Ratios of Quadrupole Splittings: Determination of Quadrupole Parameters for Ruthenium-99 and Tin-119

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Partial quadrupole splitting values from Fe^{II} low-spin compounds are used to obtain the sign of e^2qQ^* for nine Ru^{II} compounds; from the ratios of quadrupole splittings of Ru^{II} and Fe^{II} analogues, the ^{99}Ru quadrupole moment, Q^*, has been calculated to be $|0{\cdot}34| \pm 0{\cdot}07 \times 10^{-28}$ m^2. The Ru quadrupole splittings and centre shifts for $[Ru(NH_3)_5L]^{2+}$ compounds (L = N_2, CO, or MeCN) indicate that N_2 is relatively a poor σ donor but a moderate π acceptor.

By comparing ^{119}Sn and ^{121}Sb e^2qQ values for isoelectronic and isostructural compounds, the quadrupole moment of ^{119}Sn is calculated to be $-0{\cdot}062 \pm 0{\cdot}02 \times 10^{-28}$ m^2. The quadrupole splitting of the $SnCl_5^-$ ion is deduced to be negative.

A NUMBER of excited-state quadrupole splittings for $^{99}Ru^{II}$ compounds have now been determined[1-4] but rationalization of these splittings has not yet been attempted because the signs of e^2qQ^* are not known. Since the quadrupole splittings of these compounds are small, and often barely resolvable, there is little possibility of these signs being measured. In addition, the magnitude and sign of the quadrupole moment $Q^*_{^{99}Ru}$ is not well established. A lower limit of $0{\cdot}15 \times 10^{-28}$ m^2 has been calculated for $Q^*_{^{99}Ru}$ from the measured e^2qQ for RuO_2 by assuming that the fourth d electron in Ru^{4+} occupies solely the d_{xz} or d_{yz} orbital.[5] However, with spin–orbit coupling and crystal field effects, $Q^*_{^{99}Ru}$ may well be much larger than this preliminary value.

Despite the large body of data on ^{119}Sn quadrupole splittings, some of the quadrupole parameters are not yet well established. For example, the sign and magnitude of the ^{119}Sn quadrupole moment have been reported[6,7] but the magnitude of $Q_{^{119}Sn}$ is uncertain. In addition, confirmatory evidence for the negative sign of $Q_{^{119}Sn}$ would be welcome,[8] since this sign was postulated[6] on the basis of bonding schemes which are too empirical to be entirely reliable.

To obtain some of the above unknown or uncertain quadrupole parameters for ^{99}Ru and ^{119}Sn, we use the ratio method outlined previously.[9] If one takes two corresponding isoelectronic compounds such as *trans*-$Fe(NH_3)_4Cl_2$ (1) and *trans*-$[Co(NH_3)_4Cl_2]^+$ (2)[9] and assumes (a) that the bonding is identical in both compounds, (b) that the small contributions to e^2qQ from the small $4p$-orbital occupation can be neglected, and (c) that the Sternheimer antishielding factors $(1 - R)$ are the same in both compounds, then one obtains equation (1). This formula can be used in two ways.

$$(e^2qQ)_2 = \left[\frac{e^2q_{3d(2)}Q_2}{e^2q_{3d(1)}Q_1}\right](e^2qQ)_1 \qquad (1)$$

First, the sign of $(e^2qQ)_2$ can be obtained if the sign of $(e^2qQ)_1$ is known, or can be calculated from partial quadrupole splitting (p.q.s.) values. For example, the calculated sign of e^2qQ for *trans*-$Fe(NH_3)_4Cl_2$ was positive; therefore, the sign of e^2qQ for *trans*-$[Co(NH_3)_4Cl_2]^+$ must also be positive (for Q_1 and Q_2 both positive). Secondly, either one of the Q or q parameters in equation (1) can be obtained if the other five quantities are known. In our comparison of Fe^{II} and Co^{III} complexes[9] a semiempirical value for $Q_{^{57}Fe}$ was thus obtained, which was in reasonable agreement with other published values of $Q_{^{57}Fe}$.

For a number of analogous compounds of electronically isosymmetric metal ions M_1 and M_2, it is convenient to plot $(e^2qQ)_{M_2}$ against $(e^2qQ)_{M_1}$. The intercept should be zero, and the slope given by (2). From such a graph,

$$\frac{e^2q_{ndM_2}Q_{M_2}}{e^2q_{mdM_1}Q_{M_1}} \qquad (2)$$

the signs of $(e^2qQ)_{M_2}$ can be obtained if those of $(e^2qQ)_{M_1}$ are known, and the slope can be used to obtain one of the quadrupole moments.

