Notes

Solvothermal Synthesis, Crystal Structure, and Characterization of an Oxothiomolybdate, $[N(CH_3)_4]_4Mo_6O_6S_{14}$, Exhibiting a New $Mo_6O_6S_{14}$ Core

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Introduction

During the past few years solvo- or hydrothermal techniques have been successfully applied for the syntheses of new and fascinating multinary chalcogenides. The new compounds show interesting structural features as well as physical properties.[1−3] The structures of these compounds range from discrete molecular anions to three-dimensional frameworks. Due to the relatively mild conditions in the superheated solvents crystals of polymeric species or of salts can be grown that are nearly insoluble in any conventional solvent at room temperature. The crystals are often of a good quality and are obtained in a satisfactory yield. In our studies we use solvothermal methods to prepare new thio- and oxothiomolybdates. A large number of oxothiomolybdates were reported in the literature,[4] ranging from simple anions of the type $[MoO_{4-n}S_n]^{2-}$ (with $n = 1$ to 3) to anions containing four molybdenum atoms such as in $[Mo_4O_4S_{14}]^{2-}$ [5] or $[Mo_4O_4S_{18}]^{2-}$.[6,7] The number of oxothiomolybdate anions is completed by a multitude of bi- and trinuclear molybdenum clusters. Many of the trinuclear or multinuclear thiomolybdate clusters contain the Mo_3S_4 core,[8,9] where a Mo_3 triangle is capped by a S atom and bridged by three μ_2-S atoms or by three μ_2-disulfido groups and one μ_3-S yielding the Mo_3S_7 core.[10] In contrast to the large number of clusters capped by one S atom, there are only a few examples in which capping by S atoms occurs on both sides of the triangle as in Mo_3X_5-type clusters (X = S, Cl).[11−13] Most species are well characterized[14] such as the $[Mo_2O_2S_6]^{2-}$-anion,[15,16] whose properties are comparable to the new $[Mo_6O_6S_{14}]^{4-}$-anion of the title compound. The $[Mo_6O_6S_{14}]^{4-}$-anion is the first example of a bicapped molybdenum cluster in which the edges of the Mo_3 triangle are not bridged by three X atoms (X = Cl, S), but each Mo atom of the triangle is bonded to one O atom and is connected to another Mo atom of the anion by two μ_2-S atoms. The chemical flexibility in the Mo−S system under solvothermal conditions is demonstrated by the fact that under similar conditions the $[Mo_3S_{13}]^{2-}$ anion will be frequently obtained.[17] The present contribution deals with the solvothermal synthesis, crystal structure and vibrational spectra of the new oxothiomolybdate $[N(CH_3)_4]_4Mo_6O_6S_{14}$.

Experimental Section

Preparation of $[N(CH_3)_4]_4Mo_6O_6S_{14}$. Syntheses were performed in Teflon-lined autoclaves with an inner volume of 50 mL. Single crystals of $[N(CH_3)_4]_4Mo_6O_6S_{14}$ were first obtained in a solvothermal reaction of MoO_3 with TiO_2, elemental sulfur and tetramethylammonium hydroxide pentahydrate (molar ratio = 1:1:3:1) in 5 mL of 0.2 mol aqueous ammonia solution. The mixture was heated at 130 °C for 6 days. After washing with water and acetone, there were two phases remaining: a white powder of TiO_2 (~60%) and red rodlike crystals of the title compound (~40%). Crystals of good quality were obtained suitable for crystal structure determination. After the structure was determined a rational synthesis was found using sodium molybdate dihydrate, elemental sulfur and tetramethylammonium hydroxide pentahydrate (molar ratio = 1:5:1) in 5 mL of 0.2 mol aqueous ammonia solution. The mixture was heated at 130 °C for 5 days and after washing with water, CS_2 and acetone the title compound was obtained as phase pure product (yield: ~70% based on Mo). The purity was checked by comparison of the X-ray powder diffraction pattern with that calculated from single-crystal X-ray data. The crystals are stable on air and insoluble in water and acetone.

