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Apical cyanide ligands substitution in heterometallic clusters $[Re_3Mo_3Q_8(CN)_6]^{n-}$ (Q = S, Se)

Viktoria K. Muravieva, [a, b] Yakov M. Gayfulin,[a] Tatiana I. Lappi,[a, c] Vincent Dorcet,[b] Taisiya S. Sukhikh,[a, c] Pierric Lemoine,[b] Maxim R. Ryzhikov,[a, c] Yuri V. Mironov,[a, c] Stéphane Cordier,[b] Nikolay G. Naumov* [a, c]

Abstract: A number of transition metal cluster compounds can be obtained only in the melt of inorganic cyanides and, therefore, contain terminal cyanide ligands. Substitution of these ligands, which is often necessary to change the physicochemical properties of the clusters, is an urgent problem because of their low reactivity in substitution reactions. In this work, a synthetic approach has been developed for the substitution of CN-ligands in the heterometallic cluster anions $[Re_3Mo_3Q_8(CN)_6]^{n-}$ (Q = S, n = 6; Q = Se, n = 5) by the 4-*tert*-butylpyridine (TBP) molecules. Two new compounds, namely $[Re_3Mo_3S_8(TBP)_6]$ (**1**) and $[Re_3Mo_3Se_8(TBP)_6]$ (**2**), were obtained with high yields and crystallized in solvothermal conditions. It has been shown that the compounds **1** and **2** are based on the paramagnetic cluster cores $\{Re_3Mo_3Q_8\}^0$ containing 23 cluster valence electrons (CVE). Geometry of the new compounds has been investigated using the X-Ray structural analysis. The electronic structure has been analyzed using the DFT calculations showing large distortion of M_6 cluster core.

Introduction

Octahedral rhenium and molybdenum cluster complexes have been intensively studied over the past decades due to their versatility: a number of the useful chemical and physical properties, e.g. adjustable solubility, rich redox chemistry, red to NIR luminescence and radiopacity.[1] Properties of these compounds may be varied in a wide range depending strongly on the nature of apical ligands. Obtaining of the desired set of properties of the cluster compound (e.g. for construction of functional materials) requires the detailed study of the chemical approaches to the modification of the ligand environment. An outstanding feature of the rhenium and molybdenum octahedral clusters is the possibility to be prepared by a high-temperature synthesis, which results in the formation of the compounds with relatively labile halide apical ligands.[2] It was shown that various molecules and ions could substitute halide apical ligands by the use of several synthetic approaches, e.g. removal of the halide in reaction with Ag(I) salts [3] or ligand exchange in the molten organic compounds.[4]

While the homonuclear hexacyano clusters of molybdenum and rhenium are being known since a long time, the heterometallic octahedral chalcogenide cluster complexes based on $\{Re_3Mo_3Q_8\}$ (Q = S, Se) cores have been prepared only recently.[5] The investigation of these clusters is of great interest because the heterometallic substitution within the cluster core is a useful tool for tuning the cluster charge, redox potentials and chemical properties. However, further study of the reactivity of the novel cluster complexes is hampered by the fact that they can be obtained only in the high-temperature melt of inorganic cyanides. Therefore, they contain the strongly coordinated apical cyanide ligands at the preparation stage. Ambidentate nature of the cyanide is widely exploited for the design of cluster-based coordination polymers with a number of transition, post transition and rare earth metal cations.[6] However, cyanide cluster complexes are generally inert toward the ligand exchange reactions. There is a lack of literature examples of the apical cyanide ligand exchange in the chemistry of transition metal clusters despite of numerous examples in the chemistry of mononuclear cyanometallates.[7] In that frame, development of a convenient method for substitution of the apical cyanide ligands is important for further application of the heterometallic structural units in material design.

The present work deals with the cyanide exchange reactions in the mixed-metal rhenium-molybdenum clusters. We have found that substitution of the cyanide ligands for 4-*tert*-butylpyridine (TBP) is possible under solvothermal conditions. During the reaction, two new neutral complexes with general formula $[Re_3Mo_3Q_8(TBP)_6]$ (Q = S, Se) were obtained. The preparation, the geometric and electronic structures of the novel compounds are discussed.

