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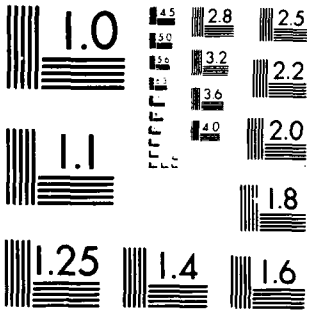

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Cation or Solvent-Induced Supermolecular Phthalocyanine Formation: Crown Ether Substituted Phthalocyanines

By

N. Kobayashi and A.B.P. Lever

in

Journal of the American Chemical Society

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Phthalocyanines with four 15-crown-5 ether voids at the 3,4 positions (MtCRPc) (Mt = H_2, Zn, Co, Ni and Cu) have been synthesized and characterised. Dimerisation of MtCRPc is induced in solvents such as methanol and by addition of some cations (K^+, Ca^{2+}, and NH_4^+), especially K^+. Cofacial dimer formation in the presence of these cations proceeds in a two-step three stage process, as indicated by absorption and emission spectroscopy. These species have a highly specific D_{4h} eclipsed configuration providing well defined dimeric species for spectroscopic analysis. The ESR spectrum of the cation induced dimeric CuCRPc shows axial symmetry and may be analysed in terms of an inter-planar separation of 4.1 Ångstroms. The ^1H NMR spectra (#19 con'd over)

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of the cation induced metal free and zinc dimers are consistent with an eclipsed configuration. Upper excited state (Soret, S_2) emission is observed for the first time in the phthalocyanine series.

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Cation or Solvent-Induced Supermolecular Phthalocyanine Formation: Crown Ether Substituted Phthalocyanines.

by Nagao Kobayashi[1*] and A.B.P.Lever[*]

Abstract

Phthalocyanines with four 15-crown-5 ether voids at the 3,4 positions (MtCRPc) (Mt = H_2, Zn, Co, Ni and Cu) have been synthesized and characterised. Dimerisation of MtCRPc is induced in solvents such as methanol and by addition of some cations (K^+, Ca^{2+}, and NH_4^+), especially K^+. Cofacial dimer formation in the presence of these cations proceeds in a two-step three stage process, as indicated by absorption and emission spectroscopy. These species have a highly specific D_{4h} eclipsed configuration providing well defined dimeric species for spectroscopic analysis. The ESR spectrum of the cation induced dimeric CuCRPc shows axial symmetry and may be analysed in terms of an inter-planar separation of 4.1 Ångstroms. The ^1H NMR spectra of the cation induced metal free and zinc dimers are consistent with an eclipsed configuration. Upper excited state (Soret, S_2) emission is observed for the first time in the phthalocyanine series.

Introduction

Dimerization, often through aggregation of porphyrins[2] and phthalocyanines[3] has been intensively investigated. In general the mechanism of aggregation is poorly understood, the product may be contaminated with monomer and perhaps with higher aggregates, and the relative orientation of the components is obscure. We report here the preparation of phthalocyanines functionalized at the 3,4-positions with four crown ether voids (MtCRPc),[4] together with their cation or solvent induced dimerization.[5] Unambiguous evidence is presented which indicates the step-wise formation of two dimeric species induced by K^+ ions. The first is non-cofacial, while the second is a rigidly cofacial eclipsed D_{4h} species. This provides the opportunity to study the uv/visible absorption and emission, ESR, and NMR spectra of well defined dimeric species (metal-free, Zn,Cu,Co and Ni) in terms of exciton theory. Upper excited state S_2 emission is observed in phthalocyanine chemistry for the first time. The results are compared with corresponding data for the tetra-crowned porphyrins,[6,7] where the orientation is twisted. We refer to the dimerisation of the monomeric MtCRPc units for ease of discussion while noting that the binuclear products contain one or more main group ions and are therefore not, strictly speaking, dimers of the mononuclear unit.

Experimental

i) Measurements: Electronic absorption spectra were recorded with a Perkin Elmer-Hitachi model 340 microprocessor spectrometer. Emission and excitation spectra were obtained with a Varian SF330 spectrofluorimeter with appropriate filters to eliminate scattered light. Fluorescence quantum yields were determined by the use of quinine bisulfate in 1N H_2SO_4 (Φ_F = 0.55 at 296 K),[8a,b] or free base tetraphenylporphyrin in benzene (Φ_F

= 0.11).[8c] Data were obtained by a comparative calibration method using the same excitation wavelength and absorbance for the crown species and the calibrants, and the same emission energies.

ESR measurements were obtained using a Varian E4 spectrometer, calibrated with DPPH. FTIR spectra were recorded on a Nicolet SX20 spectrometer using KBr discs. ^1H NMR spectra were recorded on a Varian LH360 spectrometer using deuteriochloroform alone, or containing deuteromethanol or tetramethylsilane as internal standard. The FAB mass spectra were obtained by courtesy of the Nebraska Center for Mass Spectroscopy by the same method as described previously.[9] Solvents, dimethylformamide, 1,2-dichloroethane, diethylether, methanol, ethanol, etc were either distilled or Spectrograde.

ii) Synthesis:

2,3-(3',4'-Dibromobenzo)-1,4,7,10,13-pentaoxacyclopentadeca-2-ene.

Following the dibromination of 1,2-dimethoxybenzene[10], so-called benzo-15-crown-5[11] was reacted with 2 equivalents of bromine in acetic acid, using a small crystal of iodine as initiator. Recrystallisation from ethanol gave colorless plates in 51% yield. Anal.calcd. for $C_{14}H_{18}Br_2O_5$: C,39.5; H,4.3. Found: C, 39.6; H,4.3%. ^1H NMR ($CDCl_3$, internal Me_4Si) 7.06(2H,s), 4.25-3.70(16H,m). m.p. 80-81°C.

2,3-(3',4'-Dicyanobenzo)-1,4,7,10,13-pentaoxacyclopentadeca-2-ene.

The above dibrominated benzo-15-crown-5 (8.52g, 0.02mol) and CuCN (5.4g, 0.06mol) were refluxed in dry DMF (80mL) for 5h. After rotary evaporation of about 50-60mL of DMF, concentrated ammonia (200mL, 28%) was added, and air bubbled through the solution for 12h. After washing copiously with water, the dry olive-green product was soxhlet extracted with diethyl ether for 3 days. Benzene recrystallisation provided 2.02g (31%) of colorless small needles. Anal. calcd. for $C_{16}H_{18}N_2O_5$ C, 60.4; H,

5.7; N,8.8. Found: C,60.1; H, 5.8; N, 8.5%. ^1H NMR($CDCl_3$) 7.14(2H,s), 4.35-3.70(16H,m). IR(KBr) ν 2223(C≡N) cm^{-1}, m.p. 151-2°C.

Non-metallated (H_2CRPc) and metallated (MtCRPc) crowned phthalocyanines

H_2CRPc was prepared by refluxing benzo-15-crown-5 dicyanide (1.24g, 3.9 x 10^{-3} mol) in 2-dimethylaminoethanol (5mL) for 17h while passing ammonia gas through the solution. The precipitate was re-precipitated from diethylether, washed with water, dried and then chromatographed on basic alumina, initially with chloroform as eluant. The initial yellow band, which was discarded, was followed by a blue band which was eluted with ethanol-chloroform, providing 0.468g (38%) of slightly bluish green powder (Anal, see Table I). ^1H NMR($CDCl_3$) 8.02(8H,s), 4.7-3.6(64H,m), -3.41(2H,s).

ZnCRPc was obtained by reaction of H_2CRPc with a large excess of zinc acetate in refluxing DCE/ethanol, for several days in the dark, until the 4-band Q spectrum of H_2CRPc had disappeared. After removal of the solvent, the residue was washed with water and recrystallised from chloroform-ethanol (78% yield). The FAB mass spectrum showed peaks at m/e values of 1339(M^+,7), 956(68), 522(22), 460(58), 424(23), 307(46) and 154(100) (relative intensities in parentheses).

Other MtCRPcs (Mt = Co(II), Fe(II), Ni(II), Cu(II)) were prepared by the "nitrile" method.[12] The benzo-15-crown-5 dinitrile and the appropriate metal acetate were refluxed gently in ethylene glycol[10] for several hours. The solution was filtered while hot, and the residue washed with hot ethanol, hot water, and hot ethanol, then chromatographed on basic alumina, resulting in yields between 26 and 51% of the metallated products. Elemental analyses are presented in Table I.

Results and Discussion

i) Cation complexation leading to step-wise cofacial dimer formation.

In chloroform solution, the several MtCRPc species exhibit spectra typical of well behaved mononuclear metallophthalocyanines[12] generally with a single intense π-π^* transition in the range 667-708nm with associated higher energy vibrational components, commonly referred to as the Q band, and a second intense and broader π-π^* transition at 300-360nm called the Soret[12] (Table II, Fig.1). The metal free species, H_2CRPc is similar but shows two closely spaced Q bands because of its lower (D_{2h}) symmetry. As will be demonstrated below, dimerization occurs in many other solvents or when certain cations are added to this solution. Such dimerization is readily monitored by the dramatic change in absorption, and in particular by a blue shift in both the Soret and Q band absorption.[13]

In the case of porphyrins functionalised at the methine positions with four benzo-15-crown-5[7a], increasing addition of K^+, NH_4^+, and Ba^{2+} ions affected the porphyrin Q band absorption by a) a reduction in intensity, b) broadening and c) a <u>red</u> shift of ca 10nm. On the other hand, Na^+, Mg^{2+} and Ca^{2+} did not cause any appreciable change in the visible region absorption. Note that the potassium ion is sandwiched between two crown ether units, and does not reside within the ether ring.

The MtCRPc species behave quite differently. Thus K^+, NH_4^+, Ca^{2+} and Na^+ all alter the spectra appreciably, though not all in the same fashion, while Ba^{2+}, Cs^+ and Mg^{2+} have little effect. The ionic radii of cations which produce significant changes in the electronic spectra of the MtCRPc species, are equal or smaller than those required in the porphyrin series.[14] In the crown phthalocyanine case, addition of K^+, NH_4^+ and Ca^{2+}

causes a) a reduction in Q band intensity around 660-700nm (the so-called monomer peak) and an increase in peak intensity around 620-640nm, (the so-called dimer peak) i.e. a blue shift of the Q band of ca 30-60nm, b) a blue shift in the Soret (10-20nm) and c) some broadening in the Q band region (Fig.1A, Table II). Such changes are most obvious for K^+ with respect to the amount needed to affect them.

Absorbance intensities in the 660-700 and 620-640nm ranges change markedly with K^+ concentration up to $[K^+]/[MtCRPc]$ = ca 2. Previous experience with aggregated[3] and binuclear phthalocyanines[13] shows that the loss of low energy Q band absorption, near 660-700nm, of the monomeric species, and the shift to a broad absorption near 620-640nm is consistent with electronic coupling between a pair (or more) of phthalocyanine units. In this case, as will be documented more fully below, dimerisation is the exclusive process.

