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ORIGINAL PAPER

Computational analysis of tris(1,2-ethanediamine) cobalt(III) complex ion: calculation of the ^{59}Co shielding tensor using LF-DFT

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Abstract The ligand-field density functional theory (LF-DFT) approach is employed for calculations of the ^{59}Co nuclear magnetic resonance (NMR) shielding tensor of all four diastereoisomers ($\lambda\lambda\lambda$, $\lambda\lambda\delta$, $\lambda\delta\delta$, and $\delta\delta\delta$) of tris(1,2-ethanediamine) cobalt(III) complex ion, $[Co(en)_3]^{3+}$. The obtained values split into two groups according to the point group of the diastereoisomers. The influence of the individual ring conformation on the ^{59}Co NMR shielding tensor is small. Comparisons with results obtained with conventional DFT and experimental values are given. The good agreement between calculated and experimental values demonstrates the validity of LF-DFT for calculating the shielding tensor for transition-metal complexes.

Keywords Computational chemistry · Conformation · Coordination chemistry · Density functional theory · NMR spectroscopy · Ligand-field DFT

Introduction

The tris(1,2-ethanediamine) cobalt(III) ion, $[Co(en)_3]^{3+}$, is a chiral coordination cation, thoroughly studied over the years both experimentally and theoretically. Theoretical studies were in the past usually performed with the molecular mechanics (MM) approach [1]. Since the mid 1990s, the tools of density functional theory (DFT) have successfully been employed to calculate a molecular structure and related chemical and physical properties of similar molecules [2, 3].

As already pointed out by Corey and Bailar [4] in the first publication dealing with conformations of chelate rings, $[Co(en)_3]^{3+}$ is inherently chiral through the helical arrangements of the nonplanar bidentate ligands, which can adopt either the δ or the λ conformation (Fig. 1). For this coordination unit, the combination of δ/λ twists of the three five-membered rings yields four diastereoisomers in one absolute configuration (Δ or Λ): $\lambda\lambda\lambda$, $\lambda\lambda\delta$, $\lambda\delta\delta$, and $\delta\delta\delta$ [5]. Homoconformational isomers belong to the D_3 point group, while for the heteroconformational complexes the symmetry is reduced to C_2.

As part of our efforts to determine the influence of the chelate ring conformation on various properties in this type of coordination compounds [6], in the present work we investigated the importance of the ligand conformation on the ^{59}Co NMR shielding tensor (σ).

It is well known that ^{59}Co was one of the first nuclei for which a dependency of the resonance frequency was observed [7], and it therefore occupies a special place in the history of NMR. The large shielding tensor of this nucleus makes ^{59}Co NMR spectroscopy a highly sensitive probe for the electronic structure, geometrical parameters, and reactivities of cobalt complexes [8] and permits experimental determination of not only the isotropic shift but also the components of the anisotropic shielding tensor [9]. Although commonly accessible quantum chemistry programs, such as ADF [10–12], enable calculation of the magnetic shielding tensor, in this work we present the ability of ligand-field density functional theory (LF-DFT)

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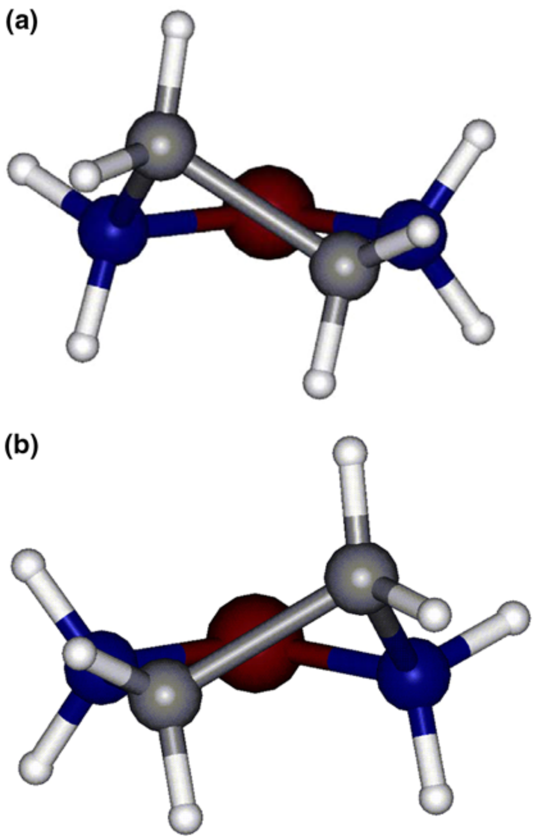

Fig. 1 Stereochemistry of the five-membered 1,2-ethanediamine chelate ring: **a** δ conformation and **b** λ conformation

to calculate the shielding tensor for transition-metal complexes [13]. The concepts used in LF-DFT [14, 15] are familiar to all chemists and give chemical insight into the problem under study. All the quantities involved in calculations are obtained in a nonempirical way, thus this model allows not only interpretation but also the prediction of properties of coordination compounds. Furthermore, comparisons with results obtained with ADF are given.