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Results and Discussion

Preparation and Structure. As it was mentioned above, substitution chemistry of coordinated cyanides is quite developed for mononuclear cyanometallates.[7a] At the same time, the cyanide cluster complexes of rhenium and molybdenum are kinetically inert toward the ligand exchange. Our first attempts to replace the terminal cyanides of the $[Re_3Mo_3Q_8(CN)_6]^{n-}$ cluster anions showed that the salts of these anions are insoluble in 4-*tert*-butylpyridine and other pyridine derivatives and hence inert in reactions with them up to 200–220°C. The use of these neat solvents did not lead to the reaction and formation of cluster products containing the pyridine ligands. To make this reaction possible, we examined mixtures of solvents in which the reaction equilibrium shifts to the right due to the increase of solubility of the starting material and formation of insoluble products. In the conditions described in Experimental Section, the crystalline compounds **1** and **2** were obtained using a mixture of TBP, acetonitrile and water at 160°C. It was also found that the reaction of $CaK_4[Re_3Mo_3S_8(CN)_6]\cdot 8H_2O$ and $K_5[Re_3Mo_3Se_8(CN)_6]\cdot 11H_2O$ with TBP proceeds only in high excess of the latter. Note that the starting cluster anion $[Re_3Mo_3S_8(CN)_6]^{6-}$ contains 23 cluster valence electrons (CVE) while the $[Re_3Mo_3Se_8(CN)_6]^{5-}$ anion contains 22 CVE. Nevertheless, products **1** and **2** are both paramagnetic and contain the $\{Re_3Mo_3Q_8\}^0$ cores with 23 CVE. Therefore, the reduction of the $\{Re_3Mo_3Se_8\}^+$ cluster core takes place during the ligand exchange reaction forming the neutral complexes in both cases. EPR spectra of polycrystalline samples of compounds **1** and **2** demonstrate broad signals with g-values of 2.245 and 2.299, respectively (Figure 1); those are substantially higher than the conventional electron spin g-factor. Similar broad signals were observed in numerous rhenium and molybdenum octahedral clusters with g = 2.44–2.56 for $([Re_6Q_8L_6]^{3-}$ (Q = S, Se, Te; L = CN, Cl) [8] and 2.289 for $K_6Mo_6Se_8(CN)_5$.[9]

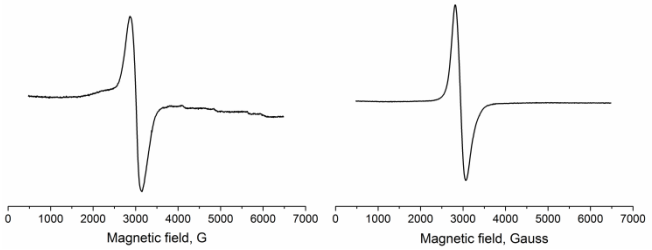


Figure 1 EPR spectra for **1** (left) and **2** (right) measured at 77K.

The compounds **1** and **2** crystallize in the tetragonal space group $P4_2/n$ and the triclinic space group $P\text{-}1$, respectively. The structures represent crystal packings of the cluster units $[Re_3Mo_3S_8(TBP)_6]$ and $[Re_3Mo_3Se_8(TBP)_6]$ (Figure 2). While the metallic core in the fragment $\{Re_3Mo_3S_8\}$ is a nearly perfect octahedron (the M–M distances vary in the range of 2.6078(6) – 2.6157(6) Å), the structure of **2** comprises the slightly distorted octahedrons M_6 of two crystallographically non-equivalent cluster complexes. This distortion is caused by the notable difference in lengths of eight bonds between the apical and the basal metal atoms and four bonds between the basal metal atoms only. The M-M bond lengths vary from 2.6316(6) to 2.6561(7) Å. Note that the two possible isomers of the mixed-metal octahedron may be presented, namely a *fac*-isomer with C_{3v} symmetry and a *mer*-isomer with C_{2v} symmetry. One can notice that the symmetry of the isomers of the $\{Re_3Mo_3\}$ metallocluster is different than the point group symmetry of the crystals of **1** and **2**. To fit the lattice symmetry, the isomers must be disordered between possible orientations. Apparently, the average structures do not allow us to analyze the real Re–Re, Re–Mo, Mo–Mo bond lengths in the crystal structures and to compare them with the DFT calculations.

