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NUCLEAR QUADRUPOLE RESONANCE IN COORDINATION COMPOUNDS

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I. INTRODUCTION

From the hyperfine structure of the atomic spectra of europium, Schuler and Schmidt [1] first indicated that a nucleus may possess an electric quadrupole moment and a magnetic dipole moment, the former having its origin in a non-spherical distribution of the nuclear charge. As a result of the non-spherical distribution of the nuclear charge, the nucleus has an orientation-dependent electrostatic interaction with its environment. Nuclear quadrupole resonance (NQR) spectroscopy is a branch of radiofrequency spectroscopy which has been adapted to study the small interaction energies which nuclear moments give rise to.

Since the NQR frequency depends on the electric field gradient at the nucleus under study, the NQR data can provide valuable information about the electronic structure of the molecules in the solid state. As the distortion of the core electrons due to polarization effects can modify the field gradient at the nucleus appreciably, the calculation of internal field gradients, effective in the nuclear quadrupole interaction, represents a delicate and often difficult problem. It follows that it is often difficult to interpret observations in highly quantitative terms.

The nuclear quadrupole interaction is affected by the internal motions of atoms, groups of atoms or molecules in the solid state. The two types of molecular motions which are expected to have an appreciable effect on the NQR frequency are torsional oscillations and hindered rotations. The frequencies of molecular motions are orders of magnitude higher than the Larmor frequencies of the quadrupolar nuclei and hence the nuclei see only the average value of the electric field gradient. As these motions are temperature dependent, NQR frequency shows variation with temperature. The temperature coefficient $(\partial \nu/\partial T)_P$ of the NQR frequency is generally negative. Apart from giving valuable information about bonding in molecules, temperature dependence studies throw light on phase transitions and hydrogen bonding in solids.

NQR is useful in detecting chemical and physical inequivalences in solids. While chemical inequivalence gives a multiplet of pure NQR lines, the physical inequivalence can be detected only through a study of the Zeeman NQR in single crystals. Also, a study of Zeeman NQR, particularly for nuclei having spin quantum number $I = 3/2$, will yield the asymmetry parameter, η, which is related to the electronic configuration of the atom under study. In favourable cases it is also possible to obtain η in polycrystalline solids.

The first observation of NQR was made by Dehmelt and Kruger [2] in *trans*-dichloroethylene, while Kruger and Meyer-Berkhout [3] were the first to observe NQR in a coordination compound (^{63}Cu NQR in $K[Cu(CN)_2]$). Since then many organic and inorganic compounds have been studied by NQR. The NQR effect, the techniques involved, the application and the interpretation of NQR results have been dealt with in a number of review articles [4—18]. Two excellent books have also appeared on the subject [19,20].

The present review is concerned with the application of NQR in coordination chemistry. The review is divided into two major parts, viz. basic theory and application. The basic theory is dealt with only briefly as an introduction to the applications. The literature covered is through 1975; most of the Russian work dealt with is based on "Chemical Abstracts".

II. BASIC THEORY

1. Nuclear quadrupole Hamiltonian and energy levels

In the multipole expansion of the electrostatic interaction of a quadrupolar nucleus with the surrounding charge distribution, the only orientation dependent term is that due to the quadrupolar interaction between the quadrupole moment of the nucleus and the electric field gradient (EFG) at the site of the nucleus produced by surrounding electric charges, the higher order terms (like the hexadecapole term) being negligible [21]. The nuclear quadrupole interaction can conveniently be expressed in terms of nuclear spin operators using the Wigner—Eckart theorem. The Hamiltonian so derived can be expressed in the principal axis of the EFG, obtaining

$$\mathcal{H}_Q = A\left[(3I_z^2 - I^2) + \frac{\eta}{2}(I_+^2 + I_-^2)\right] \qquad (1)$$

where $A = e^2Qq/4I(2I - 1)$ and $\eta = (V_{xx} - V_{yy})| V_{zz}$ with the convention $|V_{xx}| \leqslant |V_{yy}| \leqslant |V_{zz}|$. V is the electrostatic potential at thesite of the nucleus and V_{xx}, V_{yy} and V_{zz} are the EFGs along the prinzipal x, y and z directions. Conveniently, V_{zz} is written as eq. Since $V_{xx} + V_{yy} + V_{zz} = 0$ (Laplace equation), η lies in the range zero to 1. eQ is called the quadrupole moment of the nucleus and is defined as

$$eQ = \int (3z^2 - r^2)\rho(r)\,\mathrm{d}\tau$$

where $\rho(r)$ is the nuclear charge density at the point r inside the nucleus. The x, y, z axes with respect to which eQ is defined are the same as the principal x, y, z axes of the EFG.

The matrix elements of $\mathcal{H}_Q$ in the case of axially symmetric EFG ($\eta = 0$) are

$$\langle Im|\mathcal{H}_Q|Im'\rangle = \frac{e^2Qq}{4I(2I - 1)}[3m^2 - I(I + 1)]\,\delta_{mm'} \qquad (2)$$

For $\eta \neq 0$, I_+^2 and I_-^2 operators in eqn. (1) lead to a mixing up of states giving matrix elements of the type

$$\langle Im|\mathcal{H}_Q|Im'\rangle = \frac{e^2Qq}{4I(2I - 1)}[3m^2 - I(I + 1)]\,\delta_{mm'} +$$

$$\tfrac{1}{2}\eta[(I \mp m)(I \mp m - 1)(I \pm m + 1)(I \pm m + 2)]^{1/2}\delta_{m\pm2,m'} \qquad (3)$$

The degree of mixing increases as η increases and as η tends to zero, eqn. (3) reduces to eqn. (2). In the case of half integral spins, there are $I + \frac{1}{2}$ energy levels, all doubly degenerate. For $I = 3/2$ (e.g. ^{35}Cl, ^{37}Cl, ^{79}Br, ^{81}Br, ^{63}Cu etc.) the energy matrix can be solved exactly [19] giving (Fig. 1)

$$E_{\pm 3/2} = \frac{e^2Qq}{4h}\,[1 + (\eta^2/3)]^{1/2}$$

$$E_{\pm 1/2} = \frac{-e^2Qq}{4h}\left[1 + \left(\frac{\eta^2}{3}\right)\right]^{1/2} \tag{4}$$

with the single transition frequency

$$\nu = \frac{e^2Qq}{2h}\left[1 + \left(\frac{\eta^2}{3}\right)\right]^{1/2} \tag{5}$$

Thus, for $I = 3/2$, NQR does not permit the evaluation of e^2Qq and η simultaneously. However, by the application of a small magnetic field (ca. 20—100 gauss), the I degeneracy can be lifted and a study of the resulting Zeeman spectrum will give information about η and the orientation of EFG axes (in single crystals). For higher half integral spins, the secular equations are not exactly soluble, and the transition frequencies are available, for small η values, in literature [22]. However, for moderately large η values, the Hamiltonian must be diagonalized by numerical methods [23—25].

Among the nuclei with integral spins, nitrogen is one of the most impor-

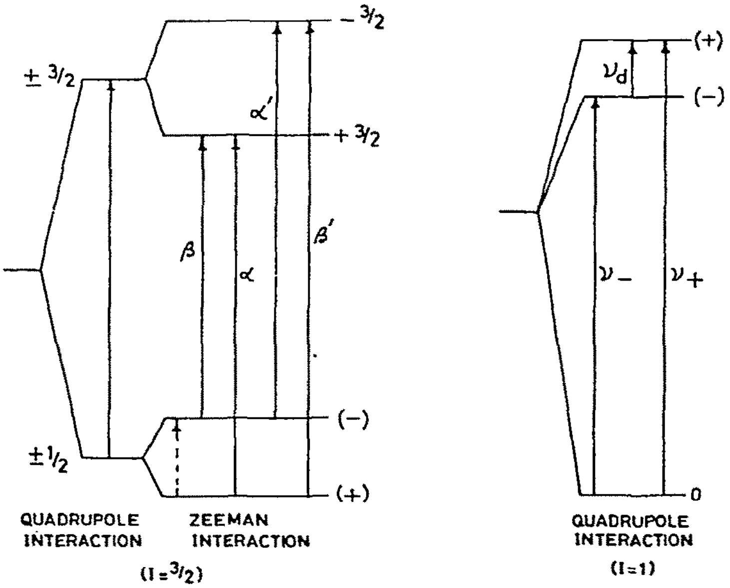

Fig. 1. Energy levels and allowed transitions for $I = 1$ and $I = 3/2$ nuclei.

tant ($I = 1$) and in this case the eigenvalue problem can be solved exactly giving

$$E_1 = \frac{e^2Qq}{4}(1 + \eta)$$

$$E_2 = \frac{e^2Qq}{4}(1 - \eta) \tag{6}$$

$$E_3 = \frac{-e^2Qq}{2}$$

with the transition frequencies

$$\nu_{\pm} = \frac{3e^2Qq}{4h}\left[1 \pm \left(\frac{\eta}{3}\right)\right] \tag{7}$$

$$\nu_d = \frac{e^2Qq}{2h}(\eta) \tag{8}$$

2. *Temperature dependence of NQR*

As mentioned earlier, the NQR frequency is affected by molecular motions, particularly the torsional oscillations. Bayer [26] was the first to analyse the temperature dependence of NQR and to show that the torsional motion affects the NQR spectrum in two ways: (i) the resonance frequency is shifted since the nucleus sees a temperature dependent average field gradient, (ii) the relaxation processes are affected leading to a variation of line shape and intensity. Bayer assumed that these motions are harmonic and are taking place about the three principal axes of the EFG tensor. His calculations show that the NQR frequency at any temperature T is given by

$$\nu_T = \nu_Q\left[1 - \frac{3h}{8\pi^2}\sum_i \frac{1}{I_i\nu_i}\left(\frac{1}{2} + \frac{1}{\exp(h\nu_i/kT) - 1}\right)\right] \tag{9}$$

where ν_Q is the NQR frequency of the stationary molecule (which is given by the extrapolated frequency at 0 K in good approximation), ν_i and I_i are the frequency and the corresponding moment of inertia of the torsional motion about the ith axis and the summation is over the x and y modes. It is further assumed that the effect of η is negligible in the first order. Bayer's results have been generalized by Kushida [27] who expressed the motions about the EFG axes in terms of normal coordinates and an equation similar to eqn. (9) was obtained involving normal modes and equivalent moments of inertia.

The effect of volume changes on the NQR frequency was first considered by Kushida et al. [28]; their calculations require a knowledge of parameters like the coefficient of thermal expansion, Grüneisen constant etc., and so are not generally practicable. Brown [29] tried to include the effect of volume change, in a molecular crystal, in a simple way by assuming that torsional frequencies (ν_i) themselves are temperature dependent. He further assumed, on the basis of the results of Ichishima [30], that ν_i varies linearly with temperature. With such simplifying assumptions, Brown [29] showed that the NQR data at high temperature, $h\nu_i/kT << 1$, can be used to evaluate the average weighted temperature coefficient of torsional frequencies.

3. Zeeman NQR and the determination of η

The application of a weak magnetic field (20—100 gauss) splits the pure NQR spectrum of an $I = 3/2$ nucleus into four lines. An angular variation study of these lines leads to the determination of η [19,23,31] in single crystals. Even in the case of polycrystalline samples, it is still possible to estimate η through a study of certain characteristic features of the Zeeman NQR spectrum [32—35]. As it is not always possible to grow big single crystals suitable for single crystal Zeeman NQR studies, Zeeman NQR of polycrystalline samples is attractive even though the information about the EFG directions is lost. Further, the powder Zeeman NQR method is especially suitable for low melting (below room temperature) substances.

4. NQR and chemical binding

Accurate interpretation of e^2Qq and η in terms of charge distribution in a given molecule may prove to be difficult; however, approximate calculations with a few simplifying assumptions may be useful, particularly in a comparative study of a family of compounds. Townes and Dailey [36] were the first to introduce certain approximations and express the coupling constant in terms of bond characters and their procedure has been extensively applied by a number of workers. Also, their work formed the basis of later modifications (e.g. Cotton and Harris [37]).

a. Townes and Dailey treatment. The contribution to EFG at the nucleus A due to an electron in the ith M.O. of the molecule is given by

$$(q_z^A)_i = \int \psi_i^* \left(\frac{3\cos^2\theta - 1}{r^3}\right) \psi_i \mathrm{d}\tau \tag{10}$$

where ψ_i is the wave function of an electron in the ith M.O. Expressing ψ_i in terms of atomic orbitals,

$$\psi_i = \sum_{j=1}^{j=n} C_i\phi_j \tag{11}$$

one may arrive at the total field gradient at A, given by

$$q_z^A = \sum_i N_i \left\{ \sum_j C_j^2 q^{jj} + \sum_k C_k^2 q^{kk} + \sum_j \sum_{\substack{k \\ j \neq k}} C_j C_k q^{jk} + \sum_k \sum_{\substack{l \\ k \neq l}} C_k C_l q^{kl} \right\} + q_{\text{nuclei}} \tag{12}$$

where N_i is the population of the ith M.O. and q_{nuclei}, the contribution from charges outside the atom A under consideration.

The following assumptions have been made to simplify eqn. (12); (i) q^{kk} arising from core electrons of atoms other than A and q_{nuclei} are negligible, (ii) the EFG due to overlap of atomic orbitals of A with those of other atoms, q^{jk}, is negligible, (iii) q^{kl} arising from the overlap between atomic orbitals of atoms other than A is negligible and (iv) in the absence of polarizing effects, the contribution to EFG from the core orbitals of A (q^{jj}_{core}) is negligible. Under the above assumptions, the contribution to EFG from the valence electrons can be expressed as

$$q_z^{\mathrm{A}} = \sum_i N_i \left\{ \sum_j C_j^2 q^{jj} + \sum_j \sum_{j'} C_j C_{j'} q^{jj'} \right\} \tag{13}$$

where $q^{jj'}$ due to the cross terms is negligible unless the difference in orbital quantum number of ϕ_j and $\phi_{j'}$ (Δl) is equal to 2. When only s and p orbitals are considered (as in the case of chlorine) $q^{jj'} = 0$ and when d orbitals are required to describe the bonding, the small, but finite, value of $s - d$ integral is usually neglected.

Further simplification can be effected on the first term in eqn. (13). Since the s orbitals are spherically symmetrical, they do not contribute to the EFG. Contribution from d and f orbitals to the EFG is comparatively smaller than that of the p orbital and can be neglected. Thus, the EFG at A (e.g. a chlorine atom) due to p orbitals alone can be expressed to a good approximation by

$$(q_z^{\mathrm{A}})_i = C_x^2 q_z^x + C_y^2 q_z^y + C_z^2 q_z^z \tag{14}$$

with

$$q_m^n = \int p_n^* \, v_{mm} p_n \mathrm{d}\tau$$

But

$$q_x^x = q_y^y = q_z^z = q_p \tag{15}$$

and

$$q_x^y = q_x^z = q_y^x = q_y^z = q_z^x = q_z^y = -q_{p/2} \tag{16}$$

Here q_p is the EFG due to an unbalanced p electron and is experimentally determined. Thus,

$$(q_z^{\mathrm{A}})_i = [C_z^2 - \tfrac{1}{2}\,(C_x^2 + C_y^2)]\, q_p \tag{17}$$

and

$$e^2Qq = \sum_i N_i [(C_z^i)^2 - \tfrac{1}{2}\{(C_x^i)^2 + (C_y^i)^2\}] e^2Qq_p \tag{18}$$

or

$$e^2Qq = \alpha \cdot e^2Qq_p \tag{19}$$

where

$$\alpha = \sum_i N_i[(C_z^i)^2 - \tfrac{1}{2}\{(C_x^i)^2 + (C_y^i)^2\}]$$

Here the coefficients $(C_z^i)^2$, $(C_y^i)^2$ and $(C_x^i)^2$ are the weights of the p_z, p_y and p_x orbitals respectively used in the M.O. which describes the bond. Assuming s and d hybridization in the bonding orbital of chlorine, it can be shown that

$$\alpha = (1 - s^2 + d^2 - i - \pi) + i(s^2 - d^2) \qquad (20)$$

where i is the ionic character and π is the π character of the bond between chlorine and another atom. s^2 and d^2 are the amounts of s and d characters in the bonding atomic orbital of chlorine. When d^2 and π are small, eqn. (20) reduces to eqn. (21).

$$\alpha = (1 - i)(1 - s^2) \qquad (21)$$

Similarly when only one of the p_x and p_y orbitals is involved in the π bond, eqn. (20) can be written as

$$\alpha = (1 - s^2)(1 - i) - (\pi/2) \qquad (22)$$

The problem of hybridization of the halogen bonding orbitals has been dealt with by many authors [36,38,39]. According to Townes and Dailey, the s hybridization is taken as 15% when the halogen is bound to an atom whose electronegativity is less than that of the halogen by 0.25 units. In all the other circumstances s character is taken as zero. The amount of d character is proposed to be 5% or less and in most cases considered negligible. Thus according to Townes and Dailey, the changes in e^2Qq for different molecules are due mainly to changes in the ionic character of the bond. Gordy [38] has preferred to take s hybridization always equal to zero. Bersohn and Shulman [39] have concluded from their NQR and ESR studies with the transition metal chlorides that s hybridization in the bonding orbital of chlorine in these compounds is negligible.

b. Cotton and Harris treatment. Cotton and Harris [37] have shown through a molecular orbital procedure that

$$e^2Qq = \sum f_j \cdot e^2Qq_{\text{atom}} \qquad (23)$$

where

$$f_j = \sum_i N_i(C_j^2 + C_j \sum_{k>j} C_k S_{jk}) \qquad (24)$$

Here S_{jk} is the overlap integral between atomic orbitals ϕ_j and ϕ_k and the other terms have the same meaning as in Sect. II.4.a. Equation (23) is the M.O. analogue of Townes and Dailey expression (19) and reduces to the same when S_{jk} is zero.

c. Point charge model calculations. In addition to the contribution from the charges within a given molecule, lattice contributions to the EFG become significant in the case of ionic solids. The observed e^2Qq is in fact a sum of contributions from the electrons within the molecule, q_{bound}, and those from the lattice, q_{lattice}. Hence,

$$q_{\text{total}} = q_{\text{lattice}} + q_{\text{bound}} \tag{25}$$

q_{lattice} can further be resolved into q_{dir}, EFG due to direct electrostatic effect of external ions, and q_{ind} which takes into account the indirect effect (e.g. the distortion or polarization of the ion in question) caused by the external ions.

q_{dir} can be calculated from the known crystal structure by considering the charges in a sphere of chosen radius using a point charge model [40]. Thus,

$$q_{\text{dir}}^{ij} = \sum_{\text{B}} Z_{\text{B}}(3x_i^{\text{B}}x_j^{\text{B}} - r_{\text{B}}^2\delta_{ij})/r_{\text{B}}^5 \tag{26}$$

where Z_{B} is the charge on the ion B having coordinates x_i^{B} at a distance r_{B} from the origin. $\delta_{ij} = 1$ when $i = j$, and zero when $i \neq j$. The polarization effect [41] due to the lattice is difficult to estimate and is generally taken into account by multiplying q_{dir} with a suitable numerical factor. Hence, the EFG at the origin is given by

$$q^{ij} = (1 - \gamma_{\infty})q_{\text{dir}}^{ij} \tag{27}$$

where γ_{∞} is the Sternheimer antishielding factor. In solids with appreciable asymmetry values, the point charge model fails in predicting the value of η. Several authors have tried to improve the point charge model by introducing effects due to dipoles and multipoles on q^{ij}. Attempts have also been made to consider the overlap of orbitals in computing the EFG.

III. INVESTIGATIONS IN COORDINATION CHEMISTRY

A. Halogen resonances

(^{35}Cl, ^{37}Cl, ^{79}Br, ^{81}Br, ^{127}I).

