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

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The peculiarities of the ^{35}Cl, ^{79}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}Cl spectra of $[TeCl_3]_2[OsCl_6]$ **1**, $[SeCl_3]_2[OsCl_6]$ **2** and $[TeCl_3]_2[ReCl_6]$ **3** the 7–10% increase in frequency in the low-frequency multiplet are accounted for by the disturbance of the p_{Hal}-d_M π-interaction due to the formation of the peripheral coordination polyhedra $[SeCl_6]$ and $[TeCl_6]$. The peculiarities of the ^{35}Cl and ^{79}Br spectra of $[MoS_2Cl_3(SeCl_2)]_2$ **4**, $[MoS_2Br_3(SeCl_2)]_2$ **5**, $[WS_2Cl_3(SeCl_2)]_2$ **6** and $[WS_2Br_3(SeBr_2)]_2$ **7** are attributed to the disturbance of the p_{Hal}-d_M π-interaction under the influence of the coordination of the $SeCl_2$ and $SeBr_2$ ligands and formation of secondary intramolecular bonds. For $[RhCl_3(SeCl_2)_2]_2$ **8**, $[IrCl_3(SeCl_2)_2]_2$ **9** and $[SCl_3][IrCl_4(SCl_2)_2]$ **10**, the appearance of frequencies at 25 MHz in low-frequency triplets is attributed to the intraspheric effect of weak donors-neutral SCl_2 and $SeCl_2$ 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}Cl and ^{79}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 η of chlorine and bromine is zero and that the frequency ν found experimentally is connected with the quadrupole interaction constant $e^2 Q q$ by the simple relation $\nu = \frac{1}{2} e^2 Q q (1 + \eta^{2/3})^{1/2}$. 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 $e^2 Q q_{\text{com.}} = U_p e^2 Q q_{\text{at.}}$, where U_p is the number of unbalanced p electrons, which is defined as $U_p = \frac{N_x + N_y}{2} - N_z$. The p_z electrons are involved in the formation of the σ bond, and the p_x and p_y electrons are involved in the formation of the possible π-bond.

On the basis of these premises, we interpreted the ^{35}Cl and ^{79}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}^1(W, Mo), t_{2g}^3(Re) and t_{2g}^4(Os), which opens a possibility for evaluating the contribution of the p_{Cl}–d_M π-interaction to the metal-halogen coordination bond. To explain the above peculiarities of the ^{35}Cl and ^{79}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–Cl–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: $[TeCl_3]_2\,[OsCl]_6$ (**1**), $[SeCl_3]_2\,[OsCl_6]$ (**2**), $[TeCl_3]_2\,[ReCl_6]$ (**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 $SeCl_4$ and $TeCl_4$ and of the groups $[SeCl_3]$ and $[TeCl_3]$ in the chalcogenchloride complexes of most metals [1–4]. The low-frequency triplets are related to the frequencies of chlorine bonded to Os^{IV} and Re^{IV}, and they are higher than those of the octahedral $[MCl_6]$ anion in complexes with alkali metals: by up to 7% in osmium complexes and up to 10% in rhenium complexes. These peculiarities of the ^{35}Cl NQR spectra of osmium and rhenium chalcogenchloride 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 $[MCl_6]$ in **1**–**3** forms a peripheral polyhedron $[ACl_6]$ through extra bonds to chalcogen atoms. The formation of these bonds disturbs the p_{Cl}–d_M π-interaction, which makes a great contribution to the Cl–M bond of the central polyhedron for transition metals with the electronic configurations t_{2g}^3 and t_{2g}^4, which have two or three electron vacancies in the relatively low-lying t_{2g} orbitals. The participation of chlorine pπ-electrons in additional bonding to chalcogen atoms of the peripheral polyhedron is competitive and weakens the pπ-d π-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 t_{2g}^6 and hence with no vacancies on the t_{2g} level, where the contribution from pπ–dπ is small. Indeed, in chalcogen chloride complexes of platinum, $[ACl_3]_2[PtCl_6]$ (A = Se, Te), which have a similar heteronuclear structure, there is some decrease in NQR frequency in the octahedron $[PtCl_6]$ due to the involvement of chlorine pπ electrons in the formation of extra M–Cl–A bridge bonds.

Table 1. ^{35}Cl NQR Spectra of Osmium and Rhenium Complexes.

$[TeCl_3]_2$ MHz	$[OsCl_6]$ S/N	$[SeCl_3]_2$ MHz	$[OsCl_6]$ S/N	$[TeCl_3]_2$ MHz	$[ReCl_6]$* S/N	Assignment
29.896	10	37.194	10	30.158	10	Cl–Te Cl–Se
29.392	10	36.616	10	29.715	10	
28.935	10	34.644	10	29.270	10	
18.144	10	18.057	2	15.650	1.5	Cl–M
17.654	10	16.890	2	15.130	1.5	
17.444	10	16.777	2	14.980	1.5	

* The spectrum was obtained by S. I. Kuznetsov and Y. V. Bryukhova at the Institute of Organoelement Compounds (Moscow, Russia).

b) Molybdenum and tungsten complexes: $[MoS_2Cl_3(SeCl_2)]_2$ (**4**), $[MoS_2Br_3(SeBr_2)]_2$ (**5**), $[WS_2Cl_3(SeCl_2)]_2$ (**6**), $[WS_2Br_2(SeBr_2]_2$ (**7**)

The ^{35}Cl and ^{79}Br 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 S_2^{2-} groups. Two $SeCl_2$ or $SeBr_2$ 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 t_{2g}^1.

^{35}Cl NQR spectra consist of high-frequency doublets and strongly split low-frequency triplets. The

Table 2. ^{35}Cl and ^{79}Br NQR Spectra of Molybdenum and Tungsten Complexes.

