

Table I. Atomic Coordinates in Crystalline $OP(O_2C_5H_{10})(O_2C_{14}H_9)$ with Standard Deviations in Parentheses

atom ^a	10 ⁴ x	10 ⁴ y	10 ⁴ z
P	3705.3 (8)	9352 (4)	6464 (1)
O ₁	4282 (2)	11056 (9)	6914 (2)
O ₂	3394 (2)	8405 (8)	7207 (3)
O ₃	3202 (2)	11156 (8)	5869 (2)
O ₄	3899 (2)	7387 (10)	5978 (3)
O ₅	2876 (2)	7287 (11)	4590 (3)
C ₁	4209 (3)	12610 (15)	7634 (5)
C ₂	3990 (3)	11257 (12)	8355 (4)
C ₃	3341 (3)	10033 (15)	7925 (5)
CM ₁	4501 (4)	9383 (17)	8789 (5)
CM ₂	3885 (4)	13043 (16)	9040 (5)
CP ₁	2543 (3)	10523 (14)	5407 (4)
CP ₂	2421 (3)	8748 (14)	4809 (4)
CP ₃	1748 (3)	8290 (15)	4313 (4)
CP ₄	1627 (4)	6440 (18)	3686 (5)
CP ₅	984 (5)	5969 (20)	3192 (5)
CP ₆	481 (5)	7420 (22)	3330 (6)
CP ₇	594 (4)	9174 (20)	3944 (6)
CP ₈	1243 (3)	9724 (14)	4469 (5)
CP ₉	1384 (3)	11568 (15)	5133 (5)
CP ₁₀	902 (4)	13045 (18)	5367 (6)
CP ₁₁	1059 (4)	14858 (18)	5971 (6)
CP ₁₂	1712 (4)	15340 (16)	6417 (5)
CP ₁₃	2201 (3)	13927 (15)	6215 (4)
CP ₁₄	2052 (3)	12028 (13)	5606 (4)

^a Atoms are labeled to agree with Figure 1.**Table II.** Selected Bond Lengths (Å) and Angles (Deg) in $OP(O_2C_5H_{10})(O_2C_{14}H_9)$ with Standard Deviations in Parentheses

Bond Lengths			
P-O ₁	1.559 (5)	O ₁ -C ₁	1.452 (8)
P-O ₂	1.558 (4)	C ₁ -C ₂	1.516 (8)
P-O ₃	1.577 (4)	C ₂ -C ₃	1.522 (9)
P-O ₄	1.443 (5)	C ₃ -O ₂	1.463 (8)
Bond Angles			
O ₁ -P-O ₂	107.5 (2)	P-O ₁ -C ₁	118.8 (4)
O ₁ -P-O ₃	102.2 (3)	O ₁ -C ₁ -C ₂	112.9 (6)
O ₁ -P-O ₄	113.6 (3)	C ₁ -C ₂ -C ₃	107.8 (6)
O ₂ -P-O ₃	107.5 (2)	C ₂ -C ₃ -O ₂	112.1 (5)
O ₂ -P-O ₄	111.3 (3)	C ₃ -O ₂ -P	119.1 (4)
O ₃ -P-O ₄	114.2 (3)	P-O ₃ -CP ₁	124.1 (4)

lengths and angles are listed in Table II. A complete compilation of bond parameters for the nonhydrogen atoms, thermal parameters, and refined parameters for hydrogen atoms are provided as supplementary material.

In compound I the six-membered ring is in a distorted chair conformation with the P=O bond occupying an equatorial position. The chair conformation is partly flattened at the O-P-O end of the ring. The dihedral angle between planes O₁C₁C₃O₂ and O₁PO₂ is 32.2°. Between planes O₁C₁C₃O₂ and C₁C₂C₃ the angle is 51.6°. In the comparable cyclohexane molecule, these dihedral angles are 49.2°. ⁵

This ring flattening observed in related compounds has been attributed to two factors: ^{1e}

1. The C-O-P ring angles are much larger than the C-C-C ring angles of cyclohexane, resulting in ring flattening at the phosphorus end. In compound I, these C-O-P angles are about 119°, as compared to the C-C-C angles of 111.5° in cyclohexane.

