

Synthesis and structure of supramolecular polyoxothiometalate nanocluster containing 52 metal atoms $[\{\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_5\}_4(\gamma\text{-SiW}_{10}\text{O}_{36})_4]^{16-}$

N. V. Izarova,^a M. N. Sokolov,^a E. Cadot,^b J. Marrot,^b F. Secheresse,^b and V. P. Fedin^{a*}

^aA. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 3 prosp. Akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation.

Fax: +7 (383 2) 34 4489. E-mail: cluster@che.nsk.su

^bUniversity of Versailles, Institute Lavoisier, 78035 Versailles, France.*

Fax: +33 (1 39) 25 4381. E-mail: secheres@chimie.uvsq.fr

The polyoxothiometalate complex $[\{\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_5\}_4(\gamma\text{-SiW}_{10}\text{O}_{36})_4]^{16-}$ was prepared by the reaction of the cationic triangular molybdenum aqua complex $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ (electrophile) with the lacunary polyoxotungstate complex $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ (nucleophile). According to the results of single-crystal X-ray diffraction analysis of the dimethylammonium salt, the anionic nanocluster contains 52 molybdenum and tungsten atoms and has a cyclic porphyrin-like structure.

Key words: polyoxometalates, chalcogenide clusters, molybdenum, tungsten, supramolecular chemistry.

The chemistry of large nanosized complexes containing tens or even hundreds of metal atoms (nanoclusters, giant clusters) is a relatively new and still extensively developing area of research. Giant palladium clusters¹ and polyoxometalate clusters (for example, $[\text{Mo}_{132}\text{O}_{372}(\text{RCOO})_{30}(\text{H}_2\text{O})_{72}]^{42-}$ is the giant cluster with icosahedral symmetry)^{2,3} are glowing examples. Such complexes are of considerable interest and can have unique applications. Our recent studies have been aimed at elaborating scientific basics for the target synthesis of nanosized complexes and supramolecular compounds containing several tens of metal atoms starting from relatively large molecular building fragments/blocks, such as chalcogenide clusters, polyoxometalate complexes, and large macrocyclic cavitands of the cucurbituril type.^{4–12} These studies are examples of interdisciplinary research in supramolecular chemistry.^{13,14}

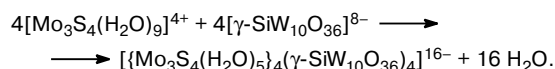
Results and Discussion

The anionic complex $[\{\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_5\}_4(\gamma\text{-SiW}_{10}\text{O}_{36})_4]^{16-}$ was synthesized by the reaction of the cationic triangular molybdenum chalcogenide cluster $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ with the Keggin-type anionic lacunary $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ complex in an aqueous solution. The starting chalcogenide cluster $[\text{Mo}_3(\mu_3\text{-S})(\mu_2\text{-S})_3(\text{H}_2\text{O})_9]^{4+}$

contains the triangular molybdenum fragment, in which the Mo atoms are linked by Mo—Mo single bonds (formal oxidation state of the Mo atoms is +4), one μ_3 -bridging S atom, and three μ_2 -bridging S atoms. Each Mo atom is additionally coordinated by three water molecules, two of which are located on the μ_3 -S side relative to the plane of the Mo_3 triangle (*cis*- H_2O), whereas the third water molecule is located on the μ_2 -S side (*trans*- H_2O).^{15,16} The coordinated water molecules are labile and are readily replaced with various nucleophiles.^{17,18}

The $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ complex is the divacant lacunary derivative of the Keggin anion $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ and differs from the latter in that it lacks two $\{\text{WO}_2\}^{2+}$ fragments.^{19,20} It is known^{20,21} that lacunary polyoxometalates act as strong nucleophiles and form complexes with a broad spectrum of metals.

