

20. Nitrotri-*ammine*palladium(II) Chloride and the Supposed Existence of *cis*-Dinitrodiamminepalladium(II).

By J. S. COE, R. HULME, and A. A. MALIK.

The preparative method reported in earlier work to yield *cis*-dinitrodiamminepalladium(II) yields instead nitrotri-*ammine*palladium(II) chloride. The original data relating to the *cis*-dinitrodiammine and the results of some more recent work have been reinterpreted to accord with this conclusion. The results of a partial X-ray structure analysis of nitrotri-*ammine*palladium(II) chloride are given.

THE preparation and X-ray examination of *cis*-dinitrodiamminepalladium(II) have been described by Mann *et al.*,¹ and several workers have since used their method to prepare the compound. The mechanism of the reaction in which the compound is formed and the mechanisms of analogous reactions have been studied by Jonassen *et al.*² Kinetic,³ polarographic,⁴ infrared,⁵ and refractive index⁶ measurements have also been carried out on the substance. Our attempts to prepare this product, *cis*-Pd(NO₂)₂(NH₃)₂, have been unsuccessful. Preparations carried out under the conditions described by earlier workers yielded a substance having general properties similar to those described, but closer examination showed the substance to be nitrotri-*ammine*palladium(II) chloride. This is the first fully authenticated example of a palladium(II) tri-*ammine*.

EXPERIMENTAL

*Nitrotri-*ammine*palladium(II) Chloride*.—The compound, *trans*-PdCl₂(NH₃)₂ (4 g.), was dissolved in a mixture of water (20 ml.) and aqueous ammonia (*d* 0.880; 10 ml.). The solution was cooled, mixed with a cold solution of sodium nitrite (10.4 g.) in water (30 ml.), and kept at <15° in a desiccator over concentrated sulphuric acid. After a period varying from 12 hr. to several days in different preparations, pale yellow crystals began to separate. These were washed with cold water, alcohol, and ether. Each sample blackened without effervescence when heated to 230–231°. Recrystallisation of the *product* from water gave pale yellow crystals which decomposed with effervescence at ~227°. Addition of concentrated aqueous potassium iodide to a solution of the original crystals in water or in acetone produced an orange precipitate and a supernatant liquid which remained colourless for several hours.

Compound	Ref.	Pd (%)	N (%)		Cl (%)
			total	as NH ₃	
[PdNO ₂ (NH ₃) ₃]Cl, sample 1	This work	44.3	24.1	17.7	14.7
" " 2	"	44.4	24.0	17.7	14.9
" " 3	"	44.3	23.9	17.9	14.7
<i>trans</i> -Pd(NO ₂) ₂ (NH ₃) ₂	"	45.8	24.4	12.1	0
<i>cis</i> -Pd(NO ₂) ₂ (NH ₃) ₂	1	44.8	23.5	—	*
"	2 _c	45.6	—	—	—
"	3	45.41	24.29	—	—
"	4	46.2	24.3	—	—
[PdNO ₂ (NH ₃) ₃]Cl, theor.	—	44.5	23.4	17.6	14.9
Pd(NO ₂) ₂ (NH ₃) ₂ , theor.	—	45.85	24.05	12.0	0

* Cl reported as impurity.

Palladium and chlorine were determined gravimetrically. Nitrogen was determined by the Kjeldahl method, with Devarda's alloy in the determination of total nitrogen. The Table gives details of the analyses of three samples of nitrotri-*ammine*palladium(II) chloride and one sample

