faster motions and to which extent it is only another expression for the increased randomness of the motion. Deuterium labeling may again be helpful in solving this problem. The relaxation times of a deuterium resonance line are determined essentially by quadrupole relaxation. The interpretation of relaxation times becomes thus much simpler than that of $^1$H or $^{13}$C nuclei.

During the preparation of this manuscript a brief report appeared on the intercalation of selectively deuterated lauric acid in lecithin bilayers.[21] The authors observed a sharp deuterium signal in sonicated bilayer dispersions. No information about order parameters was deduced, but from the line width the authors could give an estimate of the correlation time.

(21) H. Saito, S. Schreier-Muccillo, and I. C. P. Smith, *FEBS (Eur. Biochem. Soc.) Lett.*, 33, 281 (1973).

# Cobalt-59 Nuclear Quadrupole and Nuclear Magnetic Resonance Spectra of Cobaloximes[1]

**Robert A. LaRossa[2] and Theodore L. Brown\***

*Contribution from the School of Chemical Sciences and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801. Received September 26, 1973*

**Abstract:** Cobalt-59 nuclear quadrupole and nuclear magnetic resonance spectra are reported for a series of compounds XCo(dh)$_2$L, where dh = dimethylglyoxime monoanion, X$^-$ = CH$_3^-$, CHCl$_2^-$, Cl$^-$, and Br$^-$, and L = Lewis base. Chlorine-35 nqr signals were observed in a few compounds. Interpretation of the $^{59}$Co quadrupole coupling constants and asymmetry parameters in terms of bonding and electron distribution in the molecules requires an understanding of the orientation of and contributions to the electric field gradient tensor. By taking into account the known geometry of these complexes, a "donated charge" model is used to describe the changes in the quadrupole coupling constant and asymmetry parameter which result from changes in the interactions between the cobalt atom and the ligands. Taken in conjunction with the $^{59}$Co chemical shifts, the measured nqr parameters are interpreted in terms of the relative partial field gradient contributions of the axial and planar nitrogen ligands, [X] and [N], respectively. Comparison of calculated $eq_{zz}$ and $\eta$ values with experimental values of $e^2q_{zz}Q/h$ and $\eta$ shows that the value of [N] depends on the nature of the axial ligands in such a manner that the total of the partial field gradient contributions from all the ligands about Co is approximately constant. The axial ligands are ordered in terms of their interaction with Co as measured by the ratio [N]/[X].

A knowledge of the electronic charge distribution in molecules and ions is essential in attempts to understand bonding and the manner in which bonding is altered as a result of structural variations. Unfortunately, few experimental techniques provide observables which are directly related to the charge distribution.

Nuclear quadrupole resonance (nqr) spectroscopy provides a direct measure of the charge distribution around a quadrupolar nucleus in the electronic ground state of a molecule or ion through the interaction of the nuclear quadrupole moment ($eQ$) with the electric field gradient (efg). The interaction is expressed in terms of the two independent components of the field gradient tensor, the quadrupole coupling constant, $e^2q_{zz}Q/h$, and asymmetry parameter

$$\eta = \frac{q_{xx} - q_{yy}}{q_{zz}} \tag{1}$$

where $q_{xx}$, $q_{yy}$, and $q_{zz}$ are the principal components of the efg tensor. The asymmetry parameter reflects the extent of deviation of the tensor from axial symmetry.[3–5]

In the application of nqr spectroscopy to the nucleus of a multiply connected atom in a complex compound, the interpretation of the observed quadrupole coupling constant and asymmetry parameter may become quite difficult. If all the information from nqr spectroscopy is to be utilized effectively, the geometrical parameters must be known. Bis(dimethylglyoximato)cobalt(III) compounds (cobaloximes) are a series in which the geometry about the cobalt atom is well known and nearly invariant upon changes in ligation along the vertical axis.[6–8]

These compounds provide not only an interesting test of the utility of the nqr technique in the study of complex molecules but also provide a good basis for the evaluation of currently popular models which describe the origin of electric field gradients in semiempirical

(1) This research was supported by the National Science Foundation through Research Contract GH-33634 and Research Grant GP-30256X.

(2) University of Illinois Fellow, 1971–1972.

(3) T. P. Das and E. L. Hahn, "Nuclear Quadrupole Resonance Spectroscopy," Academic Press, New York, N. Y., 1958.

(4) E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants," Academic Press, New York, N. Y., 1969.

(5) E. Schempp and P. J. Bray in "Physical Chemistry. An Advanced Treatise," Vol. IV, D. Henderson, Ed., Academic Press, New York, N. Y., 1970, Chapter 11.

(6) J. S. Swanson, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1971.

(7) (a) P. G. Lenhert, *Chem. Commun.*, 980 (1967); (b) W. W. Adams and P. G. Lenhert, *Acta Crystallogr., Sect. B*, 29, 2412 (1973).

(8) K. S. Viswanathan and N. R. Kuncher, *Acta Crystallogr.*, 14, 675 (1961). The structure reported, [(NH$_3$)$_2$Co(dh)$_2$]NO$_3$, was not determined with high accuracy, and the reported N–Co–N angle of 78° is subject to considerable uncertainty.

terms.[9] An understanding of the electron distribution and bonding in these molecules is interesting in its own right. The cobaloximes, of general formula XCo-(dh)$_2$L, where (dh) = dimethylglyoximato monoanion and L is a Lewis base, contain, among a wide variety of Co–X units, stable Co–alkyl bonds. Alkylcobaloximes have gained considerable attention as models for vitamin B$_{12}$ and its derivatives,[10,11] and in studies of alkyl transfer reactions.[12]

Investigations of quadrupole splittings observed in Mössbauer spectroscopy of iron and tin compounds have led to the development of a field gradient model which involves expressing the total efg at the metal center as the sum of partial field gradient (pfg) parameters for various ligands.[9] In its conception the additive ligand model has been approached from both point-charge (or more precisely, donated charge[9b]) and molecular orbital viewpoints. Additivity follows from the assumptions that bond distances do not vary from complex to complex, external lattice contributions are negligible, the same charge is donated by a given ligand regardless of the presence of other ligands, and Sternheimer corrections are constant from ligand to ligand. The pfg parameter [L] for a ligand L may be defined in terms of the net charge centered on the ligand ($q_L$), the charge donated by the ligand to the metal valence orbitals ($q_L'$), the respective Sternheimer factors $\gamma_r$ and $R$, and the $1/r^3$ dependences on the separation between metal nucleus and the effective centers of the charge distributions.

$$[L] = e^2 Q\left[\frac{q_L(1 - \gamma_r)}{r_L{}^3} + \frac{q_L'(1 - R)}{\langle r_L{}'^3\rangle}\right] \quad (2)$$

It has been concluded that, for transition metal complexes, the donated charge or covalency term dominates in this expression.[13–16] The principal components of the field gradient tensor, in the principal axis system, are given by eq 3a–c

$$eq_{zz} = \sum_L [L](3\cos^2\theta_L - 1) \quad (3a)$$

$$eq_{xx} = \sum_L [L](3\sin^2\theta_L \cos^2\phi_L - 1) \quad (3b)$$

$$eq_{yy} = \sum_L [L](3\sin^2\theta_L \sin^2\phi_L - 1) \quad (3c)$$

where $\theta_L$ and $\phi_L$ are the angles designating the position of the ligand L in the principal axis system.

This approach has been used with some success in predicting signs and magnitudes of quadrupole coupling constants in certain Fe(II) complexes.[17,18] As Ban-

croft has pointed out,[19] the results should be applicable to $^{59}$Co nqr results in Co(III) compounds since bonding in Fe(II) and Co(III) compounds should be similar. Unfortunately, the number of compounds from which pfg parameters have been assigned is fairly limited, and one must be cautious about transferring ligand properties between sets of different compounds. Further, the model has not been fully tested, in the sense that the asymmetry parameter has usually been neglected in the Mössbauer studies. The determination of accurate asymmetry parameters is possible in nqr spectroscopy but is fairly difficult in the Mössbauer experiment and is not done routinely. A case in point is the Mössbauer data for Fe(niox)$_2$L$_2$ complexes (niox = cyclohexyldioxime monoanion and L = NH$_3$, imidazole, etc.[20,21]). Large unexplained asymmetry parameters were found for these complexes, and Bancroft and Platt report that the field gradients are not well characterized by the additivity model.[9a]

Several authors have recognized the potential for relating quadrupole coupling constants and nmr chemical shift data for $^{55}$Mn compounds,[22,23] but their efforts have been hampered by the lack of accurate quadrupole coupling constants. They have relied primarily on estimates of $e^2q_{zz}Q/h$ from nmr line width data. It is not unreasonable that such a correlation should exist, especially if one considers the efg in terms of the donated charge model noted above. This model and the concept that a particular ligand generates a pfg contribution resemble a ligand field approach for the description of electronic spectra in transition metal complexes (and for the description of $^{59}$Co nmr chemical shifts).

