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Electronic Spectra and DFT Calculations of Hexanuclear Chalcocyanide Rhenium Clusters

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The reaction of one-electron oxidation $[Re_6Se_8(CN)_6]^{4-} - [e]^- \rightarrow [Re_6Se_8(CN)_6]^{3-}$ is studied in liquid solution of the hexanuclear cluster compound $(NBu_4)_4[Re_6Se_8(CN)_6]$. The electronic absorption spectra and DFT calculations indicate that the reaction and the final compound $(NBu_4)_3[Re_6Se_8(CN)_6]$ production may be accomplished through the excited state of paramagnetic hexanuclear chalcocyanide rhenium clusters.

1. Introduction

In recent years the compounds containing hexarhenium cluster anions $[Re_6Q_8X_6]^{3-/4-}$ where Q = S, Se, and Te and X = Cl, Br, I, CN, NCS, etc., have been intensively investigated. Interest to these compounds is caused, in particular, by their luminescence characterized by long emission lifetimes, by their low electrochemical potentials, axial ligand kinetic lability and other remarkable physical properties including Jahn−Teller and relativistic effects.[1,2] Knowledge of the electronic structure of these complexes is very important, because it can explain the essential differences arising in the electronic spectra and luminescent behavior of compounds containing paramagnetic $[Re_6Q_8X_6]^{3-}$ or diamagnetic complexes $[Re_6Q_8X_6]^{4-}$.[3]

In the present work, the quantum-chemical calculations of UV−vis absorption spectra were carried out for the dia- and paramagnetic complexes $[Re_6Se_8(CN)_6]^{4-/3-}$ (Figure 1) in organic solutions of their $(NBu_4)_4$ salts.

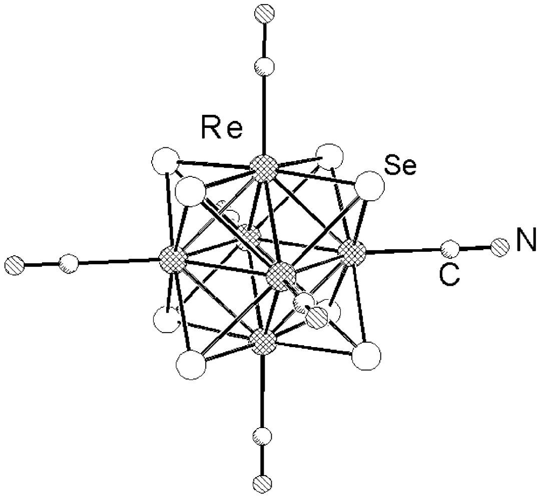

Figure 1. Structure of cluster anions $[Re_6Se_8(CN)_6]^{n-}$.

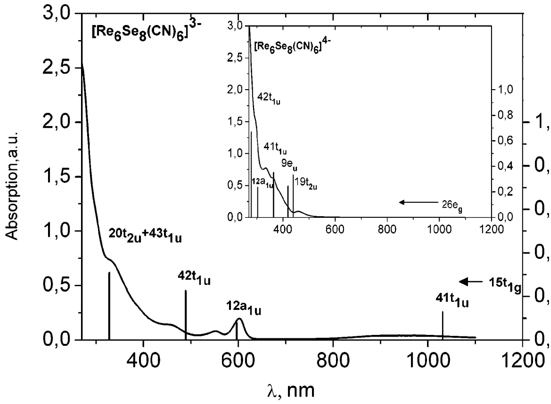

Figure 2. Observed UV−vis and near-infrared spectra of solutions of $(Bu_4N)_3[Re_6Se_8(CN)_6]$ and $(Bu_4N)_4[Re_6Se_8(CN)_6]$, and the calculated spectra for $[Re_6Se_8(CN)_6]^{3-/4-}$ complexes.

2. Experiment and Details of the Calculations

UV−vis absorption spectra were recorded on Ultraspec 3300 Pro spectrophotometer. Preparation of $(NBu_4)_4[Re_6Se_8(CN)_6]$ was described previously.[4−6] A dimethylformamide solution of diamagnetic compound $(NBu_4)_4[Re_6Se_8(CN)_6]$ was used with concentration 3×10^{-4} mol/L.

