the remaining $d_{5/2}$ proton into the $h_{11/2}$ proton orbital. Thus, the two decays, ^{139g}Nd and ^{139m}Nd, give us a wealth of information about high-spin, low-spin, single-particle, and three-particle states in ^{139}Pr, far more than one could ever get from a single decay or, for that matter, from nuclear reaction experiments.

It would be possible to go on at length about the intriguing facts that have been found or will be found from the decay of nuclei far from stability: strange and unusual nuclear configurations, odd transition rates, shape isomers (in which the metastable state actually has a different degree of deformation than the ground state), fundamental changes required in weak interaction theory from what had been expected, etc. The important thing, however, is that from isomer pairs one gets at least twice as much information as from a single decay. Another aspect that will probably be of more and more importance in the future is the added stability that the high-spin isomers give nuclei far from stability. Mostly because of their more complex configurations and the relative dearth of high-spin states to decay to, the high-spin states far from stability become longer lived than the low-spin states, even when the low-spin state is the ground state. Thus, it may well be high-spin isomers that will allow us to study the more exotic nuclei.

Isomers and the Future

Figure 3 shows almost 350 isomer pairs; yet hundreds more will likely be found. Many of these will lie far from stability, but many others, both very long- and very short-lived, will probably be found among known nuclei. A rather unnerving fact is that, whenever one irradiates a target in a particular beam to produce a particular nuclide, he almost invariably observes "unidentified" short-lived activities that have not yet been tracked down. In brief, there are isomers waiting to be identified almost everywhere.

Even aside from their value in probing nuclear structure, the uses of isomers will continue to be legion. There will be many applications in biology and medicine, where the search for shorter-lived tracers continues. They will find uses in metallurgy for quality control or for gauge monitors. They will furnish added tracers for chemistry, and a few may even be used as probes for atomic and molecular structure—for example, 26.1-min ^{235m}U lies only 73 eV above the ground state,[12] and chemical effects can significantly affect its decay rate because its decay is by conversion in the P electron shell.

Finally, nuclear isomers should make possible the eventual production of a γ-ray laser, with all its awsome implications. In fact, a γ-ray laser appears to be more feasible than an X-ray laser because it is easy to obtain population inversions with nuclear metastable states. The main difficulty will be how to stimulate emission, for nuclear states are far narrower than atomic states. It will be necessary to compensate for recoil, quadrupole shifts, and a host of other small, but important perturbations.

In this Account I have tried to give a short overview of what nuclear isomers are and how they can be of use to us. In this, I hope that I have conveyed some of the excitement engendered by the elusive, antisocial nucleus. In its isolation, providing us with the strange high-multipolarity forbidden transitions and metastable states of wildly differing half-lives, it has provided science with powerful tools found nowhere else.

(12). M. Neve de Mevergnies, *Phys. Lett. B*, **32**, 482 (1970).

Cobalt-59 Nuclear Quadrupole Resonance Spectroscopy

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Since the original observation in 1950 of a pure nuclear quadrupole resonance (nqr) transition in a solid,[1] a substantial literature dealing with nqr spectroscopy has developed.[2-4] Nevertheless, it is fair to say that it remains a rather specialized tool. In part this derives from the inherent limitations of the technique. Pure nuclear quadrupole resonance spectroscopy must be carried out on crystalline solids. The nqr spectrum is simpler, and therefore less liable to provide interesting and instructive detail than is often seen in nuclear magnetic resonance spectra of solutions. In addition, the instrumental requirements are considerably more varied than is the case for nmr. Finally, the acquisition of nqr data has proven quite difficult for several nuclear quadrupole systems which would be of great chemical interest, *e.g.*, ^{14}N, ^{2}H.

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(1) H. G. Dehmelt and H. Krüger, *Naturwissenschaften*, **37**, 111 (1950).

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

(3) 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 II.

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

Table I
Selected Quadrupolar Nuclides of Transition Elements[a]

Isotope	% abundance	Spin I	Electric quadrupole moment, eQ[b]
^{51}V	99.8	$\frac{7}{2}$	−0.04
^{53}Cr	9.54	$\frac{3}{2}$	+0.04[c]
^{55}Mn	100	$\frac{5}{2}$	0.40[d]
^{59}Co	100	$\frac{7}{2}$	0.40
^{63}Cu	69.1	$\frac{3}{2}$	−0.16
^{65}Cu	30.9	$\frac{3}{2}$	−0.15
^{95}Mo	15.72	$\frac{5}{2}$	0.12
^{97}Mo	9.46	$\frac{5}{2}$	1.1
^{101}Ru	16.98	$\frac{5}{2}$	?
^{105}Pd	22.2	$\frac{5}{2}$	0.73[e]
^{185}Re	37.1	$\frac{5}{2}$	2.8
^{187}Re	62.9	$\frac{5}{2}$	2.6
^{191}Ir	38.5	$\frac{3}{2}$	1.5
^{193}Ir	61.5	$\frac{3}{2}$	1.5

[a] Data from "Handbook of Chemistry and Physics," 54th ed, R. C. Weast, Ed., Chemical Rubber Company, Cleveland, Ohio, 1973, unless otherwise indicated. [b] Units are 1×10^{-24} cm². [c] J. A. Thompson, R. P. Scharenberg, W. R. Lutz, and R. D. Larsen, *Phys. Rev. C*, **7**, 1413 (1973). [d] E. Handrick, A. Steudel, and H. Walther, *Phys. Lett. A*, **29**, 486 (1969). [e] H. Leelavathi, S. Ismail, and K. H. Channappa, *Ind. J. Pure Appl. Phys.*, **10**, 820 (1972).

Despite these limitations, nqr spectroscopy is an important technique because it provides almost unique information about charge distribution. Furthermore, the continuing development of pulse techniques as the basis for commonly available laboratory instrumentation has provided the possibilities for much more sensitive and reliable methods for detection of nqr transitions in solids.

