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Hydrogen and Nitrogen NMR Chemical Shifts of Pentaamminecobalt(III) Complexes: Correlations with Parameters Calculated from Ligand Field Spectra

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The differences between the chemical shifts of cis and trans protons of pentaamminecobalt(III) complexes, $[Co(NH_3)_5X]^{n+}$, are clearly mainly an effect of the magnetic anisotropy of the cobalt central ion. This anisotropy is here discussed on the basis of the parametrical d^6 model, and it is found that the influence of the tetragonal ligand field on the relative magnitudes of the three Cartesian components of the orbital angular momentum operator is insignificant within the model. The expression thus obtained predicts a relation between the chemical shifts and the position of the ligand X in the spectrochemical series, but this relation is not borne out by experiment. Actually the trend of the proton and nitrogen-14 chemical shifts is the same as that previously found for cobalt-59 shifts; i.e., the shifts follow the internal field strength parameter, $\Sigma = \Delta/B$. This observation has been rationalized through an empirical modification of the parameter, which expresses the susceptibility anisotropy, by the incorporation of anisotropic nephelauxetism. A qualitative theoretical interpretation of the model, which involves anisotropic nephelauxetism, can be made on the basis of orbital angular momentum reduction.

Introduction

In the course of studies of reactions of cobalt(III) pentaammines $[Co(NH_3)_5X]^{n+}$ ($n = 1$–3), a large number of chemical shifts for ^{59}Co, ^{14}N, and ^{1}H have been collected. These d^6 cobalt complexes all have low-spin ground states and accordingly show no first-order paramagnetism. However, when a pentaammine complex is placed in a magnetic field (e.g. of an NMR spectrometer), excited ligand field states are mixed into the ground state whose orbital angular momentum component along the direction of the magnetic field thus becomes different from zero. This effect of the magnetic field gives rise to the so-called second-order paramagnetism (or temperature-independent paramagnetism (TIP)) and is also of importance for the chemical shifts of the different nuclei in the complexes and, in particular, for their variation with the ligand X. Theoretically, the NMR screening can be calculated by using the Ramsey equation, but this equation can only be used directly (vide infra) for the cobalt nucleus.

The cobalt shifts have been discussed in detail in ref 1, and it was found that they follow the internal field strength series of ligands rather than the spectrochemical series as had originally been suggested. This was taken as an indication that other quantities besides the energies of the excited states vary in the Ramsey equation. The internal field strength parameter, Σ, is defined as the ratio Δ/B where Δ is the spectrochemical parameter and B is one of the Racah interelectronic repulsion parameters. When B is determined from the UV–vis spectrum of a complex, it is generally found that its value is reduced relative to that of the corresponding gaseous metal ion. This semiempirical phenomenon is called nephelauxetism, and it has been explained as a consequence of the formation of covalent bonds between metal and ligands. However, a quantitative or even semiquantitative treatment of nephelauxetism has never been advanced.

Actually the discovery that the internal field strength series reflects the order of the cobalt shifts was based upon the observation that the same is true for the hydrogen shifts of the pentaammines. These latter shifts will be the subject of the present paper together with those of the nitrogen nuclei. Many of the concepts and methods to be used here have been discussed in the paper[1] dealing with the ^{59}Co shifts, which should be consulted.

Experimental Section

Proton magnetic resonance spectra were recorded with a Varian HA-100 spectrometer equipped with heteronuclear decoupling facilities for $^{1}H\{^{14}N\}$ and $^{1}H\{^{59}Co\}$ INDOR experiments.[2] Chemical shifts are referred to sodium 3-(trimethylsilyl)propanesulfonate as internal reference, and ^{14}N decoupling was used to sharpen and resolve the peaks where necessary. Solutions were saturated by using the solvents and temperatures noted in Table II. Many of the proton shifts have been published elsewhere.[3]

^{14}N spectra were determined by INDOR with protons used as the observing nucleus. $[Co(NH_3)_6]Cl_3$ (saturated in H_2O) was chosen as reference. Care was taken with deuterium solvents to choose an acid concentration such that insignificant replacement of H by D took place during the experiments.[4]

The sign convention used here for the chemical shift δ has been discussed in ref 1 and is that recommended by IUPAC.[5] The use of this convention leads to some apparent inconsistencies with the earlier literature[6–9] dealing with proton and/or nitrogen NMR shifts of pentaamminecobalt(III) complexes. As the conventions used in the literature are seldom explicitly given, they must be uncovered indirectly, e.g. from convention-independent statements in the text. It turns out that in all the papers mentioned, except ref 8, the shifts are in agreement with ours although the sign conventions are opposite. In ref 8 both proton and nitrogen-15 shifts are given, but their signs disagree with each other.

Ramsey and McConnell Equations

The Ramsey equation[10] allows the calculation of the NMR screening constant for a nucleus from the electronic wave functions of the molecule in which the nucleus is situated. The equation consists of two terms, referred to as the diamagnetic and the paramagnetic terms. The paramagnetic term contains matrix elements of the orbital angular momentum operator referred to the nucleus for which the screening is desired. For cobalt[1] the evaluation of these matrix elements presented no problem because the d functions by which the open subshell may be described are eigenfunctions of this operator. However, when the problem is to discuss the effect of the cobalt d electrons upon the shifts of the hydrogen and nitrogen nuclei, the situation is different and a transformation of the equation is necessary.

This transformation is not simple at all, but it was partially accomplished by Buckingham and Stephens[11] in order to treat the screening of the protons in hydride transition-metal complexes using a crystal field model. Their expressions are manageable

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in a literal crystal field model (point charge model) but cannot be used in a parametrical ligand field model.

