Redox Properties of Paramagnetic "Platinum Uracil Blues"

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Considerable effort is currently devoted towards elucidating the molecular conformation of antitumor active "Platinum Pyrimidine Blues" which form a class of amorphous compounds derived from cis-$Pt(NH_3)_2(H_2O)_2$, (PDDa), a cis-$Pt(NH_3)_2Cl_2$ hydrolysis product. The "Blues" exhibit weak paramagnetism due to low spin d^7 Pt(III) in what is generally assumed to be a chainlike structure, held together by bridging ligandsbound to a backbone of Pt-Pt bonds (1). Accordingly, esr along with optical absorption spectroscopy was employed in studying a number of "Pt Uracil Blues".

In one type of experiment we studied the effect of reducing and oxidizing agents on the "Blues". 250 µl aliquots of a solution of PDDa-6-methyl-ura which had been allowed to react at 70°C for about 4h, were mixed with 20 µl of reducing and oxidizing agents, respectively. As a result, esr spectra of differing signal intensities and line patterns were obtained. Taking into account optical absorption studies, at least three different types of spectra can be identified. They correspond to a blue "reduced" species (type II esr spectrum, ε(605 nm) $\approx$ 70), a green "moderately oxidized" species (type I esr spectrum, ε(740 nm) $\approx$ 210), and a tan species with an esr spectrum (type III) which is different in line pattern observed in the above spectra, although parts of the type I pattern can clearly be recognized.

In a second type of experiment the esr and optical absorption spectra of a number of compounds formed between PDDa and various substituted uracil ligands were compared after a given reaction time. The analysis revealed the presence of the types of spectra obtained from the redox experiments and comprised by the tentative classification described above.

From the findings one can conclude that the paramagnetism seems to arise in the course of a slow oxidation reaction driven by oxygen. This reaction is accelerated by additional oxidizing agents. It is reversed by reducing agents. Under identical conditions, large π-electron densities at the proposed ligand binding sites N(3), O(7), and/or O(8) (2) contribute to producing stronger oxidized forms of the compounds.

(1) J.K. Barton, C. Caravana, S.J. Lippard, J.Am.Chem.Soc. 101, 7269, 1979

(2) G.Y.H. Chu, R.E. Duncan, R.S. Tobias, Inorg.Chem. 16, 2625, 1977