2. Steric interactions between the axial group bonded to phosphorus and the axial methylene hydrogens of the ring may result in a flattening of the ring at the phosphorus end. The phenanthrene quinone ring in the axial site in compound I is both large and planar. It avoids these steric interactions not only by the above ring flattening mechanism but also by a tilting of the quinone ring with respect to the O₁C₁C₃O₂ plane

(the dihedral angle between these planes being 50°). As a result of this tilting, the shortest distance between the axial ring hydrogens and the quinone ring hydrogens is 2.5 Å, slightly larger than the sum of the van der Waals radii (2.4 Å). ⁶

Perhaps the most unique feature of I is the presence of a strong intramolecular hydrogen bond between O₄ and O₅. The following distances are observed: O₄...O₅ = 2.635 (6) Å; O₅-H₁₉ = 0.82 (7) Å, O₄...H₁₉ = 1.82 (6) Å. The O₄-H₁₉-O₅ angle is 176 (9)°. For O-H...O hydrogen bonds, the O...O distances fall in the range 2.5-3.5 Å while the O-H...O angles are between 140 and 180°. ⁷ This hydrogen bond results in the formation of a seven-membered ring, with the O₅, CP₂, CP₁ and O₃ atoms lying in a plane and the P, O₄ and H₁₉ atoms lying on one side of this plane.

A short intermolecular distance of 3.26 Å is present between the O₅ atom and the C₃ atom in the symmetry-related molecule at $x, \frac{3}{2}-y, z-\frac{1}{2}$. The C₃-H₉...O₅ angle is 150°, with the H₉...O₅ distance being 2.30 Å. A survey of C-H...O hydrogen bonds in crystals, where the carbon is either part of a CH, CH₂, or CH₃ group, gives the C...O distances in the range 3.00-3.24 Å, with the C-H...O angle between 102.6 and 173.3°. ⁸

Acknowledgment. The generous support for this investigation by the National Institutes of Health is gratefully acknowledged. We are indebted to the University of Massachusetts Computing Center for generous allocation of computing time on the CDC 6600 system. We are also indebted to Professor Roberta O. Day for helping with the X-ray interpretation.

Registry No. I, 74577-94-9; phenanthrene quinone, 84-11-7; phenyl 2,2-dimethyl-1,3-propanediol cyclic phosphite, 3057-08-7.

Supplementary Material Available: A compilation of observed and calculated structure factor amplitudes, bond parameters for nonhydrogen atoms, thermal parameters, and refined hydrogen parameters for 2-oxo-2-(phenanthrenequinoxyl)-5,5-dimethyl-1,3,2-dioxaphosphorinane (10 pages). Ordering information is given on any current masthead page.

(6) Pauling, Linus. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.

(7) Jeffrey, G. A.; Takagi, S. *Acc. Chem. Res.* **1978**, *11*, 264.

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Electrosynthesis of the Metal Phthalocyanine Complexes

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Since their discovery in the early 1930s the metal phthalocyanine complexes (MPc) have been intensively investigated and have found industrial application as pigments and dyeing agents, owing to their intense colors, chemical inertness, and thermal stability. Because of their resemblance to the porphyrins, an understanding of the physical and chemical behavior of the MPc might provide an important clue to the biological process. The metal phthalocyanines can be prepared by various methods; however, the routes based upon phthal-

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(1) (a) Provincial Hsinchu Teachers' College, Hsinchu, Taiwan. (b) Department of Chemistry, Polytechnic Institute of New York.

Table I. Analytical Data for the Metal Phthalocyanine Obtained from Electrolysis

reagent	solvent	product	% C ^a	% H ^a	% N ^a	current efficiency, %
CuSO ₄	CH ₃ OH	CuPc	66.45 (66.72)	2.92 (2.78)	19.41 (19.45)	38.9
NiSO ₄	CH ₃ OH	NiPc	67.23 (67.28)	2.82 (2.80)	19.45 (19.63)	37.9
Co ^{II} (OAc)	CH ₃ OH	CoPc	67.22 (67.25)	2.91 (2.80)	19.55 (19.67)	11.2
MgSO ₄	CH ₃ OH	MgPc	71.53 (71.60)	3.03 (2.98)	20.81 (20.88)	11.2
Pb(NO ₃) ₂	C ₂ H ₅ OH	PbPc	53.21 (53.39)	2.32 (2.22)	21.65 (21.79)	15.6
	CH ₃ OH	H ₂ Pc	74.06 (74.71)	4.01 (3.50)	21.10 (21.79)	15.8
UO ₂ (OAc)	DMF	H ₂ Pc				9.5

^a Calculated figures in parentheses.

onitrile and its derivatives in the presence of metal halides, hydrides, or oxides as templates are most commonly used.² The reactions typically require relatively high temperature for a prolonged time. Although the template reaction might play a key role in the cyclization reaction leading to the macrocyclic phthalocyanines, very little work has been done toward the elucidation of the reaction mechanisms.

