

## Ab Initio Calculations of Co Shielding in Model Complexes

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**Abstract:** Recent ab initio calculations of cobalt NMR shielding show that DFT-GIAO calculations using hybrid functionals are found to reproduce experimental values well. This method is used to calculate the variation of the cobalt NMR shielding tensor of square pyramidal nitrosyl complexes with respect to the CoNO geometry and to differing basal ligands. The isotropic shielding is shown to have a large negative derivative with respect to CoX distance where X is a ligating atom.; the derivative with respect to NO distance is smaller but still significant. The zz component where z is along the CoN(NO) bond is more sensitive to the basal ligands but the other two principal components are sensitive to the CoNO geometry.

**Keywords:**  $^{59}\text{Co}$ , NMR shielding, DFT, ab initio calculations, NO

### Introduction

The scope of cobalt NMR spectroscopy was illustrated in a recent review [1].  $^{59}\text{Co}$  was one of the first nuclei to be studied using NMR spectroscopy. It is a nucleus with a high receptivity and the largest known chemical shift range of around 20 000 ppm. There are a large number of stable low-spin Co(III) complexes which are diamagnetic and hence well-suited to NMR studies.  $^{59}\text{Co}$  chemical shifts were also the subject of early theoretical considerations. Ramsey [2] derived an approximate formula for the paramagnetic term in the shielding of the cobalt atom in terms of ligand field theory.

$$\sigma_{\text{iso}}^{\text{p}} = -\frac{8\mu_0\mu_{\text{B}}^2}{\pi} \frac{\langle r^{-3} \rangle_{3d} \left| \left\langle {}^1A_{1g} \left| L_z \right| {}^1T_{1g} \right\rangle \right|^2}{\Delta E({}^1A_{1g} \rightarrow {}^1T_{1g})} \quad (1)$$

where  $\Delta E$  is the average excitation energy from the ground state to the excited states linked by the shielding operator, replaced in this case by the ligand field transition ( ${}^1A_{1g} \rightarrow {}^1T_{1g}$  in the case of octahedral complexes) to a low-lying excited state. This led to a prediction that  ${}^{59}\text{Co}$  shieldings would correlate with the ligand field splitting energies,  $\Delta_o$ , of cobalt complexes and such a correlation was found for measured spectra of simple complexes [3]. In later work [4-6], the  $r^{-3}$  term and the orbital angular momentum integral which determine the covalency or nephelauxetic effect were also shown to be important. In a series of Co(III) pentammine complexes, the angular momentum integral was shown to be of negligible influence in determining the change in chemical shift and a plot of isotropic chemical shift gave a better correlation with the ratio of the nephelauxetic factor,  $\beta_{35}$ , to the excitation energy than with the reciprocal of the excitation energy alone [7]. The nephelauxetic factor,  $\beta$ , is a function of interelectron repulsion and is defined as the ratio of the Racah B parameter (obtained from optical spectra) in the complex and in the gaseous metal ion. Recently [8], Chan and Au-Yeung have shown that the angular momentum integral is related to the nuclear quadrupole coupling constant, QCC. For  ${}^{59}\text{Co}$  solution spectra, quadrupole relaxation is the dominant mechanism and QCC can be obtained from the half-width of the resonance. Correlations were obtained for complexes  $[\text{Co}(\text{NH}_3)_5\text{X}]^{(3+n)+}$ ,  $[\text{Co}(\text{CN})_5\text{X}]^{(2-n)-}$  and  $\text{trans-}[\text{Co}(\text{en})_2\text{X}_2]^{(3+n)+}$  between the  ${}^{59}\text{Co}$  chemical shift and  $(\Delta\nu_{1/2})^{1/2}/\Delta E_{\text{av}}$  where  $\Delta\nu_{1/2}$  is the solution linewidth and  $\Delta E_{\text{av}}$  is the energy of the  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  transition. This suggests that the angular momentum integral is important in determining the chemical shift. The data for each type of complex lay on two lines, one for complexes with hard ligands, X, and one for those where X is a soft ligand. The differences between the hard and soft ligands is attributed to the increased covalency of the Co-X bond for soft ligands which causes a quenching of the angular momentum.

Full ab initio calculations of  ${}^{59}\text{Co}$  chemical shieldings have only recently been feasible however. The low energy excitations which give rise to the large chemical shifts observed and to the simplification of the denominator in Ramsey's formula pose problems for ab initio calculations and gave rise to large errors in Hartree-Fock calculations. For molecules containing light elements, the introduction of MP2 correlation corrections [e.g. 9,10] and multi-configurational methods [e.g. 11] have led to considerable success in calculating chemical shielding tensors in cases where there are low excitation energies. For a transition metal complex, however, very large computer resources would be needed for such methods. The advent of density functional methods has made possible the ab initio calculation of NMR shielding of transition metal complexes with reasonable accuracy with less computer resource.