1. Hexahalometallates

The group of coordination compounds most extensively studied by NQR spectroscopy is the hexahalometallates [42—95]. The first NQR signal in this series of compounds was observed by Nakamura et al. [42] in the compound K_2PtCl_6. A number of reports on a variety of hexahalometallates with different central metal ions in their various oxidation states has appeared since then [43—95]. These studies have been successfully employed in understanding the electronic structure and other physical and chemical properties of these complexes.

a. Metal—halogen bonding in hexahalometallates. Nakamura et al. [11,42—58] have analysed the halogen NQR data in a number of hexahalometallates in terms of Townes—Dailey treatment assuming negligible *d* character and 15% *s* character in the M—X bond. The results of the analyses show the following trend:

(i) the covalent character of the M—X bond increases with decreasing electronegativity of the halogen;

(ii) the covalent character of the M—X bond increases with decreasing difference between the electronegativities of the atoms forming the bond.

A plot of the ionic character of the M—X bond against the electronegativity difference between the atoms involved in the bond (Fig. 2) shows a few distinct features. The complexes studied fall into three distinct classes comprising complexes derived from metal ions having the same outer electronic configuration. The higher degree of ionic character shown by Sn—Cl, Pb—Cl, Se—Cl and Te—Cl bonds is consistent with the completely filled *d*-shells of these metal ions which use only *s* and *p* orbitals for M—X bonding. Although Sn^{IV} and Pb^{IV} are more electropositive than tellurium(IV), the ionic character of the M—X bond in hexachlorostannates(IV) and hexachloroplumbates(IV) is almost equal to that of the hexachlorotellurates(IV). This has

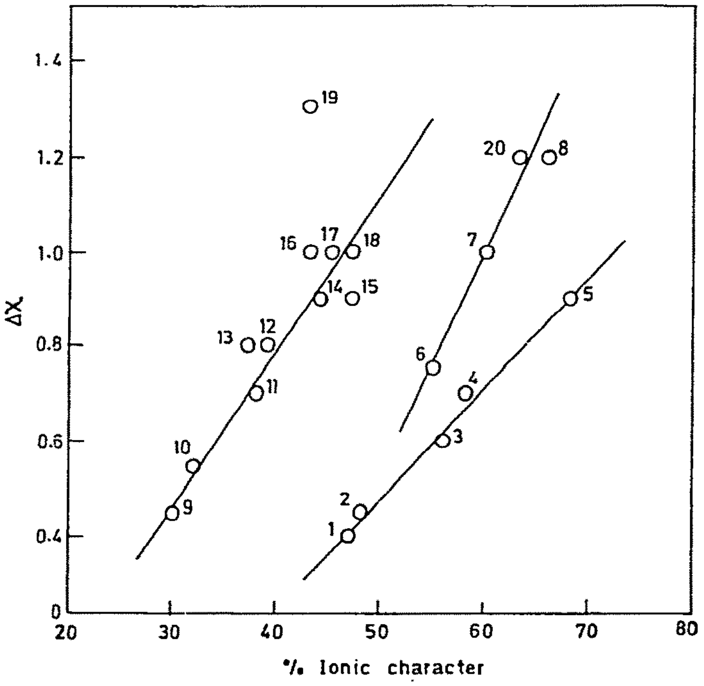

Fig. 2. Correlation between the percent ionic character of the M—X bond and the electronegativity difference between M and X. (Figure redrawn with the permission of the publisher, Academic Press, and the authors from ref. 11.) 1. Se—Br; 2. Te—I; 3. Se—Cl; 4. Te—Br; 5. Te—Cl; 6. Sn—I; 7. Sn—Br; 8. Sn—Cl; 9. Pt—I; 10. Re—I; 11. Pt—Br; 12. Re—Br; 13. Pd—Br; 14. Pt—Cl; 15. Ir—Cl; 16. Pd—Cl; 17. Re—Cl; 18. Os—Cl; 19. W—Cl; 20. Pb—Cl.

been attributed to the difference in the electronic structure of the central metal ions [41]. Even though, Nakamura et al. [45,51] have not considered the possibility of M—X π-bonding in $[SnCl_6]^{2-}$ and $[PbCl_6]^{2-}$, there are evidences [59,60] to show that Ge—Cl, Sn—Cl and Pb—Cl bonds have definite though small π-character. For example, Brill and co-workers [59] have shown that Ge—Cl bond in $[GeCl_6]^{2-}$ ion has a "non-negligible" π-character.

The hexahalometallates of Ir^{IV}, Os^{IV}, Re^{IV}, Mn^{IV}, Tc^{IV}, Mo^{IV} and W^{IV}, in which the central metal ion has vacancies in the t_{2g} orbitals, show resonances at lower frequencies than the corresponding hexahaloplatinate(IV) and hexahalopalladate(IV). The change in the NQR frequency with the d-electron configuration is approximately linear. Nakamura et al. [48,49] have explained the lower coupling constants in these paramagnetic complexes in terms of the π-character of M—X bonds involving p_x and p_y orbitals of halogens and vacant t_{2g} orbitals of metal ions. Using the equation,

$$e^2Qq = [(1 - s^2)(1 - i - \pi) - (\pi/2)]e^2Qq_{\text{atom}} \tag{28}$$

Nakamura et al. have calculated the ionic character of the M—X bond in these complexes. Based on the work of Owen and co-workers [96—99], Nakamura and co-workers [48,53] have assumed that the degree of π-bonding is 5.4% per vacancy in the metal t_{2g} orbital. Thus, for the ions Ir^{IV}, Os^{IV}, Re^{IV} and W^{IV}, which have one, two, three and four vacancies respectively in the t_{2g} orbitals, the percentage of π-character in the M—X bond will be 5.4, 10.8, 16.2 and 21.6 respectively [48,53]. Calculations using eqn. (28) show that with increasing π-character of the M—X bond, the M—X σ-character decreases (Table 1). The ionic character of the M—X bonds calculated for the paramagnetic complexes correlates well with the electronegativity differences between the halogen and the metal ion (Fig. 2). The hexachlorotungstate(IV) ion shows a deviation from this trend and this has been attributed to errors, which are large for this complex ion [11], due to various assumptions involved in the calculation.

TABLE 1

σ and π contributions to the M—X bond in a few hexahalometallates(IV) as calculated by Nakamura et al.

Complex	Electronic configuration	σ-character	π-character	Ionic character	Ref.
K_2PtCl_6	d^6	0.560	—	0.440	42
K_2IrCl_6	d^5	0.480	0.054	0.466	48
K_2OsCl_6	d^4	0.430	0.108	0.462	48
K_2ReCl_6	d^3	0.390	0.160	0.450	53
K_2WCl_6	d^2	0.350	0.220	0.430	53
K_2ReBr_6	d^3	0.450	0.160	0.390	53
K_2ReI_6	d^3	0.520	0.160	0.320	53

Although Nakamura et al. assumed 15% *s* character in the M—X bond when the halogen is bonded to an atom more electropositive than the halogen by 0.25 units, recent experimental data suggest that the value of *s*-character might be overestimated [39]. The assumption that the π-character increases linearly with the t_{2g} "hole" population has also recently been questioned [61].

Brown et al. [61] have assumed that the number of electrons transferred to the metal orbitals per metal t_{2g} vacancy in the hexachlorometallates(IV) is inversely proportional to the difference in the optical electronegativities of the central metal ion and chlorine. Based on the value of 5.4% π-character in the M—X bond of potassium hexachloroiridate(IV) [96—99], the value of π-charge transferred to the metal ion per chlorine is given by

$$\pi = 0.054\,n\,(\Delta\chi_{\mathrm{Ir}}/\Delta\chi_{\mathrm{M}}) \tag{29}$$

where $\Delta\chi_{\mathrm{M}} = \chi_{\mathrm{M}}^{\mathrm{opt}} - \chi_{\mathrm{Cl}}^{\mathrm{opt}}$. Here $\chi_{\mathrm{M}}^{\mathrm{opt}}$ is the optical electronegativity of the metal M and n is the number of vacancies in the t_{2g} orbitals of M. Thus, the π-character of M—X bonds in the complex species $[\mathrm{PtCl_6}]^{2-}$, $[\mathrm{IrCl_6}]^{2-}$, $[\mathrm{OsCl_6}]^{2-}$, $[\mathrm{ReCl_6}]^{2-}$ and $[\mathrm{WCl_6}]^{2-}$ has been calculated to be 0, 5.4, 8.1, 9.7 and 10%, respectively. The σ-character of the M—X bond has then been calculated using the equation

$$e^2Qq = [0.85\,\sigma - (\pi/2)]e^2Qq_{\mathrm{atom}} \tag{30}$$

Estimation of π-character in these complexes by Brown et al. [61] is expected [72] to provide better results than that by Ikeda et al. [53], as Brown et al. have based their analysis on optical electronegativity [100] which depends on the transfer of electrons localized in the $p\pi$ orbitals of ligands to the $d\pi$ orbitals of central atoms.

A correlation between optical electronegativity of the central metal atom and halogen nuclear quadrupole coupling constants of hexahalometallates(IV) of the second row transition metal ions has been shown to exist by Machmer [62,63]. The quadrupole coupling constant is related to the electronegativity of the central metal ion by eqn. (31)

$$\chi_{\mathrm{M}}^{\mathrm{opt}} = C + \left(\frac{e^2Qq}{h}\right)^{1/2} \tag{31}$$

where C is a constant equal to 0.38 for ^{35}Cl and 0.134 for ^{79}Br resonances. The values of electronegativity thus obtained are very similar to the optical electronegativity values obtained from electronic absorption spectral data [100]. But Brown et al. [61] have shown that the above relation breaks down completely when hexahalometallates of the same metal ion, such as tungsten, in different oxidation states are considered. A linear relationship between the NQR frequencies and optical electronegativities of the central metal ions has been reported by Cresswell et al. [64]. A plot of optical electronegativity against ^{35}Cl NQR frequency (Fig. 3) gives two straight lines, one for the second row transition metals and the other for the third row transition metals. It has also been shown [64] that the chlorine quad-

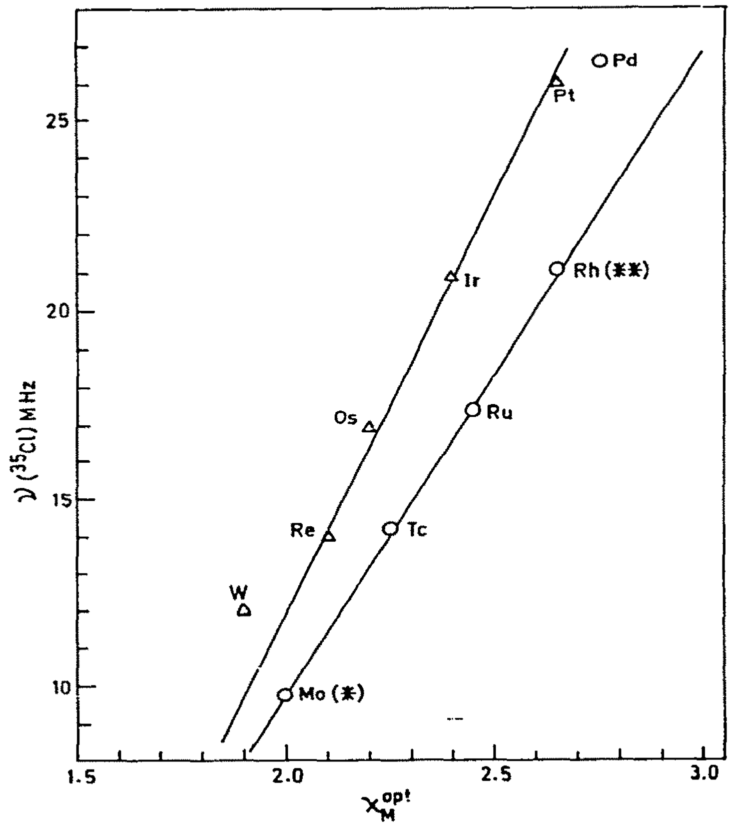

Fig. 3. Correlation between optical electronegativity of the central metal ion and ^{35}Cl NQR frequencies in K_2MCl_6.
△ = resonances at 77 K; ○ = resonances at 300 K; * = average of 3 resonances; ** = calculated approximately from the resonance for Cs_2RhCl_6.

rupole coupling constant decreases on going from the second to the third row transition metal hexachloro complexes. However, calculation of π-character based on optical electronegativity differences using eqn. (29) shows that the π-character is greater for the second row transition metal—halogen bonds [64]. (π-character of M—X in Ir^{VI}, Os^{IV} and Re^{IV} is 0.054, 0.081 and 0.097 respectively; for Rh^{IV}, Ru^{IV}, and Tc^{IV} the corresponding values are 0.093, 0.118 and 0.130.)

b. Effect of cations on the NQR frequency of hexahalometallates. The NQR frequency of halogens in various hexahalometallates with the same anion but different cations increases with increase in size of the cation (Table 2). The variation of NQR frequency upon changing the cation has been attributed to (i) electrostatic contributions to the EFG [65—67], (ii) changes in the electronic structure of the $[MX_6]^{n-}$ ion [52,68], (iii) anion—cation covalency

TABLE 2

Chlorine-35, bromine-79, bromine-81 and iodine-127 NQR frequencies in hexahalometallates

Compound [a]	Nucleus	Temperature [b] (°K)	NQR frequency (MHz)	Ref.
K_2SeCl_6	^{35}Cl	77	20.576	47
K_2TeCl_6	^{35}Cl	298	15.13, 14.99	69
Rb_2TeCl_6	^{35}Cl	298	15.14	69
Cs_2TeCl_6	^{35}Cl	298	15.60	61,68,69
$(NH_4)_2TeCl_6$	^{35}Cl	298	14.98	44,61,68
$(CH_3NH_3)_2TeCl_6$	^{35}Cl	298	15.52	69
$[(CH_3)_4N]_2TeCl_6$	^{35}Cl	298	16.29	59,69
$[(C_2H_5)_2NH_2]_2TeCl_6$	^{35}Cl	298	15.91	69
$[(C_2H_5)_3NH]_2TeCl_6$	^{35}Cl	298	15.48	69
$(PyH)_2TeCl_6$	^{35}Cl	298	16.49	69
$(4\text{-}PiCH)_2TeCl_6$	^{35}Cl	298	16.68	69
$(4\text{-}ClPyH)_2TeCl_6$	^{35}Cl	298	16.66, 16.37, 15.56	69
$(2,6\text{-}LutH)_2TeCl_6$	^{35}Cl	298	16.54	69
$MgTeCl_6 \cdot 6H_2O$	^{35}Cl	298	15.55	69
$(I_2Cl)SbCl_6$	^{35}Cl	R.T.	20.778, 21.011, 24.829, 25.689	270
$(PCl_4)SbCl_6$	^{35}Cl	77	22.80, 23.02	109, 272
$[(C_2H_5)_4N]SbCl_6$	^{35}Cl	77	24.01, 24.21, 24.67, 24.86	109
$NOSbCl_6$	^{35}Cl	77	22.35, 22.97, 23.15, 23.37, 25.03, 25.48	109
$[(CH_3)_4N]_2GeCl_6$	^{35}Cl	298	19.61	59
Rb_2GeCl_6	^{35}Cl	298	18.87	114
K_2SnCl_6	^{35}Cl	77	15.73	51,61,65
Rb_2SnCl_6	^{35}Cl	77	15.63	51,61,65
Cs_2SnCl_6	^{35}Cl	300	16.057	61,65,68
$(NH_4)_2SnCl_6$	^{35}Cl	77	15.61, 15.65	51,56,61,65
$(ND_4)_2SnCl_6$	^{35}Cl	273	15.477	56
$(CH_3NH_3)_2SnCl_6$	^{35}Cl	296	15.811	65
$[(CH_3)_3NH]_2SnCl_6$	^{35}Cl	296	16.635	65
$[(C_2H_5)_3NH]_2SnCl_6$	^{35}Cl	298	14.94	69
$[(CH_3)_4N]_2SnCl_6$	^{35}Cl	296	16.663	65
$(PyH)_2SnCl_6$	^{35}Cl	298	17.37	69
$(2,6\text{-}LutH)_2SnCl_6$	^{35}Cl	298	17.02	69
$(4\text{-}PiCH)_2SnCl_6$	^{35}Cl	298	17.81	69
$(4\text{-}ClPyH)_2SnCl_6$	^{35}Cl	298	17.52, 17.32, 14.97	69
$MgSnCl_6 \cdot 6H_2O$	^{35}Cl	300	15.836	60,65
$CaSnCl_6 \cdot 6H_2O$	^{35}Cl	300	15.904	60
$MnSnCl_6 \cdot 6H_2O$	^{35}Cl	300	15.770	60
$CoSnCl_6 \cdot 6H_2O$	^{35}Cl	296	15.752	65
$NiSnCl_6 \cdot 6H_2O$	^{35}Cl	300	15.716, 15.719	60,65
$ZnSnCl_6 \cdot 6H_2O$	^{35}Cl	300	15.720, 15.763	60,65

TABLE 2 (continued)

Compound [a]	Nucleus	Temperature [b] (°K)	NQR frequency (MHz)	Ref.
$CdSnCl_6 \cdot 6H_2O$	^{35}Cl	300	15.907	60
Cs_2PbCl_6	^{35}Cl	300	17.705	68
$(NH_4)_2PbCl_6$	^{35}Cl	77	17.26	51,61
$(CH_3NH_3)_2PbCl_6$	^{35}Cl	298	17.50	69
$[(C_2H_5)_3NH]_2PbCl_6$	^{35}Cl	298	15.39	69
$[(CH_3)_4N]_2PbCl_6$	^{35}Cl	298	18.54	69
$(PyH)_2PbCl_6$	^{35}Cl	298	19.44, 19.30	69
$(4\text{-}PiCH)_2PbCl_6$	^{35}Cl	298	19.87, 19.63, 18.58	69
$(2,6\text{-}LutH)_2PbCl_6$	^{35}Cl	298	18.75	69
$(4\text{-}ClPyH)_2PbCl_6$	^{35}Cl	298	15.53	69
K_2PdCl_6	^{35}Cl	77	26.75	43,82
$Na_2PtCl_6 \cdot 6H_2O$	^{35}Cl	296.5	25.73, 26.47, 27.04	46
K_2PtCl_6	^{35}Cl	77	26.021	44,46,61, 68,82
Rb_2PtCl_6	^{35}Cl	77	26.44	52,81
Cs_2PtCl_6	^{35}Cl	77	26.70	52,61,68, 81
$(NH_4)_2PtCl_6$	^{35}Cl	77	26.282	52
$H_2PtCl_6 \cdot 6H_2O$	^{35}Cl	298	26.55	46
$MnPtCl_6 \cdot 6H_2O$	^{35}Cl	77	25.870	58
$FePtCl_6 \cdot 6H_2O$	^{35}Cl	77	25.837	58
$CoPtCl_6 \cdot 6H_2O$	^{35}Cl	77	25.815	58
$NiPtCl_6 \cdot 6H_2O$	^{35}Cl	77	25.789	58
$CuPtCl_6 \cdot 6H_2O$	^{35}Cl	77	25.524, 25.788, 26.097	58
$ZnPtCl_6 \cdot 6H_2O$	^{35}Cl	77	25.810	58
$CdPtCl_6 \cdot 6H_2O$	^{35}Cl	77	25.823	58
$BaPtCl_6 \cdot 6H_2O$	^{35}Cl	77	25.442, 26.574, 26.698	58
Cs_2RhCl_6	^{35}Cl	298	21.859	64
$K_3RhCl_6 \cdot H_2O$	^{35}Cl	298	18.292, 18.497, 19.463	64
$Na_3RhCl_6 \cdot 2H_2O$	^{35}Cl	298	17.618	64
$Na_3RhCl_6 \cdot 10H_2O$	^{35}Cl	298	17.664	64
K_2IrCl_6	^{35}Cl	77	20.841	48,61,82
$K_3IrCl_6 \cdot H_2O$	^{35}Cl	298	16.754, 16.939, 17.505, 18.109, 18.251, 18.800	64
K_3IrCl_6	^{35}Cl	298	16.639, 17.690, 17.845, 18.435	64
$(NH_4)_3IrCl_6 \cdot H_2O$	^{35}Cl	298	17.526, 17.758, 18.038	64
K_2RuCl_6	^{35}Cl	298	17.345	64,94
K_2OsCl_6	^{35}Cl	77	16.897	48,61,68, 75
K_2MnCl_6	^{35}Cl	77	18.843	64

