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Mixed-Ligand Cluster [$Mo_3S_4(Dtp)_2(\mu\text{-}AcO)Cl(Me_2Bipy)$]: Synthesis and Structure

A. L. Gushchin[a, b, *], **Yu. A. Laricheva**[a], **D. A. Piryazev**[a], **and M. N. Sokolov**[a, b]
[a] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, pr. akademika Lavrent'eva 3, Novosibirsk, 630090 Russia*
[b] *Novosibirsk State University, ul. Pirogova 2, Novosibirsk, 630090 Russia*
**e-mail: gushchin@niic.nsc.ru*

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Abstract—Mixed-ligand cluster [$Mo_3S_4(Dtp)_2(\mu\text{-}AcO)Cl(Me_2Bipy)$] · $CHCl_3$ (**I** · $CHCl_3$), where Dtp is $(EtO)_2PS_2$, was synthesized by the reaction of the molybdenum aqua complex $[Mo_3S_4(H_2O)_9]^{4+}$ with 4,4'-dimethyl-2,2'-bipyridine (Me_2Bipy) and phosphorus sulfide (P_4S_{10}) in ethanol followed by chromatographic separation on silica gel and crystallization in the presence of acetic acid. The crystal structure of **I** · $CHCl_3$ was determined by X-ray diffraction analysis. The synthesized compound was characterized by the IR and NMR spectra and elemental analysis. The electronic structure of the synthesized compound was established, and its electrochemical behavior in a solution was studied.

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INTRODUCTION

Chalcohenide clusters of molybdenum and tungsten containing the triangular cluster core $\{M_3Q_4\}^{4+}$ (M = Mo, W; Q = S, Se) represent a large family of coordination compounds [1–4]. The sulfide complexes of molybdenum containing aqua or cyclopentadienyl ligands show a high activity in the catalytic systems of water decomposition [5, 6]. The complexes of $\{M_3Q_4\}^{4+}$ with diphosphine ligands were studied in most detail [7, 8]. The recent works in this area provide new prospects for using these complexes in catalysis [9–12]. For example, the hydride complexes Mo_3S_4 functionalized by diphosphine ligands are efficient catalysts for the selective reduction of nitroarenes to the corresponding anilines [9] and also catalyze the selective hydrogenation of pentafluoropyridine [10]. The diphosphine complexes $[Mo_3S_4(Dmpe)_3(MPTES)_3]PF_6$ (MPTES is (3-mercaptopropyl)triethoxysilane) are capable of incorporating into mesoporous silica [13], which is interesting for heterogeneous catalysis.

The works on studying the triangular clusters with the cluster core $\{M_3Q_7\}^{4+}$ (M = Mo, W; Q = S, Se) and polypyridyl ligands have recently been published. For instance, the homoleptic complexes with 1,10-phenanthroline $[M_3Se_7(Phen)_3]^{4+}$ (M = Mo, W), which undergo a complicated reversible three-electron reduction involving both the metal and 1,10-phenanthroline, were synthesized [14]. The first heteroleptic complexes with *ortho*-phenanthroline $[Mo_3S_7Br_4L]$ (L = Phen, Me_2Phen) were obtained [15]. The heteroleptic complex $\{[Mo_3S_7Br_4(DcmBipy)]Br\}^-$ with the coordinated dicarboxymethylbipyridine molecule (DcmBipy = 4,4'-$(CO_2Me)_2$-2,2'-Bipy) was reported [16]. This complex can act as a chromophore for water photolysis with the formation of hydrogen. However, no derivatives of the triangular $\{M_3Q_4\}^{4+}$ clusters with polypyridyl ligands are yet known.

In this work, we report the synthesis and structure of a new complex [$Mo_3S_4(Dtp)_2(\mu\text{-}AcO)Cl(Me_2Bipy)$] (**I**), being the first example for the coordination of the polypyridyl ligand to the $\{M_3Q_4\}^{4+}$ cluster, and discuss the electronic structure and electrochemical behavior in a solution of the synthesized compound.

EXPERIMENTAL

All processes were carried out in air. The aqua complex $[Mo_3S_4(H_2O)_9]^{4+}$ was synthesized from $Mo_3S_7Br_4$ according to a described procedure [17]. Commercially available Me_2Bipy, P_4S_{10}, and other compounds were used as received. Solvents were purified using standard procedures.

