Luminescence of salts and copolymers containing the $(Mo^{II}{}_6Cl_8)^{4+}$ cluster

O. A. Adamenko, G. V. Loukova,* and V. A. Smirnov

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
14 Institutskii prosp., 142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 524 4401. E-mail: gloukova@cat.icp.ac.ru

The photophysical properties (absorption, emission) of the $(Bu_4N)_2[(Mo^{II}{}_6Cl_8)L_6]$ (L = CF_3COO^-, $CH_2{=}CHCOO^-$) cluster salts and $(Bu_4N)_2[(Mo^{II}{}_6Cl_8)(CF_3COO)_{6-n}]$—polyacrylic acid copolymers were studied. Both the cluster-containing monomers and corresponding copolymers phosphoresce intensely (τ ~0.2—0.4 ms at 77—300 K).

Key words: molybdenum clusters, cluster-containing polymer, charge transfer, luminescence.

One of the key problems of the modern macromolecular chemistry and photochemistry is the development of new photosensitive polymeric materials,[1—3] materials and molecular systems for the molecular electronics,[4,5] chemical sensors,[6] and photocatalysis.[7] The general principle of molecular design of such materials implies the inclusion of chromophoric units into the polymer with specified physicochemical and mechanical properties. Polymeric systems based on transition metal compounds are of special interest.[8] The photophysical and photochemical properties of such chemically stable macromolecular systems and materials can be controlled by insignificant changes in the coordination sphere of the central metal ion and the nature of the transition metal.

Previously[9] we studied a possibility of synthesis of stable compounds and copolymers containing the inorganic high-symmetry $Mo_6(\mu_3\text{-}Cl)_8$ cluster units: $(Bu_4N)_2[(Mo^{II}{}_6Cl_8)L_6]$, where L = Cl^- (**1**), CF_3COO^- (**2**), $CH_2{=}CHCOO^-$ (**3**), and $(Bu_4N)_2[(Mo_6Cl_8)(CF_3COO)_{6-n}]$—polyacrylic acid (**4**). These units are found in structures of many inorganic compounds. For example, they are incorporated in crystalline lattices of lowest chlorides of heavy transition metals and superconducting Chevrel phases,[10] clusters with internal chalcogenide ligands of the $PbMo_6S_8$ type. The structure of the $[Mo^{II}{}_6(\mu_3\text{-}Cl)_8]^{4+}$ internal cluster characteristic of compounds of this type is composed of a weakly distorted octahedron of six Mo atoms inscribed into a cube (Fig. 1). The octahedral homometallic $Mo^{II}{}_6$ core has eight internal μ_3-Cl ligands forming bridges at all faces of the octahedron and six external carboxylic residues in clusters **2** and **3** and copolymer **4**, each of which is coordinated to the molybdenum atom through one O atom. Thus, the resulting formula is $[(Mo^{II}{}_6Cl_8)(RCOO)_6]^{2-}$. The averaged Mo—Mo, Mo—Cl, and Mo—O bond lengths are[11] 2.59, 2.47, and 2.09 Å, respectively. In the $[Mo^{II}{}_6(\mu_3\text{-}Cl)_8]^{4+}$ internal cluster, the formally bivalent molybdenum atoms with the d^4 electron configuration efficiently interact with each other and Cl atoms. The high-symmetry structure of the Mo_6 cluster core is stable, and the core must participate in chemical transformations as a "collective metal fragment."

In this work, we studied the properties of the electronically excited states and changes occurring in the electronic structure of the $[(Mo_6Cl_8)L_6]^{2-}$ cluster when the terminal ligands are replaced in the monomer and the cluster units containing the polymerizing external ligands are introduced into the macromolecular matrix by radical copolymerization in the bulk.

