^{35}Cl and ^{79}Br NQR Spectra and the Secondary Bonding of Chalcogen Halide Complexes

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The ^{35}Cl and ^{79}Br NQR spectra of chalcogen halide complexes of aluminium, gallium, titanium, zirconium, hafnium, niobium, tantalum, molybdenum, tungsten, rhenium, iron, ruthenium, osmium, iridium, rhodium, platinum, palladium and gold are discussed.

Three structure types of these complexes have been distinguished by X-ray structure analysis: type I with AX_2 ligand and $[MX_nA_m]$ coordination polyhedron; type II with AX_3 ligand and $[MX_{n+m}]$ coordination polyhedron; type III, dimeric complexes with M-X-M bridge (where X = Cl, Br and A = S, Se, Te). The formation of secondary M-X-A or M-X-M bonds is characteristic of most structures. The spectra were interpreted by a Townes-Dailey approximation with allowance for the electronic configuration of the metal, mutual influence of ligands and structure features of complexes. Systematic investigation of a big series of chalcogen halide complexes-analogues allowed the following changes in ^{35}Cl and ^{79}Br NQR frequencies on secondary bonding to be established for intraligand halogen atoms: A decrease in frequency for type I complexes and an increase in frequency for type II complexes; for halogen atoms in the coordination polyhedron: a decrease in frequency for p metals and transition metals with $d > 6$, and an increase in frequency for metals with $d < 6$.

Key words: Electronic Configuration; Mutual Influence of Ligands; Coordination Polyhedron; Peripheral Polyhedron.

1. Introduction

At the Institute of General and Inorganic Chemistry of the Ukrainian Academy of Sciences about 100 novel complex compounds of metal halides with chalcogen halides have been synthesized and studied. The molecular structure has been established by X-ray structure analysis for most of them, which allowed three structure types of chalcogen halide complexes to be distinguished:

Type I: Complexes based on chalcogen dihalides, $[MX_n(AX_2)_m]$, with the coordination polyhedron $[MX_nA_m]$ (where X = Cl, Br; A = S, Se);
Type II: Complexes based on chalcogen tetrahalides, $[MX_{n+m}](AX_3)_m$, with the coordination polyhedron $[MX_{n+m}]$ (where X = Cl, Br; A = S, Se, Te);
Type III: Complexes with a bridging halogen atom M-X-M.

In the chalcogen halide complexes of all three types, the formation of intramolecular or intermolecular secondary bonds has been detected: M-X-A, M-X-M [1–11]. NQR spectra of chalcogen halide complexes have been found for aluminium, thallium, titanium, zirconium, hafnium, niobium, tantalum, molybdenum, tungsten, rhenium, iron, ruthenium, osmium, rhodium, iridium, platinum, palladium and gold [12–23] [1]. The resonance frequencies of halogen in the ligand (X-A bond) and coordination polyhedron (X-M bond) lie in the remote parts of the spectrum and can be easily assigned.

Using the Townes-Dailey approximation $e^2Qq_{\text{comp}} = U_p e^2Qq_{\text{at}}$ [24], which gives the simple relation for the experimental frequency $2\nu = e^2Qq$ in the case of halogen atoms with zero asymmetry parameter, the variation of the state of the valence electrons of these atoms during complexation and secondary bonding can be examined. Since p_x and p_y electrons participate in the formation of secondary (bridge) bonds, the occupancies N_x and N_y decrease, and the value of $U_p = \frac{1}{2}(N_x + N_y) - N_z$ and the NQR frequency for this atom must also decrease. However, an opposite picture can be observed for transition metal complexes with a strong contribution of the $p_X - d_M$ π-interaction to the metal-halogen bond. In the present study, a systematic examination of ^{35}Cl and ^{79}Br NQR

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[1] NQR spectra of all complexes were obtained at the Institute of Organoelement Compounds (Moscow, Russia).

Table 1. ^{35}Cl and ^{79}Br NQR frequencies of intraligand halogen atoms in type I complexes (77 K).

