

⁵⁹Co NMR Chemical Shifts of Cobalt(III) Complexes: Correlations with Parameters Calculated from Ligand-Field Spectra

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Abstract: The effect of nephelauxetism has been incorporated empirically into the theoretical relation between ⁵⁹Co NMR chemical shifts and the optical transition energies for cobalt(III) complexes. By doing this, an empirically found correlation between the chemical shift and the internal ligand-field strength parameter $\Sigma = \Delta/B$ can be rationalized. A linear relation between the ⁵⁹Co magnetogyric ratio for orthoaxial complexes and the optical parameter $(h_1/\beta)^{-1}$, where h_1 is the energy of the first spin-allowed absorption band (¹A_{1g} → ¹T_{1g}) and β is the nephelauxetic ratio, allows an extrapolation to infinite internal ligand-field strength, i.e., to a situation where the temperature-independent paramagnetic contribution to the screening vanishes. Assuming that the diamagnetic screening in this situation is the same as that for the free atom, the magnetogyric ratio for the bare ⁵⁹Co nucleus is found to be 10.048 MHz T⁻¹. This value differs considerably from that originally determined on the basis of optical spectra but is in agreement with two previous values, determined by independent methods, so that there are now three independent values. Nonorthoaxial complexes are found to behave considerably more irregularly, and the probable reasons for this are discussed. All calculations of ligand-field parameters and angular momentum matrix elements are made without approximations within the parametrical d⁶ model. Formulas are presented which allow, without the use of a computer, calculation of the spectrochemical parameter Δ and the Racah parameter B from the positions of the two spin-allowed absorption bands of an octahedral d⁶ low-spin complex.

1. Introduction

Cobalt-59 occupies a unique place in NMR history,¹ as it was one of the first nuclei for which it was observed that the resonance frequency depends on the compound.² This "chemical shift", which is very large for ⁵⁹Co, about 1%, can in the case of low-spin cobalt(III) complexes be explained² on physical grounds which are closely related to those of temperature-independent paramagnetism. In a crystal-field interpretation, a linear relation between the chemical shift and the wavelength of the first optical transition is expected.³ This was originally found⁴ for ligands with second-period ligands, but the linear relation was later questioned⁵ when also third- and fourth-period ligands were considered. It has been found by us⁶ and independently by Juranic^{7,8} that the deviations from a linear relation can be rationalized in terms of nephelauxetism and that there exists a linear relation between the chemical shift and the wavelength of the first optical transition multiplied by the nephelauxetic ratio. In the present paper we examine the influence of nephelauxetism in determining screening constants for ⁵⁹Co in a variety of cobalt(III) complexes. A successive reformulation of the fundamental Ramsey equation is presented so that the consequences of each step carried out without approximations can be appreciated. As the Ramsey equation relates screening with optical spectroscopic data, the paper consists of some sections concerned essentially with NMR, others essentially with ligand-field theory and still others discussing their interrelations under specified circumstances.

2. Experimental Section

⁵⁹Co spectra were recorded with a Varian HA-100 spectrometer equipped with heteronuclear decoupling facilities for ¹H-⁵⁹Co INDOR experiments⁹ or by direct measurement either with a Varian VF-16 attachment to a Varian V-4502-12 EPR spectrometer or a hybrid pulsed spectrometer based on a Bruker 322S high-powered radio frequency console. During the course of the experiments, we discovered a systematic error in early papers quoting data from which $\bar{\gamma}$ could be calculated. This error persists in the recent literature. We believe the error has come from measuring the field at some point other than the sample position. For this reason, we describe our procedures for determining $\bar{\gamma}$ free from this error.

Method 1. Since $\bar{\gamma}$ is defined as the frequency-to-field ratio, measurement of both gives $\bar{\gamma}$ directly. Frequency measurement is comparatively trivial; field measurement was based on a proton NMR gaussmeter placed at the sample position (sample removed), first checking that the presence or absence of each probe next to the other did not produce a significant resonance shift in either.

Method 2. By observing proton NMR in [Co(en)₃]³⁺, for example, whilst decoupling cobalt, it is possible to get *that* frequency ratio very accurately. Since $\bar{\gamma}$ for protons in any environment is known from proton shift values and the nuclear magnetic moment of the bare proton, we can get the field of the decoupling experiment and thus $\bar{\gamma}$ for ⁵⁹Co in that compound. The results agree for [Co(en)₃]³⁺ and [Co(NH₃)₆]³⁺ with those of method 1.

Method 3. Here the field is left fixed (locked to the sample), and the resonance frequencies of an unknown and a standard are compared. Our standard is freshly prepared saturated aqueous K₃[Co(CN)₆] whose $\bar{\gamma}$ has been repeatedly determined by method 1 to be 10.1020 ± 0.0001 MHz T⁻¹ at 20 °C; see ref 4 for the temperature coefficient. This gives the field and thus $\bar{\gamma}$ for the unknown. Bulk susceptibility shifts are insignificant here.

With the exception of *cis*-[Co(NH₃)₄(CN)₂]Cl and *mer*-[Co(NH₃)₃(CN)₃] (see Acknowledgement section), all complexes were synthesized in our laboratories by standard literature methods. Analyses for C, H, and N were within at least 1% of the calculated content. The compounds were characterized by vis-UV absorption spectra and probed on NMR.

3. NMR Experiment and Ramsey's Theory of Nuclear Screening

The nuclear magnetic resonance spectrum of a molecule tumbling in solution may be observed at fixed frequency by varying the magnetic field B . Under these conditions a signal from the nucleus i , that is, a given nuclide in a given molecular species in

(1) Kidd, R. G.; Goodfellow, R. J. In "NMR and the Periodic Table"; Harris, R. K., Mann, B. E., Eds.; Academic Press: New York, 1978; Chapter 8, pp 225-244.

(2) Proctor, W. G.; Yu, F. C. *Phys. Rev.* **1951**, *81*, 20-30.

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

(4) Freeman, R.; Murray, G. R.; Richards, R. E. *Proc. R. Soc. London, Ser. A* **1957**, *242A*, 455-466.

(5) Martin, R. L.; White, A. H. *Nature (London)* **1969**, *223*, 394-396.

(6) Bramley, R.; Sargeson, A. M.; Schäffer, C. E. Paper presented at The National NMR Conference, Australian National University, Canberra, May 1979.

(7) Juranic, N. *Inorg. Chem.* **1980**, *19*, 1093-1095.

(8) Juranic, N. *J. Chem. Phys.* **1981**, *74*, 3690-3693.

(9) Bramley, R.; Peppercorn, A. E.; Whittaker, M. J. *J. Magn. Reson.* **1979**, *35*, 139-144.

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a given position in that species, is obtained when ν is connected to the fields B_i^{obsd} and B^{nucl} through the relations 1. These relations

$$\nu = \bar{\gamma}_i B_i^{\text{obsd}} = \bar{\gamma}_0 B^{\text{nucl}} = \bar{\gamma}_0 B_i^{\text{obsd}}(1 - \sigma_i) \quad (1)$$

contain the natural definition of the screening constant σ_i . The combined measurement of ν and B_i^{obsd} may be expressed in terms of the magnetogyric ratio $\bar{\gamma}_i$ for the nucleus i . The corresponding quantity for the bare nucleus $\bar{\gamma}_0$ is not generally measurable in the NMR experiment because, except in the case of very light nuclei, it is very difficult to strip off all the electrons. This is the nuclear physicist's dilemma. The chemist's dilemma is that according to (1), it is impossible to determine absolute values of screening constants without knowledge of $\bar{\gamma}_0$.

Often the position of the resonance signal of the nucleus i is communicated as a dimensionless chemical shift, δ_i . Defining δ_i as the difference between the screening constant, σ_r , of the nuclide in question as observed in a reference compound and σ_i gives (2).

$$\delta_i \equiv \sigma_r - \sigma_i = \frac{\bar{\gamma}_i - \bar{\gamma}_r}{\bar{\gamma}_0} = \frac{\nu_i - \nu_r}{\nu_0} \quad (2)$$

The sign of δ_i is here in accordance with the IUPAC recommendation. The ν 's occurring in the last part of (2) are resonance frequencies for constant external field, ν_0 being that of the bare nuclide. The usefulness of (2) depends on the degree of accuracy by which ν_0 (or $\bar{\gamma}_0$) is known. In the case of ⁵⁹Co, we therefore use $\bar{\gamma}$ rather than δ to express a resonance signal.

Equation 1 contains the conventional definition of the screening constant σ , the sign of which is positive when the screening is positive (diamagnetic screening) and negative when the screening is negative (paramagnetic screening, descreening, or antiscreening). It should be noted that these signs are the opposite of those of the magnetic susceptibilities carrying the same attributes, diamagnetic and paramagnetic.

