. 32 (1993) 1751.

[26] V.P. Fedin, V.E. Fedorov, H. Imoto, T. Saito, Polyhedron 16 (1997) 995.

[27] J. Rijnsdorp, F. Jellinek, J. Solid State Chem. 28 (1979) 149.

[28] H. Schäfer, W. Beckmann, Z. Anorg. Allg. Chem. 347 (1966) 225.

[29] R. Allmann, I. Baumann, A. Kutoglu, Z. Naturwiss. 51 (1964) 263.

[30] A. Meerschaut, L. Guemas, R. Berger, J. Rouxel, Acta Cryst. B. 35 (1979) 1747.

[31] S. Furuseth, B. Klewe, Acta Chem Scand. A. 38 (1984) 467.

[32] A. Meerschaut, P. Palvadean, J. Rouxel, J. Solid State Chem. 20 (1977) 21.

[33] V.E. Fedorov, V.K. Evstafiev, Izv. Sib. Otd. AN SSSR. Ser. Khim. 5 (1981) 79.

[34] R. Brec, G. Ouvrard, M. Evain, J. Solid State Chem. 7 (1983) 174.

[35] R. Brec, P. Grenouilleau, J. Rouxel, Rev. Chem. Miner. 20 (1983) 295.

[36] R. Brec, P. Grenouilleau, J. Rouxel, Rev. Chem. Miner. 20 (1983) 283.

[37] R. Brec, P. Grenouilleau, J. Rouxel, Rev. Chem. Miner. 20 (1983) 628.

[38] M. Evain, R. Brec, G. Ouvrard, J. Rouxel, Mater. Res. Bull. 19 (1984) 41.

[39] (a) Ch. Kim, H. Yun, Acta Cryst. C. 58 (2002) 53;
(b) J. Do, H. Yun, Inorg. Chem. 35 (1996) 3729.

[40] M. Evain, M. Queignec, R. Brec, J. Rouxel, J. Solid State Chem. 56 (1985) 148.

[41] M. Sokolov, A. Virovets, V. Nadolinnyi, K. Hegetschweiler, V. Fedin, N. Podberezskaya, V. Fedorov, Inorg. Chem. 33 (1994) 3503.

[42] M. Sokolov, R. Hernandez-Molina, M.R.J. Elsegood, S.L. Heath, W. Clegg, A.G. Sykes, J. Chem. Soc., Dalton Trans. (1997) 2059.

[43] A.V. Mishchenko, V.E. Fedorov, B.A. Kolesov, M.A. Fedotov, Koord. Khim. 15 (1989) 200.