Compound	Frequency range, ν (MHz)	Ref.	Compound	Frequency range, ν (MHz)	Ref.
SCl_2	39.0–40.2	[27]	$[PtCl_4(SeCl_2)_2]$	38.0–38.9	[16]
$[PtCl_4(SCl_2)_2]$	41.5–42.7	[13]	$[PdCl_2(SeCl_2)_2]$	36.6–37.4	[16]
$[PdCl_2(SCl_2)_2]$	41.0–41.3	[15]	$[AuCl_3(SeCl_2)]$	37.3–39.0	[19]
$[AuCl_3(SCl_2)]$	42.5–43.2	[19]	$[MoS_2Cl_3(SeCl_2)]_2$	33.5–35.1	[21]
$[PdBr_2(SeBr_2)]$	304	[17]	$[WS_2Cl_2(SeCl_2)_2]_2$	33.8–35.4	[22]
$[MoS_2Br_3(SeBr_2)]_2$	271–276	[22]	$[RhCl_3(SeCl_2)_2]_2$	35.9–38.1	[23]
$[WS_2Br_3(SeBr_2)]_2$	273–278	[22]	$[IrCl_3(SeCl_2)_2]_2$	34.5–37.7	[18]

spectra of a large number of chalcogen halide complexes with known structure was undertaken to establish the regularities of changes in the NQR spectrum of halogen atoms on secondary-bond formation.

2. Experimental

All chalcogen halide compounds were prepared in nonaqueous solvents from corresponding metal halides and chalcogen halides. The structure of these new complexes has been studied by spectroscopic methods: IR, Raman, NQR and X-ray structure analysis, which was performed using monocrystals sealed in thin-walled capillaries. Diffraction data were recorded using the ω-scanning method.

Structures were solved by the Patterson method and refined more exactly by a full-matrix least squares (LSM) anisotropic approximation for the thermal parameters of the atoms. NQR spectra were recorded on ISP-1, ISSh-1, ISSh-2-13; ISSh-1-12 pulse spectrometers at 77 and 296 K, the samples were sealed in glass cells to protect them from moisture and oxidants.

3. NQR Spectra and their Interpretation

Type I. Complexes with AX_2 Ligands

$[PtCl_4(SCl_2)_2]$ **1**, $[PtCl_4(SeCl_2)_2]$ **2**, $[PdCl_2(SCl_2)_2]$ **3**, $[PdCl_2(SeCl_2)_2]$ **4**, $[PdBr_2(SeBr_2)_2]$ **5**, $[AuCl_3(SCl_2)]$ **6**, $[AuCl_3(SeCl_2)]$ **7**, $[MoS_2Cl_3(SeCl_2)]_2$ **8**, $[WS_2Cl_3(SeCl_2)]_2$ **9**, $[MoS_2Br_3(SeBr_2)]_2$ **10**, $[WS_2Br_3(SeBr_2)]_2$ **11**.

The NQR spectra of the halogen atoms of complexes **1**–**11** consist of two strongly frequency – separated multiplets. In the high-frequency region are the frequencies assigned to the chlorine and bromine atoms in the ligand, and in the low-frequency region are the frequencies assigned to the halogen atoms bonded to metals in the coordination polyhedron. In the high-frequency multiplet of platinum, palladium and gold complexes (see Table 1), there is a tendency of an increase in A-X frequency on the coordination of chalcogen dihalide molecules. These changes are caused by a decrease in electron density on chalcogen atoms owing to transfer to the central metal atom to form a coordination bond M-A. This leads, it its turn, to a change in electron density distribution in the A-X bond of the coordinated AX_2 molecule: the occupancy pN_z decreases, and the number of unbalanced electrons U_p increases. Thus, the increase in the NQR frequency of the intraligand halogen of AX_2 molecules results from the coordination of these molecules through a chalcogen atom.

