245. *Metal Chelates. Part II.* Phthalocyanine–Chromium Complexes and Perpendicular Conjugation.*

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The phthalocyanine derivatives of chromium(II) and chromium(III) have been isolated and a number of octahedral derivatives—cationic, neutral, anionic complexes—have been prepared. Magnetic moments and light absorptions are recorded. These data and perpendicular conjugation are discussed.

Chromium derivatives of phthalocyanine have not before been properly authenticated.[1,2] We have now obtained pure both chromium(II) and chromium(III) phthalocyanine, the latter as hydroxide and acetate, and have made several 6-co-ordinate (octahedral) derivatives for the first time. Properties of the octahedral complexes suggest that the groups attached to the metal in the plane perpendicular to the aromatic phthalocyanine system (*i.e.*, in the fifth and the sixth co-ordination position) are conjugated to it. The feasibility of perpendicular conjugation (through a metal atom) was discussed by us in a preliminary communication.[3] Further comment is made below.

Tervalent Chromium Phthalocyanines.—(a) *Cationic complexes.* Interaction of chromium salts with phthalonitrile, *o*-cyanobenzamide, or 1,3-di-iminoisoindoline gave mixtures of chromic complexes together with chromous material, which could not be separated satisfactorily by chromatography or fractional crystallisation. The preferred, exothermic reaction of chromium(III) acetate with phthalonitrile at 270° afforded a product which contained phthalocyanine chromium(II) (II) and phthalocyanine chromium(III) acetate (I) from which some hydroxide (IV) was apparently formed during preliminary washing. When the washed product was heated at 400° under reduced pressure, the hydroxide and the chromium(II) complex sublimed, the latter with considerable oxidation, so that repeated sublimation at a low pressure of air afforded pure phthalocyanine chromium(III) hydroxide, PcCr·OH. This appeared as dark purple needles: its solution in, *e.g.*, chlorobenzene was green, like that of many other metal phthalocyanines. Support for the constitution (IV) came from quantitative oxidation, the magnetic moment (Table 1), similarity of the light absorption to that of established 4-co-ordinate metal phthalocyanines (Tables 2, 3), and the ready solvation of the cation by *two* molecules of, *e.g.*, water and methanol (see below). Treatment with cold acetic anhydride gave the acetate

Table 1. *Magnetic moments at room temperature.*

Structure	Assumed metal-ligand bonding	No. of unpaired electrons	Theor. moment (B.M.)	Found	
				$\mu_{\text{eff.}}$* (B.M.)	θ (°K)
PcCr (II)	*dsp*^{2}	4	4·90	3·49	−306
PcCr,2py (V)	d^2sp^3	2	2·83	3·16	−35
PcCr·OH (IV)	*dsp*^{2}	3	3·87	4·03	−15
PcCr(H_2O)·OH (VII)	d^2sp^3	3	3·87	3·69	0
$2Na^+[PcCr(OH)O]^{2-}$ (VIII; M = Na)	d^2sp^3	3	3·87	3·91	−155
$2pyH^+[PcCr(OH)O]^{2-}$ (VIII; M = C_5H_6N)	d^2sp^3	3	3·87	4·06	−15

* Calc. from $\mu_{\text{eff.}} = 2{\cdot}839(\chi'_{\text{m}}T)^{\frac{1}{2}}$.

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* Part I, *J.*, 1961, 869.

[1] Barrett, Dent, and Linstead, *J.*, 1936, 1719.

[2] B.P. 457,526/1936; Anderson, Bradbrook, Cook, and Linstead, *J.*, 1938, 1151; Bigelow and Perkins, " Chemistry of Synthetic Dyes and Pigments," A.C.S. Monograph No. 127, Reinhold Publ. Inc., New York, 1955, Chapter 9.

[3] Elvidge and Lever, *Proc. Chem. Soc.*, 1959, 123.

PcCr·OAc, which appears better represented as a 6-co-ordinate lattice compound (I) than as the 4-co-ordinate ionic acetate corresponding to the hydroxide (IV). Reasons are that it is involatile even at 400° in a vacuum, it is highly insoluble (unlike the hydroxide), it

TABLE 2. *Infrared absorptions* (3—14 μ) *of phthalocyanines*, PcM, *in Nujol mull.*

