

Density Functional Study of Cobalt-59 Nuclear Magnetic Resonance Chemical Shifts and Shielding Tensor Elements in Co(III) Complexes

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Abstract: A density functional method has been used to successfully predict the isotropic ⁵⁹Co nuclear magnetic resonance (NMR) chemical shifts of the following anionic, cationic and neutral Co(III) complexes: [Co(CN)₆]³⁻, [Co(NH₃)₆]³⁺, [Co(NO₂)₆]³⁻, [Co(NH₃)₄CO₃]⁺, Co(acac)₃, and [Co(en)₃]³⁺. Isotropic chemical shifts are well-reproduced by using Wachters' cobalt basis set and uniform 6-31G* basis sets on the light atoms, together with the use of the B3LYP hybrid functional. In addition, the principal elements of the ⁵⁹Co shielding tensor (σ_{11} , σ_{22} , and σ_{33}), the absolute shieldings of Co(CN)₆³⁻ and Co(acac)₃, and the Co–C bond length shielding derivative for Co(CN)₆³⁻ are also in good agreement with previous experimental estimates. There are no obvious distinctions between the predicted shifts (or shielding tensor elements) of anionic and cationic complexes. The ability to successfully predict both shift trends, absolute shieldings, shielding tensor elements, and a vibrational shielding derivative for d⁶ transition metal complexes opens up new possibilities for probing metal ions in biological systems by using NMR spectroscopy.

Introduction

During the past few years there has been increasing interest in the use of *ab initio* quantum chemical methods to evaluate nuclear magnetic resonance (NMR) chemical shifts, with the hope that improved insights into structure, bonding, and potentially “functional” questions—such as catalysis, ligand binding in proteins etc., might be obtained.¹ To date, most work has concentrated on the lighter elements (C, N, O, F), with very few studies of metal and especially transition metal chemical shifts being reported. This is perhaps surprising, since as noted by Bramley et al.² “Cobalt-59 occupies a unique place in NMR history, as it was one of the first nuclei for which it was observed that the resonance frequency depends on the compound.”³ The chemical shift range for cobalt is also very large, about 15 000 ppm, so it is an interesting candidate for *ab initio* quantum chemical investigation. Indeed, cobalt-59 shifts were considered in very early work by Ramsey,⁴ and important correlations between chemical shift and crystal field splittings which supported Ramsey's ideas were made in the 1950s in work by Freeman, Murray, and Richards.⁵

More recently, Chan et al.⁶ have investigated the *ab initio* calculation of ⁵⁹Co shifts and shift tensors in a series of diamagnetic Co(III) complexes using density functional theoretical (DFT) methods. They concluded that there was poor agreement between the calculated and experimental results, and suggested that this might be due to a lack of low-temperature NMR data, the absence of f-type functions in the metal basis

set, relativistic effects, a poor description of the excited states, and possible problems related to systematic errors due to the different charge states in the various systems investigated. Similarly poor accord between theory and experiment was also experienced by Bühl et al.⁷ when investigating ⁵⁷Fe NMR shifts in a series of (neutral) d⁶ and d⁸ complexes, but when hybrid functionals were used,⁸ there was a marked improvement, for both ⁵⁷Fe and ¹⁰³Rh NMR chemical shifts.⁸ It therefore seemed reasonable to us to reinvestigate the topic of the *ab initio* calculation of ⁵⁹Co NMR shifts, this time using hybrid functionals, as well as testing the effects of f-type functions in the cobalt basis. Here, an advantage of ⁵⁹Co NMR over Fe, Rh NMR is that the exceptionally high sensitivity of the ⁵⁹Co nucleus permits the ready experimental determination of not only the isotropic chemical shifts but also the elements of the anisotropic chemical shift (or shielding) tensors as well. This enables a more stringent test of the quality of the calculations, since there is less chance of an accidental cancellation of errors, as may occur with purely isotropic shift/shielding calculations. Moreover, there are several experimentally-independent estimates of the absolute shielding of the bare cobalt nucleus, so that the absolute shieldings computed theoretically can be compared with the experimental results. Plus, the topic of the temperature dependence of the isotropic shifts can be probed, by using the vibrational shielding derivatives.⁹ The ability to successfully predict isotropic shifts, shift (shielding) tensors, as well as absolute shieldings and shielding derivatives for d⁶ (Co^{III}) complexes is thus of considerable interest, since it should form the foundation for future studies of other d⁶ transition metal complexes, such as Fe^{II} in metalloproteins,^{10,11} as well as for example Co^{III} in vitamin B₁₂ and other metalloporphyrins.¹²

