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Cluster Complexes $[Mo_3O_2S_2(Acac)_3(Amine)_3]PF_6$[1]

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Abstract—New mixed-ligand cluster complexes $[Mo_3O_2S_2(Acac)_3(Amine)_3]PF_6$ (Amine = morpholine (Mor), 4-cyanopyridine (PyCN), pyrazine (Pz)) have been synthesized. The compounds were characterized by IR spectroscopy and mass spectrometry (ESI-MS). The crystal structure of the Mor complex, which was isolated as $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_2(\mu_2\text{-}S)(Acac)_3(Mor)_3]PF_6 \cdot 0.5Mor \cdot 0.3(CH_3)_2CO$ was determined. The stability of the complexes in methanolic solutions decreases in a row: Mor > PyCN > Pz.

Keywords: molybdenum, oxo-sulfide clusters, morpholine, 4-cyanopyridine, pyrazine

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INTRODUCTION

Mixed oxo-sulfide clusters of molybdenum and tungsten $\{M_3O_xS_{4-x}\}^{4+}$ remained little studied for a long time due to the lack of convenient methods for their selective synthesis and separation [1–3]. Recently we developed new approaches to the synthesis of such clusters [4, 5], in particular of the clusters with the $\{Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}O)_2\}^{4+}$ cluster core. In our earlier work mixed-ligand complexes $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}O)_2(Acac)_3(Py)_3]PF_6$ and $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}O)_2(Acac)_3(DMSO)_3]PF_6$ (DMSO = $(CH_3)_2SO$) were prepared starting from the aqua complex $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}O)_2(H_2O)_9]^{4+}$ [4, 6]. In this paper we report synthesis and characterization of the new heteroligand complexes of the type $[Mo_3O_2S_2(Acac)_3(Amine)_3]PF_6$ (where Amine is morpholine (Mor), 4-cyanopyridine (PyCN), and pyrazine (Pz)).

EXPERIMENTAL

Starting solutions of $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}O)_2(H_2O)_9]^{4+}$ in hydrochloric acid were prepared as previously reported [4]. Molar concentrations of the solutions were determined spectrophotometrically from the reported values of molar extinction [3]. All other reagents and solvents were commercially available and of analytical grade. The silica gel was of 40/100 porosity grade.

IR spectra were recorded on a spectrometer Scimitar FTS 2000. The electronic absorption spectra (UV–Vis) were recorded on a Helios γ (Thermo Scientific). Electro-spray mass spectra were recorder on a Quattro LC (quadrupole—hexapole—quadrupole) mass spectrometer with an orthogonal Z-spray electrospray interface (Micromass, Manchester, UK). Nitrogen was used as both as drying gas and working gas at a flow rate of 400 and 80 L/h, respectively. Sample solutions were injected via a syringe pump at a rate of 6 μL/min. Capillary voltage was set at 3.5 kV and the voltage in the cell varied from –10 to –60 V. The chemical composition of each peak in the scan mode was assigned by comparison of the experimental isotopic distribution pattern with calculated values using the MassLynx 3.5 program (MassLynx 3.2; Micromass: Manchester, UK, 1998).

Synthesis of $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_2(\mu_2\text{-}S)(Acac)_3(Mor)_3]PF_6$ (I) and $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_2(\mu_2\text{-}S)(Acac)_3(Mor)_3]PF_6 \cdot 0.5Mor \cdot 0.3(CH_3)_2CO$ (Ia). To a solution of 5.0 mL $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}O)_2(H_2O)_9]^{4+}$ in 4 M HCl (0.15 mmol) 0.1 mL of acetylacetone was added with stirring. Solid $KHCO_3$ was added to the solution until the termination of CO_2 evolution (just to achieve neutral pH, respectively, because the alkaline hydrolysis induces rapid cluster fragmentation), then 0.08 mL of morpholine and 0.015 g (0.09 mmol) NH_4PF_6 were quickly added. Almost immediately a dark oil was formed and the solution was stirred an hour. The oil was extracted with 10 mL CH_2Cl_2 ($CHCl_3$ can also be used), the extract was dried over $CaCl_2$ and the volume was reduced in vacuo to 0.5 mL. and this solution was purified by the column chromatography on silica gel. Chloroform and its mixture with CH_3OH (1 : 1 and 1 : 2 v/v) were used as an eluents. A pale yellow front was eluted with pure $CHCl_3$, proved to be a mixture of unreacted morpholine and acetylacetone. The main dark brown band was moving along column very slowly in pure $CHCl_3$,

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[1] The article was translated by the authors.

so the polarity of the eluent had to be increased by the addition of CH_3OH. The resulting solution was collected and evaporated in vacuo. The product was extracted with 3 mL of chloroform. Small black crystals of the complex **I** formed by layering excess of toluene on the chloroform solution in a narrow tube. Yield 78%. Extraction of a crude product with acetone followed by vapor diffusion of diethyl either resulted in single crystals of acetone solvate **Ia**, suitable for X-ray analysis.

