

Oxidation of triphenylarsine in the iron(III) thiocyanate complexes

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Triphenylarsine (AsPh_3) is oxidized by dioxygen in acetonitrile at elevated temperature in the presence of iron(III) thiocyanate complexes to triphenylarsine oxide (OAsPh_3). From the system $\text{Fe}(\text{NCS})_3\text{—AsPh}_3\text{—O}_2\text{—acetonitrile}$, the triphenylarsine oxide complexes have been obtained with the composition $\text{Fe}(\text{NCS})_3(\text{OAsPh}_3)_2$ and $\text{Fe}(\text{NCS})_3(\text{OAsPh}_3)_{1.5}$. Their stereochemistry is discussed on the basis of magnetic and spectral data.

Трифениларсин (AsPh_3) окисляется кислородом в ацетонитриле при повышенной температуре в присутствии тиоцианатных комплексов железа(III) с образованием окиси трифениларсина (OAsPh_3). Из системы $\text{Fe}(\text{NCS})_3\text{—AsPh}_3\text{—O}_2\text{—ацетонитрил}$ были получены комплексы окиси трифениларсина состава $\text{Fe}(\text{NCS})_3(\text{OAsPh}_3)_2$ и $\text{Fe}(\text{NCS})_3(\text{OAsPh}_3)_{1.5}$. Обсуждается стереохимия этих комплексов на основании данных магнитного и спектроскопического изучения.

In the previous works, our attention was focused on the studies of triphenylphosphine (PPh_3) [1] and triphenylarsine (AsPh_3) [2] oxidations with dioxygen in acetonitrile. We have found that oxidations of PPh_3 and AsPh_3 to triphenylphosphine oxide (OPPh_3) and triphenylarsine oxide (OAsPh_3), respectively, require the presence of Fe(III) complexes. We have investigated the systems $\text{FeX}_3\text{—}i\text{PrPh}_3\text{—O}_2\text{—acetonitrile}$ ($\text{X} = \text{Cl, Br, NCS}$) and isolated the corresponding phosphine oxide $\text{FeX}_3(\text{OPPh}_3)_2$ complexes, which had also been prepared by the reaction of FeX_3 and OPPh_3 in ethanol and studied by *Cotton and Gibson* [3].

Thus far, we have studied AsPh_3 oxidation with dioxygen only in the presence of Fe(III) chloro complexes [2]. In this contribution, we present the results obtained by the use of iron(III) thiocyanate complexes in the reaction of AsPh_3 and O_2 .

Experimental

The acetonitrile solution of $\text{Fe}(\text{NCS})_3$ was prepared by mixing acetonitrile solutions of FeCl_3 and KNCS in the mole ratio 1 : 3. KCl was filtered off after cooling.

AsPh₃ pure (Jansen Chimica, Belgium) was purified by dissolving in acetone with an addition of charcoal. After filtration it was precipitated with water and dried at 105°C. OAsPh₃ was prepared by the reaction of AsPh₃ and H₂O₂ and purified by crystallization from benzene [4]. Purity of both compounds was checked by melting point measurement and elemental analysis. Acetonitrile, anal. grade (Apolda, GDR), was rectified after drying with CaH₂. A fraction having b.p. = 81.5°C was used.

The Fe(III) content in the solid compounds prepared was determined after their decomposition with HNO₃ complexometrically by Chelaton 3 to sulfosalicylic acid; carbon, hydrogen, and nitrogen contents were determined by the elemental analysis.

IR spectra of the Fe(NCS)₃(OAsPh₃) and Fe(NCS)₃(OAsPh₃)_{1.5} complexes were measured with a Zeiss UR-20 spectrometer in the range of $\tilde{\nu}$ = 400—3500 cm⁻¹ and with a Perkin—Elmer spectrometer at $\tilde{\nu}$ = 200—400 cm⁻¹. A nujol suspension was used over all the region.

EPR spectra were measured at room temperature with a Varian E 4 apparatus in the band of 0 to 600 mT at a frequency of 9.3 MHz. DPPH was used as the standard. Magnetic susceptibility of the complexes was measured in the range of 93 to 295 K by the Gouy method. Mercury(II) tetracyanocobaltate(II) was used for calibration [5].