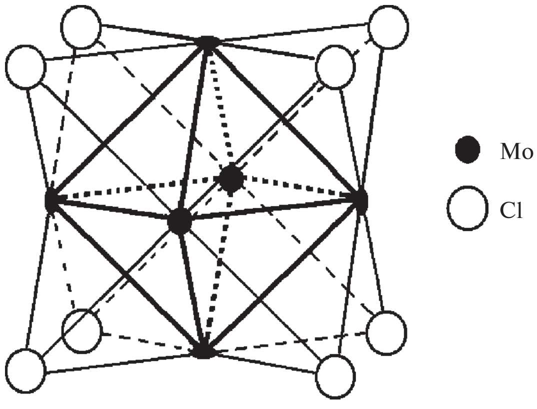

Fig. 1. Structure of the $(Mo^{II}{}_6Cl_8)$ internal cluster: the Mo atoms are in the vertices of the octahedron, and Cl atoms are in the vertices of the cube.

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Experimental

All procedures related to the preparation of samples of cluster salts and cluster-containing copolymers were carried out in an inert argon atmosphere using a standard Schlenk technique or a dry box filled with argon.[12] Argon was dehydrated by passing through a column packed with active molecular sieves 5Å.

All solvents used in syntheses were purified and successively dehydrated. Methylene chloride (Aldrich, 99.9%, A.C.S. HPLC) used for spectral measurements were successively dehydrated over P_2O_5 and CaH_2. Dioxane was boiled with concentrated HCl for 3 h, stored over KOH and refluxed for 1 h in a nitrogen atmosphere, distilled off, additionally dehydrated (or purified by staged distillation in an atmosphere of dried purified argon over $LiAlH_4$), and stored in an argon atmosphere over the Na wire. Clusters $(Bu_4N)_2[(Mo^{II}{}_6Cl_8)L_6]$, where L = Cl^- (**1**), CF_3COO^- (**2**), and $CH_2{=}CHCOO^-$ (**3**), were synthesized according to previously described procedures,[9,11] and their structure was confirmed[9,11] by XRD, NMR, optical, and IR spectroscopies, and electrochemical measurements. In the crystalline state compounds **1—3** are stable in an anhydrous inert atmosphere but decompose slowly (during several days) in air. These compounds are soluble in polar organic solvents and stable in weakly solvating solvents, such as CH_2Cl_2. Cluster-containing copolymer **4** is stable in solutions of anhydrous organic solvents and in air. Samples of cluster compounds **1—3** were recrystallized before use. Freshly prepared samples of cluster-containing copolymer **4** were used after thorough washing with CH_2Cl_2 and drying (~12 h) *in vacuo* (10^{-3} Torr, 20 °C).

Concentrations of the compounds in solutions were varied in a region of 10^{-5}—10^{-4} mol L^{-1}. Compounds **1—4** were stable during optical measurements. Absorption spectra of solutions were monitored on a Hewlett Packard 8452A Diode Array spectrophotometer, and luminescence spectra of crystalline and polymeric samples were recorded with a spectrofluorimeter.[13] Spectral measurements were performed using a previously described procedure.[14] Radiative lifetimes were determined from the single-exponential decrease of the emission intensity upon excitation with pulse light ($\tau < 10$ ns) from an N_2 laser with $\lambda = 337$ nm. The accuracy of absolute measurements of the lifetime of the excited states was ~10%, and that of the relative measurements was ~5%.

Results and Discussion

Absorption of solutions of cluster salts and cluster-containing copolymers. The absorption spectra of cluster salts with varied terminal ligands **1—3** are very close to each other: their spectra exhibit two poorly resolved shoulders at 300 and 347 nm along with a sharp decrease in absorption at 500 nm, $\varepsilon_{347} = 3100$ and $\varepsilon_{500} = 6$ L mol^{-1} cm^{-1} for compound **2** (Fig. 2). The absorption spectrum of cluster-containing copolymer **4** (dioxane solution) in the same spectral region (Fig. 3) is poorly resolved, although it resembles the spectra of initial clusters **1—3**. In the compounds with $[Mo_6(\mu_3\text{-}Cl)_8]^{4+}$ internal cluster, the first electron transitions are virtually indifferent to the replacement of the external ligands ($Cl^- \rightarrow CF_3COO^- \rightarrow CH_2{=}CHCOO^-$). The low-energy absorption of a solution of the copolymer is in the same spectral region (350—355 nm) as that of solutions of cluster salts **1—3**, but the second intense absorption band that appeared in the spectra of individual clusters **1—3** overlaps in the spectrum of copolymer **4** with the absorption of the polyacrylate matrix.

