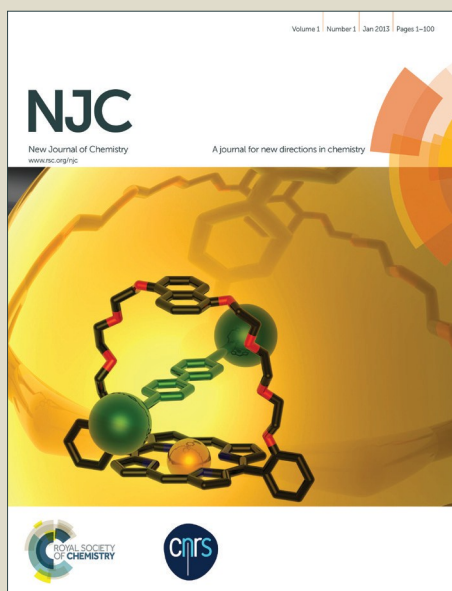


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Complexes of {Mo₆I₈} with nitrophenolates: synthesis and luminescenceReceived 00th January 20xx,
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www.rsc.org/Maksim A. Mikhailov,^a Konstantin A. Brylev,^{a,b} Alexandr V. Virovets,^{a,b} Marsel R. Gallyamov,^a Igor Novozhilov,^a Maxim N. Sokolov*^{a,b}

New bright-red luminescent nitrophenolate complexes (Bu₄N)₂{[Mo₆I₈](OR)₆} (R = C₆H₄-p-(NO₂) (1), C₆H₃-2,4-(NO₂)₂ (2)) have been prepared from (Bu₄N)₂{[Mo₆I₈]I₆} and AgOR, characterized by X-ray analysis, UV-Vis and IR spectroscopies and ESI-mass spectrometry. Both complexes are stable in solutions, and show multiple quasi-reversible reduction waves at highly negative potentials in CV studies. Complex 2 shows a quasi reversible oxidation at E_{1/2} = 1.41 V (vs. Ag/AgCl). Both 1 and 2 are intensely coloured with very high very high molar absorption coefficients in near-ultraviolet region, 143380 and 151050 l·mol⁻¹·cm⁻¹ for 1 and 2, respectively. Similarly to other {[Mo₆I₈]L₆}²⁻ clusters 1 and 2 upon UV photoexcitation display relatively narrow red emission.

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Introduction

Octahedral halide bridged clusters of molybdenum $\{[Mo_6(\mu_3-X)_8]L_6\}$ ($X = Cl, Br, I$; $L =$ inorganic or organic ligands; $\{Mo_6(\mu_3-X)_8\}^{4+}$ is the cluster core)^[1] emit relatively long-living (10^{-6} – 10^{-4} s range) red phosphorescence which can be used for energy transformation and photooxidation, for generation of singlet oxygen, and for sensing.^[2–4] The luminescence properties of the clusters generally depends on both inner ligands X and external (or terminal) ligands L , and a large series of the complexes within clusters with given X and various L are needed in order to reveal, understand and explain dependencies. Up to date, hexamolybdenum complexes with chloride and bromide bridges have received much more attention than their iodide analogues. Coordination chemistry of the $\{[Mo_6X_8]L_6\}^{2-}$ complexes ($X = Cl$ or Br) has been studied extensively during the last three decades and a large variety of the complexes with O-donor (carboxylates, alkoxo, sulfonates, nitrate, nitrite), N-donor (acetonitrile, N_3^- , NCO^- , NCS^- , $NCSe^-$, pyridines), P- and S-donor (phosphines, thiolates) ligands have been reported.^[5] Many of these complexes emit red phosphorescence upon UV-visible excitation, with microsecond length excited-state lifetimes. Contrary to this, until recently few studies on the luminescence properties of the $\{Mo_6\}^{4+}$ -based clusters were reported. Only lately it was demonstrated that complexes with fluorinated carboxylates $\{[Mo_6\}(OOCR)_6\}^{2-}$ ($R = CF_3, C_3F_7$) show luminescence properties superior (in terms of lifetime and quantum yield values) to those of any other member of the $\{M_6X_8\}$ cluster family (even including $M = Re$ and $X = S, Se, Te$).^[5d, 5f] Alkynyl $\{[Mo_6\}(C\equiv CC(O)OMe)_6\}^{2-}$ and nitrate $\{[Mo_6\}(NO_3)_6\}^{2-}$ complexes were also found to be strongly luminescent with a sharp emission spectrum.^[5s, 5t] Replacement of the external chloride ligands in $\{[Mo_6Cl_8]Cl_6\}^{2-}$ by thiolate ions results in a significant decrease of the luminescence quantum yield (Φ_{em}) and lifetime (τ_{em}).^[5o, 5p] Contrary to this, as was demonstrated by the example $(Bu_4N)_2\{[Mo_6\}(SC_6F_4H)_6\}$,^[5u] ligation of the fluorinated thiolate to $\{Mo_6\}^{4+}$ resulted in changeless Φ_{em} along with a significant increase in τ_{em} (relative to the parent complex $\{[Mo_6\}(Cl)_6\}^{2-}$). It is obvious that for a given Mo octahedral cluster complex, the photophysical characteristics are a complicated function of at least three main factors, namely: i) the identity of the capping (inner) halide; ii) the donor atom in the terminal (external) ligand; iii) the organic substituents (with different electronic and steric effects) in a given ligand set. In this paper we report the synthesis, structure and luminescence properties of two new nitrophenolate complexes of the general formula $(Bu_4N)_2\{[Mo_6\}(OR)_6\}$ ($R = C_6H_4-p-(NO_2), C_6H_3-2,4-(NO_2)_2$).

