Spin−Orbit Effects on the Aromaticity of the Re₃X₉²⁻ (X = Cl, Br) Cluster Ions

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In our recent article (*Chem. Phys. Lett.* **2008**, *467*, 94−96), we reported the aromaticity via NICS calculations of the neutral Re_3Cl_9 and Re_3Br_9 clusters. Spin−orbit effects decrease their aromaticity due to the fact that the $5d_{3/2}$ spinors are mostly occupied and are more contracted than the scalar 5d orbitals. Here, we report that the title anions are also aromatic but, oppositely, spin−orbit effects increase the clusters' aromaticity due to the fact that the $5d_{5/2}$ spinors are now being populated and are more expanded than the scalar 5d orbital. All the clusters discussed here have larger induced diatropic ring currents than benzene.

1. Introduction

Frequently, the phenomenon of electronic delocalization is used for understanding the unusual stability of planar cyclic molecules that exhibit delocalized π-bonds. Initially, aromaticity was developed only for organic compounds, but today, this concept has been extended to a large number of compounds, such as inorganic and organometallic complexes,[1−4] as well as molecular metal clusters by a combination of photoelectron spectroscopy and ab initio calculations.[5] Recent experimental reports and theoretical calculations show evidence of d-orbital aromaticity in 4d and 5d transition metal oxide clusters; namely, $[M_3O_9]^{2-}$ (M = Mo, W).[6]

In recent years, we have seen a resurgence in the development of various evaluation criteria of aromaticity of a molecular system, Schleyer and co-workers developed the concept of nucleus-independent chemical shift (NICS), which was tested in the Al_4^{2-} dianion.[7,8] The NICS index has become a popular probe delocalization in a variety of molecules and is now well-accepted by the chemical community as an efficient way to evaluate aromaticity.[9,10] Negative NICS values in interior positions of rings or cages indicate the presence of induced diatropic ring currents, which is interpreted as aromaticity, whereas positive values at each point denote paratropic ring currents, which is interpreted as antiaromaticity.[9,10]

Many attempts to evaluate the electron delocalization in inorganic systems by magnetic criteria have been made in the last two decades,[1−6,10] in which a variety of theoretical calculations including scalar relativistic effects with pseudopotentials have been reported for estimating NICS values.[1−6,10,20,21] The first good evidence of metalloaromaticity was recognized more than a decade ago by Robinson in the Ga_3^{2-} ring due to two π electrons for delocalization, thus becoming isoelectronic with the aromatic triphenylcyclopropenium species.[20] A year later, the aromatic character of the gallium ring was supported by NICS calculations, in which the NICS(0) value is evaluated at the center in the plane, and the NICS(1) value is evaluated 1 Å´ out of the plane, (NICS(0) = −45.4 ppm and NICS(1) = −23.5 ppm) at the GIAO-B3LYP/6-311+G*// B3LYP/6-

TABLE 1: Cluster NICS Values (ppm)

Cluster	NICS (0)	NICS (1)
$Re_3Cl_9^{2-}$	−31.79[a]	−46.60[a]
	−33.03[b]	−58.44[b]
$Re_3Br_9^{2-}$	−31.99[a]	−48.33[a]
	−32.18[b]	−54.60[b]
Re_3Cl_9	−29.42[a,c]	−57.58[a,c]
	−28.07[b,c]	−53.58[b,c]
Re_3Br_9	−32.25[a,c]	−64.89[a,c]
	−29.77[b,c]	−57.26[b,c]
C_6H_6	−9.94[a]	−7.98[a]
	−9.91[b]	−7.89[b]

[a] Scalar ZORA calculations. [b] Scalar plus spin−orbit (ZORA + SO) calculations. [c] Ref 22.

311+G* level.[21] Another well-known case is the Al_4^{2-} dianion, for which the calculated total NICS(0) is −30.9 ppm. These results have expanded this concept to all-metal systems.[9] The observation of d-orbital aromaticity in neutral and charged $[M_3O_9]$ (M = Mo, W) clusters was nicely explained by Huang et al.[6]

Here, we report the calculated electronic structure and NICS values of the hypothetical $Re_3Cl_9^{2-}$ and $Re_3Br_9^{2-}$ ions, taking into account scalar and spin−orbit relativistic effects.