A theoretical expression for σ was first obtained by Ramsey by using a nonrelativistic spin-free Hamiltonian.¹⁰ His expression contains two terms: a diamagnetic term and a second-order (or temperature-independent) paramagnetic one. Taking this result for σ , we can write eq 3.

$$\bar{\gamma}_i = \bar{\gamma}_0 (1 - \sigma_i^{\text{d}} - \sigma_i^{\text{p}}) \quad (3)$$

Screening is actually a tensorial property, and the scalar quantity σ for a given nucleus in an isotropic fluid medium is the average of the components on the principal diagonal of a second-rank tensor $\sigma_{\alpha\beta}$ whose nine components are obtained by replacing α and β by Cartesian coordinates x , y , and z . The physical meaning of the tensor component σ_{xx} , say, is that if a molecule is exposed to an external magnetic field whose component is B_x^{obsd} along the X axis of the reference system chosen, then the z component of the induced screening field is $-\sigma_{zx} B_x^{\text{obsd}}$ (the product of two numbers). For any coordinate system, the scalar screening constant σ is given by eq 4. The Ramsey expression for the

$$\sigma = 1/3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \quad (4)$$

general tensor component, $\sigma_{\alpha\beta}$ is the sum of $\sigma_{\alpha\beta}^{\text{d}}$ in eq 5 and $\sigma_{\alpha\beta}^{\text{p}}$ in eq 6. Here $|0\rangle$ and $|n\rangle$ represent ground-state and excited state

$$\sigma_{\alpha\beta}^{\text{d}} = \frac{\mu_0 e^2}{8\pi m_e} \langle 0 | \sum_j r_j^{-3} (r_j^2 \delta_{\alpha\beta} - r_{j\alpha} r_{j\beta}) | 0 \rangle \quad (5)$$

$$\sigma_{\alpha\beta}^{\text{p}} = - \frac{\mu_0 e^2}{8\pi m_e^2} \sum_{n,n \neq 0} (E_n - E_0)^{-1} [\langle 0 | \sum_j r_j^{-3} \hat{I}_{j\alpha} | n \rangle \times \langle n | \sum_j \hat{I}_{j\beta} | 0 \rangle + \langle 0 | \sum_j \hat{I}_{j\beta} | n \rangle \langle n | \sum_j r_j^{-3} \hat{I}_{j\alpha} | 0 \rangle] \quad (6)$$

wave functions which have the energies E_0 and E_n , respectively. It is essential to note that for the present form of the Ramsey equation to be valid, the angular momentum operator \hat{I}_j and the coordinate r_j of the j th electron should be defined relative to the nucleus for which σ is desired.

(10) Ramsey, N. F. *Phys. Rev.* 1950, 78, 699-703.

The magnetic vector potential which enters into the derivation of the Ramsey equation can be chosen with respect to any origin, leaving the total σ unaffected by this choice (gauge invariance).¹⁰ However, the balance between σ^{d} and σ^{p} , which are *not* separately measurable, does depend on the gauge.

When discussing the screening at the ⁵⁹Co nucleus, this nucleus is used as the origin of the coordinate frame. Thereby the evaluation of the matrix elements in the expression for σ^{p} becomes easy. Under these conditions, σ^{d} gives rise to a lowering of the magnetic field B^{nucl} as compared with the external field, B^{obsd} , while the opposite is true of σ^{p} . The expression for σ^{d} (eq 5) shows that this contribution to the total screening is not likely to vary much with the ligands since it is strongly dominated by the inner electrons in heavy atoms such as cobalt. We have calculated σ^{d} for Co(0) by using Slater orbitals to reproduce the Hartree-Fock value¹¹ of 0.0022 (or 2200 ppm) to within 1%. This calculation shows that the inner electron shells make by far the greater contribution to σ^{d} , and since σ for ⁵⁹Co in its cobalt(III) complexes varies¹ by some 15000 ppm, variations in σ^{d} can safely be neglected. The first- and second-shell electrons account for some 84% of σ^{d} .

4. ⁵⁹Co Screening and Ligand-Field Theory

Griffith and Orgel³ and Freeman, Murray, and Richards⁴ (FMR) were the first to use ligand-field theory to interpret ⁵⁹Co NMR data in terms of second-order paramagnetic screening. Cobalt(III) complexes have low-lying excited states which make the paramagnetic term σ^{p} dominate both the screening itself and its variation with the chemical environment.

We shall here use the parametrical d^q model¹² which allows every wave function in Ramsey's equation to be split up into a radial and an angular part. Since the orbital angular momentum operator only acts on the angular part, the expectation value of r_j^{-3} for the electrons in the unfilled shell, in casu $\langle r_{3d}^{-3} \rangle$, may be removed from the integrations involving \hat{I}_{jk} ($k = x, y, \text{ or } z$). The scalar σ^{p} can thus be written as eq 7, where σ_{xx}^{p} , σ_{yy}^{p} , and σ_{zz}^{p}

$$\sigma^{\text{p}} = - \frac{\mu_0 e^2}{12\pi m_e^2} \langle r_{3d}^{-3} \rangle \sum_{n,n \neq 0} \sum_{k=x,y,z} \frac{|\langle 0 | \hat{L}_k | n \rangle|^2}{E_n - E_0} \quad (7)$$

(eq 6) have been added according to eq 4. In eq 7, $|0\rangle$ and $|n\rangle$ only refer to the angular part of the d^6 functions and $\sum_j \hat{I}_{jk}$ have been replaced by \hat{L}_k . The ground state of cubic low-spin d^6 complexes is of symmetry ${}^1A_{1g}(O_h)$. Since \hat{L}_k transforms as $T_{1g}(O_h)$, only matrix elements connecting the ground state with the excited ${}^1T_{1g}$ terms of the d^6 configuration are nonvanishing. The values of these matrix elements will be calculated by using the parametrical d^6 model.

In ref 3 and 4, the strong-field approximation to eq 7 was used. According to this approximation, the ground-state ${}^1A_{1g}$ is represented by the pure cubic configuration $(t_{2g})^6$. Correspondingly, the lowest excited state ${}^1T_{1g}$ is associated with the subconfiguration $(t_{2g})^5(e_g)$. Since \hat{L}_k is a sum of one-electron operators, the only nonvanishing strong-field matrix elements in eq 7 are $\langle {}^1A_{1g}(t_{2g})^6 | \hat{L}_k | {}^1T_{1g}(\kappa)(t_{2g})^5(e_g) \rangle$ ($\kappa = x, y, \text{ or } z$). Inserting the value $2(2)^{1/2} \hbar$ calculated for these elements into eq 7 gives eq 8, where h_1 denotes the energy of ${}^1T_{1g}$ relative to the ground state.

$$\sigma^{\text{p}} = - \frac{\mu_0 e^2 \hbar^2}{12\pi m_e^2} \langle r_{3d}^{-3} \rangle \left[\frac{24}{h_1} \right] \quad (8)$$

FMR measured ⁵⁹Co NMR spectra of a number of cobalt(III) complexes which were to have the same value of $\langle r_{3d}^{-3} \rangle$. If the small variation in σ^{d} is neglected, eq 8 predicts a linear relation

(11) Malli, G.; Froese, C. *Int. J. Quantum Chem., Quantum Chem. Symp.* 1967, 1, 95-98.

(12) The parametrical d^q model is the mathematical model on which present-day ligand-field theory is based. It is identical with C. K. Jørgensen's "expanded radial function model"¹³ but the name has been changed because the radial functions never occur explicitly in the calculations with the model. Furthermore, the old name is based on an interpretation of the values of the empirical repulsion parameters (nephelauxetism) which is exterior to the mathematical model.

between σ and $[h_1]^{-1}$ or, alternatively—cf. eq 1—between $\bar{\gamma}$ and the wavelength of the first absorption band. Although a correlation was obvious, the data did not, however, fit a straight line very well. We shall in section 7 examine the influence of possible noncubic ligand-field components and the effect of the strong-field approximation on this expected linear relation. But first we shall in sections 5 and 6 discuss the necessary ligand-field theory.

5. Intermediate-Field Energy Matrices and Angular Momentum Matrices

Energy Matrices. A typical vis-UV spectrum of an octahedral low-spin d^6 complex contains two spin-allowed transitions: $a^1A_{1g} \rightarrow a^1T_{1g}$ and $a^1A_{1g} \rightarrow a^1T_{2g}$ with energies h_1 and h_2 , respectively. An a in front of a term symbol indicates that this is the lowest term of the symmetry type in question. In the strong-field approximation, the interaction of the a^1A_{1g} , a^1T_{1g} , and a^1T_{2g} terms with higher terms of the same symmetries is neglected. In the intermediate-field approach, however, this interaction is taken into account, and the transition energies are found by diagonalization of a ${}^1A_{1g}$ matrix (5×5), a ${}^1T_{1g}$ matrix (4×4), and a ${}^1T_{2g}$ matrix (7×7). These matrices were first set up in a cubic strong-field scheme by Tanabe and Sugano.¹⁴ In this basis the off-diagonal elements represent the interelectronic repulsion interaction between terms of the same symmetry, each belonging to a pure cubic subconfiguration.