TABLE 2 (continued)

Compound [a]	Nucleus	Temperature [b] (°K)	NQR frequency (MHz)	Ref.
Cs_2MnCl_6	^{35}Cl	77	19.539	64
K_2TcCl_6	^{35}Cl	77	14.148	64,94
K_2ReCl_6	^{35}Cl	77	13.986, 13.966	50,53,61, 68,75
Rb_2ReCl_6	^{35}Cl	77	14.248	54
Cs_2ReCl_6	^{35}Cl	77	14.604	54,61,68
$(NH_4)_2ReCl_6$	^{35}Cl	77	14.125	54
K_2MoCl_6	^{35}Cl	300	9.541, 9.795, 9.876	68
Cs_2MoCl_6	^{35}Cl	300	10.732	61,68
K_3MoCl_6	^{35}Cl	300	9.83, 8.54	61
$KWCl_6$	^{35}Cl	300	11.455, 11.335	61,68
$RbWCl_6$	^{35}Cl	300	11.546, 11.320	61,68
$CsWCl_6$	^{35}Cl	300	11.748, 11.605, 11.281	61,68
K_2WCl_6	^{35}Cl	300	10.195	53,61,68
Rb_2WCl_6	^{35}Cl	300	10.575	61,68
Cs_2WCl_6	^{35}Cl	300	10.913	61,68
Cs_2NbCl_6	^{35}Cl	300	8.589, 9.245	61,68
Cs_2TaCl_6	^{35}Cl	300	9.127, 8.803	61,68
K_2SeBr_6	^{79}Br	77	173.599, 173.285, 172.389	47
Cs_2SeBr_6	^{79}Br	77	177.44	47
$(NH_4)_2SeBr_6$	^{79}Br	77	172.623	47
K_2TeBr_6	^{79}Br	77	135.946, 135.670, 134.496	44
Cs_2TeBr_6	^{79}Br	77	135.962	44
$(NH_4)_2TeBr_6$	^{79}Br	77	135.062, 143.258, 129.946	44
$[(CH_3)_4N]_2TeBr_6$	^{79}Br	77	142.58	44
$[(C_2H_5)_2NH_2]_3SbBr_6$	^{79}Br	298	126.19	92
$[(C_2H_5)_2NH_2]_3BiBr_6$	^{79}Br	298	87.38	92
K_2SnBr_6	^{79}Br	77	130.53, 129.17, 132.00	45
Rb_2SnBr_6	^{79}Br	77	128.91	51
$(NH_4)_2SnBr_6$	^{79}Br	296	126.53	45
Cs_2SnBr_6	^{81}Br	300	110.01	61,68
K_2PdBr_6	^{79}Br	77	205.43	43
K_2PtBr_6	^{79}Br	77	204.11, 202.25	42,61,68
$H_2PtBr_6 \cdot 9H_2O$	^{79}Br	292.8	201.52	52
$Na_2PtBr_6 \cdot 6H_2O$	^{79}Br	77	207.44	52
Rb_2PtBr_6	^{79}Br	77	205.63	52
Cs_2PtBr_6	^{79}Br	77	208.32	52,61,68
$(NH_4)_2PtBr_6$	^{79}Br	77	203.983	52,61
K_2OsBr_6	^{81}Br	300	111.78	61,68
Cs_2OsBr_6	^{81}Br	300	116.83	61,68
$(NH_4)_2OsBr_6$	^{81}Br	300	112.78	61
K_2ReBr_6	^{79}Br	77	115.09, 115.86, 116.06	50,53,68

TABLE 2 (continued)

Compound [a]	Nucleus	Temperature [b] (°K)	NQR frequency (MHz)	Ref.
Rb_2ReBr_6	^{79}Br	77	115.73	54
Cs_2ReBr_6	^{79}Br	77	118.41	54
$(NH_4)_2ReBr_6$	^{79}Br	77	113.95	54
Cs_2WBr_6	^{81}Br	300	75.28	61,68
K_2TeI_6	^{127}I	77	ν_1 = 154.250, 154.095, 151.878 ν_2 = 307.353, 300.603, 303.230	44
Rb_2TeI_6	^{127}I	77	ν_1 = 153.903, 153.240, 151.995 ν_2 = 306.619, 305.636, 303.688	52
Cs_2TeI_6	^{127}I	77	ν_1 = 154.140 ν_2 = 308.288	44
$(NH_4)_2TeI_6$	^{127}I	77	ν_1 = 153.831, 152.165, 148.173 ν_2 = 306.192, 302.335, 295.123	44
Rb_2SnI_6	^{127}I	77	ν_1 = 132.57	51
K_2PtI_6	^{127}I	77	ν_1 = 204.68, 203.70, 202.60 ν_2 = 408.28, 407.18, 405.02	42
Rb_2PtI_6	^{127}I	77	ν_1 = 205.33 ν_2 = 410.66	51
$(NH_4)_2PtI_6$	^{127}I	77	ν_1 = 205.69, 205.48	51
K_2ReI_6	^{127}I	77	ν_1 = 122.92, 123.73, 124.58 ν_2 = 245.52, 246.55, 247.45	50,53
Rb_2ReI_6	^{127}I	77	ν_1 = 122.8, 122.4 ν_2 = 244.8	54
Cs_2ReI_6	^{127}I	77	ν_1 = 124.49 ν_2 = 249.01	54

TABLE 2 (continued)

Compound [a]	Nucleus	Temperature [b] (°K)	NQR frequency (MHz)	Ref.
$(NH_4)_2ReI_6$	^{127}I	77	ν_1 = 122.62, 122.10, 119.73 ν_2 = 242.03, 241.03, 239.42	54

[a] Abbreviations: PyH = pyridinium ion; 4-PiCH = 4-picolinium ion; 4-ClPyH = 4-chloropyridinium ion; 2,6-LutH = 2,6-lutidinium ion.
[b] R.T. = Room temperature.

[65,95], and (iv) changes in the M—X bending vibrations [52].

Calculations, using the point charge model, on the complexes K_2PtCl_6 and Cs_2PtCl_6 have shown [52] that the direct electrostatic effect of the charges of other ions on the EFG at the chlorine nucleus under observation is insignificant. The EFG is supposed to originate largely from the charge distribution within the complex anion whose electronic structure is affected by the surrounding cations. Similar results have been obtained [54] for the complexes A_2ReCl_6 where A = K^+, NH_4^+, Rb^+ and Cs^+. The changes in the charge distribution in the anion may be attributed to (i) the polarization of the complex ion by the electrostatic field from neighbouring ions and (ii) the suppression of bending vibrations of the M—X bonds [52]. Ikeda et al. [54] have shown that the introduction of Sternheimer antishielding effect [41] in the calculation of EFG due to external ions (point charge model) accounts for the large indirect effect, at least with respect to the sign and the order of magnitude of $q_{\text{ind.}}$ relative to $q_{\text{dir.}}$. Smith and Stoessiger [66] have shown that the introduction of Sternheimer antishielding factor, as well as the effect of multipoles on the EFG at the halogen into the point charge model calculations, largely accounts for the observed difference in frequencies (but see ref. 81).

Brill et al. [65] have performed point charge model calculations to evaluate the EFG at the chlorine nuclei due to external ions for certain hexachlorostannates(IV) such as K_2SnCl_6, Rb_2SnCl_6 and Cs_2SnCl_6. Their results show that a simple point charge model does not account for the difference in frequencies of these three salts. However, introduction of the effect of anion—cation covalency involving the overlap of the cation *p*-orbitals with the chlorine *s* and *p* orbitals, to the q_{lattice} accounts for the differences in the resonance frequencies [65,95]. Further, the overlap integrals for the three salts mentioned above show a trend which may be related to the resonance frequencies [65]. In salts of the type $A(H_2O)_6SnCl_6$, the variation of EFG at the chlorine site could be interpreted in terms of point charge model [65].

Brown and Kent [68] have observed in a series of hexahalometallates (including WCl_6, Cs_2WCl_6, K_2ReCl_6, Cs_2SnCl_6, K_2OsCl_6, K_2PtCl_6, Cs_2PtCl_6 and the corresponding bromides) that the ratio of the ^{35}Cl NQR frequency to the corresponding ^{81}Br NQR frequency is very close to the ratio of their nuclear quadrupole coupling constants (Fig. 4), even though the Sternheimer antishielding factor γ_∞ for Br^- is twice as large as that for Cl^-. This is taken as indicative of the fact that the field gradients due to lattice charge distribution do not contribute significantly to the halogen coupling constant. This led Brown and Kent [68] to suggest that the variation in frequency due to changes in cation is mainly due to covalency changes within the complex anion.

Brill et al. [65,67,69—71] have studied the effect of cations on the halogen NQR in a number of hexahalometallates. They have observed [70] that in a series of $[SnCl_6]^{2-}$ salts, the resonance frequencies do not correlate well

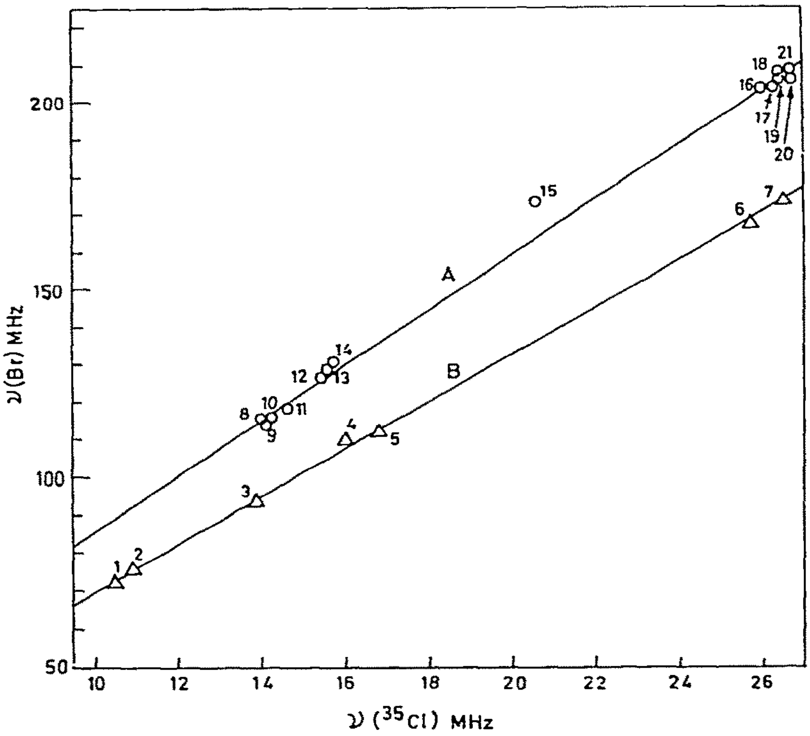

Fig. 4. Plot of ^{35}Cl NQR frequencies in hexahalometallates versus ^{79}Br (A) and ^{81}Br (B) NQR frequencies in the corresponding bromo complexes. Resonances at 77 K have been used for (A) and those at 300 K have been used for (B) (ref. 68).
1. WX_6; 2. Cs_2WX_6; 3. K_2ReX_6; 4. Cs_2SnX_6; 5. K_2OsX_6; 6. K_2PtX_6; 7. Cs_2PtX_6; 8. K_2ReX_6; 9. $(NH_4)_2ReX_6$; 10. Rb_2ReX_6; 11. Cs_2ReX_6; 12. $(NH_4)_2SnX_6$; 13. Rb_2SnX_6; 14. K_2SnX_6; 15. K_2SeX_6; 16. K_2PtX_6; 17. $(NH_4)_2PtX_6$; 18. $Na_2PtX_6 \cdot 6H_2O$; 19. Rb_2PtX_6; 20. K_2PdX_6; 21. Cs_2PtX_6.

with the Sn—Cl bond lengths, but correlate with the cation size (cation—anion contact distance) and the anion—anion contact distance. The ^{35}Cl NQR frequency in the $[SnCl_6]^{2-}$ salts is shown to be very sensitive to the anion—anion contact distance. The sensitivity gradually drops with the increase in separation of the anions till a limiting value is reached. After this value is reached, the changes in lattice dimensions do not produce any appreciable change in the NQR frequency [70]. Further, the repulsive potential between ions in $[SnCl_6]^{2-}$ salts closely follows the NQR frequency trend and may be a dominant factor in determining NQR frequencies [70,71]. An increase in the repulsive potential decreases the polarization of the halogen atoms, and hence the Sternheimer antishielding effect is suppressed [68,70,71,101]. This leads to the experimental observation that the electric field gradient decreases with increasing repulsive forces between the ions [70,71].

c. Effect of temperature on the halogen NQR frequencies in hexahalometallates [72]. One of the simplest applications of NQR is the study of phase transitions taking place in solids (Table 3). Many hexahalometallates of the type A_2MX_6 exhibit a cubic antifluorite structure at room temperature. As the temperature is decreased, some of these compounds have been observed to undergo structural phase transformations to lower symmetry forms. For example, the phase transition observed at 111 K for K_2ReCl_6 has been shown by O'Leary and Wheeler [73,74] as due to a change from cubic to tetragonal structure. The $[MX_6]^{2-}$ ions have been taken to be rigid octahedral structures situated within cages defined by A ions. At the phase transition, the cage dimensions change and the octahedra reorient themselves to the principal axis of the cage, but the octahedra themselves remain unaltered. The angle of rotation of the octahedron is taken as the order parameter and the observed changes in the NQR frequencies are associated with the change in the order parameter. The phase transition may be caused by the condensation of a particular normal mode of the phonon in the cubic phase whose eigenvector corresponds to atomic displacements in the structure stabilized below the transition temperature [74,75]. Recent advances in the understanding of phase transitions in K_2PtBr_6, K_2ReCl_6 and K_2OsCl_6, as revealed by NQR data, have been reviewed by Armstrong [75].

Armstrong and co-workers [75—90] have analysed the temperature dependence of halogen NQR frequencies in a number of hexahalometallates containing $[SnCl_6]^{2-}$ [76], $[PtCl_6]^{2-}$ [77—82], $[PtBr_6]^{2-}$ [83,84], $[PdCl_6]^{2-}$ [79,80,82], $[IrCl_6]^{2-}$ [85,86], $[OsCl_6]^{2-}$ [87,90] and $[ReCl_6]^{2-}$ [88]. The pressure dependence of the NQR frequency in a few of these complexes, as well as spin lattice and spin—spin relaxation measurements, have also been reported by Armstrong and co-workers [78,81,85,87—89].

The temperature dependence of the ^{35}Cl NQR frequency in K_2PtCl_6 and K_2PdCl_6 has been analysed using Bayer's equation [77,79]. It has been shown [79] that a single low frequency vibrational mode (~42 cm^{-1} for K_2PtCl_6 and ~32 cm^{-1} for K_2PdCl_6) dominates the motional averaging of the electric

TABLE 3

Phase transitions observed by halogen NQR in hexahalometallates

Complex	Transition temperature (°C)	Ref.
K_2SeBr_6	−33, −52, −64	47
K_2TeBr_6	−40	44
$(NH_4)_2TeBr_6$ [a]	−52	44
Rb_2TeI_6	−40, −16, +55	52
K_2SnCl_6	−17, −8.5	56
$(NH_4)_2SnCl_6$ [b]	ca. −85	56
$(ND_4)_2SnCl_6$ [b]	ca. 10	56
K_2SnBr_6	98, 123	56
$(NH_4)_2SnBr_6$	−129, −116	56
$(NH_4)_2PtCl_6$ [b]	[c]	52
$CuPtCl_6 \cdot 4H_2O$	−136	58
K_2PtBr_6	−104, −130, −136, −168, −195	84,75
$(NH_4)_2PtBr_6$	0—1 [b], −215	52,83
$K_2RhCl_6 \cdot H_2O$	[c] (<-30)	64
K_2IrCl_6	[c] (<0, >-51, <-51)	64
K_2ReCl_6	−199, −170, −162	74
K_2ReBr_6	−4, −16, −27	50,53
K_2ReI_6	ca. 166	53
$(NH_4)_2ReI_6$	ca. 46 [c]	53
Rb_2ReI_6	[c]	54
Cs_2ReI_6	[c]	54

[a] Another transition is expected to exist between −8.5°C and −196°C.

[b] Rotational transition of $(NH_4)^+$ and $(ND)_4^+$ ions.

[c] Transition point has not been observed definitely, but the range of temperature in which transition is expected is indicated.

field gradient at the chlorine site. This mode has been identified as the rotary F_{1g} mode which corresponds to torsional oscillations of the $[PtCl_6]^{2-}$ and $[PdCl_6]^{2-}$ ions about their axes of symmetry. However, stimulated by a suggestion by O'Leary [74], that rotary modes and internal bending modes may be important in the averaging process, Armstrong et al. [80,81] have shown that a multiple mode analysis of the ^{35}Cl NQR data for K_2PtCl_6 and K_2PdCl_6 based on the Bayer—Kushida model provides a convincing explanation of the motional averaging of the electric field gradient at the chlorine sites. Thus, using the multiple mode analysis, Armstrong et al. [80] have calculated the torsional oscillation frequencies ~58 cm^{-1} and ~64 cm^{-1} for K_2PtCl_6 and K_2PdCl_6 respectively. In carrying out the multiple mode analysis, two important assumptions have been made: (i) that bond stretching motions internal to the $[MX_6]^{2-}$ ion are of negligible importance relative to bond bending motions as a means of averaging the field gradient and for the destruction of π-bonding, and (ii) that $(\partial \nu/\partial T)_p = (\partial \nu/\partial T)_v$, which is reasonably valid for compounds having no π-character in the M—X bond [75]. Baker and Armstrong

[85] extended the multiple mode analysis to include the effect of the destruction of π-bonding [53] in K_2IrCl_6 by the lattice vibrations.

The temperature coefficient $(\partial \nu/\partial T)_p$, of the halogen NQR frequency is usually negative due to the Bayer effect [26]. For the hexahalometallates generally, $(\partial \nu/\partial T)_p$ increases with the decrease in size of the cation and increasing temperature (Table 4). Compounds such as $(NH_4)_2PtCl_6$, $(NH_4)_2PtBr_6$, [52], $(NH_4)_2SnCl_6$ and $(ND_4)_2SnCl_6$ [56] show a deviation from this trend, *and exhibit a second order phase transition, attributed to the rotation of* NH_4^+ and ND_4^+ ions in the crystal lattice [52,56]. It has been observed that the NQR frequency of $(ND_4)_2SnCl_6$ is always higher than that of $(NH_4)_2SnCl_6$ at a given temperature. Further, the phase transition for $(ND_4)_2SnCl_6$ occurs at a higher temperature (283 K) than for $(NH_4)_2SnCl_6$ (188 K). These results have been presumed to be due to the secondary hydrogen isotope effect. Since deuterium atoms undergo tunnelling less readily than hydrogen atoms in the ammonium ion, it has been presumed [56] that the averaging of EFG takes place to a smaller extent in the ND_4^+ compound resulting in a higher resonance frequency at a particular temperature.