Results and discussion

In this work we investigated the four diastereoisomers of $[Co(en)_3]^{3+}$ species in one absolute configuration (Δ), as enantiomers have identical stabilities. Our recent investigation on $[Co(en)_3]^{3+}$ [6] showed good ability of DFT to distinguish different stabilities of the diastereoisomers. Results obtained by DFT calculations with different functionals (LDA [16], PW91 [17], and BP86 [18, 19]) were shown to be consistent amongst themselves as well as with the results obtained by MM calculations. The minimum on the potential-energy surface corresponds to the Δ-$\lambda\lambda\lambda$ isomer of the $[Co(en)_3]^{3+}$ coordination unit in all calculations. In agreement with these theoretical arguments, the majority of X-ray structure determinations on tris(ethylenediamine) cobalt complex ions have revealed a Δ-$\lambda\lambda\lambda$ or Λ-$\delta\delta\delta$ configuration, according to the Cambridge Structural Database (CSD) [20]. All the calculations showed the same order of stability: $\lambda\lambda\lambda > \lambda\lambda\delta > \lambda\delta\delta > \delta\delta\delta$ [6]. Structural parameters for optimized minimum-energy structures revealed that the local density approximation (LDA) geometry is in excellent agreement with the X-ray structure [21]. Generalized gradient approximation (GGA) results showed an overestimation of the bond lengths. Comparison of the structural parameters between isomers obtained by the same calculation procedure showed that bond lengths and angles are almost the same for all the isomers, and the difference is in the sign of the N–C–C–N torsion angle.

Since it is known that the chemical shift of the cobalt atom is sensitive to a small perturbation of the environment, in the present work we investigate the importance of ligand conformation on the ^{59}Co NMR shielding tensor. This is of interest because, to our knowledge, solid-state NMR has been done for only one diastereoisomer (Δ-$\lambda\lambda\lambda$) [21]. On the other hand, the solution spectra give only the dynamic average of the equilibrium mixture, since the energy difference between the isomers is very small, and there is rapid interconversion of the λ and δ conformations [22].

The reference value of the shielding tensor ($\sigma_{ii}^{\mathrm{ref}}$) for aqueous $K_3[Co(CN)_6]$ was calculated and taken into account for each method [13]. Paramagnetic, σ_{ii}^{p}, and diamagnetic, σ^{d}, parts of the absolute shielding tensor, σ, and isotropic relative shielding tensor, δ_{iso}, for each of the isomers are reported in this work (details of the computational procedure are given in the "Methodology" section):

$$\sigma_{ii} = \sigma_{ii}^{\mathrm{p}} + \sigma^{\mathrm{d}}, \tag{1}$$

$$\delta_{ii} = \sigma_{ii}^{\mathrm{ref}} - \sigma_{ii}, \tag{2}$$

$$\delta_{\mathrm{iso}} = \frac{1}{3}\mathrm{Tr}(\delta). \tag{3}$$

The results for the calculated relative shielding tensor on the X-ray geometry of Δ-$\lambda\lambda\lambda$ $[Co(en)_3]^{3+}$ [21] obtained by LF-DFT as well as comparison with experimental values are given in Table 1. The good agreement between the values demonstrates the validity of our approach.

The chemical shifts of the cobalt centers computed for all investigated isomers of $[Co(en)_3]^{3+}$ in solution are listed in Table 2.