In this paper, $^{59}$Co nqr and nmr and a few $^{35}$Cl nqr results are reported for a broad series of complexes. A model for the description of field gradients in cobaloximes and other compounds of analogous structure is presented, and the relation between $^{59}$Co nqr and nmr results is discussed.

## Experimental Section

**Sample Preparation.** Alkylcobaloximes were prepared by established procedures.[24,25] Most products were recrystallized from hot ethanol, but CH$_3$Co(dh)$_2$CH$_3$OH was recrystallized from hot methanol.

ClCo(dh)$_2$L (and BrCo(dh)$_2$L) complexes were prepared according to the method of Schrauzer[24] or by adding the base L to a hot suspension of ClCo(dh)$_2$H$_2$O in ethanol. Complexes with L = P(OCH$_3$)$_3$ and P($n$-C$_4$H$_9$)$_3$ were recrystallized from a mixture of ethanol and dichloromethane. The complexes with L = NC$_5$H$_5$ and PPh$_3$ were crystallized by slow evaporation from CH$_2$Cl$_2$.

N(C$_2$H$_5$)$_4$[Br$_2$Co(dh)$_2$] and N(C$_2$H$_5$)$_4$[Cl$_2$Co(dh)$_2$] were prepared according to the method of Ablov and Samus[26] by first forming the acid, H[X$_2$Co(dh)$_2$]. This product was then recrystallized from warm ethanol–water containing excess N(C$_2$H$_5$)$_4$X (X$^-$ = Cl$^-$, Br$^-$) to yield large, dark brown crystals of the desired product.

(9) (a) G. M. Bancroft and R. H. Platt, *Advan. Inorg. Chem. Radiochem.*, **15**, 59 (1972); (b) R. V. Parish, *Progr. Inorg. Chem.*, **15**, 101 (1972).

(10) J. M. Pratt, "Inorganic Chemistry of Vitamin B$_{12}$," Academic Press, New York, N. Y., 1972.

(11) J. M. Pratt and P. J. Craig, *Advan. Organometal. Chem.*, **11**, 331 (1971), and references therein.

(12) J. H. Espenson and J. S. Shveima, *J. Amer. Chem. Soc.*, **95**, 4468 (1973).

(13) G. M. Bancroft, R. E. B. Garrod, A. G. Maddock, M. J. Mays, and B. E. Prater, *Chem. Commun.*, 200 (1970).

(14) G. M. Bancroft, R. E. B. Garrod, and A. G. Maddock, *J. Chem. Soc. A*, 3165 (1971).

(15) R. V. Parish and C. E. Johnson, *Chem. Phys. Lett.*, **6**, 239 (1970).

(16) J. Danon and L. Iannarella, *J. Chem. Phys.*, **47**, 382 (1967).

(17) G. M. Bancroft, M. J. Mays, and B. E. Prater, *J. Chem. Soc. A*, 956 (1970).

(18) J. C. Dabrowiak, P. M. Merrell, J. A. Stone, and D. H. Busch, *J. Amer. Chem. Soc.*, **95**, 6613 (1973).

(19) G. M. Bancroft, *Chem. Phys. Lett.*, **10**, 449 (1971).

(20) B. W. Dale, R. J. P. Williams, P. R. Edwards, and C. E. Johnson, *Trans. Faraday Soc.*, **64**, 620 (1968).

(21) B. W. Dale, R. J. P. Williams, P. R. Edwards, and C. E. Johnson, *Trans. Faraday Soc.*, **64**, 3011 (1968).

(22) S. Onaka, T. Mujamota, and Y. Sasaki, *Bull. Chem. Soc. Jap.*, **44**, 1851 (1971).

(23) G. M. Bancroft, H. C. Clark, R. G. Kidd, A. T. Rake, and H. G. Spinney, *Inorg. Chem.*, **12**, 728 (1973).

(24) G. N. Schrauzer, *Inorg. Syn.*, **11**, 61 (1968).

(25) N. Yamazaki and Y. Hokokabe, *Bull. Chem. Soc. Jap.*, **44**, 63 (1971).

(26) A. V. Ablov and N. M. Samus, *Russ. J. Inorg. Chem.*, **5**, 410 (1960).

**Table I.** ⁵⁹Co Chemical Shifts for Cobaloximes

| Compound | $\delta$,[a] ppm | Compound | $\delta$,[a] ppm |
|---|---|---|---|
| CH₃Co(dh)₂- | | CHCl₂Co(dh)₂S(CH₃)₂ | 4560 |
| CH₃OH | 4040[b] | ClCo(dh)₂- | |
| N(CH₃)₃ | 4360 | NC₅H₅ | 2980 |
| NC₅H₅ | 4490 | PPh₃[d] | 3360 |
| β-Picoline | 4490 | P(n-C₄H₉)₃ | 4020 |
| γ-Picoline | 4490 | P(OCH₃)₃ | 4550 |
| "Imid"[c] | 4560 | | |
| S(CH₃)₂ | 4960 | | |
| AsPh₃[d] | 5200 | | |
| P (p-PhOCH₃)₃ | 5340 | | |
| PPh₃ | 5350 | | |
| CNCH₃ | 5470 | | |
| P(n-C₄H₉)₃ | 5530 | | |
| P(OCH₃)₃ | 6570 | | |

[a] Measured upfield from an aqueous solution of [Co(NH₃)₆]Cl₃ with accuracy of ±20 ppm for the alkylcobaloximes ±50 ppm for the halocobaloximes. [b] Measured in CH₃OH solution; solvent shift is less than 50 ppm. [c] "imid" = 1-(2-trifluoromethylphenyl)-imidazole. [d] Ph = phenyl.

Analytical data for the cobaloximes may be found in the microfilm edition.[27]

The crystallinity of the complexes is a critical requirement for success of the nqr experiment. Great care was taken in recrystallization of all complexes. The problem was especially evident in the halocobaloximes, for which variable nqr signal intensities were observed for different samples of apparently identical purity. Observations of this type suggest that crystal strains arising from inclusion of impurities result in broad resonances which were frequently not detectable. Attempts were made to remove the strains by annealing the samples, but no signal improvement was observed, except in the case of BrCo(dh)₂NC₅H₅.

**Nqr Spectra.** The nqr data were obtained on two instruments of the superregenerative type. A Wilks NQR-1A spectrometer was used primarily to detect ³⁵Cl signals in the chlorocobaloximes. This spectrometer was insufficiently sensitive for detection of most of the ⁵⁹Co signals. The second instrument, constructed at the University of Illinois, is based on the design of Yim, Whitehead, and Lo,[28] with several modifications.[27] The usable frequency range of this superregenerative oscillator is about 2.5–14 MHz. An electronic coherence control unit, based on the design of Peterson and Bridenbaugh,[29,30] was used to maintain constant gain during searches.[27]

Either frequency modulation or Zeeman modulation may be employed with this spectrometer, but Zeeman modulation with a bidirectional square wave provided the best arrangement for detection of weak signals. Phase-sensitive detection was accomplished with a Princeton Applied Research Labs Model HR-8 lock-in amplifier. The output time constant was usually 30 sec, but occasionally a 100-sec time constant was used for direction of very weak signals. Very slow scan rates were obtained by driving the tuning capacitor with a stepping motor controlled by a binary divider network. Typical scan rates were 100–400 kHz/hr. Frequency measurements were made with an accuracy of at least ±0.01 MHz as described elsewhere.[31]

**⁵⁹Co Nuclear Magnetic Resonance Spectra.** ⁵⁹Co nmr spectra were obtained on a field-swept Varian WL-115 wide line spectrometer. Solution spectra of the complexes in CH₂Cl₂ were recorded at 16 kG and are reported relative to the signal for an aqueous solution of [Co(NH₃)₆]Cl₃. CH₃Co(dh)₂CH₃OH was run in CH₃OH solution; the solvent shift is less than 50 ppm. While a complete evaluation of the concentration dependence of the chemical shifts was not made, the magnitude of such shifts is undoubtedly small compared to the observed shift differences.

