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A Kinetic Study of the Hydrolysis of Acetonitrile Co-ordinated to Platinum, Yielding Platinblau

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Molecular orbital and crystal field calculations suggest that for iron phthalocyanine the $^3A_{2g}$ ground state corresponds to the electronic configuration $e_g^2\ b_{2g}^2\ a_{1g}^2$, while for cobalt phthalocyanine the ground state is $^2A_{1g}$–$e_g^4\, b_{2g}^2\, a_{1g}^1$. The MO results imply a differential covalency within the set of orbitals d_{xy}, d_{xz}, d_{yz} and d_{z^2} and it is necessary to invoke this concept in the crystal field calculations in order to reproduce the ground state of iron phthalocyanine and the low energy electronic transitions of both molecules. The calculations indicate that, contrary to a recent suggestion, the medium intensity bands in the near infra-red region of both these complexes are due to d → d electronic transitons. The bands are assigned $^2A_{1g} \rightarrow {}^2E_g$ and $^2B_{2g}$ for cobalt phthalocyanine and $^3A_{2g} \rightarrow$ either or both ^3E_g and $^3B_{2g}$ for iron phthalocyanine.

Introduction

We have recently become interested in locating low energy d → d electronic absorption in complexes which are lower than octahedral in symmetry. Of particular interest is the low energy near infra-red spectral region (4–12,000 cm^{-1}) of metal porphyrin and phthalocyanine complexes, since this region is believed to contain a number of different types of transitions including perhaps both d → d and spin-forbidden $\pi \rightarrow \pi^*$ singlet → triplet transitions as well as ring C–C and C–H vibrational overtones [1–3].

Information concerning the metal–ring bonding in these compounds is difficult to obtain from the d → d absorption spectra because most of the d → d bands are obscured by the intense $\pi \rightarrow \pi^*$ transitions of the organic ring which occur in the visible region. Fielding and Mackay [4] have recently reported the near infra-red spectra of a variety of metal phthalocyanines and rather surprisingly came to the conclusion that the low energy bands are not due to d → d transitions. Other workers have however assigned certain low energy bands in cobalt phthalocyanine to d → d transitions on the basis of polarised electronic absorption and electron spin resonance measurements [5].

A $^3B_{2g}$ ground state was originally proposed for iron phthalocyanine (d^6) on the basis of magnetic work [6], but later magnetic circular dichroism spectra have shown that the ground state is in fact $^3A_{2g}$ [7]. For cobalt phthalocyanine (d^7), the g-factors are consistent with a $^2A_{1g}$ ground state [5]. Konig *et al.* [8] using a crystal field approach, have examined the various possibilities for the ground state of tetragonal and trigonal d^6 metal ions in terms of the one-electron Dq, Ds and Dt parameters. Initially they found [8] that for tetragonal symmetry five different electronic states, $^5B_{2g}$, ^5E_g, ^3E_g, $^3A_{2g}$ and $^1A_{1g}$ could constitute the ground state within the chosen parameter range, with the $^3A_{2g}$ state corresponding to the electron occupation $e_g^4\ b_{2g}^1\ b_{1g}^1\ a_{1g}^0$. A later paper [9] showed that two other states, including another $^3A_{2g}$ level were also feasable ground states.

We report here some results of our SCF MO calculations on both cobalt and iron porphyrins and on model tetragonal $[M(NH_3)_4]^{2+}$ (M = Fe, Co) systems to ascertain which is the correct ground state configuration in these complexes and also to attempt to identify their low energy d → d transitions. The MO calculations and the poor fit of the low energy bands to the energy levels obtained from crystal field calculations suggest a differential covalency within the subset of 3d-orbitals d_{xy}, d_{xz}, d_{yz} and d_{z^2}.

Method and Results

The MO calculations use the previously reported [10] INDO method for transition metals. Crystal field analyses of the energy levels for Fe(II)-d^6 and Co(II)-d^7 have been made using the matrices for tetragonal symmetry [11] with the one-electron diagonal terms appropriate for M porphyrin, M-$(NH_3)_4^{2+}$ and $M(N)_4^{2+}$, where M = Fe and Co, taken from the MO calculations. A range of M–N distances (1.9–2.1 Å) was considered for the latter complexes.