The results of the calculations make clear that the isomers that belong to the same point group have similar values of σ, while there is a slightly larger difference between the isomers of different symmetry. Therefore, the obtained values split into two groups according to the point group of the molecule (D_3 or C_2). To check the reliability

Table 1 LF-DFT and experimental shielding tensors for Δ-$\lambda\lambda\lambda$ $[Co(en)_3]^{3+}$

	δ			δ_{iso}	Ω
LF-DFT[a]	7,363	−4	2	7,563	609
	−4	7,368	1		
	2	1	7,972		
Exp. [21]	7,301	0	0	7,202	285
	0	7,290	0		
	0	0	7,016		

δ relative shielding tensor, δ_{iso} isotropic relative shielding tensor, Ω the span

[a] Geometry of the complex ion is taken from ref. [21]

Table 2 LF-DFT results of the ^{59}Co shielding tensor for different isomers of $[Co(en)_3]^{3+}$

Isomer	σ^p			σ^d	δ_{iso}
$\delta\delta\delta$	−14,951	0	0	1,685	7,858
	−0	−14,951	0		
	0	0	−15,241		
$\lambda\lambda\lambda$	−14,817	0	0	1,704	7,908
	0	−14,817	0		
	0	0	−15,717		
$\delta\lambda\lambda$	−15,179	−549	0	1,697	7,457
	−549	−14,166	0		
	0	0	−14,632		
$\delta\delta\lambda$	−15,206	−812	0	1,697	7,519
	−814	−14,208	0		
	0	0	−14,749		

σ^p paramagnetic, σ^d diamagnetic part of the absolute shielding tensor, δ_{iso} isotropic relative shielding tensor

of these reasonable and intuitive results, we performed conventional DFT calculations for σ using the ADF program package [10–12]. Comparison of the two different methods is presented in Table 3.

Although somewhat different splitting between the δ_{iso} values for distinct isomers were obtained, the general trend is confirmed (Table 3). It seems that LF-DFT slightly overestimates while ADF slightly underestimates the δ value in comparison with the experimental value obtained for $[Co(en)_3]^{3+}$ in aqueous solution ($\delta = 7{,}146$ ppm [23]). Still, considering the large range of possible ^{59}Co NMR shifts [9], the experimental result is of the same order as the calculated values, although of course not comparable to any of the diastereoisomers, due to their rapid interconversion in solution [22].

Table 3 Comparison of isotropic relative shielding tensor values (δ_{iso}) for $[Co(en)_3]^{3+}$ isomers obtained from LF-DFT and ADF calculations

Isomer	δ_{iso} (LF-DFT)	δ_{iso} (ADF)
$\lambda\lambda\lambda$ (X-ray)	7,563	7,088
$\delta\delta\delta$	7,858	6,823
$\lambda\lambda\lambda$	7,908	6,822
$\delta\lambda\lambda$	7,457	6,572
$\delta\delta\lambda$	7,519	6,780

Conclusions

It can be concluded that the influence of the individual ring conformation on the ^{59}Co NMR shielding tensor is negligible, but the latter depends on the species symmetry. Furthermore, these calculations show that the paramagnetic shielding tensors, σ^p, are very sensitive to the geometries. This is very useful for confirming shielding tensors for a given geometry. The good agreement between calculated and experimental values demonstrates once more the validity of LF-DFT for calculating the shielding tensor. Its applicability to relatively large molecules as well as for other *d* elements is especially noteworthy.

Methodology

LF-DFT, a DFT-based ligand-field theory, was used as a tool for parameter-free calculation of optical and magnetic properties of transition-metal complexes [14, 15]. The LF-DFT method has been extended for the calculation of a variety of molecular properties, e.g., zero-field splitting and spin–orbit coupling [24], magnetic exchange coupling, *g*- and *A*-tensor [25], etc. Recently, we have presented a scheme for calculation of ^{59}Co shielding tensors within the framework of this approach [13], and here we give just an overview.

We are working in a LF approach and therefore treat the complex as an "ionic molecule." We interpret the residual paramagnetism of the ^{59}Co complexes like in the work of Griffith and Orgel [26] as arising from the electrons in orbitals being predominantly cobalt 3*d* orbitals and thus interpret it as behavior of cobalt *d* electrons. Therefore, we work in the basis of the ten cobalt 3*d* spin orbitals. The description of the multiplet structure and energies of states in this given basis are obtained with LF-DFT [14, 15]. Mapping the energies of the microstates in the LF manifold from DFT single-determinant calculations to the corresponding LF microstates allows us to estimate all Racah and LF parameters in a least-squares sense.

