Paramagnetic Anisotropy of Planar Cobalt(II) and Copper(II) Phthalocyanine, Bis(pentane-2,4-dionato)copper(II), and Bis(pentane-2,4-dithionato)cobalt(II)

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The principal crystalline and molecular susceptibilities, and their orientations, of cobalt(II) phthalocyanine, [Co(pc)], bis(pentane-2,4-dithionato)cobalt(II), [Co(pdt)$_2$], copper(II) phthalocyanine, [Cu(pc)], and bis-(pentane-2,4-dionato)copper(II), [Cu(pd)$_2$], are reported. The diamagnetic anisotropy of the two pc derivatives makes a significant contribution to the observed anisotropy, especially in the copper compound. The resulting paramagnetic anisotropy {and e.s.r. data in the case of [Co(pdt)$_2$]} is then used to confirm the $S = \frac{1}{2}$ ground state of each compound [... $d_{z^2}{}^1$ in both the cobalt(II) derivatives and $d_{xy}{}^1$ in both the copper(II) derivatives]. The marked in-plane anisotropy in [Co(pdt)$_2$], compared with the in-plane isotropy of [Co(pc)], is shown to arise from both the abnormally large splitting of the d_{xz}, d_{yz} pair of orbitals and the mixing of the d_{xy} and d_{z^2} orbitals in low symmetry. An unambiguous assignment of two of the excited states in [Cu(pc)] can be made but ambiguities remain in [Cu(pd)$_2$].

THE study of planar transition-metal compounds has generated much interest in their electronic structures,[1-4] mainly because an *a priori* determination of the ground state is often not possible. This is in contrast to complexes with octahedral or tetrahedral geometries where the total spin multiplicity uniquely determines the ground state. Apart from their intrinsic interest, investigations of transition-metal-ion materials of lower than cubic symmetry, particularly those with a square-planar configuration, are of increasing importance because of the relation between these types of molecules and those of biological interest.[5]

Apart from the measurement of the average magnetic moment, the only widely used techniques for investigating the electronic properties of planar complexes have been optical-absorption and electron spin resonance (e.s.r.) spectroscopy. Although much useful information is often obtained from these techniques, they suffer from several limitations, for example assignment problems involving the *d–d* and charge-transfer transitions in the former and relaxation phenomena in the latter.

Recently we have been interested in applying the paramagnetic-anisotropy technique to problems of electronic structure and in particular to planar complexes containing first-row transition-metal ions. The method is very useful, a determination of the sign of the molecular magnetic anisotropy often being enough to characterize, or at least indicate, a particular ground state. Also, paramagnetic-anisotropy data are essential for describing quantitatively the isotropic shifts observed in the n.m.r. spectra of paramagnetic compounds.

In the planar series of compounds full reports have appeared describing our results for the phthalocyanines of Fe^{II} (ref. 6) and Mn^{II},[7,8] and also for the diamagnetic nickel(II), zinc(II), and metal-free phthalocyanines,[9] [M(pc)]. In this paper we elaborate on our preliminary reports concerning [Co(pc)],[10] bis(pentane-2,4-dithionato)cobalt(II) [Co(pdt)$_2$],[11] [Cu(pc)],[12] and also bis-(pentane-2,4-dionato)copper(II), [Cu(pd)$_2$]. Single-crystal *X*-ray structural data on all these compounds are available. Both [Co(pc)] and [Cu(pc)] are almost perfectly planar and have nearly perfect D_{4h} symmetry[13] (Figure 1). In [Co(pdt)$_2$] the metal environ-