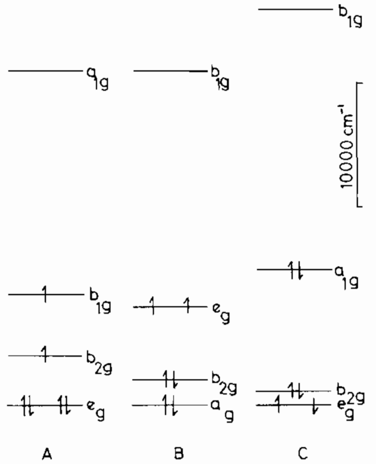

Figure 1. One-electron d-orbital energy levels a) required to give the $^3A_{2g}$–$e_g^4\,b_{2g}^1\,a_{1g}^1$ and b) $^3A_{2g}$–$e_g^2\,b_{2g}^2\,a_{1g}^2$ states using the Dq, Ds and Dt values in ref. 9. c) present M.O. values for iron porphyrin.

The magnetic circular dichroism work of Stillman and Thomson [7] has shown that the ground state of iron phthalocyanine is an intermediate spin triplet $^3A_{2g}$ state, and Konig's crystal field calculations [8, 9] have indicated the existence of two such low lying states of this symmetry. Which of these two states is actually the ground state is governed by the one-electron energies of the various d-orbitals which, on a crystal field picture, are in turn determined by the tetragonal crystal field parameters Ds, Dt and also Dq. However, the relationship between these parameters and physically meaningful quantities such as σ- and π- bonding is difficult to assess. It is for this reason that we have decided to select the one-electron d-orbital energies from the MO calculations and to use these values in the crystal field matrices for obtaining the d → d transition energies. Thus the two $^3A_{2g}$ states, $e_g^4\,b_{2g}^1\,b_{1g}^1$ and $e_g^2\,b_{2g}^2\,a_{1g}^2$, arising from Konig's calculations require Ds, Dt and Dq parameters which produce the one-electron d-orbital orderings of Figure 1a and 1b, whereas our MO results for Fe porphyrin, $Fe(NH_3)_4^{2+}$ and $Fe(N)_4^{2+}$ at each of the Fe–N distances 1.9, 2.0, 2.1 Å all yield d-orbital sequences, Fig. 1c, which are very similar. Moreover this pattern (1c) is more in keeping with traditional ideas of the d-orbital splitting in square planar complexes [12].

It should be pointed out that although Konig described his second $^3A_{2g}$ state as an approximately 50:40 mixture of the $^3T_1$ $[t_2^4(^3T_1)\ e^2\ (^1A_1)]$ and $^3T_1[t_2^4(^3T_1)\ e^2\ (^1E)]$ parent octahedral levels [9], our results show that this $^3A_{2g}$ state does correspond to an almost pure state with the occupations of the tetragonally split d-orbitals of Figure 1b. The sequence in Fig. 1a appears to correspond to some sort of tetragonal compression, while that in Fig. 1b, where the e_g level lies highest of the group of d-orbitals a_{1g}, b_{2g} and e_g, is extremely unlikely in a porphine or phthalocyanine complex which contain low lying vacant π* ligand orbitals of e_g symmetry which will tend to depress the energies of the d_{xz}, d_{yz} orbitals.

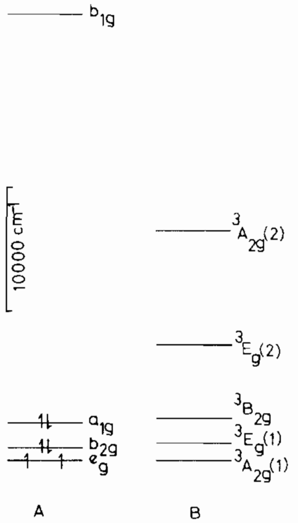

Figure 2. a) One-electron orbital energies for tetragonal $Fe(NH_3)_4^{2+}$ using Fe–N = 1.95 Å. b) INDO calculated total energies relative to the ground state for $Fe(NH_3)_4^{2+}$; $^3A_{2g}(1)$–$e_g^2\,b_{2g}^2\,a_{1g}^2$, $^3E_g(1)$–$e_g^3\,b_{2g}^2\,a_{1g}^1$, $^3B_{2g}$–$e_g^4\,b_{2g}^1\,a_{1g}^1$, $^3E_g(2)$–$e_g^3\,b_{2g}^1\,a_{1g}^2$, $^3A_{2g}(2)$–$e_g^4\,b_{2g}^1\,b_{1g}^1$.

