On the Correlation of $^{35}$Cl Nuclear Quadrupole Coupling Constants with $\pi \rightarrow \gamma_3$ and $\pi \rightarrow \gamma_5$ Optical Electron Transfer Bands of Transition Metal Complexes and its Significance in Pi-Bonding

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From a consideration of odd-even intramolecular electron transfer processes in octahedrally co-ordinated transition metal complexes, two relationships have been derived. The first correlation describes $\pi \rightarrow \gamma_3$ optical electron transfer bands of the complexes $K_2OsCl_6$, $K_2IrCl_6$, $K_2PtCl_6$, $K_2PtCl_4$ as a function of the respective $^{35}$Cl nuclear quadrupole coupling constants. The second relationship, correlates $\gamma_5$ optical charge transfer transitions of the substances $K_2OsCl_6$, $K_2IrCl_6$, $K_2PtCl_4$, $K_2PtCl_6$, $K_2PtCl_4$ with the $^{35}$Cl nuclear quadrupole coupling constants of these compounds. By using this charge transfer model, a linear relationship has been verified between the optical electronegativity values of the quadrivalent transition metal ions $W^{4+}$, $Re^{4+}$, $Os^{4+}$, $Ir^{4+}$, $Pt^{4+}$ and the $^{35}$Cl nuclear quadrupole coupling constants of their hexachloro complexes. The empirically established equation $\chi \lambda_{\text{e}} = 0.537 \left( \frac{\alpha^2 Q q_{\text{mol}}}{{^{35}\text{Cl}}} \right)$, which describes the $^{35}$Cl n.q.r. frequencies of the hexachloro complexes of $Re^{4+}$, $Os^{4+}$, $Ir^{4+}$, $Pt^{4+}$ and $Pd^{4+}$ as a function of the optical electronegativity values $\chi$ of these metal ions, has been used to estimate $^{35}$Cl nuclear quadrupole resonance frequencies of chloro complexes as yet not probed by nuclear quadrupole resonance spectroscopy, e.g. Zeise’s salt ($KPtCl_3C_2H_4$), $K_2IrCl_6$, $K_2RuCl_6$, $K_2RhCl_6$ and $K_3MoCl_6$. Conversely, by the same procedure the optical electronegativity $\chi$ of $W^{4+}$ and $Au^{3+}$ has been estimated from the $^{35}$Cl quadrupole resonance frequency of $K_2WCl_6$ and $KAuCl_4$ ($\chi W^{4+} = 1.71$ and $\chi Au^{3+} = 2.80$). In the case of analogous bromo complexes, the equation $\mu_{\text{Br}} = 0.19 \left( \frac{\alpha^2 Q q_{\text{mol}}}{{^{79}\text{Br}}} \right)$ accounts for the dependence of the $^{79}$Br nuclear quadrupole resonance frequencies upon the optical electronegativity of the metal ions. The assignment of electron transfer bands in other chloro complexes is discussed in the light of this “nuclear quadrupole resonance criterion” of optical charge transfer bands.

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3 P. MACHMER, J. inorg. nuclear Chemistry 30, 2627 [1968].
8 H. G. DEHMELT and H. KRÜGER, Naturwissenschaften 37, 111 [1950].
electron donor to the lowest lying empty m.o. of the acceptor. On the other hand, the same electron transfer phenomenon gives rise to a new and distinct uv-absorption band and a simple relationship should therefore hold for both the n.q.r. and uv-parameters of structurally related species. In particular, a series of transition metal complexes of the K₂PtCl₆-antifluorite type (hereafter referred to as K₂MeCl₆ with Me = Re, Os, Ir and Pt) is utilized to demonstrate a relationship between their n.q.r. and uv-features which are characteristic of intramolecular charge transfer.

With reference to the relationships developed in the following section, it should be mentioned that correlations were previously noted between n.q.r. coupling constants of substituted chlorobenzenes and the Hammett σ-values of their substituents. Also Taft's induction constants have been related to n.q.r. parameters. Data from polargraphic half-wave potentials, infrared, and n.m.r. spectroscopy have been used as further evidence of a linear dependence on nuclear quadrupole coupling constants. Results of theoretical calculations have been rationalized in a similar way. Also the unusual temperature dependence of nuclear quadrupole frequencies has been related to the π-bonding parameter which in turn may depend upon superexchange.