**Table II.** ⁵⁹Co Chemical Shifts for Complexes with Planar Ligands Other Than (dh)₂

| Compound[a] | $\delta$,[b] ppm | Ref |
|---|---|---|
| CH₃Co(bae) | 730 | This work |
| CH₃Co(bae)NC₅H₅[c] | 980 | This work |
| CH₃Co(salen) | 975 | 37 |
| BrCo(salen)PPh₃ | 590 | 37 |

[a] Abbreviations: bae = N,N'-ethylenebis(acetylacetoneiminato), salen = N,N'-ethylenebis(salicylideneiminato), Ph = phenyl. [b] Measured upfield from an aqueous solution of [Co(NH₃)₆]Cl₃. [c] Observed in 3:1 NC₅H₅–CH₂Cl₂ solution.

## Results and Discussion

**⁵⁹Co Nmr.** The theory of ⁵⁹Co nmr chemical shifts in Co(III) complexes has been described by Griffith and Orgel,[32] Freeman, et al.,[33] and more recently by Betteridge and Golding.[34] The chemical shifts may be related to the ligand field strengths of the bound ligands and energies of the electronic d–d transitions. Increased ligand $\sigma$ donation and/or $\pi$ back-bonding results in an increased energy separation between the ground and excited states and, therefore, decreased residual paramagnetism and decreased downfield chemical shift. The chemical shift is thus affected in the same sense by $\sigma$-donor and $\pi$-acceptor characteristics of the ligands in the complex, as discussed previously.[22,33] Unfortunately, the d–d transitions of the cobaloximes are masked by intense charge transfer transitions, so a correlation with the electronic spectra does not appear feasible.

The ⁵⁹Co chemical shifts for cobaloxime compounds are listed in Table I. In the methylcobaloxime series the oxygen base, CH₃OH, gives the smallest shift upfield from [Co(NH₃)₆]³⁺, indicating the weakest interaction with Co, followed by the nitrogen bases. Note that pyridine and the picolines give the same shifts, indicating that minor steric perturbations are not important factors in determining the shift values. It is noteworthy that the chemical shifts are not merely a consequence of the position of the bound atom in the periodic table, as is evident from the position of CNCH₃. This ligand is capable of $\sigma$ donation and $\pi$ acceptance n interactions with metals.[35] Herlinger and Brown[36] report an increase in $\nu_{CN}$ of 62 cm⁻¹ for bound CNCH₃ over free CNCH₃ which suggests that $\sigma$-bonding is dominant in the interaction with cobaloxime. The nmr result indicates that the interaction is quite strong.

It appears that $\pi$-bonding effects may be important in determining the magnitude of the chemical shifts, as illustrated by the shift of the P(OCH₃)₃ complex relative to P(n-C₄H₉)₃. P(OCH₃)₃ is expected to be a moderately strong $\sigma$-donor and a fairly strong $\pi$-acceptor, while P(n-C₄H₉)₃ is a comparatively stronger donor and weaker $\pi$-acceptor; the observed shifts reflect the presence of a $\pi$-interaction in the phosphite complex.

The observed ⁵⁹Co shifts for the chlorocobaloximes reveal similar trends. Replacement of CH₃⁻ by Cl⁻ results in a smaller shift from [Co(NH₃)₆]Cl₃, consistent

(27) See paragraph at end of paper regarding supplementary material.
(28) C. T. Yim, M. A. Whitehead, and D. H. Lo, Can. J. Chem., **46**, 3595 (1968).
(29) G. E. Peterson and P. M. Bridenbaugh, Rev. Sci. Instrum., **35**, 698 (1964).
(30) P. M. Bridenbaugh and G. E. Peterson, Rev. Sci. Instrum., **36**, 702 (1965).
(31) T. L. Brown, P. A. Edwards, C. B. Harris, and J. L. Kirsch, Inorg. Chem., **8**, 763 (1969).

(32) J. S. Griffith and L. E. Orgel, Trans. Faraday Soc., **53**, 601 (1957).
(33) R. Freeman, G. R. Murray, and R. E. Richards, Proc. Roy. Soc., Ser. A, **242**, 455 (1957).
(34) G. P. Betteridge and R. M. Golding, J. Chem. Phys., **51**, 2497 (1969).
(35) L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals," Wiley, New York, N. Y., 1969, p 26.
(36) A. W. Herlinger and T. L. Brown, J. Amer. Chem. Soc., **93**, 1790 (1971).

**Table III.** $^{59}$Co Nqr Data for Cobaloximes

| Compound[a] | $|e^2q_{zz}Q/h|$[b] | $\nu_3$ | $\nu_2$ | $\nu_1$ | $\eta$ |
|---|---|---|---|---|---|
| CH$_3$Co(dh)$_2$- | | | | | |
| PPh$_3$ | 28.12 | 5.65 (7)[c] | 3.66 (4) | 4.42 (3) | 0.77 |
| NC$_5$H$_5$ | 29.52 | 6.30 (25) | 4.13 (12) | 2.40 (3)[d] | 0.22 |
| S(CH$_3$)$_2$ | 30.30 | 6.26 (3)[d] | 3.96 (2)[d] | 3.91 (2)[d] | 0.58 |
| P($p$-PhOCH$_3$)$_3$[e] | | 6.42 (2)[d] | | | |
| AsPh$_3$ | 30.59[f] | 6.47 (8) | 4.15 (3) | | 0.35 |
| | (32.02) | | | | (0.73) |
| N(CH$_3$)$_3$[g] | 30.55[f] | 6.53 (9) | 4.31 (6) | | 0.16 |
| | (32.93) | | | | (0.84) |
| | 31.34[f] | 6.66 (9) | 4.40 (6) | | 0.14 |
| | (33.61) | | | | (0.83) |
| "Imid" | 31.34[f] | 6.69 (10) | 4.40 (6) | | 0.18 |
| | (33.69) | | | | (0.82) |
| P(OCH$_2$)$_3$CC$_2$H$_5$ | 40.24 | 8.40 (25) | 5.33 (12) | 4.76 (2)[d] | 0.50 |
| CH$_3$OH | 41.62 | 8.84 (2)[d] | 5.72 (10) | 3.79 (13) | 0.30 |
| CNCH$_3$[e] | | 8.52 (4) | | | |
| P(OCH$_3$)$_3$ | 43.33 | 8.97 (15) | 5.67 (7) | 5.58 (5) | 0.57 |
| P($n$-C$_4$H$_9$)$_3$ | 46.20 | 9.59 (12) | 6.07 (6) | 5.77 (5) | 0.55 |
| CHCl$_2$Co(dh)$_2$S(CH$_3$)$_2$ | 36.93 | 7.39 (3) | 4.81 (2) | 5.95 (5) | 0.79 |
| N(C$_2$H$_5$)$_4$[Br$_2$Co(dh)$_2$] | 75.88 | 15.46[h] | 9.86 (3) | 11.02 (5) | 0.68 |
| N(C$_2$H$_5$)$_4$[Cl$_2$Co(dh)$_2$] | 73.15 | 14.81 (3)[d] | 9.50 (6) | 10.68 (12) | 0.72 |
| BrCo(dh)$_2$NC$_5$H$_5$[e] | | | 9.14 (8) | | |
| ClCo(dh)$_2$NC$_5$H$_5$ | 64.82 | 13.31 (6) | 8.44 (15) | 8.90 (20) | 0.63 |
| ClCo(dh)$_2$PPh$_3$ | 60.45 | 12.04 (3) | 7.90 (5) | 9.91 (10) | 0.81 |
| ClCo(dh)$_2$P($n$-C$_4$H$_9$)$_3$[g] | 40.91[f] | 8.55 (10) | 5.55 (4) | | 0.35 |
| | (42.76) | | | | (0.72) |
| | 41.49[f] | 8.86 (15) | 5.81 (6) | | 0.20 |
| | (44.53) | | | | (0.82) |

[a] Abbreviations: Ph = phenyl, "imid" = 1-(2-trifluoromethylphenyl)imidazole. [b] Quadrupole coupling constant and transition frequencies have units of MHz. [c] Numbers in parentheses are the signal:noise ratios for 30-sec RC time constant unless indicated otherwise. [d] Signal:noise ratio for 100-sec RC time constant. [e] $(e^2q_{zz}Q/h)$ could not be determined since only one resonance was observed. [f] Two values of $(e^2q_{zz}Q/h)$ are reported corresponding to the two possible values of $\eta$. See text. [g] For this compound, each of the two observed transitions consisted of a pair of lines due to crystallographically distinct cobalt nuclei. [h] Signal not observed; $\nu_3$ calculated from $\nu_2$ and $\nu_1$.

with the expectation that methide is a much stronger field ligand than chloride. The trend in shifts, which result from the variation of the axial bases, is as described above.