ESI–MS(+)(CH_2Cl_2): $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}O)_2(Acac)_3(Mor)_3]^+$ (*m/z* 942 and signals corresponding to the sequential loss of morpholine ligands.

IR (KBr, ν, cm^{-1}): 2960 w., 2922 w., 1570 v.s., 1532 v.s., 1423 m., 1366 s., 1284 m., 1030 m., 843 v.s., 671 m., 559 s.

Synthesis of $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}O)_2(Acac)_3(PyCN)_3]PF_6$ (II). To a solution of 5.0 mL $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}O)_2(H_2O)_9]^{4+}$ in 4 M HCl (0.15 mmol) 0.1 mL of acetylacetone was added under stirring. Solid $KHCO_3$ was then added portionwise until the termination of CO_2 evolution, followed by quick addition of 0.1 g (0.1 mmol) of PyCN and 0.015 g (0.09 mmol) NH_4PF_6. Almost immediately a dark oil appeared, and the solution was left stirring for an hour. The oil was extracted with 10 mL CH_2Cl_2, and the extract was dried over $CaCl_2$. Toluene was layered on the extract in a narrow tube to produce a brown precipitate of **II**. Yield 82%.

ESI–MS(+) (CH_3OH): $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}O)_2(Acac)_3(PyCN)_3]^+$ (*m/z* = 993) and signals corresponding to the sequential loss of 4-cyanopyridine ligands.

IR (KBr, ν, cm^{-1}): 2964 w., 2852 w., 2237 w., 1686 m., 1574 v.s., 1527 v.s., 1416 s., 1362 s., 1261 s., 1024 s., 800 v.s., 667 m., 561 s.

Synthesis of $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}O)_2(Acac)_3(Pz)_3]PF_6$ (III). To a solution of 5.0 mL $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}O)_2(H_2O)_9]^{4+}$ in 4 M HCl (0.15 mmol) 0.1 mL of acetylacetone was added under stirring. Solid $KHCO_3$ was added to the solution until the termination of carbon dioxide evolution followed by quick addition of 0.08 g of Pz and 0.015 g (0.09 mmol) NH_4PF_6. Almost immediately a dark oil appeared, and the solution was left stirring for an hour. The oil was extracted into 10 mL of CH_2Cl_2, and the extract was dried over anhydrous $CaCl_2$. The resulting solution was rota-evaporated to a minimum volume and absorbed on a silica gel column. Excess of pyrazine and acetylacetone was eluted with chloroform. The main dark brown band was eluted with $CHCl_3/CH_3OH$ (1 : 1 v/v) mixture. The resulting solution was evaporated to dryness and the residue was extracted with 3 mL of $CHCl_3$. Layering of toluene yielded small black crystals of **III** in few days. Yield 67%.

ESI–MS(+) (CH_2Cl_2): $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}O)_2(Acac)_3(Pz)_3]^+$ (*m/z* = 921) and signals corresponding to the sequential loss of pyrazine ligands.

IR (KBr, ν, cm^{-1}): 2962 w., 2922 m., 2070 m., 2017 m., 1734 w., 1574 v.s., 1529 v.s., 1418 s., 1366 s., 1284 m., 1261 m., 1028 m., 845 v.s., 669 w., 559 s.

X-ray analysis. All measurements were performed according to standard procedures on an automated diffractometer Super Nova (Agilent Technologies), equipped with a CCD detector, at 123.0(2) K using a Cu*K* radiation (λ = 1.54178 Å) from Super Nova X-ray Source. The reflections intensities were measured by ω-scanining of 1° frames up to 2θ = 135°. Absorption correction was done empirically using SCALE3 ABSPACK (CrysAlisPro software package) [7]. The structure was solved by direct methods and refined by full-matrix anisotropic approximation for non-hydrogen atoms with SHELXTL program set [8]. The hydrogen atoms of the organic ligands were refined in their geometrically calculated positions. Cluster core $\{Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_2(\mu_2\text{-}S)\}$ in **Ia** features a positional disorder. Clarification of the occupancies of μ_2-positions occupied by O and S atoms with equal coordinates and atomic displacement parameters leads to values of 1/0, 0.67/0.33 and 0.33/0.67, respectively. The occupancies for the bridging O and S atoms were fixed in calculated values, and refined with equal coordinates and atomic displacement parameters. The solvate molecules of morpholine and the PF_6^- anions were disordered over three and two positions, respectively, with the relative weights of 0.2/0.3 and 0.5/0.5. The crystallographic data, refinement details and CSD depository number for the structure **Ia** are given in Table 1, the main bond lengths—in Table 2, the characteristics of hydrogen bonds—Table 3.

