

9; [Co(DSB)<sub>3</sub>]<sup>3+</sup>, 106735-54-0; [Co(DSB)<sub>3</sub>]<sup>+</sup>, 106735-55-1; [Co(MeDSB)<sub>3</sub>]<sup>3+</sup>, 106735-56-2; [Co(MeDSB)<sub>3</sub>]<sup>+</sup>, 106735-57-3; poly-[Fe(DSB)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>, 106761-91-5; poly-[Fe(DSB)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub>, 106761-92-6; poly-[Fe(MeDSB)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>, 106761-93-7; poly-[Fe(MeDSB)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub>, 106761-94-8; poly-[Co(DSB)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub>, 106761-96-0; poly-[Co(DSB)<sub>3</sub>]-

(PF<sub>6</sub>)<sub>3</sub>, 106761-97-1; poly-[Co(DSB)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub>, 106761-98-2; Re(CO)<sub>5</sub>Cl, 14099-01-5; (bpy)<sub>2</sub>RuCl<sub>2</sub>, 15746-57-3; (NH<sub>4</sub>)<sub>2</sub>OsCl<sub>6</sub>, 12125-08-5; Os(bpy)<sub>2</sub>Cl<sub>2</sub>, 15702-72-4; Pt, 7440-06-4; 4,4'-dimethyl-2,2'-bipyridine, 1134-35-6; 4-methylbenzaldehyde, 104-87-0; benzaldehyde, 100-52-7; iodine, 7553-56-2; formic acid, 64-18-6; carbon dioxide, 124-38-9.

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## Synthesis, Aggregation, Electrocatalytic Activity, and Redox Properties of a Tetranuclear Cobalt Phthalocyanine

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Using pentaerythritol as a framework, it has been possible to synthesize a tetranuclear phthalocyanine with a spiro type linkage. Electrochemical and spectroelectrochemical data are presented for the cobalt complex in the Co<sup>III</sup>Pc(-2), Co<sup>II</sup>Pc(-2), Co<sup>I</sup>Pc(-2), Co<sup>III</sup>Pc(-1), Co<sup>II</sup>Pc(-1), and Co<sup>I</sup>Pc(-3) oxidation levels. The Co(II) species aggregates very strongly, dimerizing with an aggregation constant in *o*-dichlorobenzene of  $2.4 \times 10^5 \text{ M}^{-1}$ , 2 orders of magnitude greater than for the parent Co<sup>II</sup>TNPc. Monolayers of the cobalt(II) species laid upon an ordinary pyrolytic graphite electrode are shown to electrocatalytically reduce oxygen more efficiently than previously described analogous mononuclear and binuclear phthalocyanines. The Co(II) tetranuclear species disproportionates into a 1:1 mixture of Co(I) and Co(III) species upon reaction with hydroxide ion in a nondonating or weakly donating solvent. A film containing [Co<sup>I</sup>TrNPc(-2)]<sub>4</sub><sup>4+</sup> reduces nitrite ion in NaOH slowly, with oxidation to the Co(II) tetranuclear species.

Metal phthalocyanines (generally containing either cobalt or iron) have been implicated as electrocatalysts for the reduction of oxygen at a fuel cell cathode.<sup>2-6</sup> Ill-defined "dimeric" and polymeric phthalocyanines<sup>6,7</sup> are revealed to be more effective oxygen reduction electrocatalysts than their mononuclear congeners perhaps because the electrocatalyst can participate in a concerted fashion with the multielectron reduction (two electrons to hydrogen peroxide or four to water). This prompted us to design a series of polynuclear phthalocyanines, with the expectation that a multielectron redox catalyst might be designed, having enhanced properties relative to those of the common one-electron electrocatalysts.

The preparations of trinuclear<sup>8</sup> and binuclear phthalocyanines covalently linked by one,<sup>8</sup> two,<sup>9</sup> four,<sup>9</sup> and five-atom<sup>10,11</sup> bridges have recently been described. These phthalocyanines are linked

at one benzene ring, the remaining benzene rings being substituted with neopentoxy groups to confer solubility in organic solvents. A preliminary discussion of the oxygen reduction capability of cobalt derivatives of these species has been reported.<sup>12</sup>

In general, we noted that these binuclear cobalt species were indeed more effective oxygen reduction catalysts to hydrogen peroxide (as indicated by kinetic current evaluation, of monolayers on ordinary pyrolytic graphite, immersed in 0.1 M NaOH) than their mononuclear analogues, though the improvement was not dramatic.

To be effective, it was necessary to reduce these electrocatalysts to form binuclear Co(I) species. Mechanistically, oxygen activation is believed to occur through formation of binuclear Co(III) peroxy species, but the degree of coupling between the halves of the binuclear species appears minimal, though not negligible, in the binuclear complexes.

We wished to prepare multinuclear phthalocyanines in which the phthalocyanine groups would be constrained to be cofacial. The previously prepared binuclear and trinuclear compounds could partially attain a cofacial conformation but were free to rotate so that a dynamic equilibrium existed between intramolecularly aggregated phthalocyanines in cofacial and isolated conformations. We believed that a tetranuclear phthalocyanine based on a pentaerythritol nucleus (Figure 1) could provide a multinuclear phthalocyanine in which two coupled pairs of phthalocyanine moieties would be so constrained by the geometry of the system, effectively a spiro arrangement, that the tetranuclear phthalocyanine would always consist of two pairs of phthalocyanines in a cofacial conformation.

This then suggested that a tetranuclear cobalt(II) phthalocyanine might be reduced to Co(I) with the possibility of four Co(I) atoms then being oxidized in a concerted fashion to Co(II) (four electrons) or Co(III) (eight electrons). Indeed the cobalt

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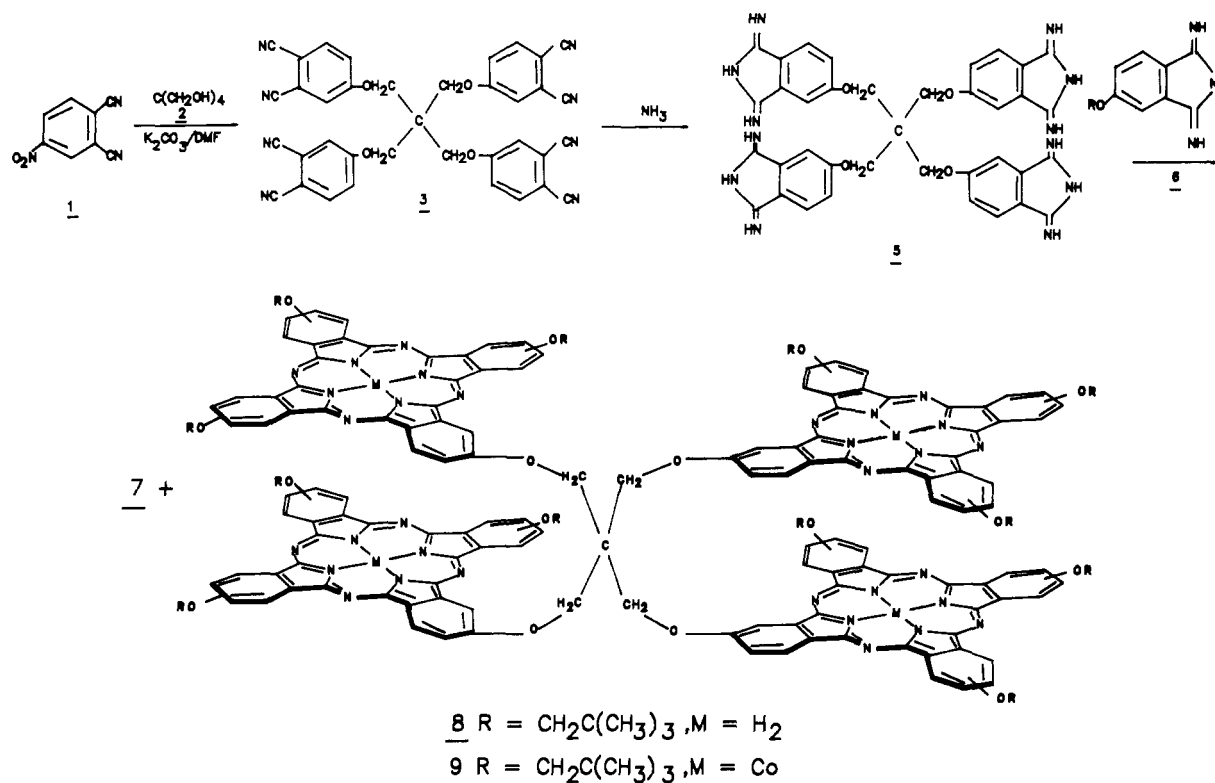


Figure 1. Scheme of preparation.

complex of this tetranuclear species does prove to be a better oxygen reduction catalyst than its binuclear analogues and confirms the strategy that increased coupling between the cobalt halves does improve oxygen reduction efficiency. However, only two-electron reduction processes have yet been identified.

Rather unexpectedly, the tetranuclear species is subject to aggregation to a much greater degree than the binuclear species under similar conditions. This provides the possibility that an octanuclear bisaggregated species might prove to be a useful electro- or photocatalyst, with an appropriate central metal.

