Submitted to J. of Chemical Physics

UCRL-19740
Preprint

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Effects of Ring Geometry on Triplet and Singlet Energies of the Metal Mesoporphyrins*

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Correlations were found between the hole size of ten metalloporphyrins, determined by X-ray crystallography, and the ionic radius of the central metal atom, derived from a new compilation of ionic radii as a function of coordination number, spin state, and valence. These correlations were used to define representative porphyrin geometries for each of three different hole sizes. We recommend the use of these geometries for future molecular orbital calculations.

Molecular orbital calculations based on these porphyrin geometries predict a decrease in the phosphorescence

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*Work performed with the financial support of the U. S. Atomic Energy Commission.

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energy as the hole size increases, a prediction in agreement with data in the literature on metal mesoporphyrins. Experimental excitation energy of the singlet Soret (but not the visible) band also decreases with increasing hole size, a result not given by calculations using either four orbital or extensive configuration interaction models. Electronegativity has a statistically significant effect on the lowest excited singlet and to a lesser extent, the lowest triplet energy. Changes in hole size produce little change in calculated bond order, indicating that structural changes induced by increased hole size are due to strain induced in sigma bonds. There is no correlation between either singlet or triplet energy and the charge density of the central metal atom as determined by previous molecular orbital calculations. Thus, the primary effect of changing metals on the lowest triplet state of metal porphyrins is due to effects on the pi electrons of the geometric distortion of the porphyrin ring imposed by the steric requirements of the central metal atom. The effect of the central metal on the singlet energies remains to be fully explained.

The electronic absorption spectra of metalloporphyrins vary depending on the central metal ion. Gouterman[1] showed that the oscillator strength of the 0-0 absorption band of the relatively weak visible (Q) transition could be correlated with the energies of both the Q band itself and the extremely intense Soret (B) transition in the blue or near-ultraviolet. He tried with the limited data then available to establish a correlation between these three quantities and the electronegativity of the central metal. Becker measured the spectra of the mesoporphyrin derivatives of nineteen different metals and found that they "cannot be related in a simple way with electronegativity."[2]

In this paper, we present a statistical correlation between spectroscopic energy levels and the structures of metal porphyrins as determined by X-ray crystallography. To do this, we first needed a way of expressing differences in porphyrin structure in terms of a single controlling parameter. Through analysis of the results of ten published crystal structures of porphyrin derivatives (as listed in Table I), we found that the molecular bond distances and angles vary in a systematic way with hole size. The hole size of a porphyrin

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[1] M. Gouterman, J. Chem. Phys. 30, 1139 (1959).

[2] a) R. S. Becker and J. S. Allison, J. Phys. Chem. 67, 2663 (1963); b) J. B. Allison and R. S. Becker, ibid. 67, 2667 (1963); c) R. S. Becker and J. B. Allison, ibid. 67, 2675 (1963).

can be defined[3] as half the average distance between diagonally opposite nitrogen atoms.

There are four independent bond distances and six independent bond angles in a square planar (D_{4h}) porphyrin ring. We determined each of these for each of the ten porphyrins by averaging the experimentally determined values according to D_{4h} symmetry. We then used the method of least squares to obtain the best linear relationship between hole size and bond angle or bond distance. Each experimental value was weighted by $1/\sigma^2$, where σ^2 is the larger of two numbers: the r.m.s. difference from the average value and the average standard deviation of the individual measurements.

These linear correlations between hole size and molecular parameters (bond angles and bond distances) made it possible to establish a standard geometry corresponding to a metalloporphyrin with a "large" and a "small" hole. For this purpose, we used hole sizes of 2.062 Å and 1.960 Å, respectively the largest and smallest measured holes for metalloporphyrins. We also calculated a "medium" geometry for a hole size of 2.011 Å. The molecular parameters corresponding to the largest and smallest hole sizes are listed in Table II, along with the linear correlation coefficient,[13] r, which is a measure

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[3] J. L. Hoard, in Structural Chemistry and Molecular Biology, A. Rich and N. Davidson, Eds. (W. H. Freeman and Co., San Francisco, Calif., 1968) pp. 573-594.