From the plot (Fig.2) of the intensity changes with $[K^+]$, there is evidence for a two-step three stage process. The first, second and third stages occur approximately at $[K^+]/[MtCRPc]$ values of 0-0.5, 0.5 - 1.5 and over 1.5, respectively. The K^+ induced two-step three stage process is also obvious from the shift in position of the isosbestic points (Fig.1).[15]

Assuming the monomer-dimer equilibrium (eq.1) for the K^+ triggered spectroscopic change:

$$nK^+ + 2\ \text{monomer} \xleftrightarrow{K} \text{dimer}.K^+_n \qquad (1)$$

the specific monomer and dimer concentrations were derived using the method of West and Pearce[16], using as data the changes of intensity at two wavelengths, as a function of $[K^+]$. The pure monomer spectrum[17] was assumed to be present in the absence of K^+. Using this procedure, proof

of formation of the dimer may be obtained by plotting the calculated log[monomer] against calculated log[dimer].[18] A slope of 2 will be obtained if eqn.(1) is applicable. Formation of higher oligomers would cause the slope to be more steep than 2. Indeed as revealed in Fig.3 there is a region where the slope is 2.0. When K^+ ions are added to a MtCRPc solution, the monomer concentration decreases sharply, and a region with slope = ca 2.0 continues until $[K^+]/[MtCRPc] = 0.5$. After this point, the slope of the plot approaches zero, especially beyond the region $[K^+]/[MtCRPc] \geq 1.0$.

Thus the monomer-dimer conversion proceeds with a very high formation constant (K for eqn.1 with n = 1, (6±2) x 10^9 L^2 mol^{-2}) until two MtCRPc units bind ONE cation. Subsequently the spectroscopic changes in the $[K^+]/[MtCRPc] \geq 1.0$ region are no longer a monomer to dimer transformation process, but, rather rearrangement of one form of dimer to another. The region $0.5 \leq [K^+]/[MtCRPc] \leq 1.5$ can be considered to be the transition stage where the MtCRPc-cation-MtCRPc complex combines with a 2nd and 3rd cation. Considering that the blue shift in the Q and Soret absorption in the dimers can be explained by an exciton interaction[19], and that the ESR data for CuCRPc in the presence of K^+ or Ca^{2+} (vide infra) will indicate the presence of two copper atoms in very close proximity, the last stage ($[K^+]/[MtCRPc] \geq 1.5$ in Fig.2) can be ascribed to cofacial complex formation. Thus after formation of a non-cofacial MtCRPc-cation-MtCRPc dimeric complex, increasing cation concentration causes a conformational change in the dimer wherein the two phthalocyanine halves encapsulate two or more cations leading to the formation of the cofacial dimer, i.e. a supermolecular phthalocyanine is attained. Probably encapsulation continues until the available sites are saturated, i.e. until two MtCRPc units bind four cations in rigid eclipsed dimer. The inset of Fig.3 shows

the calculated monomer and dimer concentrations of NiCRPc as a function of $[K^+]/[NiCRPc]$. Although not shown, similar behaviour is observed with the other MtCRPc species; thus dimerisation is essentially complete (but not cofacial dimerisation) when $[K^+]/[MtCRPc] > 1.0$.

The addition of sodium ions did lead to a change in spectrum (Fig.1B) in contradistinction to the porphyrin series.[7a] The band due to the monomer species decreases in intensity, while there is growth in the band due to the dimeric species. Sodium ions are, however, unable to effect the complete conversion to a spectrum, obtained with potassium ions, typical of the cofacial species.

ii) Solvent induced dimerisation.

The intensity of the MtCRPc Q band peak (around 660-700nm) decreases if the solvent is changed from chloroform to methylene chloride, benzene, DMF, dimethyl sulfoxide, toluene, THF, ethyl acetate, methanol etc. In such circumstances the change in spectrum exactly parallels that observed upon K^+ addition. Such spectroscopic changes are also observed in mixed solvents, e.g. Fig.4a shows the effect of mixing methanol into chloroform, upon the CoCRPc spectrum. With increasing ratio of methanol to chloroform, the peak height at 668nm (mainly monomer) decreases but that at 625nm (mainly dimer) increases. For comparison, Fig.4b shows the corresponding data for addition of K^+. The dimeric spectrum induced by the methanol solvent ($CHCl_3$:MeOH = 2:1 v/v) is essentially identical to that obtained at a $[K^+]/[CoCRPc] = 1.6$ ratio which demonstrates that the mixed solvent is giving rise to cofacial dimer formation. Unfortunately the very low solubility of the metallated crown phthalocyanines in dimer-forming solvents (ca. 1×10^{-5}M) precludes other methods of characterisation. Note that the solubility of the monomers in chloroform is several orders greater.

iii) Electron Spin Resonance.

Of the several MtCRPc species investigated, CuCRPc is expected to provide the most definitive ESR spectra. Preliminary studies showed that data collection in a chloroform-methanol mixture provided better data than pure chloroform. The spectrum of CuCRPc obtained in the absence of any cations (Fig.5A) is structureless and seems to be that of a somewhat aggregated species.[20]

Addition of an excess of sodium ions led to the development of a well defined structured signal (Fig.5B-a) in frozen solution, basically very similar to previously observed monomeric copper porphyrin and phthalocyanine species, e.g. copper(II) tetraphenylporphyrin.[21] The spectrum is clearly axial and contains both copper hyperfine and nitrogen (from the four coordinating phthalocyanine nitrogen atoms) super-hyperfine structure. The parameters ($g_{\parallel}$ = 2.166, $g_{\perp}$ = 2.049, and $A_{\parallel}^{Cu}$ = 228 x 10^{-4}, $A_{\perp}^{N}$ = 16.7 x 10^{-4}, $A_{\parallel}^{N}$ = 14.3 x 10^{-4} cm^{-1}) are typical values for a species of this type. As developed further below, the solution giving rise to this spectrum contains about 50% mononuclear species, and 50% of the non-cofacial dimer almost certainly with sodium ions occupying the ether voids in both cases. In the absence of sodium ions, the solution is partially aggregated resulting in broadening of the resonance signals. In the presence of sodium ions, the resulting positive charge keep the copper atoms separated and a clean highly resolved ESR spectrum is observed.

Dramatic changes in the ESR spectrum of CuCRPc occur when K^+ or Ca^{2+} ions are added (Fig.5C,D). This observation differs from the corresponding Cu(II) crown porphyrin where K^+, but not Ca^{2+}, was effective.[7a] Thus with CuCRPc both cations yield two strong perpendicular transitions in the g = 2 region. These transitions do not exhibit nitrogen super-hyperfi coupling but do show the characteristic seven line pattern expected for

two equivalent Cu(II) ions coupled together.[22] In the half-field region ($\Delta M = \pm 2$), seven equally spaced lines (87-88 gauss separation) are observed. These data provide unmistakable evidence for the formation of a symmetric dimeric molecule. The absence of any ESR signal originating from a monomeric CuCRPc molecule, under these conditions, attests to a high formation constant. Moreveor the overall band envelope is essentially identical to those of various well defined symmetric binuclear and coupled copper complexes in the literature.[23] The data in Figs. 5C and 5D also exclude any significant proportion of higher aggregate.

The ESR parameters for these spectra are collected in Table III, having been evaluated by standard procedures.[24] Most importantly it is possible to evaluate the Cu-Cu distance from the zero field splitting parameters.[25] In this fashion the calculated Cu-Cu distance is found to be ca. 4.1 Angstroms, in the presence of both K^+ or Ca^{2+}. This is nearly identical to the distance estimated from CPK molecular models.[26] Note that in the presence of ammonium ions, dimerisation does occur and two strong perpendicular transitions are observed, but the seven line pattern is not resolved.

iv) ^1H NMR Spectra.

The ^1H NMR spectrum of ZnCRPc is shown in Fig.6, both in the presence and absence of cations. The spectrum of mononuclear ZnCRPc is complex, in the high field region, due to a large number of chemically inequivalent ether fragments, but the signals are well separated by the ring current anisotropy of the phthalocyanine core. Assignments are shown in Fig.6.

The addition of $CaCl_2$ to a solution of ZnCRPc ($[Ca^{2+}]/[ZnCRPc]$ ca. 10) increases the complexity of the high field region (Fig.6b) and the signals spread out, especially downfield. These data are consistent with cofacial dimer formation (Fig.7). The singlet of aromatic protons does not

significantly shift but becomes sharper, due, probably to the restricted rotation of the $O-CH_2-CH_2-O$ groups or to the greater rigidity imposed by encapsulation of the cations. The negligible shift of the singlet is expected since the 3,4-protons of one phthalocyanine fall in the "black region" of the anisotropic shielding effect of the second ring,[27] assuming the interplanar distance is close to 4.1 A.[28]

The pyrrole protons of H_2CRPc shift from -3.41 ppm to -8.09 ppm with cofacial dimer formation consistent with the structure in Fig.7. This large upfield shift indicates an intense diamagnetic ring current interaction in this dimer.[29]

v) Emission spectroscopy.

Fluorescent emission from the lowest $\pi-\pi^*$ (Q band) state is common in metal free, zinc and other main group phthalocyanines.[30,31] Both mononuclear H_2CRPc and ZnCRPc exhibit such emission near 700nm. The excitation spectrum of this emission (Fig.8a) parallels that of other mononuclear phthalocyanines[13] except for a rather prominent excitation near 430nm which is also observed in absorption (Table II). This is rather unusual for a phthalocyanine unit and may involve the ether oxygen lone pairs.

Emission from the upper excited $\pi-\pi^*$ state (Soret), so-called S_2 emission is not uncommon in porphyrin chemistry.[32-34] We have recently noted that several binuclear and tetranuclear phthalocyanines also exhibit upper excited state emission[35] and also find that both metal free and zinc crown phthalocyanine <u>monomer</u> species exhibit emission in chloroform near 430nm (Fig.8). These are the first examples of phthalocyanine upper excited state emission.

The crown S_2 emission is broader than the S_1 emission and the band shape is similar to that observed for tetrabenzporphyrin free base and its

zinc derivative.[32] The excitation spectra of the S_2 emission is similar, but not identical, to the S_1 excitation spectra (Fig.8A, Table II). Assuming that the S_2 emission originates in the same transition which gives rise to the well developed 420nm absorption, then the Stokes shift for S_2 emission is, as in the porphyrin species, very small.