The average M–M distances of 2.612 Å in **1** and 2.640 Å in **2** lie between the respective values reported for the 23 CVE $\{Re_6Q_8\}^{3+}$ core in $(Ph_4P)_2(H)[Re_6Se_8(CN)_6]\cdot 8H_2O$ and $(Ph_4P)_3[Re_6S_8(CN)_6]$ [10] and $\{Mo_6Q_8\}$ cores in $La_{0.94}Mo_6Se_8$ [11] and $HoMo_6S_8$.[12] The same tendency can be found for the corresponding M–Q distances. Each M_6 octahedron is coordinated with eight Q ligands and six TBP ligands via the nitrogen atoms of the pyridine rings. The average M–N distances are slightly longer than the typical Re–N distances found in the octahedral rhenium clusters with the terminal TBP or pyridine ligands.[4h, 13] They are close to the Mo–N distances found in the compounds $[Mo_6S_8(py)_6]$ and $[Mo_6S_8(TBP)_6]$.[14] Presence of the voluminous *tert*-butyl group in the aromatic rings prevents the formation of π-π stacking between the terminal ligands of the nearby clusters. However, the structure **1** present the close packing of the cluster units without any solvent-accessible voids. On the contrary, the structure **2** contains the large cavities filled by the electron density originating from disordered solvate CH_3CN molecules. This difference of structure packings may be caused by the different volumes of S- and Se- containing cluster units. According to the electron count found by the SQUEEZE procedure, the structure **2** contains about 8 extra CH_3CN molecules. Solvate molecules in **2** can be easily removed during the experimental procedures, and the elemental analysis did not show the presence of CH_3CN molecules in the dried sample of compound **2**.

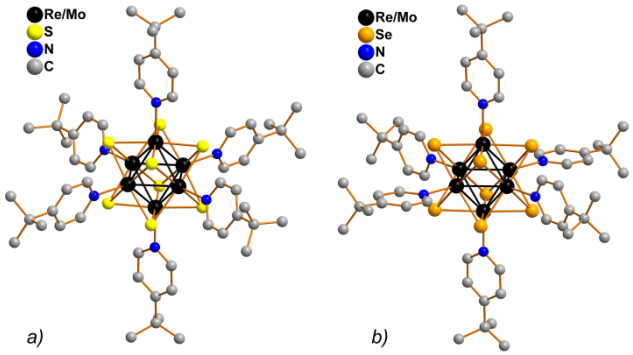


Figure 2. Ball-and-stick representation of the cluster complexes $[Re_3Mo_3S_8(TBP)_6]$ (*a*) and $[Re_3Mo_3Se_8(TBP)_6]$ (*b*) in the structures of compounds **1** and **2**, respectively. Hydrogen atoms are not shown. Disordered *tert*-butyl groups are shown in one orientation for clarity.

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The compound **1** is insoluble in common solvents, while the compound **2** dissolves in CH_2Cl_2 forming the dark-brown solution. Cyclic voltammetry showed that the compound **2** has a quasi-reversible one-electron oxidation process (ΔE = 0.16 V) with $E_{1/2}$ = 0.027 V *vs* Ag/AgCl electrode. This process corresponds to the formation of the $[Re_3Mo_3Se_8(TBP)_6]^+$ cluster with 22 CVE. The reduction of the compound **2** was detected as the irreversible process with E_{pc} at about -1.26 V vs Ag/AgCl electrode. The irreversibility indicates, most probably, a decomposition of the cluster during its reduction. Our attempts to carry out the chemical oxidation or reduction of the $[Re_3Mo_3Se_8(TBP)_6]$ cluster led to the irreversible chemical transformations giving the unidentified products.

DFT calculations.

Molecular orbital (MO) diagrams for the *fac*- and *mer*- isomers of the $[Re_3Mo_3Q_8(py)_6]$ (Q = S, Se) clusters calculated with C_1 symmetry are similar in the near frontier orbital region (Figure 3). In the region from -6.0 eV to -4.4 eV the MOs are primarily localized on atomic orbitals (AO) of the $\{M_6Q_8\}$ core atoms with minor contribution from AO of the terminal ligands. HOMO and HOMO-1 have similar energies with 0.2 eV splitting and separated from HOMO-2 by ~0.8 eV gap. LUMO separated from HOMO and HOMO-1 by ~1.1 eV. Thus in all $[Re_3Mo_3Q_8(py)_6]$ clusters the MOs are characterized by the bi-gap structure. LUMO and orbitals up to ~-1.2 eV are primarily localized on AO of the py ligand atoms with minor contribution from the AO of the metal atoms. HOMO, HOMO-1 and HOMO-2 are primarily localized on the AO of the $\{M_6Q_8\}$ core atoms. The dominant contributions in HOMO, HOMO-1 and HOMO-2 come from AO of the Mo atoms, the exceptions are HOMO-1 in the *mer*-isomers of both sulfide and selenide clusters (Table 1, Figure 4). Figure S1 in Supplementary presents isosurfaces and energies of molecular orbitals in the near frontier orbital region for LUMO, HOMO and lower lying molecular orbitals. Energy analysis shows that the *mer*-isomers are slightly more stable than the *fac*-isomers (ΔE = 0.1 eV).

