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Cubane Pyridine–Acetylacetonate Cluster Complexes with the $M_3CuS_4^{5+}$ Core (M = Mo, W)

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Abstract—The reactions between $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(Acac)_3(Py)_3]PF_6$ (HAcac is acetylacetone, Py is pyridine) and CuX (X = Cl, I, SCN) afford heterometallic cubane clusters $[Mo_3(CuX)(\mu_3\text{-}S)_4(Acac)_3(Py)_3]PF_6$. The structures of two new compounds, $[Mo_3(CuCl)S_4(Acac)_3(Py)_3]PF_6 \cdot 3.25CH_2Cl_2 \cdot 0.5C_6H_5CH_3$ and $[Mo_3(CuI)S_4(Acac)_3(Py)_3]PF_6 \cdot 4C_6H_6$, are determined by X-ray diffraction analysis. All synthesized compounds are characterized by elemental analysis and IR spectra. According to the vibrational spectra, the thiocyanate complex in the solid state is a mixture of the bond isomers $[Mo_3(CuNCS)S_4(Acac)_3(Py)_3]PF_6$ and $[Mo_3(CuSCN)S_4(Acac)_3(Py)_3]PF_6$, whereas in solution this complex exists as a isothiocyanate form.

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INTRODUCTION

Interest in clusters with the $M_3M'Q_4^{n+}$ cubane core (M = Mo, W; Q = Se, S; M' = Ru, Os, Ir, Ni, Pd, Pt, and others) is due to the high reactivity of the heterometal in the cluster and wide possibilities of the modification of the properties by the variation of the main cluster-forming metal (Mo, W), bridging chalcogen atoms, and the ligands coordinated to Mo or W [1]. The copper-containing clusters can exist in two oxidation states: both the diamagnetic $M_3CuQ_4^{5+}$ and paramagnetic $Mo_3CuQ_4^{4+}$ derivatives. According to the quantum-chemical calculations, copper exists in the oxidation state +1 in the clusters of both types [2]. It was recently shown that the $[Mo_3(CuCl)S_4(Dmpe)_3Cl_3]$ cluster (Dmpe is 1,2-bis(dimethylphosphino)ethane) and its analogs are efficient catalysts in the reactions of organic diazo compounds, for instance, for the intramolecular cyclopropanation of 1-diazo-5-hexen-2-one [3]. The nonlinear optical properties of the $[M_3(CuX)Q_4(diphosphine)_3X_3]$ clusters (diphosphine is Dppe, Dmpe; M = Mo, W; Q = S, Se; X = Cl, Br) make them promising optical filters [4, 5]. Other copper-containing clusters of the $M_3CuQ_4^{5+}$ family are also described: in them the molybdenum (tungsten) atoms are coordinated by the dithiophosphate [6, 7], dithiocarbamate [8], dithiophosphinate [9, 10], and cyclopentadienyl ligands [11], triaminocyclohexane derivatives [12], ammonia molecules [13], and nitrilotriacetate [14]. The aqua complexes, which are stable only in strongly acetic media, are also known [15–17]. We recently described the oxalate complexes [18]. The reactivity of the above-mentioned compounds is almost unstudied. In particular, it can be expected that the copper-containing clusters can catalyze the reactions of alkynes [19].

In the present work, we report the synthesis of a series of new acetylacetonate complexes $[Mo_3(CuX)S_4(Acac)_3(Py)_3]^+$ (Q = S, X = Cl, I, NCS).

EXPERIMENTAL

The syntheses were carried out in air. The solvents were purified by standard procedures. The other substances were of reactive purity and used without additional purification. The $[M_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(Acac)_3(Py)_3]PF_6$ complexes (M = Mo, W) were synthesized by a described procedure [20], and CuCl was prepared according to [21].

Analyses for C, H, N, and S were carried out at the Laboratory of Microanalysis of the Novosibirsk Institute of Organic Chemistry (Siberian Division, Russian Academy of Sciences). IR spectra in a region of 4000–375 cm^{-1} were recorded on a Scimitar FTS 2000 instrument with a resolution of 1 cm^{-1} (KBr pellets and solutions in CH_3CN and CH_2Cl_2, KBr cells 0.13 mm thick).