Using the known quantum yields of quinine sulfate[8a,b] (for S_2) and free base tetraphenylporphyrin[8c] for calibration, the quantum yields for S_1 and S_2 emission were determined to be, in chloroform, 0.7 and 1 x 10^{-2} for H_2CRPc. Some solution instability precluded an accurate determination for ZnCrPc. The S_1 quantum yield is very similar to those observed earlier for unsubstituted metal free and zinc phthalocyanine species.[30,31]

Addition of K^+ to metal free and zinc crown Pc monomers in chloroform (concentration < 5 x 10^{-6}M) leads to quenching of both the S_1 and S_2 emission, in a parallel fashion (Fig.8b). The concentration of K^+ ion required to quench the fluorescence intensity of a crowned porphyrin is apparently very much less than the concentration of the cation required to reduce the optical density of the porphyrin in the ground state.[7a] In the crowned phthalocyanine system (Fig.9), on the other hand, the quenching behaviour corresponds almost exactly to that in the absorption study (Fig.2). The Stern-Volmer plot for S_1 emission (Fig.9A) is clearly consistent with step-wise encapsulation of the K^+ ions. In the 0 < $[K^+]/[H_2CRPc]$ < 0.5 region where the non-cofacial H_2CRPc-K^+-H_2CRPc species forms (Figs.2,3), quenching is not marked, though it does occur to a small degree. However with further increase in $[K^+]$, quenching is greatly enhanced while above $[K^+]/[H_2CRPc]$ = ca. 1.5 the emission intensity become almost constant. The residual emission intensity has an excitation spectrum identical to that of the monomer species and an intensity about 1/700 of the initial intensity. It is due to the small amount of monomer

species in equilibrium with the cofacial species, implying that the cofacial dimer does not emit.[33]

The quenching of the S_2 emission parallels that of the S_1 quenching except that the degree of quenching is much less marked (Fig.9b). There is also some remaining S_2 emission which appears to arise from the cofacial dimer since it is relatively very much more intense than can be reconciled with the equilibrium monomer content (intensity 2/5 of initial value, upon cofacial dimer formation) (Fig.9b). However the excitation spectrum of this residual S_2 emission is the same as in the monomeric species. There remains the suspicion that the S_2 emission does not indeed originate from the phthalocyanine but from an impurity. This possibility appears excluded by the similarity of its excitation spectrum to the Soret absorption, and the similarity of its quenching behaviour to that of S_1, but, as noted above, there are some inconsistencies.

The addition of Na^+ ion to a chloroform H_2CRPc solution also quenches, to some degree, both the S_1 and S_2 emission (Fig.9C). However much higher concentrations of Na^+ are needed and it is clearly much less efficient. In the crown porphyrin case,[7a] Na^+ did not perturb emission. As indicated above, Na^+ ion only takes the species to the second non-cofacial dimer stage.

(vi) Absorption spectra (Table II).

a) Mononuclear species and cofacial dimer.

The mononuclear species have absorption spectra in chloroform (Fig.2, Table II) typical of mononuclear MtPc species[3] though with a prominent shoulder or peak near 420nm which is not so common. Its appearance is reminiscent of the hyper-porphryin spectra, showing similar additional absorption but the latter arises as a consequence of the central ion

having an $(np_z)^2$ pair of electrons, e.g. Pb(II).[30] This 420nm band shifts but does not disappear upon cofacial dimer formation.

The formation of the cofacial dimeric species provides a convenient method of studying exciton coupling in an eclipsed phthalocyanine species. Some spectra of fully eclipsed cofacial species are shown in Fig. 10, and the data collected in Table II. Note that under the conditions $[K^+]/[MtCRPc] > 1.5$, the quantity of mononuclear species in equilibrium with the cofacial dimer is less than 0.2% and therefore its spectrum makes no significant contribution to the spectra reported here for the cofacial species. The most interesting feature of the cofacial dimeric spectra is the single rather broad (compared to the monomer) and symmetrical Q band absorption. Although the molar extinction coefficients of the cofacial dimer Q bands are approximately one-half of the corresponding monomer Q bands, the oscillator strengths are essentially identical, i.e. there is no loss in transition probability in forming the dimer (see Table II).

Thus exciton coupling of the two Q S_1 states leads to two new levels corresponding to an in-phase and out-of-phase coupling. Transitions to the lower, out-of-phase, component are forbidden rigorously in an eclipsed D_{4h} species.[36] For compounds which show typical monomeric and dimeric spectra (MtCRPc, M = Zn, Cu, Ni and Cu), the Q band blue shift upon dimerization is about 880 - 980 cm^{-1}. For parallel eclipsed dimers with negligible distortion from D_{4h} symmetry, the dipole-dipole excitation splitting, V, is given by eqn.(2):[37]

$$V = e^2M^2/4\pi hc\varepsilon_0R^3 \qquad (2a)$$

$$= 1.16 \times 10^5M^2/R^3 \qquad (2b)$$

where M, and R are the dipole length, and the inter-molecular separation respectively, ε_0 is the permitivity in a vacuum and the other parameters have their usual meaning. V is given in wavenumbers in (2b) if

M and R are expressed in Angstroms. The dipole length in Angstroms can be estimated from eqn.(3):[30]

$$M^2 = (\epsilon_{max}/2513G)(\Delta\lambda/\lambda) \quad (3)$$

where G is the degeneracy, 2 in this case, $\Delta\lambda$ is the halfbandwidth, λ is the wavelength and ϵ_{max} is the molar extinction coefficient of the dimer Q band, respectively. In this fashion the M values are estimated to be about 0.68 - 0.98Å (Table IV). Alternatively M may be estimated from the oscillator strength[38] yielding the same result. Assuming a distance of R = 4.1Å, from ESR, the exciton splitting is calculated to be about 770 - 1600 cm^{-1}. The exciton splitting may also be estimated as twice the energy difference between the mononuclear Q band and dimeric Q band peak energies, yielding about 1760, 1960, 1910 and 1960 cm^{-1} for Ni, Co, Cu and ZnCRPcs respectively. This compares with an exciton splitting of about 2500cm^{-1} for the binuclear bridged cofacial phthalocyanine species.[13] Using these data and eqn.(3), provides an alternate route to estimating inter-metallic distances, leading to the data shown in Table IV; the electronic spectra and electron spin resonance experiments yield comparable results.

The Soret band is much less obviously affected by formation of the cofacial dimer. There is generally a small blue shift but little change in intensity. Nevertheless the shift is comparable to that seen in the Q band.[5a] Thus coupling of the Soret states does appear to have taken place even though little quenching of the S_2 emission apparently occurs.

b) Non-cofacial dimer.

The spectra of the non-cofacial dimer, obtained with $[K^+]/[MtCRPc]$ = 0.5, are collected in Fig.10, while the spectrum of the sodium ion induced non-cofacial dimer of CuCRPc is shown in Fig.1, in both cases in admixture with the monuclear species. With $[K^+]/[MtCRPc]$ = 0.5, there is

approximately 50% of monomeric species in equilibrium with the non-cofacial dimer. In Fig.11 the spectra of several non-cofacial dimeric species are shown, obtained by subtracting the spectrum of the mononuclear species from the admixed spectra. One observes that the resulting spectrum is very similar to that of the cofacial species and with an intensity, per dimeric unit, slightly less than that of the cofacial dimer. There is also evidence for the existence of a new shoulder or peak to the blue of the main Q band absorption, and little evidence for any additional absorption to the red of the Q dimer peak. There is no shifting in the Soret band (Fig.1).

The initial non-cofacial dimer, second stage product, reasonably consists of a dimeric molecule whose two halves are joined together at one ether unit by a bridging potassium ion. In fluid solution there may be many conformational forms of this dimeric unit. The electronic spectrum will consist of a 'snap-shot' of all possible conformations. If there is free rotation about the potassium ion, then many conformational forms will have symmetry much lower than D_{4h}. Such a situation will give rise to substantial absorption to the red of the cofacial dimeric peak,[18,36] yet this does not appear to be observed, rather, additional absorption is seen to the blue. Suppose instead that the ether voids, which are rather bulky, inhibit such rotation, and restrict the molecule to an end-to-end stretched out 180° conformation of C_{2h} symmetry, viewed edgeways-on as a step conformation. Such a conformation would show two higher energy peaks due to the splitting of the otherwise degenerate exciton coupled state, but transitions to the two lower energy states remain strictly forbidden.[36] Thus the data appear to support such a linear step conformation. Recall, further, that the ESR spectrum of the CuCRPc-Na^+-CuCRPc solution shows no evidence for Cu-Cu coupling,

consistent with the stretched out formulation.

Note further that the two parts of the step must be parallel - if their angle were greater than 180°C, i.e. they were tilted away from each other, absorption to the red of the dimer peak would be expected. Such tilting must be absent or small.

It is noteworthy that the mononuclear emission from S_1 is not quenched to any significant extent upon formation of the stage 2 non-cofacial dimer irrespective of whether it is potassium or sodium ion induced. Since the electronic spectra of these species show significant electronic coupling effects, such an observation is rather surprising.

Concluding Remarks

The structure of the final stage 3 dimeric species, assigned to a fully eclipsed cofacial D_{4h} dimer is required when we assume that the two halves are held together by potassium ions bridging crown ether units. With four K^+ ions shared by two MtCRPc units, a parallel arrangement of the Pc planes can surely be anticipated. This structure is supported by the Cu ESR spectrum, by the presence of a single very symmetric, rather weak and rather narrow Q absorption band (compared with the half-bandwidths for more flexible binuclear phthalocyanine species) by the emission and also by the NMR spectra. Note, too, that the cofacial free base $[H_2CRPc]_2K^+_4$ species also possesses a single relatively narrow Q band absorption suggesting it too possesses D_{4h} symmetry and that the four hydrogen atoms are, therefore, equally shared between the four pyrrole nitrogen atoms.

This result is contrasted with the cation induced porphyrin dimer[7a]. Due to the position of the 15-crown-5 units (meso position) they were constrained to adopt a lateral complexation of the cation. Consequently,

the macrocyclic rings are rotated by ca. 45° (usually) with respect to each other in a staggered dimer.

This difference in coordination style may explain the difference in cation behaviour in the two series. Thus the larger Ba^{2+} ion, ineffective in the MtCRPc series, can dimerize the porphyrin whose inter-crown distance can be expanded by further rotation of the porphyrin rings, without weakening the porphyrin-porphyrin π-π stabilisation. In the MtCRPc case, expanding the crown-crown distance, will weaken the Pc-Pc interaction.

It is also interesting that Ca^{2+} which does not dimerise the crown porphyrin and which forms a 1:1 (internal) adduct with 15-crown-5, is, nevertheless, able to generate a cofacial bridged MtCRPc dimer. It is evident that the free energy gained by forming a 1:1 crown ether complex is exceeded, in this case, by forming a 1:2 Ca^{2+}:crown species and the cofacial dimeric $[MtCRPc]_2[Ca^{2+}]_4$.

Lastly we would like to stress the importance of the eclipsed cofacial dimers realized in the present study. Although several covalently bound cofacial porphyrin[39] and phthalocyanine[27] dimers have been reported, they are all skewed[39] and/or staggered.[7,27] While not yet proven by x-ray studies, it is likely from the data presented here, that these cofacial crown MtCRPc phthalocyanines are perfectly eclipsed and will therefore be archetypes for future studies in this area.

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FIGURE CAPTIONS

Figure 1. Change of absorption spectra of (A) H_2CRPCc and (B) CuCRPc (below) by the addition of CH_3COOK or CH_3COONa respectively. to 3ml of a $CHCl_3$ solution of H_2CRPc or CuCRPc in a 10mm cell. The CH_3COOK and CH_3COONa were each dissolved in $CHCl_3$-MeOH(95:5 v/v) and were added using a microsyringe. 60μL were added in all. Arrows indicate the direction of the spectroscopic change. In (B) the final spectrum is that of a CH_3COONa saturated solution.

Figure 2. The dependence of absorbance of several MtCRPcs on $[K^+]$/[MtCRPc] for several wavelengths. Experiments were conducted as described in Fig. 1.