RESULTS AND DISCUSSION

The problem of selective synthesis of trinuclear oxo-sulfide cluster complexes of molybdenum and tungsten $\{M_3O_xS_{4-x}\}^{4+}$ appeared from the pioneering works by A.G. Sykes and T. Shibahara on sulfide clusters [1–3]. Original method of preparation consisted in reduction of the binuclear sulfide-bridged complexes in aqueous solution, followed by tedious separation of products mixtures containing all possible species $\{M_3O_xS_{4-x}\}^{4+}$ (x = 0–4). The main disadvantages of these method were low selectivity prom the point of view of individual forms with specific values of x, and difficulty of separating mixtures, because for complete separation of the aqua complexes chromatographic columns of over one meter height had to be used. Recently we proposed to use reactions of easily accessible binuclear oxide-sulfide $\{M_2O_2(\mu\text{-}S)_2\}^{2+}$ complexes with metal carbonyls ($Mo(CO)_6$, $W(CO)_6$, $Cr(CO)_6$, $Re(CO)_5Cl$) as reducing agents. In these reactions two possible ways of cluster core transformations have been identified: (a) simple reduction to a homometallic trinuclear cluster without incorporation of the metal from carbonyl, or, (b) by formation of heterometallic derivatives by [2 + 1] cluster assembly, involving incorporation of the heterometal form carbonyl. These reactions allow the synthesis of $\{Mo_3O_2S_2\}^{4+}$, $\{W_3O_2S_2\}^{4+}$, $\{Mo_3O_3S\}^{4+}$, $\{W_2MoO_2S_2\}^{4+}$ clusters as aqua complexes in high yield [4]. From the point of view of possible applications [9, 10] complexes of these cluster cores with different organic ligands are of interest, in particular those where three coordination sites at each metal are occupied by a bidentate ligand, leaving one coordination position free for coordination of labile unidentate ligands [11, 12]. Ligands coordination and exchange can be conveniently studied in $[M_3Q_4(L\text{-}L)_3L'_3]$ (M = Mo, W; Q = S, Se; L-L = bidentate ligand, L' = a monodentate ligand) complexes, in particular with L-L = acetylacetone and L' = various N-donor amines. Such complexes have been for chalcogenide clusters $\{M_3Q_4\}^{4+}$ (M = Mo, W; Q = S, Se) and for some of the $\{M_3O_xS_{4-x}\}^{4+}$ mixed oxide/sulfide bridged clusters. Only complexes with pyridine as L' = amine have been reported. The synthesis is quite simple, and the product yields are close to quantitative [13]:

$$[M_3Q_4(H_2O)_9]^{4+} + 3Acac^- + 3Py$$
$$= [M_3Q_4(Acac)_3(Py)_3]^+ + 9H_2O.$$

The acetylacetonate ligands are always coordinated by the *cis-cis* type (relatively μ_3-Q), and the pyridine molecules occupy *trans* positions. Use of a ditopic ligand, such as pyrazine, could allow preparation of more complicated aggregates by uniting together several cluster cores, as was shown, e.g., by preparation of $[\{Mo_3S_4(\eta_2\text{-}Dtp)_3(\mu\text{-}AcO)\}_2(\mu\text{-}Pz)]$ (Dtp is $(EtO)_2PS_2$), in which the pirazine molecule connects two cluster units [14]. In this paper, we used the aqua complex $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}O)_2(H_2O)_9]^{4+}$ [4] in order to prepare of several heteroligand complexes with other heterocyclic amines, namely, 4-cyanopyridine (PyCN), pyrazine (Pz) and morpholine (Mor) and to study the stability of resulting $[Mo_3O_2S_2(Acac)_3(Amine)_3]^+$ complexes in organic solvents.

IR spectra $[Mo_3O_2S_2(Acac)_3(Amine)_3]PF_6$ (**I**) shows the vibration bands routinely observed in the regions 1570–1574, 1527–1532, 1362–1366 and 1261–1284 cm^{-1} for coordinated acetylacetonate (ν(C=C), ν(C=O), δ(CH)). The ρ(CH) vibrational bands of acetylacetone methyl groups are observed at 1024–1030 cm^{-1}. The two very strong bands at 840–845 and 559–561 cm^{-1} are due to the presence of PF_6^-. The bands in the region of 1416–1420 cm^{-1} come from the ν(C–N) vibrations of coordinated *N*-heterocyclic ligands. In the region 2960–2964,

Table 1. Crystallographic characteristics and X-ray experiment details for **Ia**

Parameter	Value
Formula	$C_{29.60}H_{54.30}F_6N_{3.50}O_{11.80}PS_2Mo_3$
Molecular weight	1144.98
Crystal system	Tetragonal
Space group	$P4_12_12$
a, Å	16.20840(10)
c, Å	34.1584(3)
V, Å^3	8973.83(11)
Z	8
ρ_{calcd}, g/cm^3	1.695
μ, mm^{-1}	8.692
F(000)	4622
Crystal shape, dimensions, mm	0.088 × 0.049 × 0.040
θ Range, deg	3.02–73.75
h, k, l range	$-19 \le h \le 19$, $-16 \le k \le 19$, $-42 \le l \le 41$
No. of measured reflections	39033
No. of independent reflections (R_{int})	8674 (0.0409)
No. of observed reflections, $I \ge 2\sigma(I)$	7606
Refinement method	594
GOOF	1.009
R_1 ($I > 2\sigma(I)$)	0.0352
wR_2, all reflections	0.0896
$\Delta\rho_{min}/\Delta\rho_{max}$, e/Å^3	–0.530/1.292