Triacetylacetonatopyridinetetrasulfidomonochlorocopper trimolybdenum hexafluorophosphate $[Mo_3(CuCl)S_4(Acac)_3(Py)_3]PF_6 \cdot 3.25CH_2Cl_2 \cdot 0.5C_6H_5CH_3$ (I). Copper chloride (CuCl, 34 mg, 34 mmol) was added to a solution of $[Mo_3S_4(Acac)_3(Py)_3]PF_6$

Table 1. Crystallographic data and parameters of X-ray diffraction experiment for compounds **I** and **II**

Parameter	Value	
	I	**II**
Empirical formula	$C_{36.75}H_{46.50}Cl_{7.50}CuF_6Mo_3N_3O_6PS_4$	$C_{54}H_{60}CuF_6IMo_3N_3O_6PS_4$
Temperature, K	100.0(2)	100.0(2)
M	1516.71	1598.52
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	*Pbcm*
a, Å	24.0839(8)	12.0045(3)
b, Å	10.2220(4)	27.4318(9)
c, Å	24.8725(8)	18.6049(5)
β, deg	112.8350(10)	90
V, Å^3	5643.3(3)	6126.7(3)
Z	4	4
ρ(calcd), g/cm^{-3}	1.785	1.733
μ, mm^{-1}	1.617	1.676
$2\theta_{max}$, deg	55	55
Crystal sizes, mm	0.29 × 0.13 × 0.01	0.64 × 0.37 × 0.02
2θ range, deg	1.70–27.50	1.78–27.50
Number of measured/independent/observed ($I > 2\sigma(I)$) reflections	40314/12949/9945 (R_{int} = 0.0333)	28158/7075/4998 (R_{int} = 0.0524)
Number of refined parameters	651	369
R_1 ($I > 2\sigma(I)$)	0.0462	0.0438
wR_2 (for all reflections)	0.1386	0.1108
Goodness-of-fit	1.022	1.084
Residual electron densit (max/min), *e* Å^{-3}	3.136/–1.782	1.103/–0.686

(370 mg, 34 mmol) in CH_2Cl_2 (10 ml). The solution turned brown and was filtered into a thin tube, and toluene was carefully deposited. After three days, brown crystals of complex **I** were formed. The yield was 400 mg (99%).

IR, cm^{-1}: 3404 s, 1565 s, 1528 s, 1442 m, 1359 m, 1283 m, 1222 w, 1068 w, 1026 m, 844 s, 760 m, 697 m, 670 w, 559 m, 479 m, 439 m.

Found (%): C 29.31; H 2.99; N 3.05.

For $C_{30}H_{36}ClCuF_6Mo_3N_3O_6PS_4$ (after the loss of crystallization molecules CH_2Cl_2 and $C_6H_5CH_3$)

anal. calcd. (%): C 30.16; H 3.04; N 3.52.

Triacetylacetonatotripyridinetetraselenidomonoiodocopper trimolybdenum hexafluorophosphate $[Mo_3(CuI)S_4(Acac)_3(Py)_3]PF_6 \cdot 4C_6H_6$ (II). Copper iodide (CuI, 17 mg) was added to a solution of $[Mo_3S_4(Acac)_3(Py)_3]PF_6$ (100 mg, 91 μmol) in CH_2Cl_2 (10 ml). The solution gradually turned brown. The solution was evaporated to dryness, the residue was dissolved in CH_3CN, and benzene was deposited. After three days, needle-like brown crystals of compound **II** were formed. The yield was 115 mg (99%).

IR, cm^{-1}: 3430 s, 1565 s, 1528 s, 1443 m, 1358 m, 1284 m, 1223 w, 1069 w, 1026 w, 844 s, 696 w, 559 m, 440 m.

Found (%): C 27.04; H 3.37; N 3.12.

