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DFT Calculations, Fulminate Complexes, IR Spectra

The structural parameters and IR frequencies of the following anionic fulminate complexes were computed at the density functional BWP91 level of theory using a 6-31++G(2d) basis for C, N, O, Co, Ni, and Zn and quasi-relativistic ECP60MBW core potentials for Pt, Au, and Hg: \([\text{Co(CNO)}_6]^{3-}\) (Oh), \([\text{Ni(CNO)}_4]^{2-}\) (D_4h), \([\text{Zn(CNO)}_4]^{2-}\) (D_oh), \([\text{Pt(CNO)}_4]^{2-}\) (D_oh), \([\text{Au(CNO)}_2]^{-}\) (D_oh) and \([\text{Hg(CNO)}_4]^{2-}\) (D_oh). The structures were optimised within the symmetries stated above and were found to represent true minima (number of imaginary frequencies, \(\text{NIMAG} = 0\)). The agreement between the calculated structural parameters and characteristic asymmetric and symmetric CNO stretching frequencies is very good for all complexes.

Introduction

All anionic fulminate complexes studied theoretically in this work are experimentally known and have been characterized by infrared (IR) spectroscopy [1–4] and X-ray diffraction analysis [5–8]. In the present study we now computed the structural parameters and vibrational frequencies at the BWP91 level of theory to compare experimental and calculated data in order to get an appreciation for the quality of calculated data for those complexes for which at present no experimental structural data are available.

Methods

All calculations were carried out using the Gaussian G98W program package [9]. The structures and frequencies were computed at the density functional (DFT) BWP91 level of theory, using Becke’s exchange functional, which includes the Slater exchange along with corrections involving the gradient of the density [10] and Perdew and Wang’s gradient-corrected correlation functional [11, 12]. For C, N, O, Co, Ni, and Zn a standard double-zeta basis [13–17] supplemented with two sets of diffuse functions [18] and two sets of d polarization functions [19] was used: 6-31+G(2d).

In calculations for molecules containing platinum, gold and mercury for these elements (Pt, Au, Hg) a quasirelativistic Wood-Boring Stuttgart/Dresden (SDD) ECP60MBW pseudopotential for the 60 core electrons was applied with a (8s7p6d)/[6s5p3d] valence basis [20–24].

The energy-consistent pseudopotentials are semi-local pseudopotentials adjusted to reproduce atomic valence-energy spectra. The adjustment of the pseudopotential parameters has been done in fully numerical calculations. Valence basis sets have been generated a-posteriori via energy optimization. The complete set of potentials includes one-component (non-relativistic and scalar-relativistic) effective-core potentials (ECP) [20].

Table 1. Observed (X-ray) and computed energies and structural parameters.

<table>
<thead>
<tr>
<th>Complex anion</th>
<th>sym.</th>
<th>(-E/\text{a.u.})</th>
<th>(d(\text{M}–\text{C})/\text{Å}) calcd/exppl.</th>
<th>(d(\text{C}–\text{N})/\text{Å}) calcd/exppl.</th>
<th>(d(\text{N}–\text{O})/\text{Å}) calcd/exppl.</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Co(CNO)}_6]^{3-})</td>
<td>D_oh</td>
<td>3290.910327</td>
<td>1.919/1.915(6)</td>
<td>1.181/1.130(6)</td>
<td>1.269/1.269(6)</td>
</tr>
<tr>
<td>([\text{Ni(CNO)}_4]^{2-})</td>
<td>D_4h</td>
<td>2180.527310</td>
<td>1.863/1.875(5)</td>
<td>1.184/1.138(5)</td>
<td>1.259/1.261(4)</td>
</tr>
<tr>
<td>([\text{Zn(CNO)}_4]^{2-})</td>
<td>T_4</td>
<td>2451.488915</td>
<td>2.044/2.005(4)</td>
<td>1.187/1.140(4)</td>
<td>1.253/1.250(4)</td>
</tr>
<tr>
<td>([\text{Pt(CNO)}_4]^{2-})</td>
<td>D_4h</td>
<td>791.676170</td>
<td>2.008/2.00(2)</td>
<td>1.184/1.16(3)</td>
<td>1.257/1.25(2)</td>
</tr>
<tr>
<td>([\text{Au(CNO)}_2]^{-})</td>
<td>D_4h</td>
<td>472.022399</td>
<td>1.985/2.01(2)</td>
<td>1.187/1.10(3)</td>
<td>1.241/1.25(2)</td>
</tr>
<tr>
<td>([\text{Hg(CNO)}_4]^{2-})</td>
<td>T_3</td>
<td>825.681990</td>
<td>2.248/2.218(8)</td>
<td>1.188/1.150(9)</td>
<td>1.252/1.256(8)</td>
</tr>
</tbody>
</table>