### Experimental Section

**Materials.** Tetrabutylammonium perchlorate (TBAP; Kodak) was recrystallized from absolute ethanol and dried in a vacuum oven at 50 °C for 2 days. Toluene (Aldrich, Gold Label), *o*-dichlorobenzene (DCB; Aldrich, Gold Label), *N,N*-dimethylformamide (DMF; Aldrich, anhydrous Gold Label), tetrabutylammonium hydroxide ((TBA)OH; 1 M in methanol, Kodak), tetraethylammonium chloride ((TEA)Cl; Aldrich), and polystyrene (p(sty); Scientific Products) were used as supplied. Water was purified by double distillation over  $\text{KMnO}_4$ , followed by passage through a Barnstead organic removal cartridge and two Barnstead mixed-resin Ultrapure cartridges. Fisher Certified 1 M sodium hydroxide was diluted as required for the aqueous oxygen reduction studies. All other chemicals used were of analytical grade.

Argon gas (Linde) was purified by passage through heated copper filings, anhydrous  $\text{CaSO}_4$  (Drierite), molecular sieves (BDH type 3A), and glass wool. Oxygen gas (Linde) was purified by passage through anhydrous  $\text{CaSO}_4$ , NaOH pellets (AnalaR analytical grade), anhydrous  $\text{CaSO}_4$ , molecular sieves, and glass wool.

Ordinary pyrolytic graphite (OPG), obtained from Union Carbide, was used as the electrode material for the oxygen reduction studies. The graphite was mounted in Teflon to expose a circular area of 0.493  $\text{cm}^2$ .

**Methods.** Mass spectra were obtained courtesy of the Midwest Center for Mass Spectrometry, Lincoln, NE (with thanks to K. B. Tomer) by using a system described in full elsewhere.<sup>8-11</sup>

Electronic spectra were recorded with a Hitachi Perkin-Elmer Microprocessor Model 340 spectrometer. Cyclic and differential pulse voltammetry were performed with a Princeton Applied Research (PAR) Model 174A polarographic analyzer coupled to a PAR Model 175 universal programmer. Measurements were carried out under an atmosphere of nitrogen in a Vacuum Atmospheres Drilab. A platinum disk described by the cross-sectional area of a 27-gauge wire (area ca.  $10^{-3} \text{cm}^2$ ), sealed in glass, was used as the working electrode, a platinum wire as the counter electrode, and a silver wire as the quasi-reference electrode.

Potentials were referenced internally to the ferrocenium/ferrocene ( $\text{Fc}^+/\text{Fc}$ ) couple.<sup>13</sup>

Potential scans for oxygen reduction were performed with a Pine Instruments RD3 potentiostat and the rotation studies with a Pine Instruments PIR rotator. The cell for the adsorption experiments employed a medium frit to separate a silver-wire quasi-reference electrode from the main chamber containing the OPG working electrode and a platinum-wire counter electrode. The cell for the aqueous studies comprised a separate chamber for each electrode, with a Luggin capillary extending from the reference chamber to the proximity of the OPG surface. For the aqueous experiments, the potential was measured vs. a saturated calomel electrode (SCE).

Spectroelectrochemical measurements were made with an optically transparent thin-layer electrode (OTTLE) utilizing a gold minigrid (500 lines/in.), with platinum counter and silver quasi-reference electrodes<sup>14</sup> designed to fit into the sample compartment of the spectrometer. Solutions for electrochemistry or spectroelectrochemistry contained 0.3 M TBAP as the supporting electrolyte and  $2.5 \times 10^{-5}$  and  $(2-5) \times 10^{-5}$  M  $[\text{Co}^{\text{II}}\text{TrNPc}]_4$ , respectively.

For the adsorption studies, ca.  $2.5 \times 10^{-5}$  M  $[\text{Co}^{\text{II}}\text{TrNPc}]_4$  solutions were prepared in DCB, with 0.1 M TBAP. After the solution was purged with argon for 1 h, the OPG working electrode was scanned at a rate of 100 mV/s over the potential range 0.00 to +1.00 V vs. the silver wire. Adsorbed layers on OPG were obtained by cycling until the anodic and cathodic peak currents associated with the adsorbed species remained constant over 5 min of continuous scanning. When this condition was satisfied, the adsorbed layer was assumed to have reached a steady coverage. Scans at various rates were then recorded to determine the surface coverage.

The catalytic efficiency of the  $[\text{Co}^{\text{II}}\text{TrNPc}]_4$  adsorbed on the OPG electrode was investigated as follows: the modified electrode was removed from the phthalocyanine solution, washed with ethanol and then with water, and placed in the cell for the aqueous studies. The 0.1 M NaOH solution in this cell had been purged with oxygen for several hours to ensure saturation. The electrode was then scanned over the range 0.00 to -1.00 V vs. SCE at a rate of 10 mV/s for rotation rates ranging from 400 to 10000 rpm. After each scan, the electrode was held at 0.00 V for 60 s to permit the rotation rate to be changed for the next scan.

Films of  $[\text{Co}^{\text{II}}\text{TrNPc}]_4$  in p(sty) were prepared by dissolving the phthalocyanine in a solution of p(sty) in toluene and (diffusion) pumping off the solvent from the surface of a quartz cuvette. The cuvette was

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attached to a degassable cell, such that degassed solutions (prepared by repeated freeze-pump-thaw cycles) could be contacted with the film on the quartz surface without breaking the vacuum seal. Films containing Co(I) and Co(III) phthalocyanine species were obtained by adding a 300-fold excess of (TBA)OH to the p(sty)-[Co<sup>II</sup>TrNPc]<sub>4</sub> solution prior to evaporation.

Solutions for aggregation studies were prepared by dilution of a freshly prepared stock solution of phthalocyanine. Spectra were recorded immediately after each dilution, and solutions were shielded from room light to minimize any photochemical decomposition of the phthalocyanine.

**Synthesis.** Coupling of 4-nitrophthalonitrile (1) and pentaerythritol (2) using anhydrous potassium carbonate in DMF by methods previously described<sup>11,15,16</sup> yielded tetrakis[(3,4-dicyanophenoxy)methyl]methane (3) in 36% yield and bis(3,4-dicyanophenyl) ether (4) as a minor byproduct. Compound 3 was only sparsely soluble in organic solvents and hence was converted into the tetrakis(diiminoisindoline) 5 by a procedure slightly modified from that previously published.<sup>11,17,18</sup> A mixed condensation of the tetrakis(diiminoisindoline) 5 with an excess of the diiminoisindoline 6 derived from 4-neopentoxypthalonitrile gave by methods<sup>8-11</sup> previously described 2,9,16,23-tetraeneopentoxypthalocyanine (7) in 61% yield and tetrakis[(9,16,23-trieneopentoxypthalocyanin-2-yl)oxy)methyl]methane (8) in 12% yield after the use of flash chromatography<sup>19</sup> followed by gel permeation chromatography.<sup>20</sup> As phthalocyanines aggregate, it was difficult to remove the last traces of 7 from 8 on silica, but the use of gel permeation chromatography ensured that the bulky 8 eluted before any residual traces of 7 and that 8 was completely free of 7. In addition, mass spectroscopic analysis of 8 did not exhibit the presence of mononuclear 7. A tetracobalt(II) derivative (9) was readily prepared from 8.<sup>8-11</sup>

**Tetrakis[(3,4-dicyanophenoxy)methyl]methane (3).** A solution of 4-nitrophthalonitrile (1) (10.50 g, 60.69 mmol), pentaerythritol (2) (1.02 g, 7.47 mmol), and anhydrous potassium carbonate (12 g, 86.96 mmol) in 40 mL of dry DMF was stirred at room temperature under exclusion of moisture (CaCl<sub>2</sub> drying tube) for 7 days. The potassium carbonate was added in portions. The reaction mixture was filtered and washed thoroughly with ethyl acetate. The filtrate was diluted with ethyl acetate to form a precipitate, which was filtered off to yield 2.5 g of the desired product. The crude product was recrystallized from acetonitrile to give, in 36% yield, 1.70 g of tetrakis[(3,4-dicyanophenoxy)methyl]methane (3) as slightly yellow crystals, mp 253–254 °C. IR (KBr): 3080 (m), 2240 (s), 1600 (vs), 1560 (s), 1490 (s), 1470 (s), 1310 (vs), 1250 (vs), 1100 (s), 1040 (s), 1030 (s), 840 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (in CD<sub>3</sub>CN): δ 7.80 (d, J = 8.8 Hz, 1 H), 7.47 (d, J = 2.5, 1 H), 7.31 (dd, J = 8.8, 2.5 Hz, 1 H), 4.43 (s, 2 H). MS (*m/e* (relative intensity, %)): 640 (M<sup>+</sup>, 8), 497 (M<sup>+</sup> - 143, 27), 157 (92), 144 (100), 127 (51). Anal. Calcd for C<sub>37</sub>H<sub>20</sub>N<sub>8</sub>O<sub>4</sub>: C, 69.37; H, 3.15; N, 17.49. Found: C, 69.61; H, 3.22; N, 17.77.