The known homometallic Re_6 clusters with the pyridine derivatives, namely, *trans*-$[Re_6S_8Cl_4(ppy)_2]^{2-}$ (ppy = 4-phenylpyridine) and *trans*-$[Re_6S_8Cl_4(bpy)_2]^{2-}$ (bpy = 4,4'-bipyridine), have considerably larger HOMO-LUMO gap of about 3.6 eV in comparison with the $[Re_3Mo_3Q_8(py)_6]$ (Q = S, Se) clusters.[15] Similar to the $[Re_3Mo_3Q_8(py)_6]$ clusters, HOMO and HOMO-1 in these $\{Re_6\}$ complexes are mainly metal-centered and split by a small gap. LUMO in *trans*-$[Re_6S_8Cl_4(ppy)_2]^{2-}$ is localized on the bpy ligands, while in *trans*-$[Re_6S_8Cl_4(bpy)_2]^{2-}$ it is localized on the $\{Re_6\}$ core. Interestingly, the bi-gap structure of the $[Re_3Mo_3Q_8(py)_6]$ clusters was not observed in the case of the homometallic species.

Optimized geometries for the *mer*-isomers of the clusters are quite far from octahedral, however, the $\{Re_3Mo_3\}$ core have almost perfect C_{2v} symmetry, which is the highest possible symmetry for such spatial distribution of the atoms (Figure 5). Geometry of the *mer*-isomer of the $\{Re_3Mo_3\}$ core can be represented as the asymmetric rhombic bipyramid with the Re–Mo–Re–Mo rhomb on the base, molybdenum and rhenium atoms as the apexes of the bigger and smaller pyramids (Mo–M_{rhomb} distances are longer than Re–M_{rhomb} distances), respectively.

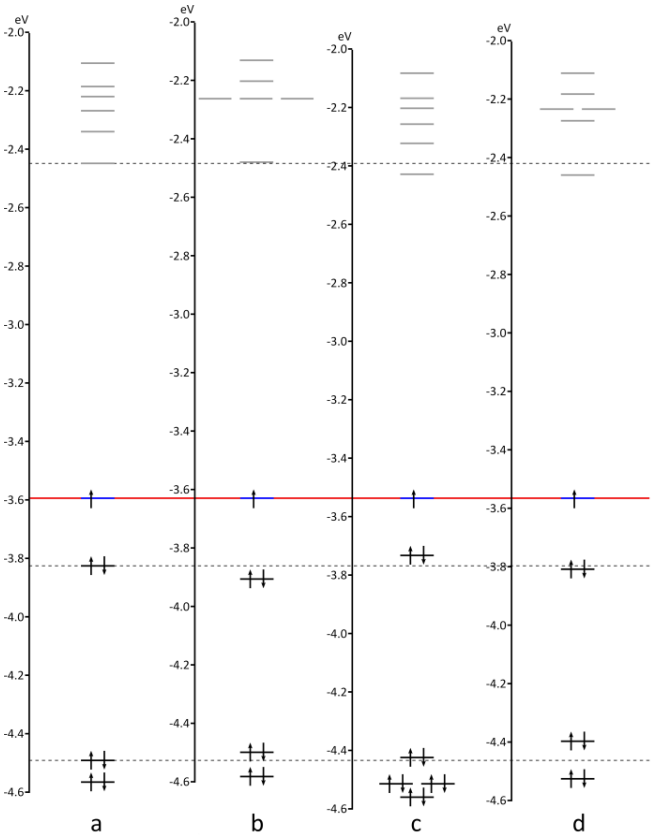


Figure 3. The energy levels diagram in the near frontier orbital region for *fac*- and *mer*- isomers of the $[Re_3Mo_3Q_8(py)_6]$ clusters. a – *fac*-$[Re_3Mo_3S_8(py)_6]$, b – -*mer*-$[Re_3Mo_3S_8(py)_6]$, c – *fac*-$[Re_3Mo_3Se_8(py)_6]$, d – *mer*-$[Re_3Mo_3Se_8(py)_6]$.

