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SPIN-ORBIT AND SOLVENT EFFECTS IN THE LUMINESCENT
 $[Re_6Q_8(NCS)_6]^{4+}$, $Q = S, Se, Te$ CLUSTERS: MOLECULAR SENSORS AND MOLECULAR DEVICES

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ABSTRACT

Relativistic time-dependent density functional (TDDFT) calculations including spin orbit interactions via the zero order regular approximation (ZORA) and solvent effects using the COSMO model were carried out on the $[Re_6Q_8(NCS)_6]^{4+}$ ($Q = S, Se, Te$) clusters. These calculations indicate that the lowest energy allowed electronic transitions are characterized by being of LMCT type. The calculated absorption maximum tends to shift to longer wavelengths as the face-capping chalcogenide ligand becomes heavier. Thus our calculations predict that the $[Re_6Te_8(NCS)_6]^{4+}$ cluster might be also luminescent. Due to the unusual properties exhibited by these and other isoelectronic and isostructural hexarhenium (III) chalcogenide clusters, hexamolybdenum halide clusters and hexatungsten halide clusters, we propose here the design of nanodevices, such as, molecular sensors and molecular nanocells for molecular electronics.

INTRODUCTION

In 2007, the Republic of Chile remained the world's leading copper producer and exporter, accounting for 36.5% of the total world mine production of copper. The country was also the world's leading producer of lithium (mostly in the form of lithium carbonate) and rhenium, accounting for about 38% and 46%, respectively, of global mine production. Chile was estimated to be the world's second ranked producer of arsenic (which was produced mostly as a byproduct of copper smelting) and was estimated to have accounted for about 19% of global production. The country was the world's third ranked producer of molybdenum and the fourth ranked producer of refined selenium, accounting for about 22% and 5.4%, respectively, of global production. In Chile, production of molybdenum, rhenium, selenium, and silver was either mostly or exclusively a byproduct of copper processing [1]. Thus, Chile has great potential to add value to its minerals through the design of molecular nanocells and molecular nanodevices.

The development of metal cluster-based inorganic and hybrid materials of technological interest calls for an understanding of their electronic structure, spectroscopy, photophysical and structural properties. The chemistry of the hexarhenium (III) chalcogenide cluster complexes is particularly attractive due to their synthetic versatility, photoluminescent and redox active properties [2-8,16-23]. The hexarhenium (III) chalcogenide clusters, the hexamolybdenum halide clusters and the hexatungsten halide cluster [9-25] complexes are characterized by showing long emission lifetimes (μs), electronic absorption spectra which are mostly characterized by intense LMCT transitions, emission spectra which arises from closely spaced excited states localized on the $[M_6(Q,X)_8]^{4+}$ cluster core with significant metal and bridging ligand content, and, all the cluster undergoes reversible oxidation process at a remarkable low potential, indicating that it can easily be switched between two stable oxidation states. In all cases we predicted that the terminal iodide ligands are the most kinetically labile and are the molecular precursor for functionalizing the hexanuclear clusters [19-25].

In this paper we report the calculated electronic structure, theoretical and experimental results on the optical properties of the $[Re_6Q_8(NCS)_6]^{4+}$; $Q = S, Se, Te$ clusters and we extend our analysis to propose the design of nanodevices based on the unusual properties of these type of heavy metal clusters.

COMPUTATIONAL DETAILS

Our current calculations for the $[Re_6Q_8(NCS)_6]^{4+}$ clusters were carried out by using the Amsterdam Density Functional (ADF) code [26,27]. The scalar and spin orbit relativistic effects were incorporated by using the zero order regular approximation (ZORA) [27,28]. All the molecular structures were fully optimized via analytical energy gradient method implemented by Verluise and Ziegler employing the local density approximation (LDA) within the Vosko-Wilk-Nusair parametrization for local exchange correlations [29,30]. We also used the GGA (Generalized Gradient Approximation) SAOP (Statistical

Average of Orbital model) exchange-correlation Potential) [31] functional which is specially designed for calculating optical properties, although it has a dubious asymptotic behavior.

The excitation energies were estimated by the spin orbit time-dependent perturbation density functional theory (TDDFT). Solvation effects were modeled by a conductor-like screening model for real solvents (COSMO) [32, 33] using acetonitrile (CH_3CN), as solvent. The cluster geometry optimizations and the excitations energies were calculated using a standard Slater-type-orbital (STO) basis sets with triple-zeta quality plus double polarization functions (TZ2P) for all the atoms.