In the course of the reaction of equimolar amounts of the $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ and $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ complexes in aqueous solutions at pH from 1.0 to 5.0, the color of the reaction solution rapidly changed from emerald-green (color of a solution of $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$) to brown



The choice of pH was determined by the fact that the lacunary anion $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ is unstable in strongly acidic solutions, whereas the triangular molybdenum aqua complex is readily hydrolyzed at higher pH. When the reaction was performed in an acetate buffer followed by

* Université de Versailles, Institut Lavoisier, 45 avenue des Etats-Unis, 78035 Versailles, France.

the addition of an excess of dimethylammonium chloride, an amorphous substance and brown truncated-octahedral crystals precipitated from the aqueous reaction solution after 7–10 days. According to the results of elemental analysis, the dimethylammonium salt dried in air has the composition $[\text{Me}_2\text{NH}_2]_{16}\{[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_5]_4(\gamma\text{-SiW}_{10}\text{O}_{36})_4\} \cdot (\sim 20\text{H}_2\text{O})$. The synthesis is well reproducible but the yield of the crystalline complex is low (8–10%).

In the IR spectra of the reaction product, silic tungstate is easily identified from the stretching vibrations $\nu(\text{SiO})$ at 808 cm^{-1} and $\nu(\text{WO})$ at 970 , 950 , and 803 cm^{-1} . The stretching vibrations of the Mo–O bonds are observed at 950 and 863 cm^{-1} . The stretching bands of the dimethylammonium cations almost completely overlap with intense stretching bands of the $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ anion. The bending bands of the water molecules are observed at 1610 – 1620 cm^{-1} .

X-ray diffraction study of the crystal hydrate demonstrated that the compound has an island (cationic-anionic) structure. The structure of the anionic cluster $[(\gamma\text{-SiW}_{10}\text{O}_{36})_4\{\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_5\}_4]^{16-}$ is shown in Fig. 1. The complex contains 52 transition metal atoms and has a porphyrin-like cyclic structure. The reaction of the $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ and $[\text{SiW}_{10}\text{O}_{36}]^{8-}$ complexes is accompanied by the replacement of four water molecules in *cis* positions with respect to $\mu_3\text{-S}$ in the molybdenum aqua complex. Each two adjacent $\{\gamma\text{-SiW}_{10}\}$ fragments are linked to the $\{\text{Mo}_3\text{S}_4\}$ fragment through the bridging oxygen atoms so that one molybdenum atom of each $\{\text{Mo}_3\text{S}_4\}$ triangle is linked to two W atoms of one of the $\{\gamma\text{-SiW}_{10}\}$ complexes through two bridging oxygen atoms (Mo–O, $2.133(9)\text{ \AA}$; W–O, $1.798(1)\text{ \AA}$), and each of two other molybdenum atoms of the $\{\text{Mo}_3\text{S}_4\}$ fragment is linked to

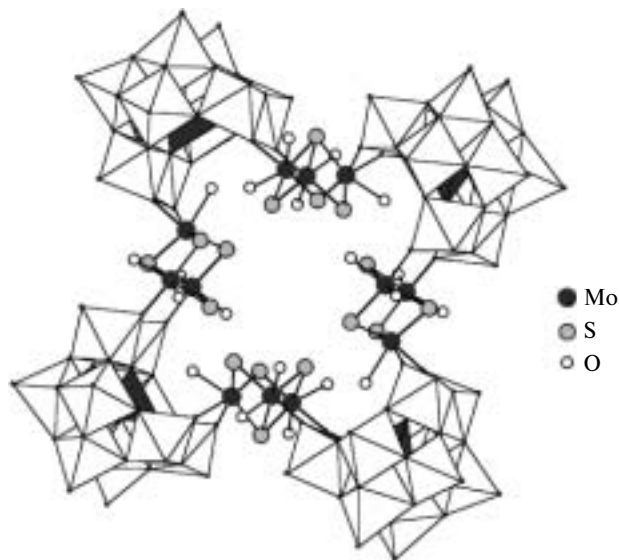


Fig. 1. Structure of the anionic complex $[(\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_5)_4(\gamma\text{-SiW}_{10}\text{O}_{36})_4]^{16-}$; the $\{\text{SiW}_{10}\text{O}_{36}\}$ fragments are represented as polyhedra.