A crystal field calculation using a B value of 700 cm^{-1} and with the one-electron d-energies corresponding to iron porphyrin gives rise to a non-degenerate $^1A_{1g}$ $(e_g^4\,b_{2g}^2)$ ground state with the lowest triplet state of ^3E_g symmetry $(e_g^3\,b_{2g}^2\,a_{1g}^1)$ lying 3,000 cm^{-1} higher in energy. The experimentally indicated symmetry state $^3A_{2g}$ lies some 14,000 cm^{-1} above this ground state and corresponds to the electronic arrangement $e_g^2\,b_{2g}^2\,a_{1g}^2$; the other $^3A_{2g}$ state $(e_{2g}^4\,b_{2g}^1\,b_{1g}^1)$ is higher still. Additional crystal field calculations using the eigen-values from the model $Fe(N)_4^{2+}$ system for the range of Fe–N distances 1.9–2.1 Å show that although the $^1A_{1g}$ and ^3E_g states may interchange, the $^3A_{2g}$ state always lies considerably above (>8,000 cm^{-1}) either of these states and with these parameters can never act as the ground state.

It seems therefore that on a crystal field approach the use of one-electron parameters which are realistic for a square planar geometry places the d_{xz}, d_{yz} orbitals so low in energy that complete, or three-electron, filling of these orbitals occurs and the desired $^3A_{2g}$ ground state is not achieved.

In order to examine whether this behaviour arises through the assumptions of the crystal field theory we have undertaken total energy calculations within the INDO approximate scheme for the variety of possible ground states, $^3A_{2g}$ $(e_g^2\,b_{2g}^2\,a_{1g}^2)$, ^3E_g $(e_g^3\,b_{2g}^2\,a_{1g}^1)$, ^3E_g $(e_{2g}^3\,b_{2g}^1\,a_{1g}^2)$ and $^3B_{2g}$ $(e_g^4\,b_{2g}^1\,a_{1g}^1)$ of the model $Fe(NH_3)_4^{2+}$ species. The results show, Fig. 2, that despite an unfavourable orbital energy ordering

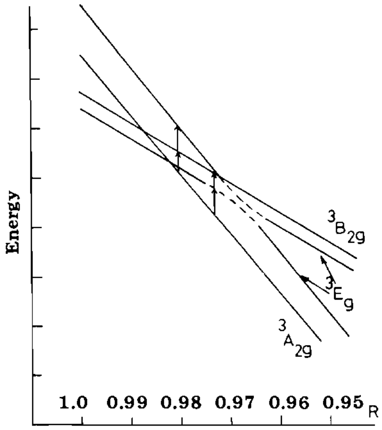

Figure 3. Dependence of the energies of the lowest four triplet states of the d^6 configuration under tetragonal symmetry with the differential covalency reduction parameter R (see text) using the Racah parameters A = 120,000 cm^{-1}, B = 700 cm^{-1} and C = 2,800 cm^{-1}, and the one-electron d-orbital energies of Fig. 1c. Energy divisions correspond to 10,000 cm^{-1}.

the $^3A_{2g}$ state, which has only two electrons in the e_g level, has lower energy than any other state.

In view of the fact that both the INDO MO results and the crystal field analysis include the effects of differing coulomb and exchange terms between the various d-orbitals, one must look further to ascertain the discrepancies between the two methods. An examination of the INDO eigenvectors for the principally 3d orbitals reveals that while the d-orbital coefficients of the e_g and b_{2g} molecular orbitals are close to unity (0.98 and 0.97 respectively) there is considerably greater mixing of the d_{z^2} orbital in the a_{1g} molecular orbital (82%) as well as a small contribution from the metal 4s orbital. Because of this greater delocalisation, electron(s) in this a_{1g} molecular orbital experience a smaller repulsion between each other and the other d electrons than do electrons in either the e_g or the b_{2g} molecular orbitals. This feature makes complete occupancy of the a_{1g} molecular orbital more favourable than complete filling of the e_g or b_{2g} orbitals and therefore stabilises the $^3A_{2g}$ (e_g^2 b_{2g}^2, a_{1g}^2) state relative to the $^3E_g(e_g^3b_{2g}^2a_{1g}^1)$ and $3B_{2g}$ ($e_g^4b_{2g}^1a_{1g}^1$) levels.