The chemical shifts observed for the cobaloxime complexes are much larger than those of complexes with salen (salen = $N,N'$-ethylenebis(salicylideneiminato))[37] and bae (bae = $N,N'$-ethylenebis(acetylacetoneiminato)) (Table II). Both of these ligands bond to the cobalt through two nitrogen and two oxygen atoms and both form stable five-coordinate complexes, unlike the cobaloximes which are always six-coordinate. The shift difference is not surprising on the basis of the expected relative ligand field strengths of N and O ligands.

$^{59}$Co Nqr. The measured $^{59}$Co nqr transition frequencies, asymmetry parameters, and quadrupole coupling constants for the cobaloxime compounds are listed in order of increasing magnitude of $e^2q_{zz}Q/h$ in Table III. $^{59}$Co has $I = {}^7/_2$ so that three transitions should be observed: $\nu_1$ ($\pm {}^1/_2 \leftrightarrow \pm {}^3/_2$), $\nu_2$ ($\pm {}^3/_2 \leftrightarrow \pm {}^5/_2$), $\nu_3$ ($\pm {}^5/_2 \leftrightarrow \pm {}^7/_2$). Observation of all three transitions permits unambiguous assignment of both $e^2q_{zz}Q/h$ and $\eta$. It was not possible to observe all three signals in every case. Where only two transitions were seen, assignment of the signals to particular transitions was made on the basis of observed signal intensities and expectations regarding the relative ordering of the compounds. When the two observed transitions can reasonably be assigned, e.g., as $\nu_3$ and $\nu_2$, two possible values of $\eta$ and $|e^2q_{zz}Q/h|$ may still exist. For this reason,

(37) C. Floriani, M. Puppis, and F. Calderazzo, J. Organometal. Chem., 12, 209 (1968).

two values of these parameters are listed for the compounds for which only two signals were observed.

Rationalization of the quadrupole coupling data in terms of the bonds between ligands and the metal requires a knowledge of the sign and orientation of the major component, $q_{zz}$, of the field gradient tensor. These properties depend on the geometry of the molecule. Neglecting minor distortions, the cobaloximes have a $C_2$ axis along the X–Co–L bond axis,[6–8] requiring that one of the principal efg tensor axes lies along this direction. In the Mössbauer studies of Fe(II) complexes having comparable planar ligands, it has been assumed that the molecules may be treated as having a $C_4$ axis by neglecting the lack of symmetry in the dimethylglyoxime-type ligands;[20,21] the z axis then lies along the $C_4$ axis. The analogous assumption in the cobaloxime case leads to the conclusion that the quadrupole coupling constant has a large positive value ($eQ$ is positive) for axial ligands which donate much less electron density to the cobalt than the planar ligand system. As the combined axial ligand strength increases, the quadrupole coupling constant decreases to zero, at which point the axial and planar ligand systems generate equal but opposite field gradient contributions. Finally, the quadrupole coupling constant becomes negative as the interaction with the axial ligands increases relative to the planar ligand interaction. The asymmetry parameter is required to be zero in the case of fourfold symmetry. In the simplest possible approach to the nqr results, we might assume that for all the methylcobaloxime compounds the averaged donor strength of the methyl group and axial base is greater than the donor
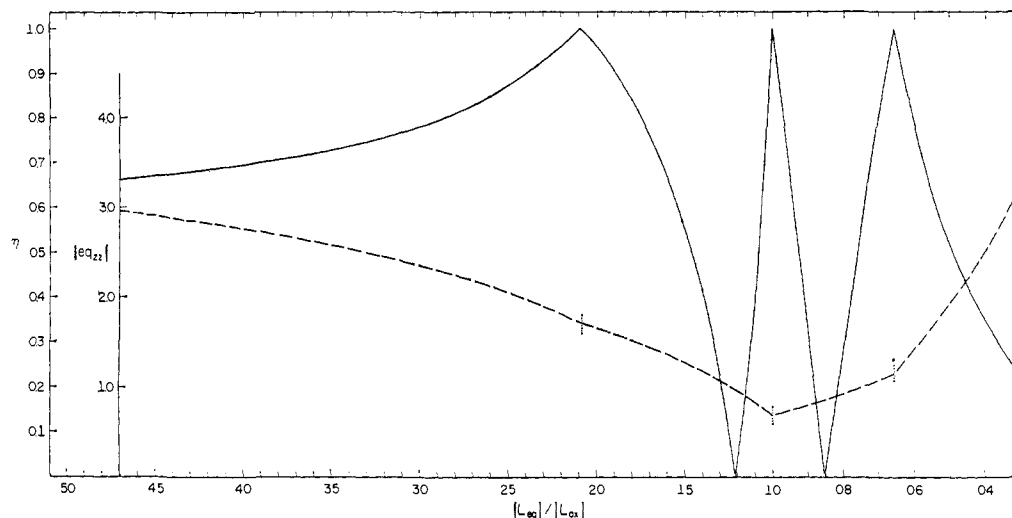
**Figure 1.** Asymmetry parameter and relative magnitude of the scaled quadrupole coupling constant *vs.* the ratio of partial field gradient contributions from equatorial and axial ligands; the N–Co–N angles in the planar ligand system are 80 and 100°. The dashed line refers to the scaled values of $eq_{zz}$ and the solid line refers to $\eta$. Vertical dotted lines indicate sign changes of $eq_{zz}$.
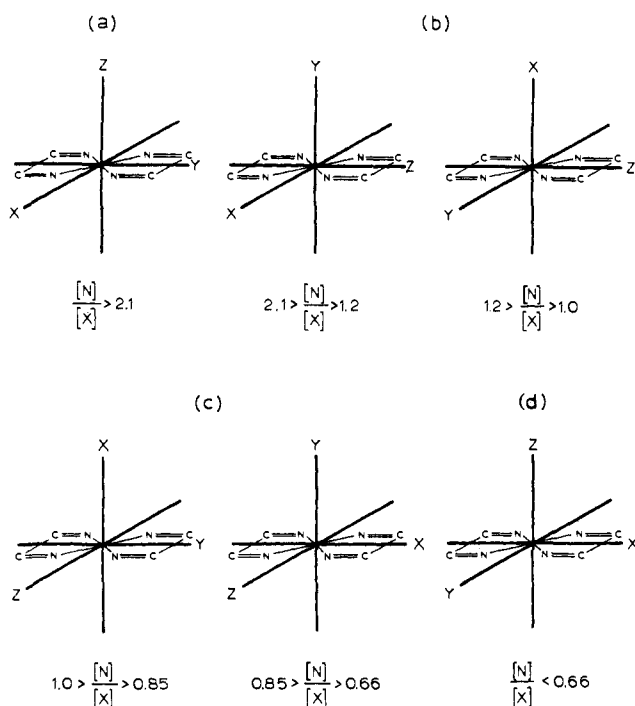


**Figure 2.** Orientation of the efg axis system for (a) [N]/[X] > 2.1, (b) 2.1 > [N]/[X] > 1.0, (c) 1.0 > [N]/[X] > 0.66, and (d) [N]/[X] < 0.66. Two axis systems are shown for conditions b and c to demonstrate the interchange of $x$ and $y$ when $\eta = 0$.

strength of a nitrogen of the planar ligand system, so that the quadrupole coupling constant is negative. In the halocobaloximes, on the other hand, the averaged donor strength of the axial ligands might be assumed to be less than for a nitrogen of the planar ligand. While these assumptions are in very rough accord with the results, the asymmetry parameter is often very seriously different from zero, the value corresponding to axial symmetry. It is therefore necessary to consider a more detailed model for the complexes, which takes account of the known geometry about cobalt.

**Development of a Field Gradient Model.** Any useful field gradient model must explain the observed variations in quadrupole coupling constants and asymmetry

parameters and make chemically reasonable predictions. We present an approach which accounts for the results reported here and which should be generally applicable to other systems with analogous geometry, including many low spin Fe(II) systems.