The temperature coefficient of the NQR of hexahalometallates of the transition elements increases progressively with increasing vacancy in the t_{2g} orbitals of the central metal ion (Table 4). The temperature coefficient becomes positive for K_2ReCl_6 and K_2WCl_6 in the K_2MX_6 series. This progressive increase in $(\partial \nu/\partial T)_p$ with t_{2g} vacancy has been attributed by Ikeda et al. [53] to the π-character in the M—X bond. A more quantitative treatment relating the π-character of the M—X bond to the observed $(\partial \nu/\partial T)_p$ values has been presented by Hass and Marram [91]. According to them, an increase in temperature will result in exciting the M—X bending vibrations. This in turn, will

TABLE 4

Temperature coefficients of ^{35}Cl NQR frequencies for some hexachlorometallates(IV) [a]

Complex	Cation radius (Å)	Electronic configuration	Temperature range (°K)	$(\partial \nu]\partial T)_p$ (kHz/°K)	Ref.
K_2PtCl_6	1.33	d^6	77—196	−0.92	52
K_2IrCl_6	1.33	d^5	204—297	−0.54	53
K_2OsCl_6	1.33	d^4	203—299	−0.22	53
K_2ReCl_6	1.33	d^3	197—294	+0.13	53
K_2WCl_6	1.33	d^2	283—308	+0.44	53
Rb_2PtCl_6	1.48	d^6	77—196	−0.59	52
Cs_2PtCl_6	1.69	d^6	77—196	−0.33	52
Cs_2RhCl_6	1.69	d^5	~298	−0.50	64
K_2RuCL_6	1.33	d^4	~298	−0.04	64
K_2TcCl_6	1.33	d^3	~298	+0.15	64

[a] $(\partial \nu/\partial T)_p$ data for a number of hexahalometallates have been reported by Brown and Kent [68].

result in the decrease in the overlap of the halogen p_x and p_y orbitals with the metal t_{2g} orbitals, thereby increasing the electronic population in the p_x and p_y orbitals of the halogen atoms. This leads to an increase in the coupling constant (eqn. 18). Comparison of the $(\partial \nu/\partial T)_p$ data for the hexahalometallates of second and third row transition elements (Table 4) indicates that the M—X π-bonding is greater for the second row transition metals, especially with the electronic configuration d^3 and d^4 [94].

Brown and Kent [68] have suggested that the positive $(\partial \nu/\partial T)_p$ in some of the paramagnetic complexes is due to the M—X stretching mode rather than the M—X bending mode. If there is a greater decrease in the metal—halogen orbital overlaps in the π-system than in the σ-system upon stretching the M—X bond, the relative loss in the π-bond order is amplified by the concommitant increase in the σ-covalancy [61,68]. Thus the coupling constant of halogen, which depends upon the difference in σ- and π-orbital population (eqns. 20—22), might increase markedly with vibrational excitation of the stretching mode.

Another explanation for the observed positive $(\partial \nu/\partial T)_p$ has been given by O'Leary [74]. According to him, the positive temperature coefficient in K_2ReCl_6 is due to the soft librational mode which is highly temperature-dependent above the highest crystallographic phase transition of K_2ReCl_6. He rules out the π-bonding theory on the basis of observed negative $(\partial \nu/\partial T)_p$ in K_2ReCl_6 below the transition temperature 110.9 K. If the π-bonding were the cause of the anomalous behaviour, one would expect a positive $(\partial \nu/\partial T)_p$ even at low temperatures. O'Leary has further pointed out that an alternative explanation [28] that the EFG might itself increase with increasing volume so as to produce a positive $(\partial \nu/\partial T)_p$ may not be applicable in the case of hexahalometallates.

A number of factors other than π-bonding, expansion of volume and temperature dependence of soft librational modes also have to be considered in explaining the $(\partial \nu/\partial T)_p$ data. For example, Ikeda et al. [54] have observed a negative $(\partial \nu/\partial T)_p$ for the ^{35}Cl NQR frequency in the compound $(NH_4)_2ReCl_6$, even though the corresponding potassium salt exhibits a positive $(\partial \nu/\partial T)_p$ above the transition point (110.9 K). It has been suggested [54] that hydrogen bonding or some electrostatic interaction between hydrogen and chlorine atoms is responsible for the observed negative $(\partial \nu/\partial T)_p$ in $(NH_4)_2ReCl_6$. The normal negative $(\partial \nu/\partial T)_p$ is not followed by the ^{79}Br resonances in $[(C_2H_5)_2NH_2]_3[SbBr_6]$ and $[(C_2H_5)_2NH_2]_3$ $[BiBr_6]$. An inversion of sign of $(\partial \nu/\partial T)_p$ has been observed in both these complexes. Brill and Long [92] have interpreted this observation as due to the effect of phase transition on the NQR frequency. However, similar results for the ^{35}Cl resonances in $Mg(H_2O)_6[SnCl_6]$ and $Ca(H_2O)_6[SnCl_6]$ have been attributed [60] to the presence of Sn—Cl π-bonding in these complexes.

The ^{35}Cl NQR frequencies for some hexahydrates of hexachloroplatinates(IV) such as $BaPtCl_6 \cdot 6H_2O$, $CuPtCl_6 \cdot 6H_2O$ etc., show low values of $(\partial \nu/\partial T)_p$ (0.23—0.33 kHz deg^{-1}) which are much smaller than the value

(0.95 kHz deg^{-1}) for K_2PtCl_6. It has been suggested [58] that torsional oscillations of $[PtCl_6]^{2-}$ octahedra are strongly hindered in these crystals. Broad line NMR spectra of these complexes suggest [58] that water molecules in these crystals do not have any freedom of rotation. Hence, it might be that the hydrogen bond formation between chlorine atoms and water molecules is responsible for the small $(\partial \nu/\partial T)_p$ [58].

Lindop [93] has studied the ^{35}Cl NQR in K_2IrCl_6 as a function of temperature and magnetic field. The compound exhibits a single resonance above the Neel point (3.05 K) and seven resonances below this point. The result has been interpreted in terms of hyperfine interaction at each of the chlorine nuclei in $[IrCl_6]^{2-}$ ion.

2. *Tetrahalometallates*

Compared to the number of hexahalometallates studied by NQR, studies on tetrahalometallates are very few (Table 5). The NQR of the first compound of this series, K_2HgI_4, was reported by Nakamura et al. in 1959 [102]. Other tetrahalomercurates studied by NQR include $K_2HgCl_4 \cdot 2H_2O$, $(PyH)_2HgCl_4$ [103] and Cs_2HgI_4 [104].

The resonance frequencies of tetrahaloplatinate(II) and tetrahalopalladate(II), where the central metal ions have a d^8 configuration, are considerably lower than those of the corresponding hexahalocomplexes of these metals in their higher oxidation state (IV) [43,105]. Analysis of the NQR data using the Townes—Dailey approach indicates that the covalency of the M—X bond in the hexahalometallate(IV) is larger than that in the tetrahalometallate(II) of the same central metal ion [43]. As the metal becomes increasingly electronegative in the order $Ni^{II} < Pd^{II} < Pt^{II}$, the covalency of the M—X bond has been found to increase in this order in compounds of the type A_2MX_4. Even though the expected order has been observed when the cation is the same [43], deviations have been observed when compounds containing different cations are considered [106]. This may indicate the importance of q_{lattice} in these compounds [106].

Compounds containing the $[AlCl_4]^-$ ion have been studied widely [107—112]. Merryman et al. [107] have shown that the observation of one, two, four or some multiplet of four resonances within a range of 1 MHz about an average of 10.6 to 11.3 MHz is an indication of the presence of a salt-like compound $A^+[AlCl_4]^-$. Observation of resonances at higher frequencies, with a wider range will mean either the presence of $[Al_2Cl_7]^-$ (or $[Al_3Cl_{10}]^-$) anions or $[AlCl_4]^-$ ions which are strongly bound to the cation [107]. In compounds containing $[Al_2Cl_7]^-$ (or $[Al_3Cl_{10}]^-$) ions which show resonances in a wider range of frequencies (10—13 MHz), the higher frequency resonances have been attributed to the terminal chlorines while those occurring at lower frequencies have been assigned to the bridging chlorines [107].

Okuda et al. [112] have observed the halogen NQR and the Zeeman effect on the resonances in $AlX_3 \cdot SbX_3$ (X = Br or I) and $AlBr_3 \cdot BiBr_3$. The former adducts have been shown to consist of $[AlX_4]^-$ and $[SbX_2]^+$ ions with a weak

TABLE 5

Halogen NQR frequencies in tetrahalometallates

Compound	Nucleus	Temperature [a] (°K)	ν (MHz)	Ref.
$Na_2ZnCl_4 \cdot 3H_2O$	^{35}Cl	298	7.680, 9.150	121
Cs_2ZnCl_4	^{35}Cl	77	8.893, 9.175, 9.628	121
$(PyH)_2ZnCl_4$	^{35}Cl	298	8.890, 9.477	121
$(N_2H_5)_2ZnCl_4$	^{35}Cl	298	7.854, 8.596, 9.117, 9.900	121
$K_2HgCl_4 \cdot H_2O$	^{35}Cl	298	16.24	103
$(PyH)_2HgCl_4$	^{35}Cl	298	11.99, 14.25, 15.72	103
Cs_2CuCl_4	^{35}Cl	77	10.484, 10.593, 10.856	121
$(CH_3NH_3)_2CuCl_4$	^{35}Cl	77	10.78, 12.157	116
$(C_2H_5NH_3)_2CuCl_4$	^{35}Cl	77	10.817, 12.074	116
$(C_3H_7NH_3)_2CuCl_4$	^{35}Cl	298	11.315, 11.645	116
$(enH_2)CuCl_4$	^{35}Cl	77	10.271, 11.901	116
$NaAuCl_4 \cdot 2H_2O$	^{35}Cl	77	25.356, 27.998, 28.867, 29.466	106,122, 123
$KAuCl_4$	^{35}Cl	77	27.320, 27.598 27.907, 28.214	122
$KAuCl_4 \cdot 2H_2O$	^{35}Cl	77	27.137, 28.183	122
$(NH_4)AuCl_4$	^{35}Cl	77	27.300, 28.130	122
$(NH_4)AuCl_4 \cdot 2/3\ H_2O$	^{35}Cl	293	26.617, 26.979, 27.431, 27.627	122
$RbAuCl_4$	^{35}Cl	77	27.651, 28.319	122
$CsAuCl_4$	^{35}Cl	77	28.419, 27.800	122
$[N(CH_3)_4]_2NiCl_4$	^{35}Cl	273	8.85, 9.05, 9.2—9.4	106
$[N(C_2H_5)_4]_2NiCl_4$	^{35}Cl	—	8.95, 8.64 (77 K), 8.96, 9.45 (220 K)	106
$(CH_3NH_3)_2MnCl_4$	^{35}Cl	R.T.	7.711, 4.564	120
$(PyH)_2PdCl_4$	^{35}Cl	273	17.97	43
K_2PtCl_4	^{35}Cl	273	17.93	138,105
$[N(CH_3)_4]_2PtCl_4$	^{35}Cl	273	18.38, 19.16	138
$(PyH)_2PtCl_4$	^{35}Cl	273	18.41, 18.60	138
$NaAlCl_4$	^{35}Cl	R.T.	11.009, 11.272, 11.385, 11.583	107
$Te_4(AlCl_4)_2$	^{35}Cl	R.T.	10.201, 11.138	107
ICl_2AsCl_4	^{35}Cl	R.T.	10.802, 10.843, 11.297, 11.413	107
$Bi_5(AlCl_4)_3$	^{35}Cl	R.T.	10.479, 10.779	107
$GaAlCl_4$	^{35}Cl	R.T.	10.813, 11.115, 12.491, 12.959	107
$Hg_3(AlCl_4)_2$	^{35}Cl	R.T.	10.417, 10.676, 10.812, 11.383, 11.433, 11.843, 12.568, 12.597	107

TABLE 5 (continued)

Compound	Nucleus	Temperature [a] (°K)	ν (MHz)	Ref.
$Co(AlCl_4)_2$	^{35}Cl	R.T.	10.813, 11.115, 12.491, 12.959	107
SCl_3AlCl_4	^{35}Cl	R.T.	9.91, 10.18, 10.46, 11.04	107
$[P(C_6H_5)_4]AlCl_4$	^{35}Cl	R.T.	11.23	111
$CsGaCl_4$	^{35}Cl	77	15.456, 15.468, 15.485, 15.524, 16.325, 16.604, 16.755, 16.958	114
$NaGaCl_4$	^{35}Cl	77	16.118, 16.370, 16.825, 16.961	114
$RbGaCl_4$	^{35}Cl	77	15.182, 16.001, 16.349, 16.587	114
$KGaCl_4$	^{35}Cl	77	16.483, 16.553	114
$GaGaCl_4$	^{35}Cl	77	16.072, 16.250	114
$[P(C_6H_5)_4]TlCl_4$	^{35}Cl	77	19.86	111
$[As(C_6H_5)_4]TlCl_4$	^{35}Cl	77	20.00	111
Cs_2ZnBr_4	^{81}Br	77	59.008, 61.266, 63.240	121
Rb_2ZnBr_4	^{81}Br	77	56.898, 62.533, 68.171	121
$(PyH)_2ZnBr_4$	^{81}Br	77	57.944, 59.801, 60.657, 61.182	121
$NaAuBr_4 \cdot 2H_2O$	^{79}Br	77	201.70, 217.66, 224.48, 229.43	122
$KAuBr_4$	^{79}Br	77	215.88, 214.64, 219.54, 217.73	122
$KAuBr_4 \cdot 2H_2O$	^{79}Br	77	212.75, 214.15, 217.97, 219.84	122
$NH_4AuBr_4 \cdot 2/3\ H_2O$	^{79}Br	77	207.03, 214.43, 215.52, 217.43	122
$RbAuBr_4$	^{79}Br	77	215.69, 219.53	122
$CsAuBr_4$	^{79}Br	77	216.85, 222.00	122
K_2PdBr_4	^{79}Br	300	129.34	43
K_2PtBr_4	^{79}Br	77	139.84	43
Cs_2ZnI_4	^{127}I	77	79.037 (ν_1)	121
K_2HgI_4	^{127}I	293	123.46, 129.30, 148.49 (ν_1)	102
$NH_4TlI_4 \cdot 2H_2O$	^{127}I	291	157.19 (ν_1), 312.50 (ν_2)	118
NH_4TlI_4	^{127}I	291	155.88, 153.77 (ν_1)	118
$KTlI_4 \cdot 2H_2O$	^{127}I	291	157.45 (ν_1)	118
$KTlI_4$	^{127}I	291	154.94 (ν_1)	118
$RbTlI_4 \cdot 2H_2O$	^{127}I	291	157.78 (ν_1), 313.7 (ν_2)	118
$CsTlI_4 \cdot 2H_2O$	^{127}I	291	157.85 (ν_1)	118

[a] R.T. = Room temperature.

bonding between them through the halogens of the $[AlX_4]^-$ group. $AlBr_3 \cdot BiBr_3$ showed spectral features which are different from those of $AlX_3 \cdot SbX_3$. Poleshchuk and Maksyutin [113] have studied the compounds $AlBr_3 \cdot SbBr_3$ and $AlBr_3 \cdot BiBr_3$ by halogen, antimony and bismuth NQR.

^{35}Cl, ^{69}Ga and ^{81}Br NQR spectra in a series of halogallates(III) including tetrahalogallate(III), $MGaCl_4$ (M = Na, K, Rb, Cs and Ga^I) have been reported by Deeg and Weiss [114]. Temperature dependence of the ^{35}Cl resonances in $KGaCl_4$ and $GaGaCl_4$ has shown that these compounds exhibit polymorphism. The phase transition on going from low to high temperatures in these two compounds is accompanied with the lowering of symmetry of the $GaCl_4$ tetrahedron and an increase in the crystal field splitting. From ^{35}Cl and ^{69}Ga NQR data, compounds of the type MGa_2Cl_7 have been assigned a bridge structure analogous to KAl_2Br_7 and $Te_4(Al_2Cl_7)_2$ [114]. Alymov et al. [115] have observed halogen NQR in compounds of the type $Bu_4^nN[GaX_4]$ (X = Cl, Br, I). $Bu_4^nN[GaI_4]$ has two non-equivalent $[GaI_4]^-$ ions in the unit cell. The covalency character of the M—X bond in these compounds is shown to increase in the order $GaCl_4^- < GaBr_4^- < GaI_4^-$.

Scaife [111,117] has suggested an empirical relationship between (i) the covalent character, σ, of the M—X bond, (ii) covalent radius of the metal M, r_M, and that of the halogen, r_X, and (iii) the M—X bond length d:

$$d = r_M + r_X - 0.61 \log \sigma \tag{32}$$

Substitution of different values in eqn. (32) for both $[Tl_2Cl_9]^{3-}$ and $TlCl_3$ led to the evaluation of $r_{Tl} = 1.24$ Å. This was used in the prediction of the Tl—Cl bond distance in $[TlCl_4]^-$ ($d_{Tl-Cl} = 2.50$ Å), which agrees well with 2.47 Å calculated from Pauling's tetrahedral radius for Tl^{III})[117]. The small asymmetry parameter ($\eta = 6.8\%$) observed for ^{127}I in $[TlI_4]$ ion has been attributed to the electrostatic effect of the external ions [118].

The two ^{35}Cl resonance frequencies observed [116] for compounds of the type A_2CuCl_4, (A = $CH_3NH_3^+$, $CH_3CH_2NH_3^+$, $CH_3CH_2CH_2NH_3^+$) and $(NH_3CH_2CH_2NH_3)CuCl_4$ have been assigned to "bridging" and non-bridging halogen atoms based on the structural data for the complex $(NH_4)_2CuCl_4$ [119]. The higher frequency resonance has been shown to be due to the "bridging" chlorine atoms of a $[CuCl_4]^-$ unit which are long bridging to the neighbouring $[CuCl_4]^-$ unit at a distance of about 2.8 Å to 2.9 Å. Similar assignments have been made for the NQR frequencies in $(CH_3NH_3)_2MnCl_4$ [120], based on studies involving single crystal rotation patterns in a small magnetic field of 40 G. The temperature dependence of NQR in $(CH_3NH_3)_2MnCl_4$ indicates a first order phase transition at 256.5 K and a second order phase transition at 393.7 K [120]. $(CH_3CH_2NH_3)_2[CuCl_4]$ shows a phase transition at ca. 360 K [120]. Halogen NQR in $[ZnX_4]^{2-}$ has been reported by Scaife [121].

Temperature dependence of ^{35}Cl NQR frequencies in $Na(AuCl_4) \cdot 2H_2O$ is interesting in that, of the four resonance signals ovserved, the lowest frequency line showed a positive $(\partial\nu/\partial T)_p$ while the others showed a normal negative $(\partial\nu/\partial T)_p$ [122,123]. The positive $(\partial\nu/\partial T)_p$ of the low frequency line has been shown to be due to the hydrogen bond formation between the chlorine responsible for the signal and the water molecule [123]. This assignment has been confirmed by the temperature dependence of the NQR spectrum of the compound $Na(AuCl_4) \cdot 2D_2O$ which showed a still more positive $(\partial \nu/\partial T)_p$ for the lower frequency line [106]. The anhydrous compounds $NaAuCl_4$ and $KAuCl_4$ show only two frequencies which exhibit negative $(\partial \nu/\partial T)_p$ [124]. The temperature dependence of ^{35}Cl NQR in $HAuCl_4 \cdot 4H_2O$ ($H_5O_2^+AuCl_4^- \cdot 2H_2O$) shows two phase transitions, one at 298 K and the other at 218 K. However, only one phase transition (at 252 K) was observed in $DAuCl_4 \cdot 4D_2O$ [125].

3. *Other halometallates*

Bowmaker et al. [128] have discussed the ^{127}I spectrum in $[Ph_3MeP]Cu_2I_3$ in terms of covalent character of the Cu—I bond as well as in terms of contributions from the Sternheimer antishielding effect.

