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## Abstract

## Full Text

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## Synthesis and Study of the Structure of Double Diazonium Salts of Aluminum Halides

A systematic study of the infrared spectra of double diazonium salts of heavy-metal chlorides in the region 2100–2300 $cm^{-1}$ led us to the conclusion that the frequency of the stretching vibrations of the triple bond N N ($\nu_{N\equiv N}$) is an individual characteristic of these compounds, depending on the initial aryldiazonium, the metal chloride, the valence of the metal, and the composition of the salt ([1–3]). This enabled us to sort out complex mixtures of double diazonium salts of thallium and bismuth of various compositions and to isolate analytically pure substances ([2,3]).

The formation of double diazonium salts of heavy-metal chlorides (Fe, Sb, Zn, Cd, Hg) always leads to a decrease in $\nu_{N\equiv N}$, which characterizes the initial aryldiazonium chloride. This property of absorption by the N N triple bond allowed us to propose the existence of a certain, probably weak, interaction between the metal atom and the nitrogen of the diazonium group ([1]). On the basis of a study of the ultraviolet spectra of double aryldiazonium salts of cobalt and copper chlorides, we obtained confirmation of this hypothesis ([4]).

At present we have begun studying the infrared spectra of double diazonium salts of halides of light metals, not only in the region 2100–2300 $cm^{-1}$, but also in the region 400–1500 $cm^{-1}$, where the appearance of absorption bands corresponding to vibrations of anions of light metals of the type $[MeX_n]^-$ may be expected.

The present paper describes the synthesis and study of the IR spectra of double diazonium salts of aluminum chloride and bromide. These salts have not been described in the literature.

The methods developed for the synthesis of double diazonium salts of heavy metals proved inapplicable to the preparation of double diazonium salts of aluminum, because water and alcohol, used as solvents, readily hydrolyze aluminum halides. The use of salts of the type $NaAlX_4$ instead of aluminum halides in an exchange reaction

$$ArN_2X + NaAlX_4 \rightleftharpoons ArN_2AlX_4 + NaX$$

also did not give positive results.

We succeeded in obtaining double diazonium salts of aluminum halides by using the etherates of the latter. In this case the reaction proceeds according to the following scheme:

$$ArN_2Cl + (C_2H_5)_2O \cdot AlCl_3 \rightarrow ArN_2AlCl_4 + (C_2H_5)_2O.$$

The resulting aryldiazonium aluminum chloride dissolves in an excess of the etherate and can be isolated in a sufficiently pure state by precipitation with anhydrous ether. By this method we synthesized, for the first time, aryldiazonium aluminum chlorides of the type $p$-$XC_6H_4N_2AlCl_4$, where $X = CH_3O,\ CH_3,\ Br,\ H,\ NO_2$.

The compounds obtained are white or yellowish ($n$-$NO_2C_6H_4N_2AlCl_4$) crystalline substances, insoluble in ether, benzene, carbon tetrachloride, and chloroform. They react vigorously with water and alcohol with evolution of hydrogen chloride, deliquesce in air, but are fairly stable on storage in an atmosphere of dry air, with the exception of $C_6H_5N_2AlCl_4$, which begins to decompose with liberation of nitrogen already during synthesis.

In an analogous manner we obtained aryldiazonium aluminum bromides of the type $n$-$XC_6H_4N_2AlClBr_3$, where $X = CH_3O, CH_3, Br, H, NO_2$, whose properties are similar to those of the aryldiazonium aluminum chlorides described above. Attempts to obtain aryldiazonium aluminum iodides by the described method were unsuccessful (violent decomposition of the reaction mixture).

The IR spectra of the aryldiazonium aluminum chlorides and aluminum bromides obtained in the regions 2200–2300 $cm^{-1}$ and 400–600 $cm^{-1}$ are summarized in Tables 1 and 2.

For comparison, Table 1 gives the vibration frequencies of the corresponding diazonium chlorides. For all the compounds studied, absorption bands of the triple bonds $N \equiv N$ are observed in the region 2200–2300 $cm^{-1}$. Relative to the starting diazonium chlorides, they are shifted downward by 8 to 28 $cm^{-1}$ for the aryldiazonium aluminum chlorides and by 15 to 33 $cm^{-1}$ for the aryldiazonium aluminum bromides. Thus, in the spectra of the double diazonium salts of aluminum halides in the region 2200–2300 $cm^{-1}$, the regularity previously established by us for double diazonium salts of heavy metals is observed (1).

