28-29 September 2023,
Kragujevac, Serbia

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2nd International Conference on Chemo and Bioinformatics
ICCBIKG_2023

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International Conference on Chemo and BioInformatics

BOOK OF PROCEEDINGS

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Sponsored by

2nd International Conference on Chemo and BioInformatics, Kragujevac, September 28-29, 2023, Serbia.

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Proofreading:

Marijana Dimović

Publisher:

Institute for Information Technologies, University of Kragujevac, Serbia, Jovana Cvijića bb, 2023

Press:

„Grafo Ink“, Kragujevac

Impression:

120 copies

CIP - Каталогизација у публикацији - Народна библиотека Србије, Београд

54:004(048)(0.034.2)
57+61]:004(082)(0.034.2)

INTERNATIONAL Conference on Chemo and BioInformatics (2 ; 2023 ;
Kragujevac) Book of Proceedings [Elektronski izvor] / 2nd International Conference on
Chemo and BioInformatics, ICCBIKG 2023, September 28-29, 2023 Kragujevac,
Serbia ; [editors Zoran Marković, Nenad Filipović]. - Kragujevac : University,
Institute for Information Technologies, 2023 (Kragujevac : Grafo Ink). - 1 USB
fleš memorija ; 1 x 2 x 6 cm

Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Tiraž
120. - Bibliografija uz svaki rad.

ISBN 978-86-82172-02-4

a) Хемија -- Информациона технологија -- Зборници b) Биомедицина --
Информациона технологија -- Зборници

COBISS.SR-ID 125908489

Table of contents

Relativistic DFT calculation and their effect on the accuracy of results

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DOI: 10.46793/ICCBI23.653R

Abstract: This study explores the significance of density functional theory (DFT) calculations with relativistic effects for two ethylenediaminetetraacetate (edta) type complexes: *trans*(O_5)-[M(eddadp)]- (M = Rh^{3+}, Co^{3+}). Relativistic effects affect the electronic structure of a molecule and, thus, its chemical and spectroscopic properties. With the use of scalar relativistic corrections (SR-ZORA), as implemented in the ADF package, with the B3LYP functional, the TZP basis set and the COSMO solvation model, structural analyses show improved predictions for the geometries of both complexes. In the case of the Rh^{3+} complex, the differences in metal-ligand bond lengths with and without the relativistic effects were small. In the case of the Co^{3+} complex, the changes in metal-ligand bond lengths due to the relativistic effects were slightly more pronounced. Compared to experimental values, excitation energies are better when including relativistic corrections, especially for the Rh^{3+} complex. These results indicate the importance of relativistic DFT calculations for heavy element compounds.
Keywords: DFT, Relativistics, ZORA, $[Rh(eddadp)]^-$, $[Co(eddadp)]^-$

1. Introduction

Chemistry and physics are tightly interconnected, and fundamental ideas and laws of physics often find rapid application in chemistry. Einstein's theory of special relativity, proposed in 1905, was one of the most significant breakthroughs in physics. For a long time, it was thought this theory would not significantly impact chemistry. This view changed in the 1970s when it was realized that (nonrelativistic) Schroedinger quantum mechanics yields results on molecular properties that differ considerably from experimental results, particularly for heavy element compounds [1]. As the atomic number increases, the electron velocities approach a significant fraction of the speed of light, leading to a relativistic increase in mass and by that changing the energies of orbitals [1]. As a result, relativistic effects influence compounds' electronic structure, leading to deviations from nonrelativistic predictions [2]. Irregularities in the trends in

the periodic table of elements, such as the yellow color of gold [3], the melting point of mercury [4], and the voltage of lead batteries [5], are attributed to relativistic effects.

While successful for many chemical systems, traditional nonrelativistic (NR) Density Functional Theory (DFT) calculation falls short in describing the behavior of heavy element-containing compounds by neglecting the relativistic effects [6]. Thus, relativistic corrections for heavy-element compounds are essential to model their properties accurately.

In this study, we aim to highlight the importance of relativistic DFT calculations through a comparative analysis of the structural and spectroscopic properties of two ethylenediaminetetraacetate (edta) - type complexes with respect to the atomic number of the central metal ion. Specifically, we investigated the *trans*(O_5)-[M(eddadp)]$^-$ (M = Rh^{3+}, Co^{3+}; eddadp^{4-} = ethylenediamine-N,N-diacetate-N'N'-dipropionat) complexes (**Figure 1**) and compared results with available experimental data.

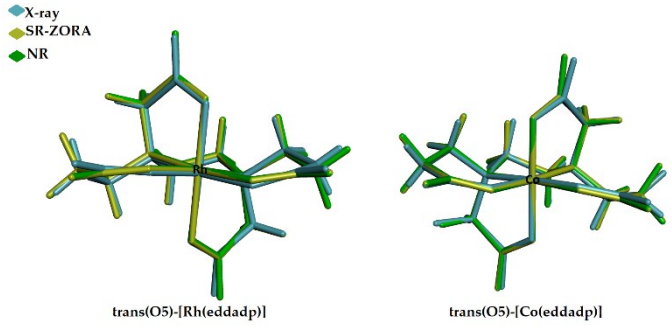

Figure 3. Overlay of X-ray structure, SR-ZORA optimized and NR optimized structures.

