

One of its more important aspects is the standardization it offers to the study of the electronic spectra of noncubic molecules as a whole. Such standardization is vital, especially where rhombic systems are concerned, if real progress in our understanding of noncubic complex electronic spectra is to be made and if useful chemical information is to be derived therefrom. There can be little doubt that the lack of such standardization in the study of molecules whose symmetry is less than tetragonal has inhibited the development of the area. NSH Hamiltonians provide a unique and unambiguous solution to this problem.¹⁶ The data discussed in this paper provide a basis for comparison of the results to be obtained in the future with less symmetric systems. Indeed it is the fact that the parameters are linearly independent of each other and of the coordinate axis of choice, which provides a means by which data from molecules of two different symmetry groups may be directly related.¹⁶ From a computational point of view the procedure offers ease and simplicity in setting up the Hamiltonian itself and, perhaps more importantly, provides a framework in which sign (phase) ambiguities do not exist.¹⁶

The ground-state energy space diagrams constitute not only a means of answering specific questions concerning possible ground states of the molecule but also provide a challenge to the synthetic chemist.

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Supplementary Material Available. A complete listing of the matrices of Hamiltonian (2) for all spin states of d^2 and d^3 will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number AIC40389D.

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Contribution from the Chemistry Department,
York University, Downsview, Ontario M3J 1P3, Canada

Higher Oxidation Level Phthalocyanine Complexes of Chromium, Iron, Cobalt, and Zinc. Phthalocyanine Radical Species

J. F. MYERS, G. W. RAYNER CANHAM, and A. B. P. LEVER*

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Radical phthalocyanine(1-) complexes of chromium(III), iron(III), cobalt(III), and zinc(II) are reported and characterized by electronic and vibrational spectroscopy, magnetism, electron spin resonance, and Mössbauer spectroscopy and through oxidative titrations. Further elucidation of the reaction of iron(II) and of cobalt(II) phthalocyanine with the hydrohalic acids is presented. It is suggested that most of the previously reported manganese(III) phthalocyanine derivatives are five-coordinate. A survey of the first-row transition metal phthalocyanines reveals that only the above-mentioned metal ions will form radical phthalocyanine species under the conditions used.

In recent years there has been considerable interest in high oxidation level porphyrin complexes, as such species may well occur in biological environments.¹⁻²⁰ There is interest concerning the nature of the oxidized species, *i.e.*, oxidation of metal or ligand, and in the latter case concerning the nature of the electronic configuration^{16,18} so produced. Evidence that radical porphyrin cations with different ground states have

quite different chemical properties¹⁸ leads to a belief that porphyrin radical species have a dominant role to play in biological electron transfer, *e.g.*, in photosynthesis.¹⁸

The phthalocyanines, while of similar structure to the porphyrins, exhibit nevertheless characteristic differences which may be ascribed to differing electronic structure and "hole" size.²¹ Previous studies have characterized a wide range of

metal phthalocyanines of the divalent metals,²² and certain groups, particularly Taube and coworkers,²³⁻²⁵ have synthesized a range of reduced species in which the formal oxidation level of the system has been reduced by as much as 5 electrons, e.g., [LiMnPc]. While M(III) and M(IV) phthalocyanine complexes of those metals whose common oxidation state is III or IV, e.g., Sc(III) and Ti(IV), have been prepared,²² there have been few attempts to isolate oxidized phthalocyanine species in the solid state. Oxidation of phthalocyanines in solution to form poorly characterized radical species, is, however, well known.²⁶⁻²⁸

Where attempts have been made to isolate and characterize solid oxidation products, the literature is often contradictory or incomplete. In particular the use of hydrohalic acids, in the presence of air, to oxidize metal phthalocyanines has led to considerable confusion. Some aspects of this problem are discussed below.

We have recently reported²⁸ our observation that oxidation of iron(II) and cobalt(II) phthalocyanines with various oxidizing agents using procedures first mentioned in the patent literature³⁰ leads to the formation of complexes containing the trivalent ion and an oxidized radical phthalocyanine species, $X_2M^{III}Pc(1-)$. This paper surveys the oxidation behavior of the metal phthalocyanines, from vanadium through zinc, discusses the cobalt and iron radical species, and introduces new radical species of chromium, $Cl_2Cr^{III}Pc(1-)$, and zinc, $[ClZn^{II}Pc(1-)]_2$. The phthalocyanine ligand carrying two negative charges has previously been designated Pc. The characterization of one-electron-oxidized species, carrying one negative charge, and logically designated $Pc(1-)$, suggests that $Pc(2-)$ should henceforth be used for the conventional ligand. This nomenclature will be used in this paper except that Pc will be used as a general name when no especial oxidation state is implied.

Experimental Section

The metallophthalocyanines were prepared by standard methods²² and were purified by vacuum sublimation or Soxhlet extraction with dichlorobenzene.

General Procedure for the Preparation of the Radical Phthalocyanine Species. Chloride Complexes. A small and carefully dried vacuum distillation apparatus was set up and three 50-ml receiving flasks were connected to the water condenser. Two reactions could be carried out simultaneously by placing a metal phthalocyanine (approximately 0.3 g) into each of two of the flasks. Nitrobenzene (dried overnight over molecular sieves) was distilled *in vacuo*, the initial distillate being run into the third, initially empty, flask. Some 10 ml of the pure distillate was allowed to run into each of the flasks containing the metal phthalocyanines. The nitrobenzene in the boiler was then replaced by thionyl chloride, and the latter distilled, at atmospheric pressure, onto the metal phthalocyanines, once again rejecting the initial distillate. About 2 ml of thionyl chloride suffices for the reaction. A temperature of approximately 40° was sufficient to distill both liquids.

Once the flasks were charged with the three reactants, a water bath was moved into position to maintain the flasks at 60–80° for about 2 hr. Subsequently the pure products, which were not recrystallized, were filtered, washed with ethanol and then ether, and dried *in vacuo* at 80–100°. Once reaction is complete, precautions to keep water absolutely absent are no longer necessary. In the case of the cobalt complex the above stringent precautions need not be taken. The radical species may be prepared by direct reaction of the three components taken from their respective stock bottles.

Bromide Complexes. These may be prepared in a similar fashion from thionyl bromide or by the use of a stoichiometric amount of molecular bromine dissolved in dry chloroform. Only the cobalt derivative could be obtained analytically pure.

