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REDOX PROPERTIES OF T (U) YORK UNIV TORONTO (ONTARIO)
DEPT OF CHEMISTRY W A NEVINS ET AL SEP 86

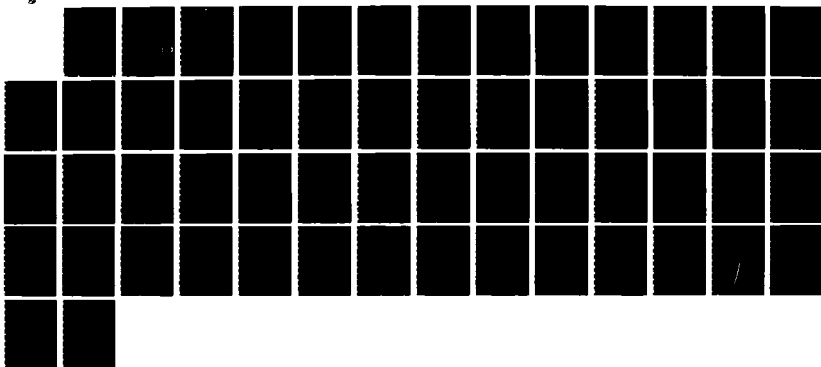
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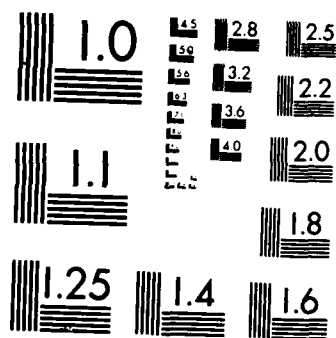
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Task No. 0051-865

Technical Report #9

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

By

W.A. Nevin, W. Liu, S. Greenberg, M.R. Hempstead, S.M. Marcuccio,
M. Melnik, C.C. Leznoff and A.B.P. Lever

in

Inorganic Chemistry

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REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION			1b RESTRICTIVE MARKINGS		
2a SECURITY CLASSIFICATION AUTHORITY Unclassified			3 DISTRIBUTION/AVAILABILITY OF REPORT As it appears on the report		
2b DECLASSIFICATION/DOWNGRADING SCHEDULE					
4 PERFORMING ORGANIZATION REPORT NUMBER(S) Report #			5 MONITORING ORGANIZATION REPORT NUMBER(S)		
6a NAME OF PERFORMING ORGANIZATION A.B.P. Lever, York University Chemistry Department		6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION Office of Naval Research		
6c ADDRESS (City, State, and ZIP Code) 4700 Keele St., North York, Ontario M3J 1P3 Canada			7b ADDRESS (City, State, and ZIP Code) Chemistry Division 800 N. Quincy Street Arlington, VA 22217 U.S.A.		
8a NAME OF FUNDING/SPONSORING ORGANIZATION		8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-84-G-0201		
8c ADDRESS (City, State, and ZIP Code)			10 SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
					WORK UNIT ACCESSION NO.
11 TITLE (Include Security Classification) Synthesis, Aggregation, Electrocatalytic Activity, and Redox Properties of Tetranuclear Cobalt Phthalocyanine					
12 PERSONAL AUTHOR(S) Nevin, William Andrew; Liu, Wei; Greenberg, Shafira; Hempstead, Michael R.; Marcuccio, Sebastian, M.; Melnik Milan; Leznoff, Clifford C.; and Lever, Alfred Beverley P.					
13a TYPE OF REPORT Technical		13b TIME COVERED FROM Oct. 84 TO		14 DATE OF REPORT (Year, Month, Day) September, 1986	
15 PAGE COUNT					
16 SUPPLEMENTARY NOTATION					
17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	Tetranuclear phthalocyanines, Spectro-electrochemistry		
			electrocatalytic oxygen reduction, aggregation, electro-		
			chemistry, disproportionation		
19 ABSTRACT (Continue on reverse if necessary and identify by block number) Using pentaerythritol as a framework, it has been possible to synthesize a tetranuclear phthalocyanine with a spiro type linkage. Electrochemical and spectro-electrochemical data are presented for the cobalt complex in the Co(III)Pc(-2), Co(II)Pc(-2), Co(I)Pc(-2), Co(III)Pc(-1), Co(II)Pc(-1) and Co(I)Pc(-3) oxidation levels. The Co(II) species aggregates very strongly, dimerising with an aggregation constant, in o-dichlorobenzene of $2.4 \times 10^5 M^{-1}$, two orders of magnitude greater than for the parent Co(II)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 non- or weakly donating solvent. A film containing [Co(I)TrNPC(-2)] ₄ reduces nitrite ion in NaOH slowly, with oxidation to the Co(II) tetranuclear species.					
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION Unclassified/unlimited		
22a NAME OF RESPONSIBLE INDIVIDUAL Dr. Harold E. Guard			22b TELEPHONE (Include Area Code)		22c OFFICE SYMBOL

DL/1113/86/2

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SYNTHESIS, AGGREGATION, ELECTROCATALYTIC ACTIVITY, AND REDOX PROPERTIES
OF TETRANUCLEAR COBALT PHTHALOCYANINE.

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Melnik,^{1b} C.C. Leznoff* and A.B.P.Lever*

Abstract

Using pentaerythritol as a framework, it has been possible to synthesize a tetranuclear phthalocyanine with a spiro type linkage. Electrochemical and spectro-electrochemical data are presented for the cobalt complex in the Co(III)Pc(-2), Co(II)Pc(-2), Co(I)Pc(-2), Co(III)Pc(-1), Co(II)Pc(-1) and Co(I)Pc(-3) oxidation levels. The Co(II) species aggregates very strongly, dimerising with an aggregation constant, in o-dichlorobenzene of $2.4 \times 10^5 \text{M}^{-1}$, two orders of magnitude greater than for the parent Co(II)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 non- or weakly donating solvent. A film containing $[\text{Co(I)TrNPc(-2)}]_4^{4-}$ 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.²⁻⁶ Ill-defined 'dimeric' and polymeric phthalocyanines,^{6,7} 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 multi-electron reduction (2 electrons to hydrogen peroxide, or 4 to water). This prompted us to design a series of polynuclear phthalocyanines, with the expectation that a multi-electron redox catalyst might be designed, having enhanced properties relative to the common one-electron electrocatalysts.

The preparations of trinuclear⁸, and binuclear phthalocyanines covalently linked by one⁸, two⁹, four⁹, and five^{10,11} atom 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.¹²

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 0.1N NaOH) than their mononuclear analogs, 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 two 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 oxidised in a concerted fashion to Co(II) (4-electrons) or Co(III) (8-electrons). Indeed the cobalt complex of this tetranuclear species does prove to be a better oxygen reduction catalyst than its binuclear analogs, 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 bis-aggregated species might prove to be a useful electro- or photocatalyst, with an appropriate central metal.

Experimental

Materials

Tetrabutylammonium perchlorate (TBAP) (Kodak) was recrystallized from absolute ethanol and dried in a vacuum oven at 50°C for two days. Toluene (Aldrich, Gold Label), o-dichlorobenzene (DCB) (Aldrich, Gold Label), N,N-dimethylformamide (DMF) (Aldrich, anhydrous Gold Label), tetrabutylammonium hydroxide (TBAOH) (1M in methanol, Kodak), tetraethylammonium chloride (TEACl) (Aldrich) and polystyrene (p(sty)) (Scientific Products) were used as supplied. Water was purified by double distillation over KMnO_4 , followed by passage through a Barnstead organic removal cartridge and two Barnstead mixed resin ultrapure cartridges. Fisher certified 1 N 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 CaSO_4 (Drierite), molecular sieves (BDH type 3A) and glass wool. Oxygen gas (Linde) was purified by passage through anhydrous CaSO_4 , NaOH pellets (AnalaR analytical grade), anhydrous 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 cm^2 .

Methods

Mass spectra were obtained courtesy of the Midwest Centre for Mass Spectrometry, Lincoln, Nebraska (with thanks to K.B.Tomer) using a system described in full elsewhere.⁸⁻¹¹

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 (PARC) model 174A Polarographic Analyser coupled to a PARC model 175 Universal Programmer. Measurements were carried out under an atmosphere of nitrogen in a Vacuum Atmospheres Drilab. A platinum disc described by the cross-sectional area of a 27 gauge wire (area ca. 10^{-3} cm²), sealed in glass, was used as the working electrode, a platinum wire as counter, and a silver wire as quasi-reference. Potentials were referenced internally to the ferrocenium/ferrocene (Fc⁺/Fc) couple.¹³

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 versus a saturated calomel electrode (SCE).

Spectro-electrochemical measurements were made with an optically transparent thin layer electrode (OTTLE) utilising a gold minigrad (500 lines/in), with platinum counter and silver quasi-reference electrodes¹⁴ designed to fit into the sample compartment of the spectrometer. Solutions for electrochemistry or spectro-electrochemistry contained 0.3 M TBAP as the supporting electrolyte, and 2.5×10^{-5} M and $2-5 \times 10^{-5}$ M [Co(II)TrNPc]₄, respectively.