Fig. 2. Molecular packing of the cyclic anionic complexes $[(\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_5)_4(\gamma\text{-SiW}_{10}\text{O}_{36})_4]^{16-}$ within one layer projected onto the *ab* plane (atoms are represented as van der Waals spheres).

one W atom of the adjacent $\{\gamma\text{-SiW}_{10}\}$ fragment through one bridging oxygen atom (Mo–O, $2.021(10)\text{ \AA}$; W–O, $1.852(10)\text{ \AA}$).

The maximum and minimum van der Waals sizes of the cyclic anionic complex $[(\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_5)_4(\gamma\text{-SiW}_{10}\text{O}_{36})_4]^{16-}$ are ~ 30 and $\sim 16\text{ \AA}$, respectively. The van der Waals diameter of the inner cavity of the cyclic anion is $\sim 4.4\text{ \AA}$, and the cavity is occupied only by water molecules of crystallization. In the crystal, the anions are packed to form parquet-like layers in such a way that the narrow fragment of one anion is adjacent to the broad fragment of another anion (Fig. 2). These layers alternate in the *ABAB* order along the crystallographic axis *c*. The dimethylammonium cations and some water molecules of crystallization are located in complex channels formed in each layer as well as between these layers.

The main geometric parameters of the $[(\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_5)_4(\gamma\text{-SiW}_{10}\text{O}_{36})_4]^{16-}$ anion are somewhat different from those of the starting building blocks. The main bond lengths in the anionic complex that formed and in the initial $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ and $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ complexes are given in Table 1. The formation of the $[(\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_5)_4(\gamma\text{-SiW}_{10}\text{O}_{36})_4]^{16-}$ anion is accompanied by a slight increase in the Mo–Mo distances. In the $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9][\text{H}_3\text{CC}_6\text{H}_4\text{SO}_3]_4$ complex,¹⁶ these distances are in the range of 2.726 – 2.741 \AA , whereas the Mo–Mo distances in the $[(\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_5)_4(\gamma\text{-SiW}_{10}\text{O}_{36})_4]^{16-}$ complex are in the range of 2.733 – 2.778 \AA . The Mo– $\mu_3\text{-S}$ and Mo–O(H_2O) distances are also slightly longer and are in the ranges of 2.322 – 2.342 and 2.311 – 2.324 \AA , respectively. The for-

Table 1. Selected bond lengths (Å) in the $[\{\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_5\}_4(\gamma\text{-SiW}_{10}\text{O}_{36})_4]^{16-}$, $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$, and $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ complexes

Bond	$[\{\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_5\}_4(\gamma\text{-SiW}_{10}\text{O}_{36})_4]^{16-}$	$[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$	$[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$
Mo—Mo	2.733(2)—2.778(2)	2.726(33)—2.741(11)	—
Mo— μ_3 -S	2.311(5)—2.324(4)	2.322(20)—2.342(30)	—
Mo— μ_2 -S	2.264(4)—2.312(4)	2.277(26)—2.289(20)	—
Mo—O _{H₂O}	2.193(11)—2.293(9)	2.158(282)—2.197(52)	—
Si—O	1.631(13)—1.676(15)	—	1.734(28)—1.736(26)
W—O _{term}	1.667(11)—1.804(12)	—	1.618(38)—1.792(31)
W— μ_2 -O(2W)	1.688(11)—2.121(10)	—	1.701(39)—2.264(40)
W— μ_3 -O	2.249(10)—2.277(8)	—	2.153(25)—2.158(21)
W— μ_4 -O	2.258(10)—2.35(1)	—	2.272(25)—2.299(24)

mation of the $[\{\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_5\}_4(\gamma\text{-SiW}_{10}\text{O}_{36})_4]^{16-}$ anion results in a noticeable decrease in the Si—O and W— μ_3 -O bond lengths (from 1.734—1.736 to 1.631—1.676 Å and from 2.153—2.158 to 2.249—2.277 Å, respectively) and a decrease in the W— μ_3 -O—W bond angles (from 98.37 to 92.10—94.32°) compared to those observed in $\text{Cs}_8[\text{SiW}_{10}\text{O}_{36}] \cdot 9\text{H}_2\text{O}$.¹⁹