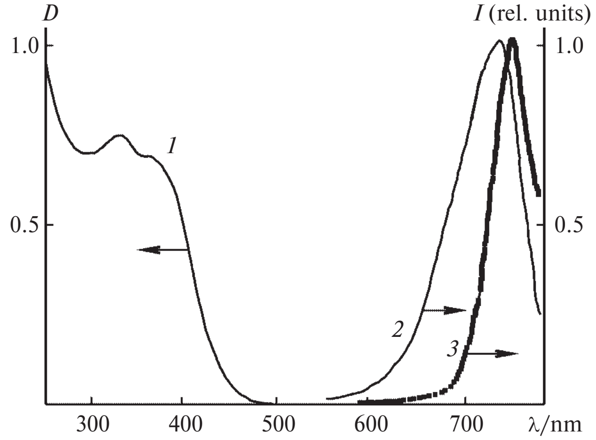

Fig. 2. Absorption spectrum of a solution of cluster **2** in CH_2Cl_2 at 291 K (*1*) and luminescence spectra of **2** in the polycrystalline state at 291 (*2*) and 77 K (*3*) (emission spectra were corrected).

Available quantum-chemical models often ignore the influence of orbitals of internal and especially outer-sphere ligands on the character of multicentered frontier MO in such cluster derivatives and the nature of Mo—Mo interactions in the cluster core. Nevertheless, in most cases calculations indicate that the LUMO in these clusters is mainly localized on the octametallic core.[15—18] Thus, for a series of molybdenum cluster derivatives, the

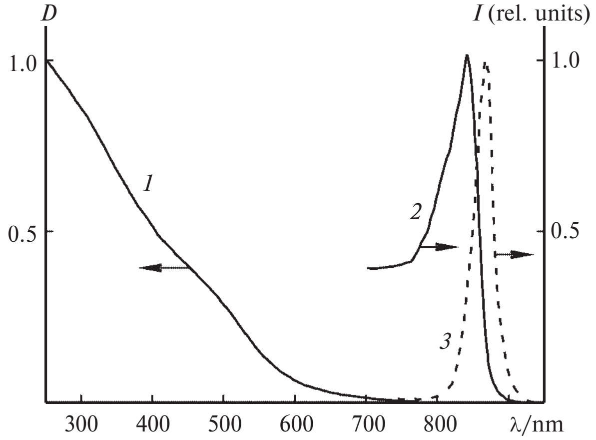

Fig. 3. Absorption spectrum of a solution of the $(Bu_4N)_2[(Mo_6Cl_8)(CF_3COO)_{6-n}]$—polyacrylic acid copolymer (**4**) in a dioxane—water mixture at 293 K (*1*) and luminescence spectra of **4** without a solvent at 293 (*2*) and 77 K (*3*) (emission spectra *2* and *3* were corrected).

intense optical absorption bands should be attributed to the allowed electron transition, namely, charge transfer from the ligands to the Mo^{II}_6 metallic core.

Luminescence of clusters 1—3 and copolymers 4 in a solution and in the polycrystalline or amorphous state. In the $[Mo_6(\mu_3\text{-}Cl)_8]^{4+}$ cluster derivatives, the low-energy absorption in the visible and near-UV regions results in the electronically excited states that lie higher than the radiative level. The samples of clusters **1—3** and copolymers **4** possess a very high stability toward the intense irradiation in the visible and near-UV regions.