The first density functional (DFT) calculations on cobalt complexes [12] were performed using the SOS-DFT-IGLO method of Malkin et al [13] in the deMon suite of programs [14-16]. The complexes studied covered both neutral and ionic species -  $[\text{Co}(\text{CN})_6]^{3-}$ ,  $[\text{Co}(\text{NO}_2)_6]^{3-}$ ,  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Co}(\text{en})_3]^{3+}$ ,  $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$  and  $[\text{Co}(\text{acac})_3]$ . The best results were found for the Becke-Perdew [17] exchange correlation potential with the TZVP basis set of Malkin et al [13-16,18, 19] on the cobalt and the

IGLO-II basis set of Kutzelnigg [20] on the surrounding ligands. Although a considerable improvement on previous semi-empirical calculations [21], the calculated values were considerably more shielded than the experimental values e.g. -3159 ppm for  $[\text{Co}(\text{CN})_6]^{3-}$  compared to the currently accepted absolute shielding of -5400 ppm [6]. Possible reasons for the discrepancy were put forward including absence of 4f functions in the Co basis set and the description of the excited state in DFT theory.

Chan and Au-Yeung [22] compared the DFT-IGLO method used in this study with the DFT-GIAO option in Gaussian94 [23] using the Becke-Perdew functional on 13 hexacoordinated complexes of Co(III) involving the ligands en,  $\text{NH}_3$ ,  $\text{SCN}^-$ ,  $\text{N}_3^-$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}_2^-$ ,  $\text{CN}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}$ ,  $\text{ONO}^-$ ,  $\text{CO}_3^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$ . They concluded that DFT-GIAO produced results closer to experiment than DFT-IGLO. Using the DFT-GIAO method with the hybrid functional B3LYP gave results even closer to experiment. A subsequent paper [24] calculated chemical shift spans and skews for several complexes using the DFT-GIAO-B3LYP method and 6-311G basis sets with varying numbers of polarisation functions and obtained satisfactory agreement with experiment.

More recent studies of the complexes studied in ref. 12 [25] using DFT-GIAO-B3LYP in Gaussian94 with Wachters basis set (62111111/3311111/3111) [26, 27] on cobalt and the 6-31G\* basis set on the ligand atoms also gave reasonable results. These authors found that the addition of f functions to the cobalt basis set and the use of larger basis sets gave little improvement.

The DFT-GIAO studies not only reproduce the chemical shift well but also yielded a remarkably good value for the absolute shielding of  $[\text{Co}(\text{CN})_6]^{3-}$ . Godbout and Oldfield [25] plotted the calculated absolute chemical shieldings against the experimental chemical shifts and obtained a value for the absolute shielding of -5162 ppm as the intercept compared to the experimentally determined value of -5400 ppm.

The success of hybrid DFT methods has been analysed [28] and attributed to more diffuse virtual orbitals, coupling due to Hartree-Fock exchange and the increase of the HOMO-LUMO gap relative to that obtained using pure DFT methods.

Because of their use as models for biological systems such as Vitamin B12 and the isoelectronic Fe(II) hemes, cobalt complexes with macrocyclic ligands such as porphins have been of considerable recent interest. A recent paper [29] reports a calculation of cobalt chemical shielding for the porphin complex  $[\text{Co}(\text{TDCPP})(\text{MeIm})_2]^+$  in which the TDCPP (tetra(dichlorophenyl)porphyrin) group forms a plane around the cobalt and two methylimidazole groups occupy positions above and below this plane. The calculations used the DFT-GIAO-B3LYP method with a 6-311G basis set on the lighter atoms, the Maclean-Chandler basis set [30, 31] on chlorine and the Wachters-Hay all-electron basis set [26, 32] for cobalt. Although chemical shift tensors are more difficult to calculate than the isotropic shift, these authors obtained very close agreement with the experimental chemical shift tensor. Zhou et al [33] considered a set of complexes in which  $[\text{Co}(\text{CN})_6]^{3-}$  was bound to protonated polyammonium macrocyclics. They reproduced the  $^{59}\text{Co}$  chemical shifts by altering the Co-C and  $\text{C}\equiv\text{N}$  distances and the symmetry of  $[\text{Co}(\text{CN})_6]^{3-}$  to fit the geometry found in the macrocycles.