Results and Discussion

The number of reported alkoxo- and aryloxo complexes of $\{Mo_6X_8\}^{4+}$ is very limited. Mo_6Cl_{12} reacts with NaOMe with the formation, depending on the reagents ratio, of $\{[Mo_6Cl_8](OMe)_6\}^{2-}$ ^[6] or *trans*- $\{[Mo_6Cl_8]Cl_4(OMe)_2\}^{2-}$.^[2] The sodium salt of $\{[Mo_6Cl_8](OMe)_6\}^{2-}$ is insoluble in organic solvents, but it can be solubilized by sequestration of Na^+ with [2,2,2]-cryptand and further used as precursor for synthesis of other $\{[Mo_6Cl_8](OR)_6\}^{2-}$ derivatives. Complexes *trans*- $\{[Mo_6Cl_8]Cl_4(OCH_2C_{14}H_9)_2\}^{2-}$

($C_{14}H_9CH_2OH$ is 9-anthracenemethanol)^[8] and $\{[Mo_6Cl_8](OPh)_6\}^{2-}$ were prepared by reacting $\{[Mo_6Cl_8]Cl_4(OMe)_2\}^{2-}$ and $\{[Mo_6Cl_8](OMe)_6\}^{2-}$, respectively, with corresponding ROH.^[6b, 7] The driving force for the substitution is ROH being more acidic than terminal ligands in the starting methoxide complex. $Na_2\{[Mo_6Br_8](OCH_3)_6\}$ was also reported.^[6a] Another recent example is $Na_2\{[Mo_6\}(OCH_3)_6\}$.^[9] The methoxides were successfully used for preparation of other complexes $\{[Mo_6X_8]L_6\}^{2-}$ by reactions with various acidic ligands LH, such as thiols and carboxylic acids, which are driven by CH_3OH elimination.^[5o, 5p, 10] The phenolates received less attention than alkoxides. In this paper we used direct substitution of terminal iodide ligands in $\{[Mo_6I_8]I_6\}^{2-}$ by reaction with silver salts of *p*-nitrophenolate and 2,4-dinitrophenolate. The driving force is the formation of insoluble AgI. This approach allows us to skip the step of preparation of the $\{[Mo_6I_8](OCH_3)_6\}^{2-}$ complex. The reactions proceed smoothly and give acceptable yields of $(Bu_4N)_2\{[Mo_6\}(OC_6H_4-p-(NO_2))_6\}$ (**1**) (52%) and $(Bu_4N)_2\{[Mo_6\}(OC_6H_3-2,4-(NO_2)_2)_6\}$ (**2**) (62%). Complexes **1** and **2** are air-stable solids soluble in common organic solvents, such as CH_2Cl_2 , CH_3CN , DMF, DMSO. The IR spectra show typical bands of ν_s vibrations of NO_2 groups at 1284 (**1**) and 1317 (**2**) cm^{-1} . The ν_{as} vibrations (around 1550–1500 cm^{-1}) are obscured by the vibrations of the aromatic rings that occur between 1600 and 1450 cm^{-1} . Both **1** and **2** maintain their integrity in solutions. Electrospray mass-spectra in CH_3CN show the signals of double-charge anionic species with $m/z = 1209.7$ ($\{[Mo_6\}(OC_6H_4NO_2)_6\}^{2-}$) for **1** and $m/z = 1344.5$ ($\{[Mo_6\}(OC_6H_3(NO_2)_2)_6\}^{2-}$) for **2** with no evidence for unreacted precursor $\{[Mo_6I_8]I_6\}^{2-}$ or partially substituted $\{[Mo_6I_8]I_{6-x}(OR)_x\}^{2-}$ ($x \leq 5$) species. 1H NMR spectra show the correct ratio between the ligand protons and the protons from Bu_4N^+ cations in **1** and **2**, and can be used to control the purity of the samples.

Cyclic voltammograms for **1** and **2** show quasi reversible waves at highly negative potentials (between -0.6 and -1.8 V) that have to be attributed to one or two-electron reduction of the nitro groups, which is typical for reduction of the nitroarenes in aprotic media. For **1**, a quasi reversible multielectron wave was observed with $E_c = -1.55$ V, $E_a = -1.36$ V at scan rate of 20 mV/s, which became less reversible at the rate of 1 V/s ($E_c = -1.57$ V, $E_a = -1.21$), Fig 3S. Complex **2** is reducible in a sequence of quasi reversible steps with $E_c = -0.94, -1.30, -1.80$ V and $E_a = -1.42, -0.97, -0.64$ V at scan rate of 1 V/s, Fig. 4S. Complex **1** does not show well-defined oxidation waves up to +1.5 V, while **2** shows a quasi reversible oxidation at $E_{1/2} = +1.41$ V ($E_c = +1.35$ V, $E_a = +1.47$ V), independently on the scan rate from 0.1 to 1.0 V/s.

