NUCLEAR QUADRUPOLE RESONANCE AND ITS APPLICATION IN INORGANIC CHEMISTRY

Masaji Kubo and Daiyu Nakamura

Department of Chemistry, Nagoya University, Chikusa, Nagoya, Japan

I. Introduction

Pure quadrupole resonance or nuclear quadrupole resonance (NQR) was first observed by Dehmelt and Krüger (*17*), who published in 1950 the results of their study on the chlorine resonance absorption of solid *trans*-dichloroethylene. Since then, the method has been applied to a number of organic as well as inorganic compounds and has yielded valuable information on the electronic structure of chemical bonds. Inorganic compounds having a simple chemical formula are not necessarily simple from the standpoint of nuclear quadrupole spectroscopy. On the other hand, some metal complex compounds are amenable to this method of attack, because to the first approximation one can discuss the electronic state of a single complex ion. The first experimental observation of the NQR absorption of coordination compounds was reported in 1959 by Nakamura *et al.* (*61*) on potassium tetraiodomercurate. Among various metal complexes, perhaps those of $R_2[MX_6]$ type have been most extensively studied partly because a systematic investigation was feasible with a variety of such complexes and also because the intensity of absorption is relatively high and serious trouble is not involved as regards the asymmetry parameter discussed below. For this reason, the present review is focused largely on this type of metal complex having halogen atoms as ligands. Readers interested in results obtained for the NQR of a wider variety of inorganic as well as organic compounds are directed to excellent reviews already published (*9, 13, 16, 42, 63, 72*). Detailed numerical data are available from some recent compilations (*71, 75*).

In discussing the nature of metal-ligand bonds in metal complexes, use is often made of rather vague terms such as covalent character, ionic character, and the hybrid of these to explain various properties of complex compounds such as, for instance, spectroscopic data, magnetic behavior. However, in order to establish these concepts in a quantitative manner and to express the transition from an ideal covalent bond to a pure ionic bond, we must define the extent of covalent character by resorting to some experimental parameters that are characteristic of metal-ligand bonds and are measurable accurately. Pure quadrupole resonance frequencies can give the necessary information.

Another advantage of pure quadrupole resonance spectroscopy arises from the high accuracy of frequency measurements obtainable in radiowave spectroscopy. The statement that, for instance, a certain quadrupole resonance line is characteristic of a Pt—Cl bond or a $[PtCl_6]^{2-}$ ion might imply that the frequency is independent of temperature and the kinds of cations with which the complex anions form crystals with possible participation of water of crystallization. This is true within the accuracy of a few per cent, and this experimental accuracy is more than enough for discussing the nature of chemical bonds in view of the present stage of development in the theory of chemical bonds. Nevertheless, owing to the high accuracy, we can determine the temperature coefficient of resonance frequencies accurately and discuss the effect of neighboring cations in some detail, and thus can provide additional information on the nature of some metal-ligand bonds.

Natural limitation is imposed on the application of NQR spectroscopy to inorganic chemistry by the fact that only a limited number of isotopic nuclei have an electric quadrupole moment and are accessible to NQR spectroscopy. Another disadvantage is that a fairly large amount of sample is needed for detecting resonance lines. Especially when complex ions are less symmetrical, signals are in general weak and often escape detection when a small amount of sample is available. From the technical point of view, a single NQR spectrometer cannot cover the whole wavelength range of importance, as for instance infrared spectrometers or NMR spectrometers do. The most serious trouble we encounter in the analysis of NQR data is that, although theories have been developed to relate NQR frequencies to a so-called percentage ionic character (*25*), the theories are not mature enough to eliminate unavoidable assumptions being made in the analysis. In the last decade, nuclear magnetic resonance spectroscopy (*54*) has given an impetus to incorporate the nuclear quadrupole moment in discussing chemical shifts as well as line broadening. It is hoped that in the future nuclear quadrupole resonance along with other closely related physical methods of attack will contribute much to the elucidation of the electronic structure of inorganic compounds.

A. QUADRUPOLE COUPLING CONSTANT

Atomic nuclei having a nuclear spin equal to or greater than unity possess a nuclear quadrupole moment. The scalar electric quadrupole moment eQ of a nucleus is defined as

$$eQ = \int \rho r^2(3\cos^2\theta - 1)d\tau \qquad (1)$$

where e is the absolute value of the electronic charge, ρ is the charge density in a volume element $d\tau$ inside the nucleus at a distance r from the center, and θ is the angle which the radius vector r makes with the nuclear spin axis (*13*).

Chlorine isotopes, ^{35}Cl and ^{37}Cl, and bromine isotopes, ^{79}Br and ^{81}Br, have a nuclear spin $I = 3/2$, while ^{127}I has $I = 5/2$. Unfortunately, fluorine consists of a single isotopic species ^{19}F having $I = 1/2$ and therefore does not show NQR absorption.

Let it be supposed that a nucleus having an electric quadrupole moment, a chlorine nucleus for instance, is placed in an inhomogeneous electric field due to the charges of all surrounding electrons and nuclei other than the nucleus in question. Let the electric field be assumed to have an axial symmetry (threefold or higher axial symmetry), say about a Pt—Cl bond, and the symmetry axis be taken as the z-axis. According to the Laplace equation, the sum of field gradients or the sum of the second derivatives of electrostatic potential V vanishes:

$$\partial^2V/\partial x^2 + \partial^2V/\partial y^2 + \partial^2V/\partial z^2 = 0 \qquad (2)$$

For the axially symmetrical field, one has

$$\partial^2V/\partial x^2 = \partial^2V/\partial y^2 \qquad (3)$$

Hence a single parameter q suffices to describe the field inhomogeneity:

$$q \equiv \partial^2V/\partial z^2 = -2\partial^2V/\partial x^2 = -2\partial^2V/\partial y^2 \qquad (4)$$

According to quantum mechanics (*13*), the orientation of the axis of nuclear spin is quantized with respect to the z-axis and the contribution E_Q to the potential energy arising from the interaction of a nuclear quadrupole moment eQ with its surroundings is given by

$$E_Q = eQq\,\frac{3M_I^2 - I(I+1)}{4I(2I-1)} \qquad (5)$$

Here, I denotes the nuclear spin, and M_I is its component along the z-axis, i.e., the magnetic quantum number for the nuclear spin. The energy levels are shown in Fig. 1 for chlorine and bromine isotopes ($I = 3/2$) and iodine ($I = 5/2$). Thus we can observe a single NQR line (M_I: $\pm 1/2 \leftrightarrow \pm 3/2$) for each isotope of chlorine or bromine, and two lines, ν_1 ($\pm 1/2 \leftrightarrow \pm 3/2$) and ν_2 ($\pm 3/2 \leftrightarrow \pm 5/2$), of frequency ratio equal to 1:2 for iodine in accordance with the selection rule $\Delta M_I = \pm 1$, provided that all halogen atoms are crystallographically equivalent:

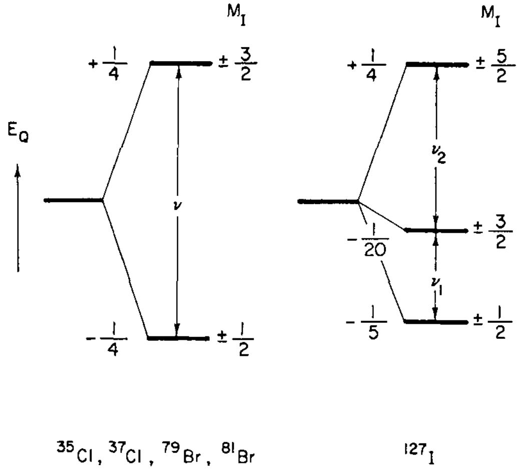

FIG. 1. Energy diagram for nuclei having an electric quadrupole moment placed in an inhomogeneous electric field.

$$\nu = \tfrac{1}{2}|eQq| \text{ for } I = 3/2 \tag{6}$$

$$2\nu_1 = \nu_2 = \tfrac{3}{10}|eQq| \text{ for } I = 5/2 \tag{7}$$

It should be noted that the sign of eQq is trivial in NQR spectroscopy and observed frequencies give only the absolute values of eQq. By convention, the quadrupole coupling constant, $|eQq|$, having the dimension of energy is divided by the Planck constant h and expressed in frequency units, Mc/sec. The ratio of resonance frequencies of different isotopes corresponding to one and the same transition is constant. For instance (*15*),

$$\nu(^{35}\text{Cl})/\nu(^{37}\text{Cl}) = Q(^{35}\text{Cl})/Q(^{37}\text{Cl}) = 1.269 \tag{8}$$

$$\nu(^{79}\text{Br})/\nu(^{81}\text{Br}) = Q(^{79}\text{Br})/Q(^{81}\text{Br}) = 1.197 \tag{9}$$

These relations merely serve for the identification of observed signals.