There have been some studies of how  $^{59}\text{Co}$  shielding varies with changes in geometry. Experimentally the variation of shielding with geometry shows up as temperature dependence and isotope shifts. Cobalt chemical shifts have extremely large temperature dependence and large isotope shifts indicating a strong dependence on geometry. In simple cases, such data can be analysed to obtain derivatives of shielding with respect to bond extensions and angle deformations. By analysing isotope shifts, Jameson et al [34] found for  $[\text{Co}(\text{CN})_6]^{3-}$  that the first order derivative of the shielding with respect to the Co-C bond distance was  $-7\,500\text{ppm}\,\text{\AA}^{-1}$ , that is the cobalt nucleus becomes more deshielded as the Co-C distance increases. The thermal shielding derivative of  $[\text{Co}(\text{NO}_2)_6]^{3-}$  has been measured [34] as  $-2.85\text{ppm}\,\text{K}^{-1}$ , over twice that observed for  $[\text{Co}(\text{CN})_6]^{3-}$ , but the vibrational motion is more complicated than that of the cyano complex and there is the possibility of internal rotation of the nitrito group so that the thermal shielding derivative is not easily linked to the derivative of the shielding with Co-N distance. Godbout and Oldfield [25] have calculated the variation of cobalt shielding with Co-C bond distance in  $[\text{Co}(\text{CN})_6]^{3-}$  and with Co-N distance for  $[\text{Co}(\text{NO}_2)_6]^{3-}$ . They used a geometry-optimised structure for the free ion with a range of Co-C or Co-N distances. In both cases, the plots were linear with slopes of  $-4\,856\text{ppm}\,\text{\AA}^{-1}$  for  $[\text{Co}(\text{CN})_6]^{3-}$  and  $-6\,180\text{ppm}\,\text{\AA}^{-1}$  for  $[\text{Co}(\text{NO}_2)_6]^{3-}$ . They thus correctly predict that the slopes are negative, 1-2 orders of magnitude larger than the shielding derivatives of first row atoms and that the magnitude of the derivative for the nitrito complex is larger than that for the cyano-complex.

We report here a study of 5-coordinate cobalt nitrosyl complexes with particular focus on the response of  $^{59}\text{Co}$  shielding to variation in the geometry of the CoNO grouping.

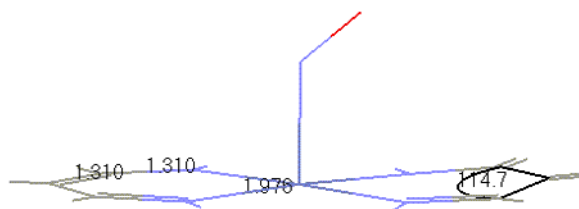
Square-pyramidal nitrosyl porphyrin complexes have been studied as models for NO and  $\text{O}_2$  binding to heme-like systems. The CoNO group can adopt two distinguishable geometries, linear with a CoNO angle of  $180^\circ$  and bent where the CoNO angle is about  $130^\circ$ , resembling the FeOO arrangement in heme. Godbout and Oldfield [25] noted that they had determined the  $^{59}\text{Co}$  shielding in a nitrosyl cobalt tetraphenylporphyrin as  $-13\,530\text{ppm}$ . They remarked that this was considerably more deshielded than anticipated. However this value yields a chemical shift of  $8086\text{ppm}$  which is in fact very close to the measured value [35] of  $7\,909\text{ppm}$  for cobalt nitrosyl tetraphenylporphyrinate in solution.

In addition to the data on porphyrinato complexes, there are also experimental measurements of solution chemical shifts for Co in nitrosyl complexes with polydentate ligands coordinating through N and O and nitrosyl dithiocarbamate complexes.

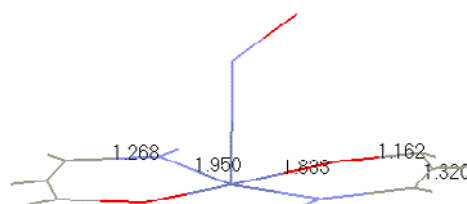
Because of the lower symmetry, square-pyramidal nitrosyl complexes would be expected to show greater asymmetry than the complexes previously studied and the different components of the shielding tensor can be shown to respond differently to geometry changes.

## Computational method

The structures of the model complexes used were



for the porphyrin complexes, with a N-Co-N angle of  $76^\circ$  and a Co-N-C angle of  $137^\circ$ ,



for the Schiff base complexes with an N-Co-O angle of  $89^\circ$ , a Co-N-C angle of  $129.5^\circ$ , a Co-O-C angle of  $136^\circ$  and a C-C-C angle of  $162^\circ$  and



for the dithiocarbamate-complexes, with a Co-S-C angle of  $68^\circ$ . All three ligands were kept planar. The arrangement of the basal ligands was kept symmetrical as shown and fixed for most calculations. Optimisation gave shorter Co-basal atom distances on the side nearest the nitrosyl oxygen when these distances were allowed to vary. Full optimisation of the CoNO group generally led to a tilt of the CoN axis away from the perpendicular to the plane, and together with the shorter Co-basal atom distance and the orientation of the nitrosyl oxygen over a basal ligand atom, this allowed stabilisation of the structure through O-basal ligand atom interaction. In experimental structures, the Co-basal atom distances are kept fixed in the symmetrical position by the rest of the molecule as in the porphyrates and/or by the crystal packing, so it was considered a better model to retain the symmetry of the basal ligands. In most of the results reported here, only one parameter (bond distance or angle) was varied at a time keeping all others fixed. The nitrosyl oxygen was positioned between the basal atoms for some runs and over one basal atom for others. Both arrangements are found experimentally. However we also calculated changes in shielding for dithiocarbamate complexes allowing the CoNO geometry to relax as the Co-N distance and CoNO angle were changed.