Structures of both complexes were determined by single-crystal X-ray analysis. The single crystals were obtained as solvates **1**· CH_3CN · H_2O and **2**·3THF by slow diffusion of diethyl ether into solution of **1** in CH_3CN , and by diffusion of hexane into a solution of **2** in THF in air. The solvent molecules are easily lost when crystals are taken out of their mother liquors, which also affect the elemental analysis data. In this paper they refer to desolvated samples. The cluster anions in **1** and **2** (Figure 1) have crystallographic C_i site symmetry. There are two crystallographically independent anions in **1**, which have similar geometrical characteristics. Average Mo–Mo and Mo– μ_3 -I distances in **1** and **2** are similar to those found in the previously reported $\{Mo_6\}^{4+}$ cluster complexes (Table 1). The Mo–O (Table 1) distances are in the expected range. The only remarkable geometric feature is a large variation of the Mo–O–C angles,

132.2(7)-146.7(8)° in **1** and 137.3(8)-166.1(8)° in **2**. For comparison, in the phenolate complex $[\text{Na}(\text{18C6})]_2[\text{Mo}_6\text{Cl}_8(\text{OC}_6\text{H}_5)_6]$ the M–O–C angles are close to 136°, whereas in the methoxocomplex $[\text{Na}(\text{18C6})]_2[\text{Mo}_6\text{Cl}_8(\text{OCH}_3)_6] \cdot 6\text{CH}_3\text{OH}$ they are much smaller (124°).^[7] In fact, the bottom values of these variations found in **1** and **2** are close to typical values found in the complexes of *p*-nitrophenolate and 2,4-dinitrophenolate ligands with electron-rich d^{10} , d^9 and d^8 ions, or with non-transition metals (Sn(IV), Ga(III)) where π -donating from O to M is not favored. To the contrary, M–O–C angles $\geq 140^\circ$ are typical for electron-deficient and π -accepting d^0 metal cations such as Ti^{4+} and Zr^{4+} . Thus the largest reported M–O–C angle (161°) is found in $[\text{LZr}(\text{O}-\text{C}_6\text{H}_4-\text{NO}_2)_3]$ (L = hydridotris(3,5-dimethylpyrazolyl)borate).^[10] This implies a large degree of π -donating from O to M. In our case in the structure of **2** there are distinct Mo–O–C sets: bent 137.3(8)° (two) and 146.7(9)° (two), and close to linear 166.1(8)° (two) (Figure 1).

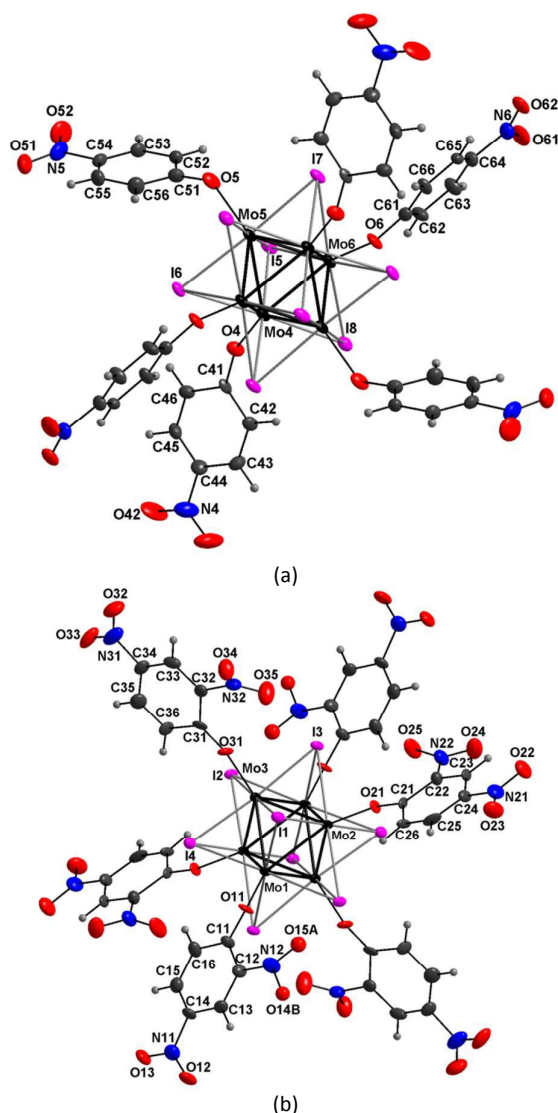


Figure 1. Cluster anions in **1** (a) and **2** (b), a.d.p. ellipsoids are at 50% probability level.

The ligands with identical Mo–O–C angles are mutually *trans*. The Mo–O–C angle 166.1(8)° is the largest reported for a *p*-

nitrophenolate or 2,4-dinitrophenolate complex. Perhaps steric demands of bulky organic ligands contribute more to such variation than electronic effects.

Table 1. Main bond distances (Å) in **1** and **2** in comparison with Cambridge Structural Database (CSD) data on similar compounds.

Compound	Mo–Mo	Mo– μ_3 -I	Mo–O
1	2.6596(14)-2.6700(13) av. 2.664[4]	2.7789(15)-2.8157(12) av. 2.795[8]	2.079(9)-2.120(9) av. 2.092[15]
2	2.6444(15)-2.6822(14) av. 2.663[12]	2.7624(13)-2.8025(16) av. 2.784[11]	2.069(7)-2.105(8) av. 2.088[15]
CSD	2.641-2.701 ¹ av. 2.672[14]	2.756-2.858 ¹ av. 2.782[17]	2.114-2.141 ² av. 2.126[10]

¹ Average data over 13 crystal structures of compounds containing $\{\text{Mo}_6\text{I}_8\}$ cluster core^[16]

² Average data over 3 crystal structures of compounds containing $\{[\text{Mo}_6\text{I}_8](\text{OR})_6\}$ fragment^[16]

In both crystal structures the cluster anions weakly interact with each other and with the Bu_4N^+ cations. Only a few shortened O...O contacts involving NO_2 groups were found in **2**, namely, O(34)...O(34') of 3.06 Å, and O(23)...O(35) of 3.07 Å. In addition, water solvent molecule in **1** makes the hydrogen bond of 2.83 Å with a phenolic oxygen atom of the nitrophenolate ligand (Figure 2).

