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Porphyrins

XX. Theory for the States of Ni(d^8) Complexes* **

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The odd electron perturbation method earlier used to explain the anomalous emissions of porphyrins with one unpaired d electron is now applied to the d^8 configuration of Ni porphyrin. Many extra states occur because the metal can be $^1A_{1g}$, $^3B_{1g}$, or $^1B_{1g}$. Absorption spectra are calculated for both $^1A_{1g}$ and $^3B_{1g}$ ground states. In the case of $^3B_{1g}$ ground state the normal porphyrin states are augmented by several others. Lack of emission from Ni porphyrins is explained by these extra states. The strong phosphorescence of Pd and Pt porphyrins is attributed to a very high energy $^3B_{1g}$.

Eine spezielle Form der Störungsrechnung für ungepaarte Elektronen, mit der früher die anormale Emission des Porphyrins erklärt wurde, wird auf die d^8 Konfiguration des Ni-Porphyrins angewendet. Viele weitere Zustände treten auf, weil die Metallzustände die Symmetrie $^1A_{1g}$, $^3B_{1g}$ oder $^1B_{1g}$ haben können. Absorptionsspektren werden sowohl für $^1A_{1g}$ als auch $^3B_{1g}$ als Grundzustände berechnet. Im letzteren Falle treten neben den normalen Porphyrinzuständen weitere auf, wodurch sich das Fehlen einer Emission bei Ni-Porphyrin erklärt. Die starke Phosphoreszenz des Pd- und Pt-Porphyrins wird mit der sehr hohen Energie von $^3B_{1g}$ begründet.

La méthode de perturbation à électron célibataire utilisée auparavant pour expliquer les émissions anormales des porphyrines avec 1 électron d célibataire est maintenant appliquée à la configuration d^8 de la porphyrine du nickel. De nombreux états supplémentaires apparaissent car le métal peut être $^1A_{1g}$, $^3B_{1g}$, ou $^1B_{1g}$. Les spectres d'absorption sont calculés pour les états $^1A_{1g}$ et $^3B_{1g}$. Dans le cas de $^3B_{1g}$, aux états normaux de la prophyrine s'en ajoutent plusieurs autres. L'absence d'émission des porphyrines du nickel s'explique par la présence de ces etats supplémentaires. La forte phosphorescence des porphyrines de Pd et Pt est attribuée à un état de haute énergie $^3B_{1g}$.

Introduction

Nickel porphyrin complexes are generally diamagnetic, but certain nickel porphyrin complexes can become paramagnetic in the presence of pyridine [1]. This is a common phenomenon with d^8 complexes and is referred to as solution paramagnetism [2]. The complexes involved are generally square planar and the pyridine applies a strong axial perturbation to this ligand field. The additional interaction raises the energy of the $a_{1g}(d_{z^2})$ ligand field orbital to the point where it becomes energetically favourable to unpair the electrons in this orbital and place one electron in the $b_{1g}(d_{x^2-y^2})$ orbital. The configuration becomes $(a_{1g})^1\,(b_{1g})^1$ with the triplet lying lower. This paper considers the interaction of this configuration with the low lying states of porphyrin. The problem is some-

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what analogous to that which arises in VO, Co, Cu complexes, which have one unpaired d electron [3, 4]. However, the d^8 problem has many more states. We shall in this paper present detailed calculations only on Ni complexes, but will use the results to attempt to explain the luminescence properties of the three d^8 metals Ni, Pd, Pt.

Electronic States and Energies

The formation of states proceeds analogously to that of the case with one d electron [3]. The spectra of closed shell metal porphyrins arise from transitions between top filled orbitals a_{2u}, a_{1u} to lowest empty orbitals e_g. We shall as before denote the ground state ${}^1\psi_0$. The states associated with $a_{1u} \rightarrow e_g$ we denote ${}^{3,1}\psi_1$ and those associated with $a_{2u} \rightarrow e_g$ we denote ${}^{3,1}\psi_2$. We note that there is no configuration interaction between the triplets, which have also been denoted ${}^3T_1$, ${}^3T_2$. The singlets have strong configuration interaction and give rise to the weak ${}^1Q$ and intense ${}^1B$ states [3].

