^{67}Zn NMR Chemical Shifts and Electric Field Gradients in Zinc Complexes: A Quantum Chemical Investigation

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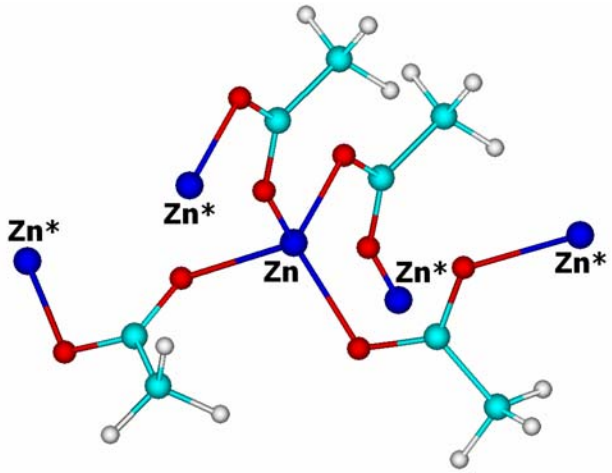
Details of SC-CFP calculations:

In each polymeric structure, the zinc atom and other atoms in the ligands of the first coordination shell were treated as real atoms using the basis set described in the Text. The Zn atoms connected to the terminal atoms in this shell were treated as point charges, using Mulliken charges from *ab initio* calculation on the first coordination shell. This process was iterated until the calculated point charges converged at 0.01 *e*, associated with precisions of ≤2 ppm and ≤0.01 MHz for computed σ_i and C_Q, respectively.

By way of example, we show the process for polymer **2**. As shown below, the central zinc atom (Zn) is coordinated by four acetate ligands (O–red; C–cyan; H–grey). This zinc atom and the four acetate ligands were treated as real atoms using the basis set described in the Text. Because in the polymeric structure each terminal oxygen atom is connected to a zinc atom (Zn*), which is identical to the central zinc atom due to crystallographic symmetry, each of the four Zn* were included in the calculation as point charges and their values were taken as the charge of the central zinc atom from the Mulliken population analysis on the real-atom system (Zn + 4 acetate). Then, the calculation on the whole system of Zn + 4 acetate + 4 Zn* was performed. The Mulliken charge of the central real zinc atom was then used for Zn* in the next run on the whole system of Zn + 4 acetate + 4 Zn*. This process was iterated until the calculated point charge of this central zinc atom converged (at < 0.01 *e*). The Gaussian 03 input file of the final run of this type of calculation is given below, where the last four lines contain the description of 4 Zn* in Gaussian 03 format. Each line has four values: the first three are (*x,y,z*) coordinates from the experiment and the last one is the quantity of the calculated point charge, in atomic units. This value is 1.24 *e* in this case, which is the same (difference < 0.01 *e*) as that for the central zinc atom in the output file (not shown) of the final run. As a result of this convergence, the iterative calculations were stopped and the predicted NMR properties from this run are the ones reported for this system (**2**) in Table 1.



```
%mem=360MB
%nproc=4
%chk=znaceu01-charge
# b3lyp/gen nmr prop=efg charge

znaceu01, ZnO4

-2 1
  O      3.19100      2.10700      6.45400
  O      4.25900      3.96900      6.87900
  C      4.10000      2.72800      7.03400
  C      5.04200      2.03700      7.96800
 Zn      2.76100      5.01800      6.20100
  H      4.60100      1.16300      8.44700
  H      5.28600      2.74600      8.75900
  H      5.93900      1.74000      7.42500
  O      3.19100      6.90600      6.45400
  O      4.25900      8.76800      6.87900
  C      4.10000      7.52700      7.03400
  C      5.04200      6.83600      7.96800
  O      1.01500      4.38600      6.82300
  O      1.85300      4.66800      8.81100
  C      0.97200      4.19800      8.06100
  C     -0.13100      3.35000      8.61500
  O      2.61700      4.93000      4.24400
  H      4.60100      5.96200      8.44700
  H      5.28600      7.54500      8.75900
  H      5.93900      6.53900      7.42500
  H      0.23600      2.44900      9.10600
  H     -0.74700      3.03200      7.77400
  H     -0.71900      3.93500      9.32200
  O      1.77900      5.21200      2.25700
  C      1.73500      5.40000      3.49400
  C      0.63200      6.24800      4.04900
  H      0.99800      7.14900      4.54100
  H      0.11900      5.65400      4.80500
  H     -0.05200      6.52400      3.24700

zn 0
6-311G*
****
C 0
6-311G*
****
H 0
6-31G*
****
2 9 13 17 0
6-311++G(2d)
****
1 10 14 24 0
6-311G*
****

2.761   0.219   6.201 1.24
2.761   9.817   6.201 1.24
1.998   4.580  10.768 1.24
3.524   4.580   1.635 1.24
```

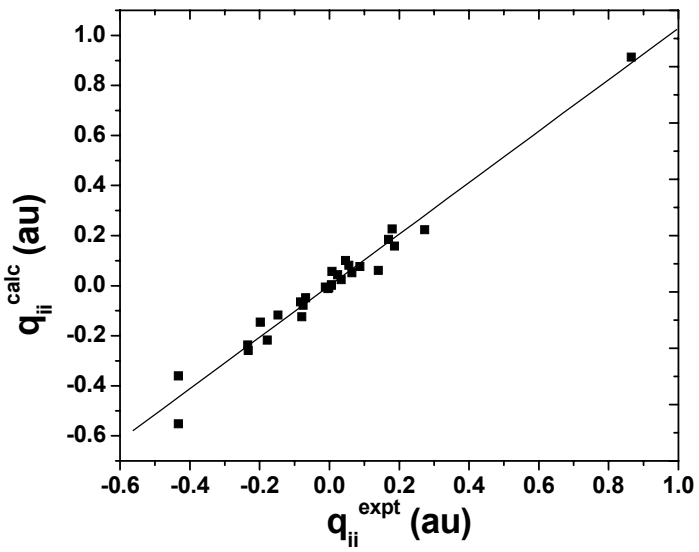


Figure S1. Calculated versus experimental ^{67}Zn electric field gradient tensor elements (q_{ii}). The regression line has a slope of 1.029 and an intercept of 0.0000 au with an R^2=0.972.