Many of the transition elements possess in significant abundances isotopes with $I > \frac{1}{2}$, a condition necessary for the presence of a nonzero nuclear quadrupole moment (Table I). Nuclear quadrupole resonance spectroscopy utilizing these nuclides is a potentially valuable, but largely untapped, source of bonding and structural information. The nqr spectroscopy of cobalt-59 is perhaps best developed of that for any transition element. This account of the present state of the art regarding cobalt-59 nqr spectroscopy provides an indication of the scope of the technique and its potential for application to many other elements.

Theory

For a nucleus with spin $I > \frac{1}{2}$, an energy term arises due to the interaction of the nuclear quadrupole moment, eQ, with the components V_{ij} of the electric field gradient (efg) at the nucleus.[5] The Hamiltonian is written as

$$\mathcal{H}_Q = \frac{1}{6}\sum_{i,j} V_{ij} Q_{ij} \qquad (1)$$

In the principal axis system, the off-diagonal elements of the field gradient tensor V_{ij} are zero. The divergence theorem leads to the LaPlace equation, $V_{xx} + V_{yy} + V_{zz} = 0$, i.e., the tensor is traceless. Thus, it possesses two independent components. The largest efg component is defined as V_{zz}; it is frequently referred to as eq_{zz} or just q. The departure

(5) See ref 4, Chapters 3–7, and ref 2 and 3 for more detailed exposition of theory.

of the efg tensor from axial symmetry is given by the asymmetry parameter η (eq 2). The axes are chosen

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \qquad (2)$$

so that $|V_{xx}| < |V_{yy}| < |V_{zz}|$; this means that $0 < \eta < 1$. Using these conventions, the most common form of the Hamiltonian is given by

$$\mathcal{H}_Q = \frac{e^2 q_{zz} Q}{4I(2I-1)}[3(I_z^2 - I^2) + \eta(I_x^2 - I_y^2)] \qquad (3)$$

The product $e^2 q_{zz} Q$ or $e^2 q_{zz} Q/h$ is termed the quadrupole coupling constant. The quadrupole coupling constant and the asymmetry parameter, η, reflect the two independent components of the field gradient tensor.

The energy level diagram for spin $I = \frac{7}{2}$ is shown in Figure 1. It follows from the expression for $\mathcal{H}_Q$, eq 3, that the energy depends only on the absolute value of m, the nuclear magnetic spin quantum number. The selection rules for quadrupole transitions in the limiting case $\eta = 0$ require that $\Delta m = \pm 1$. When η departs significantly from 0, a mixing of spin states occurs, and other transitions become allowed. Transitions between the allowed nuclear quadrupole energy states can be produced by interaction of the magnetic component of a radiofrequency field of appropriate frequency with the nuclear magnetic moment, which is collinear with the nuclear quadrupole moment. When $\eta = 0$ the three allowed transitions for $I = \frac{7}{2}$ are in the frequency ratio 3:2:1 (Figure 1). As the asymmetry parameter departs from 0, however, the transition energies change, as shown in Figure 1.

In the presence of a magnetic field, the degeneracy of m states of equal absolute value is removed. We will not be concerned, however, in this account with experiments involving significant Zeeman contributions to the Hamiltonian.

Origins of Field Gradients

The observed quadrupole coupling constant represents the product of the nuclear quadrupole moment eQ and the major component V_{zz} ($=eq_{zz}$) of the electric field gradient tensor. The quantity q_{zz} represents the expectation value for the one-electron field gradient operator, taken over the entire charge distribution external to the nucleus

$$q_{zz} = \left\langle \psi_{el} \left| \frac{3\cos^2\theta - 1}{r^3} \right| \psi_{el} \right\rangle + \sum_i Z_i \left(\frac{3\cos^2\theta_i - 1}{r_i^3} \right) \qquad (4)$$

The summation is taken over all of the nuclei and electrons in the space surrounding the nucleus in question. In practice, in dealing with neutral molecules or polyatomic ions in lattices, it is frequently necessary to consider only those atoms and electrons in the molecule or ion containing the quadrupolar nucleus. The effect of external nuclear charges is largely canceled by the spherical electron distributions centered on those nuclei. Further, because of the r^{-3} dependence of the field gradient operator, only charges in the close vicinity of the quadrupolar nucleus affect the field gradient significantly. Ac-
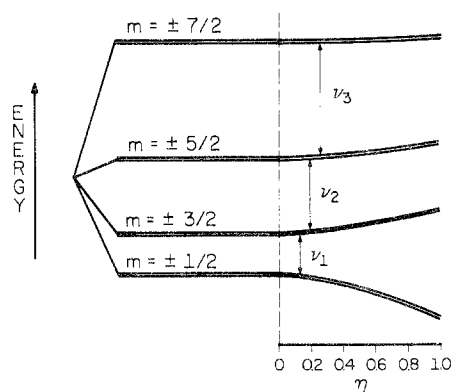
Figure 1. Nuclear quadrupole energy level diagram for $I = \frac{7}{2}$.

cordingly, it is generally possible to consider the field gradient as arising from electrons in valence orbitals centered on the quadrupolar nucleus, and—in some cases—a set of effective charges on immediately adjacent atoms.

