AN ELECTRON PARAMAGNETIC RESONANCE (EPR) STUDY OF A MOLYBDENUM-PHTHALOCYANINE POWDER

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(recibido septiembre 19, 1985; aceptado mayo 28, 1986)

ABSTRACT

EPR measurements of the spin-Hamiltonian parameters of a molybdenum-phthalocyanine powder sample and its solution in sulphuric acid are reported. The EPR spectra are analyzed in terms of an axial spin-Hamiltonian \( (S=\frac{3}{2}) \) and computer spectra simulations using these parameters are presented, together with suggestions on the structure of this compound.

RESUMEN

Se reportan los valores de RPE de los parámetros de hamiltoniano de espín de un polvo de ftalocianina de molibdeno y su disolución en ácido sulfúrico. Se analizan los espectros de RPE en términos de un hamiltoniano de espín \( (S=\frac{3}{2}) \) axial y se presentan simulaciones de los espectros en la computadora usando estos parámetros, junto con sugerencias sobre la estructura de este compuesto.
INTRODUCTION

The metal-phthalocyanines are an important class of organic compounds. They have been widely used in industry as pigments, and there is a growing interest in their catalytic, semiconductive and photoconductive behaviour\(^1,2\). Additional interest in these substances exist as some of them are closely related to biologically important metalloporphyrins, such as chlorophyll and haemoglobin.

Although the structures of most of these molecules are rather well known, some important complexes have not been yet extensively studied or adequately characterized. Such is the case of molybdenum derivatives of phthalocyanines (Mo-Pc)\(^1\).

Perhaps the only successful attempt to characterize a Mo-Pc complex has been that of Hill and Norgett\(^3\). These authors reported a diamagnetic species which they identified as oxymolybdenum (IV) phthalocyanine (Mo-Pc).

In the present paper we report the results of our investigation on a paramagnetic molybdenum phthalocyanine. This paper is arranged as follows: we first describe very briefly the preparation method of the complex and its infrared (I.R.) spectrum. We then analyze its Electron Paramagnetic Resonance (EPR) powder spectrum in terms of an axial spin-Hamiltonian.

Then, using the measured spin-Hamiltonian parameters we simulated the observed Mo-Pc EPR powder spectrum with aid of a computer. We then analyze the spectra of the Mo-Pc sample in concentrated and fuming sulphuric acid solutions.

Finally, in the light of these results we present suggestions for a possible structure for this Mo-Pc compound. We also present a brief discussion on the origins of the isotropic superhyperfine interaction observed for the sample in acid solution.

As some of our purposes in these paper is to characterize the Mo-Pc, it is important to mention very briefly the structures of phthalocyanines.

Metal-free phthalocyanine (designated as \(H_2\)-Pc) is a planar aromatic system consisting of four isoindole units linked by aza nitrogen
atoms, as show in Fig. 1.

The two central hydrogen atoms can often be replaced by a transition metal ion. This central metal ion is commonly in an oxidation state of 2; however, a great many complexes are known to be in other oxidation states. Therefore, the coordination number of this central metal ion can be 4, 5, or 6 depending on the ion's oxidation state. This is shown in Fig. 2.

The Pc derivatives can form also polymeric structures, where the first and second axial coordination positions (i.e., those perpendicular to the aromatic phthalocyanine system) may form links of the polymeric chain.

Fig. 1. Metal free phthalocyanine.
Fig. 2. Structures of metal phthalocyanine derivatives. The macrocycle has been omitted for clarity.

EXPERIMENTAL PROCEDURE

Methods of preparation of metal-Pc's are various$^{(1)}$ and the one used here was the following.

The Mo-Pc complex was prepared by one of us (M.A.G.G.) by means of a condensation reaction in which phthalonitrile and molybdenum trichloride were mixed homogeneously at 290°C for four hours. The product was soxhlet-extracted with several solvents and dried for 20 minutes at 250°C "in vacuo" ($10^{-4}$ torr).

The infrared spectrum (I.R.) of the sample was obtained in a Perkin-Elmer spectrometer model 337 using potassium bromide as the matrix
material. This I.R. spectrum in the mid-frequency range is shown in Fig. 3.