In order to correlate the chemical shifts of the ligand nuclei with optical spectroscopic data by using a semiempirical ligand field model, McConnell's approximation[12] to the Ramsey equation can be used (eq 1). It is possible on the basis of the McConnell

$$\Delta\sigma_{\mathrm{i}}(\mathrm{G}) = -\frac{1}{4\pi}\left(\frac{\Delta\chi_{\mathrm{mol}}(\mathrm{G})}{N_{\mathrm{A}}}\right)\frac{\langle 3\cos^2\theta_{\mathrm{i}} - 1\rangle}{3R_{\mathrm{i}}^3} \qquad (1)$$

equation (eq 1) to calculate the effect of a distant group of electrons, G, on the screening of a nucleus i. The equation is based on the assumption that the distance, R_{i}, between the nucleus i and the group of electrons G is large enough to validate the magnetic point–dipole approximation. If this assumption is fulfilled, the contribution to the screening arising from the group G is proportional to its molar magnetic susceptibility anisotropy, $\Delta\chi_{\mathrm{mol}}(\mathrm{G})$.

An ammonia proton (or nitrogen-14 nucleus) in a pentaammine complex sees three rather distinct distant groups of electrons: the electrons associated with the four other ammonia ligands, the electrons associated with the X ligand, and the electrons associated with the cobalt central ion. Since the ammonia parts of the complexes $[\mathrm{Co(NH_3)_5X}]^{n+}$, common to all members of the pentaammine series, are only influenced by the X ligands by the indirect contact through cobalt, any anisotropy in the electronic clouds of the ammonia parts of the complexes is likely to be roughly invariant within the pentaammine series. Anisotropies within the electronic clouds of the ligands X we cannot account for and therefore hope are small.[3] We are thus left with the anisotropy of the electronic cloud around Co caused by the tetragonal component of the ligand field.

Equation 1 is valid in the case of "axial" symmetry of the group of electrons G. This condition is fulfilled for the cobalt of the pentaammines, though only rigorously so when X is linearly ligating, i.e. when the Co–X subsystem has $C_{\infty v}$ symmetry. θ_{i} denotes the angle between the symmetry axis and the direction from the cobalt central ion to nucleus i. The geometrical factor in eq 1, which takes the approximate values −1 and 2 for cis ($\theta \approx 90°$) and trans ($\theta \approx 180°$) protons, respectively, has been used by Yoneda and Nakashima[13] to explain the observation[6,14] that cations of the type $[\mathrm{Co(NH_3)_5X}]^{n+}$ give ^{1}H NMR spectra for which the protons cis to X usually have chemical shifts of opposite sign to those trans to X, when both shifts are referred to the collapsed signal of $[\mathrm{Co(NH_3)_6}]^{3+}$ ($\delta = 0$). Yoneda and Nakashima[13] have also tried to explain the magnitudes of the shifts by using an explicit expression for the cobalt anisotropy, $\Delta\chi_{\mathrm{mol}}(\mathrm{Co})$.[15] We shall start out from the same expression.

According to van Vleck[16] the quantum-mechanical expression for the magnetic susceptibility of a molecule without angular momentum contains two terms: a diamagnetic and a TIP term. As discussed in ref 1, it is only the sum of these terms—and not the individual terms—that is measurable. However, if one assumes that the diamagnetic susceptibilities of the individual components of the complex are additive, it is possible to calculate the TIP as a difference. From powder measurements on two pentaamminecobalt(III) salts, Kernahan and Sienko[17] used this method to find that the diamagnetic and the TIP terms are of almost equal magnitudes and thus to a large extent cancel each other in the pentaammine salts.

The situation here is different for two reasons: We have focused on the susceptibility of the cobalt central ion, and it is the *anisotropy* of this susceptibility that is relevant in eq 1. Since the diamagnetism is strongly dominated by the inner electrons,[1] which are relatively unaffected by the anisotropy associated with the bond formation, it is not unreasonable to assume that the diamagnetic term $\Delta\chi^{\mathrm{d}}_{\mathrm{mol}}(\mathrm{Co})$ is vanishing in comparison with the TIP term $\Delta\chi^{\mathrm{p}}_{\mathrm{mol}}(\mathrm{Co})$. Accordingly we shall in the following neglect possible diamagnetic contributions to $\Delta\chi_{\mathrm{mol}}(\mathrm{Co})$.

The expression for the TIP susceptibility term is, apart from a factor $\langle r^{-3}\rangle$ and some fundamental constants, identical with the expression for the paramagnetic screening. The latter has in ref 1 been applied to the cobalt(III) complexes to give eq 17 of that reference. We can therefore easily obtain the corresponding susceptibility expression to be used here. Due to the tetragonal symmetry of the complexes in question the TIP susceptibility tensor is naturally diagonal and the $\kappa\kappa$ component ($\kappa\kappa = xx$, yy, or zz) is given in eq 2. Here $h(a^1\mathrm{T}_{1g}(\kappa))$ is the energy of the κ component

$$\chi^{\mathrm{p}}_{\mathrm{mol},\kappa\kappa}(\mathrm{Co}) = N_A\frac{\mu_0 e^2}{2m_{\mathrm{e}}^2}\left(\frac{|\langle a^1\mathrm{A}_{1g}|\hat{L}_\kappa|a^1\mathrm{T}_{1g}(\kappa)\rangle|^2}{h(a^1\mathrm{T}_{1g}(\kappa))}\right) \qquad (2)$$

of the cubic parentage transition $a^1\mathrm{A}_{1g} \rightarrow a^1\mathrm{T}_{1g}$, which is the first spin-allowed band in the UV–vis spectrum of a low-spin d^6 complex. Choosing Z as the tetragonal axis and using eq 2 with the definition $\Delta\chi^{\mathrm{p}}_{\mathrm{mol}} = \chi^{\mathrm{p}}_{\mathrm{mol},zz} - \chi^{\mathrm{p}}_{\mathrm{mol},xx}$, we obtain eq 3. Since the

