

Table III. Important Bond Lengths (Å) and Angles (deg)

bond	av ^a	range	
Zr-O	2.081 (43)	1.913 (20)-2.212 (16)	
P1-O	1.544 (20)	1.501 (24)-1.588 (19)	
P2-O	1.507 (32)	1.418 (18)-1.550 (19)	
O7-H1	1.008 (31)		
O10-H1	1.565 (32)		
O7-O10 (short)	2.461 (21)		
angle	av ^a	range	
O-Zr-O	88.9 (16)	81.0-95.5	
O-P-O	109.2 (16)	102.7-121.7	
O7-H1-O10	145.2 (28)		
K coord ^b	length	K coord ^b	length
K1-O3	2.744 (15)	K2-O1	2.688 (21)
K1-O5	2.834 (18)	K2-O6	2.974 (15)
K1-O7	2.814 (25)	K2-O7	2.895 (20)
K1-O10	2.794 (21)	K2-O10	3.019 (26)

^aThe esd of N observations is calculated as $[\sum |av - obsd|^2 / N(N-1)]^{1/2}$. ^bAll two contacts.

Å using a five-term refinable background function. No thermal diffuse scattering (TDS) background corrections were included in this function. No corrections were made for multiple scattering as the oscillatory nature of the background, characteristic of multiple scattering, was not observed. Refinement proceeded slowly until the [001] preferred orientation vector was assumed to have a Gaussian distribution about the axis of the sample. This preferred orientation factor is refinable as part of the least-squares technique. Refinement of better crystal and atom parameters now proceeded smoothly to convergence, at which stage a difference Fourier synthesis revealed the position of the hydrogen atom. Refinement of all parameters (including the hydrogen) was conducted to convergence, following which the non-hydrogen atoms were refined with anisotropic temperature factors.

Results and Discussion

Details of the refinement parameters are given in Table I while the positional parameters are contained in Table II. The final difference plot for the neutron Rietveld refinement is shown in Figure 1, and a summary of the bond distances and angles is given in Table III. Comparison of the results with those obtained in the X-ray study^{1,5} reveals agreement within 3σ of the quoted esd's except for two K-O interatomic distances that exceed the 3σ criterion by about 10%. It should be remembered that the subject compound is layered so that the intensity data suffer from severe preferred orientation effects. Better handling of this error would undoubtedly improve matters considerably.

The hydrogen atom occupies a position between the P-O⁻ (O7 and O10) groups, as predicted previously.⁵ It is bonded to O7 at a distance of 1.0 Å and hydrogen bonds to O10 at 1.57 Å. The hydrogen bond angle is 145°. This positioning of the hydrogen atom makes O7 four-coordinate since it bridges two potassium ions as well as bonding to hydrogen and phosphorus. The arrangement is a highly distorted tetrahedron.

It appears from this study that the structure of an unknown compound can be deduced from a minimal data set (40-50 reflections) by using deconvoluted powder X-ray intensity data to obtain a starting model for both X-ray and neutron Rietveld refinement with satisfactory results. We are in the process of applying this technique to a variety of compounds.

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Registry No. ZrKH(PO₄)₂, 54408-13-8.

Supplementary Material Available: Listings of positional parameters and anisotropic temperature factors (1 page). Ordering information is given on any current masthead page.

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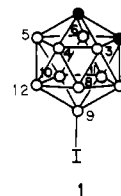
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9-Iodo-*o*-carborane¹

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Although the synthesis of 9-iodo-*o*-carborane (**1**) has been described in the literature³ we have experienced difficulty in making this useful intermediate in the synthesis of 9-alkyl-*o*-carboranes.⁴ We describe here a simple modification of the published³ procedure that gives high yields of pure **1**.



The published synthesis calls for treatment of *o*-carborane with I₂ and AlCl₃ in CCl₄ for 3 h.³ We found that this procedure leads to a mixture of halogenated carboranes containing, along with the desired **1** (28%), 9-chloro-*o*-carborane (**2**, 13%), 9,12-dichloro-*o*-carborane (**3**, 11%), 9-chloro-12-iodo-*o*-carborane (**4**, 28%), and 9,12-diiodo-*o*-carborane (**5**, 20%). That chlorinated carboranes should be present was perhaps not unexpected given the report⁶ that *o*-carborane could be chlorinated in the presence of CCl₄ and AlCl₃.