Dichloro(phthalocyaninato(1-))cobalt(III), $Cl_2Co^{III}Pc(1-)$. *Anal.* Calcd for $CoC_{32}H_{16}N_8Cl_2$: C, 58.9; H, 2.5; N, 17.4; Cl, 11.0; Co, 9.2. Found: C, 59.2; H, 2.9; N, 17.5; Cl, 10.9; Co, 9.2.

Dibromo(phthalocyaninato(1-))cobalt(III), $Br_2Co^{III}Pc(1-)$. *Anal.* Calcd for $CoC_{32}H_{16}N_8Br_2$: C, 52.6; H, 2.2; Br, 21.8; Co, 8.1. Found: C, 52.6; H, 2.6; Br, 21.7; Co, 8.3.

Dichloro(phthalocyaninato(1-))iron(III), $Cl_2Fe^{III}Pc(1-)$. *Anal.* Calcd for $FeC_{32}H_{16}N_8Cl_2$: C, 60.1; H, 2.5; N, 17.5; Cl, 11.1; Fe, 8.7. Found: C, 60.1; H, 2.9; N, 17.9; Cl, 10.7; Fe, 9.6.

Dichloro(phthalocyaninato(1-))chromium(III), $Cl_2Cr^{III}Pc(1-)$. *Anal.* Calcd for $C_{32}H_{16}Cl_2CrN_8$: C, 60.5; H, 2.5; Cl, 11.2; Cr, 8.2. Found: C, 59.5, 61.2; H, 2.5; Cl, 10.9; Cr, 8.5. Difficulty was experienced in obtaining an adequate carbon analysis for this complex.

Chloro(phthalocyaninato(1-))zinc(II), $ClZn^{II}Pc(1-)$. *Anal.* Calcd for $C_{32}H_{16}ClN_8Zn$: C, 62.6; H, 2.6; Cl, 5.8. Found: C, 62.5; H, 2.8; Cl, 5.8.

Chloro(phthalocyanato(2-))manganese(III), $ClMn^{III}Pc(2-)$. This compound was prepared by a procedure similar to the preparation of radical chloro species except that manganese(II) phthalocyanine and "neat" thionyl chloride were used. Alternately the compound could be prepared by extracting manganese(II) phthalocyanine with dichlorobenzene. Preparations using the thionyl chloride route gave the more acceptable carbon analysis, although the values were never as good as for the iron and cobalt derivatives. *Anal.* Calcd for $MnC_{32}H_{16}N_8Cl$: C, 63.8; H, 2.7; N, 18.6; Cl, 5.9; Mn, 9.1. Found: C, 62.5; H, 2.6; N, 18.2; Cl, 6.1; Mn, 8.9.

Bromo(phthalocyanato(2-))manganese(III), $BrMn^{III}Pc(2-)$. Manganese(II) phthalocyanine was treated with "neat" thionyl bromide or alternatively was extracted with bromobenzene, both routes yielding the same product. It was difficult to obtain a satisfactory carbon analysis. *Anal.* Calcd for $MnC_{32}H_{16}N_8Br$: C, 59.4; H, 2.5; Br, 12.3; Mn, 8.5. Found: C, 62.0; H, 2.6; Br, 12.6; Mn, 8.6.

Magnetic Measurements. A variable-temperature Faraday balance³¹ was used and calibrated with mercury tetrathiocyanatocobaltate(II). The results of the measurements are given in Table I.

Infrared Spectra. These were obtained as Nujol mulls using a Beckman IR 12 spectrometer.

Oxidation titrations used the dichromate method³² with the indicator 5,6-dimethylphenanthrolineiron(II) in place of barium diphenylaminesulfonate. **Electronic spectra** were obtained from solids which had been sublimed onto quartz disks located in the cool portion of the sublimation apparatus (<100°) or by using a microsublimation apparatus with quartz flats. Reactions with halogenating agents were performed by suspending the disks in the vapor atmosphere of reagent created by heating the reagent under investigation after the system had been thoroughly flushed with N₂. The original spectrum of $M^{II}Pc(2-)$ could be restored by heating the "reacted" disk *in vacuo* at ~200° for 2 hr. Alternatively thionyl chloride was added directly to the microsublimation apparatus.

Epr and Mössbauer spectra were performed by other laboratories (see Acknowledgment). Elemental analyses (C, H, N) were obtained from A. B. Gygli (Toronto, Canada). Metal analyses were performed in our laboratories by atomic absorption (Varian Techtron 1200). Halide analyses were obtained potentiometrically by using silver nitrate after liberating the halide by alcoholic KOH treatment. Several halide analyses were also obtained commercially for comparison (Gygli).

Results and Discussion

Various groups²⁶⁻²⁸ have reported the generation of phthalocyanine radical species through oxidation of metal phthalocyanine solutions with reagents such as the ceric ion. It is of historical interest that as early as 1939 it was reported: "At room temperature chlorine gas converts free phthalocyanine and many of its metallic derivatives into brown chlorides, from which the halogen is completely liberated by warm alkali."³³ This reaction must certainly have generated radical phthalocyanine species but would be unreliable as a preparative method since many complexes can further undergo ring halogenation yielding products difficult to characterize.²² Our interest in higher oxidation level metal phthalocyanines was renewed by an observation in the patent literature^{29,30} that complexes X_2CoPc (X = Cl, Br) could be obtained through treatment of cobalt phthalocyanine with reagents such as thionyl chloride, sulfuryl chloride, phosphorus oxychloride, phosphorus pentachloride, chlorine, bromine, and iodine.

Halochromium, -cobalt, -iron, and -zinc Phthalocyanines. Using a modification of the procedure reported in the patent³⁰ we have reprepared Cl_2CoPc and Br_2CoPc and extended the reaction to prepare Cl_2CrPc , Br_2FePc , Cl_2FePc , and $ClZnPc$.