Figure 3. Plots of log [Monomer] versus log [Dimer] for several MtCRPc in $CHCl_3$ solution. Experimental data as appeared in Fig. 1 were analyzed using a computer program based on the approximation method of West and Pearce.[16] The solid lines are drawn with the theoretical slope of 2. The inset shows the dependence of monomer and/or dimer concentration of NiCRPc on $[K^+]$/NiCRPc] calculated for our experimental system.

Figure 4. (A) Absorption spectra of CoCRPc in $CHCl_3$-MeOH mixtures, a; $CHCl_3$ alone, b; $CHCl_3$:MeOH = 2.9:0.1 v/v, c; $CHCl_3$: MeOH = 2.8:0.2 v/v, d; $CHCl_3$:MeOH = 2.4:0.6 v/v, e; $CHCl_3$:MeOH = 2.0:1.0 v/v.

(B) Change in absorption spectrum of CoCRPc by the addition of CH_3COOK. Experiments were carried out as described for Fig.1 The spectrum shown by an open arrow was recorded at $[K^+]$/[CoCRPc] = 1.63.

Figure 5. ESR spectra of CuCRPc in $CHCl_3$ - MeOH (ca. 4:1 v/v), A; in the absence of any cation, and in the presence of B; saturated CH_3COONa at (a) 77 K, and b) room temperature, C; CH_3COOK, ($[K^+]/[CuCRPc]$ = 4) and D; $CaCl_2$ ($[Ca^{2+}]/[CuCRPc]$ = 10) [CuCRPc]mM = 1.

Figure 6. 300 MHz proton NMR spectra of ZnCRPc in A; $CDCl_3$ and B; $CDCl_3$ containing trace amount of CD_3OD in the presence of $CaCl_2$. Signals marked X and * are due to solvents.

Figure 7. A proposed structure for the cation-induced dimer of MtCRPc. Solid circles indicate cations such as K^+ and Ca^{2+}.

Figure 8. Emission and excitation spectra of H_2CRPc in A; $CHCl_3$ (emission excited at 350nm) B; in the presence of CH_3COOK in $CHCl_3$ containing 0.1 v/v percent of MeOH and C; in the presence of CH_3COONa in $CHCl_3$ containing 0.1% v/v MeOH. $[H_2CRPc]/M = 4.91 \times 10^{-6}$. $[CH_3COOK]/[H_2CRPc] = 2.62$. $[CH_3COONa)/[H_2CRPc] = 98$. Excitation spectra were recorded for emission peaks at A; 704 nm and B; 429nm and C; 429nm.

Figure 9. Stern-Volmer plots of the emission of H_2CRPc. (a) S_1 emission quenched by K^+ ion; (b) S_2 emission quenched with K^+ ion; (c) S_2 emission quenched with Na^+ ion.

Figure 10. Absorption spectra of several MtCRPc species as indicated. Monomeric species (_____)(in chloroform), cofacial $[MtCRPc]_2K^+_4$ species (-----)(in chloroform with 0.1% methanol), and solutions with $[K^+]/[MtCRPc] = 0.5$ containing a roughly 50:50 mixture of monomeric and non-cofacial $[MtCRPc]-K^+-[MtCRPc]$ species (.....) (in chloroform with 0.02% methanol).

Figure 11. Estimated spectra of several non-cofacial [MtCRPc]-K^+-[MtCRPc] species obtained from data in Fig.10 by subtraction of the monomeric component. The spectra in the region of the dotted lines are approximate due to uncertainty in the amount of monomeric species to subtract (ca. 40-50%).

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4) Abbreviations used in this study: Pc, phthalocyaninato dianion; CRPc, tetra(15-crown-5)ed phthalocyaninato dianion; ESR, electron spin resonance; FAB, fast atom bombardment; NMR, nuclear magnetic resonance; DPPH, diphenylpicrylhydrazyl; DCE, 1,2-dichloroethane; DMF, dimethylformamide; THF, tetrahydrofuran; FTIR, fourier transform infrared.

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1.7-2.2 Å. The ionic diameters of the cations used in this paper are Mg^{2+} 1.60, Na^{+} 1.90, Ca^{2+} 1.98, K^{+} 2.66, Ba^{2+} 2.70, NH_4^{+} 2.84, Cs^{+} 3.34Å.

15) The shift in the position of the isosbestic points were most clearly observed for the CuCRPc and NiCRPc system. For the CuCRPc system, the isosbestic points of the 1st and 2nd stages appeared at 370 and 641nm, while those for the 2nd and 3rd emerged at ca. 418 and 665nm. For NiCRPc, isosbestic points were similarly observed at 378 and 632nm, and at 404 and 672nm respectively.

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Table I. Elemental Analytical Data of MtCRPcs.[a]

Compound	C		H		N	
	Found	Calcd(%)	Found	Calcd(%)	Found	Calcd(%)
H_2CRPc	59.83	60.27	5.74	5.85	8.78	8.79
ZnCRPc	57.25	57.42	5.37	5.42	8.37	8.37
CuCRPc	57.33	57.50	5.36	5.43	8.29	8.38
NiCRPc	57.51	57.71	5.35	5.45	8.30	8.41
CoCRPc	57.54	57.70	5.38	5.45	8.29	8.41

[a] Theoretical values are calculatedfor $C_{64}H_{72}N_8O_{20}Mt_1$ except for H_2CRPc ($C_{64}H_{72}N_8O_{20}H_2$).

Table II Characteristic Absorption Bands of MtCRPcs[a], nm(ε)

Compound	Monomeric Species	f[b,c]	Half-Bandwidth cm^{-1}	Dimeric Cofacial Species	f	Half-Bandwidth cm^{-1}
H_2CRPc	700(33400)			639(17500)		
	662(27500)					
	645(11800)					
	601(6200)					
	421(8100)			402(sh)[d]		
	347(30800)			333(26400)		
ZnCRPc	677(96700)	0.16	350	635(51000)	0.17	730
	610(17300)			580(sh)		
	420(sh)					
	352(61200)			342(53800)		
CuCRPc	676(129400)	0.29	480	635(74000)	0.35	1050
	610(31200)					
	409(23300)			389(21400)		
	338(57400)			328(51400)		
	292(54100)					
NiCRPc	667(70000)	0.17	520	630(47000)	0.18	845
	638(22300)					
	603(17700)					
	401(14900)			385(13700)		
				360(13400)		

CoCRPc	668(59400)	0.20	750	627(41200)	0.26	1400
	608(19800)			571(sh)		
	400(13400)			390(sh)		
	329(sh)					
	297(49300)			300(45900)		

[a] Monomer spectra were collected in $CHCl_3$, while those of dimer were in $CHCl_3$ containing ca 0.1% MeOH and in the presence of $K^+(CH_3COOK)$. $[K^+]/[MtCRPc]=4$. Extinction coefficient (ϵ) is per phthalocyanine unit.

[b] Oscillator strength. [c] Oscillator strengths for the monomeric species are lower limits excluding higher energy vibrational satellites.

[d] sh means shoulder.

Table III. Magnetic Parameters[24] of Cation-Induced CuCRPc Cofacial Dimers[a]

Compound	g_1	g_2	A_1	A_h	D_1	D_2	Frequency (MHz)	Cu-Cu[b] distance/Å
			(gauss)					
$[CuCRPc]_2(K^+)_4$	2.050	2.152	107	103	371	407	9093	4.2
$[CuCRPc]_2(Ca^{2+})_4$	2.047	2.141	105	104	375	425	9096	4.1

[a] See Fig.5 for definition of parameters.

[b] Calculated via $r^3 = 1.39 \times 10^4 \times g_2/D_2$, where D is in gauss and r is in Ångstroms.[24]

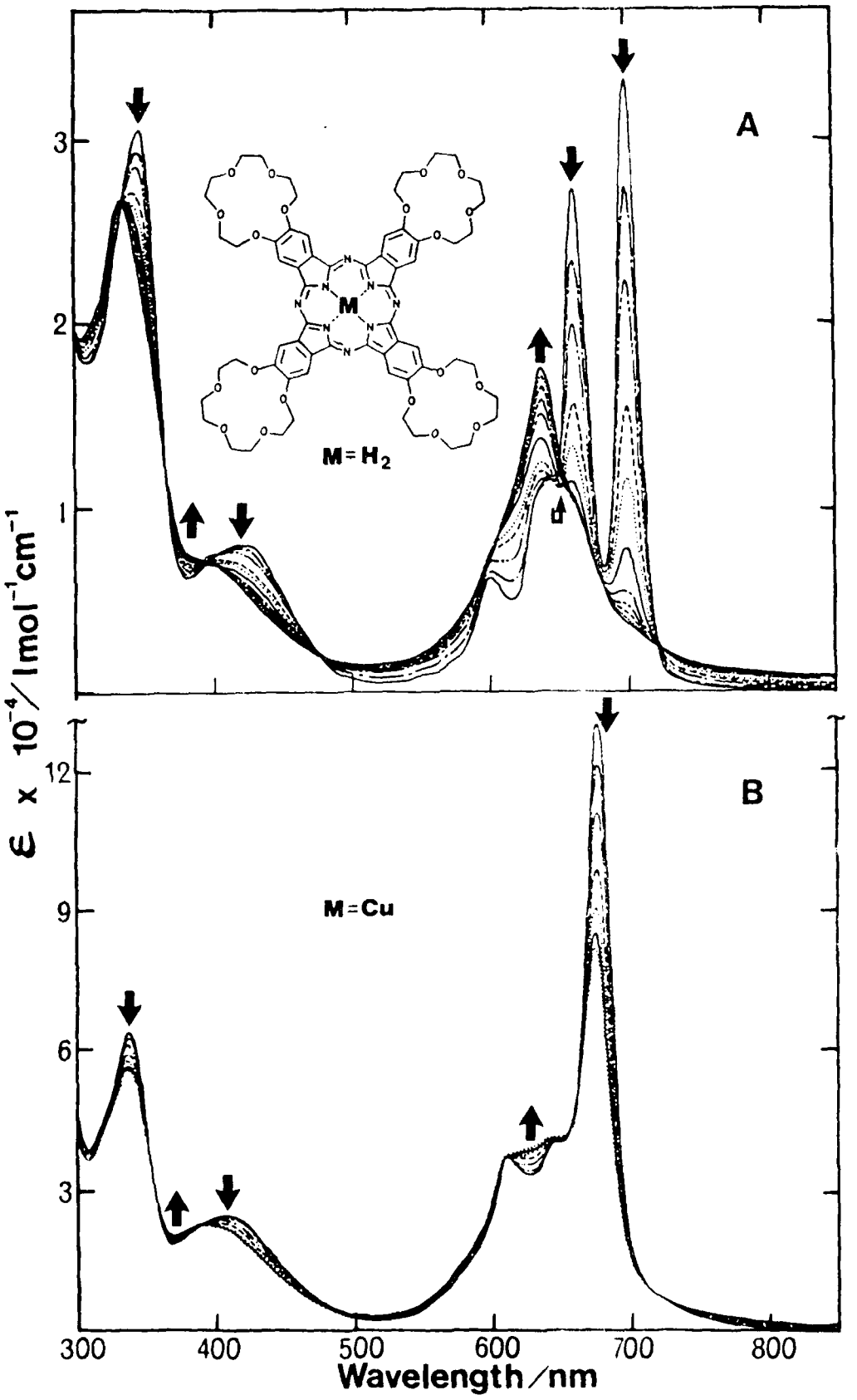
A
M=H2
M
B
M=Cu
ε x 10⁻⁴/lmol⁻¹cm⁻¹
Wavelength/nm
300
400
500
600
700
800
1
2
3
3
6
9
12

