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# Scalar Relativistic Effects on $^{17}O$ NMR Chemical Shifts in Transition-Metal Oxo Complexes. An ab Initio ECP/DFT Study

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Semiempirical MO studies have shown that spin−orbit coupling makes an important relativistic contribution to NMR chemical shifts in molecules containing heavy elements.[1] However, in this context nothing is known about the influence of scalar relativistic effects, as the identification of these contributions is difficult in semiempirical calculations. Ab initio investigations on NMR chemical shifts of heavy-element compounds are rare and have always been at nonrelativistic (and uncorrelated) levels.[2−4]

As scalar relativistic effects influence other properties of heavy-element compounds dramatically (e.g., structures, stabilities, vibrational and electronic spectra),[5] it is important also to assess the magnitude of scalar relativistic contributions to NMR properties. We have recently[6] reported the use of effective core potentials (ECPs) in the calculation of ligand NMR chemical shifts of organometallic compounds, based on density functional theory (DFT).[7] With this new combination of methods, electron correlation is taken care of approximately via the exchange-correlation functional, at modest computational cost. Additionally, scalar relativistic effects pertaining to the presence of heavy elements can be included by using quasirelativistic ECPs to replace the core electrons of these heavy atoms, when calculating the chemical shielding tensor for neighboring, lighter nuclei.[6] A comparison to nonrelativistic ECP results allows the magnitude of relativistic effects to be evaluated.

In the present paper we report scalar relativistic effects on the $^{17}O$ chemical shifts of high-valent, tetrahedral, group 6−8 transition-metal oxo complexes $MO_4^{n-}$ ($n = 0, 1, 2$), encompassing all three transition-metal rows. The ligand chemical shifts of these complexes were among the first $^{17}O$ shieldings measured.[8,9] Figgis, Kidd and Nyholm[8] found that these compounds exhibit resonances at the deshielded end of the oxygen chemical shift range and show a remarkably large dependence on the nature of the central metal (which correlated well with optical excitation energies[8]). Table 1 compares experimental data and results calculated at various nonrelativistic and quasirelativistic ECP/DFT(IGLO) levels.[6,7,10,11] Using experimental M−O distances and quasirelativistic metal pseudopotentials (QR//expt), the calculations reproduce the experimental values to within better than 70 ppm, except for the 3d species $CrO_4^{2-}$ and $MnO_4^-$ (too shielded by ca. 100 and 150 ppm, respectively). In view of various uncertainties pertaining to solvation, structures in solution, rovibrational corrections, etc., and given the large oxygen chemical shift range (more than 1200 ppm[9]), this agreement is remarkable. All experimentally observed trends, both down a given triad and within a given transition-metal row (to lower frequency in going down and in going to the right), are well reproduced. The somewhat larger deviation from experiment for the 3d complexes may be related to the particular difficulty of describing correlation contributions to the ground states of these species, arising from the compact 3d shell.[12,13] Inclusion of positive point charges in our calculations to take some rough account of the solvent and counterion effects for the negative ions[14] has a small effect for the dianions and a negligible effect for the monoanions (Table

**Table 1.** Comparison of Experimental and Calculated $^{17}O$ Chemical Shifts (ppm vs $H_2O$ vapor)[a] in Some Transition-Metal Oxo Complexes

| | | calc[c] | | | | |
|---|---|---|---|---|---|---|
| compd | expt[b] | QR//expt[d] | QR//QR[d] | QR//NR[d] | NR//NR[d] | NR//expt[d] |
| $CrO_4^{2-}$ | 786, 799 | 697 (704[e]) | 736 | 744 | 771 | 718 |
| $MoO_4^{2-}$ | 496, 524 | 547 (512[e]) | 601 | 611 | 650 | 585 |
| $WO_4^{2-}$ | 384 | 455 (429[e]) | 489 | 525 | 666 | 646 |
| $MnO_4^-$ | 1183 | 1028 (1024[e]) | 984 | 991 | 1009 | 1045 |
| $TcO_4^-$ | 713 | 696 (697[e]) | 772 | 791 | 827 | 728 |
| $ReO_4^-$ | 543 | 585 (584[e]) | 646 | 711 | 811 | 665 |
| $FeO_4$ | | | 1355 | 1376 | 1401 | |
| $RuO_4$ | 1070[f] | 1014 | 1059 | 1105 | 1156 | 1062 |
| $OsO_4$ | 760 | 811 | 879 | 996 | 1125 | 920 |

[a] The experimental data have been converted using the experimental vapor/liquid shift of 36 ppm.[9] [b] Cf. refs 8 and 9, except for $RuO_4$. [c] Cf. refs 6, 7, 10, 11, and 15 for computational details. [d] Cf. Table 2 for structures used (the standard notation employed is as follows: method for shift calculation//structure used). Shift calculations: QR//, quasirelativistic ECP used; NR//, nonrelativistic ECP used.[10] [e] With point charges added.[14] [f] Cf.: Brevard, C.; Granger, P. *J. Chem. Phys.* **1981**, *75*, 4175.