Bowmaker et al. [126] have observed only a single set of halogen resonance frequencies for the $[CuX_2]^-$ ion in $[Bu^n_4N]CuCl_2$, $[Ph_4As]CuCl_2$ and $[Bu^n_4N]CuBr_2$ and have interpreted the data in terms of centrosymmetric, linear $[CuX_2]^-$ ions. The ionic character of the M—X bond in these complexes is found to be more in the Cu—Br bond than in the Cu—Cl bond [126].

NQR spectra of a number of compounds containing $[CuCl_3]^-$ anion have been reported by Scaife [116]. The data for these complexes have been interpreted on the basis of predominent covalent character of the Cu—Cl bond with only 10% contribution to the EFG from the lattice charges. The low frequency resonances in these compounds have been assigned to chlorine atoms engaged in long bridging interactions while the higher frequency resonances have been assigned to the terminal chlorines. Positive $(\partial \nu/\partial T)_p$ was observed for all the three resonances in NH_4CuCl_3 while the normal negative $(\partial \nu/\partial T)_p$ was observed in $KCuCl_3$. The difference in the temperature dependence of NQR spectra of these two complexes has been explained as due to a change in the degree of magnetic ordering [116]. While $KCuCl_3$ is not magnetically ordered even at 1.3 K, $CsCuCl_3$ is magnetically ordered below 10 K [127]. Zeeman experiments on ^{35}Cl NQR in $KCuCl_3$ show [127] that the asymmetry parameter for the bridging chlorine is larger (91.6%) than that for terminal chlorines (22.5 and 51.3%).

$[Co(NH_3)_6]CuCl_5$ exhibits two ^{35}Cl resonances (77 K) at 10.453 MHz and 9.642 MHz. The higher frequency resonance has been assigned [116] to axial chlorine atoms (of the trigonal bipyramidal arrangement of chlorines around Cu^{II}) and that occurring at 9.642 MHz to equatorial chlorine atoms. While the low frequency signal shows a negative $(\partial \nu/\partial T)_p$, the high frequency signal shows a moderate positive $(\partial \nu/\partial T)_p$. As the frequency due to axial chlorine atoms is lower than the expected value (based on the Cu—Cl bond length) and it shows a positive temperature coefficient, Scaife [116] has suggested that the π-character of the axial Cu—Cl bond is more than that for the equatorial Cu—Cl bond.

Compounds of the type AGa_2Cl_7 (A = Na, K, Rb and Ga^I) show two groups of ^{35}Cl resonances, one containing six resonances and the other only one. A structure similar to that of $(Al_2Cl_7)^-$ [107] involving a chlorine bridge has been suggested [114] for the ion $Ga_2Cl_7^-$ and the low frequency resonance has been assigned to the bridging chlorine. The sextet at higher frequencies is due to the "chemically inequivalent" terminal chlorine atoms [114]. Deeg and Weiss [114] have found that the ratios of the terminal halogen frequencies (average) to the bridging halogen frequencies in compounds having the anion $M_2X_7^-$ (M = Al, Ga) are greater for the Ga^{III} compounds than for the Al^{III} compounds. This has been explained [114] as due to the greater degree of terminal M—X $p\pi \rightarrow d\pi$ bonding in Al^{III} compounds than that in Ga^{III} compounds.

Bridging and terminal halogen resonances have been observed in $ACuCl_3$ [116,127], $AMnCl_3$ [129,130], $[HgI_3]^-$ [131], $AHgCl_3$ [117,132], $CsPbCl_3$ [133—135], KAl_2Br_7 [114] and $A_3Sb_2X_9$ [136]. Only two resonances which could be assigned to the $\pm 1/2 \rightarrow \pm 3/2$ transition have been observed in $(CH_3NH_3)_3Sb_2I_9$ [136]. The low frequency resonance in this compound has been assigned to the bridging iodine [136]. The terminal halogen resonances in $[Sb_2Br_9]^{3-}$ are lower than those in $[SbBr_6]^{3-}$ even though the Sb—Br bond lengths in the former are less than those in the latter. This has been attributed [136] to the distortion of the Sb^{III} kernel to decrease the electron density in the region of the bridging halogen atoms. The terminal chlorine frequencies have not been observed in $[(CH_3)_4N]_2$-$[(Nb_6Cl_{12})Cl_6]$. Based on structural and chemical facts, it has been suggested [137] that the terminal halogens in the cluster anion are ionic in nature and that the resonance frequencies for them are much lower than those for the bridging halogens.

Hydrogen bonding in hydrated salts has been shown to cause large frequency shifts in NQR spectra [122,138]. The presence of water molecules apparently increases the spread of resonance frequencies as in $Na_2ZnCl_4 \cdot 3H_2O$ or increases the resonance frequency as in the salts $KZnX_3 \cdot 2H_2O$ [139]. The frequencies of bridging and terminal halogen atoms are also affected by the formation of hydrogen bonds [129].

4. *Miscellaneous*

^{127}I NQR in simple iodates such as $KCrIO_6$ and complex iodates such as $K_2Sn(IO_3)_6$ has been reported by Shishkin et al. [195]. The e^2Qq values in these compounds show a linear dependence on the ionic radius and oxidation state of the cation. Further, e^2Qq and η values in these complexes depend on the oxidation state of the central metal ion of the $[M(IO_3)_6]^{n-}$ octahedron.

A number of complexes of mercury(II) halides with various oxygen donor ligands has been studied by NQR spectroscopy [117,140—148] (Table 6). The ^{35}Cl NQR in $HgCl_2$(dioxane) occurs at a lower frequency than the parent halide, while those of $HgBr_2$(dioxane) and HgI_2(dioxane) occur at a higher frequency than the parent halide. This has been explained by Brill [141] as

TABLE 6

Halogen NQR frequencies of complexes of mercury(II) halides

Compound	Nucleus	Temperature [a] (°K)	Halogen frequency (MHz)	Ref.
$HgCl_2$(dioxane)	^{35}Cl	R.T.	20.454	141
$HgCl_2(dioxane)_2$	^{35}Cl	R.T.	21.15	144
$HgCl_2(methanol)_2$	^{35}Cl	298	20.205, 20.052	142
$HgCl_2$(THF) [d]	^{35}Cl	298	21.014, 19.628	142
$HgCl_2$(DMSO) [c]	^{35}Cl	296	21.184, 20.075	143
$HgCl_2$(acetophenone)	^{35}Cl	298	20.872, 19.396	143
$HgCl_2$(benzophenone)	^{35}Cl	298	21.685, 20.742	143
$HgCl_2$(benzoquinone)	^{35}Cl	296	20.540	143
$HgCl_2$(2,6-dimethyl-γ-pyrone)	^{35}Cl	296	19.155	143
$HgCl_2$(PyO)	^{35}Cl	298	19.461, 19.022	142
$HgCl_2$(4-MePyO)	^{35}Cl	298	21.451, 20.050	142
$HgCl_2 \cdot$ DMF	^{35}Cl	—	20.208, 20.456	140
$HgCl_2 \cdot$ dimethoxyethane	^{35}Cl	—	21.326	140
$HgCl_2 \cdot CH_3SCH_2CH_2\text{-}SCH_3$	^{35}Cl	77	16.89, 16.92	150
$HgCl_2(CH_3)_2NCH_2CH_2\text{-}N(CH_3)_2$	^{35}Cl	77	17.96	150
$HgBr_2$(dioxane)	^{79}Br	R.T.	160.03	141
$HgBr_2(dioxane)_2$	^{79}Br	R.T.	170.07	144
$HgBr_2$(THF)	^{81}Br	298	136.74, 130.22	142
$HgBr_2$(acetophenone)	^{81}Br	298	135.73, 128.49	142
$HgBr_2$(benzophenone)	^{81}Br	298	139.17, 136.26	142
$HgBr_2$(2-phenoxathiin)	^{81}Br	298	130.14, 128.87	142
$HgBr_2$(PyO)	^{81}Br	298	141.21, 132.03	142
$HgBr_2$(4-MePyO)	^{81}Br	298	141.33, 131.55	142
$HgBr_2 \cdot$ 2DMSO	^{81}Br	—	128.08, 134.78, 141.45, 141.84	140
$HgBr_2 \cdot$ DMF	^{81}Br	—	122.87, 134.60, 136.00	140
$HgBr_2$(dimethoxyethane)	^{81}Br	—	141.23, 140.40	140
$HgBr_2(CH_3SCH_2CH_2\text{-}SCH_3)$	^{81}Br	77	116.00, 116.44	150
$HgBr_2(CH_3)_2NCH_2\text{-}CH_2(CH_3)_2$	^{81}Br	77	117.56, 123.05	150
HgI_2(dioxane)	^{127}I	R.T.	172.77 [b]	141
HgI_2(PyO)	^{127}I	298	172.51, 164.63 [b]	142
HgI_2(4-MePyO)	^{127}I	298	174.53, 167.13 [b]	142
$HgI_2(CH_3SCH_2CH_2\text{-}SCH_3)$	^{127}I	77	152.93, 156.44 [b]	150
$HgI_2(CH_3)_2NCH_2CH_2\text{-}N(CH_3)_2$	^{127}I	77	148.13, 153.84 [b]	150

[a] R.T. = Room temperature (not specified).

[b] Resonance due to ±1/2→±3/2 transition.

[c] Resonances for this compound have been obtained at 19.878 and 19.484 MHz [140].

[d] Resonances have been reported at 20.584 and 19.272 MHz [140].

due to a weak interaction of dioxane with $HgBr_2$ and HgI_2 such that no significint charge transfer takes place in these complexes. The Hg^{II} halides are considered to act more as free but ordered molecules in a lattice containing dioxane molecules of crystallization [141]. The trend in strength of interaction of Hg^{II} with dioxane appears to be in the order of $HgCl_2 > HgBr_2 > HgI_2$. The shift of NQR to higher frequencies in $HgBr_2$ and HgI_2 complexes may also be due to changes in Hg—X π-bond character [140].

Similar trends have been observed in the Hg^{II} halide complexes with tetrahydrofuran (THF), benzophenone, acetophenone, phenoxathiin, methanol, pyridine-1-oxide (PyO) and 4-methylpyridine-1-oxide (4-MePyO) [142]. Patterson et al. [144] have interpreted the halogen NQR spectra in HgX_2-(dioxane) and $HgCl_2(dioxane)_2$ in terms of substituting oxygen for halogen in the highly distorted octahedral coordination about Hg^{II} in $HgCl_2$. The presence of two widely separated ^{35}Cl resonances in $HgCl_2$ complexes with THF, dimethylsulphoxide (DMSO), acetophenone, PyO and 4-MePyO has been attributed to the presence of both bridging and terminal chlorine atoms in these complexes [141,143], (however, see ref. 149). Temperature dependence of ^{35}Cl NQR in $HgCl_2 \cdot 4MePyO$ has also been reported [147].

More recently [273] the appearance of two NQR signals separated by a few MHz in mercuric halide complexes has been suggested to be due to differences in the intermolecular interactions experienced by the two halogens of the same HgX_2 group. The extent of splitting depends on the number of nearest neighbours of Hg^{II} as well as that of the halogen. From a study of ^{35}Cl, ^{79}Br, ^{81}Br and ^{127}I NQR in a number of mercuric halide adducts of polyethers such as glyme and diglyme and a crown ether (18-crown-6) and from the data available in literature, Wulfsberg [273] has proposed that the possible structure of the adducts of HgX_2 may be postulated from NQR data.

Complexes of the type $HgX_2 \cdot D$ (X = Cl, Br or I; D = $—SCH_3$, $N(CH_3)_2$, $—OCH_3$, disubstituted ethanes) have been studied by Bryukhova et al. [150] by halogen NQR spectroscopy. The results show that in the complexes where X = Cl or Br, the halogens are equivalent indicating a linear X—Hg—X group. For the X = I compounds, the tetrahedral coordination around Hg^{II} is destroyed and the asymmetry parameter, η, is severely decreased. Babushkina et al. [151] have studied the covalency changes in the M—X bond in complexes of the type $MX_2 \cdot L_2$ (where M = Zn, Cd, Hg, X = Br and I and L = nitrogen containing heterocyclic ligand) using ^{79}Br, ^{81}Br and ^{127}I NQR. The covalent character of the M—X bond decreases when Hg^{II} and Zn^{II} halides are complexed. However, in the case of $CdBr_2$ and CdI_2, the covalent character of the M—X bond increases on complexing with the ligand.

^{35}Cl NQR in $CuCl_2 \cdot PyO$ complexes has been studied by Frausto da Silva et al. [152,153]. The chlorine resonances observed for $CuCl_2 \cdot PyO$ complexes have been assigned to terminal halogens which differ in the Cu—Cl bond length [153]. While the DMSO adduct of $CuCl_2(PyO)$ shows an increase in both the resonance frequencies relative to those of $CuCl_2(PyO)$ by about

0.2 MHz, the PyO adduct shows a decrease of about 0.24 MHz for both the resonances. This may be due to the possible hydrogen bond formation in the PyO adduct which cannot happen in the DMSO adduct [153].

^{35}Cl NQR frequencies of BCl_3 and its amine complexes [154] and nitrile complexes [155,156] have been reported. The coupling constants have been interpreted in terms of two molecular theories, BEEM-π and CNDO [156]. ^{35}Cl and ^{69}Ga NQR have been reported for a number of 1 : 1 complexes of $GaCl_3$ with a variety of donor ligands [157—160]. Only the adduct of $GaCl_3$ with CH_3CN gives a single resonance line indicating a C_{3v} symmetry for the complex in the solid [158]. Structures involving halogen bridges and $[GaCl_4]^-$ ion have been ruled out by halogen NQR data [157,158]. From the ^{35}Cl NQR data on $GaCl_3$ complexes with different ligands, Carter et al. [159] have concluded that the basicity of the ligands increases in the order $R_3P < R_3As < R_2S < R_2O$ where R = Me or Et.

Rogers and Ryan [161] have partly used the point charge model calculations in assigning the frequencies in the complexes of $POCl_3$ with a number of metal halides. Analysis of the result using the Townes—Dailey approach indicates the decrease in Lewis acid strength of the metal halides studied in the order $SbCl_5 > FeCl_3 > SnCl_4 > TiCl_4$. Temperature dependence of the ^{35}Cl NQR in these complexes has indicated [161] the internal motion of the $-PCl_3$ group about its three-fold axis. The observation of only two resonance frequencies for $POCl_3$ in $SnCl_4 \cdot POCl_3$ (the crystal structure demands the observation of four resonances) has been explained by assuming a lower barrier for rotation in one $-PCl_3$ group so that even at 77 K, the resonances for that set would be lost while those for the second set would only disappear at higher temperature [161]. In $SbCl_5 \cdot POCl_3$, there is evidence for a hindrance of vibration of one of the chlorines and extensive rotational (or librational) motion of the $POCl_3$ group about the PO bond at room temperature [271]. Rotation of $SnCl_3$ group has been reported by Kume et al. [162] in the complex $SnCl_3Mn(CO)_5$

The frequency splitting and shifts of the ^{35}Cl resonance frequencies in complexes of the type $SnCl_4 \cdot L_2$ are based on the *cis* or *trans* structure of the complex [163,164]. As all the four chlorines are equivalent in the *trans* isomer and two pairs of equivalent chlorines are present in the *cis* isomer, the complexes showing two sets of resonances have been assigned the *cis* configuration [163]. Of the two sets of resonances exhibited by the *cis* complexes, the higher frequency resonances have been assigned to the equatorial chlorine atoms and the low frequency resonances to the axial chlorine atoms [163]. The splitting of the spectra is maximum at the lowest charge transfer and decreases with increasing charge transfer, finally giving a single intense line.

^{35}Cl, ^{79}Br, and ^{81}Br NQR spectra in a number of charge transfer complexes (Menshutkin complexes) of $AsCl_3$, $AsBr_3$, $SbCl_3$ and $SbBr_3$ with aromatic hydrocarbons, ethers and amines have been studied [165—185]. The shifts in the halogen NQR frequencies in these compounds compared to the parent halides have been attributed to the charge transfer from the donor to the metal atom (As or Sb) or to the halogen by the interaction of the acceptor atom with either the π-system or the lone pair of electrons on the heteroatom of the donor. Steric effects of the donor ligands also play an important role in deciding the extent of shift in the NQR frequency as well as the splitting pattern in the spectra. Zeeman effect on the NQR frequencies in $2AlBr_3 \cdot C_6H_6$, $2SbCl_3 \cdot C_6H_6$, $2SbBr_3 \cdot C_6H_6$ and $2SbCl_3 \cdot C_{10}H_8$ has also been studied [168,181—183]. The Cl—Sb—Cl bond angles obtained in these complexes (ca. 90—95°) show satisfactory agreement with those obtained by X-ray diffraction method. The value of η for the halogens in the SbX_3 complexes varies from 5 to 17%. ^{81}Br spectrum and the Zeeman study of the complex $AlBr_3 \cdot C_6H_6$ [182] show that this complex is a dimer. The interbond angle, obtained by the Zeeman study, at the bridging bromine in this complex is 95.5 ± 0.2° and the bond angle between the two terminal bromines is 117.3 ± 0.5°. The corresponding values obtained from the X-ray diffraction method are 87 ± 2° and 122 ± 2° respectively. The difference between the values obtained by these two methods has been attributed [182] to the presence of bent bonds. The asymmetry parameter obtained for this complex at the bridging bromine site is 28.9 ± 1.1% and those obtained for the two terminal bromine sites are 8.6 ± 1.1 and 6 ± 0.9%.

Poleshchuk et al. [186,187] have studied the chlorine NQR in the 1 : 1 complexes of $SbCl_5$ with donors such as pyridine, ammonia, diethylether, dioxane, benzonitrile and quinoline. Analysis of the results by the Townes—Dailey procedure indicates that the charge has been largely transferred to chlorine rather than to antimony. ^{35}Cl and ^{121}Sb (^{123}Sb) resonances in $SbCl_5$ CH_3CN are consistent with a covalent structure in which Sb^V is hexacoordinated [271]. ^{35}Cl NQR studies have been made by Makridin et al. [188] on $SbCl_5(ClCH_2)_2O$. Burgard and Lucken [189] have reported the ^{35}Cl NQR in $SbCl_5 \cdot CNCl$. 1 : 1 and 1 : 2 complexes of $TeCl_4$ with donors such as $(C_3H_7)_2S$ and DMSO have been studied by ^{35}Cl NQR [190].

Observation of two ^{35}Cl resonances (at 9.265 and 9.592 MHz) in Rb_2VOCl_4 has been attributed [191,192] to the existence of two sets of chlorine nuclei in non-equivalent positions. Safin [193] has observed two types of bromine sites in $Rb_2UO_2Br_4$ by temperature dependence of the ^{81}Br NQR. The difference in $(\partial\nu/\partial T)_p$ for the two sites is shown to be due to bromine to water hydrogen bonding. The temperature dependence of halogen NQR frequencies in acetic acid complexes of vanadium(III), $[(CH_3)_4N][VCl_4(AcOH)_2]$ and $[(CH_3)_4N][VBr_4(AcOH)_2]$, has shown [194] some interesting results. While the higher frequency line shows a normal negative $(\partial\nu/\partial T)_p$ the low frequency resonance exhibits a positive $(\partial\nu/\partial T)_p$. The higher frequency resonance disappears at 77 K. This observation has been explained [194] by assigning the low frequency line to a pair of halogens which are π-bonded but not hydrogen bonded and the higher frequency lines to a pair of halogens which are both π-bonded and hydrogen bonded.