All the matrices are expressed in terms of the spectrochemical parameter Δ , which measures the energy difference between the e_g and t_{2g} orbitals, and the interelectronic repulsion parameters B and C (Racah parameters). The parameters are taken as empirical and are determined as those which reproduce the observed transition energies h_1 and h_2 as differences between the lowest eigenvalues of the appropriate matrices. In order to determine the three parameters from two observables, it is customary to keep the ratio C/B fixed at a constant value. We chose¹⁵ $C/B = 4$ as previously.¹⁶

Even though these calculations are easily performed by means of a small computer, they do require certain program facilities. It is therefore often seen that Δ and B are determined by Jørgensen's expressions^{17,18} or by the strong-field approximation, where the diagonal elements of the strong-field matrices are used as an approximation to the eigenvalues. In this approximation the energies h_1 and h_2 are $\Delta - C$ and $\Delta + 16B - C$, respectively. For $C = 4B$, we then have eq 9 and 10. Both the strong-field

$$\Delta = h_1 + C = h_1 + \frac{1}{4}(h_2 - h_1) \quad (9)$$

$$B = \frac{1}{16}(h_2 - h_1) \quad (10)$$

approximation and Jørgensen's expressions may in some cases give results which differ substantially from the true parameter values.¹⁹

For the benefit of those who don't have the above mentioned hard- and software facilities, we provide a method by which the intermediate-field values of Δ and B can easily be found. To this end, eq 9 and 10 have been modified to eq 11 and 12. The values

$$\Delta = h_1 + [d(h_2/h_1)](h_2 - h_1) \quad (11)$$

$$B = [b(h_2/h_1)](h_2 - h_1) \quad (12)$$

of d and b , which are functions of h_2/h_1 , have been determined

(13) Jørgensen, C. K. *Discuss. Faraday Soc.* **1958**, *26*, 110–115.

(14) Tanabe, Y.; Sugano, S. *J. Phys. Soc. Jpn.* **1954**, *9*, 753–766.

(15) This choice is based on the C/B ratio in the free Co^{3+} ion.³⁴ The questions of whether this ratio takes the same value in complexes and whether the ratio varies from one complex to the other are not easy to answer. Varying the fixed value of C/B between 3 and 6 does not, however, change the spectrochemical or the nephelauxetic series.

(16) Schäffer, C. E.; Jørgensen, C. K. *J. Inorg. Nucl. Chem.* **1958**, *8*, 143–148.

(17) Jørgensen, C. K. *Adv. Chem. Phys.* **1963**, *5*, 33–146.

(18) Lever, A. B. P. "Inorganic Electronic Spectroscopy"; Elsevier: Amsterdam, London, New York, 1968; p 304.

(19) For $[Co(H_2O)_6]^{3+}$, for example, the true parameter values are $\Delta = 18\,157\text{ cm}^{-1}$ and $B = 666\text{ cm}^{-1}$. Jørgensen's formulas¹⁷ give by an iteration $\Delta = 16\,926\text{ cm}^{-1}$ and $B = 660\text{ cm}^{-1}$, while the strong-field approximation gives $\Delta = 18\,600\text{ cm}^{-1}$ and $B = 525\text{ cm}^{-1}$. Generally Jørgensen's formulas give relatively accurate results for B , while Δ is determined with a large inaccuracy. The opposite is true for the strong-field approximation.

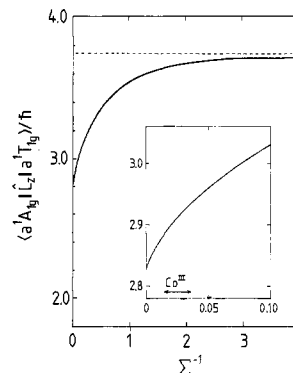


Figure 1. Value of the matrix element $\langle a^1A_{1g} | \hat{L}_z | a^1T_{1g} \rangle$ as a function of $1/\Sigma$. When the ratio C/B is fixed, in casu to 4, the angular momentum matrix only depends on the ratio $\Sigma = \Delta/B$, which we call the internal field strength. In the strong-field limit, where $\Delta/B = \infty$ and $1/\Sigma$ therefore is equal to 0, the matrix element takes its strong-field value of $(2(2))^{1/2}$. As $1/\Sigma$ increases, the value of the matrix element asymptotically approaches the weak-field value $(14)^{1/2}$. However, for $1/\Sigma \geq 0.06$, the ground term of the d^6 configuration is no longer low-spin and the matrix element is of little interest. The subfigure shows the abscissa range of chemical relevance. The interval of $1/\Sigma$ values spanned by low-spin cobalt(III) complexes known at present has been indicated. In this interval, the values of $\langle a^1A_{1g} | \hat{L}_z | a^1T_{1g} \rangle$ are only slightly larger than the strong-field value.

by diagonalization of the Tanabe–Sugano matrices. In the interval $1.10 \leq h_2/h_1 \leq 1.55$, which contains all d^6 complexes known at present (i.e., not only $Co(III)$ complexes), d and b may be approximated by polynomials of degree 2. The approximations in eq 13 and 14 are so good that values of Δ and B determined by using them in combination with eq 11 and 12 only deviate 1 to 2 cm^{-1} from the exact values found by diagonalization of the Tanabe–Sugano matrices. This error is well below the experi-

$$d(h_2/h_1) \approx 0.1824 (h_2/h_1)^2 - 0.5531 (h_2/h_1) + 0.6165 \quad (13)$$

$$b(h_2/h_1) \approx 4.077 \times 10^{-2} (h_2/h_1)^2 - 7.090 \times 10^{-2} (h_2/h_1) + 9.352 \times 10^{-2} \quad (14)$$

mental uncertainties in the determination of the transition energies. In this way, we have obtained a practical device that serves a numerical purpose. However, it should be stressed that the set of equations 11–14 has no theoretical content. Equations 13 and 14 have been obtained by a nonlinear regression procedure.

Angular Momentum Matrices. To find the intermediate-field values of the L matrix elements of eq 7, the following method was adopted. When tensorial methods²⁰ are used, an energy matrix and a matrix for \hat{L}_z can be set up in the same weak-field scheme. The basis, which consists of $d^6\text{ }^{2S+1}L$ functions, comprises in this case the 50 singlet states of the d^6 configuration. The weak-field energy matrix is expressed in terms of the parameters Δ , B , and C and contains altogether the same information as the Tanabe–Sugano matrices involving all the singlet states. Accordingly, the weak- and strong-field matrices have the same eigenvalues for a given parameter set (Δ, B, C) , but they have different eigenvectors.

Having found the values of the parameters Δ , B , and C corresponding to the transition energies h_1 and h_2 as described in the preceding subsection, the weak-field matrix is diagonalized for this particular set of parameters. The eigenvectors found in this diagonalization are then used to transform the matrix for \hat{L}_z to the eigenbasis for the complex of interest. It now remains to identify the ground-state ${}^1A_{1g}$ and excited-state ${}^1T_{1g}$ functions in the eigenbasis. This can be done, for example, by comparison of the eigenvalues of the weak-field energy matrix with those of the Tanabe–Sugano matrices.

When the parameter ratio C/B is fixed (in casu to 4), then the eigenvectors for the weak-field matrix depend on the ratio $\Sigma = \Delta/B$ only and not on the absolute magnitudes of Δ and B . Σ is

(20) Harnung, S. E.; Schäffer, C. E. *Struct. Bonding (Berlin)* **1972**, *12*, 257–295.

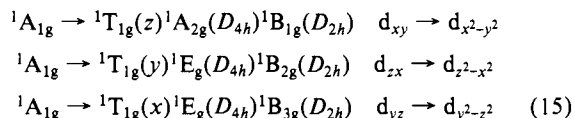
the so-called *internal-field-strength* parameter and will be discussed in section 8. The variation of the matrix element $\langle a^1A_{1g}|\hat{L}_z|a^1T_{1g}\rangle$, relevant in the Ramsey equation, is shown in Figure 1 as a function of $1/\Sigma$. As it is seen, the value of the matrix element increases monotonically as one goes from the strong-field limit ($1/\Sigma = 0$) to the weak-field limit. This is in disagreement with ref 21 where configurational mixing is found to lower the value of $\langle a^1A_{1g}|\hat{L}_z|a^1T_{1g}\rangle$. However, the calculation of ref 21 is not exact, and, in actual fact, the many small terms which were neglected turn out to add up so as to result in a net increase rather than a decrease in the value of this matrix element.

From magnetic susceptibility measurements, it is known that covalent bonding can change the value of the matrix elements of \hat{L}_z relative to those calculated by the parametrical d^6 model. This effect can be described²² symmetrywise by two parameters, $k_{\sigma\pi}$ and $k_{\pi\pi}$, which are introduced as factors on to the L matrix elements of the model, thus changing and probably, in general, reducing their effective value.²³ As there is no independent way of measuring the magnitude of this reduction by the techniques used in this paper, we shall not consider it here. All values of orbital angular momentum matrix elements are thus calculated by the parametrical d^6 model on the basis of the information contained in the optical spectra.