For the d^8 metal complexes we need to consider three metal states ${}^1A_{1g}$, ${}^3B_{1g}$, ${}^1B_{1g}$. The first arises when the two d holes are in $d_{x^2-y^2}$, while the latter two arise when one hole is in each of d_{z^2}, $d_{x^2-y^2}$. Table 1 gives the energy expressions for the combination states. The wavefunctions for these states are written out elsewhere [4]. The energy for ${}^1\Psi_0 = {}^1\psi_0 \cdot {}^1A_{1g}$ is taken as zero. The values ET 1, ES 1, ET 2, ES 2 are similar to those that occur for the closed shell metal states ${}^{3,1}\psi_1$, ${}^{3,1}\psi_2$ and are determined from spectral data in a manner analogous to that used for VO, Co, Cu complexes [3]. The exchange integrals K' and K'' are calculated as discussed below. If the ground state is ${}^1\Psi_0$, the only states which are radiatively allowed are ${}^1\Psi_4$ and ${}^1\Psi_5$. As in the earlier study [3] we shall assume

$$({}^1\Psi_0|er|{}^1\Psi_4) = ({}^1\Psi_0|er|{}^1\Psi_5) = \boldsymbol{R}_q .$$

Similarly, if the ground state is ${}^3\Psi_0$, only transitions to ${}^3\Psi_7$ and ${}^3\Psi_8$ are allowed. Again, the transition dipole to each is $\boldsymbol{R}_q$. As in the closed shell case, there is strong configuration between pairs of states: ${}^1\Psi_4$ and ${}^1\Psi_5$, ${}^1\Psi_6$ and ${}^1\Psi_7$, ${}^3\Psi_7$ and ${}^3\Psi_8$ giving rise to analogues to the Q and B states. As a result, we can adopt the short notation for all the resulting states given in Table 2. This is used in the Figures and in subsequent discussion.

All the singlets ${}^1\psi_{2-7}$ are of E_u symmetry and some of them mix through two electron terms. Below are given the nonzero off-diagonal matrix elements

$$H_{24} = -(\sqrt{6}/2)\,(e_{gy}a_{1g}|b_{1g}e_{gy}) ,$$
$$H_{26} = (\sqrt{3}/2)\,(K(e_{gy}, a_{1g}) + K(a_{2u}, b_{1g}) + K(e_{gy}, b_{1g}) + K(a_{2u}, a_{1g})) ,$$
$$H_{35} = -(\sqrt{6}/2)\,(e_{gx}a_{1g}|b_{1g}e_{gx}) ,$$
$$H_{37} = (\sqrt{3}/2)\,(K(e_{gx}, a_{1g}) + K(a_{1u}, b_{1g}) + K(e_{gx}, b_{1g}) + K(a_{1u}, a_{1g})) ,$$
$$H_{45} = 2(a_{1u}e_{gy}|e_{gx}a_{2u}) = CI = H_{67} ,$$
$$H_{46} = (1/\sqrt{2})\,(2(e_{gy}a_{1g}|e_{gy}b_{1g}) - (e_{gy}a_{1g}|b_{1g}e_{gy})) ,$$
$$H_{57} = (1/\sqrt{2})\,(2(e_{gx}a_{1g}|e_{gx}b_{1g}) - (e_{gx}a_{1g}|b_{1g}e_{gx})) .$$

