Cluster Compounds

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Niobium Alcoholate Clusters with an Octahedral Arrangement of Metal Atoms: $[K(CH_3OH)_4]_2[Nb_6(OCH_3)_{18}]$ and $[Na([18]crown\text{-}6)(C_2H_5OH)_2]_2[Nb_6(OC_2H_5)_{12}(NCS)_6]$**

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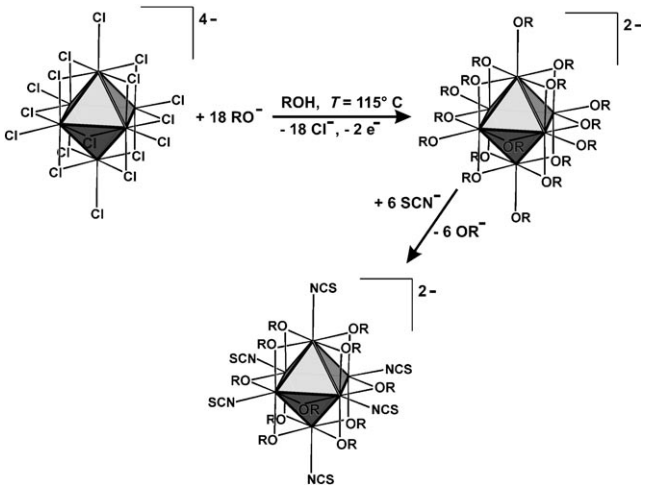
Owing to their enormous structural diversity and remarkable physical properties, reduced transition-metal halides and chalcogenides have attracted great interest for many years.[1] These compounds often contain hexanuclear cluster units with an octahedral arrangement of metal atoms. The cluster units contain either eight bridging ligands with one above each triangular face ($[M_6X_8]$ type) or 12 bridging ligands with one above each edge of the octahedron of metal atoms ($[M_6X_{12}]$ type) (M = metal of the Group 3–8 of the periodic table; X = halogenido or chalcogenido ligand).[1] In addition to a multitude of compounds, which are synthesized by solid-state high-temperature routes and contain cluster units linked by halogenido or chalcogenido bridges, also compounds with isolated cluster units synthesized by solution chemical routes by cluster excision starting from a solid phase are described.[2] In such isolated cluster units, the ligands at the *exo* positions of the octahedron of metal atoms can be substituted by other ligands, resulting in $[M_6X^i_{12}Y^a_6]$ units (X^i = inner, edge bridging ligand; Y^a = outer, apical capping ligand)[3] of diverse charge. In the case of niobium clusters with X^i = halogenido, such complexes with Y^a = cyanido,[4,5] isothiocyanato,[5,6] azido,[7] other halogenido,[8] nitrile,[9] water,[10] or methanol[11] have been described. The number of compounds with isolated cluster units of the type $[Nb_6X^i_{12}]$ with X^i = Cl or Br is large. Yet, similar compounds with isolated cluster units for X^i = O and F are missing, not only for M = Nb but for all the metals in the 4th and 5th Groups of the periodic table. Although oxido niobates with $[Nb_6O^i_{12}]$ units, which are three-dimensionally connected through intercluster-bridging oxido ligands, are thoroughly investigated, in particular by Simon et al.,[12] cluster compounds with isolated $[M_6O^i_{12}]$ cluster units linked to their neighbors merely by weak interactions are unknown.[13]

We report herein the first two representatives of a new class of compounds,[13] reduced niobium alcoholates of the $[M_6X_{12}]$ type: $[K(CH_3OH)_4]_2[Nb_6(OCH_3)_{18}]$ (**1**) and $[Na([18]crown\text{-}6)(C_2H_5OH)_2]_2[Nb_6(OC_2H_5)_{12}(NCS)_6]$ (**2**). They have been characterized by single-crystal X-ray diffraction,[14] elemental analyses, IR, FIR, and UV/Vis spectroscopic measurements and thermal analyses.

Both new cluster compounds are prepared in good yields by heating the chloride-based cluster precursor with alcoholates in sealed glass ampoules. During the reaction the outer as well as the inner chlorido ligands are completely substituted by alcoholate ions. Simultaneously, an oxidation of the cluster unit takes place (Scheme 1).