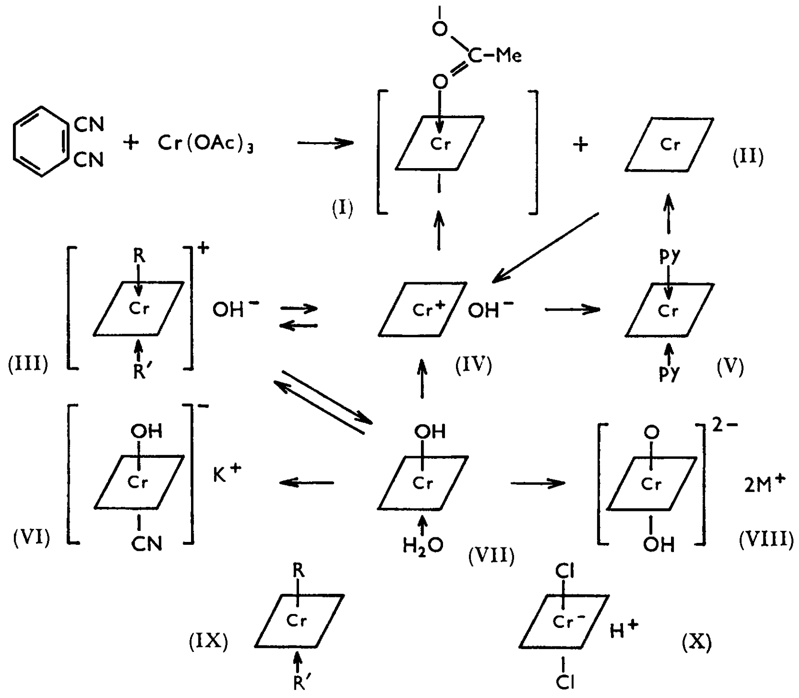
Common vibrations (cm.$^{-1}$) for all complexes listed below: 1609 ± 10 w—m, 1420 ± 10, 1333 ± 6 m—s, 1287 ± 4, 1164 ± 6, 1120 ± 4 s, 1085 ± 6 m—s, 1071 ± 8, 903 ± 13 m—s,* 779 ± 4 w—s, 755 ± 2 s, 726 ± 9 s.

* w, in $PcCr^{II},2py$.

Additional (*characteristic*) *vibrations*:

$PcCr^{III}{\cdot}OH$	1503w, 1035
$PcCr^{III}{\cdot}OAc$	1709, 1504w, 1486, 1000w, 769w
$PcCr^{III}(H_2O)_2{\cdot}OH$	1565s, 1488, 1390w, 1079s, 1016
$PcCr^{III}(MeOH)_2{\cdot}OH$ ...	1505w, 1484w, 1032, 871, 783
$PcCr^{III}(H_2O){\cdot}OH$	1568s, 1507w, 1486, 1390w, 1079s, 1016
$PcCr^{III}(H_2O){\cdot}OAc$	1715w, 1569s, 1487, 1015
$PcCr^{III}(H_2O){\cdot}O{\cdot}CO{\cdot}Et$	1715w, 1582w, 1487, 1188w, 951, 874w
$PcCr^{III}(MeOH){\cdot}OAc$ ...	1715w, 1543s, 1487, 1024
$PcCr^{III}(AcOH){\cdot}OAc$ ...	1718w, 1493, 1403, 1164w, 1046, 1000
$HPcCr^{III}Cl_2$	1514, 1502w, 1487, 1305w, 1219w, 1143w, 1096w, 952, 899, 739w, 705
$2Na^+[PcCr^{III}(O)OH]^{2-}$	1484w, 1051w
$K^+[PcCr^{III}(OH)CN]^-$ ...	2137w, 1486, 956w, 695w
$2pyH^+[PcCr^{III}(O)OH]^{2-}$	2527w, 1715w, 1626, 1571w, 1486, 1343, 1301, 1220, 1153w, 1046w, 1012, 941w, 875w, 702
$PcCr^{II},2py$	1600w, 1485w, 1216w, 1150, 1043, 760, 629
$PcCo^{II}$ [a]	1515, 879, 774
$PcFe^{II}$ [a]	1505, 872, 769w
$PcFe^{II},2py$ [a]	1584w, 1501s, 1480w, 1211w, 1146w, 1112, 1100, 930w, 866w, 761w, 691

[a] Whalley, *J.*, 1961, 866.



These rhombs represent square planar 4-co-ordinate bivalent phthalocyanine ligand, $C_{32}H_{16}N_8$.
py = pyridine.

shows carbonyl absorption at 1709 cm.$^{-1}$ (Table 2) which indicates that the acetate grouping is covalently linked, and it absorbs at 1486 cm.$^{-1}$, a frequency at or near which all the undoubted 6-co-ordinate complexes (described below) show a maximum.

The 4-co-ordinate cation of phthalocyanine chromium(III) hydroxide (IV) was readily solvated to the 6-co-ordinate state, and the products were unusual amongst phthalocyanines in being noticeably soluble in simple solvents such as methanol, ether, acetic acid. Boiling methanol afforded the dimethanol solvate (III; $R = R' = MeOH$), warm aqueous methanolic acetic acid the aquo-methanolate (III; $R = H_2O$, $R' = MeOH$), and aqueous ethanolic acetic acid the dihydrate (III; $R = R' = H_2O$). The cationic nature of these phthalocyanine complexes was demonstrated by electrophoresis on paper.