6. Noncubic Orthoaxial Complexes

For orthoaxial^{24,25} complexes whose holohedrized symmetry is lower than cubic, the $^1T_{1g}(O_h)$ terms are split. Thus, in tetragonal symmetry, each one is split into a $^1A_{2g}(D_{4h})$ and a $^1E_g(D_{4h})$ term, while in orthorhombic symmetry each is split into three terms of symmetries $^1B_{1g}(D_{2h})$, $^1B_{2g}(D_{2h})$, and $^1B_{3g}(D_{2h})$. In order to perform the summation in eq 7, it is necessary to know the energies of all the components. However, often the splittings are not resolved in the spectra, and it is impossible to determine the energies directly. FMR have circumvented this problem by using the energy of the maximum of the first unsplit absorption band as an average energy for its components. In a tetragonal complex, for example, the unsplit band may be viewed as consisting of two overlapping Gaussian components, one representing the transition to the doubly degenerate excited term $^1E_g(D_{4h})$ and the other to the nondegenerate excited term $^1A_{2g}(D_{4h})$. Now, it is only if the former of these components is twice as intense as the latter that the observed curve's maximum will represent reasonably well this average energy.

We have used the results of Yamatera,²⁶ who treats the low-symmetry part of the ligand field as a first-order perturbation on the cubic parentage functions.²⁷ In the approximation of pure cubic subconfigurations, the three components of the $a^1A_{1g}(O_h) \rightarrow a^1T_{1g}(O_h)$ transition can be associated with the one-electron transitions²⁸ given in (15). As the one-electron transitions in (15)



describe the excitation of an electron from a t_{2g} to an e_g orbital

(21) Betteridge, G. P.; Golding, R. M. *J. Chem. Phys.* **1969**, *51*, 2497-2500.

(22) Stevens, K. W. H. *Proc. R. Soc. London, Ser. A* **1953**, *A219*, 542-555.

(23) Accordingly, the parameters have been given the name "orbital angular momentum reduction parameters". This name is often, very confusingly, abbreviated as "orbital reduction parameters", indicating a reduction in the size of the d orbitals. This is, in fact, the opposite of what the nephelauxetic phenomenon seems to indicate (see Section 8).

(24) Schäffer, C. E.; Jørgensen, C. K. *Kgl. Dan. Vidensk. Selsk., Mat.-Fys. Medd.* **1965**, *34*, no. 13.

(25) Schäffer, C. E. *Theor. Chim. Acta* **1966**, *4*, 166-173.

(26) Yamatera, H. *Bull. Chem. Soc. Jpn.* **1958**, *31*, 95-108.

(27) The interaction between low-symmetry components of a^1T_{1g} and a^1T_{2g} is thus neglected. For the effectively tetragonal complex $trans-[Co(en)_2Cl_2]^{2+}$, this interaction has the effect that the energy of $a^1T_{1g}(O_h)^1E_g(D_{4h})$ is decreased by approximately 500 cm^{-1} , while that of $a^1T_{2g}(O_h)^1E_g(D_{4h})$ is increased by a similar amount.

(28) In ref 24, $B_2(D_2)$ and $B_3(D_2)$ were permuted in order to make B_1 , B_2 , and B_3 correspond to the cyclic order z , x , and y . However, here we return to custom, which is the anticyclic order z , y , and x .

having the same nodal axis as the t_{2g} orbital, their energies are largely independent of the nature of the ligands on this axis and are predominantly determined by the four ligands in the orthogonal Cartesian plane. Thus, for a $[Co(NH_3)_5X]$ -type complex the $a^1A_{1g}(O_h) \rightarrow a^1T_{1g}(z)(O_h)$ transition is observed close to the wavelength of the first band in $[Co(NH_3)_6]^{3+}$ (ref 29). The $a^1A_{1g}(O_h) \rightarrow a^1T_{1g}(y)(O_h)$ and $a^1A_{1g}(O_h) \rightarrow a^1T_{1g}(x)(O_h)$ transitions are associated with planes containing one X ligand and three ammonia ligands. The energy of the $^1A_{1g}(D_{4h}) \rightarrow ^1E_g(D_{4h})$ transition is therefore taken as the weighted average of the first band energies in the chromophores $[CoX_6]$ (25%) and $[Co(NH_3)_6]^{3+}$ (75%). In some of the cases where CoX_6 complexes have not been synthesized, we have inferred their transition energies from the corresponding Rh and Ir complexes (see Appendix section).

7. Application of Ramsey's Equation by Using the Intermediate Cubic-Field Approach and Including First-Order Low-Symmetry Corrections to the Cubic Field

Rewriting eq 7 in the form appropriate for the parametrical d^6 model gives eq 16 where $h(q^1T_{1g}(\kappa))$ is the energy of the κ component of q^1T_{1g} relative to the ground state. Contrary to eq

$$\sigma^p = -\frac{\mu_0 e^2}{12\pi m_e^2} \langle r_{3d}^{-3} \rangle \left[\sum_{q=a,b,c,d} \sum_{\kappa=x,y,z} \frac{|\langle a^1A_{1g}|\hat{L}_z|q^1T_{1g}(z)\rangle|^2}{h(q^1T_{1g}(\kappa))} \right] \quad (16)$$

7, only the \hat{L}_z matrix elements appear in eq 16. This is because their values are the same as those of the corresponding \hat{L}_x and \hat{L}_y matrix elements when the basis functions are symmetry-adapted to cubic symmetry as supposed here.³⁰ The difference between eq 16 and that of FMR (eq 8) is that in eq 16, all four $^1T_{1g}$ terms appear through their intermediate-field matrix elements and that it is taken into account that these terms split in symmetries that are lower than cubic. As the following example will show, the three highest $^1T_{1g}$ terms only contribute insignificantly to the sum but the lowest $^1T_{1g}$ term gives a different contribution from that of the strong-field approximation. For $[Co(H_2O)_6]^{3+}$, for example, we have the relative summation terms

$$\frac{(2.936)^2}{16.500} + \frac{(6.133 \times 10^{-2})^2}{39.315} + \frac{(1.422 \times 10^{-2})^2}{57.035} + \frac{(2.410 \times 10^{-2})^2}{69.414} = 0.5224 + 9.567 \times 10^{-5} + 3.646 \times 10^{-6} + 8.367 \times 10^{-6}$$

where only the first term contributes within the first four significant figures.

It may be noted that the first term contains an \hat{L}_z matrix element of 2.936. This value is, as expected by Griffith and Orgel,³ larger than the strong-field value of $2(2)^{1/2} = 2.828$. Griffith and Orgel estimated the error of using the strong-field approximation to determine the value of this matrix element of \hat{L}_z to be approximately 10%, and this is indeed what is found when the squared values appearing in Ramsey's equation are considered. As $[Co(H_2O)_6]^{3+}$ is the low-spin cobalt(III) complex which is most distant from the strong-field situation, the error is smaller for all other known complexes.

Dropping the three insignificant terms ($q = b, c$, and d) in eq 16, we get eq 17.

$$\sigma^p = -\frac{\mu_0 e^2}{12\pi m_e^2} \langle r_{3d}^{-3} \rangle \left[\sum_{\kappa=x,y,z} \frac{|\langle a^1A_{1g}|\hat{L}_z|a^1T_{1g}(z)\rangle|^2}{h(a^1T_{1g}(\kappa))} \right] \quad (17)$$

(29) Linhard, M.; Weigel, M. Z. *Phys. Chem. (Frankfurt am Main)* **1957**, *11*, 308-317.

(30) This is only strictly true for the absolute values. The L matrix elements may generally have both real and imaginary values depending on the basis functions chosen. The 50 singlet $|SLM_S T\rangle$ functions²⁰ used by us give purely imaginary values for the matrix elements of all three L components. However, in the main text, we use the corresponding real numbers.

Table I. Optical Spectroscopic Parameters and $\bar{\nu}({}^{59}\text{Co})$ Values for Orthoaxial Cobalt(III) Complexes^a

	h_1 , cm ⁻¹	h_2 , cm ⁻¹	B , cm ⁻¹	Σ	$\frac{\langle a^1A_{1g} \hat{L}_z a^1T_{1g}\rangle}{\hbar}$	b , nm	c , nm	d , nm	$\bar{\nu}({}^{59}\text{Co})$, ^e MHz T ⁻¹
Cs[Co(H ₂ O) ₆](SO ₄) ₂ ·6H ₂ O ^f	16 500	24 900	666	27.26	2.936	606	653	388	10.2540 (1)
[Co(NH ₃) ₆]Cl ₃	21 200	29 550	616	37.12	2.917	472	502	276	10.1849 (1)
K ₃ [Co(CN) ₆]	32 000	38 800	460	72.76	2.884	313	325	133	10.1020 (1)
heteropolymolybdate ^g	16 530	24 270	597	30.25	2.929	605	649	346	10.2288 (1)
[Co(NH ₃) ₅ OH](ClO ₄) ₂	20 250	28 425	607	36.08	2.918	494	526	285	10.1949 (1)
[Co(NH ₃) ₅ H ₂ O](ClO ₄) ₃	20 417	28 775	622	35.50	2.919	490	522	290	10.1944 (2)
[Co(NH ₃) ₅ Cl](CF ₃ SO ₃) ₂	19 750	27 692	589	36.24	2.918	506	540	284	10.1918 (1)
[Co(NH ₃) ₅ Br](ClO ₄) ₂	19 617	27 425	577	36.67	2.917	510	544	280	10.1921 (3)
[Co(NH ₃) ₅ CN](ClO ₄) ₂	23 000	31 092	584	42.20	2.910	435	462	241	10.1695 (2)
<i>cis</i> -[Co(NH ₃) ₄ (CN) ₂]Cl ^h	24 800	32 633	555	47.57	2.903	403	426	211	10.1530 (2)
<i>mer</i> -[Co(NH ₃) ₃ (CN) ₃] ⁱ	26 600	34 175	529	53.26	2.898	376	397	188	10.1356 (1)
[Co(NH ₃) ₅ F](NO ₃) ₂									10.2000 (2)
[Co(NH ₃) ₅ (O ₂ CCH ₃)]Cl ₂									10.1940 (1)
[Co(NH ₃) ₅ I](ClO ₄) ₂									10.1914 (3)
[Co(NH ₃) ₅ (N ₃)](ClO ₄) ₂									10.1897 (1)
[Co(NH ₃) ₅ NH ₂ OSO ₂](ClO ₄) ₂									10.1873 (2)
[Co(NH ₃) ₅ NCS](CH ₃ COO) ₂									10.1863 (2)
[Co(NH ₃) ₅ SCN]Cl ₂									10.1846 (1)
[Co(NH ₃) ₅ S ₂ O ₃]ClO ₄									10.1840 (1)
[Co(NH ₃) ₅ NO ₂](CH ₃ SO ₃) ₂									10.1792 (1)