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(1) Cf., e.g.: Pyykkö, P.; Görling, A.; Rösch, N. *Mol. Phys.* **1987**, *61*, 195 and references cited therein.

(2) A good overview of the state of the art may be found in the following: Tossel, J. A., Ed. *Nuclear Magnetic Shieldings and Molecular Structure*; Kluwer Academic Publishers: Dordrecht, 1993.

(3) Cf., e.g.: (a) Nakatsuji, H. In ref 2, p 263 and cited literature. (b) Kutzelnigg, W.; v. Wüllen, C.; Fleischer, U.; Franke, R.; v. Mourik, T. In ref 2, p 141. (c) Tossel, J. A. In ref 2, p 279. (d) Ellis, P. D; Odom, J. D.; Lipton, A. S.; Chen, Q.; Gulick, J. M. In ref 2, p 539. (e) Cremer, D.; Olson, L.; Reidel, F.; Kraka, E. *Isr. J. Chem.* **1993**, *33*, 369.

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(10) (a) Quasirelativistic and nonrelativistic energy-adjusted semilocal ECPs for the metals and flexible GTO spd-valence basis sets were taken from ref 10b. The ECPs were transformed to nonlocal form.[10c] The IGLO-II basis[10d] was used for oxygen. Auxiliary basis sets to fit charge density and exchange-correlation potential were of the size 3,4 (three s functions plus four spd sets) for the metals and 5,2 for oxygen. (b) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1987**, *86*, 866. Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123. (c) Pelissier, M.; Komiha, N.; Daudey, J. P. *J. Comput. Chem.* **1988**, *9*, 298. Kaupp, M.; Flad, H.-J.; Köster, A.; Stoll, H.; Salahub, D. R. To be published. (d) Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR—Basic Principles and Progress*; Springer Verlag: Heidelberg, 1990; Vol. 23, p 165.

(11) (a) All calculations were carried out with a modified version of the deMon program.[11b] The Perdew−Wang-91 exchange-correlation functional[11c] and the LOC1 approximation of the SOS-DFPT method[7] were used in the chemical shift calculations. The IGLO gauge origin method[11d] was used. A "fine" integration grid was employed (cf. ref 7). (b) Salahub, D. R.; Fournier, R.; Mlynarski, P.; Papai, I.; St.-Amant, A.; Ushio, J. In *Density Functional Methods in Chemistry*; Labanowski, J. K., Andzelm, J. W., Eds.; Springer: New York, 1991. (c) Perdew, J. P.; Wang, Y. *Phys. Rev.* **1992**, *B45*, 13244. (d) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193. Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919.

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1). An all-electron treatment for Mn in $MnO_4^-$ [15] gives practically the same result (1060 ppm) as the pseudopotential calculations. Coupled Hartree–Fock calculations (using the LORG procedure) on $MoO_4^{2-}$ and related ions give oxygen shift values too deshielded by ca. 300–600 ppm,[4] probably due to the neglect of electron correlation. For $FeO_4$, the only experimentally unknown species, we predict a $^{17}O$ shift of ca. 1400–1500 ppm (and an Fe–O distance of ca. 1.57–1.58 Å), based on our computational results.

