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Synthesis and Study of Thiocyanato(*N*)iodocuprates(I) and -Argentates(I) of Quaternary Arsonium Cations

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Abstract—The reactions of triarylalkylarsonium acetates with CuI and AgI in the presence of excess potassium thiocyanate yield the corresponding triarylalkylarsonium thiocyanato(*N*)iodocuprates(I) and -argentates(I). The composition, structure, and thermal behavior (in the range 20–1000°C) of these compounds were studied by chemical analysis, IR spectroscopy, conductometry, and differential thermal analysis.

Tetraalkyl(aryl)arsonium halides are excellent precipitants for both relatively simple [1] and complex [2, 3] anions. In this connection, it was suggested [4] that quaternary ammonium salts could be successfully used as reagents for quantitative determination of some elements capable of forming anionic complexes. The reactions of soluble arsonium salts with anionic complexes containing different acido ligands were not studied previously. In this study we prepared mixed-ligand anionic complexes of Cu(I) and Ag(I) with quaternary arsonium cations and examined their structure and thermal behavior in the range 20–1000°C.

Definite amounts of CuI and AgI were dissolved in an aqueous solution containing excess potassium thiocyanate. The resulting mixture was treated with the filtrate from the reaction of equivalent amounts of a triarylalkyl(alkenyl)arsonium iodide with lead(II) acetate in aqueous alcohol. Precipitates formed immediately; they were identified, using physicochemical methods, as quaternary arsonium thiocyanato(*N*)iodocuprates(I) and -argentates(I).

The target products are formed by the following sequence of reactions:

$$\mathrm{MI + KSCN \longrightarrow K[M(NCS)I]}, \qquad (1)$$

$$\mathrm{2[Ar_3AsR]I + Pb(CH_3COO)_2 \cdot 3H_2O \longrightarrow PbI_2\downarrow + 2[Ar_3AsR]OCOCH_3 + 3H_2O}, \qquad (2)$$

$$\mathrm{[Ar_3AsR]OCOCH_3 + K[M(NCS)I] \longrightarrow [Ar_3AsR][M(NCS)I]\downarrow + CH_3COOK}. \qquad (3)$$

The overall reaction is as follows:

$$\mathrm{2MI + 2KSCN + 2[Ar_3AsR]I + Pb(CH_3COO)_2 \cdot 3H_2O \rightarrow PbI_2\downarrow + 2[Ar_3AsR][M(NCS)I] + 2CH_3COOK + 3H_2O},$$

$\mathrm{Ar} = \mathrm{C_6H_5}$ or $m\text{-}\mathrm{CH_3C_6H_4}$; $\mathrm{R} = \mathrm{CH_3}$, $\mathrm{C_2H_5}$, or $\mathrm{CH_2{=}CHCH_2}$; $\mathrm{M} = \mathrm{Cu}$ or Ag.

The compounds prepared are white finely crystalline substances insoluble in water, alcohol, and nonpolar organic solvents but soluble in dimethylformamide. Their composition and structure were determined by elemental analysis (see table) and physicochemical methods.

The ionic structure of the compounds was proved by measuring the molar electrolytic conductivity of their dilute solutions in dimethylformamide (the compounds are insoluble in water). It is known [5, 6] that the molar electrolytic conductivity in dimethylformamide of 1–1 ionic coordination compounds containing single-charged cations and anions varies from 60 to 90 $\Omega^{-1}\,\mathrm{cm^2\,mol^{-1}}$. In our case, it varies within 62–77 $\Omega^{-1}\,\mathrm{cm^2\,mol^{-1}}$ (see table), unambiguously confirming that the compounds dissociate in DMF:

$$\mathrm{[Ar_3AsR][M(NCS)I] \rightleftarrows [Ar_3AsR]^+ + [M(NCS)I]}.$$

The structures of the compounds were studied by IR spectroscopy. It is known [7, 8] that the thiocyanato group can coordinate with the metal via either N or S atom to form a thiocyanato(*N*) or thiocyanato(*S*) complex, respectively. Also, being potentially a bidentate ligand, it can form a bridge between two metal ions. The IR spectra (Fig. 1) show that the $\mathrm{NCS^-}$ groups coordinate with the Cu and Ag atoms via N atom. Indeed, the ν(CN) bands in the IR spectra of $\mathrm{[Ar_3AsR][M(NCS)I]}$ are observed at approximately 2085–2100 $\mathrm{cm^{-1}}$, suggesting the isothiocyanate structure of the substances [9]. It should be noted, however, that in the spectra of $\mathrm{[Ar_3AsR][Ag(NCS)I]}$ the band at 2050–2090 $\mathrm{cm^{-1}}$ corresponding to ν(CN) of the $\mathrm{NCS^-}$ groups is slightly split, which may be due to the packing effect in the crystals. The absorption spectra of all the compounds contain absorption bands originating from vibrations of phenyl groups and other