Little has been reported concerning the electrosynthesis of MPc. Recently we have employed a two-compartment cell separated with an ion-exchange membrane for the reduction of uranium ions in an aqueous solution.³ A similar cell with a slight modification has been found to be useful for the synthesis of MPc in organic solvents under ambient conditions. A simple route for some divalent metal phthalocyanines is demonstrated here.

Experimental Section

The electrolytic cell is similar to that described elsewhere.³ However, since the present investigation was conducted in organic solutions, the cell was made of Pyrex glass instead of acrylic resin. A Nafion cation-exchange membrane (Du Pont Co.) was fixed between the cathode and anode compartments. A Hastelloy C and a Pt plate of 3 × 3 cm² served as cathode and anode, respectively. The cathode was pretreated with dilute HNO₃ before use. The electrolysis was conducted with a Nichia HP-L5A potentiostat equipped with a Nichia N-CR646 digital coulometer, and the cathode potential was monitored with a calomel electrode. A total of 100 mL of catholyte containing 0.02 M tetrabutylammonium perchlorate or sodium xylenesulfonate and 0.02 M phthalonitrile was placed in the cathode compartment, whereas 100 mL of the alcoholic solution of the respective metallic salts served as anolyte. The solubility of the respective salt is the main consideration taken in the choice of the solvents. The electrolyses were carried out at -1.6 V vs. SCE and 60–100 mA for 3–5 h at room temperature. The catholyte gradually became red-brown in the course of the electrolysis. The electrolysis was terminated when a substantial decrease of current was noticed. The solid formed in the cathode compartment was filtered and washed with 2 M NaOH, hot water, and acetone, and the solution was Soxhlet extracted with ethanol to remove the impurities and finally sublimed in vacuo.

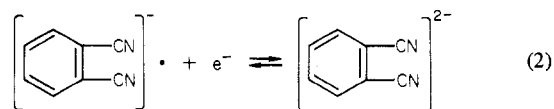
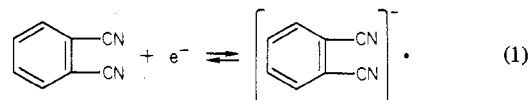
The cyclic voltammogram was obtained on the same potentiostat equipped with a Nichia S-5A potential programmer using a Pt wire as working electrode, at a scan rate of 50 mV s⁻¹. Infrared spectra were obtained on a Perkin-Elmer 580 IR spectrophotometer. The solvents were distilled prior to use. All chemicals used were of CP grade, and no further purification was made. The analytical data for the major products, MPc, together with the working conditions are shown in Tables I and II. The IR spectra are in good agreement with published data.^{4–7}

Table II. Infrared Data (KBr Pellet)

CuPc	PbPc	H ₂ Pc	MgPc	CoPc	NiPc
1590 w	1608 m	1600 m	1609 s	1525 s	1600 m
1509 sh	1484 vs	1510 s	1586 s	1425 s	1500 s
1464 s	1404 m	1495 s	1481 s	1332 vs	1426 s
1333 vs	1330 vs	1360 sh	1408 s	1219 s	1333 s
1287 s	1282 vs	1315 s	1325 s	1171 vs	1288 s
1164 s	1160 m	1295 s	1160 m	1126 vs	1164 s
1120 vs	1114 vs	1195 m	1112 s	1098 vs	1120 vs
1090 vs	1078 s	1160 m	1082 s	1080 m	1086 vs
1068 s	1059 vs	1156 s	1052 s	1055 sh	915 s
900 s	1002 w	1122 s	942 m	773 s	876 m
775 s	951 s	1010 vs	888 m	760 vs	780 s
760 vs	889 vs	870 vs	870 m	726 vs	755 s
728 vs	815 w	782 m	805 w	570 m	731 s
	780 s	775 s	774 m	513 m	578 m
	771 vs	745 s	752 s		521 m
	742 vs	724 s	725 vs		
	643 m	688 m	646 w		
	481 m	672 m	506 w		
		620 m	434 w		

Results and Discussions

The earlier polarographic study on phthalonitrile in DMF gave two half-wave potentials at -2.12 and -2.76 V, corresponding to two successive reductions⁸ (eq 1 and 2). Our



cyclic voltammetric result showed that phthalonitrile in ethanol had two peaks at -1.1 and -1.62 V. In a blank run a single peak at -1.1 V was also observed. The peak at -1.62 V might correspond to the first wave in the polarographic investigation, i.e., the formation of the nitrile anion radical. No other peaks were observed, because the decomposition of ethanol ensued.