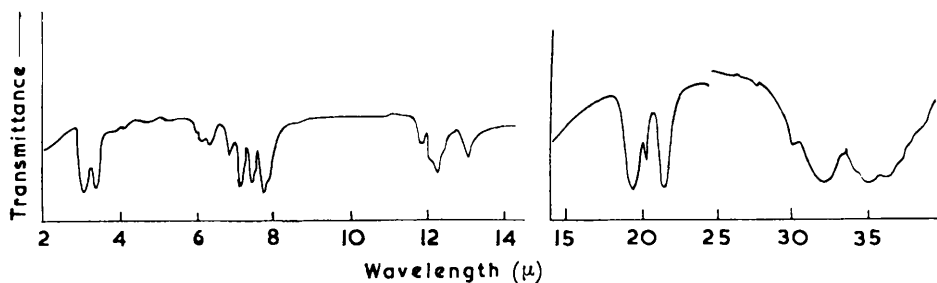
¹ Mann, Crowfoot, Gattiker, and Wooster, *J.*, 1935, 1642.² (a) Jonassen and Cull, *J. Amer. Chem. Soc.*, 1951, **73**, 274; (b) Jonassen, Sistrunk, Oliver, and Helfrich, *J. Amer. Chem. Soc.*, 1953, **75**, 5216; (c) Jonassen and Sistrunk, *J. Phys. Chem.*, 1955, **59**, 290.³ Banerjea and Tripathi, *J. Inorg. Nuclear Chem.*, 1958, **7**, 78.⁴ Chakravarty and Banerjea, *J. Inorg. Nuclear Chem.*, 1961, **16**, 288.⁵ Powell, *Chem. and Ind.*, 1956, 314.⁶ Bokii and Sokol, *Russ. J. Inorg. Chem.*, 1959, **4**, 29.

of *trans*-dinitrodiamminepalladium(II) (prepared by the method of Mann *et al.*¹). The analyses of samples of *cis*-dinitrodiamminepalladium(II) obtained by other workers, and the calculated values, are given for comparison.

Nitrotri-aminepalladium(II) Bromide.—The bromide, $[\text{PdNO}_2(\text{NH}_3)_3]\text{Br}$, was prepared as described for the chloride, from the bromo-ammine, *trans*- $\text{PdBr}_2(\text{NH}_3)_2$ (1.5 g.) in water (5 ml.) and aqueous ammonia (d 0.880; 2.5 ml.), and a solution of 2.6 g. potassium nitrite (2.6 g.) in water (7.5 ml.). Pale yellow crystals of the *product* separated after 16–24 hr. They blackened without effervescence at 220° (Found: Pd, 38.2; total N, 20.7; N as NH_3 , 15.2; Br, 27.5. $[\text{PdNO}_2(\text{NH}_3)_3]\text{Br}$ requires Pd, 37.55; total N, 19.8; N as NH_3 , 14.8; Br, 28.2%).

Reaction of Ammonia with Potassium Tetranitropalladate(II).—The palladate, $\text{K}_2\text{Pd}(\text{NO}_2)_4$ (1 g.), was dissolved in water (10 ml.), and ammonia (d 0.880; 3 ml.) was added. The mixture was treated as in the preparation of nitrotri-aminepalladium(II) chloride. Pale yellow crystals separated after 1–3 days. Each sample decomposed with effervescence at 225°, and with concentrated aqueous potassium iodide gave the red colour characteristic of the ammine, *trans*- $\text{Pd}(\text{NO}_2)_2(\text{NH}_3)_2$.

Infrared Results.—Samples of nitrotri-aminepalladium(II) chloride were examined in Nujol mulls on Grubb-Parson and Perkin-Elmer infrared spectrometers. The spectra are shown in the Figure.



Infrared spectra of $[\text{PdNO}_2(\text{NH}_3)_3]\text{Cl}$. (A thinner mull was used for the measurements beyond 25 μ .)

X-Ray Results.—Our crystals form flat, fairly thick plates and show a considerable tendency to aggregate in clusters. Oscillation and Weissenberg photographs taken with CuK_α radiation show that the single crystal is orthorhombic with $a = 9.70$, $b = 5.46$, $c = 12.57$ Å. Systematic absences are $0kl$ when l is odd, and $h0l$ when h is odd, so that the space group must be either the non-centric $Pca2_1$ (No. 29), or the centric $Pcam$ (No. 57). Both these space groups give the same ($h\bar{h}0$) projection (*pmg*). By flotation we found a density of 2.31 g./c.c. which, for 4 molecules in the unit cell, gives a molecular weight of 231 ± 8 , the formula weight of nitrotri-aminepalladium(II) chloride requiring 239.2. An electron-density projection, constructed from limited intensity data obtained about the c -axis, showed palladium to be located at 0.077, 0.231 and chlorine at 0.238, 0.742. The distance Pd–Cl is far too great for the chlorine to be co-ordinated to the metal, and it must therefore be ionic, as required by our formula.