Compounds **2**, **3**, and **5** are known, and their physical and spectroscopic properties could be compared to those reported in the literature (**2**,⁷ **3**,⁹ **5**,^{7b,10}). Compound **4** is new and was identified by high-resolution mass spectrometry and ¹¹B NMR spectroscopy.

We found the composition of products not to vary with time, but reducing the temperature to 40 °C did increase the percentage of **1**, although the other halogenated carboranes were still present. We were finally successful in obtaining a high yield of pure **1** by combining low temperature with a change of solvent. Methylene chloride seemed less likely than CCl₄ to contribute a chlorine to the reaction pool, and this proved to be the case.⁸ Treatment of *o*-carborane with iodine and AlCl₃ in CH₂Cl₂ gave **1** in good yield and high purity. Traces of **5** and a compound believed to be

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9-iodo-12-(chloromethyl)-*o*-carborane are formed but are easily removed by a single crystallization.

Experimental Section

Iodination of *o*-Carborane in CCl₄. A solution of 3.3 g of I₂, 2.1 g of *o*-carborane, and 0.3 g of AlCl₃ in 80 mL of CCl₄ was refluxed under N₂ for 3 h. The mixture was poured into 100 mL of distilled water and the organic layer separated and dried over MgSO₄. The filtered solution was concentrated at the water pump to give a residue that was analyzed by gas chromatography on a 6 ft × 1/4 in. 15% OV 101 on Gaschrom Q 60/80 column at 200 °C. Preparative gas chromatography gave known compounds **1**, **2**, **3**, and **5** as well as the unknown **4** (mp 163–164 °C). Precise mass for B₁₀C₂ClH₁₀I: calcd, 306.0448; found, 306.0442 ± 0.003.

Iodination of *o*-Carborane in CH₂Cl₂. A mixture of 10.35 g of *o*-carborane and 18.2 g of I₂ was refluxed in 250 mL of CH₂Cl₂ with a catalytic amount of AlCl₃ for 16.5 h. The clear yellow solution was poured into distilled water and the organic layer separated. The water was extracted once with 100 mL of ether, and the combined organic layers were dried over MgSO₄. The filtered solvent was removed at the water pump and the residue recrystallized from hexane to give 18 g of **1** (93%; mp 125–126 °C, lit.^{7b,10} mp 122–123 °C).

Registry No. **1**, 17830-03-4; **2**, 19513-12-3; **3**, 98330-58-6; **4**, 98330-59-7; **5**, 17702-35-1; *o*-carborane, 16872-09-6.

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Kinetics of Reduction of Cobalt(III) Porphyrins by Fe^{II}-EDTA²⁻

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Kinetics studies on the mechanisms of reduction of cobalt(III) porphyrins to their divalent states have employed chromium(II),¹⁻³ vanadium(II),² dithionite,^{4,5} hexaammineruthenium(II),^{2,6} radiolysis-produced radicals,⁷ superoxide,⁸ cobalt(II) porphyrins,⁹ and metalloporphyrin anion radicals.⁷ In contrast to many of these reagents, iron(II) ethylenediaminetetraacetate (Fe^{II}-EDTA²⁻) is a weak reductant that will attack only the coordinated metal ion and not reduce the metalloporphyrin ring system itself. We report the kinetics of reduction of five water-soluble positively and negatively charged cobalt(III) porphyrins with Fe^{II}-EDTA²⁻. The observed rate laws are a function of the porphyrin charge type, and the corresponding Co^{III/II}-porphyrin self-exchange rate constants are calculated.

Experimental Section

The cobalt(III) forms of tetrakis(4-sulfonatophenyl)porphyrin (TPPS), tetrakis(*N,N,N*-trimethylammonium)porphyrin (TAP), and tetrakis(*N*-methyl-4-, -3-, or -2-pyridinium)porphyrin (TMPyP(X)) were prepared and purified by literature methods.¹⁵⁻¹⁷ Iron(II) in the form