The ethyl acetate filtrate was washed with water, dried over anhydrous magnesium sulfate, and evaporated to give 2.3 g of crude bis(3,4-dicyanophenyl) ether (4) as a byproduct. The crude product was purified by silica gel column chromatography using acetonitrile-benzene (1:7) as the eluting solvent. It was then recrystallized from a mixture of acetonitrile-water to give in 14% yield 1.18 g of bis(3,4-dicyanophenyl) ether (4), mp 259–260 °C (lit.<sup>15</sup> mp 254–256 °C).

**Preparation of the Tetrakis(diiminoisindoline) Compound 5.** Gaseous ammonia was bubbled vigorously into a slurry of 258 mg of tetrakis[(3,4-dicyanophenoxy)methyl]methane (3) in 80 mL of a 3:1 mixture of dry methanol-dioxane containing 50 mg of sodium methoxide. After the ammonia was introduced for 3 h at room temperature, a very slight green color developed. The mixture was then heated to reflux while gaseous ammonia was continuously introduced to it for an additional 5 h. After the mixture was cooled to room temperature and the solvent was evaporated, the crude isindoline was used directly in the condensation reaction without further purification. The crude isindoline did not exhibit nitrile absorption in its IR spectrum.

**Tetrakis[(9,16,23-trieneopentoxypthalocyanin-2-yl)oxy)methyl]methane (8), [H<sub>2</sub>TrNPc(-2)]<sub>4</sub>.** The two crude diiminoisindolines 5 and 6, obtained from 324 mg (0.51 mmol) of 3 and 9.0 g (42 mmol) of 4-neopentoxypthalonitrile, respectively, were heated at 165 °C (oil bath) in 30 mL of 2-(dimethylamino)ethanol for 60 h under an argon atmosphere. After it was cooled to room temperature, the dark blue mixture

was diluted with water and the residue filtered and washed thoroughly with water, followed by methanol, until the filtrate was colorless. The residue was then dried and continuously extracted with methanol in a Soxhlet apparatus for 8 h until the extract was almost colorless. This process removed most of the green and yellow impurities. Further purification of the product was achieved by flash chromatography<sup>19</sup> using a 5 cm wide column packed with silica gel 15 cm high. The crude product was preadsorbed on silica and eluted with 2000 mL of toluene-hexanes (4:1) to give 4.76 g of the mononuclear 2,9,16,23-tetraeneopentoxypthalocyanine 7. Further elution with 700 mL of toluene yielded an additional 714 mg of mononuclear 7. Thus the total yield of the mononuclear 7 was 5.47 g (61%). Further elution with 2000 mL of toluene-2-methoxyethanol (100:1) yielded after solvent evaporation a mixed mononuclear-tetranuclear fraction. This fraction was further purified by gel permeation chromatography<sup>20</sup> using a 5 cm wide column packed with SX1 BioBeads 50 cm high. The mononuclear-tetranuclear fraction was eluted with freshly distilled tetrahydrofuran (THF). The faster moving band consisting of tetranuclear species was further purified by flash chromatography using toluene followed by toluene-2-methoxyethanol (100:1) as eluant and gave 200 mg of the tetranuclear 8 (12%) while the slower moving band of the mononuclear species was not further purified. IR (KBr): 3300 (w), 1620 (vs), 1485 (vs), 1245 (vs), 1100 (s), 1020 (vs), 750 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (in CDCl<sub>3</sub>): δ 1–2 (broad m, *t*-Bu), -3 (broad s, NH). UV-vis (*o*-dichlorobenzene; λ<sub>max</sub> (log ε)): 338 (5.12), 642 (5.00), 674 (4.96), 715 (4.86) nm. MS (*m/e* (relative intensity, %)): 3221.6 (48.1), 3220.6 (75), 3219.6 (100), 3218.6 (82), 3217.6 (M<sup>+</sup>, 59). Anal. Calcd for C<sub>193</sub>H<sub>196</sub>N<sub>32</sub>O<sub>16</sub>: C, 71.99; H, 6.14; N, 13.92. Found: C, 72.26; H, 6.44; N, 13.65.

**Tetrakis[(cobalt(II) 9,16,23-trieneopentoxypthalocyanin-2-yl)oxy)methyl]methane (9), [Co<sup>II</sup>TrNPc(-2)]<sub>4</sub>.** A mixture of metal-free tetranuclear species (8) (30 mg, 0.0093 mmol), anhydrous cobalt(II) chloride (60 mg, 0.46 mmol), 2-methoxyethanol (3 mL), and toluene (7 mL) was heated at 120 °C for 20 h under an argon atmosphere. The solution was cooled and the product was purified by flash chromatography using a 1.5 cm wide column packed with silica gel 8 cm high, by direct application of the mixture to the column. Elution with toluene gave, after solvent evaporation, 28.5 mg (89%) of the cobalt tetranuclear species 9 as a very dark blue shining solid. IR (KBr): 1615 (vs), 1240 (s), 1100 (s), 750 (m) cm<sup>-1</sup>. UV-vis (*o*-dichlorobenzene, aggregated; λ<sub>max</sub> (log ε)): 380 (sh, 4.56), 625 (4.89), 676 (4.85) nm. MS (*m/e*): 3447.2 (M<sup>+</sup>). Anal. Calcd for C<sub>193</sub>H<sub>188</sub>N<sub>32</sub>O<sub>16</sub>Co<sub>4</sub>: C, 67.24; H, 5.50; N, 13.00; Co, 6.84. Found: C, 67.50; H, 5.74; N, 12.54; Co, 6.50.

## Results and Discussion

With use of the procedures discussed elsewhere,<sup>8-11</sup> four *o*-benzenedinitrile (phthalonitrile) units were attached to a pentaerythritol residue and converted to the tetrakis(diiminoisindoline) 5, which was then condensed with excess 5-neopentoxydiiminoisindoline to obtain the desired metal-free product, [H<sub>2</sub>TrNPc(-2)]<sub>4</sub> (8) (Figure 1). Under the conditions of synthesis, a mixture of isomers is obtained in which the neopentoxy groups are substituted randomly in the 4- or 5-positions of the unlinked benzene rings. Characterization of the product was achieved through elemental analysis, NMR and IR spectroscopy, and, most importantly, the observation of a parent ion at *m/e* 3217.6 by FAB mass spectroscopy. Aspects of the emission of the metal-free species will be discussed elsewhere.<sup>21</sup> It appears facile to incorporate metal ions into this species by standard methods. Here we are concerned with the characterization of the tetranuclear cobalt trineopentoxypthalocyanine [CoTrNPc]<sub>4</sub> in its various oxidation states and comparison with the mononuclear tetraeneopentoxypthalocyanine (CoTNPc) as a control molecule.

**Aggregation Phenomena.** Aggregation of phthalocyanines in solution to form dimers and higher aggregated forms has been extensively studied, mainly for the tetrasulfonated phthalocyanines (TsPc) in aqueous and alcohol solution<sup>22</sup> with some work also

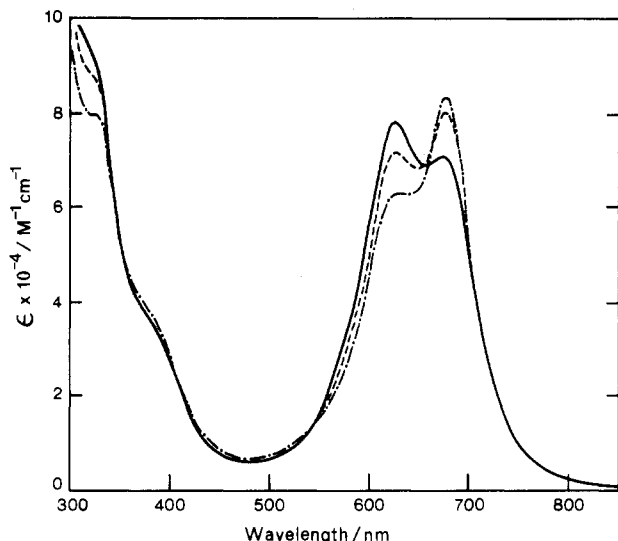
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**Table I.** Electronic Absorption Maxima of [CoTrNPc]<sub>4</sub> Species

species <sup>a</sup>	$\lambda_{\text{max}}$ , nm ( $10^{-4}\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> ) <sup>d</sup>									
[Co <sup>II</sup> TrNPc(-2)] <sub>4</sub> <sup>b</sup>	326 (8.41)	380 sh						625 sh		676 (9.61)
[Co <sup>I</sup> TrNPc(-3)] <sub>4</sub> <sup>b</sup>	315 sh		476 sh	520 s						672 w
[Co <sup>I</sup> TrNPc(-2)] <sub>4</sub> <sup>b</sup>	312 (15.4)	350 sh	435 sh	472 (7.07)	524 w	564 w	590 (3.49)	643 (5.22)	680 sh	708 (9.39) 1040 (0.2)
[Co <sup>II</sup> TrNPc(-2)] <sub>4</sub>	325 sh	380 sh						625 (7.82)		676 (7.15)
[Co <sup>II</sup> TrNPc(-1)] <sub>4</sub> <sup>b</sup>	320 (5.96)	365 sh		496 (3.44)			590 (3.89)			690 (3.83) 975 br (0.4)
[Co <sup>III</sup> TrNPc(-1)] <sub>4</sub> <sup>b</sup>	330 s	370 sh				554 m				780 w
[Co <sup>III</sup> TrNPc(-2)] <sub>4</sub> <sup>b,c</sup>	336 (12.0)	350 sh	395 sh					614 (6.02)		676 (14.9)

<sup>a</sup>In DCB solution with  $2 \times 10^{-5}$  M [CoTrNPc]<sub>4</sub> and 0.3 M TBAP, except where noted. <sup>b</sup> $5 \times 10^{-7}$  M [CoTrNPc]<sub>4</sub> in DCB. <sup>c</sup> $2 \times 10^{-5}$  M [CoTrNPc]<sub>4</sub> with 0.3 M TBAP in DMF. <sup>d</sup>Abbreviations: sh = shoulder; w = weak; m = medium; s = strong; br = broad.