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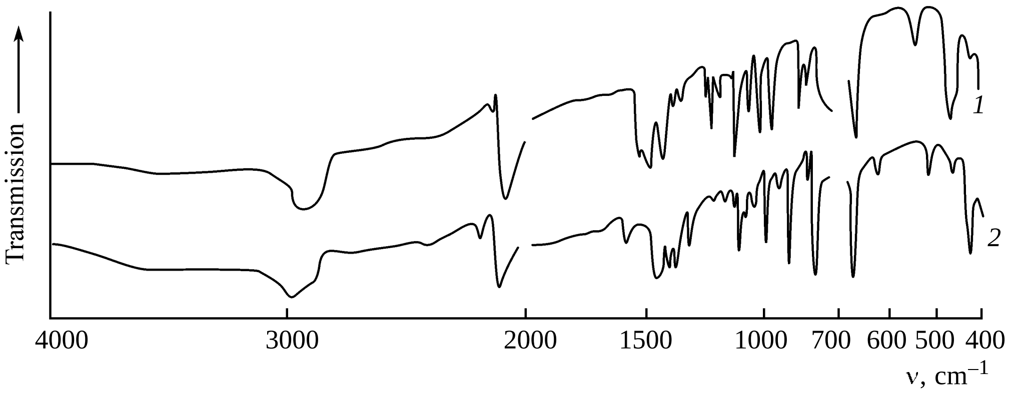

Fig. 1. IR spectra of allyltriphenylarsonium (*1*) thiocyanato(*N*)iodoargentate(I) and (*2*) thiocyanato(*N*)iodocuprate(I).

substituents at the As atom and benzene ring. These bands are virtually the same as in the spectra of the corresponding quaternary arsonium iodides [10, 11], which also indicates that the quaternary arsonium moiety remains essentially unchanged in going from the iodides to thiocyanatoiodometallates.

The As–C$_{Alk}$ bands are observed at about 620–625 cm^{-1}, suggesting the *sp*^{3} hybridization of the As atom [10].

The thermal stability of the thiocyanato(*N*)iodocuprates(I) and -argentates(I) was studied by thermogravimetric analysis. The thermograms are similar. Figure 2 shows as example the thermogravigram of tri-*m*-tolylallylarsonium thiocyanato(*N*)iodocuprate(I). It demonstrates a 16.0% weight loss in the range 120–230°C (T_{min} 170°C) corresponding to the elimination of allyl thiocyanate (calculated for the elimination of $CH_2{=}CH–CH_2SCN$: 15.53%) with the formation of CuI and $As(C_6H_4–CH_3\text{-}m)_3$, which apparently form a complex. Thermolysis of this complex starts at 230°C and is complete at 470°C.

In this range, there are several thermal effects caused, apparently, by elimination of tri-*m*-tolylarsine and its oxidation. The total weight loss is 53.0%. The final thermolysis products were not identified.

Thus, an IR study showed that the copper(I) and silver(I) thiocyanate compounds prepared are actually thiocyanato(*N*)iodocuprates(I) and -argentates(I). According to thermogravimetric analysis, the Cu–NCS bond in the complex anion [Cu(NCS)I]$^-$ is weaker than the Cu–I bond. Another evidence of the stability of the Cu–I bond is that, to dissolve MI (M = Cu,

Yields, melting points, molar electrolytic conductivities (μ), and elemental analyses of quaternary arsonium thiocyanato(*N*)iodocuprates(I) and -argentates(I) [Ar$_3$AsR][M(NCS)I]

