Electronic Spectral Simulation for Dinuclear Zinc (II) Complexes Bridged by a 2,3,5,6-Tetrahydroxy-1,4-benzoquinonate Ion and by a Rhodizonate Ion

Hiroshi SAKIYAMA, a, * Syoji MIYAZATO, b Satoshi TAKARA, b Eiji ASATO b

a Department of Material and Biological Chemistry, Faculty of Science, Yamagata University, Kojirakawa 1-4-12, Yamagata 990-8560, Japan
b Department of Chemistry, Biology and Marine Science, Faculty of Science, University of the Ryukyus, Nishihara, Nakagami-gun, Okinawa 903-0213, Japan
*e-mail: saki@sci.kj.yamagata-u.ac.jp

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The electronic spectra of dinuclear zinc (II) complexes were simulated for [Zn₂(μ-H₂THBQ)(TPA)_2](ClO₄)₂ (1) and [Zn₂(μ-RHOD)(TPA)_2](ClO₄)₂ (2) [H₂THBQ₂⁻: 2,3,5,6-tetrahydroxy-1,4-benzoquinonate, TPA: tris (2-pyridylmethyl) amine, RHOD²⁻: rhodizonate] using the methods of density functional theory (DFT). A band at 361 nm for 1 was assigned to a (2nd HOMO)-LUMO transition, which originates from a bridging benzoquinonate moiety; a band at 502 nm and a band at 449 nm for 2 were assigned to a HOMO-LUMO transition and a HOMO-(2nd LUMO) transition, respectively, and both are originated from a bridging rhodizonate moiety.

Keywords: Dinuclear zinc (II) complex, Electronic spectra, DFT computation, Benzoquinonate, Rhodizonate

1 Introduction

Tetraoxoles, congeners of benzoquinone (BQ), are capable of bridging two metal ions with the four oxygen donors in the bis-bidentate fashion [1–7]. Not only with the bridging ability, tetraoxoles are superior to BQ in creating novel multi-redox molecular systems due to their non-innocent characteristics. The derivatives of 1,4-dihydroxybenzoquinone (H₂DHBQ), chloranilic acid (H₂CA) for instance, have hence been used to synthesize dinuclear metal complexes that exhibit intriguing redox- and magneto-chemistry [8–13]. Introducing two more hydroxyl groups to H₂DHBQ affords 2,3,5,6-tetrahydroxy-1,4-benzoquinonine (H₄THBQ) which is more attractive to inorganic synthetic chemists. Surprisingly, metal complexes of deprotonated forms of H₄THBQ such as THBQ⁺ or H₂THBQ⁻ are scarcely reported due to their poor stability in solution. As far as we realize, only five examples are reported thus far [14–18]. The fully deprotonated ligand THBQ⁺ binds three Mo(VI) ions by usual σ-donation with three pairs of adjacent O-O-chelation from the C₆O₆ ring to produce a Mo₃(THBQ) core in the [Mo₆O₁₅(C₆O₆)₂]⁴⁻ cluster [14]. Another example, by our group, is the mixed valence heptapalladium cluster, in which the tetraanion bridges three Pd(II) ions in the same chelation mode to generate a Pd(II)₃(THBQ) unit [15]. Interestingly, the THBQ ligand in the Pd(II)₃(THBQ) unit was found to coordinate to another Pd (0) center in a η⁶-fashion yielding the [Pd₄(THBQ)₂(tben)]⁴⁺ cluster, where tben is N,N,N',N'-tetrabenzylethylenediamine. Thus, tetraanion THBQ⁴⁻ shows rich coordination chemistry. On the other hand, the di-deprotonated ligand H₂THBQ⁻ is more important because the quinonate is expected to give the dinuclear [M(μ-H₂THBQ)M] core, which is capable of giving up two protons and two electrons to generate dinuclear species [M(μ-RHOD) M], where RHOD²⁻ is rhodizonate. Recently, Miller et al. has reported the first example of the dinuclear [M(μ-H₂THBQ)M] core, as [Fe₂(μ-H₂THBQ)(TPA)]²⁺, TPA=tris (2-pyridyilmeth-
2 Computational methods

DFT computations were performed using WinGAMESS program [19,20] and Gaussian 03 software (Gaussian, Inc.). Structural optimization was performed with several DFT methods (LC-BLYP/6-31G [21], LC-BOP/6-31G [21], B3LYP/6-31G [22–24], BLYP/6-31G [25], and BOP/6-31G [26]), using the crystal structures as initial structures. The electronic spectral simulation was performed with the TD-DFT methods (TD-LC-BLYP/6-31G, TD-LC-BOP/6-31G, TD-B3LYP/6-31G, TD-BLYP/6-31G, and TD-BOP/6-31G) using the corresponding optimized structures. In all the computations, the solvation effect was not taken into account.