These 6-co-ordinate cationic complexes were not thermally stable. At 180°/20 mm., the dimethanolate (III; $R = R' = MeOH$) was desolvated to the starting material (IV), but the aquo-methanolate lost only methanol, and the dihydrate only a mol. of water, both yielding the compound $PcCr{\cdot}OH,H_2O$. That this new product was still a tervalent chromium complex was shown by the magnetic moment (Table 1), so it seems best formulated as (VII), covalent 6-co-ordinate phthalocyanine hydroxoaquochromium(III). Only at 400° under a vacuum could it be dehydrated to yield, as sublimate, phthalocyanine-chromium(III) hydroxide (IV). On the other hand, it combined readily with hot water to regenerate the dihydrated ionic hydroxide (III; $R = R' = H_2O$), in this respect behaving as a base. The thermal conversion of the aquo-methanolate hydroxide (III; $R = H_2O$, $R' = MeOH$) into the hydroxoaquo-complex (VII) is typical. Thus the complex salt $[Cr(NH_3)_5H_2O]^{3+}\ 3Cl^-$ is transformed[4] by heat into $[Cr(NH_3)_5Cl]^{2+}\ 2Cl^-$ and not into $[Cr(NH_3)_5OH]^{2+}\ 2Cl^-$, an anion substituting a co-ordinate position rather than abstracting a proton.

Mild treatment of the covalent hydroxoaquo-complex (VII) with acetic anhydride and with propionic anhydride gave respectively phthalocyanine acetatoaquochromium(III) (IX; $R = OAc$, $R' = H_2O$) and the corresponding propionatoaquo-complex (IX; $R = O{\cdot}CO{\cdot}Et$, $R' = H_2O$). The infrared absorptions (Table 2) of these complexes, and of others described below, confirmed the covalent bonding of the carboxylate residues. Boiling acetic anhydride converted the hydroxoaquo-complex (VII), and also phthalocyanine chromium(III) hydroxide (IV) into a complex containing two acetic residues. This may be formulated as (covalent) phthalocyanine acetato(acetic acid)chromium(III) (IX; $R = OAc$, $R' = HOAc$). Each of the foregoing complexes (IX) was stable at 180°/20 mm. A less stable analogue, phthalocyanine acetatomethanolchromium(III) (IX; $R = OAc$, $R' = MeOH$), was formed from phthalocyanine chromium(III) hydroxide (IV) and boiling methanolic acetic acid; at 180°/20 mm., the complex lost methanol to yield the previously encountered phthalocyanine chromium(III) acetate (I).

It seems possible in these conversions of phthalocyanine chromium(III) hydroxide (IV) into the covalent diacetate and acetato-methanolate, that the cation is first solvated to labile 6-co-ordinate species which then undergo anion attack (by OAc^-, here), analogously to the conversion of the aquo-methanolate (III; $R = H_2O$, $R' = MeOH$) (and presumably the related diaquo-complex) into phthalocyanine hydroxoaquochromium(III) (VII).

When dry hydrogen chloride was passed into a boiling methanolic suspension of phthalocyanine chromium(III) hydroxide (IV), a dichloro-complex was formed. The stability of this at 180°/20 mm. and its infrared absorption (Table 2) suggested its formulation as the 6-co-ordinate hydrogen [phthalocyanine dichlorochromate(III)] (X), rather than as the hydrochloride of 4-co-ordinate phthalocyanine chromium(III) chloride. The dichloro-complex was readily hydrolysed by aqueous alcohol to hydrogen chloride and phthalocyanine diaquochromium(III) hydroxide (III; $R = R' = H_2O$).

(b) *Anionic complexes.* The observation that phthalocyanine chromium(III) hydroxide (IV) and the covalent hydroxoaquo-complex (VII) dissolved appreciably in alcoholic

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[4] Benrath, *Z. anorg. Chem.*, 1928, **177**, 286.

potassium cyanide led to the discovery of potassium [phthalocyanine hydroxocyanochromate(III)] (VI). This showed similar infrared absorption to other metal phthalocyanines but with an additional band at 2137 cm.$^{-1}$ (Table 2), which is close to the C≡N stretching at 2127 cm.$^{-1}$ in the hexacyanochromate(III) anion.[5] The visible-light absorption of a methanol solution of the monocyano-complex (VI) soon changed in the absence of cyanide ion, indicating hydrolysis. Addition of an excess of potassium cyanide, however, caused further changes in the light absorption (Table 3) suggestive of the formation of potassium [phthalocyanine dicyanochromate(III)]. Similar indications of the formation of thiocyanato- and selenocyanato-anionic complexes were obtained on dissolution of phthalocyanine chromium(III) hydroxide (IV) in methanolic potassium thiocyanate and selenocyanate; unfortunately, attempts to isolate these complexes failed.

It was also found that the slight solubility of the hydroxoaquo-complex (VII) in ethanol was much increased by addition of sodium hydroxide. Evidently the complex was acidic, and this was further indicated by electrophoresis of a drop of the alkaline solution on paper whereupon the coloured spot migrated towards the anode. That *two* protons were displaceable from the complex (VII) was indicated by the isolation of disodium [phthalocyanine oxohydroxochromate(III)] (VIII; M = Na). With liquid ammonia, the hydroxoaquo-complex (VII) gave a diammonium salt, but this was unstable at room temperature. Treatment of the complex (VII) with pyridine, however, gave a well-defined dipyridinium salt (VIII; M = C_5H_6N), the constitution of which was supported by the magnetic moment (Table 1), stability at 180°/15 mm., electrophoretic migration of the coloured ion towards the anode, and infrared absorption (Table 2).