![Infrared absorption spectrum in the 700-1300 cm\(^{-1}\) region. The arrow in the figure shows the Mo-O stretching frequency.](image)

The I.R. frequencies in the 625-200 cm\(^{-1}\) band, are given in Table I, together with the main frequencies of \(\alpha\)- and \(\beta\)-iron phthalocyanines and the ones obtained by Hill and Norgett\(^{(3)}\) for MoO\(_2\)Pc. The numbering system of these bands is that of Lever\(^{(1)}\).

The spectra of almost all metal Pc's are independent of the central metal ion\(^{(1,4,5)}\). The I.R. spectrum shown in Fig. 3 was found to be closely similar (see Table I) to other metal phthalocyanines, thereby establishing that the compound was indeed a phthalocyanine.

The spectral characteristics of four compound show better agreement with the \(\beta\) polymorph modification than the \(\alpha\)-modification. The I.R. spectrum in the 2000-625 cm\(^{-1}\) region displayed three additional absorptions
at 977, 1380 and 1540 cm\(^{-1}\) (see Table I). The one at 977 cm\(^{-1}\) (shown by an arrow in Fig. 3) can be confidently attributed to a terminal Mo = 0 stretching frequency. This assignment is based on data published in the literature\(^{(6,7,8)}\) for Mo = 0 stretching frequencies in molybdenum compounds. This conclusion is further verified by the assignment by Hill and Norgett\(^{(3)}\) of the 973 cm\(^{-1}\) line in MoOPc which they attributed to Mo = 0.

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Table I. Infrared spectra of some phthalocyanines in the range 625 - 2000 cm\(^{-1}\)
Frequencies assigned in the literature to Mo-O-Mo\(^{(6,7)}\)
Mo-O\(_2\)-Mo\(^{(6,8)}\) and O = Mo-O-Mo = O\(^{(9)}\) did not appear in the I.R. spectrum of our sample, decreasing support for an eventual formation of a dimeric compound. Further evidence diminishing the possibility of a dimer will be given in the discussion of the EPR spectrum.

The EPR spectra were recorded at room temperature in a Varian E-15 X band spectrometer with 100-Khz field modulation. DPPH was used for field marking.

A chemical microanalysis of the sample was carried out by the Departamento de Análisis Químicos, ININ. The results were as follows: C = 60.1%, H = 3.0%, N = 18.0%, Mo = 14.1%, Cl = 0.1%.

**POWDER SPECTRUM RESULTS**

The powder spectrum shown in Fig. 4 is typical of an axially symmetric spin-one half powder sample, and therefore it has been analyzed in terms of a spin-Hamiltonian for an axially symmetric system,

\[
H = \beta_e \left( g_\| H S_z + g_\perp (H_x S_x + H_y S_y) \right) + A S_z I_z + B(S_x I_x + S_y I_y),
\]

where \(S = \frac{1}{2}\), \(\beta_e\) is the Bohr magneton, \(H\) the applied magnetic field, \(g_\|\) and \(g_\perp\) the components of the g tensor, \(A\) and \(B\) are the hyperfine couplings constants, between the unpaired electron and the molybdenum isotopes with nuclear spin (I = 5/2). Molybdenum has two types of isotopes; the even ones \(^{94,96,98,100}\)Mo having zero nuclear spin, and the odd ones \(^{95,97}\)Mo having spin 5/2 with nuclear moments differing only by 2%. The latter two together having a natural abundance of 25%.

In a powder sample, the molecular axes of symmetry are randomly distributed. The overall resonance lineshape is the weighted average of the contributions of the individual resonance centres. Sands\(^{(10)}\) has shown that for such a system the derivative spectrum shows a set of weak lines at the resonance field \(H_\|\), corresponding to those molecules with their symmetry axes parallel to the applied magnetic field, and a set of strong lines at the resonance field \(H_\perp\), corresponding to those molecules with
symmetry axes perpendicular to the applied magnetic field.