Table I

Dichloro(phthalocyanato(1-))chromium(III) ^a (Diamagnetic Correction 481×10^{-6} cgsu)							
Temp, °K	88.6	103.9	115.1	123.1	137.2	146.1	169.2
$10^6 \chi_g$, cgsu	32.47	29.11	27.06	25.58	23.61	22.37	19.91
μ_{eff} , BM	3.87	3.97	4.03	4.06	4.12	4.145	4.22
Temp, °K	185.8	196.0	211.2	229.0	253.1	275.9	298.5
$10^6 \chi_g$, cgsu	18.43	17.52	16.37	15.30	13.98	12.83	11.92
μ_{eff} , BM	4.26	4.27	4.29	4.32	4.36	4.365	4.39
Chloro(phthalocyanato(2-))manganese(III) (Diamagnetic Correction 458×10^{-6} cgsu)							
Temp, °K	85.4	99.4	116.4	144.9			179.9
$10^6 \chi_g$, cgsu	55.42	48.53	41.63	33.31			26.69
μ_{eff} , BM	4.81	4.86	4.88	4.88			4.88
Temp, °K	214.2	250.1	287.1	305.6			324.6
$10^6 \chi_g$, cgsu	22.31	19.01	16.43	15.45			14.56
μ_{eff} , BM	4.88	4.89	4.88	4.89			4.90
Dichloro(phthalocyanato(1-))cobalt(III) (Diamagnetic Correction 481×10^{-6} cgsu)							
Temp, °K	85.6	103.2	120.6	137.9	155.4	172.75	190.1
$10^6 \chi_g$, cgsu	2.57	2.49	2.35	2.205	2.06	1.93	1.79
μ_{eff} , BM	1.21	1.31	1.385	1.45	1.50	1.54	1.57
Temp, °K	208.1	226.2	245	263	281.6		299.9
$10^6 \chi_g$, cgsu	1.68	1.58	1.475	1.37	1.29		1.21
μ_{eff} , BM	1.61	1.645	1.67	1.69	1.72		1.74
Dichloro(phthalocyanato(1-))iron(III) (Diamagnetic Correction 478×10^{-6} cgsu)							
Temp, °K	85.5	102.2	119.3	136.2	153.1	170.4	188.0
$10^6 \chi_g$, cgsu	14.99	13.70	12.345	11.19	10.22	9.32	8.57
μ_{eff} , BM	2.62	2.75	2.83	2.88	2.93	2.96	2.99
Temp, °K	223.75	242.15	259.9	277.85	296.4	314.45	332.4
$10^6 \chi_g$, cgsu	7.30	6.77	6.29	5.90	5.54	5.21	4.89
μ_{eff} , BM	3.05	3.05	3.06	3.07	3.09	3.10	3.10
Dibromo(phthalocyanato(1-))cobalt(III) (Diamagnetic Correction 505×10^{-6} cgsu)							
Temp, °K	85.3	102.2	119.4	136.5	153.4	170.8	188.4
$10^6 \chi_g$, cgsu	2.37	2.24	2.04	1.88	1.76	1.64	1.52
μ_{eff} , BM	1.24	1.32	1.38	1.43	1.48	1.53	1.56
Temp, °K	206.2	224.3	242.9	260.6	278.6		296.9
$10^6 \chi_g$, cgsu	1.42	1.34	1.29	1.21	1.15		1.09
μ_{eff} , BM	1.60	1.63	1.68	1.70	1.73		1.76

^a Different samples of this complex gave slightly differing magnetic behavior. While this is regarded as the best data set, it is clear that there is some doubt concerning the magnetic purity of this species.

These derivatives are a golden brown or dark brown, which is atypical for phthalocyanine derivatives. Halogen analyses reveal that the total halogen content is released upon reaction of these derivatives with ethanolic potassium hydroxide. Such lability would not be anticipated for aromatic ring substituted halogen. The complexes are all stable to cold water once prepared. However considerable care has to be taken to exclude water during the preparation of the iron, chromium, and zinc derivatives to avoid formation of a hydrochloride

derivative which does not contain the radical phthalocyanine species. Cobalt phthalocyanine is much less susceptible to the formation of a hydrochloride (*vide infra*). While the cobalt bromide phthalocyanine radical species is cleanly prepared from the parent phthalocyanine and molecular bromine, some difficulty was experienced in obtaining a pure sample of the corresponding iron derivative. In the case of chromium and zinc even more difficulty was experienced and hence these derivatives are not reported. The reaction does not stop after the addition of one molecule of bromine per metal atom.

The chromium, iron, and cobalt complexes may be regarded as two-electron oxidation products of $M^{II}Pc(2-)$, containing a radical phthalocyanine species and M^{III} and possessing a six-coordinate octahedral structure with two trans M-X bonds.²⁹

The zinc complex appears to be a dimeric derivative containing Zn(II) and the phthalocyanine radical species. The data upon which these conclusions rest follow.

(i) **Oxidation Titrations.** Elvidge³² developed a procedure for the quantitative oxidative degradation of metal phthalocyanines. The phthalocyanine unit requires one atom of oxygen (loses two electrons) for such destruction. By the careful oxidative destruction of the halometal derivatives, their oxidation level, relative to the parent metal phthalocyanines, can, in most cases, be unequivocally determined. These data are reported in Table II. Thus while $Co^{II}Pc(2-)$ requires 1 g-atom of oxygen per mole, for destructive oxidation, Cl_2CoPc requires no oxygen. The latter complex is therefore at an oxidation level of two electrons above the parent compound, inferring the formulation $Cl_2Co^{IV}Pc(2-)$ or $Cl_2Co^{III}Pc(1-)$. The data for the chromium and iron compounds lead to the same two alternate formulations, $Cl_2M^{IV}Pc(2-)$ or $Cl_2M^{III}Pc(1-)$. The complex $ClZnPc$ is only one electron above $ZnPc(2-)$ inferring the alternate formulations $ClZn^{III}Pc(2-)$ or $ClZn^{II}Pc(1-)$.

A third possibility to formulate these complexes as derivatives of phthalocyanine(0) seems remote, the weight of evidence greatly mitigating against such a proposal. In the case of the zinc complex, for example, it would infer the presence of zinc(I), an improbable oxidation level, particularly in view of the mode of preparation. Moreover phthalocyanine(0) is a 36-electron system possessing no special (Hückel) stability. Similarly Zn(III) is an improbable oxidation level. Thus the mere existence of this zinc complex is good evidence for the radical formulation.

While Elvidge's method is inappropriate for bromide-containing complexes, there can be no doubt from other physical data that the chloro and bromo complexes are strictly analogous.