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Computational Section

Cobalt chemical shieldings were all evaluated by using the Gaussian-94 program¹³ on a cluster of RISC workstations: IBM RS/6000 Models 340, 350, 360, 365, and 3CT (International Business Machines, Austin, TX), together with a 4-processor Silicon Graphics (Mountain View, CA) Origin-2000, the latter calculations being carried out in parallel. We investigated the following complexes: $K_3[Co(CN)_6]$,¹⁴ $[Co(NH_3)_6]Cl_3$,¹⁵ $K_2Na[Co(NO_2)_6]$,¹⁶ $[Co(NH_3)_4CO_3]Br$,¹⁷ $Co(acac)_3$ ¹⁸ (acac = acetylacetonate), and $[Co(en)_3]I_3 \cdot H_2O$ ¹⁹ (en = ethylenediamine). In each case, we used purely experimental geometries, and the structures chosen were those which appeared to be well-refined. Hydrogen atoms were incorporated by using the Builder module in Cerius (Version 2.0, Biosym/Molecular Simulations Inc., San Diego, CA). For the cobalt atoms, we used Wachters' basis set^{20,21} ((62111111/3311111/3111); basis set 1, in the Huzinaga notation²²), which we then augmented with f-type functions²³ ((62111111/3311111/3111/3); basis set 2) for some calculations. For the light elements, we used the 6-31G* basis sets of Pople.²⁴ We have also used the Wachters basis set in a highly decontracted scheme, namely $(14 \times 1/3, 8 \times 1/6 \times 1)$ where the notation indicates that 14 contractions made of one primitive each were used for the s-type orbitals, for example. In the case where the latter basis set was used, 6-311G(2d) basis sets were employed for carbon and nitrogen. For the charged complexes, we considered only the complex ion, without any additional corrections for charge field effects, since in preliminary studies this procedure was shown to give very good results for isotropic, anisotropic, as well as absolute shieldings, and crystal-solution shifts in all cases are known to be small.²⁵ We also used the B3LYP hybrid functional,¹³ which denotes a functional built from Becke's three-parameter functional²⁶ with a nonlocal correlation term given by the Lee, Yang, and Parr²⁷ expression, since in the case of ⁵⁷Fe and ¹⁰³Rh shieldings,⁸ this has previously been found to give excellent accord between theory and experiment, at least for

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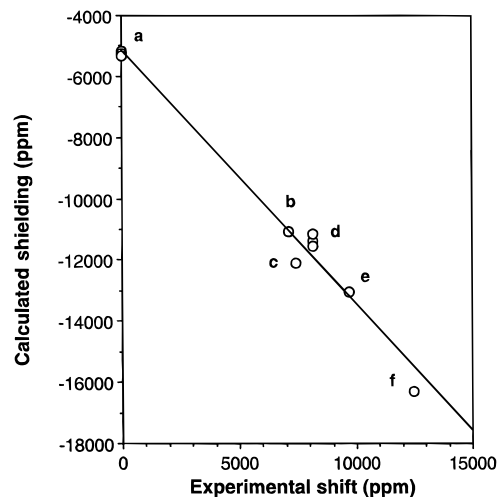


Figure 1. Graph showing correlation between experimental ⁵⁹Co NMR chemical shifts and theoretical shieldings (B3LYP functional, basis set 1). Slope = -0.83 and $R^2 = 0.98$. The systems shown are (a) $[Co(CN)_6]^{3-}$, (b) $[Co(en)_3]^{3+}$, (c) $[Co(NO_2)_6]^{3-}$, (d) $[Co(NH_3)_6]^{3+}$, (e) $[Co(NH_3)_4CO_3]^+$, and (f) $Co(acac)_3$.

isotropic shifts in neutral complexes. In all cases, the gauge-including atomic orbital (GIAO) method was used.^{28–32}