The molecular geometry of the cobaloximes may be described as pseudo-$D_{2h}$, rather than $C_{2v}$, by denoting the complex as *trans*-$X_2CoN_4$, where the two different axial ligands in each complex are replaced by two ligands, X, having partial field gradient (pfg) parameters which are the average of the pfg parameters for the two original axial ligands, *i.e.*, [X] = $\frac{1}{2}$([A] + [B]). This replacement in no way alters the quadrupole coupling constant or $\eta$. [N] represents the pfg parameter for a nitrogen of the dimethylglyoxime ligands. The calculation of relative efg tensor components is now quite simple. Using eq 3a–c, the following expressions result

$$eq_{kk} = 4[X] - 4[N] \tag{4a}$$

$$eq_{jj} = -2[X] + 4[N](3\cos^2\phi - 1) \tag{4b}$$

$$eq_{ii} = -2[X] + 4[N](3\sin^2\phi - 1) \tag{4c}$$

The subscripts $i$, $j$, and $k$ denote the three axes. The positions of the tensor axes are fixed since one must lie along the X–Co–X axis, and the other two must lie in the dimethylglyoxime plane, bisecting the N–Co–N angles. The angle $\phi$ is measured in this plane by arbitrarily choosing one axis as $x$. At this point no assumption has been made about the actual assignment of the three axes in terms of $q_{xx}$, $q_{yy}$, and $q_{zz}$.

Using eq 4a–c and the observed geometry about the cobalt in the plane of the dimethylglyoxime groups, values for $eq_{zz}$ and $\eta$ can be calculated for a wide range of relative pfg's of [N] and [X]. The three tensor components of the overall field gradient tensor are assigned in accord with the requirement that $|q_{zz}| \geq |q_{yy}| \geq |q_{xx}|$. For any particular values chosen for [N] and [X] the calculated value for $eq_{zz}$ is related to the observed $e^2Qq_{zz}/h$ value by a scaling factor. The *relative* values for [N] and [X] are of prime importance, since for any given total values for the two parameters this ratio determines both $e^2Qq_{zz}/h$ and $\eta$. We shall
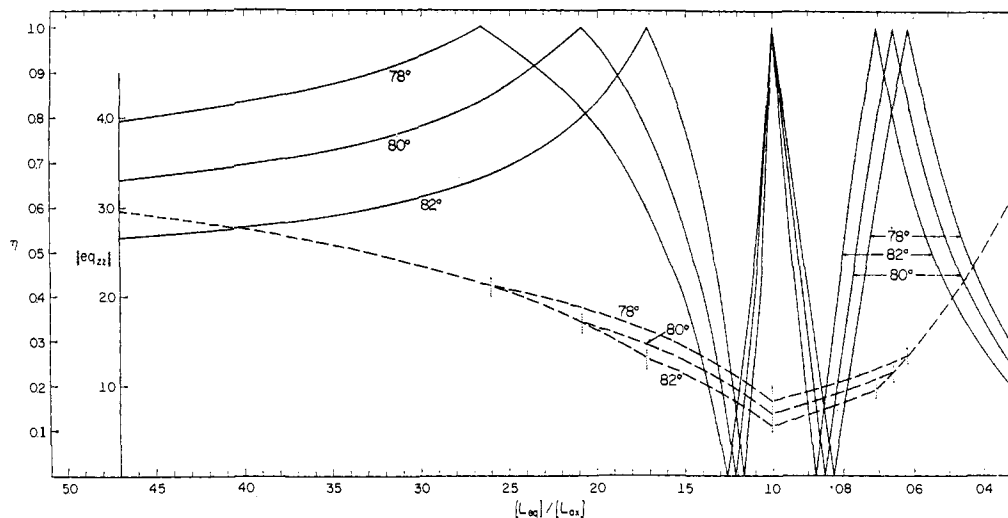
**Figure 3.** Asymmetry parameter and relative magnitude of the scaled quadrupole coupling constant $vs.$ the ratio of partial field gradient contributions from equatorial and axial ligands for three N-Co-N angles. Solid lines refer to $\eta$, and dashed lines refer to the scaled values of $eq_{zz}$. Vertical dotted lines indicate sign changes of $eq_{zz}$.

thus be interested in examining how the ratio [N]/[X] varies as we change the nature of the axial ligands in the cobaloxime series, and how the value assigned for [N] varies as we change the value for the ratio.

We assume that $N(C_2H_5)_4[Cl_2Co(dh)_2]$ represents one extreme among the compounds studied, in which the interaction of the axial ligands with the cobalt is much weaker than the interaction of the planar ligands ([N]/[X] > 1). The opposite extreme, in which the axial ligands interact more strongly with cobalt than the planar ligand ([N]/[X] < 1), is represented by $CH_3Co$-$(dh)_2P(n$-$C_4H_9)_3$. We begin by assigning [N] = $-1.0$ and [X] = $-0.1$ and increase [X] in increments up to values larger than $-1.0$, keeping [N] constant and assuming that $\phi$ = 40°. This generates a set of values of $eq_{zz}$ and $\eta$, and it is possible to fit both the compounds mentioned above to the resulting curves of $eq_{zz}$ and $\eta$ $vs.$ the ratio [N]/[X]. However, the scaling factor relating $eq_{zz}$ to the observed values for $e^2q_{zz}Q/h$ is vastly different in the two cases. This indicates that it is not correct to assume that the contribution for [N] is a constant, independent of the value chosen for [X]; $i.e.$, the assumption of constancy for the planar ligand pfg parameters fails. Rather, it works out that for each increment of $-0.01$ in [X] one must increment [N] by $+0.006$. When this is done, the two compounds which represent an extreme difference among the compounds studied in terms of the ratio [N]/[X] can be fitted to the calculated field gradient tensor quantities with the same scaling factor of 27 relating the calculated $|eq_{zz}|$ and observed coupling constants.

A plot of $eq_{zz}$ and $\eta$ $vs.$ the ratio [N]/[X] generated as described above reveals the entire range of nqr parameters generated by ligands of different relative strengths. The results are presented in Figure 1 for a N-Co-N angle of 80° ($\phi$ = 40°). The graph is cut off at the extremes where the nqr parameters become unrealistic for the systems studied. The ratio [N]/[X] is indicated in the figure in a more general way as the ratio of equatorial and axial ligand contributions [$L_{eq}$]/[$L_{ax}$], and $|eq_{zz}|$ is the magnitude of the major component of the field gradient, scaled to the arbitrary units of the calculations. In the present instance each unit corre-

sponds to about 27 MHz in $e^2q_{zz}Q/h$. It is obvious from this figure that neglecting the details of the molecular geometry, as has been done in considering the Mössbauer data for Fe(II) complexes, cannot result in a complete picture of the changes in the nqr parameters. Each time $\eta$ = 1, the orientation of the major component of the field gradient changes and the sign of $e^2q_{zz}Q/h$ changes (denoted on the graph by the vertical dotted lines). When $\eta$ = 0, the $x$ and $y$ directions interchange. Initially, when the Co-N interaction is very large compared to the Co-X interaction ([N]/[X] > 2.1), the axis system is that shown in Figure 2a. In the region 2.1 > [N]/[X] > 1.0, when [X] becomes comparable to [N], the $z$-axis shifts into the dimethylglyoxime plane and the $x$ and $y$ axes interchange as shown in Figure 2b; $eq_{zz}$ is negative. Between the [N]/[X] values of 1.0 and 0.65, $eq_{zz}$ is positive and the $z$ axis has been rotated by 90°, still in the dimethylglyoxime plane (Figure 2c). Once again, $q_{xx}$ and $q_{yy}$ interchange directions at the point $\eta$ = 0. Finally, when the axial ligands produce a much larger contribution to $q_{zz}$ than the planar ligand, $eq_{zz}$ is negative and increases in magnitude very rapidly. The $z$ axis is again along the X-Co-X direction (Figure 2d). It is noteworthy that the quadrupole coupling constant never goes to zero as it would if the molecule had $D_{4h}$ or $C_{4v}$ symmetry.

It is of importance to explore the effect of small geometrical distortions on the quadrupole coupling constant and asymmetry parameter. Cobaloxime compounds for which crystal structure information is available exhibit N-Co-N angles in the plane ranging from 78 to 81.5°.[6-8] The effect of a ±2° change from the 80° angle on the calculated nqr parameters is shown in Figure 3. The change in quadrupole coupling constant is fairly substantial for a 2° change in the region near [$L_{eq}$]/[$L_{ax}$] = 1, whereas the modification of $\eta$ is most noticeable in the region [$L_{eq}$]/[$L_{ax}$] > ~1.5. It is evident that, in systems where substantial variation in the details of the geometry about the central metal is possible, it will be difficult to fit observed nqr data to the model unless accurate structural data are available for each compound of interest. In the case of the

cobaloximes, however, we can safely assume that the N–Co–N angle remains within about 1° of 80°.