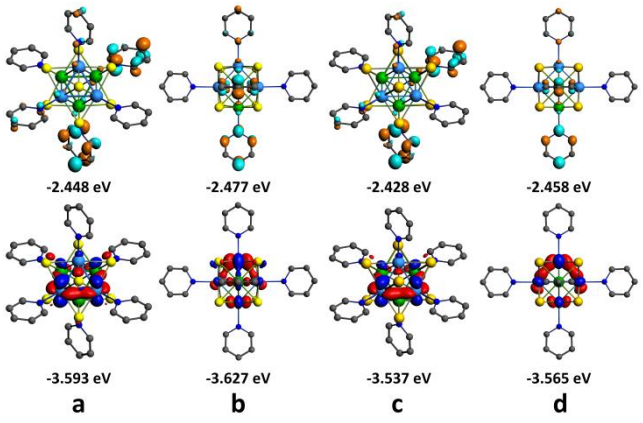


Figure 4. HOMO (bottom) and LUMO (top) orbitals of the different isomers of the $[Re_3Mo_3Q_8(py)_6]$ (Q = S, Se) clusters. a – *fac*-$[Re_3Mo_3S_8(py)_6]$, b – -*mer*-$[Re_3Mo_3S_8(py)_6]$, c – *fac*-$[Re_3Mo_3Se_8(py)_6]$, d – *mer*-$[Re_3Mo_3Se_8(py)_6]$.

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Table 1. Composition of MOs in near frontier orbital region.

	Mo	Re	Q	tbp
fac-$[Re_3Mo_3S_8(py)_6]$				
LUMO	4%	3%	0%	92%
HOMO	56%	19%	24%	0%
HOMO-1	58%	22%	20%	0%
HOMO-2	59%	21%	19%	0%
fac-$[Re_3Mo_3Se_8(py)_6]$				
LUMO	4%	3%	0%	93%
HOMO	55%	18%	27%	0%
HOMO-1	55%	21%	23%	0%
HOMO-2	59%	23%	18%	0%

	Mo	Re	Q	tbp
mer-$[Re_3Mo_3S_8(py)_6]$				
LUMO	5%	10%	0%	85%
HOMO	51%	26%	23%	0%
HOMO-1	38%	41%	21%	0%
HOMO-2	74%	2%	24%	0%
mer-$[Re_3Mo_3Se_8(py)_6]$				
LUMO	4%	9%	0%	87%
HOMO	53%	13%	34%	0%
HOMO-1	31%	40%	29%	0%
HOMO-2	79%	9%	11%	0%

Optimized geometries for the *fac*-isomers calculated in C_1 symmetry (Figure 5) are far from possible C_{3v} symmetry showing large distortion of both $[Re_3Mo_3Q_8(py)_6]$ clusters characterized by the one specific Mo–Mo distance (marked by red arrow in Figure 5), which is ~0.05 Å longer than the other metal-metal distances (Tables S1, S2).

Considering that the $[Re_3Mo_3Q_8(TBP)_6]$ clusters have an odd number of electrons, the *fac*-isomers may undergo the Jahn-Teller (JT) effect. Previously, JT distortion was reported for 23 CVE $[Re_6Q_8X_6]^{3-}$ (Q = S, Se; X = Cl, CN) clusters.[16]

It is known that the character table for C_{3v} point group contains the **E** irreducible representation with doubly degenerate orbitals. Thus, energy levels diagram for the *fac*-isomer of the $[Re_3Mo_3Se_8(py)_6]$ with C_{3v} symmetry was calculated in order to verify possible JT effect. According to the calculations, it contains doubly degenerate orbitals occupied by three electrons, that results in the JT instability of *fac*-isomers and in geometry distortion with the split of degenerate orbitals (Figure 6).