IR spectra were recorded on a Scimitar FTS-2000 spectrometer in a range of 4000–400 cm^{-1} (KBr pellets). The ^{31}P NMR spectrum was measured on a Bruker Avance 500 spectrometer at room temperature using H_3PO_4 as a standard. Analyses to C, H, N, and S were carried out on an EuroEA3000 Eurovector analyzer. Cyclovoltammograms were obtained with a 797 VA Computrace instrument (Metrohm, Switzerland). A platinum rod (2 × 20 mm) served as an auxiliary electrode, and a silver chloride (Ag/AgCl) electrode filled with a 3 M KCl solution was a reference electrode. The working electrode was a glassy carbon disk electrode. The supporting electrolyte was a 0.05 M solution of tetrabutylammonium hexafluorophosphate in CH_2Cl_2, and a scan rate was 0.1 V/s. Quantum-chemical calculations were performed by the DFT method with the ADF2012 program using the TZ2P basis set [18].

Synthesis of $[Mo_3S_4(Dtp)_2(\mu\text{-}AcO)Cl(Me_2Bipy)] \cdot CHCl_3$ ($I \cdot CHCl_3$). A solution of 4,4'-dimethyl-2,2'-bipyridine (56 mg, 305 μmol) in ethanol (5 mL) and a solution of P_4S_{10} (68 mg, 153 μmol) in ethanol (3 mL) were added to an ethanol solution (5 mL) of $[Mo_3S_4(H_2O)_9]Cl_4$ (220 mg, 305 μmol). The reaction mixture was stirred at room temperature for 3 h. A brown precipitate was formed from a dark brown solution. Then the reaction mixture was evaporated on a rotary evaporator to dryness and chromatographed on silica gel (40/100). The sequence of eluents was chloroform, acetone–chloroform (1 : 1, 1 : 2, 1 : 3) mixtures, and acetoneL. The obtained fractions were evaporated to dryness, and solid residues were dissolved in chloroform. Several droplets of concentrated acetic acid were added to all solutions, and the mixtures were left to evaporate slowly. Crystals of the products were obtained from a solution of the second fraction. They were separated and washed with alcohol and ether. The yield was 53 mg (15%).

For $C_{22}H_{35}N_2O_6P_2S_8ClMo_3$ (without $CHCl_3$)

anal. calcd., %:	C, 24.8;	H, 3.3;	N, 2.6;	S, 24.1.
Found, %:	C, 25.3;	H, 3.7;	N, 2.3;	S, 24.4.

IR (ν, cm^{-1}): 2977 m, 2928 w, 2899 w, 2860 w, 1616 m, 1519 w, 1429 s, 1287 w, 1162 m, 1009 vs, 961 vs, 817 s, 789 s, 673 w, 640 s, 523 w, 449 w.

^{31}P NMR ($CDCl_3$; δ, ppm): 109.4 (s); 108.6 (s).

X-ray diffraction analysis of $I \cdot CHCl_3$. Diffraction data were obtained on a Bruker X8Apex automated four-circle diffractometer equipped with a CCD detector [19, 20] (MoK_α radiation, graphite monochromator). The crystallographic characteristics and X-ray diffraction experimental details are presented in Table 1. Selected bond lengths are listed in Table 2.

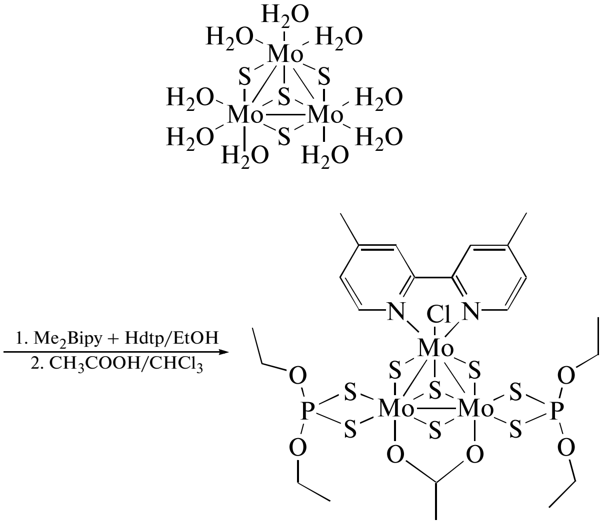
The full information on the studied structure was deposited with the Cambridge Crystallographic Data Centre (CCDC) (no. 935265; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Chalcogenide clusters containing polypyridyl ligands are very rare. There are no such examples in the chemistry of triangular molybdenum and tungsten clusters $\{M_3Q_4\}^{4+}$. Although the synthesis and X-ray diffraction analysis of the mixed-ligand complex $[Mo_3S_4(Dtp)_4(Bipy)]$ are briefly reported [21], neither the synthetic procedure, nor spectral characteristics of this complex were presented and the structural data were not deposited with the CCDC. In this work, the aqua complexes $[M_3S_4(H_2O)_9]Cl_4$ (M = Mo, W) obtained using known procedures were used as the starting compounds. The reactions of these complexes with 2,2'-bipyridine or 1,10-phenanthroline afford poorly soluble products. The elemental analysis data show that the products of these reactions are mixtures of bis- and tris-substituted polypyridyl complexes. The singly charged bidentate dithiophosphate anion (Dtp, $(EtO)_2PS_2$) was introduced into the reaction to increase the solubility. This anion forms stable and suitable for crystallization complexes with the M_3Q_4 core [22, 23]. The reaction of phosphorus sulfide P_4S_{10} with ethanol was used as a source of Dtp in situ. The reaction affords $(EtO)_2PS_2H$ (HDtp)