Results and Discussion

1. Isotropic Chemical Shifts and Absolute Shieldings. We first consider the isotropic chemical shift or shielding results we have obtained. We show in Figure 1 the correlation between the experimentally determined solution NMR chemical shifts and the computed absolute shieldings obtained by using the Wachters' all electron Co/6-31G* basis set DFT/B3LYP method outlined above, for $[Co(CN)_6]^{3-}$, $[Co(NH_3)_6]^{3+}$, $[Co(NO_2)_6]^{3-}$, $[Co(NH_3)_4CO_3]^+$, $Co(acac)_3$, and $[Co(en)_3]^{3+}$. For $K_3Co(CN)_6$, there are three crystallographically distinct sites, and the shifts for each site were computed, while for $Co(NH_3)_6Cl_3$, there are four crystallographically distinct sites, and again the shieldings for each site were computed and are included in Figure 1. For the isotropic shifts, we used the average experimental shifts reported in solution,³³ since in several cases the solid state results are complicated by the presence of multiple crystallographic sites and/or the complex interplay between the chemical shielding tensor and the second-order quadrupolar interaction.²⁵ The individual shielding tensor predictions, together with the predicted isotropic shieldings and experimental isotropic shifts, are all presented in Table 1.

The slope of the theory-versus-experiment correlation shown in Figure 1 for basis set 1 is -0.83 with an R^2 value of 0.98. There is thus an excellent correlation, together with a respectable slope. In an earlier study,⁶ the magnitudes of the calculated isotropic shifts versus experiment were smaller by scaling factors of 1.68–2.44, which we believe can be mainly attributed to the use of the Perdew–Wang exchange-correlation (PW91) functional.³⁴ The effect of the type of exchange-correlation functional used has been shown to be particularly important in previous ⁵⁷Fe shielding calculations on neutral d⁶ and d⁸ metal

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Table 1. Calculated ⁵⁹Co NMR Absolute Shieldings and Experimental Chemical Shifts of Cobalt(III) Complexes

compd	basis set	σ_{11} (ppm)	σ_{22} (ppm)	σ_{33} (ppm)	σ_i (ppm)	$\delta_{i,\text{expt}}$ (ppm)	
[Co(CN) ₆] ³⁻ site 1	1	-5432	-5280	-4798	-5170	0	
	2	-5435	-5280	-4799	-5171	0	
	site 2	1	-5460	-5252	-5099	-5270	0
		2	-5493	-5279	-5127	-5300	0
	site 3	1	-5532	-5318	-5198	-5349	0
		2	-5566	-5345	-5224	-5378	0
[Co(NH ₃) ₆] ³⁺ site 1	1	-11237	-11195	-10985	-11139	8153	
	2	-11251	-11209	-10992	-11151	8153	
	site 2	1	-11579	-11536	-11496	-11537	8153
		2	-11590	-11545	-11504	-11546	8153
	site 3	1	-11575	-11555	-11473	-11534	8153
		2	-11586	-11566	-11479	-11544	8153
	site 4	1	-11607	-11541	-11039	-11396	8153
		2	-11618	-11552	-11049	-11406	8153
	[Co(NH ₃) ₄ CO ₃] ⁺	1	-13688	-13178	-12272	-13046	9691
		2	-13736	-13163	-12276	-13058	9691
	[Co(NO ₂) ₆] ³⁻	1	-12121	-12115	-12114	-12117	7424
		2	-12140	-12135	-12133	-12136	7424
Co(acac) ₃	1	-16844	-16210	-15929	-16328	12500	
[Co(en) ₃] ³⁺	1	-11260	-11146	-10798	-11068	7110	

complexes,⁸ and can be expected to be likewise important in the case of the d⁶ Co(III) shieldings as well. The B3LYP functional contains a significant Hartree–Fock contribution to the exchange functional and, when combined with the large all-electron representation for ⁵⁹Co (basis set 1), gives almost a factor of 2 improvement in slope, as well as an increase in R² (from 0.913 to 0.98) over the earlier results. We also found that the addition of f-type functions to cobalt caused very little change in the calculated shieldings, and selected shielding calculations containing f-type functions on cobalt (basis set 2) are also given in Table 1, an observation consistent with previous findings by Bühl.⁸ We also investigated the isotropic shielding for [Co(CN)₆]³⁻ with an extended Wachters basis set and the 6-311G(2d) sets on the carbon and nitrogen atoms. The shielding of -5147 ppm obtained represents a difference of only 23 ppm with respect to the calculation with basis set 1 for site 1, even though the number of basis functions increased from 214 to 347. Bühl⁸ has examined the effect of the use of an even larger, well-tempered, basis set on ⁵⁷Fe shielding, and based on these results it is unlikely that a further enlargement of the basis set on the metal would modify the overall agreement with experiment significantly.