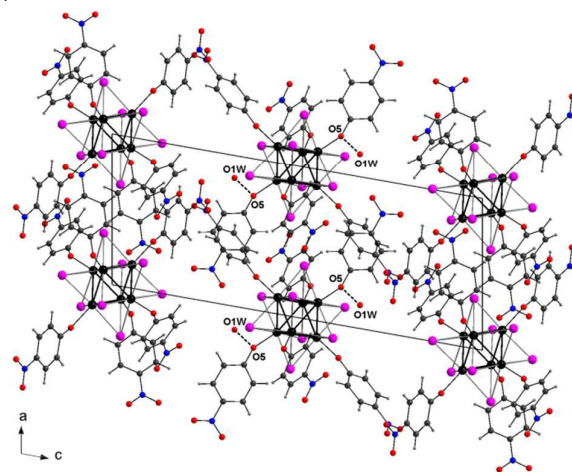


Figure 2. The hydrogen bond of a water solvent molecule with a phenolic oxygen atom of the nitrophenolate ligand in **1**.

Similarly to other $\{[\text{Mo}_6\text{I}_8]\text{L}_6\}^{2-}$ clusters with L different from iodide, **1** and **2** upon UV photoexcitation display relatively narrow (in comparison with $\{\text{Mo}_6\text{Cl}_8\}^{4+}$ and $\{\text{Mo}_6\text{Br}_8\}^{4+}$ -based complexes) emission spectra in both acetonitrile and solid state (Figure 3).

The emission maximum wavelengths (λ_{em}), the full-width at half-maximum of the emission spectra (fwhm), quantum yields (Φ_{em}) and lifetimes (τ_{em}), related to the powdered samples and aerated as well as deaerated acetonitrile solutions of **1** and **2**, are summarized in Table 2.

For each complex, the emission spectral band shapes of the aerated and deaerated solutions are essentially identical, while the oxygen-free solutions are characterized by significantly higher values of Φ_{em} and τ_{em} , in comparison with those found for the aerated solutions, in which the luminescence is efficiently quenched by dioxygen.^[5r-t]

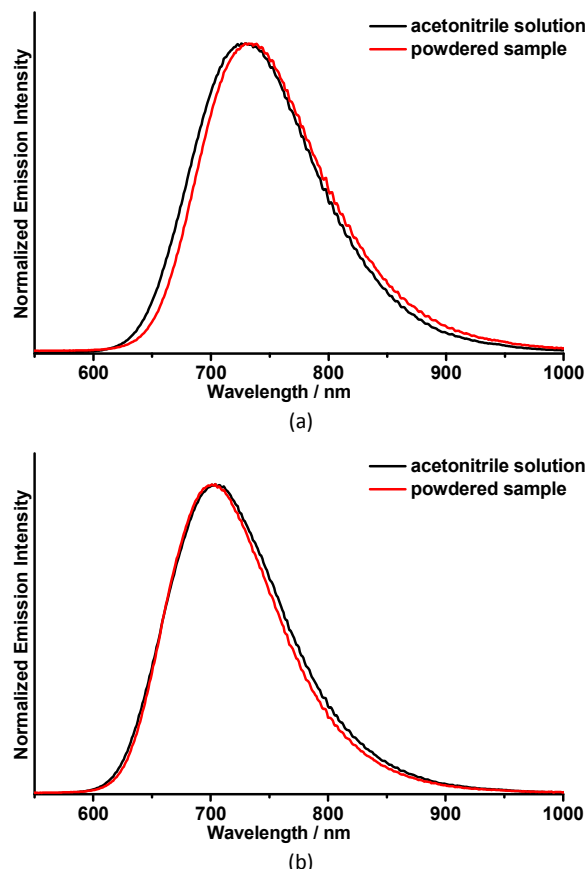


Figure 3. Normalized emission spectra of **1** (a) and **2** (b) in the solid state and in a deaerated acetonitrile solution.

In the solid state the luminescence spectra are slightly narrower than in acetonitrile (see corresponding fwhm values in Table 2), and the emission decay profiles were fitted by double-exponential functions with decay constants (τ_{em}) of 30 and 6.4 μ s for **1** and 52 and 14 μ s for **2**, with emission quantum yields of 0.03 and 0.05, respectively. In deaerated acetonitrile solutions, **1** and **2** showed single-exponential emission decays with higher emission lifetimes and quantum yields (Table 2).

Luminescence spectra of powdered samples as well as solutions of **1** and **2** have very similar shape. However, the spectra of **1** are red-shifted; and the Φ_{em} and τ_{em} values for both the powder and solution of **1** are lower and shorter, respectively, than those of **2** (Table 2).

As can be seen from Table 2, emission spectra of **1** and **2** are as narrow (≤ 2500 cm^{-1}) as the spectra of recently reported $[\{\text{Mo}_6\text{I}_8\}(\text{OCC}_3\text{F}_7)_6]^{2-}$ and $[\{\text{Mo}_6\text{I}_8\}(\text{NO}_3)_6]^{2-}$.^[5r, 5i] However, the latter complexes show significantly higher Φ_{em} and their spectra are appreciably blue shifted than those of **1** and **2**. It is curious that λ_{em} , Φ_{em} and λ_{em} values of powdered sample and deaerated acetonitrile solution of **1** are very similar to those of $[\{\text{Mo}_6\text{I}_8\}(\text{SC}_6\text{F}_4\text{H})_6]^{2-}$,^[5u] while the photophysical parameters of **2** in both the solid phase and solution are almost identical with those of $[\{\text{Mo}_6\text{I}_8\}(\text{C}\equiv\text{CC}(\text{O})\text{OMe})_6]^{2-}$.^[5j] At the same time, the emission spectra of **1** and **2** are considerably narrower than those of $[\{\text{Mo}_6\text{I}_8\}(\text{SC}_6\text{F}_4\text{H})_6]^{2-}$ and $[\{\text{Mo}_6\text{I}_8\}(\text{C}\equiv\text{CC}(\text{O})\text{OMe})_6]^{2-}$.