$$\Delta\chi^{\mathrm{p}}_{\mathrm{mol}}(\mathrm{Co}) = N_{\mathrm{A}}\frac{\mu_0 e^2}{2m_{\mathrm{e}}^2}\left[\frac{|\langle a^1\mathrm{A}_{1g}|\hat{L}_z|a^1\mathrm{T}_{1g}(z)\rangle|^2}{h(a^1\mathrm{T}_{1g}(z))} - \frac{|\langle a^1\mathrm{A}_{1g}|\hat{L}_x|a^1\mathrm{T}_{1g}(x)\rangle|^2}{h(a^1\mathrm{T}_{1g}(x))}\right] \qquad (3)$$

parameters R_{i} and θ_{i} of eq 1 are expected to be almost independent of X in the $[\mathrm{Co(NH_3)_5X}]^{n+}$ series of complexes it is thus $\Delta\chi^{\mathrm{p}}_{\mathrm{mol}}(\mathrm{Co})$ that determines the relative magnitudes of the chemical shifts for a given nucleus. We shall in the following section discuss how $\Delta\chi^{\mathrm{p}}_{\mathrm{mol}}(\mathrm{Co})$ is calculated for different $[\mathrm{Co(NH_3)_5X}]^{n+}$ complexes by using the parametrical d^6 model.[1]

Susceptibility Anisotropy and the Parametrical d^6 Model

The expression for the susceptibility anisotropy (eq 3) contains the energies of the tetragonal split components of the cubic $a^1\mathrm{A}_{1g} \rightarrow a^1\mathrm{T}_{1g}$ transition. Although a splitting of the cubic band is often observed in the spectrum of a specific pentaammine complex, it is not easy to obtain accurate wavelengths for the components.[1] Therefore, instead of using the observed spectrum of a $[\mathrm{Co(NH_3)_5X}]^{n+}$ complex, we calculate the energies of the two tetragonal split components on the basis of the transition energies obtained from the spectra of the cubic chromophores $[\mathrm{Co(NH_3)_6}]^{3+}$ and $[\mathrm{CoX_6}]^{m+}$. These calculations are performed by using the scheme of Yamatera.[1,18]

Besides the energies, the term in brackets of eq 3 also contains matrix elements of components of the orbital angular momentum operator $\hat{L}$. These elements have hitherto been assumed to take the cubic strong-field value $2(2)^{1/2}\,\hbar$, i.e. the same value irrespective of the component and the complex concerned. However, within the parametrical d^6 model it is possible to calculate their values for a particular pentaammine complex on the basis of the energies of certain ligand field transitions. As described in ref 1, this is done by setting up a matrix for the desired component of $\hat{L}$ and transforming it to the eigenbasis of the model Hamiltonian of the particular complex. Such a transformation has elsewhere[19] been called a rediagonalization. In ref 1 the values of the $\hat{L}$ matrix elements were calculated by rediagonalizations of the $\hat{L}$ matrices with respect to *cubic* model Hamiltonians. For each complex the Hamiltonian was specified by the two parameters Δ and B obtained from the average energies corresponding to the two cubic transitions $a^1\mathrm{A}_{1g} \rightarrow a^1\mathrm{T}_{1g}$ and $a^1\mathrm{A}_{1g} \rightarrow a^1\mathrm{T}_{2g}$.

As a consequence of the cubic symmetry of the model Hamiltonian, the same values were obtained for all three components

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Table I. Transition Matrix Elements of the Three Components of the Orbital Angular Momentum Operator[a]

	cubic basis	tetragonal basis
$\langle a^1A_{1g}\|\hat{L}_z\|a^1T_{1g}(z)\rangle/\hbar$	2.918	2.910
$\langle a^1A_{1g}\|\hat{L}_y\|a^1T_{1g}(y)\rangle/\hbar$	2.918	2.902
$\langle a^1A_{1g}\|\hat{L}_x\|a^1T_{1g}(x)\rangle/\hbar$	2.918	2.902

[a] The values have been calculated within the parametrical d^6 model on the basis of ligand field parameters that are likely to describe the pentaammine complex $[Co(NH_3)_5Cl]^{2+}$. The approximate calculation based on only the cubic ligand field component gives the same values for all three components of $\hat{L}$. Inclusion of the tetragonal field components described by the two parameters $\Delta(e)$ and $\Delta(t_2)$ brings about a distinction between $\hat{L}_z$ on the one side and $\hat{L}_y$ and $\hat{L}_x$ on the other side. The difference between these values is, however, too small to be of importance. It should be noted that what we call here $a^1T_{1g}(x)$ and $a^1T_{1g}(y)$ correspond to $a^1E(D_{4h})$ when the tetragonal field components are present and what we call $a^1T_{1g}(z)$ corresponds to $a^1A_{2g}(D_{4h})$. The usage of cubic designations is justified by the fact that the mixing of tetragonal terms of different cubic parentages is small. Thus $a^1E(D_{4h})$ only contains a small fraction of $a^1T_{2g}(O_h)^1E(D_{4h})$.

of $\hat{L}$. In the Ramsey equation used for the cobalt shifts, matrix elements of the three components are added, and if deviations from the cubic average values were more or less barycentered, these deviations would partially cancel each other. In the anisotropy equation (eq 3), however, the elements are subtracted, and in this case differences between the magnitudes of the $\hat{L}_z$ and $\hat{L}_x$ (or $\hat{L}_y$) matrix elements might be more important. We have therefore by means of an example examined the effect of the tetragonal components of the ligand field on the relative magnitudes of the matrix elements of the three components of $\hat{L}$. As it will appear (Table I), partial barycentration does not apply to these relative magnitudes, but the tetragonal deviations are so small that they can be safely be ignored independently of whether the components are added or subtracted.