Physical Methods. far-IR spectra (range 80−530 cm^{-1}) were measured on a Bruker IFS 66 Infrared-Spectrometer at a resolution of 2 cm^{-1} in pressed polyethylene disks. MIR spectra of the compound were recorded in a KBr matrix. The sample was ground with dry KBr into a fine powder and pressed into a transparent pellet. The spectra were recorded in the IR region of 450−3000 cm^{-1}, resolution 2 cm^{-1}, with a ATI Mattson Genesis infrared spectrometer. Raman spectra were measured in the region from 100 to 3500 cm^{-1} with a Bruker IFS 66 Fourier transform Raman spectrometer. Magnetic properties were measured on a Bruker B−SU 20 instrument with a Satorius 4411 vacuum microbalance.

X-ray Structure Determination. Intensity data were collected using a STOE AED II four-circle diffractometer using the $\omega-\theta$ mode with

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(1) Sheldrick, W. S.; Wachhold, M. S. *Angew. Chem.* **1997**, 109, 214−234; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 206−224.
(2) Bowes, C. L.; Ozin, G. A. *Adv. Mater.* **1996**, *8*, 13−28.
(3) Rabenau, A. *Angew. Chem.* **1985**, *97*, 1017−1032; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1026−1041.
(4) Bergmann, H.; Czeska, B.; Haas, I.; Katscher, H.; Mohsin, B.; Wandner, K.-H. In *Gmelin Handbook of Inorganic and Organometallic Chemistry*; Springer: Berlin, 1995; Mo Suppl., Vol. B8.
(5) Coucouvanis, D.; Toupadakis, A.; Lane, J. D.; Koo, S. M.; Kim, C. G.; Hadjikyriakou, A. *J. Am. Chem. Soc.* **1991**, *113*, 5271−5282.
(6) Hadjikyriakou, A. I.; Coucouvanis, D. *Inorg. Chem.* **1989**, *28*, 2169−2177.
(7) Coucouvanis, D.; Hadjikyriakou, A. *Inorg. Chem.* **1987**, *26*, 1−2.
(8) Shibara, T. *Adv. Inorg. Chem.* **1991**, *37*, 143−173 and references therein.
(9) Shibara, T. *Coord. Chem. Rev.* **1993**, *123*, 73−147 and references therein.
(10) Mayor-López, M. J.; Weber, J.; Hegetschweiler, K.; Meienberger, M. D.; Joho, F.; Leoni, S.; Nesper, R.; Reiss, G. J.; Frank, W.; Kolesov, B. A.; Fedin, V. P.; Fedorov, V. E. *Inorg. Chem.* **1998**, *37*, 2633−2644.
(11) Tsuge, K.; Yajima, S.; Imoto, H.; Saito, T. *J. Am. Chem. Soc.* **1992**, *114*, 7910−7912.
(12) Tsuge, K.; Imoto, H.; Saito, T. *Inorg. Chem.* **1995**, *34*, 3404−3409.
(13) Huang, J.; Shang, M.; Liu, S.; Lu, J. *Sci. Sinica, Ser. B (Engl. Transl.)* **1982**, *25*, 1269−1270.
(14) Coucouvanis, D.; Toupadakis, A.; Koo, S.-M.; Hadjikyriakou, A. *Polyhedron* **1989**, *8*, 1705−1716.
(15) Müller, A.; Rittner, W.; Neumann, A.; Sharma, R. C. *Z. Anorg. Allg. Chem.* **1981**, *472*, 69−74.
(16) Clegg, W.; Mohan, N.; Müller, A.; Neumann, A.; Rittner, W.; Sheldrick, G. M. *Inorg. Chem.* **1980**, *19*, 2066−2069.
(17) Bensch, W.; Schur, M. *Z. Kristallogr.* **1997**, *212*, 303−304.