For the adsorption studies, ca. 2.5×10^{-5} M [Co(II)TrNPc]₄ solutions were prepared in DCB, with 0.1 M TBAP. After purging the solution with

argon for 1h, the OPG working electrode was scanned at a rate of 100 mV/s over the potential range 0.00 to +1.00 V versus 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 five minutes 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 $[\text{Co(II)TrNPc}]_4$ adsorbed on the OPG electrode was investigated as follows: the modified electrode was removed from the phthalocyanine solution, washed with ethanol, 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 versus SCE at a rate of 10 mV/s for rotation rates ranging from 400 to 10,000 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 $[\text{Co(II)TrNPc}]_4$ 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 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 TBAOH to the $\text{p(sty)}/[\text{Co(II)TrNPc}]_4$ 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 minimise 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^{11,15,16} yielded 1,1,1,1-tetrakis-(3',4'-dicyanophenoxy-methyl)methane (3) in 36% yield and bis-(3,4-dicyanophenyl) ether (4) as a minor by-product. Compound (3) was only sparsely soluble in organic solvents and hence was converted into the tetradiiminoisoindoline (5) by a procedure slightly modified from that previously published.^{11, 17,18} A mixed condensation of the tetradiiminoisoindoline (5) with an excess of the diiminoisoindoline (6) derived from 4-neopentoxypthalonitrile gave by methods⁸⁻¹¹ previously described 2,9,16,23-tetraneopentoxypthalocyanine (7) in 61% yield and 1,1,1,1-tetrakis-[2'-(9',16',23'-tri-neopentoxypthalocyaninoxymethyl)]methane (8) in 12% yield after the use of flash chromatography¹⁹ followed by gel permeation chromatography²⁰. 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 8⁸⁻¹¹.

1,1,1,1-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 (CaCl₂ 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 1,1,1,1-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^{-1} . ^1H NMR (in CD_3CN): δ 7.80 (d, $J=8.8$ Hz, 1H), 7.47 (d, $J=2.5$, 1H), 7.31 (dd, $J=8.8$, 2.5 Hz, 1H), 4.43 (s, 2H). MS, m/e (relative intensity): 640 (M^+ , 8%), 497 (M^+-143 , 27%), 157 (92%), 144 (100%), 127 (51%). Anal. calcd for $\text{C}_{37}\text{H}_{20}\text{N}_8\text{O}_4$: 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 and dried over anhydrous magnesium sulfate and evaporated to give 2.3 g of crude bis-(3,4-dicyanophenyl)ether (4) as a by-product. 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.¹⁵ mp 254-256).

Preparation of the Tetradiiminoisoindoline (5).

Gaseous ammonia was bubbled vigorously into a slurry of 258 mg of 1,1,1,1-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 5 additional h. After

cooling to room temperature and evaporating the solvent the crude isoindoline was used directly in the condensation reaction without further purification. The crude isoindoline did not exhibit nitrile absorption in its ir spectrum.

1,1,1,1-Tetrakis-[2'-(9',16',23'-trineopentoxypthalocyaninoxymethyl)] methane (8), [H₂TrNPc(-2)]₄.

The two crude diiminoisoindolines (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-N,N-dimethylaminoethanol for 60 h under an argon atmosphere. After cooling 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 chromatography¹⁹ using a 5 cm wide column packed with silica gel 15 cm high. The crude product was pre-adsorbed on silica and eluted with 2000 mL of toluene/hexanes (4:1) to give 4.76 g of the mononuclear 2,9,16,23-tetraneopentoxypthalocyanine (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 chromatography²⁰ using a 5 cm wide column packed with Bio beads SX1 50 cm high. The mononuclear/tetranuclear fraction was eluted with freshly distilled tetrahydrofuran (THF). The faster moving band

consisting of tetranuclear 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 was not further purified, IR (KBr): 3300 (w), 1620 (vs), 1485 (vs), 1245 (vs), 1100 (s), 1020 (vs), 750 (m) cm^{-1} . ^1H NMR (in CDCl_3): 1-2 (broad m, ^tBut), -3 (broad s, NH) UV-VIS (o-dichlorobenzene) λ_{max} (loge): 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^+ , 59%). Anal. Calcd for $\text{C}_{193}\text{H}_{196}\text{N}_{32}\text{O}_{16}$: C, 71.99; H, 6.14; N, 13.92. Found: C, 72.26; H, 6.44; N, 13.65.

1,1,1,1-Tetrakis-[2'-(9',16',23'-trineopentoxypthalocyaninoxymethyl Cobalt(II))]methane (9), $[\text{Co(II)TrNPc(-2)}]_4$.

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 $^{\circ}\text{C}$ 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^{-1} . UV-VIS (o-dichlorobenzene, aggregated) λ_{max} (loge): 380 (sh, 4.56), 625 (4.89), 676 (4.85), nm. MS, m/e: 3447.2 (M^+). Anal. Calcd for $\text{C}_{193}\text{H}_{188}\text{N}_{32}\text{O}_{16}\text{Co}_4$: 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

Using the procedures discussed elsewhere⁸⁻¹¹, four o-benzenedinitrile (phthalonitrile) units were attached to a pentaerythritol residue, converted to the tetra-diiminoisoindoline (5), which was then condensed with excess 5-neopentoxydiiminoisoindoline to obtain the desired metal-free product (8), $[H_2TrNPc(-2)]_4$ (Figure 1). Characterisation of the product was achieved through elemental analysis, NMR, IR and most importantly, the observation of a parent ion at 3217.6 using FAB mass spectroscopy. Aspects of the emission of the metal-free species will be discussed elsewhere.²¹ It appears facile to incorporate metal ions into this species by standard methods. Here we are concerned with the characterisation of the tetra-nuclear cobalt trineopentoxypthalocyanine, $[CoTrNPc]_4$ in its various oxidation states and comparison with the mononuclear tetraneopentoxypthalocyanine (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 tetra-sulphonated phthalocyanines (TsPc) in aqueous and alcohol solution²² with some work also having been done on tetraalkyl phthalocyanines (PcX_4) in organic solvents²³. Typically the aggregate has a Q band absorption at 30-50nm 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 8 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 dimerisation 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 $[\text{Co(II)TrNPc(-2)}]_4$ 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 $\text{Co(II)TrNPc(-2)}^{24,25}$; and a band at 625 nm, which increases in intensity relative to the 676 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 7×10^{-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 coupling²⁶). In the limit of strict four-fold 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 (5×10^{-7} M), where only monomeric $[\text{Co(II)TrNPc(-2)}]_4$ exists, a substantial amount of absorption still occurs at 625 nm (ca. 50% relative to 676 nm), compared with mononuclear Co(II)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

complexes²⁶. 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 $[\text{Co(II)TrNPc}(-2)]_4$ are given in Table I. Aggregation of $[\text{Co(II)TrNPc}(-2)]_4$ occurs at much more dilute solution than for $\text{Co(II)TNPc}(-2)$, which exhibits deviation from Beer's Law only at concentrations greater than $1 \times 10^{-5}\text{M}$.²⁷

In the case of a simple monomer-dimer equilibrium, a plot of $\log_{10}C_M$ against $\log_{10}C_D$ will give a straight line with a slope of 2, as has been found for Co(II)TNPc in DCB²⁷ and several mononuclear PcX_4 complexes in organic solution²³. Calculation of the values of C_M and C_D at any given total concentration is normally carried out using the relative intensities at the wavelengths of the Q bands of the monomeric and dimeric species.^{22,23,28} 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 $[\text{Co(II)TrNPc}(-2)]_4$ 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 undimerised 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 7.6×10^{-7} to 2.3×10^{-5} M in DCB using the approximation method of West and Pearce²⁸ (Table II). The spectrum at 5×10^{-7} M was taken as that of the pure unaggregated monomer (see Table I). A plot of $\log_{10} C_D'$ versus $\log_{10} C_M'$ gave a slope of 1.6 (Figure 3a), indicating that indeed a dimer is not formed by coupling 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 $[\text{Co(II)TrNPc}]_4$ species, and plots of $\log_{10} C_D$ versus $\log_{10} C_M$ 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). 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 which 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 (2.3×10^{-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 two orders of magnitude higher than the dimerisation constant measured for

mononuclear Co(II)TNPc in DCB ($2.6 \times 10^3 \text{ M}^{-1}$).²⁷ 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 $[\text{Co(II)TrNPc(-2)}]_4$ in DCB over the potential range +1.0 to -2.1 V, versus Fc^+/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 Co(II)TNPc(-2) and binuclear $[\text{Co(II)TrNPc(-2)}]_2$ complexes,²⁵ although the waves were much less well defined than for the cyclic voltammogram of Co(II)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. see²⁹.

No evidence was seen for any splitting of the redox peaks, such as observed for cofacial and "clamshell" cobalt porphyrins³⁰. It appears that the four Co(II)TNPc units of each molecule reduce or oxidise simultaneously. By analogy to Co(II)TNPc²⁵, 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 Co(II)TNPC units at each redox couple.