Ar	R	mp, °C	Yield, %	μ, Ω^{-1} cm^2 mol^{-1}	Found, %				Formula	Calculated, %			
					As	I	M	S		As	I	M	S
C_6H_5	CH_3	76–77	79.3	65.8	12.5	20.6	17.9	5.6	$C_{20}H_{18}AgAsINS$	12.2	20.6	17.5	5.2
m-$CH_3C_6H_4$	CH_3	54	83.3	76.6	11.7	19.4	16.8	5.4	$C_{23}H_{24}AgAsINS$	11.4	19.3	16.4	4.8
C_6H_5	$CH_2{=}CH–CH_2$	111–112	79.8	81.4	11.9	19.7	17.2	5.4	$C_{22}H_{20}AgAsINS$	11.7	19.8	16.8	5.0
m-$CH_3C_6H_4$	$CH_2{=}CH–CH_2$	105–106	83.8	67.3	11.3	18.5	16.1	4.8	$C_{25}H_{26}AgAsINS$	11.0	18.6	15.8	4.6
m-$CH_3C_6H_4$	C_2H_5	87–88	79.7	62.1	11.5	18.8	16.5	4.9	$C_{24}H_{26}AgAsINS$	11.1	18.9	16.1	4.7
C_6H_5	CH_3	132–133	73.3	78.8	13.4	23.1	11.4	5.9	$C_{20}H_{18}AsCuINS$	13.1	23.3	11.1	5.6
m-$CH_3C_6H_4$	CH_3	114–115	86.1	86.7	12.5	20.5	10.7	5.6	$C_{23}H_{24}AsCuINS$	12.2	20.7	10.3	5.2
C_6H_5	$CH_2{=}CH–CH_2$	117	86.5	84.2	12.8	21.1	10.9	5.8	$C_{22}H_{20}AsCuINS$	12.6	21.3	10.6	5.3
m-$CH_3C_6H_4$	$CH_2{=}CH–CH_2$	118–119	87.2	72.5	11.9	20.0	10.3	5.4	$C_{25}H_{26}AsCuINS$	11.7	19.9	9.9	5.0
m-$CH_3C_6H_4$	C_2H_5	68–69	84.6	69.3	12.2	20.0	10.5	5.5	$C_{24}H_{26}AsCuINS$	11.9	20.3	10.1	5.1

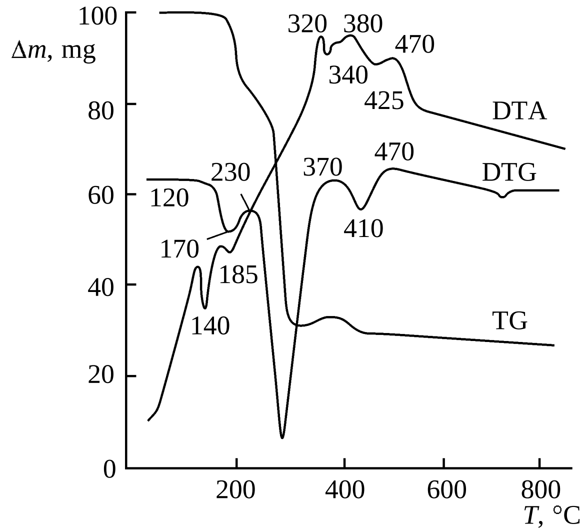

Fig. 2. Thermogram of tri-*m*-tolylallylarsonium thiocyanato(*N*)iodocuprate(I).

Ag), potassium thiocyanate was taken in an approximately ninefold excess relative to the stoichiometry. Nevertheless, treatment of the resulting solutions with quaternary arsonium acetates resulted in precipitation of only monothiocyanate complexes, i.e., even under these conditions the iodide ion was not displaced by the thiocyanato group.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer in the range 400–3700 cm^{-1} in KBr.

The molar electolytic conductivity of the compounds in DMF was measured 25°C on an Impul's conductometer with a ±1.5% accuracy. The temperature was kept constant with a ±0.5°C accuracy. The molar electrolytic conductivity was calculated by the formula $\mu = 1000\chi/c$ [Ω^{-1} cm^2 mol^{-1}], where χ and c are the specific electrical conductivity and concentration of the solution, respectively.

The thermogravimetric analysis was performed with a Paulik–Paulik–Erdey Q-1500D derivatograph (heating rate 10 deg min^{-1} in air, 0.1-g samples, Pt crucible).

As starting compounds we used triarylalkyl(alkenyl)arsonium iodides prepared by alkylation of symmetrical arsines according to [11] and CuI and AgI prepared by the standard procedure [12].

Triphenylmethylarsonium thiocyanato(*N*)iodoargentate(I). A 1.06-g portion of lead(II) acetate was dissolved in 40 ml of distilled water and treated with 2.5 g of triphenylmethylarsonium iodide dissolved in 30 ml of alcohol. A yellow precipitate of PbI_2 formed immediately; it was filtered off. The filtrate was added with continuous stirring to a solution prepared by dissolving 1.31 g of AgI in 40 ml of water in the presence of 4.86 g of potassium thiocyanate. The microcrystalline precipitate was left overnight in the mother liquor, after which it was filtered off, thoroughly washed with water and alcohol, and dried in a desiccator over phosphorus pentoxide and paraffin to constant weight. Triphenylmethylarsonium thiocyanato(*N*)iodoargentate(I) was obtained as a colorless or light grayish powder; yield 2.72 g, mp 76–77°C.

The other complexes were prepared similarly; their physicochemical constants are given in the table.

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