RESULTS AND DISCUSSION

The results of the geometry optimization which includes spin-orbit interaction were performed in the vacuum. These are listed in Table 1 and the clusters molecular structure is depicted in Figure 1. All the calculated bond distances are in quite good agreement with the observed averaged experimental values [4], indicating that this method which includes scalar and spin-orbit effects is quite efficient for optimizing geometries of heavy metal clusters. These $24e [Re_6Q_8(NCS)_6]^{4+}$, $Q = S, Se, Te$ clusters ions exhibit a singlet ground state and are therefore diamagnetic. The calculated composition, location, and ordering of the occupied and unoccupied molecular orbitals of each cluster are very much alike. The lowest closely spaced manifold of unoccupied molecular orbitals indicates that these are mainly centered on the $[Re_6Q_8]^{2+}$ core, while the highest molecular orbitals (HOMO's) of all the cluster ions are mainly centered on the apical ligands. All the HOMO's are antibonding in character, this fact may suggest that these clusters may undergo facile electrochemical one-electron reversible oxidation at low half-wave values. The HOMO-LUMO gap decreases as the capping chalcogenide ligand becomes heavier (2.41, 2.38 and 2.24 eV), respectively.

As reported by Sasaki et al. the $[Re_6S_8(NCS)_6]^{4+}$ and $[Re_6Se_8(NCS)_6]^{4+}$ clusters show the characteristic absorption and emission spectra [4], but, the absorption and emission spectra of the heavier $[Re_6Te_8(NCS)_6]^{4+}$ clusters have not been yet reported. However, our results indicate that due to their electronic similarities with the lighter clusters, as shown in Table 2, these might be also luminescent. It is thus also interesting to see the effect on the absorption spectra by changing the capping halide and to extrapolate toward the possible consequences on their emission spectra. The manifold of closely spaced excited states localized in the $[Re_6Q_8]^{2+}$ core consist of more than three triplet excited states. The calculations of excitation energies involving LMCT transitions are in error by about 0.5 eV, as usual. By considering spin-orbit effects we should be careful in selecting the allowed excitations because of the double point group selection rules. Therefore, the calculated allowed electronic transitions are summarized in Table 3, where it can be noted the absorption maximum (λ_{max}) tends to shift to longer wavelengths as the face-capping halide ligand becomes heavier.

Table 1. Calculated and Observed Bond lengths (in Å).

	I. $\text{Re}_6\text{S}_8(\text{NCS})_6^{4+}$		II. $\text{Re}_6\text{Se}_8(\text{NCS})_6^{4+}$		III. $\text{Re}_6\text{Te}_8(\text{NCS})_6^{4+}$	
	Calc.	Exp. ^a	Calc.	Exp. ^a	Calc.	Exp.
Re-Re	2.62	2.59	2.64	2.62	2.68	?
Re-Q	2.42	2.40	2.53	2.52	2.71	?
Re-N	2.01	2.07	2.02	2.09	2.02	?
N-C	1.18	1.11	1.18	1.14	1.18	?
C-S	1.62	1.66	1.62	1.63	1.62	?

^a Ref. 4.

Figure 1. The optimized geometry of the octahedral $\text{Re}_6\text{Q}_8(\text{NCS})_6^{4+}$ clusters.

Table 2. Percent composition (%) of the frontier molecular orbitals of $[\text{Re}_6\text{Q}_8(\text{NCS})_6]^{4+}$, Q = S, Se, Te clusters [Other metal (s,p) contributions are less than 10%].