The complex chosen for this illustration is $[Co(NH_3)_5Cl]^{2+}$. Being tetragonal, its complete model Hamiltonian may be specified by the values of the following parameters: the cubic parameter Δ, the two tetragonal parameters $\Delta(e)$ and $\Delta(t_2)$,[20,21] and the repulsion parameter B (C is assumed to be equal to $4B$). As in ref 1, Δ and B are determined on the basis of the average transition energies of $[Co(NH_3)_6]^{3+}$ (weight $^5/_6$) and (hypothetical) $[CoCl_6]^{3-}$ (weight $^1/_6$). A set of tetragonal parameters that suffices for the present purpose can be obtained from the spectrum of the complex *trans*-$[Co(en)_2Cl_2]^+$, which has been studied in detail.[22,23] The parameters of *trans*-$[Co(en)_2Cl_2]^+$ can be transferred into those of $[Co(NH_3)_5Cl]^{2+}$ if we first assume that 1,2-ethanediamine is not spectrally very different from NH_3 and if we then use the relation that exists in the additive ligand field models between the parameters of a *trans*-tetraammine complex and those of the corresponding pentaammine complex (e.g. ref 18 or 24). According to this relation the values of the tetragonal parameters for the pentaammine are half those of the *trans*-tetraammine complex.

Having now obtained a complete set of parameters for $[Co(NH_3)_5Cl]^{2+}$, we calculate the $\hat{L}$ matrix elements, as described above, both for the cubic component of the field alone and for the total tetragonal field. The results are given in Table I. As in ref 1, one notices that the cubic value is somewhat larger than the strong-field value $2(2)^{1/2}\hbar = 2.828\hbar$. The effect of the tetragonal field components upon the $\hat{L}$ matrix elements is very small, and the anisotropy of $\hat{L}$ can therefore safely be ignored. Accordingly, we can use the cubic values from ref 1 for these matrix elements. For the pentaammines these happen to be almost invariant[1] through the whole series and we thus expect the chemical shifts to depend on parameter 4.

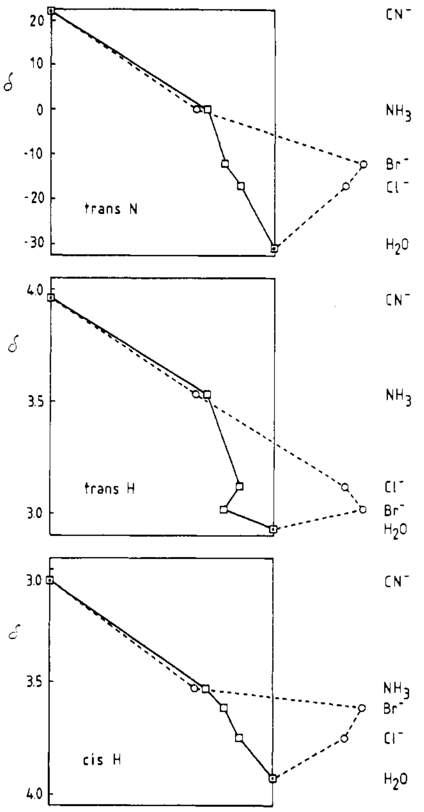

Figure 1. Relations between the chemical shifts of ammonia protons and nitrogen-14 nuclei of cobalt pentaammines and two different spectroscopic parameters. The spectroscopic parameter that corresponds to the circles is that of the parametrical d^6 model (expression 4) and does not give rise to monotonic relations (broken lines). When this parameter is modified through the inclusion of anisotropic nephelauxetism, the new parameter (expression 6) corresponding to the squares is obtained, and for this parameter the monotonicity is almost perfect (full lines). One small anomaly is observed for the trans protons of $[Co(NH_3)_5Br]^{2+}$. The lines connecting the points follow the order of the observed shift values. The abscissa axes of the two parameters have been chosen with respect to origins and scalings such that the parameter values for the two pentaammines giving extreme shift values coincide. These coinciding points have been indicated by squares with dots in the middle. The similarity among the three plots strongly suggests that the proton and nitrogen shifts have a common cause. In order to visualize this similarity we have reversed the direction of the ordinate axis of the cis ^1H plot and thereby eliminated the effect of a geometrical factor, which causes values of different signs for the cis and trans nuclei.

$$\left[\frac{1}{h(a^1T_{1g}(z))} - \frac{1}{h(a^1T_{1g}(x))}\right] \tag{4}$$

As remarked by Yoneda and Nakashima[13] the variation of parameter 4 within the pentaammine series depends practically only on the position of the ligand X in the spectrochemical series. In the approximation of pure cubic subconfigurations each of the components of the first cubic parentage absorption band ($a^1A_{1g} \rightarrow a^1T_{1g}$) corresponds to a one-electron excitation of a t_{2g} electron to an e_g orbital (ref 1, expression 15). As these component transitions take place between orbitals with coinciding nodal axes, their energies are little influenced by the ligands placed on these axes and are predominantly determined by the remaining four ligands, which are situated in the respective orthogonal planes. It follows that the transition energy $h(a^1T_{1g}(z))$ is determined largely by the four ammonia ligands bound to cobalt in the *xy*

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(23) From Table III of ref 22 we obtain for *trans*-$[Co(en)_2Cl_2]^+$ the following transition energies and assignments: 16 225 ($^1A_{1g} \rightarrow {}^1E_g$), 22 500 ($^1A_{1g} \rightarrow {}^1A_{2g}$), 24 250 ($^1A_{1g} \rightarrow {}^1B_{2g}$), and 27 100 cm^{-1} ($^1A_{1g} \rightarrow {}^1E_g$). An iterative fitting procedure using the energy matrices of the d^6 model yields the parameter values $\Delta = 20.09 \times 10^3\ cm^{-1}$, $\Delta(e) = 5.50 \times 10^3\ cm^{-1}$, $\Delta(t_2) = -1.70 \times 10^3\ cm^{-1}$, and $B = 0.526 \times 10^3\ cm^{-1}$.