Bivalent Chromium Phthalocyanines.—When treated with acid-free pyridine, phthalocyanine chromium(III) hydroxide (IV) underwent rapid reduction to phthalocyanine dipyridinechromium(II), PcCr py$_2$. This is a very dark green solid which gives rich blue solutions, in contrast to the dull green solutions of the starting material (IV). The bivalency of the metal in this dipyridine complex (V) was shown by quantitative oxidation, whilst the 6-co-ordinate nature of the complex, suggested by the thermal stability, was supported by the magnetic moment (Table 1). The pyridine was removed only at 400° under very low pressure, whereupon, provided oxygen was absent, a dark purple sublimate of phthalocyanine chromium(II) (II) was obtained. This compound (II), if regarded as a planar 4-co-ordinate complex of bivalent chromium, would belong to a rare class of compound: however, the magnetic properties (Table 1)—low moment and large negative value of θ—indicate that there is electron-spin coupling between chromium atoms. Therefore, there is some degree of bonding between them and they may be regarded as effectively in a 6-co-ordinate lattice. The thinness of the unit cell, determined as 3·4 Å by electron diffraction, compared with ~4·7 Å in many bivalent metal phthalocyanines,[6] is in agreement with chromium–chromium interaction.

The phthalocyanine chromium(II) (II) tended to be oxidised in air, but the dipyridine complex (V) was stable, as it was also in pyridine solution in the absence of acid. Addition of acid resulted in rapid oxidation and transformation into the 6-co-ordinate hydrated chromium(III) state, the light absorption indicating that the previously encountered dipyridinium salt (VIII; M = C_5H_6N) was formed. If sodium hydroxide (in excess of the acid) was then added to the pyridine solution, no reduction occurred. Nor did reduction occur when the hydroxoaquochromium(III) complex (VII) was treated with acid-free pyridine—again the dipyridinium salt (VIII) resulted. Evidently, the chromium has to be in the 4-co-ordinate state, as in phthalocyanine chromium(III) hydroxide (IV), before it can be approached and reduced by the pyridine. It is also evident that displacement of the pyridine by water is strongly catalysed by acid, and the metal then returns to the normally more stable tervalent state. On addition of sodium dithionite to the dipyridinium

Caglioti, Sartori, and Scrocco, *J. Inorg. Nuclear Chem.*, 1958, **8**, 87.

[6] Linstead and Robertson, *J.*, 1936, 1736.

salt (VIII) in pyridine, the green solution became blue and then purple, the measured light absorption changes indicating that reduction occurred to the chromium(II) state and then to a hydrophthalocyanine complex. Aerial oxidation reversed these changes, as expected.

Magnetic Moments.—These were measured for the pure compounds by the Gouy method over the temperature range 110—295° K. Each compound obeyed the Curie–Weiss law. In Table 1, the effective moment[7] at room temperature is given together with the theoretical value required by each structure, inner orbital bonding being assumed. The experimental moments support the assigned structures unambiguously except for phthalocyanine chromium(II) (II) and the disodium salt (VIII; M = Na). In these two cases the plots give a large intercept θ on the temperature axis. The probable significance for the chromium(II) complex has already been discussed; that for the disodium salt is at present unclear.

Light Absorptions.—For reasons of symmetry, the infrared spectra of phthalocyanine complexes of closely related transitional metals should be similar. The spectra of the established square-planar cobalt(II) and iron(II) complexes[1,6] are indeed very much alike, there being 15 corresponding maxima in the 3—14 μ region (Table 2). Within small limits, 13 of these maxima are common also to the spectrum of phthalocyanine chromium(III) hydroxide, which is excellent support for its constitution (IV), and 12 of these maxima are common to the spectra of all of the other phthalocyanine chromium complexes. There are additional vibrational modes in the latter because of the ligand groupings in the fifth and sixth co-ordination positions and there is a rough correlation between spectral and chemical complexity, but only the few assignments already mentioned can readily be made. In the spectra of the hydrated and hydroxylated complexes there are bands in the 1400—950 cm.$^{-1}$ region which may represent O–H deformations, whilst in the spectra of the pyridine-containing complexes there are bands in the 1600—1480 cm.$^{-1}$ region and near 1215 cm.$^{-1}$ which are probably pyridine skeletal vibrations. The diacetic complex appears best represented by the constitution (IX; R = OAc, R′ = HOAc) because of the similarity of its infrared spectrum to those of the preceding 6-co-ordinate complexes listed in Table 2. The dichloro-complex, on the other hand, has a more complex spectrum suggestive of a major structural difference, and therefore the constitution (X) is preferred, in which the phthalocyanine ring system is protonated.

TABLE 3. *Light absorptions* (230—1000 mμ) (*in methanol unless otherwise indicated*).