[44] M.N. Sokolov, S.V. Tkachev, V.E. Fedorov, V.P. Fedin, Zh. Neorg. Khim. 41 (1996) 1124.
[45] M.N. Sokolov, V.P. Fedin, K. Hegetschweiler, A. Müller, V.E. Fedorov, Zh. Neorgan. Khim. 39 (1994) 1663.
[46] M. Sokolov, D.Sc. Thesis, Novosibirsk, 2003.
[47] A.V. Virovets, M.N. Sokolov, N.V. Podberezskaya, V.E. Fedorov, Zh. Struct. Khim. 37 (1996) 525.
[48] M. Sokolov, H. Imoto, T. Saito, V. Fedorov, J. Chem. Soc., Dalton Trans. (1999) 85.
[49] X.F. Fan, B.L. Fox, E.R.T. Tiekink, Ch.G. Young, J. Chem. Soc., Dalton Trans. (1994) 1765.
[50] M. Sokolov, A. Virovets, O. Oeckler, A. Simon, V. Fedorov, Inorg. Chim. Acta 331 (2002) 25.
[51] T. Halbert, L.L. Hutchings, R. Rodes, E.I. Stiefel, J. Am. Chem. Soc. 108 (1986) 6437.
[52] Y. Yang, L. Huang, Q. Liu, B. Kang, Acta Cryst. C47 (1991) 2085.
[53] S.A. Duraj, M.T. Andras, P.A. Kibala, Inorg. Chem. 29 (1990) 1232.
[54] E.T.R. Tiekink, X.-F. Wan, C.G. Yang, Aust. J. Chem. 45 (1992) 897.
[55] S.C. Sendlinger, J.R. Nickolson, E. Lobkovsky, J.C. Huffmann, D. Rehder, G. Christou, Inorg. Chem. 32 (1993) 204.
[56] C.N. Chau, R.W.M. Wardle, J.A. Ibers, Inorg. Chem. 26 (1987) 2741.
[57] G. Matsubayashi, K. Natsuaki, M. Nakano, H. Tamura, R. Arakawa, Inorg. Chim. Acta 262 (1997) 103.
[58] M. Sokolov, H. Imoto, T. Saito, Inorg. Chem. Commun. 2 (1999) 422.
[59] V.P. Fedin, A.V. Virovets, D.N. Dybtsev, O.A. Gerasko, K. Hegetschweiler, M.R.J. Elsegood, W. Clegg, Inorg. Chim. Acta 304 (2000) 301.
[60] M. Sokolov, H. Imoto, T. Saito, V. Fedorov, Z. Anorg. Allg. Chem. 625 (1999) 989.
[61] M.G.B. Drew, D.A. Rice, D.M. Williams, J. Chem. Soc., Dalton Trans. (1984) 1087.
[62] M.G.B. Drew, D.A. Rice, D.M. Williams, Acta Crystallogr. C40 (1984) 1547.
[63] M. Sokolov, O. Gerasko, A. Virovets, V. Fedorov, K. Hegetschweiler, Inorg. Chim. Acta 271 (1998) 222.
[64] M.N. Sokolov, O.A. Gerasko, A.P. Majara, P.P. Semyannikov, V.M. Grankin, S.V. Belaya, I.K. Igumenov, Electrochem. Soc. Proc. 25 (1997) 836.
[65] M.N. Sokolov, O.A. Gerasko, H. Imoto, T. Saito, V.E. Fedorov, Koord. Khim. 26 (2000) 361.
[66] M. Sokolov, A. Virovets, W. Clegg, Z. Anorg. Allg. Chem. 627 (2001) 119.
[67] A.V. Virovets, M.N. Sokolov, D. Fenske, Zh. Struct. Khim. 41 (2001) 1028.
[68] M.N. Sokolov, O.A. Gerasko, A.V. Virovets, V.E. Fedorov, Koord. Khim. 24 (1998) 828.
[69] M. Sokolov, H. Imoto, T. Saito, Inorg. Chem. Comm. 3 (2000) 96.
[70] M.G.B. Drew, D.A. Rice, D.M. Williams, J. Chem. Soc. Dalton Trans. (1983) 2251.
[71] A.J. Benton, M.G.B. Drew, D.A. Rice, J. Chem. Soc. Chem. Comm. (1981) 1241.
[72] M.G.B. Drew, D.A. Rice, D.M. Williams, J. Chem. Soc. Dalton Trans. (1985) 417.
[73] J. Rijnsdorp, F. Jellinek, J. Solid State Chem. 25 (1978) 325.
[74] M. Yoon, V. Young Jr., G.J. Miller, Acta Cryst. C53 (1997) 1041.
[75] A.J. Benton, M.G.B. Drew, R.J. Hobson, D.A. Rice, J. Chem. Soc. Dalton Trans. (1981) 1304.
[76] E. Babaian-Kibala, F.A. Cotton, Inorg. Chim. Acta 182 (1991) 77.
[77] E. Babaian-Kibala, F.A. Cotton, P.A. Kibala, Inorg. Chem. 29 (1990) 4002.
[78] U. Winkler, M.A. Khan, K.M. Nicholas, Inorg. Chem. Comm. 1 (1998) 317.
[79] M. Moore, K. Feghali, S. Gambarotta, Inorg. Chem. 36 (1997) 2191.
[80] C.P. Gerlach, J. Arnold, Inorg. Chem. 35 (1996) 5770.
[81] H. Zhu, Q. Liu, X. Huang, T. Wen, C. Chen, D. Wu, Inorg. Chem. 37 (1998) 2678.