**Figure 2.** Electronic absorption spectra of [Co<sup>II</sup>TrNPc(-2)]<sub>4</sub> in DCB at concentrations of  $2.3 \times 10^{-5}$  M (—),  $3.8 \times 10^{-6}$  M (---), and  $1.5 \times 10^{-6}$  M (-·-·).

having been done on tetraalkylphthalocyanines (PcX<sub>4</sub>) in organic solvents.<sup>23</sup> Typically the aggregate has a Q-band absorption at 30–50 nm to the blue of the unaggregated species Q-band. Before a detailed study of this new species can be carried out, it is important to know to what extent it too is susceptible to aggregation. Clearly an aggregated dimeric species would contain eight potentially active cobalt atoms, which could perturb the chemistry of the monomeric species in a dramatic fashion.

Usually, an equilibrium exists between the monomer (M) and dimer (D) of the type



where  $K_D$  is the dimerization constant, given by  $K_D = C_D/C_M^2$ , and  $C_M$  and  $C_D$  are the concentrations of monomer and dimer, respectively, at a given total concentration,  $C_T$ , of phthalocyanine.

Figure 2 shows the UV-visible absorption spectrum of [Co<sup>II</sup>TrNPc(-2)]<sub>4</sub> in DCB at concentrations in the range of  $10^{-5}$ – $10^{-6}$  M. The Q-band region consists of two bands: a band at 676 nm, at the same position as the Q band of mononuclear Co<sup>II</sup>TNPc(-2),<sup>24,25</sup> and a band at 625 nm, which increases in intensity relative to that of the 676-nm band with increasing phthalocyanine concentration, indicating a substantial formation of aggregates of the tetranuclear molecules. Deviation from Beer's law is seen for the 676-nm band at concentrations greater than  $7 \times 10^{-7}$  M, a remarkably low concentration.

The 625-nm band arises from the coupling through space of the transition moments of the excited Q states between the

phthalocyanine units of the aggregated molecules (exciton coupling<sup>26</sup>). In the limit of strict fourfold symmetry, two pairs of doubly degenerate states will then arise, with transitions to the two upper states allowed, resulting in a blue-shifted band relative to the monomer Q band. In very dilute solution ( $5 \times 10^{-7}$  M), where only monomeric [Co<sup>II</sup>TrNPc(-2)]<sub>4</sub> exists, a substantial amount of absorption still occurs at 625 nm (ca. 50% relative to the band at 676 nm), compared with mononuclear Co<sup>II</sup>TNPc(-2) in DCB. This is the result of intramolecular coupling between the phthalocyanine units of the tetranuclear molecule, also giving rise to absorption at 625 nm through exciton coupling, as previously observed for metal-free binuclear TrNPc complexes.<sup>26</sup> It may be useful to view the molecule as containing, per molecule, some fraction of coupled and some fraction of uncoupled rings.

Electronic absorption data for monomeric [Co<sup>II</sup>TrNPc(-2)]<sub>4</sub> are given in Table I. Aggregation of [Co<sup>II</sup>TrNPc(-2)]<sub>4</sub> occurs at much more dilute solution than for Co<sup>II</sup>TNPc(-2), which exhibits deviation from Beer's law only at concentrations greater than  $1 \times 10^{-5}$  M.<sup>27</sup>

In the case of a simple monomer-dimer equilibrium, a plot of  $\log C_M$  against  $\log C_D$  will give a straight line with a slope of 2, as has been found for Co<sup>II</sup>TNPc in DCB<sup>27</sup> and several mononuclear PcX<sub>4</sub> complexes in organic solution.<sup>23</sup> Calculation of the values of  $C_M$  and  $C_D$  at any given total concentration is normally carried out by using the relative intensities at the wavelengths of the Q bands of the monomeric and dimeric species.<sup>22,23,28</sup> However, for a tetranuclear phthalocyanine, this approach is only valid for the case of a dimer formed through coupling between all four phthalocyanine rings of each molecule, which is improbable for the [Co<sup>II</sup>TrNPc(-2)]<sub>4</sub> molecule because of stereochemical constraints. For dimeric aggregates formed by bridging between less than the total number of phthalocyanine rings, only coupled rings will contribute to the dimer spectrum. The monomer spectrum will thus contain contributions from both the uncoupled rings of the dimer aggregates and from the undimerized monomeric molecules, i.e.

$$C_M' = C_M + C_M'' \quad (2)$$

where  $C_M'$  is the apparent monomer concentration calculated from the absorption spectrum and  $C_M''$  is the effective concentration of monomer resulting from the uncoupled dimer aggregate rings. The apparent dimer concentration,  $C_D'$ , is then given by the relationship

$$C_D' = (C_T - C_M')/2 \quad (3)$$

Note for further clarification that if the dimer were formed by coupling between all four rings of each tetranuclear molecule,  $C_M = C_M'$  and  $C_D = C_D'$ .

Values of  $C_M'$  and  $C_D'$  were calculated for total concentrations of  $7.6 \times 10^{-7}$  to  $2.3 \times 10^{-5}$  M in DCB using the approximation method of West and Pearce<sup>28</sup> (Table II). The spectrum at  $5 \times 10^{-7}$  M was taken as that of the pure unaggregated monomer (see Table I). A plot of  $\log C_D'$  vs.  $\log C_M'$  gave a slope of 1.6 (Figure 3a), indicating that indeed a dimer is not formed by coupling

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**Table II.** Dimerization Constants,  $K_D$ , of  $[\text{Co}^{\text{II}}\text{TrNPc}]_4$  in DCB at 20 °C<sup>a</sup>

$10^6 C_T$ , M	$L$ , cm	$\text{OD}_{\text{obsd}}$ (676 nm)	$\text{OD}_M$	$10^6 C_M'$ , M	$10^6 C_D'$ , M	$10^6 C_M^b$ , M	$10^6 C_D^b$ , M	$10^{-5} K_D$ , M <sup>-1</sup>
23.4	1.0	1.66	1.33	13.5	4.95	3.60	9.90	7.64
9.43	1.0	0.704	0.632	6.41	1.51	3.40	3.02	2.62
3.77	1.0	0.300	0.281	2.85	0.459	1.93	0.919	2.46
0.76	2.0	0.140	0.135	0.69	0.038	0.610	0.075	2.01

<sup>a</sup> Legend:  $L$  = Cell path length;  $\text{OD}_{\text{obsd}}$  = observed optical density;  $\text{OD}_M$  = corrected optical density of the monomeric species (see text). <sup>b</sup>  $C_M$  and  $C_D$  are calculated for a dimer coupled through two phthalocyanine rings of each monomeric unit, from the relationships  $C_M = 2C_M' - C_T$  and  $C_D = (C_T - C_M)/2$ .

**Table III.** Electrochemical Data for  $[\text{Co}^{\text{II}}\text{TrNPc}]_4$  in *o*-Dichlorobenzene,  $E_{1/2}$  (V), with Reference to the Ferrocenium/Ferrocene Couple<sup>a,b</sup>

$\text{Co}^{\text{III}}\text{Pc}(0)/\text{Co}^{\text{III}}\text{Pc}(-1)$	$\text{Co}^{\text{III}}\text{Pc}(-1)/\text{Co}^{\text{II}}\text{Pc}(-2)$	$\text{Co}^{\text{II}}\text{Pc}(-2)/\text{Co}^{\text{I}}\text{Pc}(-3)$	$\text{Co}^{\text{II}}\text{Pc}(-2)/\text{Co}^{\text{I}}\text{Pc}(-3)$	$\text{Co}^{\text{I}}\text{Pc}(-2)/\text{Co}^{\text{I}}\text{Pc}(-3)$
+0.86	+0.50	+0.05	-0.92	-2.06

<sup>a</sup>  $\text{Fc}^+/\text{Fc}$  lies at +0.40 V vs NHE. Data were collected by differential pulse polarography at 2 mV/s. <sup>b</sup> Conditions:  $[(\text{Co}^{\text{II}}\text{TrNPc})_4] = 2.5 \times 10^{-5}$  M;  $[\text{TBAP}] = 0.3$  M.

