336. The Magnetic Behaviour of Transition-metal Phthalocyanines

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The magnetic behaviour of the square-planar Cr^{II}, Cr^{III}, Mn^{II}, Fe^{II}, and octahedral Cr^{II}, Cr^{III}, and Mn^{IV} phthalocyanines has been investigated over the temperature range 90—300°K. The results, together with those of other authors, are discussed, with the help of electron spin resonance data, in terms of the relative energies of the metal-ion 3*d* orbitals. It is suggested that phthalocyaninechromium(II) and phthalocyaninechloroiron(III) have structures involving metal–metal bonds.

THE transition-metal phthalocyanines represent a novel class of complexes in which a square-planar configuration, proved by *X*-ray studies,[1] is conferred upon the metal ion through the geometry of the ligand. Despite the apparent ease with which one might expect also to form octahedral complexes, by adding two further ligands to the square, it is possible to isolate square-planar complexes of the Cr^{II}, Cr^{III}, and Mn^{II} ions. The phthalocyanines offer a unique opportunity to study and compare the magnetic properties of a considerable number of first-row transition-metal ions in the comparatively rare square-planar configuration.

Previous workers [2-5] studied the magnetic properties of the Ti^{III}, OV^{VI}, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, and Cu^{II} phthalocyanine derivatives, in some cases at more than one temperature, but only in the case of cobalt [5] has a detailed temperature study been undertaken. We now present detailed temperature studies of most of the first-row elements, including Cr^{II}, Cr^{III}, and Mn^{IV} derivatives which were not available to earlier workers. A summary of the magnetic properties of some of the chromium and manganese derivatives has already been reported.[6-8] Data are also included for the many octahedral phthalocyanine derivatives which are now known.

Square-planar Derivatives.—Gibson, Ingram, and Schonland [9] and Griffith [10] have investigated the electron paramagnetic resonance (e.p.r.) spectra of cobalt and copper phthalocyanines in order to determine the 3*d* orbital energies. In the case of phthalocyaninecopper the orbitals are believed to lie in the order indicated in Fig. 1*a*, the calculated energies being appended. In the case of phthalocyaninecobalt there is some uncertainty regarding the relative order of the orbitals. The e.p.r. measurements are consistent both with the d_{z^2} orbital being of high energy, as in Fig. 1*a*, or with its being of comparatively low energy as in Fig. 1*b*. The square-planar phthalocyanines belong to the point group D_{4h}. Gray and Ballhausen [11] have carried out a simple molecular orbital study of a metal ion in a ligand environment of D_{4h} symmetry, assuming an intramolecular π system on the ligands. They conclude that the order of *d* orbitals is $e_g < a_{1g} < b_{2g} < b_{1g}$. However this order will not necessarily apply to the metal phthalocyanines since, in their calculation, Gray and Ballhausen assume the presence of ligand π orbitals both perpendicular and parallel to the molecular plane. In the phthalocyanine complexes, there are no π orbitals parallel to the molecular plane.

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[1] Linstead and Robertson, *J.*, 1936, 1195, 1736.

[2] Klemm and Klemm, *J. prakt. Chem.*, 1935, **143**, 82; Senff and Klemm, *ibid.*, 1940, **154**, 73.

[3] Engelsma, Yamamoto, Markham, and Calvin, *J. Phys. Chem.*, 1962, **66**, 2517.

[4] Havemann, Haberditzl, and Mader, *Z. phys. Chem. (Leipzig)*, 1962, **218**, 71.

[5] Figgis and Nyholm, *J.*, 1959, 338.

[6] Elvidge and Lever, *J.*, 1961, 1257.

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

[8] Elvidge and Lever, *Proc. Chem. Soc.*, 1959, 195.

[9] Gibson, Ingram, and Schonland, *Discuss. Faraday Soc.*, 1958, **26**, 72.

[10] Griffith, *Discuss. Faraday Soc.*, 1958, **26**, 81.

[11] Gray and Ballhausen, *J. Amer. Chem. Soc.*, 1963, **85**, 260.