[82] J.H. Liao, L. Hill, M.G. Kanatzidis, Inorg. Chem. 32 (1993) 4650.
[83] H. Zhu, Ch. Chen, X. Zhang, Q. Liu, D. Liao, L. Li, Inorg. Chim. Acta 328 (2002) 96.
[84] J.K. Money, J.C. Huffman, G. Christou, Inorg. Chem. 27 (1988) 507.
[85] C.M. Bolinger, T.B. Rauchfuss, A.L. Rheingold, J. Am. Chem. Soc. 105 (1983) 6321.
[86] M. Herberhold, M. Kuhnlein, New J. Chem. 12 (1988) 357.
[87] M. Herberhold, M. Kuhnlein, M. Schrepfermann, M.L. Ziegler, B. Nuber, J. Organomet. Chem. 398 (1990) 259.
[88] C.M. Bolinger, T.B. Rauchfuss, A.L. Rheingold, Organometallics 1 (1982) 1551.
[89] J. Darkwa, D.M. Giolando, C.J. Murphy, T.B. Rauchfuss, Inorg. Synth. 27 (1990) 51.
[90] (a) E.G. Muller, J.L. Petersen, L.F. Dahl, J. Organomet. Chem. 111 (1976) 91;
(b) R.A. Schunn, C.J. Fritchie Jr., C.T. Prewitt, Inorg. Chem. 5 (1966) 892.
[91] W.A. Herrmann, H. Biersck, M.L. Ziegler, B. Balbach, J. Organomet. Chem. 206 (1981) C33.
[92] A. Meerschaut, P. Grenouillieau, J. Rouxel, J. Solid State Chem. 61 (1986) 90.
[93] H. Böhm, H.-G. von Schnering, Z. Kristallogr. 171 (1985) 41.
[94] J.K. Money, J.C. Huffman, G. Christou, Inorg. Chem. 27 (1988) 507.
[95] F.A. Cotton, M.P. Diebold, R. Llusar, W.J. Roth, J. Chem. Soc. Chem. Commun. (1986) 1276.
[96] N.S. Dean, K. Folting, E. Lobkovsky, G. Christou, Angew. Chem. Int. Ed. Engl. 32 (1993) 594.
[97] Y. Yang, Q. Liu, D. Wu, Inorg. Chim. Acta 208 (1993) 85.
[98] H. Zhu, Q. Liu, Y. Deng, T. Wen, C. Chen, D. Wu, Inorg. Chim Acta 286 (1999) 7.
[99] F. Lin, R.L. Beddoes, D. Collison, C.D. Garner, F.E. Mabbs, J. Chem. Soc. Chem. Commun. (1993) 496.
[100] H. Brunner, G. Gehart, B. Nuber, J. Wachter, M.L. Ziegler, Angew. Chem. Int. Ed. Engl. 31 (1992) 1021.
[101] H. Kawaguchi, K. Tatsumi, Organometallics 16 (1997) 307.
[102] K. Tatsumi, Y. Inoue, H. Kawaguchi, M. Kohsaka, A. Nakamura, R.E. Cramer, W. Van Coone, G.J. Taogoshi, P.N. Richmann, Organometallics 12 (1993) 352.
[103] D. Fenske, P.G. Maue, Z. Naturfosch. B44 (1989) 531.
[104] H. Brunner, W. Meier, J. Wachter, B. Nuber, M.L. Ziegler, J. Organomet. Chem. 381 (1990) C7.
[105] G. Khvorykh, A.V. Shevelkov, V.A. Dolgikh, B.A. Popovkin, J. Solid State Chem. 120 (1995) 311.
[106] (a) G.J. Miller, J. Alloys Compds. 229 (1995) 93;
(b) G.J. Miller, J. Alloys Compds. 217 (1995) 5.
[107] (a) M. Smith, G.J. Miller, J. Solid State Chem. 140 (1998) 226;
(b) M.D. Smith, G.J. Miller, J. Am. Chem. Soc. 118 (1996) 12238.
[108] H.-J. Meyer, Z. Anorg. Allg. Chem. 620 (1994) 863.
[109] (a) K. Selte, A. Kjekshus, Acta Cryst. 17 (1964) 1568;
(b) A.F.J. Ruysink, F. Kadijk, A.J. Wagner, F. Jellinek, Acta Cryst. B24 (1968) 1614;
(c) J.G. Smeggil, J. Solid State Chem. 3 (1971) 248.
[110] G.J. Miller, J. Lin, Angew. Chem. Int. Ed. Engl. 33 (1994) 334.
[111] M.D. Smith, G.J. Miller, Inorg. Chem. 42 (2003) 4165.
[112] W. Tremel, J. Chem. Soc., Chem. Commun. (1992) 126.
[113] P. Grenouilleau, A. Meerschaut, L. Guemas, J. Rouxel, J. Solid State Chem. 66 (1987) 293.
[114] H. Zhu, Q. Liu, C. Chen, D. Wu, Inorg. Chim. Acta 306 (2000) 131.
[115] A.A. Pasynski, I.L. Eremenko, A.S. Katugin, G.Sh. Gasanov, E.A. Turchanova, O.G. Ellert, Yu.T. Struchkov, V.E. Shklover, N.T. Sogomonova, O.Yu. Okhlobystin, J. Organomet. Chem. 344 (1988) 195.