(ii) **Magnetism.** Before discussing the magnetic data recall that the moment to be expected from a molecule containing

Table II. Oxidation Titrations

Complex	No. of runs	Oxygen equiv		Calcd ^b	Electrons consumed
		Found in this study ^a	Found previously ³²		
$Co^{II}Pc(2-)$	3	1.02	1.06, 1.15	1.00	2
$Cl_2Co^{III}Pc(1-)$	3	0.02		0.00	0
$Fe^{II}Pc(2-)$	Many	1.46 ^c	1.41, 1.46, 1.47	1.50	3
$ClFe^{III}Pc(2-)$ ^d	5	0.83	0.96, 0.99	1.00	2
$Cl_2Fe^{III}Pc(1-)$	2	0.51		0.50	1
$ClMn^{III}Pc(2-)$	3	0.50		0.50	1
$Cl_2Cr^{III}Pc(1-)$	2	0.54		0.50	1
$Zn^{II}Pc(2-)$	2	0.98	1.03	1.00	2
$Zn^{II}Pc(2-)HCl$	2	0.97	0.91, 1.01	1.00	2
$(ClZn^{II}Pc(1-))_2$	2	0.51 ^e		0.50	1

^a Except where indicated, this is the mean value obtained for the number of runs indicated. With the exception of $ClFe^{III}Pc(2-)$ and $Fe^{II}Pc(2-)$, the mean deviation was very small. ^b Calculated number of oxygen equivalents consumed on the basis of the proposed formula.

^c This is the best of many values. Difficulty was experienced in dissolving this complex (and also $ClFe^{III}Pc(2-)$) fully in the acid solution.

^d This sample was prepared under a nitrogen atmosphere (see text). Elvidge³² would have used a sample prepared in air. ^e Per monomer unit.

Table III. Magnetism and Electronic Spectra^a

Complex	Magnetic moment (~ 298° K), ^a BM	Electronic spectrum ^b						
Cl ₂ Cr ^{III} Pc(1-)	4.40	12,540 s	13,270 m	14,710 w	17,350 s	22,470 s	27,590 s	(35,700)
ClMn ^{III} Pc(2-)	4.90	7,280 w	13,090 s	(14,705)	19,040 m	27,420 vs	36,325 vs	
Cl ₂ Fe ^{III} Pc(1-)	3.10	12,220 s	13,070 w	(14,290)	16,740 s	22,960 s	27,030 vs	(36,360)
Cl ₂ Co ^{III} Pc(1-)	1.74 ^d	13,370 s			18,000 s	22,570 s	28,550 vs	35,640 vs
Br ₂ Co ^{III} Pc(1-)	1.76 ^e	7,170 vw ^c (11,680)	13,380 s		17,910 vs	21,430 s	28,570 vs	36,170 vs
[ClZn ^{II} Pc(1-)] ₂	0	9,130 w	13,460 s	(15,150)	18,150 s	22,430 s	26,360 vs	30,980 vs

^a Variable-temperature data given in Table I. ^b Films on quartz disks except where noted; shoulders in parentheses. ^c Solid-state transmittance spectra. ^d $J = 56 \text{ cm}^{-1}$; $N\alpha = 200 \times 10^{-6}$ cgsu; standard deviation 0.017 BM [eq 3, ref 35, p 77]. ^e $J = 53 \text{ cm}^{-1}$; $N\alpha = 150 \times 10^{-6}$ cgsu; standard deviation 0.03 BM [eq 3, ref 35, p 77]. ^f Note that these data represent the major features of the spectra. Minor features, barely perceptible shoulders, are not recorded.

two magnetic centers is the square root of the sum of the squares of the individual moments. The magnetic behavior of Cl₂CrPc is of particular significance. The moment, 4.4 BM, is close to the predicted value of 4.24 BM for three unpaired electrons on the metal and one on the ligand, consistent with the Cr^{III}Pc(1-) formulation. This moment is quite inconsistent with any Cr(IV) formulation which would only contain two unpaired electrons. While these data provide no direct evidence for the coordination number, the Cr(III) species almost invariably forms octahedral species. The slight temperature dependence of the magnetic moment probably arises as a consequence of a small exchange interaction (see Cl₂CoPc below). The manganese(III) complexes exhibit temperature-independent moments corresponding to the presence of four unpaired electrons. Since there is no evidence that these complexes contain a radical species, such data are readily interpreted in terms of d⁴ manganese(III) (see below).

The magnetic data for the iron complex, Cl₂FePc, are consistent with both an iron(IV) and an iron(III) radical formulation. In the former case an octahedral d⁴ Fe(IV) low-spin system would exhibit two unpaired electrons with a temperature-dependent moment, as is indeed observed (Tables I and III). A low-spin octahedral d⁵ Fe(III) would contribute one unpaired electron, also with a temperature-dependent moment, which together with the spin on the radical could readily lead to an observed room-temperature moment near 3.0 BM. Since there will be an orbital contribution to the moment of the iron(III) atom, it is not realistic simply to predict a moment of 2.45 BM arising from two isolated unpaired electrons, in this case. Low-spin octahedral iron(III) in a hemoprotein environment exhibits moments ranging³⁴ from about 2.2 to 2.8 BM. Such moments if observed in this case would lead to moments for the radical complex of 2.8–3.3 BM. The data do argue against a five-coordinate formulation which would have in excess of two unpaired electrons. The moment of the iron radical complex is in agreement with the approximate value recorded⁴ for the corresponding iron tetraphenylporphyrin radical complex.

The cobalt complexes exhibit a magnetic moment at room temperature close to the value expected for one unpaired electron; the moment decreases slightly with decreasing temperature (see Tables I and III). These data are inconsistent with the postulate of a five-coordinate Co(III) radical phthalocyanine species or a five-coordinate Co(IV) species. They are however consistent with expectation for a six-coordinate Co(III) radical phthalocyanine species, for a diamagnetic metal ion, or for a six-coordinate cobalt(IV) species. A temperature-dependent magnetic moment, as is observed, would be expected for the Co(IV) formulation but not, at first sight, for the radical formulation. An isolated free radical should have a temperature-independent moment of 1.73 BM. Temperature dependence in this case could only arise through an exchange process causing partial spin pairing.

Noting that low-spin d⁶ octahedral cobalt(III) complexes are not strictly diamagnetic but have a sizable temperature-independent paramagnetic term³⁵ and assuming a pairwise interaction between adjacent radicals, the magnetic data may be fitted³⁵ with an exchange energy of 50–60 cm⁻¹ (see Tables I and III). Such exchange energies do not seem out of line given that the octahedral metal atom will inhibit close intermolecular contacts. Note that this exchange provides a mechanism for energy transfer. Unfortunately, while a corresponding cobalt tetraphenylporphyrin radical derivative has been reported,⁴ no magnetic data were included.

While a Co(IV) formulation would also provide a temperature-dependent moment, it is hard to reconcile the detail of this temperature dependence with low spin d⁵.