[13] W. C. Hamilton, Statistics in Physical Sciences (Ronald Press Co., New York, N. Y., 1964) p. 31.

of the correlation between parameters, as well as the r.m.s. difference between the observed and the calculated bond parameters. We recommend the use of one of these geometries--or one determined in a similar way from future crystallographic studies--in future molecular orbital calculations on porphyrins.*

The numbering scheme and the general changes produced by enlarging the hole size are shown in Figure 1, which is a threefold exaggeration of the change from small to large hole size. As the hole size increases, the nitrogens are forced farther from the geometric center of the ring, the α-N-α angle increases and the α-N distance decreases. The α carbons are forced outward, lengthening the α-m distance and increasing the angle α-m-α.

The molecular orbitals for a general metalloporphyrin were calculated using the self-consistent molecular orbital method of Pariser, Parr and Pople (SCMO-PPP)[15] and the "traditional" parameters of Weiss,

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*After the completion of this work, Hoard[14] announced a new, very precise structure of the "large hole" compound α,β,γ,δ-tetra(4-pyridyl) porphinatomonopyridine zinc(II). The bond distances and bond angles of this compound agree with our large hole geometry within our standard deviation.

[14] D. M. Collins and J. L. Hoard, J. Amer. Chem. Soc., in press (Feb. 1969).

[15] R. Pariser and R. G. Parr, J. Chem. Phys. 21, 466, 467 (1953); J. A. Pople, Trans. Faraday Soc. 49, 1365 (1953); R. G. Parr, Quantum Theory of Molecular Electronic Structure (W. A. Benjamin, New York, N. Y., 1964).

Kobayashi, and Gouterman.[16] The calculations use the input geometry to calculate repulsion and resonance integrals. Since these parameters were originally chosen[16] to minimize the effects of the geometry, any dependence of a calculated quantity on the input geometry should be significant. Both four-orbital and extended configuration interaction (to 150 nm) basis sets were used for the singlet calculations; for the triplets, only the four-orbital model was used. The calculations predict that the bond orders and the lowest two (B and Q) excited singlet energies should be invariant to changes in the input geometry, but that the lowest excited triplets should show a measurable dependence on the hole size. Four-orbital model calculations using the interpolation formula for interatomic electron repulsion of Pariser and Parr[15] gave the same qualitative prediction. This formula is the one used by Sundbom[17] in her recent molecular orbital calculation on porphyrins.

The lowest triplet energies of a variety of metalloporphyrins have been measured by Becker.[2] Many of these data relate to compounds whose hole sizes have not been accurately determined. We therefore developed a method of estimating the hole sizes of metalloporphyrins from ionic radii determined from X-ray measurements of inorganic crystals.

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[16] C. Weiss, H. Kobayashi and M. Gouterman, J. Mol. Spectr. 16, 415 (1965).

[17] M. Sundbom, Acta Chem. Scand. 22, 1317 (1968).

This undertaking was complicated by the demonstration by Shannon and Prewitt[18] that the effective ionic radius in metal fluorides and oxides depends not only on ionic charge but also on coordination number and electronic spin state. Using their data, we estimated the effective ionic radius of tetracoordinated Ni(II), $r(^{IV}Ni(II))$, from ionic radii of $^{VI}Ni(II)$, Cu(II) and Zn(II) by using the relationship: $r(^{IV}Ni(II)) = r(^{VI}Ni(II)) + 1/2[r(^{IV}Cu(II)) - r(^{VI}Cu(II)) + r(^{IV}Zn(II)) - r(^{VI}Zn(II))]$. (Cu and Zn are adjacent to Ni on the periodic table.) The ionic radius of the vanadium atom was estimated from the vanadium oxygen distances of vanadyl bisacetylacetonate.[19] The "effective radius" of the oxygen atoms of the acetylacetonate group was found by subtracting the effective ionic radii of $^{VI}Mn(III)$, $^{VI}Zn(II)$, $^{VI}Ni(II)$, $^{VI}Cr(III)$, and $^{VI}Fe(III)$ from the metal oxygen distances of their respective acetylacetonates.[20-24] The other three values of ionic radius were obtained directly from Shannon and Prewitt.[18] Figure 2 shows a good correlation between the

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[18] R. D. Shannon and C. T. Prewitt, Acta Crystallogr. 25, 925 (1969).

[19] R. P. Dodge, D. H. Templeton and A. Zalkin, J. Chem. Phys. 35, 55 (1961).

[20] B. Morosin and J. R. Brathovde, Acta Crystallogr. 17, 705 (1964).

[21] H. Montgomery and E. C. Lingafelter, ibid. 16, 748 (1964).

[22] H. Montgomery and E. C. Lingafelter, ibid. 17, 1481 (1964).