Considering only the $p\pi(p_z)$ orbital on each co-ordinating nitrogen atom of the phthalocyanine unit, the π orbitals span e_g, a_{2u}, and b_{2u} in D_{4h} symmetry. The σ orbitals span a_{1g}, b_{1g}, and e_u. The metal orbitals transform as shown

$$d_{z^2},\, s \longleftrightarrow a_{1g} \qquad d_{xy} \longleftrightarrow b_{1g}$$
$$d_{x^2-y^2} \longleftrightarrow b_{1g} \qquad p_z \longleftrightarrow a_{2u}$$
$$d_{xz},\, d_{yz} \longleftrightarrow e_g \qquad p_x,\, p_y \longleftrightarrow e_u$$

It follows that the d_{xy} orbital will be formally non-bonding, since neither the σ nor π combinations of the phthalocyanine unit include b_{2g}. The d_{z^2} and $d_{x^2-y^2}$ orbitals will be σ anti-bonding, the latter strongly so, since its charge density lies mainly in the xy plane. The e_g pair will be π anti-bonding, though there may well be some stabilisation through interaction with the empty π anti-bonding orbitals on the phthalocyanine unit. This interaction could be important since the lowest empty π orbital on the phthalocyanine unit has e_g symmetry.[12] This arrangement differs radically from that in complexes such as $[PdCl_4]^{2-}$, where the presence of chlorine π orbitals in the molecular plane leads to a destabilisation of the d_{xy} orbital, twice as great as the destabilisation of the d_{xz} and d_{yz} pair.

The relative position of the $d_{z^2}(a_{1g})$ orbital will depend upon the degree of axial perturbation in the molecule. In the crystal the co-ordination about the metal is tetragonal, with nitrogen atoms of adjacent parallel molecules lying above and below the molecular plane at distances of about 3·4 Å from the metal atom.[1] The orbital energies illustrated in Fig. 1*a* are more consistent with this treatment than are those in Fig. 1*b*. The electron spin resonance data for phthalocyaninecopper [9] however, show that the e_g and b_{2g} orbitals are fairly close together, and hence may well cross over in some complexes.

TABLE 1

Complex	Oxidation state	Co-ordination number	Number of unpaired electrons	μ_e (B.M.) * (25°)	θ (°K)	Theoretical spin-only moment	Ref.†
Pc(Cl)Ti	3	6?	1	1·79		1·73	28
Pc(O)Ti	4	5	0	0 ¶		0	28
Pc(O)V	4	5	1	1·71	4	1·73	2
PcCr	2	4	4	3·49	306	4·89	t.p.
Pc(Py)$_2$Cr	2	6	2	3·16	35	2·83	t.p.
[PcCr]$^+$ OH$^-$	3	4	3	4·03	15	3·87	t.p.
Pc(H$_2$O)(HO)Cr	3	6	3	3·69	0	3·87	t.p.
[Pc(HO)(O)Cr]$^{2-}$ 2Na$^+$	3	6	3	3·91	155	3·87	t.p.
[Pc(HO)(O)Cr]$^{2-}$ 2PyH$^+$	3	6	3	4·06	15	3·87	t.p.
PcMn	2	4	3	4·34	−6	3·87	t.p.
				4·33		3·87	3
				4·55		3·87	2
Pc(MeOH)(HO)Mn	3	6	4	4·87		4·89	3
Pc(Py)(OAc)Mn	3	6	4	4·76		4·89	3
[Pc(O)$_2$Mn]= 2Na$^+$	4	6	3	4·00	49	3·87	t.p.
Pc(HO)(CN)Mn	4	6	3	3·88	5	3·87	t.p.
Pc(O)Mn	4	6	3	3·77	46	3·87	t.p.
PcFe	2	4	2	3·85	9	2·83	t.p.
				3·96		2·83	2
				4·51		2·83	4
Pc(Py)$_2$Fe	2	6	0	0 ‡	—	0	2
Pc(Cl)Fe	3	6?	3?	3·32	53	3·87	t.p.
PcCo	2	4	1	2·72	60	1·73	5
				2·66		1·73	4
				2·14		1·73	2
PcNi	2	4	0	0 §	—	0	2
PcCu	2	4	1	1·73		1·73	2
				1·75		1·73	4
				1·73		1·73	38

* Calc. from $\mu_e = 2{\cdot}839(\chi'_m T)^{\frac{1}{2}}$, by assuming a diamagnetic correction for phthalocyamine of 290×10^{-6} c.g.s. units. † t.p., this Paper. ‡ $\chi_g = -0{\cdot}3 \times 10^{-6}$ c.g.s. unit. § $\chi_g = -0{\cdot}4 \times 10^{-6}$ c.g.s. unit. ¶ $\chi_g = -0{\cdot}6 \times 10^{-6}$ c.g.s. unit.

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[12] Basu, *Indian J. Phys.*, 1954, **37**, 511.

A compilation of all the available magnetic data on the metal phthalocyanines is listed in Table 1. In the discussion which follows we shall treat each phthalocyanine individually.