For $C_{30}H_{36}CuF_6IMo_3N_3O_6PS_4$ (after the loss of crystallization molecules of benzene)

anal. calcd. (%): C 28.02; H 2.82; N 3.27.

Triacetylacetonatotripyridinetetrasulfidomonothiocyanatocopper trimolybdenum hexafluorophosphate $[Mo_3(CuSCN)S_4(Acac)_3(Py)_3]PF_6$ (III). Cop-

per thiocyanate (CuSCN, 11 mg, 99 μmol) was added to a solution of $[Mo_3S_4(Acac)_3(Py)_3]PF_6$ (100 mg, 91 μmol) in CH_2Cl_2 (10 ml). The solution turned brown and filtered, and benzene was deposited. The yield was 105 mg (95%).

IR (KBr), cm^{-1}: 3464 w, 2923 w, 2155 s, 2081 m, 1565 s, 1529 s, 1444 m, 1424 m, 1360 m, 1283 m, 1223 m, 1069 m, 1027 m, 936 m, 843 s, 759 m, 697 m, 670 w, 558 m, 483 w, 438 m.

IR (CH_3CN), cm^{-1}: 3632 m, 3546 m, 2088 m, 1633 m, 1582 m, 1533 w, 1284 w, 1223 w, 938 w, 848 vs, 700 w, 669 w, 559 w, 482 w, 438 w.

Found (%): C 31.48; H 3.54; N 3.97; S 12.78.
For $C_{31}H_{36}CuF_6Mo_3N_4O_6PS_5$
anal. calcd. (%): C 30.59; H 2.98; N 4.60; S 13.17.

Triacetylacetonatotripyridinetetrasulfidomonothiocyanatocopper tritungsten hexafluorophosphate $[W_3(CuSCN)S_4(Acac)_3(Py)_3]PF_6$ (IV). Copper thiocyanate (CuSCN, 2 mg, 18 μmol) was added to a solution (20 ml) of $[W_3S_4(Acac)_3(Py)_3]PF_6$ (25 mg, 18 μmol) in CH_2Cl_2 (10 ml). The solution gradually turned brown and filtered, and benzene was deposited. The yield was 26 mg (96%).

IR, cm^{-1}: 3649 w, 3443 w, 3114 w, 2923 w, 2153 m, 2075 m, 1669 w, 1565 s, 1532 s, 1443 m, 1362 s, 1288 m, 1222 w, 1068 w, 1029 m, 941 w, 842 s, 760 w, 696 m, 672 w, 557 m, 444 m.

Found (%): C 25.98; H 2.68; N 3.03.
For $C_{31}H_{36}CuF_6N_4O_6PS_5W_3$
anal. calcd. (%): C 25.14; H 2.45; N 3.78.

X-Ray diffraction analyses for compounds I and II. Diffraction data were obtained on a Bruker X8APEX four-circle automated diffractometer [22] (CCD two-coordinate detector at 100 K for PF_6^- disordering decoupling, MoK_α radiation, λ = 0.71073 Å, graphite monochromator). The crystallographic data and experimental parameters are presented in Table 1. An absorption correction was applied semiempirically on the basis of the equivalent reflection intensities using the SADABS program [22]. Structures **I** and **II** were determined by a direct method and refined by the full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms (SHELXTL) [23]. Hydrogen atoms were specified in the geometrically calculated positions. In structure **I**, the toluene molecule is disordered over two equally probable positions. The hydrogen atoms of the disordered molecule were not localized. The multiplicities of site occupancies of the atoms of one of the disordered CH_2Cl_2 molecules were equalized, refined with the thermal parameter values held stationary, and then fixed in an obtained value of 0.25. Selected bond lengths are given in Table 2. The atomic coordinates