Both valence electrons and charges external to the atom (ion) containing the quadrupolar nucleus can contribute to polarization of the inner core electrons to produce Sternheimer shielding or antishielding contributions to the field gradients.[6]

Occupancy of the 4s, 4p, and 3d orbitals of the first-row transition element may be expected to lead to significant nonzero contributions to q_{zz}. Table II shows the calculated field gradient due to a single electron in a metal $3d_{z^2}$ orbital (q_{320}) for three isoelectronic metals with a $4s^2 3d^6$ configuration (^{5}D state), based upon Clementi's Hartree–Fock SCF atomic functions.[7,8] The value for q_{320} increases markedly with increasing nuclear charge. The table also shows the value of q_{320} for Fe(0) in the $4s^1 3d^6 4p^1$ configuration (^{7}P state).[8] The change in configuration does not produce a large change in q_{320}. The field gradient due to the $4p_z$ electron, q_{410}, for the ^{7}P state of Fe is calculated to be -4.97×10^{-15} esu cm^{-3}.[8] This is not a great deal smaller than q_{320}. Thus, although in general the 4p orbitals have much lower occupancies than the 3d, it may not always be justifiable to dismiss the 4p electron contribution to q_{zz}.

$$q_{zz} = q_{320}[N_{d_{z^2}} + \tfrac{1}{2}(N_{d_{xz}} + N_{d_{yz}}) -$$
$$(N_{d_{xy}} + N_{d_{x^2-y^2}})] + q_{410}[N_{p_z} - \tfrac{1}{2}(N_{p_x} + N_{p_y})] \quad (5)$$

The major component of the electric field gradient may be expressed in terms of valence orbital populations as in eq 5.[9]

Accounting for the quadrupole coupling constant in terms of the valence orbital populations in this manner amounts to the assumption that external charge distributions are of negligible consequence. This is likely to be a safe assumption in many organometallic compounds of cobalt, in which the metal has a near-zero charge, and the charges on atoms immediately adjacent to the metal are also small. On the other hand, in coordination compounds of Co(II) and

(6) Reference 4, Chapter 3.
(7) G. Malli and S. Fraga, *Theor. Chim Acta*, **6**, 54 (1966).
(8) C. D. Pribula, T. L. Brown, and E. Münck, *J. Amer. Chem. Soc.*, **96**, 4149 (1974).
(9) T. L. Brown, P. A. Edwards, C. B. Harris, and J. L. Kirsch, *Inorg. Chem.*, **8**, 763 (1969).

Table II
Comparative Calculated Field Gradients for a 3d Electron

Atom (ion)	Configuration	State	q_{320}, 10^{15} esu cm^{-3}
Mn$^-$	$4s^2 3d^6$	^{5}D	-6.70
Fe	$4s^2 3d^6$	^{5}D	-9.23
Co$^+$	$4s^2 3d^6$	^{5}D	-12.16
Fe	$4s^1 3d^6 4p^1$	^{7}P	-8.79

Co(III), the external charge distribution around the metal may make a major contribution to the field gradient. It is essentially impossible to separate contributions to the field gradient due to point charges located external to the valence orbitals from contributions due to donation of electrons into valence orbitals of the metal. The "donated-charge" model[10] treats the elements of the field gradient tensor as arising from a summation of effective contributions from individual ligands, as in eq 6–8, where the an-

$$V_{zz} = \sum_i [L_i](3 \cos^2 \theta_i - 1) \quad (6)$$

$$V_{xx} = \sum_i [L_i](3 \sin^2 \theta_i \cos^2 \phi - 1) \quad (7)$$

$$V_{yy} = \sum_i [L_i](3 \sin^2 \theta_i \sin^2 \phi_i - 1) \quad (8)$$

gles θ_i and ϕ_i are measured from the Z and X axes to each of the i ligands. In these equations the parameter $[L_i]$ associated with each ligand may be viewed as the sum of two contributing terms

$$[L_i] = e^2 Q \left[\frac{q_i(1 - \gamma_{r_i})}{r_i^3} + \frac{q'_i(1 - R)}{\langle r'_i^3 \rangle} \right] \quad (9)$$

The symbol γ_{r_i} represents the Sternheimer correction factor for charges q_i resident on the ligand atom i at distance r_i.[6] Since these charges are external to the valence orbitals of the central atom, γ_{r_i} will in general be negative, i.e., an antishielding contribution. The Sternheimer shielding correction for charge donated by the ligands to the valence orbitals is represented by R. The "lattice" or external charge contribution to [L] may be viewed as an effective point charge q_i located at the donor atom, at distance r_i from the quadrupolar nucleus. The covalency contribution is more subtle; $q'_i/\langle r'_i^3 \rangle$ represents the expectation value for the radial component of the field gradient due to charge donated from L into valence orbitals of the central atom.

Even when the bond to L is quite polar, the second, covalency, term is the more important, because $\langle r'_i^{-3} \rangle$ is much larger than r_i^{-3}. The magnitudes of the Sternheimer terms are not well known. R is in general on the order of 0 to 0.2. γ_{r_i}, as computed for free atoms and ions, is large at large distances from the central nucleus.[6] (For example, γ_∞ has been estimated to be about 8 for Co metal.[11]) At typical metal–ligand distances γ_{r_i} may be far from attaining the maximum value. Furthermore, the effect of the ligand field on the central atom may be to quench antishielding contributions.[12,13]

(10) See R. V. Parish, *Prog. Inorg. Chem.*, **15**, 124 (1972), for discussion.
(11) T. P. Das and M. Pomerantz, *Phys. Rev.*, **123**, 2070 (1961).
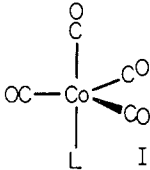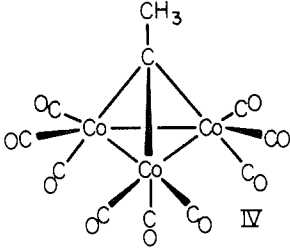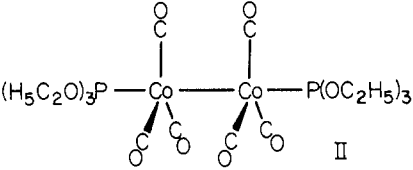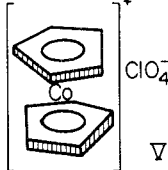(12) H. W. deWijn, *J. Chem. Phys.*, **44**, 810 (1966).

Figure 2. Geometrical structures and field-gradient tensor parameters for several organometallic cobalt compounds.

This empirical approach, which treats the contribution from each ligand as a parameter characteristic of that ligand, gives rise to the additive partial field gradient (pfg) model, which has been employed extensively in interpretation of ^{57}Fe and ^{119}Sn Mössbauer quadrupole splittings.[10,14,15] We shall remark upon applications of this model to ^{59}Co nqr spectra in a later section.