This model has direct application to the Mössbauer investigations of Fe(niox)$_2$L$_2$ complexes referred to previously. Dale, et al.,[20,21] found a large $\eta$ for the compound with L = imidazole and $\eta \approx 1$ for L = NH$_3$. The quadrupole coupling constants have been thought to have positive signs by analogy with the measured sign for phthalocyanine complexes (the N–Co–N angles in the niox ligand are 79 and 101°, whereas phthalocyanine has 90° angles). The pfg parameters reported by Bancroft and Platt[9a] indicate that niox generates a larger field gradient contribution than imidazole or NH$_3$, so, in terms of the model presented here, the data fall in the region where [N]/[X] > 1. Since $e^2q_{zz}Q/h$ for L = NH$_3$ is greater than that for L = imidazole, and $\eta_{NH_3} > \eta_{im}$, the compounds probably fall in the region just below [N]/[X] = 2.7 probably at about 2.0. We suggest that the sign of the quadrupole coupling constant is *negative* for the imidazole complex, not positive as previously thought.

**Correlation of Nqr and Nmr Results.** A cursory comparison of the data in Tables I and III reveals that the ordering of ligands is not likely to be exactly the same in the two techniques. For example, the P($n$-C$_4$H$_9$)$_3$ and P(OCH$_3$)$_3$ complexes are reversed in order in the two sets of results. It seems most likely that the $\sigma$ and $\pi$ effects in the two compounds influence the chemical shift and quadrupole coupling constant differently. $\pi$-Bonding cannot be evaluated as a separate effect in the efg model. For example, a ligand situated on the $z$ axis which is capable of acting as a $\pi$-acceptor with respect to the metal $d_{xz}$ and $d_{yz}$ orbitals, thereby reduces the magnitude of $q_{zz}$ in that direction. Some fraction of the electronic charge so removed is redirected into the $d_{z^2}$ orbital by means of the familiar synergism between $\pi$-acceptor and $\sigma$-donor actions, resulting in a partial restoration of the efg component. While the net ($\sigma + \pi$) bonding interaction for a ligand like P(OCH$_3$)$_3$ may be as large as it is for a strongly donating ligand like P($n$-C$_4$H$_9$)$_3$, the result of the larger $\pi$ interaction in the case of the phosphite is a reduction of $eq_{zz}$ relative to phosphine (assuming [N]/[X] < 1). The $^{59}$Co nmr shift, on the other hand, depends on the d–d separation, which is increased by *both* $\sigma$- and $\pi$-bonding. Any two otherwise similar ligands capable of different degrees of $\pi$-bonding may therefore exhibit an inversion of ordering between the two techniques. If [N]/[X] > 1, the quadrupole coupling constant increases with increased $\pi$-bonding, and if [N]/[X] < 1, the quadrupole coupling constant decreases.

While $\pi$-bonding effects may operate thus to alter the effect of a given ligand, $\pi$-bonding is not expected to be a major component of the binding of any of the ligands to Co. We thus assume that $\pi$-bonding exerts at most a relatively minor perturbative effect on the expected monotonic relationship between $^{59}$Co chemical shifts and the ratio [L$_{eq}$]/[L$_{ax}$] as deduced from nqr. We are then in a position to order the axial ligands from largest to smallest [L$_{eq}$]/[L$_{ax}$] ratio, taking into account the changes in sign and variations in asymmetry parameter. In the following discussion it will be helpful to refer closely to Tables I and III and Figure 1.

The quadrupole coupling constants for the halo-

cobaloximes decrease in an order consistent with varying metal–axial ligand interaction in the order Br$^-$ < Cl$^-$ < NC$_5$H$_5$ < PPh$_3$ < P($n$-C$_4$H$_9$)$_3$. The decrease in $|e^2q_{zz}Q/h|$ with increasing donor ability corresponds to the region [N]/[X] > 1 in Figure 1. In this region, the sign of $eq_{zz}$ changes from positive to negative, so in order to determine the sign of $eq_{zz}$ in each compound, it is necessary to determine the value of [N]/[X] for each axial ligand pair. N(C$_2$H$_5$)$_4$[Br$_2$Co(dh)$_2$] and N(C$_2$H$_5$)$_4$[Cl$_2$Co(dh)$_2$] have asymmetry parameters of 0.68 and 0.72, respectively. Using these values of $\eta$, the two compounds may be assigned [N]/[X] values of 4.3 and 3.6, assuming N–Co–N angles in the planar arrangement of 80 and 100°. These positions correspond to +2.85 for the trans-dibromo complex and +2.65 for the trans-dichloro complex. When a stronger base is substituted for Cl$^-$, [N]/[X] should decrease and $\eta$ should increase. The observed $\eta$ for ClCo(dh)$_2$NC$_5$H$_5$ is 0.63, whereas the model predicts $\eta$ > 0.7. This instance is probably exemplary of the level of agreement generally obtainable with the model. $\eta$ is quite sensitive to small changes in geometry (and may even be sensitive to the orientation of the pyridine ring in the crystal), while the quadrupole coupling constant is unaffected by small structural changes. It is not unreasonable, therefore, that the observed asymmetry parameter is too small. The relative position of the pyridine complex on the [N]/[X] curves may still be determined from the observed value of $e^2q_{zz}Q/h$, by employing the scaling factor of $^1/_{27}$ to reduce the observed value to $eq_{zz}$. Using this relation, the scaled value is +2.40 corresponding to [N]/[X] = 3.1, with a predicted $\eta$ = 0.76. This same relation predicts [N]/[X] = 2.8 for ClCo(dh)$_2$PPh$_3$ with $\eta$ = 0.81, in excellent agreement with the observed value of 0.81. The halocobaloximes described so far all have positive quadrupole coupling constants.

The predictive capability of the model may be tested further with the results for ClCo(dh)$_2$P($n$-C$_4$H$_9$)$_3$. Since only two of the three nqr signals for the $^{59}$Co nqr of this compound have been observed (consider an average of the crystallographically split signals, Table III) and have been assigned as $\nu_3$ and $\nu_2$, two values of $|e^2q_{zz}Q/h|$ may be calculated—43.6 MHz corresponding to $\eta$ = 0.80 or 40.5 MHz with $\eta$ = 0.23. The model may be used to distinguish between these two possible quadrupole coupling constants. We enter Figure 1 with the scaled values of $eq_{zz}$ to determine [N]/[X] and $\eta$ for the two cases for ClCo(dh)$_2$P($n$-C$_4$H$_9$)$_3$. The predicted asymmetry parameters are 0.96 and 0.88, corresponding to $|e^2q_{zz}Q/h|$ = 43.6 and 40.5, respectively. This suggests that $e^2q_{zz}Q/h$ = 43.6 MHz, since this choice leads to large $\eta$. The value of [N]/[X] for this choice is 1.9.

It is extremely unlikely that [N]/[X] > 1 for all the cobaloximes. If the nmr chemical shifts for $^{59}$Co reflect the same relative interactions as the nqr data, then we should expect a continuous distribution of the observed efg's over a range of [N]/[X] values. For example, the complex CH$_3$Co(dh)$_2$CH$_3$OH has approximately the same quadrupole coupling constant and chemical shift as ClCo(dh)$_2$P($n$-C$_4$H$_9$)$_3$. Since bonding to the cobalt center from both CH$_3$OH and P($n$-C$_4$H$_9$)$_3$ should be dominated by $\sigma$-effects, it is not unreasonable to expect that both compounds have similar [N]/[X]

values. That is, the average of $Cl^-$ and $P(n\text{-}C_4H_9)_3$ generates a partial field gradient contribution comparable to the average of $CH_3^-$ and $CH_3OH$. If the $N(CH_3)_3$ adduct follows the nmr results as well, then it should have a smaller $[N]/[X]$ value than the oxygen base but larger than the other nitrogen bases. Using the average of the split signals for this compound (Table III), and assuming that the in-plane angles are 80 and 100°, the value for $[N]/[X]$ is about 1.35, with an asymmetry parameter of 0.3, for the quadrupole coupling constant corresponding to small $\eta$. Alternatively, the larger quadrupole coupling constant may be chosen. In his case $[N]/[X]$ is about 1.4, and a fairly large asymmetry parameter is predicted. Because of the steepness of the curves for $\eta$ in this region, this compound represents a case in which predictions regarding the magnitude of the asymmetry parameter are difficult without accurate structural data. Tentatively, however, we choose the larger $e^2q_{zz}Q/h$ as the more likely possibility.

