Structures of hexanuclear molybdenum chalcocyanide complexes: electronic absorption spectra and DFT calculation

S. G. Kozlova, S. P. Gabuda, K. A. Brylev, Yu. V. Mironov, and V. E. Fedorov*

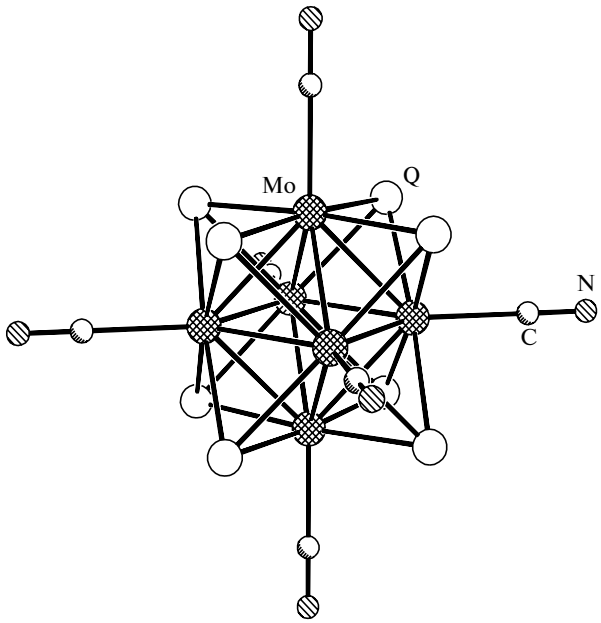
A. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 3 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation. Fax: +7 (383 2) 34 4489. E-mail: sgk@che.nsk.su

Electronic absorption spectra of aqueous solutions of the clusters $K_6[Mo_6Q_8(CN)_6]$ and $K_7[Mo_6Q_8(CN)_6]$ (Q = S, Se) were studied. The electronic structures of the $[Mo_6Q_8(CN)_6]^{6-}$ and $[Mo_6Q_8(CN)_6]^{7-}$ cluster anions were calculated by the DFT method. The absorption spectra observed agree with the results of calculation in the framework of the electron-dipole transition model.

Key words: electronic structure, octahedral molybdenum chalcocyanide clusters, Jahn—Teller effect.

Chalcogenide complexes $M_6Q_8L_6$ (M = Mo, W, Re; Q = S, Se, Te; L = Cl, Br) containing octahedral cluster fragments are typical of transition metals. New hexanuclear molybdenum chalcocyanide complexes $K_6[Mo_6Q_8(CN)_6]$ and $K_7[Mo_6Q_8(CN)_6]$ (Q = Se [1] and S [2]) containing different numbers of valent electrons (20 and 21) in the Mo_6 metal octanedron have recently been synthesized. The different number of valent electrons is manifested as different colors and magnetic properties of the compounds with even and odd numbers of electrons. These differences are caused, perhaps, by specific features of the electronic structure and the character of filling of the highest occupied and lowest unoccupied electronic levels in the clusters under consideration.

Information on the electronic structures of the complexes can be obtained from analysis of the UV-vis absorption spectra in combination with theoretical calculations of the electronic structure and electron transitions. In this work, we studied the electronic absorption spectra of the clusters $K_6[Mo_6Q_8(CN)_6]$ and $K_7[Mo_6Q_8(CN)_6]$ (Q = S, Se) and calculated the electronic structures of diamagnetic and paramagnetic clusters $[Mo_6Q_8(CN)_6]^{n-}$ (n = 6, 7) in the framework of the density functional theory (DFT) method.



Q = S, Se

Fig. 1. Structure of the cluster anion $[Mo_6Q_8(CN)_6]^{n-}$ (for the case Q = S, n = 7 in the $K_7[Mo_6S_8(CN)_6]\cdot 8H_2O$ complex).[2]

Experimental

The compounds $K_7[Mo_6Q_8(CN)_6]$ and $K_6[Mo_6Q_8(CN)_6]$ (Q = S, Se) were synthesized according to previously described procedures.[1,2] The structure of the cluster anion $[Mo_6Q_8(CN)_6]^{n-}$ is shown in Fig. 1. Since the paramagnetic $K_7[Mo_6Q_8(CN)_6]$ complexes are easily oxidizable, we studied only freshly prepared samples under the conditions of restricted contact of solutions with air. To record electronic absorption spectra, aqueous solutions with concentrations $5\cdot 10^{-5}$ (Q = Se) and $6.8\cdot 10^{-5}$ mol L^{-1} (Q = S) were used. Electronic absorption spectra were recorded on an Ultraspec 3300 Pro spectrophotometer at 290 K in a range of 200—1100 nm.