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Table II. Calculated Optical Data and ^{1}H and ^{14}N Chemical Shifts for Substituted Pentaamminecobalt(III) Complexes[a]

	$h(a^1T_{1g}(x))$/cm^{-1}	$h(a^1T_{2g}(\xi))$/cm^{-1}	$B(yz)$/cm^{-1}	$[h(a^1T_{1g}(z))]^{-1} - [h(a^1T_{1g}(x))]^{-1}$/nm	$\beta(xy)[h(a^1T_{1g}(z))]^{-1} - \beta(yz)[h(a^1T_{1g}(x))]^{-1}$/nm	^{1}H chem shifts		^{14}N chem shifts[e]	
						δ_{trans}	δ_{cis}	δ_{trans}	δ_{cis}
$[Co(NH_3)_5CN](CH_3SO_3)_2$	23900	31863	569	53	47	3.96	3.05	22 (3)	−14 (2)
$[Co(NH_3)_5\mathit{S}CN]Cl_2$						3.64	3.54	*f*	−5 (2)
$[Co(NH_3)_5\mathit{S}_2O_3]ClO_4$						3.59	3.31		
$[Co(NH_3)_6](CH_3SO_3)_3$	21200	29550	616	0	0	3.53	3.53		
$[Co(NH_3)_6]Cl_3$	21200	29550	616	0	0			0	0
$[Co(NH_3)_5\mathit{N}O_2](CH_3SO_3)_2$[c]						3.45	3.45	10 (3)[d]	10 (3)[d]
$[Co(NH_3)_5\mathit{N}CS](CH_3SO_3)_2$[b]						3.32	3.77	−18 (2)	3 (2)
$[Co(NH_3)_5N_3](ClO_4)_2$[c]						3.26	3.41	−26 (3)	−1 (3)
$[Co(NH_3)_5I](ClO_4)_2$						3.13	3.50	13 (3)	−9 (3)
$[Co(NH_3)_5Cl](ClO_4)_2$[c]	19025	26763	575	−54	−10	3.12	3.75	−17 (3)	−2 (3)
$[Co(NH_3)_5Br]ClO_4)_2$	18825	26363	558	−60	−5	3.02	3.62	−12 (3)	−5 (3)
$[Co(NH_3)_5H_2O](ClO_4)_3$	20025	28388	626	−28	−20	2.93	3.93	−31 (2)	−2 (2)
$[Co(NH_3)_5O_2CNH_2](ClO_4)_2$						2.88	3.87	−20 (2)	−4 (2)
$[Co(NH_3)_5O_2CCH_3]Cl_2$[b]						2.77	3.87	−25 (2)	−1 (2)
$[Co(NH_3)_5F](NO_3)_2$[c]						2.51	3.90	−26 (3)	−1 (3)

[a] All the proton shifts, except those for the thiosulfato complex are from ref 3. The ^{14}N shifts were measured at 30 ± 1 °C in 0.01 M DCl/D_2O (unless otherwise noted) with $[Co(NH_3)_6]Cl_3$ as the reference. The value of the anisotropic repulsion parameter $B(xy)$ is common to all the pentaammines and identical with the value of $B(yz)$ for $[Co(NH_3)_6]^{3+}$. The nephelauxetic ratios have been calculated using $B_{gas} = 1120$ cm^{-1} (ref 1). [b] ^{14}N shifts measured in 0.12 M $DClO_4$. [c] ^{14}N shifts measured in 0.012 M $DClO_4$. [d] Only one unresolved ^{14}N signal was observed. [e] Standard deviations in parentheses. [f] The trans ^{14}N signal was not resolved (shoulder).

plane and thus takes the same value for all members of the pentaammine series, while $h(a^1T_{1g}(x))$, which appears in the second term of parameter 4, is determined by the three ammonia ligands and one X ligand in the yz plane. Since the contribution from the ammonia ligands in both terms of (4) is invariant, it is thus mainly the spectrochemical property of Co–X that determines the variation of parameter 4 with X.

In Figure 1 the shift data (Table II) have been plotted against parameter 4. Although, it may be argued that the point–dipole approximation is not valid for the nitrogen nuclei, the shifts of the trans N nuclei seem to vary much the same with the spectroscopic parameter as do the proton shifts. The smaller range of cis nitrogen shifts and the comparative inaccuracy of ^{14}N shift measurements give a less conclusive result (plot not shown).

Involvement of Nephelauxetism

We have now seen that it is impossible to rationalize even the order of the shifts of the ligand nuclei using the expression of the parametrical d^6 model for the magnetic anisotropy.

The data of Table II show that the shifts associated with $[Co(NH_3)_5CN]^{2+}$ lie at one end of the scale and those associated with $[Co(NH_3)_5F]^{2+}$ and $[Co(NH_3)_5H_2O]^{3+}$ at the other end, with the shifts for the pentaammine complexes of the heavy halides in between. As noted by Nakashima et al.,[25] this order is also observed for the ^{59}Co shifts. These have been found[1] to follow the internal field strength, Σ, of the complexes, an observation that has been described by the inclusion of the nephelauxetic ratio $\beta = B_{complex}/B_{gas}$ in the parameter that determines the order of the shifts. Modification of our parameter 4 in the same empirical fashion leads to parameter 5. However, a plot of the shifts against

$$\left[\frac{\beta}{h(a^1T_{1g}(z))} - \frac{\beta}{h(a^1T_{1g}(x))}\right] \qquad (5)$$

parameter 5 is only insignificantly different from that of Figure 1 for parameter 4. In order to try to introduce nephelauxetism with more weight, we have used the concept of *anisotropic nephelauxetism* inspired by Jørgensen's idea of symmetry-restricted covalency.[26] The anisotropic nephelauxetism is expressed in terms of two different nephelauxetic parameters of β type for the tetragonal complexes.[27,28] One of these parameters, $\beta(xy)$, refers to the xy plane and is chosen to be equal to the β value of $[Co(NH_3)_6]^{3+}$, and the other one, $\beta(yz) = \beta(zx)$, refers to the two orthogonal planes. Since each of these orthogonal planes contain three ammonia ligands and one X ligand, their β parameters have been defined as follows. Transition energies $h(a^1T_{1g})$ and $h(a^1T_{2g})$ for a hypothetical complex have been calculated as 75% $h([Co(NH_3)_6]^{3+})$ + 25% $h([CoX_6]^{m+})$ ($h = h(a^1T_{1g})$ or $h(a^1T_{2g})$) and the usual formula (ref 1, eq 12) has been used to calculate the Racah parameter B for this system. B/B_{gas} has then been used as $\beta(yz) = \beta(zx)$, now different from $\beta(xy)$ which is the β value of the hexaammine.