The zinc complex was observed to be diamagnetic over an extended temperature range from -196 to +100°. Since there can be no doubt from the oxidative titration data that ClZnPc contains an odd number of electrons, the diamagnetism must arise through spin pairing. The most simple procedure to accommodate this pairing would be dimerization, and a dimeric radical structure [ClZn^{II}Pc(1-)]₂ is therefore proposed for this species. This observation parallels zinc porphyrin chemistry where diamagnetic dimeric zinc porphyrin complexes have been characterized.³⁶ While the detailed structure of such a dimer is not known, it seems probable that, in our case, two five-coordinate ClZn^{II}Pc(1-) units are stacked with their phthalocyanine bases parallel and with electron coupling through the π clouds. It is relevant that, in porphyrin chemistry, a monomeric paramagnetic radical species is obtained when the zinc porphyrin has bulky substituents which presumably prevent the π clouds from getting sufficiently close together.¹⁹ The possibility that these complexes be formulated M^{II}Pc(2-)X₂ with molecular halogen is, on the basis of all the data, extremely remote.

(iii) **Electron Spin Resonance Data.** Cl₂Co^{III}Pc(1-) and BrCo^{III}Pc(1-) exhibit very intense signals at $g = 2.003$ and 2.004 , respectively, with a bandwidth of less than 5 G. Such an intense narrow signal is typical of a radical species of this type.^{1,5,9,10} It is true that esr signals at $g \approx 2.0$ reported³⁷⁻³⁹ for free unmetalated phthalocyanine and for various metal phthalocyanines, which have been sublimed, are attributed to partial oxidation or impurities. Nevertheless we believe that the exceptionally high intensity of the signals reported here, together with the fact that these derivatives are not freshly sublimed but have been reacted in a solvent phase, argue for a stoichiometrically oxidized product. No hyperfine structure was observed on these signals either at room temperature or at liquid nitrogen temperature. The iron complexes did not exhibit any esr signal. This is not surprising; analogous metal porphyrin complexes exhibit no signal from the radical electron when the central ion is paramagnetic.^{4,9,10} There is evidently sufficient coupling to wipe the signal out.

(iv) **Electronic Spectra.** Table III and Figures 1 and 2

Table IV: Far-Infrared Vibrational Data (cm^{-1})

Complex	$\nu(\text{M-Br})$		$\nu(\text{M-Cl})$			
$\text{Cl}_2\text{Cr}^{\text{III}}\text{Pc}(1-)$		288.5 s	332 s	360.5 s	366 s	426 m
$\text{Cl}_2\text{Fe}^{\text{III}}\text{Pc}(1-)$		292 s	332 vs ^a	358 w	391 s	428 m
$\text{Br}_2\text{Fe}^{\text{III}}\text{Pc}(1-)$	244 vs	308 s		354 s	374 m	400 w, 426 m
$\text{Cl}_2\text{Co}^{\text{III}}\text{Pc}(1-)$		292.5 m	329.0 vs ^a		407.0 s	439.0 m
$\text{Br}_2\text{Co}^{\text{III}}\text{Pc}(1-)$	253 vs			310 s	397 m	434 s
$\text{ClMn}^{\text{III}}\text{Pc}(2-)$		258 sh	269 vs	297 vs	342 m	432 vs
$\text{BrMn}^{\text{III}}\text{Pc}(2-)$	211 vs			292 s	342 m	432 s
$\text{ClZn}^{\text{II}}\text{Pc}(1-)$		213 s	279 vs		342 m	421.5 s
		237.5 m				
		262 w				

^a Identified by ^{35}Cl , ^{37}Cl isotopic substitution.⁴⁰

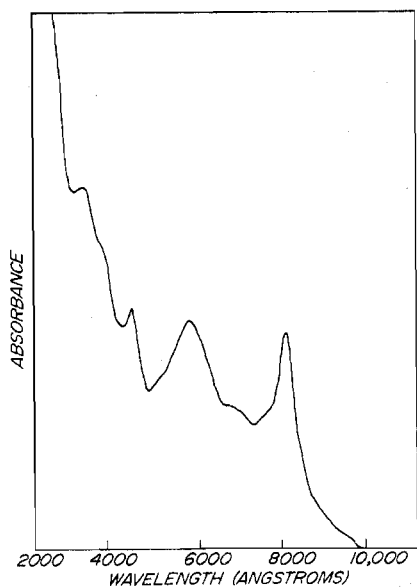


Figure 1. The electronic spectrum of $\text{Cl}_2\text{Fe}^{\text{III}}\text{Pc}(1-)$ (recorded as a film on a quartz disk at room temperature).

illustrate the electronic spectra of these complexes, obtained on a quartz disk (see Experimental Section). They are richer than the spectra of the $\text{M}^{\text{II}}\text{Pc}(2-)$ species²² especially in the 400–600-nm region, which absorption is responsible for the atypical golden brown color of these derivatives. By analogy with the porphyrin radical species data,^{16,20} these spectra provide further definitive evidence for the presence of a radical phthalocyanine species. Heating of the quartz disks to 200° *in vacuo* restores the electronic spectrum of $\text{M}^{\text{II}}\text{Pc}(2-)$, providing further evidence for the absence of ring halogenation.

(v) **Infrared Data (Conventional Region).** The infrared spectra of metallophthalocyanines are very similar and are almost independent of the nature of the central ion.²² Consequently the observation that these chromium, iron, and cobalt complexes have infrared spectra markedly different from their $\text{M}^{\text{II}}\text{Pc}(2-)$ precursors provides additional evidence for a serious perturbation of the phthalocyanine ligand (see Figure 3), lending support to their formulation as radical species and not complexes of $\text{M}(\text{IV})$. The most prominent change in the infrared spectra upon oxidation of the $\text{M}^{\text{II}}\text{Pc}(2-)$ complex is a decrease in the intensity of the bands in the region 800–1300 cm^{-1} , together with the appearance of a strong new band at 1050 cm^{-1} . This new band is observed for all the X_2MPc species within ± 2 cm^{-1} and appears to be diagnostic of the uncoupled phthalocyanine radical species. When $\text{X} = \text{Br}$, a second fairly strong band, present weakly in the chlorides, appears at 1158 cm^{-1} . The complex $\text{Br}_2\text{Fe}^{\text{III}}\text{Pc}(1-)$ is included in this report, even though we were unable to obtain really satisfactory analytical data, because its infrared spectrum in the 800–1300- cm^{-1} region, in particular, is essentially identical with the spectrum of $\text{Br}_2\text{Co}^{\text{III}}\text{Pc}(1-)$.