Our calculations used the DFT-GIAO-B3LYP method in Gaussian98 [36] on the DEC8400/CompaqES40 cluster, Columbus, at the Rutherford Appleton Laboratory. The basis set used was Ahrlich's VTZ basis set [37] plus polarisation functions on all atoms. Convergence was found to be easier using the same basis set on all atoms. Triple zeta basis sets, as noted in earlier work described in the Introduction, give good results for Co shielding when used with hybrid functionals. The absolute shielding of  $[\text{Co}(\text{CN})_6]^{3-}$  using the optimised geometry with a Co-C distance of 191pm and  $\text{C}\equiv\text{N}$  distance of 117pm was calculated to be  $-5\ 882\text{ppm}$  and using the experimental geometry for  $\text{K}_3[\text{Co}(\text{CN})_6]$  of Co-C 190pm and  $\text{C}\equiv\text{N}$  113pm  $-5\ 360\text{ppm}$  with this method and basis set. These values are very close to the experimentally determined one and give us confidence in our method.

## Results

The calculated shielding tensors for our model complexes are shown in Table 1 along with the Mulliken charges on Co.  $\Omega$  is the span and  $\kappa$  the skew. In terms of the principal components of the tensor,  $\sigma_{11}$ ,  $\sigma_{22}$  and  $\sigma_{33}$  where  $\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$ ,  $\Omega = \sigma_{33} - \sigma_{11}$  and  $\kappa = 3 \times (\sigma_{\text{iso}} - \sigma_{22})/\Omega$ .

We define molecular axes so that the CoN(NO) bond forms the z axis and the y axis is between the basal ligands. For the majority of the porphyrin and thiocarbamate complexes where the CoNO group is in the xz plane and the CoNO angle is in the range  $115\text{-}140^\circ$ , one principal component, usually  $\sigma_{33}$  but in some cases  $\sigma_{22}$ , is  $\sigma_{yy}$ . The 1 axis is rotated by an angle of  $5\text{-}15^\circ$  from the x axis towards the z axis in the xz plane for the dithiocarbamate complexes. For the porphyrin complexes the 1 axis is rotated by a slightly larger angle ( $12\text{-}20^\circ$ ) from the z axis towards the x axis. The Schiff base complexes and those where the CoNO group is not in the xz plane are less symmetrical and none of the principal axes coincides with x, y or z. The principal axes of the Schiff base complexes are however close to those of the porphyrin complexes. For large CoNO angles,  $\sigma_{xx}$  and  $\sigma_{yy}$  become more nearly equal as the complex approaches  $\text{C}_{2v}$  symmetry.

An analysis of the d energy levels in square-pyramidal nitrosyl complexes of iridium was obtained by Mingos [38] using the Wolfsberg-Helmholtz method. Using the orientation just described, the HOMO was the a' orbital including contributions from  $d_{z^2}$ ,  $d_{xz}$  and the  $\pi^*$  and  $\sigma$  orbitals on NO and the LUMO an a'' orbital with contributions from  $d_{yz}$  and the  $\pi^*$  on NO. These would be expected to provide a large contribution to the paramagnetic shielding, particularly  $\sigma_{xx}$ , for Co from  $d_{z^2}$  to  $d_{yz}$  which will be dependent on the Co-NO bond. However there is another contribution, primarily to  $\sigma_{zz}$ , from  $d_{xy}$  to  $d_{x^2-y^2}$  which does not involve NO orbitals and will be highly dependent on the Co-basal ligand interaction [39]. Thus if this latter contribution predominates we should expect little dependence of the shielding on the CoNO geometry. Our calculations on the dithiocarbamate complexes indicate that the HOMO is the  $d_{z^2}/\text{NO}$  bonding a' orbital and the LUMO the  $d_{yz}/\text{NO}$   $\pi^*$  a'' orbital. Both orbitals become lower in energy as the CoN bond distance increases or the CoNO angle decreases but the