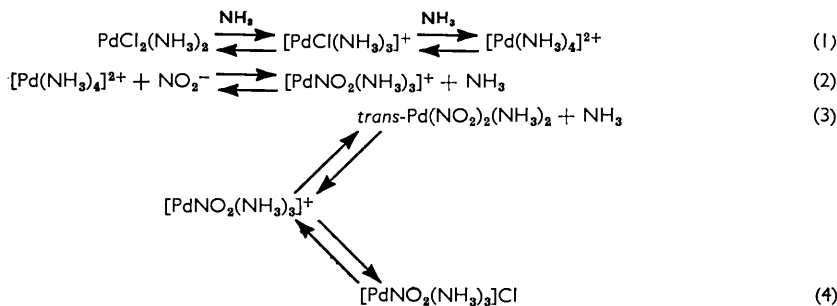
Examination of a Sample of "cis-Dinitrodiamminepalladium(II)" Supplied by Dr. D. B. Powell.—This sample, which appeared to have decomposed slightly, had been used by Dr. Powell in preliminary infrared studies.⁵ In the region 15–38 μ it gave a spectrum (including absorptions at 20.2 and 21.6 μ , as previously reported) identical with that of our salt, $[\text{PdNO}_2(\text{NH}_3)_3]\text{Cl}$. An X-ray oscillation photograph showed Dr. Powell's sample to have all dimensions identical with those of our compound.

DISCUSSION

By the action of sodium nitrite on an ammoniacal solution of the complex, *trans*- $\text{PdCl}_2(\text{NH}_3)_2$, at low temperature a compound is formed which, on the basis of analyses and the presence of ionic chlorine, has the formula $[\text{PdNO}_2(\text{NH}_3)_3]\text{Cl}$. Nitrotri-aminepalladium(II) bromide is formed in a similar reaction from the complex *trans*- $\text{PdBr}_2(\text{NH}_3)_2$. These reactions have previously been reported^{1, 2a, 2c, 3, 4} to yield a compound,

cis-Pd(NO₂)₂(NH₃)₂. In most cases samples of the latter are not now available,⁷ but one sample was shown by infrared and X-ray measurements to be identical with our salt, [PdNO₂(NH₃)₃]Cl. Further, the general properties of our compound (appearance, density, temperature and nature of decomposition, reaction with potassium iodide) correspond closely to those reported for the complex, *cis*-Pd(NO₂)₂(NH₃)₂, by the other workers. One crucial point concerns the original X-ray work. Mann *et al.*¹ reported crystals of their *cis*-compound to be monoclinic, with $a = 11.0$, $b = 12.4$, $c = 10.8$ Å, $\beta = 59^\circ 48'$, space group $P2_1$, and eight molecules in the unit cell, although the work was not carried to completion.⁸ It is possible by using the annexed transformation matrix to deduce their cell from ours, giving $a = 11.13$, $b = 12.57$, $c = 10.92$ Å, and $\beta = 60^\circ 37'$. All these dimensions are about 1.2% greater than those of Mann *et al.* Further, the new space groups are more satisfactory than those of Mann *et al.*, the four molecules in the new unit cell being related by symmetry. In their case it would be necessary to make the unusual assumption that there were four unrelated pairs of molecules in the unit cell.

The whole evidence indicates strongly that our salt, [PdNO₂(NH₃)₃]Cl is the same substance as that described previously as *cis*-Pd(NO₂)₂(NH₃)₂. Most of the results of earlier work can be accounted for on this basis. The two tests previously claimed^{1,2} to distinguish *cis*- from *trans*-dinitrodiamminepalladium(II) are now to be seen as distinguishing the covalent *trans*-dinitrodiammine from the ionic nitrotri-*ammine* chloride. The Table shows that the theoretical analyses of the chloride are very close to the results of Mann *et al.*,¹ and their sample was reported to contain chlorine.* Analyses obtained by other workers are close to the values expected for *cis*-Pd(NO₂)₂(NH₃)₂ but it is evident that figures for palladium and total nitrogen are not sensitively diagnostic.