$$P_4S_{10} + 8EtOH = 4(EtO)_2PS_2H + 2H_2S.$$

The scheme of the synthesis of compound $I \cdot CHCl_3$ can be presented as follows:



A solution of the starting aqua complex $[Mo_3S_4(H_2O)_9]Cl_4$ in hydrochloric acid was evaporated to dryness on a rotary evaporator, and the solid product was dissolved in ethanol. Solutions of Me_2Bipy and $(EtO)_2PS_2H$ (in a ratio of 1 : 2) were added to the obtained solution. After the reaction mixture was stirred at room temperature and evaporated to dryness, the solid product was deposited on a column with silica gel. Chloroform, acetone–chloroform mixtures (in ratios of 1 : 3, 1 : 2, and 1 : 1), and acetone were used as eluents. After chromatographic separation, the obtained fractions were evaporated to dryness, dissolved in chloroform, and crystallized by the addition of concentrated acetic acid and slow evaporation. The first fraction gave crystals of the complex with three coordinated dithiophosphate ligands $[Mo_3S_4(Dtp)_3(CH_3CO_2)(H_2O)]$, which was identified by elemental analysis data. The crystals of complex $I \cdot CHCl_3$ were isolated from the second fraction in a low yield (15%). All subsequent fractions included, most

Table 1. Main crystallographic characteristics and X-ray diffraction experimental details for compound **I** · $CHCl_3$

Parameter	Value
Empirical formula	$C_{23}H_{36}N_2O_6P_2S_8Cl_4Mo_3$
FW	1184.58
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	10.5900(2)
b, Å	14.0125(2)
c, Å	14.9798(4)
α, deg	89.0610(10)
β, deg	69.5820(10)
γ, deg	86.4070(10)
V, $Å^3$	2079.10(7)
Z	2
ρ_{calcd}, g/cm^3	31.12.91
μ, mm^{-1}	1.665
F(000)	1176.0
Crystal size, mm	0.2 × 0.2 × 0.15
Scan θ range, deg	4.90–63.40
Reflection index ranges	$-14 \le h \le 14$, $-20 \le k \le 13$, $-21 \le l \le 20$
Measured reflections	27129
Independent reflections (R_{int})	11385 (0.0251)
Number of refined parameters	440
T_{max}/T_{min}	0.612/0.746
Goodness-of-fit for F^2	1.030
R factors for $F > 4\sigma(F)$	$R_1 = 0.0332$, $wR_2 = 0.0828$
R factors for all reflections	$R_1 = 0.0444$, $wR_2 = 0.0893$
Residual electron density (max/min), e/Å^3	1.100/–1.340

likely, complexes with a large amount of Me_2Bipy; however, the products were not identified.

The IR spectrum of complex **I** contains characteristic absorption bands of the coordinated Me_2Bipy and Dtp ligands. The very intense bands at 1009 and 961 cm^{-1} correspond to the bending vibrations δ(POC), and the bands at 817 and 789 cm^{-1} correspond to the stretching vibrations ν(P–S) of the dithiophosphate ligand. The characteristic bands of the ν(C–H) stretching vibrations of the Me_2Bipy ligand lie at 2977–2860 cm^{-1}. The bands at 1616 and 1430 cm^{-1} correspond to the stretching vibrations of the pyridine rings (ν(C=C), ν(C=N), and ν(C–C)).