Phthalocyaninechromium(II).—The chromium(II) ion, having a d^4 configuration, is expected to give rise to square-planar complexes, but in practice only two such complexes, $PcCr^{II}$ (Pc = phthalocyanine) and $CrCl_2,2Py$ are known.[13] Most metal phthalocyanines have a unit-cell width [1] of 4·7—4·8 Å. This corresponds to the nearest approach of the two phthalocyanine units in the cell, such that the rings are just touching, the van der Waals repulsion keeping them apart. The unit-cell width of phthalocyanine chromium(II) [6] however is only 3·4 Å, the implication being that the phthalocyanine units are held closer together by the presence of a chromium–chromium interaction. This would give rise to a magnetic moment lower than the expected 4·90 B.M. and the moment would be strongly temperature-dependent. This is in fact observed. The coupling of the chromium atoms will give rise to a series of spin states, the lowest having $S = 0$ and the highest $S = 4$, whose energies will be related to the exchange integral J as indicated in Fig. 2. The magnetic moment then arising will depend upon the temperature, in that the observed moment will be equal to the sum of the moments of each spin state multiplied by the Boltzmann distribution for that state. In view of the small unit cell, it seems likely that the chromium–chromium interaction extends continuously through the crystal, rather than being between adjacent pairs of molecules. Figgis and Lewis [14] have calculated the temperature-dependence of the magnetic moment for such a system. They find that once eight or nine atoms have been strung together, the expected moment is almost independent of further polymerisation. The theoretical curve of μ_e *versus* J/kT is illustrated in Fig. 3 for nine atoms each of $S = 2$ interacting together. The experimental results fit this curve extremely well with $J = -38{\cdot}2°$. We conclude that phthalocyanine-chromium(II) exists as a continuous polymer (Fig. 4*a*) with the chromium atoms stacked on top of one another giving rise to an interaction with an exchange energy of $-38{\cdot}2°$.

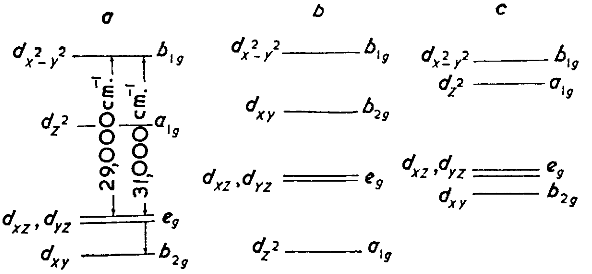

FIG. 1. *a*, Energy levels in phthalocyanine copper(II). *b*, Possible order of energy levels in phthalocyanine cobalt(II). *c*, Energy levels in six-co-ordinate D_{4h} metal phthalocyanines.

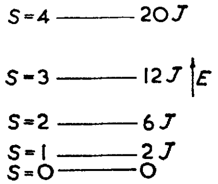

FIG. 2. Spin states in phthalocyanine chromium(II).

Phthalocyaninechromium(III) *hydroxide*. The observed moment of 4·0 B.M. accompanied by a small Curie–Weiss temperature is consistent with three unpaired spins with a small but definite orbital contribution. This contribution may arise from a high frequency temperature independent term through coupling with a higher excited state, perhaps $(b_{2g})^1(e_g)^1(a_{1g})^1$ or $(a_{1g})^1(e_g)^1(b_{2g})^1$. Such terms are unimportant for the chromic ions in an ordinary octahedral environment, since the $^4T_{2g}$ state lies too far above the $^4A_{2g}$ state to be mixed in appreciably.[15] However the excited states mentioned above for the phthalocyanine, are likely to be very much closer to the orbitally non-degenerate ground state.

Phthalocyaninemanganese(II). The manganous ion has five d electrons. The electron

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[13] Gill, Nyholm, Barclay, Christie, and Pauling, *J. Inorg. Nucl. Chem.*, 1961, **18**, 88

[14] Figgis and Lewis, unpublished work; Lewis, personal communication.

[15] Griffith, " The Theory of Transition Metal Ions," Cambridge University Press, Cambridge, 1961.

configuration will be orbitally non-degenerate, $(b_{2g})^2(e_g)^2(a_{1g})^1$ or less likely $(a_{1g})^2(e_g)^2(b_{2g})^1$, with three unpaired electrons. A moment somewhat in excess of 3·87 B.M. is observed (Table 1) with a small Curie–Weiss constant. An orbital contribution could arise through the mixing-in of higher orbitally degenerate states, such as $(b_{2g})^1(e_g)^3(a_{1g})^1$.