All the above-mentioned changes in the geometric parameters of the $\{\text{SiW}_{10}\text{O}_{36}\}$ and $\{\text{Mo}_3\text{S}_4\}$ structural fragments upon the formation of the $[\{\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_5\}_4(\gamma\text{-SiW}_{10}\text{O}_{36})_4]^{16-}$ complex are, on the whole, small. Hence, the starting compounds can be considered as building blocks, and the preparation of the $[\{\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_5\}_4(\gamma\text{-SiW}_{10}\text{O}_{36})_4]^{16-}$ anion is an example of the target synthesis according to the method of building blocks.

An interesting structural feature of the cyclic complex $[\{\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_5\}_4(\gamma\text{-SiW}_{10}\text{O}_{36})_4]^{16-}$ is the presence of a rather large inner cavity formed by 12 sulfur atoms of four $\{\text{Mo}_3(\mu_3\text{-S})(\mu_2\text{-S})_3\}$ fragments. It is well known from the coordination chemistry of the $[\text{M}_3(\mu_3\text{-S})(\mu_2\text{-S})_3(\text{H}_2\text{O})_9]^{4+}$ clusters (M = Mo, W; Q = S, Se) that the μ_2 -bridging chalcogen atoms are coordinatively unsaturated and can coordinate a broad spectrum of transition and main-group metals (M') to form heterometallic cuboidal complexes $\text{M}_3(\mu_3\text{-S})_4\text{M}'$.²² The porphyrin-like complex $[\{\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_5\}_4(\gamma\text{-SiW}_{10}\text{O}_{36})_4]^{16-}$ would be expected to possess an analogous reactivity.

To summarize, the reaction of the electrophilic $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ cluster with nucleophilic polyoxotungstate $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ under strictly controlled conditions in aqueous solutions affords the nanosized (~3 nm) anionic cyclic cluster containing 52 molybdenum and tungsten atoms.

Experimental

A solution of the $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ complex in 2 M HCl and the $\text{K}_8[\gamma\text{-SiW}_{10}\text{O}_{36}] \cdot 12\text{H}_2\text{O}$ salt were prepared according to known procedures.^{23–26} Other reagents of analytical grade were

Table 2. Principal crystallographic characteristics and details of X-ray diffraction study of complex **1**

Parameter	Characteristic
Molecular formula	$\text{C}_{32}\text{H}_{224}\text{Mo}_{12}\text{N}_{16}\text{O}_{192}\text{S}_{16}\text{Si}_4\text{W}_{40}$
Molecular weight	13036.87
Crystal system	Tetragonal
Space group	$I4/m$
Unit cell parameters/Å	
<i>a</i>	24.1514(7)
<i>b</i>	24.1514(7)
<i>c</i>	21.8711(9)
<i>V</i> /Å ³	12757.2(7)
<i>Z</i>	2
<i>d</i> _{calc} /g cm ^{−3}	3.394
Temperature/K	293(2)
Diffractometer	«Siemens SMART CCD»
λ /Å	0.71073 (Mo-K α)
$2\theta_{\text{max}}$ /deg	46.52
Ranges of <i>h</i> , <i>k</i> , <i>l</i> indices	−21 ≤ <i>h</i> ≤ 26, −25 ≤ <i>k</i> ≤ 26, −24 ≤ <i>l</i> ≤ 21
Crystal dimensions/mm	0.08 × 0.08 × 0.04
μ /mm ^{−1}	1.790
<i>T</i> _{min} / <i>T</i> _{max}	0.315/0.521
Number of measured reflections	23613
Number of independent reflections	4733
<i>R</i> _{int}	0.1425
Number of reflections with <i>F</i> _o > 4σ(<i>F</i> _o)	2618
Number of parameters in refinement	356
Number of restrictions	4
<i>R</i> factors based on reflections with <i>F</i> _o > 4σ(<i>F</i> _o)	<i>R</i> ₁ = 0.0784, <i>wR</i> ₂ = 0.1900
<i>R</i> factors based on all reflections	<i>R</i> ₁ = 0.1497, <i>wR</i> ₂ = 0.2229
Goodness-of-fit on <i>F</i> ²	1.035
Residual electron density (min/max)/e Å ^{−3}	−2.376/2.788

