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Electronic structure and molecular properties of the octacyanorhenate $[Re(CN)_8]^{3-}$ and $[Re(CN)_8]^{2-}$ complexes

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Abstract

We report scalar and four component relativistic density functional calculations on octacyanorhenate $[Re(CN)_8]^{2-}$ and $[Re(CN)_8]^{3-}$ complexes. The relativistic calculations predict that the molecular *g*-tensor of the paramagnetic $[Re(CN)_8]^{2-}$ complex is isotropic. The calculated optical electronic transitions for both complexes with a polarizable continuum model using a time dependent density functional (TDDFT)/B3LYP formalism suggest that the $[Re(CN)_8]^{3-}$ complex may distort towards dodecahedral geometry in solution. The electronic excitations of LMCT type of $[Re(CN)_8]^{2-}$ are displaced at very high wavelengths with significant oscillator strength values which is characteristic of Re compounds having luminescent behaviour. Thus, our calculations predict that $[Re(CN)_8]^{2-}$ could be luminescent.

1. Introduction

In recent years there has been great interest in the chemistry and properties of metal–cyanide complexes and clusters due to their possible use for an assortment of applications that include electronics, magnetism and catalysis [1–3]. Thus, the title metal–cyanide complexes are viewed as useful molecular precursors, which can be, incorporated into high-nuclearity clusters with adjustable magnetic properties and could be of utility in the design of cyano-bridged materials with potentially technological applications [1,4,5]. It is expected that the incorporation of third-row transition metal complexes may enhance the utility of such materials since these third-row transition metals possess higher-energy valence d orbitals that may induce interesting magnetic properties due to the effects of significant spin–orbit coupling [3–5].

In particular, the low-spin (d^2) $[Re(CN)_8]^{3-}$ complex have been structurally characterized [5]. The X-ray analysis of single crystals of the $[Re(CN)_8]^{3-}$ salt has indicated that adopt the square antiprismatic (D_{4d}) geometry, while the paramagnetic (d^1) $[Re(CN)_8]^{2-}$ complex has been postulated as the photo-oxidized product of $[Re(CN)_8]^{3-}$ [5]. The electronic structure and spectral assignments of the octacyanide rhenium complexes were discussed in 1963 by Perumareddi et al. [6] and Griffith et al. [7] using ligand field theory, and no other studies on these complexes are currently known. However, recent ab initio CASSCF and CASPT2 calculations for the assignment of the electronic spectra of the (d^2) $[Mo(CN)_8]^{4-}$, $[W(CN)_8]^{4-}$, and (d^1) $[Mo(CN)_8]^{3-}$ complexes have been reported by Hendrickx et al. [8,9].

In view of the current interest in metal–cyanide materials, we have investigated in this Letter, the electronic structure and spectral properties of above mentioned rhenium–octacyanide complexes using scalar and four component relativistic (DSW) calculations with the purpose of identifying relativistic and electron correlation effects on the ground and excited states properties of both complexes. We also performed time-dependent density functional (TDDFT) calculations including solvent effects to rationalize their optical spectra, ZORA [13] and DSW first-order perturbational calculations to estimate the molecular *g*-tensor of the (d^1) $[Re(CN)_8]^{2-}$ complex.

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2. Details of the calculations

The geometry optimizations of each complex in a vacuum were carried out using the Amsterdam density functional code (ADF) [10] developed by Baerends and co-workers [11–13]. Electron correlation was treated within the LDA approximation, and non-local Becke exchange [14] and Perdew correlation gradient corrections [15,16] were included in the calculations. Solvation effects were estimated in a polarized continuum model (PCM) [17–19] of acetonitrile solutions using the GAUSSIAN98 package [20] with the B3LYP functional, where for Re the 15 valence electrons quasirelativistic pseudopotentials of Andrae et al. [21] was employed, while for the C and N atoms, pseudopotentials using double-ξ basis sets with the addition of one d-type polarization function were employed [22]. The calculation of the excitation energies of each complex in a PCM were done at the B3LYP level using the time-dependent perturbation density functional theory approach (TDDFT) [23,24]. The TDDFT approach provides an alternative to computationally demanding multireference configuration interaction methods for the calculation of excitation energies [24].

