Name	Student Code

32nd IChO • Problem 3 — 9 points

Bioinorganic Chemistry

The square planar complex *cis*-diamminedichloroplatinum(II) is an important drug for the treatment of certain cancers.

3-1 Draw the structures of *cis*- and *trans*-diamminedichloroplatinum(II) and label each structure as *cis* or *trans*.

A number of ionic compounds are also compatible with the empirical formula $Pt(NH_3)_2Cl_2$.

3-2 Write precise molecular formulas for all possible ionic compounds which comply with the following conditions: each compound has 1) empirical formula $Pt(NH_3)_2Cl_2$, 2) is composed of discrete, monomeric ionic platinum(II) complex entities, and 3) contains only one type of cation and one type of anion. The answer must clearly reveal the composition of each discrete platinum(II) complex entity in each compound.

3-3 How many 5d electrons does the platinum(II) ion have?

The valence d-orbital energy splitting diagram for a square planar complex can be regarded as being derived from that for an octahedral complex in which the metal-ligand interactions due to the two ligands coordinated along the *z* axis vanish, while the bonds to the four remaining ligands (coordinated along the *x* and *y* axes) become stronger.

3-4 Which of the five 5d orbitals attain the highest energy (*i.e.* is the least likely to be occupied by electrons) in the general case of a square-planar Pt(II) complex?

Serum transferrin (abbreviated: Tf) is a monomeric protein whose main function in the human body is the transport of iron(III). Each transferrin molecule can bind up to two iron(III) ions with stepwise overall binding constants K_1 and K_2 at biological conditions (but at 25 °C) corresponding to the overall reactions:

$Fe^{III} + Tf \rightleftharpoons (Fe^{III})Tf$ $\qquad K_1 = 4.7 \times 10^{20}\ M^{-1}$

$Fe^{III} + (Fe^{III})Tf \rightleftharpoons (Fe^{III})_2Tf$ $\qquad K_2 = 2.4 \times 10^{19}\ M^{-1}$

In the diferric protein, $(Fe^{III})_2Tf$, the two iron(III) ions are bound at two similar, but non-identical sites, and the two possible monoferric protein products, $(Fe^{III})Tf$, can be denoted $\{Fe^{III}\cdot Tf\}$ and $\{Tf\cdot Fe^{III}\}$. Their relative abundance at equilibrium is given by the constant $K = [\{Tf\cdot Fe^{III}\}][\{Fe^{III}\cdot Tf\}]^{-1} = 5.9$.

3-5 Calculate the values of the two constants $K_1' = [\{Fe^{III}\cdot Tf\}][Fe^{III}]^{-1}[Tf]^{-1}$ and $K_1'' = [\{Tf\cdot Fe^{III}\}][Fe^{III}]^{-1}[Tf]^{-1}$, respectively, corresponding to the formation of each monoferric form of transferrin.

3-6 Calculate the values of the two constants $K_2' = [(Fe^{III})_2Tf][Fe^{III}]^{-1}[\{Fe^{III}\cdot Tf\}]^{-1}$ and $K_2'' = [(Fe^{III})_2Tf][Fe^{III}]^{-1}[\{Tf\cdot Fe^{III}\}]^{-1}$ respectively, corresponding to the formation of diferric transferrin from each of the monoferric forms

The bound iron(III) ion at each binding site is surrounded by six donor atoms from various ligands. Thus, two oxygen atoms of a carbonate anion coordinate to the metal, and the following amino acid side chains from the protein primary structure also coordinate to the iron(III) ion with one potential donor atom each: one aspartate, one histidine and two tyrosine residues.

3-7 What is the total number of oxygen donor atoms that surround a 6-coordinate iron(III) ion in transferrin?