Preparation of complexes

Acetonitrile solution of Fe(NCS)₃ was mixed with acetonitrile solution of AsPh₃ ($n(\text{Fe(NCS)}_3) : n(\text{AsPh}_3) = 1 : 2$) and the resulting solution was heated on water bath under reflux at about 80°C for 18—20 h. After evaporation *in vacuo*, a mixture of two types of crystals was available: orange and dark red ones. They were separated on the basis of their different solubility in ethanol (the orange ones are poorly soluble in ethanol in contrast to the dark red ones).

For Fe(NCS)₃(OAsPh₃)₂ (dark red) $w_i(\text{calc.})$: 6.38 % Fe, 53.56 % C, 3.46 % H, 4.80 % N; $w_i(\text{found})$: 6.30 % Fe, 53.00 % C, 3.57 % H, 4.18 % N.

For Fe(NCS)₃(OAsPh₃)_{1.5} (orange) $w_i(\text{calc.})$: 7.83 % Fe, 50.89 % C, 3.18 % H, 5.89 % N; $w_i(\text{found})$: 7.64 % Fe, 50.42 % C, 3.27 % H, 5.49 % N.

The Fe(NCS)₃(OAsPh₃)₂ complex was also prepared by the direct reaction of Fe(NCS)₃ and OAsPh₃ in the mole ratio 1 : 2 in ethanol at room temperature. However, Fe(NCS)₃(OAsPh₃)_{1.5} can be prepared only indirectly, *i.e.* by the reaction of acetonitrile solutions of Fe(NCS)₃ and AsPh₃ in the mole ratio 1 : 1.5 and in the presence of oxygen at about 80°C. The direct reaction of Fe(NCS)₃ and OAsPh₃ in ethanol in the mole ratio 1 : 1.5 leads to formation of Fe(NCS)₃(OAsPh₃)₂ only.

Results and discussion

Triphenylarsine is oxidized with dioxygen to triphenylarsine oxide in the presence of iron(III) thiocyanate complexes in acetonitrile at the elevated temperature. A mixture of two crystal types having a composition Fe(NCS)₃(OAsPh₃)₂ (dark red) and Fe(NCS)₃(OAsPh₃)_{1.5} (orange) is formed in

the system $\text{Fe}(\text{NCS})_3\text{—AsPh}_3\text{—O}_2\text{—acetonitrile}$ with the mole ratio 1 : 2. Both compounds were separated by extraction with ethanol.

Besides the elemental analysis, the presence of OAsPh_3 was confirmed by the analysis of its IR spectra.

A similar AsPh_3 oxidation to the corresponding oxide takes place also in the presence of iron(III) chloride complexes [2] not only in acetonitrile but also in some other nonpolar or slightly polar solvents, *e.g.* benzene, methanol or ethanol. AsPh_3 dissolved in acetonitrile is not oxidized by the air oxygen [2]. Under the given experimental conditions, the AsPh_3 oxidation to OAsPh_3 takes place only in the presence of $\text{Fe}(\text{III})$ complexes.

We have proved by the spectrophotometric study of the system $\text{Fe}(\text{NCS})_3\text{—AsPh}_3\text{—acetonitrile}$ without the presence of dioxygen that binding of AsPh_3 to the central $\text{Fe}(\text{III})$ atom (characterized by the shift of charge transfer band from $\tilde{\nu} = 21\,580\text{ cm}^{-1}$ for pure $\text{Fe}(\text{NCS})_3$ to $\tilde{\nu} = 20\,600\text{ cm}^{-1}$) results in the reduction of $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$. The reduction was followed by the absorption band increase of the complex $[\text{Fe}(\text{2,2'}\text{-dipyridyl})_3]^{2+}$ at $\tilde{\nu} = 19\,100\text{ cm}^{-1}$.

Further, we assume the reaction of $\text{Fe}(\text{II})\text{—AsPh}_3$ complex with dioxygen according to [6] with the simultaneous oxidation of the bound AsPh_3 to OAsPh_3 .

We obtained information on the coordination of the ligands in the $\text{Fe}(\text{NCS})_3(\text{OAsPh}_3)_2$ and $\text{Fe}(\text{NCS})_3(\text{OAsPh}_3)_{1.5}$ complexes by the analyses of IR and EPR spectra and by the measurements of the magnetic susceptibility in dependence on temperature.

IR spectra of the complexes (Table 1) show typical bands corresponding to the coordinated OAsPh_3 . Absorption band of the stretching vibration $\nu(\text{As—O})$ is shifted from the value $\tilde{\nu} = 879\text{ cm}^{-1}$ for noncoordinated OAsPh_3 [7] to $\tilde{\nu} = 842\text{ cm}^{-1}$ for $\text{Fe}(\text{NCS})_3(\text{OAsPh}_3)_2$ and to $\tilde{\nu} = 815\text{ cm}^{-1}$ for $\text{Fe}(\text{NCS})_3\text{—}(\text{OAsPh}_3)_{1.5}$, which points to different mode of OAsPh_3 coordination.

