FORMATION OF NEW MONOMERIC Pd(III) COMPLEX SPECIES WITH 8-AMINOQUINOLINE

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Abstract--By means of EPR and magnetochemical methods the formation of 3 new Pd(III) complex species is proved resulting from the reaction of $PdCl_4^{2^2}$ and 8-aminoquinoline (8-AQ) in basic (aqueous or aqueous-methanolic) medium. Elemental analysis, visible and IR data for the complexes are also obtained.

In the course of our systematic study on formation and stabilization of intermediate Pt(III) and Pd(III) species we have already proven that in basic-water medium and presence of oxygen (aerobic conditions) Pt(II) and Pd(II) are oxidized to Pt(III) and Pd(III) respectively [1-7]. The latter compounds being in general rather unstable transients, can be stabilized either through complexation with proper bridging ligands as oligomeric mixed-valent species (Platinum Blues) [1,2] or through chelation with N-containing ligands [3-7]. Therefore it can be expected that 8-aminoquinoline (8-AQ) also will be able to stabilize Pd(III). At the same time its complexation properties are relatively scarcely studied, due most likely to its insolubility in water. Only complexes of some transition and platinum group metal ions obtained in acidic solution are known up to now [8-13].

In the present paper the results obtained regarding the reaction of $PdCl_4^{2-}$ and 8-AQ in strongly basic medium (pH > 12) and in basic-methanolic medium (CH₃OH + KOH) are reported.

EXPERIMENTAL

Synthesis of the Complexes

 $[Pd(8-AQ_{-H})_2(OH)] \bullet H_2O 1$. 0.0324 g (0.225 mMol) 8-AQ dissolved in 10 ml KOH solution (pH ~12) is added to 1.00 ml of $PdCl_4^{2-}$ (5 x 10⁻² M) (M:L = 1:5). The pH of the reaction mixture is adjusted to pH 12-13 by adding KOH solution. Dark blue-violet residue is formed immediately, which was filtered off, washed repeatedly with chloroform and water and dried for 2 weeks above P_4O_{10} . The elemental analysis data

are shown in Table 1. The complex is soluble in CH₃OH, CHCl₃, acetonitrile (An) and dimethylsulfoxide (DMSO).

 $[Pd(8-AQ_{-H})_2Cl]$ •CH₃OH **2**. 0.100 g 8-AQ dissolved in 10.0 ml CH₃OH is mixed with 7.0 ml water solution of PdCl₄²⁻ (5 x 10⁻² M), and methanolic solution of tetramethyl ammonium hydroxide $[(CH_3)_4N]^+(OH)$ is added up to pH \approx 12 (uncorrected value) (M:L = 1:2). The dark blue residue formed is filtered off, washed repeatedly with water and chloroform and dried for 2 weeks above P₄O₁₀. The complex is soluble in DMSO.

The elemental analysis data are shown in Table 1.

 $[Pd(8-AQ_{-H})_2OH] \bullet CH_3OH 3$. 0.100 g 8-AQ dissolved in 10.0 ml CH₃OH is mixed with 7.0 ml water solution of $PdCl_4^{2-}$ (5 x 10^{-2} M) and water solution of KOH is added up to pH ~13 (uncorrected value) (M:L = 1:2). The dark blue residue formed is filtered off, washed repeatedly with chloroform and water and dried for 2 weeks above P₄O₁₀. The complex is soluble in DMSO.

The elemental analysis data are shown in Table 1.

Materials and Apparatus

The reagents $(NH_4)_2$ PdCl₄ and 8-aminoquinoline were used as purchased from Aldrich. All other reagents and solvents used were of AR grade.

The electronic and IR spectra (KBr disks) were recorded on spectrometers "Specord UV-Vis" (Carl-Zeiss-Jena) and "Perkin-Elmer 983" respectively. The EPR spectra were taken on X-band spectrometer "Bruker B-ER 420" in the temperature range 130-300 K.

The magnetochemical measurements were performed in argon atmosphere according to Faraday's method. The Pd content was determined gravimetrically after treatment of the samples with conc. H_2SO_4 and calcination at 800 °C up to constant weight.

RESULTS AND DISCUSSION

The complexation of $PdCl_4^{2-}$ with 8-AQ was studied at different reaction conditions, varying the nature of the reaction medium. The experimental data obtained show that both in aqueous basic and methanolic basic media in the course of the reaction a redox process proceeds together with the complexation resulting in formation of Pd(III) species. Similar results were obtained in the course of $PdCl_4^{2-}$ interaction with some amide-containing ligands in basic medium [3-6].