In Table 2, in addition to data on the absorption spectra of diazonium aluminum chlorides, spectra recorded by us in the same region are given for diazonium chlorides, complexes of aluminum chloride with pyridine and trimethylamine, and the spectra of the following compounds: $KAlCl_4$, $C_5H_5NHAlCl_4$, and $(CH_3)_3NHAlCl_4$. The latter were obtained by the reaction:

$$C_5H_5NHCl + AlCl_3 \rightarrow C_5H_5NHAlCl_4.$$

As can be seen from the data presented and from the absorption curves shown in Fig. 1, the spectra of such ionically constructed compounds as $KAlCl_4$, $C_5H_5NHAlCl_4$, and $(CH_3)_3NHAlCl_4$ are characterized by a very broad and intense band in the region 550–440 $cm^{-1}$, with maxima at 500–480 $cm^{-1}$. This band is absent in the complexes of aluminum chloride with pyridine and trimethylamine.

Consequently, the broad absorption band in the region 550–440 $cm^{-1}$ may be assigned to the anion $[AlCl_4]^-$.

In the case of an ionic structure of the aryldiazonium aluminum chlorides, one should expect in their spectra an absorption band corresponding to the anion $[AlCl_4]^-$. Indeed, all the investi-

**Fig. 1.** IR absorption spectra in the region 550–400 $cm^{-1}$.
*a*–*n*-$NO_2C_6H_4N_2AlCl_4$ (1), *n*-$NO_2C_6H_4N_2Cl$ (2);
*b*–*n*-$BrC_6H_4N_2AlCl_4$ (1), *n*-$BrC_6H_4N_2Cl$ (2);
*c*–$KAlCl_4$;
*d*–$C_5H_5NHAlCl_4$ (1); $C_5H_5N \cdot AlCl_3$ (2)

**Table 1**

Values of the frequencies $\nu_{N\equiv N}$ ($cm^{-1}$) of the absorption maxima of diazonium aluminum halides of composition *n*-$XC_6H_4N_2AlX_4$ in the region 2200–2300 $cm^{-1}$

| Anion | $CH_3O$ | $CH_3$ | Br | H | $NO_2$ |
|---|---|---|---|---|---|
| $AlCl_4^-$ | 2233 | 2255 | 2266 | 2270 | 2286 |
| $AlClBr_3^-$ | 2227 | 2242 | 2262 | 2265 | 2279 |
| $Cl^-$ | 2248 | 2266 | 2278 | 2298 | 2294 |

Table 2

Absorption spectra in the region 400-600 $cm^{-1}$

| Compound | $\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ |
|---|---|---|---|---|
| *n*-$CH_3OC_6H_4N_2AlCl_4$ | 520 s | 500 sh | 480 s | |
| *n*-$CH_3C_6H_4N_2AlCl_4$ | 520 s | 500 sh | 480 s | 440 m |
| *n*-$BrC_6H_4N_2AlCl_4$ | 520 s | 500 sh | 484 s | 440 m |
| *n*-$NO_2C_6H_4N_2AlCl_4$ | 520 m | 500 s | 484 s | |
| *n*-$CH_3OC_6H_4N_2Cl$ | 518 m | 494 m | | |

| Compound | $\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ | $\nu$, $cm^{-1}$ |
|---|---|---|---|---|
| *n*-$CH_3C_6H_4N_2Cl$ | 520 s | | | 440 m |
| *n*-$BrC_6H_4N_2Cl$ | 516 s | | | 440 m |
| *n*-$NO_2C_6H_4N_2Cl$ | 518 m | | | |
| $KAlCl_4$ | | 500 s | 484 s | |
| $C_5H_5NHAlCl_4$ | | 500–480 br | | |
| $(CH_3)_3NHAlCl_4$ | | 500–480 br | | |
| $C_5H_5N \cdot AlCl_3$ | 452 s | 446 m | | |
| $(CH_3)_3N \cdot AlCl_3$ | in the region 600–400 $cm^{-1}$ bands are absent | in the region 600–400 $cm^{-1}$ bands are absent | in the region 600–400 $cm^{-1}$ bands are absent | in the region 600–400 $cm^{-1}$ bands are absent |

Note: s –strong band; br –broad; m –medium; sh –shoulder.

The aluminum chlorides studied by us have a band at 500-580 $cm^{-1}$, which in its shape, intensity, and position is analogous to the band of $KAlCl_4$ and other ionically constructed compounds. In addition to the characteristic band indicated above, the spectra of aryldiazonium aluminum chlorides contain absorption maxima at 520 $cm^{-1}$ (for all compounds investigated) and 440 $cm^{-1}$ (for *n*-$CH_3C_6H_4N_2AlCl_4$ and *n*-$BrC_6H_4N_2AlCl_4$). These bands are characteristic of aryldiazonium chlorides (Table 2), in the spectra of which, however, the broad and intense band $[AlCl_4]^-$ is absent.