By using as abscissa for the shift plots the spectroscopic parameter 6 rather than parameters 4 or 5, one obtains almost

$$\left[\frac{\beta(xy)}{h(a^1T_{1g}(z))} - \frac{\beta(yz)}{h(a^1T_{1g}(x))}\right] \qquad (6)$$

monotonic relationships (Figure 1). Except for one small anomaly that is observed for the trans protons of $[Co(NH_3)_5Br]^{2+}$, the inclusion of anisotropic nephelauxetism in the parameter has the effect that the data points for the chloro- and bromopentaammines are moved so much relative to the rest of the data points that the relationship between the NMR shift data and the new spectroscopic parameter 6 becomes monotonic.

For the pentaammine series $\beta(xy)/h(a^1T_{1g}(z))$ in parameter 6 is a constant determined only by the properties of the central ion and the ammonia ligands. The relative shifts are thus determined by the term $\beta(yz)/h(a^1T_{1g}(x))$, whose connection with the internal field strength we shall here discuss. Let us first consider the ratio $\beta/h(a^1T_{1g})$ for cubic complexes. Since $h(a^1T_{1g})$ primarily is determined by Δ, this ratio is expected to vary in the same way as $\Sigma^{-1} = B/\Delta$. The parameter $\beta(yz)/h(a^1T_{1g}(x))$ can be interpreted in the same way, only in this case we are dealing with an averaged cubic system where 25% of the perturbation is of X type and 75% is of NH_3 type. When we are to relate this parameter to the average internal field strength of the pentaammine complex in question it is noted that the latter refers to a system where 16.67% of the perturbation is of X type and 83.33% is of NH_3 type. Since the numerator and denominator are varied simultaneously when going from one kind of averaged system to the other, a general relation between the parameters cannot be given. In practice it turns out, however, that $\beta(yz)/h(a^1T_{1g}(x))$ is monotonically related to the average internal field strength of the pentaammine.[29] Also, graphs of the shift data vs. Σ^{-1} are

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(25) Nakashima, Y.; Sakaguchi, U.; Yoneda, H. *Chem. Lett.* **1974**, 503–508.

(26) Jørgensen, C. K. *Prog. Inorg. Chem.* **1962**, *4*, 73–124.

(27) A similar anisotropy has been suggested before in connection with the relationship between empirically found intensities of tetragonal split components and the position of the ligands involved in the hyperchromic series.[28]

(28) Schäffer, C. E.; Glerup, J. *Proc. Int. Conf. Coord. Chem., 9th*, **1966**, 113.

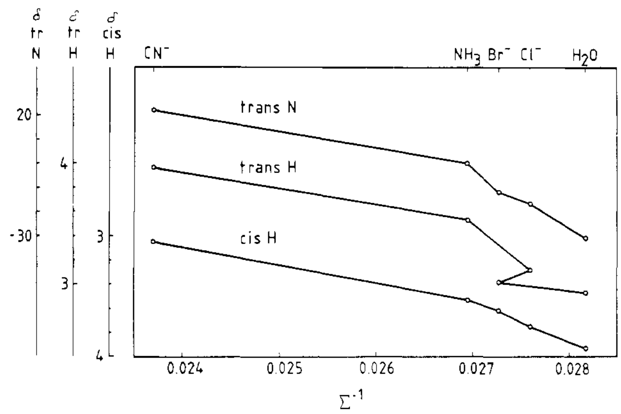

Figure 2. Relations between the chemical shifts and the reciprocal average internal field strength parameters. These relations are very similar to those of Figure 1, and this is due to the connection discussed in the main text between the average internal field strength parameter and parameter 6, containing anisotropic nephelauxetism. The values of the Σ parameters have been taken from ref 1, Table I.

found to be monotonic (Figure 2).

The plots of Figure 2 show a numerical connection between the relative shifts and the internal field strength parameter. The connection only comprises five of the pentaammines but is, as the following discussion will show, at least qualitatively more general. For ligands whose position in the internal field strength series cannot be calculated due to the lack of spectroscopic data, one can often make a plausible guess of their positions. For example, $S_2O_3^{2-}$ and SCN^-, both S bonded to the metal, are known to be low in the spectrochemical series, but because of their large nephelauxetism, they are expected to be found relatively much higher in the Σ series. On the other hand, $CH_3CO_2^-$ and F^- are placed in the middle of the spectrochemical series, but because of their small nephelauxetism they are found in the low end of the Σ series. The observed NMR shifts are qualitatively in agreement with these estimated positions.

In Table II the pentaammine complexes have been ordered on the basis of the trans proton shifts. Ideally one would expect this order to be exactly the opposite of that which is based on the cis shifts, but since this is not the case, an alternative way of ordering may be desirable. Here one may use the difference between the trans and cis proton shifts. This ordering principle has two advantages. First, it is based on experimental data for both types of protons and, second, there may be certain shift causes that are common and give rise to equal shift contributions for both types of protons, which cannot be accounted for by our model. These shift causes may in this way be eliminated. The following order of the pentaammines, here denoted by their X ligands, is obtained by this difference method: $CN^- >> S_2O_3^{2-} > \mathit{S}CN^- > NH_3 \approx NO_2^- > N_3^- > I^- > \mathit{N}CS^- > Br^- \approx Cl^- > H_2O \approx NH_2CO_2^- > CH_3CO_2^- >> F^-$. This order is in good agreement with the expected internal field-strength series.