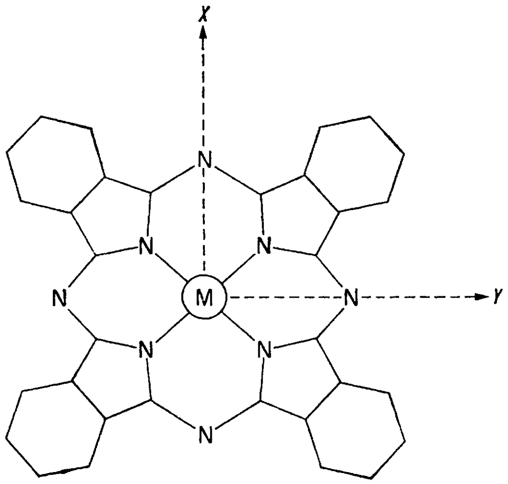

FIGURE 1 Molecular geometry of the planar bivalent metal phthalocyanines. The unlabelled atoms are carbon atoms; hydrogen atoms are not shown (M = Co or Cu)

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[1] H. B. Gray, 'Transition Metal Chemistry,' ed. R. L. Carlin, Marcel Dekker, New York, 1966, ch. 4.

[2] T. S. Piper and R. L. Belford, *Mol. Phys.*, 1962, **5**, 169 and refs. therein.

[3] A. H. Maki, N. Edelstein, A. Davisson, and R. H. Holm, *J. Amer. Chem. Soc.*, 1964, **86**, 4580.

[4] J. S. Griffith, *Discuss. Faraday Soc.*, 1958, **26**, 81.

[5] Many examples are scattered through the excellent chapters of 'Inorganic Biochemistry,' vols. 1 and 2, ed. G. L. Eichhorn, Elsevier, Amsterdam, 1973.

[6] C. G. Barraclough, R. L. Martin, S. Mitra, and R. C. Sherwood, *J. Chem. Phys.*, 1970, **53**, 1643.

[7] C. G. Barraclough, R. L. Martin, S. Mitra, and R. C. Sherwood, *J. Chem. Phys.*, 1970, **53**, 1638.

[8] C. G. Barraclough, A. K. Gregson, and S. Mitra, *J. Chem. Phys.*, 1974, **60**, 962.

[9] C. G. Barraclough, R. L. Martin, and S. Mitra, *J. Chem. Phys.*, 1971, **55**, 1426.

[10] R. L. Martin and S. Mitra, *Chem. Phys. Letters*, 1969, **3**, 183.

[11] A. K. Gregson, R. L. Martin, and S. Mitra, *Chem. Phys. Letters*, 1970, **5**, 310.

[12] R. L. Martin and S. Mitra, *Inorg. Chem.*, 1970, **9**, 182.

[13] J. M. Robertson, *J. Chem. Soc.*, 1935, 615.

ment is conveniently described as square planar (Figure 2) although the molecule as a whole is not planar, being

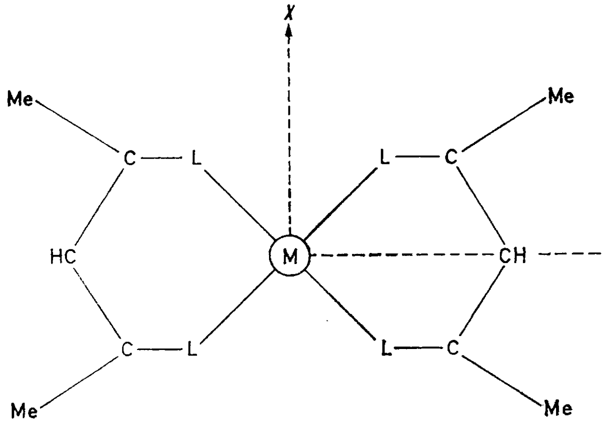

FIGURE 2 Molecular geometry of [Co(pdt)$_2$] (L = S, M = Co) and [Cu(pd)$_2$] (L = O, M = Cu)

folded so that the dihedral angle between the MS$_4$ and the ligand planes is *ca.* 6°.[14] The compound [Cu(pd)$_2$] is not strictly square planar and the true symmetry is lower than D_{4h} (Figure 2).[15] However, e.s.r.[16] and other evidence (below) suggest that the symmetry of the ligand field acting on Cu^{II} in [Cu(pd)$_2$] has nearly axial symmetry.