2. Computational Details

Our calculations for the $Re_3X_9^{2-}$ clusters were carried out by using the Amsterdam density functional code.[12] The spin orbit and scalar relativistic effects were incorporated via the zeroth order regular approximation (ZORA Hamiltonian).[12−14] All the molecular structures were fully optimized via the analytical energy gradient method implemented by Verluis and Ziegler employing the local density approximation within the Vosko−Wilk−Nusair parametrization for local exchange correlations.[15,16]

The nucleus-independent chemical shifts were calculated using the generalized gradient approximation OPBE functional,[17] which is specially designed for the calculation of chemical shifts. The clusters' geometry optimizations were calculated using a

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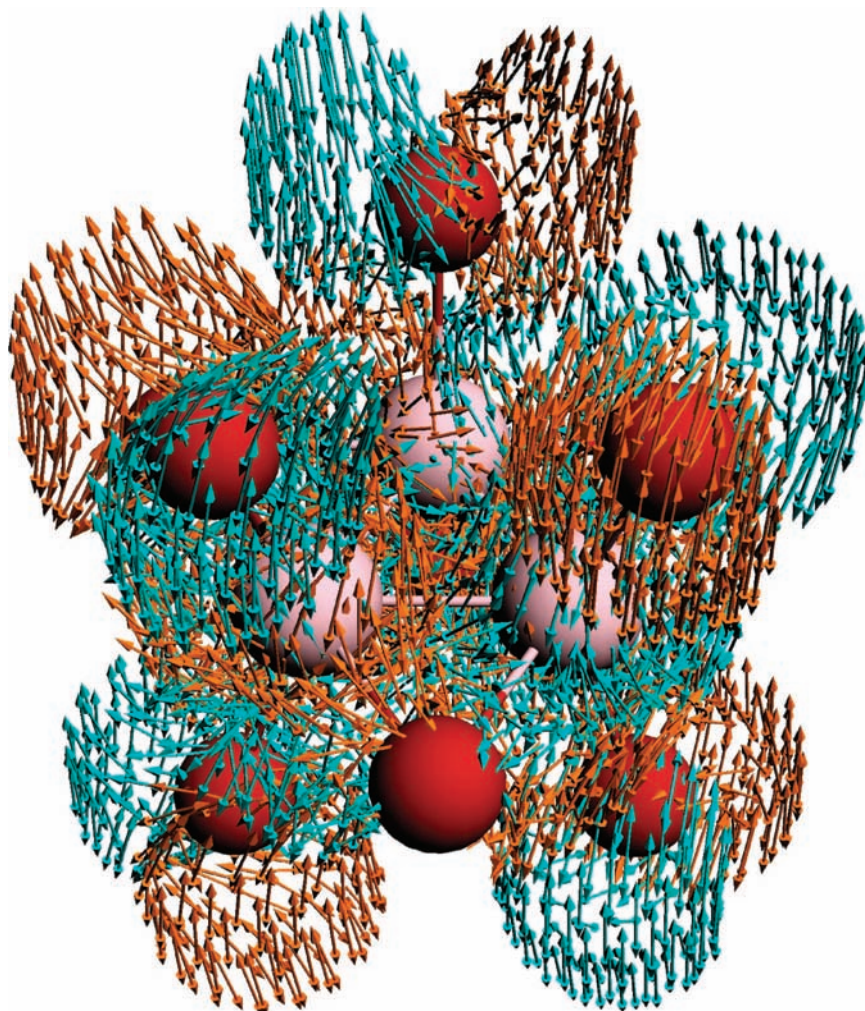
Figure 1. Spin magnetization density plot of the highest occupied molecular orbital ($E_{5/2}$, HOMO) of the $Re_3Br_9^{2-}$ cluster.

TABLE 2: Total Valence Populations (e/atom)

	l	j	Re_3Br_9	$Re_3Br_9^{2-}$
Re	s	1/2	0.600	0.611
	p	1/2	0.283	0.283
		3/2	0.433	0.435
	tot p		0.716	0.718
	d^a	3/2	2.523	2.640
		5/2	3.169	3.340
	tot d		5.692	5.980
	tot Re		7.008	7.309
Br_{ax}	s	1/2	1.942	1.953
	p	1/2	1.723	1.727
		3/2	3.350	3.472
	tot p		5.073	5.199
	tot Br_{ax}		7.015	7.152
Br_{pl}	s	1/2	1.951	1.965
	p	1/2	1.692	1.705
		3/2	3.319	3.385
	tot p		5.011	5.090
	tot Br_{pl}		6.962	7.055

^{a} The ratios of $j = l + 1/2$ to $j = l - 1/2$ population for $l = 2$ are 1.25 and 1.26, respectively.

standard Slater-type-orbital basis set with triple-ζ quality plus double polarization functions for the all the atoms.