Scheme 1. Conversion of the halogenide-based niobium clusters with octahedral metal-atom arrangement with alcoholate ions into the new niobium alcoholate clusters.

To prepare **2**, a further substitution reaction is required in which the six *exo* positions of the cluster are occupied by isothiocyanato ligands. Reports on the substitution of the inner ligands of clusters which have an octahedral metal-atom arrangement are rare.[2f,13,15] Both title compounds contain Nb_6 octahedra like the ones found in reduced transition-metal halides and chalcogenides.[1] All the edges of the octahedra in **1** and **2** are bridged by the O atoms of the alcoholate ions resulting in $[Nb_6(OR)_{12}]^{4+}$ units (**1**: R = CH_3; **2**: R = C_2H_5). The *exo* positions of the octahedron of niobium atoms are occupied either by further alcoholate ions (**1**) or by isothiocyanate ions (**2**). In **1**, two opposing faces of the metal-atom octahedron have their three edge-bridging O atoms coordinated to a potassium atom, whose coordination sphere is completed by the O atoms of four methanol molecules. Thus,

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the neutral centrosymmetric $[K(CH_3OH)_4]_2[Nb_6(OCH_3)_{18}]$ ion triple, which is shown in Figure 1, is present in **1**.

Compound **1** crystallizes in the monoclinic space group *C*2/*c*. Figure 2 shows the ion triples are lined up along [101] in

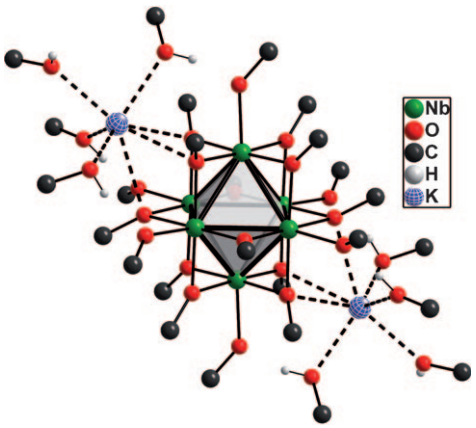

Figure 1. Molecular structure of the ion triple **1** with cluster anion (without methyl H atoms, Nb_6 octahedron in polyhedral representation).

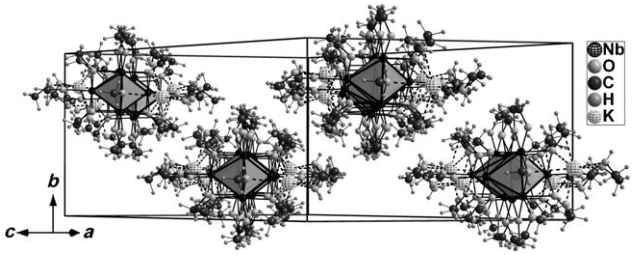

Figure 2. View of the arrangement of the isolated $[K(CH_3OH)_4]_2[Nb_6(OCH_3)_{18}]$ ion triples **1** with cluster anion in the unit cell.

the crystal. Between the methanol molecules surrounding the potassium ions of adjacent ion triples short H···OH distances are found. The O···O distances are in the range of 2.549 to 2.750 Å, so they can be interpreted as hydrogen bonds.

Compound **2** crystallizes in the tetragonal space group $I4_1/a$. In this compound, the charge of the $\bar{4}$ symmetry $[Nb_6(OC_2H_5)_{12}(NCS)_6]^{2-}$ cluster ion (Figure 3), is compensated by two sodium ions, each coordinated to a [18]crown-6 molecule.

As a result of the cations being coordinated to the crown ethers there are no short distances between the cations and the cluster anion in **2**. Figure 4 depicts the arrangement of the isolated cluster ions as well as the cations within the unit cell. In addition to the O atoms of the crown ether molecule, ethanol molecules are coordinated to the sodium ion on both sides of the macrocyclic ligand. Thus, short Na···S contacts are absent.