Compound	$\lambda_{max.}$ (mμ), with $\log_{10} \varepsilon$ in parentheses								
$PcCr^{III}{\cdot}OH$ [a]	689 (4·92)	621 (4·14)	502 (3·91)			347 (4·62)			
$PcCr^{III}(H_2O)_2{\cdot}OH$	676 (5·17)	610 (4·48)	502 (4·05)	477 (3·99)		344 (4·60)			268 (4·48)
$PcCr^{III}(MeOH)_2{\cdot}OH$	670 (5·11)	605 (4·40)	505 (3·82)	475 (3·79)		340 (4·55)			
$2Na^+[PcCr^{III}(O)OH]^{2-}$ [b]	669 (5·25)	604 (4·47)		475 (3·56)		337 (4·71)		278 (4·59)	268 (4·63)
$K^+[PcCr^{III}(OH)CN]^-$ [c]	677	611	515			345	321	308	271
$K^+[PcCr^{III}(CN)_2]^-$ [d]	675	615	518	490	380	345	322	309	258
$K^+[PcCr^{III}(SCN)_2]^-$ [d]	682	617	511			349		298	270
$HPcCr^{III}Cl_2$ [e]	682 (5·15)	615 (4·30)	507 (4·03)	495 (3·93)	355 (4·70)	347 (4·71)		282 (4·57)	
$PcCr^{II},2py$ [f]	687 (4·85)	632 (4·20)	560 (3·70)	525 (3·86)	500 (3·70)	345 (4·59)			

[a] In PhCl; and in propylene carbonate which is transparent to 230 mμ. [b] +0·25% NaOH. [c] Intensities not measured because of hydrolysis. [d] See text. [e] +trace of HCl. [f] In pyridine.

The visible and near-ultraviolet absorption characteristics of the phthalocyanine chromium complexes are listed in Table 3. The use of methanol as a solvent is noteworthy and reflects the greater solubility of the 6-co-ordinate complexes over the majority of

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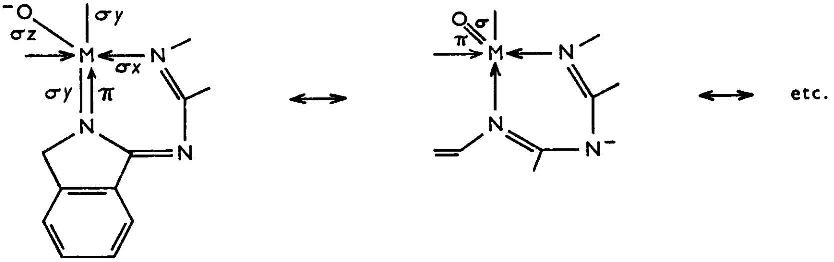
[7] Figgis and Nyholm, *J.*, 1959, 331.

4-co-ordinate phthalocyanine transition-metal derivatives. The present spectra are typical in that the most intense band is in the visible region at 670—690 mμ with the second most intense band at 330—350 mμ.[8] All of the 6-co-ordinate chromium complexes have subsidiary maxima which are atypical. These new bands (in the blue and/or ultraviolet) must result (ultimately) from electronic interactions of the groupings in the fifth and sixth co-ordination positions with the rest of the system. This may be likened to cross-conjugation superimposed on the phthalocyanine chromium chromophore so that new partial chromophore bands are to be expected.

Comparison of present results (Table 3) with data given by Williams *et al.*[9] for octahedral protoporphyrin iron(II) complexes suggests that the weakish absorption band of our chromium complexes in the 502—518 mμ region may result from a π–π* transition. Williams *et al.* point out that the energy of such a transition will be affected by the degree of coupling between d_ϵ electrons on the metal with π-states of the macrocycle. Good π-acceptor ligands in the fifth and sixth co-ordination positions will reduce or prevent the coupling, so reducing the electron density in the π-states of the porphyrin. The absorption is then expected to move to longer wavelengths (and *vice versa* for π-donor ligands). This is indeed as observed for the symmetrical phthalocyanine chromium complexes, the ligand sequence H_2O, MeOH, Cl^-, CNS^-, CN^- resulting in the bathochromically changing sequence 502, 505, 507, 511, 518 mμ (see Table 3).

Perpendicular Conjugation.—This idea[3] arose from attempts to explain the properties of the octahedral phthalocyanine chromium and manganese complexes. That the complexes $PcCr^{III}(H_2O)\cdot OH$ (VII) and $PcMn^{IV}(OH)_2$[10] each behaved as a *di*basic acid was unexpected. It seemed that there must be means for stabilizing the anions $[PcCr(O)OH]^{2-}$ and $[PcMnO_2]^{2-}$ and that this could be achieved through distribution of the negative charge (formally on oxygen) over the π-electron system of the macrocycle. Such a sharing of charge with the aromatic ring is accepted, for example, in the phenoxide anion. For the sharing to be possible in the phthalocyanine complex anions, it was necessary to assume that there was conjugation between the mutually perpendicular phthalocyanine and oxy-groups. How this might be possible, through simple overlap of a d_{xz}(or d_{yz})-orbital of the metal with *p*-orbitals of nitrogen and oxygen along the *x*(or *y*)- and *z*-axes has been indicated.[3,11] It was pointed out that the sets of canonical structures which might then be written could not be hybridised because of the symmetry of the *d*-orbitals. Nevertheless the limited conjugation allows the required distribution of negative charge, as indicated by the partial formulæ (A).



(A)

The process indicated in (A) could operate only if a d_{xz}(or d_{yz})-orbital of the metal were vacant. If the anion is an inner orbital complex (as is most probable), then the perpendicular conjugation must be through 4*d*-orbitals (which are capable of accepting electrons

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[8] Linstead, *J.*, 1953, 2873.