Spectro-electrochemistry

As indicated above, the visible spectrum of the monomeric $[\text{Co(II)TrNPc}(-2)]_4$ species is dominated by an intense Q band at 676 nm, resulting from the $a_{1u} \rightarrow e_g(\pi^*)$ transition, similar to mononuclear Co(II)TNPC. In 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 non-aggregated species. In the presence of the supporting electrolyte used here for electrochemistry and spectro-electrochemistry, $[\text{Co(II)TrNPc}(-2)]_4$ is extensively aggregated and this is seen in the spectrum, given in Table I, of a typical $[\text{Co(II)TrNPc}]_4$ solution prepared for electrolysis in the OTTLE, 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 oxidised and reduced states, from our laboratory^{24,25,31-35}, and others³⁶⁻⁴⁴, 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 $[\text{Co(II)TrNPc}(-2)]_4$ in DCE at ca. 200 mV positive of the first oxidation potential results in formation of $[\text{Co(II)TrNPc}(-1)^+]_4$ by analogy with the corresponding reaction for the mononuclear species²⁵ (Figure 4, Table I). Thus all four rings of the tetranuclear molecule oxidise at the same potential. Interestingly a broad band is seen in the nir region, centred at 975 nm. Weak nir bands have previously been observed for the phthalocyanine and octaethylporphyrin

(OEP) dimeric radical cations, $[\text{ClZn(II)Pc(-1)}^+]_2^{33}$, $[\text{MOEP(-1)}]_2^{2+}$ $\text{M} = \text{Zn}^{45}$ and Mg^{46} , at 1095, 945 and 950 nm respectively.

Re-reduction to $[\text{Co(II)TrNPc(-2)}]_4$, by polarising the OTTLE at 200 mV negative of the first oxidation potential, is reversible, 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 re-reduction.

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 $[\text{Co(III)TNPc(-1)}]^{2+}$ indicating that the tetranuclear oxidation mirrors that of the mononuclear species.

Oxidation of $[\text{Co(II)TrNPc(-2)}]_4$ in DCB in the presence of TEACl or in DMF at +0.7 V versus Ag^+/Ag , results in the formation of the $[\text{Co(III)TrNPc(-2)}]_4^{4+}$ species, characterised 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 stabilises 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.^{25,38}

As a consequence of the axial ligation, $[\text{Co(III)TrNPc(-2)}]_4^{4+}$ is much less aggregated than $[\text{Co(II)TrNPc(-2)}]_4$, as evidenced by the weak intensity at 614nm. Nevertheless, the relative intensity of the band at

614nm is higher than for the mononuclear Co(III)TNPC complex,²⁵ indicating that some intra- or intermolecular coupling is taking place. Moreover the halfbandwidth of the lower energy Q band, 1000cm⁻¹, is also indicative of substantial coupling between the rings. Re-reduction to [Co(II)TrNPc(-2)]₄ is reversible, with the final solution having an increase in intensity of the 676 nm band relative to 625 nm, compared with the initial solution, as was the case with oxidation in DCB.

Reduction of a [Co(II)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 Co(II)TrNPc units to give the [Co(I)TrNPc(-2)]₄⁴⁻ species, shown in Figure 5. The spectrum is very similar to that of mononuclear [Co(I)TNPC(-2)]⁻, characterised by the intense metal to ligand charge transfer (MLCT) band near 470nm,^{24,25,32,40} [Co(I)TrNPc(-2)][d(x₂,yz)]⁻ → π*(1b_{1g}).

Although the Co(I) species is expected to be much less inter-molecularly 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 in DMF than in DCB. This extra absorption at 640 nm indicates, in part, formation of aggregates of [Co(I)TrNPc(-2)]₄⁴⁻. No such aggregation was observed for mononuclear [Co(I)TNPC]⁻, 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 halfbandwidth for the 708 nm band, 890cm⁻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 re-oxidation to Co(II), and was not seen for mononuclear $[\text{Co(I)TNPc}(-2)]^-$.²⁵ An additional weak absorption is seen near 590 nm (Figure 5) reminiscent of vibrational absorption seen in oligomeric silicon phthalocyanines.⁴⁷ 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 676 nm, as for the oxidations.

Polarisation 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, $[\text{Co(I)TrNPc}(-3)]_4^{8-}$, as seen previously for mononuclear Co(II)TNPc and other phthalocyanines.^{25,37,41} The MLCT band is red-shifted by about 40 nm with respect to the mononuclear species (Figure 4). Re-oxidation gives the $[\text{Co(II)TrNPc}(-2)]_4$ 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 $[\text{Co(II)TrNPc}(-2)]_4$ towards the reduction of oxygen was investigated by means of rotating disc 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 expression⁴⁸

$$i_L = 1000nAF\bar{C}u^{1/2}\omega^{1/2} \left[0.62048S^{-2/3} \right] (2\pi/60)^{1/2} \\ \hline [1 + 0.2980S^{-1/3} + 0.14514S^{-2/3}] \quad (5)$$

where ν is the kinematic viscosity (cm^2/s), ω is the rotation rate (rpm), S is the Schmidt number, and the other parameters have their normal electrochemical significance. The remaining term in equation (4), i_k , is that current which would flow if the concentration of 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 O_2 could be reduced at the catalyst-modified electrode at a given potential⁴⁹. The kinetically limited current can be related to a rate constant by an appropriate kinetic model⁵⁰, but here we shall use i_k directly as a measure of the catalytic efficiency.

It follows from equations (4) and (5) that a plot of i^{-1} versus $\omega^{-1/2}$ will give a linear fit with a slope proportional to n , the number of electrons transferred to the O_2 molecule, and an intercept which is the reciprocal of i_k . The value of n establishes whether the modified OPG surface is reducing 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 $1.67 \times 10^{-5} \text{ cm}^2/\text{s}$ ⁵¹ and $1.38 \times 10^{-6} \text{ mol}/\text{cm}^3$ ⁵² for the diffusion coefficient and concentration of O_2 , respectively, and $9.97 \times 10^{-3} \text{ cm}^2/\text{s}$ ⁵³ for the kinematic viscosity of the 0.10 M NaOH solution.

The reduction of 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 those given in Figure 7 for 100 mV/s scan rate. A Koutecky-Levich plot for O_2 reduction at -0.450 V vs SCE on a $[Co(II)TrNPc(-2)]_4$ modified OPG surface is presented in Figure 8. Following the procedures presented by Frumkin and Tedoradse⁵⁴ and discussed in depth elsewhere⁵⁵, Koutecky-Levich plots were obtained at -0.450 V, -0.500 V, -0.550 V, and -0.600 V vs. SCE, under conditions where the reverse reaction is unimportant. These plots were all very well behaved ($R > .999$) and the calculated n values indicated that the 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.¹²

The kinetic currents for O_2 reduction on OPG electrodes modified with $[Co(II)TrNPc(-2)]_4$ are presented with those from similar studies¹² 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 in the average normalized kinetic currents is less than 15% which is similar to the deviation reported in another study⁵⁶. These normalized kinetic currents indicate that, other than $C(2)[Co(II)TrNPc(-2)]_2$, which only shows a 10% increase in catalytic efficiency over CoTNPc, the binuclear species are about 50% more efficient than CoTNPc towards O_2 reduction and $[Co(II)TrNPc(-2)]_4$ shows an improvement of about 75%.

Although $[Co(II)TrNPc(-2)]_4$ has proven to be the most effective of our CoTNPc species towards 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 analog. Such studies parallel those of Collman, Anson, Chang and their co-workers on the electrocatalytic reduction of oxygen with binuclear cobalt porphyrin derivatives.⁵⁷

Disproportionation and Redox Reactions

Following previous work on mononuclear and binuclear Co(II)TNPC complexes,⁵⁸ the addition of tetrabutylammonium hydroxide, TBAOH, in an 80-fold excess with respect to the phthalocyanine rings, to a solution of $[\text{Co(II)TrNPc(-2)}]_4$ in DCB, DMF or toluene under 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 Co(III)Pc(-2) but not at all to Co(II)Pc(-2) and as a consequence the $(\text{OH})_2\text{Co(III)Pc}/\text{Co(II)Pc}$ couple is more negative than the $\text{Co(II)Pc}/\text{Co(I)Pc}$ couple, thereby rendering Co(II)Pc unstable with respect to disproportionation.⁵⁸

The disproportionation products are readily identifiable through their electronic spectra. Computer addition of the spectra of equal amounts of pure $[\text{Co(I)TrNPc(-2)}]_4^{4-}$ and pure $[\text{Co(III)TrNPc(-2)}]_4^{4+}$ gives an identical spectrum to 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 $[\text{Co(I)TrNPc(-2)}]_4^{4-}$ and $[\text{Co(III)TrNPc(-2)}]_4^{4+}$, rather than $\{[\text{Co(I)TrNPc(-2)}]_2[\text{Co(III)TrNPc(-2)}]_2\}$ molecules.