^aNMR determined at 20 ± 1 °C with water as solvent unless otherwise noted. For the cubic chromophores, h_1 and h_2 are the observed optical transition energies. For the low-symmetry chromophores, h_1 and h_2 are calculated as the weighted averages of those for the associated cubic ones. B , Σ , and $\langle a^1A_{1g}|\hat{L}_z|a^1T_{1g}\rangle$ are calculated on the basis of the average cubic energies under the assumption that $C/B = 4$. ^b $1/3 \sum_{\kappa=x,y,z} 1/[h(a^1T_{1g}(\kappa))]$. ^c $(\langle (a^1A_{1g}|\hat{L}_z|a^1T_{1g})^2 \rangle / 8) / (1/3 \sum_{\kappa=x,y,z} 1/[h(a^1T_{1g}(\kappa))])$. ^d $\beta(\langle (a^1A_{1g}|\hat{L}_z|a^1T_{1g})^2 \rangle / 8) / (1/3 \sum_{\kappa=x,y,z} 1/[h(a^1T_{1g}(\kappa))])$. ^eStandard deviation in parentheses. ^fIn 4 M H₂SO₄ at 18 °C. ^g28 °C; (NH₄)₃(CoMo₆O₂₄H₆), 7H₂O. A crystal structure determination³¹ of Na₃(CrMo₆O₂₄H₆), 8H₂O shows that the Cr^{III} site is not completely orthoaxial. The two compounds are, however, not isomorphous and the much smaller Co³⁺ ion may well fit the polymolybdate structure better. At any rate the Co compound fits the plot of Figure 2b very well. ^h30 °C. ⁱ30 °C. This compound has a chemical shift of 3344 ppm relative to K₃[Co(CN)₆]. The meridional configuration has been confirmed by a ¹³C NMR spectrum which shows two peaks. Earlier ⁵⁹Co NMR papers,^{32,33} which report chemical shifts of approximately 3300 ppm for *fac*-[Co(NH₃)₃(CN)₃] and approximately 4000 ppm for *mer*-[Co(NH₃)₃(CN)₃], seem to have assigned the configurations differently.

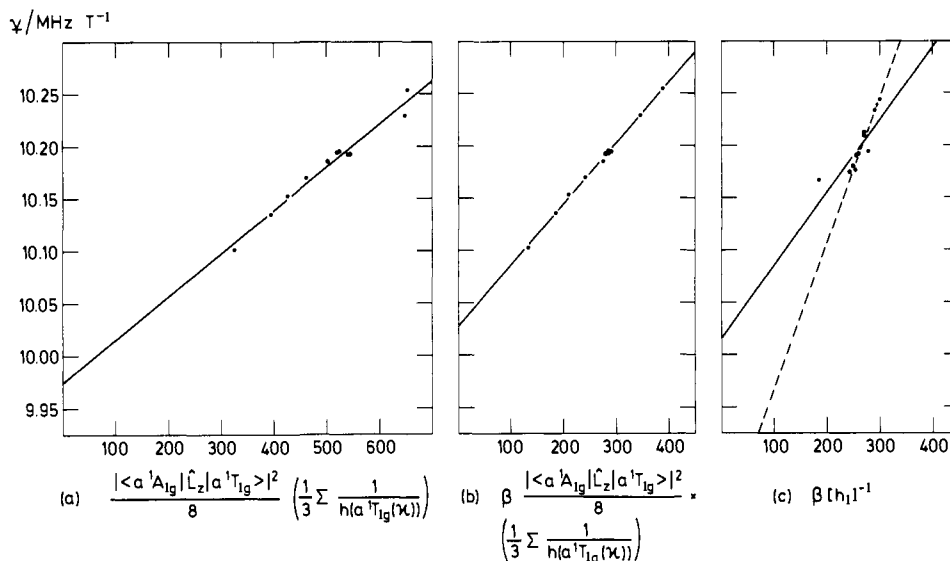
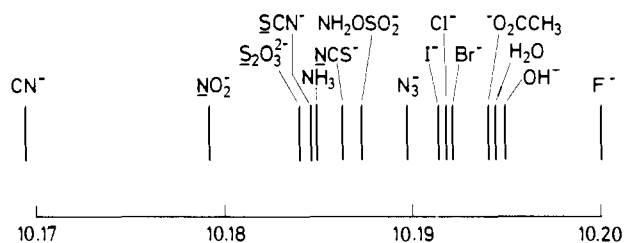


Figure 2. (a) Freeman, Murray, and Richards-type plot of $\bar{\nu}({}^{59}\text{Co})$ vs. wavelengths for orthoaxial cobalt(III) complexes. For the noncubic complexes, the low-symmetry splitting of the $a^1T_{1g}(O_h)$ term has been taken approximately into account. The values of the angular momentum matrix element are based on intermediate ligand-field calculations. The factor 8 in the denominator of the abscissa is the squared strong-field value of this matrix element. (b) As Figure 2a but with the nephelauxetic ratio β incorporated in the optical parameter. This produces a better fit to a straight line and makes the intercept in agreement with $\bar{\nu}({}^{59}\text{Co})$ values found by other methods. (c) Plot of $\bar{\nu}({}^{59}\text{Co})$ vs. $\beta[h_1]^{-1}$ for nonorthoaxial complexes. In the calculation of the optical parameters, these complexes have been treated as cubic ones. As discussed in section 10, this is probably not justified. The full line arises from a linear regression of the data for all the nonorthoaxial complexes. Excluding the two complexes with sulfur ligands changes the intercept drastically (broken line).

In Table I, optical transition energies, ligand-field parameter values, and ⁵⁹Co NMR measurements for a number of orthoaxial cobalt(III) complexes have been collected. Those complexes for which there is sufficient optical information have in Figure 2a been presented in a FMR-like plot of $\bar{\nu}$ vs. wavelength. However, the above mentioned improvement of using wavelengths which are the average of the wavelengths of the components of the $a^1A_{1g} \rightarrow a^1T_{1g}$ transitions has been made relative to FMR. Further, the strong-field approximation to the \hat{L}_z matrix element has been avoided, and Figure 2a is based on intermediate-field calculations.

Compared to the original FMR plot,⁴ the points fit a straight line very well. We see two reasons for this. Firstly, we have taken the low-symmetry splitting explicitly, although only approximately, into account. Secondly, we have only used orthoaxial complexes, thus avoiding trigonal ones. We shall in section 10 give an explanation of why trigonal complexes are not expected to fit a straight line as well as the orthoaxial complexes. The effect of the strong-field approximation on $\langle a^1A_{1g}|\hat{L}_z|a^1T_{1g}\rangle$ is not important for the fit. The main difference between Figure 2a and a corresponding plot based on the strong-field approximation is the

Scheme I



slope, which is lower in the intermediate field case (cf. Figure 1). The extent to which the data points fit a straight line in the two cases is the same.

8. Involvement of Nephelauxetism and Internal Field Strength

The expectation that all the data points of Figure 2a would fall on one straight line is based on the assumption that $\langle r_{3d}^{-3} \rangle$ takes the same value for all the complexes examined. This is probably not a good assumption, as it is known¹⁶ that the value of the repulsion parameter B , which depends on the reciprocal interelectronic distances in the 3d shell, varies from one complex to the other. It is generally found that the *nephelauxetic ratio*, i.e., the ratio between the value of B for the complex and for the corresponding gaseous ion (eq 18), is less than one. The value of this

$$\beta = B_{\text{complex}}/B_{\text{gas}} \quad (18)$$

ratio generally increases with the ligands in the order $I^- < Br^- < CN^- \approx Cl^- < NH_3 < H_2O < F^-$. If β is small for a complex, this indicates that the nephelauxetism (cloud expansion) is large. The value of B_{gas} for Co^{3+} has been determined³⁴ to be 1120 cm^{-1} . Nephelauxetism has been invoked before in connection with chemical shifts which do not follow simple excitation energy predictions, for example, by Kidd and Truax.³⁶ They found that ²⁷Al shifts for tetrahalidoaluminate anions can be rationalized if the physical idea of cloud expansion is introduced. Unfortunately, there is no spectroscopic way of estimating nephelauxetism for these compounds. Yamasaki et al.³⁷ seems to have been the first to notice the significance of nephelauxetism for the ⁵⁹Co chemical shifts of cobalt(III) complexes.