**Table 1.** Calculated Co shielding tensors for model square pyramidal nitrosyl complexes.

r(Co-basal atom) /pm	r(Co-N(NO))/pm	r(NO) /pm	$\angle\text{CoNO} /^\circ$	$\sigma_{\text{iso}}/\text{ppm}$	$\sigma_{11}/\text{ppm}$	$\sigma_{22}/\text{ppm}$	$\sigma_{33}/\text{ppm}$	$\Omega/\text{ppm}$	$\kappa$	Mulliken charge
<i>Porphin complexes</i>										
197.6	173.8	101	120	-15542	-21851	-15902	-8871	12900	0.08	0.243
“	“	112	“	-16057	-21373	-16990	-9807	11566	0.24	0.259
“	“	“	130	-16528	-21809	-17688	-10086	10723	0.32	0.253
“	“	“	140	-17460	-22853	-18628	-10898	11955	0.29	0.244
“	“	114	120	-16157	-21348	-17153	-9969	11379	0.26	0.261
“	“	116	“	-16257	-21345	-17300	-10126	11219	0.28	0.263
“	183.3	112	“	-17576	-22245	-18695	-11789	10456	0.02	0.297
<i>Schiff base complexes</i>										
195.0/ 183.3	173.0	101	125	-13142	-18634	-13220	-7571	11063	0.22	0.327
“	173.8	112	120	-13760	-18432	-14374	-8474	9958	0.18	0.348
“	“	116	120	-13993	-18478	-14759	-8441	10037	0.23	0.352
“	“	112	130	-14128	-18889	-14762	-8734	10155	0.19	0.342
“	“	116	129	-14337	-19002	-15021	-8988	10074	0.20	0.347
“	“	112	140	-14864	-19872	-15224	-9496	10376	0.10	0.335
“	180.6	112	127	-14888	-19207	-15695	-9762	9445	0.26	0.372
“	183.3	101	130	-14398	-19196	-14936	-9062	10134	0.16	0.367
“	193	101	125	-15230	-19466	-15928	-10296	9170	0.23	0.403
“	“	110	140	-17685	-22727	-17220	-13109	21408	-0.07	0.417
“	“	116	120	-17274	-23250	-16977	-11595	11655	-0.08	0.432
<i>Dithiocarbamate complexes</i>										
200	172.8	110	120	-5713	-9074	-5388	-2677	6397	-0.15	-0.241
210	172.8	101	115	-6922	-9798	-6025	-4944	4854	-0.55	-0.142
“	177	“	120	-7443	-11338	-5963	-5028	6310	-0.70	-0.129
“	172.8	110*	120	-7761	-11836	-5871	-5576	6266	-0.90	-0.135
“	“	“	“	-7848	-12553	-5794	-5198	7355	-0.84	-0.146
“	“	“	130	-8074	-13072	-5694	-5456	7616	-0.94	-0.143
“	“	“	140	-8711	-14238	-6407	-5488	8750	-0.79	-0.142
“	“	“	150	-10036	-16659	-8360	-5087	11272	-0.43	-0.143
“	“	“	160	-12904	-22024	-12393	-4296	17728	-0.09	-0.147
“	“	“	170	-19965	-33982	-22636	-3279	30703	0.26	-0.152
210	172.8	112	120	-8023	-12959	-5777	-5333	7626	-0.88	-0.145
“	173.8	“	“	-8085	-12301	-6136	-5818	6483	-0.90	-0.127
“	175	117*	135	-9422	-15016	-7733	-5518	9498	-0.53	-0.124
“	177	110	120	-8380	-13515	-5845	-5779	7736	-0.98	-0.124
210	183	101	120	-8053	-12367	-6054	-5737	6630	-0.90	-0.09
“	“	110	“	-9191	-14995	-6684	-5894	9101	-0.83	-0.093

**Table 1.** (continued)

r(Co-basal atom) /pm	r(Co-N(NO))/pm	r(NO) /pm	$\angle$ CoNO / $^\circ$	$\sigma_{\text{iso}}$ /ppm	$\sigma_{11}$ /ppm	$\sigma_{22}$ /ppm	$\sigma_{33}$ /ppm	$\Omega$ /ppm	$\kappa$	Mulliken charge
“	“	116	“	-9928	-16694	-7291	-5798	10896	-0.73	-0.099
“	193	110	“	-10685	-17718	-8411	-5928	11790	-0.58	-0.046
“	“	“	130	-11096	-18580	-8880	-5829	12751	-0.52	-0.040
“	“	“	140	-12264	-21000	-10216	-5575	15425	-0.40	-0.036
226.5	172.8	110	120	-11632	-16300	-11881	-6715	9585	0.08	0.046
	175	111*	130	-12536	-16297	-11985	-9325	6972	-0.24	0.057
“	175	116.6 <sup>#</sup>	129.5 <sup>#</sup>	-12757	-18754	-11704	-7814	10940	-0.29	0.058
“	183	116.25 <sup>#</sup>	127.3 <sup>#</sup>	-14240	-21366	-12180	-9174	12192	-0.51	0.091
“	193	115.86 <sup>#</sup>	124.8 <sup>#</sup>	-16284	-25185	-12588	-11077	14108	-0.79	0.129
“	187.85 <sup>#</sup>	116.23 <sup>#</sup>	120	-14936	-22490	-12502	-9817	12673	-0.58	0.11
“	183.57 <sup>#</sup>	116.12 <sup>#</sup>	130	-14535	-21980	-12143	-9481	12499	-0.57	0.093
“	180.8 <sup>#</sup>	115.89 <sup>#</sup>	140	-14907	-22965	-11683	-10072	12893	-0.75	0.078
“	191.0 <sup>#</sup>	101	127.7 <sup>#</sup>	-13822	-18922	-13503	-9040	9882	-1.10	0.108
“	186.04 <sup>#</sup>	112	127.1 <sup>#</sup>	-14359	-21167	-12569	-9342	11825	-0.45	0.100
“	185.34 <sup>#</sup>	114	126.9 <sup>#</sup>	-14455	-21545	-12417	-9402	12143	-0.50	0.099
240.0	173.8	101*	120	-16943	-23093	-14668	-13067	10026	-0.68	0.237