This differential covalency [13] is automatically taken into consideration in the calculation of the electronic energy from the SCF MO eigen-functions, but is not accounted for in the crystal field calculations where 'pure' d-functions are assumed. However, it may be treated empirically on the crystal field picture by reducing those electronic repulsions pertaining to the d_{z^2} orbital and Figure 3 shows the dependence of the energies of the lowest four triplet states with this reduction parameter R. Although the differential covalency parameter R is related to the orbital mixing coefficient of the d_{z^2} orbital in the a_{1g} molecular orbital, these two quantities are not equal; this is due to the fact that electronic repulsions between a_{1g} electrons, which are now delocalised, and other d-electrons are determined not only from one-centre d-d repulsions but also from two-centre d-ligand terms.

The diagram shows that for R = 1, *i.e.* pure d-orbital wavefunctions the ^3E_g level lies lowest but as R is decreased the $^3A_{2g}$ state, and also the other ^3E_g state, become more favoured. This effect is brought about mainly through the large reduction of the Racah A term for the d_{z^2} orbital.

Our powder reflectance spectral measurements for iron phthalocyanine show bands of medium intensity at 5,500 and 8,200 cm^{-1} with a weaker band at 6,400 cm^{-1} in good agreement with the vapour and film spectra of Fielding and Mackay [4]. Two possibilities therefore arise for the assignment of these bands in terms of d → d excitations. Firstly, the complex lies only slightly to the right of the $^3A_{2g}$–^3E_g crossover point (R = 0.98) so that the transition $^3A_{2g} \rightarrow {}^3E_g$ is too low in energy to be observed and the transition at 5,500 cm^{-1} corresponds to $^3A_{2g} \rightarrow {}^3B_{2g}$, and the 8,200 cm^{-1} peak is due to the transition $^3A_{2g} \rightarrow {}^3E_g$. The INDO total energies for $Fe(NH_3)_4^{2+}$ (Figure 2) provide support for this assignment. The alternative explanation is to attribute the band at 5,500 cm^{-1} to $^3A_{2g} \rightarrow {}^3E_g$ excitation with the band at 8,200 cm^{-1} corresponding to excitation to either $^3B_{2g}$ or ^3E_g states (R = 0.975). Any transitions to the b_{1g} molecular orbital are expected, by analogy with similar nickel complexes [14], to occur at energies greater than 20,000 cm^{-1} and will be difficult to locate among the fully allowed $\pi \rightarrow \pi^*$ bands of the phthalocyanine ring; the weaker bands observed in the low energy region could correspond to either spin-forbidden d → d transitions since many of these occur at such energies in the crystal field calculations, or to spin-forbidden transitions within the organic ring.

There is less uncertainty for cobalt phthalocyanine. For instance, the ground state is known [5] to be $^2A_{1g}$–e_g^4 b_{2g}^2 a_{1g}^1, however, there still remains some doubt over the nature of the low energy bands. Two bands of medium intensity, which could therefore be attributed to d → d excitations, are observed around 5,000 and 9700 cm^{-1}. Fielding and Mackay [4] have recently discounted the possibility that these bands in cobalt phthalocyanine are due to metal d → d transitions because of an erroneous assumption of a ^2E_g ground state and also through the incorrect use of an octahedral rather than a tetragonal crystal field energy level diagram to estimate energy differences. However, some assignments in terms of d-electron transitions have been made using single crystal measurements on the α and β modifications of cobalt phthalocyanine in conjunction with electron spin resonance data [5]. The INDO calculations give

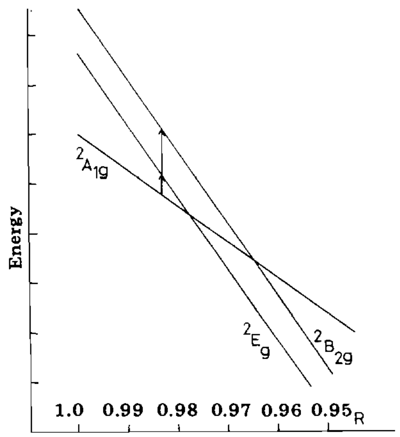

Figure 4. Dependence of the energies of the lowest three doublet states of the d^7 configuration under tetragonal symmetry with the differential covalency reduction parameter R using the Racah parameters A = 120,000 cm^{-1}, B = 700 cm^{-1} and C = 2,800 cm^{-1}, with one-electron d-orbital energies appropriate for cobalt porphyrin. Energy divisions correspond to 10,000 cm^{-1}.