Five-Coordinate Co(I) Compounds

During the past few years an extensive body of ^{59}Co nqr data for 5-coordinate cobalt carbonyl compounds has accumulated. It is useful to think of these compounds as derived from a parent $Co(CO)_5^+$ species isostructural with $Fe(CO)_5$ and $Mn(CO)_5^-$, which are trigonal bipyramidal. From Mössbauer spectra[16,17] and ^{55}Mn nqr spectra,[8] respectively, the field gradients eq_{zz} for the latter two species are +4.4 and 2.2, in units of 10^{15} esu cm^{-3}. Stable $Co(CO)_5^+$ salts are not known to date, but phosphite- and phosphine-substituted derivatives are. Comparisons of eq_{zz} for these and the analogous iron compounds suggest that eq_{zz} for $Co(CO)_5^+$ should be on the order of 5.4 × 10^{15} esu cm^{-3},[8] corresponding to an e^2Qq_{zz}/h of about 156 MHz.

The sign of q_{zz} in $Fe(CO)_5$ is known from the Mössbauer work to be positive. Since q_{320} and q_{410} (eq 5) are both negative, this requires that the negative terms within the brackets dominate. (It might be noted parenthetically that the 3d orbital populations make the major contribution to q_{zz}.) The evidence

strongly suggests that q_{zz} has the same sign for the cobalt species. A larger value of eq_{zz} for the cobalt as compared with the iron species is consistent with the calculated effect of increasing nuclear charge on the values for q_{320}, as indicated in Table II.

Replacement of all five CO groups by $P(OCH_3)_3$ groups results in only a very small change in field gradient at cobalt; e^2Qq_{zz}/h for [Co-$(P(OCH_3)_3)_5$]BPh$_4$ is 153.7 MHz.

Replacement of one of the axial CO groups in $Co(CO)_5^+$ by a ligand of formal negative charge produces a series of trigonal 5-coordinate cobalt species of the geometry shown as I in Figure 2. Table III lists values of quadrupole coupling constants for several $Co(CO)_4X$ compounds.[9,18-21] These results show that groups which are poor σ donors and/or strong π acceptors cause large quadrupole coupling constants at the metal. This is consistent with the assumption that the d_{xy} and $d_{x^2-y^2}$ orbitals are more highly populated than the d_{x^2} and d_{xz}, d_{yz}. Strongly σ-donor groups should increase the populations of the d_{z^2} orbital, thus decreasing the deficiency of electron density in the region of positive contribution to q_{zz}. On the other hand, π-acceptor ligands, by removing electron density principally from d_{xz} and d_{yz}, should increase this difference, and thus increase q_{zz}. The σ-donor and π-acceptor characteristics of the ligands thus work in opposite directions in the sense that σ donation toward cobalt from axial ligands tends to decrease q_{zz}, whereas π-acceptor action tends to increase it.

(13) G. Burns and E. G. Wikner, *Phys. Rev.*, **121**, 155 (1961).
(14) G. M. Bancroft and R. H. Platt, *Advan. Inorg. Chem. Radiochem.*, **15**, 59 (1972).
(15) G. M. Bancroft, *Coord. Chem. Rev.*, **11**, 247 (1973).
(16) R. L. Collins and R. Pettit, *J. Amer. Chem. Soc.*, **85**, 2332 (1963).
(17) P. Kienle, *Phys. Verd.*, **3**, 33 (1963).

(18) D. D. Spencer, J. L. Kirsch, and T. L. Brown, *Inorg. Chem.*, **9**, 235 (1970).
(19) A. N. Nesmeyanov, G. K. Semin, E. V. Bryuchova, K. N. Anisimov, N. E. Kolobova, and V. N. Khandozhko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1936 (1969).
(20) H. W. Spiess and R. K. Sheline, *J. Chem. Phys.*, **53**, 3036 (1970).
(21) T. E. Boyd and T. L. Brown, *Inorg. Chem.*, **13**, 422 (1974).

Table III
Cobalt-59 Nqr Data for Co(CO)₄X Compounds

X^a	e^2Qq_{zz}, MHz^b	η	Ref
$-SnCl_3$	161.45	0.0	9
$-SnBr_3$	159.88	0.072	9, 20
$-SnI_3$	153.04	0.06	9
$-GeCl_3{}^c$	161.48	0.030	9, 20
	159.37	0.039	
$-SiCl_3$	130.67	0.13	9
$-HgCo(CO)_4{}^c$	112.0	0.05	18
	110.8	0.0	
$-SiPh_3$	101.09	0.0	9
$-GePh_3$	109.63	0.05	21
$-SnPh_3$	104.00	0.285	9, 20
$-PbPh_3$	110.82	0.05	9
$-Sn(CH_3)_3$	96.8	0.03	18

^{a} Ph = C_6H_5. ^{b} At 298 K. Data at 77 K are reported in ref 19. ^{c} Separate resonances due to crystallographically distinct species.

For compounds of the form $X_n Sn[Co(CO)_4]_{4-n}$ (X = Cl, Br, CH₃; n = 1, 2, or 3), the variation in quadrupole coupling constant at cobalt[18,19] correlates smoothly with the highest frequency CO stretching mode for the compounds measured in hexane solution. In the case of neither observable, however, is it readily possible to separate the σ and π effects.

Other Organometallic Cobalt Compounds

Figure 2 shows nqr data for several organometallic compounds in which the chemical environment and symmetry about cobalt change. The nqr data listed beside each structure clearly reflect the symmetry of the environment about the metal. In I and II the cobalt is in an essentially axial environment. In $Co_2(CO)_8$, III, on the other hand, the environment is decidedly nonaxial. Mooberry, Pupp, Slater, and Sheline[22] have carried out an elegant single-crystal ^{59}Co broad-line nmr study of $Co_2(CO)_8$.