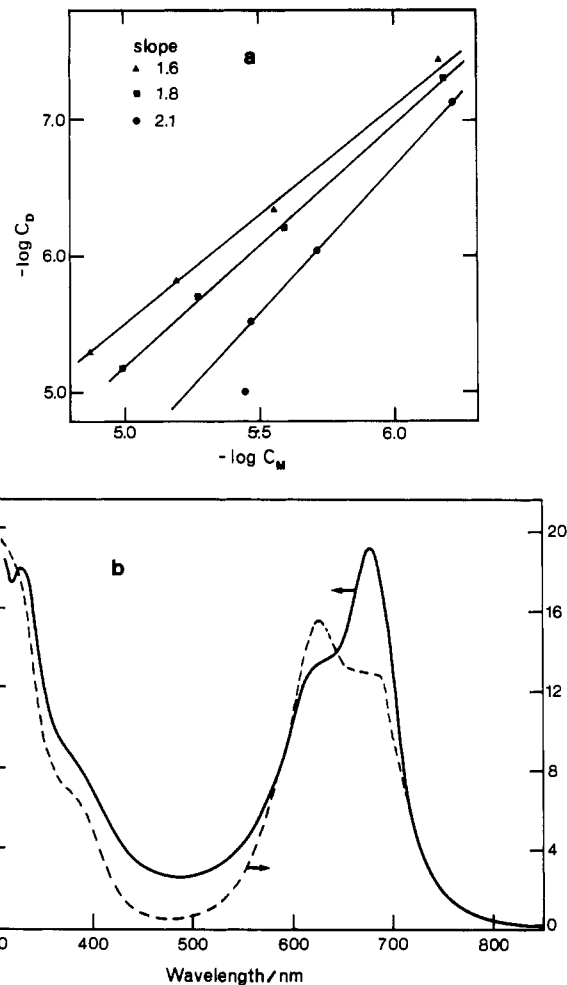
between all four rings of each tetranuclear molecule. The values of  $C_M'$  were used to calculate  $C_M$  and  $C_D$  for possible coupling configurations involving dimeric and trimeric  $[\text{Co}^{\text{II}}\text{TrNPc}]_4$  species and plots of  $\log C_D$  vs.  $\log C_M$  made in each case.

The closest fit to a slope of 2, expected for a monomer-dimer equilibrium, was found to be given by the dimer formed through coupling between two rings of each tetranuclear molecule, which gave a slope of 2.1 (see Figure 3a and Table II). The next best fit was for the dimer involving aggregation via three rings of each molecule, giving a slope of 1.8 (also shown in Figure 3a), though this is also difficult to conceive of geometrically. The true situation will inevitably be more complex than simple coupling between two rings of each molecule: any association between the rings via aggregation will, to a lesser extent, also affect those rings that are not directly bridged. Hence, the unaggregated rings will also show a small coupling effect. This is apparent in the observed slope of 2.1, which indicates a net coupling effect of greater than two rings per tetranuclear molecule. At the highest concentration studied ( $2.3 \times 10^{-5}$  M), significant deviation from the straight-line plot is seen, possibly indicating formation of higher aggregates than dimers. An average value of  $2.4 \times 10^5 \text{ M}^{-1}$  is obtained for  $K_D$  (Table II). This is 2 orders of magnitude higher than the dimerization constant measured for mononuclear  $\text{Co}^{\text{II}}\text{TNPC}$  in DCB ( $2.6 \times 10^3 \text{ M}^{-1}$ ).<sup>27</sup> Using the aggregation constant data, it is possible to deduce the spectrum of the pure dimeric aggregate; this is shown in Figure 3b.

One might speculate why such a large and cumbersome molecule as the tetranuclear species should aggregate to such a large degree. Since two Pc rings, per tetranuclear species, are involved, one may imagine that a pair of rings from one molecule interpolate between a pair of rings in another molecule to create a stack of four aggregatively coupled Pc rings. This would provide an interaction nominally twice as strong as the simple aggregation between monomer units.

**Electrochemistry.** Cyclic voltammetry of  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$  in DCB over the potential range +1.0 to -2.1 V, vs.  $\text{Fc}^+/\text{Fc}$ , gave a series of shallow anodic and cathodic peaks, consisting of three oxidation and two reduction couples. The half-wave potentials measured by differential pulse polarography (Table III) are similar to those measured for the related mononuclear  $\text{Co}^{\text{II}}\text{TNPC}(-2)$  and binuclear  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_2$  complexes,<sup>25</sup> although the waves were much less well defined than for the cyclic voltammogram of  $\text{Co}^{\text{II}}\text{TNPC}$ . The poorly defined waves obtained for the tetranuclear complex are likely the result of aggregation effects certainly present at the concentrations employed for the electrochemical measurements (e.g. see ref 29).

No evidence was seen for any splitting of the redox peaks, such as observed for cofacial and "clamshell" cobalt porphyrins.<sup>30</sup> It



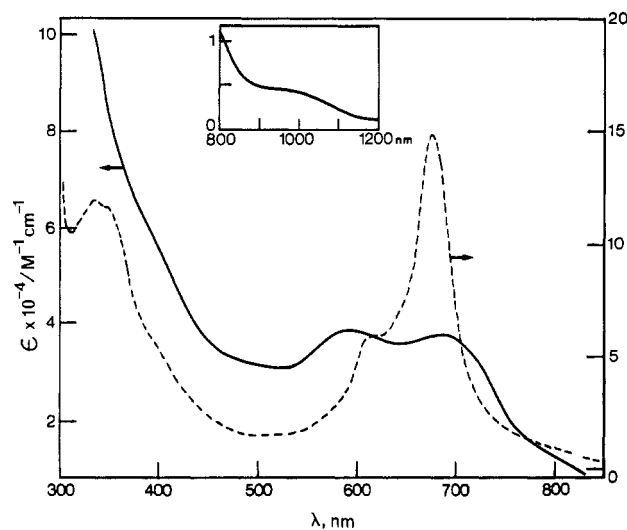
**Figure 3.** (a) Plots of  $-\log C_D$  vs.  $-\log C_M$  for  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$  in DCB. Values of  $C_M$  and  $C_D$  are calculated for the conditions of coupling between four ( $\blacktriangle$ ), three ( $\blacksquare$ ), and two ( $\bullet$ ) phthalocyanine rings of each unit of  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$ . (b) Experimental spectrum of monomeric  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$  (—) and calculated spectrum of dimeric aggregated  $[(\text{Co}^{\text{II}}\text{TrNPc}(-2))_4]_2$  (---) in DCB.

appears that the four  $\text{Co}^{\text{II}}\text{TNPC}$  units of each molecule are reduced or oxidized simultaneously. By analogy to the case for  $\text{Co}^{\text{II}}\text{TNPC}$ ,<sup>25</sup> the redox couples can be assigned as metal or ligand processes (Table III), assuming each peak corresponds to four "simultaneous" one-electron transfers. In agreement, the spectroelectrochemical studies (below) showed no evidence for any mixed-valence states, and the spectra obtained were those expected for complete oxidation or reduction of the four  $\text{Co}^{\text{II}}\text{TrNPc}$  units at each redox couple.

**Spectroelectrochemistry.** As indicated above, the visible spectrum of the monomeric  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$  species is dominated by an intense Q band at 676 nm, resulting from the  $a_{1u} \rightarrow e_g(\pi^*)$  transition, similar to the case for mononuclear  $\text{Co}^{\text{II}}\text{TNPC}$ . In

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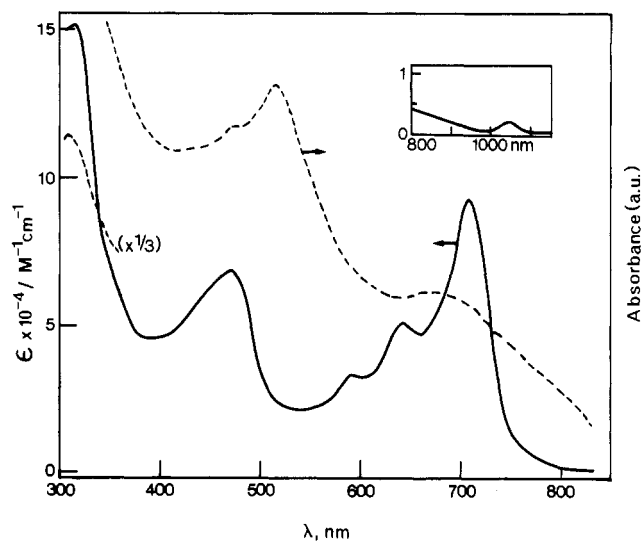
**Figure 4.** Electronic absorption spectra of electrochemically generated  $[\text{Co}^{\text{II}}\text{TrNPc}(-1)]_4^{4+}$  in DCB (—) and  $[\text{Co}^{\text{III}}\text{TrNPc}(-2)]_4^{4+}$  in DMF (---) ( $[\text{TBAP}] = 0.3 \text{ M}$ ;  $[(\text{CoTrNPc})_4] = 5 \times 10^{-5} \text{ M}$ ).

addition, in limiting dilute solution ( $< 5 \times 10^{-7} \text{ M}$ ) there is a shoulder at 625 nm, of intensity ca. half that of the 676-nm band, due to the intramolecularly coupled but nonaggregated species. In the presence of the supporting electrolyte used here for electrochemistry and spectroelectrochemistry,  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$  is extensively aggregated and this is seen in the spectrum, given in Table I, of a typical  $[\text{Co}^{\text{II}}\text{TrNPc}]_4$  solution prepared for electrolysis in the OTTE, where the intensity of the Q band at 625 nm is greater than that at 676 nm.