As in the case of the Co(II)TNPC system,⁵⁸ irradiation with white light or with monochromatic light into the Q band, of a disproportionated

solution, under inert gas, or vacuo, 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 $[\text{Co(I)TrNPc}(-2)]_4^{4-}$ in DCB in the presence of hydroxide may be due to a reaction with the solvent, as has been found for Co(I)Pc species in chlorinated solvents.⁵⁹ Interestingly, the tetranuclear Co(I) species is stable in DCB in the absence of hydroxide. If a disproportionated solution is left in air, or electrochemically oxidised in the OTTLE, $[\text{Co(III)TrNPc}(-2)]_4^{4+}$ is formed directly from Co(I), as in the case of the mononuclear complex.⁵⁸ 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 8-electron transfer between the Co(I) and Co(III) states. Hence, the possibility exists to utilise this feature in the form of a multi-electron redox catalyst. This was investigated by preparing thin films of Co(I)/Co(III), irradiating under vacuo to give Co(I) and reacting with a number of degassed reagents under vacuo. The films reacted with solutions of H_3O^+ (aqueous HCl), CO_3^{2-} (aqueous $\text{Na}_2\text{CO}_3/\text{NaOH}$) and slowly with SO_3^{2-} (aqueous $\text{Na}_2\text{SO}_3/\text{NaOH}$) to give $[\text{Co(II)TrNPc}(-2)]_4$, with no obvious increase in efficiency relative to the mononuclear species.⁵⁸ Under the conditions used (see experimental), 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 multi-electron redox reaction, but the above reactions probably proceed through one-electron pathways, since mono-

nuclear Co(II)TNPc is equally effective.

However, in addition, a reaction was also seen with NO_2^- (aqueous $\text{NaNO}_2/\text{NaOH}$), with which the cobalt(I) tetranuclear species was re-oxidised 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 multi-electron 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 which is not possible with the mononuclear complex, possibly via a nitrosyl intermediate.^{60, 61} Work is presently in progress to characterise 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 Co(II)Pc(-2) state. The improvement in oxygen reduction capability over model mononuclear and binuclear phthalocyanines is ascribed, in part, to this interaction. The nitrite reduction reaction is indicative of incipient concerted multi-electron behaviour but this remains yet to be clearly identified in this system. The very strong aggregation effects seen with the Co(II) tetranuclear species merits further consideration in this

respect.

Acknowledgements: We are indebted to the Natural Sciences and Engineering and Research Council (Ottawa) and the Office of Naval Research (Washington) for financial support.

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Figures

Figure 1. Scheme of Preparation.

Figure 2. Electronic absorption spectra of $[\text{Co(II)TrNPc}(-2)]_4$ in DCB at concentrations of $2.3 \times 10^{-5}\text{M}$ (—), $3.8 \times 10^{-6}\text{M}$ (----), and $1.5 \times 10^{-6}\text{M}$ (-.-.-.).

Figure 3. a) Plots of $\log C_M$ versus $\log C_D$ for $[\text{Co(II)TrNPc}(-2)]_4$ 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 $[\text{Co(II)TrNPc}(-2)]_4$. b) Spectra of experimental monomeric $[\text{Co(II)TrNPc}(-2)]_4$, and calculated dimeric aggregated $\{[\text{Co(II)TrNPc}(-2)]_4\}_2$ in DCB.

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

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

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

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

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

Table I Electronic Absorption Maxima of [CoTrNPc]₄ Species

Species ^a	λ_{max} ($\times 10^{-4}$ M ⁻¹ cm ⁻¹)					
[Co(II)TrNPc(-2)] ₄ ^b	326(8.41)	380 sh		625 sh		676(9.61)
[Co(II)TrNPc(-3)] ₄ ^c	315 sh		476 sh		520 s	672 w
[Co(II)TrNPc(-2)] ₄ ^d	312(15.4)	350 sh	435 sh	564 w	590(3.49)	680 sh 1040(0.2)
[Co(II)TrNPc(-2)] ₄	325 sh	380 sh			625(7.82)	676(7.15)
[Co(II)TrNPc(-1)] ₄ ^e	320(5.96)	365 sh		590(3.89)		690(3.83)
[Co(III)TrNPc(-1)] ₄ ^f	330 s	370 sh		554 m		780 w
[Co(III)TrNPc(-2)] ₄ ^g	336(12.0)	350 sh	395 sh		614(6.02)	676(14.9)

^a In DCB solution with 2×10^{-5} M [CoTrNPc]₄ and 0.3M TBAP, except for ^b 5×10^{-7} M [CoTrNPc]₄ in DCB, ^c 2×10^{-5} M [CoTrNPc]₄ with 0.3 M TBAP in DMF.

sh = shoulder, w = weak, m = medium, s = strong, br = broad

Table II Dimerisation Constant, K_D of $[\text{CoTrNPc}]_4$ in DCB at 20°C^a

$C_T \times 10^6$	L	OD_{obs}	OD_M'	C_M'	C_D'	C_M^b	C_D^b	$K_D \times 10^{-5}$
M	cm	(676nm)		$\times 10^6 \text{M}$	$\times 10^6 \text{M}$	$\times 10^6 \text{M}$	$\times 10^6 \text{M}$	M^{-1}
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

^aL = Cell pathlength; OD_{obs} = observed optical density; OD_M' = corrected optical density of the monomeric species (see text). ^b C_M and C_D are calculated for a dimer coupled through two phthalocyanine rings of each monomeric unit, using the relationships, $C_M = 2C_M' - C_T$ and $C_D = (C_T - C_M)/2$.

Table III Electrochemical Data for $[\text{CoTrNPc}]_4$ in o-Dichlorobenzene, $E_{1/2}$ V, with Reference to the Ferrocenium/Ferrocene Couple. ^{a, b}

Co(III)Pc(0)/	Co(III)Pc(-1)/	Co(II)Pc(-1)/	Co(II)Pc(-2)/	Co(I)Pc(-2)/
Co(III)Pc(-1)	Co(II)Pc(-1)	Co(II)Pc(-2)	Co(I)Pc(-2)	Co(I)Pc(-3)
+0.86	+0.50	+0.05	-0.92	-2.06V

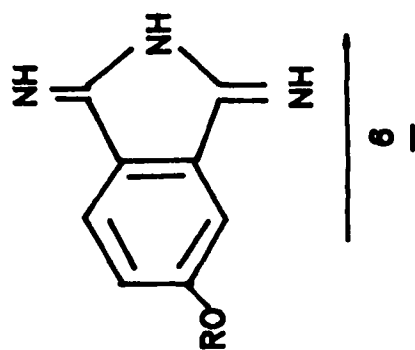
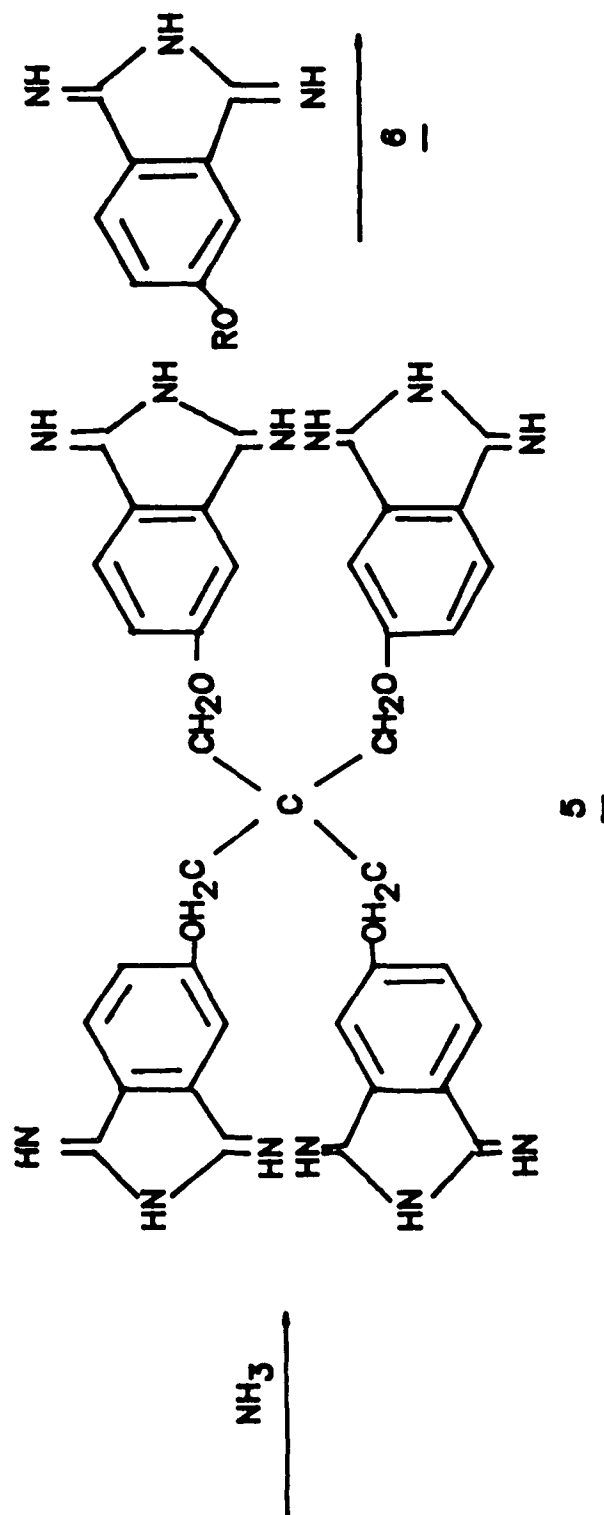
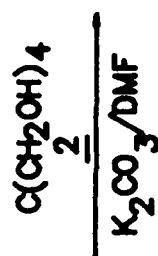
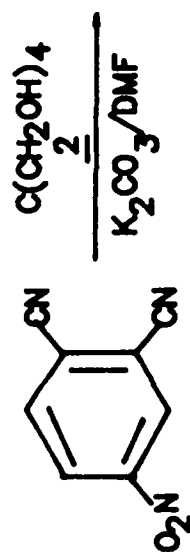
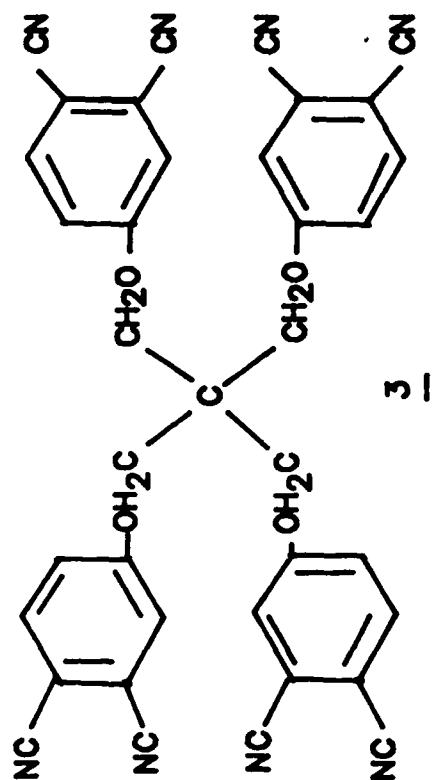
^a Fc^+/Fc lies at +0.44V vs NHE. Data collected by differential pulse polarography at 2mV/s. ^bConditions $[(\text{CoTrNPc})_4] = 2.5 \times 10^{-5}\text{M}$, $[\text{TBAP}] = 0.3\text{M}$.