A well resolved absorption band at 460 nm (Figure 2) was observed for the diamagnetic complexes. The electronic absorption spectra have undergone essential changes after addition of bromic water (concentration 0.188 mol/L) to a tetraanion $[Re_6Se_8(CN)_6]^{4-}$ solution according to the reaction:

$$[Re_6Se_8(CN)_6]^{4-} + {}^1\!/_2Br_2 = [Re_6Se_8(CN)_6]^{3-} + Br^-$$

Bromine was added in double surplus relative to the quantity which is necessary for one-electron oxidation as follows from the above reaction. As a result, well resolved bands are centered at ∼ 950, 600, and 550 nm, as can be seen in the absorption spectrum depicted in Figure 2. Undoubtedly, the observed spectral changes are caused by oxidation of the tetraanion cluster and by formation of the paramagnetic $[Re_6Se_8(CN)_6]^{3-}$ cluster anion. This oxidation process is accompanied by a color change of the solution, where the red-orange solution becomes green. The chemical composition of the salts containing oxidized anions, corresponds to the known $(NBu_4)_3[Re_6Se_8(CN)_6]$ formula. Earlier this compound was prepared by oxidizing the same cluster anion with iodine in methanol.[7] Several paramagnetic crystals based on the $[Re_6Se_8(CN)_6]^{3-}$ anion have been isolated and characterized.[4−6] The received deposits were kept for a long time, giving at dissolution in water and organic solvents appropriate for the UV−vis absorption spectra of the oxidized form. Similar spectra were received by the one-electron oxidation of the diamagnetic complexes $[Re_6S_8Cl_6]^{4-}$.[1]

Density functional calculations (DFT) were carried out on

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TABLE 1: Optimized Geometries and Averaged Distances of the Structurally Characterized Compounds Containing Complexes $[Re_6Se_8(CN)_6]^{n-}$

	D(Re−Re), Å		D(Re−Se), Å		D(Re−C), Å	
complex	calcd	ref 16	calcd	ref 16	calcd	ref 16
$[Re_6Se_8(CN)_6]^{4-}$	2.675	⟨2.632⟩	2.553	⟨2.527⟩	2.125	2.11
$[Re_6Se_8(CN)_6]^{3-}$	2.671	⟨2.630⟩	2.550	⟨2.518⟩	2.113	2.10

different $[Re_6Se_8(CN)_6]^{3-/4-}$ models using the ADF2000 code.[8] In the present letter, we used the spin-restricted and spin-unrestricted formalisms of the DFT method. The local-exchange VWN correlation potential[9] was used for the local density approximation (LDA), Becke's nonlocal corrections[10] to the exchange energy, and Perdew's nonlocal corrections[11] to the correlation energy were added. The triple-ζ STO basic set without core-potential was used for all atoms.[8] The relativistic corrections for atoms were accounted by the scalar ZORA (zeroth-order relativistic approximation) method.[12] The electronic structure calculations for the all model systems $[Re_6Se_8(CN)_6]^{n-}$ were carried out with full optimization under the O_h and D_{4h} single point group symmetries. The calculations of the electronic binding energy[13,14] for the complexes have been performed for the formal reaction $6Re + 8Se + 6C + 6N + ne^- = [Re_6Se_8(CN)_6]^{n-}$.

The calculations of the electronic transitions and their probabilities have been carried out in the dipole approximation for systems with center of symmetry.[15] Additionally, it was supposed that observed spectra are related to electron excitations from the highest occupied molecular orbitals (HOMO) to the vacant, LUMO orbitals.

3. Results and Discussion

The optimized calculated and experimental geometrical parameters of the $[Re_6Se_8(CN)_6]^{n-}$ complexes are presented in Table 1. In the solid state these complexes are distorted; therefore, in Table 1 we report their averaged values. The reported geometrical results are in quite good agreement with the experimental data. The good agreement with experiment obtained for the geometrical parameters gives the basis for comparing the calculated electronic transitions of these complexes with the experimental electronic spectra.

According to the spin-restricted calculations of the electronic structure under the O_h symmetry, we obtained the ground HOMO states for both diamagnetic $[Re_6Se_8(CN)_6]^{4-}$ and paramagnetic $[Re_6Se_8(CN)_6]^{3-}$ complexes, which are characterized by the same orbital e_g symmetry. However, the occupation of the e_g state is different in the two cases: in the diamagnetic complex it is completely occupied with electronic configuration e^4_g, term $^1A_{1g}$ (singlet), and is partially occupied for the paramagnetic one, which is characterized by the electronic configuration e^3_g, term ^2E_g (doublet) (Figure 3). We should note that the obtained electronic structures of the complexes $[Re_6Se_8(CN)_6]^{3-/4-}$ agree with previous electronic structure calculations of the complexes $[Re_6Q_8X_6]^{3-/4-}$.[17]