Table 1. *States and energies for d^8 metals*

Singlet states	Energy	Triplet states	Energy	Quintet states	Energy
${}^1\Psi_0 = {}^1\psi_0 \cdot {}^1A_{1g}$	O	${}^3\Psi_0 = {}^1\psi_0 \cdot {}^3B_{1g}$	ETM	${}^5\Psi_1 = {}^3\psi_2 \cdot {}^3B_{1g}$	ET 2 + ETM − K'
${}^1\Psi_1 = {}^1\psi_0 \cdot {}^1B_{1g}$	ETM + K''	${}^3\Psi_1 = {}^3\psi_2 \cdot {}^1A_{1g}$	ET 2	${}^5\Psi_2 = {}^3\psi_1 \cdot {}^3B_{1g}$	ET 1 + ETM − K'
${}^1\Psi_2 = {}^3\psi_2 \cdot {}^3B_{1g}$	ET 2 + ETM + 2K'	${}^3\Psi_2 = {}^3\psi_1 \cdot {}^1A_{1g}$	ET 1		
${}^1\Psi_3 = {}^3\psi_1 \cdot {}^3B_{1g}$	ET 1 + ETM + 2K'	${}^3\Psi_3 = {}^3\psi_2 \cdot {}^3B_{1g}$	ET 2 + ETM + K'		
${}^1\Psi_4 = {}^1\psi_2 \cdot {}^1A_{1g}$	ES 2	${}^3\Psi_4 = {}^3\psi_1 \cdot {}^3B_{1g}$	ET 1 + ETM + K'		
${}^1\Psi_5 = {}^1\psi_1 \cdot {}^1A_{1g}$	ES 1	${}^3\Psi_5 = {}^3\psi_2 \cdot {}^1B_{1g}$	ET 2 + ETM + K''		
${}^1\Psi_6 = {}^1\psi_2 \cdot {}^1B_{1g}$	ES 2 + ETM + K''	${}^3\Psi_6 = {}^3\psi_1 \cdot {}^1B_{1g}$	ET 1 + ETM + K''		
${}^1\Psi_7 = {}^1\psi_1 \cdot {}^1B_{1g}$	ES 1 + ETM + K''	${}^3\Psi_7 = {}^1\psi_2 \cdot {}^3B_{1g}$	ES 2 + ETM		
		${}^3\Psi_8 = {}^1\psi_1 \cdot {}^3B_{1g}$	ES 1 + ETM		

$2K' \equiv K(e_g, a_{1g}) + K(e_g, b_{1g}) + K(a_{2u}, a_{1g}) + K(a_{1u}, a_{1g})$; $K'' \equiv 2K(a_{1g}, b_{1g})$.

Table 2. *Short notation for d^8 states*[a]

Metal Porphyrin	$^1A_{1g}$	$^3B_{1g}$	$^1B_{1g}$
$^1\psi_0$	$^1A_{1g}$	$^3B_{1g}$	$^1B_{1g}$
$^3\psi_1$, $^3\psi_2$	$^3T_1$, $^3T_2$	$^{1,3,5}T_1'$, $^{1,3,5}T_2'$	$^3T_1''$, $^3T_2''$
$^1\psi_1$, $^1\psi_2$	^1Q, ^1B	$^3Q'$, $^3B'$	$^1Q''$, $^1B''$

[a] There is little configuration interaction between $^3\psi_1$, $^3\psi_2$ but it is strong between $^1\psi_1$, $^1\psi_2$. See text.

For the triplets eight states of E_u symmetry exist and can mix. The following nonzero matrix elements are obtained:

$$\begin{aligned}
&H_{13} = -(e_{gy}a_{1g}|b_{1g}e_{gy}) = \sqrt{2}\,H_{17}\,,\\
&H_{15} = (1/\sqrt{2})\,(2(e_{gy}a_{1g}|e_{gy}b_{1g}) - (e_{gy}a_{1g}|b_{1g}e_{gy}))\,,\\
&H_{24} = -(e_{gx}a_{1g}|b_{1g}e_{gx}) = \sqrt{2}\,H_{28}\,,\\
&H_{26} = (1/\sqrt{2})\,(2(e_{gx}a_{1g}|e_{gx}b_{1g}) - (e_{gx}a_{1g}|b_{1g}e_{gx}))\,,\\
&H_{35} = (1/\sqrt{2})\,(K(e_{gy}, a_{1g}) + K(a_{2u}, a_{1g}) - K(e_{gy}, b_{1g}) - K(a_{2u}, b_{1g}))\,,\\
&H_{37} = (1/\sqrt{2})\,(K(e_{gy}, a_{1g}) - K(a_{2u}, a_{1g}) + K(e_{gy}, b_{1g}) - K(a_{2u}, b_{1g}))\,,\\
&H_{46} = (1/\sqrt{2})\,(K(e_{gx}, a_{1g}) + K(a_{1u}, a_{1g}) - K(e_{gx}, b_{1g}) - K(a_{1u}, b_{1g}))\,,\\
&H_{48} = (1/\sqrt{2})\,(K(e_{gx}, a_{1g}) - K(a_{1u}, a_{1g}) + K(e_{gx}, b_{1g}) - K(a_{1u}, b_{1g}))\,,\\
&H_{57} = \tfrac{1}{2}(K(e_{gy}, a_{1g}) - K(a_{2u}, a_{1g}) - K(e_{gy}, b_{1g}) + K(a_{2u}, b_{1g}))\,,\\
&H_{68} = \tfrac{1}{2}(K(e_{gx}, a_{1g}) - K(a_{1u}, a_{1g}) - K(e_{gx}, b_{1g}) + K(a_{1u}, b_{1g}))\,,\\
&H_{78} = CI\,.
\end{aligned}$$

