I. Introduction

The $^{35}$Cl NQR spectra for iridium complexes are known only for the coordination anions $[\text{Ir}^{III} \text{Cl}_6]^{3-}$ and $[\text{Ir}^{I V} \text{Cl}_6]^{-2}$, where iridium has the electronic configurations $t_{2g}^5$ and $t_{2g}^6$, respectively [1]. Unlike platinum and palladium chloro complexes, in which a strong increase of the platinum and palladium chloro complexes, in

In the present paper, $^{35}$Cl NQR spectra for iridium complexes are studied by spectroscopic methods (IR, Raman, diffuse reflection spectroscopy), their magnetic properties have been investigated [2], and an X-ray structure analysis has been carried out for complex 5 [3]. Difficulties in the synthesis of chlorochalcogenide complexes iridium made it impossible to obtain sufficient amounts of each compound which were necessary for $^{35}$Cl NQR spectra measurements. Whereas the synthesis of chalcogen chloride complexes of other platinum metals (Pt, Pd, Os, Rh, Ru) proceeds within several hours and involves the formation of one molecular species, state of iridium, the structure of these compounds and the influence of ligands in the coordination sphere.

II. Synthesis and Characterization of the Complexes

We have synthesized and studied iridium chlorocomplexes with the chalcogen chlorides AC$_2$ (where A=S, Se) and AC$_4$ (where A=S, Se, Te) of the following compositions: (SCl$_2$)$_2$[IrCl$_6$] $^1$, (TeCl$_2$)$_2$[IrCl$_6$] $^2$, (SeCl$_2$)$_2$[IrCl$_6$] $^3$, [IrCl$_4$(SCl$_2$)$_2$] $^4$, (SCl$_3$)[IrCl$_4$(SCl$_2$)$_2$] $^5$, [IrCl$_5$(SeCl$_2$)$_2$] $^6$.

The structure of these new compounds has been studied by spectroscopic methods (IR, Raman, diffusive reflection spectroscopy), their magnetic properties have been investigated [2], and an X-ray structure analysis has been carried out for complex 5 [3]. Difficulties in the synthesis of chlorochalcogenide complexes iridium made it impossible to obtain sufficient amounts of each compound which were necessary for $^{35}$Cl NQR spectra measurements. Whereas the synthesis of chalcogen chloride complexes of other platinum metals (Pt, Pd, Os, Rh, Ru) proceeds within several hours and involves the formation of one molecular species.
the preparation of iridium complexes takes longer
time and in some cases leads to the formation of a
mixture of complexes. For example, when a seleni­
um complex was synthesized, unreacted starting
selenium tretrachloride was detected in the reac­
tion mixture after 20 h heating (Fig. 1) and the
transformation was complete after about 100 h.

![Fig. 1. The $^{35}$Cl NQR spectrum of reaction mixture after
20 h heating (SCl$_3$)$_2$[IrCl$_6$] complex with SeCl$_4$.]

Since all the iridium complexes 1–6 are air-moisture
sensitive, they were prepared and purified in sealed ampules or closed vessels in order to avoid
hydrolysis. The starting compound for producing
all chalcogen chloride complexes of iridium was
IrCl$_4$·nH$_2$O. By synthesis in the presence of
chlorine gas, the oxidation state Ir(IV) remains in
1, 2 and 3, while in 4, 5 and 6 the reduction Ir(IV)
Ir(III) takes place in the solvents SCl$_2$ and SeCl$_2$.

Complex 1 was produced by heating a solution
of IrCl$_4$·nH$_2$O in SCl$_2$ for 20 h in a chlorine stream
containing wine-red crystals.

Analysis for (SCl$_3$)$_2$[IrCl$_6$]
Calcd Ir 28.17 S 9.40 Cl 62.43%,
Found Ir 28.10 S 9.20 Cl 61.30%.

Since the crystals of this complex possess piezo­
electric properties, we could not obtain any $^{35}$Cl
NQR spectrum.

Complex 2 was produced by heating 1 with a stoichiometric amount of TeCl$_4$ in thionyl chloride
under passing of chlorine for 20 h by the reaction:
(SCl$_3$)$_2$[IrCl$_6$] + 2 TeCl$_4$ = (TeCl$_3$)$_2$[IrCl$_6$] + 2 SCl$_2$ +
2 Cl$_2$ containing precipitated black crystals and
gave a well resolved $^{35}$Cl NQR spectrum.

Analysis for (TeCl$_3$)$_2$[IrCl$_6$]
Calcd Ir 22.01 Te 29.10 Cl 47.80%,
Found Ir 22.00 Te 29.10 Cl 47.80%.