Table 2. Main distances in a crystal structure of **Ia**

Bond	*d*, Å	Bond	*d*, Å
Mo(1)–Mo(2)	2.7143(6)	O(21)–C(22)	1.291(6)
Mo(1)–Mo(3)	2.6049(6)	O(22)–C(24)	1.267(6)
Mo(2)–Mo(3)	2.6767(6)	O(31)–C(32)	1.262(8)
Mo(2)–S(1)	2.3446(14)	O(32)–C(34)	1.272(7)
Mo(2)–S(2)/O(2c)	2.3239(16)	O(1*A*)–C(112)	1.428(8)
Mo(2)–S(3)/O(3c)	2.293(2)	O(1*A*)–C(113)	1.428(7)
Mo(3)–S(1)	2.3661(14)	O(2*A*)–C(212)	1.408(7)
Mo(3)–S(3)/O(3c)	2.267(2)	O(2*A*)–C(213)	1.421(9)
Mo(1)–S(1)	2.3591(15)	O(3*A*)–C(312)	1.435(7)
Mo(1)–S(2)/O(2c)	2.3101(16)	O(3*A*)–C(313)	1.429(7)
Mo(1)–O(11)	2.134(4)	C(11)–C(12)	1.487(8)
Mo(1)–O(12)	2.074(3)	C(12)–C(13)	1.384(8)
Mo(1)–N(1)	2.279(4)	C(13)–C(14)	1.370(8)
Mo(1)–O(1)	1.918(4)	C(14)–C(15)	1.496(8)
Mo(2)–N(2)	2.299(4)	C(21)–C(22)	1.475(8)
Mo(2)–O(21)	2.098(4)	C(22)–C(23)	1.392(7)
Mo(2)–O(22)	2.123(3)	C(23)–C(24)	1.396(8)
Mo(3)–N(3)	2.302(4)	C(24)–C(25)	1.516(7)
Mo(3)–O(1)	1.923(4)	C(31)–C(32)	1.495(9)
Mo(3)–O(31)	2.103(4)	C(32)–C(33)	1.405(8)
Mo(3)–O(32)	2.111(3)	C(33)–C(34)	1.392(8)
N(1)–C(111)	1.498(6)	C(34)–C(35)	1.489(8)
N(1)–C(114)	1.489(7)	C(111)–C(112)	1.516(8)
N(2)–C(211)	1.470(7)	C(113)–C(114)	1.513(9)
N(2)–C(214)	1.487(7)	C(211)–C(212)	1.521(8)
N(3)–C(311)	1.482(7)	C(213)–C(214)	1.491(9)
N(3)–C(314)	1.475(6)	C(311)–C(312)	1.517(8)
O(11)–C(12)	1.275(6)	C(313)–C(314)	1.497(9)
O(12)–C(14)	1.304(6)		

~2920 and 2851–2854 cm^{-1}, there are medium intensity bands from ν(C–H) vibrations of the organic ligands.

The IR spectrum of $[Mo_3O_2S_2(Acac)_3(PyCN)_3]PF_6$ (**II**) has a weak ν(C≡N) vibration band at 2237 cm^{-1}, a ν(C=N) ring vibration band at 1686 cm^{-1}, and a medium intensity vibration band at ~561 cm^{-1}, which can be attributed to a superposition of PF_6 and δ_{sh}(C≡N) deformation vibrations bands. The IR spectrum of $[Mo_3O_2S_2(Acac)_3(Pz)_3]PF_6$ (**III**) exhibits two strong vibration bands at 2012 and 2070 cm^{-1}, corresponding to the vibrations of the aromatic ring.

Mass spectrometry data for **I–III** reveal some differences in their behavior in solution. Characteristic peaks corresponding to the $[Mo_3O_2S_2(Acac)_3(Amine)_3]^+$ cations in the case of morpholine (**I**) and 4-cyanopyridine (**II**), respectively, were observed using of freshly prepared starting aqua complex $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}O)_2(H_2O)_9]^{4+}$ in the synthesis. A mass spectrum of complex **I** is shown in Fig. 1. In the case of pyrazine complex (**III**) dissolved in methanol, substitution of pyrazine by methanol (Fig. 2) was found. Variation of the ionization potential has shown that the substitution is not caused by the mass spectrometry experimental conditions. Thus $[Mo_3O_2S_2(Acac)_3(Pz)_3]^+$ is unstable in methanol to substitution of pyrazine ligands in the coordination sphere of molybdenum. However, mass spectrometry data show perfect stability of **III** in CH_2Cl_2, because methylene chloride can not compete with pyrazine for coordination sites. Reducing the basicity in a row Mor (pK_a 8.70) > Py (pK_a 5.23) > PyCN (pK_a 1.90) > Pz (pK_a 0.65) explains lesser stability of the pyrazine complex [15]. It should be noted that the final product of the ionization under a mass spectrometry conditions is $[Mo_3O_2S_2(Acac)_3]^+$ in all cases (including Py), wherein all of the molybdenum atoms either have one vacant coordination site, or hydrogen atoms of CH_3-groups in acetylacetonate ligands are involved in an agostic interaction.