2. Methods

All DFT calculations were carried out by using the Amsterdam Density Functional (ADF) code, version 2017.01 [7], incorporating scalar relativistic (SR) corrections via the Zero Order Relativistic Approximation (ZORA) [8]. The hybrid B3LYP functional [9] and the all-electron TZP basis set for all atoms were used. Calculations were carried out with water as a solvent using the Conductor-like Screening solvation model (COSMO) [10].

The Ligand Field Density Functional Theory (LFDFT) [Ref] was used to study the excited state energies. LFDFT calculations were performed on the structures determined by geometry optimizations and X-ray structures. The SR-ZORA-B3LYP/TZP(COSMO-water) level of theory was used for LFDFT calculations.

The calculations were also performed without the SR corrections to see the influence of the relativistic effects (NR calculations).

3. Results and discussions

Structural data for X-ray, SR-ZORA-optimized, and NR-optimized geometries are presented in Table 1. For both complexes, SR-ZORA improves the accuracy of the structural predictions. The metal-ligand (M-L) bond lengths in both complexes are shorter when SR calculations are employed. M-L bond lengths are similar with and without relativistic effects for the Rh^{3+} complex, while these differences are more

pronounced for the Co^{3+} complex. However, the root mean square deviation (RMSD) of all atoms between X-ray and optimized structures, Table 1, indicates that relativistic effects cause slightly more distinct structural changes in the case of the Rh^{3+} complex.

The energies of the excited states calculated by LFDFT corresponding to the spin-allowed transitions are given in Table 2 and compared with the available experimental values. Relativistic effects are important for the accuracy of computed transitions, Table 2. In the case of a unified effect of relativistic on geometry and excited state energies, compared to NR calculations, MAE shows a significant improvement in the case of the Rh^{3+} complex.

Table 1. Comparison of structural data of X-ray and optimized geometries.

	Refs.		X-ray	SR-ZORA	NR
trans(O5)-[Co(eddadp)]$^-$	[11]	average (Co-N)	1.948	1.986	1.992
		average (Co-O)[a]	1.926	1.926	1.932
		average (Co-O)[b]	1.892	1.910	1.915
		RMSD (Å)[c]		0.167	0.168
trans(O5)-[Rh(eddadp)]$^-$	[12]	average (Rh-N)	2.022	2.078	2.082
		average (Rh-O)[a]	2.045	2.070	2.073
		average (Rh-O)[b]	2.008	2.048	2.050
		RMSD (Å)[c]		0.199	0.203

[a] Average length of M-O (M = Rh, Co) of equatorial oxygen; [b] Average length of M-O (M = Rh, Co) of axial oxygen [c] RMSD is the root mean square deviation of all atoms overlaid X-ray and DFT optimized geometries.

Table 2. Energies (10^3 cm^{-1}) of the singlet excited states from LFDFT and comparison with available experimental data.

Transition[c]	*trans*(O5)-[Co(eddadp)]$^-$					*trans*(O5)-[Rh(eddadp)]$^-$				
	x-ray[a]	x-ray[b]	Opt[a, d]	Opt[b, e]	Exp.[13]	x-ray[a]	x-ray[b]	Opt[a]	Opt[b]	Exp.[13]
$^1A_{1g}\rightarrow{}^1T_{1g}$	15.59	15.44	14.94	14.49	18.55	26.18	26.18	23.53	22.54	26.45
	16.36	16.20	15.04	14.60		26.79	26.30	23.95	22.98	
	16.46	16.25	15.16	14.77		28.07	27.73	25.16	24.12	29.85
$^1A_{1g}\rightarrow{}^1T_{2g}$	23.12	22.93	22.03	21.53		33.55	33.44	30.67	29.52	
	23.98	23.79	22.76	22.24	25.64	34.06	33.82	31.10	30.06	33.89
	24.89	24.67	24.45	23.92		36.27	36.03	33.96	32.80	
MAE[f]	2.03	2.22	3.03	3.50		0.85	0.96	3.12	4.17	

[a] SR-ZORA LFDFT calculations; [b] NR LFDFT calculation; [c] Oh point group assignment; [d] SR-ZORA geometry optimization[e] NR geometry optimization; [f] Mean average error in 10^3 $cm^{-1.}$

3. Conclusions

In conclusion, scalar-relativistic corrections in DFT calculations are crucial for accurately predicting the chemical properties of heavy-element complexes. By taking the effects of relativity into account, we can obtain more accurate results and better understand the properties of these molecules.

Acknowledgment

This research is funded by the Ministry of Science, Technological Development and Innovation, Republic of Serbia, Grants: No. 451-03-47/2023-01/200122, 451-03-47/2023-01/200026. This research was supported by the Science Fund of the Republic of Serbia, #7750288, Tailoring Molecular Magnets and Catalysts Based on Transition Metal Complexes – TMMagCat.

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