Scheme I shows the ⁵⁹Co gyromagnetic ratios for some complexes of the pentaamminecobalt(III) series. This ratio lies at one end of the scale for $[Co(NH_3)_5CN]^{2+}$ and at the other end for $[Co(NH_3)_5F]^{2+}$ with gyromagnetic ratios for $X = I^-, Br^-,$ and Cl^- in between. This distribution excludes a simple dependence of the shift data on the energy of the first cubic absorption band ($a^1A_{1g} \rightarrow a^1T_{1g}$) which follows the *spectrochemical series* (Δ series) of ligands X ; $CN^- > NH_3 > H_2O > F^- > Cl^- > Br^- > I^-$. However, the data indicate that the *internal-field-strength* parameter,³⁸ $\Sigma = \Delta/B$, might be governing the order of the chemical shifts. This indication is also brought out by the position of the S-bonded $S_2O_3^{2-}$ and SCN^- which both are low in the spectrochemical series but, since they are quite nephelauxetic, high in the internal-field-strength series.

The name change from the field-strength series³⁸ to "internal-field-strength series" has been introduced to avoid ambiguities. In the crystal-field model, if this is defined to involve only the repulsion parameters of the *gaseous* ions and the energy

difference between the e_g and t_{2g} orbitals, Δ represents the concept of field strength. In the parametrical d^q model, where individual repulsion parameters are associated with the different complexes of the same metal ion, $\Sigma = \Delta/B$ becomes a measure of the field strength. For an octahedral complex, the field-strength parameters of each model are, respectively, solely responsible for the mixing of cubic subconfigurations. Therefore, unless the model is specified, the term "field strength" is ambiguous. Accordingly, Σ has in this paper been renamed "the internal-field-strength parameter". The name internal has been introduced on the basis of the following consideration. The parameter $\Sigma = \Delta/B$ consists of an energy difference divided by an interelectronic repulsion parameter *for the same chemical system*. This means that Σ is a dimensionless parameter, being the ligand-field energy parameter Δ measured with an internal energy unit.

The internal-field-strength series for ligands runs as $CN^- > NH_3 > Br^- \approx Cl^- > H_2O > F^-$; the heavy halides have been moved forward with respect to the spectrochemical series due to their high nephelauxetism (low B values).

The qualitative empirical observation that there appears to be a relationship between the chemical shift and the internal field strength cannot be understood theoretically at the present time. This follows alone from the fact that even though the regular behavior of nephelauxetism has been known for more than 25 years, not even a semiquantitative theoretical account of this phenomenon has been advanced.

The problem is how to introduce nephelauxetism into Ramsey's equation while expressing it in a way which can be determined from optical data. A possible solution is given in eq 19 which is derived from eq 17 by multiplying *and* dividing with β (eq 18).

$$\sigma^p = -\frac{\mu_0 e^2}{12 \pi m_e^2} \left(\frac{\langle r_{3d}^{-3} \rangle}{\beta} \right) \left[\beta \sum_{\kappa=x,y,z} \frac{|\langle a^1A_{1g} | \hat{L}_z | a^1T_{1g}(z) \rangle|^2}{h(a^1T_{1g}(\kappa))} \right] \quad (19)$$

For noncubic complexes, we have here determined B , and thus β , from the average cubic transition energies inferred from cubic cobalt(III) complexes of the ligands in question.

The value of the factor in brackets in eq 19 can be determined solely from optical spectroscopic information by means of an intermediate ligand-field representation of the data. This term actually contains a slightly modified form of the internal-field-strength parameter Σ , namely, $h(a^1T_{1g})/\beta$. As the energy of the first cubic transition, $h(a^1T_{1g})$, is predominantly determined by Δ , and as β is proportional to B for the complex, then $h(a^1T_{1g})/\beta$ will vary with the chemistry in much the same way as Σ .

In the cases where sufficient optical information is available, the gyromagnetic ratios from Table I have been plotted vs. the optical factor in square brackets of eq 19 (Figure 2b). It is seen that the involvement of nephelauxetism makes the data points fall almost exactly on a straight line or, at least, much closer to a straight line than in the intermediate-field FMR plot of Figure 2a.

9. Results and Discussion

The intercepts for the plots of Figure 2 are equal to $\bar{\gamma}_0(1 - \sigma_{sf}^d)$ where σ_{sf}^d is the shielding term left when the cubic ligand field is infinitely strong (sf = strong field) so that σ^p vanishes. It is customary to assume that σ_{sf}^d is equal to the free atom value $\sigma^d = 0.0022$. By an extrapolation from the measured data to the intercept, one can thereby obtain the value of $\bar{\gamma}_0$.

This extrapolation to the cubic strong-field limit, i.e., to an infinitely strong internal field strength, is from a practical point of view an easy matter. Conceptually, there is, however, a little problem. Formally, the parametrical d^q model embodies a spherical component of the ligand-field operator which, though not an observable of the model, is hard to ignore conceptually.³⁹

(39) In the semiclassical electrostatic model, the potential is expanded in a multipole series and the spherical term there has to be larger than the cubic term. An extrapolation to an infinitely large cubic term is thus particularly difficult to associate with a free ion situation.

(31) Perloff, A. *Inorg. Chem.* **1970**, *9*, 2228-2239.
 (32) Juranic, N.; Celap, M. B.; Vucelic, D.; Malinar, M. J. *Radivoja, P. N. Spectrochim. Acta, Part A* **1979**, *35A*, 997-1002.
 (33) Au-Yeung, S. C. F.; Eaton, D. R. *J. Magn. Reson.* **1983**, *52*, 351-365.
 (34) Since the energies of the atomic levels of Co^{3+} only recently have become available,³⁵ the free ion repulsion parameters have hitherto been determined by extrapolation from those of an isoelectronic series (e.g., ref 14). We have performed a least-squares fitting of all the terms (their energies being found by degeneracy weighted averaging over the J levels) of the d^6 configuration given in ref 35. This gives as a result $B = 1120 \pm 25 \text{ cm}^{-1}$ and $C = 4430 \pm 85 \text{ cm}^{-1}$, corresponding to $C/B = 4.0$.
 (35) Sugar, J.; Corliss, C. *J. Phys. Chem. Ref. Data* **1981**, *10*, 1097-1174.
 (36) Kidd, R. G.; Truax, D. R. *J. Am. Chem. Soc.* **1968**, *90*, 6867-6869.
 (37) Yamasaki, A.; Yajima, F.; Fujiwara, S. *Inorg. Chim. Acta* **1968**, *2*, 39-42.
 (38) Schäffer, C. E. *Proc. R. Soc. London, Ser. A* **1967**, *A297*, 96-133.

The extrapolation to the cubic strong-field limit brings us to the situation which is as far away from a spherical situation as possible. Yet we want to represent the diamagnetic part of the screening constant here by that of the free atom. In addition to this problem within the d^q model, there is the more general problem associated with an extrapolation to an extreme situation by using a theoretical equation (the Ramsey equation) which has been derived by using second-order perturbation methods.

From a least-squares fit to a straight line of the data points in Figure 2b and from the value of σ_{sd}^d mentioned above, we obtain the following value of the gyromagnetic ratio for the bare ^{59}Co nucleus. (The standard deviation is that obtained from the linear regression.)

$$\bar{\gamma}_0(^{59}\text{Co}) = 10.048 \pm 0.003 \text{ MHz T}^{-1} \quad (20)$$

This value is in excellent agreement with those previously found by completely different methods. Walstedt, Wernick, and Jaccarino⁴⁰ reported their value, based on careful studies of the susceptibilities and Knight shifts of intermetallic compounds of cobalt and silicon, to be $\bar{\gamma}_0 = 10.054 \pm 0.02 \text{ MHz T}^{-1}$. In another study, Spiess, Haas, and Hartmann⁴¹ reported ^{59}Co NMR in single crystals of bis(η^5 -cyclopentadienyl)cobalt(III) nitrate. Their results correspond⁴² to $\bar{\gamma}_0 = 10.057 \pm 0.01 \text{ MHz T}^{-1}$. This value is based on the perhaps not completely justified assumption of unfettered magnetic-field-induced electron currents about the molecular axis.

The three values mutually support each other by being experimentally quite independent. From the intercept of the intermediate-field FMR plot (Figure 2a), $\bar{\gamma}_0 = 9.995 \text{ MHz T}^{-1}$ is obtained. This is in agreement with the observation⁴⁰ that the FMR plot underestimates the value of $\bar{\gamma}_0$. Although it would seem that the difference of about 0.05 MHz T^{-1} between the FMR value and that of eq 20 is small, it should be compared with the total range of gyromagnetic ratios for the ^{59}Co compounds which is 0.15 MHz T^{-1} .

