Inorganica Chimica Acta, 53 (1981) L157–L159
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Photochemical Formation of a Mixed Valence Platinum Compound

CARLO BARTOCCI*, CARLO A. BIGNOZZI, ANDREA MALDOTTI

Centro di Studio sulla Fotochimica e Reattività degli Stati Eccitati dei Composti di Coordinazione del C.N.R., Istituto Chimico dell'Università, Via L. Borsari 46, Ferrara, Italy

and FRANCESCO FAGIOLI

Istituto Chimico dell'Università, Via L. Borsari 46, Ferrara, Italy

Received November 4, 1980

The chemistry of *cis*- and *trans*-$Pt(NH_3)_2X_2$ (X = Cl, H_2O, Br) complexes has acquired in recent years, considerable importance after the discovery of the powerful antitumoral activity of *cis*-$Pt(NH_3)_2Cl_2$ [1].

Another class of platinum(II) complexes which has recently attracted the attention of many researchers is that known as 'platinum blue compounds' [2]. The chemistry and structure of these complexes, the first of which was prepared by Hofmann and Bugge in 1908 [3], are still not clear and several hypotheses have been reported concerning the mechanism of their formation on reaction of platinum(II) complexes with organic ligands such as CH_3CN [2a, 4], uracil [2b, 2d] *etc.*

We wish to report here some preliminary results on the photochemical formation of a blue platinum compound upon U.V. irradiation of [*cis*-$Pt(NH_3)_2(H_2O)_2$] SO_4 aqueous solution**.

The absorption spectra of the aquo-complex solution at two different pH values are reported in Fig. 1. The irradiation of these solutions with 254 nm light gave the following results. The absorbance increased with the irradiation time over the whole wavelength range; after about 40 minutes of irradiation a blue color was observed; this color became deeper and deeper as the irradiation continued, while a dark blue precipitate formed. If the irradiation was stopped after the first 30 minutes and the reaction vessel was kept in the dark, the formation of some blue compound was also observed. The spectral variations observed during irradiation indicated that the rate of formation of the blue product increased with increasing pH in the range 2.5–6.5†. If the solutions were previously carefully deoxygenated, the irradiation led to spectral variations quite similar to those described above for the irradiation of aerated solutions; however, the blue compound was not observed to form for long irradiation periods; if air was allowed to flow into the reaction vessel after the irradiation, the blue compound was formed.

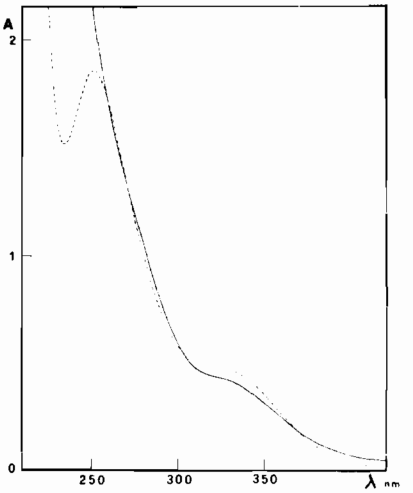


Fig. 1. Absorption spectra of [*cis*-$Pt(NH_3)_2(H_2O)_2$] SO_4 in aqueous solution 1.33×10^{-2} *M*. ------ pH = 2.9 —— pH = 6.5.

A spectrophotometric investigation did not give sufficient information in order to identify the photoreaction product; in fact, the unsolubility of the blue compound in all the common inorganic and organic solvents did not allow us to perform UV–VIS absorption spectra, while IR spectra showed diffuse, unresolved, not assignable bands.

Elemental analysis (Found (%): Pt, 67.53; N, 6.20; O, 18.27; H, 1.80; S, 3.44) is in sufficiently good agreement with the simplest formula $Pt_3N_4O_{10}H_{18}S$ (Calculated (%): Pt, 68.73; N, 6.58; O, 18.79; H, 2.13; S, 3.76).

The blue product reacts with diluted (0.1 *M*) aqueous hydrogen chloride, giving a pale yellow solution which: *i*) oxidizes hydrazine sulfate, *ii*) reduces $Ce(SO_4)_2$, iii) precipitates $BaSO_4$ from a solution of $BaCl_2$.

Since points *i* and *ii* suggest the presence of platinum in different oxidation states, the Pt(II) was

---

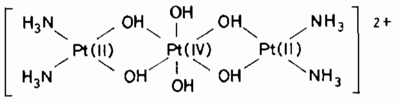
*Author to whom correspondence should be addressed.

**The photochemical behavior of *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ complex ion was previously studied by Perumareddi and Adamson [5]; however, as far as the irradiation of this complex at 254 nm is concerned, definitive results have not been reported by these authors.

†The photochemical behavior at pH values higher than 6.5, which seems to be quite different from that at lower pH, is under investigation.

determined in the solution in HCl by potentiometric titration with $Ce(SO_4)_2$: the result gave a Pt(II) concentration which is one third of the total platinum concentration, suggesting a Pt(II)/Pt(IV) ratio of 2.