[9] Cowan, Drake, and Williams, *Discuss. Faraday Soc.*, 1959, **27**, 217.

[10] To be described later in full.

[11] Elvidge and Lever, *Proc. Chem. Soc.*, 1959, 171.

for π-bonding). (It is much less likely that the anion is spin-free and that a $3d_{xz}$- or $3d_{\gamma}$-orbital is freed by promotion of an electron to one of the vacant $3d_{\gamma}$-orbitals, as previously implied.[3]) $4d$-Orbitals are diffuse and so the overlap with p-orbitals of the ligand atoms would become increasingly poor along the first-row transition-metal series from titanium to copper, and perpendicular conjugation in suitable derivatives might vanish by about cobalt. It is perhaps significant that the light absorptions (visible and ultraviolet) of the analogues of vitamin B_{12} (B_{12a}, etc.) are closely similar,[12] but that those of the octahedral phthalocyanine chromium (and manganese) complexes show variations which appear too large (Table 3) to be ascribed solely to inductive effects of the ligands. There may be evidence here of the operation of perpendicular conjugation.

Williams's observations [9,13] concerning the spectra of some octahedral porphyrin complexes appear to provide evidence for perpendicular conjugation in these compounds. Chatt and his co-workers [14] explain the physical properties of some 4-co-ordinate platinum complexes in terms of a "*cis*-effect," whereby the electron push or pull of a ligand affects the bond strength of the ligand *cis* to it, *i.e.*, attached to the metal in the perpendicular direction. Thus electronic effects can certainly be transmitted through $3d_{\epsilon}$-orbitals, but this only becomes conjugation if one or other of the ligands is unsaturated so that the effects can be carried further. Such a case would differ from the example of perpendicular conjugation presented by the phthalocyanine complexes because all of the atoms concerned would be coplanar. The essential point concerning the octahedral phthalocyanine derivatives is that conjugation is postulated through a series of atoms which are not all coplanar (see A).

Craig's treatment [15] of conjugation in the phosphonitrilic halides, from which our postulate of perpendicular conjugation is ultimately derived,[3] proposed π-bond formation by the overlap of each nitrogen p-orbital with the adjacent phosphorus d_{xz}-orbital. Interactions with the phosphorus d_{yz}-orbital were taken to be negligible. Recently, Dewar *et al.*[16] concluded that this was unjustified and that the pair of phosphorus d_{xz}- and d_{yz}-orbitals should be combined linearly to give two new d_{π}-orbitals, each of which would overlap with just one of the adjacent nitrogen p-orbitals. This treatment thus leads to the conclusion that each nitrogen atom is at the mid-point of a 3-centre π-bond formed with the two neighbouring phosphorus atoms, and that the conjugation is broken at each phosphorus atom so that there is no through conjugation. It was further suggested that no significant through conjugation should therefore be observed in other examples of d_{π}–p_{π} π-bonding. That electronic effects appear to be transmitted perpendicularly through the d-orbitals of suitable metals must nevertheless be admitted, and their magnitude suggests through conjugation—which is indeed implied by the interpretation of the spectra of octahedral protoporphyrin iron(II) complexes given by Williams and his colleagues.[9] A compromise explanation seems necessary. Further experimental evidence is needed and is being sought.

EXPERIMENTAL

As in previous work in this series, the progress of reactions and of purifications was followed by quantitative measurements of visible-light absorption.

Phthalocyanine Chromium(III) *Hydroxide* (IV).—An intimate mixture of chromic acetate (3 g.) and phthalonitrile (6 g., purified) was heated to 270°. After 15 min., the melt thickened and was allowed to cool. The solid was powdered and triturated in turn with benzene, methanol, water, methanol, and ether. The product (8 g.), mainly phthalocyanine chromium(II) and phthalocyanine chromium(III) acetate, was heated at 400°/10^{-6} mm., whereupon the

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[12] Kaczka, Wolf, Kuehl, and Folkers, *J. Amer. Chem. Soc.*, 1951, **73**, 3569.

[13] Williams, *Chem. Rev.*, 1956, **56**, 299.

[14] Chatt, Duncanson, Shaw, and Venanzi, *Discuss. Faraday Soc.*, 1958, **26**, 131.

[15] Craig and Paddock, *Nature*, 1958, **181**, 1052; Craig, *J.*, 1959, 997.

[16] Dewar, Lucken, and Whitehead, *J.*, 1960, 2423.

chromous complex sublimed but underwent oxidation. Further sublimation afforded *phthalocyanine chromium*(III) *hydroxide* as long purple needles (Found: C, 66·1, 66·0; H, 3·55, 3·0; Cr, 9·4, 9·0; N, 19·4. $C_{32}H_{17}CrN_8O$ requires C, 66·1; H, 2·95; Cr, 8·95; N, 19·3%). On quantitative oxidation[17] the pigment consumed 1·03 atom-equiv. of O ($PcCr^{III}OH$ requires 1·0 atom-equiv. of O).[18]

Phthalocyanine Chromium(III) *Acetate* (I).—The preceding hydroxide (50 mg.) was kept with acetic anhydride for 24 hr. The product was washed with anhydrous ether and dried at 180°/15 mm. to give the *acetate* (Found: C, 65·4; H, 3·1; Cr, 8·55. $C_{34}H_{19}CrN_8O_2$ requires C, 65·5; H, 3·1; Cr, 8·3%).