B. Asymmetry Parameter

When the electric field is not exactly axially symmetrical, theoretical calculations lead to the following equations (*9*, *14*, *18*). For $I = 3/2$, one has

$$\nu = \tfrac{1}{2}|eQq|(1 + \tfrac{1}{3}\eta^2)^{1/2} \tag{10}$$

and for $I = 5/2$

$$\nu_1 = \tfrac{3}{20}|eQq|(1 + 1.0926\eta^2 - 0.634\eta^4 + \cdots) \tag{11}$$

$$\nu_2 = \tfrac{3}{10}|eQq|(1 - 0.2037\eta^2 + 0.162\eta^4 - \cdots) \tag{12}$$

where the asymmetry parameter η is defined as

$$\eta = |\partial^2 V/\partial x^2 - \partial^2 V/\partial y^2|/|\partial^2 V/\partial z^2| \tag{13}$$

Therefore, from the two frequencies, ν_1 and ν_2, observed for iodine, one can evaluate both the quadrupole coupling constant and the asymmetry parameter (*49*). On the other hand, the quadrupole coupling constant cannot be calculated for chlorine and bromine, unless some reasonable assumption is made. The asymmetry parameters η observed for hexaiodo complexes $R_2[MI_6]$ are only a few per cent, as shown in Table I with potassium hexaiodoplatinate(IV) as an example. Hence η^2 amounts to at most 0.1%. It is not unreasonable to assume that $\eta = 0$ in evaluating eQq of hexachloro and hexabromo complexes, $R_2[MX_6]$. The small nonvanishing asymmetry parameters are attributable to the effect of neighboring ions in a crystal (*77*) and also to thermal motion: no finite asymmetry parameter is expected

TABLE I

Quadrupole Coupling Constant and Asymmetry Parameter of ^{127}I in Potassium Hexaiodoplatinate(IV)[a]

Temperature (°C)	eQq (Mc/sec)	η
26	1346.32 ± 0.05	0.034 ± 0.004
	1345.43 ± 0.05	0.029 ± 0.005
	1325.7 ± 0.5	0.02
−72	1355.31 ± 0.05	0.038 ± 0.004
	1352.51 ± 0.05	0.025 ± 0.005
	1339.3 ± 0.8	0.01
Liquid N_2	1361.50 ± 0.05	0.045 ± 0.004
	1357.38 ± 0.05	0.020 ± 0.007
	1350.2 ± 0.8	0.02

[a] Reference (*60*).

for an isolated $[MX_6]^{2-}$ ion having a perfect octahedral structure of O_h symmetry.

From Eqs. (11) and (12), one has $2\nu_1 \geq \nu_2$. This relation must be satisfied whenever two frequencies, ν_1 and ν_2, originate from equivalent atoms having one and the same value for q. When there are two or more kinds of crystallographically nonequivalent halogen atom in crystals and multiplet components appear, the correspondence between ν_1 and ν_2 must be made with due regard to this relation.

II. Phase Transition in Solids

Perhaps the simplest application of NQR spectroscopy to inorganic chemistry is in the study of phase transitions in solids. As an example (*58*), Fig. 2 shows the temperature dependence of NQR frequencies of ^{79}Br in potassium hexabromoselenate(IV). A single resonance line is observed at

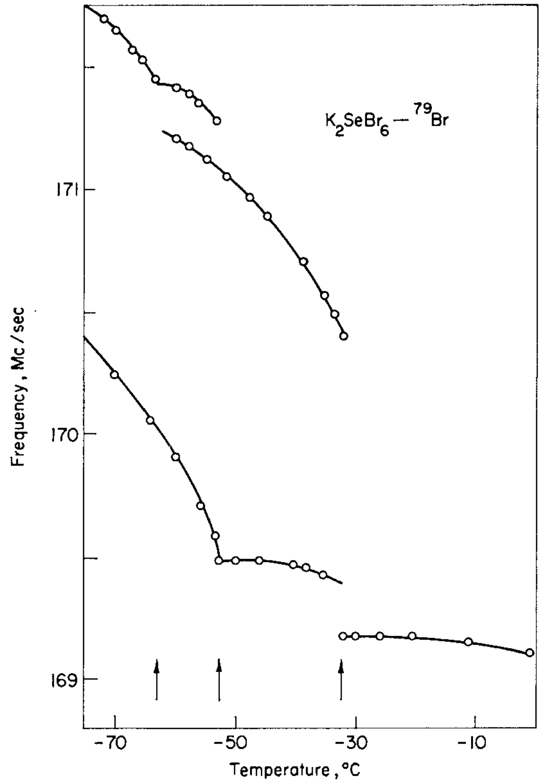

FIG. 2. Transition points of potassium hexabromoselenate(IV) as revealed by the temperature dependence of NQR frequencies.

temperatures above a transition point at −33°, indicating that all bromine atoms are crystallographically equivalent, in agreement with the results of X-ray analysis that this compound forms cubic crystals of the potassium hexachloroplatinate(IV) type at room temperature (*33*). Below −33°, two resonance lines appear, the signal-to-noise ratio of one line at a lower frequency being about twice that of the other line. The appearance of multiplet components indicates the existence of two kinds of crystallographically nonequivalent bromine atom in crystals having a lower than cubic symmetry (tetragonal in all likelihood). Below the second transition point at −52°, another line is observable. The resulting three resonance lines show almost equal intensity. Evidently the crystal lattice is less symmetrical (rhombic or lower symmetry). One of the triplet lines disappears below the third transition point at −64°. At liquid nitrogen temperature (not shown in Fig. 2), three resonance lines are observable. Accordingly, at least one transition point exists between dry ice and liquid nitrogen temperatures. In general, the NQR frequency decreases with increasing temperature ($d\nu/dT < 0$) and the curve of the frequency versus temperature is concave toward the abscissa ($d^2\nu/dT^2 < 0$) as in this special case.

The transition points of $R_2[MX_6]$ type complexes, located by the temperature dependence of NQR frequencies, are listed in Table II. Some of them have been observed by heat capacity measurements also (*5*, *36*, *52*).

TABLE II
TRANSITION POINTS OBSERVED BY NQR SPECTROSCOPY

Compound	Transition point (°C)	Reference
K_2SeBr_6	−64, −52, −33	(*58*)
$(NH_4)_2TeBr_6$	−52	(*56*)
Rb_2TeI_6	−40, −16, 55	(*59*)
K_2SnCl_6	−8.5	(*55*)
$(NH_4)_2PtBr_6$	0.5	(*59*)
K_2ReBr_6	−27, −16, −4	(*35*, *36*)
K_2ReI_6	166	(*36*)

An interesting feature of the transition of potassium hexabromoselenate(IV) (*58*) at −52° (Fig. 2) and potassium hexabromorhenate(IV) (*36*) at −16° (Fig. 3) is that one of the multiplet components is insensitive to the transition. In other words, whereas two lines of the triplet observed below the transition temperature either disappear above this temperature or show a discontinuity of the slope, $d\nu/dT$, one line exhibits no discontinuity of frequency and intensity at the transition point. It is evident that bromine atoms responsible for this line suffer no change in the field gradient

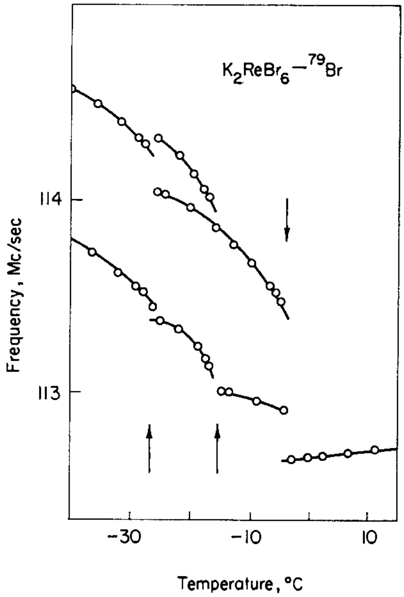

FIG. 3. NQR frequencies of ${}^{79}Br$ in potassium hexabromorhenate(IV) showing the existence of three transition points at about −4, −16, and −27°C.

at this temperature. Presumably the transition is related to the torsional oscillation or rotation of hexabromoselenate(IV) or hexabromorhenate(IV) ions about Se—Br or Re—Br axes involving the bromine atoms in question, as pointed out by Morfee *et al.* (*52*) for hexachlorostannate(IV) ions in potassium hexachlorostannate(IV). A phase transition of similar nature has been observed for rubidium hexaiodotellurate(IV) (*59*) at −40°.