Ingram and Bennett [16] have measured the electron spin resonance spectrum of powdered phthalocyaninemanganese(II). They found $\bar{g} = 2{\cdot}0$. The $\bar{g}$ value is related to the magnetic moment by the equation

$$\mu^2_e = \bar{g}^2 S(S + 1) \tag{1}$$

where S = total spin angular momentum and $\bar{g}$ is the mean g value ($\bar{g} = 1/3[2g\perp + g\|]$). Hence we should expect a spin-only moment for phthalocyaninemanganese(II) on this basis. It is not clear why the electron spin resonance data and the magnetic data should disagree. Both Klemm [2] and Engelsma and their co-workers [3] have measured the magnetic moment of this complex.

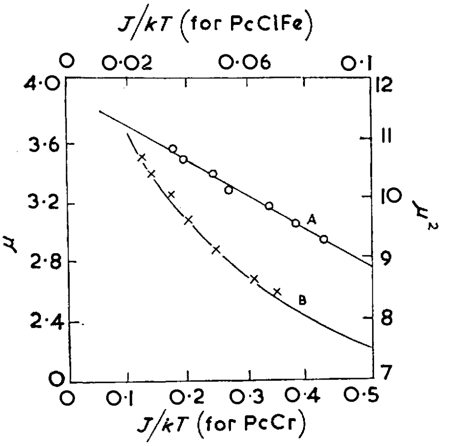

FIG. 3. *A*, Phthalocyanine chloroiron(III) [top and right scales]. Theoretical line $J = -10{\cdot}4^\circ$K, $g = 1{\cdot}77$. *B*, Phthalocyanine chromium(II) [bottom and left scales]. Theoretical line $J = -38{\cdot}2^\circ$K, $g = 2{\cdot}0$.

FIG. 4. *a*, Possible structure of phthalocyanine chromium(II). Each line represents an edge view of the phthalocyanine molecule. *b*, Possible structure of phthalocyanine chloroiron(III).

Phthalocyanineiron(II). Phthalocyanineiron(II) has been the subject of much discussion since Klemm's early measurement indicated a moment roughly halfway between the spin-free and spin-paired predicted values. The discussion [17] concerns the possibility of a complex exhibiting a thermal admixture of the spin-free ($S = 2$) and spin-paired ($S = 1$) states; in other words, a compound where the energy levels of the two possible magnetic states lie close together within kT. E.p.r. measurements indicate that ferrihæmoglobin hydroxide [18] is of this type, whilst some authors [19] claim spectral evidence for the existence of such closely lying magnetic states in a number of other ferriporphyrin complexes, which exhibit abnormal magnetic moments. Orgel [17] has suggested that phthalocyanineiron(II) may also be of this type, and hence a reinvestigation of the complex seemed warranted. A new study over a larger temperature range (100—340°K) has substantially confirmed Klemm's findings. The complex obeys the Curie–Weiss law though there is a tendency to swing away from a straight line towards lower than calculated susceptibility at the higher temperatures (Fig. 5) which is not understood. A Curie–Weiss temperature of only 9°K rules out any possibility of anti-ferromagnetism.

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[16] Ingram and Bennet, *J. Chem. Phys.*, 1954, **22**, 1136; *Discuss. Faraday Soc.*, 1955, **19**, 140.

[17] Orgel, " 10e Conseil de l'Institut International de Chimie, Solvay," Stoops, Brussels, 1956.

[18] Ingram, *Discuss. Faraday Soc.*, 1958, **26**, 93.

[19] Griffith, *Discuss. Faraday Soc.*, 1958, **26**, 94.

If ferrous phthalocyanine did contain two closely lying magnetic states, then reduction of temperature should lead to an increased population of the lower lying ($S = 1$) level. In other words the moment would change with temperature and there would be a concomitantly high Curie–Weiss temperature. The fact that the moment is virtually independent of temperature precludes this system. Indeed it seems inconceivable that the $S = 2$ state could be populated when we consider that the $d_{x^2-y^2}$ orbital must be of the order of 20,000—30,000 cm.$^{-1}$ above the lower levels. The moment is therefore deemed to arise from the spin-paired $S = 1$ state, with a considerable orbital contribution. The relative order of the orbitals however cannot be determined, since both arrangements would give rise to an orbital contribution when six electrons are fed in. Havemann and Haberditzl[4] have measured the moment of phthalocyanineiron(II), but their value of 4·56 B.M. disagrees with both our work and that of Klemm. Ingram and Bennett[16] were unable to observe an electron spin signal from phthalocyanineiron(II).