The results obtained testify in favor of an ionic structure of aryldiazonium aluminum halides:

$$[Ar - \overset{+}{N} \equiv N][AlCl_4]^-.$$

Therefore, one may consider that the systematic decrease observed by us in the frequency of the triple bond ($\nu_{N\equiv N}$) on passing from aryldiazonium chlorides to aluminum chlorides and further to aluminum bromides is caused by the different influence of the anions $Cl^-$, $[AlCl_4]^-$, $[AlClBr_3]^-$ on the triple bond

$$N \equiv N.$$

## Experimental Part

The aryldiazonium chlorides corresponding to aniline, *n*-toluidine, *n*-bromoaniline, *n*-nitroaniline, and *n*-anisidine were prepared by Knoevenagel' s

method ([5]) and dried in a vacuum desiccator over $P_2O_5$. Aluminum chloride was sublimed before use; aluminum bromide and aluminum iodide were distilled in vacuum. Etherates of aluminum halides were prepared by adding small portions of the corresponding aluminum halide to cooled ether in an atmosphere of dry nitrogen.

Aryldiazonium aluminum chlorides and aluminum bromides were prepared by adding the diazonium chloride to an excess of the corresponding etherate of the aluminum halide at room temperature. The contents were stirred for several minutes until complete dissolution of the diazonium chloride. The resulting double salt was precipitated with absolute ether. The precipitate was washed four times with ether and dried in a vacuum desiccator. In the case of $C_6H_5N_2AlCl_4$, the diazonium chloride was added to aluminum chloride etherate cooled to $-10^\circ$. The analyses and melting points of the compounds obtained are given in Table 3.

Table 3

| Compound | M.p., °C | Gross formula | C, % found | C, % calculated | H, % found | H, % calculated | N, % (diazo) found | N, % (diazo) calculated |
|---|---|---|---|---|---|---|---|---|
| *n*-$CH_3OC_6H_4N_2AlCl_4$ | 72–73* | $C_7H_7ON_2Cl_4Al$ | 27,29 | 27,66 | 1,53 | 1,33 | 9,30 | 9,22 |
| *n*-$CH_3C_6H_4N_2AlCl_4$ | 82 | $C_7H_7N_2Cl_4Al$ | 28,47 | 29,19 | 1,70 | 1,40 | 9,37 | 9,73 |
| *n*-$BrC_6H_4N_2AlCl_4$ | 94–95 | $C_6H_4N_2Cl_4BrAl$ | 19,68 | 20,52 | 1,87 | 1,14 | 7,69 | 7,94 |
| $C_6H_5N_2AlCl_4$ | 43–45 | $C_6H_5N_2Cl_4Al$ | | | | | 8,75 | 10,2 |
| *n*-$NO_2C_6H_4N_2AlCl_4$ | 95 | $C_6H_4O_2N_3Cl_4Al$ | 23,41 | 22,58 | 1,52 | 1,26 | 8,85 | 8,78 |
| *n*-$CH_3OC_6H_4N_2AlClBr_3$ | 97–98* | $C_7H_7ON_2ClBr_3Al$ | | | | | 6,38 | 6,40 |
| *n*-$CH_3C_6H_4N_2AlClBr_3$ | 92–93 | $C_7H_7N_2ClBr_3Al$ | | | | | 6,40 | 6,64 |
| *n*-$BrC_6H_4N_2AlClBr_3$ | 104–105 | $C_6H_4N_2ClBr_4Al$ | | | | | 5,51 | 5,76 |
| $C_6H_5N_2AlClBr_3$ | 76–78 | $C_6H_5N_2ClBr_3Al$ | | | | | 6,83 | 6,87 |
| *n*-$NO_2C_6H_4N_2AlClBr_3$ | 65 | $C_6H_4O_2N_3ClBr_3Al$ | | | | | 5,97 | 6,19 |

* The substance melts; in the other cases it decomposes.

The IR spectra of the compounds in the region 2100–2300 $cm^{-1}$ were recorded on an IKS-11 spectrophotometer with a lithium fluoride prism; the spectra in

the region 400–680 $cm^{-1}$ were recorded on an IKS-14 spectrophotometer with a potassium bromide prism.

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*Note: Figure translations are in progress. See original paper for figures.*