III. Nature of Metal-Ligand Bonds

A. THEORY

The field gradient $q \equiv \partial^2 V/\partial z^2$ is completely determined by the charge distribution around a nucleus in question. Since a charge $-e$ at a distance r from the nucleus contributes $-e/r$ to the potential at the origin, it gives rise to the field gradient,

$$\frac{\partial^2}{\partial z^2}\left(-\frac{e}{r}\right) = -e\,\frac{3\cos^2\theta - 1}{r^3} \tag{14}$$

where θ is an angle between the radius vector r and the z-axis. Accordingly, the field gradient q originating from an electron in a state described by a wave function ψ is given by

$$q = -e\int \psi^*[(3\cos^2\theta - 1)/r^3]\psi\,d\tau \tag{15}$$

Owing to the factor $1/r^3$, the field gradient is determined for the most part by charge distribution in the vicinity of the nucleus, contributions from charges belonging to other ions being of minor importance. However, the reverse is not true: *s*-electrons having a spherically symmetrical charge distribution do not contribute to the field gradient, because $\langle 3\cos^2\theta - 1\rangle = 0$. For the same reason, a closed shell of electrons yields a vanishing field gradient at its center. On the other hand, *p*-electrons give rise to an appreciable field gradient. Contributions from *d*- and *f*-electrons can be ignored in comparison with those from *p*-electrons (*76*).

Let the contributions of single electrons in p_x, p_y, and p_z orbitals to the field gradient be denoted by q_x, q_y, and q_z, respectively, and the number of electrons in these orbitals be N_x, N_y, and N_z, respectively. One has

$$q = N_xq_x + N_yq_y + N_zq_z \tag{16}$$

Since, for $N_x = N_y = N_z$, the charge distribution is spherically symmetrical and hence $q = 0$, one has

$$q_x + q_y + q_z = 0 \tag{17}$$

Because p_x and p_y orbitals are equivalent, one has

$$2q_x = 2q_y = -q_z \tag{18}$$

From Eqs. (16) and (18),

$$q = -[(N_x + N_y)/2 - N_z]q_z \tag{19}$$

The number of unbalanced *p*-electrons U_p defined as

$$U_p = (N_x + N_y)/2 - N_z \tag{20}$$

is zero for a halogen ion ($N_x = N_y = N_z = 2$), while it is equal to unity for a halogen atom ($N_x = N_y = 2$, $N_z = 1$). Accordingly, Eq. (19) can be rewritten as

$$|eQq| = U_p|eQq_z| = U_p|eQq|_{\text{atom}} \tag{21}$$

where $|eQq|_{\text{atom}}$ stands for the quadrupole coupling constant of a halogen atom. The atomic quadrupole coupling constants for halogens have been obtained from the hyperfine splitting of atomic beam magnetic resonance, as shown in Table III (*15*).

A chlorine molecule, in which two chlorine atoms are bonded by a covalent $p\sigma$-bond, has $N_x = N_y = 2$ and $N_z = 1$, because two electrons involved in the bond belong to two nuclei. Accordingly, the number of unbalanced *p*-electrons U_p is equal to unity as in a chlorine atom. In fact, the pure quadrupole spectrum of solid chlorine at liquid nitrogen temperature yields a frequency practically identical with that evaluated from atomic beam experiments (*20*, *46*, *48*).

Since $U_p = 0$ for a halogen ion and $U_p = 1$ for a halogen atom par-

TABLE III

ATOMIC QUADRUPOLE COUPLING CONSTANTS eQq_{atom} OF HALOGENS[a]

Nucleus	Spin	$\frac{1}{2}eQq_{\text{atom}}$ (Mc/sec)	Reference
^{35}Cl	3/2	-54.873 ± 0.005	*(40)*
^{37}Cl	3/2	-43.255 ± 0.010	*(40)*
^{79}Br	3/2	$+384.878 \pm 0.008$	*(44)*
^{81}Br	3/2	$+321.516 \pm 0.008$	*(44)*
^{127}I	5/2	-1146.356 ± 0.010	*(41)*
$Cl_2(^{35}Cl)$		$+54.248$	*(46)*

[a] Q is negative for chlorine and iodine.

ticipating in a pure $p\sigma$-type covalent bond, one may define the extent of covalent character σ of a bond involving a halogen atom as $\sigma = U_p$ or

$$|eQq| = \sigma|eQq|_{\text{atom}} = (1 - i)|eQq|_{\text{atom}} \tag{22}$$

where i denotes the extent of ionic character of the bond. However, the bonding orbitals of halogen atoms are not always of a pure p-type: one must take into account the sp hybridization of the bonding orbitals. Townes and Dailey (*12*, *76*) have shown that Eq. (22) must be modified to

$$|eQq| = (1 - i)(1 - s)|eQq|_{\text{atom}} \tag{23}$$

where s denotes the extent of s character in the bonding orbital of the halogen. Accordingly, from the observed quadrupole coupling constant one can evaluate the ionic character i, provided that the extent of s character is reasonably estimated. Gordy (*22*, *23*) disregarded the hybridization, while Dailey and Townes (*12*) assumed that the atomic orbital of a halogen atom has 15% s character when the halogen atom is bonded to an atom more electropositive than the halogen by as much as 0.25 unit. For the present discussion, let $s = 15\%$ be accepted because this assumption seems to be closer to the truth than Gordy's simpler assumption that $s = 0$. This is a debatable problem and is discussed in some detail in the succeeding section after some quantitative data become available.

The net charge ρ (in electronic units) on the central metal atom M of a complex ion is calculated by

$$\rho = F - Z(1 - i) \tag{24}$$

where F and Z denote the formal charge and the coordination number of the central metal ion M, respectively ($F = 4$ and $Z = 6$ for $R_2[MX_6]$ type complexes). This is because, in this type of complex, the central metal ion is formally tetrapositive but is surrounded by six halogen ions, from which charges migrate toward the central metal ion through coordination bonds.

B. Ionic Character of Metal-Halogen Bonds

Before discussing the nature of metal-ligand bonds in complexes, some comment is necessary on the observed frequencies. In the first place, it is desirable to eliminate a possible effect of molecular vibrations or temperature in order to evaluate the ionic character of the bonds. However, the effect is very small. For instance, the NQR frequency of potassium hexachloroplatinate(IV) (*60*) is 25.813, 25.910, and 26.021 Mc/sec at room, dry ice, and liquid nitrogen temperatures, respectively. Since the absolute value of the temperature coefficient $|d\nu/dT|$ decreases with decreasing temperature and approaches zero at the absolute zero of temperature (*3*, *47*), the data at liquid nitrogen temperature are taken as a good approximation for the following discussion. Second, for some complexes multiplet components appear, indicating that not all metal-ligand bonds are equivalent in crystals. However, the separation between the multiplet components usually amounts to less than a few per cent (see Table I). Therefore, the frequencies are averaged over multiplet components. Lastly, the quadrupole coupling constants of compounds having the same complex anion are close to one another regardless of the kind of cation eventually accompanied by difference in crystal structure (Table IV) (*38*). This suggests that the NQR frequency of halogens in a complex compound $R_2[MX_6]$ is determined primarily by the electronic distribution in the complex ion $[MX_6]^{2-}$ without being affected greatly by neighboring cations and complex anions (*11*, *73*).

TABLE IV

NQR Frequencies of ^{35}Cl in $R_2[PtCl_6]$ Complexes[a]

Compound	Temperature (°C)	Frequency (Mc/sec)
$H_2PtCl_6 \cdot 6H_2O$	25.0	26.55 ± 0.05
$Na_2PtCl_6 \cdot 6H_2O$	23.5	25.730 ± 0.005 26.470 ± 0.005 27.040 ± 0.005
K_2PtCl_6	23.5	25.813 ± 0.001

[a] Reference (*38*).

The ionic character of M—X bonds and the net charge on the central metal atom M of various $R_2[MX_6]$ type complexes are shown in Table V.