MO Level	Single point group irrep	Occup.	Double point Group irrep	% 5d Re	% Total S	%Total NCS
$[\text{Re}_6\text{S}_8(\text{NCS})_6]^{4+}$						
LUMO+4	$17t_{1u}$	0.0	$U_{3/2u} \oplus E_{1/2u}$	48.5	21.4	30.8
LUMO+3	$3e_u$	0.0	$U_{3/2u}$	42.8	57.9	0.0
LUMO+2	$9t_{2u}$	0.0	$U_{3/2u} \oplus E_{5/2u}$	59.1	26.4	14.6
LUMO+1	$2a_{2g}$	0.0	$E_{5/2g}$	100.0	0.0	0.0
LUMO	$7t_{1g}$	0.0	$U_{3/2g} \oplus E_{1/2g}$	56.4	14.7	24.4
HOMO	$4e_g$	4.0	$U_{3/2g}$	74.6	26.9	0.0
HOMO-1	$8t_{2u}$	6.0	$U_{3/2u} \oplus E_{5/2u}$	32.7	13.2	67.9
HOMO-2	$16t_{1u}$	6.0	$U_{3/2u} \oplus E_{1/2u}$	24.6	35.4	41.3
HOMO-3	$10t_{2g}$	6.0	$U_{3/2g} \oplus E_{5/2g}$	24.0	16.2	61.0
$[\text{Re}_6\text{Se}_8(\text{NCS})_6]^{4+}$						
LUMO+4	$10t_{2g}$	0.0	$U_{3/2g} \oplus E_{5/2g}$	40.9	56.1	0.0
LUMO+3	$5e_u$	0.0	$U_{3/2u}$	45.4	54.2	0.0
LUMO+2	$11t_{2u}$	0.0	$U_{3/2u} \oplus E_{5/2u}$	56.7	29.5	13.7
LUMO+1	$2a_{2g}$	0.0	$E_{5/2g}$	100.0	0.0	0.0
LUMO	$9t_{1g}$	0.0	$U_{3/2g} \oplus E_{1/2g}$	56.1	19.4	23.1
HOMO	$4e_g$	4.0	$U_{3/2g}$	71.7	30.8	0.0
HOMO-1	$10t_{2u}$	6.0	$U_{3/2u} \oplus E_{5/2u}$	32.7	14.3	66.0
HOMO-2	$8t_{1g}$	6.0	$U_{3/2g} \oplus E_{1/2g}$	4.1	55.8	38.5
HOMO-3	$19t_{1u}$	6.0	$U_{3/2u} \oplus E_{1/2u}$	20.9	40.1	40.5
$[\text{Re}_6\text{Te}_8(\text{NCS})_6]^{4+}$						
LUMO+4	$13e_g$	0.0	$U_{3/2g}$	52.4	41.8	7.4
LUMO+3	$5e_u$	0.0	$U_{3/2u}$	39.4	60.3	0.0
LUMO+2	$11t_{2u}$	0.0	$U_{3/2u} \oplus E_{5/2u}$	53.1	36.0	9.9
LUMO+1	$9t_{1g}$	0.0	$U_{3/2g} \oplus E_{1/2g}$	53.2	27.2	19.5
LUMO	$2a_{2g}$	0.0	$E_{5/2g}$	100.0	0.0	0.0
HOMO	$8t_{1g}$	6.0	$U_{3/2g} \oplus E_{1/2g}$	10.0	58.0	30.0
HOMO-1	$12e_g$	4.0	$U_{3/2g}$	63.9	38.2	0.0
HOMO-2	$10t_{2u}$	6.0	$U_{3/2u} \oplus E_{5/2u}$	34.9	16.7	48.3
HOMO-3	$19t_{1u}$	6.0	$U_{3/2u} \oplus E_{1/2u}$	14.5	56.9	27.3

Table 3. TD-DFT +SO excitation energies calculated in a continuum solvation model for acetonitrile.

Cluster	$\lambda_{\max}$ (nm)	f^a	Contributions ^b	Type transition
$\text{Re}_6\text{S}_8(\text{NCS})_6^+$	441 (430) ^c	0.002273	$25\text{E}_{g/2u} \rightarrow 63\text{U}_{3/2g}$ (79) HOMO-1 $\rightarrow$ LUMO+1	LMCT
	428 (330) ^c	0.009552	$61\text{U}_{3/2u} \rightarrow 41\text{E}_{1/2g}$ (25) HOMO-2 $\rightarrow$ LUMO	LMCT
	405 (290) ^c	0.007727	$61\text{U}_{3/2u} \rightarrow 63\text{U}_{3/2g}$ (45) HOMO-2 $\rightarrow$ LUMO+1	LMCT
$\text{Re}_6\text{Se}_8(\text{NCS})_6^+$	447 (455) ^c	0.000033	$74\text{U}_{3/2u} \rightarrow 32\text{E}_{5/2g}$ (96) HOMO-3 $\rightarrow$ LUMO+1	LMCT
	429 (340) ^c	0.007307	$74\text{U}_{3/2u} \rightarrow 32\text{E}_{5/2g}$ (67) HOMO-3 $\rightarrow$ LUMO+1	LMCT
	420 (310) ^c	0.000035	$46\text{E}_{1/2u} \rightarrow 47\text{E}_{1/2g}$ (63) HOMO-8 $\rightarrow$ LUMO	LMCT
$\text{Re}_6\text{Te}_8(\text{NCS})_6^+$	542	0.000341	$86\text{U}_{3/2u} \rightarrow 38\text{E}_{5/2g}$ (96) HOMO-2 $\rightarrow$ LUMO+1	LMCT
	485	0.000669	$37\text{E}_{5/2u} \rightarrow 38\text{E}_{5/2g}$ (51) HOMO-2 $\rightarrow$ LUMO+1	LMCT
	476	0.001803	$85\text{U}_{3/2g} \rightarrow 87\text{U}_{3/2u}$ (40) HOMO $\rightarrow$ LUMO+4	LMCT