**Results**

It should be noted that in the series of transition metal complexes under investigation, both the first strong π→γ₃ and π→γ₅ optical charge transfer bands are linearly related to the intrinsic ³⁵Cl nuclear quadrupole coupling constants (see figs. 1 and 2; the n.q.r. and uv-data relevant to the figs. 1 and 2 are collected in the appendix). Alternatively, it is not possible to accommodate the crystal field bands and the ³⁵Cl n.q.r. results by a smooth curve.

![Fig. 1. Linear plot of ³⁵Cl nuclear quadrupole coupling constants versus wavelength of the respective first strong π→γ₃ charge transfer band (slope: 0.5).](image-url)

**References**

16. R. S. Mulliken, J. Amer. chem. Soc. 72, 600 [1950].
24c. C. K. Joergensen, Molecular Physics 2, 329 [1959].
An examination of both figs. shows that the linearity of the two plots is satisfactory, although the uv-data refer to solution spectra whereas the n.q.r. spectra characterize the K₂MeCl₆ complexes in the solid state. However, for practical reasons it is necessary to use the uv-spectra of the solutions for the production of figs. 1 and 2 since diffuse reflectance spectroscopic data are only available for the complexes K₂OsCl₆ and Na₂IrCl₆. The procedure adopted here seems to be justifiable because it has been established that the position of an optical absorption band of solid K₂MeCl₆ complexes is only slightly shifted towards shorter wavelengths upon dissolution. For a series of homologous compounds such as the K₂MeCl₆ complexes, the shift is of the same order of magnitude for all members of the series since the environmental difference is the same in each case. With regard to K₂OsCl₆, the relevant shifts is 17 m/μ whereas Na₂IrCl₆ displays a greater change (50 m/μ) presumably on account of the different cation.

Unfortunately, optical data on K₂WCl₆ have not yet been reported. To the author's knowledge, only the uv-spectrum of Rb₂WCl₆ has been recorded and a band has been located at 235 m/μ.

That a linear relationship also exists between the Cl nuclear quadrupole coupling constants and the optical electronegativities of the central quadrivalent metal ions of K₂MeCl₆ complexes, can be seen from fig. 3.

The data graphically represented on fig. 3 are summarized in the appendix.

**Discussion**

In the uv-spectra of octahedrally co-ordinated chloro complexes of the general formula K₂MeCl₆ with Me = Re, Os, Ir and Pt, two groups of optical bands with varying intensities are displayed. The theory concerning the intensity of these bands will be summarized only briefly in the present instance since it is well outlined in the literature.

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From a consideration of selection rules, the weak hands are assigned to forbidden crystal field transitions ($\gamma_5 \rightarrow \gamma_3$) which occur between the subshells of the $5d$-orbitals of the metal ions. In contrast, the more intense spectral bands are attributed to metal-ligand interactions which involve the back-donation of lone-pair electrons from the chlorine ligands to the respective metal ion ($\pi$-bonding).

The linear and simultaneous shift of the $^{35}\text{Cl}$ nuclear quadrupole coupling constants as a function of the positions of the first strong electron transfer bands $\tau \rightarrow \gamma_3$ and $\tau \rightarrow \gamma_5$ (see figs. 1 and 2) suggests that the successive displacement of the $^{35}\text{Cl}$ nuclear quadrupole coupling constants from 51.64 MHz to 20.44 MHz (see appendix) represents an increasing $\pi$-electron transfer from the respective chlorine ligands to the central metal ion (the plots 1 and 2 imply that the shift is due to the co-operative effect of $\tau \rightarrow \gamma_3$ and $\tau \rightarrow \gamma_5$ electron transfer respectively or in other words: the change of the $^{35}\text{Cl}$ nuclear quadrupole coupling constants monitors the change of the electric field gradient at the chlorine 35 nuclei as caused by $\tau \rightarrow \gamma_3$ and $\tau \rightarrow \gamma_5$ electron transfer). This hypothesis explains the steadily decreasing $^{35}\text{Cl}$ n.q.r. coupling constants in the observed order $\text{K}_2\text{PtCl}_6 > \text{K}_2\text{IrCl}_6 > \text{K}_2\text{OsCl}_6 > \text{K}_2\text{ReCl}_6 > \text{K}_2\text{WC1}_6$ because increasing transfer of lone-pair electrons results in a more spherical charge distribution which in turn lowers the $^{35}\text{Cl}$ nuclear quadrupole coupling constant. This effect of $\pi$-bonding on the n.q.r. coupling constant is quantitatively accounted for by the eq. $^{44a-b}$