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Results and Discussion

Initially, all six complexes were computed without any symmetry constraints and were fully optimised to the experimentally observed symmetries indicated in Tables 1 and 2. Consequently, we then computed all complexes again within the experimentally observed symmetries (cf. Table 1) and found them to represent true minima (number of imaginary frequencies, $N_{\text{IMAG}} = 0$) at the level of theory applied. The experimentally obtained and computed structural parameters are summarized in Table 1, the vibrational data are given in Table 2. Generally, the agreement between the computed and observed structural parameters is good (Table 1). The agreement between the calculated and observed characteristic IR frequencies is very good (cf. Table 2 contains the unsealed computed values) with an empirical scaling factor of 0.98 which would give the best fit.

Acknowledgements

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Table 2. Observed (IR) and computed zero point energies (zpe) and infrared (IR) frequencies and intensities for the symmetric and asymmetric CNO stretch.

<table>
<thead>
<tr>
<th>Complex anion</th>
<th>sym.</th>
<th>zpe/ kcal mol$^{-1}$</th>
<th>$v_{\text{sym}}$(CNO)/cm$^{-1}$ (Int.)</th>
<th>$v_{\text{asym}}$(CNO)/cm$^{-1}$ (Int.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{[Co(CNO)}_6\text{P}^{-}$</td>
<td>$O_h$</td>
<td>44.1</td>
<td>$T_{1u}$: 1123 (1.0)/1114 vvs</td>
<td>$T_{1u}$: 2166 (0.5)/2167 m</td>
</tr>
<tr>
<td>$\text{[Ni(CNO)}_4\text{P}^{-}$</td>
<td>$D_{4h}$</td>
<td>29.7</td>
<td>$E_u$: 1156 (1.0)/1126 vs</td>
<td>$E_u$: 2196 (0.7)/2185 vs</td>
</tr>
<tr>
<td>$\text{Zn(CNO)}_4^{2-}$</td>
<td>$T_1$</td>
<td>28.5</td>
<td>$T_2$: 1177 (0.5)/1155 vs</td>
<td>$T_2$: 2162 (1.0)/2128 vs</td>
</tr>
<tr>
<td>$\text{Pt(CNO)}_4^{2-}$</td>
<td>$D_{4h}$</td>
<td>29.5</td>
<td>$E_u$: 1157 (1.0)/1122 vs</td>
<td>$E_u$: 2219 (0.6)/2193 vs</td>
</tr>
<tr>
<td>$\text{[Au(CNO)}_2\text{]}^{-}$</td>
<td>$D_{2h}$</td>
<td>14.7</td>
<td>$\Sigma_u$: 1220 (0.9)/1180 vs</td>
<td>$\Sigma_u$: 2207 (1.0)/2173 vs</td>
</tr>
<tr>
<td>$\text{[Hg(CNO)}_4\text{]}^{2-}$</td>
<td>$T_d$</td>
<td>28.0</td>
<td>$T_2$: 1164 (0.5)/1143 vs</td>
<td>$T_2$: 2160 (1.0)/2130 vs</td>
</tr>
</tbody>
</table>

$^a$ IR frequencies unsealed; IR intensities calibrated to int. = 1.0 for the strongest absorption.