Knowing $\bar{\gamma}_0(^{59}\text{Co})$, absolute values of screening constants can be calculated. Thus, for both extremes of the cobalt(III) low-spin systems $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Co}(\text{CN})_6]^{3-}$, one obtains antiscreening, expressed by the constants of -0.0205 and -0.0054 , respectively.

According to eq 19, the slope of the straight line of Figure 2b formally⁴³ reflects the magnitude of $\langle r_{3d}^{-3} \rangle / \beta$. This quantity is established as a good constant for the series of complexes examined and, thereby, $\langle r_{3d}^{-3} \rangle / B$ is also a constant. The Racah parameter B of the parametrical d^q model may be interpreted as being

(40) Walstedt, R. E.; Wernick, J. H.; Jaccarino, V. *Phys. Rev.* **1967**, *162*, 301-311.

(41) Spiess, H. W.; Haas, H.; Hartmann, H. *J. Chem. Phys.* **1969**, *50*, 3057-3064.

(42) This value is not that explicitly given by Spiess et al.⁴¹ For the field along the 5-fold axis of the cation, an upfield chemical shift of 6700 ppm relative to $\text{K}_3[\text{Co}(\text{CN})_6]$ solution was found in ref 41. The effective ligand field was taken to be of D_{5h} symmetry which is strictly true for a d^6 model since the d electrons cannot distinguish between an ∞ -fold and a 5-fold axis. Under the conditions of the experiment and the assumptions stated, it is a symmetry property that the paramagnetic shielding tensor component σ_{zz}^p (eq 6) vanishes. In the calculation of $\bar{\gamma}_0$ in ref 41, it is assumed that also the diamagnetic tensor component σ_{zz}^d is vanishing. Avoiding this assumption and taking $\sigma^d = 0.0022$ and $\bar{\gamma}[\text{Co}(\text{CN})_6^{3-}] = 10.1020 \text{ MHz T}^{-1}$ (Table I), $\bar{\gamma}_0$ can be obtained from eq 1 and 2 as

$$\begin{aligned} \delta[\text{Co}(\text{C}_5\text{H}_5)_2^+] &= \delta[\text{Co}(\text{C}_5\text{H}_5)_2^+] - \delta[\text{Co}(\text{CN})_6^{3-}] \\ &= \sigma[\text{Co}(\text{CN})_6^{3-}] - \sigma[\text{Co}(\text{C}_5\text{H}_5)_2^+] \\ &= \sigma[\text{Co}(\text{CN})_6^{3-}] - \sigma^d[\text{Co}(\text{C}_5\text{H}_5)_2^+] \\ -0.0067 &= \sigma[\text{Co}(\text{CN})_6^{3-}] - 0.0022 \\ \sigma[\text{Co}(\text{CN})_6^{3-}] &= -0.0045 \rightarrow \end{aligned}$$

$$\bar{\gamma}_0 = \bar{\gamma}[\text{Co}(\text{CN})_6^{3-}] / (1 - \sigma[\text{Co}(\text{CN})_6^{3-}]) = 10.1020 / (1 + 0.0045) = 10.057 \text{ MHz T}^{-1}$$

The error was not quoted for the above screening tensor component; however, two significant figures were given, so $\pm 0.01 \text{ MHz T}^{-1}$ should be the maximum error for $\bar{\gamma}_0$.

(43) Note that if the parametrical d^q model is unable to describe the values of the L matrix elements correctly (see section 5), the errors will appear implicitly in the value of the slope.

Table II. Optical Spectroscopic Parameters and $\bar{\gamma}(^{59}\text{Co})$ Values for Nonorthoaxial Cobalt(III) Complexes^a

	h_1 , cm ⁻¹	h_2 , cm ⁻¹	B , cm ⁻¹	$\beta[h_1]^{-1}$, nm	$\bar{\gamma}(^{59}\text{Co})$, ^b MHz T ⁻¹
$[\text{Co}(\text{en})_3]\text{Cl}_3$	21 550	29 600	587	243	10.1742 (1)
$[\text{Co}(\text{en})_2(\text{ox})]\text{Cl}\cdot\text{H}_2\text{O}$	19 900	27 650	570	256	10.1902 (1)
$\text{Na}[\text{Co}(\text{en})(\text{ox})_2]$	18 250	25 700	554	271	10.2088 (1)
$\text{K}_3[\text{Co}(\text{ox})_3]$	16 610	23 750	538	289	10.2332 (2)
$[\text{Co}(\text{en})_2(\text{mal})]\text{Hmal}^c$	20 160	28 090	585	259	10.1916 (2)
$\text{K}[\text{Co}(\text{en})(\text{mal})_2]^c$	18 590	26 180	565	271	10.2119 (2)
$\text{K}_3[\text{Co}(\text{mal})_3]^c$	16 450	23 700	550	299	10.2436 (1)
$[\text{Co}(\text{tame})_2]\text{Cl}_3^d$	21 320	29 500	600	251	10.1770 (1)
$[\text{Co}(\text{tacn})_2]\text{Br}_3^e$	21 810	30 300	625	256	10.1666 (1)
$[\text{Co}(\text{exan})_3]^f$	16 000	20 750	334	186	10.1658 (1)
$[\text{Co}(\text{dtp})_3]^g$	13 570	19 230	423	278	10.1934 (1)

^a NMR measurements at 30 °C in water. B is calculated under the assumption that the observed energies h_1 and h_2 represent the average cubic energies. ^b Standard deviation in parentheses. ^c mal = malonate. ^d tame = $\text{CH}_3\text{-C}(\text{CH}_2\text{-NH}_2)_3$. ^e tacn = $-(\text{CH}_2\text{-CH}_2\text{-NH})_3$. ^f exan = $\text{CH}_3\text{-CH}_2\text{-O-C}(\text{S})_2$. ^g dtp = $(\text{CH}_3\text{-CH}_2\text{-O})_2\text{P}(\text{S})_2$.

proportional to $\langle r_{ij}^{-1} \rangle$ (where r_{ij} is the distance between the electrons i and j). On the basis of a linear scaling of the d orbitals, one would rather have expected $\langle r_{3d}^{-3} \rangle / B^3$ to be a constant.

When one examines the few ^{103}Rh NMR data available for rhodium(III) complexes, it becomes clear that the quantitative way in which the cobalt(III) shifts depend on the nephelauxetic ratio is not unique. Thus, the chemical shifts of complexes of the types $[\text{Rh}(\text{H}_2\text{O})_{6-n}\text{Cl}_n]^{3-n}$ (ref 44) and $[\text{RhCl}_{6-n}\text{Br}_n]^{3-}$ (ref 45) are better described by an optical parameter⁴⁶ containing β^3 rather than β^1 (cf. eq 19). Thus, we must conclude that although no globally valid relation has been found between the chemical shifts and optical data, the effect of nephelauxetism is certainly significant and the shifts are determined by some combination of the nephelauxetic ratio and the spectrochemical parameter. This is especially evident for the rhodium(III) data just mentioned. The traditional FMR plot here gives the wrong sign of the correlation (i.e., rhodium(III) shows inverse halogen dependence), but this is corrected when the nephelauxetic ratio is incorporated in the abscissa.

10. Nonorthoaxial Complexes

The theoretical development so far has been concerned with orthoaxial²⁴ complexes, i.e., complexes having ligands which are linearly ligating and for which the angles subtended at the metal by adjacent ligating atoms are all 90°. The situation for non-orthoaxial complexes, e.g., those of the tris-bidentate type, is not so simple.

Trigonal complexes are described by three ligand-field parameters; the cubic parameter Δ and two low-symmetry parameters B and D (of ref 38, p 104). There are two reasons why the energies of the maxima for the first and second cubic parentage bands to *not* represent the average cubic energies very well.

First, the ligand-field parameter B (not to be mistaken for the repulsion parameter, which in this section will be called B_{Racah}) is in the cubic strong-field approximation responsible for an equal splitting of each of the cubic terms, a^1T_{1g} and a^1T_{2g} , into two components. The $^1T_{1g}(O_h)$ term splits into $^1A_2(D_3)$ and $^1E(D_3)$, while the $^1T_{2g}(O_h)$ term splits into $^1A_1(D_3)$ and $^1E(D_3)$. Supposing that the component bands can be approximated by Gaussian functions; then it is only if the transitions to the doubly degenerate $^1E(D_3)$ terms are twice as intense as those to the nondegenerate terms that the maxima of the observed curves will represent the average cubic energies reasonably well. This is likely to be roughly true for the vibronic part of the intensity. For the static part, however, application of circular dichroism sum rules³⁸ provides

(44) Mann, B. E.; Spencer, C. *Inorg. Chim. Acta* **1982**, *65*, L57-L58.

(45) Mann, B. E.; Spencer, C. M. *Inorg. Chim. Acta* **1983**, *76*, L65-L66.