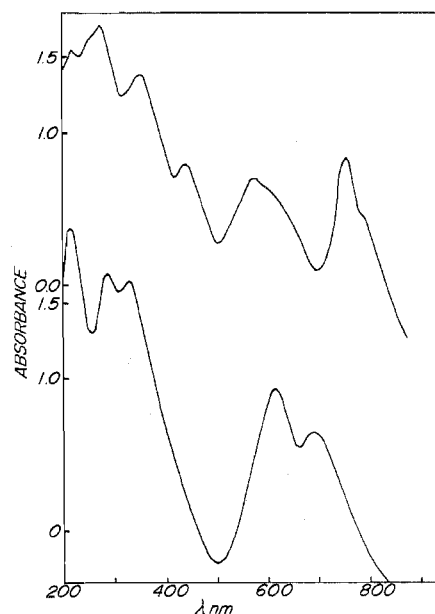


Figure 2. The electronic spectra of $\text{Co}^{\text{II}}\text{Pc}(2-)$ (lower) and $\text{Cl}_2\text{-Co}^{\text{III}}\text{Pc}(1-)$ (upper) (recorded as films on quartz disks at room temperature).

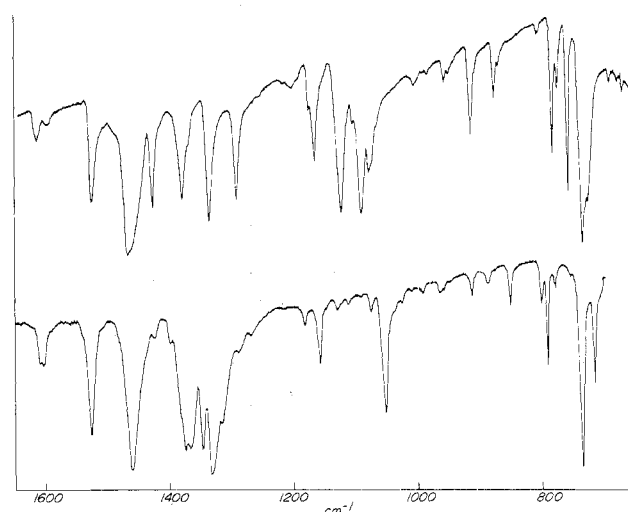


Figure 3. Comparison of the infrared spectra of $\text{Co}^{\text{II}}\text{Pc}(2-)$ (upper) and of $\text{Cl}_2\text{Co}^{\text{III}}\text{Pc}(1-)$ (lower).

The infrared spectrum of $\text{ClZn}^{\text{II}}\text{Pc}(1-)$ differs both from the spectra of the radical species described above and from the spectra of conventional metal phthalocyanines. This may be construed as further evidence for the ring-ring interaction proposed to exist in this dimeric species.

(vi) **Far-Infrared Spectra (550–200 cm^{-1}).** Far-infrared data are reported for these compounds in Table IV. Met-

al-halogen modes are identified but a full discussion of these assignments which are based upon isotopic substitution and upon a comparison of the spectra of appropriate pairs of compounds, will be presented elsewhere.⁴⁰ It is important to note that the frequencies are compatible with the presence of a trivalent metal ion correlating well with previously reported $\nu(\text{M}^{\text{III}}-\text{X})$ stretching vibrations.^{6,40,41} These data confirm the presence of at least one M-X bond in these radical species.

(vii) Mössbauer Spectra. The Mössbauer spectrum of $\text{Cl}_2\text{Fe}^{\text{III}}\text{Pc}(1-)$ shows an isomer shift of 0.35 mm/sec and a quadrupole splitting of 2.15 mm/sec. This isomer shift is markedly lower than that of $\text{Fe}^{\text{II}}\text{Pc}(2-)$ (various values reported from 0.63 to 0.72 mm/sec)^{25,42-44} consistent with a higher oxidation level in the former complex. The validity of such conclusions is however questioned since in a study of iron complexes it is observed that quite large variations in isomer shift can occur as a function of the σ and π characteristics of the ligand without necessarily changing the formal oxidation number of the iron.⁴⁵ Nevertheless the isomer shift is lower than any other previously reported iron phthalocyanine derivative including $\text{Fe}^{\text{III}}\text{Pc}(2-)(p\text{-toluenesulfonate})$.²⁵

Oxidative Experiments with Other Metallophthalocyanines. Electrochemical studies⁴ with the metal phthalocyanines reveal that the ligand has a relatively low potential for oxidation when $\text{M} = \text{Fe}, \text{Co},$ and Zn and relatively high for $\text{M} = \text{Ni}$ and Cu and for H_2 . Various molecular orbital studies of the metal phthalocyanines have been published.^{21,25,46} While they differ in fine detail, all agree that there are filled molecular orbital energy levels on the ligand lying at energies within the d orbital manifold, for most first-row transition element phthalocyanines. The question of whether successive oxidation will occur at the ligand or at the metal is therefore a rather subtle problem involving the changes in charge distribution and interelectronic repulsion which take place. In this study we have surveyed the behavior of transition metal phthalocyanines from vanadium through zinc, with thionyl chloride. Only chromium, iron, cobalt, and zinc phthalocyanines yield a radical species.

Vanadyl phthalocyanine does not react under the conditions used to prepare the radical species discussed above.

While on the basis of its electronic structure^{21,25,46} manganese phthalocyanine might be expected to yield a radical oxidation product, this does not appear to be the case. Evidence exists in the literature for both manganese(III) and manganese(IV) phthalocyanine derivatives.^{22,47} The manganese(III) complexes are usually dark green and have magnetic moments consistent with the presence of high-spin octahedral Mn(III) (but see below). Manganese(II) phthalocyanine is a moderately reactive compound which is easily oxidized, apparently to Mn(III). Thus while most metallophthalocyanines may be purified by Soxhlet extraction with halogenated solvents, such as the chlorobenzenes,²² manganese(II) phthalocyanine extracts chlorine to form chloromanganese(III) phthalocyanine. This fact has also been observed very recently⁴⁸ in a mass spectroscopic study of metallophthalocyanines. The corresponding bromide may be prepared *via* Soxhlet extraction with bromobenzene. These same compounds are produced by the action of thionyl chloride and bromide, respectively, upon manganese(II) phthalocyanine. The formulation of these as manganese(III) complexes follows from the similarity of their infrared spectra in the 800-1400- cm^{-1} region with other common metallophthalocyanines and from their magnetic moments which correspond to four unpaired electrons and which are essentially temperature independent over the range studied (Tables I and III). Although there was no evidence of a radical species being formed in these reactions, we were unable to obtain adequate carbon analyses with these compounds suggesting the reaction may not be as straightforward as suggested. Methanol adducts of