$$\frac{e^2 \frac{Q}{\text{mol}}}{h} = \left[ (1 - s^2 + d^2) (1 + i) - \pi \right] \frac{e^2 Q_{\text{atomic}}}{h} \quad (1)$$

with $e^2 Q_{\text{mol}}/h = \text{molecular nuclear quadrupole constant}$, $e^2 Q_{\text{atomic}}/h = \text{nuclear quadrupole coupling constant of atomic }^{35}\text{Cl}$, $i$ = ionicity of the o-bond, $s^2 = \text{s-hybridisation of the o-bond}$, $\pi = \text{double bond character}$.

Indeed, it is justified to attribute the n.q.r. shift of $\text{K}_2\text{MeCl}_6$ complexes to the action of the $\pi$-bonding parameter $^{46, 47a-b}$ since neither the ionicity $i$ nor the s-hybridisation on chlorine 35 accounts for the varying $^{35}\text{Cl}$ nuclear quadrupole coupling constants. In particular, it has been confirmed by n.q.r. data $^{46}$ that the ionicity $i$ of the respective metal-chlorine $\sigma$-bond is virtually the same in all $\text{K}_2\text{MeCl}_6$ complexes under consideration. Further, in the series of the structurally correlated $\text{K}_2\text{MeCl}_6$ complexes with $d^{5}\text{sp}^3$-hybridisation on the metal ion, the degree of s-contribution is, to a good approximation, constant on the various metal ions as well as on their chlorine ligands. Also crystal lattice effects cannot cause the shift from 51.64 MHz to 20.44 MHz since the order of magnitude of this effect $^{48}$ is $\pm 0.6$ MHz. Finally, it should be noted that the possible influence of metal-oxidation bands ($\gamma_3 \rightarrow \tau$ and $\gamma_5 \rightarrow \pi$) on the $^{35}\text{Cl}$ nuclear quadrupole coupling constants can be neglected as long as only metal-reduction bands ($\tau \rightarrow \gamma_3$ and $\tau \rightarrow \gamma_5$) are identified in the relevant uv-spectra $^{25}$. In conclusion, the present approach confirms the trend in the numerical values of the $\pi$-bonding parameter $^{46}$ but no inference is possible concerning the accuracy of the percentage values estimated $^{46}$.

It is reassuring to have available some critical test of the performance of the charge transfer model as adopted and applied here in conjunction with n.q.r. spectroscopy. It is felt that its validity may be tested by examining the implications inherent in the charge transfer model, one of them being a linear relationship between $^{35}\text{Cl}$ nuclear quadrupole coupling constants $^{18-24}$ and the optical electronegativity values $^{44a-b}$ of the transition metal ion. This relationship is a consequence of the intrinsic equation $^{49}$

$$h\nu_{CT} = \nu \chi \quad \text{or} \quad \chi$$

which applies to both intermolecular and intramolecular charge transfer by relating the electron withdrawing power $E$ of the acceptor (as characterized $^*$ by its electron affinity $E$ or the electronegativity $\chi$) to the positions of the respective charge transfer bands. However, according to figs. 1 and 2, these

$^{44}$ D. Biedenkapp and A. Weiss, Ber. Bunsenges., 70, 788 [1966].
$^{46}$ The electron affinity $E$ and the electronegativity $\chi$ are related to each other by

$$\chi = \frac{1}{2} \left( \nu + E \right).$$

optical charge transfer bands are correlated with the 
$^{35}$Cl nuclear quadrupole coupling constants and there­
fore, in conformity to equation (2), a linear relation­
ship should also exist between the electronegativity 
values $^{41a-b}$ of the acceptor metal ions and the $^{35}$Cl 
nuclear quadrupole coupling constants $^{18-24}$ of the 
donor ligands. The verification of a linear relation­
ship between $^{35}$Cl nuclear quadrupole coupling con­
stants $^{18-24}$ and the optical electronegativities $^{41a-t}$ on 
fig. 3 thus stresses the correctness of the model inferred 
from the plots on figs. 1 and 2. In the case of the com­
plexes $K_2PdCl_6$, $K_2ReCl_6$, $K_2OsCl_6$, $K_2IrCl_6$, $K_2PtCl_6$ and $K_2PtCl_4$, the empirically established 
equation

$$
\chi_{Me} = 0.537 \sqrt{ \frac{e^2 Q q_{mol}}{2 \hbar}} ^{35}Cl
$$

relates the intrinsic optical electronegativities of the 
acceptor metal ions to the $^{35}$Cl n.q.r. frequencies of 
the donor ligands (see table I which displays experi­mental and calculated $^{35}$Cl n.q.r. frequencies).