Fig 1

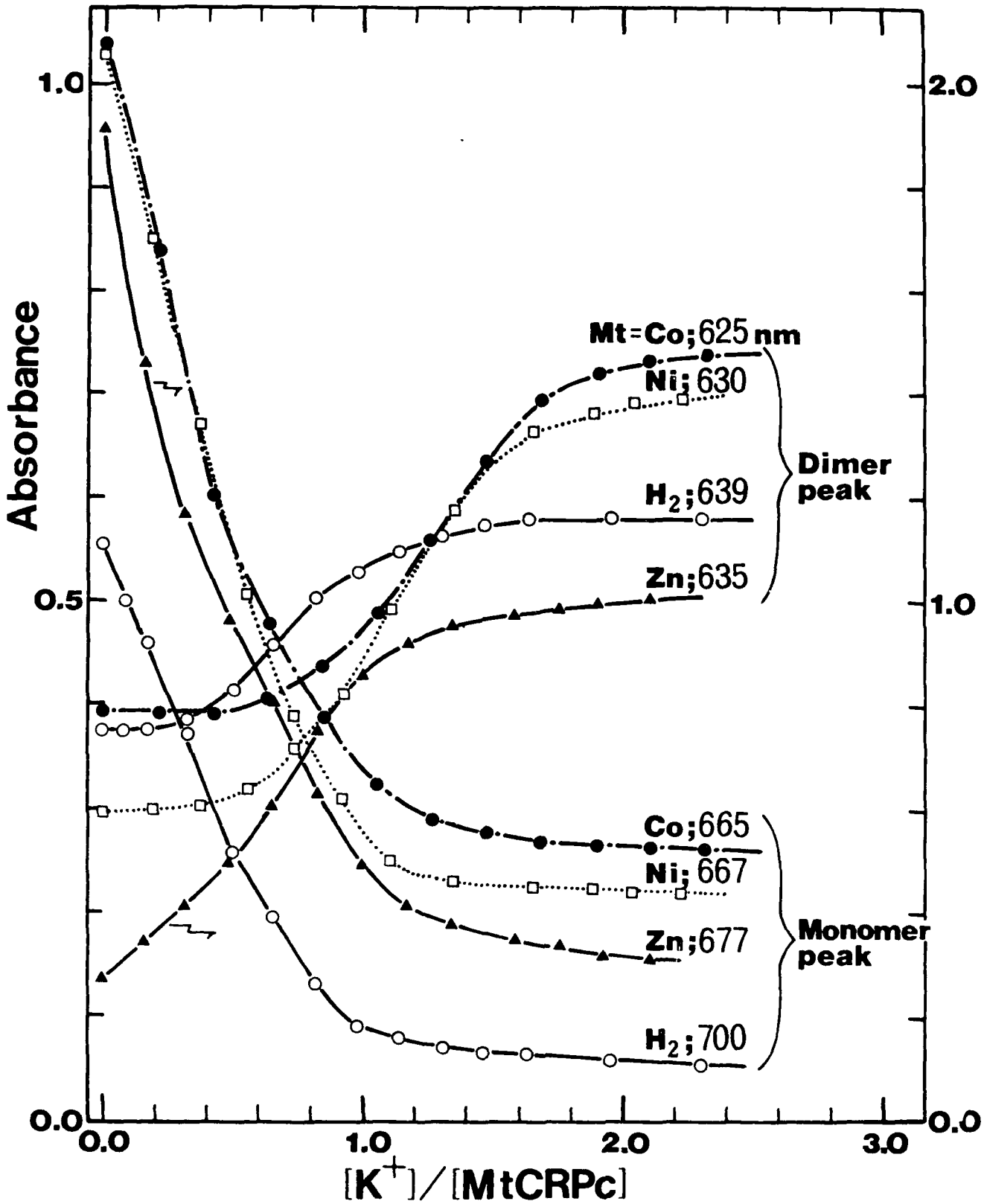
Absorbance
1.0
0.5
0.0
2.0
1.0
0.0
0.0
1.0
2.0
3.0
[K+]/[MtCRPc]
Mt=Co;625 nm
Ni;630
H2;639
Zn;635
Dimer peak
Co;665
Ni;667
Zn;677
H2;700
Monomer peak

Fig 2

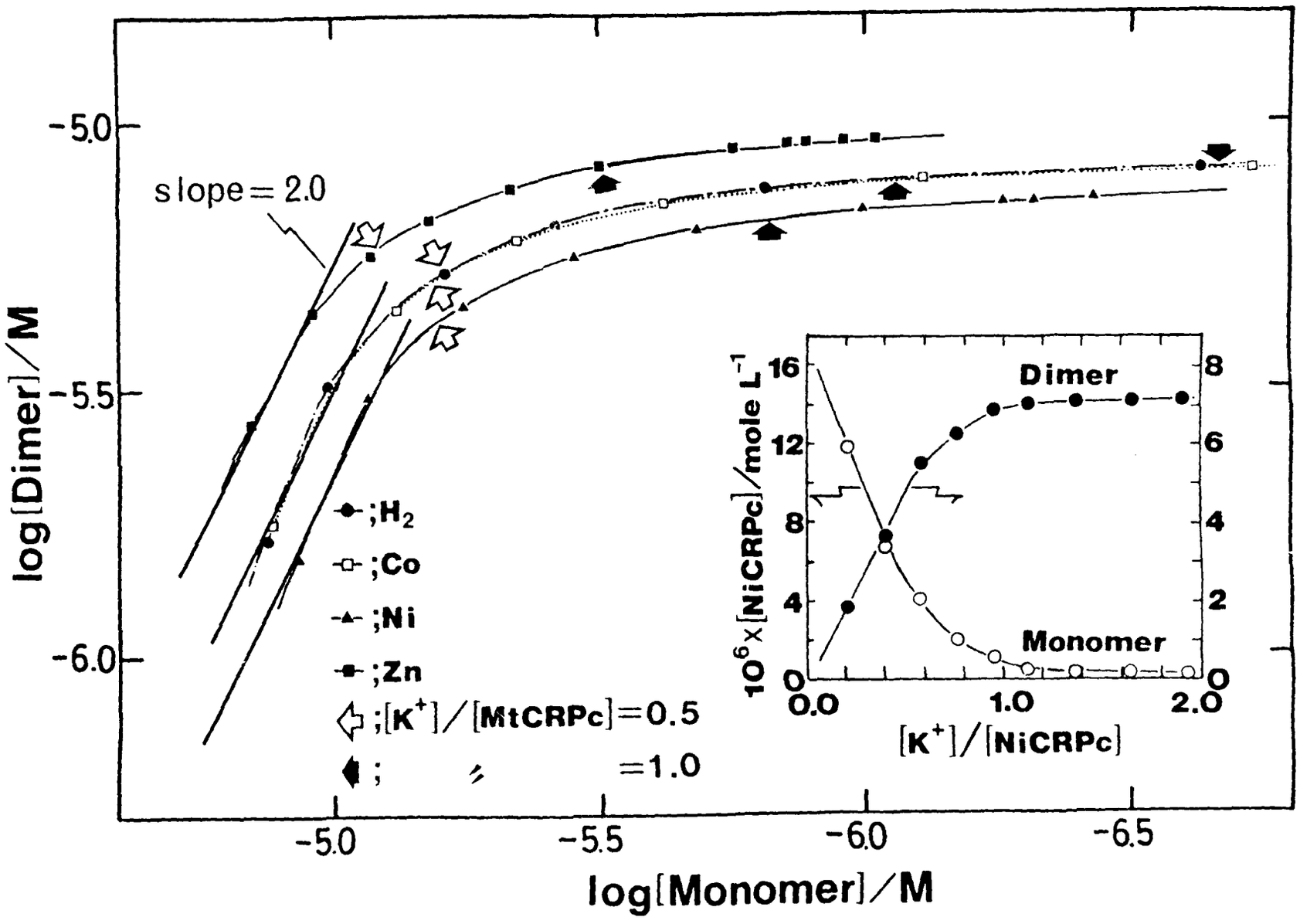
slope = 2.0
-5.0
-5.5
-6.0
log[Dimer]/M
-5.0
-5.5
-6.0
-6.5
log[Monomer]/M
;H2
;Co
;Ni
;Zn
;[K+]/[MtCRPc]=0.5
; =1.0
Dimer
Monomer
10^6 x [NiCRPc]/mole L^-1
16
12
8
4
0
8
6
4
2
0
0.0
1.0
2.0
[K+]/[NiCRPc]

Fig 3

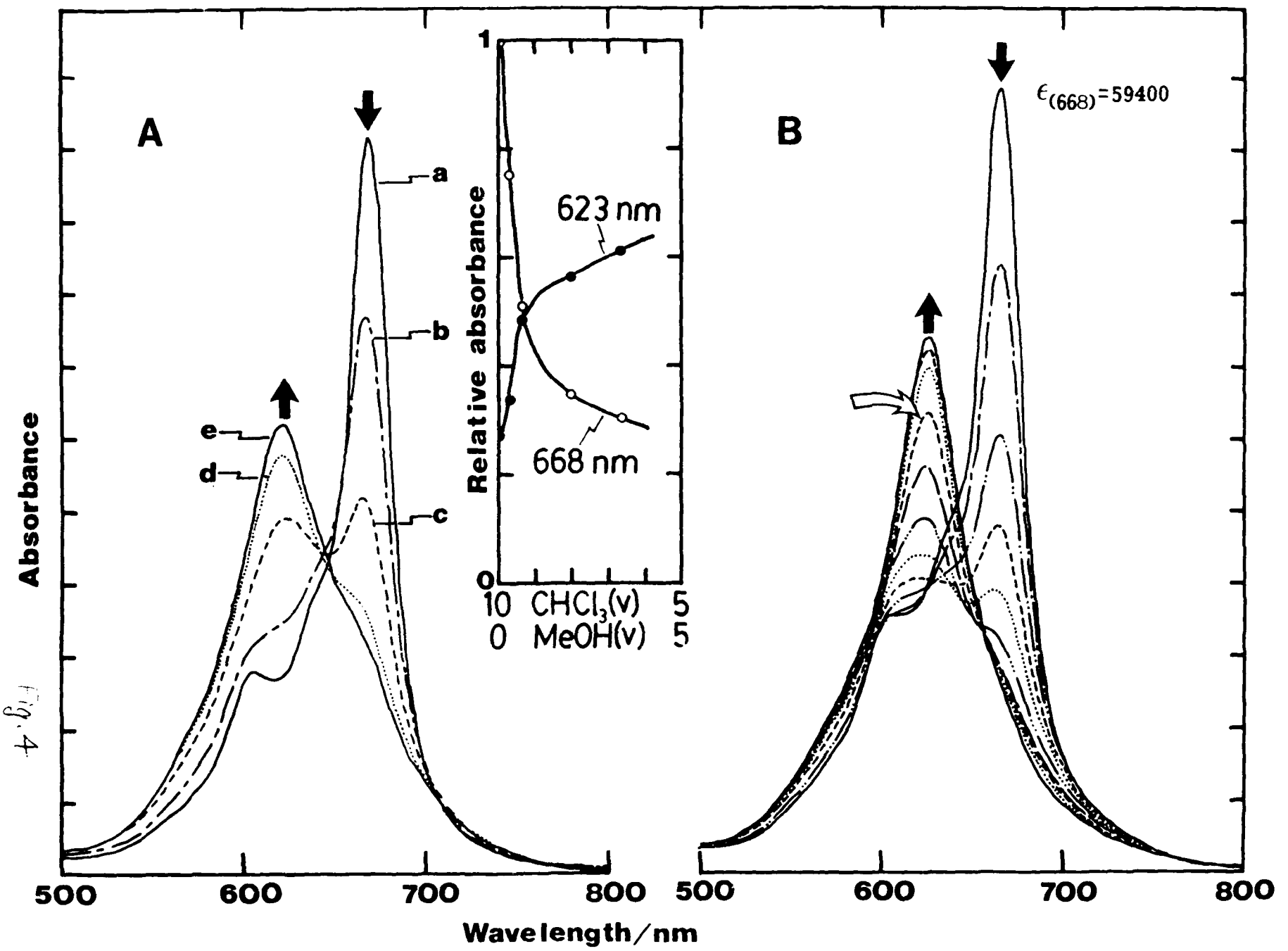
A
B
a
b
c
d
e
Absorbance
Relative absorbance
623 nm
668 nm
1
0
10 CHCl3(v) 5
0 MeOH(v) 5
ε(668)=59400
500
600
700
800
Wavelength/nm