The formation of Pd(III) complexes is proven both by the EPR and magnetochemical methods. All three complexes are paramagnetic and EPR active. The

1	tical data (%) ^a , magnetochemical and visible data ^b for the complexes.
Table 1	Analytical

Complex	С	Н	N	CI	Pd	µ _{eff} /µ _B	λ_{max} (nm)
[Pd(8-AQ _{.H}) ₂ (OH)]•H ₂ O 1	50.8 (50.5)	3.7 (4.0)	13.4 (13.1)		24.8 (24.9)	1.76	380, 520
[Pd(8-AQ. _H) ₂ Cl]•CH ₃ OH 2	49.1 (49.6)	3.9 (3.9)	12.0 (12.2)	7.7 (7.7)	22.7 (23.1)	1.38	sh370, sh500
[Pd(8-AQ. _H) ₂ OH]•CH ₅ OH 3	51.5 (51.7)	4.8 (4.3)	12.9 (12.7)		24.5 (24.1)	1.70	385, 520
^a Mean values of 3 samples from 3 d	lifferent batches; ca	alculated values	are in parentheses.				

^bSolvent DMF.

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corresponding μ_{eff} -values (Table 1) are close to the theoretical one (1.73 μ_B) for one unpaired electron thus suggesting low-spin d⁷ configuration.

The EPR data obtained (Table 2) are in agreement with this assumption. The g-values observed are typical for low-spin Pd(III) complexes [14,15]. The complexes 1 and 3 are showing nearly isotropic spectra, thus indicating the realization of almost regular structure e.g. *trans*-configuration. This fact might be explained assuming octahedral coordination, the 5th and 6th sites being occupied by OH⁻ and solvent molecule. As it can be expected complex 2, which contains Cl⁻ in its coordination sphere, exhibits an anisotropic 3-component EPR spectrum (Table 2) which shows a strong deviation from the regular octahedral structure, most likely *cis*-configuration.

Table EPR sj	2 pectral data.				
	ТК	g _{iso} ±0.001	g _x ±0.001	g _y ±0.001	g _z ±0.001
1	130 293	1.990 1.948			
2	130 293	2.000 ^a 2.000 ^a	2.014 2.014	2.005 2.006	1.982 1.982
3	130 293	2.003 2.003			

^aCalculated according the relation $g_{iso} = 1/3 (g_x + g_y + g_z)$.

The formation of Pd(III) complexes is supported by the visible spectral data also. In the spectra of the complexes (Table 1) two new weak bands at 380 and 520 nm are observed, ascribed to d-d transitions. On the basis of these data the following structures for 1-3 can be proposed:

Selected IR data for the 8-AQ and	d the complexes (cm^{-1})					×
Compound	∿(OH)	$v^{as}(NH_2)$	∿ ^s (NH ₂)	(HN)v	v(CH ₃)	v(aromatic ring)
		3440	3350			~1420; ~1450; 1495; ~1550; 1590; 1605
[Pd(8-AQ _{-H}) ₂ (OH)]•H ₂ O 1	3100-3600 v.br	,		3350 br.		~1450; ~1500; 1570; 1540
[Pd(8-AQ. _H) ₂ Cl]•CH ₃ OH 2	3100-3600 v.br			3350 br.	2962; 2918	1460; ~1560; 1660
[Pd(8-AQ _{.H}) ₂ OH]•CH ₅ OH 3	3100-3600 v.br		,	3350 br.	~2960 sh; 2923	1470; ~1500; 1530; 1570; 1590

Table 3

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The IR data obtained (Table 3) are indicative of coordination of deprotonated ligand: in the $3450-3200 \text{ cm}^{-1}$ range of the ligand spectrum a couple of intense bands ascribed to the symmetric and asymmetric NH₂ vibrations are observed, while in the spectra of the complexes in the same range only one band (due to NH vibration) is present.

At the same time in the spectra of the complexes very broad bands, due to OH^{-} , -OH and H₂O engaged in H-bonding are observed. The presence of a CH₃OH molecule in **2** and **3** is also supported by existence of two new bands in the 3000-2900 cm⁻¹ range ascribed to CH₃-vibrations.

Summarizing all these data it can be concluded that reacting $PdCl_4^{2-}$ and 8-AQ in basic medium octahedral Pd(III) complexes are formed including 2 deprotonated ligands, OH⁻ or Cl⁻ ions and a solvent molecule.

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