Table 2. Selected bond lengths and bond angles in structures **I** and **II***

Bond	*d*, Å	Bond	*d*, Å
I		**II***	
Mo(1)–Mo(2)	2.7683(6)	Mo(1)–Mo(2)	2.7749(7)
Mo(1)–Mo(3)	2.7668(6)	Mo(1)–Mo(2)^i	2.7749(7)
Mo(2)–Mo(3)	2.7756(6)	Mo(2)–Mo(2)^i	2.7652(8)
Mo(1)–S(1)	2.3433(12)	Mo(1)–S(1)	2.3369(13)
Mo(1)–S(3)	2.3383(12)	Mo(1)–S(1)^i	2.3369(13)
Mo(1)–S(4)	2.3385(12)	Mo(1)–S(3)	2.3437(19)
Mo(2)–S(1)	2.3515(12)	Mo(2)–S(1)	2.3354(13)
Mo(2)–S(2)	2.3363(12)	Mo(2)–S(2)	2.3412(14)
Mo(2)–S(4)	2.3365(12)	Mo(2)^i–S(2)	2.3412(14)
Mo(3)–S(1)	2.3424(12)	Mo(2)–S(3)	2.3435(14)
Mo(3)–S(2)	2.3366(12)	Mo(2)^i–S(3)	2.3435(14)
Mo(3)–S(3)	2.3430(12)		
Mo(2)–Cu(1)	2.8303(7)	Mo(1)–Cu(1)	2.8507(10)
Mo(1)–Cu(1)	2.8424(7)	Mo(2)–Cu(1)	2.8476(8)
Mo(3)–Cu(1)	2.8237(7)	Mo(2)^i–Cu(1)	2.8476(8)
Mo(1)–O(11)	2.096(3)	Mo(1)–O(3)	2.087(3)
Mo(1)–O(12)	2.087(3)	Mo(2)–O(1)	2.082(3)
Mo(2)–O(21)	2.101(3)	Mo(2)–O(2)	2.094(3)
Mo(2)–O(22)	2.076(3)	Mo(1)–O(3)^i	2.087(3)
Mo(3)–O(31)	2.080(3)		
Mo(3)–O(32)	2.105(3)		
Mo(1)–N(1)	2.270(4)	Mo(1)–N(1)	2.252(6)
Mo(2)–N(2)	2.277(4)	Mo(2)–N(2)	2.277(4)
Mo(3)–N(3)	2.271(4)		
Cu(1)–S(2)	2.2939(13)	Cu(1)–S(1)	2.2825(13)
Cu(1)–S(3)	2.2782(13)	Cu(1)–S(1)^i	2.2825(13)
Cu(1)–S(4)	2.3172(13)	Cu(1)–S(2)	2.287(2)
Cu(1)–Cl(1)	2.1785(13)	Cu(1)–I(1)	2.4716(9)
Angle	ω, deg	Angle	ω, deg
I		**II**	
S(4)Cu(1)Cl(1)	113.24(5)	S(1)Cu(1)I(1)	113.55(4)
S(3)Cu(1)Cl(1)	115.91(5)	S(2)Cu(1)I(1)	117.93(6)
S(2)Cu(1)Cl(1)	115.02(5)	S(1)^{i}Cu(1)I(1)	113.55(4)
S(4)Cu(1)S(3)	103.20(5)	S(1)^{i}Cu(1)S(1)	103.37(7)
S(2)Cu(1)S(3)	104.33(5)	S(1)Cu(1)S(2)	103.40(5)
S(2)Cu(1)S(4)	103.67(5)	S(1)^{i}Cu(1)S(2)	103.40(5)

* Symmetry procedures for the multiplication of atoms: ^{i} x, y, $-z + 1/2$.