Results and Discussion

The electronic absorption spectra of aqueous solutions of the $[Mo_6Q_8(CN)_6]^{n-}$ complexes are presented in

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1598—1603, August, 2004.

1066-5285/04/5308-1661

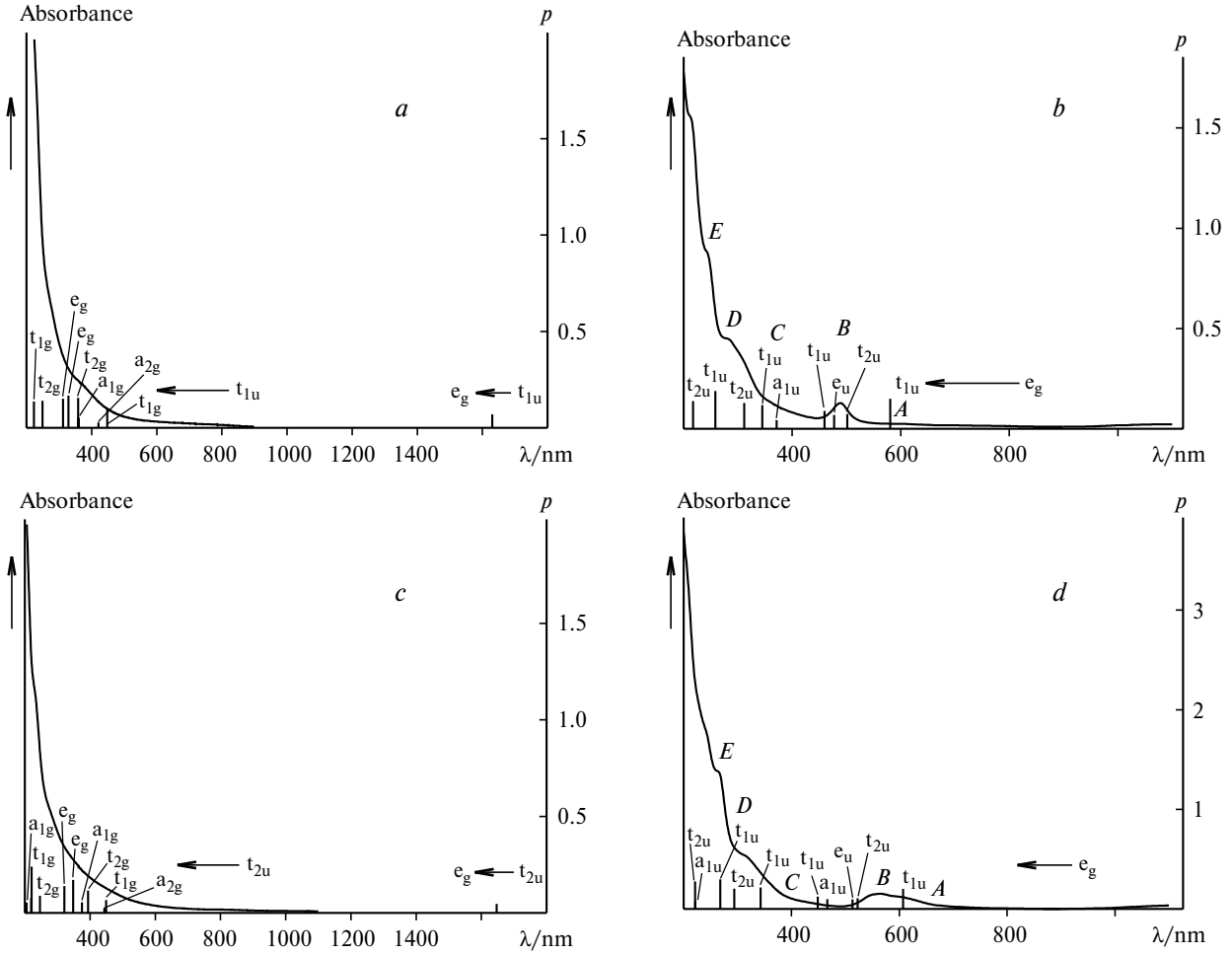


Fig. 2. UV-vis electronic absorption spectra and calculated intensities (p) of transitions for the $K_6Mo_6S_8(CN)_6$ (*a*), $K_7Mo_6S_8(CN)_6$ (*b*), $K_6Mo_6Se_8(CN)_6$ (*c*), and $K_7Mo_6Se_8(CN)_6$ (*d*) complexes (for points *A*—*E*, see notes in the text).