In molybdenum **8**, **10** and tungsten **9**, **11** complexes, an opposite trend is observed: a decrease in the intraligand halogen frequency on the coordination of the molecules $SeCl_2$ and $SeBr_2$. An X-ray structure analysis established the dimeric structure of the complexes **8**–**11** with metal-metal bond, $[S]^{2-}$ groups and the coordinated SeX_2 molecule [10]. This molecule is attached through a selenium atom and two extra M-X-Se bonds to the halogen atoms of the coordination environment of the metal. Secondary intramolecular bonding in complexes **8**–**11** to form M-X-Se bonds leads to an increase in negative charge on the selenium atom and hence to electron a density redistribution in the Se-X bond, viz to a decrease in the number of unbalanced electrons U_p and a decrease in the NQR frequency of the intraligand atoms of halogens. Thus, the structure features of complexes **8**–**11** with secondary M-X-Se bonds are the cause of abnormal changes in the NQR frequency of the intraligand halogen on the coordination of AX_2 molecules. The low frequencies of 35.935 and 34.530–35.403 MHz in the intraligand multiplets of rhodium 53 and iridium 52 complexes, respectively, relate to the group AX_2 with secondary bonds.

The interpretation of the low-frequency multiplet and changes in the coordination sphere due to the coordination of chalcogen dichloride molecules must take into ac-

Table 2. ^{35}Cl and ^{79}Br NQR frequencies of halogen atoms in the coordination polyhedron of type I complexes (77 K).

Compound	Frequency range, ν (MHz)	Ref.	Compound	Frequency range, ν (MHz)	Ref.
$[PtCl_6]^{2-}$	26.0 – 26.7	[25]	$[PdCl_4]^{2-}$	17 – 18*	[33]
$[PtCl_4(SCl_2)_2]$	28.6 – 29.5	[15]	$[PdCl_2(SCl_2)_2]$	18.467	[15]
$[PtCl_4(SeCl_2)]$	28.2 – 28.4	[16]	$[PdCl_2(SeCl_2)_2]$	17.353	[16]
$[MoCl_6]^{2-}$	~ 10 – 11**	[34]	$[PdBr_4]^{2-}$	129.8	[32]
$[MoS_2Cl_3(SCl_2)]_2$	15.8 – 21.7	[21]	$[PdBr_2(SeBr_2)]$	131.169	[17]
$[WCl_6]^{-}$	10 – 11**	[34]	$[WBr_6]^{2-}$	90.3**	[34]
$[WS_2Cl_3(SeCl_2)]_2$	15.9 – 21.2	[22]	$[WS_2Br_3(SeBr_2)_2]$	133 – 182	[22]
			$[MoS_2Br_3(SeBr_2)_2]$	133 – 182	[22]

* 273 K, ** 300 K.

count the peculiarities of the electronic configuration of the central atom: its charge, occupancy of d orbitals, environment geometry and appearance of neutral ligands (AX_2 molecules instead of Cl^-, Br^- acidoligands). The replacement of Cl^- (Br^-) by a relatively weak donor, which is AX_2 molecules, must lead to an enhancement of electron density transfer from the neighbouring Cl^-, Br^- ligands. Owing to this, the electron occupancy N_z in the M-Cl Br bond decreases, and U_p and the NQR frequency increase.

For example, from Table 2 it is evident that the frequency in the Pt-Cl bond in the platinum complexes **1** and **2** with the electronic configuration t_{2g}^6 increases by 10% as compared with the octahedral anion $[Pt^{IV}\,Cl_6]^{2-}$. A similar increase in halogen frequency in the M-X bond is observed in the gold complexes **6** and **7** and in the molybdenum and tungsten complexes **8 – 11**. In these complexes, the disturbance of $p_X - d_M$ π-interaction, whose contribution to the M-X bond is substantial for W^V and Mo^V with the electronic configuration t_{2g}^1, acts in the same direction. The strong splitting in these spectra is due to the low symmetry of the coordination polyhedron. For the complexes **8 – 11**, the doublets 15.9 – 16.1 MHz and 132 – 135 MHz may be assigned to the halogen atoms participating in the formation of two secondary M-X-Se bonds (see above). In consequence of the formation of these additional bonds, a disturbance of the $p_X - d_M - \pi$-interaction takes place: the U_p value and the ^{35}Cl and ^{79}Br NQR frequency in the bond to metal increase.