Decomposition of starting aqua complex $[Mo_3O_2S_2(H_2O)_9]^{4+}$ over a long period leads to the appearance of $[Mo_3O_3S(H_2O)_9]^{4+}$ and

Table 3. Hydrogen bonds characteristics in a crystal structure of **Ia**

Type of the hydrogen bond, D–H	Distances, Å			Angle DHA, deg	Symmetry codes
	D–H	H···A	D···A		
N(1)–H(1*A*)...O(2*A*)	0.930	2.049	2.977(6)	175.05	*x* + 1/2, –*y* + 3/2, –*z* + 3/4
N(2)–H(2*A*)...O(3*A*)	0.930	2.222	3.141(5)	169.36	–*y* + 1, –*x* + 1, –*z* + 1/2
N(3)–H(3*A*)...S(2)	0.930	2.855	3.758(5)	164.03	*x* + 1/2, –*y* + 3/2, –*z* + 3/4

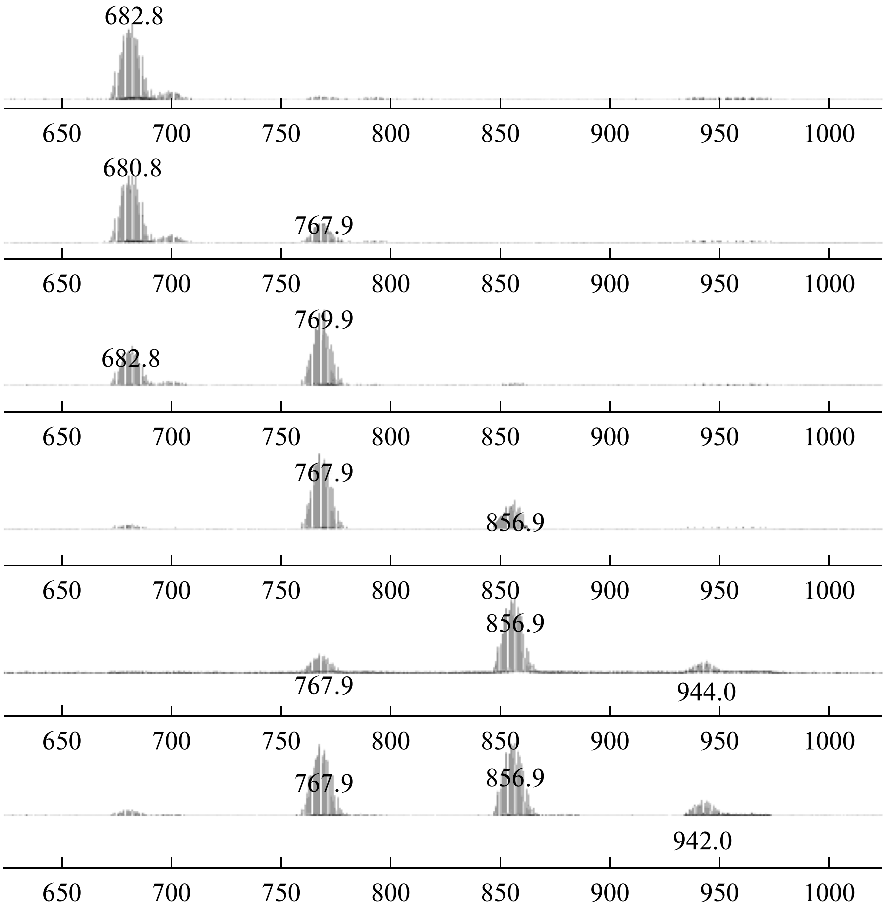

Fig. 1. ESI–MS spectra of **I** in methanol: $[Mo_3O_2S_2(Acac)_3Mor)_3]^+$ (*m/z* 943), $[Mo_3O_2S_2(Acac)_3(Mor)_2]^+$ (*m/z* 856), $[Mo_3O_2S_2(Acac)_3(Mor)]^+$ (*m/z* 768), $[Mo_3O_2S_2(Acac)_3]^+$ (*m/z* 681). Cone voltage increases from down to up.