(46) Although the optical parameters calculated for geometrical isomers of the type $[\text{Rh}(\text{H}_2\text{O})_{6-n}\text{Cl}_n]^{3-n}$ are almost identical, the isomers show large differences in chemical shifts. These large differences are not seen for $[\text{RhCl}_{6-n}\text{Br}_n]^{3-}$, and it is therefore natural to ascribe the phenomenon to the irregular spectrochemical behavior of the ligand H_2O .⁴⁷

Table III. Calculated Optical Transition Energies and Ligand-Field Parameters for Hypothetical Cubic Complexes

	h_1, cm^{-1}	h_2, cm^{-1}	Δ, cm^{-1}	B, cm^{-1}
[Co(OH) ₆] ³⁻	15 500	22 800	16 943	564
[CoCl ₆] ³⁻	12 500	18 400	13 666	456
[CoBr ₆] ³⁻	11 700	16 800	12 713	386

reasons to believe that the intensity ratios are the reverse for the first cubic parentage absorption band. Moreover, the component transition ¹A_{1g}(O_h)¹A₁(D₃) → ¹T_{2g}(O_h)¹A₁(D₃) of the second cubic parentage absorption band is a forbidden transition in a static trigonal field. This means that in the absence of vibronic intensity contributions, the second cubic parentage band will actually give the energy of the transition ¹A_{1g}(O_h)¹A₁(D₃) → ¹T_{2g}(O_h)¹E(D₃) rather than the weighted average of this transition and the forbidden one.

Second, the generally larger one of the two trigonal ligand-field parameters, *D* mixes ¹T_{1g}(O_h)¹E(D₃) with ¹T_{2g}(O_h)¹E(D₃) with the consequence that the two ¹E(D₃) terms "repel" each other. Since *B*_{Racah} is largely determined by the energy difference between the two cubic parentage bands, there will be a systematic error in its value depending on the magnitude of *D* and thereby also in the value of the internal-field-strength Σ, which is the essential parameter in the present context. One might have thought that a similar problem existed with the orthoaxial complexes when, for example, in a tetragonal complex *a*¹T_{1g}(O_h)¹E_g(D_{4h}) and *a*¹T_{2g}(O_h)¹E_g(D_{4h}) will also "repel" each other. However, by using calculated cubic average energies to estimate the actual transition energies, we have avoided the influence of the mixing of cubic parentage terms upon the value determined for *B*_{Racah} and thereby for the field-strength parameter Σ (see also ref 27).

Table II contains experimental data concerning ligand-field transitions and ⁵⁹Co magnetogyric ratios for some nonorthoaxial complexes. The data for these complexes have in Figure 2c been presented in the same way as the data for the orthoaxial complexes in Figure 2b by treating the transition energies as if they referred to cubic complexes. All the nonorthoaxial complexes, except those with sulfur-containing ligands, surprisingly fit on one straight line but with a much higher slope and smaller intercept than that belonging to the orthoaxial complexes.

Whilst our work was in progress, Juranic^{7,8} also realized the significance of nephelauxetic⁴⁸ variations within cobalt(III) complexes and found $\bar{\gamma}_0(^{59}\text{Co}) = 10.06 \pm 0.01 \text{ MHz T}^{-1}$ by extrapolation.⁴⁹ Considering that the majority of complexes chosen by Juranic were of trigonal symmetry, this value is in remarkably good agreement with our value found from orthoaxial complexes (eq 20). A least-squares fit to all our nonorthoaxial data yields $\bar{\gamma}_0 = 10.04 \pm 0.05 \text{ MHz T}^{-1}$. However, if the two complexes with sulfur ligands, [Co(exan)₃] and [Co(dtp)₃], are excluded, the intercept changes dramatically and $\bar{\gamma}_0 = 9.85 \pm 0.04 \text{ MHz T}^{-1}$ is obtained. We are therefore of the opinion that *not much confidence should be placed in $\bar{\gamma}_0(^{59}\text{Co})$ values found by extrapolation from nonorthoaxial data.*

11. Conclusion

Juranic has recently rationalized^{50,51} the chemical shifts of cobalt(III) and other d⁶ complexes in ways different from those of his earlier papers.^{7,8} We do not consider the approaches of the recent papers^{50,51} to be fruitful. Juranic has apparently realized that not all the quantities on the right-hand side of the Ramsey

equation that vary with the chemistry ($\langle r_{nd}^{-3} \rangle$, $\langle a^1A_{1g} | \hat{L}_z | a^1T_{1g} \rangle$, and $h(a^1T_{1g})$) are measurable by presently available experimental techniques. The author therefore introduces ad hoc parameters which are meant to describe the combined variation of some of the quantities mentioned, but their values are determined on the basis of the same chemical shifts as they are to rationalize. Thereby, the whole discussion becomes almost impenetrable from a point of view of logic.

Instead we are presenting an empirical relation between two experimentally completely independent quantities: the chemical shift on the one hand and an optical parameter which can be calculated from the vis-UV spectrum of the complex on the other hand. Our optical parameter is modified relative to that appearing in the Ramsey equation through the incorporation of the nephelauxetic ratio. This ratio is calculated (together with the orbital angular momentum matrix elements) within the framework of the parametrical d⁶ model on the basis of the two cubic parentage bands of the complex in question. Besides giving an improved linear correlation, our new optical parameter has the advantage that extrapolation to the intercept is only 50% of the observed abscissa range whereas the unmodified wavelength extrapolation is as large as the total spread of wavelengths. Nonorthoaxial complexes are found to give a much more uncertain linear relation than orthoaxial ones. In a future publication, it will be shown that the hydrogen and nitrogen chemical shifts of complexes of the type [Co(NH₃)₅X] follow the trend of the ⁵⁹Co shifts, i.e., vary with the internal ligand field strength series.

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Appendix

The transition energies, *h*₁ and *h*₂, for the hypothetical cubic complexes [Co(OH)₆]³⁻, [CoCl₆]³⁻, and [CoBr₆]³⁻ were obtained indirectly as follows. For a series of rhodium(III) and iridium(III) complexes of the type [MX₆]³⁺, spectroscopic data are available,⁵² and it was noted that the ratio h^{Rh}/h^{Ir} for corresponding transitions was constant for each X to within 1%. This was found to be also true for the h^{Rh}/h^{Co} ratios for the complexes [M(H₂O)₆]³⁺ and [M(NH₃)₆]³⁺. We have used this fact as an empirical aid to obtain transition data for the hypothetical cobalt(III) complexes. These calculated transition energies are given in Table III.

Registry No. Cs[Co(H₂O)₆](SO₄)₂, 95388-50-4; [Co(NH₃)₆]Cl₃, 10534-89-1; K₃[Co(CN)₆], 13963-58-1; [Co(NH₃)₅OH](ClO₄)₂, 18885-27-3; [Co(NH₃)₅H₂O](ClO₄)₃, 13820-81-0; [Co(NH₃)₅Cl](CF₃SO₃)₂, 95388-51-5; [Co(NH₃)₅Br](ClO₄)₂, 14591-65-2; [Co(NH₃)₅CN](ClO₄)₂, 14216-98-9; *cis*-[Co(NH₃)₄(CN)₂]Cl, 20394-57-4; *mer*-[Co(NH₃)₃(CN)₃], 20394-56-3; [Co(NH₃)₅F](NO₃)₂, 14240-02-9; [Co(NH₃)₅(O₂CCH₃)]Cl₂, 16073-49-7; [Co(NH₃)₅I](ClO₄)₂, 14972-83-9; [Co(NH₃)₅(N₃)](ClO₄)₂, 14283-04-6; [Co(NH₃)₅NH₂OSO₂](ClO₄)₂, 95120-87-9; [Co(NH₃)₅NCS](CH₃COO)₂, 65888-17-7; [Co(NH₃)₅SCN]²⁺, 15005-69-3; [Co(NH₃)₅S₂O₃]ClO₄, 14972-92-0; [Co(NH₃)₅NO₂](CH₃SO₃)₂, 95388-52-6; [Co(en)₃]Cl₃, 13408-73-6; [Co(en)₂(ox)]Cl, 17439-00-8; Na[Co(en)(ox)₂], 36527-85-2; K₃[Co(ox)₃], 14239-07-7; [Co(en)₂(mal)]Hmal, 95388-53-7; K[Co(en)(mal)]₂, 15079-76-2; K₃[Co(mal)₃], 25373-79-9; [Co(tame)₂]Cl₃, 60909-16-2; [Co(tacn)₂]Br₃, 36426-19-4; [Co(exan)₃] (coordination compound entry), 14916-47-3; [Co(exan)₃] (salt entry), 3444-56-2; [Co(dtp)₃] (coordination compound entry), 14177-94-7; [Co(dtp)₃] (salt entry), 15232-73-2; Co, 7440-48-4.

(47) Glerup, J.; Mønsted, O.; Schäffer, C. E. *Inorg. Chem.* **1976**, *15*, 1399-1407.

(48) The origin of Juranic's β values is unclear. They deviate both from those obtained by Jørgensen's expressions¹⁷ and from those found by a complete intermediate-field calculation.

(49) We have noticed a systematic shift of the $\bar{\gamma}$ values measured by Juranic by +0.004 MHz T⁻¹ relative to our values.

(50) Juranic, N. *Inorg. Chem.* **1983**, *22*, 521-525.

(51) Juranic, N. *J. Chem. Soc., Dalton Trans.* **1984**, 1537-1540.

(52) Jørgensen, C. K. "Absorption Spectra and Chemical Bonding in Complexes"; Pergamon Press: Oxford, London, New York, Paris, 1962; Table 30.