Using the above method for pairs of Ru and Fe compounds, and Sb and Sn compounds, we have obtained the signs of the quadrupole splittings for Ru and Sn compounds which cannot be obtained from experimental data. Using equation (1), we have calculated new values of the quadrupole moments, $Q^*_{^{99}Ru}$ and $Q_{^{119}Sn}$ which, despite the assumptions noted above, appear to be more accurate than those reported previously.

RESULTS AND DISCUSSION

Ru and Fe Quadrupole Splittings.—Table 1 lists reported $\frac{1}{2}e^2qQ^*$ values for nine Ru^{II} compounds.[1-4] Because values obtained by different groups vary markedly sometimes, we have averaged the reported quadrupole splittings.[10] Very small quadrupole splittings have been arbitrarily assigned to the $[Ru(NH_3)_5L]^{2+}$ (L = CO and MeCN) compounds. The large

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linewidth in the CO compound definitely indicates unresolved splitting. The choice of $\frac{1}{2}e^2qQ^*$ values for these two compounds makes little difference to the later analysis.

TABLE 1

Quadrupole splittings for Ru compounds, and calculated quadrupole splittings for analogous Fe compounds

	$\lvert\frac{1}{2}e^2qQ^*\rvert$(Ru) mm s^{-1}	$\frac{1}{2}e^2qQ$(Fe) mm s^{-1}
$[M(NH_3)_5CO]^{2+}$	$>0(0{\cdot}10)$	$-0{\cdot}08$
$[M(NH_3)_5MeCN]^{2+}$	$\sim0(0{\cdot}05)$	$-0{\cdot}16$
$[M(NH_3)_5N_2]^{2+}$	0·23	+0·28
$[MBr_5NO]^{2-}$	0·08	+0·60
$[MCl_5NO]^{2-}$	0·21	+0·64
$[M(CN)_5NO_2]^{4-}$	0·28	+0·86
$[M(NCS)_5NO]^{2-}$	0·24	+1·02
$[M(NH_3)_5NO]^{3+}$	0·36	+1·06
$[M(CN)_5NO]^{2-}$	0·42	+1·72

Most of the Fe^{II} analogues are unknown, but the quadrupole splittings for hypothetical compounds can be calculated by use of partial quadrupole splittings (Table 2). Most of these values are taken from a previous paper,[11] but those for N_2 and MeCN have been calculated from the quadrupole splittings of *trans*-$[FeHL'(depe)_2]^+BPh_4^-$ ($L' = N_2$ and MeCN).[12] The value for CO is taken from a recent paper,[13] and our present studies[14] indicate that this is a reasonable value. The p.q.s. values for N_2 and CO are expected to vary over a range of *ca.* 0·1 mm s^{-1},[14] but those quoted appear to be good working values.

TABLE 2

Partial quadrupole splittings/mm s^{-1} for ligands in Fe^{II} compounds

NO^+	+0·02	MeCN	−0·43
Br^-	−0·28	NCS^-	−0·49
Cl^-	−0·30	NH_3	−0·51
N_2	−0·37	CO	−0·55
NO_2^-	−0·41	CN^-	−0·84
		H^-	−1·04

The quadrupole splittings in Table 1 for the Fe^{II} compounds can then be calculated simply. The Z e.f.g. axis is along the four-fold molecular axis, and for a species $FeAB_5$, the quadrupole splitting is given by $2(\text{p.q.s.})_A - 2(\text{p.q.s.})_B$.[15]

A plot of $\lvert(\frac{1}{2}e^2qQ^*)\rvert_{Ru}$ against $(\frac{1}{2}e^2qQ)_{Fe}$ is given in Figure 1 and the nine points have been fitted to a least-squares straight line with slope +3·0 and intercept +0·1 mm s^{-1}. If the CO and MeCN compounds are omitted, then the slope is +3·2 and the intercept +0·05 mm s^{-1}. The possible errors in the Ru quadrupole splittings, and the assumption of identical bonding on both Ru and Fe compounds being considered, there is a reasonably good linear correlation and the intercept is remarkably close to zero.

Except for the first two Ru compounds in Table 1, the signs of q for the other Ru compounds can be confidently assigned as positive: if Q^* is positive, then e^2qQ^* for these compounds is also positive, as for the analogous Fe compounds. Because of the very small e^2qQ values for $M(NH_3)_5(MeCN)^{2+}$ and $M(NH_3)_5(CO)^{2+}$, and the variable bonding of CO, the signs of q for these compounds are more tentative.