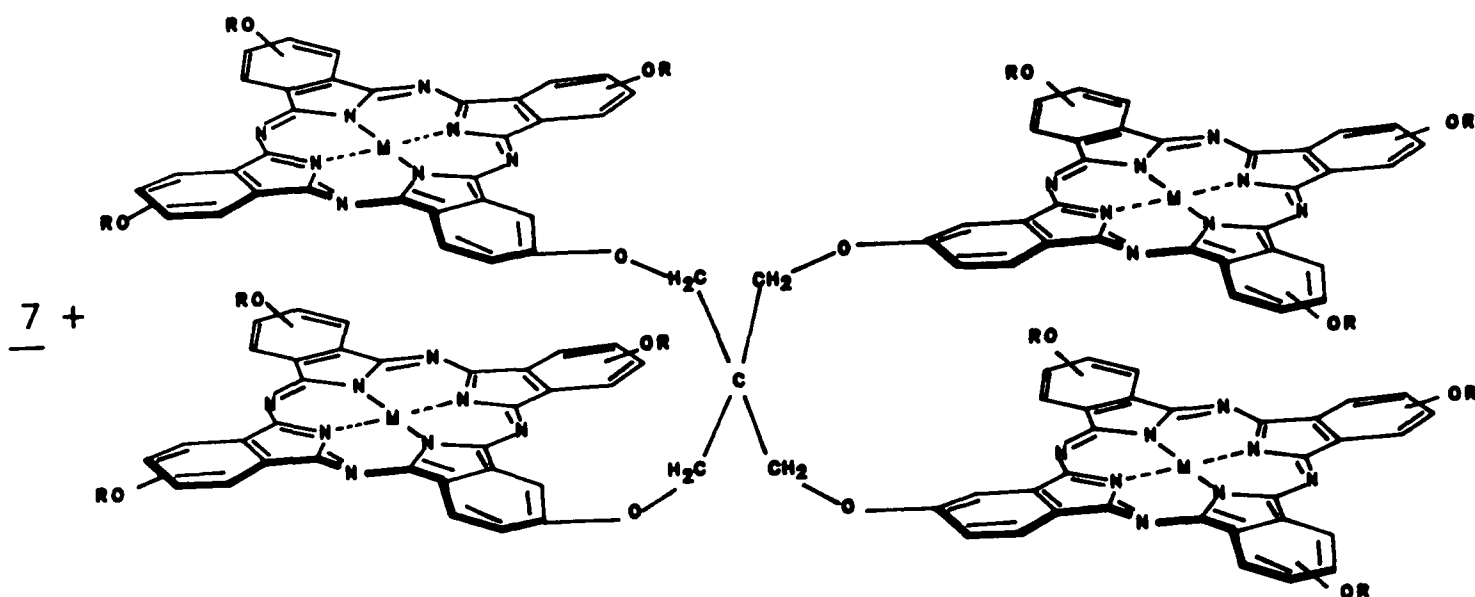
Table IV Kinetic Currents, in mA, for OPG Electrodes Modified with a Variety of Cobalt Neopentoxy Phthalocyanine Compounds in 0.10 M NaOH.

Compound	Potential versus SCE/V			
	-0.450	-0.500	-0.550	-0.600
CoTNPc	1.51	3.00	5.58	9.95
C(2)[CoTrNPc] ₂	1.64	3.20	5.90	11.01
Cat(4)[CoTrNPc] ₂	1.84	3.91	7.95	16.01
EtMeO(5)[CoTrNPc] ₂	2.35	4.38	7.68	13.08
O(1)[CoTrNPc] ₂	2.45	4.61	8.15	13.89
[CoTrNPc] ₄	2.65	5.22	9.84	18.24

Table V Normalized Kinetic Currents for OPG Electrodes Modified with a Variety of Cobalt Neopentoxo Phthalocyanine Compounds in 0.10 M NaOH.

Compound	Potential versus SCE/V				AVERAGE	s
	-0.450	-0.500	-0.550	-0.600		
CoTNPC	1	1	1	1	-	-
C(2)[CoTrNPc] ₂	1.09	1.07	1.06	1.11	1.08	0.02
Cat(4)[CoTrNPc] ₂	1.22	1.30	1.42	1.61	1.39	0.17
EtMeO(5)[CoTrNPc] ₂	1.56	1.46	1.38	1.31	1.43	0.10
O(1)[CoTrNPc] ₂	1.62	1.54	1.46	1.40	1.50	0.10
[CoTrNPc] ₄	1.75	1.74	1.76	1.83	1.77	0.04