The three crystallographically nonequivalent cobalt atoms in the solid-state structure of IV[23] possess closely similar field gradient tensor parameters.[24] The essentially axial symmetry about cobalt in structures V and VI is reflected in the near-zero values for η. Several other cationic cobalt carbonyl species have been reported.[8]

Cobalt (III) Complexes

Among the earliest ^{59}Co nqr measurements of chemical interest were those on diamagnetic, low-spin d⁶ complexes of cobalt(III).[26-28] In these compounds the metal is surrounded by six coordinated ligands in a roughly octahedral array. In some attempts to interpret the nqr data explicit account has been taken of three contributions to the efg tensor at cobalt: (a) the valence electrons of the central metal

(22) E. S. Mooberry, M. Pupp, J. L. Slater, and R. K. Sheline, *J. Chem. Phys.*, **55**, 3655 (1971).

(23) P. W. Sutton and L. F. Dahl, *J. Amer. Chem. Soc.*, **89**, 261 (1967).

(24) T. L. Brown and J. P. Yesinowski, unpublished observations. ^{59}Co field gradient tensor parameters in $C_6H_5CCo_3(CO)_9$ and $ClCCo_3(CO)_9$ are very similar to those for $CH_3CCo_3(CO)_9$.

(25) (a) J. Voitländer and R. Longino, *Naturwissenschaften*, **46**, 664 (1959); (b) J. Voitländer, H. Klocke, R. Longino and H. Thiene, *ibid.*, **49**, 491 (1962).

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

(27) H. Hartmann and H. Sillescu, *Theor. Chim. Acta* **2**, 371 (1964).

(28) I. Watanabe and Y. Yamagata, *J. Chem. Phys.*, **46**, 407 (1967).

Table IV
^{59}Co Nqr Data for Cobalt (III) Complexes

Compound	$e^2q_{zz}Q/h$	η	Ref
$[Co(NH_3)_5Cl]Cl_2$	31.74	0.215	29
trans-$[Co(NH_3)_4Cl_2]Cl$	59.23	0.136	28
cis-$[Co(en)_2Cl_2]NO_3$	33.71	0.173	32
trans-$[Co(en)_2Cl_2]NO_3$	62.78	0.132	28
trans-$[Co(en)_2Cl_2]Cl$	60.63	0.272	28
trans-$[Co(en)_2Cl_2]ClO_4$	60.22,	0.149	33
	59.92	0.149	
trans-$[Co(en)_2Cl_2]Cl \cdot H_2O_5{}^+Cl^-$	71.73	0.222	26

ion, (b) the ionic charges on the ligand atoms bonded to the central atom, and (c) the ionic charges external to the complex ion (lattice charges). In the compound $[Co(NH_3)_5Cl]Cl_2$, for example,[29] the chlorine nqr resonances provide, *via* the Townes–Dailey model, an estimate of the ionicity of the Co–Cl bond. Contribution b was evaluated by assuming that net charges reside at the sites of the ligated atoms and that the operative value for $1 - \gamma$ is 8. Contribution c is easily evaluated from a knowledge of the crystal structure, assuming that $1 - \gamma_\infty = 8$; it proves to be negligibly small. Thus, contributions a and b must sum to give the observed field gradient at cobalt. If it is assumed that $q > 0$, as seems much the more reasonable choice,[30] the charges on the atoms involved are: Co, -0.48; N, $+0.63$; Cl, -0.67. The last of these comes from the assumption that the Townes–Dailey model is applicable to the nqr data for the chlorine bound to cobalt. The fact that the charges on nitrogen and cobalt turn out unreasonable is probably the result of the assumptions made in evaluating contribution b. Unfortunately, there is at the present no compelling theoretical model on the basis of which one might choose an appropriate value for $1 - \gamma_r$ in dealing with ligands, and $1 - \gamma_\infty$ in dealing with external lattice charges. For this reason it is useful to formulate a model for the efg tensor at the metal in terms of partial field gradient contributions from the ligands attached to the metal, as expressed in eq 6–8. The concept of partial field gradient parameters leads at once to a few simple predictions.[30,31] If it is assumed that the pfg parameter for a ligand is relatively insensitive to the other ligands bound to the metal and that 90° ligand–metal–ligand bond angles obtain around the metal, then the quadrupole coupling constant for CoA_5X should be about half that for *trans*-CoA_4X_2 and equal to that for *cis*-CoA_4X_2.

Table IV shows data for several cobalt(III) complexes.[26,28,29,32,33] The first and second pairs of compounds illustrate the "rules" stated above. The last four compounds in the table show the degree to which the ions external to the coordination sphere itself affect the efg at the metal. Except for the last compound listed, in which strong hydrogen bonding to the axial chlorides seems possible,[34] the field gra-

(29) I. Watanabe, H. Tanaka, and T. Shimizu, *J. Chem. Phys.*, **52**, 4031 (1970).

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

(31) R. R. Berrett and B. W. Fitzsimmons, *J. Chem. Soc. A*, 525 (1967).

(32) I. Watanabe, *J. Chem. Phys.*, **57**, 3014 (197).

(33) T. B. Brill and Z. Z. Hugus, Jr., *J. Phys. Chem.*, **74**, 3022 (1970).

(34) Brill and Hugus account for the larger value for *trans*-$[Co(en)_2Cl_2]Cl \cdot H_2O_5^+Cl^-$ in terms of a larger calculated lattice contribution. However, they employ the estimated free atom value of 8^{11} for $(1 - \gamma_\infty)$.
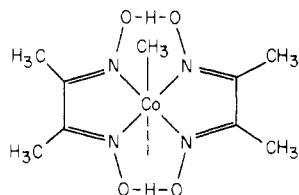
Figure 3. Structure of bis(dimethylglyoximato)cobalt(III) complexes (cobaloximes).