[23] B. Morosin, ibid. 19, 131 (1965).

[24] R. B. Roof, ibid. 9, 781 (1956).

ionic radius as determined by these methods and the experimental hole size in the five metalloporphyrins for which both data are available.[5,6,11,26]

The existence of correlations between the ionic radius and hole size and between hole size and porphyrin geometry implies that there should be a correlation between the ionic radius and porphyrin geometry. Our molecular orbital calculations therefore predict that the ionic radius should be correlated with the phosphorescence energy and the singlet-triplet separation. Figure 3 shows the experimental phosphorescence energy (^3E_Q) and the excitation energies of the visible (^1E_Q) and Soret (^1E_B) singlet bands,* as functions of the ionic size derived from the data of Shannon and Prewitt for the eight metalloporphyrins for which the necessary data are available. The data clearly point to correlations between ionic radius and ^3E_Q and ^1E_B. As the metal gets bigger, the phosphorescence drops in energy and the singlet-triplet splitting increases--in agreement with the theoretical prediction also shown in Figure 3.

The solid line in Figure 3 shows the dependence of the energy of the lowest triplet as calculated with "traditional" parameters for the geometry corresponding to the ionic radius shown. The calculated energies are too low by some 2600 cm^{-1}, and the slope agrees with experiment quite

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*The Soret band of manganic porphyrin is split into three bands covering a region of 5700 cm^{-1},[27] presumably by mixing with a charge transfer band from the ring to the metal. For this reason, ^1E_B for manganic mesoporphyrin is omitted from Figure 3.

[26] R. C. Pettersen, Acta Crystallogr., in press.

[27] P. A. Loach and M. Calvin, Biochemistry 2, 361 (1963).

well. The singlet-triplet splitting increases since the singlet energy is nearly stationary, again in agreement with theory.

Calculated values for the second lowest triplet energy increase from 13810 cm^{-1} for "small" hole to 14340 cm^{-1} for "large" hole. A plot of ^1E_Q vs. electronegativity is found in Figure 2 of reference 2c. Our Figure 4 shows the dependence of the phosphorescence energy ^3E_Q on electronegativity. In both the scatter is considerable.

The Soret (B) band also decreases in energy as the hole size increases, as is shown in our Figure 3.* This means that the energy

*This correlation was suggested to us by Dr. M. Zerner.

split between B and Q decreases with increasing hole size. Since the oscillator strength of the B band is known[27] to increase with increasing B-Q splitting, this too should decrease with increasing hole size. These effects are not predicted by the calculations. Because of the relatively small number of data and the narrow range of ionic radii--a problem common to all studies of bond length--we excluded the hypothesis of random correlations by appropriate statistical tests.

Table III lists several possible correlations, the linear correlation coefficient for each and its associated probability.[28] The most significant experimental correlation is between the triplet energy and the ionic radius of the central metal atom (Figure 3). For triplets, the direct geometric effect of the sigma strain due to increased ionic size is enough to explain the triplet dependence on ionic radius.

For singlets, statistical analysis of the data shows that ^1E_Q varies in a significant way with the metal's electronegativity.[29] The correlation is masked, however, by a strong dependence on some other variable. In statistical terminology,[28] the linear correlation is significant but accounts for only $r^2 = 50\%$ of the variation. The singlet Q dependence on ionic radius is not due to a direct geometric effect, at least according to our calculations, but must be due to some

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[27] M. Gouterman and C. Weiss, unpublished work.

[28] K. W. Smillie, An Introduction to Regression and Correlation (Academic Press, New York, 1966).

[29] A. F. Clifford, J. Phys. Chem. 63, 1227 (1959).

other unknown factor. In an attempt to pin down this unknown variable, we looked for a correlation between experimental singlet and triplet energy and the metallic charge as calculated by Zerner and Gouterman.[30] No correlation was found in either case.

The bond orders predicted by these calculations are independent of hole size. This suggests that the changes in the π system induced by changes in hole size are small, and hence that the geometric effects of increased hole size are due to strain in the sigma bond system.

At hole sizes larger than 2.01 Å, an increase in metal ionic radius correlates not only with ring expansion, but also with an equilibrium position of the metal out of the plane of the ring.[3] The hole sizes of 2.03 Å and 2.11 Å for two diacid porphyrins[31] suggest that the maximum possible hole size is about 2.0-2.1 Å. The hole sizes of mercury and cadmium porphyrins are therefore much smaller than their ionic radii would indicate from a simple linear extrapolation. This may explain why the Cd and Hg points of Figure 3 fall to the right of the best line through the other points.