Two signals at 109.4 and 108.6 ppm corresponding to two nonequivalent phosphorus atoms of the Dtp ligand are detected in the ^{13}P NMR spectrum ($CDCl_3$).

The structure of **I** · $CHCl_3$ is shown in Fig. 1. The main geometric parameters of the complex are given in Table 2. The $\{Mo_3S_4\}^{4+}$ cluster core is based on a distorted triangle of Mo_3 in which the average Mo–Mo distance is 2.748 Å. The Mo–Mo distance in the fragment with the coordinated acetate ion is 2.689 Å, and two other Mo–Mo distances are 2.773 and 2.783 Å.

The shortening of one of the metal–metal bonds due to the "contraction" effect of the bidentate-coordinated carboxylate ligand is a general regularity in compounds $[M_3Q_4(Dtp)_3(\mu\text{-}RCOO)(L)]$ [3, 21, 24]. For example, in complex $[Mo_3S_4(Dtp)_3(S\text{-}Lac)(Py)]$ [25] (S-Lac is anion of the S-isomer of lactic acid), the shortened Mo–Mo distance is 2.690 Å and other bond lengths range from 2.74 to 2.75 Å. It should be mentioned that in compounds of the $[Mo_3S_4(Dtp)_3(\mu\text{-}Dtp)(L)]$ type with the bridging dithiophosphate ligand all metal–metal bonds are equivalent and the average Mo–Mo distance is 2.73–2.77 Å [21, 26].

Each molybdenum atom in the $[Mo_3S_4(Dtp)_2(\mu\text{-}AcO)Cl(Me_2Bipy)]$ molecule has a distorted octahe-

Table 2. Average bond lengths (Å) in the structure of compound **I** · $CHCl_3$

Bond	*d*, Å*	*d*, Å**
Mo–Mo***	2.7484(3)	2.762
Mo–μ_3-S	2.3426(7)	2.359
Mo–μ_2-S	2.2986(8)	2.307
Mo–S_{Dtp}	2.5438(8)	2.580
Mo–O_{OAc}	2.196(2)	2.244
Mo–Cl	2.5078(8)	2.471
Mo–N_{Me_2Bipy}	2.2700(2)	2.310

* The values of experimental bond lengths obtained from the X-ray diffraction data.

** The optimized distances.

*** The distance between the Mo atoms bonded by the acetate bridge is shortened being 2.6891(3) Å (calculated 2.696 Å). The average distance between other molybdenum atoms is 2.7780(3) Å (calculated 2.794 Å).

dral structure (ignoring the metal–metal bonds). Each of two molybdenum atoms is coordinated by three sulfur atoms of the bridging sulfide ligands, two sulfur atoms of the dithiophosphate ligand, and the oxygen atom of the acetate bridge. The coordination environment of the third molybdenum atom consists of three sulfur atoms of the sulfide ligands, two nitrogen atoms of bipyridine, and the chloride ligand. The values of the Mo–(μ_3-S), Mo–(μ_2-S), and Mo–S_{Dtp} bond lengths in the cluster are typical of this class of compounds. The average Mo–N distance is 2.27 Å. A similar distance in the $[Mo_3S_4Cl_4(Py)_5]$, $[Mo_3S_4Cl_3(Py)_6]I$, and $[Mo_3S_4(Dtp)_3(\mu\text{-}RCO_2)(Py)]$ pyridine complexes varies from 2.28 to 2.39 Å [22, 23, 27–29].

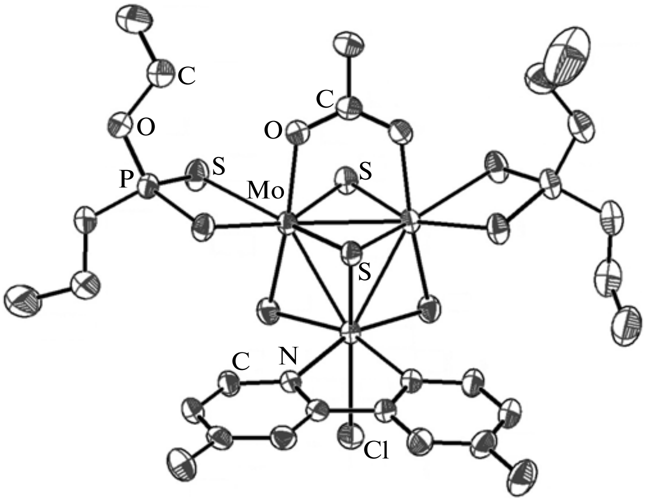


Fig. 1. Structure of cluster $[Mo_3S_4(Dtp)_2(\mu\text{-}AcO)Cl(Me_2Bipy)]$ (**I**) (atomic shift ellipsoids of 50% probability).