Table 2. Spectroscopic and photophysical parameters of **1** and **2** and some compounds based on $\{\text{Mo}_6\text{I}_8\}^{4+}$ at room temperature.

Sample	λ_{em} [nm] (fwhm [cm^{-1}])	Φ_{em}	τ_{em} [μ s] (Amplitude)
1 (aerated acetonitrile solution)	730 (2400)	0.001	1.7
1 (deaerated acetonitrile solution)	730 (2400)	0.14	187
1 (powdered sample)	733 (2300)	0.03	30 (0.30), 6.4 (0.70)
2 (aerated acetonitrile solution)	705 (2400)	0.002	2.0
2 (deaerated acetonitrile solution)	705 (2400)	0.18	210
2 (powdered sample)	703 (2250)	0.05	52 (0.25), 14 (0.75)
$[\{\text{Mo}_6\text{I}_8\}(\text{SC}_6\text{F}_4\text{H})_6]^{2-}$ [5u] (deaerated acetonitrile solution)	726 (3080)	0.13	179
$[\{\text{Mo}_6\text{I}_8\}(\text{SC}_6\text{F}_4\text{H})_6]^{2-}$ [5u] (powdered sample)	713 (3140)	0.04	39 (0.4), 11 (0.6)
$[\{\text{Mo}_6\text{I}_8\}(\text{C}\equiv\text{CC}(\text{O})\text{OMe})_6]^{2-}$ [5j] (aerated acetonitrile solution)	707 (3100)	0.002	1.8
$[\{\text{Mo}_6\text{I}_8\}(\text{C}\equiv\text{CC}(\text{O})\text{OMe})_6]^{2-}$ [5j] (deaerated acetonitrile solution)	707 (3100)	0.18	164
$[\{\text{Mo}_6\text{I}_8\}(\text{C}\equiv\text{CC}(\text{O})\text{OMe})_6]^{2-}$ [5j] (powdered sample)	700 (2600)	0.05	67 (0.45), 24 (0.55)
$[\{\text{Mo}_6\text{I}_8\}(\text{NO}_3)_6]^{2-}$ [5r] (aerated acetone solution)	669 (2500)	<0.01	3.4
$[\{\text{Mo}_6\text{I}_8\}(\text{NO}_3)_6]^{2-}$ [5r] (deaerated acetone solution)	669 (2500)	0.25	185
$[\{\text{Mo}_6\text{I}_8\}(\text{NO}_3)_6]^{2-}$ [5i] (powdered sample)	666 (2350)	0.26	93 (0.7), 26 (0.3)
$[\{\text{Mo}_6\text{I}_8\}(\text{OCCF}_3)_6]^{2-}$ [5d] (deaerated acetonitrile solution)	673	1.0	182
$[\{\text{Mo}_6\text{I}_8\}(\text{OCCF}_3)_6]^{2-}$ [5d] (powdered sample)	670	-	215
$[\{\text{Mo}_6\text{I}_8\}(\text{OCC}_3\text{F}_7)_6]^{2-}$ [5r] (aerated acetonitrile solution)	668 (2390)	<0.01	2.2
$[\{\text{Mo}_6\text{I}_8\}(\text{OCC}_3\text{F}_7)_6]^{2-}$ [5r] (deaerated acetonitrile solution)	668 (2390)	0.59	303
$[\{\text{Mo}_6\text{I}_8\}(\text{OCC}_3\text{F}_7)_6]^{2-}$ [5r] (powdered sample)	659 (2170)	0.36	150
$[\{\text{Mo}_6\text{I}_8\}(\text{OOC-pyrene})_6]^{2-}$ [9a] (deaerated THF solution)	698	0.60	210
$[\{\text{Mo}_6\text{I}_8\}(\text{OOC-anthracene})_6]^{2-}$ [9a] (deaerated THF solution)	700	0.02	1200
$[\{\text{Mo}_6\text{I}_8\}(1\text{-OOC-1,2-closo-C}_2\text{B}_{10}\text{H}_{11})_6]^{2-}$ [9b] (deaerated acetonitrile solution)	685	0.70	320
$[\{\text{Mo}_6\text{I}_8\}(1\text{-OOC-1,7-closo-C}_2\text{B}_{10}\text{H}_{11})_6]^{2-}$ [9b] (deaerated acetonitrile solution)	685	0.93	320
$[\{\text{Mo}_6\text{I}_8\}(1\text{-OOC-1,12-closo-C}_2\text{B}_{10}\text{H}_{11})_6]^{2-}$ [9b] (deaerated acetonitrile solution)	685	0.77	330