The validity of our statistical analyses does not depend on the assumption that the correlation between hole size and ionic radius is linear beyond the range of the data of Figure 2. We need assume only a monotonic relationship between the two variables, and a corresponding correlation between the ionic radius and the other observables we have

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[30] M. Zerner and M. Gouterman, Theoret. Chim. Acta 4, 44 (1966); M. Zerner and M. Gouterman, Inorg. Chem. 5, 1699 (1966).

[31] A. Stone and E. B. Fleischer, J. Amer. Chem. Soc. 90, 2735 (1968).

studied. Additional crystallographic data would make possible a more elaborate correlation treatment.

We conclude that changes in the ring geometry of metalloporphyrins produce small but significant changes in the electronic properties of these molecules, as far as can be judged from the small sample of data available. The correlations between hole size and phosphorescence energy and Soret band energy should be confirmed and extended by additional spectroscopic and crystallographic measurements on metalloporphyrins. This means that differences in ground state geometry should be taken into account in detailed theoretical explanations of porphyrin spectra, and that the coordination number of the central metal atom should be specified.

No satisfactory general theory for the effect of ligands on porphyrin spectra exists (see, however, ref. 32). From the present study we conclude that the coordination number may have a small but significant effect on metalloporphyrin absorption energy levels simply by virtue of the change in ionic radius of the central metal. For example, the ionic radius of Pd^{+2} in the square planar arrangement is 0.64 Å,[18] but the ionic radius increases to 0.86 Å [18] when the Pd^{+2} increases its coordination to sixfold. From Figure 3 we estimate that the increased hole size alone should be enough to red shift the phosphorescence energy by as much as 1800 cm^{-1} when the number of ligands of the Pd^{+2} is increased from four to six. A similar change in the coordination number of Mg^{+2} from four to six should also red shift the phosphorescence energy by as much as 1800 cm^{-1}.

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[32] R. L. Ake and M. Gouterman, Theoret. Chim. Acta, in press.

If these predictions are confirmed, it may be possible to use experimental measurements of the phosphorescence energies of other metalloporphyrins together with published values of the ionic radius of the cations themselves to determine the coordination number of the metals in the metalloporphyrins in varied chemical environments. If the overall correlation of phosphorescence energy with hole size is confirmed, it may be possible to use phosphorescence energy as a "spectroscopic ruler" of hole size without the necessity of gathering X-ray data.

TABLE I. Porphyrin structures used in the analysis of hole size.

Porphyrin	Reference
Nickel(II) 2,4-diacetyldeuteroporphyrin dimethyl ester	4
Copper(II) tetraphenylporphin	5
Chlorohemin (Chloroiron(III) protoporphyrin-IX)	6
Palladium(II) tetraphenylporphin	5
Chloroiron(III) tetraphenylporphin	7
Methoxyiron(III) mesoporphyrin-IX dimethyl ester	8
Aquozinc(II) tetraphenylporphin	9
Porphin	10
Tetraphenylporphin in tetragonal crystals	11
Tetraphenylporphin in triclinic crystals	12

[4]T. A. Hamor, W. S. Caughey and J. L. Hoard, J. Amer. Chem. Soc. 87, 2305 (1965).

[5]E. B. Fleischer, C. K. Miller and L. E. Webb, ibid. 86, 2342 (1964).

[6]D. F. Koenig, Acta Crystallogr. 18, 663 (1965).

[7]J. L. Hoard, G. H. Cohen, and M. D. Glick, J. Amer. Chem. Soc. 89, 1992 (1967).

[8]J. L. Hoard, M. J. Hamor, T. A. Hamor and W. S. Caughey, ibid. 87, 2312 (1965).

[9]M. D. Glick, G. H. Cohen, and J. L. Hoard, ibid. 89, 1996 (1967).

[10]L. E. Webb and E. B. Fleischer, ibid. 87, 667 (1965).

[11]M. J. Hamor, T. A. Hamor, and J. L. Hoard, ibid. 86, 1938 (1964).

[12]S. J. Silvers and A. Tulinsky, ibid. 89, 331 (1967).

Table II. Porphyrin geometry as a function of the hole size.

