Characterisation of the Structure of Inorganic Chloride Salts with Chlorine Solid State N.M.R.

Tina L. Weeding and Wiebren S. Veeman*

Department of Molecular Spectroscopy, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

The ^{35}Cl and ^{37}Cl solid state n.m.r. chemical shifts are highly correlated with the interionic separation and with the electronegativity of the cation in inorganic chloride salts with cubic structures.

Solid state n.m.r. is finding ever greater acceptance as a method for providing structural information. Chlorine has been used in solution n.m.r. studies but, as yet, there have been few reports of solid state n.m.r. of either the ^{35}Cl or ^{37}Cl isotopes. This is probably due to their typically large quadrupole coupling constants (q.c.c.) which make them ideal candidates for nuclear quadrupole resonance (n.q.r.) spectroscopy, but less suited for n.m.r. However, when the nucleus is in a position of high symmetry, the q.c.c. is small and either isotope is a good candidate for solid state n.m.r. because natural abundances are high (75% for ^{35}Cl and 25% for ^{37}Cl), the gyromagnetic ratios give Larmor frequencies which are high enough to be conveniently measured on a high field instrument (49 MHz for ^{35}Cl and 41 MHz for ^{37}Cl at 11.7 Tesla), and the chemical shift ranges are large. Here we report on the ^{35}Cl and ^{37}Cl solid state n.m.r. of five chloride salts with cubic structures.

The n.m.r. spectra were measured at room temperature on a Bruker AM 500 spectrometer equipped with a Bruker double bearing CP/MAS probe. The chemical shifts were measured by comparison with an external dilute solution of Cl^-, the resonance of which was assigned 0.0 p.p.m. Of the five salts, two (CsCl and NH_4Cl) have the CsCl structure in which the Cl^- ion has eight cation neighbours at equal distances, and three (NaCl, KCl, and RbCl) have the NaCl structure in which the Cl^- ion has six cation neighbours at equal distances.

The measured chemical shifts are given in Table 1 and the spectra of two of the salts are shown in Figure 1. For each salt, both isotopes give peaks at the same chemical shift value. This equality of chemical shifts shows that there are no quadrupole effects which would produce unequal shifts in the resonance positions because of the unequal values of the quadrupole moments (Q) of the two isotopes [Q of ^{35}Cl is -0.0789 barns and Q of ^{37}Cl is -0.0621 barns (1 barn = 10^{-24} cm^2 per nucleus)]. To interpret these data we therefore need only to consider chemical shift effects.

Table 1. ^{35}Cl and ^{37}Cl Chemical shifts[a] and structural data.

Sample	Structure	^{35}Cl	^{37}Cl	R(Å)	S.e.n.
$Cl^-_{(aq)}$		0.0	0.0		
CsCl	CsCl	109.4	109.6	3.560	0.2200
NH_4Cl	CsCl	74.0	73.8	3.357	0.3075
RbCl	NaCl	44.7	44.8	3.285	0.3120
KCl	NaCl	3.07	2.8	3.139	0.4450
NaCl	NaCl	−46.1	−42.0	2.814	0.5600

[a] Chemical shifts are measured in p.p.m. relative to an external standard of dilute Cl^-. The least squares fits to the data gave the relations: δ(p.p.m.) = -2264 (s.e.n./c.n.) + 166, where s.e.n. is the Sanderson electronegativity and c.n. is the co-ordination number of the Cl^-; δ(p.p.m.) = $216(R) - 660$ where R is the internuclear separation in Å.

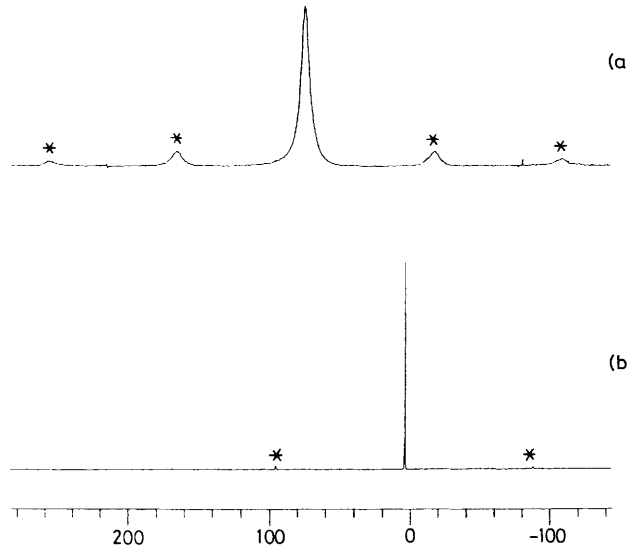

Figure 1. ^{35}Cl spectra of (a) NH_4Cl and (b) KCl. Magic angle spinning (MAS) rate was 4.5 KHz, spinning side bands are indicated by the stars. The NH_4Cl line is broadened by the protons which were not decoupled.

