Peculiarities of the $^{35}\text{Cl}$ and $^{79}\text{Br}$ NQR Spectra of Chalcogenhalide Complexes of Some Transition Metals

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The peculiarities of the $^{35}\text{Cl}$, $^{79}\text{Br}$ NQR spectra of the chalcogenhalide complexes are explained in terms of intraspheric effect of ligands, formation of secondary intra- and intermolecular bonds, and electronic structure of metal atom. In the $^{35}\text{Cl}$ spectra of [TeCl$_3$]$[\text{ReCl}_4]$ $I$, [SeCl$_3$]$[\text{OsCl}_4]$ $2$ and [TeCl$_3$]$[\text{ReCl}_4]$ $3$ the 7–10\% increase in frequency in the low-frequency multiplet are accounted for by the disturbance of the $p_d^2-d_m$ $\pi$-interaction due to the formation of the peripheral coordination polyhedra [SeCl$_3$] and [TeCl$_3$]. The peculiarities of the $^{35}\text{Cl}$ and $^{79}\text{Br}$ spectra of [Mo$_2$Cl$_3$(SeCl)$_3$]$^+$ $4$, [Mo$_2$Br$_3$(SeCl)$_3$]$^+$ $5$, [WS$_2$Cl$_3$(SeCl)$_3$]$^+$ $6$ and [WS$_2$Br$_3$(SeBr)$_3$]$^+$ $7$ are attributed to the disturbance of the $p_{d_{z^2}}-d_m$ $\pi$-interaction under the influence of the coordination of the SeCl$_3$ and SeBr$_3$ ligands and formation of secondary intramolecular bonds. For $[\text{RhCl}_4(\text{SeCl}_3)]^-$ $8$, $[\text{IrCl}_4(\text{SeCl}_3)]^-$ $9$ and [SCl$_4$][IrCl$_4$(SCl)$_3$]$^-$ $10$, the appearance of frequencies at 25 MHz in low-frequency triplets is attributed to the intraspheric effect of weak donors-neutral Cl$_2$ and SeCl$_3$ molecules; the frequencies at 18 MHz are assigned to bridging chlorine atoms. This assignment was confirmed by the dimeric structure, which was established by an X-ray structure analysis.

Key words: Molybdenum (V), tungsten (V), rhenium (IV), osmium (IV), rhodium (III), iridium (III), electronic structure.

1. Introduction

In recent years, we have examined the $^{35}\text{Cl}$ and $^{79}\text{Br}$ NQR spectra of a number of chalcogenhalide complexes of group III–VIII metals [1–9]. The spectra were interpreted by the Townes-Dailey approximation, which gives good results for halogen atoms with one valence $p$-electron. The interpretation of the spectra is simplified by the fact that the asymmetry parameter $\eta$ of chlorine and bromine is zero and that the frequency $v$ found experimentally is connected with the quadrupole interaction constant $e^2Qq$ by the simple relation $v=\frac{1}{2}e^2Qq(1+\eta^{3/2})^{1/2}$. The state of the valence electrons of a halogen is characterized by the occupancies $N_x$, $N_y$, and $N_z$. The constant of quadrupole interaction in a complex is connected with the free halogen atom constant by the relation $e^2Qq_{com.}=U_p e^2Qq_{max.}$, where $U_p$ is the number of unbalanced $p$ electrons, which is defined as $U_p=\frac{N_x+N_z}{2}-N_y$. The $p_x$ electrons are involved in the formation of the $\sigma$ bond, and the $p_y$ and $p_z$ electrons are involved in the formation of the possible $\pi$-bond.

On the basis of these premises, we interpreted the $^{35}\text{Cl}$ and $^{79}\text{Br}$ NQR spectra of most chalcogenhalide complexes synthesized. However, this simple interpretation proved to be inadequate. For example, it was impossible to explain such peculiarities of NQR spectra as the substantial decrease in NQR frequencies in the $AX_2$ ligand (where $A=S$, Se and $X=Br$, Cl) in molybdenum, tungsten [7, 8] and iridium [9] complexes, whereas according to the theory the frequency must increase with coordination. The strong splitting and considerable increase in the NQR frequencies of chlorine and bromine in the coordination polyhedron of molybdenum, tungsten [7, 8], osmium, rhenium [6] and iridium [9] remained to be unusual.

