Nuclear Quadrupole Resonance Spectra and π-Bonding of some Nickel(II) Complexes

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Summary The nuclear quadrupole resonance spectra of some tetrahedral and square-planar nickel(II) complexes are reported: it is shown that the π-bonding character of the metal–halogen bond is *ca.* 10%.

RECENTLY Fryer and Smith[1] have reported ^{35}Cl nuclear quadrupole resonance (n.q.r.) spectra for the planar compound $(Bu^n_3P)_2NiCl_2$ and for the tetrahedral compounds $[Me_4N]_4NiCl_4$ and $[Et_4N]_2NiCl_4$.

We have independently observed the n.q.r. spectra of the tetrahedral complexes $(Ph_3P)_2NiCl_2$ and $(Ph_3P)_2NiBr_2$ and of the square-planar complexes $(Pr^n_3P)_2NiCl_2$, $(Pr^n_3)_2NiBr_2$, and $(Bu^n_3P)_2NiBr_2$. The n.q.r. frequencies (ν) are given in Table 1 together with reported data on some other nickel complexes for comparison. The paramagnetic triphenylphosphine complexes have been studied at 77 K as well as at room temperature and show normal negative temperature coefficients in their n.q.r. frequencies. The instrumentation and precision of measurement were as described previously.[2] A spectrum analyser was used to select the central radiofrequency from the side bands. Where necessary the resonant frequency was distinguished from the side band responses by varying the quench frequency. The compounds were prepared by standard methods.[3]

The notable feature of the observed resonances is the large frequency shift between the square planar and the tetrahedral complexes. This shift[1] can be associated with the presence of partly filled metal orbitals suitable for halogen–metal π-bonding in the tetrahedral complexes and the absence of such orbitals in the planar complexes. Our results make possible an estimation of the π-bonding in the case of these uncharged $(R_3P)_2NiX_2$ species where there are no cation effects and where any lattice effects can be ignored.

TABLE 1

N.q.r. frequencies of nickel(II) complexes

Compound	Stereochemistry	Nucleus	Frequency (MHz)	Temperature (K)	Signal : noise
$(Ph_3P)_2NiCl_2$	Tetrahedral	^{35}Cl	9·471	298	2
		^{35}Cl	9·723	77	4
$(Pr^n_3P)_2NiCl_2$	Planar	^{35}Cl	15·852	298	5
$(Bu^n_3P)_2NiCl_2$	Planar	^{35}Cl	15·99[a]	273	medium[a]
$(Me_4N)_2NiCl_4$	Tetrahedral	^{35}Cl	8·85, 9·05[a]	273	medium[a]
$CsNiCl_3$	Octahedral	^{35}Cl	8·349[b]	300	—
$(Ph_3P)_2NiBr_2$	Tetrahedral	^{79}Br	71·07, 75·15[c]	298	6
		^{79}Br	71·77, 77·16[c]	77	6
$(Pr^n_3P)_2NiBr_2$	Planar	^{79}Br	126·26[c]	308	15
$(Bu^n_3P)_2NiBr_2$	Planar	^{79}Br	126·53[c]	308	2
$(Ph_3P)_2NiI_2$	Tetrahedral	^{127}I	71·04, 138·0	298	3

[a] From ref. 1. [b] From ref. 4. [c] The ^{81}Br frequencies were observed with the correct frequency ratio.

If the degree of π-bonding is given by π, the s-hybridisation by s, and the ionic character by i, then it has been shown[5] that

$$e^2Qq_{\mathrm{mol}}/e^2Qq_{\mathrm{at}} = (1-s)(1-i-\pi)-\pi/2 \tag{1}$$

where e^2Qq_{mol} is the quadrupole coupling constant in the molecule and e^2Qq_{at} is that of the free atom. For spin 3/2 nuclei (*e.g.* ^{35}Cl, ^{79}Br)

$$e^2Qq_{\mathrm{mol}} = 2\nu(1 + 1/3\eta^2)^{\frac{1}{2}}$$

where η is the assymmetry parameter. For tetrahedral complexes, symmetry requires that η be small, and for $(Ph_3P)_2NiI_2$ where the spin 5/2 nucleus allows η to be determined, the value $\eta = 0{\cdot}15$ is obtained. There is evidence that η is also small in planar complexes.[1] Hence we can take $e^2Qq_{\mathrm{mol}} = 2\nu$ for these compounds. Following Kubo *et al.* we assume 15% s-hybridisation as the most reasonable value.[5] Then equation (1) becomes

$$e^2Qq_{\mathrm{mol}}/e^2Qq_{\mathrm{at}} = 0{\cdot}85\ (1 - i) - 1{\cdot}35\pi \tag{2}$$

We now take $\pi = 0$ for the square planar complexes, with no available $d\pi$ orbitals, and calculate i. If we assume the same ionic character for the corresponding tetrahedral complex then we can evaluate the degree of π-bonding from equation (2). The results obtained are given in Table 2. The same values of i and π are obtained when the tributyl phosphine complexes are considered. This estimate of 10% π-bonding is the first obtained from n.q.r. studies of metal complexes.

While the approximations made in this analysis are such that the results in Table 2 must be regarded as an order of magnitude estimate only, two observations support them. Firstly, the decrease in ionic character and increase in π-bonding between the chloride and bromide is as expected. Secondly, the classical measurement of the π-bond character of a metal–halogen bond by Griffiths *et al.*[6] gave the value 5·3% for the hexachloroiridate(IV) ion. Our value of *ca.* 10% is significantly higher than this as expected for compounds with two d-orbitals available for π-bonding.

TABLE 2

Bonding parameters

Compound		$e^2Qq_{\mathrm{mol}}/e^2Qq_{\mathrm{at}}$	i	π
$(Ph_3P)_2NiCl_2$ ..	..	0·173	0·66	0·09
$(Pr^n_3P)_2NiCl_2$ ..	..	0·289	0·66	—
$(Ph_3P)_2NiBr_2$ ..	..	0·190	0·61	0·10
$(Pr^n_3P)_2NiBr_2$	..	0·328	0·61	—

For the pseudo-octahedral compound $CsNiCl_3$ the n.q.r. data suggest that the extent of π-bonding is quite similar. The effects of the cations and the bridging nature of the chlorine atoms would need to be considered in any further analysis of π-bonding.

The two n.q.r. frequencies observed for $(Ph_3P)_2NiBr_2$ suggest that the compound is further distorted than the chloride,[7] with two different nickel–bromine bond lengths.

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