The values calculated for the ionic character of metal-halogen bonds range from 0.30 to 0.68. This shows definitely that the assumption of pure ionic bonding, as is often made in a simple form of the crystalline field theory, is a poor approximation. On the other hand, the result shows also

TABLE V

THE IONIC CHARACTER OF M—X BONDS, THE NET CHARGE ON THE CENTRAL METAL ATOM M, AND THE ELECTRONEGATIVITY DIFFERENCE $\Delta\chi = \chi_X - \chi_M$ BETWEEN ATOMS INVOLVED IN THE BONDS OF $R_2[MX_6]$ TYPE COMPLEXES

Complex ion	Ionic character i	Net charge ρ	$\Delta\chi$	Reference
$[SeCl_6]^{2-}$	0.56	1.36	0.6	(*58*)
$[SeBr_6]^{2-}$	0.47	0.82	0.4	(*58*)
$[TeCl_6]^{2-}$	0.68	2.08	0.9	(*56*)
$[TeBr_6]^{2-}$	0.58	1.48	0.7	(*56*)
$[TeI_6]^{2-}$	0.48	0.88	0.45	(*56*)
$[SnCl_6]^{2-}$	0.66	1.96	1.2	(*55*)
$[SnBr_6]^{2-}$	0.60	1.60	1.0	(*55, 57*)
$[SnI_6]^{2-}$	0.55	1.30	0.75	(*55*)
$[PbCl_6]^{2-}$	0.63	1.78	1.2	(*55*)
$[PdCl_6]^{2-}$	0.43	0.58	1.0	(*37*)
$[PdBr_6]^{2-}$	0.37	0.22	0.8	(*37*)
$[PtCl_6]^{2-}$	0.44	0.64	0.9	(*60*)
$[PtBr_6]^{2-}$	0.38	0.28	0.7	(*60*)
$[PtI_6]^{2-}$	0.30	−0.20	0.45	(*60*)

that too much emphasis should not be laid on the covalency of metal-ligand bonds, because even the so-called hyperligated (formerly described as essentially covalent) complexes (*67*) show ionic character as high as 0.44.

An alternative measure for the ionic character of metal-ligand bonds is provided by the difference between the electronegativities of atoms involved in a bond (*12*, *23*). The ionic character evaluated from the NQR data is plotted against the electronegativity difference (*24*, *29*, *68*) in Fig. 4. Instead of having a single curve, one has three straight lines, each of which comprises complex ions having a central atom of the same outer electronic configuration.

The net charge on palladium(IV) and platinum(IV) ions is reduced significantly owing to the charge migration from ligands. It is as small as a positive fraction of an electronic charge, in good agreement with the neutrality principle proposed by Pauling (*65*). On the other hand, the net charge on the central atom of Group IVB and Group VIB elements in the periodic table amounts to almost a unit charge or more. The reason for this must be looked for in the electronic configuration of the central ions. Since platinum(IV), for instance, can form as many as six equivalent bonding orbitals from six atomic orbitals $5d^26s6p^3$, resonance is possible for a hexahaloplatinate(IV) ion among various electronic structures in which the platinum atom carries no formal charge. On the other hand, tellurium(IV), for instance, having an outer electronic configuration $4d^{10}5s^2$, can avail

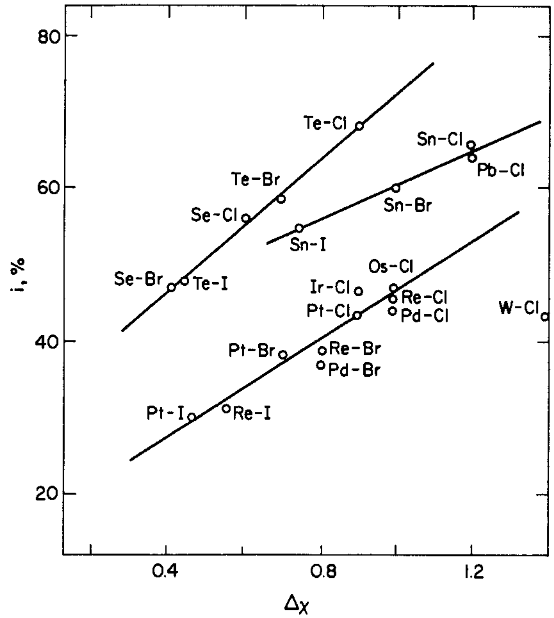

FIG. 4. Dependence of the ionic character of metal-ligand bonds in hexahalo complexes on the difference between the electronegativities of the ligands and the central atom.

itself of only three 5*p* orbitals for forming bonds with halogen in a $[TeX_6]^{2-}$ ion, because 5*d* and 6*s* orbitals are energetically higher than 5*p* orbitals by 6–7 ev in a neutral tellurium atom. Therefore, the nature of the Te—X bonds can be represented by a resonance hybrid among various electronic

TABLE VI

THE IONIC CHARACTER OF M—X BONDS AND THE NET CHARGE ON THE CENTRAL METAL ATOM M OF SOME COMPLEX IONS

Complex ion	Ionic character i	Net charge ρ	Reference
$[PdBr_4]^{2-}$	0.60	0.40	*(37)*
$[PtCl_4]^{2-}$	0.61	0.44	*(51)*
$[PtBr_4]^{2-}$	0.57	0.28	*(37)*
$[AuCl_4]^-$	0.40–0.42	0.61–0.68	*(6, 7)*
trans-$[Coen_2Cl_2]^-$	0.75–0.80	—	*(31, 32)*
trans-$[Coen_2Br_2]^-$	0.60[a]	—	*(32)*

[a] Calculated by the present authors without correction for field gradient due to other ions in a crystal.

structures, in all of which the tellurium atom bears at least one positive charge. It should be noted that no resonance structures having a vanishing formal charge on the central atom are conceivable (*56*). Reasoning along a similar line leads to a conclusion that, for hexahalostannates(IV) and hexahaloplumbates(IV), resonance structures having a single or double positive charge on the central atom are predominant (*57*).

A negative value for the net charge on the platinum atom in a hexaiodoplatinate(IV) ion is fortuitous and is apparently due to the overestimation of the *s* character in the bonding orbital of iodine.

The halogen NQR data of metal complexes other than those of the $R_2[MX_6]$ type are quite meager. Table VI shows the ionic character of M—X bonds and the net charge on the central metal atom M evaluated from these data published prior to 1965.

C. PARAMAGNETIC COMPLEXES

It has been believed for some time that the quadrupole resonance of atoms directly bonded to a paramagnetic atom or ion escapes detection owing to the Zeeman splitting of signals due to the magnetic field of unpaired electron spins. Barnes and Segel (*2*) were the first to observe the NQR of a few paramagnetic halides of transition elements. However, no paramagnetic complexes had ever been reported to show observable NQR spectra until Ito *et al.* (*39*) observed resonance lines for potassium hexachloroiridate(IV) and hexachloroosmate(IV). Since then, an increasing number of simple as well as complex inorganic compounds have been found to show NQR absorptions (*4, 34, 43, 53, 62*). The fact that resonance lines have been observed for paramagnetic compounds indicates that the magnetic field of unpaired electron spins is effectively averaged to zero at halogen nuclei, because of the rapid relaxation of unpaired electron spins in paramagnetic ions.

Unlike hexahaloplatinates(IV) and hexahalopalladates(IV), which are diamagnetic by having the d_ϵ orbitals of the central atom completely filled with electrons, the hexahalo complexes of iridium, osmium, etc., are paramagnetic (*10, 21, 78*) owing to the presence of one or more vacancies in the d_ϵ orbitals. It is conceivable that partial π-bonds are formed between the $d\pi$ orbitals of the central atom and the $p\pi$ orbitals of halogen atoms. In fact Griffiths, Owen, and others (*8, 26, 27, 64*) have observed the electron-spin resonance of some hexachloroiridates(IV) and concluded that the π-bond character is involved in the metal-ligand bonds. Accordingly, Eq. (23) must be modified by taking into account the π-bond character (*39*).