^{35}Cl NQR in a few cobaloximes shows [197] that the covalency of the Co—Cl bond gets reduced by the electron-donor ligand present *trans* to the chlorine, the interaction of $P(C_6H_5)_3$ being more than that of pyridine. No such trend has been observed for *trans*-dichlorocobaloximes. A number of complexes of ethylenediamine (en) and NH_3 with Co(III) salts have been studied by ^{35}Cl NQR [198—204]. *Trans*-$[Co(en)_2Cl_2]ClO_4$ [198] and $[Co(NH_3)_5Cl]SO_4 \cdot H_2SO_4$ [204] show two ^{35}Cl resonances consistent with two inequivalent cobalt sites observed by ^{59}Co NQR. Analysis of ^{35}Cl NQR data using Townes—Dailey procedure indicates ~35% covalent character in the Co—Cl bond of these complexes. The ^{35}Cl resonance in *trans*-$[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$ is similar to that in *trans*-$[Co(tn)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$ (tn = trimethylenediamine) indicating that the Co—Cl interaction and population of the Co(d_{z^2}) orbital which is involved in Cl—Co—Cl bonds are virtually unchanged in these complexes [203].

A number of *cis—trans* isomers of the type MX_2L_2 (M = Ni^{II}, Pd^{II} or Pt^{II}) have been studied by Fryer and Smith [106,205,206]. The *trans*-$PtCl_2 \cdot L_2$ complexes exhibit resonances at higher frequencies than the *cis*-$PtCl_2 \cdot L_2$ complexes (Table 7). The difference between the ^{35}Cl NQR frequencies of the *trans* complex and those of the *cis* complex, is a measure of the *trans* influence of the ligand L [206]. On changing the ligand L, resonances due to both

TABLE 7

Chlorine-35 NQR frequencies of some square planar platinum(II) and palladium(II) complexes

Compound [a]	Temperature (°K)	ν (MHz)	Ref.
trans-$(piperidine)_2PdCl_2$	273	16.11, 16.31	205
trans-$(pyridine)_2PdCl_2$	273	17.72	205
trans-$(Bu^n_3As)_2PdCl_2$	273	18.23, 18.59	205
trans-$(Bu^n_3P)_2PdCl_2$	273	18.37, 18.50, 18.58, 18.63	205
trans-$(EtCN)_2PdCl_2$	273	20.30	205
trans-$(C_6H_5CN)_2PdCl_2$	273	20.58	205
trans-$[(CH_3)_2NH]_2PtCl_2$	273	18.16	205
trans-$(NH_3)_2PtCl_2$	273	17.30	205
trans-$(pyridine)_2PtCl_2$	273	19.62	205
trans-$(Et_3P)_2PtCl_2$	273	20.99	205
trans-$[(C_6H_5)Bu^n_2P]_2PtCl_2$	273	21.32, 21.64	106
cis-$[(CH_3)_2NH]_2PtCl_2$	273	17.21	206
cis-$(pyridine)_2PtCl_2$	273	17.65	206
cis-$(Bu^n_3P)_2PtCl_2$	273	17.73, 17.79, 17.89, 17.96	106
cis-$[(C_6H_5)Et_2P]_2PtCl_2$	273	17.82, 17.99	106
cis-$[(C_6H_5)Bu^n_2P]_2PtCl_2$	273	18.33	106
cis-$(bipyridine)PtCl_2$	273	18.98	106
cis-$(EtCN)_2PtCl_2$	273	21.05, 21.33	106
$(bipyridine)PdCl_2$	273	17.82, 18.35	106
$(DMSO)_2PdCl_2$	273	19.75	106
trans-$(Bu^n_3P)_2PtCl_2$	273	20.90, 21.04, 21.08	106

[a] Bu^n = *n*-butyl; Et = ethyl; DMSO = dimethylsulphoxide.

trans and *cis* complexes move in the same direction [206]. In the *trans* Pt^{II} series the decrease in the ^{35}Cl NQR frequency has been correlated to the increase in the Pt—Cl bond length [106]. A greater spread of Pt—Cl bond distances for a given range of ^{35}Cl resonances has been observed when the *trans* ligand is changed, than when the *cis* ligand is changed. In the *trans*-$PdCl_2L_2$ series, the charge on the chlorine atom increases as L is changed in the following sequence: PhCN, EtCN, Bu^n_3P, Bu^n_3As, pyridine and piperidine. A similar trend has been observed for the corresponding Pt^{II} complexes also. The increase in the charge on chlorine indicates a weakening of the M—Cl bond which appears to assist nucleophilic substitution reactions of the chlorine. The above order of *cis* influence of the nucleophiles has been explained by Fryer and Smith [205] as due to either (i) the increasing charge donation from left to right in the series allowing the *cis* M—Cl bond to become increasingly polarized or (ii) the possibility that the ligands which weaken the *trans* bond simultaneously strengthen the *cis* bond. An interpretation of the *cis* effect in planer d^8 complexes of the type $PtCl_2XY$ based on experimental NQR data has been presented by Schreiner and Brill [207]. No appreciable *cis* effect on ^{35}Cl NQR has been observed in $PtCl_2(C_2H_4)L$ compounds [208].

A common feature in the spectra of mono-olefin complexes of the type $[PtCl_3L]^-$ is the presence of a pair of higher frequency resonances and one low frequency resonance [138,209]. The low frequency resonance has been assigned to the *trans* chlorine. Temperature dependence studies on Zeise's salt reveal that, of the two *cis* chlorine atoms which are responsible for the pair of high frequency resonances, the one responsible for the higher frequency resonance is involved in a stronger hydrogen bond than the other [138]. The observed order of the olefins in terms of increasing ^{35}Cl frequencies, ethylene < butene < styrene, is probably influenced by both inductive effect and steric character of the substituents on ethylene [138]. Yesinowski and Brown [209] have studied the ^{81}Br NQR in $K[PtBr_3(C_2H_4)]\cdot H_2O$, K_2PtBr_4 and $PtBr_2L$ (L = cyclooctatetraene). As in the corresponding chloro complex, the low frequency resonance (103.2 MHz) and the high frequency resonances (130.9 and 132.5 MHz) have been assigned to *trans* and *cis* bromine atoms respectively [209] in $K[PtBr_3(C_2H_4)]H_2O$.

In complexes of the type *trans*-$(LPtCl_2)_2$ and *trans*-$(LPdCl_2)_2$, where both bridging and terminal chlorines are present, the higher frequency resonance has been assigned to the terminal halogen [174]. This assignment has been supported by photoelectron spectroscopic studies on *trans*-$[(Et_3P)_2Pt_2Cl_4]$ which show lower binding energy for the bridging chlorines than that for the terminal chlorines [210]. A correlation between the (Cl $2p_{3/2}$) binding energy and ^{35}Cl NQR frequency has also been obtained for these compounds (Fig. 5) [210].

Differences in NQR frequencies of tetrahedral and square planar complexes of Ni^{II} have been observed by Smith and Stoessiger [211] (Table 8). The differences have been attributed to the presence of partially filled metal orbitals suitable for M—X π-bonding in the tetrahedral complexes and the absence of

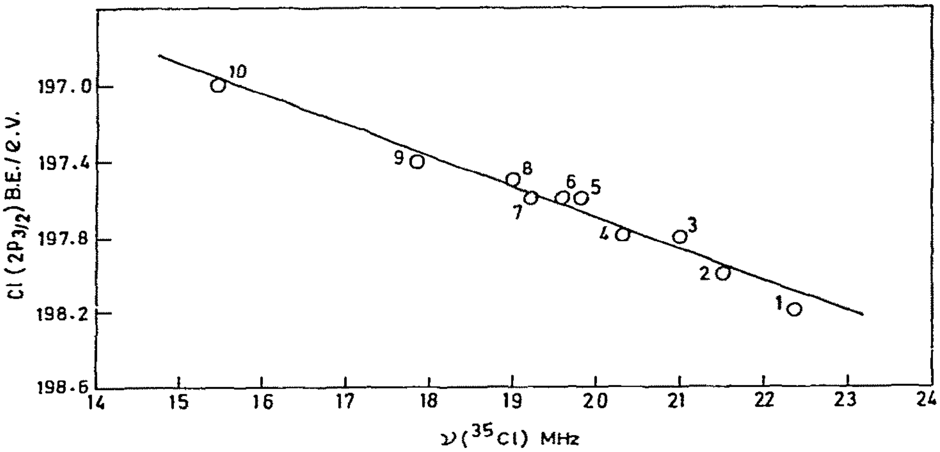

Fig. 5. Correlation between the ^{35}Cl NQR frequency and the binding energy [Cl($2p_{3/2}$)] in a few Pt$^{\mathrm{II}}$ complexes.
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such orbitals in the square planar complexes [211]. An estimation of π-bonding in tetrahedral complexes has been made by comparing the ^{35}Cl e^2Qq of the squre planar and tetrahedral complexes.

^{35}Cl NQR in tris-(sarcosine)calcium chloride has been studied [212] as a function of temperature in the range 127—320 K. The measured NQR frequency at room temperature (2.175 MHz) is one of the lowest reported ^{35}Cl NQR frequencies so far. Point charge model calculations indicate that the EFG at the chlorine site is mainly determined by the hydrogens involved in three hydrogen bonds, N—H...Cl, around each chlorine [212]. Blinc et al.

TABLE 8

Halogen NQR frequencies of some square planar and tetrahedral nickel(II) complexes [211].

Compound	Stereochemistry	Temperature (°K)	Nucleus	ν (MHz)
$[(C_6H_5)_3P]_2NiCl_2$	Tetrahedral	298	^{35}Cl	9.471
$[(CH_3)_4N]_2NiCl_4$	Tetrahedral	273	^{35}Cl	8.85, 9.05
$[(C_6H_5)_3P]_2NiBr_2$	Tetrahedral	298	^{79}Br	71.07, 75.15
$[(C_5H_5)_3P]_2NiI_2$	Tetrahedral	298	^{127}I	71.04 (ν_1) 138.00 (ν_2)
$[(n\text{-}C_3H_7)_3P]_2NiCl_2$	Square planar	298	^{35}Cl	15.852
$[Bu^n_3P]_2NiCl_2$	Square planar	273	^{35}Cl	15.99
$[(n\text{-}C_3H_7)_3P]_2NiBr_2$	Square planar	308	^{79}Br	126.26
$[Bu^n_3P]_2NiBr_2$	Square planar	308	^{79}Br	126.53

[213] have observed that the chlorine environment and the lengths of the N—H...Cl hydrogen bonds significantly change on going through the phase transition in this complex. The hydrogen bonded chlorine atoms seem to play an important role in the transition mechanism in addition to the rotational distortion of the sarcosine octahedron.

Halogen NQR in compounds such as $C_5H_5Fe(CO)_2X$ (X = Cl, Br or I), $[C_5H_4 \cdot C_2H_2B_{10}Hg]Fe(CO)_2Br$ [214] and $Cl_nTi(C_5H_5)_{4-n}$ (n = 2—4) [215] has been reported. Halogen NQR in other organometallic complexes where the chlorine is a part of the ligand has also been reported [for example 162, 217—222]. ^{35}Cl NQR in a few complexes of 3-chloroacetylacetone with different metal ions has been shown [216] to vary markedly according to the polarity or charge of the complex. The non-polar complexes show resonances around 36 MHz while the polar or charged complexes show resonances around 38 MHz [216].

B. Copper-63 and copper-65 resonances (Table 9)

The first NQR report [3] on a coordination compound is the ^{63}Cu resonance in $KCu(CN)_2$. Zeeman NQR [223] study of this complex has yielded the asymmetry parameter η as 78 ± 7%.

^{63}Cu and ^{65}Cu resonances in a few $(CuX_2)^-$ compounds have been interpreted [126] in terms of *ds* hybridization on the Cu^I ion. ^{63}Cu and ^{65}Cu NQR frequencies in $(Ph_3MeP)Cu_2I_3$ have shown [128] the presence of two crystallographically inequivalent copper sites in this compound. Based on the signal to noise ratio for the two crystallographically inequivalent copper sites, the compound is shown [128] to have the tetramolecular $[Cu_4I_6]^{2-}$ species.

Cu—S bonds in complexes of copper(I) with thiourea (and substituted thiourea) have been shown to be quite covalent by ^{63}Cu and ^{65}Cu NQR studies [224,225]. The observed resonance frequencies have been shown to be dependent on the metal—ligand bond lengths and inductive effects of the substituents in the substituted thiourea complexes [224]. ^{63}Cu and ^{65}Cu NQR frequencies in some copper-N,N′-dialkyldithiocarbamates are relatively constant [226], lying within 0.5 MHz of 26.5 MHz. This constancy has been explained as due to the fact that the basic Cu_4 tetrahedral unit with its interlocked dithiocarbamate groups is a rigid structure less susceptible to distortion due to packing or solvation.

^{63}Cu and ^{65}Cu NQR in a few complexes of trimethylphosphine sulphide [227,228] and trimethylarsine sulphide [228] with Cu^I salts has been interpreted in terms of partial *d*-orbital vacancy which arises due to the promotion of the electronic charge density from the $3d_{z^2}$ orbital to the vacant 4*s* orbital of the copper atom. Graybeal et al. [227] have calculated the EFG at the Cu^I site in $[Cu((CH_3)_3PS)_3]^+$ by an extended Hückel molecular orbital EHMO method. The calculated e^2Qq is only 30% of the observed value. This difference in the e^2Qq may be due to (i) the use of Slater type basis orbitals in

TABLE 9

Copper-63 and copper-65 resonance frequencies of some copper(I) complexes

Compound [a]	Temperature (°K)	Cu-63 resonance (MHz)	Cu-65 resonance (MHz)	Ref.
$K[Cu(CN)_2]$	289	33.479	30.221	3
$(Bu^n_4N)CuCl_2$	77	30.7	28.3	126
$[(C_6H_5)_4As]CuCl_2$	77	31.15	28.75	126
$[Bu^n_4N]CuBr_2$	77	28.85	26.60	126
$[(C_6H_5)_3(CH_3)P]Cu_2I_3$	77	26.8, 26.15	24.55, 23.95	128
$Cu(tu)_2Cl$		22.115, 19.296	20.465, 17.856	224
$Cu(tu)_2Br$		16.443, 16.181	—	224
$Cu_4(tu)_9(NO_3)_4$		25.088	23.280	224
$Cu(etu)_2ClO_4$		22.881	—	224
$[Cu(etu)_4]_2SO_4$		31.562	29.250	224
$Cu(etu)_2Cl$		27.860	25.753	224
$Cu(etu)_2Br$		32.010	29.620	224
$Cu(dtu)_3Cl$		38.804	36.825	224
$Cu[(CH_3)_3PS]_3ClO_4$ [b]	77	26.35	24.39	228
$Cu[(CH_3)_3AsS]_3ClO_4$	77	24.16	22.35	228
$[(CH_3)_3PSCuCl]_3$	77	29.24, 28.44	26.77, 26.34	228
$[(CH_3)_3PSCuBr]_n$	77	27.53, 27.18	25.49, 25.16	228
$[(CH_3)_3PSCuI]_n$	77	24.91, 24.92	—	228
$[(CH_3)_3AsSCuCl]_n$	77	29.05, 28.25	26.86, 26.10	228
$Cu[(CH_3)_3PS]_3BF_4$	300	24.838	22.985	227
Cu(dtc)	293	26.956	24.949	226
$Cu[Bu^n_2dtc]$	293	25.949, 26.824	23.997, 24.827	226
$Cu[(n\text{-}C_3H_7)_2dtc]\text{-}1/8\ CS_2$	293	26.238, 26.432, 26.476	24.278, 24.461, 24.497	226
$Cu[(n\text{-}C_3H_7)_2dtc]\text{-}1/2\ CHCl_3$	293	26.270, 26.343, 26.504, 26.765	24.313, 24.375, 24.525, 24.764	226

[a] Abbreviations: tu = thiourea; etu = ethylenethiourea; dtu = N,N′-dimethylthiourea; dtc = N,N-diethyldithiocarbamate; Bu^n_2dtc = N,N-di-*n*-butyldithiocarbamate.

[b] Graybeal et al. [227] have reported ^{63}Cu and ^{65}Cu resonances (300 K) at 24.815 and 22.968 MHz respsectively.

the calculation and (ii) the value of Sternheimer antishielding factor used in the calculation [227].

C. Gallium-69 resonances

Tong [158] has reported ^{69}Ga NQR in a number of donor—acceptor complexes containing $GaCl_3$ as the acceptor. ^{69}Ga resonances in these complexes are more sensitive to the changes in the ligands than the ^{35}Cl resonances [158]. In most of these complexes $(\partial \nu / \partial T)_p$ values for the ^{69}Ga resonances are positive. All these complexes are shown to be monomeric from their ^{69}Ga and

^{35}Cl NQR spectra. It has been suggested [158] that ^{69}Ga NQR frequency might be a useful guide to the relative strength of coordination in different complexes; the weaker the donor the higher the frequency. Good correlation of the ^{69}Ga and average ^{35}Cl frequencies with gas phase heats of formation has also been obtained [158]. ^{69}Ga resonances in compounds such as $GaCl_3 \cdot O(C_2H_5)_2$ [157] and compounds containing the anions $[Ga_2Cl_7]^-$ and $[GaCl_4]^-$ [114] have also been reported.

D. Arsenic-75 resonances

^{75}As NQR in a few substituted dithiocarbamates and *O*-ethylxanthate complexes of As^{III} has been studied by Bastow and Whitefield [226]. ^{75}As frequencies in these complexes show a marked variation upon changing the substituent in the dithiocarbamate ligand. This may be due to changes in the S—As—S pyramidal angle in these complexes [226]. It has been observed that $(\partial \nu/\partial T)_p$ for the As^{III} *O*-ethylxanthate complex in the temperature range 77—195 K is approximately three times that in the range 195—293 K.

Grechishkin et al. have studied the ^{75}As NQR in a number of Menshutkin complexes based on $AsCl_3$ and $AsBr_3$ [229—234]. Extraordinary frequency shifts have been observed for the ^{75}As resonances in these complexes. Comparison of ^{75}As spectra with ^{121}Sb spectra of similar complexes indicates that the arsenic *d*-orbitals have more tendency to form $d\pi$—$p\pi$ bonds than those of antimony. Multiplicity of ^{75}As resonances also surpasses that of ^{121}Sb and ^{123}Sb frequencies in similar compounds. Shift in the ^{75}As resonance frequencies of the complex compared to the parent halide is usually towards the lower frequency region. The shifts correlate linearly with the ionization potential of the donor ligands: the lower the ionization potential of the ligand, the greater will be the shift. Patterson and Carnevale [235] have reported the ^{75}As NQR in $(CH_3)_3In \cdot As(CH_3)_3$.

E. Mercury-201 resonances

Patterson et al. [144] have reported ^{201}Hg NQR in the complexes $HgCl_2$(dioxane)$_2$ (323.38 MHz) and $HgBr_2$(dioxane)$_2$ (313.23 MHz). ^{201}Hg and ^{35}Cl NQR data in these complexes have been discussed [144] in terms of finer details of the structure of these complexes.

F. Nitrogen-14 resonances

Nitrogen-14 is one of the important nuclei which can be studied by NQR. However, ^{14}N NQR has been studied only in a few metal complexes [213, 236—239]. Nakamura and co-workers [236] have studied ^{14}N NQR in Zn^{II}, Cd^{II}, Hg^{II}, Cu^{I}, Pt^{II} and Co^{II} cyano complexes. The quadrupole coupling constant of ^{14}N in complexes of the metal ions having no vacant *d*-orbitals (e.g. Zn^{II}, Cu^{I}) are higher than those of Pt^{II} and Co^{II} complexes (Table 10).

TABLE 10

Nitrogen-14 NQR parameters for some metal cyano complexes at 77 K [236]

Compound	ν_+ (kHz)	ν_- (kHz)	ν_0 (kHz)	e^2Qq/h (kHz)	η (%)
$K_2Zn(CN)_4$	—	—	3104.2	4139.0	0.00
$K_2Cd(CN)_4$	—	—	3149.1	4198.8	0.00
$K_2Hg(CN)_4$	—	—	3035.6	4047.5	0.00
	3069.4	3041.4	—	4073.9	1.37
$K_2Cu(CN)_4$	3002.1	2943.8	—	3963.9	2.94
$K_2Pt(CN)_4 \cdot 3H_2O$	2641.2	2594.7	—	3467.0	3.2
	2614.2	2549.7			
$K_3Co(CN)_3$	2794.5	2709.9	—	3684.0	3.0
	2789.2	2706.3			
	2787.8	2688.8			

It has been suggested [236] that the metal—ligand bonds in Pt^{II} and Co^{II} complexes have greater *dπ—pπ* bond character than those in Zn^{II}, Cd^{II}, Hg^{II} and Cu^{I} complexes. Saruwatari et al. [237] have studied the temperature dependence of ^{14}N NQR in $K_2Hg(CN)_4$ and located a phase transition at 111 K. The temperature dependence of the ^{14}N NQR in this compound has been shown to be determined mostly by the rotational oscillation of the cyanide group [237].

