ETHYLENEDIAMINE COMPLEXES OF TETRAVALENT PALLADIUM OF THE TETRAMMINE TYPE

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Abstract

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ETHYLENEDIAMINE COMPLEXES OF TETRAVALENT PALLADIUM OF THE TETRAMMINE TYPE*

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Tetrammines of tetravalent palladium had not until recently been reported in the literature. We have synthesized (1) ammine complexes of tetravalent palladium, which are only slightly stable in solutions because of readily occurring reduction.

The present article describes the synthesis of ethylenediamine tetrammines of Pd(IV) and some of their properties.

When the divalent palladium complex $[Pden_2]Cl_2$ was treated in the cold with concentrated nitric acid, we isolated a green crystalline compound. According to chemical analysis, it is the complex $[Pden_2Cl_2](NO_3)_2$. In addition to the nitrate, the chloride, chloropalladite, chloroplatinate, and picrate of dichloroethylenediaminepalladium(IV) were obtained.

When the reaction between $[Pden_2]Br_2$ and nitric acid is carried out, analogously to the reaction for preparing $[Pden_2Cl_2](NO_3)_2$, a crystalline compound $[Pden_2Br_2](NO_3)_2$ of dark-bronze color is formed.

Keeping the powder $[Pden_2]Cl_2$ for 24 hours in an atmosphere of gaseous chlorine leads to the formation of a light-green product. According to chemical analysis, this substance has the composition $Pden_2Cl_3$. It dissolves in concentrated hydrochloric acid with formation of $[Pden_2Cl_2]Cl_2$ and $[Pden_2]Cl_2$. This reaction gives grounds to suppose that $Pden_2Cl_3$ is a compound of divalent and tetravalent palladium, $[Pden_2Cl_2]Cl_2[Pden_2]Cl_2$. Similar compounds have been described both for palladium ([2,3,1]) and for platinum ([4]).

On oxidation of $[Pden_2]Cl_2$ with a solution of bromine in carbon tetrachloride, the analogous bromide compound $[Pden_2Br_2]Br_2[Pden_2]Br_2$ was isolated.

A study of the molecular electrical conductivity and pH of aqueous solutions of the nitrates $[Pden_2Cl_2]^{2+}$ and $[Pden_2Br_2]^{2+}$ indicated rapid reduction of the bromide compound and processes of hydration and hydrolysis of the chloride compound, followed by reduction with time.

When $[Pden_2Cl_2](NO_3)_2$ is treated in the cold for half an hour with an excess of hydrochloric acid, an orange substance is formed. Its chemical analysis, as well as the liberation of iodine in its reaction with potassium iodide ([5]), indicates the formation of a complex with chloramine in the inner sphere as a ligand. Similar compounds for tetravalent platinum have been described by Yu. N. Kukushkin ([5]). Reaction of the resulting complex with ammonium chloropalladite led to isolation of the compound $[PdenCH_2NH_2CH_2NHClCl_2][PdCl_4]$, which indicates that the complex cation is divalent and, consequently, that the complex contains mono-, and not dichloramine. Thus, the orange compound synthesized by us has the formula $[PdenCH_2NH_2CH_2NHClCl_2]Cl_2$.

Green crystals of $[Pden_2Cl_2](NO_3)_2$, when treated with dilute alkali, give an orange-colored solution. In the electronic absorption spectrum—

* A detailed account of the work will be published in the *Journal of Inorganic Chemistry*.

of this solution, a shift of the absorption band $\lambda = 390$ mμ toward the long-wavelength region is observed in comparison with the absorption band of the aqueous solution. Probably, in an alkaline solution of this tetrammine Pd(IV), as also in ammine compounds of Pt(IV), an amidation reaction occurs. Some indication of this may also be provided by the formation of chloramine in the reaction of dichlorodiethylenediaminepalladium nitrate with hydrochloric acid.

Despite the easy reducibility of Pd(IV) complexes in aqueous medium, we succeeded in carrying out several inner-sphere substitution reactions in $[Pden_2Cl_2](NO_3)_2$. Thus, chlorine in this complex could be replaced by bromine and iodine with the aid of potassium bromide and iodide, yielding $[Pden_2Br_2]Br_2$ and $[Pden_2J_2]J_2$ in yields of about 20%. Attempts to replace the halogen by nitro and rhodano groups in the inner sphere of the Pd(IV) tetrammine led, as was to be expected, to reduction of the Pd(IV) compound to a Pd(II) compound.

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