As it seems rather difficult to justify equation (3) 
theoretically and to establish the physical significance 
of the factor 0.537, the fit of calculated to experi­mental $^{35}$Cl n.q.r. frequencies (see table I) appears 
to be the important feature in the present instance.

The satisfactory performance of equation (3) in 
the cases of the six $K_2MeCl_6$ complexes under in­vestigation (see table I) makes it possible to estimate 
the $^{35}$Cl n.q.r. frequency of complexes when the optical 
electronegativity of the respective central metal ion is available from other sources. The reverse procedure is, of course, equally well applicable, i.e. 
the calculation of optical electronegativity values from experimental $^{35}$Cl n.q.r. frequencies. The present work offers examples of both approaches. Thus 
are set out in table II the calculated $^{35}$Cl n.q.r. frequencies of the complexes $KPtCl_3C_2H_4$ ($Zeise$'s salt), $K_3IrCl_6$, $K_3RhCl_6$, $K_2RuCl_6$, $K_3MoCl_6$ and $K_2TeCl_6$. To date, these compounds have not been 
probed experimentally by n.q.r. 

<table>
<thead>
<tr>
<th>Complex</th>
<th>optical electronegativity of the metal ion. (Ref. $^{41a-b}$)</th>
<th>$^{35}$Cl n.q.r. frequency [MHz] estimated with the aid of equation (3)</th>
<th>Probable limit of error: = 5%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$KPtCl_3C_2H_4$</td>
<td>2.3</td>
<td>18.3</td>
<td></td>
</tr>
<tr>
<td>$K_3IrCl_6$</td>
<td>2.25</td>
<td>17.5</td>
<td></td>
</tr>
<tr>
<td>$K_2RuCl_6$</td>
<td>2.4</td>
<td>19.9</td>
<td></td>
</tr>
<tr>
<td>$K_3RhCl_6$</td>
<td>2.3</td>
<td>18.3</td>
<td></td>
</tr>
<tr>
<td>$K_3MoCl_6$</td>
<td>1.7</td>
<td>10.9</td>
<td></td>
</tr>
<tr>
<td>$K_2TeCl_6$</td>
<td>2.2</td>
<td>16.7</td>
<td></td>
</tr>
</tbody>
</table>

Table II. Approximate values of $^{35}$Cl n.q.r. frequencies of transition metal chloro complexes which have not yet been 
probed by n.q.r. (The estimates were performed with the aid of equation (3).)

An estimate of the optical electronegativity of $W^{4+}$ and $Au^{3+}$ is also made with the aid of equation (3) from the experimental $^{35}$Cl n.q.r. frequency $^{21,24b}$ of $K_2WCl_6$ and $KAuCl_4$. For $W^{4+}$ and $Au^{3+}$ the values 1.71 and 2.80 are proposed. These results com­

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^{35}$Cl n.q.r. frequency (MHz) at 300 °K. (Ref. $^{18-24b}$)</th>
<th>$^{35}$Cl n.q.r. frequency (MHz). Calculated with the aid of equation (3)</th>
<th>$\Delta e^2 Q q_{mol}/2 \hbar$, i.e. the deviation of the calculated n.q.r. frequencies from the experimental n.q.r. data</th>
<th>optical electronegativity values of the respective metal ions. (Ref. $^{41a-b}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_2WCl_6$</td>
<td>10.22</td>
<td>10.22</td>
<td>0</td>
<td>1.71 (present work)</td>
</tr>
<tr>
<td>$K_2ReCl_6$</td>
<td>13.89</td>
<td>13.87</td>
<td>0</td>
<td>2.0</td>
</tr>
<tr>
<td>$K_2OsCl_6$</td>
<td>16.84</td>
<td>16.78</td>
<td>- 0.06 MHz ($= 0.03^\circ$)</td>
<td>2.2</td>
</tr>
<tr>
<td>$K_2IrCl_6$</td>
<td>20.73</td>
<td>19.97</td>
<td>- 0.76 MHz ($= 3.7^\circ$)</td>
<td>2.4</td>
</tr>
<tr>
<td>$K_2PtCl_6$</td>
<td>25.82</td>
<td>25.28</td>
<td>- 0.54 MHz ($= 2^\circ$)</td>
<td>2.7</td>
</tr>
<tr>
<td>$K_2PtCl_4$</td>
<td>17.92</td>
<td>18.34</td>
<td>+ 0.42 MHz ($2.3^\circ$)</td>
<td>2.3</td>
</tr>
<tr>
<td>$K_2PdCl_6$</td>
<td>26.55</td>
<td>25.28</td>
<td>- 1.27 MHz ($= 4.8^\circ$)</td>
<td>2.7</td>
</tr>
<tr>
<td>$KAuCl_4$</td>
<td>27.36</td>
<td>27.36</td>
<td>0</td>
<td>2.80 (present work)</td>
</tr>
</tbody>
</table>