Since the MO arrangements in the two cases are practically the same, it is evident that the electronic transitions for dia- and paramagnetic complexes should be similar according to the symmetry rules for systems with center of inversion.[15] However, the experimental electronic spectra of the oxidized complexes strongly differ from the spectra of the starting reduced complexes (Figure 2). It would be possible to assume that the Jahn−Teller effect operating in the paramagnetic complexes might complicate the electronic spectra.[17] The Jahn−Teller theory arguments that the adiabatic surface of an E-term octahedral system can holds either of the three types of minima: three equivalent minima corresponding to the elongation to D_{4h} symmetry ($D_{4h}{}^{el}$); three equivalent minima corresponding to the compression to D_{4h} symmetry ($D_{4h}{}^{com}$); and six equivalent minima corresponding to the elongation to D_{2h} symmetry.[18] Our calculations converged to these minima of different energy as: $E(D_{4h}{}^{comp}) < E(D_{2h}) < E(D_{4h}{}^{el})$ or -202.594 eV < -202.590 eV < -202.557 eV. However, the electronic structure for complexes obtained in $D_{4h}{}^{comp}$ symmetry also does not explain the experimental observation (Figure 3). The e_g level splits into $b^2{}_{1g}$ and $a^1{}_{1g}$, and the value of this splitting is about 0.3 eV, which essentially has not affected the energy levels ordering.

The contradiction between experiment and theory may be explained if we suppose that the one-electron oxidation reaction $[Re_6Se_8(CN)_6]^{4-} - [e] \rightarrow [Re_6Se_8(CN)_6]^{3-}$ proceed via some intermediate excited state. This excited state may be inferred from the fact that it is nearest in energy to the quartet state where two electrons occupy the e_g state ($e_g{}^2$), and one electron

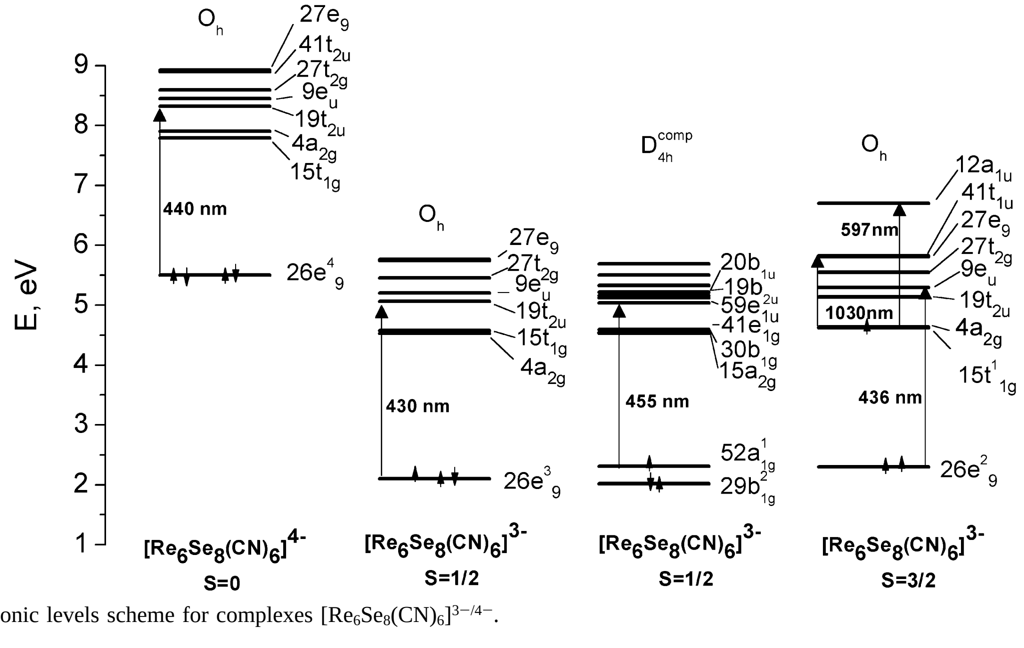

Figure 3. Electronic levels scheme for complexes $[Re_6Se_8(CN)_6]^{3-/4-}$.

TABLE 2: Binding Energy (*E*) for $[Re_6Se_8(CN)_6]^{n-}$ Models with Symmetry O_h

complex	spin	E, eV
$[Re_6Se_8(CN)_6]^{4-}$	0	−198.78
$[Re_6Se_8(CN)_6]^{3-}$	3/2	−200.49
$[Re_6Se_8(CN)_6]^{3-}$	1/2	−202.53

is excited to the lowest unoccupied molecular orbital (LUMO), giving rise to t^1_{1g} , as indicated in the scheme for O_h symmetry in Figure 3. The physical nature of appearance of this state may be related to the known “Laporte forbidden” transitions:[15] if during oxidation the term t_{1g} was occupied, the back transition to the ground-state e_g is forbidden.