We have also performed SCF-DSW four-component relativistic calculation on the neutral and charged cluster to extract the atomic spinor characters of the total valence population.[24] If the spinor density is defined as $\rho = \Psi^\dagger \Psi$, then, the spin

magnetization density is $m = \Psi^\dagger \sigma \Psi$, where σ is the vector of Pauli spin matrices. Thus, m allows us to visualize the spinor Ψ. Recently, a four-component relativistic formalism has been implemented to estimate aromaticity via the induced current density by Saue et al.[25]

3. Results and Discussion

The geometry optimization which includes spin−orbit interaction was performed in a vacuum, and according to our calculations, the $Re_3Cl_9^{2-}$ and $Re_3Br_9^{2-}$ clusters possess D_{3h} symmetry, as the neutral ones,[11,18,19] exhibiting a singlet and diamagnetic ground state. The molecular structures are characterized by having a triangle of Re atoms in one plane plus three bridges halide (μ_2) atoms in the same plane and six apical halide atoms (out of the plane).

The nuclear magnetic resonance parameters were calculated for a ghost atom and placed at the center of the ring. The NICS value is a negative of the isotropic magnetic shielding constant at the ghost atom. The NICS(0) values at the center in the plane of the ring are influenced by σ-bonds, whereas the NICS(1) values calculated 1 Å´ out of plane are affected by the π-bonds. As expected, d-orbital aromaticity requires significant d−d bonding interactions and should be found in early 4d/5d transition metal systems.[6] Here, we report theoretical evidence of d-orbital aromaticity in 5d transition metal clusters; namely, $[Re_3X_9]^{2-}$, X = Cl, Br.

As shown in Table 1, we obtained highly negative NICS values for the $Re_3Cl_9^{2-}$ and $Re_3Br_9^{2-}$ clusters, corresponding

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to their high 5d-delocalization. In Figure 1, we depict the HOMO spin magnetization density to visualize the $E_{5/2}$ spinor where the 5d delocalization can be clearly noted. Thus, the 5d spinor is fully determined by the spin magnetization density. Their NICS values are more negative than benzene. We also observe from Table 1 that the NICS(1) values are higher than NICS(0) with scalar ZORA calculations with and without spin−orbit (ZORA + SO) interaction, which indicates that the greatest contribution to the delocalization of both the hypothetical clusters $Re_3Cl_9^{2-}$ and $Re_3Br_9^{2-}$ is of π character. Interestingly, as can be seen from Table 1, the spin−orbit effects increase the aromaticity, which is opposite to the spin−orbit effects on the neutral clusters.

In the neutral clusters, the HOMO and HOMO-1 orbitals the $Re(5d^4)$ electrons occupy predominantly the $5d_{3/2}$ metal spinors. As shown in Table 2, the extra two electrons occupy a molecular spinor involved in strong metal−metal bonding. Roughly speaking, one electron is distributed as 0.35e in $5d_{3/2}$ and about 0.6e in $5d_{5/2}$; the other electron goes into the axial Br ligands. As observed in Table 2, we note that the increased population of the $5d_{5/2}$ spinors, whereas the $5d_{3/2}$ population increases to a lesser extent. We should note that in the nonrelativistic limit, the $(d_{5/2}/d_{3/2})$ ratio is required by symmetry to be $(l + 1)/l$; that is, equal to 1.50. Then, as indicated in Table 2, the ratio of $d_{5/2}$ to $d_{3/2}$ population is larger for the ionic clusters, thus confirming that the $5d_{5/2}$ population increased. In relativistic theory, it is known that 5d orbitals split into the $5d_{3/2}$ and $5d_{5/2}$ spinors,[24] the $5d_{3/2}$ spinors being more contracted that the scalar 5d orbitals. Thus, the delocalization and NICS values decrease and the aromaticity decreases, whereas in the $Re_3Cl_9^{2-}$ and $Re_3Br_9^{2-}$ clusters, the same portions of the extra two electrons now occupy the $5d_{5/2}$ spinors, which are more expanded than the scalar 5d orbital, and thus, the aromaticity increases.[23,24]

4. Conclusions

Our calculations have shown that both the hypothetical $Re_3Cl_9^{2-}$ and $Re_3Br_9^{2-}$ clusters exhibit aromaticity and that spin−orbit effects increase aromaticity due to the fact that the $5d_{5/2}$ spinors increased their population with respect to the neutral clusters, and these are more expanded than the scalar 5d orbitals.

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