Table I. Experimental $^{35}$Cl n.q.r. frequencies compared with values which were calculated with the aid of equation (3).
pare with the value $^{51a-b}$ of 1.6 and 2.9 $^{41a}$ which have been determined by a manner independent from the present method.

However, the present approach is limited in its applicability to d-group transition metal complexes since equation (3) does not rationalize the $^{35}$Cl n.q.r. frequencies of the complexes $(NH_4)_2$PbCl$_6$ and K$_2$SnCl$_6$ if for the optical electronegativity of Pb$^{4+}$ and Sn$^{4+}$ the values $^{41a-b}$ 1.9 and 1.5 are used.

The relation (4) with is similar to equation (3), namely

$$\chi_{Me} = 0.19 \sqrt{\left( \frac{e^2 Q_{mol}}{2 \hbar} \right)}$$  \(^{79}\text{Br} \) \(^{(4)}\)

has been developed to fit the $^{79}$Br n.q.r. frequencies $^{20, 21, 23}$ of K$_2$MeBr$_6$ complexes to the electronegativity values $^{41a-b}$ of their central transition metal ions. It is gratifying to note that the experimental n.q.r. results $^{20, 21, 23}$ so far available for bromo complexes, can be rationalized by equation (4). (See table III.)

As the agreement between calculated and experimental n.q.r. values is satisfactory, equation (4) is used for calculating the $^{79}$Br n.q.r. frequencies of K$_2$MeBr$_6$ complexes as yet not investigated by n.q.r. (see table IV).

With the aid of equation (4) also the “optical electronegativity” of Pd$^{2+}$ has been calculated from the $^{79}$Br n.q.r.-frequency of the complex K$_2$PdBr$_4$, the value $\chi_{Pd}$ $^{20}$ = 2.16 being obtained (the value 2.5 is proposed by JOERGENSEN $^{52}$).

With regard to iodo complexes of the type K$_2$MeI$_6$, solely K$_2$PtI$_6$ and K$_2$ReI$_6$ have been probed $^{21, 22}$ by n.q.r. At this stage any quantitative approach appears premature and only future investigations will exhibit whether the present model accommodates the uv and n.q.r. data of the iodo complexes as well as the results of the chloro and bromo complexes. However, it is already clear that the linear relationship between uv and nuclear quadrupole coupling parameters applies also to gaseous alkali halides and a subsequent paper will illustrate how the relevant experimental data can be reconciled with the framework already developed for the K$_2$MeCl$_6$ and K$_2$MeBr$_6$ complexes.

The generalization of the approach outlined on figs. 1 and 2 may lead to a “nuclear quadrupole resonance criterion” of optical charge transfer bands which can facilitate their assignment in hexachloro complexes if dichroitic experiments cannot be performed.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^{79}$Br n.q.r. frequency [MHz] at 300 $^\circ$K. (Ref. 20, 21, 23)</th>
<th>$^{79}$Br n.q.r. frequency [MHz] calculated with aid of equation (4)</th>
<th>$\Delta e^2 Q_{mol}/2 \hbar$, i.e. the deviation of the calculated n.q.r. frequencies from the experimental n.q.r. data</th>
<th>Optical electronegativity values of the respective metal ions. (Ref. 41a—b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$ReBr$_6$</td>
<td>112.70</td>
<td>110.8</td>
<td>$-1.9$ MHz ($1.6%$)</td>
<td>2.0</td>
</tr>
<tr>
<td>K$_2$PtBr$_6$</td>
<td>201.18</td>
<td>201.9</td>
<td>$+1.7$ MHz ($=0.8%$)</td>
<td>2.7</td>
</tr>
<tr>
<td>K$_2$PdBr$_6$</td>
<td>201.81</td>
<td>201.9</td>
<td>$+0.1$ MHz ($=0.05%$)</td>
<td>2.7</td>
</tr>
<tr>
<td>K$_2$PtBr$_4$</td>
<td>138.70</td>
<td>146.5</td>
<td>$+7.8$ MHz ($=5.5%$)</td>
<td>2.3</td>
</tr>
<tr>
<td>K$_2$PdBr$_4$</td>
<td>129.34</td>
<td>129.34</td>
<td>0</td>
<td>2.16</td>
</tr>
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</table>