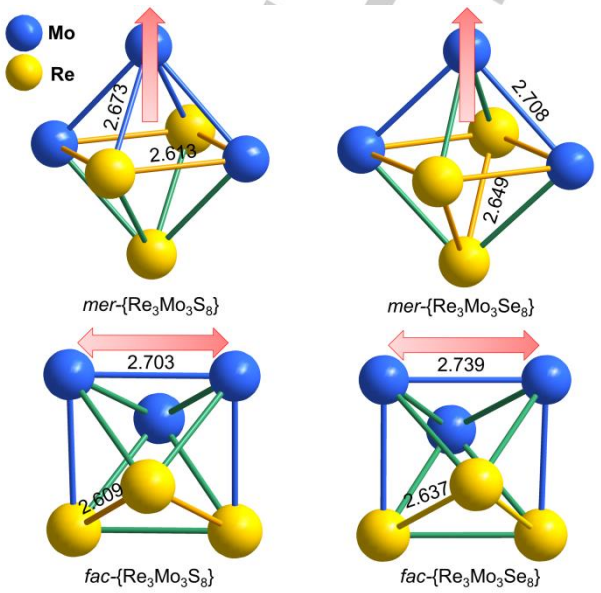


Figure 5. Optimized geometries in *fac*- and *mer*-isomers of $\{Re_3Mo_3\}$ of the $[Re_3Mo_3Q_8(py)_6]$ clusters.

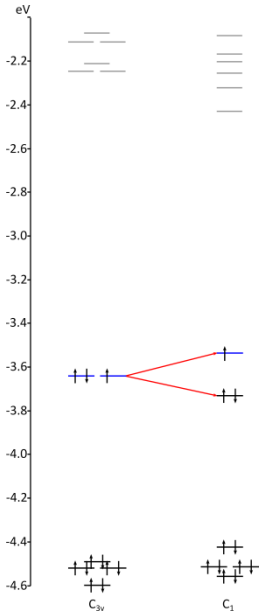


Figure 6. Energy levels diagram in near frontier orbital region for *fac*- isomer of the $[Re_3Mo_3Se_8(py)_6]$ cluster with C_{3v} (left) and C_1 (right) symmetries.

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Conclusions

We demonstrate herein an efficient exchange reaction for the substitution of the terminal cyanide ligands in the octahedral heterometallic clusters $[Re_3Mo_3Q_8(CN)_6]^{n-}$ (Q=S, Se) by 4-*tert*-butylpyridine. Two new compounds, namely $[Re_3Mo_3S_8(TBP)_6]$ (**1**) and $[Re_3Mo_3Se_8(TBP)_6]$ (**2**), were obtained and crystallized in the solvothermal conditions in high yields. It has been shown that the compounds **1** and **2** are paramagnetic with g-values of 2.245 and 2.299, respectively. The geometry of new compounds has been investigated using an X-Ray structural analysis, and their electronic structure has been analyzed using DFT calculations. The X-Ray structural analysis revealed that the cluster cores in both structures are based on the nearly perfect metal octahedron, while the DFT calculations showed that the optimized geometry is strongly distorted. This research opens the way for the ligand exchange chemistry applied to the heterometallic clusters with the $\{Re_3Mo_3Q_8\}$ cores and functional pyridine-based ligands.

Experimental Section

Materials and methods. The starting salts $CaK_4[Re_3Mo_3S_8(CN)_6]\cdot 8H_2O$ and $K_5[Re_3Mo_3Se_8(CN)_6]\cdot 11H_2O$ were prepared as described.[5c,d] Other reagents and solvents were purchased from commercial sources and used without further purification.

EPR spectra at 77 K were registered using a Bruker EMX EPR-spectrometer. FT-IR spectra in KBr pellets were recorded on a Bruker Scimitar FTS 2000 spectrometer in the range 4000–375 cm^{-1}. Energy dispersive spectroscopy (EDS) was performed on a JEOL JSM-7100F scanning electron microscope equipped with an EDS detector SDD X-Max 50mm^2 Oxford Instruments AZtecEnergy. Elemental analysis was performed with a Thermo Electron Microanalyser Flash EA1112 CHNS/O. Cyclic voltammetry was carried out on a Metrohm Computrace 797 VA voltammetry analyzer using three-electrode scheme with GC working, Pt auxiliary and Ag/AgCl reference electrodes. The investigations were carried out for $2.5\cdot 10^{-3}$ M solution of cluster salts in 0.1 M solution of Bu_4NClO_4 in CH_2Cl_2 under Ar atmosphere.