Calculations and Results

The methods used to obtain states, energies and intensities were those used previously on VO, Co and Cu porphyrin [3]. The double reduction was made on all two electron integrals except $K(a_{1g}, b_{1g})$. In the calculation of the σ-π integrals only one center integrals were included. The Ni atomic input integrals were chosen to be consistent with a $+0.3$ charge and an $s^{0.5}p^{0.5}d^{8.7}$ configuration. They are $F^2(dd) = 73{,}500\ \mathrm{cm}^{-1}$ and $G^2(sd) = 7{,}150\ \mathrm{cm}^{-1}$. The spectral input data came from Ni deuteroporphyrin [5]: $f_B = 1.18$, $f_Q = 0.134$, $E_B = 25{,}610\ \mathrm{cm}^{-1}$, $E_Q = 18{,}200\ \mathrm{cm}^{-1}$. The emitting triplet was taken from Becker [6], who reported that Ni mesoporphyrin phosphoresces weakly at 14,680 cm^{-1}. Although more recent studies suggest that this luminescence is due to a Cu impurity [7], this energy is probably quite close to the value needed to determine ET 1.

Two calculations were made. Calculation I used the molecular orbitals resulting from a planar nickel porphin extended Hückel (EH) calculation [8]. Calculation II used the corresponding molecular orbitals from an EH calculation on the Ni porphin pyridine complex. For the latter the nickel was taken to be

Table 3. *Exchange integrals* (in cm^{-1})

Integral	Calculation I	Calculation II
$K(e_{gx}, a_{1g})$	171	1817
$K(e_{gy}, a_{1g})$	171	1704
$K(a_{1u}, a_{1g})$	3	16
$K(a_{2u}, a_{1g})$	121	18680
$K(e_{gx}, b_{1g})$	371	425
$K(e_{gy}, b_{1g})$	371	430
$K(a_{1u}, b_{1g})$	16	211
$K(a_{2u}, b_{1g})$	400	1141
$(e_{gx}a_{1g} \mid e_{gx}b_{1g})$	477	415
$(e_{gx}a_{1g} \mid b_{1g}e_{gx})$	90	97
$(e_{gy}a_{1g} \mid e_{gy}b_{1g})$	477	469
$(e_{gy}a_{1g} \mid b_{1g}e_{gy})$	90	106
$K(a_{1g}, b_{1g})$	3217	3292

A reduction factor of 0.3974 was applied to all these integrals, except the last one, before they were used in the calculations.

0.5 Å out of the plane of the porphyrin ring and the pyridine nitrogen was placed 2.0 Å above the nickel with the plane of the pyridine perpendicular to the porphyrin ring and passing through two of the porphyrin nitrogen atoms.

Table 3 gives the integrals which resulted from the use of the two sets of MO's. The big difference is seen to lie in integrals involving a_{2u} and a_{1g}. The geometry of the complex destroys the center of symmetry and allows the a_{2u} porphyrin π to mix with the $a_{1g}(d_{z^2})$ metal orbital. This results in a large one center metal contribution. The effect of these larger integrals is to mix certain states more heavily in Calculation II than in Calculation I. The diagonal energies are also dependent on these integrals.