Let the ionic character of metal-halogen bonds in a paramagnetic complex of the iridium series $R_2[MX_6]$ be denoted by i. A covalent σ-bond can be formed between a central metal atom and a halogen atom when one of the $5d_\gamma^2/6s6p^3$ hybridized orbitals of the metal atom overlaps one of the sp_z hybridized orbitals of the halogen. In the light of the valence bond method, the resulting covalent σ-bond character of the metal-ligand bond is expressed by σ. Since there is a vacancy or vacancies in the d_ϵ orbitals of the central ion, π-bonds also can be formed between the two atoms in question. Depending on whether the p_x or p_y orbital of the halogen is involved in bond formation with the corresponding d_ϵ orbital (d_{xz} or d_{yz}) of the central metal atom, one has covalent π-bond character, π_x or π_y, for the metal-ligand bond. The O_h symmetry of the complex ions requires that

$$\pi_x = \pi_y = \pi/2 \tag{25}$$

where π stands for the overall covalent π character of the bond. In other words, $\pi/2$ is the extent of contribution to the normal state of the resonance structure, in which only a single π-bond is involved in the bond formation. Accordingly,

$$i + \sigma + \pi = 1 \tag{26}$$

For this electronic structure,

$$N_x = 2i + 2\sigma + \pi_x + 2\pi_y \tag{27}$$

$$N_y = 2i + 2\sigma + 2\pi_x + \pi_y \tag{28}$$

because each of the bonding orbitals contributes a single electron, while each of orbitals not participating in the bond formation contributes two electrons to N_x and N_y. On the other hand,

$$N_z = 2i + [(1 - s) + 2s]\sigma + 2\pi_x + 2\pi_y \tag{29}$$

where s denotes the s character of the sp_z hybridized bonding orbital of the halogen. The coefficient in brackets takes into account the sp_z hybridization, by which the bonding orbital having s character to some extent contributes one electron while the pair of electrons not participating in the bond formation acquires the corresponding p_z character. From Eqs. (25–29), one has

$$N_x = 2 - \pi_x \tag{30}$$

$$N_y = 2 - \pi_y \tag{31}$$

$$N_z = 2 - (1 - s)\sigma \tag{32}$$

Owing to the bond formation, the number of electrons in each of the p orbitals of the halogen is decreased from 2 for the halogen ion by half an amount allotted to the bonding electron pairs. Introducing Eqs. (30–32) into Eq. (20), followed by substitution for U_p in Eq. (21), one has

$$|eQq| = [(1 - s)(1 - i - \pi) - \pi/2]|eQq|_{\text{atom}} \tag{33}$$

Needless to say, Eq. (23) is a special case of the general Eq. (33).

From electron-spin resonance experiments carried out by Griffiths *et al.* (*8, 26, 27, 64*), the π-bond character of metal-ligand bonds in hexachloroiridates(IV) is estimated to be 5.3% or $\pi/2 = 2.7\%$. Similar experiments have been undertaken with ammonium hexachloroosmate(IV), but no resonance has been observed (*27*). The electron-spin resonance of potassium hexachlororhenate(IV) shows no observable hyperfine structure due to chlorine nuclei (*19, 69*). Therefore, the π-bond character of Re—Cl bonds is still unknown. The hexachloro complexes of tungsten(IV) have not yet been studied by the electron-spin resonance method. However, since Os^{4+}, Re^{4+}, and W^{4+} ions have two, three, and four vacancies, respectively, in their d_ϵ orbitals rather than one vacancy as in an Ir^{4+} ion, it is reasonable to assume that the number of electrons migrating from a chlorine ion to the central metal ion is proportional to the number of electronic vacancies in the d_ϵ orbitals of the central metal ion. With this assumption, the ionic character i (Eq. 33) and the σ-bond character σ (Eq. 26) can be calculated along with the net charge ρ (in electronic charge units) on the central metal ion (Eq. 24). The results are shown in Table VII.

TABLE VII

THE BOND CHARACTER OF METAL-LIGAND BONDS AND THE NET CHARGE ON THE CENTRAL METAL ATOM IN SOME PARAMAGNETIC HEXAHALO COMPLEXES

Compound	Ionic character i	σ-Bond character σ	π-Bond character π	Net charge ρ	$\Delta\chi$	Reference
$[PtCl_6]^{2-}$	0.44	0.56	0	0.64	0.9	(*60*)
$[IrCl_6]^{2-}$	0.47	0.48	0.054	0.82	0.9	(*39*)
$[OsCl_6]^{2-}$	0.47	0.43	0.108	0.82	1.0	(*39*)
$[ReCl_6]^{2-}$	0.45	0.39	0.16	0.70	0.9–1.1	(*36*)
$[WCl_6]^{2-}$	0.43	0.35	0.22	0.58	1.2–1.4	(*36*)
$[ReBr_6]^{2-}$	0.39	0.45	0.16	0.34	0.7–0.9	(*36*)
$[ReI_6]^{2-}$	0.32	0.52	0.16	−0.08	0.45–0.65	(*36*)

It is seen that with increasing π-bond character of metal-ligand bonds, the σ-bond character decreases with decreasing atomic number of the central metal atoms. On the other hand, the ionic character remains almost constant as expected from nearly the same electronegativities of the metal elements. As a result, the net charge is a positive fraction of the electronic charge throughout this series of complexes in conformity with Pauling's electroneutrality principle, the increase of the net charge on the central atom due to the decrease in the σ-bond character being compensated by the increase of the negative charge due to the π-bond formation. The ionic character of M—X bonds in these paramagnetic complexes is plotted in

Fig. 4 against the difference, $\Delta\chi = \chi_X - \chi_M$, between the electronegativities (*24*, *29*, *50*, *66*) of atoms involved in the bonds. The data lie on the straight line for platinum and palladium complexes. Potassium hexachlorotungstate(IV) shows a slight deviation, probably because errors due to various assumptions are relatively large for this complex. On the other hand, if the π-bond character is entirely disregarded, all the data of the paramagnetic complexes deviate from the straight line to a considerable extent, and the net charges on the central metal ions increase in contradiction to Pauling's principle. This indicates unequivocally the importance of the π-bond character of M—X bonds in paramagnetic complexes.

IV. Effect of Cations and Temperature

A. EFFECT OF CATIONS ON NQR FREQUENCIES

The NQR frequencies of chlorine and bromine in various hexachloroplatinates(IV) and hexabromoplatinates(IV), all of which show the same type of crystal structure, increase progressively with increasing lattice constant of these crystals, as shown in Table VIII. (Sodium salts are omitted from the discussion because they crystallize with water of crystallization.) Since X-ray crystal analysis has shown that the Pt—Cl distance (2.32–2.36 Å) in various hexachloroplatinates(IV) (*74*) is almost independent of the kind of cation, it is presumed that the frequency increase results primarily from the increasing size of cations.

TABLE VIII

NQR FREQUENCIES ν OF ^{35}Cl AND ^{79}Br AND LATTICE CONSTANTS a OF $K_2[PtCl_6]$ TYPE CRYSTALS AT ROOM TEMPERATURE[a,b]

Compound	ν (Mc/sec)	$\Delta\nu/\nu_0$ (%)	a (Å)	$\Delta a/a_0$ (%)
$K_2[PtCl_6]$	25.81	0	9.755	0
$(NH_4)_2[PtCl_6]$	26.07	1.0	9.858	1.1
$Rb_2[PtCl_6]$	26.29	1.9	9.901	1.5
$Cs_2[PtCl_6]$	26.60	3.1	10.215	4.7
$K_2[PtBr_6]$	200.2	0	10.293	0
$(NH_4)_2[PtBr_6]$	202.5	1.1	10.367	0.7
$Rb_2[PtBr_6]$	204.4	2.1	10.405	1.1
$Cs_2[PtBr_6]$	207.2	3.4	10.643	3.4

[a] $\Delta\nu = \nu - \nu_0$ and $\Delta a = a - a_0$, where subscripts 0 refer to $K_2[PtCl_6]$ and $K_2[PtBr_6]$ taken as references.

[b] Reference (*59*).