Fig. 4

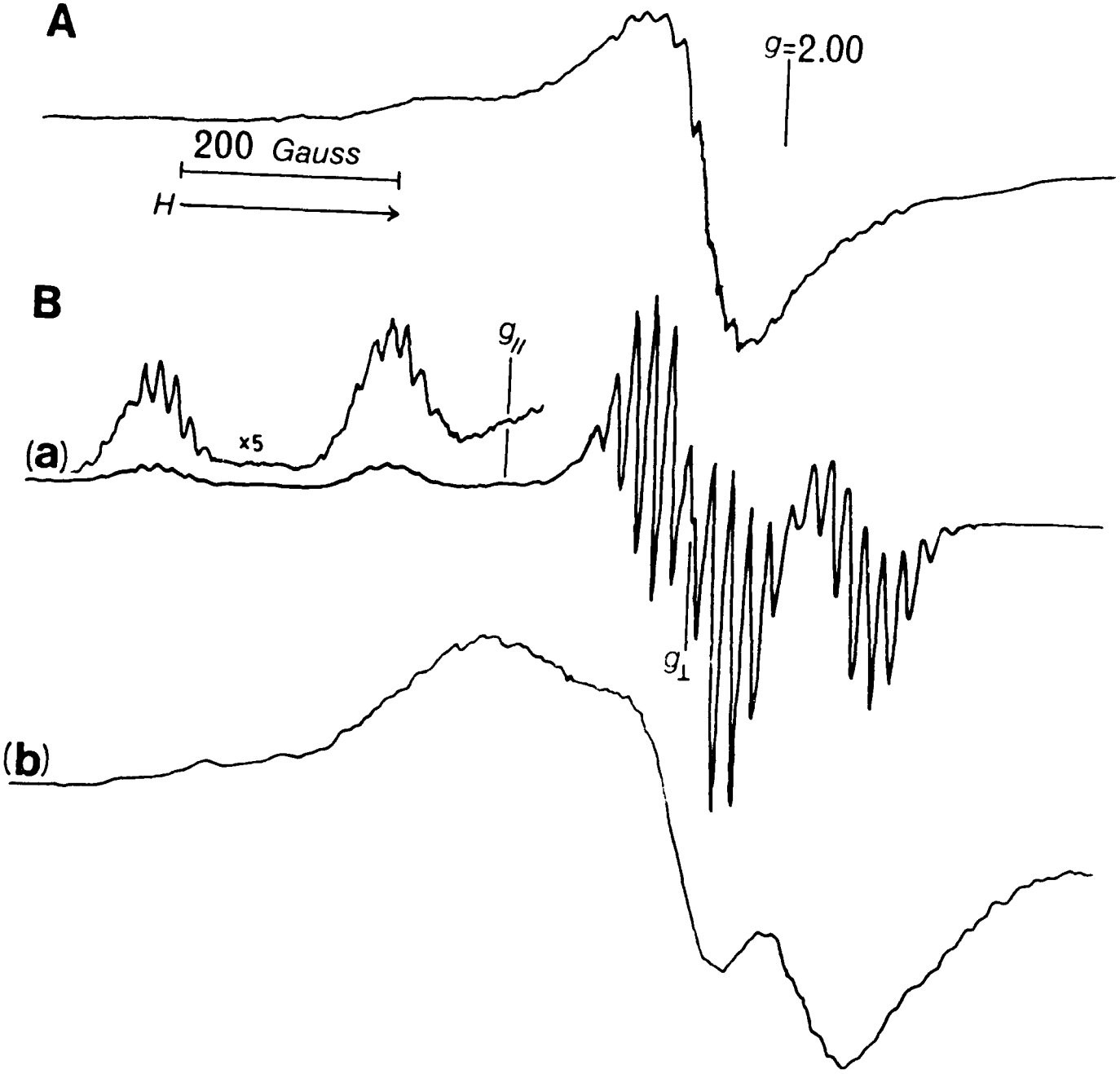

Fig. 5

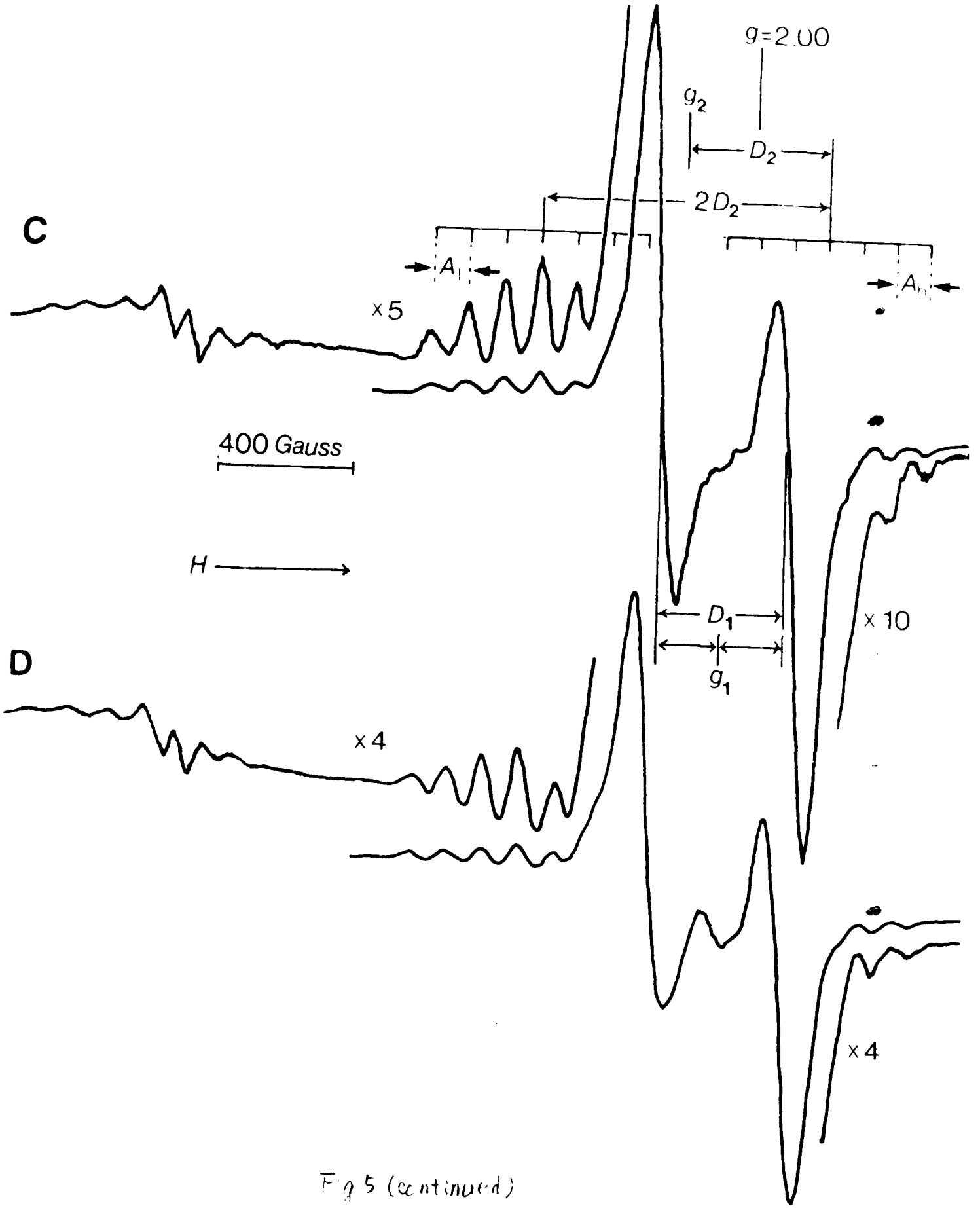

Fig 5 (continued)