![EPR powder spectrum at room temperature.](image)

The resonance fields $H_{//}$ can be derived from the spin-Hamiltonian Eq. (1). Second order perturbation theory yields

$$H_{//} = \frac{h\nu}{g_{//}\beta_e} - \frac{A}{g_{//}\beta_e} M_I - \frac{B^2}{2(g_{//}\beta_e)^2H_{//}} \left\{ I(I+1) - M_I^2 \right\} . \quad (2)$$

where $M_I$ is the molybdenum nuclear spin component and $I$ the nuclear spin.

In a similar way the resonance fields for $H$ can be obtained.

These are

$$H_{\perp} = \frac{h\nu}{g_{\perp}\beta_e} - \frac{B}{g_{\perp}\beta_e} M_I - \frac{(A^2 + B^2)}{4(g_{\perp}\beta_e)^2H_{\perp}} \left\{ I(I+1) - M_I^2 \right\} . \quad (3)$$

From an analysis of the sets of lines appearing in the spectrum it is possible to deduce tentative values for the spin-Hamiltonian parameters and with these, a computer lineshape simulation can be performed.

Preliminary values for the spin-Hamiltonian parameters were obtained as follows:

Equations (2) and (3) predict one set of six lines each. Two of
the lines, corresponding to the weak intensity sextet predicted by Eq. (2) are clearly discernible in the high field region of the spectrum. They are labelled $b_1$ and $b_2$ in Fig. 4. In a similar way, two of the lines corresponding to the strong intensity set, predicted by (3) are clearly recognizable in the low field extreme of the spectrum. These are labelled $a_1$ and $a_2$ in Fig. 4.

The separation between $a_1$ and $a_2$, $b_1$ and $b_2$ gave us respectively, preliminary values for the hyperfine coupling constants $A$ and $B$. With them, and assuming that $a_1$ and $a_2$ are respectively, the extreme low field and the extreme high field of each sextet; we used Eqs. (2) and (3) to calculate the approximate positions for the centre of each set, thereby obtaining values for $g_{//}$ and $g_{\perp}$.

Using the set of values ($g_{//}$, $g_{\perp}$, $A$ and $B$) a computer line-shape simulation was performed. The procedure followed was the developed by Galindo and González-Tovany(11). These authors obtained a Monte Carlo method for the line shape of a single hyperfine line. Their method is function of the four spin-Hamiltonian parameters and of the linewidth for a Lorentzian line-shape of individual transitions. We refer the reader to Galindo and González-Tovany's article for details(11).

Using different sets of parameters, starting from our preliminary values we calculated numerically the derivative of the lineshape. The simulated spectra were sums of spectra of single hyperfine lines, given by Galindo and González-Tovany's method, and weighted according to their natural abundances.

We then adjusted the parameters until the low and high field extremes and the zeros of the central parts of the spectrum were in good agreement with the experimental spectrum.

Calculations were performed on a PDP10 computer equipped with a Calcomp plotter. The simulated spectrum is shown in Fig. 5. The linewidth used in this case was $r = 15$ gauss.

The final set of values in this way was:

\[
g_{\perp} = 1.99 \pm 0.01
\]
\[
g_{//} = 1.95 \pm 0.01
\]
\[ A = (84 \pm 1) \times 10^{-4} \text{ cm}^{-1} \]
\[ B = (47 \pm 1) \times 10^{-4} \text{ cm}^{-1} \]

We wish to point out here that the large errors given for the above parameters are due to the fact that the spectrum could be acceptably reproduced with slightly different sets of parameters.

Therefore, we have taken into account maximum possible variations of the parameters on estimating the quoted errors.

\[ \]

**LIQUID SOLUTION SPECTRUM RESULTS**

Molybdenum phthalocyanine is an stable compound, it can only be easily dissolved in concentrated sulphuric acid. In this solvent, the compound is demetallated fairly rapidly and, as a consequence of this process the observed EPR spectrum is a mixture of the solution of Mo-Pc in \( \text{H}_2\text{SO}_4 \) spectrum and its decomposition products. The EPR overall spectrum
consist then of a series of broad, weak lines, plus an intense nine-line multiplet centred at a $g$ of $1.9796 \pm 0.0002$ (see Fig. 6). Some of the broad lines belong to the spectrum of Mo-Pc in solution, they are distinguishable from the spectra of the decomposition products by the fact that the former disappear at the same rate as the nine line multiplet and, as we shall see, the multiplet is an unmistakable feature of the Mo-Pc in solution.