used without additional purification. All experiments were carried out in air. Elemental analysis was carried out at the N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences. The IR spectra were recorded on a Bruker IFS-85 spectrometer in KBr pellets.

Hexadakis(dimethylammonium)tetrakis{pentaqua- μ_3 -sulfidotri- μ_2 -sulfidotrimolybdate(Mo—Mo)- γ -decatungstosilicate} octacosia crystal hydrate (1). The $K_8[\gamma\text{-SiW}_{10}\text{O}_{36}] \cdot 12\text{H}_2\text{O}$ complex (0.30 g, 0.101 mmol) was dissolved in an acetate buffer (0.5 M AcOH/0.5 M AcONa; 20 mL). Then a 70 mM $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ solution (1.5 mL, 0.105 mmol) in 2 M HCl was added dropwise with stirring for 3 min, the process being accompanied by a rapid change of the color of the reaction mixture from green to brown. The reaction mixture was stirred for 10 min, 6 M HCl was added to pH 2.0, and then $[\text{Me}_2\text{NH}_2]\text{Cl}$ (0.30 g, 3.68 mmol) was added. The solution was concentrated in air for one week to approximately one-half of the initial volume, which gave rise to an amorphous precipitate as well as needle-like and octahedrally shaped crystals. The latter crystals were handpicked under a microscope. The yield of the crystalline product was 0.033 g (10%). Found (%): C, 2.91; H, 1.44; N, 1.61. $\text{C}_{32}\text{H}_{208}\text{N}_{16}\text{O}_{184}\text{Mo}_{12}\text{Si}_4\text{W}_{40}\text{S}_{16}$. Calculated (%): C, 2.98; H, 1.62; N, 1.74. IR (KBr), ν/cm^{-1} : 3410 s, 3157 s (sh), 1617 m, 1460 w, 990 w, 950 m, 863 s, 803 s, 697 s, 552 m.

X-ray diffraction study. Principal crystallographic characteristics and details of X-ray diffraction study are given in Table 2. Single crystals of the $(\text{NH}_2\text{Me}_2)_{16}[\{\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9\}_4(\gamma\text{-SiW}_{10}\text{O}_{36})_4] \cdot 28\text{H}_2\text{O}$ complex were taken directly from the reaction solution. The structure was solved by direct methods and refined by the full-matrix least-squares method using the SHELX-97 program package.²⁷ The atomic coordinates were deposited with the Cambridge Structural Database and can be obtained from the authors.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 02-03-32604), the Chemistry and Materials Science Division of the Russian Academy of Sciences (Target Program of Basic Research "Chemistry and Physical Chemistry of Supramolecular Systems and Atomic Clusters"), and the INTAS (Grant 2002-2346).