Complex 3 was produced by heating 1 with a stoichiometric amount of SeCl$_4$ in thionyl chloride
under passing of chlorine for 100 h containing pre­
cipitated black crystals.

Analysis for (SeCl$_3$)$_2$[IrCl$_6$]
Calcd Ir 24.79 Se 20.33 Cl 54.88%,
Found Ir 24.70 Se 20.20 Cl 54.20%.

The corresponding $^{35}$Cl NQR spectrum was ob­
tained.

To produce 4, a weighted amount of
IrCl$_4$·nH$_2$O was heated with a twenty-fold excess
of sulfur dichloride until SO$_2$ evolution ceased and
a yellow precipitate formed by the reaction
2(IrCl$_4$·nH$_2$O) + 5 SC1$_2$ =
[IrCl$_3$(SCl$_2$)$_2$]$_2$ + SO$_2$ + 4 HCl.

The ampule was sealed, the solution was trans­
ferred to the other end of the ampule. After seal­
ing-off, the crystal were dried under vacuum.

Analysis for [IrCl$_3$(SCl$_2$)$_2$]$_2$
Calcd Ir 38.12 S 12.67 Cl 49.21%,
Found Ir 38.10 S 12.70 Cl 49.10%.

The $^{35}$Cl NQR spectrum of this sample exhibited
a broad line at 40 MHz. We succeeded in obtain­
ing a well-resolved spectrum only after a repeated
recrystallization of 4 in sulfur dichloride. It turned
out, however, that a chemical transformation
takes place by the reaction:
[IrCl$_3$(SCl$_2$)$_2$]$_2$ + 4SCl$_2$ $\rightleftharpoons$ 2(SCl$_3$)[IrCl$_4$(SCl$_2$)$_2$]
leading to the equilibrium existence of two com­
plex species, namely 4 51% and 5 49%.*

From the mixture the crystals of 5 have been se­
lected and the X-ray structure analysis has been
carried out [3]. A further heating and recrystalliza­
tion did not affect the composition. Thus, the $^{35}$Cl
NQR spectrum corresponded with the mixture of
crystals of 4 and 5 (Fig. 2).

To produce 6, a weighted amount of
IrCl$_4$·nH$_2$O was heated with selenium tetrachlo­
ride in a 1:2 ratio in a solution of thionyl chloride
until SO$_2$ evolution ceased. Then it was heated in a
sealed ampule for 20–30 h until the black precipi­
tate changed completely to orange crystals of 6.

* The content of two complex species in the mixture was
calculated from the results of a chemical analysis
(Ir 32.5; S 13.1; Cl 52.0) using the standard Gauss
method for a set of three equations in two unknowns.
III. Discussion of the $^{35}\text{Cl}$ NQR Spectra, Results

a) Complex 1–2

The $^{35}\text{Cl}$ NQR spectrum of complex 2 consists of two multiplets that are widely separated in frequency (Table I). The high-frequency multiplet lies somewhat higher than for pure tellurium tetrachloride but in the same frequency range as for platinum, gold and osmium complexes [4,5]. This indicates the presence of the TeCl$_3$ grouping. A small high-frequency shift may be due to charge transfer by complex formation. The low-frequency multiplet was assigned to chlorine bonded to iridium, the different ranges make such an assignment unambiguous. The frequency values are close to the spectrum of the [IrIVCl$_6$]$^-$ anion and confirm the presence of iridium(IV). The small multiplet separation is rather caused by the asymmetrical placing of molecules in the crystal. The nature of both the high-frequency and low-frequency multiplets indicates most probably the presence of two crystallographically non-equivalent complex molecules in the crystal.

b) Complex 3

In the $^{35}\text{Cl}$ NQR spectrum of 3, we were able to obtain only the high-frequency region, which was assigned to the resonance of chlorine atoms bonded to selenium. The frequency values fall within the range of spectra of pure SeCl$_4$. The line intensity ratio in the doublet is 1:2, which seems to be due to the complex molecule being symmetrically disposed in the crystal along the twofold axis.