[116] S.A. Duraj, M.T. Andras, B. Richter, Polyhedron 8 (1989) 2763.

[117] C.E. Davies, J.C. Green, N. Kaltsoyannis, M.A. MacDonald, J. Qiu, T.B. Rauchfuss, C.M. Redfern, G.H. Stringer, M.G. Woolhouse, Inorg. Chem. 31 (1992) 3779.

[118] (a) C.M. Bolinger, J. Darkwa, G. Gammie, S.D. Gammon, J.W. Lyding, T.B. Rauchfuss, S.R. Wilson, Organometallics 5 (1986) 2386;
(b) J. Darkwa, J.L. Lockermeyer, P.D.W. Boyd, T.B. Rauchfuss, A.L. Rheingold, J. Am. Chem. Soc. 110 (1988) 141.

[119] M. Herberhold, M. Schrepfermann, J. Darkwa, J. Organomet. Chem. 430 (1992) 61.

[120] I.L. Eremenko, A.A. Pasynskii, A.S. Katugin, O.G. Ellert, V.E. Shklover, Yu.T. Struchkov, Izv. Akad. Nauk SSSR. Ser. Khim. (1984) 1669.

[121] V.E. Fedorov, V.K. Evstafiev, S.D. Kirik, A.V. Mischenko, Zh. Neorg. Khim. 26 (1981) 2701.

[122] H.B. Yaich, J.C. Jegaden, M. Potel, M. Sergent, A.K. Rastogi, R. Tournier, J. Less-Comm. Met. 102 (1984) 9.

[123] V.P. Fedin, I.V. Kalinina, A.V. Virovets, N.V. Podberezskaya, I.S. Neretin, Y.L. Slovokhotov, Chem. Commun. (1998) 2579.

[124] V.P. Fedin, I.V. Kalinina, A.V. Virovets, D. Fenske, Russ. Chem. Bull. 50 (2001) 930.

[125] J.L. Seela, J.C. Huffman, G. Christou, J. Chem. Soc. Chem. Commun. (1987) 1258.

[126] E. Babaian-Kibala, F.A. Cotton, P.A. Kibala, Polyhedron 9 (1990) 1689.

[127] E. Babaian-Kibala, F.A. Cotton, Inorg. Chim. Acta 182 (1991) 77.

[128] J.K. Money, J.C. Huffman, G. Christou, J. Am. Chem. Soc. 109 (1987) 2210.

[129] W. Bensch, J. Koy, Inorg. Chim. Acta 206 (1993) 221.

[130] D. Fenske, A. Grissinger, M. Loos, J. Magull, Z. Anorg. Allg. Chem. 589/599 (1991) 121.

[131] H-J. Meyer, J.D. Corbett, Inorg. Chem. 30 (1991) 963.

[132] H. Womelsdorf, H.-J. Meyer, Angew Chem. Int. Ed. Engl. 33 (1994) 1943.

[133] A.M. Arif, J.G. Hefner, R.A. Jones, T.A. Albright, S.-K. Kang, J. Am. Chem. Soc. 108 (1986) 1701.