Fig. 2, *a*—*d*. The characteristic features of the spectra of the dia- and paramagnetic S complexes appear in the short-wave region compared to analogous spectra of the Se complexes. This fact can indicate a higher stability to oxidation of the thio complexes. Meanwhile, the spectra of the dia- and paramagnetic complexes differ sharply.

The spectra of the diamagnetic clusters (see Fig. 2, *a*, *c*) exhibit a gradual, rather smooth increase in the absorbance (from ~1000 nm) on going to the visible and UV regions. The maximum slope of the absorbance curve lies near 200 nm for both the S- and Se-containing compounds.

Unlike the diamagnetic clusters, the S- and Se-containing paramagnetic clusters are characterized by a single, sharply asymmetric broad absorption band, whose "head" (*B*) lies at shorter waves and a relatively broad region of a smooth decrease in the absorbance (*A*) is extended to a shorter-wave range (see Fig. 2, *b*, *d*). In addition, the spectra of both paramagnetic clusters exhibit a pronounced fine structure of the absorbance edge on going from the visible to UV region. The specific features of the fine structure are designated by letters *C*—*E* (see Fig. 2, *b*, *d*). The numeric parameters of the fine structure in the electronic absorption spectra of the paramagnetic $[Mo_6Q_8(CN)_6]^{7-}$ complexes (in nm) are presented below.

Complex	*A*	*B*	*C*	*D*	*E*
$[Mo_6S_8(CN)_6]^{7-}$	588	487	360	276	240
$[Mo_6Se_8(CN)_6]^{7-}$	600	560	402	310	263

Analysis of the electronic structure and the character of the Mo—Mo, Mo—Q, and Mo—L bonds in the molecular clusters $M_6Q_8L_6$ (see Fig. 1) is traditionally based on a formal oxidation state of constituent elements.[3,4] If the S and Se atoms in the $M_6Q_8L_6$ complexes have the highest negative oxidation state (−2), then the metal clusters Mo_6 contain 20 and 21 d electrons in $[Mo_6Q_8(CN)_6]^{6-}$ and $[Mo_6Q_8(CN)_6]^{7-}$, respectively.[4] These d electrons are assumed to participate in the formation of 12 covalent Mo—Mo bonds in the six-center metallic core due to overlapping of the electronic density of the 4d states. To

Table 1. Interatomic distances (R) in the $[Mo_6Q_8(CN)_6]^{n-}$ (Q = S, Se) complexes

Complex	R/Å					
	Mo—Mo		Mo—Q		Mo—C	
	calculation	lit. data[1,2]	calculation	lit. data[1,2]	calculation	lit. data[1,2]
$[Mo_6S_8(CN)_6]^{6-}$	2.725	—	2.491	—	2.280	—
$[Mo_6S_8(CN)_6]^{7-}$	2.738	2.666	2.505	2.457	2.305	2.204
$[Mo_6Se_8(CN)_6]^{6-}$	2.769	2.700—2.721	2.603	2.568—2.582	2.253	2.19—2.21
$[Mo_6Se_8(CN)_6]^{7-}$	2.779	2.700	2.614	2.562	2.276	2.17

form 12 two-electron covalent Mo—Mo bonds, 24 electrons are needed; therefore, for the complexes considered for both $n = 6$ and $n = 7$, the system of metal—metal bonds is electron-deficient. In this case, minimum differences in their electronic spectra can be expected. In fact, the above-presented experimental data of electronic spectroscopy demonstrate a sharp difference between the dia- and paramagnetic compounds. Thus, the model assuming the highest negative oxidation state for the S and Se atoms is not confirmed even at a qualitative level.