\* O of nitrosyl over basal ligand atom

# partially optimised geometry

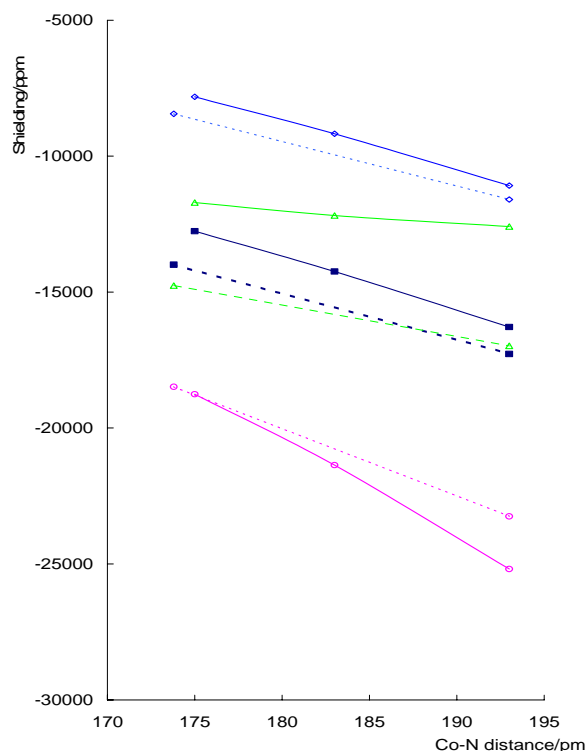
decrease in the HOMO energy is greater so that the energy gap also decreases. The Mulliken population on Co increases slightly with CoN distance and NO distance and decreases with CoNO angle, but is mainly determined by the basal ligands, increasing as the Co-basal ligand distance increases reflecting a lowering of covalency.

Figure 1 shows the variation of the isotropic shielding and the principal components with Co-N(NO) distance for both fixed NO distance and CoNO angle and when the CoNO geometry is allowed to relax. The NO distance for the series of runs in which the CoNO geometry is optimised is close to 1.16Å and so we have used a series of runs with an NO distance of 1.16Å for the fixed geometry comparison.

$\sigma_{11}$  and  $\sigma_{33}$  both decrease with increasing Co-N distance for the two sets of data shown.  $\sigma_{22}$  shows the least variation with Co-N distance as is expected for a component that is mainly  $\sigma_{zz}$ . Relaxing the CoNO geometry has little effect on the pattern of change. The notable difference in  $\sigma_{22}$  stems from the difference in the basal ligands.

The derivative of the isotropic shielding with respect to the Co-N distance is about  $-19\,000\text{ ppm \AA}^{-1}$  for the complexes in figure 1. Reference to the data in Table 1 shows a smaller derivative for complexes with shorter NO distances.





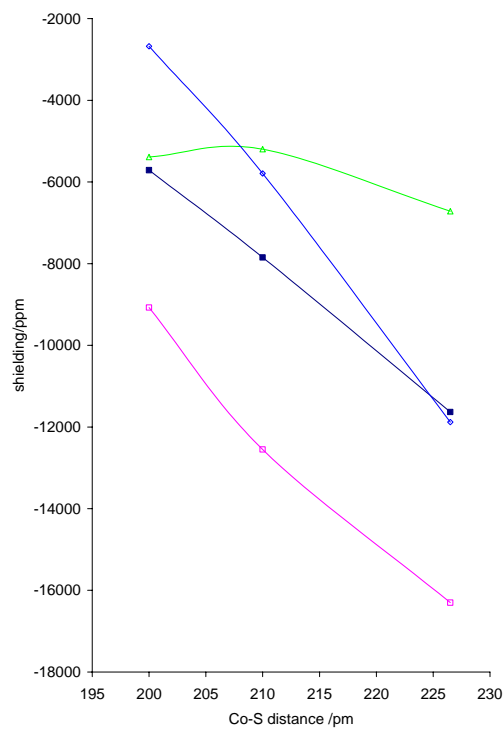
**Figure 1.** Variation of shielding with change in Co-N distance for a set of dithiocarbamato complexes for which the CoNO geometry is relaxed (solid lines) and for Schiff base complexes with CoNO  $120^\circ$  and an NO distance of  $1.16 \text{ \AA}$  (dotted lines) ■ isotropic shielding, ○  $\sigma_{11}$ , ▲  $\sigma_{22}$  and ◇  $\sigma_{33}$ .