Phthalocyaninecobalt(II). The magnetic behaviour of phthalocyaninecobalt(II), first investigated by Klemm *et al.*,[2] and then in detail by Figgis and Nyholm,[5] parallels that of other spin-paired square-planar cobaltous derivatives,[20] *i.e.*, a moment considerably above that expected for one unpaired spin, and an abnormal temperature dependence. The electron spin resonance data do not distinguish between the energy levels described in Fig. 1, *a* and *b*. However the order 1*a* seems favoured because the situation would not then be too dissimilar from that occurring in phthalocyaninecopper. The ground state is then $(b_{2g})^2(e_g)^4(a_{1g})^1$, and an orbital contribution could arise through mixing-in of higher orbitally degenerate states such as $(b_{2g})^2(e_g)^3(a_{1g})^2$. If the a_{1g} orbital lies some considerable distance from the e_g orbital then the moment should be temperature-independent. This has been so in all the preceding cases where higher states have been mixed in by spin–orbit coupling to explain the enhanced moments. However phthalocyaninecobalt does have a magnetic moment which is strongly dependent upon temperature. A plot of $1/\chi_m$ against T gives a straight line at low temperature but there is considerable deviation from this line at higher temperatures.[5] This behaviour suggests the presence of a considerable high frequency temperature-independent paramagnetic term.

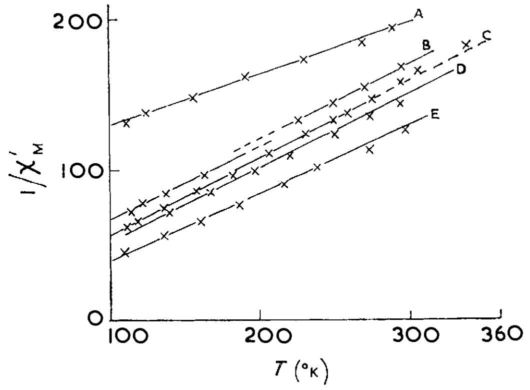

FIG. 5

A, Phthalocyaninechromium(II).
B, Phthalocyanineoxymanganese(IV).
C, Phthalocyanineiron(II).
D, Phthalocyaninehydroxychromium(III).
E, Phthalocyaninemanganese(II).

The observed g values,[9] $g\| = 1{\cdot}92$, $g_x = 2{\cdot}92$, and $g_y = 2{\cdot}88$, lead to a mean $\bar{g}$ value of 2·57 corresponding to $\mu_e = 2{\cdot}22$ B.M. (from eqn. 1). There is disagreement between the magnetic susceptibility measurements and the electron spin data. It is not yet possible to explain why this should be so. The low magnetic moment found by Klemm *et al.*[2] is probably spurious.

Phthalocyaninenickel(II). This complex is diamagnetic, having eight d electrons to place in the four lower orbitals. The paramagnetism which has sometimes been associated

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[20] Figgis and Nyholm, *J.*, 1954, 12.

with this,[21] and other supposedly diamagnetic phthalocyanines including the metal-free ligand itself, arises from an impurity which may be removed by repeated recrystallisation from concentrated sulphuric acid.

Phthalocyaninecopper(II). Phthalocyaninecopper(II) with a moment of 1·73 B.M. is a little unusual since most copper complexes have moments fairly close to 1·9 B.M. Antiferromagnetism in the phthalocyanine complex may be ruled out through the absence of any triplet structure in the e.p.r. spectrum,[9,10] whilst *X*-rays show that the metal ion has nitrogen atoms as nearest neighbours some 3·4 Å distance in the octahedral positions. The electron spin resonance data of Ingram and his co-workers [9] yields $\bar{g} = 2{\cdot}085$ for the crystalline material. Insertion of this value into eqn. (1) gives $\mu_e = 1{\cdot}81$ B.M., slightly higher than the observed result. The odd electron was placed in the b_{1g} orbital and α^2 was found to be 0·79. This value may be interpreted to mean that the electron is in an antibonding σ orbital and spends 79% of its time on the copper atom. No hyperfine interaction with the bonding nitrogen atoms was observed, however. In a later study of the complex, dissolved in concentrated sulphuric acid, Roberts and Koski [22] found $\alpha^2 = 0{\cdot}72$ and observed a hyperfine interaction with the nitrogen atoms. Malmström and Vänngård [23] also observe a hyperfine interaction in frozen solution.