The structural parameters of the $[Nb_6O_{12}]$ units of both compounds are similar. The Nb–Nb distances vary insignificantly, ranging from 2.8655(4) to 2.8808(4) Å with an average of 2.873 Å for **1** and from 2.8497(5) to 2.8576(5) Å, average of 2.855 Å for **2**. The mean values of the Nb–O^i distances are 2.081 Å in **1** and 2.068 Å in **2**. Comparing these average values to those of the $[Nb_6O^i_{12}]$ units in reduced oxido niobates with

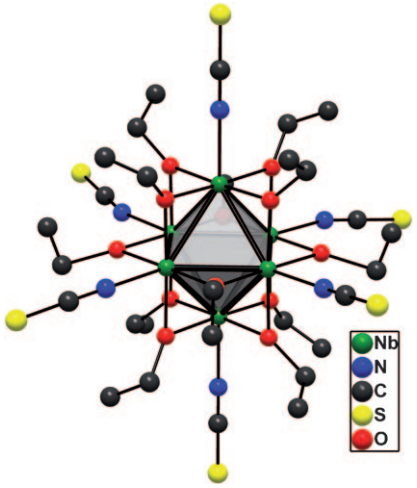

Figure 3. View of the structure of the cluster anion $[Nb_6(OC_2H_5)_{12}(NCS)_6]^{2-}$ in the crystal structure of **2** (without H atoms, Nb_6 octahedron in polyhedral representation).

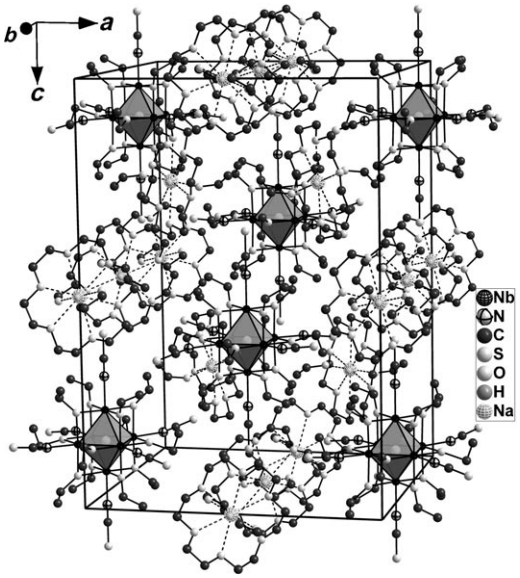

Figure 4. View of the arrangement of the complex ions in the unit cell of **2**.

discrete clusters, offering the same number of cluster-based electrons, for example, in $Mg_3[Nb_6O_{11}]$, $Mn_3[Nb_6O_{11}]$,[16] or in $Na_2(Sc_4Nb_2)[Nb_6O_{12}]_3$,[17] the Nb–$O^i$ distances are similar, while the Nb–Nb distances are in the upper range of those found in the oxido niobates. The lower charge density of the alcoholate O atoms, compared to that of the O atoms of the oxido niobates, is reflected in the metal–metal bond strength and subsequently, in the Nb–Nb distances. Comparing the Nb–Nb distances in $[Nb_6X^i_{12}]^{4+}$ units for X^i = Cl and OR, it is apparent that these bonds are significantly longer in the chlorides (in which they are around 3.02 Å).[18] The larger, so-called matrix effect of the Cl atoms compared to the O atoms is the reason for the longer metal–metal bonds.[19]

A comparison of the structural parameters of both title compounds with the known mixed oxide–halide Nb clusters, which have O atoms at edge-bridging positions, reveals the

following:[20] While the mean Nb–O^i distances, for example, in $Ti_2[Nb_6(Cl^i_8O^i_4)Cl^a_6]$ (2.026 Å), are similar to those of the title compounds, the Nb–Nb distances vary from 2.812 to 2.992 Å, with, as expected, the longer distances being found at the chloride-bridged edges of the strongly distorted octahedron of metal atoms.[21]