The isotropic shielding is also markedly dependent on the basal ligands. Adjusting the cobalt distance to the basal ligands in the dithiocarbamato complex from  $2.0 \text{ \AA}$  to  $2.1 \text{ \AA}$  to  $2.65 \text{ \AA}$  led to an increase in shielding equivalent to a derivative greater than  $-20\,000 \text{ ppm \AA}^{-1}$  due to increases in  $\sigma_{xx}$  and  $\sigma_{zz}$  arising from decreased overlap of  $d_{z^2}$  and  $d_{x^2-y^2}$  with basal ligand orbitals, as shown in figure 2. In this figure  $\sigma_{yy}$  and  $\sigma_{zz}$  refer to whichever of  $\sigma_{22}$  and  $\sigma_{33}$  are closest to these components, as the direction of the 2 and 3 axes change across the series.  $\sigma_{zz}$  is particularly sensitive to changes in Co-S distance as expected.

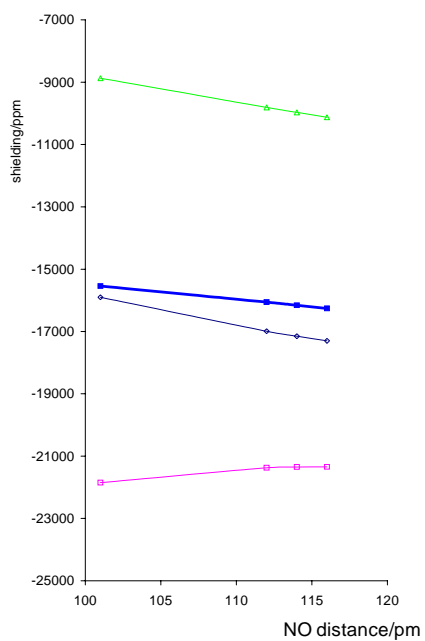
We would expect some effect from altering the NO distance because the nitrogen orbitals are used in bonding to O and Co and as the NO bond is weakened, the CoN bond is strengthened. The calculated shielding shows a decrease with increasing NO distance, figure 3, for all components except  $\sigma_{11}$ .

For the porphyrin model shown the plots are much closer to linear with derivatives of  $-4\,747 \text{ ppm \AA}^{-1}$  than those with respect to Co-ligand distance, although larger derivatives are found for some of the dithiocarbamato complexes.

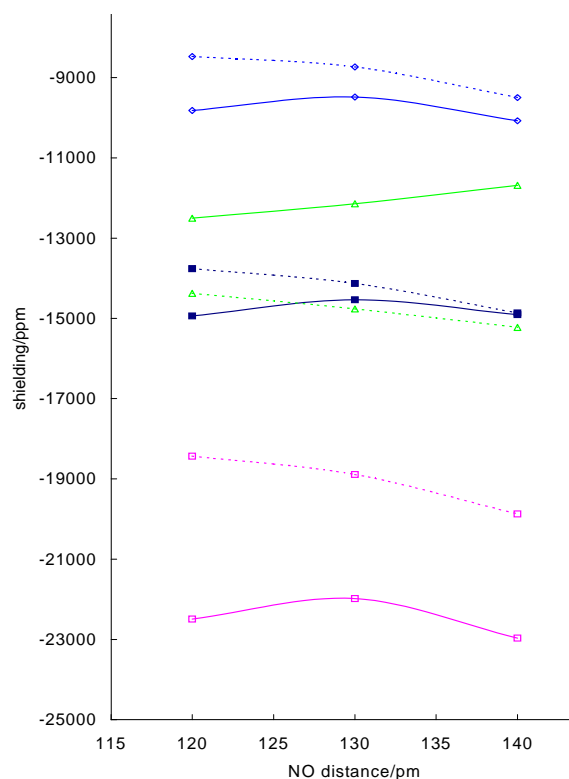
CoNO groups have the potential to wag (varying the angle) and swing (varying the position of the nitrosyl oxygen with respect to the base ligands). Varying the angle from  $120^\circ$  to  $140^\circ$ , the range of



**Figure 2.** Calculated variation of Co shielding with Co-S distance for dithiocarbamate complexes with  $r(\text{Co-N}) = 1.728 \text{ \AA}$ ,  $r(\text{NO}) = 1.10 \text{ \AA}$  and a CoNO angle of  $120^\circ$ . ■ isotropic shielding, □  $\sigma_{11}$ , △  $\sigma_{yy}$  and ◇  $\sigma_{zz}$ .