The magnitude of the quadrupole coupling constants for the pyridine, "imid," $S(CH_3)_2$, and $AsPh_3$ adducts is quite similar and it would be difficult to distinguish between the results for these compounds strictly on the basis of the nqr data. The order of ligand donor strengths which the nmr data suggest, slightly modified by the interchange of $NC_5H_5$ and "imid" to give agreement with the nqr results, is "imid" $< NC_5H_5 < S(CH_3)_2 < AsPh_3$. Since the pyridine adduct appears to exhibit a minimum $e^2q_{zz}Q/h$, the compounds probably straddle the cross-over point of $[N]/[X] = 1.0$ on the efg curves. Therefore, one might suggest that the pyridine and "imid" complexes have $[N]/[X] > 1.0$ and the sulfide and arsine have $[N]/[X] < 1.0$. The nmr and nqr data for $CHCl_2Co(dh)_2S(CH_3)_2$ provide additional evidence for this conclusion. $CHCl_2^-$ should be a significantly poorer donor than $CH_3^-$. This compound probably has a $[N]/[X]$ value of 1.6, slightly lower than the value for the $CH_3OH$ complex. If $CH_3Co(dh)_2S(CH_3)_2$ were to have $[N]/[X]$ greater than 1.0 instead of less than 1.0 as suggested above, this would imply that the difference in donor ability of $CH_3^-$ and $CHCl_2^-$ is small, which is inconsistent with the large chemical shift differences between the two compounds.

The pyridine and "imid" adducts of methylcobaloxime may be assigned $[N]/[X]$ numbers of 1.10 (corresponding to a theoretical $\eta = 0.22$) and 1.35 (corresponding to a theoretical $\eta = 0.32$), respectively. It is interesting to note that the field gradient parameters for the "imid" complex are nearly the same as those for the $N(CH_3)_3$ complex. The $^{59}Co$ chemical shift data suggest, on the ther hand, that the "imid" pfg parameters should denote an even more strongly bonding ligand than pyridine.

The phosphorus-containing complexes in the methylcobaloxime series may be expected to fall in the region of $[N]/[X]$ less than 1.0. By using the same conversion factor which was used to relate the scaled quadrupole coupling constants of Figures 1 and 3 and measured coupling constants, the model yields $[N]/[X] = 0.73$ for the $PPh_3$ adduct. The asymmetry parameter for this ratio is 0.7, which compares favorably with the observed value of 0.77. The sign of $eq_{zz}$ for this complex, as well as for the $S(CH_3)_2$ and $AsPh_3$ complexes, is positive,

and $q_{zz}$ is located in the equatorial plane (Figure 2c). The quadrupole coupling constant for the $PPh_3$ adduct is smaller than those of the sulfide and arsine complexes, contrary to the order predicted by the chemical shift data. The origin of this discrepancy is not clear.

While the remaining phosphorus bases would not be expected to be drastically different from the $PPh_3$ ligand, the quadrupole coupling constants show a dramatic increase in magnitude. As Figure 3 demonstrates, the efg model predicts this effect quite well if these compounds have $[N]/[X]$ less than about 0.65, corresponding to negative $eq_{zz}$. Since the planar ligand system for the $P(OCH_3)_3$ complex is known to have N–Co–N angles of about 81°,[6,7b] each of the remaining compounds will be assumed to have this geometry. (The effect of a 1° angle change in this region is, however, very small.) The observed quadrupole coupling constants for the $P(OCH_2)_3CC_2H_5$, $P(OCH_3)_3$, and $P(n\text{-}C_4H_9)_3$ compounds were converted to scaled values for $q_{zz}$ and these in turn were employed to obtain $[N]/[X]$ values and predicted values for $\eta$. The values predicted for $\eta$ for the three compounds are 0.65, 0.59, and 0.50, as compared with observed values of 0.50, 0.57, and 0.55 for the $P(OCH_2)_3CC_2H_5$, $P(OCH_3)_3$, and $P(n\text{-}C_4H_9)_3$ compounds, respectively.

The results of our approach to the analysis of the nqr and nmr data may be summarized in several ways. The quadrupole coupling constants and their signs are listed in Table IV along with the $[N]/[X]$ ratios used to

Table IV. Signs of the Quadrupole Coupling Constants and $[N]/[X]$ Values for Cobaloximes

| Compound | $e^2q_{zz}Q/h$, MHz | $[N]/[X]$ |
|---|---|---|
| $N(C_2H_5)_4[Br_2Co(dh)_2]$ | +75.88 | 4.3 |
| $N(C_2H_5)_4[Cl_2Co(dh)_2]$ | +73.15 | 3.6 |
| $ClCo(dh)_2\text{-}$ | | |
| $NC_5H_5$ | +64.82 | 3.1 |
| $PPh_3$ | +60.45 | 2.8 |
| $P(n\text{-}C_4H_9)_3$ | −43.64[a] | 1.9 |
| $CH_3Co(dh)_2CH_3OH$ | −41.62 | 1.8 |
| $CHCl_2Co(dh)_2S(CH_3)_2$ | −36.93 | 1.6 |
| $CH_3Co(dh)_2\text{-}$ | | |
| $N(CH_3)_3$ | −33.27[a] | 1.4 |
| "Imid" | −31.34 | 1.35 |
| $NC_5H_5$ | −29.52 | 1.10 |
| $PPh_3$ | +28.12 | 0.73 |
| $S(CH_3)_2$ | +30.30 | 0.68 |
| $AsPh_3$ | +32.02 | 0.67 |
| $P(OCH_2)_3CC_2H_5$ | −40.24 | 0.59 |
| $P(OCH_3)_3$ | −43.33 | 0.56 |
| $P(n\text{-}C_4H_9)_3$ | −46.20 | 0.54 |

[a] Average of two values. See Table III.

characterize the efg in each compound. A plot of log $[N]/[X]$ ratios vs. the $^{59}Co$ chemical shifts (Figure 4) shows a reasonably regular monotonic relationship between the nqr and nmr data. It is pointless to graph the quadrupole coupling constants against the chemical shifts because the sign changes add discontinuities in the curve which are not reflected by the nmr data.

Recently, Bancroft, et al.,[23] attempted to deduce the sign of the quadrupole coupling constant for a series of $Mn(Co)_5X$ compounds possessing $C_{4v}$ symmetry at the metal, by plotting $e^2q_{zz}Q/h$ vs. $\delta(^{55}Mn)$. The data may be arranged to yield a linear relationship, and the sign of $eq_{zz}$ may be determined. This approach is useful
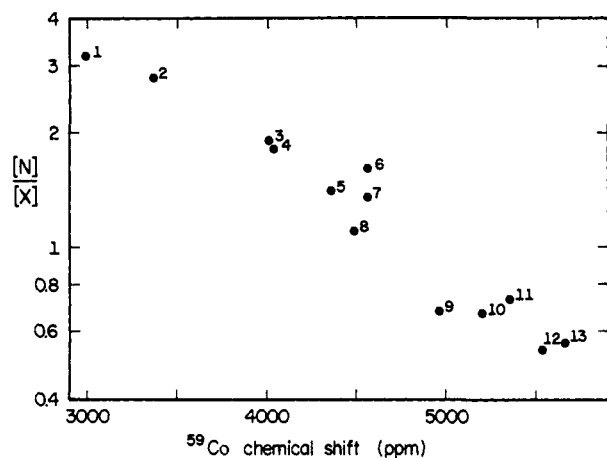
**Figure 4.** Ratio of partial field gradient contribution from the dimethylglyoxime nitrogen atoms to that from axial ligands vs. $^{59}$Co chemical shifts. Points on the graph refer to (1) ClCo(dh)$_2$-NC$_5$H$_5$, (2) ClCo(dh)$_2$PPh$_3$, (3) ClCo(dh)$_2$P($n$-C$_4$H$_9$)$_3$, (4) CH$_3$Co-(dh)$_2$CH$_3$OH, (5) CH$_3$Co(dh)$_2$N(CH$_3$)$_3$, (6) CHCl$_2$Co(dh)$_2$S(CH$_3$)$_2$, (7) CH$_3$Co(dh)$_2$"imid", (8) CH$_3$Co(dh)$_2$NC$_5$H$_5$, (9) CH$_3$Co(dh)$_2$S-(CH$_3$)$_2$, (10) CH$_3$Co(dh)$_2$AsPh$_3$, (11) CH$_3$Co(dh)$_2$PPh$_3$, (12) CH$_3$Co-(dh)$_2$P($n$-C$_4$H$_9$)$_3$, (13) CH$_3$Co(dh)$_2$P(OCH$_3$)$_3$.