Visible and UV irradiation of the samples of cluster salts **1—3** and copolymer **4** in both solutions and crystalline or amorphous states induces a fairly intense luminescence (with a considerable shift of the emission maximum relative to the absorption maximum, Table 1) in the 600—900 nm region. The observed luminescence lifetimes are very long for inorganic or coordination compounds[19—21]: τ = 0.2—0.4 ms (see Table 1). This can be caused, in particular, by the strong distortion of the high-symmetry structure of the cluster in the electronically excited states. The luminescence excitation spectra virtually coincide with the absorption spectra. The emission spectra are independent of the wavelength of the excitation light. The luminescence spectra (see Fig. 3) are very narrow (~5000 cm^{-1} at 77 K). The emission spectra contain no vibrational structure at either room or low temperatures. Since all bonding molecular orbitals in similar cluster molecules are occupied[15—18] and the ground electronic state in the molecules is singlet (S_0), the long radiation lifetimes indicate the *forbidden radiative transition* of the $T_1 \rightarrow S_0$ type. The character of the high- and low-lying excited electronic states does not basically change when the external ligand sphere is modified, so that the lowest excited state in clusters **1—4** must be triplet and emission should be the spin-forbidden electron transition to the ground state, *i.e.*, in the cases of similar clusters with the Mo^{II}_6 octahedral core, the radiative transition is attributed to phosphorescence.

Table 1. Luminescence of cluster compounds **1—3** and copolymer **4** at 293 (I) and 77 K (II)

Compound	$\lambda_{max}{}^a$/nm		τ/ms	
	I	II	I	II
1	728 (760)[b]	778	0.28 (0.18)[b]	0.3
2	713	765	0.3	0.4
3	706	760	0.26	0.4
4	706—713[c]	760	0.25	0.35

[a] The emission spectrum was corrected.

[b] A solution in MeCN.[21]

[c] A broad emission maximum.

The complete disappearance of the yellow color with the simultaneous appearance of the blue color is observed when cluster-containing copolymers **4** are aged (chemical degradation). Such aged Mo^{II}_6 copolymers completely lose the characteristic emission properties.

The intense long-lived emission spectra allow one to estimate the position of the lowest triplet level in both individual compounds **1—3** and cluster-containing copolymer **4**. The emission spectra of clusters **1—3** and copolymer **4** are not as isoenergetic as the absorption spectra. The replacement of the external ligand sphere in the $[(Mo_6Cl_8)L_6]$ cluster somewhat changes the position of luminescence maxima, in particular, the short-wave shift of the maximum decreases in the following series of the cluster compounds: **3** ≥ **2** > **1**. This order retains at room and low temperatures. The optical HOMO—LUMO gap in the compounds (energy of the intersystem crossing $T_1 \rightarrow S_0$) is fairly high ~1.6—2 eV. The excitation and luminescence spectra of cluster-containing copolymers **4** are broaden compared to the corresponding spectra of individual cluster salts **1—3**. The radiative lifetime of the excited state (λ_{exc} = 337 nm) in the series of compounds **1—4** changes insignificantly. At both low and room temperatures, the positions of emission maxima in the spectra of cluster-containing copolymers **4** virtually coincide with the positions of the corresponding luminescence maxima for monomer **3** and the phosphorescence lifetimes are slightly lower. For example, at 20 °C τ(**3**) = 0.27 ms and τ(**4**) = 0.25 ms, and at 77 K τ(**3**) = 0.40 ms and τ(**4**) = 0.35 ms. The difference in the photophysical properties of clusters **1—3** and cluster-containing copolymers **4** is insignificant, *i.e.*, the electronic optical properties of the clusters and their structure remain unchanged when they are introduced into the rigid matrix by radical copolymerization.

Thus, we were able to obtain new intensely luminescent compounds containing the octahedral homometallic Mo_6 core and the ligand sphere of two types: stable internal (of eight Cl ligands) and relatively labile external (of six different ligands, Cl, RCOO). The optical HOMO—LUMO gap (energy of the radiative transition $T_1 \rightarrow S_0$) for these molecules is ~1.6—2 eV. The electronically excited states in complexes **1—3** and copolymers **4** are predominantly localized on the high-symmetry Mo^{II}_6 core, and the radiative lifetimes are of the longest lifetimes known for inorganic or coordination compounds: τ = 0.2—0.4 ms. The character of excited states in clusters **1—3** and corresponding cluster-containing polyacrylate **4** was shown to remain unchanged.

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