Bond parameter	Small hole	Large hole	r[a]	Δ[b]
Hole size	1.960 Å	2.062 Å		
N-α	1.394	1.363	-0.62	0.010 Å
α-β	1.447	1.439	-0.33	0.010
β-β	1.351	1.350	-0.02	0.015
α-m	1.374	1.394	0.38	0.011
α-N-α	104.71°	108.31°	0.75	1.15°
N-α-β	110.24	108.96	-0.40	0.91
N-α-m	125.36	125.69	0.18	0.53
β-α-m	124.53	125.48	0.41	0.57
α-β-β	107.20	107.21	0.01	0.44
α-m-α	123.74	126.19	0.58	0.66

[a] Linear correlation coefficient.

[b] R.m.s. difference between observed and calculated parameter.

Table III. Correlations and significance levels

		Number of compounds	r^a	Significance level[b]	
Energy of lowest excited triplet (^3Q)	ionic radius[9]	7	-0.92	<<0.01	vs
	electronegativity[18]	16	0.49	0.07	s
	metallic charge[19]	9	-0.14	0.7	ns
Energy of lowest excited singlet (^1Q)	ionic radius[9]	8	-0.60	0.03	s
	electronegativity[18]	19	0.71	<0.01	vs
	metallic charge[19]	8	-0.41	0.3	ns
Singlet-triplet energy separation	ionic radius[9]	7	0.81	0.04	s
Energy of Soret (^1B) band	ionic radius[9]	7	-0.83	<<0.01	vs
	electronegativity[18]	15	0.37	0.18	ns
	metallic charge[19]	6	-0.73	0.09	s

[a] Linear correlation coefficient.

[b] vs = very significant; s = significant; ns = not significant.

FIGURE CAPTIONS

Fig. 1. Effect of expansion of the hole size on the porphyrin geometry, three times exaggerated, as derived from X-ray data. The solid lines correspond to a porphyrin with hole size of 1.858 Å, the dashed lines to a porphyrin with hole size of 2.164 Å. (These are not the values used in the calculations.)

Fig. 2. Metalloporphyrin hole size derived from X-ray data as a function of the ionic radius of the central metal in fluorides and oxides.[18]

Fig. 3. Spectroscopic energies of metal mesoporphyrins as a function of ionic radius of the central metal atom. Spectra of VO and Mn^{+3} mesoporphyrins are in ethanol and dimethyl formamide, respectively, and are from R. S. Becker (personal communication to M. Gouterman). Other spectra are from ref. 2. Solid line shows calculated energy of lowest triplet.

Fig. 4. Phosphorescence energy of metalloporphyrins as a function of the electronegativity of the metal atom. All metals are divalent unless otherwise indicated.

