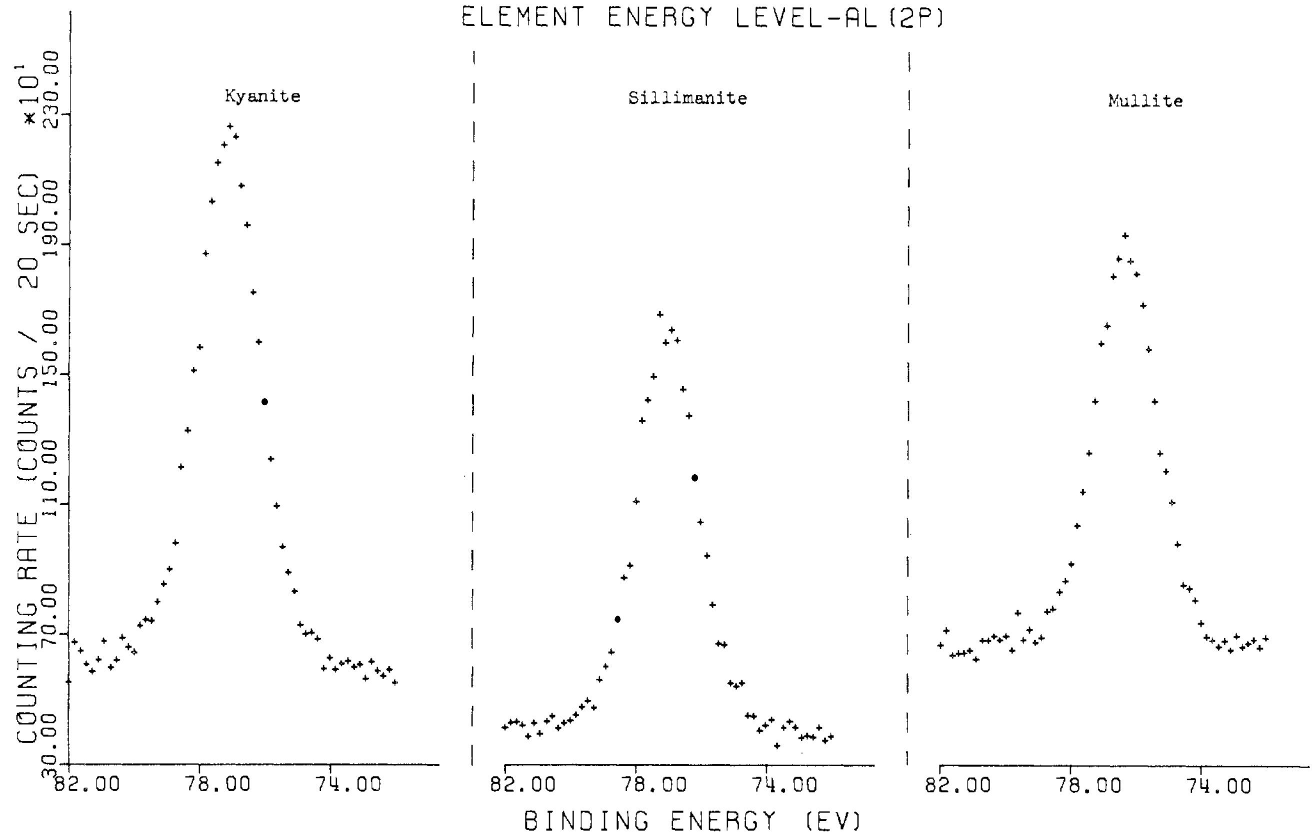

Figure 1. Photoelectron spectra of kyanite, sillimanite, and mullite.

are listed in Table I. As can be seen from Figure 1 and Table I, the binding energies and full widths at half-maximum of the aluminum 2p level are quite similar for the three materials. Indeed, the full width at half-maximum (FWHM) of the 2p level of aluminum in sillimanite, which possesses both fourfold and sixfold coordinations, is actually somewhat less than the FWHM of the 2p level of aluminum in kyanite, which has all of its aluminum in sixfold coordination. The core electron binding energies of oxygen and silicon are also observed to be the same within experimental error. The FWHM of the oxygen 1s and the silicon 2p levels of mullite are observed to be larger than the same levels in the other two aluminosilicates, but this may be due to the existence of the minor glassy phase, which is presumably SiO_2, in addition to the mullite phase.