These metals have unoccupied $t_{2g}$ levels and the electronic configurations $t_{2g}^{\text{W, Mo}}$, $t_{2g}^{\text{Re}}$ and $t_{2g}^{\text{Os}}$, which opens a possibility for evaluating the contribution of the $p_{\text{Cl}}-d_m$ $\pi$-interaction to the metal-halogen coordination bond. To explain the above peculiarities of the $^{35}\text{Cl}$ and $^{79}\text{Br}$ NQR spectra of these complexes, the present communication considers the following factors: electronic configuration of the central atom, existence of secondary contacts such as extra $M-\text{Cl}^{-}\text{A}$ bonds and effect of mutual influence of ligands in the first coordination sphere. The interpretation of the NQR spectra was made easier by the fact that these complexes were also studied by X-ray structure analysis [8, 10–12].

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2. NQR Spectra and their Interpretation

a) Osmium and rhenium complexes:

- [TeCl₃]₂ [OsCl]₆ (1)
- [SeCl₃]₂ [OsCl]₆ (2)
- [TeCl₃]₂ [ReCl₆] (3)

The spectra of 1, 2, 3 consist of strongly frequency-separated multiplets (Table 1). The high-frequency multiplet was assigned to the frequencies of the ligand chlorine. The ranges 28–30 MHz (complexes 1, 3) and 35–37 MHz (complex 2) are characteristic of SeCl₄ and TeCl₄ and of the groups [SeCl₃] and [TeCl₃] in the chalcogenchloride complexes of most metals [1–4]. The low-frequency triplets are related to the frequencies of chlorine bonded to OsIV and ReIV, and they are higher than those of the octahedral [MCl₆] anion in complexes with alkali metals: up to 7% in osmium complexes and up to 10% in rhenium complexes. These peculiarities of the ³⁵Cl NQR spectra of osmium and rhenium chalcogen chlorides complexes are due to the electronic structure of the central atom and to the structure of 1, 2 and 3.

X-ray structure investigations [12] showed that the central polyhedron [MCl₆] in 1–3 forms a peripheral polyhedron [ACl₆] through extra bonds to chalcogen atoms. The formation of these bonds disturbs the pCl–dM π-interaction, which makes a great contribution to the Cl–M bond of the central polyhedron for transition metals with the electronic configurations t₂ₑ and t₂ₑ, which have two or three electron vacancies in the relatively low-lying t₂ₑ orbitals. The participation of chlorine pπ-electrons in additional bonding to chalcogen atoms of the peripheral polyhedron is competitive and weakens the pπ–dπ-transfer in the central polyhedron, increasing the NQR frequencies of the chlorine bonded to the metal. For bridging chlorine atoms in niobium and tantalum pentachloride dimers a similar frequency increase was observed [13]. At the same time, an NQR frequency increase is not to be expected for metals with the electronic configuration t₂ₑ and hence with no vacancies on the t₂ₑ level, where the contribution from pπ–dπ is small. Indeed, in chalcogen chloride complexes of platinum, [ACL₆][PtCl₄] (A = Se, Te), which have a similar heteronuclear structure, there is some decrease in NQR frequency in the octahedral [PtCl₆] due to the involvement of chlorine pπ electrons in the formation of extra M–Cl–A bridge bonds.

b) Molybdenum and tungsten complexes:

- [MoS₂Cl₃(SeCl₂)]₂ (4)
- [MoS₂Br₃(SeBr₂)]₂ (5)
- [WS₂Cl₃(SeCl₂)]₂ (6)
- [WS₂Br₂(SeBr₂)]₂ (7)

The ³⁵Cl and ⁷⁹Br NQR spectra of 4–7 are of the same type due to the similarity of their structure (Table 2). An X-ray structure analysis [8] established the dimeric structure of molecules with a metal-metal bond and two bridging S₂⁻ groups. Two SeCl₂ or SeBr₂ molecules are coordinated to the central metal atom through a selenium atom and two extra M–X–Se bonds to halogen atoms of the coordination environment of the metal, the oxidation state of metals being V and the electronic configuration being t₁₇g.