That the electrolysis took place at a potential of -1.6 V, irrespective of the metal ions, might be indicative of the importance of the anion radicals in the cyclization leading to the formation of MPc, whereas the metal ion was not involved in the electrochemical reaction. It might be that the metal ion which played the role of a template migrated from the anode compartment and reacted with two anion radicals generated at the cathode and two phthalonitrile molecules (eq 3). Very low yields of NiPc and CuPc were obtained, when the metal ions were placed together with the phthalonitrile in the cathode compartment. Most of the metals were observed to deposit on the cathode surface; therefore the anion radicals should be generated prior to migration of the metal ions into the cathode compartment. Phthalimide arising from the hydrolysis of the

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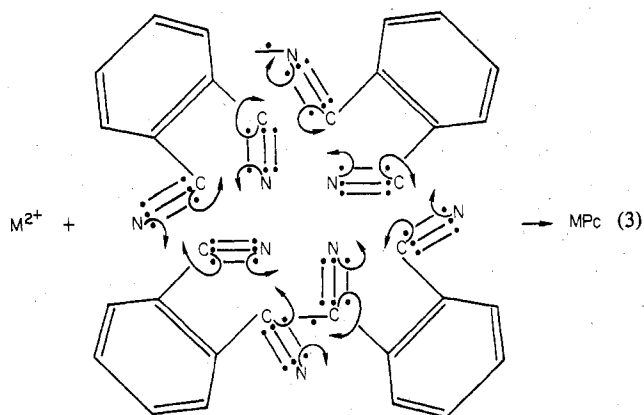
(4) The current efficiency is calculated on the basis of the assumption that two nitrile anion radicals, i.e., two electrons, are necessary in the formation of MPc.

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anion radical was the main byproduct separated and identified.

Finally, it is interesting to note that the attempts using UO_2^{2+} and Pb^{2+} ions in CH_3OH failed to produce MPc but produced instead H_2Pc .

The successful preparation of MPc using a two-compartment electrolytic cell described above might provide a valuable clue to the hitherto not well-elucidated mechanisms of the template reaction leading to the MPc. We are presently exploring the use of this method for a variety of reactions.

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Registry No. CuPc, 147-14-8; NiPc, 14055-02-8; CoPc, 3317-67-7; MgPc, 14325-24-7; PbPc, 15187-16-3; H_2Pc , 574-93-6; phthalonitrile, 91-15-6.

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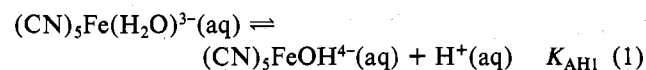
Acidity of the Aquo Ligand in Aquopentacyanoferrate(II)

Geoffrey Davies* and Alfred R. Garafalo

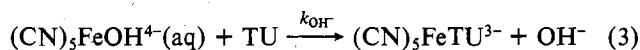
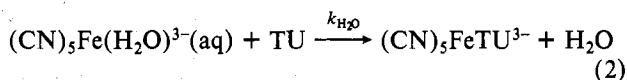
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The determination of the acidities of aquo ligands coordinated to low-spin transition-metal centers is a valuable contribution in view of their likely importance in both chemical and biochemical systems.

In a recent paper, Macartney and McAuley¹ reported a pH dependence in the visible spectrum of 10^{-4} M aqueous solutions of aquopentacyanoferrate(II) which led to an estimate of $K_{AH1} = (1.37 \pm 0.20) \times 10^{-8}$ M for equilibrium 1 at 25 °C.



The distribution of iron(II) species derived from eq 1 was found to correspond closely to the pH profiles for the rates of substitution of thioureas and *N*-alkylthioureas, TU, at these proposed pentacyanoferrate(II) centers at the $(2-4) \times 10^{-5}$ M concentration level, leading to the conclusion¹ that reactions 2 and 3 proceed at significantly different rates. We cannot support the assignment of these data to reactions of monomeric aquopentacyanoferrate(II) centers.