The optimized values of structural parameters for compound **I** are given in Table 2. The calculated interatomic distances are consistent with the experimental crystallographic data.

The scheme of the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) and the shape of the frontier orbitals are presented in Fig. 2. As can be seen from Fig. 2 and Table 3, the main contribution to the HOMO is from 4*d* atomic orbitals of molybdenum (56.5%) and 2*p* atomic orbitals of sulfur (18.5%) and chlorine (14.8%). This is qualitatively consistent with the classical scheme of bonding in the $\{M_3Q_4\}^{4+}$ clusters. In this scheme, the HOMO is the 1*e* orbital in the symmetry group C_{3v} responsible for the metal–metal bonding [30]. Thus, the metal–metal bond is retained upon the introduction of the bipyridine ligand. On the contrary, the LUMO predominantly consists of the 2*p* atomic orbitals of carbon and nitrogen (83.4%) of the bipyridine ligand forming the π* orbital of the ligand. This difference in the nature of the HOMO and LUMO is not characteristic of the M_3Q_4 complexes, because the role of the LUMO is usually performed by the weakly bonding (with respect to the metal–metal bond) metal-centered orbital ($2a_1$ for the C_{3v} symmetry). The change in the electronic structure is explained by the low-lying antibonding π orbitals of dimethylbipyridine and, therefore, it can be considered as a non-innocent ligand.

The unusual electrochemical behavior of compound **I** is a result of specific features of its electronic structure. The cyclovoltammetric data obtained for a solution of **I** in dichloromethane show the absence of

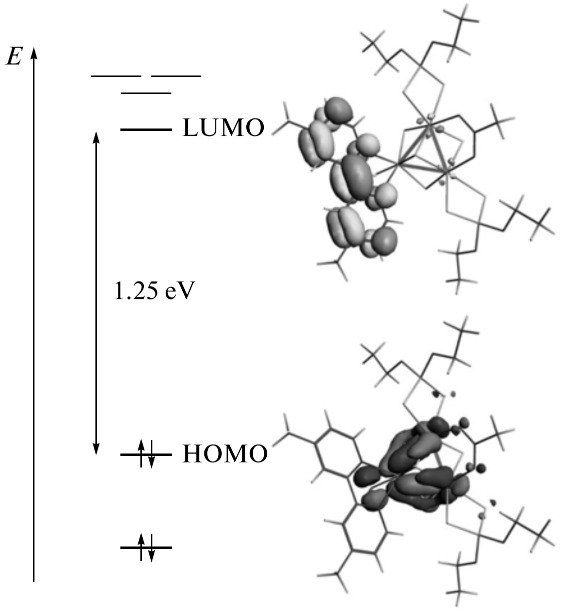


Fig. 2. Scheme of molecular orbitals and the shape of frontier orbitals of the LUMO and HOMO for **I**.

Table 3. Calculated composition of the HOMO and LUMO (%) for **I**

Frontier orbitals	Mo	S	Cl	Me_2Bipy
HOMO	56.5	18.5	14.8	
LUMO		1.3		83.4

any electrochemical processes in the negative potential region down to –2.5 V, which is not typical of this class of compounds. It is known that the M_3Q_4 complexes with diphosphines undergo the consecutive reduction in the range from – 0.4 to –1.6 V centered on the metal and formally described as $M_3^{IV} \rightleftarrows M_2^{III}M^{IV} \rightleftarrows M_3^{III}$ [7] according to the above scheme of the electronic structure. The oxalate complexes $[Mo_3(CuX)Q_4(C_2O_4)_3]^{2-}$ undergo reduction at lower potentials from –0.33 to –0.35 V, which is also related to the reduction of Mo^{IV} to Mo^{III} [31]. No reduction processes of Mo^{IV} for **I** can be explained by the ligand-centered character of the LUMO, since an additional electron should get on this orbital upon the reduction of the complex. Under these conditions, the reduction of the bipyridine ligand should proceed at higher negative potentials.

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