Various correlations between chemical shifts and structural parameters have been published. For example, in an analysis of 99 different sites in minerals, the ^{29}Si chemical shift has been shown to be sensitive to the sum of the electronegativities of the bonded groups.[1] ^{31}P chemical shifts in orthophosphates have been shown to be highly correlated with the electronegativity of the nearest neighbour divided by $\sqrt{R}$, the distance to the nearest neighbour.[2] Turner *et al.* also found that the ^{31}P chemical shift anisotropy was linearly correlated with the average deviation of the O–P–O angle from tetrahedral in orthophosphate systems.[2] In aluminophosphates, both the ^{27}Al and ^{31}P chemical shifts are correlated with the mean Al–O–P angle.[3]

The parameters which we tested for correlation with the chemical shift included R, $1/R$, $1/R^3$, $1/\sqrt{R}$, Sanderson electronegativity, Sanderson electronegativity/R, Sanderson electronegativity/$\sqrt{R}$, the volume of the unit cell, and the cation/anion radius ratio. For these Cl n.m.r. data, the chemical shifts were found to be well correlated with both the distance, R (Figure 2a), between the chloride anion and the cation, and the (Sanderson) electronegativity[4] of the electropositive element (Figure 2b). The correlation with the electronegativity of the cation is better than that with the internuclear separation. Sanderson electronegativities of the neutral atoms were used rather than the older, more common Pauling electronegativities, because the latter are less refined, and for example, show no difference between the values for Cs and Rb. The best fit was achieved when the electronegativity was adjusted for the number of nearest neighbours by dividing the electronegativity by the co-ordination number.

Not surprisingly, the Sanderson electronegativity and the interionic separation are also highly correlated. Since electronegativity values for the elements were available, but that of NH_4 was not available, the electronegativity of NH_4 was estimated *via* a least squares fit of the electronegativity *versus* R for the other four salts. The estimated value of the electronegativity of NH_4 is given in Table 1 along with the literature data for the other four crystals. The best fit equations given at the bottom of Table 1 can be used to estimate the electronegativity of, or distance to, cations in cubic chloride salts for which n.m.r. data are available.

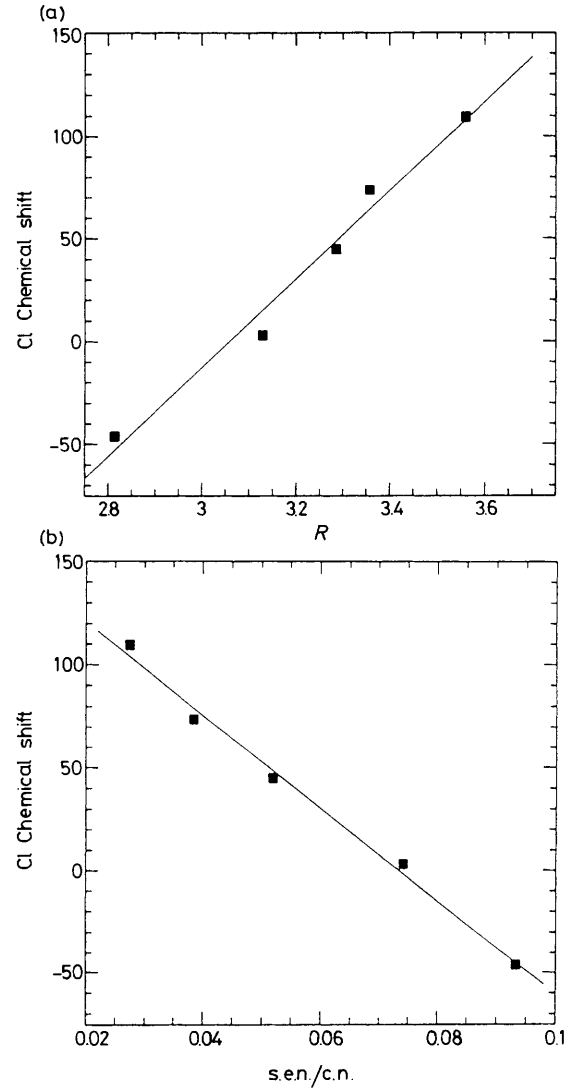

Figure 2. Least squares fits of the Cl chemical shift to (a) R, the internuclear separation in Å and (b) the Sanderson electronegativity (s.e.n.) divided by the co-ordination number (c.n.).

The Cl^- ion has a closed shell, noble gas configuration so paramagnetic contributions to the chemical shift are negligible. The deshielding of the chlorine nucleus by its electropositive neighbours shifts the resonance downfield. Larger, more electropositive cations like Cs^+ have a larger effect upon the the Cl^- electrons than smaller, less electropositive ions like Na^+. The influence of 8 neighbours is greater than that of 6 neighbours and must be divided out to compare the effects. The linear correlation in R is unusual and more difficult to understand. That the correlation with R is not caused by simple steric or packing effects which 'squeeze' the Cl^- electrons can be seen by the poor correlation with the volume of the unit cell. However, the outer electrons of the larger cations are much less tightly bound than those of the smaller cations. Perhaps the greater polarizability of the larger ions is responsible for the greater observed deshielding of the Cl nucleus and is manifested in a linear dependence upon the internuclear separation. We emphasise that the dependence is upon the internuclear separation and not upon the ionic radius, NH_4^+ and Rb^+ have the same ionic radius.

This work was performed as part of the research program of the Stichting Scheikundig Onderzoek in Nederland (S.O.N.) with financial support of the Nederlandse organisatie voor Wetenschappelijk Onderzoek (N.W.O.).

Received, 15th March 1989; Com. 9/01123D

References

1 N. James and E. Oldfield, *J. Am. Chem. Soc.*, 1985, **107**, 6769.
2 G. L. Turner, K. A. Smith, R. J. Kirkpatrick, and E. Oldfield, *J. Magn. Reson.*, 1986, **70**, 408.
3 D. Muller, E. Jahn, G. Ladwig, and H. Haubenreisser, *Chem. Phys. Lett.*, 1984, **109**, 332.
4 R. T. Sanderson, *J. Am. Chem. Soc.*, 1983, **105**, 2259.