EXPERIMENTAL

The phthalocyanine crystals were grown by the vacuum-sublimation method and were obtained as thin elongated plates with a well developed (001) plane. Single crystals of [Co(pdt)$_2$] were prepared by passing a very slow stream of H$_2$S through a very dilute ethanol–hydrochloric acid solution of pentane-2,4-dione containing the Co^{2+}. Although [Co(pdt)$_2$] can be recrystallized from benzene, crystals cannot be grown by evaporation because the compound decomposes when left in solution for more than 1 h. However, by extending the reaction time to several days and using very dilute solutions, good quality crystals prepared *in situ* were quite satisfactory. They grow as small thin plates with a well developed *bc* plane, elongated along the *c* crystallographic axis. The compound [Cu(pd)$_2$] was prepared by the published method [17] and recrystallized from chloroform. The crystals grow as thin plates with a well developed (101) plane and elongated along the *b* crystallographic axis. In all cases, the crystallographic axes were identified by *X*-ray methods. The single crystals of β-[Co(pc)], β-[Cu(pc)], and [Cu(pd)$_2$] belong to the monoclinic crystal system while [Co(pdt)$_2$] crystals are orthorhombic.

The magnetic anisotropy was measured using the apparatus described earlier.[18] The notation for the monoclinic system is the same as used in previous papers [18,19] and that for the orthorhombic system is similar to that used by Mitra.[20] For the monoclinic phthalocyanine crystals measurements were made with the '*a*' and '*b*' axes vertical, the crystal anisotropies being given by equation (1),

$$\text{'}b\text{' axis vertical, } (\Delta\chi)_b = \chi_1 - \chi_2 \qquad (1)$$

χ_1 being greater than χ_2 by definition, and by equation (2).

$$\text{'}a\text{' axis vertical, } (\Delta\chi)_a = \pm[(\chi_1 - \chi_2)\sin^2\phi - (\chi_1 - \chi_3)] \qquad (2)$$

Here ϕ is the angle between the '*a*' and χ_2 axes and the sign of equation (2) is decided by noting the position of the crystal with respect to the magnetic-field direction at the setting position. The crystal anisotropies ($\chi_1 - \chi_2$) and ($\chi_1 - \chi_3$) are then easily obtained.

In [Cu(pd)$_2$] the '*b*' axis is easily identified but the '*a*' and '*c*' axes are rather difficult to locate, as noted previously in single-crystal optical-absorption studies.[21] However, when the crystal was suspended in the magnetic field with the *b* axis vertical, the flat (101) face lay almost perpendicular to the magnetic-field direction at the setting position. This means that χ_1 lies almost perpendicular to the (101) face so that a measurement with the (101) face horizontal in the magnetic field gives a direct measure of the anisotropy in the other two principal components of the susceptibility tensor namely $\chi_3 - \chi_2$, χ_3 being observed to be greater than χ_2.

The crystalline anisotropies of orthorhombic [Co(pdt)$_2$] were measured with the *b* and *c* axes vertical, *i.e.* values of $\chi_a - \chi_c$ and $\chi_a - \chi_b$ were determined experimentally. A check was also made with the '*a*' axis vertical.

RESULTS AND DISCUSSION

(a) *Crystalline Anisotropies.*—Rather than present all the raw experimental data as has been customary in the past, we list in Table 1 the observed average values of the principal crystalline anisotropies at specified temperatures.