Although the 1.4-eV difference in the 2p binding energy of aluminum in microcline has been attributed to the different coordinations of the aluminum in the two compounds,[1] it can also be explained by using ionic model concepts. Sixfold coordinated aluminum has been shown to have a 2p binding energy that can vary by as much as 1.6 eV depending on the number of positively charged ions in the lattice.[7] The presence of additional potassium cations in the crystal lattice of microcline, $KAlSi_3O_8$, has the effect of reducing the electron-attracting ability of the oxygen atoms. This causes a decrease in Al 2p binding energy as the number of positively charged ions increases and could account for the Al 2p binding energy in microcline being 1.4 eV lower than it is in alumina. However, when materials have similar chemical compositions, this effect will be absent and binding energy shifts due only to differing coordinations can be unambiguously determined. Sillimanite and kyanite, both Al_2SiO_5, meet this requirement. Since the Al 2p spectrum for sillimanite, with the aluminum in both fourfold and sixfold coordinations, is essentially identical with that for kyanite, with aluminum only sixfold coordinated, it must be concluded that photoelectron spectroscopy of core levels is unable to differentiate between aluminum atoms in different coordinations. This conclusion is strengthened by the data for mullite which is also essentially identical with that for kyanite even though the aluminum is again both fourfold and sixfold coordinated.

Acknowledgments. We thank Professor D. R. Peacor, University of Michigan, and Professor J. T. Wilband, University of Toledo, for supplying the sillimanite and kyanite minerals.

Registry No. Kyanite, 1302-76-7; sillimanite, 12141-45-6; mullite, 1302-93-8.

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Discovery of Monoamminepalladium(II) Chloride Using Thermogravimetry

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Several workers have studied the thermal decompositions and isomerizations of a number of palladium-ammine complexes.[1,2] The most extensive studies of the thermal decompositions of tetraamminepalladium(II) chloride and *trans*-diamminepalladium(II) chloride have been reported by Wendlandt and Fumes.[3] These studies revealed that the tetraamminepalladium(II) chloride decomposed over the range of 150-200° to yield the diammine complex

$$[\mathrm{Pd(NH_3)_4}]\mathrm{Cl_2(s)} \rightarrow trans\text{-}[\mathrm{Pd(NH_3)_2Cl_2}](\mathrm{s}) + 2\mathrm{NH_3(g)} \qquad (1)$$

On further heating at rates of 7-10°/min, Wendlandt and Fumes observed that the diammine decomposed over the range of about 250-350° with a rather complex stoichiometry

$$5trans\text{-}[\mathrm{Pd(NH_3)_2Cl_2}](\mathrm{s}) \rightarrow 5\mathrm{Pd(s)} + 6\mathrm{NH_4Cl(s)} + 4\mathrm{HCl(g)} + 2\mathrm{N_2(g)} + \mathrm{H_2(g)} \qquad (2)$$

They stated: "It should be emphasized that the reaction stoichiometries determined here may apply to this set of experimental conditions such as maximum temperature, heating rate, helium flow rate, and so on. Changing these conditions may well change the decomposition stoichiometry."

We discovered that a new compound, monoamminepalladium(II) chloride, can be obtained by very carefully controlling the thermal decomposition of the *trans*-$[\mathrm{Pd(NH_3)_2Cl_2}]$

$$trans\text{-}[\mathrm{Pd(NH_3)_2Cl_2}](\mathrm{s}) \rightarrow \mathrm{Pd(NH_3)Cl_2(s)} + \mathrm{NH_3(g)} \qquad (3)$$