The proposed model was calculated using the spin-unrestricted DFT method, and the result does not contradict the assumed model for the electronic distribution of the excited states, depicted in Figure 3. It is essential that for the given configuration the electronic transitions from a level of t_{1g} symmetry to the vacant levels may occur in the long-wave range as it is really observed in the experimental spectra (see Figures 2 and 3). In Table 2, we show the calculated binding energies of the discussed complexes. The data reported here confirm the possibility of existence of these complexes and also that the process of oxidation may occur via the excited state of the paramagnetic complexes.

We emphasize that the state with maximum spin ($S = {}^3/_2$) may be not realized. The measurements of the magnetic susceptibility and ESR estimated an effective magnetic moment ($1.9-2.08\ \mu_B$) slightly higher than the spin-only value of 1.73 μ_B expected for one unpaired electron.[3,5,7] A molecular distortion invoking the Jahn−Teller effect can explain the small magnetic moment, since e_g splits into $a_{1g} + b_{1g}$.

The observed good-resolved absorption bands in both vis and near-infrared ranges correlate well with the calculated spectra of excited states of cluster complexes. However, the comparison of calculated transitions with the experimental bands is complicated for both para- and diamagnetic systems in a UV wavelength interval 200−400 nm where the experimental absorption strongly increases most probably due to combination of excitation of electron transitions from the deep-laying energy levels, and due to effect of ionization. In these cases the one-electron approach does not allow one to describe correctly the transitions in the high energy region, where a multiplet picture may be necessary to invoke. Nevertheless, UV band of absorption of calculated transitions are in qualitative agreement with UV experimental band of absorption.

4. Conclusions

The offered distribution electrons not only explain the UV−vis absorption spectra of the paramagnetic complexes but also may give an explanation for the optical and luminescence properties of compounds containing similar rhenium cluster complexes. It is necessary to notice that the obtained results for the complexes $[Re_6Q_8X_6]^{3-/4-}$ (Q = Se) give a similar picture when Q = S, Te. The distinctions make evident in the fact the characteristic features of the spectra of dia- and paramagnetic S complexes are shifted to short wavelengths, and Te complexes are shifted to longer wavelengths as compared with the analogous spectra of Se complexes.

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References and Notes

(1) Gabriel, J. P.; Boubekeur, K.; Uriel, S.; Batail, P. *Chem. Rev.* **2001**, *101*, 2037.

(2) Arratia-Perez, R.; Hernandez-Acevedo, L. *J. Chem. Phys.* **1999**, *110*, 2529; **1999**, *111*, 168.

(3) Guilbaud, C.; Deluzet, A.; Domercq, B.; Molinie, P.; Coulon, C.; Boubekeur, K.; Batail, P. *Chem. Commun.* **1999**, 1867.

(4) Naumov, N. G.; Ostanina, E. V.; Virovets, A. V.; Schmidtman, M.; Muller, A.; Fedorov, V. E. *Russ. Chem. Bull.* **2002**, *51*, 866.

(5) Larina, T. V.; Ikorsky, V. N.; Vasenin, N. T.; Anufrienko, V. F.; Naumov, N. G.; Ostanina, E. V.; Fedorov, V. E. *Russ. J. Coord. Chem.* **2002**, *28*, 554.

(6) Fedorov, V. E.; Naumov, N. G.; Mironov, Yu. V.; Virovets, A. V.; Artemkina, S. B.; Brylev, K. A.; Yarovoi, S. S.; Efremova, O. A.; Paek, U-Hyon *J. Struct. Chem. (Engl. Transl.)* **2002**, *43*, 669.

(7) Bennett, M. V.; Beauvais, L. G.; Shores, M. P.; Long, J. R. *J. Am. Chem. Soc.* **2001**, *123*, 8022.

(8) Amsterdam Density Functional (ADF) program, Release 2000.02. Vrije Universteit: Amsterdam, The Netherlands, 2000.

(9) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys. (Paris).* **1980**, *58*, 1200.

(10) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(11) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(12) Van Lenthe, E.; Ehlers, A. E.; Baerends, E. J. *J. Chem. Phys.* **1999**, *110*, 8943.

(13) Baerends, E. J.; Branchadell, V.; Sodupe, M. *Chem. Phys. Lett.* **1997**, *265*, 481.

(14) Ziegler, T.; Rauk, A. *J. Theor. Chem. Acta* **1977**, *46*, 1.

(15) Cory, M. G.; Zerner, M. C. *Chem. Rev.* **1991**, *91*, 813.

(16) Cambridge Crystallographic Data Centre nos. CCDC 170981 and CCDC 170982.

(17) Deluzet, A.; Duclusaud, H.; Sautet, P.; Borshch, S. A. *Inorg. Chem.* **2002**, *41*, 2537.

(18) Bersuker, I. B. *Vibronic Interactions in Molecules and Crystals*; Springer-Verlag: New York, 1983.