From previous studies of the electronic spectra of CoPc in its various ligand and metal oxidized and reduced states, from our laboratory<sup>24,25,31-35</sup> and others,<sup>36-44</sup> it is generally possible to use electronic spectroscopy to identify, unequivocally, the nature of the redox species formed upon controlled-potential electrolysis.

Oxidation of a solution of  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$  in DCB at ca. 200 mV positive of the first oxidation potential results in formation of  $[\text{Co}^{\text{III}}\text{TrNPc}(-1)]_4^{4+}$  by analogy with the corresponding reaction for the mononuclear species<sup>25</sup> (Figure 4, Table I). Thus, all four rings of the tetranuclear molecule are oxidized at the same potential. Interestingly, a broad band is seen in the near-IR region, centered at 975 nm. Weak near-IR bands have previously been observed for the phthalocyanine and octaethylporphyrin (OEP) dimeric radical cations  $[\text{ClZn}^{\text{II}}\text{Pc}(-1)]_2^{3+}$  and  $[\text{M}(\text{OEP}(-1))]_2^{2+}$  ( $\text{M} = \text{Zn},^{45} \text{Mg}^{46}$ ) at 1095, 945, and 950 nm, respectively.

Rereduction to  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$ , by polarizing the OTTE at 200 mV negative of the first oxidation potential, is reversible,



**Figure 5.** Electronic absorption spectra of electrochemically generated  $[\text{Co}^{\text{I}}\text{TrNPc}(-2)]_4^{4-}$  (—) and  $[\text{Co}^{\text{I}}\text{TrNPc}(-3)]_4^{8-}$  (---) in DCB ( $[\text{TBAP}] = 0.3 \text{ M}$ ;  $[(\text{CoTrNPc})_4] = 5 \times 10^{-5} \text{ M}$ ).

with less than 2% loss of the Q-band intensity. However, there are some differences in the final and initial spectra, namely an increase in intensity of the 676-nm band relative to the 625-nm band in the final spectrum. Thus, it appears that some conformational changes and/or changes in the degree of aggregation of the tetranuclear molecules have occurred upon oxidation and rereduction.

Oxidation positive of the second oxidation potential results in a rapid decrease in the visible absorption intensity, indicating destruction of the phthalocyanine ring (no decomposition products were seen in the visible region). However, the weak spectrum obtained (see Table I) is very similar to that of mononuclear  $[\text{Co}^{\text{III}}\text{TNPc}(-1)]_2^{2+}$ , indicating that the tetranuclear oxidation mirrors that of the mononuclear species.

Oxidation of  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$  in DCB in the presence of (TEA)Cl or in DMF at +0.7 V vs.  $\text{Ag}^+/\text{Ag}$  results in the formation of the  $[\text{Co}^{\text{III}}\text{TrNPc}(-2)]_4^{4+}$  species, characterized by a sharp decrease in intensity of the 625-nm band, an increase in intensity and narrowing of the 676-nm band, and a shift of the Soret band to 340 nm (Figure 4). The presence of axially coordinating ligands stabilizes the Co(III) species and shifts the potential of the Co(III)/Co(II) couple negative of the Pc(-1)/Pc(-2) couple, so that the first oxidation now ensues at the central metal rather than the TNPc ring.<sup>25,38</sup>

As a consequence of the axial ligation,  $[\text{Co}^{\text{III}}\text{TrNPc}(-2)]_4^{4+}$  is much less aggregated than  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$ , as evidenced by the weak intensity at 614 nm. Nevertheless, the relative intensity of the band at 614 nm is higher than for the mononuclear  $\text{Co}^{\text{III}}\text{TNPc}$  complex,<sup>25</sup> indicating that some intra- or intermolecular coupling is taking place. Moreover, the half-bandwidth of the lower energy Q band,  $1000 \text{ cm}^{-1}$ , is also indicative of substantial coupling between the rings. Rereduction to  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$  is reversible, with the final solution having an increase in intensity of the 676-nm band relative to that at 625 nm, compared with the initial solution, as was the case with oxidation in DCB.

Reduction of a  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$  solution in DCB or DMF at ca. 200 mV negative of the first reduction wave results in simultaneous reduction of the four  $\text{Co}^{\text{II}}\text{TrNPc}$  units to give the  $[\text{Co}^{\text{I}}\text{TrNPc}(-2)]_4^{4-}$  species, shown in Figure 5. The spectrum is very similar to that of mononuclear  $[\text{Co}^{\text{I}}\text{TNPc}(-2)]^-$ , characterized by the intense metal to ligand charge-transfer (MLCT) band near 470 nm,<sup>24,25,32,40</sup>  $[\text{Co}^{\text{I}}\text{TrNPc}(-2)][\text{d}(xz,yz)] \rightarrow \pi^*(1b_{1u})$ .

Although the Co(I) species is expected to be much less intermolecularly coupled than the Co(II) species as a result of the negative charge on the cobalt atoms, strong coupling effects are seen. The peak at 640 nm was found to increase in intensity relative to the Q band at 708 nm with increasing concentration of phthalocyanine, while the 640 nm:708 nm intensity ratio is lower

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in DMF than in DCB. This extra absorption at 640 nm indicates, in part, formation of aggregates of  $[\text{Co}^{\text{I}}\text{TrNPc}(-2)]_4^{4-}$ . No such aggregation was observed for mononuclear  $[\text{Co}^{\text{I}}\text{TNpc}(-2)]^-$ , which again shows a higher tendency for the tetranuclear complex to aggregate in solution. Some of the absorption at 640 nm is also likely due to intramolecular coupling between the phthalocyanine units of the tetranuclear molecule, as indicated by the relatively large half-bandwidth for the 708-nm band,  $890\text{ cm}^{-1}$ . A very weak band at 1040 nm was also seen for the tetranuclear Co(I) complex (Figure 5, Table I). The peak disappears on formation of the second reduction product or reoxidation to Co(II) and was not seen for mononuclear  $[\text{Co}^{\text{I}}\text{TNpc}(-2)]^-$ .<sup>25</sup> An additional weak absorption is seen near 590 nm (Figure 5) reminiscent of vibrational absorption seen in oligomeric silicon phthalocyanines.<sup>47</sup> Oxidation of the reduced species is fully reversible to the Co(II) species, but with a decrease in intensity of the 625-nm band relative to that of 676 nm, as for the oxidations.

Polarization of the OTTLE negative of the second reduction potential results in a change in solution color from yellow to pink and a spectrum characteristic of the ligand-reduced species  $[\text{Co}^{\text{I}}\text{TrNPc}(-3)]_4^{8-}$ , as seen previously for mononuclear  $\text{Co}^{\text{I}}\text{TNpc}$  and other phthalocyanines.<sup>25,37,41</sup> The MLCT band is red shifted by about 40 nm with respect to the mononuclear species (Figure 5). Reoxidation gives the  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$  species, but with a considerable decrease in phthalocyanine absorption intensity, indicating some destruction of the phthalocyanine ring has occurred.

**Electrocatalytic Reduction of Oxygen.** The electrocatalytic efficiency of  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$  toward the reduction of oxygen was investigated by means of rotating disk electrode (RDE) studies. The current for a RDE experiment is given by

$$1/i = 1/i_k + 1/i_L \quad (4)$$

in which  $i_L$  is the diffusion-limited current and  $i_k$  is the kinetically limited current. The diffusion-limited current, given in mA, is defined by the expression<sup>48</sup>

$$i_L = \frac{1000nAF\omega^{1/2}v^{1/2}[0.62048S^{-2/3}](2\pi/60)^{1/2}}{1 + 0.2980S^{-1/3} + 0.14514S^{-2/3}} \quad (5)$$

where  $v$  is the kinematic viscosity ( $\text{cm}^2/\text{s}$ ),  $\omega$  is the rotation rate (rpm),  $S$  is the Schmidt number, and the other parameters have their normal electrochemical significance. The remaining term in eq 4,  $i_k$ , is that current which would flow if the concentration of  $\text{O}_2$  at the electrode surface could be maintained at its bulk concentration during the reduction process. Therefore,  $i_k$  is directly proportional to the maximum rate at which  $\text{O}_2$  could be reduced at the catalyst-modified electrode at a given potential.<sup>49</sup> The kinetically limited current can be related to a rate constant by an appropriate kinetic model,<sup>50</sup> but here we shall use  $i_k$  directly as a measure of the catalytic efficiency.

It follows from eq 4 and 5 that a plot of  $i^{-1}$  vs.  $\omega^{-1/2}$  will give a linear fit with a slope proportional to  $n$ , the number of electrons transferred to the  $\text{O}_2$  molecule, and an intercept that is the reciprocal of  $i_k$ . The value of  $n$  establishes whether the modified OPG surface is reducing  $\text{O}_2$  by a two-electron pathway to form peroxide or by a four-electron pathway to form water. The parameters we used in the calculation of  $n$  were  $1.67 \times 10^{-5}\text{ cm}^2/\text{s}$ <sup>51</sup> and  $1.38 \times 10^{-6}\text{ mol}/\text{cm}^3$ <sup>52</sup> for the diffusion coefficient and concentration of  $\text{O}_2$ , respectively, and  $9.97 \times 10^{-3}\text{ cm}^2/\text{s}$ <sup>53</sup> for the kinematic viscosity of the 0.10 M NaOH solution.