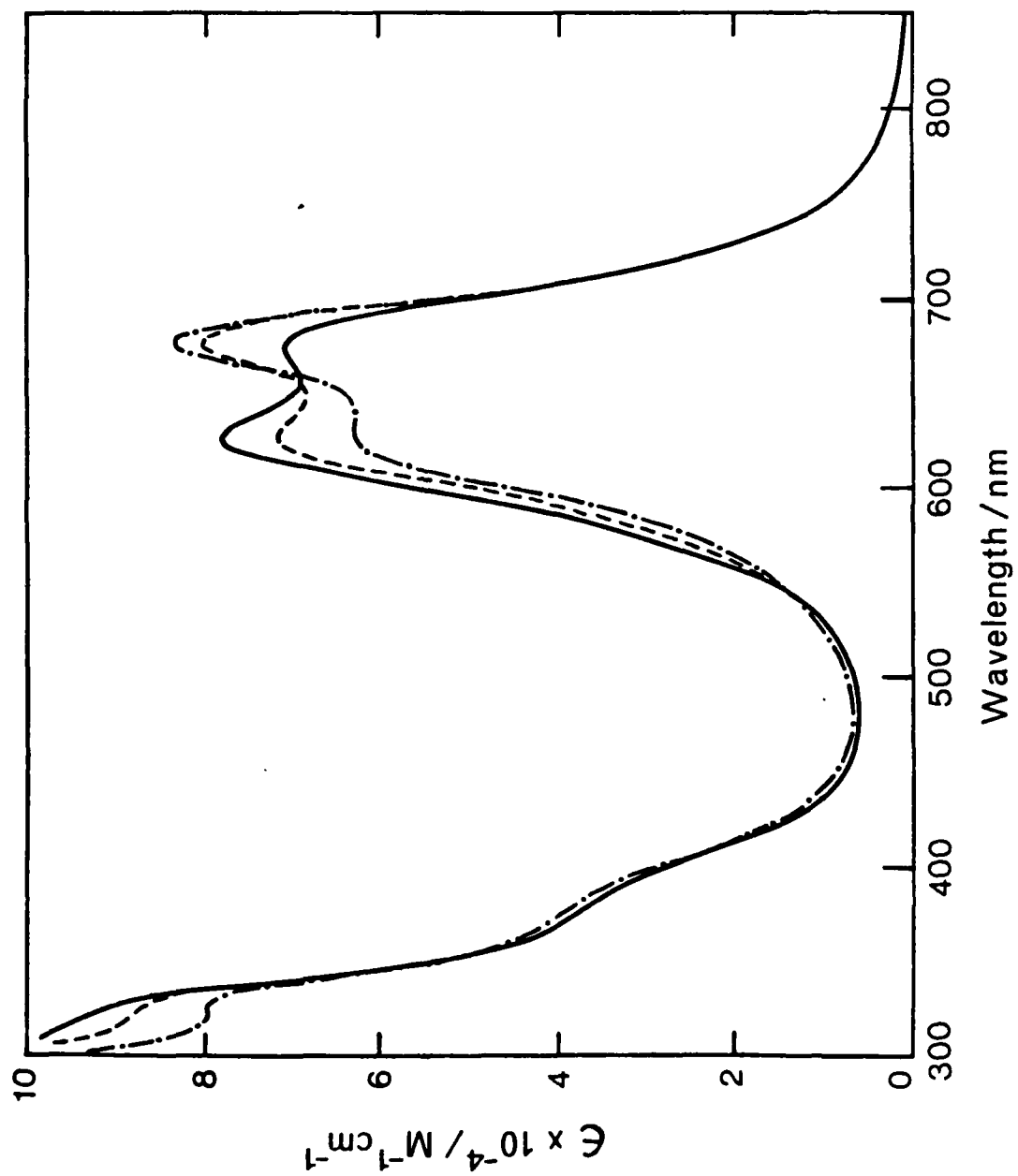




8 R = CH₂C(CH₃)₃, M = H₂

9 R = CH₂C(CH₃)₃, M = Co

fig. 2



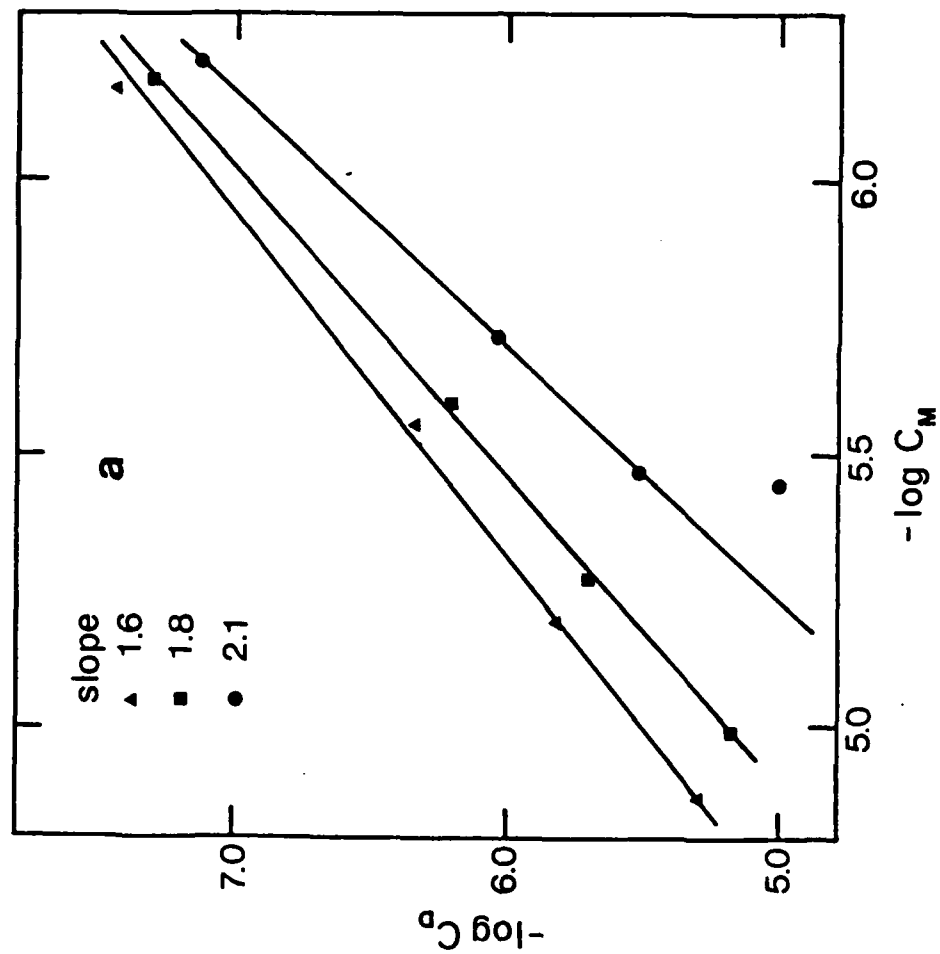


fig. 3(b)