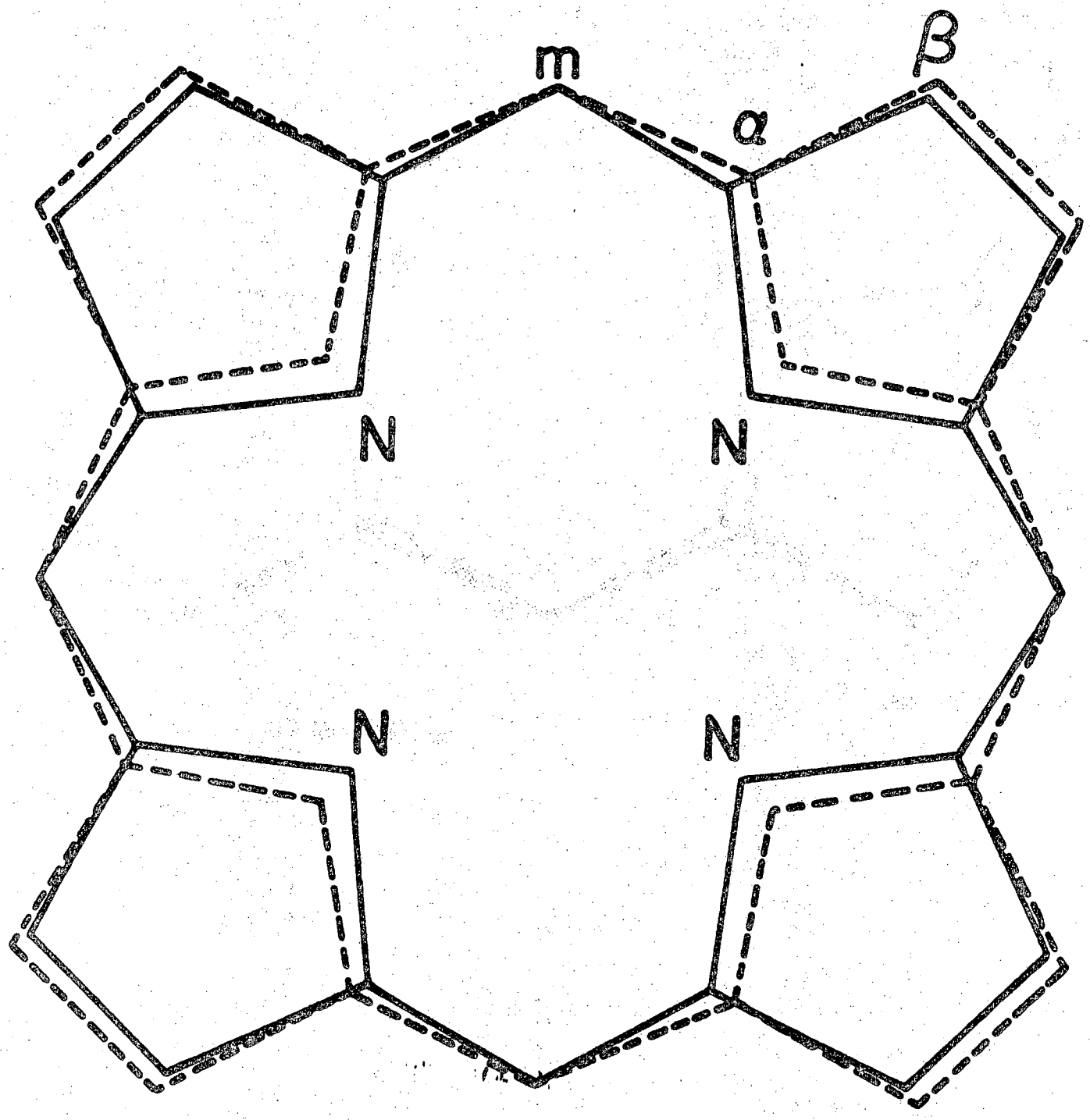

Fig. 1 - Fischer & Weiss

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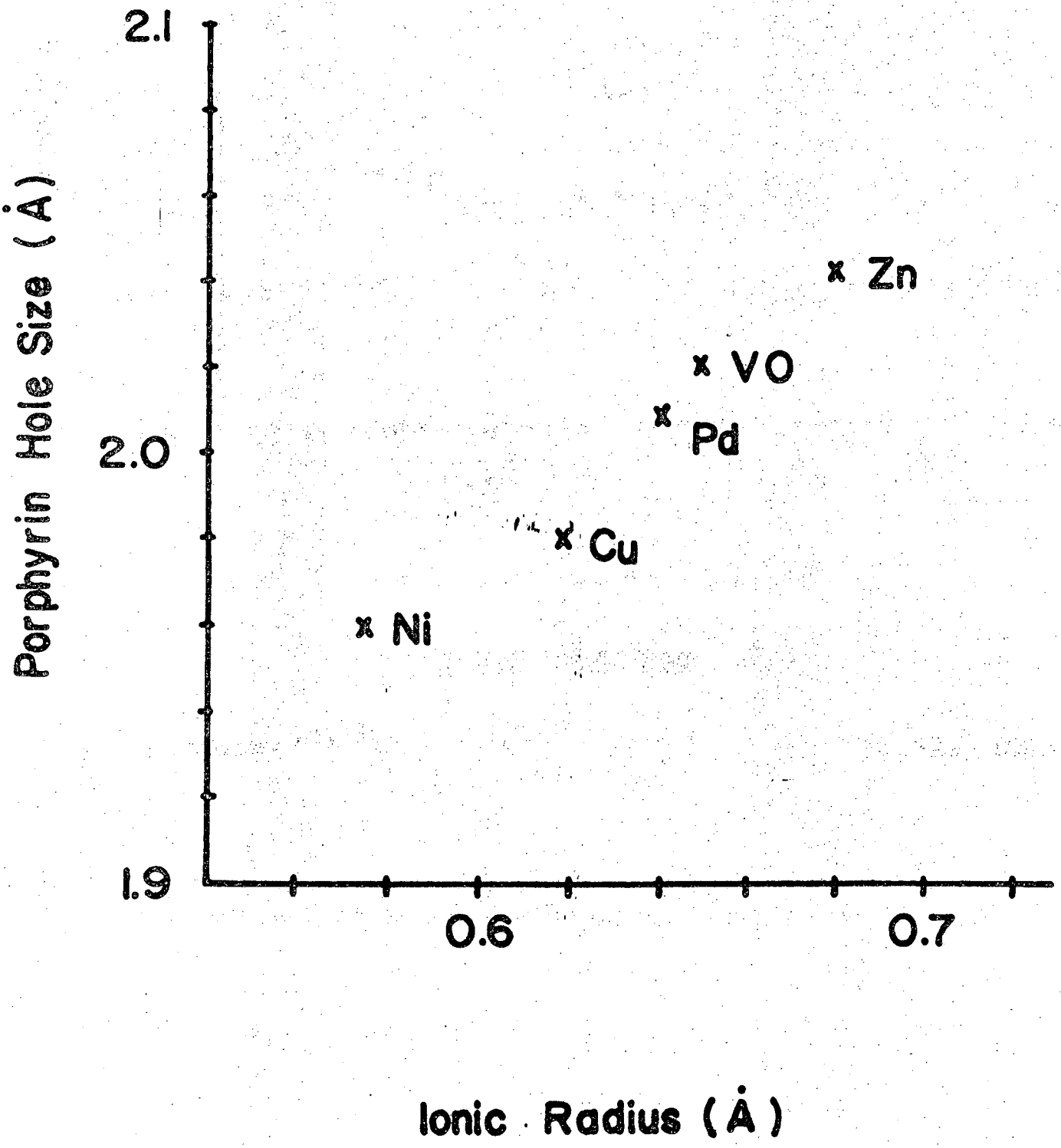