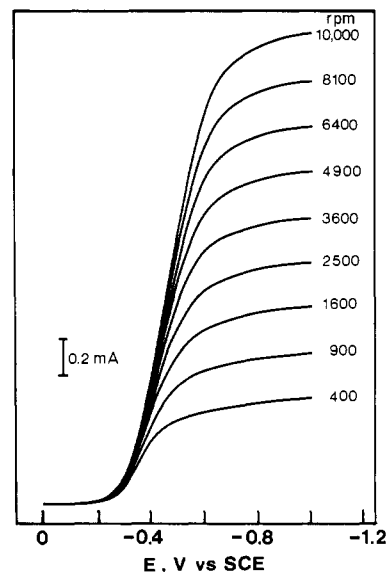


Figure 6. Reduction of molecular oxygen in 0.10 M NaOH at a rotating OPG electrode modified with 2.5 monolayers of  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$ .

Table IV. Kinetic Currents (mA) for OPG Electrodes Modified with a Variety of Cobalt Neopentoxophthalocyanine Compounds in 0.10 M NaOH<sup>a</sup>

compd	E vs. SCE			
	-0.450 V	-0.500 V	-0.550 V	-0.600 V
CoTNpc	1.51	3.00	5.58	9.95
C(2)[CoTrNPc] <sub>2</sub>	1.64	3.20	5.90	11.01
Cat(4)[CoTrNPc] <sub>2</sub>	1.84	3.91	7.95	16.01
EtMeO(5)[CoTrNPc] <sub>2</sub>	2.35	4.38	7.68	13.08
O(1)[CoTrNPc] <sub>2</sub>	2.45	4.61	8.15	13.89
[CoTrNPc] <sub>4</sub>	2.65	5.22	9.84	18.24

<sup>a</sup> Abbreviations for the binuclear complexes are defined in ref 25. The number in parentheses is the number of bridging atoms linking the two phthalocyanine rings.

The reduction of  $\text{O}_2$  at an OPG electrode modified with 2.5 layers of  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$  is shown in Figure 6. The coverage of  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$  on the electrode surface was determined from the charge under the peaks of cyclic voltammograms recorded at a number of scan rates, such as that given in Figure 7 for a 100 mV/s scan rate. A Koutecky-Levich plot for  $\text{O}_2$  reduction at -0.450 V vs. SCE on a  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$ -modified OPG surface is presented in Figure 8. From the procedures presented by Frumkin and Tedoradse<sup>54</sup> and discussed in depth elsewhere,<sup>55</sup> Koutecky-Levich plots were obtained at -0.450, -0.500, -0.550, and -0.600 V vs. SCE, under conditions where the reverse reaction is unimportant. These plots were all very well-behaved ( $R > 0.999$ ), and the calculated  $n$  values indicated that the  $\text{O}_2$  was being reduced by a two-electron process, yielding peroxide as the reduction product. Other studies in which OPG electrodes were modified with CoTNpc or one of its binuclear derivatives also indicated that peroxide was the reduction product under alkaline conditions.<sup>12</sup>

The kinetic currents for  $\text{O}_2$  reduction on OPG electrodes modified with  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$  are presented with those from similar studies<sup>12</sup> with CoTNpc and some of its binuclear derivatives in Table IV. These kinetic currents were then used to rank the catalytic efficiency of these species by normalizing them to the CoTNpc data. The normalized kinetic currents are given in Table V. The deviation ( $s$ ) in the average normalized kinetic currents is less than 15%, which is similar to the deviation reported in another study.<sup>56</sup> These normalized kinetic currents indicate that,

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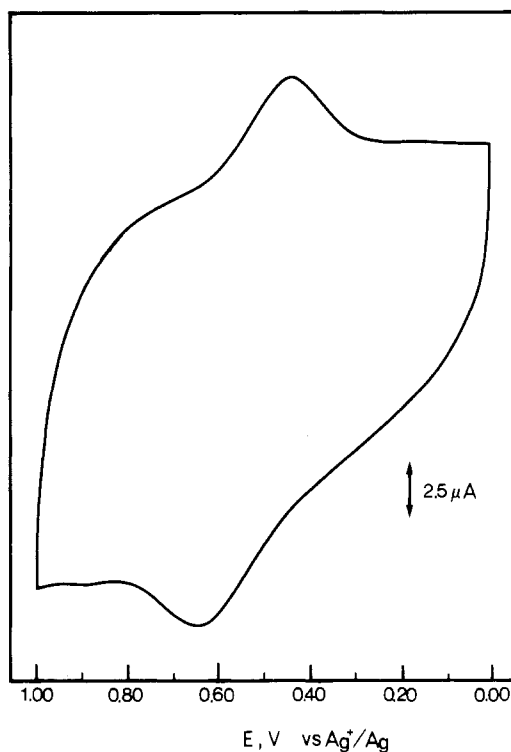
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**Table V.** Normalized Kinetic Currents (mA) for OPG Electrodes Modified with a Variety of Cobalt Neopentoxphthalocyanine Compounds in 0.10 M NaOH

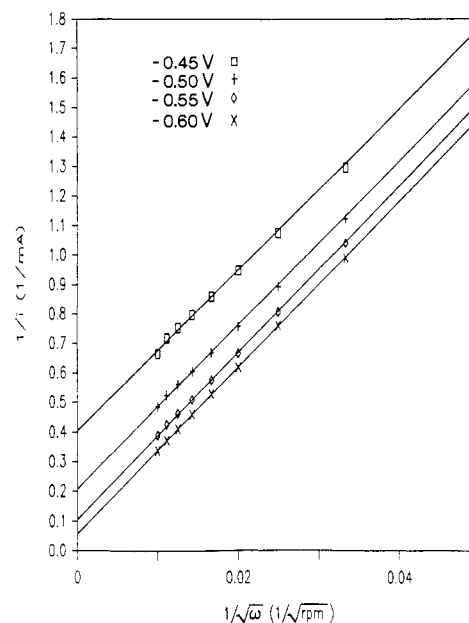
compd	E vs. SCE					av	s
	-0.450 V	-0.500 V	-0.550 V	-0.600 V			
CoTNPc	1	1	1	1			
C(2)[CoTrNPc] <sub>2</sub>	1.09	1.07	1.06	1.11	1.08	0.02	
Cat(4)[CoTrNPc] <sub>2</sub>	1.22	1.30	1.42	1.61	1.39	0.17	
EtMeO(5)[CoTrNPc] <sub>2</sub>	1.56	1.46	1.38	1.31	1.43	0.10	
O(1)[CoTrNPc] <sub>2</sub>	1.62	1.54	1.46	1.40	1.50	0.10	
[CoTrNPc] <sub>4</sub>	1.75	1.74	1.76	1.83	1.77	0.04	

**Figure 7.** Cyclic voltammogram showing adsorption of  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$  on an OPG-electrode in DCB (scan rate 100 mV/s;  $[(\text{Co}^{\text{II}}\text{TrNPc}(-2))_4] = 2.6 \times 10^{-6}$  M;  $[\text{TBA}^+] = 0.1$  M).

other than C(2)[ $\text{Co}^{\text{II}}\text{TrNPc}(-2)]_2$ , which only shows a 10% increase in catalytic efficiency over CoTNPc, the binuclear species are about 50% more efficient than CoTNPc toward  $\text{O}_2$  reduction and  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$  shows an improvement of about 75%.

Although  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$  has proven to be the most effective of our CoTNPc species toward  $\text{O}_2$  reduction, it is disappointing that it does not display a four-electron reduction process, at least under the conditions investigated so far; however, that it is more efficient than its binuclear congeners is encouraging. Further studies will include oxygen reduction with this species over a pH range and the study of the iron analogue. Such studies parallel those of Collman, Anson, Chang, and their co-workers on the electrocatalytic reduction of oxygen with binuclear cobalt porphyrin derivatives.<sup>57</sup>

**Disproportionation and Redox Reactions.** Following previous work on mononuclear and binuclear  $\text{Co}^{\text{II}}\text{TrNPc}$  complexes,<sup>58</sup> the addition of tetrabutylammonium hydroxide, (TBA)OH, in an 80-fold excess with respect to the phthalocyanine rings, to a solution of  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$  in DCB, DMF, or toluene under

**Figure 8.** Koutecky-Levich plots showing the inverse current vs. the inverse square root of the rotation rate, at the indicated potentials, with use of adsorbed  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$  on an OPG electrode in 0.10 M NaOH.

nitrogen, results in disproportionation of the phthalocyanine to a 1:1 mixture of Co(I) and Co(III) species. This reaction proceeds because hydroxyl ion binds very strongly to  $\text{Co}^{\text{III}}\text{Pc}(-2)$  but not at all to  $\text{Co}^{\text{II}}\text{Pc}(-2)$  and as a consequence the  $(\text{OH})_2\text{Co}^{\text{III}}\text{Pc}/\text{Co}^{\text{II}}\text{Pc}$  couple is more negative than the  $\text{Co}^{\text{II}}\text{Pc}/\text{Co}^{\text{I}}\text{Pc}$  couple, thereby rendering  $\text{Co}^{\text{II}}\text{Pc}$  unstable with respect to disproportionation.<sup>58</sup>

The disproportionation products are readily identifiable through their electronic spectra. Computer addition of the spectra of equal amounts of pure  $[\text{Co}^{\text{I}}\text{TrNPc}(-2)]_4^{4+}$  and pure  $[\text{Co}^{\text{III}}\text{TrNPc}(-2)]_4^{4+}$  gives a spectrum identical with that of the disproportionated Co(I)/Co(III) solution, with no evidence of any extra transitions, or wavelength shifting, which may have resulted from mixed-valence species. Thus, the disproportionated solution appears to consist of a mixture of  $[\text{Co}^{\text{I}}\text{TrNPc}(-2)]_4^{4+}$  and  $[\text{Co}^{\text{III}}\text{TrNPc}(-2)]_4^{4+}$ , rather than  $\{[\text{Co}^{\text{I}}\text{TrNPc}(-2)]_2[\text{Co}^{\text{III}}\text{TrNPc}(-2)]_2\}$  molecules.