A more realistic model should take into account a low difference between the electronegativities of the molybdenum and chalcogen atoms, which corresponds to the predominantly covalent character of the Mo—Q bonds. We analyzed interactions in the systems under study in the framework of the quantum-chemical DFT method using the ADF 2000.02 program package.[5] The DFT method is most appropriate for calculation of multi-particle systems without any theoretical restrictions on the number of atoms,[6] which justifies its application for calculation of the electronic structure of the hexanuclear molybdenum complexes. We used the spin-restricted DFT method in which the model Hamiltonian of the density functional is presented by the sum of the local density functional LDA [7] and gradient exchange functional GGA.[8,9] The three-exponent Slater orbitals without a core potential were used as basis wave functions.[5] The electronic structures of the ground state of the high-symmetry (point group O_h) model systems $[M_6Q_8(CN)_6]^{n-}$ were calculated with complete geometry optimization[10] taking into account scalar relativistic effects in the zero-order approximation (ZORA method).[11] In the framework of the program package used, the electronic bonding energy of the $[Mo_6Q_8](CN)_6{}^{n-}$ compounds were calculated according to the formal reaction

$$6\,Mo + 8\,Q + 6\,C + 6\,N + n\,e^- \longrightarrow [Mo_6Q_8(CN)_6]^{n-}.$$

The optimized calculated and experimental values of the geometric parameters of the $[Mo_6Q_8(CN)_6]^{n-}$ complexes are presented in Table 1. The results obtained indicate a good qualitative agreement between the experiment and calculations. The differences observed can be explained by the influence of the crystal field on the geometry of the $[Mo_6Q_8(CN)_6]^{n-}$ complexes in crystals, whose structures have been described previously.[1,2]

The bonding energies of the $[Mo_6Q_8(CN)_6]^{n-}$ complexes are given below.

Complex	Bonding energy/eV	
	$n = 6$	$n = 7$
$[Mo_6S_8(CN)_6]^{n-}$	−184.49	−171.04
$[Mo_6Se_8(CN)_6]^{n-}$	−179.56	−166.44

The negative values of the energies indicate that complex formation is favorable, and the thio complexes are characterized by a higher stability than the selenium complexes. This agrees, on the whole, with the higher stability of the thio complexes observed experimentally and with the fact that the energies of electron excitation in $[Mo_6Se_8(CN)_6]^{7-}$ are lower than those in $[Mo_6S_8(CN)_6]^{7-}$ (see above).

The calculated charges on the atoms in the $[Mo_6Q_8(CN)_6]^{n-}$ complexes are presented in Table 2. They were obtained by the Hirshfeld method,[12] which reflects most correctly the electronegativity of atoms.[13,14] According to the data calculated by this method, the charge on the Mo atom is weakly positive, indicating the covalent character of the bonds of the molybdenum atoms.

The quantum-chemical calculations of molecular orbitals of the complexes under study show strong mixing of the 4d orbitals of molybdenum with the 3p and 4p orbitals of S and Se, which agrees with the earlier results for related systems.[3] For the diamagnetic thio and selenium molybdenum complexes, triply degenerate levels t_{1u} and

Table 2. Calculated atomic charges (q) in the $[Mo_6Q_8(CN)_6]^{n-}$ complexes

Complex	q/e			
	Mo	Q	C	N
$[Mo_6S_8(CN)_6]^{6-}$	0.1408	−0.3342	−0.1803	−0.5149
$[Mo_6S_8(CN)_6]^{7-}$	0.1116	−0.3936	−0.1899	−0.5636
$[Mo_6Se_8(CN)_6]^{6-}$	0.1038	−0.3060	−0.1858	−0.5101
$[Mo_6Se_8(CN)_6]^{7-}$	0.0761	−0.3715	−0.1951	−0.5523