In the low-frequency part of the spectra of the palladium complexes **3**, **4** and **5** there is a different tendency: The NQR frequencies in the Pd-Cl and Pd-Br bonds remained practically unchanged in comparison with the symmetrical square-planar anion $[PdCl_4]^{2-}$ (see Table 2). However, the formation of a complex compound with square-planar geometry $[PdX_2(AX_2)_2]$ trans position of ligands and coordination via chalcogen atom is confirmed by X-ray structure analysis [3]. A substantial increase in the NQR frequencies of intraligand halogen also indicates the coordination bond to be strong, which should lead to changes in the NQR frequencies of the halogen atoms bonded to metal, as was observed in complexes **1**, **2**, **6**, **7**, **8 – 11**. The assumption that additional intramolecular Pd-X-A bonds are formed by analogy with molybdenum and tungsten complexes (see above) does not agree with the increase in the frequencies of intraligand halogen atoms in molecules on coordination.

A possible explanation of the peculiarities of the NQR spectrum of complexes **3**, **4** and **5** is connected with the electronic configuration of palladium (II). The occupied d_{xz}, d_{yz} and d_z^2 orbitals, which lie over (and under) the molecule planes, create a higher electron density, which determines square-planar geometry with the coordination number 4. Additional interaction with solvent molecules and formation of bonds to π-acceptor ligands become possible. Dative transfer from these orbitals stabilizes considerably the lowest states Rh (I), Pd (II) and Pt (II) and accounts for the high stability of cyanide carbonyl complexes, where ligands possess π-acceptor properties.

In terms of the mutual influence of ligands, π-dative transfer from the palladium atom the the AX_2 orbitals must enhance σ-donor properties and decrease electron density transfer from the neighbouring chlorine (bromine) ligands to the palladium atom. In this case the number of unbalanced electrons in the Pd-X bond and the NQR frequency change only slightly. This mechanism, which gives rise to small changes in the NQR frequency of the halogen atom bonded to palladium, is corroborated by the anomalous behavior of this frequency with temperature. Namely, as the temperature rises, π-bonds are broken, the π-dative Pd-A transfer is disturbed and the negative charge on the ligand decreases.

Table 3. ^{35}Cl and ^{79}Br NQR frequencies of intraligand halogen atoms in type II complexes (77 K).

Compound	Frequency range, ν (MHz)	Ref.	Compound	Frequency range, ν (MHz)	Ref.
$SeCl_4$	34.5–36.8	[28]	$TeCl_4$	27.3–28.5	[29]
$[SeCl_3][AlCl_4]$	38.1–39.2	[13]	$[TeCl_3][AlCl_4]$	29.5–30.9	[14]
$[SeCl_3][GaCl_4]$	37.9–39.0	[13]	$[TeCl_3][GaCl_4]$	29.4–30.8	[14]
$[SeCl_3]_2[ZrCl_6]$	35.9–37.4	[14]	$[TeCl_3]_2[ZrCl_6]$	28.1–28.5	[14]
$[SeCl_3][ZrCl_5]$	36.1–38.2	[14]	$[TeCl_3]_2[HfCl_6]$	28.4–28.5	[14]
$[SeCl_3]_2[HfCl_6]$	35.9–37.5	[14]	$[TeCl_3][NbCl_5]$	27.3–28.5	[14]
$[SeCl_3][HfCl_5]$	37.0–38.0	[14]	$[TeCl_3][TaCl_5]$	29.7–30.1	[14]
$[SeCl_3][NbCl_6]$	35.9–38.6	[14]	$[TeCl_3][FeCl_4]$	29.2–30.4	[14]
$[SeCl_3][TaCl_6]$	36.2–38.7	[14]	$SeBr_4$	293–304	[14]
$[SeCl_3][MoCl_6]$	36.2–37.3	[14]	$[SeBr_3][AlBr_4]$	314–335	[14]
$[SeCl_3][FeCl_4]$	37.7–38.7	[14]	$[SeBr_3][GaBr_4]$	312–333	[14]
$TeBr_4$	225–239	[29]	$[SeBr_3][AuBr_4]$	304–311	[17]
$[TeBr_3][AuBr_4]$	236–243	[17]			