Phthalocyanine Dimethanolchromium(III) *Hydroxide* (III; R = R′ = MeOH).—Phthalocyanine chromium(III) hydroxide (50 mg.) was heated with methanol (7 c.c.) under reflux for 2 hr. The *complex* was washed with anhydrous ether and dried in a desiccator (yield, 54 mg.) (Found: C, 63·5; H, 3·9; Cr, 8·3; N, 16·9. $C_{34}H_{25}CrN_8O_3$ requires C, 63·25; H, 3·9; Cr, 8·1; N, 17·4%). When heated at 180°/20 mm. for several hr., this complex afforded phthalocyanine chromium(III) hydroxide, as indicated by the infrared absorption.

Phthalocyanine Aquomethanolchromium(III) *Hydroxide* (III; R = H_2O, R′ = MeOH).—Phthalocyanine chromium(III) hydroxide (100 mg.) was kept with acetic acid (4·5 c.c.), water (3 c.c.), and methanol (1 c.c.) at 90° for 5 hr. After being washed with water, methanol, and then ether, the *complex* was dried in a desiccator (yield, 105 mg.) (Found: C, 63·1; H, 3·55; Cr, 8·0. $C_{33}H_{23}CrN_8O_3$ requires C, 62·75; H, 3·9; Cr, 8·25%). At 180°/20 mm., this complex lost weight (4%) and afforded phthalocyanine hydroxoaquochromium(III) with infrared absorption identical with that of authentic material (see below).

Phthalocyanine Diaquochromium(III) *Hydroxide* (III; R = R′ = H_2O) *and the* 6-*Co-ordinate Complex* (VII).—Phthalocyanine chromium(III) hydroxide (50 mg.) was warmed with 3 : 1 : 4 aqueous-ethanolic acetic acid at 95° for 3 hr. Alternatively the hydroxoaquochromium(III) compound (VII) (80 mg.) was suspended in water (5 c.c.) at 95° for 4 hr. The *complex* was washed with water, methanol and ether, and dried in a desiccator (yield, 97%) (Found: C, 62·2; H, 3·7; Cr, 8·6. $C_{32}H_{21}CrN_8O_3$ requires C, 62·2; H, 3·4; Cr, 8·4%). Sublimation of the complex (36 mg.) at 400°/10^{-6} mm. afforded phthalocyanine chromium(III) hydroxide (20 mg.) identified by its infrared spectrum. At 180°/20 mm., however, the complex yielded *phthalocyanine hydroxoaquochromium*(III) (VII) (Found: C, 64·4, 64·2; H, 3·7, 3·5; Cr, 8·6; N, 18·3. $C_{32}H_{19}CrN_8O_2$ requires C, 64·1; H, 3·2; Cr, 8·7; N, 18·7%). Sublimation of this at 400°/10^{-6} mm. afforded phthalocyanine chromium(III) hydroxide (correct infrared spectrum) in 60% yield (Found: C, 66·0; H, 3·0%).

Phthalocyanine Acetatoaquochromium(III) (IX; R = OAc, R′ = H_2O).—Powdered phthalocyanine hydroxoaquochromium(III) (50 mg.) was kept with acetic anhydride (1 c.c.) for 24 hr. The green powder (100%) was washed with ether and dried at 180°/20 mm., so affording the *complex* (Found: C, 63·4; H, 3·5; Cr, 8·5. $C_{34}H_{21}CrN_8O_3$ requires C, 63·6; H, 3·3; Cr, 8·1%). An identical product (infrared spectrum) resulted from treatment of phthalocyanine chromium(III) hydroxide with 70% aqueous acetic acid at 90° for 2 hr.

Phthalocyanine propionatoaquochromium(III) (IX; R = O·CO·Et, R′ = H_2O), formed by keeping phthalocyanine hydroxoaquochromium(III) with propionic anhydride for 1 week, was washed with ether and dried at 180°/15 mm. (Found: C, 63·85; H, 3·9; Cr, 7·6. $C_{35}H_{23}CrN_8O_3$ requires C, 64·1; H, 3·55; Cr, 7·9%).

Phthalocyanine Acetato(*acetic acid*)*chromium*(III) (IX; R = OAc, R′ = HOAc).—Phthalocyanine hydroxoaquochromium(III) (VII) (50 mg.), or phthalocyanine chromium(III) hydroxide (IV), was refluxed in acetic anhydride (10 c.c.) for 1·5 hr. The *complex* (96%) was washed with methanol and ether, and dried at 180°/15 mm. (Found: C, 63·5; H, 3·7; Cr, 7·7. $C_{36}H_{23}CrN_8O_4$ requires C, 63·25; H, 3·4; Cr, 7·6%).