Our earlier work² describes the experimental problems encountered in making spectral measurements at the 10^{-4} M iron(II) concentration levels used by Macartney and McAuley,¹ even when *analyzed samples* of the precursor³ $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$ are used.⁴ In particular, we never observed the isobestic spectral behavior anticipated from eq 1 from pH 6 to 1 M NaOH, and the time dependence of the spectra under these conditions was highly dependent on how the solutions were made up and treated.^{2,6}

Reproducible rate data for substitution and redox reactions at monomeric aquopentacyanoferrate(II) centers can be obtained under carefully controlled conditions.² Published data actually indicate that 10^{-4} M aqueous solutions of pentacyanoferrate(II) species generated by rapid aquation³ of $(\text{CN})_5\text{FeNH}_3^{3-}$ contain both monomeric and dimeric species in time- and pH-dependent proportions.² Reactions of 10^{-4} M solutions containing such species with substituting ligands like X = pyrazine, nitrite, or *tert*-butyl hydroperoxide are easily distinguishable from their different rates.² The fastest process corresponds to reactions of monomeric species, as indicated by the observation of only one substitution process, at an identical rate, at $[\text{Fe}^{II}]_{\text{TOTAL}} \lesssim 10^{-5}$ M under identical pseudo-first-order conditions. Absorbance changes associated with formation of the common product $(\text{CN})_5\text{FeX}^{n-}$ from reaction of X with monomeric and dimeric species present at higher concentration levels can be used to estimate the proportions of these species under a particular set of conditions.² At $[\text{Fe}^{II}]_{\text{TOTAL}} \lesssim 10^{-5}$ M, where monomers greatly predominate, absorption spectra exhibit a maximum at 440 nm which is unaffected by acidity variations in the pH 6-9 range.⁷

The kinetics of substitution at monomeric $(\text{CN})_5\text{Fe}(\text{H}_2\text{O})^{3-}$ centers have been investigated with a wide range of ligands X over the pH range 5.5-13. Except for X = pyrazine, which appears to be a special case,^{2,8} a pH dependence of the rate is observed only for protic ligands, e.g., H_2O_2 , where the dependence can be accounted for.² Our list² also includes kinetic data for substitution of thiourea,¹ which reacts with $(\text{CN})_5\text{Fe}(\text{H}_2\text{O})^{3-}$ in a second-order reaction whose constant

- (1) D. H. Macartney and A. McAuley, *Inorg. Chem.*, **18**, 2891 (1979).
- (2) G. Davies and A. R. Garafalo, *Inorg. Chem.*, **15**, 1101 (1976), and references therein.
- (3) J. M. Malin and H. E. Toma, *Inorg. Chem.*, **12**, 2080 (1973).
- (4) Analyzed samples of $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$ (Fisher Certified) which had been recrystallized from concentrated ammonia solution and vacuum-dried were used throughout the studies reported in ref 2. We are concerned that no analytical data for this precursor are reported in ref 1 in view of difficulties we have experienced in reproducing published syntheses for a number of pentacyanoiron(II) species. If Brauer's procedure⁵ is followed, it is likely that the product will contain significant proportions of monomeric and dimeric pentacyanoferrate(II) salts, in addition to $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$, since the ammonia ligand is known to be labile.³
- (5) G. Brauer, "Handbook of Preparative Inorganic Chemistry", 2nd ed., Academic Press, New York, 1965, p 1511.
- (6) Macartney and McAuley mention no time dependence of their spectra. As noted earlier,^{2,7} the rate of change of the spectra of 10^{-4} M $(\text{CN})_5\text{Fe}(\text{H}_2\text{O})^{3-}$ solutions was highly dependent on pH even under closely controlled conditions.
- (7) A. R. Garafalo, Ph.D. Thesis, Northeastern University, Boston, 1976.
- (8) As reported earlier,² a 15% lower rate constant for formation of the pyrazine complex is observed on decreasing the reaction pH below 9.5. We were careful to discount the apparent $K_{AH1} \approx 2 \times 10^{-7}$ M (eq 1) suggested by the data (see ref 2 and text of this paper) and noted other peculiarities of this particular substituting ligand system which make it unsuitable as a means of determining K_{AH1} . The rate of the corresponding reaction with 2-methylpyrazine is essentially independent of acidity in the range pH 6-13 (A. Kwan and J. M. Malin, unpublished observations).

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