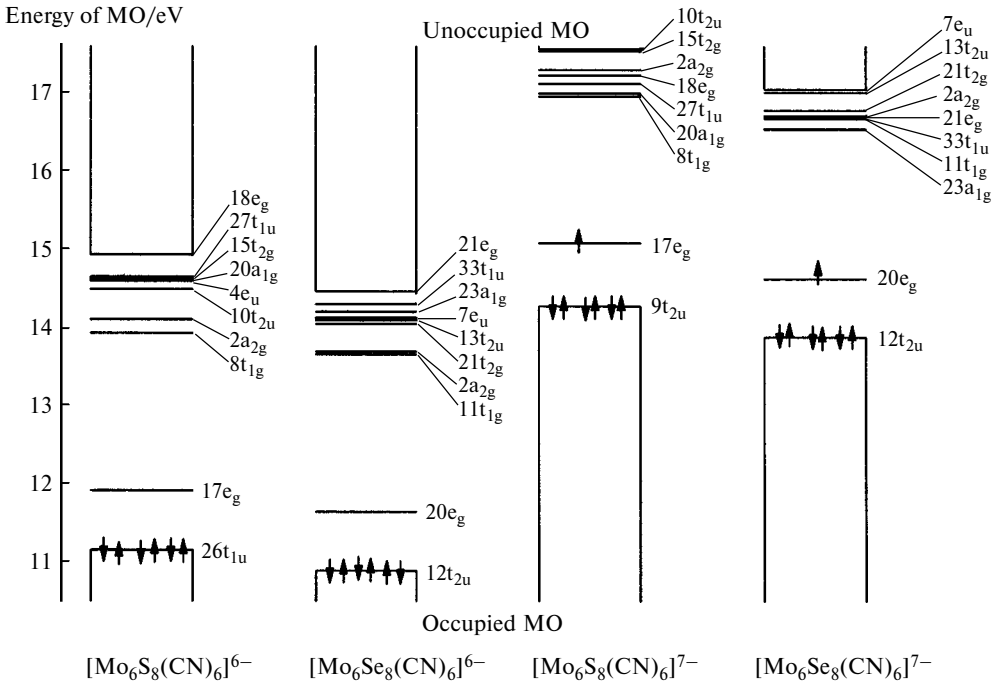


Fig. 3. Diagram of MO levels in the $[Mo_6Q_8(CN)_6]^{n-}$ complexes (Q = S, Se).

t_{2u} correspond to the highest occupied orbitals (Fig. 3). These orbitals consist predominantly of the 4d orbitals of molybdenum (~56 and ~80% for the S and Se complexes, respectively) and 3d and 4d orbitals of chalcogens (~35 and ~9%). The contribution of the p and s orbitals of the cyanide group is at most 6%. In the paramagnetic molybdenum complexes, partially occupied doubly degenerate levels e_g containing, as follows from the calculation, one unpaired electron are the highest occupied orbitals. The presence of one unpaired electron is independently confirmed by the data on magnetic susceptibility of the $K_7Mo_6Q_8(CN)_6 \cdot 8H_2O$ clusters.[1] The molecular orbitals e_g consist predominantly of the 4d orbitals of molybdenum (~60% for Q = S and Se each) and the 3d and 4d orbitals of chalcogens (~20% each). The lowest unoccupied molecular orbitals also have a mixed composition of the d, p, and s orbitals of molybdenum, chalcogens, and the cyanide group, and the contribution from the orbitals of the latter is minimum.

A good qualitative agreement of the calculated geometric parameters and the energies of formation with experiment made it possible to consider the results of calculations of the electronic structures of the molybdenum complexes as a model approximation for interpreting the electronic spectra. We believed that charge-transfer electron-dipole transitions are the most probable electron transitions due to the mixed character of molecular orbitals in the complexes. In addition, it was assumed that the electromagnetic irradiation of the complexes results in the excitation of electrons only from the highest occupied levels.

The results of calculations show that the electron transitions for the dia- and paramagnetic $[Mo_6Q_8(CN)_6]^{n-}$ complexes lie in the region of experimental values of transition energy and intensities. The fine distinctions in the spectra of the dia- and paramagnetic complexes can be attributed to specific features of filling the energy levels, the symmetry of the orbitals, and selection rules. As a whole, the $[Mo_6Q_8(CN)_6]^{n-}$ clusters under study are characterized by an inversion center (in the idealized approximation, their point symmetry group is O_h). Electron-dipole transitions for the diamagnetic complexes can occur only from the occupied odd triply degenerate level (t_{1u} and t_{2u}) to even levels e_g, t_{1g}, a_{2g}, *etc.* (see Fig. 2, *a*, *c*; Table 3).

For the paramagnetic $[Mo_6Q_8(CN)_6]^{7-}$ complexes, the most intense electron-dipole transitions are possible from the e_g level to the nearest lowest odd levels t_{1u}, t_{2u}, *etc.* (Table. 4; see Fig. 2, *b*, *d*). The intensities of the transitions were calculated in the approximation of electron-dipole transitions.[15] If we know the molecular orbitals of the electronic system

$$\Psi_s = \Sigma_m \Sigma_n C_m{}^n \varphi_m{}^n,$$

where $\varphi_m{}^n$ is the n-atomic wave function of the m-th atom (summation was performed over all atomic wave functions forming a molecular orbital Ψ, and $C_m{}^n$ are coeffi-