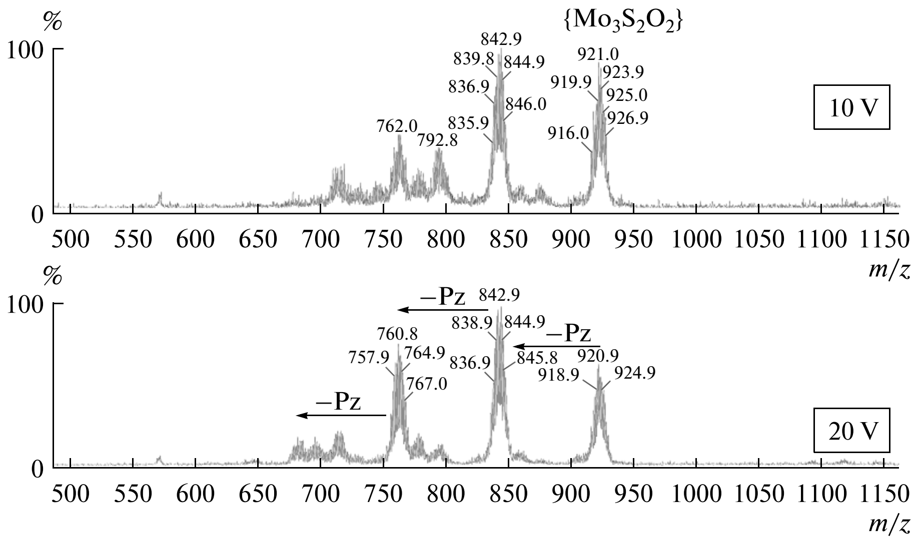

Fig. 2. ESI–MS spectra of **III** in methanol: $[Mo_3O_2S_2(Acac)_3(Pz)_3]^+$ (*m/z* 921), $[Mo_3O_2S_2(Acac)_3(Pz)_2]^+$ (*m/z* 842), $[Mo_3O_2S_2(Acac)_3(Pz)]^+$ (*m/z* 761), $[Mo_3O_2S_2(Acac)_3]^+$ (*m/z* 681); $[Mo_3O_2S_2(Acac)_3(Pz)(CH_3OH)]^+$ (*m/z* 793), $[Mo_3O_2S_2(Acac)_3(CH_3OH)_2]^+$ (*m/z* 745).

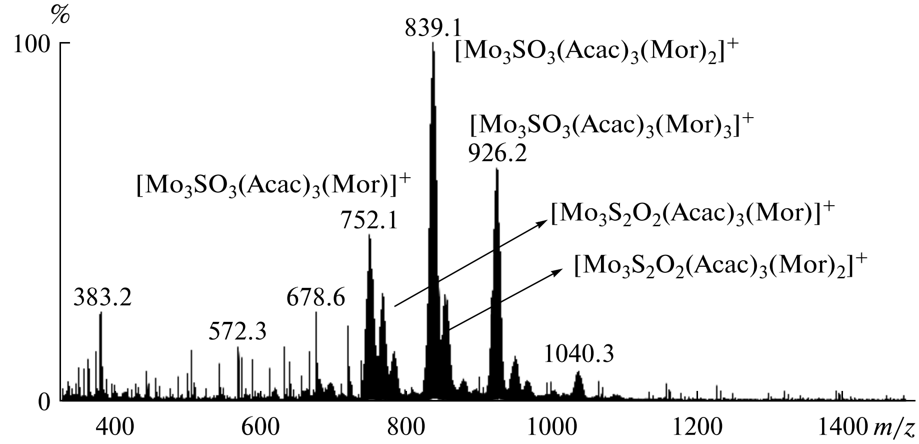

Fig. 3. ESI–MS spectra of the $[Mo_3O_{2+x}S_{2-x}(Acac)_3(Mor)_3]PF_6$ ($x = 0, 1$) mixture in methanol prepared as **I** from the mixture of initial aquacomplexes formed during keeping of $[Mo_3O_2S_2(H_2O)_9]^{4+}$ solution for a long time in air.

$[Mo_3OS_3(H_2O)_9]^{4+}$ clusters as the result of redistribution of oxide and sulfide ligands in the cluster core. This fact was confirmed by mass spectrometric experiments (Figs. 3, 4) demonstrating appearance of corresponding peaks from the complexes containing the cluster cores $\{Mo_3O_3S\}^{4+}$ and $\{Mo_3OS_3\}^{4+}$, which are less or more sulfidized analogues of the **I–III**, respectively. The mechanism of this process remains obscure.

Crystallization of $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_2(\mu_2\text{-}S)(Acac)_3(Mor)_3]PF_6$ from acetone extracts yielded small black crystals of $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_2(\mu_2\text{-}S)(Acac)_3(Mor)_3]PF_6 \cdot 0.5Mor \cdot 0.3(CH_3)_2CO$ (**Ia**). The structure of the cluster cation is typical for this type of complexes (Fig. 5), and the bond lengths in the cluster core are shown in Table. 2. Similar to the pyridine complexes [4, 5, 13, 16], coordination of morpholine molecules occurs via the nitrogen atom in *trans*-position relative to the apical μ_3-S ligand. In the crystal structure of **Ia** cluster complex occupies general positions, but in spite of this, the cluster core $\{Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}O)_2\}^{4+}$ is a positionally disordered, being in two out of three possible orientations around an imaginary third order axis, passing through the center of a molybdenum triangle and through a