**Figure 3.** Variation of calculated Co shielding with NO distance for a model porphyrin complex with  $r(\text{CoN}) = 1.74 \text{ \AA}$ . ■ isotropic shielding, □  $\sigma_{11}$ , △  $\sigma_{22}$  and ◇  $\sigma_{33}$ .



**Figure 4.** Variation of calculated  $^{59}\text{Co}$  shielding with CoNO angle for model nitrosyl complexes: dithiocarbamato complex with optimised CoNO geometry (solid line), model Schiff base complex with  $r(\text{CoN}) = 1.738\text{\AA}$  and  $r(\text{NO}) = 1.12\text{\AA}$  (dotted line) ■ isotropic shielding, □  $\sigma_{11}$ ,  $\triangle\sigma_{22}$  and  $\diamond\sigma_{33}$

angles found in most bent Co(III) nitrosyl complexes, produced a decrease in shielding of about 1 000 – 2 000 ppm about 10% of the absolute shielding. This is exemplified in figure 4 where the isotropic shielding is plotted against CoNO angle for a model Schiff base model complex. Similar changes with change in angle were obtained for a porphyrin model complex and for dithiocarbamato and Schiff base complexes with different CoN and NO distances.

In this case, the partially optimised structure displays a different pattern to the series with fixed CoNO geometry with the shielding going through a maximum. In these structure the Co-N distance decreases with increasing angle and as shown in figure 1 this will lead to an increase in shielding, offsetting the decrease due to increase in angle.

The effect of ligand swinging was investigated by calculating the shielding with the nitrosyl oxygen in two positions, between two basal ligating atoms and over one basal atom. The changes in the tensor for a typical dithiocarbamato complex can be seen by comparing the starred entries with non-starred entries for the dithiocarbamato complex with  $\text{Co-N} = 1.728\text{\AA}$ ,  $\text{N-O} = 1.1\text{\AA}$  and CoNO angle of  $120^\circ$  in Table 1.

These differences are not large but are noticeable. Averaging over these two positions would give a reduced span because the tensor principal components will not be exactly aligned for the two positions.

For the complex with the O between the ligands, then one principal axis is along the y axis with the other two rotated by  $12^\circ$  from the x and z axes, whereas all three axes are rotated for the other complex leading to one axis lying almost over Co-S direction where S is the atom over which the nitrosyl oxygen lies.

## Discussion and Conclusions

Density functional calculations of cobalt shielding in Co(III) complexes using DFT/GIAO methods with moderately-sized basis sets and hybrid density functionals have been found by several groups to give good agreement with experimental shielding values. Agreement is good not only for simple octahedral complexes but also for larger systems such as porphinato complexes. We have found that such calculations also give good results for square-pyramidal nitrosyl complexes of cobalt.

Analysis of the shielding tensors shows that the largest component arises from the  $d_{z^2}$  to  $d_{yz}$  transition. The paramagnetic part of this component increases rapidly with increasing cobalt -ligand distance. The principal component closest to zz, where the z axis is along the Co-N(NO) bond, shows a marked dependence on cobalt-basal ligating atom distance and the nature of the ligand as would be expected for a component arising primarily from orbitals in the basal plane. The third principal component by contrast is more sensitive to Co-N(NO) distance than to the basal ligands. The isotropic shielding displays large changes with Co-N and Co-basal ligating atom distance. The large changes in the shielding of the order of  $-10^3 - 10^4$  ppm/Å with variation in cobalt ligating atom distance agree with experimental observations of temperature variation and isotope shifts which indicate that cobalt shielding is very sensitive to changes in geometry. The isotropic shielding decreases with NO distance but the derivative is smaller than that with respect to Co-ligating atom distances and the most negative component of the shielding tensor can decrease with increasing NO distance. Changes in the shielding tensor with CoNO angle are much smaller. For complexes with the basal ligands arranged at the experimental distances from the cobalt, then the shielding increases  $N < N,O < S$ .

A recent study on B12 model systems [40] shows that increase in axial Co-C bond distance due to substitution of different alkyl groups leads to an increased HOMO-LUMO gap via decrease of the HOMO energy. Our studies show that increase of the Co-N(NO) distance leads to a lowering in energy of both HOMO (Co  $d_{z^2}/NO$   $\sigma/\pi$ ) and LUMO (Co  $d_{yz}/NO$   $\pi^*$ ) with a greater lowering of the LUMO leading to a decrease in HOMO-LUMO energy gap.

Ideally, for comparison with experimental chemical shifts calculations should be corrected for temperature effects, although this is difficult except for simple cases such as  $[Co(CN)_6]^{3-}$  where most of the effect comes from the variation in one distance (CoC).

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