Fig. 2 - Fischer & Weiss

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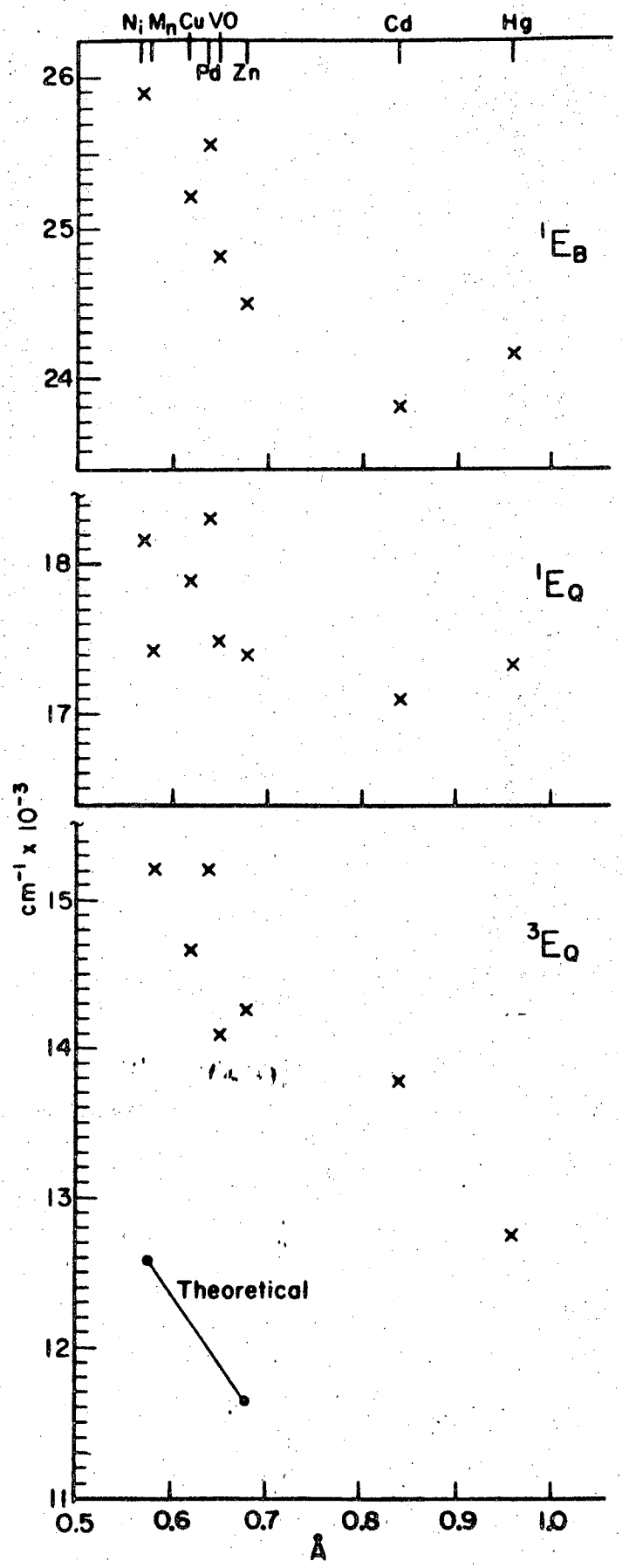