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Table 1. Crystallographic Data for $[N(CH_3)_4]_4Mo_6O_6S_{14}$

chemical formula	$[N(CH_3)_4]_4Mo_6O_6S_{14}$	space group	*P*31*c* (IT. No. 159)
$a = b$ [Å]	15.258 (1)	T [°C]	293
c [Å]	11.768 (2)	λ [Å]	0.71 073
$\alpha = \beta$ [deg]	90	D_c [g/cm^3]	1.984
$\gamma =$ [deg]	120	μ [mm^{-1}]	2.19
V [Å^3]	2372.5 (5)	R1 ($F_o > 4\sigma(F_o)$)^a	0.0255
Z	2	wR2^b (all data)^c	0.0622
fw [g/mol]	1417.02		

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o$. ^{b} $w = 1/[\sigma^2(F_o^2) + (0.0327P)^2 + 0.86P]$; $P = (\mathrm{Max}\ (F_o^2,0) + 2F_c^2)/3$. ^{c} $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Table 2. Selected Distances [Å] and Angles [deg] for $[N(CH_3)_4]_4Mo_6O_6S_{14}$

Mo(1)−O(1)	1.685 (4)		Mo(2)−O(2)	1.682 (4)	
Mo(1)−S(1)	2.463 (2)	(3×)	Mo(1)−S(3)	2.327 (2)	
Mo(1)−S(2)	2.482 (2)	(3×)	Mo(2)−S(3)	2.313 (2)	
Mo(1)−S(4)	2.319 (2)		Mo(2)−S(5)	2.373 (2)	
Mo(2)−S(4)	2.316 (2)		S(5)−S(6)	2.078 (4)	
Mo(2)−S(6)	2.405 (2)		Mo(1)−Mo(2)	2.809 (1)	
Mo(1)−Mo(1A)	3.413 (1)				
O(1)−Mo(1)−S(4)	110.32 (17)		O(1)−Mo(1)−S(3)	107.06 (16)	
S(4)−Mo(1)−S(3)	101.32 (6)		O(1)−Mo(1)−S(1)	102.84 (15)	
S(4)−Mo(1)−S(1)	82.07 (5)		S(3)−Mo(1)−S(1)	146.35 (5)	
O(1)−Mo(1)−S(2)	104.58 (15)		S(4)−Mo(1)−S(2)	141.34 (5)	
S(3)−Mo(1)−S(2)	83.43 (6)		S(1)−Mo(1)−S(2)	74.35 (5)	
O(1)−Mo(1)−Mo(2)	103.75 (15)		O(2)−Mo(2)−S(3)	111.01 (25)	
O(2)−Mo(2)−S(4)	106.06 (20)		S(3)−Mo(2)−S(4)	101.81 (5)	
O(2)−Mo(2)−S(5)	112.52 (24)		S(3)−Mo(2)−S(5)	129.16 (9)	
S(4)−Mo(2)−S(5)	90.23 (8)		O(2)−Mo(2)−S(6)	106.93 (20)	
S(3)−Mo(2)−S(6)	91.46 (8)		S(4)−Mo(2)−S(6)	136.88 (9)	
S(5)−Mo(2)−S(6)	51.54 (10)		O(2)−Mo(2)−Mo(1)	103.50 (20)	
Mo(1)−S(1)−Mo(1)	87.69 (6)	(3×)	Mo(1)−S(2)−Mo(1)	86.84 (6)	(3×)
Mo(2)−S(3)−Mo(1)	74.50 (5)		Mo(2)−S(4)−Mo(1)	74.60 (5)	
S(6)−S(5)−Mo(2)	65.02 (9)		S(6)−S(5)−Mo(2)	63.44 (9)	

graphite monochromated Mo Kα radiation. The measurement was carried out at 293 K. A crystal of approximate dimensions 0.5 × 0.02 × 0.02 mm was used for the diffraction study. The raw intensities were reduced to F_o by applying Lorentz and polarization correction. The structure was solved with direct methods using the program SHELXS-94[18] and refined by full-matrix least-squares techniques using SHELXL-93.[19] Anisotropic displacement parameters were used for C, N, Mo, S, and O atoms. The H atoms were positioned with idealized geometry and refined using the riding model and a fixed isotropic displacement parameter. The absolute structure was determined and is in agreement with the selected setting (Flack x parameter: 0.10 (6)). In addition, refinement of the inverted structure leads to a poorer reliability factor: wR2 for all data = 0.0644 compared with 0.0622 for the selected setting. Crystal data is summarized in Table 1.