For the known potassium hexachloroplatinate(IV) structure (Fig. 5), the field gradient $q_{n.i.}$ at a halogen atom X due to neighboring ions can be

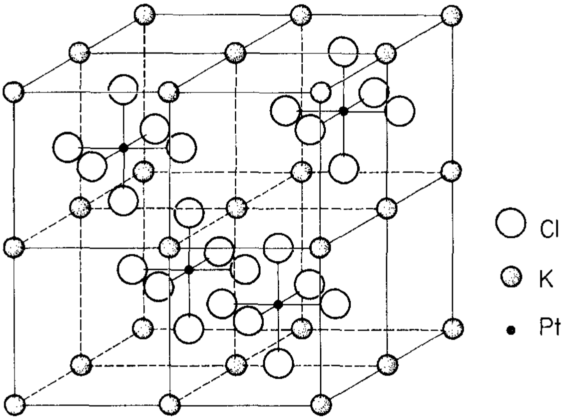

FIG. 5. Crystal structure of potassium hexachloroplatinate(IV).

calculated for a point-charge model (Eq. 15), where the z-axis is taken along the M—X direction. If only eight cations R^+ nearest to the complex anion in question are taken into account, the field gradient $q_{n.i.}^{(1)}$ is negative and is, roughly speaking, proportional to the square of the M—X bond distance and inversely proportional to the fifth power of the R—R distance. On the other hand, the field gradient $q_{c.i.}$ originating from charges within the complex ion except for the halogen nucleus in question is positive, because the halogen atom has partial vacancy in the p_z orbital, whereas both p_x and p_y orbitals are filled, i.e., the halogen nucleus has a positive charge cloud on either side along the z-axis. Accordingly, the NQR frequency given for nuclei having $I = 3/2$ by

$$\nu = \tfrac{1}{2}|eQq| = \tfrac{1}{2}|eQ|(q_{c.i.} + q_{n.i.}) \tag{34}$$

increases with increasing lattice constant in qualitative agreement with observations. Numerical calculations have been carried out (*59*) for potassium hexachloroplatinate(IV) ($a_0 = 2l(\text{K—K}) = 9.755$ Å, $l(\text{Pt—Cl}) = 2.33_0$ Å) and cesium hexachloroplatinate(IV) ($a_0 = 2l(\text{Cs—Cs}) = 10.215$ Å, $l(\text{Pt—Cl}) = 2.34_0$ Å) by including $q_{n.i.}^{(2)}$ due to 12 second neighbors (anions) and $q_{n.i.}^{(3)}$ due to 24 third neighbors (cations). One has

$$q_{n.i.}(K_2[PtCl_6]) = (-7.801 + 1.866 + 0.539) \times 10^{22}e = -5.40 \times 10^{22}e \tag{35}$$

$$q_{n.i.}(Cs_2[PtCl_6]) = (-6.680 + 1.478 + 0.435) \times 10^{22}e = -4.77 \times 10^{22}e \tag{36}$$

in c.g.s., e.s.u. The difference, $\Delta q = q(\text{Cs}) - q(\text{K})$, between calculated values is

$$\Delta q^{(1)} = 1.12 \times 10^{22}e \tag{37}$$

$$\Delta q^{(1-2)} = 0.73 \times 10^{22}e \tag{38}$$

$$\Delta q^{(1-3)} = 0.63 \times 10^{22}e \tag{39}$$

for the first, second, and third approximations, respectively. In order to check the convergence of the series expansion, further numerical calculations have been performed by including all other ions within a sphere having its center at the chlorine ion in question rather than at the center of the complex ion, the radius being 19 and 20 Å for the potassium and cesium salts, respectively. The sphere comprises 236 cations and 115 complex anions in addition to the central anion. One has

$$q_{\mathrm{n.i.}}(\mathrm{K_2[PtCl_6]}) = -6.05 \times 10^{22}e \tag{40}$$

$$q_{\mathrm{n.i.}}(\mathrm{Cs_2[PtCl_6]}) = -5.30 \times 10^{22}e \tag{41}$$

leading to

$$\Delta q = 0.75 \times 10^{22}e \tag{42}$$

This value is presumed to be correct at least with regard to its sign and the order of magnitude, although the numerical agreement with the foregoing value, $0.63 \times 10^{22}e$, is rather poor. It leads to the quadrupole frequency difference $\Delta\nu$ between the two complexes given by

$$\Delta\nu = \tfrac{1}{2}|eQ|\Delta q \tag{43}$$

where Q, the nuclear quadrupole moment of ^{35}Cl, is equal to -0.07894×10^{-24} cm^2 in electronic units (*15*). The calculated frequency difference, 0.010 Mc, is one or two orders of magnitude smaller than the difference, 0.79 Mc, observed at room temperature. Owing to the highly symmetrical structure of these crystals, the direct electrostatic effect of charges of other ions on the field gradient at the halogen nucleus under observation is rather insignificant. The field gradient comes largely from the charge distribution within the complex anion, the electronic structure of which is affected by surrounding ions. Conceivable causes are the polarization of the complex ion by the electrostatic field from neighboring ions as well as the suppression of bending vibrations of M—X bonds leading to the increased frequency of quadrupole resonance (*3*).

B. EFFECT OF CATIONS ON THE TEMPERATURE COEFFICIENT OF NQR FREQUENCIES

The average temperature coefficients, $\Delta\nu/\Delta T$, of the resonance frequencies of ^{35}Cl and ^{79}Br in potassium hexachloroplatinate(IV) type crystals have been calculated between liquid nitrogen and dry ice temperatures and between dry ice and room temperatures, as shown in Table IX. In general, the temperature coefficient $\Delta\nu/\Delta T$ increases with increasing size of cations and decreasing temperature, except for ammonium hexachloro- and hexabromoplatinates(IV), which show some deviations.

TABLE IX

TEMPERATURE COEFFICIENTS $\Delta\nu/\Delta T$ OF QUADRUPOLE RESONANCE FREQUENCIES OF ^{35}Cl AND ^{79}Br IN $K_2[PtX_6]$ TYPE CRYSTALS[a]

Compound	$\Delta\nu/\Delta T$ (kc/deg)	
	Liquid N_2–dry ice	Dry ice–room temperature
$K_2[PtCl_6]$	−0.92	−0.98
$(NH_4)_2[PtCl_6]$	−1.01	−0.94
$Rb_2[PtCl_6]$	−0.59	−0.78
$Cs_2[PtCl_6]$	−0.33	−0.61
$(NH_4)_2[PtBr_6]$	−6.7	−6.7
$Rb_2[PtBr_6]$	−5.3	−6.4
$Cs_2[PtBr_6]$	−4.5	−5.9

[a] Potassium hexabromoplatinate(IV) is omitted, because phase change takes place between dry ice and liquid nitrogen temperatures (*60*).

The exceptional behavior of the ammonium complexes must be looked for in the structure of ammonium ions. If ammonium ions rotate in crystals, they simulate spherical symmetry inherent in alkali metal ions. If the rotation does not take place, the symmetry is lowered to T_d. Therefore, the electrostatic effect of ammonium ions on halogens in $[PtX_6]^{2-}$ ions must be different from that of rotating ammonium ions. Since the fixation of ammonium ions in crystals gives rise to a discontinuous change in the field gradient about halogen atoms, one may expect some discontinuity in the temperature dependence of NQR frequencies. As shown in Fig. 6, ammonium hexabromoplatinate(IV) shows a discontinuity of $d\nu/dT$ at 0–1°. No such discontinuity has been observed for ammonium hexachloroplatinate(IV) between room and dry ice temperatures, the relation between the resonance frequency and temperature being strictly linear. However, the value at liquid nitrogen temperature deviates from this linear relation to the high-frequency side, whereas the curves of NQR frequencies plotted against temperature are normally concave to the abscissa. This suggests the existence of a rotational transition, as observed for ammonium hexabromoplatinate(IV), at some temperature between dry ice and liquid nitrogen temperatures.

So far we have discussed the effect of cations on the NQR frequency and its temperature coefficient. The observed dependence of the frequency

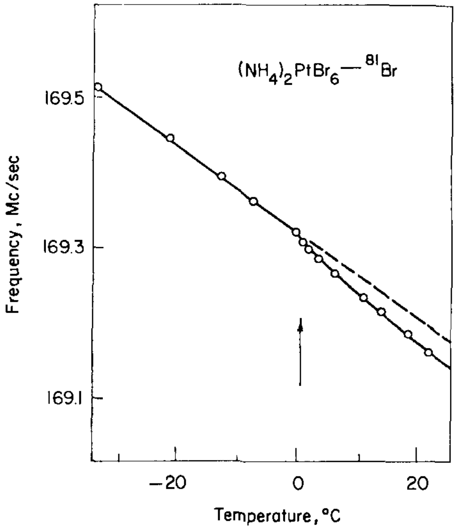

FIG. 6. Temperature dependence of the NQR frequency of ^{81}Br in ammonium hexabromoplatinate(IV).

and its temperature coefficient on the temperature and the lattice constant a_0 can be summarized by the following general expressions:

$$\left(\frac{\partial \nu}{\partial T}\right)_p < 0, \qquad \left(\frac{\partial \nu}{\partial a_0}\right)_T > 0 \tag{44}$$

$$\left\{\frac{\partial}{\partial T}\left(\frac{\partial \nu}{\partial T}\right)_p\right\}_p < 0, \qquad \left\{\frac{\partial}{\partial a_0}\left(\frac{\partial \nu}{\partial T}\right)_p\right\}_T > 0 \tag{45}$$

C. POSITIVE TEMPERATURE COEFFICIENT

The temperature coefficient of NQR frequencies is normally negative (*3*). However, potassium hexachlororhenate(IV), hexabromorhenate(IV), and hexachlorotungstate(IV) have been found to show positive temperature coefficients of NQR frequencies in the temperature range in which these complexes yield a single resonance line, i.e., they form cubic crystals of the potassium hexachloroplatinate(IV) structure (*36*). (Potassium hexaiodorhenate(IV) does not crystallize in a cubic structure at any temperature below 200°. No positive temperature coefficient has been observed in this temperature range.) This is the first instance of complex compounds ever reported to show a positive temperature coefficient, although a few simple inorganic compounds such as tungsten hexachloride (*30*), titanium tetrabromide (*1*), and thorium tetrachloride (*70*) have been reported to exhibit such temperature dependence. The change of resonance frequencies with temperature is almost linear in the temperature range of the cubic crystal structure, as shown in Fig. 3. Table X shows the NQR frequency ν and its temperature coefficient $d\nu/dT$ of the rhenium and tungsten complexes at 20° along with those of related complexes.