The presence of sulfate anion in the solution in HCl (point *iii*) indicates that the blue compound is a doubly charged cation, for which, on the basis of the above experimental results, we suggest the following tentative molecular structure:



Several years ago Babaeva and Motyagina [6] obtained by UV irradiation of aqueous *cis*-$Pt(NH_3)_2Cl_2$ a blue compound which was formulated as a mixed valence (Pt(II)/Pt(IV) $\sim$ 3) tetranuclear complex. Since we observed that the irradiation of aqueous solutions of *cis*-$Pt(NH_3)_2Cl_2$ in the presence of excess Cl^- ions does not give the blue product, the compound obtained by those authors could be considered to be formed on photoreaction of hydrolysis products of the *cis*-dichloro complex; however, the different elemental analysis, in paticular the observed presence of Cl, indicates that this compound is definitely different from ours.

Recently, thorough investigation on hydroxo-bridged Pt(II) complexes has been published [7]. The results reported in that study suggest that in aqueous solution of *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ dinuclear and trinuclear species may be present, the concentration of which should be strongly dependent on the total platinum concentration and on pH, reaching the maximum value at pH near to 7. Interestingly, as reported above, we observed that the formation rate of the blue compound increased with pH, reaching the highest value at pH 6.5. This seems to indicate that the dimer or trimer could be the species responsible for the photochemical formation of the blue product. In order to verify this hypothesis the dimer and the trimer species were isolated [7] from an aqueous solution of [*cis*-$Pt(NH_3)_2(H_2O)_2$]SO_4; aqueous solutions of these compounds were irradiated with 254 nm light. While the dimer only gave rise to the formation of yellow unidentified platinum products, the photochemical behavior of the trimer was the same as that observed for [*cis*-$Pt(NH_3)_2(H_2O)_2$]SO_4 aqueous solutions. This fact clearly indicates that the trimer species is responsible for the photoreaction which leads to the formation of the blue product.

The above experimental results do not allow a formulation of a photoreaction mechanism, since the knowledge of the nature of the intermediate, as well as of the type of the electronic transition responsible for the primary photoreaction are essential for this purpose; however, the following points can be already established:

1) The excited platinum trimer complex leads, either in the presence or in the absence of oxygen, to the formation of an intermediate which is stable in deoxygenated solution at pH 6.5 for a long time.

2) The intermediate, which is likely to be a polynuclear species, is partially oxidized by oxygen giving rise to the formation of a mixed valence (Pt(II)–Pt(IV)) dinuclear or trinuclear blue complex.

Finally, the nature of the electronic transition responsible for the deep blue color of the photoreaction product can be considered; intensely colored polynuclear complexes have been known for a long time and their color has been attributed to 'intervalence transfer absorption' [8]; we think that absorption bands of the same nature are responsible for the color of our blue compound.

Experimental

cis-Dichlorodiammineplatinum(II) was prepared according to reference [9]. Aqueous solutions of [*cis*-$Pt(NH_3)_2(H_2O)_2$]SO_4 were obtained by stirring in water *cis*-$Pt(NH_3)_2Cl_2$ with equivalent amounts of Ag_2SO_4 for 48 hours in the dark and filtering away the AgCl formed. The light sources and equipment used to obtain 254 nm radiations were the same as previously described [10]. Samples were deoxygenated before the irradiation by freeze thaw pump method. UV and IR absorption spectra were carried out with a Varian Cary 219 and Perkin-Elmer mod. 577 spectrophotometers respectively. The elemental analysis was performed in the Analytische Laboratorien of Elbach über Engelskirchen (FRG). All the chemicals were reagent grade commercial products.

Acknowledgement

C.B. is grateful to Professor T. Theophanides of the Department of Chemistry of the University of Montreal, Canada, for stimulating the beginning of this work during a stay in his laboratory in Montreal as invited researcher.

References

1 B. Rosenberg, L. Van Camp, J. E. Trosko, and V. H. Manson, *Nature, 222,* 384 (1969).

2 See for example: a) A. K. Johnson and J. D. Miller, *Inorg. Chim. Açta, 22,* 219 (1977). b) J. K. Barton, H. N. Rabinowitz, D. J. Szalda, S. J. Lippard, *J. Am. Chem. Soc., 99,* 2877 (1977) and references therein. c) C. M. Flynn, T. S. Viswanathan, and R. Bruce Martin, *J. Inorg. Nucl. Chem., 39,* 437 (1977). d) R. Faggiani, B. Lippert, and C. J. Lock, *Inorg. Chem., 19,* 295 (1980).

3 K. A. Hofmann and G. Bugge, *Ber.*, *41*, 312 (1908).

4 R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 2835 (1964).

5 J. R. Perumareddi and A. W. Adamson, *J. Phys. Chem.*, *72*, 414 (1968).

6 A. V. Babaeva and M. A. Motyagina, *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk*, 227 (1953).

7 R. Faggiani, B. Lippert, C. J. Lock, and B. Rosenberg, *J. Am. Chem. Soc.*, *99*, 777 (1977); *Inorg. Chem.*, *16*, 1192 (1977); *Inorg. Chem.*, *17*, 1941 (1978).

8 G. C. Allen and N. S. Hush, *Progr. Inorg. Chem.*, *8*, 357 (1967).

9 'Inorganic Synthesis', Vol. VII, McGraw–Hill, New York, 1963, p. 239.

10 V. Balzani, V. Carassiti, L. Moggi, and F. Scandola, *Inorg. Chem.*, *4*, 1243 (1965).