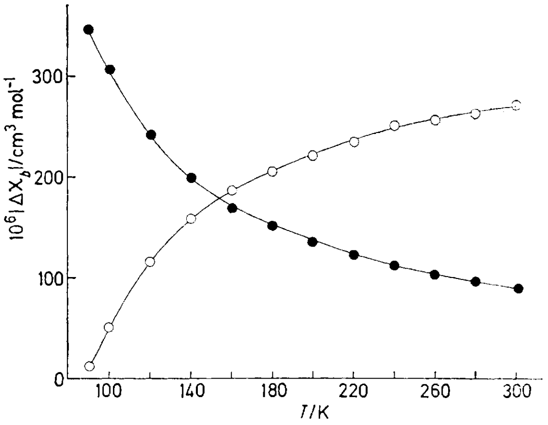

FIGURE 3 Temperature dependence of the observed (○) and corrected (for diamagnetic anisotropy) anisotropies (●) of [Cu(pc)] with the *b* axis vertical

The temperature variation of the experimental magnetic anisotropy for [Cu(pc)] appears at first sight to be anomalous (Table 1, Figure 3) because the observed anisotropy decreased with decreasing temperature. However, when the observed crystalline anisotropies are

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[14] R. Beckett and B. F. Hoskins, *J.C.S. Dalton*, 1974, 622.

[15] L. F. Dahl, 1961, personal communication, referred to in ref. 36.

[16] A. H. Maki and R. B. McGarvey, *J. Chem. Phys.*, 1958, **29**, 35.

[17] M. M. Jones, *J. Amer. Chem. Soc.*, 1959, **81**, 3188.

[18] A. K. Gregson and S. Mitra, *J. Chem. Phys.*, 1968, **49**, 3696.

[19] A. K. Gregson, R. L. Martin, and S. Mitra, *Proc. Roy. Soc.*, 1971, **A156**, 597.

[20] S. Mitra, *J. Chem. Phys.*, 1968, **49**, 4724.

[21] J. Ferguson, *J. Chem. Phys.*, 1961, **34**, 1609.

TABLE 1

Principal crystalline anisotropies (10^{-6} cm^3 mol^{-1})

$\frac{T}{\mathrm{K}}$	[Co(pc)]				[Co(pdt)$_2$]		[Cu(pc)]				[Cu(pd)$_2$]	
	$(\chi_1-\chi_2)_{obs.}$	$(\chi_1-\chi_2)_{corr.}$	$(\chi_1-\chi_3)_{obs.}$	$(\chi_1-\chi_3)_{corr.}$	$(\chi_a-\chi_b)$	$(\chi_a-\chi_c)$	$(\chi_1-\chi_2)_{obs.}$	$(\chi_1-\chi_2)_{corr}$	$(\chi_1-\chi_3)_{obs.}$	$(\chi_1-\chi_3)_{corr.}$	$(\chi_1-\chi_2)$	$(\chi_3-\chi_2)$
300	1 550	1 243	1 150	847	2 204	2 168	269	88	263	24	141	160
280	1 570	1 263	1 153	850	2 258	2 243	262	95	262	25	153	169
260	1 590	1 283	1 157	854	2 397	2 373	255	102	260	27	168	179
240	1 663	1 356	1 200	897	2 630	2 512	245	112	258	29	185	192
220	1 772	1 465	1 274	971	2 900	2 680	234	123	257	30	206	208
200	1 912	1 605	1 368	1 065	3 214	2 912	221	136	251	35	230	227
180	2 090	1 783	1 492	1 189	3 539	3 155	205	152	247	40	261	251
160	2 349	2 042	1 683	1 380	3 945	3 522	187	170	243	44	300	281
140	2 672	2 365	1 925	1 622	4 429	4 058	159	198	235	52	351	320
120	3 030	2 723	2 131	1 878	5 105	4 710	116	241	224	63	423	372
100	3 500	3 193	2 502	2 199	6 150	5 669	51	306	207	80	524	443

corrected for the diamagnetic anisotropy of [Cu(pc)], normal Curie-type behaviour emerges (Figure 3). The metal phthalocyanines have an inner macroring of delocalized π electrons and four nearly isolated benzene rings, both of which produce a large diamagnetic anisotropy. The diamagnetic anisotropies (in 10^{-6} cm^3 mol^{-1}) of the isostructural [Zn(pc)] are [9] $\chi_1 - \chi_2 = 357$ and $\chi_1 - \chi_3 = 287$, and using equation (3) the

