

Outline of the solution to Problem 4: It is in your blood

10 marks

3 September, 2020

1.

- (a) (1 point) O_2^{2+} has high stability but low persistence.
- (b) (1 point) $[Fe(TPP)(2-MeIm)]$ - TPP forms the porphyrin plane (albeit with a little doming which we can ignore) and 2-MeIm as an axial ligand] O_2^{2+} is expected to bind in linear mode to this complex
- (c) (2 points) MO for the linear and perpendicular binding mode are as follows:
For O_2^{2+} as there are no electrons in the antibonding orbitals of both linear and perpendicular

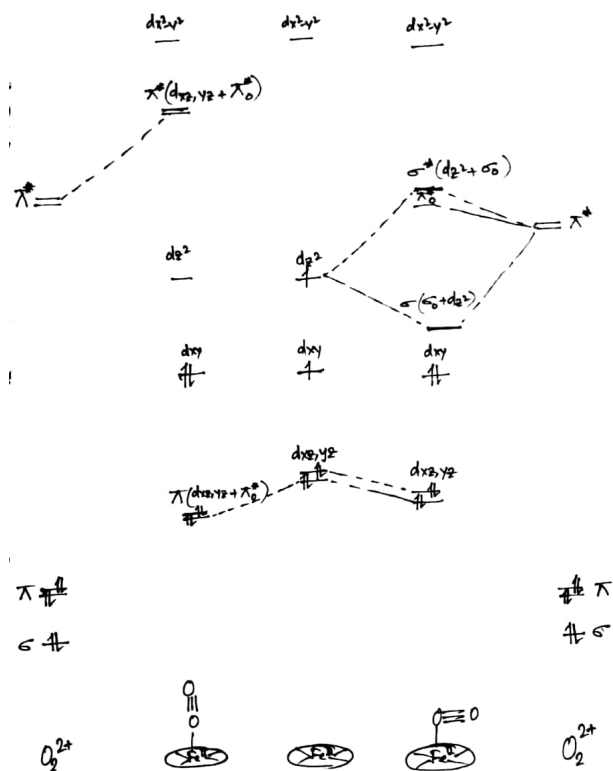


Figure 1: MO for the binding modes

modes of binding, both may seem possible. But, since the linear mode maximizes metal to ligand pi bonding, the linear mode is the preferred mode of binding. This case is exactly analogous to the linear binding of CO to hemoglobin as CO is isoelectronic with O_2^{2+} .

2. (2 points) No dimerization occurs forming (FeP)₂ O dimers. (+0.5)

In Fe-protoporphyrin complex IX the following reactions occur due to the absence of the steric bulk imposed by globin chain(+0.5 for writing about lack of steric constraints and possibility of dimerization, +1 for reactions)

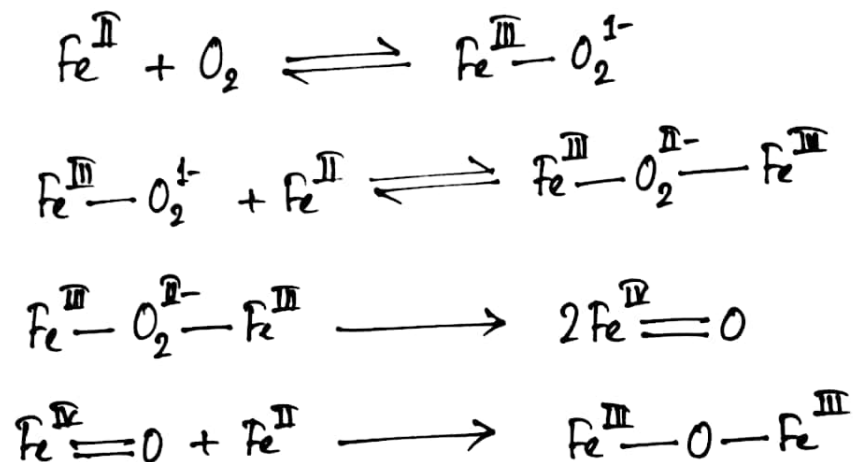


Figure 2: Reaction sequence

3. (4 points) Dimerization occurs through the double bonded oxenoid moiety obtained in reaction 3 above. In the case of Co-protoporphyrin complex, the doubled bonded oxenoid species will have one electron in the antibonding orbital as Co²⁺ is a d⁷ species. Thus, the oxenoid species will be formed less due to