Table IV. Approximate values of $^{79}$Br n.q.r. frequencies of transition metal bromo complexes which have not yet been probed by n.q.r. (The calculations were performed with the aid of equation (4).)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Optical electronegativity of the metal ion. (Ref. 41a—b)</th>
<th>$^{79}$Br n.q.r. frequency [MHz] estimated with the aid of equation (4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$WBr$_6$</td>
<td>1.71</td>
<td>83.8</td>
</tr>
<tr>
<td>K$_2$OsBr$_6$</td>
<td>2.2</td>
<td>134.0</td>
</tr>
<tr>
<td>K$_2$IrBr$_6$</td>
<td>2.4</td>
<td>159.5</td>
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Table III. Experimental $^{79}$Br n.q.r. frequencies compared with values which were calculated with the aid of equation (4).

## Appendix

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^{35}$Cl n.q.r. frequency $v$ [MHz] at 300°K. (Ref. 18–24b)</th>
<th>$^{35}$Cl n.q.r. coupling constant $e^2 Q_{q mol}$/h [MHz]</th>
<th>$^{79}$Br n.q.r. frequency $v$ [MHz] at 300°K. (Ref. 20, 21, 23)</th>
<th>$^{79}$Br n.q.r. coupling constant $e^2 Q_{q mol}$/h [MHz]</th>
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<tr>
<td>$K_2WCl_6$</td>
<td>10.22</td>
<td>20.44</td>
<td>$K_2ReBr_6$</td>
<td>112.70</td>
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<tr>
<td>$K_2ReCl_6$</td>
<td>13.89</td>
<td>27.78</td>
<td>$K_2PtBr_6$</td>
<td>200.18</td>
</tr>
<tr>
<td>$K_2OsCl_6$</td>
<td>16.83</td>
<td>33.68</td>
<td>$K_2PdBr_6$</td>
<td>201.81</td>
</tr>
<tr>
<td>$K_2IrCl_6$</td>
<td>20.73</td>
<td>41.46</td>
<td>$K_2PtBr_4$</td>
<td>138.70</td>
</tr>
<tr>
<td>$K_2PtCl_6$</td>
<td>25.82</td>
<td>51.64</td>
<td>$K_2PdBr_4$</td>
<td>129.34</td>
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<tr>
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<td>25.91</td>
<td>51.82</td>
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<td>$K_2PdCl_6$</td>
<td>26.02</td>
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<td>$K_2PdCl_4$</td>
<td>26.75</td>
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<td>$KAuCl_4$</td>
<td>27.36</td>
<td>54.72</td>
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### Single-electron spin-orbit coupling constant of the respective quadrivalent transition metal ions (Ref. 42)

<table>
<thead>
<tr>
<th>Quadrivalent metal ions</th>
<th>Single-electron spin-orbit coupling constant of the optical $\gamma_3 \rightarrow \gamma_3$ transition. (Crystal field bands). (Ref. 25) [m(\mu)]</th>
<th>Complex</th>
<th>W(^{4+})</th>
<th>2300 cm(^{-1})</th>
<th>K(_2)ReCl(_6)</th>
<th>363.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re(^{4+})</td>
<td>3300 cm(^{-1})</td>
<td>K(_2)OsCl(_6)</td>
<td>301</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Os(^{4+})</td>
<td>4000 cm(^{-1})</td>
<td>K(_2)IrCl(_6)</td>
<td>278</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir(^{4+})</td>
<td>5000 cm(^{-1})</td>
<td>K(_2)IrCl(_6)</td>
<td>255</td>
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</tbody>
</table>

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