Phthalocyanine Acetatomethanolchromium(III) (IX; R = OAc, R′ = MeOH).—Phthalocyanine chromium(III) hydroxide (30 mg.), methanol (5 c.c.), and acetic acid (3 c.c.) were refluxed together for 3 hr. The green *complex* (30 mg.) was washed with methanol and ether, and dried in a desiccator (Found: C, 63·8; H, 3·9; Cr, 7·8. $C_{35}H_{23}CrN_8O_3$ requires C, 64·1; H, 3·55; Cr, 7·9%). At 180°/20 mm., this complex was converted into phthalocyanine chromium(III) acetate (Found: C, 65·2; H, 3·1; Cr, 8·5%).

Hydrogen [*Phthalocyanine Dichlorochromate*(III)] (X).—Dry hydrogen chloride was passed

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[17] Elvidge, *J.*, 1961, 869.

[18] Cf. Dent, Linstead, and Lowe, *J.*, 1934, 1036.

into a refluxing suspension of phthalocyanine chromium(III) hydroxide (180 mg.) in methanol (15 c.c.) for 3 hr. The very dark green *product* (180 mg.) was dried at 180°/20 mm. (Found: C, 60·5; H, 3·3; Cl, 10·7; Cr, 8·3; N, 17·0. $C_{32}H_{17}Cl_2CrN_8$ requires C, 60·4; H, 2·7; Cl, 11·1; Cr, 8·2; N, 17·6%).

Potassium [Phthalocyanine Hydroxocyanochromate(III)] (VI).—Phthalocyanine chromium(III) hydroxide (80 mg.), methanol (5 c.c.), butanol (5 c.c.), and potassium cyanide (80 mg.) were refluxed together for 8 hr., and the mixture was then filtered. During 1 week at 2°, the filtrate deposited elongated prisms of the *complex* (35 mg.) which was washed with cold water, methanol and ether, and dried at 180°/20 mm. (Found: C, 61·5; H, 3·05; Cr, 7·7; K, 5·9; N, 19·4. $C_{33}H_{17}CrKN_9O$ requires C, 61·3; H, 2·65; Cr, 8·0; K, 6·05; N, 19·5%).

Disodium [Phthalocyanine Oxohydroxochromate(III)] (VIII; M = Na).—Powdered phthalocyanine hydroxoaquochromium(III) (VII) (100 mg.) was shaken with 1% sodium hydroxide in ethanol (5 c.c.) for 24 hr. The purple crystals of the complex *salt* were washed rapidly with ethanol and then with ether, and dried at 180°/20 mm. (yield, 90 mg.) (Found: C, 60·1, 59·7; H, 3·2, 3·2; Cr, 7·7; Na, 7·2. $C_{32}H_{17}CrN_8Na_2O_2$ requires C, 59·7; H, 2·7; Cr, 8·1; Na, 7·15%).

Diammonium [Phthalocyanine Oxohydroxochromate(III)] (VIII; M = NH_4).—Liquid ammonia (~10 c.c.) was filtered on to the hydroxoaquo-complex (VII) (50 mg.), cooled with liquid ammonia. After 5 hr., the ammonia had evaporated and the *salt* was then dried in a desiccator (Found: C, 61·3; H, 4·0; Cr, 7·3. $C_{32}H_{25}CrN_{10}O_2$ requires C, 60·8; H, 3·95; Cr, 8·2%). At room temperature, the salt slowly evolved ammonia.

Dipyridinium [Phthalocyanine Oxohydroxochromate(III)] (VIII; M = pyH).—The powdered hydroxoaquo-complex (VII) (100 mg.) was kept with pyridine (1 c.c.) for 24 hr. and the resulting jade-green crystals (125 mg.) of the *salt* were washed with ether and dried at 150°/20 mm. (Found: C, 66·6; H, 3·95; Cr, 7·0. $C_{42}H_{29}CrN_{10}O_2$ requires C, 66·6; H, 3·9; Cr, 6·9%). Alternatively, phthalocyanine chromium(III) hydroxide (80 mg.) was shaken for 24 hr. with pyridine (4 c.c.), acetic acid (3 c.c.), and water (0·5 c.c.). The product (100 mg.), after being washed with ether and dried at 150°/15 mm., had an infrared spectrum indistinguishable from that given by the preceding salt.

Phthalocyanine Dipyridinechromium(II) (V).—Dried, powdered phthalocyanine chromium(III) hydroxide (IV) (135 mg.) was shaken under nitrogen with pyridine (2 c.c., freshly distilled from barium oxide). After 24 hr., the olive-green chromium(II) *complex* was washed with anhydrous ether and dried at 150°/15 mm. (yield, 146 mg.) (Found: C, 69·45; H, 4·0; Cr, 7·2; N, 19·2. $C_{42}H_{26}CrN_{10}$ requires C, 69·8; H, 3·6; Cr, 7·2; N, 19·4%).

Phthalocyanine Chromium(II) (II).—Sublimation of the preceding complex at 400° in nitrogen at 10^{-6} mm. afforded the chromium(II) *complex* as dark purple needles (Found: C, 67·7, 68·45; H, 3·0, 3·1; Cr, 9·3, 9·2. $C_{32}H_{16}CrN_8$ requires C, 68·1; H, 2·9; Cr, 9·2%). On quantitative oxidation,[17] the complex consumed 1·56, 1·33 atom-equiv. of O ($PcCr^{II}$ requires 1·50 atom-equiv. of O).

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