References

1. M. N. Vargaftik, I. I. Moiseev, D. I. Kochubey, and K. I. Zamaraev, *Faraday Discuss Chem. Soc.*, 1991, N. 92, 13.
2. A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtman, and F. Peters, *Angew. Chem., Int. Ed.*, 1998, **37**, 3360.
3. A. Müller and S. Roy, *Usp. Khim.*, 2002, **71**, 1107 [*Russ. Chem. Rev.*, 2002, **71** (Engl. Transl.)].
4. F. Sécheresse, E. Cadot, and A. Dolbecq, *J. Solid State Chem.*, 2000, **152**, 78.
5. E. Cadot and F. Sécheresse, *Chem. Commun.*, 2002, 2189.
6. E. Cadot, B. Salignac, T. Loiseau, A. Dolbecq, and F. Sécheresse, *Chem. Eur. J.*, 1999, **5**, 3390.
7. E. Cadot, M.-A. Pilette, J. Marrot, and F. Sécheresse, *Angew. Chem., Int. Ed.*, 2003, **42**, 2173.
8. B. Salignac, S. Riedel, A. Dolbecq, F. Sécheresse, and E. Cadot, *J. Am. Chem. Soc.*, 2000, **122**, 10381.
9. E. Cadot, J. Marrot, and F. Sécheresse, *Angew. Chem., Int. Ed.*, 2001, **40**, 774.
10. O. A. Geras'ko, D. G. Samsonenko, and V. P. Fedin, *Usp. Khim.*, 2002, **71**, 840 [*Russ. Chem. Rev.*, 2002, **71** (Engl. Transl.)].
11. M. N. Sokolov, D. N. Dybtsev, and V. P. Fedin, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 987 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 1041].
12. A. Müller, V. P. Fedin, C. Kuhlmann, H.-D. Fenske, G. Baum, H. Bögge, and B. Hauptfleisch, *Chem. Commun.*, 1999, 1189.
13. J.-M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, VCH, Weinheim—New York—Bales—Cambridge—Tokio, 1995.
14. A. Müller, P. Kögerler, and C. Kuhlmann, *Chem. Commun.*, 1999, 1347.
15. F. A. Cotton, Z. Dori, R. Luser, and W. Schwotzer, *J. Am. Chem. Soc.*, 1985, **107**, 6734.
16. H. Alkashi, T. Shibahara, and H. Kuroya, *Polyhedron*, 1990, **9**, 1671.
17. T. Shibahara, M. Yamasaki, G. Sakane, K. Minami, T. Yabuki, and A. Ichimura, *Inorg. Chem.*, 1992, **32**, 640.
18. K. Hegetschweiler, H. Wörle, M. D. Meienberger, R. Nesper, H. W. Schmalle, and R. D. Hancock, *Inorg. Chim. Acta*, 1996, **250**, 35.
19. H. Hartl and V. Hubert, *Acta Crystallogr.*, 1996, **C52**, 757.
20. A. Müller, F. Peters, M. T. Pope, and D. Gatteschi, *Chem. Rev.*, 1998, **98**, 239.
21. E. Coronado and C. J. Gómez-García, *Comments Inorg. Chem.*, 1995, **17**, 255.
22. R. Hernandez-Molina, M. N. Sokolov, and A. G. Sykes, *Acc. Chem. Res.*, 2001, **34**, 223.
23. D. Saysell, V. P. Fedin, G. Lamprecht, M. N. Sokolov, and A. G. Sykes, *Inorg. Chem.*, 1997, **36**, 2982.
24. V. P. Fedin, M. N. Sokolov, Y. V. Mironov, B. A. Kolesov, S. V. Tkachev, and V. E. Fedorov, *Inorg. Chim. Acta*, 1990, **167**, 39.
25. V. P. Fedin, Y. V. Mironov, M. N. Sokolov, O. A. Geras'ko, A. V. Virovets, N. V. Podberezskaya, and V. E. Fedorov, *Inorg. Chim. Acta*, 1991, **187**, 81.
26. A. Teze and G. Herve, *Inorg. Synth.*, 1990, **27**, 85.
27. G. M. Sheldrick, *SHELX-97, Release 97-2*, University of Göttingen, Göttingen, Germany, 1998.

Received December 16, 2003