these complexes have been previously reported,⁴⁷ obtained through the action of methanolic hydrohalic acid on manganese(II) phthalocyanine. The complexes obtained from manganese(III) phthalocyanine *via* extraction with chlorobenzene, by extraction with methanol containing hydrochloric acid, or by reaction with thionyl chloride all have essentially identical infrared spectra in both the conventional and the far-infrared ranges. The methanol adducts, previously formulated as six-coordinate high-spin complexes, are anomalous in that no other high spin metal phthalocyanine complexes are known. In view of the apparent identity between the XMnPc complexes and the methanol adducts, we tentatively propose that all these complexes are indeed *five-coordinate (square pyramidal)*. This stereochemistry would generate a high-energy *unoccupied* $x^2 - y^2$ orbital, the four electrons being placed, unpaired, into the lower four orbitals; in this way the anomaly is removed. The only genuine six-coordinate⁴⁹ manganese(III) phthalocyanines [(base)Mn^{III}Pc(2-)]₂O are essentially diamagnetic.⁵⁰ Previously reported manganese(IV) phthalocyanines²² have properties consistent with the presence of the phthalocyanine(2-) species and not with the presence of a radical phthalocyanine species.

Nickel(II), copper(II), and unmetalated phthalocyanines do not react with thionyl chloride to form oxidized species. It is of interest that the reactivity of thionyl chloride with metal phthalocyanines parallels the reactivity of these species toward nitric oxide.⁵¹ With this latter reagent Cr^{II}, Mn^{II}, Fe^{II}, and Co^{II}Pc all react, while Ni^{II}- and Cu^{II}Pc do not. On this basis it seems probable that the initial reaction with thionyl chloride involves coordination to the metal. The fate of the SO group is unknown. Note that the oxidation process with thionyl chloride will proceed under a nitrogen atmosphere, thereby excluding oxygen from playing a role.

Reactions of Metal Phthalocyanines with Strong Acids. While a range of metal phthalocyanines has been treated with acids, the products have seldom been adequately characterized, the principal uncertainty being whether ring protonation or metal oxidation (or both) occurs. In the reaction of iron phthalocyanine with hydrochloric acid, for example, both $\text{Fe}^{\text{II}}\text{Pc}\cdot\text{HCl}$ and $\text{Fe}^{\text{III}}\text{PcCl}$ have been claimed as product.^{25,42,44,52-59} The latter compound is also believed to be formed through reaction of Ph_3CCl with $\text{Fe}^{\text{II}}\text{Pc}(2-)$.⁶⁰ Reaction of iron phthalocyanine with hydrochloric acid on a steam bath in the open atmosphere for about 1 hr yields black crystals. If this reaction is repeated using time periods of 1, 3, 5, 8, and 24 hr, and longer periods, the conventional and far-infrared spectra of the products over the different time periods vary markedly, as do the halogen analyses, the magnetic moments, and the electronic spectra. *We are convinced that this reaction yields a mixture of products.* Oxidative titration data are irreproducible but indicate that *some* oxidation has occurred. The absence of a strong peak at 1050 cm^{-1} , however, argues against Cl_2FePc being one of the major products. It seems probable that the mixed product contains primarily $\text{Fe}^{\text{II}}\text{Pc}(2-)$, $\text{Fe}^{\text{II}}\text{Pc}(2-)\cdot\text{HCl}$, $\text{Fe}^{\text{III}}\text{Pc}(2-)\text{Cl}$, and probably $\text{Fe}^{\text{III}}\text{Pc}(2-)\text{Cl}\cdot\text{HCl}$, the last being inferred from the observation that in some samples the Cl:Fe ratio exceeded unity. There is little doubt that a similar situation prevails with hydrobromic acid.

Reaction of $\text{Co}^{\text{II}}\text{Pc}(2-)$ with hydrochloric acid under the same conditions also produces mixtures but in this case the presence of some absorption at 1050 cm^{-1} infers that $\text{Cl}_2\text{Co}^{\text{III}}\text{Pc}(1-)$ is among the products although probably not to a very large extent. Samples exhibit an electron spin resonance signal at $g = 2.003$ but with a bandwidth twice as large as that exhibited by pure $\text{Cl}_2\text{Co}^{\text{III}}\text{Pc}(1-)$. Behavior with HBr is similar. We conclude that all previous work on complexes obtained by treating iron(II) or cobalt(II)

Chart I^a

Sc ⁶²	Ti ⁶³⁻⁶⁵	V ²²	Cr ^{51,66}	Mn ^{22,47}	Fe ^{22,24,29,67,68}	Co ^{22,29,30,68-70}	Ni ²²	Cu ²²	Zn ²²
	2+		2+	2+	2+	2+	2+	2+	2+
3+	3+		3+	3+	3+	3+			2+ (R)
	4+	4+	3+ (R)	4+	3+ (R)	3+ (R)			

^a R = radical phthalocyanine.

phthalocyanines with HCl or HBr in the presence of air must be considered of doubtful validity, since it is unlikely that pure products were being studied.

Reactions carried out under a nitrogen atmosphere take a somewhat different course. Cobalt(II) phthalocyanine fails to react with concentrated hydrochloric acid under a nitrogen atmosphere, at reflux, even after 6 hr. Iron(II) phthalocyanine reacts to yield a dark green product. While it is clearer than the product from the reaction in air, minor changes in the relative intensities of infrared bands and variation in magnetic data as a function of reaction time suggest that it is still a mixture, though undoubtedly a simpler one. Magnetic moments approaching 2.0 BM were achieved, much lower than previously observed. Oxidative titration data (Table II) are suggestive of iron(III). This product may, therefore, be composed primarily of ClFe^{III}Pc(2-).

Reaction of cobalt phthalocyanine with nitric acid has previously been reported to yield oxidation products.⁶¹ While we were unable to obtain a sample analyzing satisfactorily, it is worth noting that in this case the product is brown, rather than black, and the infrared spectrum exhibits a strong band at 1050 cm⁻¹. Contrary to the behavior with HCl and HBr, the electron spin resonance signal at $g = 2.0025$ is very narrow. We conclude that reaction with nitric acid does lead primarily, though not entirely, to the formation of a radical phthalocyanine species.