rise to d-orbital splittings for cobalt porphyrin and $Co(NH_3)_4^{2+}$ which are very similar to those of Figure 1c, and the total molecular ion energies for $Co(NH_3)_4^{2+}$ yield a $^2A_{1g}$ ground state with ^2E_g–$e_g^3\ b_{2g}^2\ a_{1g}^1$ and $^2B_{2g}$–$e_g^4\ b_{2g}^1\ a_{1g}^2$ higher by 4,000 cm^{-1} and 14,000 cm^{-1} respectively. The use of the cobalt porphyrin one-electron values for diagonal elements in the crystal field calculations for tetragonal d^7 symmetry [11], also yields a $^2A_{1g}$ ground state however, the next lowest state of the same spin multiplicity, ^2E_g, is calculated to lie 13,000 cm^{-1} above this ground state. It appears therefore that for both tetragonal d^6 and d^7 configurations, simple crystal field theory fails to account for either the ground state or the magnitude of the electronic energy differences between ground and excited states. The INDO MO results show that the reason for this failure is due to the differential covalency within the d-orbitals which should make double occupancy of the a_{1g} molecular orbital more favourable than anticipated for a pure d-orbital basis. A diagram similar to Figure 3, showing the dependence of the lowest doublet states for d^7–Co(II) on the reduction parameter R, is shown in Figure 4. An R value close to that found suitable for iron phthalocyanine is likewise seen to give a satisfactory transition energy for the lowest band in cobalt phthalocyanine ($^2A_{1g} \rightarrow {}^2E_g$). At this R value the $^2B_{2g}$ state is calculated to be approximately 11,000 cm^{-1} above the ground state and it is possible that the band of medium intensity at 9,700 cm^{-1} corresponds to excitation to this level.

Conclusions

The ground states of Fe(II) and Co(II) in a square planar environment have been examined using SCF molecular orbital and crystal field methods. It has been found that the crystal field theory does not reproduce the known ground state of iron phthalocyanine nor the magnitude of the transition energies in both iron and cobalt phthalocyanine if the convential splitting of the d-orbitals in a square planar geometry is used. However, these failures are overcome if the concept of differential covalency, as indicated by the MO results, is used in the crystal field calculations. The results show that the medium intensity bands between 4,000 and 10,000 cm^{-1} in these molecules correspond to spin allowed electronic transitions within the d_{xz}, d_{yz}, d_{xy} and d_{z^2} set of orbitals.

References

*Part XIV. D. W. Clack and M. Monshi, *J. Organomet. Chem., 116*, C41 (1976).

1 P. Day, G. Scregg and R. J. P. Williams, *J. Chem. Phys., 38*, 2778 (1963).

2 P. Fielding and A. G. Mackay, *J. Chem. Phys., 38*, 2777 (1963).

3 P. Fielding and A. G. Mackay, *Aust. J. Chem., 17*, 750 (1964).

4 P. Fielding and A. G. Mackay, *Aust. J. Chem., 28*, 1445 (1975).

5 F. Cariate, D. Galizzioli and F. Morlazzoni, *J. Chem. Soc. Dalton*, 556 (1975).

6 C. G. Barraclough, R. L. Martin, S. Mitra and R. C. Sherwood, *J. Chem. Phys., 53*, 1643 (1970).

7 M. J. Stillman and A. J. Thomson, *J. Chem. Soc., Far. II, 70*, 790 (1974).

8 E. Konig and R. Schnakig, *Inorg. Chim. Acta, 7*, 383 (1973).

9 E. Konig and R. Schnakig, *Theor. Chim. Acta., 30*, 205 (1973).

10 D. W. Clack, *Mol. Phys., 27*, 1513 (1974).

11 J. Otsuka, *J. Phys. Soc. Jap., 21*, 596 (1966).

12 S. F. A. Kettle, "Coordination Compounds", Nelson, 1969.

13 C. K. Jφrgensen, *Prog. Inorg. Chem., 4*, 73 (1962); *Helv. Chim. Acta (Fasc. ext., Alfred Werner)* 131 (1967).

14 B. Bosnich, M. L. Tobe and G. A. Webb, *Inorg. Chem., 4*, 1109 (1965).