The other broad lines appearing in the spectrum are produced by unidentified paramagnetic decomposition products. In contrast to the spectrum of the dissolved Mo-Pc, these lines increase in intensity with the time.

The dissolved Mo-Pc spectrum can be described by means of the same Hamiltonian of Eq. (1) plus a term representing the superhyperfine interaction of the molybdenum with the four neighbouring nitrogen ligands.

The rapid tumbling of the Mo-Pc molecule in $H_2SO_4$ averages away the anisotropic superhyperfine and hyperfine terms. The dissolved Mo-Pc spectrum can be then described by the very simple Hamiltonian:

$$H_a = g_a H \cdot S + a I \cdot S + A_N S \cdot \sum_i^N I_i$$

(4)

where $g_a = 1/3 (g_\parallel + 2g_\perp)$ and $a = 1/3 (A + 2B)$; here again, $g_\perp$ and $g_\parallel$ are perpendicular and parallel components of the $g$ factor. $B$ and $A$ are molybdenum perpendicular and parallel components of the nuclear hyperfine constant. The last term of Eq. (4) represents the superhyperfine interaction with the four neighbouring ligands where $A_N$ is the nitrogen nuclear isotropic hyperfine constant and $I_i^N$ represents the individual nuclear spin of the four equivalent first neighbour nitrogens, each with $I_i^N = 1$.

The Hamiltonian of Eq. (4) predicts a set of six weak nine line multiplets centred at $g_a$, plus a strong intensity nine line multiplet also centred at $g_a$. The central multiplet corresponds to the molybdenum having zero nuclear spin (75%), while the remaining multiplets correspond to the isotopes having spin 5/2.

Experimentally we found that the superhyperfine structure is only visible in the high intensity central line (Fig. 6), and not visible in the broad lines. This is typical of the closely related molybdenum (V)
tetraphenylporphyrin complexes (Mo(V) - TPP) in solution (12).

Fig. 6. EPR spectrum of Ma-Pc in concentrated sulphuric acid.

Measurements on the spectrum yield the following spin-Hamiltonian parameters:

\[ g_a = 1.9796 \pm 0.0002 \]
\[ a = (60 \pm 1) \times 10^{-4} \text{ cm}^{-1} \]
\[ A_N = (2.35 \pm 0.05) \times 10^{-4} \text{ cm}^{-1} \]

The calculated values for \( g_a \) (assuming both \( g_\parallel \) and \( g_\perp \) of the same sign) and "a" (assuming also A and B of the same sign), from the powder spectrum data are: \( g_a = 1.98 \pm 0.01 \) and \( a = (59 \pm 1) \times 10^{-4} \text{ cm}^{-1} \). The excellent agreement between the calculated and measured values reinforces our confidence in the set of spin-Hamiltonian parameters obtained from the computer simulations of the powder spectrum. We must also mention that the experimental \( g_a \) obtained in this work compares fairly well with the ones obtained for the closely related Mo(V) - TPP complexes (13).
The relative amplitudes of the nine-line multiplet are clearly shown in Fig. 7a and are given by the following predicted intensity distribution:

$$1 : 4 : 10 : 16 : 19 : 16 : 10 : 4 : 1$$

which agrees well with the observed:

$$1 : 4 : 8.3 : 17.9 : 21.8 : 19.1 : 12.7 : 4.1 : 1$$

distribution, the latter was obtained from a computer simulation fit to the experimental spectrum. This is shown in Fig. 7b.

For this simulation the computer was programmed to carry out summations of nine Lorentzian derivatives, and then adjust the intensities of each line to give the best fit using a computer program known as Minuit\(^{(14)}\). A line-width of $\Gamma = 1.5$ gauss was used for all the nine lines.