$$K_\perp - K_\parallel = (\chi_1 - \chi_2) + (\chi_1 - \chi_3) \qquad (3)$$

molecular diamagnetic anisotropy of [Cu(pc)] ($K_\perp - K_\parallel = 644$) is larger in magnitude and opposite in sign to the molecular paramagnetic anisotropy. Since the diamagnetic anisotropy is independent of temperature, the observed anisotropy (the sum of the diamagnetic and paramagnetic components) decreases as the temperature decreases. It may be recalled that no similar anomaly was observed for [Mn(pc)],[7] [Fe(pc)],[6] or [Co(pc)] [10] because the molecular paramagnetic anisotropies in these compounds are much larger than the diamagnetic anisotropy. Another more subtle reason why [Cu(pc)] is anomalous lies in the sign of the molecular paramagnetic anisotropy. It is only in the copper derivative that the paramagnetic anisotropy is opposite in sign to the diamagnetic anisotropy and this further complicates the apparent trends in the measured values. Even so, corrections were made for the diamagnetic anisotropies in each case using the method of Krishnan and Banerjee [22] and were found to be quite appreciable and important. Again, in the case of [Cu(pc)], care has to be exercised because the observed anisotropy is diamagnetic [$(\chi_1 - \chi_2)_{obs.}$ and $(\chi_1 - \chi_3)_{obs.}$ decrease with decreasing temperature] and from the definitions of the signs and magnitudes of χ_1, χ_2, and χ_3 it is in fact χ_2 which is parallel to the field at the setting position.

The crystals of [Co(pdt)$_2$] were extremely small so the anisotropy in the nearly isotropic *bc* plane could not be measured, although at the setting position $\chi_c > \chi_b$ which is consistent with the values $\chi_a - \chi_b = 2\,204 \times 10^{-6}$ and $\chi_a - \chi_c = 2\,167 \times 10^{-6}$ cm^3 mol^{-1}.

(b) *Molecular Susceptibilities*.—The molecular anisotropy of [Co(pc)] was calculated using equation (3). This assumes an axially symmetric susceptibility tensor which is justified from the e.s.r. data where only very slight rhombic character was noted in the plane of the phthalocyanine ring.[4] Similar comments apply to [Cu(pc)] and [Cu(pd)$_2$] where the molecular anisotropies were calculated using equation (4) and are tabulated in

$$K_\parallel - K_\perp = 2(\chi_1 - \chi_2) - (\chi_1 - \chi_3) \qquad (4)$$

Tables 2—4 together with average susceptibilities (corrected for the diamagnetic effects of the ligand atoms using Pascal's constants). Biswas and Sengupta [23] reported the molecular magnetic anisotropy of [Cu(pd)$_2$] between 300 and 90 K. Although their average mag-

TABLE 2

Principal molecular anisotropy and susceptibilities (in 10^{-6} cm^3 mol^{-1}) and magnetic moments (in B.M.) * of [Co(pc)]

T/K	$K_\perp - K_\parallel$	$\bar{K}$	$K_\parallel$	$K_\perp$	$\mu_\parallel$	$\mu_\perp$
300	2 090	2 775	1 382	3 472	1.82	2.89
280	2 113	2 940	1 531	3 644	1.85	2.85
260	2 137	3 120	1 695	3 832	1.88	2.82
240	2 253	3 315	1 796	4 049	1.85	2.78
220	2 436	3 540	1 916	4 352	1.83	2.76
200	2 670	3 780	2 000	4 670	1.79	2.73
180	2 972	4 100	2 119	5 091	1.75	2.71
160	3 422	4 550	2 269	5 691	1.71	2.70
140	3 987	5 175	2 517	6 504	1.71	2.70
120	4 601	6 100	3 033	7 634	1.73	2.71
100	5 393	7 330	3 835	9 128	1.75	2.71

* 1 B.M. ≈ 9.27×10^{-24} A m^2.