The absorption band corresponding to the stretching vibration $\nu(\text{C—S})$, which in the case of NCS group binding to the central atom through the nitrogen atom is located in the region of $\tilde{\nu} = 770\text{—}860\text{ cm}^{-1}$ [8] or $\tilde{\nu} = 820\text{—}870\text{ cm}^{-1}$ [9], is overlapped by the band assigned to $\nu(\text{As—O})$. It is possible, therefore, to draw some conclusions on the mode of NCS binding to the central atom through the nitrogen atom from the band locations of $\nu(\text{C—N})$ ($\tilde{\nu} = 2060\text{ cm}^{-1}$) and $\delta(\text{NCS})$ ($\tilde{\nu} = 472\text{ cm}^{-1}$) [9, 10].

Similarly to the chloro complexes with OAsPh_3 [2], it is possible to assign the bands in the region of $\tilde{\nu}/\text{cm}^{-1}$: 1440, 1090, 1000, and 750 to the $\nu(\text{—AsPh}_3)$ vibrations. Their locations do not change with the coordination of OAsPh_3 to $\text{Fe}(\text{III})$ [7].

A band of moderate intensity, which occurs in the spectra of all arsine oxide complexes at $\tilde{\nu} = 400\text{—}435\text{ cm}^{-1}$ [11, 12], is assigned to $\nu(\text{Fe—O})$; a similar assignment is given for arsine oxide $\text{Mn}(\text{II})$ and $\text{Ni}(\text{II})$ complexes [12] and is

Table 1

Wavenumbers of the diagnostic bands ($\tilde{\nu}/\text{cm}^{-1}$) in the infrared spectra

Type of vibration	OAsPh ₃	Fe(NCS) ₃ (OAsPh ₃) ₂ from Fe(NCS) ₃ and OAsPh ₃ $n_1 : n_2 = 1 : 2$	Fe(NCS) ₃ (OAsPh ₃) _{1.5} from Fe(NCS) ₃ and AsPh ₃ $n_1 : n_2 = 1 : 2$
$\nu(\text{As—O})$	879 s [7]	842 s	815 s
$\nu(\text{—AsPh}_3)$	1448 vs [2]	1440 vs	1440 vs
	1093 m	1090 m	1088 m
	1003 w	1000 w	1003 w
	750 vs	745 vs	750 vs
$\delta(\text{NCS})$	—	472 s	473 s
$\nu(\text{C—N})$	—	2068 sh	2070 sh
		2060 vs	2058 vs
		2030 sh	2025 s
$\nu(\text{Fe—O})$	—	420 m	420 m
$\nu(\text{Fe—NCS})$	—	339 s	
		280 s	

s — strong; vs — very strong; m — moderate; w — weak; sh — shoulder.

consistent with the value corresponding to the absorption band found for other iron complexes with the ligands containing oxygen donor atom [11].

The complexes studied exhibit two bands (at $\tilde{\nu} = 280$ and 339 cm^{-1}) in the region of $\tilde{\nu} = 200\text{--}400\text{ cm}^{-1}$ which can be assigned to $\nu(\text{Fe—NCS})$ vibrations [3].

An investigation of IR spectra has shown that in the case of the $\text{Fe}(\text{NCS})_3\text{-(OAsPh}_3)_2$ complex prepared directly (from OAsPh_3) or indirectly (from AsPh_3 and O_2) they are the same.

Studies of the magnetic properties of $\text{Fe}(\text{III})$ complexes have proved (Table 2) that the course of molar magnetic susceptibility is in agreement with the Curie—Weiss law in the form

$$\chi_m^{\text{corr}} = \frac{C}{T - \Theta}$$

where C is the Curie constant (K), T is the thermodynamical temperature and Θ is the Weiss constant (K).

The results of measurements (Table 2) revealed that the value of magnetic moment $\mu_{\text{eff}} = 5.89\mu_B$ at the temperature of 295 K of the $\text{Fe}(\text{NCS})_3(\text{OAsPh}_3)_2$ complex decreased only slowly with the decreasing temperature. The value of Weiss constant about -4 K indicates a very weak antiferromagnetic interaction in the complex studied.