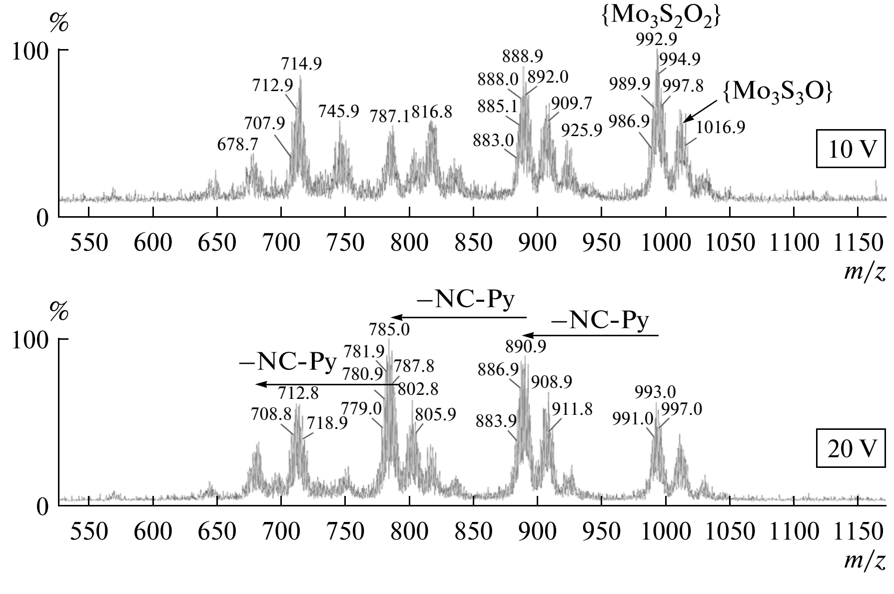

Fig. 4. ESI–MS spectra of methanolic solution of **II**: $[Mo_3O_2S_2(Acac)_3(PyCN)_3]^+$ (*m/z* 993), $[Mo_3O_2S_2(Acac)_3(PyCN)_2]^+$ (*m/z* 890), $[Mo_3O_2S_2(Acac)_3(PyCN)]^+$ (*m/z* 785), $[Mo_3O_2S_2(Acac)_3]^+$ (*m/z* 681).

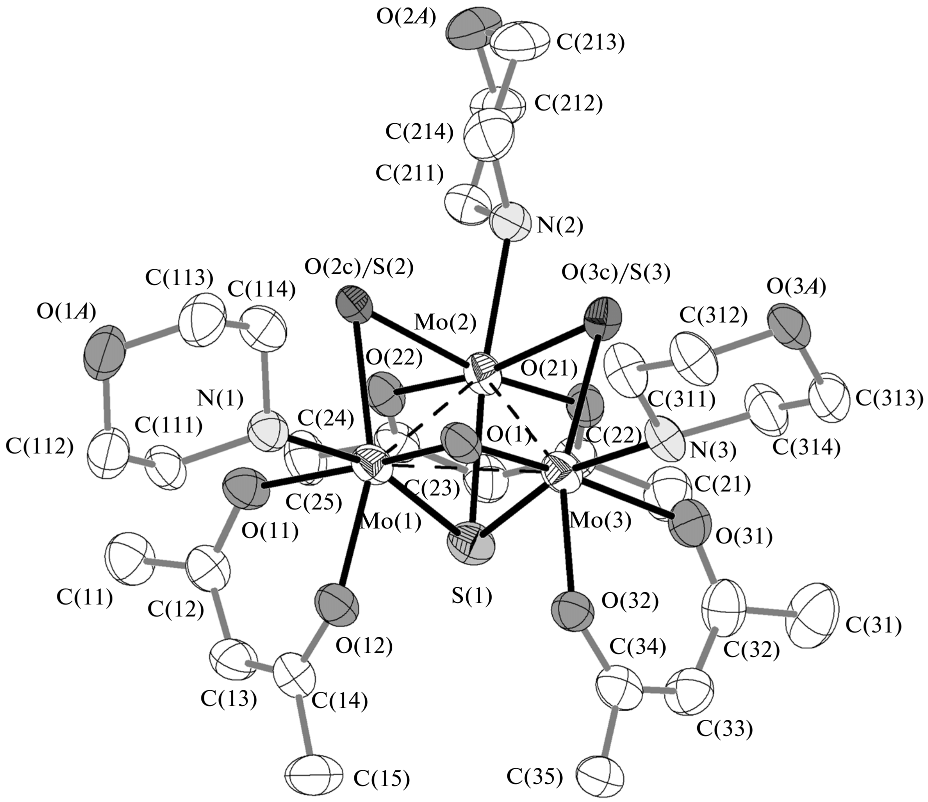

Fig. 5. Structure of $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}O)_2(Acac)_3(Mor)_3]^+$ in **Ia** (thermal ellipsoids are shown in 50% probability). Hydrogen atoms are not shown for clarity.