TABLE 3

Principal molecular anisotropy (in 10^{-6} cm^3 mol^{-1}) and magnetic moments (in B.M.) of [Cu(pc)]

T/K	$K_\parallel - K_\perp$	$\bar{K}$	$\mu_\parallel$	$\mu_\perp$
300	152	1 389	1.89	1.79
240	195	1 720	1.88	1.78
180	264	2 280	1.88	1.77
120	419	3 310	1.85	1.75
90	600	4 180	1.82	1.73

TABLE 4

Principal molecular anisotropy and susceptibilities (in 10^{-6} cm^3 mol^{-1}) of [Cu(pd)$_2$]

T/K	$K_\parallel - K_\perp$	$\bar{K}$	$K_\parallel$*	$K_\perp$*
300	306	1 460	1 664 (1 719)	1 358 (1 338)
260	345	1 690	1 913 (1 959)	1 568 (1 532)
220	409	1 980	2 253 (2 300)	1 844 (1 812)
180	502	2 380	2 715 (2 781)	2 213 (2 216)
140	667	3 055	3 500 (3 507)	2 833 (2 840)
100	958	4 095	4 737 (4 943)	3 776 (3 968)

* Calculated values are given in parentheses (see text).

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[22] K. S. Krishnan and S. Banerjee, *Phil. Trans. Roy. Soc.*, 1936, **A235**, 343.

[23] P. K. Biswas and P. Sengupta, *Phys. Stat. Solidi*, 1970, **40**, 339.

netic-susceptibility values agree quite well with those in Table 4, the molecular anisotropy is appreciably lower. The reason for this appears to lie in an erroneous identification of the external morphology of the crystal because it is well known[21,24] that when grown from chloroform [Cu(pd)$_2$] has a well developed (101), not (001), face.

As has been pointed out before,[20,25] detailed structural data are required to transform the crystalline-susceptibility tensor to the required molecular-susceptibility tensor in the orthorhombic crystal system for [Co(pdt)$_2$]. If the molecular axes are chosen {by analogy with bis(maleonitriledithiolato)cobalt(II),[3] [Co(mnt)$_2$]$^{2-}$; see discussion below} as in Figure 2, then the direction cosines of K_x, K_y, and K_z connecting the crystalline and molecular susceptibilities with respect to a, b, and c are for the first Co atom:

	a	*b*	*c*
K_x	1	0	0
K_y	0	−0.6282	−0.7780
K_z	0	0.7780	−0.6282

The set for the second inequivalent Co atom in the unit cell is related by the symmetry of the crystal (D_{2h}^{18}, no. 64). The standard equations[25] then lead to (5)—(7)

$$\chi_a = K_x \qquad (5)$$

$$\chi_b = 0.3946K_y + 0.6053K_z \qquad (6)$$

$$\chi_c = 0.6053K_y + 0.3946K_z \qquad (7)$$

which when solved simultaneously using smoothed data at regular temperature intervals give the principal susceptibilities and moments shown in Table 5 and Figure 4. The irregular variation of μ_y and μ_z with temperature appears to be real as repeated determinations of both the average susceptibility and the crystalline anisotropies always led to the same result. The very small crystals of [Co(pdt)$_2$] may have led to an unknown systematic error in the anisotropy measurements or, in explanation, the structural parameters may not remain independent of temperature. Quite small changes in molecular orientation with temperature, a not uncommon occurrence, can produce significant changes in the calculated susceptibilities. The measured diamagnetic susceptibility of [Ni(pdt)$_2$] (-185×10^{-6} cm^3 mol^{-1}) was used for the diamagnetic correction for [Co(pdt)$_2$]. The overall uncertainty in the crystalline- and molecular-susceptibility data is estimated to be better than 5%.