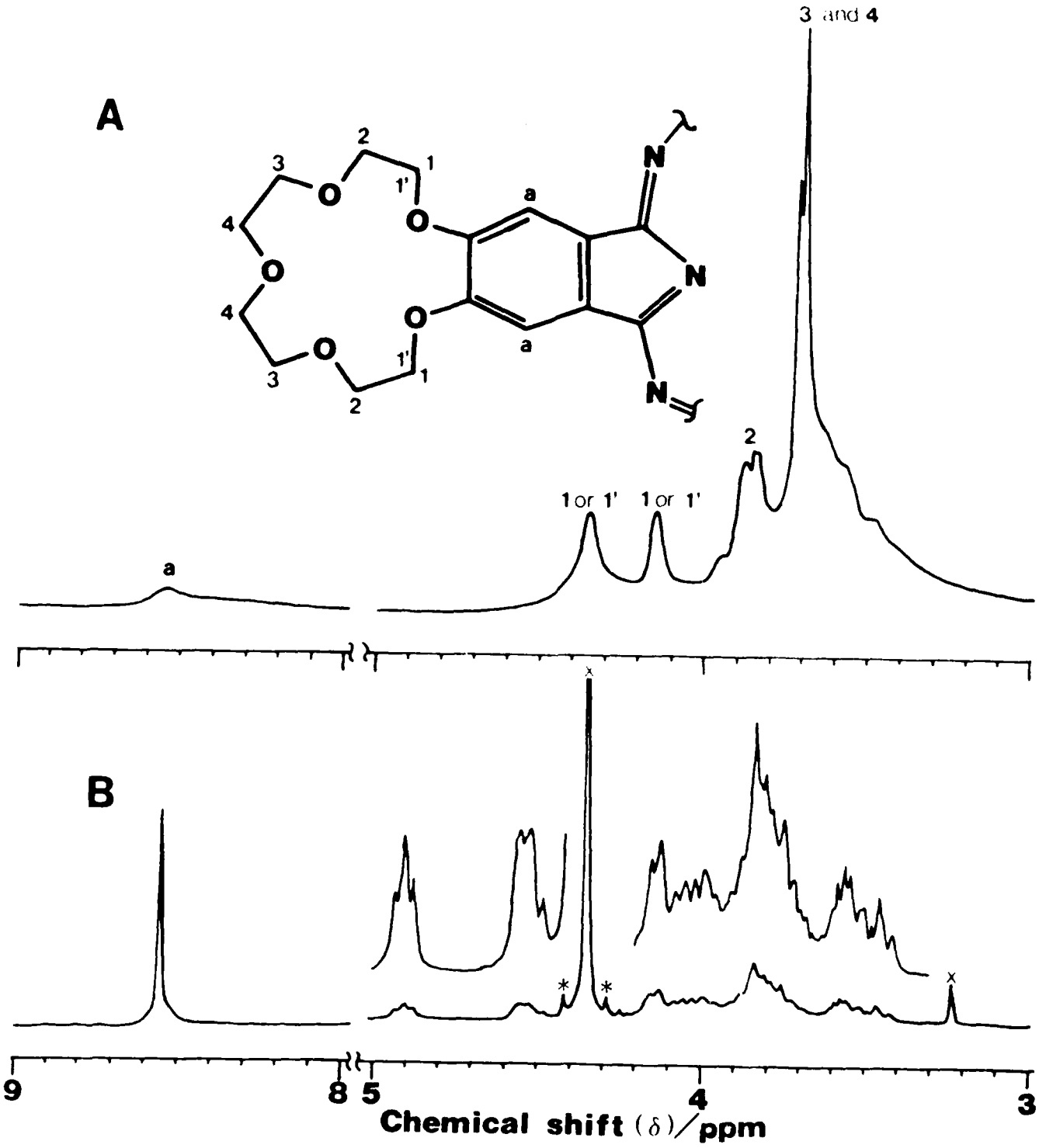

Fig 6

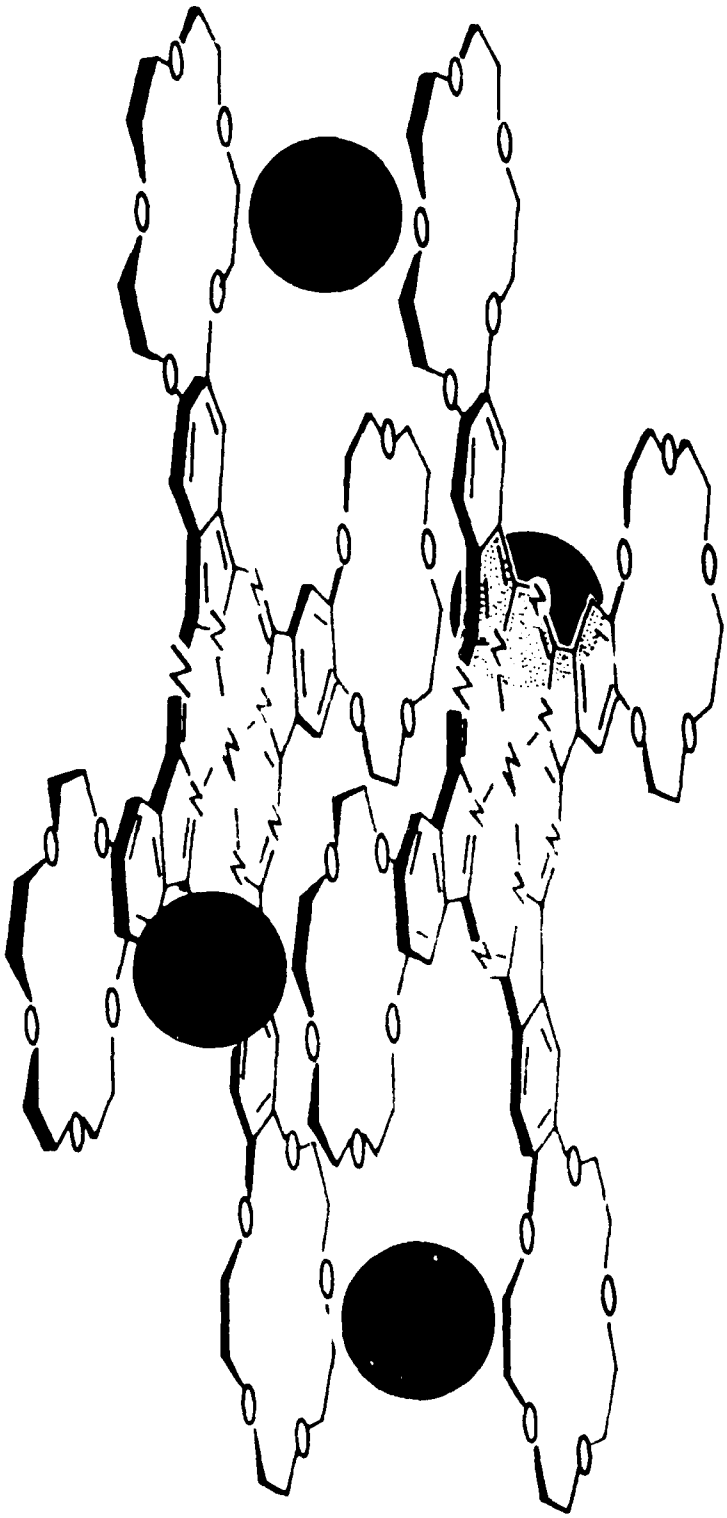

Fig. 7

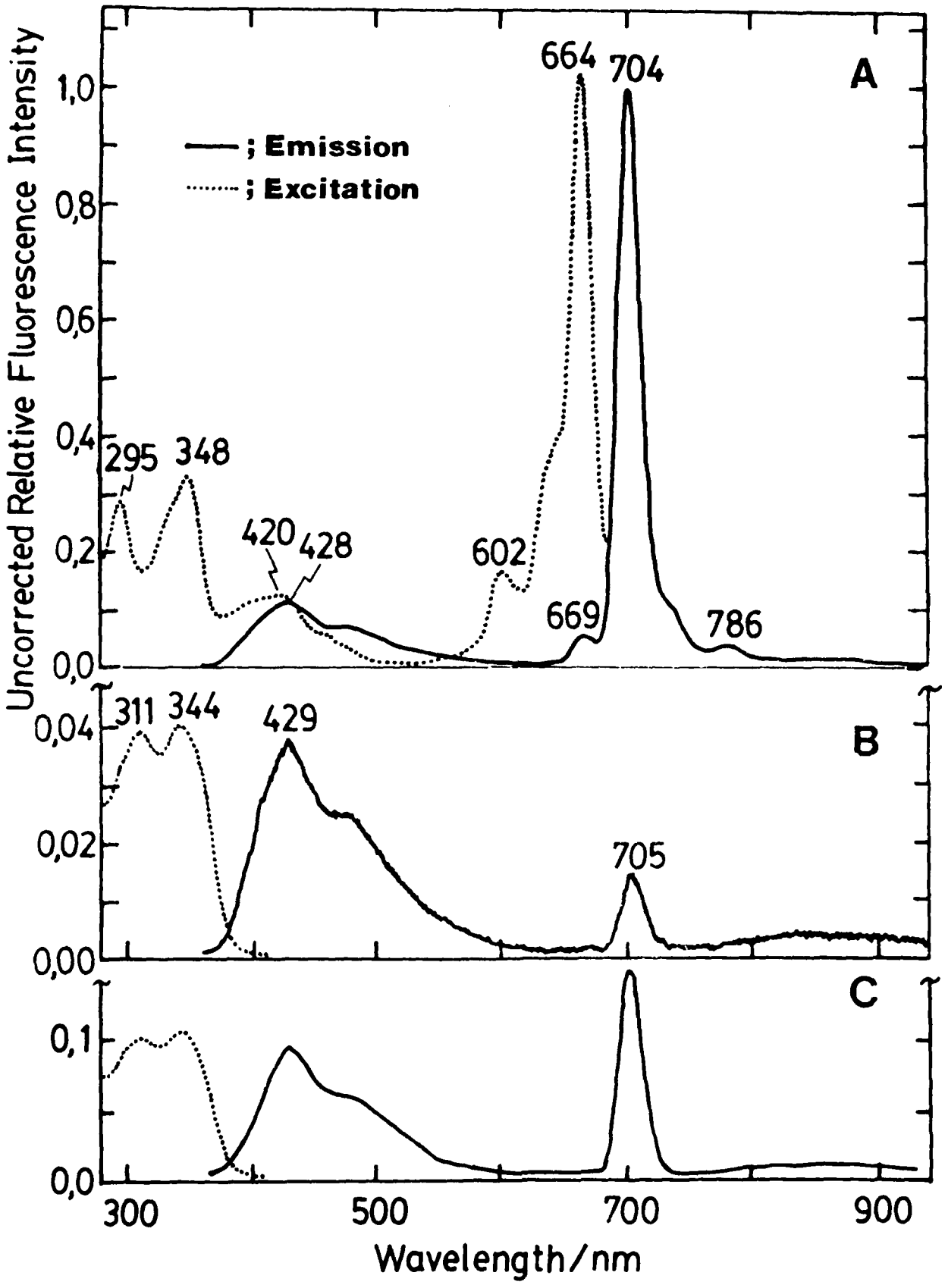
Uncorrected Relative Fluorescence Intensity
1,0
0,8
0,6
0,4
0,2
0,0
; Emission
; Excitation
664
704
A
295
348
420
428
602
669
786
0,04
0,02
0,00
311
344
429
B
705
0,1
0,0
C
300
500
700
900
Wavelength/nm