Of course, it is also very desirable in any chemical shielding calculation to obtain a good result for the absolute shielding, the shielding from the bare nucleus. For the light elements, Jameson and co-workers have established very good estimates of the absolute shielding of many nuclei using gas phase NMR and previous spin-rotation measurements.³⁵ Unfortunately, such methods are applicable to few metals, and there are no measurements for ⁵⁹Co. However, there are a number of completely different approaches which have been applied to evaluating the absolute shielding of ⁵⁹Co.^{2,36,37} Waldstedt et al.³⁶ obtained a value of $\bar{\gamma}_o = 10.054 \pm 0.02$ MHz T⁻¹ using measurements of the Knight shifts and susceptibilities of cobalt silicides, Spiess et al.³⁷ obtained $\bar{\gamma}_o = 10.057 \pm 0.01$ MHz T⁻¹, while Bramley et al.² obtained $\bar{\gamma}_o = 10.048 \pm 0.003$ MHz T⁻¹. Using the most recent and reportedly the most precise value, one obtains an absolute shielding for [Co(CN)₆]³⁻ of -0.0054, or -5400 ppm.² This value is remarkably close to the -5162

ppm shielding intercept we obtain from Figure 1, which is based on all eleven shielding calculations we have performed. Similarly, in early work by Reynhardt,³⁸ a value for the absolute shielding of Co(acac)₃ of -17 700 ppm was obtained (traceable via Lourens and Swanepol³⁹ to the Waldstedt value), which is again in quite good accord with the calculated -16328 ppm absolute shielding, although the ability of the Bramley et al.² method to also predict ¹⁰³Rh(III) data suggests that their absolute shieldings are perhaps more accurate. In any event, the absolute shieldings are good, for a transition metal. Of course, while e.g. a 1000 ppm error may sound large, the cobalt shift range is ~15 000 ppm. For a nuclide having a 150 ppm shift range, the corresponding error would only be 10 ppm, a more typical and generally acceptable error in e.g. *ab initio* ¹³C shift/shielding calculations.

2. The Chemical Shielding Tensor. Next, we investigate the chemical shielding tensors for ⁵⁹Co. We focus on the four complexes [Co(NO₂)₆]³⁻, [Co(NH₃)₄CO₃]⁺, Co(acac)₃, and [Co(en)₃]³⁺ for the following reasons: For [Co(NH₃)₆]³⁺, there are multiple sites, and the ⁵⁹Co NMR spectrum has not been interpreted. Similarly, there are three sites in K₂Na[Co(CN)₆], and the shift tensors for this species have not been reported. However, for [Co(NH)₄CO₃]Br there is a single-crystal ⁵⁹Co NMR study³⁷ together with an X-ray structure, as is the case for Co(acac)₃.³⁸ For [Co(en)₃]³⁺, the CSA has been deduced from the powder pattern line shape,²⁵ but the anion was unspecified. For Na₃[Co(NO₂)₆], again the CSA has been deduced from the powder pattern line shape,²⁵ but only the high-resolution K₂Na[Co(NO₂)₆] structure is available. Nevertheless, both the NMR and crystallographic results indicate single sites, permitting a theoretical-versus-experimental shielding correlation to be made.

We show in Figure 2 a plot of the experimentally determined chemical shielding tensor elements versus the theoretically evaluated shielding tensor elements (σ_{11} , σ_{22} , and σ_{33} ; Table 2). The traceless representation is used, i.e. relative to the isotropic average, since accurate solid-state isotropic shifts have not been reported in several cases, and in addition our aim here is to evaluate the tensor predictions, rather than any errors in absolute shielding, which were discussed above. There is clearly a very good correlation between theory and experiment, with a slope of 0.82 and an R² value of 0.88, Figure 2. Interestingly,

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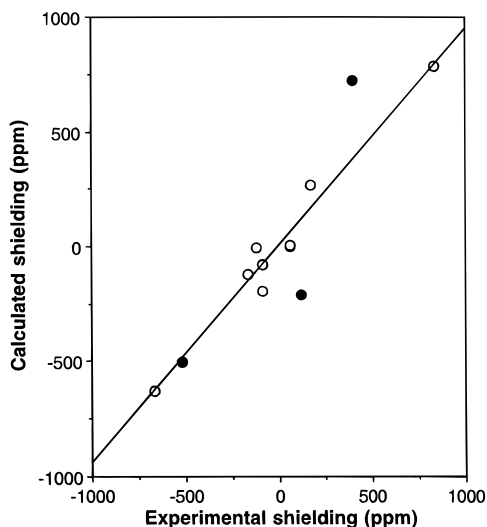