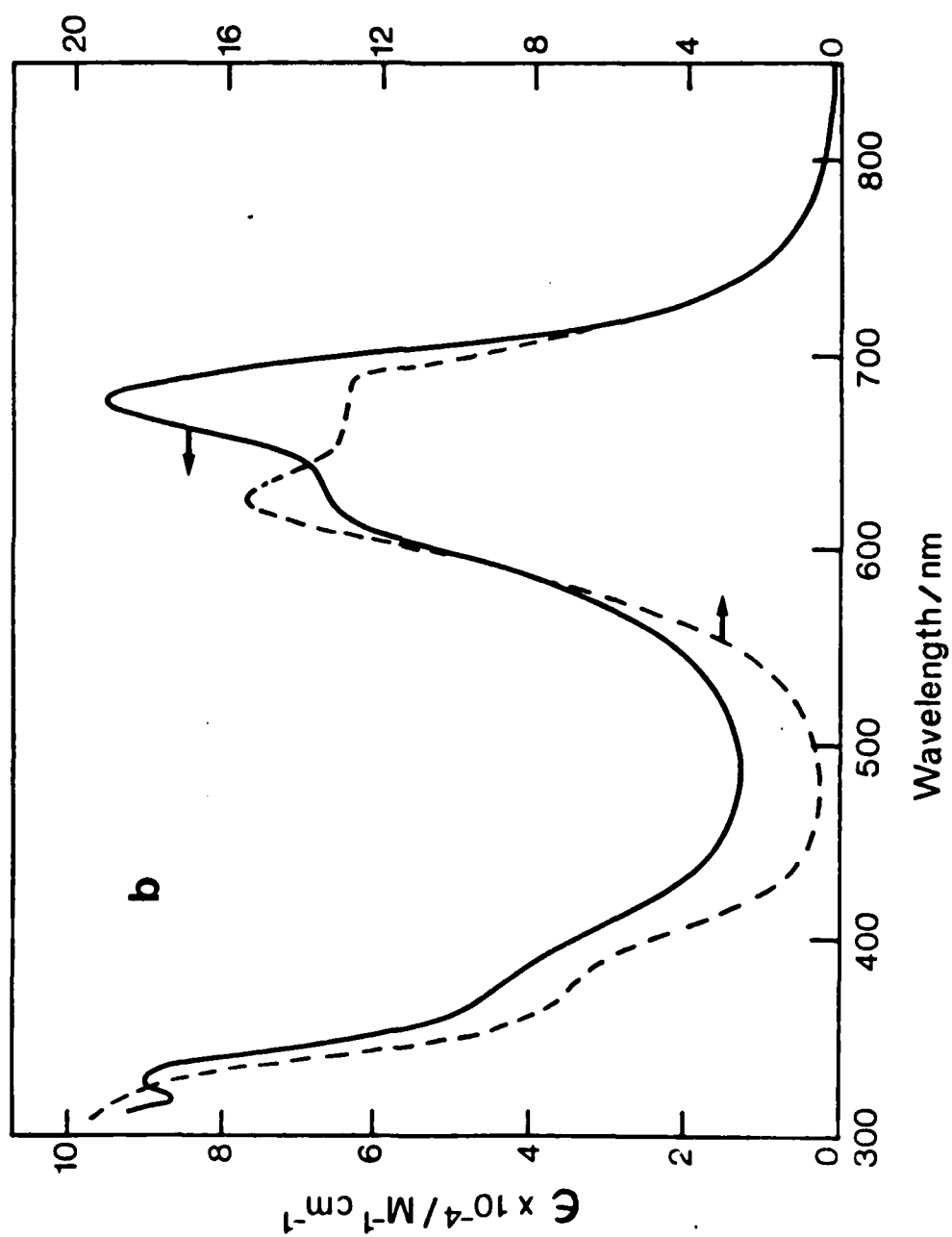


fig 4

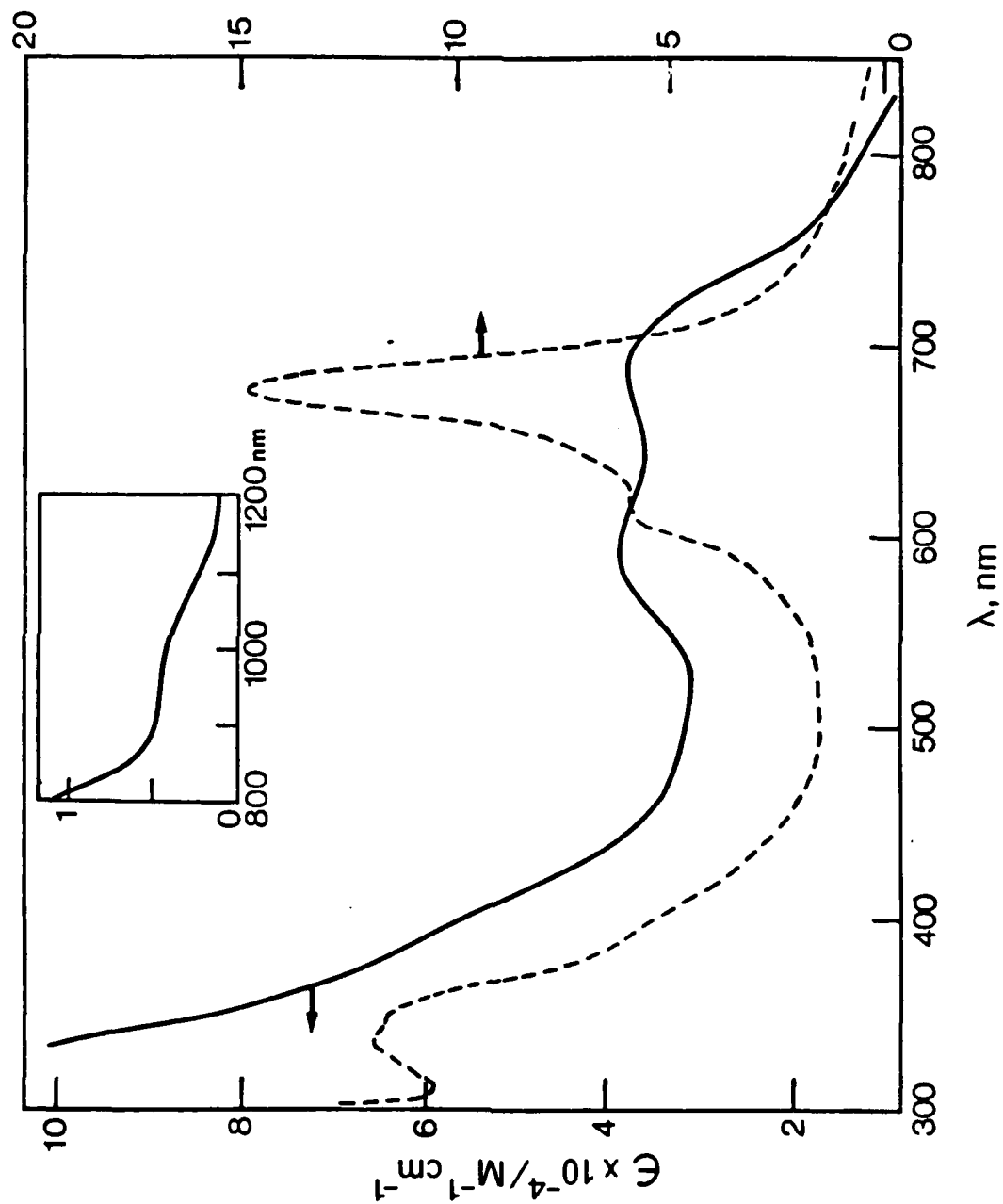


fig 5.

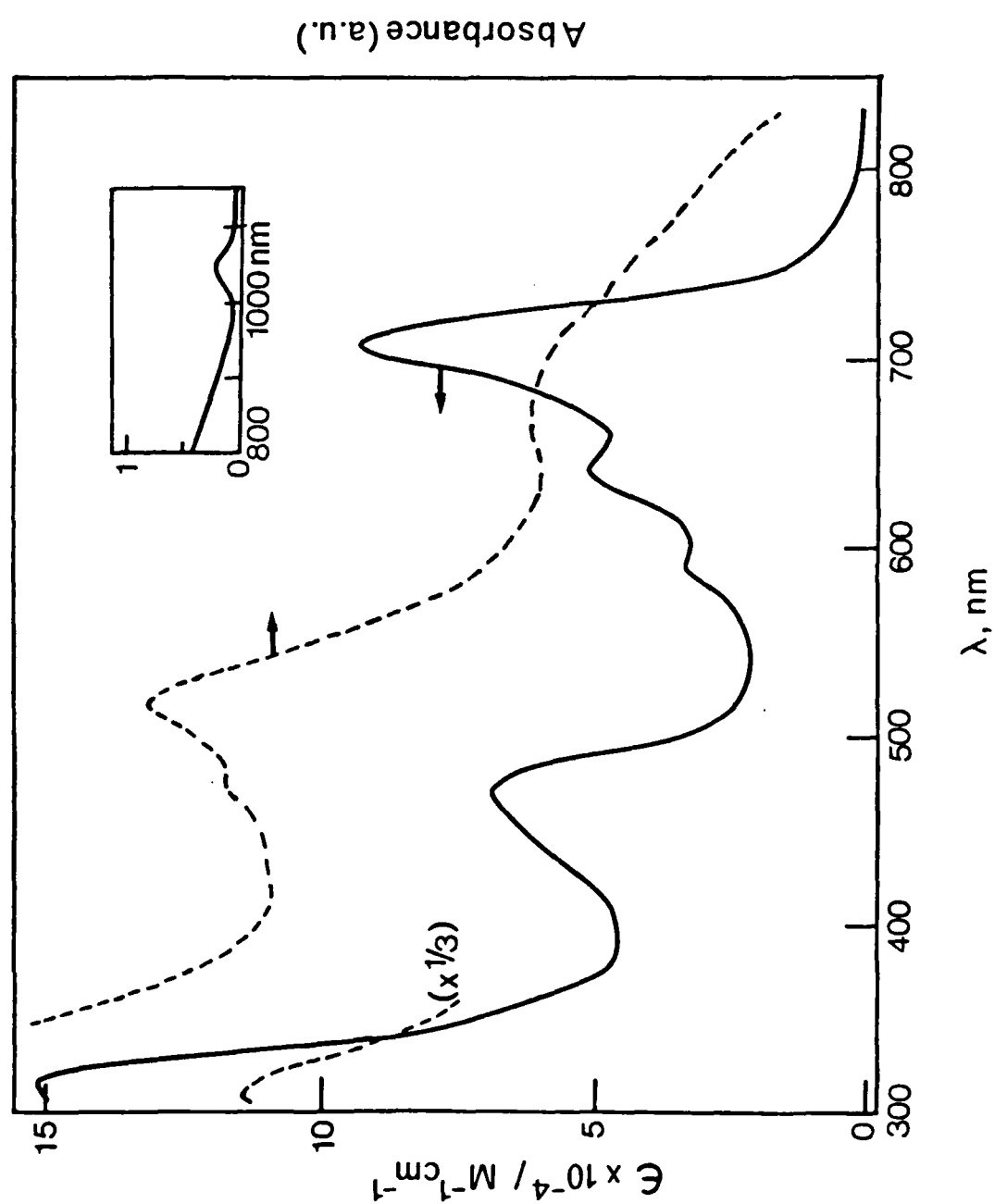


fig 6.