The compound was also studied in a fuming sulphuric acid solution Fig. 7c, shows the effects of a slower molecular tumbling rate. A computer simulation for this case is shown in Fig. 7d, where the best fit was obtained with a line-width of $\Gamma = 2.7$ gauss.

An important feature of Mo-Pc in fuming sulphuric acid is the difference in the demetallation rate as compared with the concentrated acid case. The former may be considered as stable whereas the latter labile. A complete study of the latter labile. A computer study of the demetallation kinetics as well as the variation of the line-width with the acid viscosity will be the subject of a further study.

**DISCUSSION**

We have seen in a previous section that the I.R. spectrum reveals the presence of a Mo = 0 terminal bond in the molecule. This has two implications; the first is that the complex is not square planar but five- or six-co-ordinate (see Fig. 2), secondly since the central ion has two single bonds to nitrogen atoms, the presence of a double bond to oxygen suggests that the Mo is in an oxidation state IV or possibly higher.
Fig. 7a. Observed central nine line multiplet of Mo-Pc in concentrated sulphuric acid.
b. Computer simulation.
c. Observed central nine line multiplet of Mo-Pc in fuming sulphuric acid.
d. Computer simulation.
Molybdenum IV has two 4d electrons in the outer shell and therefore its total spin must be an integer. Since we have observed a spin-one-half EPR spectrum, we can rule out Mo IV as the oxidation state of the central metal ion. That leaves Mo V as the possible oxidation state for the paramagnetic centre, and we can conclude then that we are in the presence of a six-co-ordinate species where the first axial position is occupied by an oxygen.

A problem arises then in the assignment of the ligand in the second axial position. This ligand could be either forming part of a chain bridge in case the complex being a polymer, or a terminal ligand in case being a monomer.

The EPR powder spectrum gives evidence against the former case, because the proximity of the molybdenums in a polymer could make them interact and the paramagnets will couple spins, therefore we would no longer have a spin-one-half spectrum. There is ample experimental evidence for this, showing that the proximity of molybdenum paramagnets in the same complex couples their spins giving, for instance, species with \( S = 1 \) or \( S = 0 \) \(^{(7, 15)}\).

If one then assumes the complex to be a monomer, the approximate atomic weight for the second axial ligand may be determined from the microchemical analysis. This indicates that the ligand must have an atomic weight of around 15 a.u.

On the other hand, the preparation method tells us that the elements taking part in the chemical reaction are only six (C, H, O, Mo, Cl). This fact, together with the possible weight determined by the chemical analysis suggest that the second axial ligand could be \( \text{OH}^- \), \( \text{H}_2\text{O} \), or \( \text{O}^{2-} \). For the former two cases there is no experimental evidence in our I.R. spectrum, of any band in the 3600 cm\(^{-1}\) region that could be attributable to an OH stretching vibration. This apparently does not rule out the possibility of having an OH in the molecule. Elvidge and Lever\(^{(5)}\) have reported a series of chromium phthalocyanines containing OH groups that do not exhibit I.R. bands in the 3600 cm\(^{-1}\) region, however we must mention that the presence of OH in one of their compounds have been questioned by Nill et al.\(^{(16)}\).

The difficulty in observing OH absorption bands in some of these
compounds is reinforced by experimental evidence showing that in Pc
derivatives the OH stretching frequency appears as a weak(17) or sometimes
very diffuse band(4).

On the other hand elemental analysis and EPR can not discern
between the three proposed structures i.e. (O = Mo Pc - O)\(^{-}\), (O = Mo Pc - OH)
and (O = Mo Pc - OH\(_{2}\))\(^{+}\). In view of these facts we believe that other
experimental techniques are necessary to decide on the above three options.

Finally, the g factors can be analyzed by nothingthat in the
three proposed structures, the central metal ion is surrounded by four
nitrogen situated on symmetrical positions along the x and y axes, and two
oxygens symmetrically placed along the four-fold z axis. For this situation
the local symmetry corresponds to that of a D\(_{4h}\) group, and the crystal field
can be considered as an octahedral field with a strong tetragonal distortion
due to the non-equivalence of O and N. Furthermore the I.R. results
(\(v = 977 \text{ cm}^{-1}\)) for the Mo = O terminal frequency, suggests a short Mo-O
distance(6) implying a tetragonal distortion which contracts the octahedron
along the z axis.