The interaction of a nucleus with a nonzero magnetic moment with an external magnetic field H is $-\vec{\mu}\cdot\vec{H}$. The field at the nucleus is modified by the magnetic moment induced in the electronic system by the external field. Hence, we write the actual first-order interaction with H as

$$E = \mu_0 \overrightarrow{\mu} \cdot (1 - \sigma) \cdot \overrightarrow{H}, \tag{4}$$

where μ_0 is the vacuum permeability constant and σ is the shielding tensor, which is also known as a chemical shift or as a screening constant. This, in general anisotropic, shielding tensor can be split into a so-called paramagnetic and diamagnetic part [27] as

$$\sigma = \sigma^{\mathrm{d}} + \sigma^{\mathrm{p}}. \tag{5}$$

σ^{p} originates from the nuclear hyperfine interaction and σ^{d} from the diamagnetic part of the Hamiltonian for the interaction of the electronic system with magnetic fields. For calculating σ we evaluate the expectation value of the corresponding operators over the ground state. Therefore, we use a double-perturbation approach like the authors of [28]: we perturb the ground-state wavefunction and the operators. The ground-state wavefunction is written as a nonrelativistic wavefunction without magnetic field, perturbed to first order by the Zeeman interaction. For the operator, we start from the Dirac equation with eliminated small component to obtain the electron-spin-dependent term. Then, we add the magnetic perturbation, but take the nonrelativistic limit, and thus our working equations are nonrelativistic. We need to calculate the energetic interaction coming from the interaction of μ with the magnetic field, so finally we are just interested in upcoming parts with a vector potential A and of first order in μ. Rearranging the terms leads to the following working equations for the paramagnetic shielding tensor:

$$\sigma_{\alpha_{\alpha'}} = -2k_{\mathrm{u}} g_{\mathrm{e}} \frac{\beta_{\mathrm{e}}^2}{\hbar^2} \left\langle \overline{r^{-3}} \right\rangle \sum_{n \neq 0} \frac{\langle \Psi_0 | \Omega_\alpha | \Psi_n \rangle \langle \Psi_n | Z_{\alpha'} | \Psi_0 \rangle}{\varepsilon_n - \varepsilon_0} \tag{6}$$

(where Ω_α is the α component of the operator acting on the angular momentum vector of the nucleus in the hyperfine Hamiltonian; $Z_{\alpha'}$ is the α' component of the Zeeman term; ψ is the unperturbed wavefunction; k_{u} is the unit factor) and for the diamagnetic part of the shielding tensor, written for many-electron systems,

$$\sigma^{\mathrm{d}} = k_{\mathrm{u}'} \frac{e^2}{3mc^2} \sum_{e^-} \left\langle r^{-1} \right\rangle_{e^-}, \tag{7}$$

where the sum goes over all electrons and $k_{\mathrm{u}'}$ is a unit factor.

Computational details

All DFT calculations were performed using the Amsterdam density functional (ADF) program package [10–12] (release 2007.01 was used for the calculation on the X-ray geometry; release 2004.01 when COSMO model is used; release 2009.01 for the NMR calculations with NMR utility program [28, 29–31] because of the possibility to use hybrid functionals). If not mentioned specially, the generalized gradient approximation (GGA) in the Perdew–Wang 91 (PW91) form [17] for exchange–correlation functionals was used, with an all-electron zero-order regular approximation (ZORA) triple-zeta Slater-type orbital (STO) plus one polarization function (TZP) basis set. Relativistic effects have been taken into account through the ZORA approach as implemented in ADF.

LF-DFT calculations were used to obtain the energies and wavefunctions of the ^{59}Co 3*d* spin orbitals. XATOM [32] was used for evaluation of $\langle r^{-n} \rangle$ integrals. For both of these, MatLab [33] scripts can be obtained from the authors on request.

For all calculations on crystal geometry, coordinates were taken from the published crystal structure [21]. For simulating the nonnegligible effect of counterions, we replaced all surrounding atoms in a sphere from the cobalt nuclei by their point charges, to end with a total sum of charges close to zero; more specifically, a point charge sum of −3.15 was used, and therefore a total sum of charges of −0.15, within a radius of 6.87 Å. The values of the point charges are Mulliken point charges of the corresponding atoms from a calculation on crystal geometry in vacuum.

Geometries of all diastereoisomers were obtained from gas-phase calculations with LDA/Vosko–Wilk–Nusair (VWN) [16], for the reasons mentioned in the text. To mimic effects of water, the COSMO model (with water as solvent, van der Waals radii from [20]) has been used for all corresponding calculations. ADF NMR calculations were done with hybrid B3LYP functional [34].

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