A, B	$\dfrac{[N]}{\frac{1}{2}([A] + [B])}$
Br, Br	4.3
Cl, Cl	3.6
Cl, NC$_5$H$_5$	3.1
Cl, PPh$_3$	2.8
Cl, P(n-C$_4$H$_9$)$_3$	1.9
CH$_3$, CH$_3$OH	1.8
CHCl$_2$, S(CH$_3$)$_2$	1.6
CH$_3$, N(CH$_3$)$_3$	1.4
CH$_3$, IMID^a	1.35
CH$_3$, NC$_5$H$_5$	1.10
CH$_3$, PPh$_3$	0.73
CH$_3$, S(CH$_3$)$_2$	0.68
CH$_3$, AsPh$_3$	0.67
CH$_3$, P(OCH$_2$)$_3$CC$_2$H$_5$	0.51
CH$_3$, P(OCH$_3$)$_3$	0.56
CH$_3$, P(n-C$_4$H$_9$)$_3$	0.54

^{a} IMID = 1-(2-trifluoromethylphenyl)imidazole.

dient is not markedly altered by a change in anion. The asymmetry parameter is, however, noticeably affected by lattice forces, as evidenced by the nonzero values for Co(NH$_3$)$_5$Cl^{2+} and *trans*-Co(NH$_3$)$_4$Cl$_2^+$. There is reason to believe, on the basis of calculations,[29,33] that the external lattice charge contribution to the field gradient is ordinarily too small to cause much effect on either $e^2q_{zz}Q/h$ or η. Nonzero values for η may be due to small but significant displacements of ligands away from fourfold axial symmetry. In the absence of specific interactions between ligands and external charges, and where the geometry about the metal can be well defined, it should thus be possible to interpret both $e^2q_{zz}Q/h$ and η in terms of the electronic interactions between metal and ligands.

The series of cobalt(III) complexes known as cobaloximes[35] afford an interesting series for study of ^{59}Co nqr because their geometrical structures are well defined. It is thus possible to employ the nqr data to learn something about the interaction of the ligands with the central metal.[36] The general structure of the cobaloximes is shown as in Figure 3. The cobalt is coordinated by a planar array of nitrogens which are part of two dimethylglyoxime (dh) monoanions. The axial ligands may be varied over a wide range in terms of donor capabilities.

Because the planar nitrogen atoms make two distinct angles with the metal (about 80 and 100°),[37-41] the cobaloximes do not possess fourfold axial symmetry. They should thus not be expected in general to possess small asymmetry parameters. Use of the additive ligand pfg model makes it possible to define the field gradient tensor at Co in terms of the pfg parameters for the planar nitrogens, [N], and the average pfg parameter of the two axial ligands, [X] = $\frac{1}{2}$([A] + [B]).

$$eq_{kk} = 4[X] - 4[N] \tag{10}$$

$$eq_{jj} = -2[X] + 4[N][3 \cos^2 (40°) - 1] \tag{11}$$

$$eq_{ii} = -2[X] + 4[N][3 \sin^2 (40°) - 1] \tag{12}$$

The simplest initial assumption is that [N] is independent of the pfg parameters for the axial ligands. It develops, however, that for a series of complexes CoN$_4$AB, in which the axial ligands A and B are var-

(35) G. N. Schrauzer, *Accounts Chem. Res.*, 1, 97 (1968).
(36) R. A. LaRossa and T. L. Brown, *J. Amer. Chem. Soc.*, **96**, 2072 (1974).
(37) (a) J. S. Swanson, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1971; (b) W. W. Adams and P. G. Lenhert, *Acta Crystallogr., Sect. B*, **29**, 2412 (1973).
(38) P. G. Lenhert, *J. Chem. Soc., Chem. Commun.* 980 (1967).
(39) K. S. Viswanathan and N. R. Kuncher, *Acta Crystallogr.*, **14**, 675 (1961).
(40) D. L. McFadden and A. T. McPhail, *J. Chem. Soc., Dalton Trans.*, 363 (1974).
(41) S. Brücker and L. Rondaccio, *J. Chem. Soc., Dalton Trans.*, 1017 (1974).

ied widely, the experimental data can be fitted to pfg parameters [N] and [X] only if it is assumed that [N] decreases as the ratio [N]/[X] grows smaller, *i.e.*, as the axial ligands become more strongly donating. This result is in contrast to the conclusions reached on the basis of Mössbauer studies of many low-spin Fe(II) complexes, in which the pfg parameters of ligands are generally assumed independent of the pfg parameters of other ligands on the same metal.

The complex possessing the most weakly donating axial ligand system observed is represented by Co(dh)$_2$Cl$_2^-$ (dh = dimethylglyoximato monoanion), and the strongest by CH$_3$Co(dh)$_2$P(n-C$_4$H$_9$)$_3$. If it is assumed that the pfg parameter for [N] varies smoothly between these two extreme cases, it is possible to construct a graph of eq_{zz} and η as a function of the ratio [N]/[X]. Such a graph,[36] corresponding to 80 and 100° N–Co–N bond angles, is shown in Figure 4. From the observed values for $e^2q_{zz}Q/h$ and η it is possible in principle to locate positions on the curves which give agreement between calculated and observed quantities.

If the field gradient parameters could be rigorously assumed to depend only on the effects of the immediately coordinated atoms, accurate values for $e^2q_{zz}Q/h$ and η would make it possible to assign quite accurately values to [N]/[X].

Despite certain limitations, it is possible to obtain an extensive and fairly reliable list of [N]/[X] values for a series of Co(dh)$_2$AB complexes (Table V).

If we assume that for a series of axial ligands the variations in effective distances are small with respect to the other variations, and that covalency dominates in determining the pfg value, then the variation in axial ligands which occasions variation in [N]/[X] may be associated with changes in the strength of covalent binding of the axial ligand to the metal.