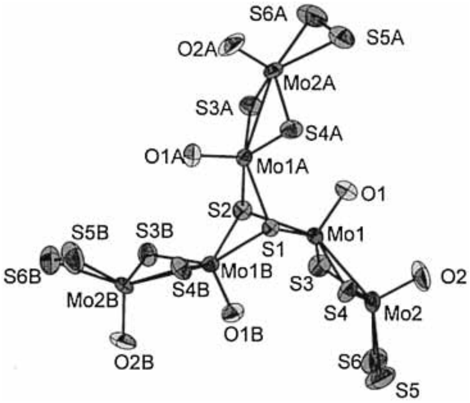

Figure 1. View of the $[Mo_6O_6S_{14}]^{4-}$anion with labeling and displacement ellipsoids drawn at the 50% probability level. Symmetry codes: (A) $1 - y$, $1 + x - y$, $+z$; (B) $-x + y$, $1 - x$, $+z$.

Results and Discussion

In the crystal structure of $[N(CH_3)_4]_4Mo_6O_6S_{14}$ the new discrete $[Mo_6O_6S_{14}]^{4-}$ anions are separated by discrete $[N(CH_3)_4]^+$ cations. The structure of the $[Mo_6O_6S_{14}]^{4-}$ anion is shown in Figure 1, and selected bond distances (Å) and angles (deg) are listed in Table 2. The anion consists of three $[Mo_2O_2S_2]^{2+}$ entities which are connected to each other by two μ_3-S atoms and every $[Mo_2O_2S_2]^{2+}$ unit has a terminal η^2-disulfido group. Therefore, each Mo atom in the $[Mo_2O_2S_2]^{2+}$ unit is bound to one O atom and two μ_2-S atoms: one of the two Mo atoms has also a η^2-disulfido ligand and the other Mo center is connected to the two central μ_3-S atoms. This connection mode yields the $[Mo_6O_6S_{14}]^{4-}$ anion. The two μ_3-S atoms, S1 and S2, are located on a 3-fold axis. The bond length for the average Mo−O distance [1.683(4) Å] is in normal range compared with other oxothiomolybdates.[14] The Mo1−Mo2 distance is 2.809(1) Å. The short distance as well as the diamagnetism of the compound demonstrate that the remaining d^1 electron of the Mo atoms are used for a Mo−Mo bond in the $[Mo_2O_2S_2]^{2+}$ unit. The Mo1−Mo2 distance is very similar to values reported for other $[^VMo_2O_2S_2]^{2+}$ containing compounds.[14] The S−S bond length in the disulfido group of 2.078(4) Å is typical for a single bond. The average Mo−S distance to the μ_2-S bridge of 2.319(8) Å is shorter than the distance from Mo2 to the S atoms in the terminal η^2-S_2^{2-} group [2.389(18) Å]. Such a difference is also observed in other binuclear thio- and oxothiomolybdates.[4,20] Significantly larger distances of 2.482(2) and 2.463(2) Å are

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(18) Sheldrick, G. M. *SHELXL-93: Program for the Refinement of Crystal Structures*; University of Göttingen: Germany, 1993.

(19) Sheldrick, G. M. *SHELXS-94: Program for Crystal Structure Determination*; University of Göttingen: Germany, 1994.

(20) Hadjikyriacou, A. I.; Coucouvanis, D. *Inorg. Chem.* **1987**, *26*, 2400−2408.