EPR spectrum of $\text{Fe}(\text{NCS})_3(\text{OAsPh}_3)_2$ is quite complicated. The strongest band is located in the area of about $g_{\perp} = 6$ and a less intensive one in the area of about $g_{\parallel} = 2$. In the area of higher field, there are some weaker, less distinguishable bands. Both the shape of spectrum and the calculated values of g factors are comparable with the $\text{Fe}(\text{III})$ complexes with phosphine oxide ligand [3].

On the basis of the experimental results obtained and the analogy with the conclusions of paper [3], it is possible to assume a pentacoordination in the $\text{Fe}(\text{III})$ atom environment of the $\text{Fe}(\text{NCS})_3(\text{OAsPh}_3)_2$ complex with participation of three NCS ligands bound to $\text{Fe}(\text{III})$ atom through the N donor atoms. The remaining two sites are occupied by OAsPh_3 molecules coordinated through the oxygen donor atoms, most probably in the trigonal-bipyramidal arrangement.

The value of magnetic moment $\mu_{\text{eff}} = 4.41\mu_B$ at 295 K measured for the complex $\text{Fe}(\text{NCS})_3(\text{OAsPh}_3)_{1.5}$ is lower than the pure spin value corresponding to five impaired electrons $5.92\mu_B$, which points to antiferromagnetic interaction. The value of magnetic moment was shown to be dependent on temperature (Table 2). With decreasing of temperature, it is possible to follow a smooth decrease of magnetic moment value from $4.41\mu_B$ at 295 K to $3.62\mu_B$ at 93 K. Similarly, the value of Weiss constant $\Theta \approx -45\text{ K}$, which corresponds to the

Table 2

Magnetic values of the complexes

<i>T</i> /K	Fe(NCS) ₃ (OAsPh ₃) ₂ (diamagnetic correction: $-\Delta = 483 \text{ m}^3 \text{ mol}^{-1}$)		Fe(NCS) ₃ (OAsPh ₃) _{1.5} (diamagnetic correction: $-\Delta = 391 \text{ m}^3 \text{ mol}^{-1}$)	
	$\chi_{\text{m,g}} \cdot 10^6 / (\text{m}^3 \text{ mol}^{-1})$	$\mu_{\text{eff}}/\mu_{\text{B}} \pm 0.03$	$\chi_{\text{m,g}} \cdot 10^6 / (\text{m}^3 \text{ mol}^{-1})$	$\mu_{\text{eff}}/\mu_{\text{B}} \pm 0.03$
295	16.24	5.89	11.00	4.41
280	17.10	5.88	11.35	4.36
260	18.24	5.85	11.77	4.28
248	19.24	5.86	12.05	4.23
235	20.56	5.89	12.15	4.13
222	21.69	5.88	12.77	4.11
215	22.39	5.88	13.00	4.08
205	23.47	5.87	13.40	4.04
196	24.64	5.88	13.95	4.02
186	25.87	5.87	14.30	3.97
165	28.82	5.83	15.92	3.94
155	30.72	5.83	16.55	3.89
142	33.69	5.83	17.56	3.83
126	37.82	5.82	19.00	3.75
112	42.46	5.81	21.12	3.72
100	47.95	5.83	23.06	3.67
93	51.30	5.81	24.08	3.62

value of exchange interaction $J = -31.3 \text{ cm}^{-1}$, indicates the presence of anti-ferromagnetic interaction in the complex.

EPR spectrum of $\text{Fe}(\text{NCS})_3(\text{OAsPh}_3)_{1.5}$ revealed two absorption bands, the first very intensive one at about $g_{\perp} = 6$ and the second one at about $g_{\parallel} = 2$.

On the basis of the results of spectral and magnetic properties we assume that the $\text{Fe}(\text{NCS})_3(\text{OAsPh}_3)_{1.5}$ complex has a binuclear structure in which two $\text{Fe}(\text{III})$ atoms are probably bridged by OAsPh_3 molecules through the oxygen donor atoms.

The complexes under study are from the point of spectral and magnetic properties very close to the $\text{FeCl}_3(\text{OAsPh}_3)_2$ and $\text{FeCl}_3(\text{OAsPh}_3)_{1.5}$ complexes [2], and therefore, we can assume an analogical stereochemical arrangement in these thiocyanate and chloride dimers. To support this assumption it might be useful to solve the structures of the complexes by X-ray analyses. However, we could not use the latter approach as we were not able to isolate these compounds in the form of crystals necessary for X-ray studies.

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