Phthalocyaninesilver(II).—No magnetic datum is available for this complex,[24] but two e.p.r. studies have been carried out. Kholmogorov and Glebovsky [25] found only a narrow line at $g = 2{\cdot}0023$, ascribed to a radical impurity, whilst MacCragh and Koski [26] found a broad line in the solid at $g\perp = 2{\cdot}016$, and lines at $g\| = 2{\cdot}093$ and $g\perp = 2{\cdot}017$ (from eqn. 1, $\mu_e = 1{\cdot}77$ B.M.) in frozen chloronaphthalene. The odd electron is placed in the b_{1g} orbital, and $\alpha^2 = 0{\cdot}54$ compared with 0·72 for phthalocyaninecopper.[22]

Phthalocyanine-oxytitanium(IV) *and -oxyvanadium*(IV). Both these compounds contain metal–oxygen double bonds [27,28] and may be regarded as five co-ordinate, and undoubtedly square pyramidal. The former, with a d^0 configuration, is diamagnetic, whilst the latter has a moment of 1·71 B.M.[2] This is in accord with other vanadyl complexes where moments within a few percent of 1·73 B.M. are always found,[29] and is in agreement with theory, since no orbital contribution is expected. An electron spin resonance study with powdered phthalocyanineoxyvanadium(IV) [16] gave $\bar{g} = 2{\cdot}0$, and hence $\mu_e = 1{\cdot}73$ B.M.

Octahedral Complexes.—In all cases where stable octahedral phthalocyanine derivatives can be isolated, spin-paired complexes are obtained. In most cases the magnetic behaviour is typical of the corresponding metal ion in an octahedral configuration. The acquisition of two further ligands by the metal ion, in these complexes, does not alter the microsymmetry, which remains D_{4h}. The presence of the extra two ligands should increase the energy of the d_{z^2} orbital relative to its energy in the square-planar complexes, and may also ensure that the order of the three lowest orbitals is $d_{xy} < d_{xz}, d_{yz}$ (Fig. 1*c*).

Phthalocyaninechlorotitanium(III). The structure of this complex [28] is not known but it seems probable that the chloride ions bridge the titanium atoms to form an octahedral polymeric arrangement. The microsymmetry will be D_{4h} so that the ground state will be $^2B_{2g}$. The moment [28] is close to the spin-only value as would be predicted for such a ground term.

Phthalocyaninedipyridinechromium(II).—This complex [6] has a moment of 3·16 B.M. and a Curie–Weiss temperature of 35°K. Since the chromous ion has a d^4 configuration, all four electrons will reside in the t_{2g} orbitals of the octahedral set which would give rise to

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[21] Tikhomirova and Chernikova, *Zhur. strukt. Khim.*, 1962, **3**, 335.

[22] Roberts and Koski, *J. Amer. Chem. Soc.*, 1961, **83**, 1865.

[23] Malmström and Vänngård, *J. Mol. Biol.*, 1960, **2**, 118.

[24] Barrett, Frye, and Linstead, *J.*, 1938, 1157.

[25] Kholmogrov and Glebovskii, *Optics and Spectroscopy*, 1962, **12**, 411.

[26] MacCragh and Koski, *J. Amer. Chem. Soc.*, 1963, **85**, 2375.

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

[28] Taube, *Z. Chem.*, 1963, **3**, 194.

[29] Asmussen, Magnetokemiske Undersögelser over Uorganiske Kompleksforbindelser, Gjellerups Forlag, Copenhagen, 1944.

two unpaired spins plus an orbital contribution. The moment observed may be compared with other octahedral chromous derivatives such as $K_4Cr(CN)_6$, $\mu_e = 3{\cdot}15$ B.M.;[30] and $[Cr(Dipy)_3]^{++}$,$2Br^-$, $\mu_e = 3{\cdot}27$ B.M.[31] Kotani[32] has shown that the magnetic moments of regular octahedral low-spin chromous complexes, having a ground state $^3T_{1g}$, should increase with decreasing temperature. In D_{4h} symmetry the degeneracy of the $^3T_{1g}$ term would be lifted. The ground term will now be $^3A_{2g}$ with a ^3E_g term lying at a distance of ΔE about it. The moment should become independent of temperature if ΔE is large. This appears to be the case. There is however a considerable temperature-independent term indicated by a deviation from Curie–Weiss behaviour at higher temperatures.

Octahedral chromium(III) *and manganese*(IV) *derivatives.* These complexes,[6] having d^3 ions, should have moments in the 3·7—3·9 B.M. region with no orbital contribution. The slightly higher moments observed in some cases (Table 1) are not understood. A number of other irregularities are also present; the sodium salt of the phthalocyaninehydroxychromate(III) has an unexpectedly high Curie–Weiss temperature of +155°K. The complex obeys the Curie–Weiss law, over the temperature range studied, and has no observable Néel point. If the sodium ions are replaced by the much larger pyridinium ions, the constant is reduced to 15°K. This behaviour suggests that the abnormality arises through some perturbation of the cubic field, experienced by the chromic ion, as a result of the proximity of the small positively charged sodium ions. Just what sort of mechanism this would involve is not clear. The corresponding disodium manganese complex also has a somewhat high Curie–Weiss constant (49°K).