**Table V.** $^{35}$Cl Nqr Data for Chlorocobaloximes

| Compound | $|e^2q_{zz}Q/h|$, MHz |
|---|---|
| N(C$_2$H$_5$)$_4$[Cl$_2$Co(dh)$_2$] | 38.72 (3)$^a$ |
| ClCo(dh)$_2$NC$_5$H$_5$ | 39.42 (3) |
| ClCo(dh)$_2$PPh$_3$ | 37.96 (3) |

$^a$ Numbers in parentheses are signal:noise ratios for 30-sec RC time constant.

only in complexes of axial symmetry, in which the $z$ axis does not change its orientation. In the cobaloxime compounds, the nmr chemical shifts parallel the sum of the interactions between cobalt and the axial and equatorial ligands, while the nqr data are indicative of the difference in charge donation from the axial and equatorial ligands. The chemical shift, therefore, does not follow the reorientation of the field gradient axis system but shows a monotonic change characteristic of the overall ligand field. Thus, caution must be exercised in suggesting quadrupole coupling constant sign changes on the basis of nmr data alone.

$^{35}$Cl **Nuclear Quadrupole Resonance.** The chlorine nqr results obtained for the cobaloximes are reported in Table V. Since the signal intensities were very low, $^{37}$Cl signals could not be observed.

A very simple trend might be expected to appear in these results. As the ligand trans to the chloride becomes a stronger donor, the electron density on the cobalt center is increased and the covalency of the Co–Cl bond is reduced, thereby reducing the $^{35}$Cl quadrupole coupling constant. This appears to be the case for the pyridine and PPh$_3$ complexes. The $^{59}$Co nqr suggests a stronger interaction with PPh$_3$ than with pyridine, and the $^{35}$Cl nqr shows the same result. However, the data for the trans-dichloro complex are inconsistent with this trend. Cl$^-$ should be the weakest axial ligand, and the $^{35}$Cl coupling constant should be highest for this compound, but it is not. Because this complex is not neutral and the chloride ligand may be affected by the lattice, rationalization of the nqr result in terms of this simple model is invalid. Attempts to

resolve this problem by observing $^{59}$Co and $^{35}$Cl nqr in cobaloxime salts having various counterions were unsuccessful. $^{35}$Cl nqr frequencies in complexes of the type [CoCl$_2$(en)$_2$]X have been found to be sensitive to the counterion.[38,39]

It is interesting to note that the $^{35}$Cl quadrupole coupling constants in Table V are about 5 MHz higher than those in the ethylenediamine complexes. This suggests that the bonding between Co and Cl is more covalent in the dimethylglyoximato complexes.

**Conclusions**

The nqr data presented here represent the most extensive body of information available regarding the field gradient about a transition metal. Nevertheless, the data are incomplete; with the present state of the art for obtaining nqr spectra, the acquisition of data is often very difficult. If the data were more complete, in that all three resonances were seen for all of the compound listed, some of the more subtle points which are at present uncertain could be cleared up. In addition it would be reassuring to have accurate bond angle information for each and every compound studied, to eliminate any uncertainties regarding variations of a degree or two in the bond angles about cobalt. However, small variations in the bond angles do not affect the actual ordering of the compounds given in Table IV.

Even in the absence of complete nqr data for every compound and with an uncertainty of perhaps a degree in the bond angles about cobalt, it has been possible to assign a reliable ordering to the axial ligands, using $^{59}$Co nmr chemical shift data for additional guidance. Since the nqr experiment provides at most two independent quantities for each compound, $e^2q_{zz}Q/h$ and $\eta$, one can expect to extract a limited amount of information for each compound regarding the coordination about cobalt. In the present model, the parameters which we extract are the ratio of partial field gradient contributions for the axial as compared with the planar ligands and a measure of the total field gradient contribution from all the ligands.

The chemical significance of the derived ligand partial field gradient parameters deserves some comment. We have shown that the model gives good agreement with experimental results only if we assume that the pfg parameter for the planar ligand nitrogens becomes more positive as the axial ligand contribution increases.[40]

(38) I. Watanabe, *J. Phys. Soc. Jap.*, 29, 1204 (1970).

(39) H. Hartmann, M. Fleissner, and H. Sillescu, *Theor. Chim. Acta*, 2, 63 (1964).

(40) In this connection it should be noted that the observed values of $e^2q_{zz}Q/h$ and $\eta$ for [Br$_2$Co(dh)$_2$]$^+$ and [Cl$_2$Co(dh)$_2$]$^+$ are both consistent only with [N] and [X] parameters of the same sign.[13,14] In eq 2 the term associated with "external" charge centered on the ligand is the term containing $\gamma_r$, the Sternheimer antishielding term.[41] The value of $\gamma_r$ varies with distance from the quadrupolar nucleus and is capable of attaining large negative values at large distances in free atoms and ions, as calculated from perturbation treatments of Hartree–Fock wave functions. At the metal–ligand distances characteristic of the ligand environment around cobalt, $\gamma_r$ could be expected to be negative, but its magnitude is not known. This is in part due to the fact that the extent to which the environment created by immediately adjacent atoms or ions quenches the antishielding term is not known. If, however, the first term on the right in eq 2 were to dominate over the second for any ligands studied here, it would be for the halides in the [X$_2$Co(dh)$_2$]$^+$ ions. However, as indicated, it is not possible to calculate $\eta$ values anywhere near the observed values by assuming [N] and [X] to be of opposite sign. We conclude, therefore, that it is resonable to assume that [N] and [X] are of the same sign and negative for all ligands studied.

(41) Reference 4, Chapter 5, and references therein.

The [N] and [X] parameters might acquire a smaller absolute value either because the effective donated ligand charge becomes smaller or because the effective distance from the central nucleus to the center of the charge distribution increases.

The empirical relationship we employed in establishing the relationships between [N]/[X] and the scaled quantity $|eq_{zz}|$ shown in Figures 1 and 3 expresses [N] as a function of X: [N] = $-1.06 - 0.6$[X]. Thus, having arrived at an appropriate [N]/[X] ratio, values for both [N] and [X] follow. It is interesting that the sum of the ligand pfg contributions so obtained in the cobaloximes is remarkably close to constant. Thus, for [N(C$_2$H$_5$)$_4$][(Cl$_2$Co(dh)$_2$] the sum of 4[N] + 2[X] is $-4.15$; for CH$_3$Co(dh)$_2$P($n$-C$_4$H$_9$)$_3$ the sum is $-3.87$. It is certain that the total charge donated by the ligands is greater in the latter instance, as evidenced, for example, by the $^{59}$Co chemical shift. A decrease in the effective value for $1/r^3$ appears to approximately cancel the increased values for the donated charges. It appears from our results that a constancy of total pfg's for the ligands about a given metal in a given oxidation state is a more accurate empirical rule of thumb than the assumption of additive fixed ligand pfg parameters. For this reason we have not attempted to derive, from the results of Table IV, a set of ligand pfg parameters. Nevertheless, the ordering of ligands implicit in Table IV is a direct measure, in the ground electronic state, of the relative strength of interaction of the ligands with the cobalt center.

The relative accuracy of the [N]/[X] values depends primarily on the validity of our assumption that the N–Co–N angles are constant in the entire series of cobaloximes. If we had chosen to assume that this angle is 81° rather than 80° we would have obtained slightly smaller values for those [N]/[X] ratios considerably greater than 1, but the ordering of [N]/[X] values would have remained unchanged. Since the [N]/[X] ratios are derived primarily by reliance on the values of $e^2q_{zz}Q/h$, minor perturbations of the field gradient tensor due to external lattice effects are not serious. Such effects generally appear as altered values for $\eta$ and affect the quadrupole coupling constant very little. This should be the case particularly in the cobaloximes, since the quadrupolar nucleus lies at the center of a large molecule with a well-defined geometry about the central atom.

To the extent that our assumptions are valid, the nqr experiment provides a unique body of information. Other spectroscopic techniques which purport to assess ligand interaction with the metal always involve excited states, either directly as in electronic spectra or indirectly as in the interpretation of data using perturbation theoretical methods. The field gradient, on the other hand, represents the expectation value for a one-electron operator and thus is interpretable in terms of the ground-state electronic wave function and a knowledge of the molecular geometry. Clearly, it would be possible to invoke a much more sophisticated model in interpretation of the nqr data than we have employed here. However, we believe that the concept of partial field gradient contributions serves to provide an important and chemically significant index of ligand behavior toward the central metal in complexes and anticipate that this model will serve well in the interpretation of field gradient data in other closed shell, six-coordinate complexes.