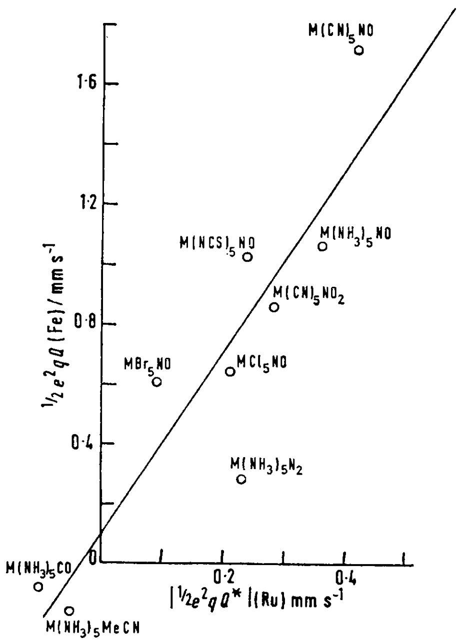

FIGURE 1 $\frac{1}{2}e^2qQ$ for Fe^{II} compounds plotted against $\lvert\frac{1}{2}e^2qQ^*\rvert$ for analogous Ru^{II} compounds

The correlation strongly suggests that the bonding in analogous Fe and Ru complexes is reasonably similar, *i.e.*, that q as defined in equation (3)[15]

$$q = K[-N_{d_{z^2}} + N_{d_{x^2-y^2}} + N_{d_{xy}} - \tfrac{1}{2}(N_{d_{xz}} + N_{d_{yz}})] \quad (3)$$

in both Ru and Fe complexes are similar. We therefore feel that it is reasonable to use equation (1) to calculate a value of $Q^*{}_{^{99}Ru}$ using the following quantities: $\langle r^{-3}\rangle_{4d}$ for Ru^{II} = 5·86 a_0^{-3},[16] $\langle r^{-3}\rangle_{3d}$ for Fe^{II} = 4·73 a_0^{-3},[16] and taking $E_\gamma(^{99}Ru) = 90$ keV and $E_\gamma(^{57}Fe) = 14{\cdot}4$ keV, $Q_{^{57}Fe} = 0{\cdot}20 \times 10^{-28}$ m^2 [9] † and $(e^2qQ^*)_{Ru}/(e^2qQ)_{Fe} = +3{\cdot}0$ from Figure 1. Substituting these values into equation (1) (using E_γ to convert the e^2qQ values from mm s^{-1} into MHz), we obtain $\lvert Q^*{}_{^{99}Ru}\rvert = 0{\cdot}34 \times 10^{-28}$ m^2. It is difficult to measure the error in this quantity owing to the errors in the e^2qQ values, $Q_{^{57}Fe}$, the $\langle r^{-3}\rangle$ values, and the assumption of identical bonding in analogous Fe and Ru compounds. However,

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† Although many values for the quadrupole moment of ^{57}Fe have been suggested, $0{\cdot}20 \times 10^{-28}$ m^2 is commonly considered to best represent $Q_{^{57}Fe}$ at present.

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we suggest that the above value is accurate to $0{\cdot}07 \times 10^{-28}$ m^2. Our value of Q^* is considerably larger than the minimum value reported previously.[5]

Having established the correlation between Ru and Fe quadrupole splittings, it is worth commenting on the variation of quadrupole splittings with bonding properties of ligands using the method outlined earlier.[12,15] For example, in the $M(NH_3)_5L$ series ($L = N_2$, MeCN, and CO), e^2qQ^* will become more negative as the σ donor ability of L increases, and as the π-acceptor ability of L decreases, *i.e.*, as $\sigma - \pi$ increases. The partial quadrupole splitting values for N_2, MeCN, and CO (Table 2), and the variation in quadrupole splittings for the above three pairs of compounds indicate that $\sigma - \pi$ increases in the order $N_2 <$ MeCN $<$ CO. Thus CO is most likely a better σ donor *and* a better π acceptor than NH_3, $[(\text{p.q.s.})_{CO} \approx (\text{p.q.s.})_{NH_3}]$ and the two almost cancel out to give a small unresolvable quadrupole splitting in $M(NH_3)_5CO$ In contrast, N_2 is probably a better π acceptor but worse σ donor than NH_3 $[(\text{p.q.s.})_{N_2}$ is more positive than $(\text{p.q.s.})_{NH_3}]$, and both σ and π terms contribute to a moderately large quadrupole splitting. Together with both Ru and Fe centre-shift data which indicate that that $\sigma + \pi$ increases in the order MeCN $< N_2 <$ CO, we conclude, as previously,[12] that N_2 is a poor σ donor and a moderate π acceptor when bonded to both Fe and Ru.