Brown and co-workers [238] have studied the ^{14}N NQR in a number of bis(glyoximato)metal complexes like bis(dimethylglyoximato)nickel(II). The ^{14}N coupling constants of the complexes have been compared with the free ligand values and have been interpreted in terms of changes in nitrogen orbital occupancies and bond angles. The nitrogen orbital directed towards the metal has been estimated to have an occupation number of 1.65 in $Ni(DMG)_2$ and 1.75 in $Pd(DMG)_2$ as compared with 2 in the free ligand.

Blinc et al. [213] have studied the ^{14}N NQR in tris(sarcosine)calcium chloride. At room temperature two nitrogen sites have been observed in this complex. On lowering the temperature the inequivalence is removed and at 77 K only one resonance line has been observed [213]. ^{14}N NQR in a series of hexamethylenetetramine complexes with lithium halide hydrates has been reported by Dresvyankin et al. [239]. ^{14}N NQR along with ^{35}Cl NQR has been used by Andreeva et al. [164] in assigning the *cis-trans* structures in a number of complexes of the type $SnCl_4 \cdot 2L$ (where L = phosphoric acid amides).

G. Manganese-55 resonances (Table 11)

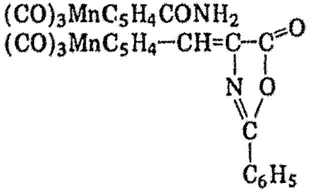
A number of ^{55}Mn NQR reports has appeared on manganese pentacarbonyl and its derivatives [220,221,240—246]. Voitländer et al. [240] first reported the ^{55}Mn NQR in manganese pentacarbonyl. From a study of a number of substituted π-cyclopentadienylmanganesetricarbonyls, Nesmeyanov et al. [221,

TABLE 11

Manganese-55 NQR parameters for manganese carbonyl and its derivatives

Compound	$\nu(\pm 1/2 \rightarrow \pm 3/2)$ (MHz)	$\nu(\pm 3/2 \rightarrow \pm 5/2)$ (MHz)	η (%)	e^2Qq/h (MHz)	Temperature (°K)	Ref.
$Mn_2(CO)_{10}$	—	19.350	—	—	293	240
$LiMn(CO)_5$	10.16	20.070	10	67.1	298	260
$NaMn(CO)_5$	10.48	19.240	26	65	298	260
$Ni(1,10\text{-phen})_3[Mn(CO)_5]$	9.45, 9.66	18.670,	8	62.4	298	260
		18.990	12	63.5		
$Ni(1,10\text{-phen})_3[Mn(CO)_4P(OCH_3)_3]_2$	11.52	22.920	5	76.5	298	260
$Ni(1,10\text{-phen})_3[Mn(CO)_4P(C_6H_5)_3]_2$	12.92	25.310,	13	84.7	298	260
		25.690,	6	85.8		
		25.690				
$(Pyrrole)Mn(CO)_3$	10.2287	19.9355	14.25	—	77	243
$(CO)_3MnC_5H_5$	9.79	19.572	1.9	65.24	77	243,240
$(CO)_3MnC_5H_4COCF_3$	9.09	17.736	13.9	59.35	77	241
$(CO)_3MnC_5H_4COOCH_3$	9.21	18.348	5.6	61.20	77	241
$(CO)_3MnC_5H_4COCH_3$	9.29	18.472	6.8	61.63	77	241
$(CO)_3MnC_5H_4COOH$	9.34	18.682	0	62.27	77	241
$(CO)_3MnC_5H_4COC_6H_5$	9.50	18.672	11.8	62.41	77	241
$(CO)_3MnC_5H_4SO_2NH_2$	9.58	19.050	6.9	63.56	77	241
$(CO)_3MnC_5H_4CH_3$	9.75	19.452	4.4	64.86	77	241
$(CO)_3MnC_5H_4CH_2Cl$	9.77	19.476	5.1	64.95	77	241
$(CO)_3MnC_5H_4SO_3^-Na^+$	9.88	19.740	2.9	65.81	77	241
$(CO)_3MnC_5H_4I$	10.07	20.094	4.3	67.00	77	241
$(CO)_3MnC_5H_4NHCOOCH_2C_6H_5$	10.17	19.860	13.8	66.45	298	220
$(CO)_3MnC_5H_4HgCl$	9.61	19.150	5.6	63.86	298	220
	9.59	18.960	9.6	63.32		
$(CO)_3MnC_5H_4CNOHCH_3$	9.65	19.060	10.2	63.72	298	220
$(CO)_3MnC_5H_4CO_2^-NH_4^+$	9.47	18.88	4.6	62.97	298	220
$(CO)_3MnC_5H_4S{-}S$	9.59	18.84	11.9	62.97	298	220
$(CO)_3MnC_5H_4SO_2H$	9.43	18.77	6.1	62.61	298	220
	9.30	18.51	6.3	61.74		
$(CO)_3MnC_5H_4CHO$	9.24	18.23	10.2	60.89	298	220

TABLE 11 (continued)

Compound	$\nu(\pm 1/2 \rightarrow \pm 3/2)$ (MHz)	$\nu(\pm 3/2 \rightarrow \pm 5/2)$ (MHz)	η (%)	e^2Qq/h (MHz)	Temperature (°K)	Ref.
$(CO)_3MnC_5H_4CO_2^-Na^+$	—	19.30	—	—	298	220
$(CO)_3MnC_5H_4CONH_2$	—	18.57	—	—	298	220
	—	17.83	—	—	298	220
$(CO)_3MnC_5H_4COCl$	—	17.960	—	—	77	241
$(CO)_3MnC_5H_4SO_2Cl$	—	18.486	—	—	77	241
$(CO)_3MnC_5H_4SO_3C_2H_5$	—	19.300	—	—	77	241
$(CO)_3MnC_5H_4C_2H_5$	—	19.380 19.760	—	—	77	241
$(CO)_3MnC_5H_4COCH_2Cl$	—	18.180	—	—	77	241
$(CO)_3MnC_5H_4COCH_2Br$	—	18.150	—	—	77	241
$(CO)_3MnC_5H_3(CH_2Cl)_2$	—	18.820	—	—	77	241
$(CO)_3MnC_5H_3(CH_3)\cdot(SO_3^-NH_3^+C_6H_4CH_3)$	—	19.610	—	—	298	220
$(CO)_3MnC_6H_6^+Br_3^-$	7.712	15.420	1.4	51.40	298	246
$(CO)_3MnC_6H_6^+I_3^-$	7.910	15.819	0.7	52.73	298	246
$(CO)_3MnC_6H_6^+BF_4^-$	7.750	15.463	4.3	51.56	298	246
$(CO)_3MnC_6H_6^+ClO_4^-$	7.742	15.460	3.4	51.55	298	246
$(CO)_3MnC_6H_6^+B(C_6H_5)_4^-$	7.898	15.726	5.9	52.45	298	246
$(CO)_3MnC_6H_5CH_3^+Br_3^-$	8.111	16.198	3.6	54.00	298	246
$(CO)_3MnC_6H_5CH_3^+I_3^-$	7.998	15.947	4.9	53.18	298	246
$(CO)_3MnC_6H_5CH_3^+BF_4^-$	8.429	16.834	3.3	56.13	298	246
$(CO)_3Mn[1,3,5\text{-}(CH_3)_3C_6H_3]^+Br_3^-$	8.676 8.733	17.356 17.490	0 0	57.84 58.22	298	246
$(CO)_3Mn[1,3,5\text{-}(CH_3)_3C_6H_3]^+I_3^-$	8.628	17.225 16.968	3.9	57.42	298	246

$(CO)_3Mn[1,3,5\text{-}(CH_3)_3C_6H_3]^+BF_4^-$	8.283	16.537	3.7	55.14	298	246
$(CO)_3Mn(CH_3)_5C_6H^+Br_3^-$	9.004	17.953	4.9	59.87	298	246
$(CO)_3Mn(CH_3)_6C_6^+Br_3^-$	9.334	18.544	7.2	61.88	298	246
$(CO)_3Mn(CH_3)C_6^+I_3^-$	9.287	18.512	5.1	61.74	298	246
$(CO)_3Mn(CH_3)_6C_6^+BF_4^-$	9.545	19.085	1.4	63.62	298	246
$(CO)_3Mn[1,4\text{-}(CH_3)_2C_6H_4]^+Br_3^-$	—	16.385	—	—	298	246
$(CO)_3Mn(CH_3)_5C_6H^+I_3^-$	—	17.959	—	—	298	246
$(CO)_3Mn(CH_3)_5C_6H^+BF_4^-$	—	17.338	—	—	298	246
$(CO)_2MnC_5H_5$(*cis*-cyclooctene)	11.12 11.15	17.930	—	61.93	298	245
$(CO)_2MnC_5H_5$(cyclopentene)	10.87	18.33	—	61.61	298	245
$(CO)_2MnC_5H_5$(cycloheptene)	11.27 11.23	17.81	—	60.77	298	245
$(CO)_2MnC_5H_5$(vinylene carbonate)	10.70	16.63	—	57.82	298	245
$(CO)_2MnC_5H_5$(norbornylene)	—	18.96	—	—	298	245
$(CO)_2MnC_5H_5L$ [a]	—	17.90	—	—	298	245
$(CO)_2MnC_5H_5L$ [b].	—	17.96	—	—	298	245
$(CO)_2MnC_5H_5$(2,5-norbornadiene)	—	17.27	—	—	298	245
$(CO)_2MnC_5H_5$(piperidine)	—	17.18	—	—	298	245
$(CO)_2MnC_5H_5$(pyridine)	—	17.62	—	—	298	245
$(CO)_2MnC_5H_5(C_6H_5CN)$	—	18.22	—	—	298	245
$(CO)_2MnC_5H_5(CH_3CN)$	—	18.71 18.63	—	—	298	245
$(CO)_2MnC_5H_5P(CH_3)_3$	—	18.13	—	—	298	245
$(CO)_2MnC_5H_5P(i\text{-}C_3H_7)_3$	—	18.44	—	—	298	245
$(CO)_2MnC_5H_5(PBu_3^n)$	—	18.66	—	—	298	245
$(CO)_2MnC_5H_5P(C_6H_5)_3$	—	18.82	—	—	298	245
$(CO)_2MnC_5H_5P(OC_6H_5)_3$	—	19.78	—	—	298	245
$(CO)_2MnC_5H_5As(C_6H_5)_3$	—	19.38	—	—	298	245
$(CO)_2MnC_5H_5As(OC_6H_5)_3$	—	20.92	—	—	298	245
$(CO)_2MnC_5H_5Sb(C_6H_5)_3$	—	19.78	—	—	298	245

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[a] *endo, cis*-Bicyclo[2,2,1]-5 heptene-2,3-dicarboxylic anhydride.

[b] 1,2,3,6-tetrahydrophthalic anhydride.

241,242] correlated the ^{55}Mn quadrupole coupling constants to σ-constants of the substituents on the cyclopentadienyl ring (eqn. 33).

$$A = A_0 + \alpha\sigma_I + \beta\sigma_R \tag{33}$$

where

A = e^2Qq/h or $\nu(\pm 3/2 \rightarrow \pm 5/2)$

σ_I, σ_R = induction and conjugation constants of the substituents

and α, β = coefficients which determine the transmission properties of a system in relation to the induction and conjugation influence of the substituent.

The results show [241] that in this system of compounds, the influence of a substituent is transmitted to the metal from the cyclopentadienyl ring in accordance with a conjugative mechanism. The asymmetry parameters for the compounds in which the substituents are of the type COR (R = CH_3, CF_3 or C_6H_5) are appreciably greater than the asymmetry parameter for C_5H_5-$Mn(CO)_3$. This has been explained [241] as due either to a direct interaction of the substituent with the metal atom giving rise to a distortion of the ideal structure of the molecule $C_5H_5Mn(CO)_3$, or to a fulvene-like rearrangement of the cyclopentadienyl ring. Temperature dependence of the ^{55}Mn NQR frequencies in π-pyrrolenylmanganesetricarbonyl and π-cyclopentadienylmanganesetricarbonyl suggest [243] that the pyrrolenyl—manganese bond is significantly distorted via a pyrrole slippage. Thus, the pyrrolenyl—manganese bond might be described [243] as a four-electron metal—heterocyclic allylic and two-electron metal—olefin bond.

Effect of substitution in the cyclopentadienyl ring on the ^{55}Mn NQR in the complexes of the series $RC_5H_4Mn(CO)_3$ has also been studied by Brill and Long [220]. The resonance frequencies and hence the coupling constants of Mn^I increase as the ring becomes electron rich. This has been explained [220] as due to the electronic polulation of d-orbitals, the population of d_{z^2}, d_{xz} and d_{yz} being greater than that of $d_{x^2-y^2}$ and d_{xy} orbitals in these compounds. Substitution of a CO group by another ligand such as $(C_6H_5)_3As$ and $(C_6H_5)_3$-Sb sharply raises the asymmetry parameter and changes the coupling constant considerably at the manganese site [244].

In compounds of the type π-$C_5H_5Mn(CO)_2L$ where L is a cycloolefin, η decreases in the order, *cis*-cyclooctene, cyclopentene and cycloheptene [245]. This order parallels an increase in the olefin ring strain; as the strain increases, the strength of the manganese—olefin bond, which acts to relieve the strain, increases [245]. When L is a group V donor atom derivative, the frequencies roughly parallel the σ-donor and π-acceptor abilities of the ligands. For example, the trend in resonance frequencies for phosphorus donor ligands, viz., $P(OC_6H_5)_3 > P(C_6H_5)_3 > P(alkyl)_3$, parallels the π-acceptor ability of the ligand and the reverse is the trend for the σ-donor ability.

In compounds of the type $[(CH_3)_nC_6H_{6-n}Mn(CO)_3]^+$, changes in size, symmetry and charge density of the anion produce a variation of about 3% in ^{55}Mn coupling constant [246]. The lattice effects in these compounds seem to be about the same magnitude as those found in organic compounds and smaller than those in hexahalometallates. The ^{55}Mn ($\pm 3/2 \rightarrow \pm 5/2$) transition frequencies for the Br_3^- and I_3^- salts of $[(CH_3)_nC_6H_{6-n}Mn(CO)_3]^+$ correlate linearly with the number of methyl groups on the aromatic ring [246].

H. Rhenium-185 and rhenium-187 resonances

^{185}Re and ^{187}Re NQR frequencies in $Re_2(CO)_{10}$ have first been observed by Segel and Barnes [247]. The large asymmetry parameter observed in this compound has been explained in terms of both anisotropic vibration [248] and electronic configuration [249]. The increase in the asymmetry parameter from 63% at 26.5° C to 88% at liquid nitrogen temperature has been explained by Harris [248] in terms of large anisotropic vibrations which leave q_{zz} relatively unaffected both in direction and in magnitude but affect q_{xx} and q_{yy} in such a way as to make q_{yy}/q_{xx} much larger than 1. The increase in η at low temperature is due to decrease in motion in both x and y directions but a greater decrease in the x-direction. On the other hand, Segel and Anderson [249] attribute the increase in η with decreasing temperature to a rearrangement of the orbital configuration so as to allow one of the components of the EFG tensor to increase to a value almost equal to q_{zz}.In fact, extrapolation of the η versus temperature curve does predict a value of η = 100% at about 0 K. It is interesting to note that the forbidden transition ($\mp 1/2 \rightarrow \pm 5/2$) of ^{185}Re and ^{187}Re has been observed [241] in this system (71.51 and 75.45 MHz respectively at 77 K).

Nesmayanov et al. [241,242] have studied the ^{185}Re and ^{187}Re NQR in substituted π-cyclopentadienylrheniumcarbonyl compounds. The η values are greater in these compounds than in the corresponding manganese compounds. Comparison of e^2Qq values for ^{55}Mn and ^{187}Re in similar compounds indicates that the EFG at the Re nucleus is about twice as large as that at the Mn nucleus.

I. Antimony-121 and antimony-123 resonances

^{121}Sb and ^{123}Sb NQR in a number of Menshutkin complexes based on $SbCl_3$ have been reported [172,174,176–178,180,229,232,250–252]. Generally the asymmetry parameter, η, at the antimony site is found to be 10—15% in these complexes except in $SbCl_3 \cdot C_6H_5NH_2$ which has η = 3% [253]. This low η for $SbCl_3 \cdot C_6H_5NH_2$ has been attributed to fortuitous balancing of EFG components from the external atoms as a result of their arrangement. A considerable change in η has been associated with a distortion of shape of $SbCl_3$ and $SbBr_3$ pyramids in their complexes with aromatic hydrocarbons. ^{121}Sb and ^{123}Sb coupling constants in a few of the Menshutkin complexes based on $SbCl_3$ and $SbBr_3$ indicate that the complexes are formed mainly through the π-electrons of the benzene ring. Zemmukhova et al. [196] have reported ^{121}Sb and ^{123}Sb resonances in a number of oxalatofluoride and nitratofluoride complexes of Sb^{III} such as $K_2Sb_2(C_2O_4)F_6$ and $K_3Sb_2(NO_3)_2F_7$.

^{121}Sb and ^{123}Sb resonances in $SbCl_5 \cdot POCl_3$ and $SbCl_5 \cdot CH_3CN$ have been observed by Schneider and Dilorenzo [271]. In $SbCl_5 \cdot POCl_3$, the ^{121}Sb and ^{123}Sb resonances are consistent with an unusually large η and the temperature dependence of ^{121}Sb and ^{123}Sb resonances indicates a large axial anisotropy in the x direction (lowest EFG direction).

J. Cobalt-59 resonances [254]

Hartman et al. [200,201] have studied the ^{59}Co, ^{35}Cl and ^{37}Cl NQR in *trans*-$[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$. The quadrupole coupling constant and η at the cobalt site have been shown to be 71.73 MHz and 0.222 respectively. Using the Townes—Dailey procedure, they have calculated an ionic character of 75—80% for the Co—Cl bond in this complex. Watanabe and co-workers [198,204,255,256] have studied ^{59}Co NQR in a number of cobalt-ammine complexes. The coupling constants for the compounds (Table 12) of the type $[Co(NH_3)_5Cl]Cl_2$ (33.71 MHz) are about half those for the corresponding praseo salts such as *trans*-$[Co(NH_3)_4Cl_2]Cl$ (59.23 MHz) and *trans*-$[Co(en)_2Cl_2]Cl$ (60.63 MHz). Comparison of the coupling constants of *cis* and *trans*-dichlorobisethylenediaminecobalt(III) complexes has shown that e^2Qq in the *cis* complexes are considerably smaller than those for the *trans* complexes and are comparable to those for $[Co(NH_3)_5Cl]^{2+}$ complexes. Large variation in ^{59}Co coupling constants have been observed in *trans*-$[Co(en)_2Cl_2]^+$ complexes when the anion is changed. For example, on going from *trans*-$[Co(en)_2Cl_2]Cl$ to *trans*-$[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$, the ^{59}Co e^2Qq increases by about 15% and on going from *trans*-$[Co(en)_2Br_2]ClO_4$ to *trans*-$[Co(en)_2Br_2]Br \cdot HBr \cdot 2H_2O$ there is an increase of ca. 25% in the ^{59}Co e^2Qq [199]. The lower value of ^{59}Co e^2Qq in *trans*-$[Co(tn)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$ compared to *trans*-$[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$ has been attributed by Brill and Hugus [203] to the difference in the interaction of the carbon atom with the cobalt valence electrons in the two compounds considered.