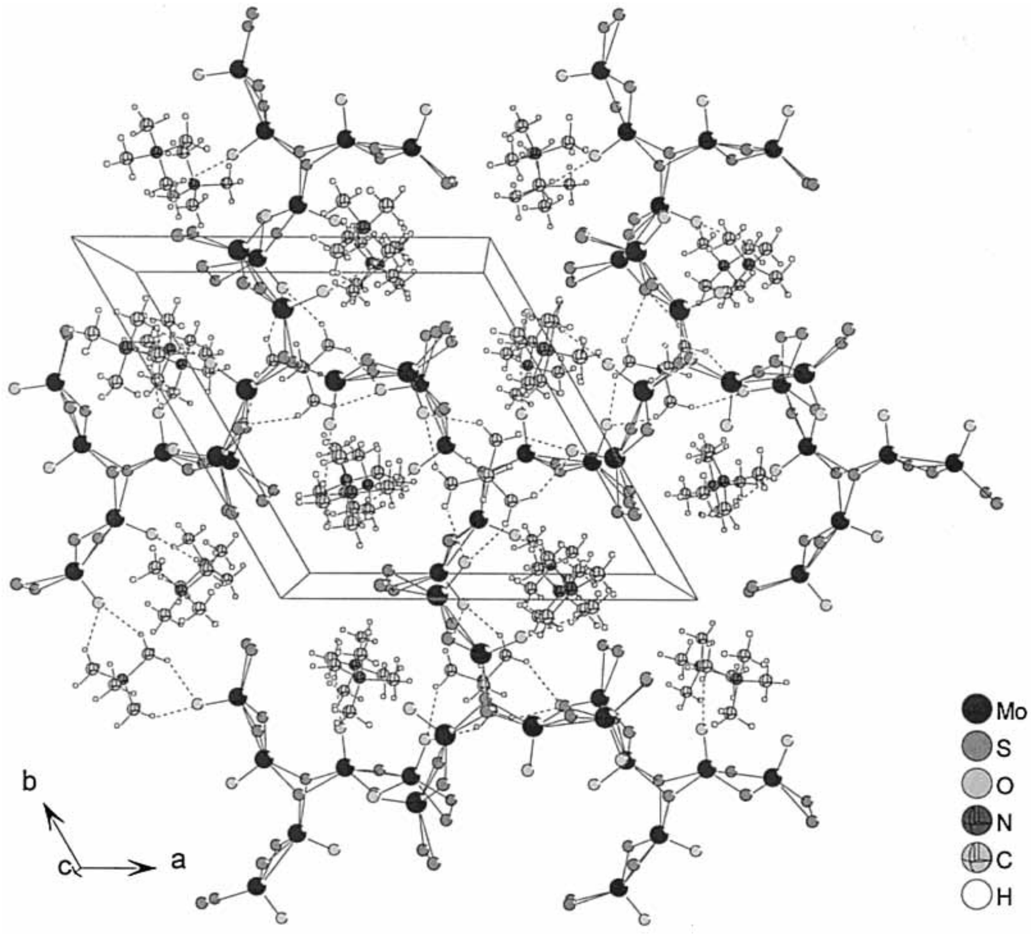

Figure 2. Crystal structure viewed along the *c* axis with short intermolecular O···H distances indicated by dotted lines.

observed between Mo1 and the S atoms of the two μ_3 coordinating S atoms.

In an alternative description the structure of the anions contains a Mo_3S_2 core in a bipyramidal arrangement with the Mo atoms in the equatorial and the sulfur atoms in the axial positions. There are two more μ_3-S bicapped thiomolybdate clusters described in the literature, $[Mo_3S_5(PMe_3)_6]$[11,12] and the $[Mo_3S_2Cl_9]^{3-}$ anion.[13] It is noted that the Mo atoms in these compounds are in a different oxidation state than the Mo atoms in the $[Mo_6O_6S_{14}]^{4-}$ anion, making a direct comparison difficult. In $[Mo_3S_5(PMe_3)_6]$ and the $[Mo_3S_2Cl_9]^{3-}$ anion the Mo atoms in the Mo_3S_2 cores are bridged by μ_2-X atoms (X = S, Cl), and the $4d^2$ electrons are involved in Mo−Mo bonds between the Mo atoms of the triangle with significantly shorter Mo−Mo distances of 2.56−2.65 Å in $[Mo_3S_2Cl_9]^{3-}$ and 2.71 Å in $[Mo_3S_5(PMe_3)_6]$. Furthermore, the distance between the Mo atoms and the μ_3-sulfur atoms becomes shorter than in the title compound [Mo1−Mo1 3.413(1) Å, Mo−μ_3-S 2.473(11) Å].

A $[Mo_6S_{20}]^{2-}$ unit was also reported, and it was claimed that the anion is a constituent of $(n\text{-}Bu_4N)_2Mo_6S_{20}$.[21] The exact structure is not known yet, but it is supposed to consist of a dimeric MoS_2Cl_3 in which the Cl atoms are substituted by MoS_4 groups. Because this structure should be dimeric, whereas the anion of the title compound is trimeric, they cannot be compared.