Type II. Complexes with AX_4 Ligands

Al(Ga)Cl_3[S(Se,Te)Cl_4] **12–17**; Al(Ga)Br_3[Se,Br_4] **18, 19**; Zr(Hf)$Cl_4$7[S(Se)Cl_4] **20–23**; Zr(Hf)Cl_4[Se(Te)Cl_4]$_2$ **24–27**; Nb(Ta)Cl_5[S(Se,Te)Cl_4] **28–33**; $MoCl_5$[S(Se)Cl_4] **34, 35**; $ReCl_4[TeCl_4]_2$ **36**; $FeCl_3$[Se(Te)Cl_4] **37, 38**; $OsCl_4$[Se(Te)Cl_4]$_2$ **39, 40**; $PtCl_4$[Se(Te)Cl_4]$_2$ **41, 42**; $PtBr_4$[Se(Te)Br_4]$_2$ **43, 44**; $IrCl_4$[Se(Te)Cl_4]$_2$ **45, 46**; $AuCl_3$[S(Se,Te)Cl_4] **47, 48, 49**; $AuBr_3$[Se(Te)Br_4] **50, 51**.

Most chalcogen halide complexes of metals belong to this type. The ^{35}Cl and ^{79}Br NQR spectra of them consist of two multiplets: a high-frequency multiplet, which relates to halogen atoms in the A-X bond in the ligand, and a low-frequency multiplet, which relates to halogen atoms in the coordination polyhedron, in the M-X bond. Unfortunately, this part of the spectrum was established not for all compounds owing to the low line intensity. The interpretation of the NQR spectra is based on the determining role of the secondary X-A-X bonding in the formation of the central $[MX_n]$ and peripheral $[AX_6]$ coordination polyhedra, the main structural units of these complexes. In the peripheral polyhedron, the chalcogen atom is surrounded by halogen atoms at the vertices of distorted octahedra; the bond length corresponds to the formula 3+3. Three A-X bonds correspond to the sum of covalent radii and are terminal. Three other bonds of chalcogen to the halogen atom of the coordination environment of the metal are 0.8–0.9 Å longer [1, 5, 9] and determine secondary bonding. Whereas the structure of the coordination polyhedra remains the same for all complexes, there are differences in the packing of molecules in the unit cell: skeleton, chain, layer structure [8, 9]; this can hardly affect, however, NQR spectra.

In the high-frequency region of the NQR spectra of all compounds, higher X-A bond frequencies as compared with free uncoordinated molecules of tetrahalides were observed. The NQR spectra of these exhibit three frequencies, which is due to their structure features: The molecules exist as cube-like tetramers $(AX_4)_4$, where the chalcogen atoms are in the centre of coordination polyhedra (AX_6) with three terminal bonds and three bridge bonds. This structure persists on the whole on coordination but undergoes slight changes depending on the nature of the metal. The ^{35}Cl and ^{79}Br NQR frequencies for $SeCl_4$, $TeCl_4$, $SeBr_4$ and $TeBr_4$ are in the ranges 34.5–36.8, 27.3–28.5, 293–304 and 225–239 MHz, respectively, and in the spectra of the complexes **12–51** these frequency ranges change as follows: 35.9–39.2, 27.5–30.9, 304–335 and 236–243 MHz (see Table 3).