Figure 2. Graph showing correlation between the experimental and theoretical principal elements of the chemical shielding tensor for $[\text{Co}(\text{NO}_2)_6]^{3-}$, $[\text{Co}(\text{en})_3]^{3+}$, $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$, and $\text{Co}(\text{acac})_3$ in the traceless representation. Data from Table 2. The straight line is fitted to the data set *minus* $\text{Co}(\text{acac})_3$ (see the text for details) and has a slope of 0.94 and an R^2 value of 0.96. With the $\text{Co}(\text{acac})_3$ data (●) the slope decreases to 0.82 and the R^2 value to 0.88.

Table 2. Calculated and Experimental ^{59}Co Shielding Tensor Elements in the Traceless Representation

system	calcd (ppm) ^a			exptl (ppm) ^b		
	σ_{11}	σ_{22}	σ_{33}	σ_{11}	σ_{22}	σ_{33}
$[\text{Co}(\text{NO}_2)_6]^{3-}$	-4.3	1.7	2.7	-120	60	60
$[\text{Co}(\text{en})_3]^{3+}$	-191.3	-77.3	268.7	-85	-85	170
$[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$	-642.2	-131.9	774.1	-666.7	-166.7	833.3
$\text{Co}(\text{acac})_3$	-516.3	117.7	398.7	-510	-210	720

^a Basis set 1. ^b From refs. 25, 37, and 38.

the results for $\text{Co}(\text{acac})_3$ appear to lie off of the general trend, as shown by the solid circles in Figure 2. In earlier work, Eaton et al.²⁵ have commented on the single-crystal $\text{Co}(\text{acac})_3$ results of Reynhardt³⁸ and have implied an inconsistency between the single crystal results and their powder spectrum.²⁵ The origin of the differences between the two groups is at present unresolved. If the controversial $\text{Co}(\text{acac})_3$ points are removed from the correlation, the slope improves to 0.94 with an R^2 value of 0.96. Further work will be necessary to resolve this point (which could also, of course, originate in crystallographic uncertainties as well). However, either with or without the $\text{Co}(\text{acac})_3$ results, the correlation between the experimental and the *ab initio* theoretical predictions for the principal elements of the ^{59}Co shielding tensor is very good, and gives additional confidence in the use of *ab initio* methods to predict both transition metal shifts and shielding tensors as well.

3. Vibrational Shielding Derivatives and the Temperature Dependence of the Cobalt Shift. Cobalt chemical shifts have been known for many years to have an extremely large temperature dependence, as well as a large isotope shift. In early work,⁴⁰ it was thought that the large temperature dependence was due to a change in crystal field splitting due to vibrations, but later isotope substitution experiments showed that the remoteness of the isotope substitution greatly influenced shielding, which would not be expected from the early model. Jameson et al.⁴¹ therefore introduced a model in which the shielding is a function of the displacement coordinates, for a diatomic:

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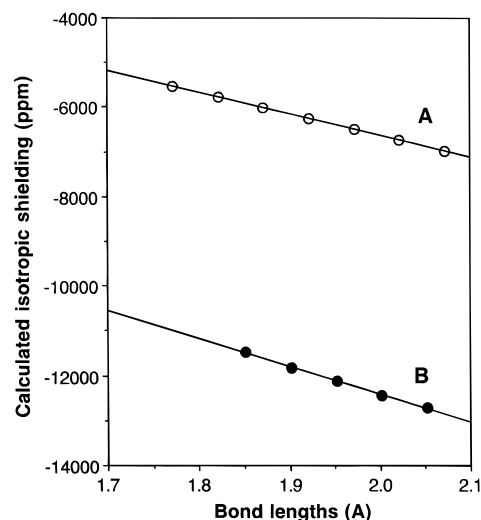


Figure 3. Graph showing variation of the calculated ^{59}Co NMR shielding as a function of cobalt-nearest neighbor bond length: (A) $[\text{Co}(\text{CN})_6]^{3-}$, slope = $-4856 \text{ ppm } \text{Å}^{-1}$, and (B) $[\text{Co}(\text{NO}_2)_6]^{3-}$, slope = $-6180 \text{ ppm } \text{Å}^{-1}$.

$$\sigma_o = \sigma_e + (\partial\sigma/\partial r)_e \langle \Delta r \rangle + 1/2 (\partial^2\sigma/\partial r^2)_e \langle (\Delta r)^2 \rangle \dots$$

in which $\partial^n\sigma/\partial r^n$ are the n 'th derivatives of the shielding, σ , with respect to a given bond displacement, r , and Δr is a generalized displacement.