La Rossa and Brown [197] have studied a number of Co^{III} complexes, known as cobaloximes, of the type $Co(dh)_2L'L''$ (dh = dimethyl glyoximatomono anion; $L',L'' = Cl^-$, Br^-, NC_5H_5, $(C_6H_5)_3P$, $(OCH_3)_3P$, $(n\text{-}C_4H_9)_3P$, $(C_6H_5)_3As$ etc.). The ^{59}Co NQR data for these complexes have been analysed in terms of a partial field gradient model. Good agreement with the experimental results could be obtained only when it is assumed that the partial field gradient tensor parameter for the equatorial ligand nitrogen becomes more positive as the axial ligand contribution increases in such a way that the total field gradient is approximately constant [197].

A large number of investigations (Table 13) have been carried out on dicobaltoctacarbonyl, $Co_2(CO)_8$, and its various substituted complexes [217—219,222,240,258—264]. From the pure quadrupole resonance of ^{59}Co in $Co_2(CO)_8$, two e^2Qq (90.19 and 89.30 MHz at 77 K), which are almost equal for the two cobalt sites, and two η values (31 and 48% respectively), which are considerably different, have been obtained [240,262]. The asymmetry

TABLE 12

Cobalt-59 NQR parameters for some cobalt(III) amine complexes

Compound	$\nu(\pm1/2\rightarrow\pm3/2)$ (MHz)	$\nu(\pm3/2\rightarrow\pm5/2)$ (MHz)	$\nu(\pm5/2\rightarrow\pm7/2)$ (MHz)	η (%)	e^2Qq/h (MHz)	Temperature [a] (°K)	Ref.
trans-$[CoCl_2(NH_3)_4]Cl$	(4.531)	8.370	12.665	13.6	59.23	R.T.	255
trans-$[CoCl_2(en)_2]Cl$	5.367	8.368	12.893	27.2	60.63	R.T.	255
trans-$[CoCl_2(en)_2]Br$	4.890	8.405	12.821	20.4	60.08	R.T.	198
trans-$[CoCl_2(en)_2]I$	4.528	8.238	12.485	15.6	58.41	R.T.	198
trans-$[CoCl_2(en)_2]SCN$	—	8.395	12.870	24.5	60.43	296	199
trans-$[CoCl_2(en)_2]ClO_4$	4.601	8.452	12.798	14.8	59.86	R.T.	198, 199
	4.614	8.494	12.858	14.6	60.14		
trans-$[CoCl_2(en)_2]NO_3$	4.777	8.877	13.426	13.2	62.78	R.T.	255
trans-$[CoCl_2(en)_2]BrO_3$	—	9.057	13.880	23.8	65.15	296	199
trans-$[CoCl_2(en)_2]Cl \cdot HCl \cdot xH_2O$	5.979	10.001	15.296	22.2	71.73	R.T.	199, 200
trans-$[CoCl_2(tn)_2]Cl \cdot HCl \cdot 2H_2O$	4.683	8.691	13.137	13.2	61.41	298	203
trans-$[CoBr_2(en)_2]Br$	(5.117)	8.392	12.860	23.5	60.36	R.T.	255
trans-$[CoBr_2(en)_2]Br \cdot HBr \cdot 2H_2O$	—	10.104	15.503	24.4	72.80	R.T.	200
trans-$[CoBr_2(en)_2]ClO_4$	—	8.096	12.264	14.9	57.38	296	199
cis-$[CoCl_2(en)_2]Cl \cdot H_2O$	3.168	4.980	7.668	26.8	36.05	R.T.	256
cis-$[CoCl_2(en)_2]NO_3$	2.654	4.741	7.201	17.3	33.71	R.T.	256
$[CoCl(NH_3)_5]Cl_2$	2.733	4.399	6.758	25.1	31.74	R.T.	204
$[CoCl(NH_3)_5]SO_4 \cdot H_2SO_4$	2.405	4.773	7.161	4.0	33.43	R.T.	204
	2.526	4.892	7.364	8.9	34.39		

[a] R.T. = Room temperature.

TABLE 13

Cobalt-59 NQR data for a few derivatives of cobalt carbonyl

Compound [a]	Temperature (°K)	$\nu(\pm 1/2 \to \pm 3/2)$ (MHz)	$\nu(\pm 3/2 \to \pm 5/2)$ (MHz)	$\nu(\pm 5/2 \to \pm 7/2)$ (MHz)	e^2Qq/h (MHz)	η (%)	Ref.
$Co_2(CO)_8$	77	8.417	12.334	19.132	90.18	31.49	262, 264
		10.344	11.818	18.671	89.30	48.37	
$Cl_3SiCo(CO)_4$	298	—	18.500	27.960	130.70	3.0	259, 217
$Cl_3SiCo(CO)_3P(n\text{-}C_4H_9)_3$	298	—	16.270	24.400	113.90	0	259
$(C_6H_5)_3SiCo(CO)_4$	298	—	14.434	21.662	101.09	0	259
$Cl_3GeCo(CO)_4$	303	11.443	22.741	34.140	159.33	3.9	217
		11.571	23.055	34.598	161.476	3.0	
$Br_3GeCo(CO)_4$	298	—	22.918	34.573	161.340	12.0	217
$I_3GeCo(CO)_4$	298	—	22.694	34.078	159.080	4.0	217
$(C_6H_5)_3GeCo(CO)_4$	300	—	15.641	22.486	109.630	5.0	258
$Cl_3GeCo(CO)_4PBu^n_3$	298	—	23.710	35.560	166.000	0	259
$Cl_3GeCo(CO)_4P(C_6H_5)_3$	298	—	22.310	33.580	156.90	8	259
			22.320	33.600	156.80	8	
$(C_6H_5)_3GeCo(CO)_3P(OC_6H_5)_3$	300	9.67	15.664	24.065	113.02	25	258
$Cl_2Ge[Co(CO)_4]_2$	298	—	22.200	33.340	155.60	4	218
			20.400	30.990	145.00	17	
$Cl_3SnCo(CO)_4$	298	11.675	23.380	35.020	163.40	0	217
$Br_3SnCo(CO)_4$	298	11.650	22.790	34.269	159.91	6	217
$I_3SnCo(CO)_4$	298	11.052	21.815	32.786	153.04	6	217
$(C_6H_5)_3SnCo(CO)_4$	298	—	14.852	22.304	104.11	5	217
$(C_6H_5CH_2)_3SnCo(CO)_4$	300	—	14.24	21.51	100.4	15	265
$(CH_3)_3SnCo(CO)_4$	298	—	13.810	20.730	96.80	3	218
				20.470			
$Cl_3SnCo(CO)_3P(OC_6H_5)_3$	300	—	22.768	34.167	159.46	3	258
$(CH_3)_3SnCo(CO)_3P(OC_6H_5)_3$	300	—	14.830	22.259	103.88	3	258
$Cl_3SnCo(CO)_3PBu^n_3$	300	—	24.800	37.190	173.60	0	217
$(C_6H_5)_3SnCo(CO)_3P(OCH_3)_3$	300	—	14.871	22.322	104.19	4	258
$(C_6H_5)_3SnCo(CO)_3P(OC_6H_5)_3$	300	—	15.264	23.491	110.44	27	258

$(C_6H_5)_3SnCo(CO)_3PBu^n_3$	338	—	14.727	22.107	103.18	4	258
$Cl_2Sn[Co(CO)_4]_2$ [b]	298	—	21.250	31.940	149.00	6	218,
			20.480	30.940	144.60	13	219
$Cl_2Sn[Co(CO)_4]_2$ [c]	298	10.81	21.640	32.490	151.60	0	218
		10.46	19.580	28.580	138.20	12	
$Br_2Sn[Co(CO)_4]_2$	298	—	20.980	31.640	148.00	16	218
			20.610	31.090	145.10	0	
$(CH_3)_2Sn[Co(CO)_4]_2$	298	8.15	15.260	22.650	105.70	0	218
$(C_6H_5)ClSn[Co(CO)_4]_2$	298	—	18.356	27.500	128.40	5	219
			18.100	27.250	126.90	9	
$(C_6H_5)_2Sn[Co(CO)_4]_2$	298	—	16.075	24.219	113.10	9	219
			16.030	24.089	112.70	6	
$ClSn[Co(CO)_4]_3$	298	—	19.480	29.340	135.90	9	218
			18.890	28.400	132.60		
$BrSn[Co(CO)_4]_3$	298	—	18.82	28.47	133.0	14	218
$(CH_3)Sn[Co(CO)_4]_3$	298	—	17.80	26.70	124.6	0	218
			17.56	26.47	122.5	0	
			17.22	25.77	120.2	0	
			16.97	22.57	119.3	10	
			16.66	25.34	118.6	18	
$(C_6H_5)_3SnCo(CO)_2[P(OCH_3)_3]_2$	300	10.496	14.088	22.017	104.20	37	258
$(C_6H_5)_3SnCo(CO)_2[P(OC_6H_5)_3]_2$	300	—	12.499	19.798	95.40	55	258
$Sn[Co(CO)_4]_4$	298	—	18.470	27.69	129.2	0	218
$(C_6H_5)_3Pb[Co(CO)_4]$	298	—	15.806	23.741	110.82	5	217
$(C_6H_5)_3PbCo(CO)_3P(OC_6H_5)_3$	300	—	16.656	25.599	120.28	26	258
$Hg[Co(CO)_4]_2$	298	—	15.99	24.000	112.0	5	218
			15.81	23.75	110.8	0	
$Hg[Co(CO)_3P(OC_6H_5)_3]_2$	300	—	15.844	24.387	114.65	27	258
			15.243	22.901	106.81	6	
$[Co(CO)_3P(C_6H_5)_3]_2$	298	—	20.96	31.46	146.8	0	217
$[Co(CO)_3P(OC_6H_5)_3]_2$	273	11.219	22.281	33.440	156.10	4	263
$[Co(CO)_3P(OCH_3)_3]_2$	273	10.372	20.573	30.868	144.08	4.6	263
$[Co(CO)_3P(OC_2H_5)_3]_2$	273	10.169	20.232	30.249	141.674	2.6	263
$[Co(CO)_3PBu^n_3]_2$	273	10.163	20.170	30.272	141.291	3.8	263
$[Co(CO)_4]Co(CO)_3[P(C_6H_5)_3]_2$	298	—	22.77	34.20	159.7	5	217
$Co(CO)_3[P(C_6H_5)_3]^+_2B(C_6H_5)^-_4$	293	—	22.006	33.641	157.75	22	260

TABLE 13 (continued)

Compound	Temperature (°K)	$\nu(\pm 1/2 \to \pm 3/2)$ (MHz)	$\nu(\pm 3/2 \to \pm 5/2)$ (MHz)	$\nu(\pm 5/2 \to \pm 7/2)$ (MHz)	e^2Qq/h (MHz)	η (%)	Ref.
$Co(CO)_3[P(OCH_3)_3]^{+}_{2}B(C_6H_4)^{-}_{4}$	298	9.7	19.26	29.12	136.1	13	260
$Co(CO)_2[P(OCH_3)_3]^{+}_{3}B(C_6H_5)^{-}_{4}$	298	15.68	18.09	28.56	136.3	47	260
$Co[P(OCH_3)_3]^{+}_{5}B(C_6H_5)^{-}_{4}$	298	—	21.93	32.92	153.7	4	260
$Co(CO)_6(HC{\equiv}CH)$	273	10.530	11.109	17.584	84.655	54.3	264
			(21.625)	(28.685)			
		10.757	11.115	17.593	84.875	55.9	
			(21.876)	(28.786)			
$Co(CO)_6(Bu^tC{\equiv}CH)$	273	9.945	10.850	17.165	82.377	51.7	264
				(20.795)			
			10.805	17.064			
$Co_2(CO)_6(HOCH_2C{\equiv}CCH_2OH)$	273	10.220	11.465	18.127	86.856	49.8	264
		10.798	11.263	17.826	86.043	55.7	
$Co_2(CO)_6(F_3C{\equiv}CF_3)$	273	10.003	8.396	13.091	64.746	73.8	264
		9.747	8.396	13.091	64.684	72.2	
		9.757	8.250	12.816	63.523	74.1	
		9.605	8.250	12.816	63.485	73.1	
$Co_2(CO)_6(C_6H_5C{\equiv}CC_6H_5)$	273	10.416	9.429	14.802	72.596	67.5	264
		11.173	10.144	15.936	78.101	67.1	
$Co_3(CO)_6(f_4fars)$	273	10.114	11.830	18.684	89.097	47.3	264
		10.564	11.940	18.870	90.306	49.2	
$Co_2(CO)_6(\pi\text{-}C_7H_8)$	273	8.125	10.98	17.17	81.14	37.1	264
		7.75	11.31	17.55	82.74	31.8	
$Co_2(CO)_4(\pi\text{-}C_7H_8)_2$	273	10.949	9.717	15.172	74.684	70.0	264
		10.793	9.485	14.873	73.212	69.7	

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[a] $f_4fars = (CH_3)_2AsC{=}C{-}As(CH_3)_2CF_2CF_2$; Bu^t = tertiary butyl; Bu^n = *n*-butyl.

[b] Powder from solution.

[c] Sublimed.

parameter for the two sites approach each other with increasing temperature. Moobery et al. [262] have attributed the two different η values and their temperature dependence to the distortion of the regular octahedron around the two cobalt sites to different extents.

^{59}Co NQR spectra of a number of derivatives of $Co_2(CO)_8$ have been reported by Chia et al. [263,264]. The NQR parameters obtained for these complexes have been interpreted in terms of the electronic population in the *d* orbitals of the cobalt atom. For the alkyne complexes such as $(RC \equiv CR')Co_2(CO)_6$ ($R = R' = H, CF_3, CH_2OH, C_6H_5$; $R = H$; $R' = C(CH_3)_3$), e^2Qq and η values have been related to the electronegativities of R and R′ and e^2Qq values have been found to be inversely proportional to η. Substantial differences in e^2Qq have also been observed with gross structural variations.

Brown et al. [217] have interpreted the variation in the EFG at the cobalt site in compounds of the type $MX_3Co(CO)_4$ (M = Si, Ge, Sn and Pb; X = Cl, Br, I and C_6H_5) in terms of σ and π bonding of MX_3 to the cobalt atom. The results show that the groups MX_3 which are poor donors and/or strong acceptors cause large ^{59}Co quadrupole coupling constants. ^{59}Co e^2Qq values have also been used [217] in studying the electronic effects within the MX_3 group. For example, the low coupling constant for $SiCl_3Co(CO)_4$ compared to other $MX_3Co(CO)_4$ compounds is shown to indicate an extensive Si—Cl $d\pi$—$p\pi$ bonding. In the series $GeCl_3$-, $GeBr_3$- and $GeI_3Co(CO)_4$, the essential constancy of the ^{59}Co coupling constants has been shown [217] to be due to variations in germanium—halogen π-bonding in the order Cl > Br > I. ^{59}Co NQR in a series of complexes derived from cobalt carbonyl and organotin (or organogermanium) compounds has been studied by Nesmeyanov et al. [222]. ^{59}Co coupling constants in these complexes increase with increasing electronegativity of the substituent on germanium or tin. ^{59}Co e^2Qq values correlate with inductive and conjugative constants of the substituents and this correlation was used [222] to show that in $RR'_2SnCo(CO)_4$, there exists some bond multiplicity in the Co—Sn bond.

Spencer et al. [218] have reported ^{59}Co NQR in compounds of the type $X_nSn[Co(CO)_4]_{4-n}$ where X = Cl, Br or CH_3 and n = 0, 1, 2 or 3. The e^2Qq values have been analysed in terms of the population of 3*d* as well as 4*p* orbitals. ^{59}Co e^2Qq in these complexes increases on increasing the value of n when X = Cl or Br and decreases on increasing the value of n when X = CH_3. It has been shown [218] that the e^2Qq values at the cobalt site correlate smoothly with the highest frequency CO stretching vibration (in hexane) of these compounds. Analysis of the coupling constants suggests that chlorine is relatively strongly π-bonded towards tin in these compounds than bromine. Pribula et al. [260] have calculated e^2Qq for the complexes $[M(CO)_{5-x}P_x]^n$ where P is $P(C_6H_5)_3$ or $P(OCH_3)_3$ and M is Mn ($n = -1$), Fe ($n = 0$) or Co ($n = 1$) in different electronic configurations using SCF atomic wave-functions. Comparison of the calculated e^2Qq with observed e^2Qq indicates [260] that the radial orbitals of the central metal ion become more populated compared to the axial orbitals with increased charge on the central metal ion.

Boyd and Brown [258] have studied ^{59}Co NQR in compounds of the type $XCo(CO)_2L_2$ where X is $Sn(C_6H_5)_3$ or other similar group IV metal derivatives and L is $P(n\text{-}C_4H_9)_3$, $P(OCH_3)_3$, $P(OC_2H_5)_3$ or $P(OC_6H_5)_3$. The σ-donor and π-acceptor characteristics of the ligand L play an important role in deciding the ^{59}Co coupling constant in these complexes. Axial substitution does not markedly change the e^2Qq at cobalt when both axial ligands are of π-acceptor character [258].

Harris [257] has observed the ^{59}Co NQR in $Cs[(1,2\text{-}B_9C_2H_{11})_2Co]$ and explained the coupling constant in terms of the bonding of the $[1,2\text{-}B_9C_2H_{11}]^{2-}$ moiety to Co^{III}. The 1,2 carbons and the 4,7,8 borons are pratically identical in their bonding to Co^{III}.

K. Niobium-93 resonances

NQR of ^{93}Nb in $[(CH_3)_4N]_2[(Nb_6Cl_{12})Cl_6]$ has been observed at room temperature by Edwards et al. [137]. An approximate population analysis for electrons in $[Nb_6Cl_{12}]^{4+}$ cluster has shown [137] that fourteen electrons are available for metal—metal bond as predicted by theory. ^{93}Nb NQR in NbF_5 and a number of its adducts have been reported [266]. NQR data for these complexes are consistent with low values for η at the niobium nucleus. The interaction of XeF^+ and NbF_6^- or $Nb_2F_{11}^-$ ions in $XeF_2 \cdot NbF_5$ complexes has been discussed [266] in terms of the point charge model.

L. Indium-115 resonances

^{115}In NQR in $(NH_4)_2\ InCl_5 \cdot H_2O$ has been studied by Carr et al. [267] as a function of temperature. The ^{115}In resonance in this complex shows an unusually large temperature dependence and the value shows a linear decrease with decrease in temperature. Analysis of both ^{115}In and ^{35}Cl NQR data in this complex indicates that the complex is predominantly ionic with greater covalent character in the indium—water bond than in the indium—chlorine bond.

^{115}In NQR parameters as well as those for ^{75}As and ^{123}Sb in the 1 : 1 complexes of $(CH_3)_3In$ with $(CH_3)_3N$, $(CH_3)_3P$, $(CH_3)_3As$ and $(CH_3)_3Sb$ are consistent with a small $d\pi$—$p\pi$ bonding between $(CH_3)_3In$ and $(CH_3)_3P$ and its heavier congeners [235].

M. Bismuth-209 resonances

Guryanova and co-workers [268,269] have studied the ^{209}Bi NQR in a number of complexes of $BiCl_3$ with different π-donors such as $CH_3OC_6H_5$, CH_3OCH_3 and CH_3CN. The variations in e^2Qq and η in these complexes depend mainly on the geometry of the complexes. The value of η in these complexes varies from 14% to 34% with the distortion of $BiCl_3$ being greater than that in similar complexes of $SbCl_3$. Bi-209 NQR in the complex $AlBr_3 \cdot BiBr_3$ has also been reported [113].

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