Table 3. Calculated electron transitions from levels $26t_{1u}$ and $12t_{2u}$ and their relative intensities (p) in the studied absorption region of the diamagnetic complexes $[Mo_6Q_8(CN)_6]^{6-}$

Transition*	λ /nm	p	Transition**	λ /nm	p
	$[Mo_6S_8(CN)_6]^{6-}$			$[Mo_6Se_8(CN)_6]^{6-}$	
$17e_g$	1630.2	0.071	$20e_g$	1647.1	0.047
$8t_{1g}$	447.65	0.099	$11t_{1g}$	449.6	0.067
$2a_{2g}$	421.1	0.028	$2a_{2g}$	443.8	0.023
$20a_{1g}$	359.9	0.052	$21t_{2g}$	393.9	0.116
$15t_{2g}$	358.3	0.156	$23a_{1g}$	375.3	0.055
$18e_g$	328.9	0.167	$21e_g$	347.9	0.171
$19e_g$	312.4	0.151	$22e_g$	320.9	0.140
$16t_{2g}$	249.2	0.140	$22t_{2g}$	246.1	0.089
$9t_{1g}$	223.1	0.137	$23t_{2g}$	220.5	0.164
			$12t_{1g}$	219.1	0.076
			$24a_{1g}$	205.2	0.054

Note. Here and in Table 4, the numbers in designation of transition show the number of molecular level.
* From level $26t_{1u}$.
** From level $12t_{2u}$.

Table 4. Calculated electron transitions from levels $17e_g$ and $20e_g$ and their relative intensities (p) in the studied absorption region of the $[Mo_6Q_8(CN)_6]^{7-}$ complexes

Transition*	λ /nm	p	Transition**	λ /nm	p
	$[Mo_6S_8(CN)_6]^{7-}$			$[Mo_6Se_8(CN)_6]^{7-}$	
$27t_{1u}$	580.7	0.150	$33t_{1u}$	607.15	0.200
$10t_{2u}$	501.3	0.074	$13t_{2u}$	522.6	0.108
$4e_u$	477.1	0.069	$7e_u$	513.3	0.095
$28t_{1u}$	459.4	0.090	$10a_{1u}$	466.5	0.099
$7a_{1u}$	371.3	0.044	$34t_{1u}$	448.8	0.125
$29t_{1u}$	344.9	0.118	$35t_{1u}$	342.9	0.215
$11t_{2u}$	311.5	0.129	$14t_{2u}$	293.9	0.203
$30t_{1u}$	258.2	0.188	$36t_{1u}$	267.9	0.296
$12t_{2u}$	217.4	0.138	$11a_{1u}$	221.5	0.079
			$15t_{2u}$	221.4	0.198

* From level $17e_g$.
** From level $20e_g$.

cients), then the intensities of electron transitions can be estimated by the formula

$$I \cong \Sigma[C_k C_i \langle\varphi_k|\hat{r}|\varphi_i\rangle]^2,$$

where k and i are indices characterizing the final and initial states of the system, $\hat{r}$ is the operator of the electron coordinate, and the dipole moment is $\langle\varphi_k|\hat{r}|\varphi_i\rangle \neq 0$ in the case when the principle quantum number of an electron l obeys a condition $\Delta l = \pm 1$.

For the paramagnetic complexes, an absorption band appears in the visible region, which can be assigned, based on the specific features (see above), with a good accuracy to the calculated electron transitions. In particular, the shoulder A (~600 nm) agrees well with the electron transition from level e_g to level t_{1u}. The B peak at ~490 nm for the S complex and at ~560 nm for the Se complex is described by a superposition of electron transitions from level e_g to levels t_{2u}, e_u, and t_{1u} (S complex) and t_{2u} and e_u (Se complex).

It is more difficult to interpret the sharp increase in the absorbance in the region of shortest wavelengths for both the diamagnetic and paramagnetic complexes (see Fig. 2, *a*—*d*). Probably, the one-electron approach used does not allow one to describe correctly probabilities of transitions in high-energy regions.