μ_3-S atom. It leads to the variations in the occupancies in the μ_2-position of the cluster core, the occupancies being O/S: 1/0, 0.67/0.33, and 0.33/0.67. This fact, coupled with our inability to separate positions of sulfur and oxygen during the refining of structure, resulted in averaging of bond lengths involving these atoms (Table 2). The distances (Mo–μ_2Q, Mo–μ_3Q and Mo–Mo) calculated as described above fall within the ranges of the bond lengths for the clusters of this family: $(Mo\text{–}\mu_2S)_{av}$ 2.257(8)–2.305(2), $(Mo\text{–}\mu_3S)_{av}$ 2.320(10)–2.367(5) Å; $(Mo\text{–}Mo(O))_{av}$ 2.5916(15)–2.635(3), $(Mo\text{–}Mo(S))_{av}$ 2.693(1)–2.734(1) Å (in brackets given are the average values of the errors, calculated for an individual cluster core) [4, 16]. In the $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(Acac)_3(Py)_3]^+$ the following geometrical parameters have been found: $(Mo\text{–}\mu_2O)_{av}$ 1.930(5), $(Mo\text{–}\mu_3S)_{av}$ 2.364(2) Å; $(Mo\text{–}MO(O))_{av}$ = 2.5939(8) [5], and for $[Mo_3(\mu_3\text{-}Se)(\mu_2\text{-}O)_3(Acac)_3(Py)_3]^+$ the values are following: $(Mo\text{–}\mu_2O)_{av}$ 1.912(3), $(Mo\text{–}\mu_3Se)_{av}$ 2.4995(6), $(Mo\text{–}Mo(O))_{av}$ 2.6063(5) Å [15].

Coordinated morpholine molecules form the hydrogen bonds N(H)···O, thus involving cluster complexes $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}O)_2(Acac)_3(Mor)_3]^+$ in the intermolecular interaction (Table 3). Each complex offers all three ligand molecules to the hydrogen bonding. Two of them form one hydrogen bond, respectively using either –NH group, or –O– groups, and the remaining morpholine molecule is involved in formation of two hydrogen bonds with both –O– and –NH groups (Fig. 6). Disordered solvate morpholine and acetone molecules, as well as PF_6^- anions are surrounded by acetylacetonate as closest neighbors and do not participate in hydrogen bonding.

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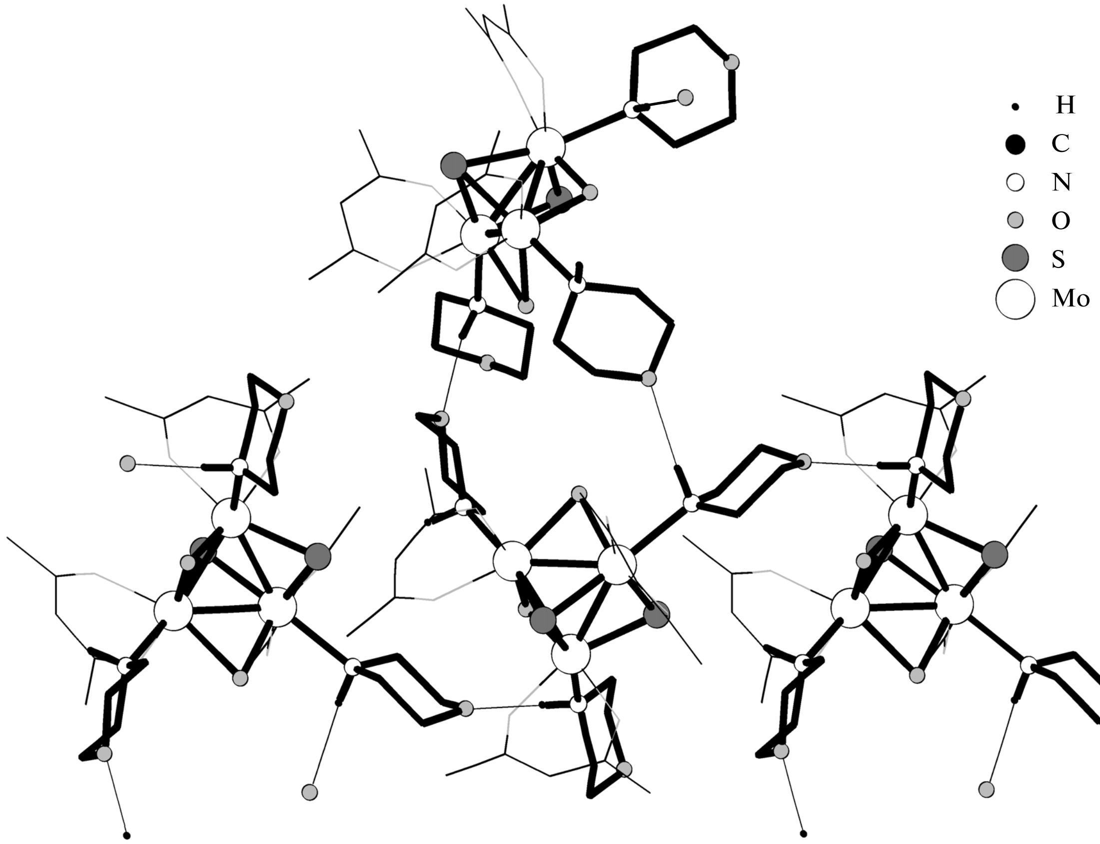

Fig. 6. Hydrogen bonding in the crystal structure of **Ia** including coordinated morpholine molecules, which involve $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}O)_2(Acac)_3(Mor)_3]^+$ complexes into intermolecular interactions. Hydrogen atoms without participation in hydrogen bonding formation are not shown for clarity.

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