For $[\text{Co}(\text{CN})_6]^{3-}$, Jameson et al.⁹ found a first-order vibrational shielding derivative, $\partial\sigma/\partial r_{\text{CoC}}$, of $-7500 \text{ ppm } \text{Å}^{-1}$, some 1–2 orders of magnitude larger than typical first-row atom shielding derivatives.⁴² That is, the ^{59}Co nucleus becomes more deshielded upon Co–C bond extension. This value was shown⁹ to account for $\sim 90\%$ of the temperature dependence of the cobalt chemical shift seen experimentally, which corresponds³³ to $\sim 1.38 \text{ ppm } \text{K}^{-1}$. Since the overall shift change seen experimentally is overwhelmingly dominated by $\partial\sigma/\partial r_{\text{CoC}}$, we evaluated this derivative by computing the ^{59}Co shieldings at a series of different Co–C bond lengths. We used a geometry optimized structure and included no counterions in the calculation. The result is shown in Figure 3. There is no curvature, and $\partial\sigma/\partial r = -4856 \text{ ppm } \text{Å}^{-1}$. This value is clearly smaller than that found from the analysis of the isotope shifts,⁹ although since our overall shift range is only 0.83 of that seen experimentally, we can use this overall shielding response as a scale factor to obtain $-4856/0.83 = -5851 \text{ ppm } \text{Å}^{-1}$, in quite good agreement with the previous estimate based on isotope shift experiments.

For $[\text{Co}(\text{NO}_2)_6]^{3-}$, the experimental thermal shielding derivative³³ is $-2.85 \text{ ppm } \text{K}^{-1}$. This is over twice that seen for $[\text{Co}(\text{CN})_6]^{3-}$. As expected, the vibrational shielding derivative, $\partial\sigma/\partial r_{\text{CoN}}$ is larger than that observed in $[\text{Co}(\text{CN})_6]^{3-}$, at $-6180 \text{ ppm } \text{Å}^{-1}$, though clearly this is only a minor increase over the $[\text{Co}(\text{CN})_6]^{3-}$ result, as can be seen in Figure 3. However, the vibrational characteristics of the NO_2^- group are quite different from those of the CN group, and in the absence of $^{15}\text{N}/^{17}\text{O}$ or ^{18}O isotope shift experiments and a detailed vibrational analysis, it is not at present possible to analyze this result in more detail. Also, the nitro group may also undergo Co–N rotational motion, which may contribute in a non-negligible way to the temperature dependence of the shielding.

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Conclusions and Prospects

The results we have discussed above are of interest for several reasons. First, they represent the accurate calculation of not only the shielding patterns but also the absolute shieldings, the principal components of the shielding tensor, and the vibrational shielding derivatives for a series of cobalt(III) complexes. Using hybrid functionals, we successfully reproduce the > 10 000 ppm range of isotropic cobalt shifts with an R^2 value of ~ 0.98 , with the chemical shielding tensor elements also being well-described (slope = 0.82–0.94; R^2 = 0.88–0.96). Second, contrary to previous suggestions, it does not appear to be essential to incorporate f -type functions into the calculations, or relativistic effects, or to obtain low-temperature NMR data to reproduce the main experimental results. Third, there are no systematic differences between the shieldings calculated for anionic and cationic complexes, implying that charge field effects are small, consistent with more recent results of Chan and Au-Yeung⁴³ which were kindly provided to us by a reviewer prior to their

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publication. The use of moderately large basis sets and hybrid exchange-correlation functionals now permits good predictions of isotropic shifts, anisotropic shieldings, absolute shieldings, and shielding derivatives for Co(III) complexes, so it seems reasonable to believe that it may soon be possible to attack even more complex systems, such as metalloporphyrins. However, in the case of complex molecules, there may be additional structural uncertainties. For example, in a nitrosyl cobalt tetraphenylporphyrin, we have determined the ⁵⁹Co shielding to be –13530 ppm using the basis set 1 scheme (437 basis function), considerably more deshielded than anticipated. Thus, while very good accord between theory and experiment is found for simple systems, challenges still remain for the analysis of macromolecular systems.

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