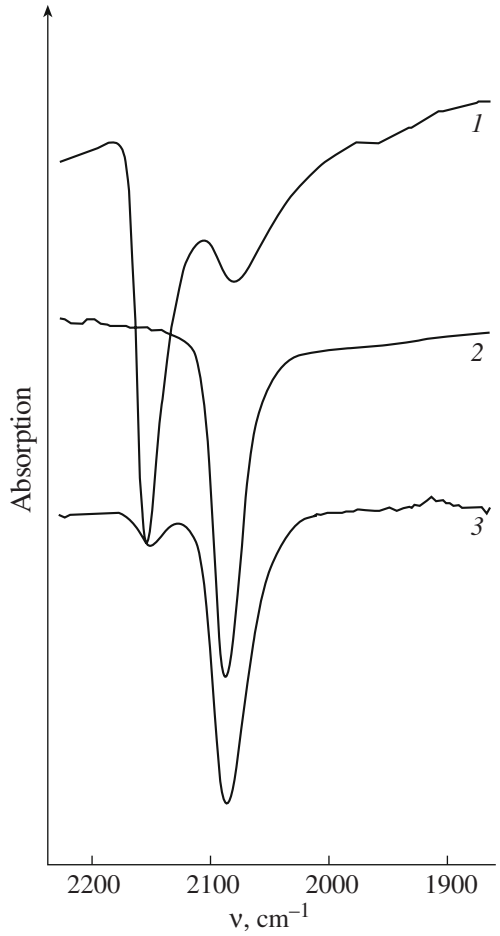

Fig. 1. IR spectra of complex **III** in the region of ν(CN) vibrations: (*1*) solid sample and its solutions in (*2*) CH_3CN and (*3*) CH_2Cl_2.

and other parameters for structures **I** and **II** were deposited with the Cambridge Structural Database (nos. 710207 (**I**) and 710208 (**II**); www.ccdc.cam.ac.uk/deposit).

Tests of catalytic activity. The reactions were carried out under argon in a toluene–triethylamine mixture (triethylamine was used to absorbed evolved HCl) at temperatures from 20 to 70°C. According to the GLC data, no formation of the expected reaction product (1,3-diphenylpropinone) was observed within 2 h after equivalent amounts of benzoyl chloride and phenylacetylene were added to the reaction mixture containing the cluster (0.01 mol), whereas the reaction ceased within 1 h under the same conditions but with CuCl.

RESULTS AND DISCUSSION

The copper-containing clusters were synthesized by the reactions of the triangular acetylacetonate molybdenum complexes with univalent copper salts. The reactions occur rapidly with an quantitative yield at room

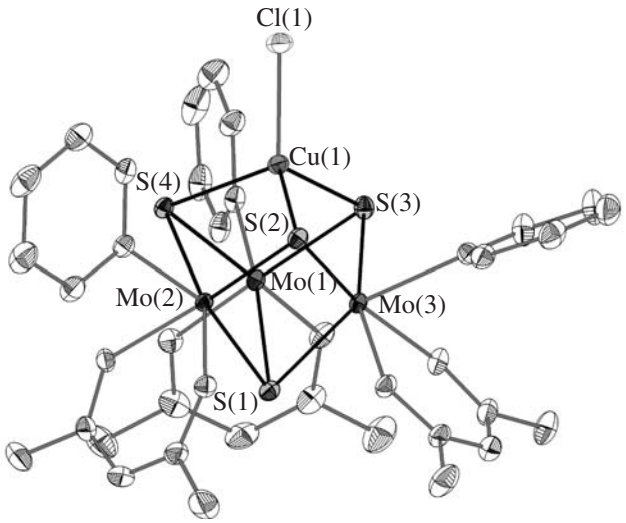

Fig. 2. Structure of the $[Mo_3(CuCl)(\mu_3\text{-}S)_4(Acac)_3(Py)_3]^+$ cluster complex in compound **I** (50% probability ellipsoids, the Mo–Mo and Mo–Cu bonds and hydrogen atoms are omitted).

temperature in acetonitrile or methylene chloride solutions

$$[Mo_3S_4(Acac)_3(Py)_3]PF_6 + CuX \longrightarrow [Mo_3(CuX)S_4(Acac)_3(Py)_3]PF_6. \quad (X = Cl, I, SCN)$$

Note that CuCN does not react. The $[W_3(CuNCS)S_4(Acac)_3(Py)_3]PF_6$ complex was obtained similarly.