Discussion

Parameter 4, which is the one used by Yoneda and Nakashima,[13] describes a situation where the shifts follow the spectrochemical properties of the X ligands. The empirical observation that the internal field strength series defined by the parameter $\Sigma = \Delta/B$ determines the order of the shifts, forced us to focus attention upon the variations of the interelectronic repulsion parameter B, i.e. upon nephelauxetism.

Although the formalism based on nephelauxetism as described in the previous section is completely well-defined, it has no direct theoretical basis. It is thus difficult to see why nephelauxetism should be of importance for the chemical shifts of the ligand nuclei when eq 3 apparently contains no terms that depend on the nephelauxetism (cloud expansion). For cobalt shifts a correlation with the internal field strength parameter was also found. However, there the problem of finding a radial cause was not pressing since the Ramsey equation contains a radial quantity, $\langle r_{3d}^{-3}\rangle$, which may be expected to vary along with the interelectronic repulsion in the d shell, i.e. with the nephelauxetism. A possible explanation for the observed situation here may be that the anisotropic nephelauxetic parameters in our optical parameter 6 simply reflect the covalency of the chemical bonds involved.

It is general empirical knowledge from ESR studies of paramagnetic d^q complexes that the magnitudes of the $\hat{L}$ matrix elements are reduced relative to the values calculated on the basis of d functions.[30] Further, when the d^q model has been used[31,32] to interpret the measured susceptibilities of low-spin cobalt(III) complexes as temperature-independent paramagnetism (after correction for diamagnetism), the transition moments of $\hat{L}$ have invariable been found to be low.

Stevens[33] explained these low values as a result of a reduction in the magnitudes of the matrix elements of the one-electron operator $\hat{l}$ caused by what Jørgensen[26] has called symmetry-restricted covalency (vide infra). Parametrically, the phenomenon is described by orbital angular momentum parameters that measure the magnitudes of the $\hat{l}$ matrix elements in units of their values calculated on the basis of pure d wave functions. For cubic (octahedral) complexes symmetry arguments require that the orbital angular momentum within an $e_g \oplus t_{2g}$ basis involves two parameters, k_{t_2e} and $k_{t_2t_2}$.

Unfortunately, the experimental data often do not contain sufficient information for such a symmetry-based model description of the angular momentum. In this case a so-called angular momentum reduction factor, k, may be used to express the ratio between the value found experimentally for a given matrix element and that calculated on the basis of the parametrical d^q model. For a series of complexes for which the same matrix element is associated with an experimentally observable quantity, it is thus possible to rationalize the data on the basis of such k factors.[34]

In the tetragonal pentaammine complexes the transition matrix elements of $a^1A_{1g} \rightarrow a^1T_{1g}$ (mainly of k_{t_2e} type) may be different for $\hat{L}_z$ on the one side and $\hat{L}_x$ and $\hat{L}_y$ on the other side. Two independent reduction factors, both of k_{t_2e} type, are thus necessary, and a reformulation of eq 3 in terms of these factors gives eq 7, where $2.92\hbar$ is the value of the parametrical d^6 model for the $\hat{L}$ matrix elements.

$$\Delta\chi_{\mathrm{mol}}^{\mathrm{p}}(\mathrm{Co}) = N_A \frac{\mu_0 e^2}{2m_e^2}(2.92\hbar)^2 \left[\frac{k_z^2}{h(a^1T_{1g}(z))} - \frac{k_x^2}{h(a^1T_{1g}(x))} \right] \tag{7}$$

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(29) A similar monotonic relationship is found between the Σ values of the $[CoX_6]^{m+}$ complexes and those of the pentaammines, $[Co(NH_3)_5X]^{n+}$. Since it is the Σ values of the $[CoX_6]^{m+}$ complexes that define the internal field strength series for ligands, we may say that the shifts follow the internal field strength of the ligand X.

(30) As mentioned above, the values calculated for these matrix elements on the basis of the parametrical d^q model only show little variation within the pentaammine series. Further, the variation found in the $\hat{L}$ transition moments from the ground state $^1A_{1g}(O_h)$ to the manifold, whose essential parentage is the lowest energy $^1T_{1g}(O_h)$ states, is caused by the concomitant influence of the ligand field and the interelectronic repulsion upon the eigenvectors of the states in question. The one-electron matrix elements of $\hat{l}$ remain, of course, constant within the parametrical d^q model.

(31) Griffith, J. S.; Orgel, L. E. *Trans. Faraday Soc.* **1957**, *53*, 601–606.

(32) Ballhausen, C. J.; Asmussen, R. W. *Acta Chem. Scand.* **1957**, *11*, 479–483.

(33) Stevens, K. W. H. *Proc. R. Soc. London A* **1953**, *219*, 542–555.

(34) In the literature the orbital angular momentum reduction is sometimes accounted for by the substitution of the operator $\hat{L}_z$ with $k\hat{L}_z$. It is thereby assumed that all matrix elements are reduced to the same extent, a situation that is not possible to interpret by symmetry. The wave functions may thus either be d functions, for which $k = 1$, or be e and t_2 functions, in which case two independent orbital angular momentum parameters are necessary. As it is often essentially one matrix element that determines the experimentally measured quantity, the value determined for k of the operator $k\hat{L}_z$ is identical with the orbital reduction factor for this specific matrix element. The assumption that all matrix elements are equally reduced is thus unnecessary and thereby conceptually confusing.

Jørgensen[26] has discussed the concept of covalency as a combination of two parts: central field covalency and symmetry-restricted covalency. For transition-metal complexes the central field covalency is caused by the penetration of ligand electrons into and behind the d shell, thereby shielding this from the nuclear charge and causing it to expand. The symmetry-restricted covalency is most easily explained within an LCAO-MO model, where the metal d orbitals are intermixed with ligand orbitals so that the resulting antibonding MO's carry less than 100% d character.

