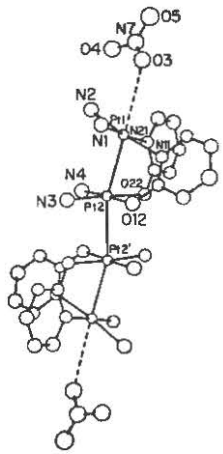
Platinblau: Recent Structural Studies

Susan L. Kaiser Literature Seminar April 5, 1983

In contrast to the yellow or colorless nature of most platinum complexes, some ligands yield intense blue or purple complexes that are referred to as platinum blues or platinblau. These blue complexes are not only interesting because of their intense color but also intriguing chemically.

Comparative studies suggest that all known blue compounds are mixed-valent, metal-metal bonded, amidate-bridged oligomers [1]. The chemistry and structures of these complexes, the first of which was prepared by Hofmann and Bugge in 1908 [2], are still not clear and several hypotheses have been reported concerning the mechanism of their function on reaction of platinum(II) complexes with organic ligands such as CH_3CN, uracil, etc. [3]. The discovery that platinum blues (e.g., platinum pyrimidine blues) possess a high index of antitumor activity with a lower associated toxicity than the parent drug, cis-$(NH_3)_2PtCl_2$ [4], stimulated efforts to characterize them. These platinum blues have also been used as cytologic stains for DNA in electron microscopy [5].

To date only cis-diammineplatinum α-pyridone blue (PPB) has been fully characterized structurally [6]. It consists of four platinum atoms bridged by α-pyridonate ligands. The tetramer is composed of two centrosymmetrically related dimers, as required by the space group symmetry. This structure determination was a step toward the understanding of the chemistry of platinum blues.



Distance	Å
Pt1····Pt2	2.779
Pt2····Pt2′	2.885
Pt-NH_3(av)	2.06
Pt-N(pyridone)	2.05
Pt-O (av)	2.04
Angle	**Deg.**
Pt1-Pt2-Pt2′	164.5°

Spectroscopic and synthetic studies on the platinum pyrimidine blues, etc., show that the solution chemistry of platinum blues is very complicated, with more than one oligomeric platinum species usually existing in solution. Attempts to crystallize other blue complexes have been largely unsuccessful due to their heterogeneous

oligomeric nature. Attention has been drawn to the non-blue structural analogues of the platinum blues in hopes of rationalizing the structures of many blue complexes by analogy. Several non-blue crystalline products have been isolated from reaction mixtures that ultimately produce cis-diammineplatinum pyrimidine blues even though crystals of the blue product have not to date been obtained [7-10]. Three structures of non-blue compounds obtained in the reaction of cis-diammineplatinum(II) with α-pyridone were reported [11]. These analogues contain one, two or four platinum atoms. Often these derivatives are "head-to-head" or "head-to-tail" dimers, or tetranuclear platinum complexes. An example of a "head-to-head" arrangement for a platinum dimer bridged by two ligands is where one platinum is bound to a nitrogen from each ligand and the other platinum is bound to an oxygen from each ligand. Conversely, the "head-to-tail" arrangement is where each platinum is bound to one nitrogen and one oxygen.

cis-Diammineplatinum α-pyrrolidone tan was obtained from the reaction of the cis-diammineplatinum(II) hydrolysis product with α-pyrrolidone [12]. It is interesting to note that the platinum oxidation state in cis-diammineplatinum α-pyridone is 2.25, whereas in cis-diammineplatinum α-pyrrolidone tan it is 2.5 [12].

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