3 Results and discussion

3.1 Structural optimization for complex 1

Before simulating the electronic spectra, the structure of the complex cation [Zn₂(μ-H₂THBQ)(TPA)₂]²⁺ was optimized using the five DFT methods, LC-BLYP/6-31G, LC-BOP/6-31G, B3LYP/6-31G, BLYP/6-31G, and BOP/6-31G. The reported crystal structure [17] was used as an initial structure for each computation. In all the cases, the structures were optimized successfully, and the discrepancy factors of bond lengths and angles were less than 0.004 (Figure 1). The crystal structure of the complex cation [Zn₂(μ-H₂THBQ)(TPA)₂]²⁺ and one of the optimized structures (LC-BLYP/6-31G) are shown in Figure 2; they look very similar to each other.

3.2 Structural optimization for complex 2

As well as we did for complex 1, the structure of the complex cation [Zn₂(μ-RHOD)(TPA)₂]²⁺ was optimized using the five DFT methods; in all the cases, the structures were optimized successfully. The discrepancy factors were less than 0.0012, and the LC-BLYP/6-31G was the best (Figure 3). The crystal structure of the complex cation [Zn₂(μ-RHOD)(TPA)₂]²⁺ and one of the optimized structures (LC-BLYP/6-31G) are shown in Figure 4; they look very similar to each other.

![Discrepancy factors of computed [Zn₂(μ-H₂THBQ)(TPA)₂]²⁺ structure for bond lengths around zinc ions (■), bond angles around zinc ions (■), and total (■).](image)
3.3 Electronic spectrum of complex 1

As mentioned in the introduction, an acetonitrile solution of 1 was green, and the UV–vis spectrum showed a characteristic intense band at 361 nm [17]. In order to assign this band, TD-DFT computations were conducted, using the optimized structures described in section 3.1. Wavelengths of the simulated bands are summarized in Table 1, and three of the related molecular orbitals are shown in Figure 5. The results obtained by the TD-LC-BLYP/6-31G(363 nm) and TD-LC-BOP/6-31G

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Observed</th>
<th>LC-BLYP</th>
<th>LC-BOP</th>
<th>B3LYP</th>
<th>BLYP</th>
<th>BOP</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2nd HOMO)-LUMO</td>
<td>361</td>
<td>363</td>
<td>362</td>
<td>-a</td>
<td>-a</td>
<td>-a</td>
</tr>
</tbody>
</table>

* Reasonable result was not observed.
The results obtained by the three methods, TD-LC-BLYP/6-31G, TD-LC-BOP/6-31G, and TD-B3LYP/6-31G were essentially the same, but the result of TD-B3LYP/6-31G (452 and 500 nm) was the closest to the observed data. Assuming a local $D_{2h}$ symmetry for the bridging $\mu$-RHOD moiety, the three orbitals $2\text{nd}$ HOMO, HOMO, and LUMO are called $b_{1u}$, $b_{2g}$, and $b_{3g}$ orbitals, respectively, where the $z$ axis is perpendicular to the THBQ plane and the $x$ axis is parallel to the Zn···Zn axis. The two observed bands were assigned to the HOMO-LUMO ($b_{1u} \rightarrow b_{2g}$) and HOMO-(2$\text{nd}$ LUMO) ($b_{1u} \rightarrow b_{3g}$) transitions from the lower energy, and both were Laporte-allowed $\pi \rightarrow \pi^*$ transitions.

When we focus on the bridging moieties of 1 and 2, the shapes of 2$\text{nd}$ HOMO, HOMO, and LUMO in 1 are similar to those of HOMO, LUMO, and 2$\text{nd}$ LUMO in 2, respectively (Figure 7). This similarity may correspond to the fact that the loss of two protons and two electrons from the H$_2$THBQ moiety results in the RHOD moiety. If we summarize the electronic spectra of 1 and 2, we obtained an energy diagram as shown in Figure 8. For 1, the band at 361 nm was assigned to the (2$\text{nd}$ HOMO)-LUMO transition; for 2, two bands at 502 and 449 nm were assigned to HOMO-LUMO and HOMO-(2$\text{nd}$ LUMO) transitions, respectively.

### 4 Concluding remarks

In this study, absorption bands were characterized for the dinuclear zinc (II) complexes 1 and 2, based on the DFT methods. For 1, the band at 361 nm was assigned to the (2$\text{nd}$ HOMO)-LUMO transition, which was characterized by a $\pi \rightarrow \pi^*$ transition.
of the bridging benzoquinonate moiety. For 2, two bands at 502 and at 449 nm were assigned to HOMO-LUMO and HOMO-
(2nd LUMO) transitions, respectively, and both were characterized by π→π* transitions of the bridging rhodizonic moiety.

As already reported by our group [17], the dinuclear unit [Zn(μ-H\(_2\)THBQ)Zn] is capable of giving up two protons and two electrons to generate dinuclear species [Zn(μ-RHOD)Zn]. This P.C.E.T. behavior may be applicable to redox active transition-metal ions. The information on the electronic structure obtained in this study would contribute to understand the P.C.E.T. chemistry using transition-metal ions as our future work. Preliminary experiments using Fe (II), Mn (II), Co (II), and Ni (II) ions applied to the [M(μ-H\(_2\)THBQ)M] core showed similar P.C.E.T. behavior. These results and the theoretical approach to understanding the behavior will be presented elsewhere.

References