The presence of the pyridine also destroys the equivalence of the E_{ux} and E_{uy} submatrices. This effect, however, is small. The off-diagonal matrix elements in the two submatrices differ by little and the EH calculations indicate that the formerly degenerate diagonal energies are now separated by about $30\,\text{cm}^{-1}$. This separation is too small to be shown in the figures illustrating our calculated spectra, but it should be understood to be present.

In both calculations the energy of the ${}^3B_{1g}$ above the ${}^1A_{1g}$, defined as ETM, was varied over a range from $18{,}000\,\text{cm}^{-1}$ to $-500\,\text{cm}^{-1}$. This energy difference is affected by porphyrin substituents and the range of values employed was meant to cover a range of situations. It should be understood that the extremely low values of ETM found in the calculations of type I as well as the extremely high values of ETM found in the calculations of type II will probably not correspond to any situation to be found experimentally. The resulting energy levels as a function of ETM for the two types of calculations are given in Figs. 1 and 2. Absorption spectra are given in Fig. 3 for two particular cases. From the type I calculations that calculation having a value of $\text{ETM} = 3{,}000\,\text{cm}^{-1}$ was chosen for the diamagnetic case because it presents the interesting situation of having

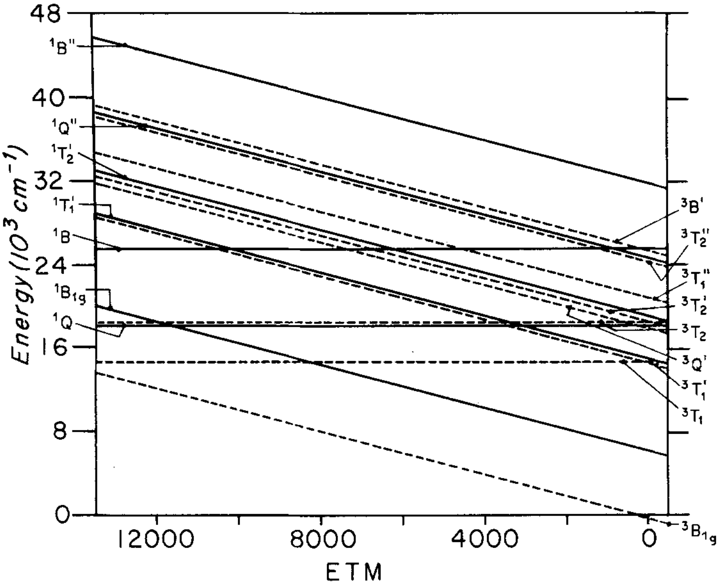

Fig. 1. Singlet energies (solid lines) and triplet energies (dashed lines) for Calculation I (planar, uncomplexed) as a function of ETM (cm^{-1}). The very low values of ETM are not expected to correspond to situations to be found experimentally

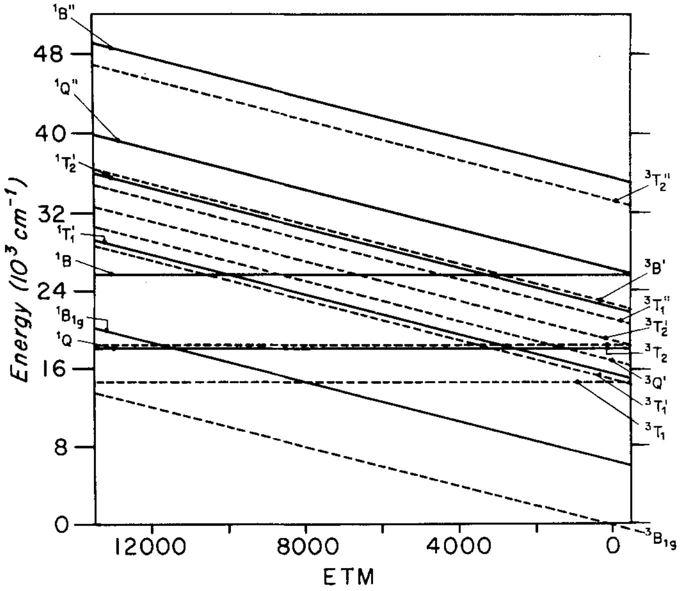

Fig. 2. Singlet energies (solid lines) and triplet energies (dashed lines) for Calculation II (nonplanar, complexed) as a function of ETM (cm^{-1}). The very high values of ETM are not expected to correspond to situations to be found experimentally