As in the case of the  $\text{Co}^{\text{II}}\text{TrNPc}$  system,<sup>58</sup> irradiation with white light or with monochromatic light into the Q band of a disproportionated solution, under inert gas or vacuum, in DCB results in the conversion of Co(III) to Co(I); however, this is more difficult to effect with the tetranuclear compound. Similarly, prolonged electrochemical reduction in DCB does not give complete conversion to Co(I). On the other hand, Co(I) is easily formed via irradiation into a disproportionated solution in DMF. The instability of  $[\text{Co}^{\text{I}}\text{TrNPc}(-2)]_4^{4+}$  in DCB in the presence of hydroxide may be due to a reaction with the solvent, as has been found for  $\text{Co}^{\text{I}}\text{Pc}$  species in chlorinated solvents.<sup>59</sup> Interestingly, the tetranuclear Co(I) species is stable in DCB in the absence of hydroxide. If a disproportionated solution is left in air, or

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electrochemically oxidized in the OTTLE,  $[\text{Co}^{\text{III}}\text{TrNPc}(-2)]_4^{4+}$  is formed directly from Co(I), as in the case of the mononuclear complex.<sup>58</sup> Thus, solutions containing 100% Co(I) or 100% Co(III) are readily obtainable from Co(II) via the hydroxide disproportionation reaction.

The tetranuclear disproportionation reaction is particularly interesting since there is effectively an eight-electron transfer between the Co(I) and Co(III) states. Hence, the possibility exists to utilize this feature in the form of a multielectron redox catalyst. This was investigated by preparing thin films of Co(I)/Co(III), irradiating under vacuum to give Co(I), and reacting with a number of degassed reagents under vacuum. The films reacted with solutions of  $\text{H}_3\text{O}^+$  (aqueous HCl) and  $\text{CO}_3^{2-}$  (aqueous  $\text{Na}_2\text{CO}_3$ -NaOH) and slowly with  $\text{SO}_3^{2-}$  (aqueous  $\text{Na}_2\text{SO}_3$ -NaOH) to give  $[\text{Co}^{\text{II}}\text{TrNPc}(-2)]_4$ , with no obvious increase in efficiency relative to that of the mononuclear species.<sup>58</sup> Under the conditions used (see the Experimental Section), the quantum yields were obviously very small (<0.1%) and so the products (probably hydrogen, formate ion, and sulfur) were not pursued. Our concern here was to identify a multielectron redox reaction, but the above reactions probably proceed through one-electron pathways, since mononuclear  $\text{Co}^{\text{II}}\text{TNpc}$  is equally effective.

However, in addition, a reaction was also seen with  $\text{NO}_2^-$  (aqueous  $\text{NaNO}_2$ -NaOH), with which the cobalt(I) tetranuclear species was reoxidized to Co(II). No similar reaction was observed in the case of the mononuclear complex. The reduction of biological nitrite to nitrogen, ammonia, or nitric oxide is multielectron in nature. The apparent observation of this reaction with the tetranuclear, but not the mononuclear or binuclear phthalocyanine species, does provide cause to believe that, with the tetranuclear phthalocyanine, some kind of low-yield concerted reaction may

be taking place that is not possible with the mononuclear complex, possibly via a nitrosyl intermediate.<sup>60,61</sup> Work is presently in progress to characterize this reaction.

The conversion of Co(III) to Co(I) by irradiation of a film occurred at a much slower rate for the tetranuclear than for the mononuclear complex. This may be the result of a shorter excited-state lifetime of Co(III) in the case of the tetranuclear molecule as a result of intramolecular quenching.

**Concluding Comments.** The phthalocyanine rings in the tetranuclear cobalt phthalocyanine are in close proximity, and coupling between these rings is evident in all the various oxidation states investigated, but most prominently in the  $\text{Co}^{\text{II}}\text{Pc}(-2)$  state. The improvement in oxygen reduction capability over that of model mononuclear and binuclear phthalocyanines is ascribed, in part, to this interaction. The nitrite reduction reaction is indicative of incipient concerted multielectron behavior, but this remains yet to be clearly identified in this system. The very strong aggregation effects seen with the Co(II) tetranuclear species merit further consideration in this respect.

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**Registry No.** 1, 31643-49-9; 2, 115-77-5; 3, 106799-31-9; 4, 23277-29-4; 5, 106799-32-0; 6, 3468-11-9; 7, 93673-00-8; 8, 106799-30-8; 9, 106782-12-1; 9 (8- ion), 106782-14-3; 9 (4- ion), 106782-13-2; 9 (4+ ion), 106782-15-4; 9 (8+ ion), 106782-16-5;  $\text{O}_2$ , 7782-44-7;  $\text{NO}_2$ , 14797-65-0.

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Kent State University, Kent, Ohio 44242

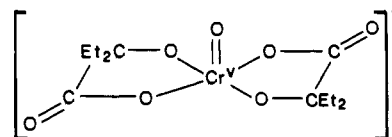
## Electron Transfer. 84. Reduction of Carboxylato-Bound Chromium(V) with Iodide<sup>1</sup>

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The chromium(V) chelate bis(2-ethyl-2-hydroxybutyrate)oxochromate(V) (I) is reduced by iodide in aqueous solution buffered by the ligand acid 2-ethyl-2-hydroxybutyric acid and its salt. Very nearly two  $\text{I}^-$  ions are oxidized per Cr(V) consumed. As in the reductions by  $\text{HSO}_3^-$  examined previously, the reaction passes through a strongly absorbing Cr(IV) intermediate, which accumulates slowly but disappears suddenly, imparting "clocklike" behavior to the system. The reaction is strongly catalyzed by the Cr(IV) intermediate and is thought also to pass through an iodine atom intermediate ( $\text{I}^*$ ), for which Cr(V) and Cr(IV) compete. The proposed reaction sequence (eq 2-7 in the text), in conjunction with rate constants for the component steps obtained by least-squares refinements based on the Runge-Kutta integration procedure, reproduces the observed kinetic profiles. The 1e transactions of  $\text{I}^-$  with both Cr(V) and Cr(IV) are accelerated by  $\text{H}^+$ , indicating that both chromium oxidation states are partially converted to a reactive protonated form with  $\text{p}K^{\text{A}}_{\text{Cr(V)}} = 2.9$  and  $\text{p}K^{\text{A}}_{\text{Cr(IV)}} < 2$ . The properties of the Cr(III) product correspond to those of a monochelated dicarboxylato derivative of  $(\text{H}_2\text{O})_3\text{Cr}^{\text{III}}$ , breakage of one chelate ring probably having occurred at the Cr(IV) level. No Cr(III)-bound iodide is detected in the reduction product. Reaction of  $\text{I}^-$  with Cr(V) is, as expected, markedly slower than with Cr(IV), which is more strongly oxidizing, but the  $\text{I}^*$  radical reacts with Cr(V) about 50 times as rapidly as with Cr(IV). This apparent inversion of relative rates points to an inner-sphere route for the Cr(V)- $\text{I}^*$  reaction. The reaction of HOI with  $\text{I}^-$  to form  $\text{I}_2$  exhibits a bimolecular rate constant of  $43 \text{ M}^{-1} \text{ s}^{-1}$  (24 °C, pH 2.75,  $\mu = 0.65 \text{ M}$ ) in the buffer system used, whereas the formation of  $\text{I}_3^-$  from  $\text{I}_2$  and  $\text{I}^-$  proceeds at a specific rate  $> 1 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ .

In 1979 Krumpolc and Roček<sup>3</sup> documented the facile preparation of a series of (bis) chelates of chromium(V), the most robust of which is the 2-ethyl-2-hydroxybutyrate derivative I. These are stable in air and dissolve in nonreducing polar solvents without



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immediate disproportionation. The availability of these chelates led not only to the mechanistic examinations of the redox reactions of this atypical oxidation state,<sup>4</sup> but also to the generation, via