Scalar relativistic effects may affect the chemical shifts in two ways: (i) an indirect change is caused by relativistic changes in the molecular structures, and (ii) a direct relativistic change of electronic structure at a given nuclear arrangement will also influence the chemical shift values. These effects are separated in Table 1 by comparing quasirelativistic ECP results obtained at the quasirelativistically optimized structures[16] (QR//QR) to those obtained at the nonrelativistically optimized structures[16] using both the quasirelativistic ECPs (QR//NR) and the nonrelativistic ones (NR//NR). As the QR-optimized M–O distances are slightly larger than the experimental ones (Table 2), the QR//QR shift values are at somewhat higher frequency than the QR//expt results (note the large dependence of chemical shift on M–O distances), without changes in the periodic trends. The NR-optimized distances are still larger, by ca. 0.003–0.006, 0.008–0.016, and 0.033–0.046 Å for the 3d, 4d and 5d metals, respectively. Therefore, the QR//NR calculated shifts are at higher frequencies, negligibly for the 3d, slightly more so for the 4d, and considerably for the 5d complexes. The NR//NR data finally are at still higher frequencies, revealing even larger relativistic effects for the heavy metals. As a result, the completely nonrelativistic NR//NR calculations do not reproduce the periodic trend to lower frequencies down a given triad, but they predict similar shielding for the 4d and 5d compounds. On the other hand, the trend to lower frequencies for the 4d compared to the 3d compounds is affected only little by the relativistic changes. The relativistic change in molecular structure and the change in electronic structure at a given nuclear arrangement do not necessarily enforce each other for the chemical shift. Preliminary results on $^{13}C$ shifts in compounds like $Pb(CH_3)_4$ and $Hg(CH_3)_2$ indicate that the relativistic bond contraction leads to more shielding but the scalar relativistic contributions at a given M–C distance are deshielding.[17]

**Table 2.** M–O Distances (Å) in Some Transition-Metal Oxo Complexes

| compd | //expt[a] | calc[b] //QR[c] | calc[b] //NR[d] |
|---|---|---|---|
| $CrO_4^{2-}$ | 1.65 | 1.669 | 1.674 |
| $MoO_4^{2-}$ | 1.76 | 1.812 | 1.820 |
| $WO_4^{2-}$ | 1.79 | 1.826 | 1.859 |
| $MnO_4^-$ | 1.629 | 1.612 | 1.615 |
| $TcO_4^-$ | 1.711 | 1.750 | 1.760 |
| $ReO_4^-$ | 1.730 | 1.768 | 1.804 |
| $FeO_4$ |  | 1.587 | 1.593 |
| $RuO_4$ | 1.705 | 1.721 | 1.737 |
| $OsO_4$ | 1.711 | 1.740 | 1.786 |

[a] Experimental distances are averages from reported solid-state structures, except for $OsO_4$ and $RuO_4$, where GED values have been used. [b] Cf. refs 10, 11, and 15 for computational details. [c] Optimized with quasirelativistic ECP.[15] [d] Optimized with nonrelativistic ECP.[15]

We also give nonrelativistic ECP results for the experimental structures (NR//expt, last column in Table 1). These data suggest that, even on the basis of experimental structures, neglect of scalar relativistic effects in the chemical-shift calculations leads to appreciable errors (ca. 80–190 ppm) for the 5d metals but may be acceptable (i.e., within the range of other possible errors) for the 4d and 3d complexes. The generally good agreement of the QR//expt calculated values with experiment suggests that spin–orbit coupling is not very important for the oxygen chemical shifts in these species.[18] Population analyses and orbital energies show an increase in HOMO–LUMO gaps and an increase in the negative charge on oxygen due to relativistic corrections. We are presently carrying out more detailed analyses of relativistic effects on ligand chemical shifts in a larger number of systems.[17]

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(14) Sixty partial point charges, adding up to a total positive charge of +2, for $MO_4^{2-}$ and to +1 for $MO_4^-$, were used to simulate the influence of a solvent field and to ensure only negative occupied orbital energies for the dianions (the free dianions all had 12 positive occupied orbital energies). The charges were located at the vertices of a "$C_{60}$-like" arrangement of $I_h$ symmetry, at a distance from the central metal nucleus of 2.18 times the M–O distance.

(15) A flexible all-electron basis for Mn (Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829) was augmented by the most diffuse (1s, 2p, 1d) functions of the Mn ECP valence basis.[10b]

(16) (a) Structures were optimized using the same metal ECPs and valence bases as the chemical shift calculations,[10b] as well as an ECP and DZP valence basis[16b] for oxygen. Becke's exchange[16c] and Perdew's correlation functional[16d] were employed for the optimizations. (b) Bergner, A.; Dolg, M.; Küchle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431. (c) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098. (d) Perdew, J. P. *Phys. Rev.* **1986**, *B33*, 8822.

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(18) Nevertheless, we are presently implementing spin–orbit coupling corrections in our program. First results are promising (Malkin, V. G.; Malkina, O. L.; Eriksson, L. A.; Salahub, D. R. To appear in the following: *Theoretical and Computational Chemistry*; Politzer, P., Seminario, J. M., Eds.; Elsevier: Amsterdam; Vol. 1, in press.