Sn *and* Sb *Quadrupole Splittings*.—A plot of $(e^2qQ)_{^{119}\mathrm{Sn}}$ against $(e^2qQ)_{^{121}\mathrm{Sb}}$ for isoelectronic Sn [17-20] and Sb [21,22] compounds is given in Figure 2. All of the Sb e^2qQ signs are negative,[21,22] while the signs of e^2qQ are known to be negative for $[Me_3SnCl_2]^-$ and $[Ph_3SnCl_2]^-$.[20] It is reasonable to assume then that e^2qQ is negative for the other $[R_3SnX_2]^-$ compounds.

The analogous Sn and Sb compounds appear to be isostructural. Both $SbCl_5$ at room temperature and $SnCl_5^-$ have trigonal bipyramidal structures with metal–chlorine bond lengths of $2{\cdot}35 \pm 0{\cdot}1$ Å.[23,24] Although several studies (see refs. in ref. 25) have suggested that $SbCl_5$ undergoes a change in structure at low temperatures, an Sb n.q.r. study showed that $(e^2qQ)_{Sb}$ is the same above and below the transition temperature.[26] The Me_3SbX_2 and Ph_3SbX_2 structures are also based on a trigonal bipyramid, with axial halogens and equatorial Me or Ph ligands.[25,27,28] There are no *X*-ray data on the analogous tin compounds, but i.r. evidence for $[Ph_3SnX_2]^-$ [29] suggests that they are isostructural with the corresponding antimony compounds.

Figure 2 shows the good linear correlation between the Sb and Sn quadrupole splittings. The slope is $+3{\cdot}40$; and once again the intercept is very close to zero ($+0{\cdot}25$ mm s^{-1}). Two facts can immediately be obtained from this graph. First, since $Q_{^{121}\mathrm{Sb}}$ is negative,[30] $Q_{^{119}\mathrm{Sn}}$ must also be negative. Secondly, the sign of e^2qQ for $SnCl_5^-$ is negative as first assumed by Parish and Platt.[18] However, the recent M.O. treatment for Sn compounds left this sign in some doubt.[31] From the treatment by Clark *et al.*,[31] it is apparent that $\sigma_{01}{}^{tba} > \sigma_{01}{}^{tbe}$ (tba = trigonal bipyramidal axial; tbe = trigonal bipyramidal equatorial).

Using equation (1), the quadrupole moment of ^{119}Sn can be calculated from: $Q_{^{121}\mathrm{Sb(gr)}} = -0{\cdot}28 \times 10^{-28}$ m^2,[30] $q_{5p(\mathrm{Sn})} = 11{\cdot}2$ $a_0{}^{-3}$, $q_{5p(\mathrm{Sb})} = 13{\cdot}0$ $a_0{}^{-3}$,[32] and $E_\gamma(\mathrm{Sb})/E_\gamma(\mathrm{Sn}) = 1{\cdot}55$.[33] Substituting these quantities and the slope of the line into equation (1) gives $Q_{^{119}\mathrm{Sn}} = -0{\cdot}062 \times 10^{-28}$ m^2, in reasonable agreement with those values given previously.[6,7] With the large error in $Q_{^{121}\mathrm{Sb}}$ ($= 0{\cdot}1 \times 10^{-28}$ m^2),[30] the absolute error in this

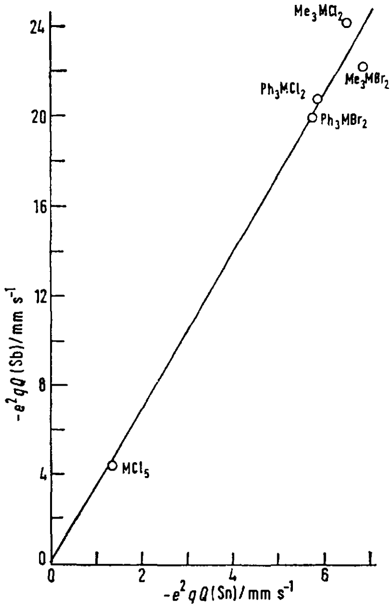

FIGURE 2 e^2qQ for Sb^V compounds plotted against e^2qQ for isoelectronic Sn^{IV} compounds

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value is probably about ±0·02 × 10^{-28} m^2, although the ratio of $Q_{Sb} : Q_{Sn}$ obtained by this method is probably more accurate.

Finally, it should be noted that with the above value of $Q_{^{119}Sn}$ and the $q_{5p(Sn)}$ value given above, the $\frac{1}{2}e^2qQ$ value for one 5_{pz} electron in ^{119}Sn ($=\Delta_0$) is *ca.* 3·4 mm s^{-1}, substantially smaller than those used for previous calculations.[34,35]

Note added in proof: A recent paper [36] reports values for $Q_{^{119}Sn}$ ($-0{\cdot}065 \times 10^{-28}$ m^2 and Δ_0 3·5 mm s^{-1}) in excellent agreement with our values.

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