$[MoS_2Cl_3(SeCl_2)]_2$		$[MoS_2Br_3(SeBr_2)]_2$		$[WS_2Cl_3(SeCl_2)]_2$		$[WS_2Br_3(SeBr_2)]_2$		Assignment
νMHz	S/N	νMHz	S/N	νMHz	S/N	νMHz	S/N	
35.092	25	276.625	3	35.420	10	278.415	15	Cl–Se Br–Se
33.470	25	271.221	4	33.806	12	273.757	20	
21.761	15	187.507	20	21.182	3	182.260	50	Cl–M Br–M
16.126	10	135.660	20	16.182	4	134.723	45	
15.840	10	131.878	15	15.956	4	132.013	40	

high-frequency doublets relate to ligand halogen atoms; however, the NQR frequencies in them lie much lower than in chalcogen halide complexes of gold, platinum and palladium, where they are 37–39 MHz and about 300 MHz for chlorine and bromine, respectively [3, 4]. The frequency decrease reaches 10% and seems to be due to 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_p, on halogen atoms in the Se-X bond and to a decrease in NQR frequency.

The low-frequency triplets were assigned to halogen atoms in the coordination polyhedron $[MX_3S_2Se]$, where X = Cl, Br, the frequencies being strongly split (up to 40%) and much higher than in the NQR spectra of the $[MoCl_6]^{2-}$, $[WCl_6]^{2-}$ and $[WCl_6]^-$: 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_X–d_M π-interaction under the influence of changes in coordination 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 of the intraspheric environment. For instance, the coordination of the SCl_2 and $SeCl_2$ molecules, which are weak σ donors as against Cl^- ion, is known to enhance electron transfer from the neighbouring Cl^- ligands in chalcogenchloride complexes of Pt^{IV}. Owing to this, the number of unbalanced electrons on them increases; the increase in NQR frequency reaches 10% in platinum complexes $[PtCl_4(ACl_2)_2]$, where A = S,Se [3, 4].

The mutual-influence effect in the NQR spectra of nitrosohalide complexes of ruthenium and osmium was observed in [15]. When there is a general increase in the NQR frequency of chlorine (up to 19 MHz) due to the weakening of the pπ–dπ-interaction under the influence of the nitrosogroup, a sharp decrease (down to 13 MHz) in the frequency of chlorine on the trans-coordinate NO–Ru–Cl is observed.

Thus the increase in ^{35}Cl and ^{79}Br NQR frequencies in **4**–**7** compared to those of the symmetrical $[MCl_6]^{2-}$ and $[MBr_6]^{2-}$ anions results from a change in the electron distribution in the M–Cl and M–Br bonds under the influence of the $SeCl_2$, $SeBr_2$ and S_2^{2-} ligands. It is more difficult to explain the strong frequency splitting in this region; it may be caused both 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.

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

$[RhCl_3(SeCl_2)_2]_2$*		$[IrCl_3(SeCl_2)_2]_2$		$[SCl_3][IrCl_4(SCl_2)_2]$		Assignment
MHz	*S/N*	MHz	*S/N*	MHz	*S/N*	
38.143	40	37.698	10	42.015	6	
37.695	20	37.300	15	41.125	8	
37.323	20	35.463	5	40.835	10	Cl–S
35.935	15	34.603	5	40.205	10	Cl–Se
		34.560	5	39.945	20	
				39.593	10	
25.748	5	22.053	10	24.542	15	Cl–M
20.188	3	21.469	20	22.054	15	
18.073	3			18.720	30	

* The spectrum was obtained by S. I. Kuznetsov and Y. V. Bryukhova at the Institute of Organoelement Compounds (Moscow, Russia).

c) *Rhodium and iridium complexes:* *$[RhCl_3(SeCl_2)_2]_2$* (8), *$[IrCl_3(SeCl_2)_2]_2$* (9), *$[SCl_3][IrCl_4(SCl_2)_2]$* (10)

The peculiarities of the ^{35}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 $SeCl_2$ and $SeCl_4$ 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}Cl frequencies in the octahedral $[RhCl_6]^{3-}$ and $[IrCl_6]^{3-}$ 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_{Cl}–d_M π-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

orbitals lie rather high and seem to be not involved in the $p_{Cl}-d_M$ π-interaction. In this case, the model for p metals must hold, according to which the bridging halogen atoms have lower NQR frequencies than the end ones. Due to the involvement of Cl bridge pπ electrons in bonding to the dimer molecules there is a decrease in the occupancy $N_y(N_x)$, 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 SCl_2 and $SeCl_2$ ligands in the coordination sphere. Replacement of chlorine ion by neutral chalcogen dichloride molecule with weak σ-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 $[RhCl_6]^{3-}$ and $[IrCl_6]^{3-}$ anions, for which the ^{35}Cl NQR frequencies are 18.7 MHz and 17.6 MHz, respectively.

Thus, the ^{35}Cl and ^{79}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 $[MX_6]$ coordination polyhedron are accounted for by changes in the electronic structure of the complex: – disturbance of the P_{Cl} – d_M π-interaction in the MCl_6 polyhedron under the influence of secondary bonding and formation of peripheral polyhedra ($[ACl_6]$) for osmium and rhenium complexes; – electron density redistribution in the M–Cl bond in the $[M-(\mu Cl)_2Cl_2S_2]$ polyhedron under the influence of the weak σ-donor $SeCl_2$ and SCl_2 molecules for rhodium and iridium complexes; – both of these effects are determining in the $[M-(\mu S_2)_2Xl_3Se]$ polyhedron for molybdenum and tungsten complexes.

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