There are several short intermolecular contacts between the hydrogen atoms of the $[N(CH_3)_4]^+$ cations and the oxygen atoms of the $[Mo_6O_6S_{14}]^{4-}$ anion. The O···H separations (C···O distances) are O1−H2B = 2.516 Å (O1−C2 = 3.427(10) Å), O1−H3C = 2.500 Å (O1−C3 = 3.402(10) Å), O2−H6B = 2.306 Å (O2−C6 = 3.172(8) Å), and O2−H6C = 2.400 Å (O2−C6 = 3.244(8) Å). The corresponding angles C−H···O range from 149(1)° to 158(3)°, indicating hydrogen bonding as depicted in Figure 2. There is also a short S···H distance between S1 and H6A of 2.824 Å (S1−C6 = 3.685(7) Å) and with a C−H···S angle of 150(1)°.

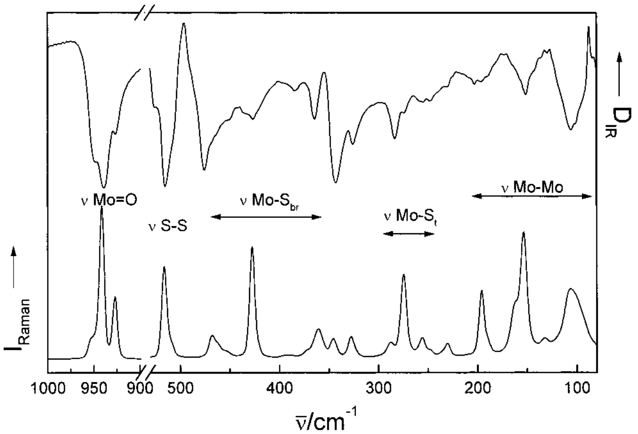

Figure 3. Raman and IR spectra of $[N(CH_3)_4]_4Mo_6O_6S_{14}$.

Vibrational Properties. The IR and Raman spectra of $[N(CH_3)_4]_4Mo_6O_6S_{14}$ are shown in Figure 3. The Mo=O vibrations can be easily identified at 930 and 940 cm^{-1}. In the region 150−200 cm^{-1} mainly the Mo−Mo vibrations are recognizable, with the peaks at lower frequencies resulting from collective lattice modes. The frequency of the terminal η^2-disulfido group vibration is found at 515 cm^{-1}. A rough

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(21) Fedin, V. P.; Mironov, Yu. V.; Sokolov, M. N.; Fedorov, V. E. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1987**, *36*, 171−172.

assignment of the Mo−S vibrations is possible on the basis of the data reported in the literature for the $[Mo_2O_2S_6]^{2-}$ anion[22] which shows several structural similarities. An exact assignment of the Mo−S frequencies is not straightforward because most of the Mo−S vibrations are strongly coupled. However it is highly likely that the Mo−S_t vibrations (S_t = terminal S atoms) are in the range from 250 to 290 cm^{-1}, whereas the most significant Mo−S_{br} modes (S_{br} = bridging S atoms) occurs between 360 and 480 cm^{-1}. The positions of the Mo−μ_3-S vibrations could not be unambiguously located, but additional signals at ∼345 and ∼465 cm^{-1} compared with the spectra of the $[Mo_2O_2S_6]^{2-}$ anion suggest these absorptions are due to Mo−μ_3-S modes. This is also in agreement with the frequencies for the Mo−μ_3-S vibrations in the $[Mo_3S_{13}]^{2-}$ anion.[23, 24]

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Supporting Information Available: Tables of atomic coordinates, isotropic and anisotropic displacement parameters, full bond lengths and angles including details of the structure determination. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Fedin, V. P.; Kolesov, B. A.; Mironov, Yu. V.; Gerasko, O. A.; Fedorov, V. YE. *Polyhedron* **1991**, *10*, 997−1005.

(23) Fedin, V. P.; Kolesov, B. A.; Mironov, Yu. V.; Fedorov, V. YE. *Polyhedron* **1989**, *8*, 2419−2423.

(24) Müller, A.; Wittenbein, V.; Krickemeyer, E.; Bögge, H.; Lemke, M. *Z. Anorg. Allg. Chem.* **1991**, *605*, 175−188.