Jonassen and Cull^{2a} proposed a mechanism for reactions in which the complex, *cis*-Pd(NO₂)₂(NH₃)₂, is formed under various conditions. It is possible to account for most of their results on the assumption that the above processes occur, our reaction (1) being identical with Jonassen and Cull's (1). The difficulty in their mechanism, that the compound, PdClNO₂(NH₃)₂, is not precipitated as expected, does not arise in our scheme. Reaction (2) accounts for their observation that the pH increases on addition of nitrite to an ammoniacal solution of the ammine, PdCl₂(NH₃)₂. Reaction (3) is likely to be slower than reaction (4) (as it involves replacement of a ligand), and the complex *trans*-Pd(NO₂)₂(NH₃)₂ is less soluble than [PdNO₂(NH₃)₃]Cl. These two points explain why only the *trans*-dinitrodiammine separates above 25° and the nitrotri-*ammine* chloride separates first at temperatures below 15°. With the nitro-ammine, *trans*-Pd(NO₂)₂(NH₃)₂, as

* Since the *cis*-isomer was found to change rapidly on recrystallisation, the analyses and X-ray investigation reported by Mann *et al.* were carried out on crystals which separated initially from the reaction mixture. The low analytical results were attributed to possible contamination by traces of sodium nitrite and sodium chloride.

⁷ Mann, Banerjee, and Jonassen, personal communications.

⁸ Ref. 1, p. 1651.

starting material in place of $\text{PdCl}_2(\text{NH}_3)_2$, Jonassen and Cull observed that none of the complex, $\text{cis-Pd}(\text{NO}_2)_2(\text{NH}_3)_2$, was formed, but on addition of sodium chloride large yields of the *cis*-product were obtained. These results, and the observation that $\text{cis-Pd}(\text{NO}_2)_2(\text{NH}_3)_2$ is converted into the *trans*-isomer at higher temperatures, can also be accounted for by reactions (3) and (4).

One result of Jonassen and Cull we are not able either to explain or to repeat. They reported the formation of the nitro-ammine, $\text{cis-Pd}(\text{NO}_2)(\text{NH}_3)_2$, from an ammoniacal solution of the salt, $\text{K}_2\text{Pd}(\text{NO}_2)_4$, in the absence of chloride ion. Our experiments yielded only the *trans*-isomer, a result also obtained by Mann *et al.*¹ There is also a discrepancy between our results and those of Jonassen and Sistrunk.^{2c} They obtained *cis*-dinitrodiamminepalladium(II) by treating an ammoniacal solution of dibromodiamminepalladium(II) with sodium nitrite at 10–15°. On repeating this experiment we obtained a compound $[\text{PdNO}_2(\text{NH}_3)_3]\text{Br}$.

Bokii and Sokol⁶ have measured refractive indices of a number of palladium(II) complexes, including a sample of $\text{cis-Pd}(\text{NO}_2)_2(\text{NH}_3)_2$ prepared, it is implied, by the method of Mann *et al.*¹ They noted a difference between the experimental co-ordinate refraction for $\text{NO}_2\text{-Pd-NH}_3$ (18.04) and the result obtained by taking the mean of values for $\text{NO}_2\text{-Pd-NO}_2$ and $\text{NH}_3\text{-Pd-NH}_3$ (16.86). Their value for the molar refraction of *cis*-dinitrodiamminepalladium(II) is 36.08. If the compound they used was in fact nitrotriamminepalladium(II) chloride, the molar refraction would be 37.05 (*i.e.*, using the molecular weight 239.2 in place of 232.7). The experimental co-ordinate refraction for $\text{NO}_2\text{-Pd-NH}_3$ would then be 16.59, in good agreement with the calculated value.

Banerjea and Tripathi³ used *cis*-dinitrodiamminepalladium(II) in kinetic studies. It is not possible to reinterpret their results as they gave no details of the conductance measurements by which the reactions were followed. It may be significant, however, that they reported an anomaly in the final conductance of a mixture of their substance, $\text{cis-Pd}(\text{NO}_2)_2(\text{NH}_3)_2$, and glycine, and also that this mixture gave an initial conductance equal to that expected for a uni-univalent electrolyte.

We thank the University of London Computer Unit for making available their facilities, and Dr. D. B. Powell for a chemical sample.