The ordering of the d orbitals predicted by the crystal field
theory for a d\(^{1}\) ion in an octahedral field with a large tetragonal distor-
tion, compared with the spin-orbit coupling, is shown in Fig. 8. We can
note that the ground state corresponds to the d\(_{xy}\) orbital. When the
unpaired electron resides in this orbital in a strong tetragonal field, \(\delta\)
is so large that the spin-lattice relaxation time is long enough to allow
EPR observation at room temperature.

The crystal field theory gives for this situation:
\[ g_{//} = g_e - 8\delta/\Delta \text{ and } g_{\perp} = g_e - 2\delta/\Delta. \]
Since \(\Delta \gg \delta\), one expects \(g_{//}\) to be
larger than \(g_{\perp}\). For the present case we experimentally observe the reverse
order (i.e. \(g_{\perp} > g_{//}\)).

Crystal field theory's failure to predict right ordering for the
g factors indicates that covalent bonding plays an important role in the
magnetic properties of the complex. This is not surprising as the high
charge (5+) of the central metal ion is expected to a strongly attract-
ligand electrons and hence increase considerably the covalency. It is
understandable then, the inaccuracy of this theory as the ligands can not
be treated as point charges.
Fig. 8. Splitting of the states of a $4d^1$ ion in an octahedral field with an added tetragonal distortion, large, compared with the spin-orbit coupling. The symbols $\Delta$ and $\delta$ represent the splittings shown above and $\lambda = 0$ is the spin-orbit coupling constant. For the present case $\Delta > \delta > \lambda > 0$.

In order to take into account ligand electrons, detailed molecular orbital (MO) calculations are required, but these calculations exhibit well known difficulties for $4d$ transition metal complexes (18). However, in a qualitative discussion in the frame of a LCAO MO model, B.R. McGarvey (19) points out that, for a $d^1$ ion in an octahedral field with a large tetragonal distortion, $g_{//}$ is affected only by bonding with the ligands in the $xy$ plane (in our case four nitrogens) while bonding to ligands on the $z$ axis affects only $g_{\perp}$. This fact together with the reverse order of the $g$ values ($g_{\perp} > g_{//}$), implies that the covalency contribution in the $xy$ plane must be significant.

Evidence for the direct participation of the ligands in the present case is provided by the presence of isotropic superhyperfine interaction in the spectrum of the Mo-Pc in solution. This isotropic
interactions results from the transfer of unpaired electron spin density (fₛ) to the s orbitals of the equatorial nitrogens ligands. The origins of this interaction can be understood in general in the context of the theory of covalent magnetic complexes (20).

In the frame of this theory, it is widely accepted that one of the main causes for the production of unpaired spin density at the ligands is the electron transfer mechanism from the ligand to the partly filled ground state orbital of the paramagnetic ion.

In the present case, this situation is represented by the molecular orbital of symmetry b₂ which involves the metal dₓᵧ orbital and the ligands pᵧ orbitals. Since b₂ has a node at the nitrogen nuclei this mechanism can not give rise directly to nitrogen isotropic interaction, but will give maximum unpaired spin density in the pᵧ part of the ligand orbital. It is then possible that part of the isotropic interaction may arise not only from the promotion of an electron from a filled molecular orbital (b₁) with nitrogen s character to an unfilled one with the same symmetry (b₁*), but indirectly from the polarization of the 2s-nitrogen orbitals by the spin density of the nitrogen 2pᵧ orbitals.

If we assume that the latter mechanism is more important, this would readily imply that the covalency contribution is significant in the xy plane, therefore affecting g//, as pointed out by McGarvey (19), and possibly explaining the ordering of the g factors.

REFERENCES

13. See Table II of Ref. 12.
14. F. James and M. Roos, *Computer Phys. Commun.*, 10 (1975) 343. Also published as CERN/DD internal report 75/20. The minimizing subroutine used in this case was MIGRAD.