The temperature dependence of the magnetic susceptibility of phthalocyanineoxymanganese(IV),[8] illustrated in Fig. 5, is noteworthy. There is a discontinuity in the curve at about 175°K, which is probably due to a phase change in the crystal structure. The moderately high Curie–Weiss constant seems almost certainly to have arisen from an antiferromagnetic interaction. The polymeric oxygen-bridged nature of the complex[8] would certainly be expected to give rise to such an interaction.[33]

Phthalocyaninemanganese(III) *derivatives.* The magnetic moments of the manganese(III) derivatives discussed by Engelsma, Yamamoto, Markham, and Calvin[3] are close to that expected for four unpaired electrons. There should be no orbital contribution.

Phthalocyanine-dipyridine- and -diquinoline-iron(II).—These complexes were investigated by Klemm *et al.*[2] and found to be diamagnetic as expected for spin-paired octahedral (or tetragonal) ferrous derivatives.

Phthalocyaninechloroiron(III).—This complex can be prepared[24] by the aerial oxidation of a suspension of phthalocyanineiron(II) in concentrated hydrochloric acid at 90°. It is the only ferric phthalocyanine known. Attempts to prepare[34] other ferric phthalocyanines by starting with ferric salts gave only phthalocyanineiron(II). Sidorov and Terenin[35] have shown that phthalocyanineiron(II) absorbs hydrogen chloride vapour reversibly which suggests that this complex should be formulated as a hydrochloride of phthalocyanineiron(II). However the magnetism of this complex is quite different from that of phthalocyanineiron(II) and hence is unlikely to be the hydrochloride. Moreover, unlike phthalocyanineiron(II), this complex exhibited electron spin resonance signals.[16] The oxidation state of three for the iron atom has been proved by quantitative oxidation.[36] A ferric phthalocyanine should have a spin of 3/2 and hence a moment near 3·87 B.M. A moment considerably below this was observed, with a fairly large Curie–Weiss temperature (Table 1).

Since the conversion to phthalocyaninechloroiron(II) proceeds so readily in the solid state, it is possible that there is little change in the crystal structure upon oxidation, *i.e.*,

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[30] Hume, *J. Amer. Chem. Soc.*, 1941, **63**, 1202.
[31] Burstall and Nyholm, *J.*, 1952, 3570.
[32] Kotani, *J. Phys. Soc. Japan*, 1949, **4**, 293.
[33] Lewis and Wilkins, " Modern Co-ordination Chemistry," Interscience, New York, 1960, p. 400.
[34] Elvidge and Lever, unpublished work.
[35] Sidorov and Terenin, *Optics and Spectroscopy*, 1961, **11**, 175.
[36] Elvidge, *J.*, 1961, 869.

the iron phthalocyanine units remain stacked together and the chloride ions find holes in the lattice to reside in. We may therefore expect iron–iron interactions to occur. As discussed in connection with phthalocyaninechromium(II), this would give low moments and a marked temperature dependence as is observed. However, in contrast to chromous phthalocyanines the experimental results cannot be fitted to the theory[14] if we assume that there is metal–metal interaction extending throughout the crystal. The metal–metal interaction may therefore be localised over a small number of metal atoms, perhaps only two.

Earnshaw and Lewis[37] have derived an equation relating the temperature dependence of the magnetic susceptibility with the exchange integral J, for binuclear complexes of $S = 3/2$. The equation given here is rearranged in terms of the magnetic moment, after

TABLE 2

Phthalocyaninechromium(II)
(290 × 10^{-6} c.g.s.)

T (°K)	$10^6\chi'_m$	μ_e (B.M.)
294	5126	3·49
268	5376	3·40
228	5709	3·25
190	6126	3·08
155	6668	2·89
124	7168	2·68
111	7544	2·60

Phthalocyaninedipyridinechromium(II)
(374 × 10^{-6} c.g.s.)

294	4197	3·16
270	4482	3·13
246	4767	3·08
223	5173	3·05
185	6109	3·02
124	8346	2·89
112	9363	2·90

Phthalocyaninehydroxychromium(III)
(298 × 10^{-6} c.g.s.)