${}^1T_1'$ lower than ${}^1Q$, thus playing a role similar to the tripdoublet in VO, Co and Cu complexes. The EH calculations predict a value more like ETM = 8,000 cm^{-1}, but this is probably an extreme value, not even encountered in the most neutral solvents. From the type II calculations a value of ETM = -500 cm^{-1} was chosen representing the paramagnetic case.

A stick representation of an absorption spectrum plotted as logε versus wavenumber is given for the two cases in Fig. 3. The diamagnetic singlet spectrum shows a normal B and Q band with some new states whose intensities are less than those of the B and Q bands by two orders of magnitude. The paramagnetic triplet-triplet absorption spectrum, however, shows a red-shifted Soret band with a new intense band appearing to the blue of it. Experimentally a red shift on the order of 1,000 cm^{-1} is observed [9]. It is interesting that a shift of the right order of magnitude can be obtained without the use of charge transfer states. It can be seen that several excited states of intensity $\varepsilon > 10^4$ are predicted for the paramagnetic ground state.

An interesting point to note is that ${}^3T_2$ lies above ${}^1Q$ (see Figs. 1 and 2). This was not found in VO, Co, Cu or Zn complexes. It is accounted for not by a greater difference in the π-π exchange integrals, but by a greater splitting of the pure configuration singlets as obtained from the spectral data.

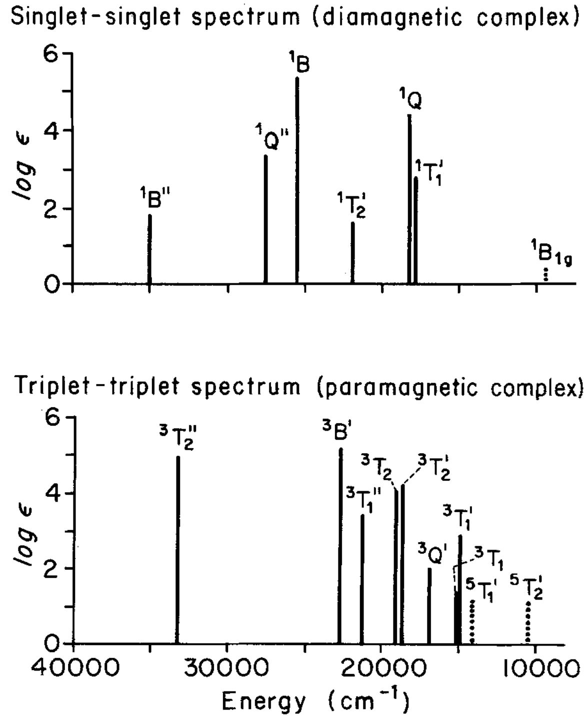

Fig. 3. Singlet-singlet absorption spectrum for ETM = 3.000 cm^{-1} (Calculation I) and triplet-triplet absorption spectrum for ETM = -500 cm^{-1} (Calculation II)

Relation to Luminescence

Recent experiments show that diamagnetic nickel porphyrins luminesce very weakly if at all [7b]. Fig. 2 provides a ready explanation. For 12,000 cm^{-1} > ETM > 8,000 cm^{-1} the state $^1B_{1g}$ lies between the normally fluorescing state ^1Q and the normally phosphorescing state $^3T_1$, and would efficiently transfer energy between them. However, phosphorescence from $^3T_1$ is likely to be quenched by the lower energy $^3B_{1g}$. For lower values of ETM, $^1B_{1g}$ is the lowest excited singlet. However, since the radiative transition from $^1B_{1g}$ to the ground state is forbidden, it most likely will decay radiationlessly. For a diamagnetic complex with ETM < 3,000 cm^{-1} the states $^1B_{1g}$ and $^3B_{1g}$ are so low in energy that radiationless decay to them might become inefficient. Conceivably, emission from $^1T_1'$ or $^3T_1$ might then be observed.