^a Oscillator strength^b Values is $|\text{coeff.}|^2 \times 100$ ^c Experimental (Ref. 4.) **Figure 2.** The active molecular orbitals: the occupied (t_{2u} , HOMO-1) and the unoccupied molecular orbital (t_{1g} , LUMO) of the octahedral $\text{Re}_6\text{S}_8(\text{NCS})_6^+$ cluster.

The decrease in the HOMO-LUMO gap and the longer wavelength as the capping halide becomes heavier may influence the photoemissive characteristics, since, it has been observed that the emission lifetime and emission quantum yield values depend on the capping ligands in the isoelectronic $[\text{Re}_6\text{Q}_8\text{X}_6]^+$ cluster series [3]. Thus, our calculations and the electronic similarities with the other clusters studied here, suggest that $[\text{Re}_6\text{Te}_8(\text{NCS})_6]^+$ cluster might be also luminescent.

These studies have found that the 24e rhenium–chalcogenide clusters display long emissive lifetimes at the microsecond scale, significant quantum yields at room temperature, and, undergo reversible oxidation process at very low potentials. It has been observed that both terminal-and capping ligands induce a modulated dependence on the luminescence quantum yield [2-5].

Due to these interesting photophysical properties, these clusters can be viewed as potential candidates for its use as x-ray contrast agents, or as useful photoredox sensitizers towards electron acceptors, or as a novel class of metal cluster photoreceptors for chemical reactions induced by light [2-25]. Moreover, the synthetic versatility of the $[\text{Re}_6\text{Q}_8]^{2+}$ cluster core has allowed the synthesis of extended new porous materials that can be used as molecular sieves, or used as starting material for designing versatile chemical sensors for the detection of a large variety of volatile organic contaminants, (VOC), because due to the labile nature of the apical ligands they get substituted by VOC ligands, thus inducing an immediate color change at very low VOC concentrations, please see Scheme 1 [5-8].

Molecular Nanosensor

Scheme 1. Molecular Sensor. VOC (Volatile Organic Contaminant).

It is worth noting that all the diamagnetic and paramagnetic cluster ions are well characterized, and, all are luminescent at room temperature with significantly long emissive lifetimes and high quantum yields. All the clusters undergoes reversible oxidation process at a remarkable low potentials, indicating that they can easily be switched between two stable oxidation states, so they can store information and serve as a molecular memory devices [34], see Scheme 2. These interesting properties suggest that the reversible redox couples could be suitable nanoscale material for applications in optical and magnetic data storage, data communication systems, and solar energy conversion devices. We postulate here that the reversible redox couples could constitute suitable molecular nanocells for applications in molecular electronics [23], please see Scheme 3.

Molecular Nanocell

Scheme 2. Molecular Nanocell

Molecular Electronics

Scheme 3. Molecular Electronics.

CONCLUSIONS

Thus, our calculations and the electronic similarities between the other clusters studied here, suggest that $[\text{Re}_6\text{Te}_8(\text{NCS})_6]^{+}$ cluster might be also

luminescent. These strongly luminescent clusters and their congeners discussed here could be incorporated into polymeric matrices, deposited on silicon surfaces for designing new nanomaterials and thus we will be able to add value to our strategic minerals. We have opened new frontiers on rhenium cluster chemistry by discovering that the Re_3X_9 clusters are aromatic, thus, paving the way for new rhenium chemistry and new cluster functionalizations [35, 36].

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