Table I. Kinetic Data for Co^{III}-P/Fe-EDTA²⁻ Reactions^a

compd	E ^{ox} , V ^b	pK ₃	k _D , M ⁻¹ s ⁻¹ ^c	K, M ⁻¹ ^c	k _C , s ⁻¹
Co ^{III} -TPPS ³⁻	+1.06	4.6	2.0 × 10 ³	<10	
Co ^{III} -TAP ⁵⁺	+1.17	3.6	7.3 × 10 ³	460	1.6 × 10
Co ^{III} -TMPyP(3) ⁵⁺	+1.19	1.8	7.8 × 10 ⁴	530	1.5 × 10 ²
Co ^{III} -TMPyP(4) ⁵⁺	+1.19	1.4	8.7 × 10 ⁴	470	1.8 × 10 ²
Co ^{III} -TMPyP(2) ⁵⁺		-0.9	1.4 × 10 ⁵	770	1.8 × 10 ²

^a Conditions: *I* = 0.5 (NaCl/HCl); pH 5; 25 °C. ^b Potential for the Co^{III}-P/Co^{II}-P⁺ oxidation vs. NHE. ^c k_D = *A*, K = *B*, and k_C = *A/B* from eq 1.

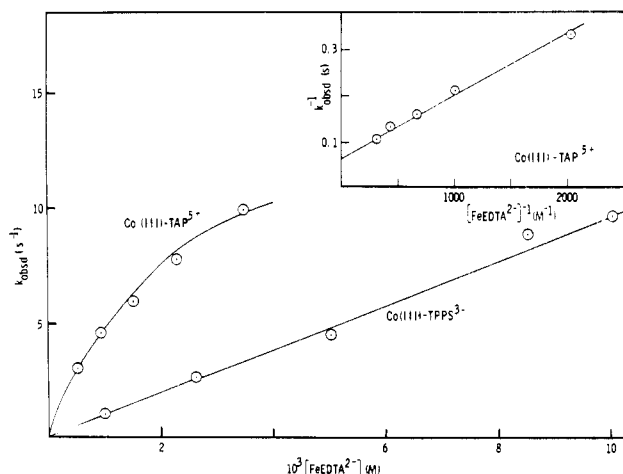


Figure 1. Graphs of k_{obs} vs. Fe-EDTA²⁻ for the Co^{III}-P/Fe-EDTA²⁻ reactions at 25 °C (Co^{III}-TPPS³⁻ data at *I* = 0.1, Co^{III}-TAP⁵⁺ data at *I* = 0.5). The insert is a plot of k_{obs} vs. [Fe-EDTA²⁻]⁻¹.

FeCl₂·4H₂O or Fe(NH₄)₂(SO₄)₂·6H₂O (both gave the same kinetic results) was dissolved in deaerated solutions and analyzed spectrophotometrically with *o*-phenanthroline.¹⁸ A stoichiometric amount of standardized deaerated EDTA was added to produce the air-sensitive Fe-EDTA²⁻. All reagents were handled in Hamilton glass syringes. The reactions were run under chromous scrubbed argon at 25 °C and followed on a Durrum-Gibson stopped-flow apparatus. The ionic strength (*I*) was maintained with NaCl/HCl, and 10⁻² M HOAc/NaOAc was the buffer. Ac and cyclic voltammetry¹⁹ using a polished glassy-carbon electrode and SCE was done on N₂-deaerated solutions at pH 4.5 (*I* = 0.1 M HCl/KCl, 0.01 M HOAc/NaOAc).

Results

While other groups have reported reduction potentials in aqueous solution for Co^{III/II} porphyrins with TMPyP(4) ($E^\circ = +0.42$ V vs. NHE²⁰), TPPS (-0.41 V²¹), TAP (+0.38 V²²), we found only broad, ill-defined peaks in the expected potential ranges using slow-sweep ac voltammetry. However, one-electron-oxidation waves assigned to the ligand oxidation process Co^{III}-P = Co^{III}-P⁺ + e⁻ were readily observed under the same conditions, and such E° values are listed in Table I. Cyclic voltammetry studies gave one-electron-reduction potentials of 0.00 V for Mn^{III/II}-TMPyP(4) and -0.21 V for Mn^{III/II}-TPPS at pH 4.5.

The kinetics were followed at the Soret bands for the cobalt porphyrins. Under pseudo-first-order conditions with at least a 50-fold excess of Fe-EDTA²⁻ to Co(III)-P (ca. 10⁻⁶ M), the reactions were all first order in porphyrin for over 90% of the reaction, with an observed rate constant k_{obs} . For Co(III)-TPPS³⁻

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