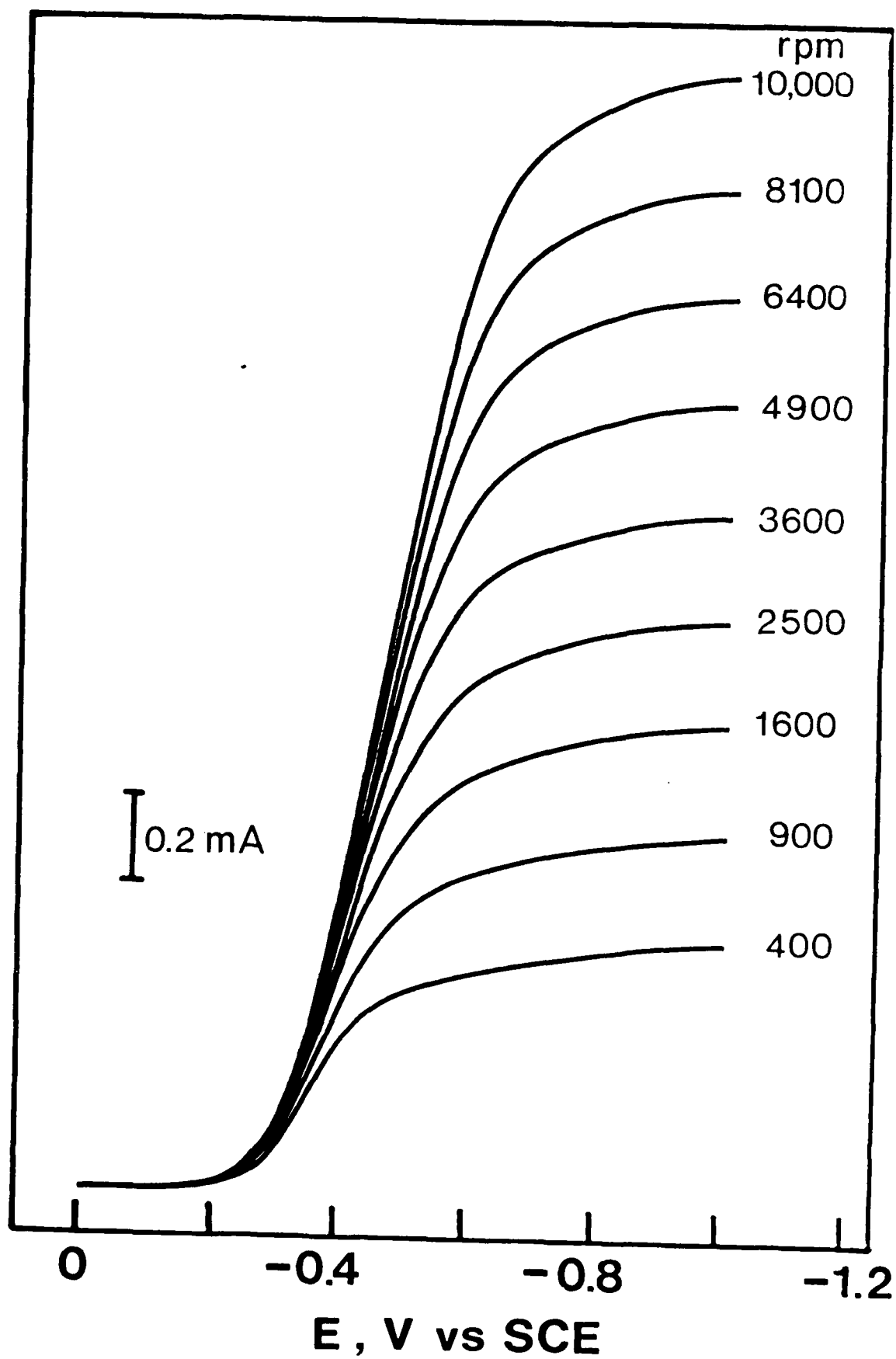


fig. 7.

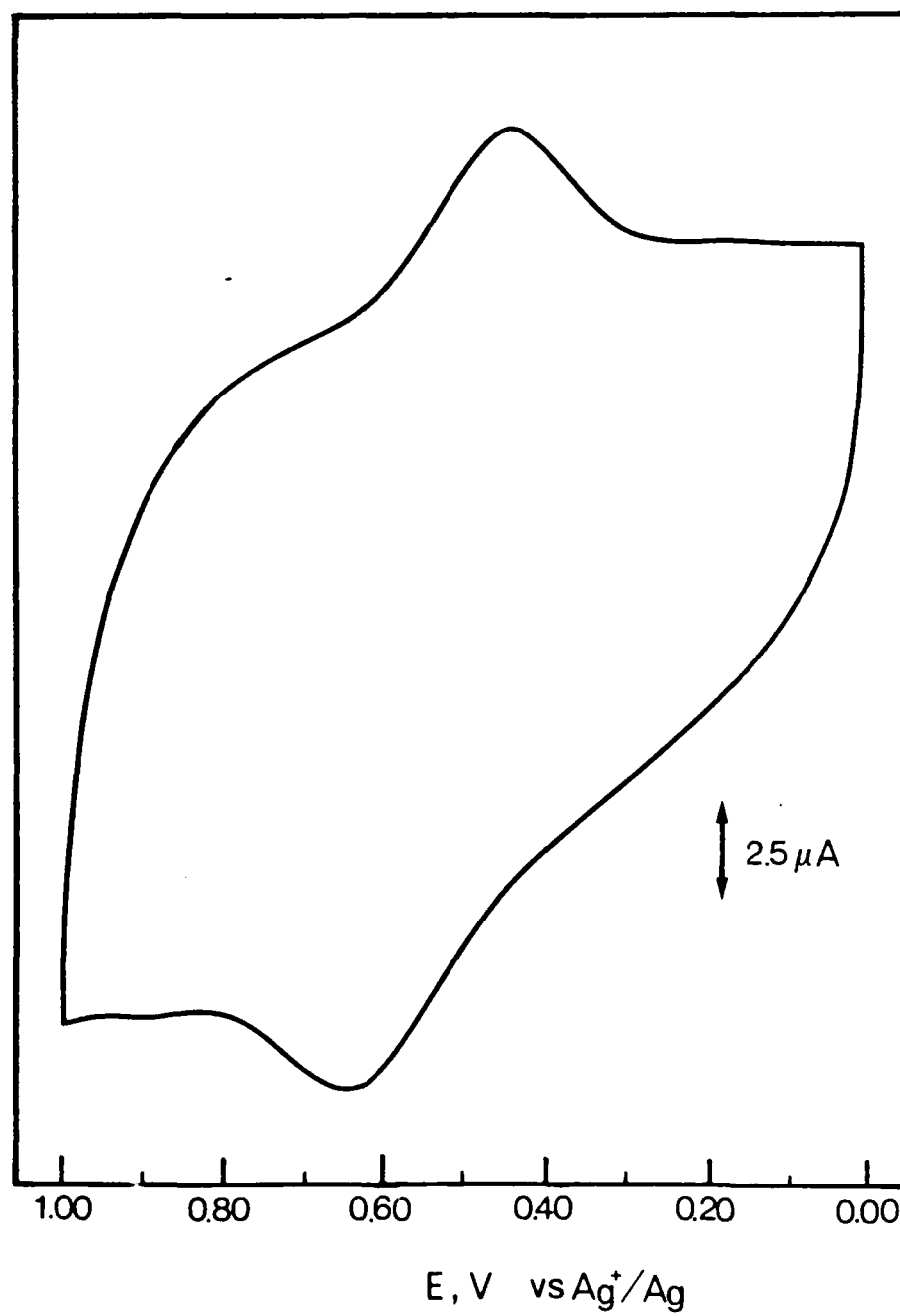
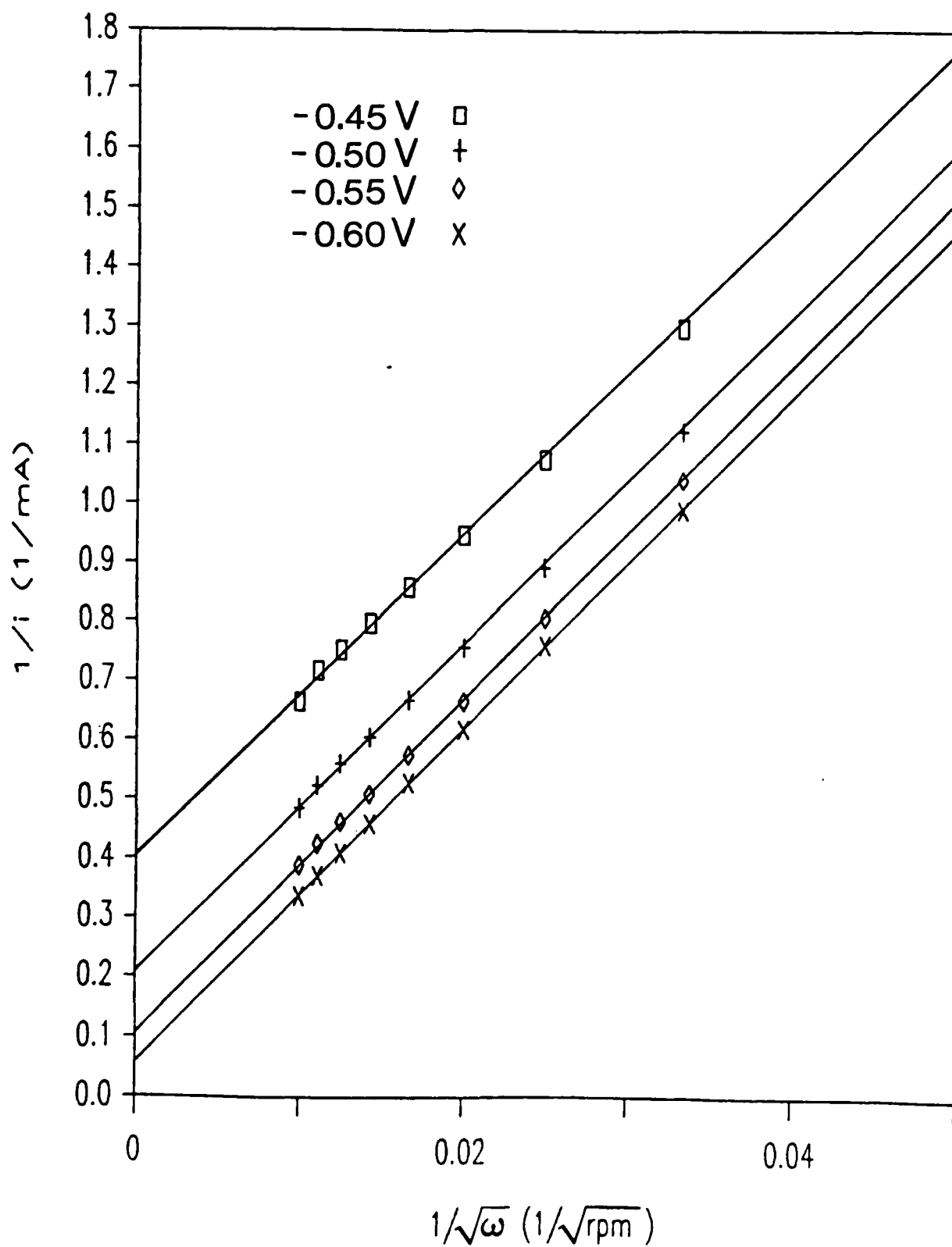


fig. 8.



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