As one would expect, the formation of additional secondary M-X-A bonds in complexes instead of A-X-A bonds in free uncoordinated chalcogen tetrahalide molecules leads to a decrease in electron density on chalcogen atoms, the transfer of p_z electrons in X-A bond is enhanced, the occupancy N_z decreases, U_p increases, and the NQR frequency rises.

The low-frequency region of the NQR spectrum relates to the halogen atoms bonded to the metal in the coordination polyhedra $[MX_6]$ and $[MX_4]$. The frequencies of these atoms undergo substantial changes, as compared with the anions $[MX_6]^{-n}$ and $[MX_4]^{-n}$, through secondary bonding and the formation of peripheral $[AX_6]$ polyhedra in the complexes. The π-electrons of halogen atoms participate in the formation of secondary M-X-A bonds; therefore the greatest changes are to be expected for metals where there is a contribution of π-electrons to bonds to halogen.

Table 4. ^{79}Br NQR frequencies in the coordination polyhedron of type II complexes (77 K).

Compound	Frequency range, ν (MHz)	Ref.	Compound	Frequency range, ν (MHz)	Ref.
Al_2Br_6	97.945 113.790 115.540	[30]	Ga_2Br_6	120.600 120.635 168.3 – 168.8	[31]
$[SeBr_3][AlBr_4]$	89.227 – 92.446	[14]	$[SeBr_3][GaBr_4]$	123.813 – 131.028	[14]
$[PtBr_6]^{2-}$	202 – 208	[35]			
$[SeBr_3][PtBr_6]$	193 – 199	[17]			
$[TeBr_3][PtBr_6]$	196 – 201	[17]			

Table 5. ^{35}Cl and ^{79}Br frequencies of halogen atoms in the coordination polyhedron $[AuX_4]$ (77 K).

Compound	Frequency range, ν (MHz)	Ref.	Compound	Frequency range, ν (MHz)	Ref.
Au_2Cl_6	23.235 33.348 – 36.316	[31]	Au_2Br_6	182 – 186 250 – 267	[17]
$[SCl_3][AuCl_4]$	25.248 – 30.613	[15]	$[SeBr_3][AuBr_4]$	182.684 – 252.976	[17]
$[SeCl_3][AuCl_4]$	24.035 – 32.670	[14]	$[TeBr_3][AuBr_4]$	203.935 – 236.919	[17]
$[TeCl_3][AuCl_4]$	25.877 – 29.505	[14]			

For p metals, there is practically no competition in the participation of π-electrons in the bonds M-X and M-X-A, and p_x and p_y electron transfer with the formation of a bridge bond leads to a decrease in the occupancies N_x and N_y, then to a decrease in U_p and hence to a decrease in NQR frequency for the halogen atoms involved in secondary bonding. This effect is observed in aluminium complexes and especially in the gallium complexes **12–17**, where splitting in the spectrum of the $[MX_4]$ polyhedron is 20%, and the low-lying frequencies in the multiplet relate to the M-X-A bond **13**, **14**: In the bromide complexes **18** and **19**, all bromine atoms seem to participate in secondary bonding, as can be seen from a comparison with the spectra of the dimeric molecules $(AlBr_3)_2$ and $(GaBr_3)_2$ (see Table 4).

The changes caused by secondary bonding in the NQR spectra of the coordination polyhedron $[MX_n]$ for d metals depend on the electronic configuration of the metal, viz on the presence of unoccupied d orbitals involved in the p_X-d_M π-interaction with the electrons of halogen atoms. In the metals of t_{2g}^6 electronic configuration, the unoccupied e_g orbitals lie relatively high and do not participate in π-bonding to halogen atoms. Therefore, in this case, like p metals, a decrease in the NQR frequency of halogen on secondary bonding is to be expected. This tendency is observed with chloride and bromide complexes of platinum with selenium and tellurium (see Table 4).