Comparing the title compounds to the reduced oxide–halides of niobium, it is interesting to note that in compounds with the general formula $[Nb_6Cl_{12-m}O_m]^{(4m)+}$, above $m = 2$, the orbital that is usually the highest occupied orbital (symmetry a_{2u}) has overall antibonding character and is thus no longer occupied.[8g,12a,22] Consequently, the number of cluster valence electrons required to fill all the bonding orbitals is reduced from 16 to 14, thus the twofold negative charge of the cluster ion is plausible. The oxidation process of the title compounds remains unclear. Cluster disproportionation reactions appear to be possible, but have not been demonstrated yet. Similar redox reactions have been observed in other cluster systems.[1c,n,15,23] Interesting in this context is the relatively high thermal stability of **2** shown by differential scanning calorimetry (DSC) measurements, in which the first exothermal effects appear above 300 °C, and are probably due to decomposition processes. In contrast, the DSC curve of **1** shows an exothermal peak at approximately 120 °C.

With respect to the known Nb_6 halide clusters with alcoholato or isothiocyanato groups as Y^a functions, both title compounds are also unique because they are the only ones that do not have 16 cluster-based electrons. Therefore the Nb–Y^a bond lengths of the title compounds cannot be compared to those of these other clusters. The average of the Nb–O^a distances in **1** is 2.148 Å, whereas in $[Na(222\text{-crypt})]_2[Na(CH_3OH)_4]_2[Nb_6Cl_{12}(OCH_3)_6]\cdot 7\,CH_3OH$ it is 2.159 Å.[11a] If the Y^a positions are not occupied by O atoms of alcoholate ions but by those of neutral alcohol molecules, the Nb–O^a distances are clearly longer, for example, 2.252 Å in $[Nb_6Cl_{14}(CH_3OH)_4]\cdot 6\,CH_3OH$[11c] or 2.233 Å in $[Nb_6Cl_{12}(C_2H_5OH)_6][Mo_6Cl_{14}]\cdot 3\,C_2H_5OH\cdot 3\,(C_2H_5)_2O$.[11e] In **2** the Nb–N distances average 2.231 Å. Among the isothiocyanato containing niobium chloride cluster compounds of the type $A_4[Nb_6Cl_{12}(NCS)_6]$ with A = K, Rb, NH_4, Cs, Ph_4P the Nb–N distances are in the range 2.211 to 2.243 Å.[5,6]

The new compounds demonstrate that not only the substitution of the outer but also of the inner ligands in $[Nb_6Cl_{18}]^{4-}$ units is feasible. The synthesis of a multitude of new cluster compounds based, for example, on pseudo halogenido ligands as the X^i functions should be possible. Likewise, the synthesis of new compounds with bi- or multifunctional ligands seems to be possible, which might contain new cross-linked cluster units featuring interesting properties.

Experimental Section

1: $K_4[Nb_6Cl_{18}]$ (100 mg; 74 mmol) and a basic solution containing 18 equivalents of potassium methanolate (93.4 mg; 1331 mmol) in methanol (4 mL) were heated to 115 °C in a sealed glass ampoule for 5 days. Afterwards, the dark solution was filtered and the solvent evaporated under reduced pressure. Dissolving the solid in CH_2Cl_2 and a further filtration improves the purity of the product (filtrate). Afterwards the solvent is replaced by methanol to crystallize the product. Brown crystals are obtained by slow evaporation of the solvent (yield: 61 mg, 57 % with respect to $K_4[Nb_6Cl_{18}]$).

2: Similar to **1**, a solution of $Na_4[Nb_6Cl_{18}]$ (100 mg, 78 mmol) and sodium ethanolate (95.1 mg, 1398 mmol) in ethanol (4 mL) was prepared. 6 equivalents (with respect to the used $Na_4[Nb_6Cl_{18}]$) of dried NaSCN (37.8 mg, 466 mmol) and 2 equivalents of dried [18]crown-6 (41.1 mg, 155 mmol) were added to the solution. Dark red crystals appear during the slow evaporation of the solvent (yield: 132 mg, 77 % with respect to $Na_4[Nb_6Cl_{18}]$).

Further experimental details concerning the syntheses, X-ray structures, elemental analyses, IR-, FIR-, UV/Vis spectroscopic measurements, and thermal analyses are given in the Supporting Information.