Emission characteristics of the paramagnetic complex can be predicted from Fig. 3. Excitation takes place in the triplet manifold followed by rapid internal conversion to $^3T_1'$, the lowest excited triplet. By intersystem crossing the $^5T_1'$ can be populated, and the energy would be degraded to $^5T_2'$. Notice here that the large value of $K(a_{2u}, a_{1g})$ has pushed the $a_{2u} \rightarrow e_g$ quintet lower than the $a_{1u} \rightarrow e_g$ quintet even though $a_{1u} \rightarrow e_g$ gives the lowest triplet. Hence, the emission would be a quintet→triplet phosphorescence and would appear at about 10,000 cm^{-1}. This is a very low energy electronic emission and probably would be radiationlessly deactivated.

In this context it becomes of interest to ask why Pd and Pt porphyrins have such strong phosphorescence [6, 7b], although having the same d^8 configuration as Ni. Unlike Ni porphyrins, Pd and Pt porphyrins do not complex with pyridine at room temperature although there is evidence for some complex formation at liquid nitrogen temperature [7b, 9]. Palladium and platinum are larger than Nickel. The Pd–Pd and Pt–Pt metal distances are 2.74 and 2.77 Å respectively compared to the Ni–Ni metal distance of 2.49 Å [10]. In dimethylglyoxime complexes the Pd–N distance is 1.93 Å, while the Ni–N distance is 1.85 Å. Palladium and platinum have greater preference for square planar complexes, which are always diamagnetic, than has nickel [11]. Based on spectroscopic shifts, Pd and Pt porphyrins are presumed to be more covalent and stable than Ni complexes [12]. Finally, we note that the Soret band of the pyridine complexes of Co and Ni TPP are shifted ~200 Å to the red of the uncomplexed compounds while in Cu and Zn TPP the complexed and uncoupled forms are at about the same wavelength [9]. This observation suggests that pyridine complexing of Co and Ni TPP leads to a geometry change, most likely the metal moving out of plane.

All of these considerations can be comprehended if we assume that the σ bonding of Pd and Pt to the porphyrin ring is stronger than for Ni. This could arise because of a greater tendency to covalency and a more favourable overlap for Pd and Pt. As a result, the empty $b_{1g}(d_{x^2-y^2})$ will have a far higher energy than in Ni. This can be related to the far weaker tendency for Pd and Pt to form pyridine complexes: Such complexes may require a paramagnetic electronic configuration and a non-planar geometry, which in Pd and Pt are resisted by the strong σ bonds. Because of the high energy of $b_{1g}(d_{x^2-y^2})$, the state $^3B_{1g}$ may lie above $^3T_1$, giving a normal phosphorescence.

Another feature that needs explanation is the lack of fluorescence of Pd porphyrins, although a weak fluorescence is observed in Cd porphyrins where the metal has a higher Z value [6, 13]. Becker and Allison [6] found that Cd mesoporphyrin IX has a medium intensity phosphorescence with a 7 msec lifetime, while the Pd complex has a very strong phosphorescence with a 2 msec lifetime. Whether or not the radiationless decays of the Cd complex occur as ${}^1Q \rightsquigarrow {}^1A_{1g}$ or ${}^3T_1 \rightsquigarrow {}^1A_{1g}$, the observed luminescence requires that the radiationless rate ${}^1Q \rightsquigarrow {}^3T_1$ and the radiative rate ${}^3T_1 \rightarrow {}^1A_{1g}$ must be faster in Pd than in Cd porphyrin. Thus spin-orbit coupling must be significantly greater in Pd in spite of its lower atomic number. One reason for this might be the presence of many more second order intersystem crossing processes due to the extra states associated with the ${}^3B_{1g}$, ${}^1B_{1g}$ metal configuration. Also we might note that our theoretical studies on VO, Co, Cu and Zn porphyrins predict that the spin-orbit interaction matrix element is 5 to 30 times larger in the open shell metals than in Zn. The same undoubtedly is true for Ni compared to Zn and for Pd compared to Cd.

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