For the metals with electron-saturated d^8 configuration, a decrease in M-X bond frequencies under the influence of secondary bonding is also to be expected. For instance, in the ^{35}Cl, ^{79}Br NQR spectra of the parent gold dimers Au_2Cl_6 and Au_2Br_6, the low-lying frequencies at 23.285 and 182–186 MHz were assigned to the bridging halogen atoms, and those at 33.348, 33.316 and 250.8–267.2 MHz to the terminal atoms [31, 17], see Table 5. The spectra of the complexes **47–51** are represented by quadruples. The strong splitting in the quadruples of the spectra of complexes with sulfur and selenium is caused by the peculiarities of their structure, which has one terminal and three bridging halogen atoms in the $[MX_4]$ polyhedron. In tellurium complexes, the splitting in the quadruple is weaker, which agrees with its structure, in which all four halogen atoms participate in secondary bonding [5]. In accordance with the proposed concept, the high frequencies in the quadruples of the spectra of gold complexes are to be assigned to the terminal halogen atoms. Though other assumptions are not ruled out.

In the NQR spectra of complexes of metals with vacancies on t_{2g} orbitals, other changes under the influence of secondary bonding are to be expected. The unoccupied, relatively low-lying t_{2g} orbitals participate in the p_X-d_M π-interaction in the M-X bond in octahedral $[MX_6]^{n-}$ anions [25]. Secondary bonding with the formation of peripheral [AX_6] polyhedra is competing. According to [26], the bridging- chlorine frequencies for dimeric niobium and tantalum pentachloride molecules are higher than for terminal atoms. Secondary bonding in rhenium, osmium, molybdenum and tungsten complexes leads to a similar frequency increase [23]. Under its influence, π-interaction in the M-X bond is disturbed, and the electron occupancies N_x and N_y increase, U_p and resonance frequency in the NQR spectrum rise. Reference [23] considers in detail changes in the spectra of these complexes on secondary bonding. The same relation must be characteristic of titanium, zirconium, hafnium, niobium, tantalum (d^0) **20–33**, molybdenum, tungsten (d^1) **8–11** and iron (d^5) **37**, **38** complexes. Indeed, strongly splitted multiplets in the ranges 8.841–10.420 MHz and 6.438–10.338 MHz were found in the spectra of niobium and tantalum complexes, respectively; the high-lying frequencies should be assigned to the chlorine atoms involved in secondary bonding. Unfortunately, this part of the spectrum could not be recorded for all complexes due to the low frequency intensity.

Type III. Dimeric Complexes with a Chlorine Bridge

$[IrCl_3(SeCl_2)_2]_2$ **52**, $[RhCl_3(SeCl_2)_2]_2$ **53**, $[Ti_2Cl_9](SCl_3)$ **54**.

The chalcogen halide complexes of the third type have dimeric structures with the M-X-M bond. For iridium and rhodium complexes with the electronic configuration d^6, a strong splitting in the NQR spectrum is observed, which is enhanced by the mutual influence of ligands in the complex coordination polyhedron [$MCl^t_2Cl^b_2A_2$]; in accordance with the concept being developed, the low frequencies in the multiplet should be assigned to the bridging chlorine atoms. More detailed information can be found in [23]. Of particular interest is the interpretation of the NQR spectrum of the titanium complex (d^0), for which an increase in the bridging chlorine frequency in the Ti-Cl-Ti bond is to be expected due to the strong $p_{Cl}-d_{Ti}$ π-interaction. The NQR spectrum of the dimeric complex **54** will be examined in a separate communication, taking into account the peculiarity of its structure.

4. Conclusions

Thus, a systematic examination of the NQR spectra of an imposing series of chalcogen halide complexes allowed us to establish the following regularities of changes in spectra, which were caused by secondary bonding involving formation of the M-X-A and M-X-M bonds: for the intraligand atoms of halogen:

- a decrease in frequency in the AX_2 ligand;
- an increase in frequency in the AX_4 ligand;

for the halogen atoms of the central polyhedron:

- a decrease in frequency in the M-X bond in p metal and d metal complexes with $d < 6$;
- an increase in frequency in the M-X bond in metal complexes with $d < 6$.

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