TABLE X

TEMPERATURE COEFFICIENT OF NQR FREQUENCIES OF POTASSIUM HEXAHALORHENATES(IV), HEXACHLOROTUNGSTATE(IV), AND RELATED COMPLEXES AT 20°C[a]

Compound	ν (Mc/sec)	$d\nu/dT$ (kc/deg)	Temperature range (°C)
$K_2[PtCl_6]$	25.82	−1.00	−75.0–23.5
$K_2[IrCl_6]$	20.73	−0.54	−69.0–24.2
$K_2[OsCl_6]$	16.84	−0.22	−70.0–26.0
$K_2[ReCl_6]$	13.89	0.13	−76.0–21.2
$K_2[WCl_6]$	10.22	0.44	10.5–35.0
$K_2[ReBr_6]$	112.71	2.8	−3.0–181.0

[a] Reference (*36*).

It is seen from Table X that the resonance frequency of the hexachloro complexes decreases while the temperature coefficient increases progressively with decreasing atomic number of the central metal atom or with increasing electron deficiency in the d_ϵ orbitals. This regularity suggests that the frequency decrease and the positive temperature coefficient are closely related to the vacancy in the d_ϵ orbitals or the partial $d\pi$-$p\pi$ bond character of the metal-ligand bonds.

With increasing π-bond character, electrons in the p_x and p_y orbitals of chlorine migrate toward the central metal ion, where the z-axis is taken along the metal-ligand bond. The resulting electron deficiency leads to the decrease in the NQR frequency of chlorine, in agreement with experimental observation.

As regards the dependence of the resonance frequency on temperature, a simple thermodynamical calculation (*28*, *45*) yields

$$(\partial\nu/\partial T)_p = (\partial\nu/\partial T)_V + (\partial\nu/\partial V)_T(\partial V/\partial T)_p \tag{46}$$

The thermal expansion $(\partial V/\partial T)_p$ is positive. In the case of potassium hexachloroplatinate(IV) type crystals, $(\partial\nu/\partial V)_T$ is also positive for the following reason. As mentioned in Eq. (34),

$$q = q_{\text{c.i.}} + q_{\text{n.i.}} \tag{47}$$

where $q_{\mathrm{c.i.}}$ originating from charges within the complex ion except for the halogen nucleus assumes a positive value (as mentioned in Section IV,A). The field gradient $q_{\mathrm{n.i.}}$ due to all neighboring ions depends directly on the lattice constant. Calculations based on a point-charge model have indicated that for crystals having the potassium hexachloroplatinate(IV) structure, $q_{\mathrm{n.i.}}$ is negative and is smaller than $q_{\mathrm{c.i.}}$, the absolute value decreasing with increasing lattice constant. Accordingly, $(\partial\nu/\partial V)_T$ is positive. This theoretical conclusion is supported by experimental observations that, at a constant temperature, the resonance frequency of chlorine or bromine in hexahaloplatinates(IV) having various cations increases with increasing lattice constant (Eq. 44).

The fact that the observed temperature coefficient $(\partial\nu/\partial T)_p$ is normally negative implies that the major term $(\partial\nu/\partial T)_V$ in the right-hand side of Eq. (46) is negative. Although this quantity is not accessible to direct measurement, it has an advantage for theoretical discussion in that it takes into account the thermal vibration of complex anions but is free from the effect of the thermal expansion of the lattice (*3*, *18*). With increasing thermal vibration of the complex ion, especially bending vibrations, the overlap of the σ orbital of the central metal ion with the p_z orbital of the halogen atom decreases, leading to decreased covalent character of the metal-ligand bond. Accordingly, the field gradient q and hence the NQR frequency also decrease with increasing temperature.

The foregoing discussion applies to complexes involving no bonds having π-bond character. However, when $d\pi$-$p\pi$ bonds are involved, as in paramagnetic complexes, the decrease of overlap due to thermal vibration leads to the decrease of π-bond character. This means that electrons in the p_x and p_y orbitals of a halogen atom migrate toward the $d\pi$ orbitals to a smaller extent, and hence the field gradient increases with increasing temperature. The key point is that, although thermal vibration gives rise to the increase of N_z and $N_x + N_y$ for the σ-bond and π-bond, respectively, N_z and $N_x + N_y$ contribute to U_p, the number of unbalanced p-electrons, with opposite signs (Eq. 20). The positive temperature coefficient of NQR frequencies results when the aforementioned effect, along with the second term of the right-hand side of Eq. (46), predominates over the normal negative temperature coefficient. This is the case with hexahalorhenates(IV) and hexachlorotungstate(IV) of the cubic structure involving metal-ligand bonds of high π-bond character.

LIST OF SYMBOLS

a_0	Lattice constant
e	Absolute value of an electronic charge
eQ	Electric quadrupole moment of a nucleus

$\lvert eQq \rvert$	Quadrupole coupling constant
$\lvert eQq \rvert_{\text{atom}}$	Atomic quadrupole coupling constant
E_Q	Energy of interaction between a nuclear quadrupole moment and its surroundings
F	Formal charge on a central metal ion M of a complex ion $[MX_6]^{2-}$
i	Extent of ionic character of a metal-ligand bond
I	Nuclear spin
l	Interatomic or interionic distance
M_I	Magnetic quantum number of nuclear spin orientation
N_x, N_y, N_z	Number of electrons in the p_x, p_y, and p_z orbitals of a halogen atom, respectively
q	Electric field gradient at a halogen atom X along a metal-halogen bond
$q_{\text{c.i.}}$	Field gradient at a halogen atom due to charges within the complex ion $[MX_6]^{2-}$ except for the halogen nucleus
$q_{\text{n.i.}}$	Field gradient at a halogen atom X due to neighboring ions in an $R_2[MX_6]$ complex
q_x, q_y, q_z	Field gradient due to an electron in the p_x, p_y, and p_z orbitals of a halogen atom, respectively
	Extent of s character in the sp hybridized bonding orbital of a halogen atom
U_p	Number of unbalanced p-electrons
V	Electrostatic potential
Z	Coordination number of a central metal atom
η	Asymmetry parameter
ν	NQR frequency, especially for a nucleus having $I = 3/2$
ν_1	NQR frequency resulting from a transition of M_I: $\pm 1/2 \leftrightarrow \pm 3/2$
ν_2	NQR frequency resulting from a transition of M_I: $\pm 3/2 \leftrightarrow \pm 5/2$
π	Extent of covalent π-bond character of a metal-ligand bond
ρ	Net charge on the central metal atom M of a complex ion in electronic units
σ	Extent of covalent σ-bond character of a metal-ligand bond
χ	Electronegativity of an element

REFERENCES

1. Barnes, R. G., and Engardt, R. D., *J. Chem. Phys.* **29,** 248 (1958).

2. Barnes, R. G., and Segel, S. L., *Phys. Rev. Letters* **3,** 462 (1959).

3. Bayer, H., *Z. Physik* **130,** 227 (1951).

4. Burgiel, J. C., Jaccarino, V., and Schawlow, A. L., *Phys. Rev.* **122,** 429 (1961).

5. Busey, R. H., and Sonder, E., *J. Chem. Phys.* **36,** 93 (1962).

6. Caglioti, V., Furlani, C., Orestano, F., and Capece, F. M., *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. Nat.* **35,** 10 (1963).