Nephelauxetism is attributed to both types of covalency. The central field covalency expands the d shell and thereby increases all interelectronic distances. The symmetry-restricted covalency reduces the charge density in the metal d orbitals (of a given size) by transferring charge to the ligand orbitals. Since nephelauxetism is a combination of two concomitant but relatively independent effects, it is fortunate that the semiempirical concept of nephelauxetism is so consistent[26,35] in chemistry that it gives a well-defined series of ligands as well as central ions.

The covalency influence upon the orbital angular momentum is easier to interpret since $\hat{L}$ only operates on the angular parts of the wave functions. The radial expansion of the d shell described by the central field covalency is thus only of importance for the angular momenta in so far as it indirectly influences the symmetry-restricted covalency, which solely becomes responsible for the orbital angular momentum reduction. A priori, one would therefore expect the angular momentum reduction to show a behavior at least as regular as that of nephelauxetism. This has, however, never been found, possibly because of inherent difficulties associated with the interplay of experiment and theory in this area. The determination of orbital angular momentum comes from ligand field analyses of magnetic susceptibilities or ESR measurements and involves the elimination or codetermination of ligand field and interelectronic repulsion parameters. The fact that small low-symmetry parameters often correlate strongly with the spin-orbit coupling in determining measured quantities combined with extra-model phenomena like intermolecular magnetic couplings in solids and diamagnetism adds difficulties and makes determinations of orbital angular momenta in chemically quite different systems hard to compare. All these problems have to be drawn in parallel with the well-defined procedure by which the nephelauxetism is determined from a UV-vis spectrum. It is thus not surprising that the orbital angular momentum reduction factors in the literature do not show the same regular behavior as do the nephelauxetic parameters. One may alternatively say that our knowledge does not exclude a monotonic relation between squared orbital angular momentum reduction and nephelauxetic ratios through the concept of covalency.

Let us now assume such a relation and compare the optical parameter in the square brackets of (7) with that in (6). Both parameters consist of a difference between what we may call a z term and an x term, where z and x refer to the components of the $a^1A_{1g} \rightarrow a^1T_{1g}$ transition. The two parameters only differ by the kind of covalency parameters that are associated with the z and x terms. In (6) the covalency parameters are anisotropic nephelauxetic parameters whereas in (7) they are squared orbital angular momentum reduction factors. The connection between the component transition energies and their associated covalency parameters are parallel in the two cases. As discussed above we may associate the z component of the transition $a^1A_{1g} \rightarrow a^1T_{1g}$ with the xy plane and the x component with the yz plane. Thereby the connections between the anisotropic nephelauxetic parameters and the component transitions were already established. For the reduction factors of the angular momentum transition matrix elements, the connection with the components of the electronic transition is obvious.

If the above mentioned monotonic relation exists between the two kinds of covalency parameters, the nephelauxetic ratios β and the squared reduction factors k^2, then a monotonic variation of the z and x terms individually will be found. A difficulty, however, is that this variation of the individual terms only allows the same conclusion about the variation of their differences if the monotonicity is a proportionality. This difficulty can be removed by an argument of the kind used in the discussion of the connection between (6) (Figure 1) and Σ^{-1} (Figure 2). Since our series of chemical systems consists of cobalt(III) pentaammines, the z terms, which according to the above are influenced by the covalency of four cobalt(III)-ammonia nitrogen bonds, are likely to be roughly constant. This means that the z terms only result in a shift along the abscissa axis in plots like those of Figure 1 while the x terms, which carry almost all the covalency influence of the X ligand upon the shifts, alone determine the shape (slope) of the curves.

Conclusion

The fact that the ^1H and ^{14}N shifts of the pentaammines $[Co(NH_3)_5X]^{n+}$ follow the same chemical trend as the ^{59}Co shifts when the X ligand is varied may be taken as an indication that the partially filled d shell is to a large extent responsible for the variations found in the chemical shifts of the ligand nuclei. The influence of the d electrons upon the shifts of the ligand nuclei can be described in the magnetic point-dipole approximation by the McConnell equation, which states that the shifts are proportional to the magnetic anisotropy of the cobalt central ion. The expression of the parametrical d^6 model for this anisotropy suggests that the shifts should follow the spectrochemical series and is thus in disagreement with the observed correlation with the internal field strength series. We have therefore made an empirical modification of the essential parameter of the susceptibility anisotropy expression by including anisotropic nephelauxetism and thereby produced parameter 6, which has the property of varying monotonically with the shift data (Figure 1).[36] These results cannot, however, be credited to the idea of anisotropic nephelauxetism since it turned out that another parameter, Σ^{-1}, based upon the average cubic complexes also has this property.

Acknowledgment. M.B. thanks the Danish Natural Science Research Council for financial support (Grant No. 11-4894).

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[35] Schäffer, C. E.; Jørgensen, C. K. *J. Inorg. Nucl. Chem.* **1958**, *8*, 143-148.

[36] The modified parameter (parameter 6), is as we have seen, capable of rationalizing the order of the shifts much better than parameter 4. Its empirical origin does, however, mean that it cannot be used for the calculation of absolute magnitudes of shifts. The equation for $\Delta\chi^{P}_{mol}(Co)$ obtained on the basis of the parametrical d^6 model allows such a calculation. As far as the protons are concerned one finds relatively good agreement between the calculated and observed magnitudes of the shifts, which at most differ by a factor of 2. Nakashima et al.[9] have noticed that the same is not true for the nitrogen shifts, where the calculated magnitudes are typically 10-15 times smaller than the observed ones. This of course reduces the confidence in the physical content of the dipole model. Nakashima et al.[9] therefore introduced an explanation for the origin of the nitrogen shifts that does not involve the magnetic anisotropy of the cobalt ion. This explanation does, however, not seem to account for the strong correlation between the ^{59}Co, ^1H, and ^{14}N shifts.