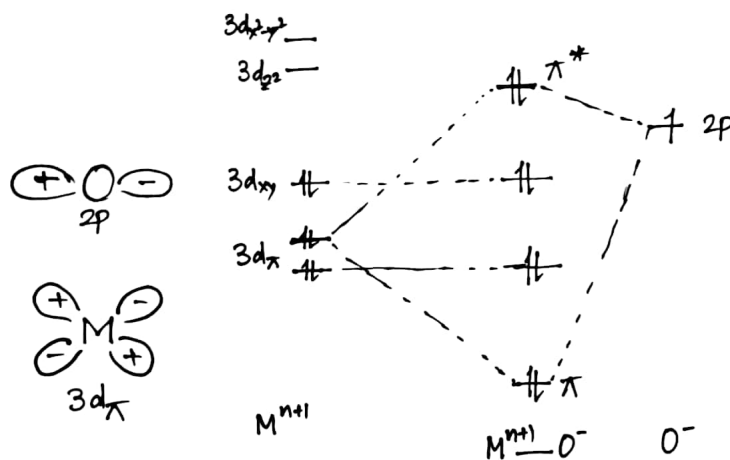


Figure 3: Orbital diagram showing stabilities of M-O species

instability and thus this complex is more likely to carry oxygen than iron protoporphyrin complex. (+2)
 The binding mode of NO to this complex will be perpendicular as the linear mode has an electron in the antibonding orbital. The bent mode may also be possible. (+2)

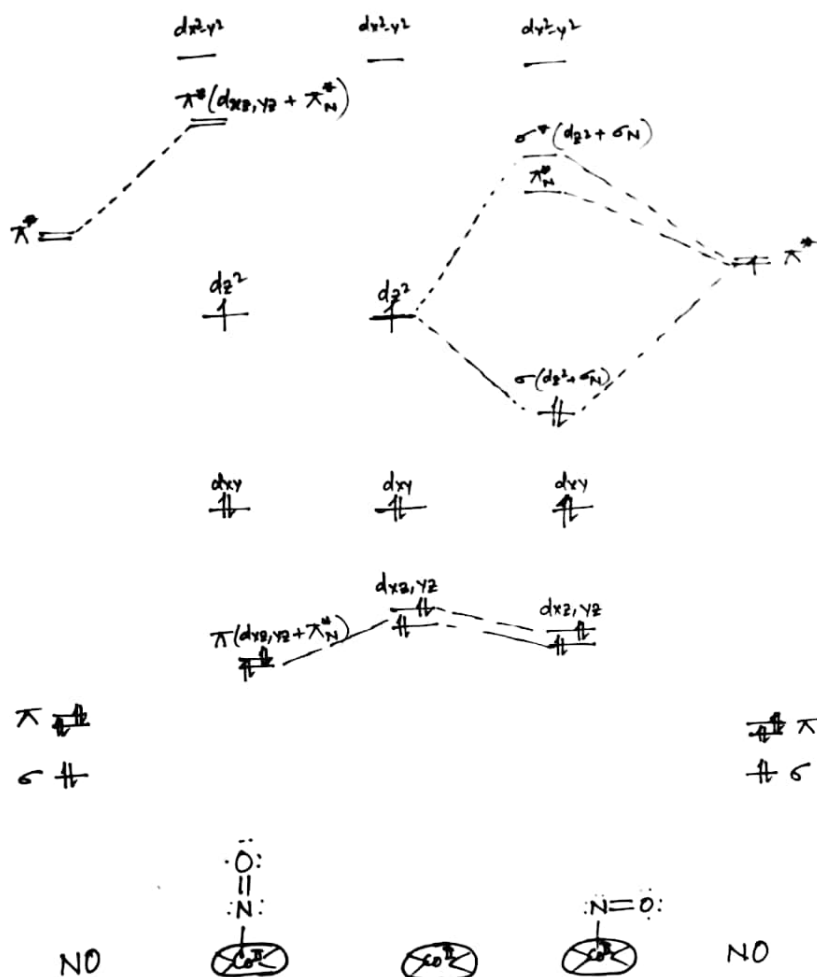


Figure 4: MO diagram for various modes in Co