^{2}H NMR calculations on polynuclear transition metal complexes: on the influence of local symmetry and other factors. Eelectronic Supporting Information

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Computational details

In nuclei like deuterium the nuclear quadrupole moment interact with the electric field gradient (EFG) arisen at these sites. This interaction is described by the quadrupolar coupling constant C_Q and the asymmetry parameter η_Q. In principle these parameters can be obtained by quantum mechanical DFT calculations[1–4] which allow the determination of the electric field tensor $\overline{\overline{V}}$. A given matrix element is calculated by the formula[3]:

$$\overline{\overline{V}}_{ij}(\mathbf{r}) = \frac{\partial E_i(\mathbf{r})}{\partial r_j} - \frac{1}{3}\delta_{ij}\sum_k \frac{\partial E_k(\mathbf{r})}{\partial r_k} \qquad (1)$$

where i, j, k stands for x, y, z and $E_k(\mathbf{r})$ is the kth component of the electric field at position $\mathbf{r}$.

C_Q (eq. 2) and η_Q (eq. 3) are calculated from the EFG tensor eigenvalues V_{11}, V_{22}, V_{33}, with the convention : $|V_{11}| \leq |V_{22}| \leq |V_{33}|$ (i.e. V_{33} is the principal component):

$$C_Q = \frac{eQV_{33}}{h} \qquad (2)$$

$$\eta_Q = \frac{|V_{22}| - |V_{11}|}{|V_{33}|} \qquad (3)$$

where Q is the nuclear quadrupole moment ($Q = 0.00286$ barns for ^{2}H). The conversion from atomic units to kHz is:

$$C_Q\,(\text{kHz}) = 672 \times V_{33}(\text{u.a.}) \qquad (4)$$

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C_Q are related to the experimental quadrupolar splitting value Δv_Q[5], which, at low temperatures where no significant motional processes on the NMR time scale occur, is directly related to the EFG eigenvalue V_{33} by

$$\Delta v_Q = \frac{3}{4}C_Q = \frac{3}{4}\frac{eQ}{h}V_{33} \qquad (5)$$

In the case of deuterium atoms, equation 5 simply writes:

$$\Delta v_Q = \frac{3}{4} \times 672 \times V_{33} = 504 \times V_{33} \qquad (6)$$

All molecular DFT calculations were performed with Gaussian03.[6] The [Ru$_4$] as well as the $H_2Ru_6(CO)_{18}$ and $[HRu_6(CO)_{18}]^-$ cluster geometries considered in the present work are taken from a previous study.[7] Geometries had been fully optimized in gas phase without symmetry constraints, employing the PBE0 functional[8] and a polarized double-zeta quality basis set. In order to be consistent with that study, the most stable geometry of $[H_3Ru_6(CO)_{18}]^+$, initially proposed in another previous work[9], has been optimized again at the same level of calculation and other isomers have been found on the potential energy surface. A small set of tetrahedral $H_4M_4(CO)_{12}$ clusters has also been considered in order to assess the possible effect of the metal M on C_Q and η_Q (M = Re, Tc, Os, Fe). Unrestricted-DFT calculations of the singlet and triplet states have been done in several cases in order to take care of the possible magnetism of some of these clusters. It could in particular have been the case for those that break the electron-counting rule, namely $H_4Ru_4(C_6H_6)_2^+$, the strongly electron deficient $H_2Ru_4(CO)_9$ cluster or $H_4M_4(CO)_{12}$ clusters (M = Re, Tc).

Calculations of EFG tensors were done using the B3PW91 functional[10–16] and the Stuttgart effective core potential for Ru, Fe, Re and Os,[17] augmented with one polarization function ($\zeta_f(\text{Ru}) = 1.235$, $\zeta_f(\text{Fe}) = 2.462$, $\zeta_f(\text{Re}) = 0.869$, $\zeta_f(\text{Os}) = 0.886$, $\zeta_f(\text{Tc}) = 1.134$). For the other elements (H, C, O, and P) Dunning's correlation consistent basis set cc-pVTZ[18,19] has been used. We have already proved on some test cases that quadrupolar coupling constants calculated on triple-ζ and double-ζ basis sets' geometries differ by less than

2%, owing to the local character of this property.[20] Due to the large dimension of some TM complexes we have considered that performing geometry optimizations and EFG tensor calculations in the same expensive triple-ζ quality basis set leads no significant enhancement of the results. The structures labelling is consistent with the one adopted in Ref. 7. The quadrupolar parameters published in Ref. 9 have been computed, with a somewhat lower accurate level of calculation, only for the carbonyl-ruthenium clusters hereafter named 1^{CO}, $1'^{CO}$, 13, $13'$, and $14a$. For the sake of consistency, they have been systematically recalculated within the cc-pVTZ basis set and the Stuttgart effective core potentials. This small sample of clusters is completed in the present work by a wide set of $[Ru_4]$ clusters with CO, PH_3, PF_3, AsH_3 and C_6H_6 ligands,[7] together with an electron deficient $[Ru_4]$ cluster, an extended set of $[H_3Ru_6(CO)_{18}]^+$ isomers and other $H_4M_4(CO)_{12}$ clusters (with M = Re, Tc, Os, Fe).

Owing to the debate about the isomerization process of $H_4Ru_4(CO)_{12}$[21,22] and for the purpose of checking the possible effect of crystal packing on the isomerization pathway of this compound, periodic boundary computations were performed on this particular case within the framework of the density functional theory (DFT) considering the spin unpolarized constraint. The exchange-correlation potential was approximated by the generalized gradient approach proposed by Perdew, Burke, and Ernzerhof (PBE).[23,24] Calculation of the energetic parameters, as well as the geometry optimizations were carried out using the projector augmented waves (PAW) full-potential reconstruction[25,26] implemented in the Vienna *ab initio* simulation package VASP.[27,28] We found that a kinetic energy cutoff of 500 eV was sufficient to achieve a total energy convergence within several millielectronvolts. Atoms were free to move until the residual forces on any direction were less than 0.02 eV/Å. Diffusion barriers were estimated by the nudge elastic band (NEB) variant recently proposed by Henkelman and co-workers,[29] with a force tolerance of 0.02 eV/Å and five intermediate geometries for the transition state search.

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