Zinc phthalocyanine reacts readily with hydrochloric acid to yield a hydrochloride previously identified³² and confirmed in this study (Table II) to contain zinc(II) phthalocyanine and therefore quite distinct from the radical species described here as the product with thionyl chloride.

Survey of Metallophthalocyanine Oxidation Levels. In Chart I are reviewed the oxidation levels (2+ and above) for which first transition metal phthalocyanines have been claimed. This would suggest that complexes of vanadium phthalocyanine should be stable in at least the 3+ oxidation level if not in 2+.

Conclusions

The characterization of this series of metal phthalocyanine radical species removes an apparent anomaly by showing that the phthalocyanines do form a series of radical cations which parallel those observed with the porphyrins. In view of the importance of the role believed played by the porphyrin radical species in electron transfer in living systems,¹⁵ this paper should provide the impetus for a detailed study of the preparation and reactivity of metal phthalocyanine radical species. In the porphyrin series such species are chemically reactive and can be used as precursors for the synthesis of various ring-substituted derivatives. Similar opportunities should prevail with the metal phthalocyanines.

The existence of porphyrin dications produced through oxidation with bromine, for example,¹⁵ suggests that further study of the reactions of metal phthalocyanines with bromine may prove profitable, particularly in view of the very high chemical reactivity of porphyrin dications.

Since there is evidence that the first step in the photosynthetic process in plants is the formation of dimeric radical chlorophyll species,^{71,72} the possibility that dimeric radical phthalocyanine species could act as models for this process is suggested. Further studies of the oxidation characteristics of non-transition-metal phthalocyanines should therefore prove profitable.⁷³

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Registry No. Cl₂Cr^{III}Pc(1-), 53466-60-7; Cl₂Fe^{III}Pc(1-), 50298-30-1; Br₂Fe^{III}Pc(1-), 53432-31-8; Cl₂Co^{III}Pc(1-), 47838-42-6; Br₂Co^{III}Pc(1-), 39019-60-8; ClMn^{III}Pc(2-), 53432-32-9; BrMn^{III}Pc(2-), 53432-33-0; ClZn^{II}Pc(1-), 53466-59-4.

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- (73) **Note Added in Proof.** The electrochemical oxidation of zinc phthalocyanine yields a paramagnetic, presumably monomeric, radical species [D. Lexa and M. Reix, *J. Chim. Phys.*, **71**, 517 (1974)].

Contribution of the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

New Multidentate Ligands. XIV. Aqueous Coordination Chemistry of *N,N'*-Bis(2-hydroxybenzyl)ethylenediamine-*N,N'*-bis(methylenephosphonic) Acid¹

D. T. MacMILLAN, I. MURASE, and A. E. MARTELL*

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The synthesis and the metal-proton-ligand aqueous solution equilibria of the novel ligand *N,N'*-bis(*o*-hydroxybenzyl)-ethylenediamine-*N,N'*-bis(methylenephosphonic) acid (HBEDPO), H₆L, are described. At 25° and $\mu = 0.100$, the logarithms of the ligand protonation constants are 13.57, 11.48, 9.67, 7.24, 5.31, and 3.61 and the stability constants for the 1:1 metal chelates, ML⁴⁻, where M = Cu(II), Ni(II), Co(II), Ca(II), and Mg(II), are respectively 24.0, 17.9, 18.0, 8.36, and 7.95 log units. In addition to the "normal" species, ML⁴⁻, other protonated forms MHL³⁻, MH₂L²⁻, MH₃L⁻ and MH₄L were found to be present with Cu(II), Ni(II), and Co(II), while MHL³⁻ and MH₂L²⁻ are present in the Ca(II) and Mg(II) systems. The protonated Fe(III) chelate is very insoluble and dissolves only after 6 mol of base/mol of iron(III) ($\alpha = 6$) have been added. The zinc chelate is insoluble between 1 and 4 mol of base/mol of ligand. The potentiometric data for copper and nickel show an inflection at $\alpha = 4$ indicating essential completion of interaction with HBEDPO at that point. In contrast, cobalt(II) and zinc(II) show complete interaction, only at and above $\alpha = 5$. Calcium(II) and magnesium(II) show the least affinity, with no interaction with the ligand below $\alpha = 3$. The spectrophotometric study of the copper(II) and cobalt(II) systems indicates appreciable phenolate coordination with these two metal ions even below $\alpha = 4$, indicating a structural rearrangement equilibrium involving the phenolate groups and the other metal ion coordinating groups in the ligand.

Introduction

The recent investigation² of the metal-binding characteristics of *N,N'*-bis(2-hydroxybenzyl)ethylenediamine-*N,N'*-diacetic acid (HBED) shows that its affinities for many metal ions in aqueous solution are considerably higher for this ligand than for EDTA. This increase in stability has been interpreted as being the result of a very favorable arrangement of its six donor groups (two basic nitrogens, two carboxylate groups, and two *o*-phenolate groups) about the metal ion as well as the high affinity of the phenolate group for certain metal ions. EHPG (*N,N'*-ethylenebis(2-hydroxyphenylglycine)),³ a structurally related ligand also containing these same six coordinating groups, shows similar high stability, although somewhat lower than that of HBED because of a less favorable steric arrangement of these donor groups. It has already been established^{4,5} in these laboratories that the stability constants, upon substituting phosphonate for the carboxylate groups in EDDA (ethylenediamine-*N,N'*-diacetic acid) to obtain

EDDPO (ethylenediamine-*N,N'*-bis(methylphosphonic) acid, are slightly better for copper(II) or slightly lower for nickel(II) and cobalt(II), compared to the model EDDA, even though the lowering of the basicities of the nitrogen atoms present in the ethylenediamine framework by the phosphonate groups would predict considerably lower metal ion affinities. Thus it seems that phenolate and phosphonate groups could be effective donors in multidentate ligands having suitable molecular geometry.

The present work was undertaken to combine these less conventional functional groups (*i.e.*, the phosphonate and phenolate groups) into a multidentate ligand having a sterically favorable arrangement of donor groups. The structure of the ligand meeting these objectives, *N,N'*-bis(*o*-hydroxybenzyl)ethylenediamine-*N,N'*-bis(methylenephosphonic) acid, is given by formula I. Because of structural similarity of I with HBED² and the fact that the latter has the highest affinity for iron(III) of any ligand previously known, the new mul-