The vibrational spectra of all the obtained compounds show the typical pattern characteristic of the bidentate-coordinated acetylacetonate ligands [24]. The most intense absorption bands corresponding to the ν(C=O) + ν(C=C) vibrations appear at 1565 and 1527–1532 cm^{-1}. The vibrations of the PF_6^- anion characterize the intense absorption bands at 840–848 and 557–559 cm^{-1}.

An unusual feature of the IR spectra of the solid samples of complexes **III** and **IV** is the presence of two absorption bands in the region of ν(CN) vibrations of the thiocyanate ligand: 2155 and 2081 cm^{-1} for molybdenum cluster **III** and 2152 and 2075 cm^{-1} for tungsten cluster **IV**. According to literature data, these vibrations appear for the N-coordinated thiocyanate ligand at ~2050 cm^{-1}, whereas those for the S-coordinated isomer lie higher than 2100 cm^{-1} [25, 26]. The IR spectral data for solid samples **III** and **IV** indicate the simultaneous presence of the both bond isomers $[M_3(CuNCS)S_4(Acac)_3(Py)_3]PF_6$ and $[M_3(CuSCN)S_4(Acac)_3(Py)_3]PF_6$. According to literature data, the vibrations of the CS group of the thiocyanate ligand should be observed at 860–780 cm^{-1} for the N-coordinated isomer and at 720–690 cm^{-1} for the S-coordinated isomer. However, the absorption bands

Table 3. Geometry of the $Mo_3CuS_4^{5+}$ cubane fragment in the structures with the Cu–X bond (X = Cl, Br, I) (value range, Å)

Compound	Mo–Mo	Mo–Cu	Mo–S	Cu–S	Cu–X	Literature
$[Mo_3(CuCl)(Acac)_3(Py)_3]PF_6 \cdot 3.25CH_2Cl_2 \cdot 0.5PhCH_3$ (**I**)	2.7668–2.7756	2.8237–2.8424	2.336–2.351	2.2782–2.3172	2.178	This work
$(NH_4)_2[Mo_3(CuCl)S_4(HNta)_3] \cdot 3H_2O$	2.778	2.838	2.323–2.343	2.300	2.279	[14]
$[Mo_3(CuCl)S_4(Cp^*)_3](p\text{-Tos})$	2.809–2.827	2.836–2.866	2.312–2.334	2.329–2.348	2.179	[11]
$[Mo_3(CuCl)S_4(Dmpe)_3Cl_3](CuCl_2)$	2.804	2.843	2.311–2.368	2.313	2.179	[3]
$[Mo_3(CuCl)S_4(Dmpe)_3Cl_3]PF_6$	2.782–2.784	2.820–2.825	2.317–2.372	2.303–2.306	2.180	[4]
$[Mo_3(CuI)S_4(Acac)_3(Py)_3]PF_6 \cdot 4C_6H_6$ (**II**)	2.7652–2.7749	2.8476–2.8507	2.3354–2.3437	2.2825–2.287	2.4716	This work
$K_2[Mo_3(CuI)S_4(C_2O_4)_3(H_2O)_3] \cdot 6H_2O$	2.741–2.764	2.817–2.841	2.320–2.343	2.302–2.319	2.449	[18]
$[Mo_3(CuI)S_4(Dtp)_3(\mu_2\text{-}CH_3COO)(DMF)]$	2.679–2.770	2.806–2.885	2.303–2.352	2.277–2.306	2.454	[29]
$[Mo_3(CuI)S_4(Dtp)_3(\mu_2\text{-}CF_3COO)(MeCN)]$	2.701–2.761	2.792–2.875	2.289–2.365	2.268–2.303	2.440	[30]
$[Mo_3(CuI)S_4(Dtp)_3(\mu_2\text{-}CH_3COO)(DMSO)]$	2.680–2.776	2.814–2.882	2.309–2.340	2.270–2.295	2.463	[31]
$[Mo_3(CuI)S_4(Dtp)_3(\mu_2\text{-}CH_3COO)(H_2O)]$	2.692–2.770	2.801–2.898	2.307–2.342	2.274–2.309	2.476	[31]
$[Mo_3(CuI)S_4(Dtp)_3(\mu_2\text{-PhCOO})(Py)]$	2.689–2.783	2.825–2.883	2.318–2.339	2.262–2.290	2.448	[31]
$[Mo_3(CuI)S_4(Dtc)_4(Py)] \cdot MeCOOEt$	2.727–2.783	2.83–2.862	2.323–2.354	2.293–2.316	2.484	[8]