Experimental Section

A modified Du Pont 950 thermogravimetric analyzer used in conjunction with a Radiometer automatic titrator has been described.[4] Heating rates and purge gases are identified in the text; a constant gas flow rate of 150 cm^3/min was used. Where NH_4Cl was evolved during tg, it condensed on the cool exit end of the quartz reactor tube. It was measured quantitatively by rinsing into a flask and distilling the NH_3 from boiling 50% NaOH solution; the NH_3 was collected and titrated as described previously.[4] X-Ray diffraction data for the new palladium compound, mixed with silicon as a standard, were obtained with a Siemens powder diffractometer using Ni-filtered Cu Kα radiation. Infrared spectra of Fluorolube and Nujol mulls of the various samples were obtained with a Beckman IR-10 spectrometer. The tetraamminepalladium(II) and *trans*-diamminepalladium(II) chlorides were prepared as previously described.[3]

Results and Discussion

Formation of $Pd(NH_3)Cl_2$. During a study of the thermal decomposition of $[Pd(NH_3)_4]Cl_2$ in a helium purge at a heating rate of 5°/min, we found, in agreement with Wendlandt and Fumes,[3] that the stoichiometric quantity of NH_3 was evolved over the range of 150-200°. Upon heating further to 350° under the same conditions, we expected to obtain only HCl, N_2, and H_2 as volatile products in accordance with reaction 2. Quite surprisingly, we obtained significant quantities of NH_3 [0.2 mol of NH_3/mol of Pd] evolved from about 210 to 265°. Suddenly, at about 270-275°, HCl was evolved and the weight of ash at 400° suggested that reduction to Pd metal was incomplete. Subsequently, we found that at still lower heating rates, even more NH_3 was evolved and still less metallic Pd was obtained at 400°. We found, ultimately, that upon heating about 10 mg of the *trans*-diammine to 215 ± 5° for about 20 hr, 0.99 mol of ammonia was evolved per mole of diammine used. The weight loss occurring during this isothermal treatment agreed exactly with the quantity of ammonia determined by automatic titration. Clearly, the weight of product of the isothermal treatment at 215 ± 5° corresponded to $Pd(NH_3)Cl_2$. X-Ray diffraction analysis (Table I) of this material indicated it was highly crystalline; the diffraction pattern does not correspond to $[Pd(NH_3)_4]Cl_2$, $[Pd(NH_3)_2Cl_2]$, $PdCl_2$, or Pd. We tentatively concluded we obtained a new compound with empirical formula $Pd(NH_3)Cl_2$. Infrared analyses supported our conclusion. The tetraammine and the diammine show $\delta_s(NH_3)$ at 1280 and 1240 cm^{-1}, respectively, whereas for $Pd(NH_3)Cl_2$, this deformation appears at 1260 cm^{-1}. Also, $\rho_r(NH_3)$ occurs at 800 and 835 cm^{-1} for the tetraammine and at 745 cm^{-1} for both the diammine and the monoammine.

Table I. X-Ray Diffraction Pattern of Monoamminepalladium(II) Chloride

d, Å	I/I_0	*d*, Å	I/I_0
7.47	50	2.53	6
5.99	100	2.49	21
4.77	5	2.43	5
3.71	12	2.327	4
3.54	4	2.221	3
3.40	36	2.205	5
3.23	6	2.065	2
3.17	10	1.997	5
3.05	4	1.914	5
2.99	2[a]	1.774	3
2.80	4	1.684	4[a]
2.65	3		

[a] Broad peak, may be an unresolved doublet.

On heating 40 mg of dichlorodiamminepalladium(II) at 215 ± 5° for 18 hr, the resulting monoamminepalladium(II) chloride was contaminated with 17 mol % (10 wt %) metallic palladium. (See footnote *c* of Table II.) The increased degree of reduction with increased sample size is attributed to higher concentrations of ammonia held within the sample, which, in turn, reduces the palladium chloride product to the metal. This observed role of sample size is similar to the behavior of ammonium zeolites during calcination wherein retention of ammonia by the sample induces labilization of chemical water in the zeolite, which, in turn, leads to hydrolysis of a portion of the tetracoordinate aluminum.[5]

Thermal Decomposition of $Pd(NH_3)Cl_2$. In Table II are tg data for the $Pd(NH_3)Cl_2$ using approximately 10-mg samples. These samples were prepared *in situ* from the diammine by isothermal treatment at 215 ± 5° for 20 hr.

