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Abstract

Full Text

Chemistry

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Complex Compounds of Pd(IV)

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Compounds of tetravalent palladium have been described in the literature ($^{1-5}$): $Me_2[PdX_6]$, where X—Cl, Br, F, as well as $[Pd(NH_3)_2Cl_4]$, [Pden Cl_4], $[PdPy_2Cl_4]$, and $[PdPy_2X_2Y_2]$, where X—Cl, Y—Br or J.

The small number of described compounds of tetravalent palladium is explained by the difficulties of synthesizing them. Their investigation is far from complete owing to their instability in solutions.

The present work is directed toward elucidating the conditions of synthesis and studying new complex compounds of Pd(IV). As a result of this work tetrammine $[Pd(NH_3)_4Cl_2]Cl_2$ was obtained; in addition, the molecular compound $[Pd(NH_3)_4]Cl_2[Pd(NH_3)_4Br_2]Br_2$ was isolated.

To obtain $[Pd(NH_3)_4Cl_2]Cl_2$, a suspension of finely crystalline $[Pd(NH_3)_4]Cl_2$ in dried CCl_4 was treated with dry gaseous chlorine until the color changed, and then for another 45 min for complete oxidation. The substance formed was filtered off and dried in a desiccator to constant weight.

$[Pd(NH_3)_4Cl_2]Cl_2$.	Found, %:	Pd 33.47, 33.56;	N 17.89, 17.21;	Cl 44.76, 44.39
	Calculated, %:	Pd 33.71	N 17.69	Cl 44.80

Chemical analysis confirms that the substance obtained is tetramminepalladium chloride.

When an attempt was made to obtain this compound by treating $[Pd(NH_3)_4]Cl_2$ with chlorine in aqueous solution, a mixture of $[Pd(NH_3)_4Cl_2]Cl_2$ and $[Pd(NH_3)_2Cl_4]$ was obtained. The appearance of the diammine of Pd(IV) is explained by cleavage of $[Pd(NH_3)_4]Cl_2$ by hydrochloric acid during the interaction of chlorine with water, followed by oxidation of the palladosammine. $[Pd(NH_3)_4Cl_2]Cl_2$ is a fine powder of dark-yellow color, sparingly soluble in water, insoluble in alcohol, ether, and carbon tetrachloride. Refractive indices*: $N_g = 1.857$, $N_p = 1.678$, $N_m = 1.785$.

By the method of I. and V. Noddack (^{6}), the tetravalency of palladium in the compound obtained was confirmed.

The tetravalent state of palladium in $[Pd(NH_3)_4Cl_2]Cl_2$ was indirectly confirmed by the study of infrared absorption spectra**. It is known that on passing from divalent platinum to tetravalent platinum the frequencies of the rocking vibrations of ammonia increase by approximately 40—100 cm^{-1} (^{7}). The obtained value of the frequencies of the rocking vibrations of ammonia in $[Pd(NH_3)_4Cl_2]Cl_2$–909 cm^{-1}–may be assigned to ammonia coordinated to tetravalent palladium, by analogy with the acidoammines of Pt(IV). The frequencies of the rocking vibrations of ammonia in known acidoammines of Pd(II) lie in the region 740—840 cm^{-1}.

In aqueous solution, $[Pd(NH_3)_4Cl_2]Cl_2$ is reduced to $[Pd(NH_3)_4]Cl_2$ with liberation of chlorine, which is confirmed by precipitation of Vauquelin' s salt $[Pd(NH_3)_4][PdCl_4]$ from this solution, as well as by measurement of the electrical conductivity. The electrical conductivity of an aqueous solution of $[Pd(NH_3)_4Cl_2]Cl_2$, measured as a function of time, changes over 30 min from 726 to 520 $ohm^{-1} \cdot cm^2$ and then remains constant. The conductivity values, which are too high for three-ion electrolytes, are explained by the presence in the solution of HCl and HOCl, formed during reduction of tetrammine Pd(IV). The decrease in conductivity with time is caused by the conversion of the electrolyte $[Pd(NH_3)_4]Cl_2$ into the nonelectrolyte $[Pd(NH_3)_2Cl_2]$.

When dry gaseous ammonia acts on solid $[Pd(NH_3)_4Cl_2]Cl_2$, the latter is reduced to $[Pd(NH_3)_4]Cl_2$.

A 30% hydrogen peroxide solution in the cold likewise reduces $[Pd(NH_3)_4Cl_2]Cl_2$ to $[Pd(NH_3)_4]Cl_2$.

When a 10% alkali solution acts on $[Pd(NH_3)_4Cl_2]Cl_2$, an orange coloration of the solution is observed, with the appearance of a small amount of orange powder. The electronic absorption spectra obtained for aqueous and alkaline solutions of $[Pd(NH_3)_4Cl_2]Cl_2$ did not give a clear indication of the nature of the substances formed, but for the alkaline solution a shift of the absorption band to the longer-wavelength region was observed, which is characteristic of an amidation reaction. Investigation of this reaction is greatly complicated by the reduction processes of tetravalent palladium in alkaline medium.

On treating $[Pd(NH_3)_4]Cl_2$ with a solution of bromine in carbon tetrachloride in the cold, a black powdery substance poorly soluble in water was obtained.

Found, %: Pd 28.61, 28.52; N 14.85, 15.29; Cl + Br 53.31, 52.52

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* The refractive indices were determined in the crystal-chemistry laboratory of the Institute of General and Inorganic Chemistry by V. I. Sokol and O. V. Popov.

** The infrared spectra were obtained by O. N. Evstaf' eva in the laboratory of complex compounds of platinum metals of our institute.

$Pd(NH_3)_4Br_2Cl$. Calculated, %: Pd 28.83; N 15.13; Cl + Br 52.79

The analyses formally correspond to a compound of tetravalent palladium. But since the substance obtained proved to be diamagnetic*, it apparently represents a molecular compound of di- and tetravalent palladium: $[Pd(NH_3)_4]Cl_2[Pd(NH_3)_4Br_2]Br_2$. The analogous chloride compound $[Pd(NH_3)_2Cl_2][Pd(NH_3)_2Cl_4]$ has been described in the literature ([1]). Compounds of this kind are also known for platinum ([8]). $[Pd(NH_3)_4]Cl_2[Pd(NH_3)_4Br_2]Br_2$ is reduced in the cold in aqueous solution, and also by 30% hydrogen peroxide, with formation of $[Pd(NH_3)_4]Cl_2$ and $[Pd(NH_3)_4]Br_2$, which is partially split to $[Pd(NH_3)_2Br_2]$.

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* The magnetic susceptibility of the compound was determined in the laboratory for the structure of matter of our institute by V. I. Belova.

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