Fig. 3 - Fischer & Weiss

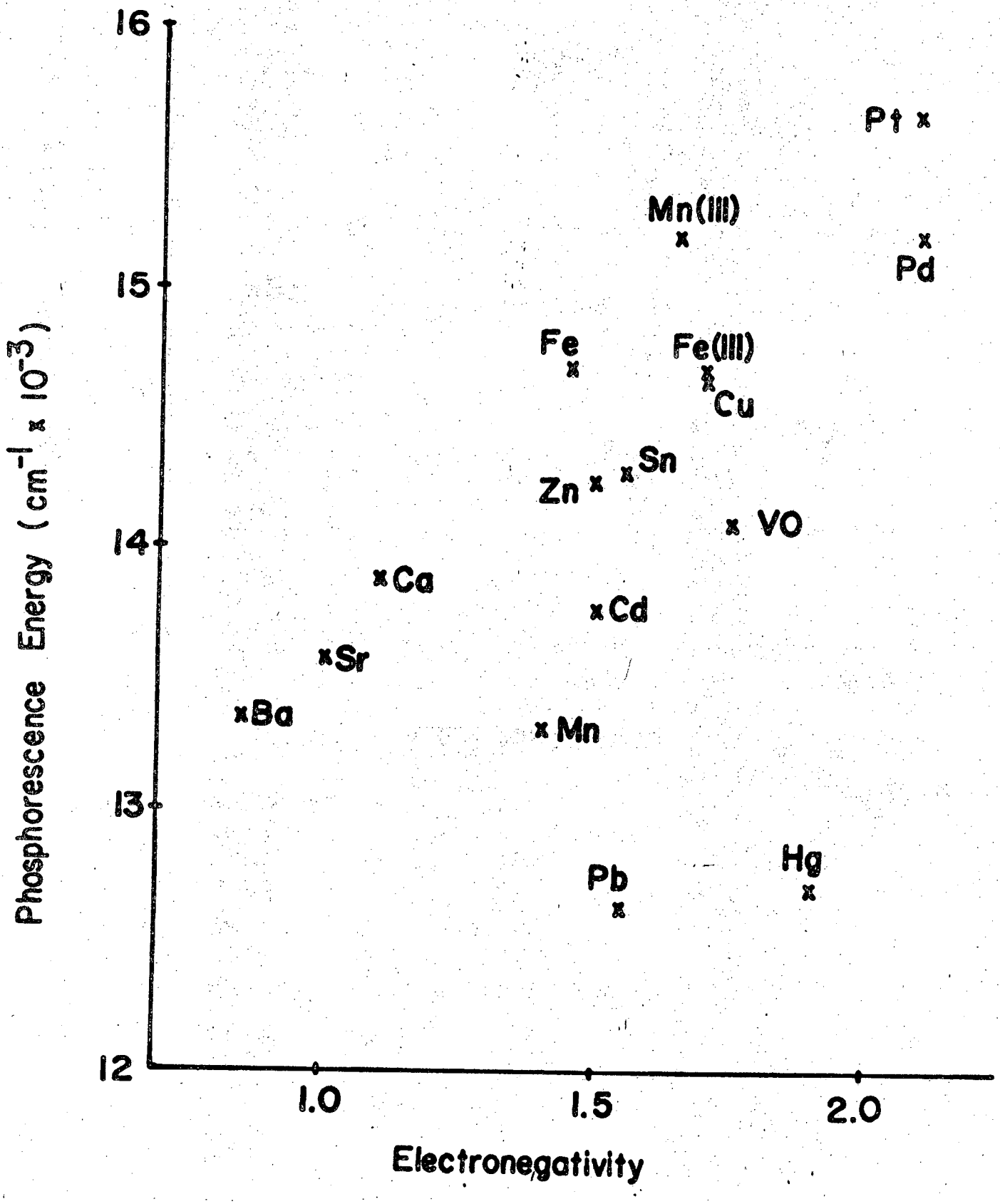

Fig. 4 - Fischer & Weiss

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