corresponding to vibrations of the organic part of the complex appear in the same region, which impedes the assignment of the ν(CS) bands. It is interesting that the IR spectrum of a solution of compound **III** in CH_3CN contains only one absorption band at 2088 cm^{-1} (Fig. 1). This indicates the absence of an isomer with coordination through the sulfur atom in the solution. Similarly, a solution of compound **III** in CH_2Cl_2 exhibits predominantly the N-coordinated isomer (the band at 2150 cm^{-1} is low-intensity).

Thus, the synthesized complexes with CuNCS supplement the series of the known compounds for which the above-mentioned isomerism was found: (*trans*-$Pd(AsPh_3)_2(NCS)_2$], [$Pd(Bipy)(NCS)_2$], [$CpMo(CO)_3(NCS)$], $K_3[Co(CN)_5(NCS)]$, and *trans*-[$Co(DMG)_2(Py)(NCS)$] [24]. At the same time, in $K_2[Mo_3(CuSCN)(\mu_3\text{-}S)_4(H_2O)_3(C_2O_4)_3] \cdot 7H_2O$ the thiocyanate group is coordinated through the sulfur atoms according to the IR spectra [18], whereas in $[W_2(CuNCS)_2S_4(NCS)_6]^{4-}$ this ligand is coordinated to the copper atom through the nitrogen atom [27].

The structure of the $[Mo_3(CuCl)S_4(Acac)_3(Py)_3]^+$ cluster complex in compound **I** is shown in Fig. 2. The iodide complex in cluster **II** has a completely analogous structure. The $Mo_3CuS_4^{5+}$ cluster core is a distorted cube with the bond lengths close for the both compounds: Mo–Mo 2.76–2.78, Mo–S 2.34–2.35, Cu–S 2.28–2.32, and Mo–Cu 2.82–2.85 Å (Table 2). The coordination numbers of the Mo and Cu atoms (ignoring the metal–metal bonds in both compounds) are six and four, respectively. Their coordination polyhedra are an insignificantly distorted octahedron and a distorted tetrahedron, respectively, in which the SCuS angles are compressed and the XCuS are increased compared to the angle ideal for tetrahedron (Table 2).

The geometric parameters of the $Mo_3CuS_4^{5+}$ cluster fragment in complexes **I** and **II** agree, as a whole, with those for eleven structurally characterized complexes (Table 3). It is of interest that in compound **I** and four other structurally studied compounds with X = Cl the corresponding bond lengths in the cluster fragment and the Cu–Cl distance are similar within the root-mean-square deviations, except for the Mo–Mo bond lengths. In compound **I**, the Mo–Mo bonds are noticeably shorter (Table 3). In complex **II**, the bond lengths in the cluster fragment are also equal (within the root-mean-square deviations) to those in seven structurally studied compounds with X= I, except for the Cu–S bonds, which change most substantially along with the Cu–I contacts (Table 3). Note that for compound **II** the Mo–Mo

and Mo–S distances are somewhat elongated compared to the average values for the known compounds.

The testing reaction between phenylacetylene and benzoyl chloride was used to determine the catalytic activity of compound **I** [28]. The cluster demonstrated no catalytic activity compared to free CuCl. It is most likely that vacant coordination sites are needed for catalytic activity to appear, and these are absent from the copper atom incorporated into the cluster.

Thus, the new copper-containing heterometallic cubane clusters with the $Mo_3CuS_4^{5+}$ and $W_3CuS_4^{5+}$. cores were synthesized and structurally characterized. A possibility of bond isomerism of the copper atom due to the coordination of the thiocyanate ligand through both the nitrogen atom and sulfur atom was shown for the first time using these compounds as an example.

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