Recently, Kirakci et al. emphasized a significant increase of the brightness of luminescent Mo_6 cluster complexes as a result of coordination of strongly absorbing ligands at apical positions of the phosphorescent $\{\text{Mo}_6\text{I}_8\}^{4+}$ core. In particular, it was shown that the complex with the pyrene apical ligands $[\{\text{Mo}_6\text{I}_8\}(\text{C}_{17}\text{H}_9\text{O}_2)_6]^{2-}$ exhibits the highest emission brightness ever achieved for a Mo_6 cluster complex, when excited in the near-UV region ($\epsilon_{355} = 2.3 \cdot 10^5$ $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$, $\Phi_{em} = 0.60$).^[9a] An interesting finding of the present work is the fact that ligation of such simple aromatic anions as *p*-nitrophenolate and 2,4-dinitrophenolate at apical positions of the $\{\text{Mo}_6\text{I}_8\}^{4+}$ core leads to the complexes that in an acetonitrile solution are characterized by very high molar absorption coefficients in near-ultraviolet region, being 143380 and 151050 for **1** and **2**, respectively, while the common ϵ values for the most of the Mo_6 cluster complexes are in the order of 10^3 $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. In contrast to the pyrene cluster complex, which

absorption spectrum consists in the additive contributions from the $\{\text{Mo}_6\text{I}_8\}^{4+}$ core and the grafted pyrene ligands,^[9a] absorption bands of *p*-nitrophenol and 2,4-dinitrophenol are not observed in the spectra of **1** and **2** (Figure 4), respectively, implying significant electronic interaction between nitrophenolates and the cluster $\{\text{Mo}_6\text{I}_8\}^{4+}$.

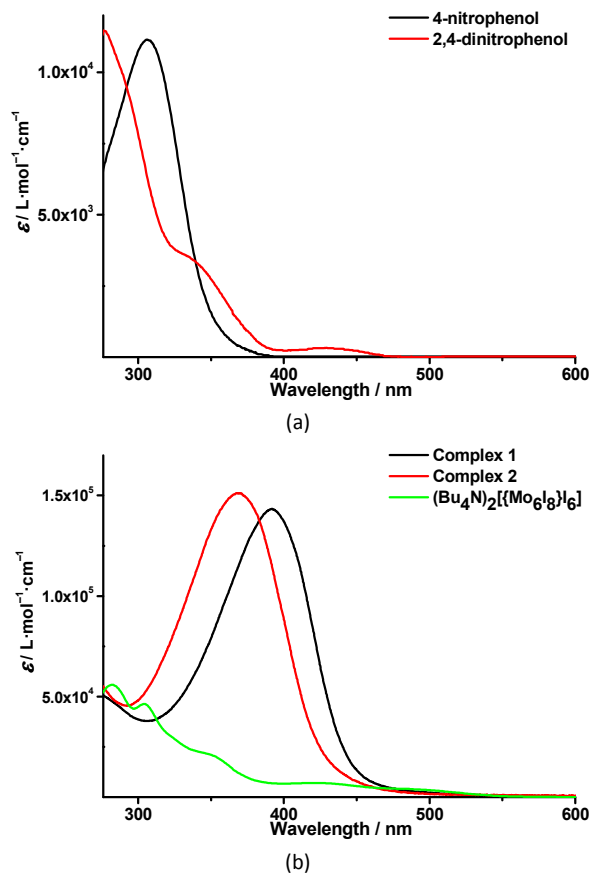


Figure 4. Absorption spectra of free phenols (a) and molybdenum cluster complexes (b) in an acetonitrile solution.

Thus, based on considerable emission quantum yields revealed for deaerated acetonitrile solution of the complexes **1** and **2** along with the high molar absorption coefficients, we can state that the solutions exhibit very bright red emission upon photoexcitation with near-UV light.

Conclusions

Two nitrophenolate complexes with $\{\text{Mo}_6\text{I}_8\}^{4+}$ core, $(\text{Bu}_4\text{N})_2[\{\text{Mo}_6\text{I}_8\}(\text{OR})_6]$ have been prepared from $[\{\text{Mo}_6\text{I}_8\}\text{I}_6]^{2-}$ and silver silver phenolates AgOR ($\text{R} = \text{C}_6\text{H}_4\text{-p}(\text{NO}_2)$, $\text{C}_6\text{H}_3\text{-2,4}(\text{NO}_2)_2$) in moderate yields. Complexes are electrochemically active both at highly negative and positive potentials. Acetonitrile solutions of the complexes are stable and show high molar absorption coefficients of the order of $10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$, which indicate strong electronic interaction between cluster core and ligands. Both solid samples and acetonitrilic solutions of the complexes exhibit very bright red emission

(ca. 730 nm for **1**, ca. 700 nm for **2**) upon photoexcitation with near-UV light.

Experimental section

General Comments: Starting $(\text{Bu}_4\text{N})_2[\{\text{Mo}_6\text{I}_8\}\text{I}_6]$ was prepared as described in [11]. Silver(I) oxide was obtained by combining aqueous solutions of silver nitrate (5 g, 29 mmol) in 500 mL of water, and potassium hydroxide (1.65 g, 29 mmol) in 100 mL of water under stirring at 0°C for 30 minutes and then for 1 hour at room temperature. The precipitate was collected by filtration and washed with water. The wet cake was dried on a rotary evaporator to produce dark brown powder of Ag_2O in a quantitative yield. Silver(I) nitrophenolates were prepared following the procedure described by Jakob et al. [12]