The single crystals of compounds **1** and **2** for diffraction studies were selected directly from the reaction mixtures. Diffraction data for **1** were collected at 296 K using a Bruker Nonius X8 Apex CCD diffractometer (graphite monochromated Mo-K_α radiation, λ = 0.71073 Å). The φ- and ω-scan techniques were employed to measure intensities. Absorption corrections were applied using the SADABS program.[17] The crystal structure was solved by direct methods and refined by the full-matrix least squares techniques with the use of the SHELX package [18] and OLEX2 GUI.[19] The structure was refined as 2-component twin with twin law (0 1 0 1 0 0 0 0 –1), BASF 0.20. All non-hydrogen atoms were refined anisotropically. Atomic coordinates and atomic displacement parameters for pairs of disordered Mo and Re atoms were fixed to be the same using EXYZ and EADP constraints. Two disordered *tert*-butyl groups were refined with SADI, SIMU and DELU restraints. Hydrogen atoms were located geometrically and refined in rigid body approximation. Diffraction data for **2** were collected using a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector, Mo-K_α radiation (λ = 0.71073 Å, multilayer monochromator). The structure was solved by dual-space algorithm using the SHELXT program,[18] and then refined with full-matrix least-squares methods based on F^2 (SHELXL).[20] The contribution of the disordered solvents to the calculated structure factors was estimated following the BYPASS algorithm[21] implemented as the SQUEEZE option in PLATON.[22] Large solvent accessible void with the volume of 571 $Å^3$ was located at (-0.002 0.000 0.000) and containing 190 e^- was removed. *R*-factor before SQUEEZE was 0.0537. A new data set, free of solvent contribution, was then used in the final refinement. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. The crystal data collection and structure refinement conditions for **1** and **2** are summarized in Table 2. Selected interatomic distances are shown in Table 3.

Table 2. Summary of single-crystal data collections and structure refinement conditions of **1** and **2**.

Compound	**1**	**2**
Chemical formula	$C_{54}H_{78}Mo_3N_6Re_3S_8$	$C_{56}H_{81}Mo_3N_7Re_3Se_8$
Formula weight	1914.12	2330.37
Space group	$P4_2/n$	P-1
a [Å]	26.7541(6)	14.431(2)
b [Å]	26.7541(6)	15.681(2)
c [Å]	9.3946(3)	18.758(2)
α [°]	90	105.580(5)
β [°]	90	103.786(5)
γ [°]	90	98.813(5)
V [$Å^3$]	6724.5(4)	3862.3(8)
Z	4	2
Crystal size [mm^3]	0.25×0.07×0.07	0.60×0.19×0.17
λ [Å]	0.71073	0.71073
T [K]	296(2)	150(2)
ρ_{calc} [g/cm^3]	1.891	2.004
μ [mm^{-1}]	6.207	8.959
Θ range [°]	0.761 – 25.701	2.930 – 27.483
Index range	$-32 \le h \le 32$	$-18 \le h \le 18$
	$-32 \le k \le 31$	$-20 \le k \le 20$
	$-11 \le l \le 11$	$-24 \le l \le 24$
Reflections collected	54716	70201
Unique reflections	6401	17687
Reflections observed (I>2σ(I))	5615	12717
R_{int}	0.0613	0.0652
Parameters refined	400	678
Restraints	126	8
GoF	1.144	1.037
R(I>2σ(I))	0.0390	0.0503
R_w(I>2σ(I))	0.0730	0.1126
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e $Å^{-3}$]	1.198, -1.046	2.857, -2.924

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Table 3. Selected interatomic distances in Å (range <average>) in the structures **1** and **2**.

	1	2
M–M	2.6078(6) – 2.6157(6) <2.612>	2.6316(6) – 2.6561(7) <2.640>
M–Q	2.419(2) – 2.440(2) <2.430>	2.5356(10) – 2.5570(10) <2.547>
M–N	2.236(8) – 2.252(7) <2.246>	2.223(8) – 2.261(8) <2.245>