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Table I. $^{35}\text{Cl}$ NQR frequencies for iridium complexes.
c) Complex 4–5

The spectrum of the mixture of 4 and 5 exhibits a complicated multiplet in the high-frequency region and a distant triplet of wide separation (Table II). Such a frequency distribution in the spectrum allows an unambiguous assignment of the high-frequency multiplet to chlorine, bonded to sulfur atoms and of the triplet to chlorine, bonded to an iridium atom. We were able to analyze the complicated multiplet after considering the intensities of the frequencies of 15 chlorine atoms bonded to sulfur (Fig. 2). The frequencies 42.015 and 41.125 MHz are appreciably higher in comparison with those of a free SC1₂ molecule [6]. This occurs due to charge transfer by complex formation and is typical for chlorochalcogenide complexes of platinum, palladium and gold [7]. They contain the SC1₂ molecule or SC1₃ groups as a component. By analogy with these complexes, the doublet 42.015, 41.123 MHz with a double-intensity line could be assigned to be SC1₃ groups in 5.

The presence of resonance lines with a low frequency (39.045 and 39.542 MHz) in the multiplet may be attributed to the formation of additional bonds formed between sulfur and chlorine atoms which are in the coordination environment of iridium. A similar frequency decrease in the ligand was observed in molybdenum and tungsten complexes [MS₂Cl₂(SeCl₂)]₂ [8]; in which selenium-chlorine contacts were revealed by X-ray structure analysis [9]. Similar extended bonds were detected in a rhodium complex [RhCl₃(SeCl₂)]₂ [3]. This additional bonding must lead to a charge increase at the sulfur atom and hence to a decrease of the ⁳⁵Cl NQR frequency in the SC1₂ ligand. If this assumption is true, the low frequencies in the multiplet can be assigned to 4.

The triplet separation reaches 30%, which indicates chemical non-equivalence of the chlorine atoms at iridium. When assigning ⁳⁵Cl NQR frequencies in this region, the peculiarities of the electronic structure of iridium(III) were taken into account. It has the electronic ³t₂g configuration with two electron vacancies on the high-lying ⁵eₕ orbitals, which are not involved in the p⁻Cl⁻dₗIr⁻π-type of interaction. The substitution of a neutral chalcogen dichloride molecule for the chloro ligand in such complexes enhances the electron density transfer from the chlorine atoms bonded to the metal and hence increases the ⁳⁵Cl NQR frequency of these atoms. In Pt(IV) complexes PtCl₄(SCl₂)₂ and PtCl₄(SeCl₂)₂ this increase reaches 10%. Thus, the appearance of an unexpectedly high frequency (24.542 MHz) in 4 and 5, which is unusual to iridium(III) complexes, may be due to the intraspheric influence of the SC1 ligand, which possesses weak σ-donor properties. The secondary-bonding effect,

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Table II. ³⁵Cl NQR frequencies for iridium complexes.
which was pointed out previously [8], must lead to some decrease in the frequency (22.054 MHz) of chlorine bonded to iridium owing to the formation of weak Ir–Cl–S bridge bonds. At last the 18.720 MHz frequency relates most probably to the bridging chlorine atoms in dimeric 4. The positive temperature coefficient value \( \frac{dv}{dT} = +0.2 \) confirms assignment.

\[ \text{d) Complex 6} \]

The \( ^{35}\text{Cl} \) NQR spectrum of complex 6 consists of a complicated high-frequency multiplet and a distant doublet with a double-intensity line, which were assigned to chlorine bonded to selenium and iridium, respectively (Table II). It was found that the character of the multiplet, considering the line intensity, corresponds to eight chlorine atoms bonded to selenium. The frequencies 37.648 and 37.300 MHz are close in value to the spectra of the complexes \( \text{PtCl}_4(\text{SeCl}_2)_2 \) and \( \text{PdCl}_2(\text{SeCl}_2)_2 \) [4], and the low-lying frequencies 34.560 and 34.603 MHz are close to the spectra of the complexes \( \text{MoS}_2\text{Cl}_4(\text{SeCl}_2)_2 \) and \( \text{WS}_2\text{Cl}_6(\text{SeCl}_2)_2 \). The latter compounds exhibit secondary bonding, which seems also occur in complex 6.

The NQR frequencies of \( ^{35}\text{Cl} \) bonded to iridium are much higher compared to the spectra of \( \text{M}_3[\text{IrCl}_6] \) complexes; this is caused by the influence of coordinated \( \text{SeCl}_2 \) molecules, which are weak \( \sigma \)-donors. Secondary bonding to the selenium atom in the \( \text{SeCl}_2 \) ligand and the formation of bridging chlorines bonding two iridium atoms must decrease the NQR frequencies of \( ^{35}\text{Cl} \) at iridium. Comparison of the spectra of 4, 5 and 6 makes it possible to assign the 24.642 MHz frequency to chlorine atom in 5. However, a more detailed assignment of \( ^{35}\text{Cl} \) NQR frequencies in this region appears to be impossible before the Zeeman split NQR measurements are accomplished.