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[1] a) A. Simon, *Angew. Chem.* **1988**, *100*, 163 – 188; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 159 – 183; b) *Metal Clusters in Chemistry* (Eds.: P. Braunstein, L. A. Oro, P. R. Raithly), Wiley-VCH, Weinheim, **1999**; c) N. Prokopuk, D. F. Shriver, *Adv. Inorg. Chem.* **1999**, *46*, 1 – 49; d) C. Perrin, M. Sergent, *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 933 – 948; e) A. Simon in *Clusters and Colloids – From Theory to Applications* (Ed.: G. Schmid), VCH, Weinheim, **1994**, pp. 373 – 458; f) J. D. Corbett in *Modern Perspectives in Inorganic Crystal Chemistry*, (Ed.: E. Parthé), Kluwer, Dortrecht, **1992**, pp. 27 – 56; g) J. D. Corbett, *J. Chem. Soc. Dalton Trans.* **1996**, 575 – 587; h) J. D. Corbett, *Inorg. Chem.* **2000**, *39*, 5178 – 5191; i) F. A. Cotton, *J. Chem. Soc. Dalton Trans.* **2000**, 1961 – 1968; j) T. Hughbanks, *J. Alloys Compd.* **1995**, *229*, 40 – 53; k) C. Perrin, S. Cordier, S. Ihmaïne, M. Sergent, *J. Alloys Compd.* **1995**, *229*, 123 – 133; l) A. Simon, H.-J. Mattausch, G. J. Miller, W. Bauhofer, R. K. Kremer in *Handbook on the Physics and Chemistry of Rare Earth*, *Vol. 15* (Eds.: K. A. Gschneider, L. Eyring), Elsevier Science, Amsterdam, **1991**, pp. 191 – 285; m) G. Meyer, *Chem. Rev.* **1988**, *88*, 93 – 107; n) T. G. Gray, *Coord. Chem. Rev.* **2003**, *243*, 213 – 235.

[2] a) S. C. Lee, R. H. Holm, *Angew. Chem.* **1990**, *102*, 868 – 885; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 840 – 856; b) J. R. Long, L. S. McCarty, R. H. Holm, *J. Am. Chem. Soc.* **1996**, *118*, 4603 – 4616; c) J. R. Long, A. S. Williamson, R. H. Holm, *Angew. Chem.* **1995**, *107*, 248 – 251; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 226 – 229; d) O. M. Yaghi, M. J. Scott, R. H. Holm, *Inorg. Chem.* **1992**, *31*, 4778 – 4784; e) X. Xie, J. N. Jones, T. Hughbanks, *Inorg. Chem.* **2001**, *40*, 522 – 527; f) C. E. Runyan, Jr., T. Hughbanks, *J. Am. Chem. Soc.* **1994**, *116*, 7909 – 7910.

[3] H. Schäfer, H. G. von Schnering, *Angew. Chem.* **1964**, *76*, 833 – 868.

[4] a) B. Yan, H. Zhou, A. Lachgar, *Inorg. Chem.* **2003**, *42*, 8818 – 8822; b) N. G. Naumov, S. Cordier, C. Perrin, *Angew. Chem.* **2002**, *114*, 3128 – 3130; *Angew. Chem. Int. Ed.* **2002**, *41*, 3002 – 3004; c) N. G. Naumov, S. Cordier, F. Gulo, T. Roisnel, V. E. Fedorov, C. Perrin, *Inorg. Chim. Acta* **2003**, *350*, 503 – 510.

[5] a) A. Flemming, A. Bernsdorf, M. Köckerling, *J. Clust. Sci.*, DOI: 10.1007/s10876-008-0217-2; b) N. G. Naumov, S. Cordier, C. Perrin, *Solid State Sci.* **2003**, *5*, 1359 – 1367.

[6] a) N. G. Naumov, S. Cordier, C. Perrin, *Chem. Commun.* **2004**, 1126 – 1127; b) O. Reckeweg, H.-J. Meyer, *Z. Anorg. Allg. Chem.* **1996**, *622*, 411 – 416.