³⁵Cl NQR spectra consist of high-frequency doublets and strongly split low-frequency triplets. The
The low-frequency triplets were assigned to halogen atoms in the coordination polyhedron $[\text{MX}_{3}\text{S}_{2}\text{Se}]$, where $X=\text{Cl, Br}$, the frequencies being strongly split (up to 40%) and much higher than in the NQR spectra of the $[\text{MoCl}_{4}]^{2-}$, $[\text{WC}_{12}]^{2-}$ and $[\text{WC}_{12}]^{-}$: 10.7, 10.7, and 11.5 MHz, respectively [14]. The complex composition of the polyhedron makes it impossible to unambiguously interpret the spectra of 4–7, but it allows one to follow the trends of Cl$^-$ frequency variation. These changes result from the disturbance of the $p_{\pi}-d_{\pi}$-interaction under the influence of changes in orientation sphere composition (see above). The effect of mutual influence of ligands in the first coordination sphere of a complex acts in the same direction. Though this effect is not discussed specially in the NQR theory, we can give characteristic examples of the change in the NQR frequencies of Cl$^-$ ligand under the influence of a change in the electronic structure of the central Rh and Ir atoms. Unlike the complexes $[\text{RhCl}_{3}(\text{SeCl}_{2})_{2}]^{-}$ against Cl$^-$ ion, is known to enhance electron transfer by the effect of the partner on the transcoordinate Cl–M–Cl or Cl–M–S$^2_2^-$, and by the formation of additional intramolecular Se–Cl–M bonds.

c) Rhodium and iridium complexes:

$[\text{RhCl}_{3}(\text{SeCl}_{2})_{2}]^{-}$ (8), $[\text{IrCl}_{3}(\text{SeCl}_{2})_{2}]^{-}$ (9), $[\text{SCl}_{3}]^{2-}$ and $[\text{IrCl}_{4}(\text{SCl}_{2})_{2}]^{-}$ (10)

The peculiarities of the $^{35}\text{Cl}$ NQR spectra of iridium complexes were discussed in detail in [9]; the fact that the NQR spectrum of the rhodium complex 8 is of the same type as the above spectra seems to be due to these compounds being similar in structure: NQR spectra are complex; the high-frequency multiplet relates to chlorine bonded to chalcogen atom, and the strongly split low-frequency triplet relates to chlorine atoms bonded to metal (Table 3).

The frequency range 35–38 MHz of the high-frequency multiplet corresponds to the chlorine frequency position in the SeCl$^-$ and SeCl$^-$ molecules. The character of splitting of the low-frequency triplet in the spectrum of rhodium complex 8 is similar to those in the spectra of the iridium complexes 9 and 10, the tendency to increase in NQR frequencies to 25 MHz as against $^{35}\text{Cl}$ frequencies in the octahedral $[\text{RhCl}_{4}]^{3-}$ and $[\text{IrCl}_{4}]^{3-}$ anions is also the same. These peculiarities of the spectra of 8, 9 and 10 can be accounted for by the electronic structure of the central Rh$^{III}$ and Ir$^{III}$ atoms. Unlike the complexes 1–7, where the $p_{\pi}-d_{\pi}$-interaction involving unoccupied $t_{2g}$ orbitals makes a great contribution to the coordination M–Cl bond, the $t_{2g}$ level in 8–10 is occupied. The unoccupied $e_g$ ligands. It is more difficult to explain the strong frequency splitting in this region; it may be caused both by an increase in negative charge on the selenium atom owing to the formation of extra bonds. This leads in turn to a decrease in the number of unbalanced electrons, $U_e$, on halogen atoms in the Se-X bond and to a decrease in NQR frequency.