The present study showed that the electronic structures of the $[Mo_6Q_8(CN)_6]^{n-}$ complexes is characterized by strong mixing of the 4d orbitals of the Mo atom with the 3p and 4p orbitals of the S and Se atoms, indicating the predominantly covalent character of the Mo—S and Mo—Se chemical bonds. The calculated weakly positive charge on the Mo atoms, which varies from 0.07 in the paramagnetic complex $[Mo_6Se_8(CN)_6]^{7-}$ to 0.14 in the diamagnetic complex $[Mo_6S_8(CN)_6]^{6-}$ also agrees with this conclusion. It follows from the mixed character of molecular orbitals that the electronic absorption spectra under question are related to the electron-dipole transitions of electrons from the highest occupied orbitals (in which the contributions of the atomic Mo(4d) orbitals are ~60%) to the lowest unoccupied orbitals with prevailing contributions from the atomic S(3p) and Se(4p) orbitals. Similar transitions can arbitrarily be ascribed to transitions from the metal to chalcogen atoms; however, in this case, some contribution is made by electron transitions between the metal atoms, as well as the electron transfer from the chalcogen to metal atoms in the $[Mo_6Q_8(CN)_6]^{n-}$ complexes under study.

In this study, the problem of symmetry of the paramagnetic $[Mo_6Q_8(CN)_6]^{7-}$ complexes is left aside. The X-ray diffraction data[1,2] show that at room temperature the crystals of $K_7Mo_6Q_8(CN)_6 \cdot 8H_2O$ belong to the cubic crystal system and the cluster anions $[Mo_6Q_8(CN)_6]^{7-}$ are characterized by the point symmetry O_h. This conclusion confirms indirectly the results of calculations for the model of high-symmetry clusters that are in good correspondence with the experimental electronic spectra obtained at room temperature. However, it can be assumed that the symmetry of the system and the electronic spectra can change. This hypothesis is based on the fact that the highest occupied level of the system is the orbital-degenerated doublet e_g; therefore, the symmetry can decrease spontaneously due to the Jahn—Teller effect. In addition, the symmetry of the paramagnetic cluster anions $[Mo_6Q_8(CN)_6]^{7-}$ is sensitive to the spatial distribution of the electron density of the single unpaired electron over six sites of the $[Mo_6]$ octahedron and over eight vertices of the cubic cell of the ligands Q_8. The complex

behavior of this system is confirmed by the preliminary ESR study, according to which the signal from an unpaired electron is determined by the superposition of two states, whose contribution and amplitude change smoothly with the temperature change in an interval of 77—300 K.

The authors thank V. A. Nadolinnyi and V. F. Anufrienko for ESR data presented and help in discussion.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 02-03-32319, 02-03-32264, and 03-03-06114), the Integration Project of the Division of Chemistry and Materials Science of the Russian Academy of Sciences (Program 4.1-15), and the INTAS (Grant 00-00689).

References

1. Y. V. Mironov, A. V. Virovets, N. G. Naumov, V. N. Ikorskii, and V. E. Fedorov, *Chem. Eur. J.*, 2000, **6**, 1361.
2. K. A. Brylev, A. V. Virovets, N. G. Naumov, Yu. V. Mironov, D. Fenske, and V. E. Fedorov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2001, 1088 [*Russ. Chem. Bull.*, *Int. Ed.*, 2001, **50**, 1140].
3. H. Imoto, T. Saito, and H. Adachi, *Inorg. Chem.*, 1995, **34**, 2415.
4. T. Saito, *Adv. Inorg. Chem.*, 1997, **44**, 45.
5. *Amsterdam Density Functional (ADF) Program, Release 2000.02*, Vrije Universteit, Amsterdam (The Netherlands), 2000.
6. V. Kon, *Usp. Fiz. Nauk*, 2002, **172**, 336 [*Physics-Uspekhi*, 1001, **45** (Engl. Transl.)].
7. S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200.
8. A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.
9. J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822.
10. L. Verluis and T. Ziegler, *J. Chem. Phys.*, 1988, **88**, 322.
11. E. Van Lenthe, A. E. Ehlers, and E. J. Baerends, *J. Chem. Phys.*, 1999, **110**, 8943.
12. F. L. Hirshfeld, *Theor. Chim. Acta.*, 1977, **44**, 129.
13. F. Ogliaro, S. Cordier, J.-F. Halet, C. Perrin, J.-Y. Saillard, and M. Sergent, *Inorg. Chem.*, 1998, **37**, 6199.
14. F. M. Bickelhaupt, N. J. R. van Eikama Hommes, C. F. Guerra, and E. J. Baerends, *Organometallics*, 1996, **15**, 2923.
15. A. B. P. Lever, *Inorganic Electronic Spectroscopy*, 2nd ed., Elsevier, Amsterdam, 1984, 493 pp.

Received April 24, 2003;
in revised form November 3, 2003