Physical Measurements: Diffraction data (Table 3) were measured at 100 K using Bruker Apex2 Duo diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) and narrow (0.5°) ϕ - and ω -scans. Structures were solved by direct methods and refined with full-matrix least squares method against F^2 using SHELXTL 6.22 programs set. [13] Absorption corrections were applied semi-empirically using SADABS program. [14] Hydrogen atoms were placed on calculated positions and refined in rigid body approximation. Our attempt to localize H atoms belonging to solvent water molecules failed. Full crystallographic data, details of diffraction experiments and structure refinement are deposited in Cambridge Crystallographic Data Center under the deposition codes CCDC 1027967 and 1027968 for **1** and **2**, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif. Complete tables of bond distances and angles in **1**: $\text{CH}_3\text{CN}\cdot\text{H}_2\text{O}$ and **2**: 3THF are given also in Supporting Information, Tables S1 and S2, respectively. IR spectra ($4000\text{--}400 \text{ cm}^{-1}$) were recorded on an IFS-85 Bruker spectrometer. UV/vis spectra were recorded on an Ultrospec 3300 pro spectrophotometer. NMR spectra were recorded on a 500 MHz, Bruker Avance 500 plus Elemental analyses were carried out by the analytical service of the Institute of Inorganic Chemistry (Novosibirsk). The samples were preliminary de-solvated by vacuum pumping until constant weight was reached. Mass spectrometry (ESI-MS) was performed on an Agilent 6100 Series Quadrupole LC/MS system. Cyclic voltammetry experiments were run on a Metrohm 797 Computrace equipment for $10^{-3}\text{--}10^{-4}\text{M}$ solutions (2 mM for **1**, 0.2 mM for **2**) in CH_3CN (0.05 M Bu_4NBF_4 was used as electrolyte). Working electrode was glassy carbon, auxiliary electrode was Pt and reference electrode was Ag/AgCl . The solutions were saturated with Ar. For emission measurements, the powdered samples **1** and **2** were placed between two non-fluorescent glass plates. The absorbance of acetonitrile solutions was set < 0.1 at 355 nm. Each solution was poured into two quartz cuvettes and one of them was deaerated by purging with an Ar stream for 30 min and then the cuvette was sealed. Measurements were carried out at 298 K. The samples were excited by 355-nm laser pulses (6 ns duration, LOTIS TII, LS-2137/3). Corrected emission spectra were recorded on a red-light-sensitive multichannel photodetector (Hamamatsu Photonics, PMA-12). For emission decay measurements, the emission was analyzed by a streakscope system (Hamamatsu Photonics, C4334 and C5094). The emission quantum yields (Φ_{em}) for the aerated and deaerated acetonitrile solutions of **1** and **2** were estimated by using $(\text{Bu}_4\text{N})_2[\text{Mo}_6\text{Cl}_{14}]$ as standard: $\Phi_{\text{em}} = 0.19$ in deaerated acetonitrile. [15] The emission quantum yields of the powdered samples were determined by an Absolute Photo-

Luminescence Quantum Yield Measurement System (Hamamatsu Photonics, C9920-03), which comprised an excitation Xenon light source (the excitation wavelength was set at 380 nm), an integrating sphere, and a red-sensitive multichannel photodetector (Hamamatsu Photonics, PMA-12).

Table 3. Selected crystallographic data for **1-CH₃CN·H₂O** and **2·3THF**.

	1-CH ₃ CN·H ₂ O	2·3THF
Formula	C ₇₀ H ₁₀₁ I ₈ Mo ₆ N ₉ O ₁₉	C ₈₀ H ₁₁₄ I ₈ Mo ₆ N ₁₄ O ₃₃
<i>M_r</i>	2963.44	3390.69
Crystal system, space group	Triclinic, <i>P1</i>	Monoclinic, <i>C2/c</i>
Temperature (K)	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.2810(6), 18.6929(13), 24.7011(16)	40.500(5), 10.2557(13), 32.799(5)
α , β , γ (°)	90.145(2), 99.641(2), 104.611(2)	90, 123.367(7), 90
<i>V</i> (Å ³)	4523.7(5)	11378(3)
<i>Z</i> , <i>D_x</i> (g·cm ⁻³)	2, 2.176	4, 1.979
μ (mm ⁻¹)	3.60	2.89
Crystal size (mm)	0.30 × 0.12 × 0.06	0.30 × 0.11 × 0.03
<i>T_{min}</i> , <i>T_{max}</i>	0.641, 0.745	0.178, 0.263
Number of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	21341, 16798, 9728	18809, 9686, 6292
<i>R_{int}</i>	0.043	0.053
θ_{max} (°)	25.73	25
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, <i>S</i>	0.055, 0.128, 0.97	0.062, 0.162, 1.09
No. of reflections	16798	9686
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	1.48, -1.11	2.58, -1.08

Preparations

[AgOC₆H₄-*p*-(NO₂)]. To a solution of *p*-nitrophenol (120 mg, 863 mmol) in 10 mL of CH₂Cl₂, 100 mg (432 mmol) of Ag₂O was added. The flask was wrapped in aluminum foil to isolate the reaction mixture from light, and the mixture was stirred overnight. The orange solid was collected by filtration and washed with diethyl ether. Yield: 163 mg (77%). AgH₄C₆NO₃ (245.97): calcd. C 29.30, H 1.64, N 5.69; found C 28.95, H 1.30, N 6.00. IR (KBr): ν = 3370 (m), 1639 (w), 1586 (s), 1556 (m), 1502 (s), 1459 (w), 1423 (m), 1390 (m), 1295 (s), 1170 (s), 1118 (s), 858 (m), 760 (w), 710 (w), 649 (m), 492 (w), 462 (w) cm⁻¹.

[AgOC₆H₃-2,4-(NO₂)₂]. The silver salt was obtained in a similar way from 2,4-dinitrophenol (239 mg, 1.30 mmol) and Ag₂O (150 mg, 646 mmol). Yield: 307 mg (1.05 mmol, 81%). AgH₃C₆N₂O₅ (290.97): calcd. C 24.77, H 1.04, N 9.63; found C 25.20, H 1.40, N 9.85. IR (KBr): ν = 3468 (m), 3101 (w), 1949 (w), 1605 (s), 1565 (s), 1534 (m), 1469 (m), 1434 (m), 1380 (m), 1329 (s), 1264 (s), 1135 (s), 1053 (w), 925 (w), 838 (m), 750 (w), 715 (w), 633 (w), 529 (w) cm⁻¹.