7. Caglioti, V., Sartori, G., and Furlani, C., *Proc. 8th Intern. Conf. Coord. Chem.*, p. 81. Springer, Vienna, 1964.

8. Cipollini, E., Owen, J., Thornley, J. H. M., and Windsor, C., *Proc. Phys. Soc. (London)* **79,** 1083 (1962).

9. Cohen, M. H., and Reif, F., *Solid State Phys.* **5,** 321 (1957).

10. Cooke, A. H., Lazenby, R., McKim, F. R., Owen, J., and Wolf, W. P., *Proc. Roy. Soc.* **A250,** 97 (1959).

11. Cornwell, C. D., and Yamasaki, R. S., *J. Chem. Phys.* **27,** 1060 (1957).

12. Dailey, B. P., and Townes, C. H., *J. Chem. Phys.* **23,** 118 (1955).

13. Das, T. P., and Hahn, E. L., *Solid State Phys.* Suppl. 1, 3 (1958).
14. Das, T. P., and Hahn, E. L., *Solid State Phys.* Suppl. 1, 14 (1958).
15. Das, T. P., and Hahn, E. L., *Solid State Phys.* Suppl. 1, 127 (1958).
16. Dehmelt, H. G., *Am. J. Phys.* **22,** 110 (1954).
17. Dehmelt, H. G., and Krüger, H., *Naturwissenschaften* **37,** 111 (1950).
18. Dehmelt, H. G., and Krüger, H., *Z. Physik* **129,** 401 (1951).
19. Dorain, P. B., and Rahn, R. O., *J. Chem. Phys.* **36,** 561 (1962).
20. Douglass, D. C., *J. Chem. Phys.* **31,** 504 (1959).
21. Figgis, B. N., Lewis, J., Nyholm, R. S., and Peacock, R. D., *Discussions Faraday Soc.* **26,** 103 (1958).
22. Gordy, W., *J. Chem. Phys.* **19,** 792 (1951).
23. Gordy, W., *Discussions Faraday Soc.* **19,** 14 (1955).
24. Gordy, W., and Thomas, W. J. O., *J. Chem. Phys.* **24,** 439 (1956).
25. Gray, H. B., *J. Chem. Educ.* **41,** 2 (1964).
26. Griffiths, J. H. E., and Owen, J., *Proc. Roy. Soc.* **A226,** 96 (1954).
27. Griffiths, J. H. E., Owen, J., and Ward, I. M., *Proc. Roy. Soc.* **A219,** 526 (1953).
28. Gutowsky, H. S., and Williams, G. A., *Phys. Rev.* **105,** 464 (1957).
29. Haïssinsky, M., *J. Phys. Radium* **7,** 7 (1946).
30. Hamlen, R. P., and Koski, W. S., *J. Chem. Phys.* **25,** 360 (1956).
31. Hartmann, H., Fleissner, M., and Sillescu, H., *Naturwissenschaften,* **50,** 591 (1963).
32. Hartmann, H., Fleissner, M., and Sillescu, H., *Theoret. Chim. Acta* **2,** 63 (1964).
33. Hoard, J. L., and Dickinson, B. N., *Z. Krist.* **84,** 436 (1933).
34. Hughes, W. E., Montgomery, C. G., Moulton, W. G., and Carlson, E. H., *J. Chem. Phys.* **41,** 3470 (1964).
35. Ikeda, R., Nakamura, D., and Kubo, M., *Bull. Chem. Soc. Japan* **36,** 1056 (1963).
36. Ikeda, R., Nakamura, D., and Kubo, M., *J. Phys. Chem.* **69,** 2101 (1965).
37. Ito, K., Nakamura, D., Kurita, Y., Ito, Ko., and Kubo, M., *J. Am. Chem. Soc.* **83,** 4526 (1961).
38. Ito, Ko., Ito, K., Nakamura, D., and Kubo, M., *Bull. Chem. Soc. Japan* **35,** 518 (1962).
39. Ito, Ko., Nakamura, D., Ito, K., and Kubo, M., *Inorg. Chem.* **2,** 690 (1963).
40. Jaccarino, V., and King, J. G., *Phys. Rev.* **83,** 471 (1951).
41. Jaccarino, V., King, J. G., Satten, R. A., and Stroke, H. H., *Phys. Rev.* **94,** 1798 (1954).
42. Jeffrey, G. A., and Sakurai, T., *in* "Progress in Solid State Chemistry" (H. Reiss, ed.), Vol. 1, p. 380. Macmillan (Pergamon), New York, 1964.
43. Jones, W. H., Jr., and Segel, S. L., *Phys. Rev. Letters* **13,** 528 (1964).
44. King, J. G., and Jaccarino, V., *Phys. Rev.* **94,** 1610 (1954).
45. Kushida, T., Benedek, G. B., and Bloembergen, N., *Phys. Rev.* **104,** 1364 (1956).
46. Livingston, R., *J. Chem. Phys.* **19,** 803 (1951).
47. Livingston, R., *J. Phys. Chem.* **57,** 496 (1953).
48. Livingston, R., *Science* **118,** 61 (1953).
49. Livingston, R., and Zeldes, H., Table of Eigenvalues for Pure Quadrupole Spectra, Spin 5/2, ONRL Rept. 1913. Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1955.
50. Lotspeich, J. F., Javan, A., and Engelbrecht, A., *J. Chem. Phys.* **31,** 633 (1959).
51. Marram, E. P., McNiff, E. J., and Ragle, J. L., *J. Phys. Chem.* **67,** 1719 (1963).
52. Morfee, R. G. S., Staveley, L. A. K., Walters, S. T., and Wigley, D. L., *Phys. Chem. Solids* **13,** 132 (1960).
53. Morosin, B., and Narath, A., *J. Chem. Phys.* **40,** 1958 (1964).

54. Muetterties, E. L., and Phillips, W. D., *Advan. Inorg. Chem. Radiochem.* **4,** 231 (1962).

55. Nakamura, D., *Bull. Chem. Soc. Japan* **36,** 1662 (1963).

56. Nakamura, D., Ito, K., and Kubo, M., *J. Am. Chem. Soc.* **84,** 163 (1962).

57. Nakamura, D., Ito, K., and Kubo, M., *Inorg. Chem.* **1,** 592 (1962).

58. Nakamura, D., Ito, K., and Kubo, M., *Inorg. Chem.* **2,** 61 (1963).

59. Nakamura, D., and Kubo, M., *J. Phys. Chem.* **68,** 2986 (1964).

60. Nakamura, D., Kurita, Y., Ito, K., and Kubo, M., *J. Am. Chem. Soc.* **82,** 5783 (1960).

61. Nakamura, D., Uehara, Y., Kurita, Y., and Kubo, M., *J. Chem. Phys.* **31,** 1433 (1959).

62. Narath, A., *J. Chem. Phys.* **40,** 1169 (1964).

63. Orville-Thomas, W. J., *Quart. Rev. (London)* **11,** 162 (1957).

64. Owen, J., *Discussions Faraday Soc.* **19,** 127 (1955).

65. Pauling, L., *J. Chem. Soc.* **1948,** 1461.

66. Pauling, L., "The Nature of the Chemical Bond," 3rd ed., p. 93. Cornell Univ. Press, Ithaca, New York, 1960.

67. Pauling, L., "The Nature of the Chemical Bond," 3rd ed., p. 162. Cornell Univ. Press, Ithaca, New York, 1960.

68. Pritchard, H. O., and Skinner, H. A., *Chem. Rev.* **55,** 745 (1955).

69. Rahn, R. O., and Dorain, P. B., *J. Chem. Phys.* **41,** 3249 (1964).

70. Reddoch, A. H., *J. Chem. Phys.* **35,** 1085 (1961).

71. Segel, S. L., and Barnes, R. G., Catalog of Nuclear Quadrupole Interactions and Resonance Frequencies in Solids, Part 1. Elements and Inorganic Compounds. Ames Laboratory Research and Development Report, U.S.A.E.C., Physics, TID 4500, 1962.

72. Semin, G. K., and Fedin, E. I., *J. Struct. Chem.* (*USSR*) (*English Transl.*) **1,** 252 and 464 (1960).

73. Sternheimer, R. M., and Foley, H. M., *Phys. Rev.* **102,** 731 (1956).

74. Sutton, L. E., "Tables of Interatomic Distances and Configuration in Molecules and Ions," p. M101. Chemical Society, London, 1958.

75. Townes, C. H., *in* "Handbuch der Physik" (S. Flügge, ed.), Vol. 38, Part 1, p. 377. Springer, Berlin, 1958.

76. Townes, C. H., and Dailey, B. P., *J. Chem. Phys.* **17,** 782 (1949).

77. Townes, C. H., and Dailey, B. P., *J. Chem. Phys.* **20,** 35 (1952).

78. Westland, A. D., and Bhiwandker, N. C., *Can. J. Chem.* **39,** 1284 (1961).