[7] a) H.-J. Meyer, *Z. Anorg. Allg. Chem.* **1995**, *621*, 921 – 924; b) O. Reckeweg, H.-J. Meyer, *Z. Naturforsch. B* **1995**, *50*, 1377 – 1381;

c) O. Reckeweg, H.-J. Meyer, A. Simon, *Z. Anorg. Allg. Chem.* **2002**, *628*, 920 – 922.

[8] a) A. Simon, H. G. von Schnering, H. Schäfer, *Z. Anorg. Allg. Chem.* **1968**, *361*, 235 – 248; b) P. B. Fleming, L. A. Müller, R. E. McCarley, *Inorg. Chem.* **1967**, *6*, 1 – 4; c) A. Broll, D. Juza, H. Schäfer, *Z. Anorg. Allg. Chem.* **1971**, *382*, 69 – 79; d) A. Broll, H. Schäfer, *J. Less-Common Met.* **1970**, *22*, 367 – 368; e) C. Perrin, M. Sergent, *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 933 – 948; f) S. Ihmaïne, C. Perrin, O. Peña, M. Sergent, *J. Less-Common Met.* **1988**, *137*, 323 – 332; g) O. Peña, S. Ihmaïne, C. Perrin, M. Sergent, *Solid State Commun.* **1990**, *74*, 285 – 290; h) S. Ihmaïne, C. Perrin, O. Peña, M. Sergent, *Physica B* **1990**, *163*, 615 – 617; i) C. Perrin, S. Cordier, S. Ihmaïne, M. Sergent, *J. Alloys Compd.* **1995**, *229*, 123 – 133; j) S. Ihmaïne, C. Perrin, M. Sergent, *Acta Crystallogr. Sect. C* **1987**, *43*, 813 – 816; k) S. Ihmaïne, C. Perrin, M. Sergent, *Acta Crystallogr. Sect. C* **1989**, *45*, 705 – 707; l) T. Duraisamy, J. S. Qualls, A. Lachgar, *J. Solid State Chem.* **2003**, *170*, 227 – 231; m) A. Nägele, E. Anokhina, J. Sitar, H.-J. Meyer, A. Lachgar, *Z. Naturforsch. B* **2000**, *55*, 139 – 144.

[9] A. Flemming, M. Köckerling, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2309 – 2315.

[10] a) M. Vojnovic, N. Brničević, I. Bašic, R. Trojko, M. Miljak, I. D. Desnica-Frankovic, *Mater. Res. Bull.* **2001**, *36*, 211 – 225; b) H. Schäfer, B. Plautz, H. Plautz, *Z. Anorg. Allg. Chem.* **1972**, *392*, 10 – 22; c) F. W. Koknat, J. A. Parsons, A. Vongvusharintra, *Inorg. Chem.* **1974**, *13*, 1699 – 1702.

[11] a) U. Beck, A. Simon, N. Brničević, S. Širac, *Croat. Chem. Acta* **1995**, *68*, 837 – 848; b) N. Brničević, F. Muštović, R. E. McCarley, *Inorg. Chem.* **1988**, *27*, 4532 – 4535; c) L. F. Piedra-Garza, M. Köckerling, *Inorg. Chem.* **2006**, *45*, 8829 – 8831; d) B. Spreckelmeyer, H. Schäfer, *J. Less-Common Met.* **1966**, *11*, 74 – 75; e) I. Bašic, N. Brničević, U. Beck, A. Simon, R. E. McCarley, *Z. Anorg. Allg. Chem.* **1998**, *624*, 725 – 732.

[12] a) J. Köhler, G. Svensson, A. Simon, *Angew. Chem.* **1992**, *104*, 1463 – 1483; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1437 – 1456; b) G. Svensson, J. Köhler, A. Simon in *Metal Clusters in Chemistry* (Eds.: P. Braunstein, L. A. Oro, P. R. Raithly), Wiley-VCH, Weinheim, **1999**, pp. 1509 – 1550, and references therein.