*Synthesis of $[Re_3Mo_3S_8(TBP)_6]$ (**1**).* Hydrothermal reaction of $CaK_4[Re_3Mo_3S_8(CN)_6]\cdot 8H_2O$ (60 mg, 0,038 mmol) and 4-tert-butylpyridine (300 µL, 2.222 mmol) in 2 ml of a mixture of H_2O and CH_3CN (1:3 *v/v*) at 160°C for 96 hours produced black rod-shaped crystals of **1**. The crystals were separated from the reaction mixture, washed with water, acetonitrile and dried in air. Yield: 50 mg (70%). EDS: Re / Mo / S = 2,8 : 3,2 : 8,3. IR (cm^{-1}): [py] 3092m, 3062s, 1598s, 1479s, 1441s, 1348m, 1232w, 1213s, 1146m, 1067s, 1039m, 1009m, 938w, 870w, 757s, 688s, 633w; [t-Bu] 2982s, 2909w, 1348m, 568w. Elemental analysis of $C_{54}H_{78}Mo_3N_6Re_3S_8$: calcd. (mass %) C 33.88, H 4.11, N 4.39, S 13.40; found C 34.03, H 4.20, N 4.45, S 13.31.

*Synthesis of $[Re_3Mo_3Se_8(TBP)_6]$ (**2**).* Compound **2** was synthesized using similar procedure as for **1**, except the use of $K_5[Re_3Mo_3Se_8(CN)_6]\cdot 11H_2O$ (60 mg, 0,030 mmol) as the starting compound. Yield: 40 mg (59%). EDS: Re / Mo / Se = 3,1 : 2,9 : 8,3. IR (cm^{-1}): [py] 3068vw 3037sh 1611s 1494m 1274m 1200vw 1226m 1067m 1019w 847sh 825m 748vw 725vw [t-Bu] 2962s 2901w 2868w 1413m 1365m 567m. Elemental analysis of $C_{54}H_{78}Mo_3N_6Re_3Se_8$: calcd. (mass %) C 28.33, H 3.43, N 3.67; found C 27.17 H 3.21, N 3.56.

Computational details. To simplify the quantum chemical calculations, the pyridine analogs of $[Re_3Mo_3Q_8(TBP)_6]$ (Q= S, Se) cluster complexes were used as a relevant approximation. Density functional theory (DFT) calculations were carried out for the clusters in *fac-* and *mer-* forms in ADF2017 program suit.[23] Geometric parameters for the clusters were optimized with PW92 for LDA part of exchange-correlation functional, PBE for correlation correction and revPBE for exchange correction of GGA part of exchange-correlation functional [24] and all-electron TZ2P basis set.[25] The zero order regular approximation (ZORA) was used in all calculations in this work to take into account of the scalar relativistic effects.[26] Effects of dichloromethane environment were added with Conductor like Screening Model (COSMO).[27] All optimized structures have no imaginary frequencies.

Supplementary data

Crystallographic data for the structures of the title compounds have been deposited at the Cambridge Crystallographic Data Center under reference numbers CCDC 1896770 for **1** and CCDC 1896176 for **2**. Copies of this information may be obtained free of charge from the CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (fax: +44 1223 336033; http://www.ccdc.cam.ac.uk/conts/retrieving.html).

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Keywords: cluster • ligand exchange • rhenium • molybdenum • electronic structure

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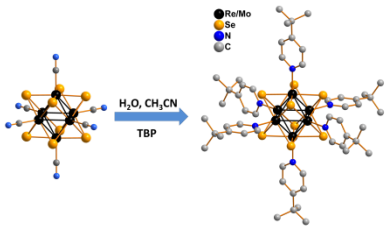
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Reaction of $[Re_3Mo_3Q_8(CN)_6]^{n-}$ (Q = S, n = 6; Q = Se, n = 5) complexes with the 4-*tert*-butylpyridine (TBP) leads to compete substitution of coordinated cyano-ligands and formation of two new heterometallic complexes $[Re_3Mo_3Q_8(TBP)_6]$ (Q = S, Se) obtained with high yields. DFT calculations shows a large distortion of M_6 metal cores in complexes.



Cluster Reactivity

*Viktoria K. Muravieva, Yakov M. Gayfulin, Tatiana I. Lappi, Vincent Dorcet, Taisiya S. Sukhikh, Pierric Lemoine, Maxim R. Ryzhikov, Yuri V. Mironov, Stéphane Cordier, Nikolay G. Naumov**

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Apical cyanide ligands substitution in heterometallic clusters $[Re_3Mo_3Q_8(CN)_6]^{n-}$ (Q = S, Se)

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