(Bu₄N)₂[(Mo₆I₈)(OC₆H₄-*p*-(NO₂)₂)₆]·CH₃CN·H₂O (**1-CH₃CN·H₂O**). To a solution of (Bu₄N)₂[(Mo₆I₈)₆] (0.15 g, 0.052 mmol) in 10 mL of CH₂Cl₂ a 12-fold excess of solid [AgOC₆H₄-*p*-(NO₂)₂] (0.156 g, 0.634 mmol) was added. The mixture was stirred for one day. Then the resulting fine suspension was filtered through a thick filter paper and the filtrate was rotary evaporated, leaving a red oil. The oil was dissolved in CH₃CN. Single crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into the CH₃CN solution. Yield: 0.08 g (0.028 mmol, 52 %). Analysis for desolvated Mo₆I₈O₁₈N₈C₆₈H₉₆ (2904.04): calcd. C 28.12, H 3.33 N 3.86; found C 28.40, H 3.50, N 3.91. IR (KBr): ν = 3065 (w), 2959 (m), 2872 (w), 2571 (w), 2389 (w), 1974 (w), 1576 (s), 1485 (s), 1284 (s), 1158

(m), 1106 (s), 992 (m), 865 (m), 831 (m), 757 (w), 700 (w), 654 (m), 404 (w) cm⁻¹. ESI-MS (MeCN, *m/z*): 1209.7 [(Mo₆I₈)(OC₆H₄NO₂)₆]²⁻ (¹H NMR (C₃D₆O, 25 °C): δ = 0.96 (t, ³*J*_{H,H} = 7.33 Hz, 24 H), δ = 1.41 (sextet, ³*J*_{H,H} = 7.32 Hz, 16 H), δ = 1.79 (p, ³*J*_{H,H} = 7.80 Hz, 16 H), δ = 3.40 (m, 16 H), δ = 6.67 (d, ³*J*_{H,H} = 9.15 Hz, 12 H, 2-H and 6-H), δ = 8.02 (d, ³*J*_{H,H} = 9.15 Hz, 12 H, 3-H and 5-H) ppm (Figure 15). UV/Vis (MeCN): λ_{max} [nm] (ϵ [L·mol⁻¹·cm⁻¹]) = 392 (143380).

(Bu₄N)₂[(Mo₆I₈)(OC₆H₃-2,4-(NO₂)₂)₆]·3THF (**2·3THF**). The complex was obtained in a similar way from (Bu₄N)₂[(Mo₆I₈)₆] (0.162 g, 0.057 mmol) and [AgOC₆H₃-2,4-(NO₂)₂] (0.10 g, 0.34 mmol). Single crystals suitable for X-ray analysis were obtained by slow diffusion of hexane into THF solution. Yield: 112 mg (0.035 mmol, 62 %). Mo₆I₈O₃₀N₁₄C₆₈H₉₀ (3174.38): calcd. C 25.73, H 1.30 N 6.17; found C 25.50, H 1.30, N 6.12. IR (KBr): ν = 3098 (w), 2961 (m), 2874 (w), 1593 (s), 1522 (s), 1474 (s), 1317 (s), 1132 (s), 1058 (m), 1329 (s), 925 (m), 848 (w), 827 (m), 748 (w), 719 (m), 689 (m), 640 (m), 513 (w), 474 (w), 418 (w) cm⁻¹. ESI-MS (MeCN, *m/z*): 1344.5 [(Mo₆I₈)(OC₆H₃-2,4-(NO₂)₂)₆]²⁻, 1344.7). ¹H NMR (CD₃CN, 25 °C): δ = 0.97 (t, ³*J*_{H,H} = 7.33 Hz, 24 H), δ = 1.35 (sextet, ³*J*_{H,H} = 7.39 Hz, 16 H), δ = 1.60 (p, ³*J*_{H,H} = 7.97 Hz, 16 H), δ = 3.07 (m, 16 H), δ = 6.87 (d, ³*J*_{H,H} = 9.37 Hz, 6 H, 6-H), δ = 8.20 (d-d, ³*J*_{H,H} = 9.37 Hz, ⁴*J*_{H,H} = 2.95 Hz 6 H, 5-H), δ = 8.53 (d, ⁴*J*_{H,H} = 2.95 Hz, 6H, 3-H) ppm (Figure 25). UV/Vis (MeCN): λ_{max} [nm] (ϵ [L·mol⁻¹·cm⁻¹]) = 368 (151050).

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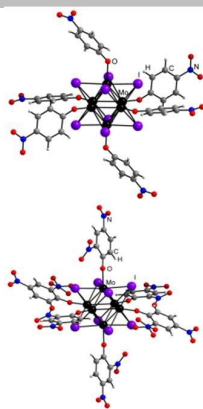
ARTICLE

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

New bright-red luminescent nitrophenolate complexes $(\text{Bu}_4\text{N})_2\{[\text{Mo}_6\text{I}_8](\text{OR})_6\}$ ($\text{R} = \text{C}_6\text{H}_4\text{-p-}(\text{NO}_2)$, $\text{C}_6\text{H}_3\text{-2,4-}(\text{NO}_2)_2$) have been prepared from $(\text{Bu}_4\text{N})_2\{[\text{Mo}_6\text{I}_8]\}$ and AgOR, characterized by X-ray analysis, UV-Vis and IR spectroscopies and ESI-mass spectrometry,



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Complexes of $\{\text{Mo}_6\text{I}_8\}$ with nitrophenolates: synthesis and luminescence