One expects that the paramagnetic contributions should dominate in determining the ^{59}Co nmr chemical shifts in cobaloximes, and that these contributions should decrease as the ligand field produced by
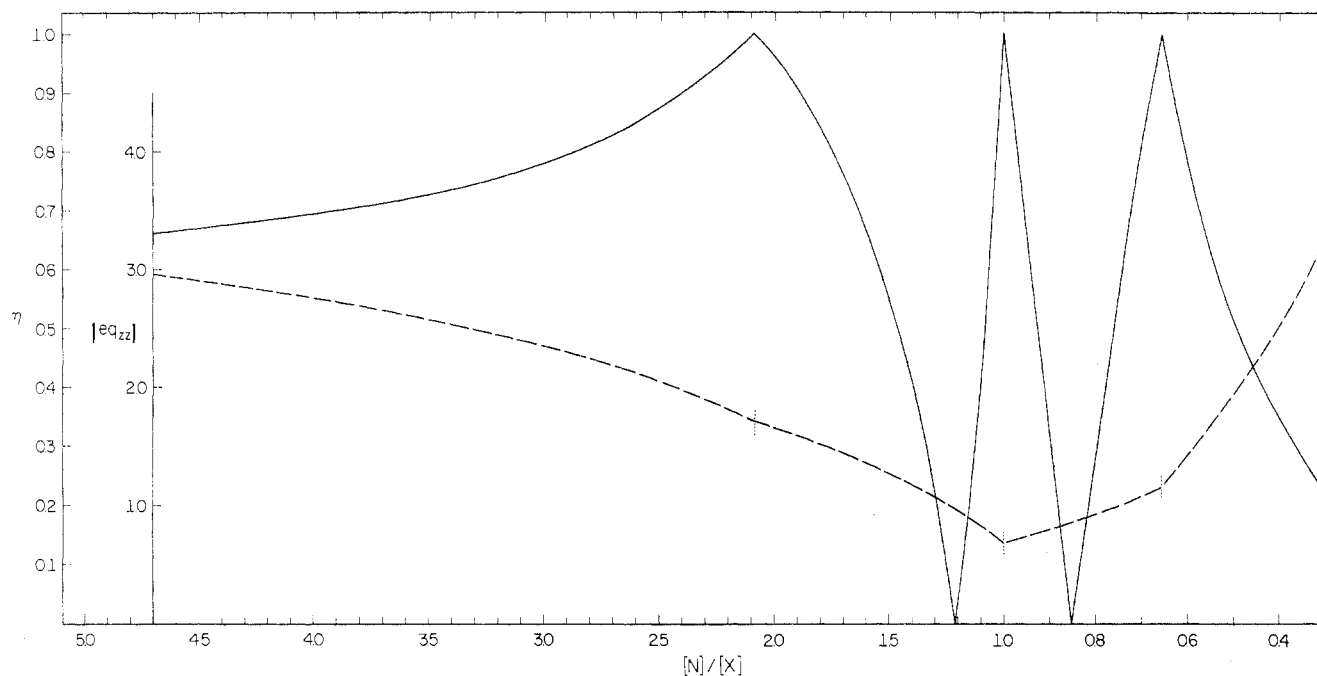
Figure 4. Scaled field-gradient and asymmetry parameter *vs.* ratio of ligand pfg parameters for [CoN₄L₂] complexes ($\angle$N–Co–N = 80 and 100°).

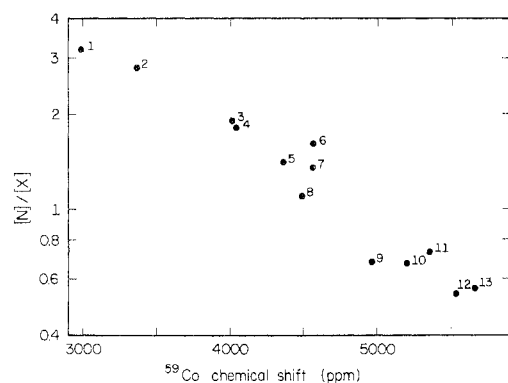**Figure 5.** ^{59}Co chemical shifts *vs.* log [N]/[X] for cobaloximes. (The numbers are identified in ref 36.)

Figure 6. Log [N]/[X] *vs.* ΔG^* for dissociation of axial ligand from $CH_3Co(dh)_2L$ compounds. L groups as follows: 1, CH_3OH; 2, $N(CH_3)_3$; 3, NC_5H_5; 4, IMID; 5, $S(CH_3)_2$; 6, $P(C_6H_5)_3$; 7, $P(OCH_3)_3$; 8, $P(n\text{-}C_4H_9)_3$. (The values of ΔG^* for the CH_3OH and NC_5H_5 complexes were estimated from the values obtained for the $[CH_3Co(tmed)CH_3OH]BPh_4$ and $CH_3Co(dh)_2$(3-fluoropyridine) complexes, respectively.[42c] Only small corrections are involved.)

the axial ligands increases. Thus, with decreasing value of [N]/[X] the ^{59}Co chemical shift should move to higher field, as observed (Figure 5).

If the [N]/[X] ratio measures the overall strength of ligand interaction with the metal, there should be a correlation between [N]/[X] and the kinetic stability of the cobalt–ligand bond. Base dissociation from $CH_3Co(dh)_2L$ complexes has been found[42] to be purely dissociative; rupture of the cobalt–ligand bond is the major contributor to the enthalpy of activation.[43] In Figure 6 is shown a graph of log [N]/[X] *vs.* ΔG^* for base dissociation. It is clear that all the compounds do not obey a single monotonic relationship. On the other hand, it is possible to discern a regular relationship in the expected direction for the third-row bases. Similarly, the second-row bases seem to follow a relationship of similar slope, but displaced upward in terms of [N]/[X].