The computed formula weight of 188.0 (Table II, run 1) indicates that this sample of monoamminepalladium(II) chloride contains an impurity of 6.6 mol % (3.7 wt %) Pd. During the isothermal treatment at 215 ± 5°, 0.12 mol of NH_4Cl/mol of initial dichlorodiamminepalladium(II) was evolved. The NH_4Cl arises from the reduction of palladium(II) to the metal; for each mole of NH_4Cl produced, 0.5 mol of palladium is reduced to metal. Hence, from the NH_4Cl evolved, the amount of palladium reduced is calculated to be 0.06 mol (0.12/2), in excellent agreement with the degree of reduction calculated from the computed formula weight.

On the basis of the results of run 2, Table II, we propose that the isothermal decomposition of the monoammine at 260 ± 5° proceeds by the stoichiometry of (4). The NH_4Cl

$$\mathrm{Pd(NH_3)Cl_2} \xrightarrow{260^\circ} {}^1\!/_2\mathrm{Pd} + {}^1\!/_2\mathrm{PdCl_2} + {}^1\!/_6\mathrm{N_2} + {}^2\!/_3\mathrm{NH_4Cl} + {}^1\!/_3\mathrm{HCl} \qquad (4)$$

is formed from NH_3 and HCl gases evolved separately. When

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[2] G. S. Muravliskaya and I. I. Chernyaev, *Russ. J. Inorg. Chem.*, 4, 690 (1959).

[3] W. W. Wendlandt and L. A. Fumes, *J. Inorg. Nucl. Chem.*, 26, 1879 (1964).

[4] G. T. Kerr and A. W. Chester, *Thermochim. Acta*, 3, 113 (1971).

[5] G. T. Kerr, *J. Catal.*, 15, 200 (1969).

Table II. Thermal Decomposition of $Pd(NH_3)Cl_2$[a]

Run	Heating rate and purge gas	Moles evolved/mole of Pd		FW of ash[b]	Ash composition,[c] mol %		H_2 reduction of ash, mol of HCl evolved/mol of Pd
		NH_4Cl	HCl		Pd	$PdCl_2$	
1	5°/min, H_2[d]	0.94	0.83	106.4	100.0		
2	260° for 18 hr, He	0.68		145.9	44.3	55.7	0.97
3	1°/min, He	0.48	0.74	130.3	66.3	33.7	0.82
4	30°/min, He	0.25	1.49	108.6	96.9	3.1	

[a] Samples contained 94 mol % $Pd(NH_3)Cl_2$ and 6 mol % Pd. [b] Computed from weight of Pd after complete reduction with H_2. [c] Computed from formula weight of ash (prior to H_2 reduction): (106.4)(mol % Pd) + (177.3)(1 − mol % Pd) = 100(FW of ash).[b] [d] Formula weight of initial sample, 188.0, computed from formula weight and mass of ash (Pd); calculated for $Pd(NH_3)Cl_2$, 194.0.

decomposition is performed by programmed heating as indicated in run 3, the NH_3 concentration in the sample and gas stream is increased and reaction 5 is induced. At high

$$PdCl_2 + NH_3 \xrightarrow{1^\circ/\text{min}} Pd + {}^1/_3N_2 + {}^1/_3NH_4Cl + 1\,{}^2/_3HCl \qquad (5)$$

heating rates (30°/min, run 4), reaction 4 is followed immediately by reaction 5 to give the *overall* stoichiometry of reaction 6.

$$Pd(NH_3)Cl_2 \xrightarrow{30^\circ/\text{min}} Pd + {}^1/_3N_2 + {}^1/_3NH_4Cl + 1\,{}^2/_3HCl \qquad (6)$$

The stoichiometry of eq 2 proposed by Wendlandt and Fumes,[3] in which 0.8 mol of HCl and 1.2 mol of NH_4Cl are evolved per mole of *trans*-dichlorodiamminepalladium(II), would be expected if eq 3-5 are occurring more or less simultaneously. Our results indicate that little ammonia cracking (to yield N_2 and H_2) is occurring.

We have also found that monoammineplatinum(II) chloride can be prepared similarly and we are investigating its preparation by several routes.

Registry No. $Pd(NH_3)Cl_2$, 51911-44-5; *trans*-$[Pd(NH_3)_2Cl_2]$, 13782-33-7.