Table 3. $^{35}\text{Cl}$ NQR Spectra of Rhodium and Iridium Complexes.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>$^{35}\text{Cl}$ NQR Spectra of Rhodium and Iridium Complexes.</th>
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<tr>
<td>MHz</td>
<td>$^3$N/S $^3$N/S $^3$N/S $^3$N/S</td>
</tr>
<tr>
<td>38.143</td>
<td>40 37.698 10 42.015 6</td>
</tr>
<tr>
<td>37.695</td>
<td>20 37.300 5 41.125 8</td>
</tr>
<tr>
<td>37.322</td>
<td>20 38.365 5 40.835 10</td>
</tr>
<tr>
<td>35.935</td>
<td>15 37.560 5 39.945 10</td>
</tr>
<tr>
<td>25.748</td>
<td>5 22.053 10 24.542 15</td>
</tr>
<tr>
<td>20.188</td>
<td>3 21.469 20 22.054 15</td>
</tr>
<tr>
<td>18.073</td>
<td>3 18.720 30</td>
</tr>
</tbody>
</table>

* The spectrum was obtained by S. I. Kuznetsov and Y. V. Bryukhova at the Institute of Organoelement Compounds (Moscow, Russia).
orbitals lie rather high and seem to be not involved in the $\text{PCl}_2\text{d}_\pi$-interaction. In this case, the model for $p\pi$ electrons in bonding to the dimer molecules there is a decrease in the occupancy $N_z(N_y)$ in the number of unbalanced electrons, $U_p$, and hence in the NQR frequency of the bridging atom. This electron transfer mechanism allows one to assign the NQR frequencies 18.720 MHz and 18.078 MHz in 9 and 8 to bridging Cl atoms.

The unexpectedly high frequencies of 24.542, 22.054 and 25.448, 20.188 MHz in complexes 9 and 8, respectively, are caused by the appearance of the SC12 and SeCl4 ligands in the coordination sphere. Replacement of chlorine ion by neutral chalcogen dichloride molecule with weak $\sigma$-donor properties stimulates electron density transfer from neighbouring chlorine atoms. In this case, the occupancy $N_z$ on these atoms decreases, and $U_p$ and the NQR frequency increase. The increase in frequency reaches here 30–40% in comparison to the octahedral $[\text{RhCl}_6]^{3-}$ and $[\text{IrCl}_6]^{3-}$ anions, for which the $^{35}\text{Cl}$ NQR frequencies are 18.7 MHz and 17.6 MHz, respectively.

Thus, the $^{35}\text{Cl}$ and $^{79}\text{Br}$ NQR spectra of chalcogenhalide complexes of some transition metals with unoccupied $d$ orbitals were interpreted as a Townes-Dailey approximation taking into account their electronic configuration, peculiarities of coordination bond and structure.

3. Conclusions

The peculiarities of NQR spectra: strong splitting and higher frequencies as against the $[\text{MX}_6]$ coordination polyhedron are accounted for by changes in the electronic structure of the complex: – disturbance of the $\text{PCl}_2\text{d}_\pi$-interaction in the $\text{MCl}_6$ polyhedron under the influence of secondary bonding and formation of peripheral polyhedra ($[\text{ACl}_6]$) for osmium and rhenium complexes; – electron density redistribution in the $\text{M}\text{Cl}_2$ bond in the $[\text{M}(-\mu\text{SCl})_2\text{Se}]$ polyhedron under the influence of the weak $\sigma$-donor SeCl2 and SC12 molecules for rhodium and iridium complexes; – both of these effects are determining in the $[\text{M}(-\mu\text{S}_2)^2\text{X}_3\text{Se}]$ polyhedron for molybdenum and tungsten complexes.

Acknowledgements

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