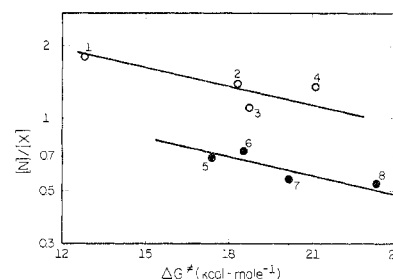The different behavior of the second-row bases from those in the third row may arise from different

relative importances of electrostatic and covalent components of the metal–ligand bond in affecting [L]. One would expect the covalent component, which gives rise to the larger field gradient contribution, to be larger for the heavier bases. Thus [N]/[X] should be smaller. The changed relative importances of the two contributions to the bonding need not, however, lead to a very great difference in metal–ligand bond strength, as reflected in ΔG^*.

The different behavior of the second and third row bases might also arise in part from π bonding to the third row axial ligands. The fact that cobalt in the methylatocobaloximes is capable of π bonding has been suggested on the basis of several lines of evidence. The presence of an additional energy term ascribable to π bonding has been noted in the cobalt–$P(OCH_3)_3$ interaction.[44]

Future Prospects

The examples described above demonstrate the potential usefulness of nqr as a tool in determining certain characteristics of the environment around a

(42) (a) T. L. Brown, L. M. Ludwick, and R. S. Stewart, *J. Amer. Chem. Soc.*, **94**, 384 (1972); (b) R. J. Guschl and T. L. Brown, *Inorg. Chem.*, **12**, 2815 (1973); (c) R. J. Guschl and T. L. Brown, *ibid.*, **13**, 959 (1974).

(43) W. Trogler, R. C. Stewart, and L. G. Marzilli, *J. Amer. Chem. Soc.*, **96**, 3697 (1974).

(44) R. L. Courtwright, R. S. Drago, J. A. Nusz, and M. S. Nozari, *Inorg. Chem.*, **12**, 2809 (1973).

transition metal. It is easy to imagine that the technique could have great value in probing the environment about cobalt in many other cobalt(III) compounds, including vitamin B_{12}, methylcobalamin, coenzyme B_{12}, and others. Similarly, compounds of several other transition elements might be studied. Unfortunately, the techniques usually employed by chemists in the past have lacked the requisite sensitivity to permit observation of nqr spectra for many nuclei of interest.

The most promising approaches for the future seem to lie in the use of double resonance techniques,[45,46] capable of providing enormously increased sensitivity in observing quadrupolar transitions, and permitting observation of transitions of very low frequency, such as in ^2H nqr spectra, where the transitions are observed in the 100–160-kHz re-

(45) S. R. Hartmann and E. L. Hahn, *Phys. Rev.*, **128**, 2042 (1962).
(46) R. E. Slusher and E. L. Hahn, *Phys. Rev.*, **166**, 332 (1968).

gion.[47] A most spectacular demonstration of the high sensitivity inherent in one of the techniques is the observation of ^{17}O nqr in natural abundance (0.037%) in several quinones, by means of an adiabatic demagnetization in the lab frame, level-crossing, double-resonance experiment.[48] Extension of these techniques to observation of the quadrupole resonance spectra of transition elements in diamagnetic compounds seems entirely feasible.

(47) J. L. Ragle and K. L. Sherk, *J. Chem. Phys.*, **50**, 3553 (1969).
(48) Y.-N. Hsieh, J. C. Koo, and E. L. Hahn, *Chem. Phys. Lett.*, **13**, 563 (1972).

Gas-Phase Carbene Reactions[1]

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The thermal or photochemical decomposition of diazo compounds is the most common method of generating species containing divalent carbon (carbenes).[2,3] As spin is conserved in the decomposition and as nitrogen is far more stable as a singlet than a triplet, the carbene is usually born in a singlet state.

$$R_2CN_2 \xrightarrow[h\nu]{\Delta} R_2C: + N_2$$
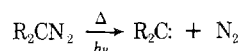
Methods have been developed for producing the triplet states, which are often the ground-state species.[2,3]

Singlet carbenes are voracious electrophiles, reacting with weak Lewis bases such as π bonds and even σ bonds to give products. The triplets are far less reactive, but also combine with multiple and single bonds to give the same overall products as the singlets (although by quite different mechanisms).

Maitland Jones, Jr., was born in New York City in 1937, and raised in the small town of Bedford, N. Y. He turned to chemistry only after the discovery of the curve ball by his contemporaries made it clear that he would never be a major league center fielder, and the intransigence of his parents removed him from the tennis circuit. He worked as a child at the Hickrill Chemical Research Foundation in Katonah, N. Y., where he acquired what experimental skill he possesses from Lawrence Knox and Gunther Laber and first came under the influence of William von Eggers Doering. He went on to Yale, where he worked for Professor Doering both as an undergraduate and graduate student. He came to Princeton in 1964 after a happy year of postdoctoral study with Professor J. A. Berson at Wisconsin, and is now Professor of Chemistry and Master of Stevenson Hall, an undergraduate college. He maintains a measure of sanity by escaping each year with his wife, Susan Hockaday, and their three children to Orangedale, Nova Scotia, in the peace and quiet of which this Account was written.
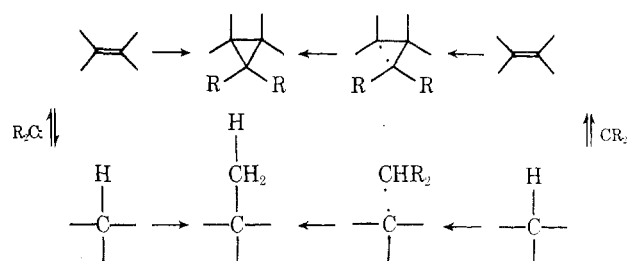
In the chemistry that follows in this Account, many intramolecular additions and insertions will appear.

Our general reason for studying carbene reactions in the gas phase, after so much effort had been applied already to studies of carbene reactions in solution,[2,3] was to examine the intramolecular reactions of carbenes. Carbenes seem to fall into two classes: one in which intramolecular reactions are virtually inevitable and another in which they are most difficult to observe. It simply depends on the ease of intramolecular reaction. If a multiple bond, carbon-hydrogen bond, or even a carbon-carbon bond is within range, and intramolecular reaction would not generate a very high energy species, then intermolec-