We also performed Dirac scattered wave (DSW) calculations to estimate spin–orbit effects and spin-dependent properties. In this formalism, an effective Coulomb and exchange-correlation potential approximate the Dirac four-component wave function as a Slater determinant. [25,26,28–30]. The exchange-correlation potential is modeled by a relativistic local density potential according to MacDonald and Vosko [31,32]. For the calculation of the Zeeman magnetic splittings we start with a Dirac self-consistent four-component wave function Φ and we employ a first-order perturbation procedure. The effects of an external magnetic field is described by a relativistic perturbation Hamiltonian $H_1 = e\boldsymbol{\alpha}\cdot\mathbf{A}$, where $\boldsymbol{\alpha}$ is the 4×4 Dirac matrix composed of zeros on the diagonal, and the Pauli spin matrices in the off-diagonal positions, and, $\mathbf{A}$ is the electromagnetic four-vector potential. When the magnetic nuclei is in the presence of an external magnetic field $\mathbf{B}$, this four-vector potential is represented by $\mathbf{A} = 1/2(\mathbf{B}\times\mathbf{r})$, and, the Zeeman magnetic interactions are then described by the perturbation Hamiltonian $H_Z = 1/2e\boldsymbol{\alpha}\cdot(\mathbf{B}\times\mathbf{r})$ [28–30,33].

Table 1
Group relationships between the D_{4d} and D^*_{4d} point groups

Direct product for the D^*_{4d} double point group

D^*_{4d}	Γ_8	Γ_9	Γ_{10}	Γ_{11}
Γ_8	$A_1 + A_2 + E_3$	$E_1 + E_2$	$B_1 + B_2 + E_1$	$E_2 + E_3$
Γ_9		$A_1 + A_2$	$E_2 + E_3$	$B_1 + B_2 + E_3$
Γ_{10}			$A_1 + A_2 + E_3$	$E_1 + E_2$
Γ_{11}				$A_1 + A_2 + E_1$

Compatibility table between $D_{4d} \rightarrow D^*_{4d}$

	A_1	A_2	B_1	B_2	E_1	E_2	E_3
Γ_8	Γ_8	Γ_8	Γ_{10}	Γ_{10}	$\Gamma_9 + \Gamma_{10}$	$\Gamma_9 + \Gamma_{11}$	$\Gamma_8 + \Gamma_{11}$

The $\langle\Phi|H_1|\Phi\rangle$ matrix elements are evaluated in the basis spanning the 'two' rows of the double valued irreducible representations of the paramagnetic complex holding the single electron spin. Since the $\boldsymbol{\alpha}$ matrices are off-diagonal, the evaluation of the matrix elements involves products of the 'large' and 'small' components of the Dirac wavefunction. The resulting perturbation energies are then fitted to the usual spin Hamiltonian $H_{spin} = \mathbf{S}\cdot\mathbf{g}\cdot\mathbf{B}$, where a convenient parameterized value of $\mathbf{S} = 1/2$ is used to describe the ground state Kramers doublet, being $\mathbf{g}$ its associated g-tensor [28,29,33,34].

To facilitate the analysis and understanding of our scalar relativistic and Dirac scattered-wave calculations, we provide in Table 1 the group relationships between the single (D_{4d}) and double (D^*_{4d}) point groups.

3. Results and discussion

The results of the geometry optimization performed in a vacuum and in a polarized continuum of acetonitrile solutions (PCM) [17–19], are listed in Table 2. It can be seen from Table 2 that the removal of one electron in $[Re(CN)_8]^{3-}$ does not induce severe alterations in their geometries. Although, no structural data are yet available for the paramagnetic $[Re(CN)_8]^{2-}$ ion, its existence is extracted from the cyclic voltammogram in acetonitrile which indicates that $[Re(CN)_8]^{3-}$ oxidizes to $[Re(CN)_8]^{2-}$ at $E_{1/2} = 0.999$ V vs. $Cp_2Fe^{0/1+}$ [5]. The computed bond distances and bond angles, in both phases, are in reasonable agreement with the averaged experimental values of $[Re(CN)_8]^{3-}$ [5].

Table 2
Bond lengths (Å) and angles (°) of the $[Re(CN)_8]^{2-}$ and $[Re(CN)_8]^{3-}$ anions

	$[Re(CN)_8]^{2-}$		$[Re(CN)_8]^{3-}$		
	Calc.[a]	Calc.[b]	Calc.[a]	Calc.[b]	Expt.[c]
Distances					
Re–C	2.09	2.15	2.11	2.15	2.09
C–N	1.17	1.16	1.16	1.15	1.16
Angles					
C–Re–C	78.9, 113.5, 142.7	72.1, 112.7, 142.8	79.3, 112.9, 142.8	75.5, 113.5, 142.7	76.0, 114.3, 142.5
Re–C–N	178.3	180.0	177.5	180.0	177.7

[a] Gas-phase optimization with ADF method.
[b] Optimization in acetonitrile solutions with GAUSSIAN98+B3LYP.
[c] X-ray structure of $K_3[Re(CN)_8]\cdot 2MeCN$, see Ref. [5].