Fig. 8

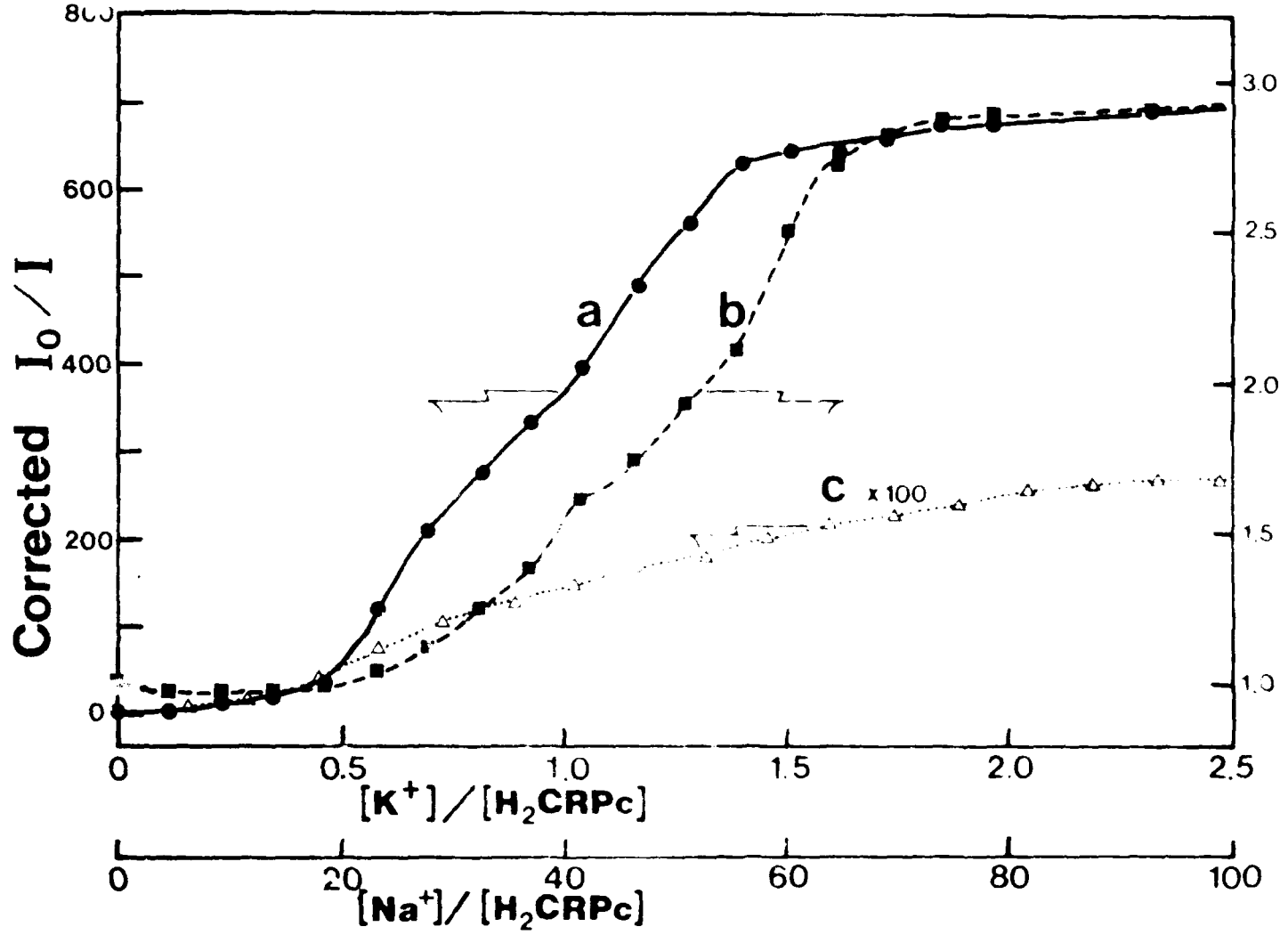
Corrected I_0/I
800
600
400
200
0
3.0
2.5
2.0
1.5
1.0
a
b
c x 100
0
0.5
1.0
1.5
2.0
2.5
$[K^+]/[H_2CRPc]$
0
20
40
60
80
100
$[Na^+]/[H_2CRPc]$

Fig. 9

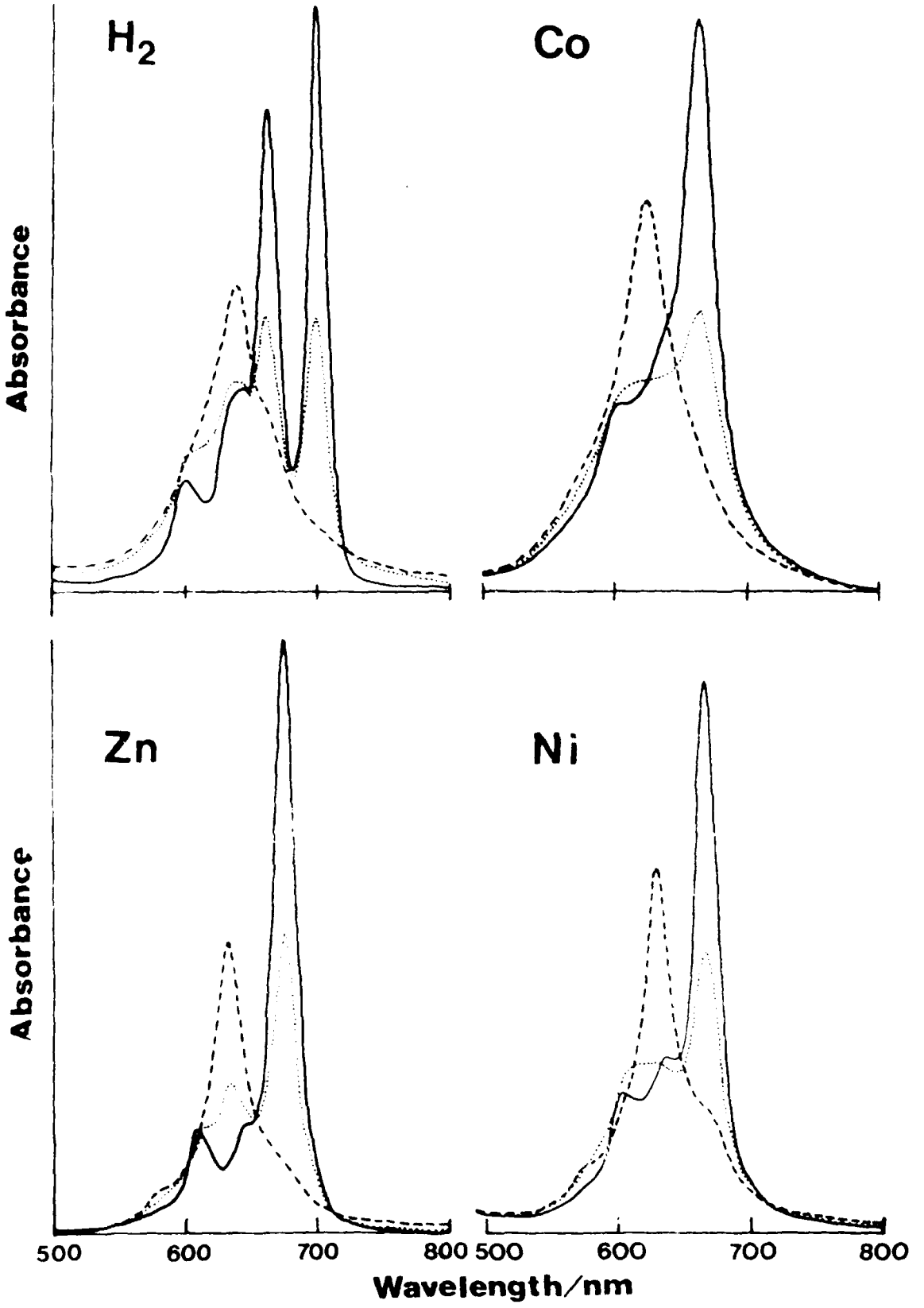
H2
Co
Zn
Ni
Absorbance
Absorbance
500
600
700
800
500
600
700
800
Wavelength/nm

Fig 10

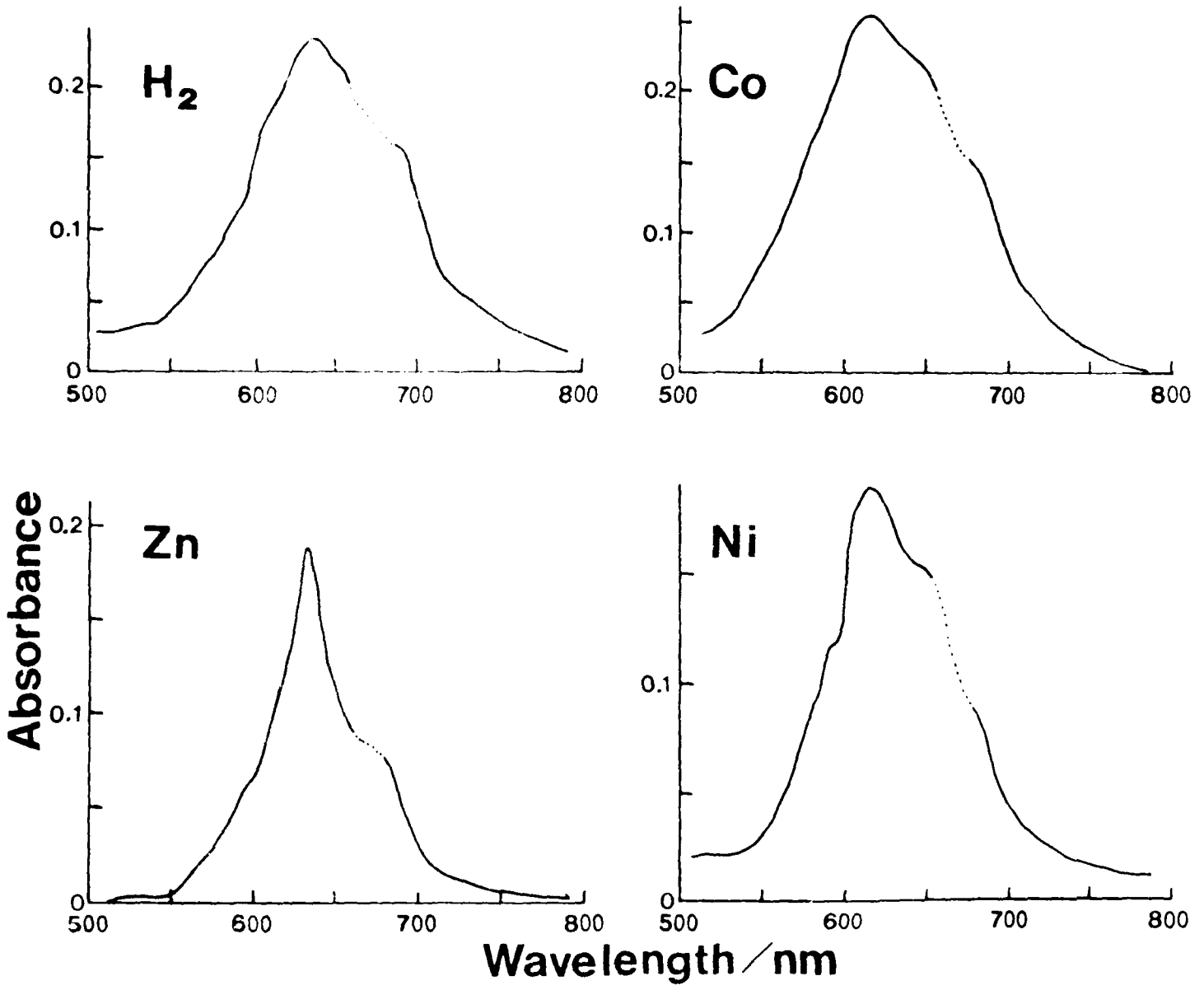

Fig 11

ED
8