[13] To date, the only example of a M_6 cluster compound with an octahedral metal atom framework, which bears exclusively methanolato ligands is of the $[M_6X_8]$ type with M = molybdenum: a) P. Nannelli, B. P. Block, *Inorg. Chem.* **1968**, *7*, 2423 – 2426; b) M. H. Chisholm, J. A. Heppert, J. C. Huffman, *Polyhedron* **1984**, *3*, 475 – 478.

[14] Single-crystal structure analyses: X-ray diffraction data were collected on a Bruker-Nonius Apex X8 diffractometer, equipped with a CCD detector. Measurements were done using monochromatic MoKα radiation ($\lambda = 0.71073$ Å, graphite monochromator). The structures were solved using direct methods and refined using Full-matrix least-squares on F^2 (Shelx-97).[24] The positions of the hydroxy H atoms of the methanol molecules were taken from the difference electron density map and refined isotropically. All further H atoms were calculated on idealized positions and refined as a riding model. **1**: brown crystals, monoclinic, *C*2/*c* (no. 15), $a = 26.177(2)$, $b = 12.1643(8)$, $c = 19.151(2)$ Å, $\beta = 117.315(5)°$, $V = 5418.0(7)$ Å^3, $Z = 4$, $R1 = 0.0295$ ($I > 2\sigma(I)$), $wR2 = 0.0747$ (all data), 6183 symmetry independent reflections, 288 parameter. **2**: dark red crystals, tetragonal, $I4_1/a$ (no. 88), $a = 19.0590(6)$, $c = 27.055(2)$ Å, $V = 9827.5(7)$ Å^3, $Z = 4$, $R1 = 0.0507$ ($I > 2\sigma(I)$), $wR2 = 0.1634$ (all data), 5842 symmetry independent reflections, 265 parameter. CCDC 697148 (**1**) and CCDC 697149 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[15] J. B. Willems, H. W. Rohm, C. Geers, M. Köckerling, *Inorg. Chem.* **2007**, *46*, 6197 – 6203.

[16] a) B. O. Marinder, *Chem. Scr.* **1977**, *11*, 97 – 101; b) R. Burnus, J. Köhler, A. Simon, *Z. Naturforsch. B* **1987**, *42*, 536 – 538.

[17] S. Cordier, K. Kirakci, B. Fontaine, J.-F. Halet, R. Gautier, C. Perrin, *Inorg. Chem.* **2006**, *45*, 883 – 893.

[18] F. W. Koknat, R. E. McCarley, *Inorg. Chem.* **1972**, *11*, 812 – 816.

[19] J. D. Corbett, *J. Solid State Chem.* **1981**, *39*, 56 – 74.

[20] a) E. Anokhina, A. Lachgar in *Inorganic Chemistry in Focus III* (Hrsg.:G. Meyer, D. Naumann, L. Wesemann), Wiley-VCH, Weinheim, **2006**, pp. 79 – 104; b) C. Perrin in *Metal Clusters in Chemistry* (Eds.: P. Braunstein, L. A. Oro, P. R. Raithby), Wiley-VCH, Weinheim **1999**, pp. 1563 – 1590, and references therein.

[21] E. V. Anokhina, M. W. Essig, A. Lachgar, *Angew. Chem.* **1998**, *110*, 538 – 540; *Angew. Chem. Int. Ed.* **1998**, *37*, 522 – 525.

[22] a) Z. Lin, I. A. Williams, *Polyhedron* **1996**, *15*, 3277 – 3287; b) F. Ogliaro, S. Cordier, J.-F. Halet, C. Perrin, J.-Y Saillard, M. Sergent, *Inorg. Chem.* **1998**, *37*, 6199 – 6207; c) T. Hughbanks, *Prog. Solid State Chem.* **1989**, *19*, 329 – 372, and references therein.

[23] a) F. Rogel, J. D. Corbett, *J. Am. Chem. Soc.* **1990**, *112*, 8198 – 8200; b) F. Rogel, Ph.D. Thesis, Iowa State University, Ames, IA **1990**.

[24] G. M. Sheldrick, ShelxS-97 and ShelxL-97, Programs for the Solution and Refinement of Crystal Structures, University of Göttingen, **1997**.