294	6855	4·03
272	7396	4·03
248	8064	4·01
219	9083	4·01
189	10,324	3·94
139	13,603	3·90
117	15,640	3·84

Phthalocyanineaquohydroxychromium(III)
(308 × 10^{-6} c.g.s.)

290	5768	3·69
252·5	6608	3·68
194	8698	3·69
151	11,008	3·66

Disodium phthalocyanineoxyhydroxychromate(III)
(320 × 10^{-6} c.g.s.)

T(°K)	$10^6\chi'_m$	μ_e (B.M.)
292	6520	3·92
263	6956	3·84
234	7492	3·76
200	8196	3·63
159	9302	3·46
130	10,139	3·26
110	11,011	3·13

Dipyridiniumphthalocyanine oxyhydroxychromate(III)
(392 × 10^{-6} c.g.s.)

294	6958	4·06
272	7412	4·04
248	8032	4·01
218	9229	4·03
196	10,096	4·00
165	11,748	3·96
138	13,937	3·94
119	15,506	3·86

Phthalocyaninemanganese(II)
(290 × 10^{-6} c.g.s.)

295	7943	4·34
272	8681	4·36
238	9807	4·34
216	10,956	4·37
186	12,965	4·41
160	15,004	4·40
134	17,929	4·40
107	23,159	4·47

Phthalocyaninecyanohydroxymanganese(IV)
(310 × 10^{-6} c.g.s.)

294	6337	3·88
272	6996	3·91
241	7875	3·92
218	8943	3·96
163	11,611	3·90
147	12,620	3·87
122	15,033	3·84
108	17,230	3·88

Disodium phthalocyaninedioxymanganate(IV)
(317 × 10^{-6} c.g.s.)

T (°K)	$10^6\chi'_m$	μ_e (B.M.)
290	6857	4·00
272	7249	3·99
248	7752	3·94
213	8814	3·90
193	9596	3·86
169	10,603	3·80
137	12,280	3·68

Phthalocyanineoxymanganese(IV)
(295 × 10^{-6} c.g.s.)

294	5927	3·75
270	6340	3·72
247	6871	3·70
224	7461	3·67
188	9112	3·72
163	10,292	3·68
137	11,707	3·59
121	12,740	3·53
115	13,536	3·54

Phthalocyanineiron(II)
(290 × 10^{-6} c.g.s.)

337	5395	3·83
303	6008	3·83
292	6300	3·85
273	6737	3·85
257	7227	3·87
249	7496	3·88
231	8021	3·86
206	9013	3·87
182	10,034	3·84
158	11,580	3·84
135	13,622	3·85
117	15,460	3·82
113	15,780	3·79

Phthalocyaninechloroiron(III)
(314 × 10^{-6} c.g.s.)

294	4647	3·32
272	4931	3·29
218	5996	3·25
194	6564	3·20
158	7843	3·16
138	8660	3·10
123	9477	3·07

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[37] Earnshaw and Lewis, *J.*, 1961, 396.

correcting the observed magnetic susceptibility for a temperature-independent contribution (assumed to be 50 × 10^{-6} c.g.s.)

$$\mu^2 = (2 \cdot 84)^2 \frac{g^2 N\beta^2}{3k}\left[\frac{42 + 15\exp(6x) + 3\exp(10x)}{7 + 5\exp(6x) + 3\exp(10x) + \exp(12x)}\right]$$

$$x = -J/kT;\ \frac{N\beta^2}{3k} = 0 \cdot 125$$

Hence $$\mu^2 = 1 \cdot 0075 g^2 \left[\frac{42 + 15\exp(6x) + 3\exp(10x)}{7 + 5\exp(6x) + 3\exp(10x) + \exp(12x)}\right]$$

The equation was solved graphically; the experimental results fitted the theory for $g = 1 \cdot 77$ and $J = -10 \cdot 4°$. This is illustrated in Fig. 3.

Although this does not prove that phthalocyaninechloroiron(III) is a dimer held together by metal–metal bonds as indicated in Fig. 4*b*, it does provide support for such a structure.

EXPERIMENTAL

The complexes were prepared by the methods of Linstead *et al.*[24,27] and of Elvidge and Lever.[6-8] All magnetic measurements were made with analytically pure samples using a Gouy balance similar in design to that described by Figgis and Nyholm.[39] The magnetic susceptibility (χ'_m) values (Table 2) include the diamagnetic correction which is quoted in parentheses after the compound.

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[38] Ray and Nath Sen, *J. Indian Chem. Soc.*, 1948, **25**, 473, in Table 1 on p. 1822.

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