TABLE 5

Principal molecular susceptibilities (in 10^{-6} cm^3 mol^{-1}) and moments (in B.M.) for [Co(pdt)$_2$]

T/K	K_x	K_y	K_z	μ_x	μ_y	μ_z
300	3 590	1 493	1 316	2.93	1.89	1.77
280	3 771	1 557	1 485	2.90	1.86	1.82
260	4 009	1 682	1 566	2.88	1.87	1.80
240	4 306	2 015	1 455	2.87	1.96	1.67
220	4 642	2 374	1 330	2.85	2.04	1.53
200	5 052	2 702	1 276	2.84	2.08	1.43
180	5 531	3 093	1 276	2.82	2.11	1.35
160	6 158	3 426	1 423	2.81	2.09	1.35
140	7 008	3 642	1 887	2.80	2.01	1.45
120	8 146	4 177	2 302	2.79	2.00	1.48
100	9 789	5 023	2 738	2.79	2.00	1.48

(c) (i) *Orientation of the Magnetic Axes in the Monoclinic System.*—The orientation of the magnetic axes in the crystal can be determined readily during the anisotropy measurement. For the two phthalocyanine derivatives ϕ (the angle between the χ_2 and a crystallographic axes) can be measured directly and quite easily since the (001) plane is well developed. It has to be remembered that these are the observed values of ϕ and in the case of [Co(pc)] this will also be the angle which the paramagnetic χ_2 makes with the a axis because (*i*) the measured anisotropy is paramagnetic and (*ii*) the sign of the paramagnetic and diamagnetic anisotropies is the same. This is not true in [Cu(pc)] where the observed angle of −17° is the angle which the diamagnetic χ_2 or the paramagnetic χ_1 makes with the a axis. (Because of the sign convention, the larger diamagnetic susceptibility is χ_2 whereas the larger paramagnetic susceptibility is χ_1, so that the measured $\chi_1 - \chi_2$ is always positive.) The angle ϕ for the paramagnetic-susceptibility tensor of the copper ion in [Cu(pc)] will be $90 - 17 = 73°$. In [Cu(pd)$_2$] the a and c crystallographic axes are not easily located but a stereographic diagram in the (010) plane indicates $\phi \simeq 47°$, although considerable temperature variation in the setting position was noted.

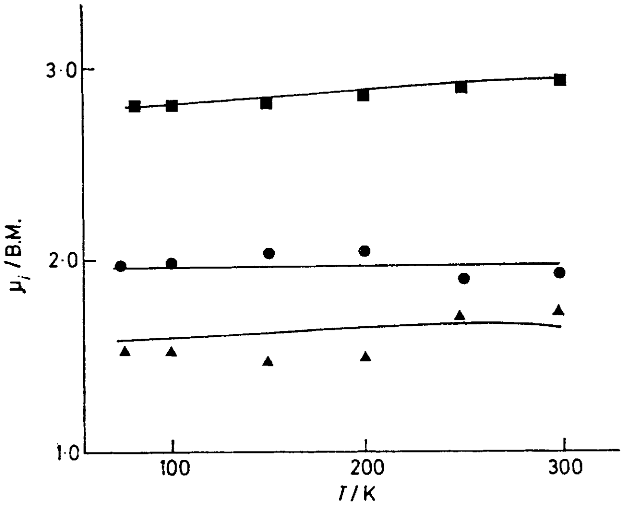

FIGURE 4 Temperature dependence of the principal magnetic moments of [Co(pdt)$_2$]: (■), (●), and (▲) represent the experimental data for μ_x, μ_y, and μ_z, and the solid lines were calculated with parameters described in the text

With the assumption of axial symmetry in the molecular-susceptibility tensor the angle ϕ can be calculated directly from X-ray structural data using the relations (8) and (9) where α_3 and γ_3 are the direction cosines of the $K_{\|}$ axis with respect to the orthogonal a and c^* axes respectively. It is not generally realised

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[24] C. Dijkgraaf, *Theor. Chim. Acta*, 1965, **3**, 38.

[25] A. K. Gregson, Ph.D. Thesis, University of Melbourne, 1971.

that there is a separate relation for each sign of the molecular anisotropy.[26] Using the structural data for

$$\tan\phi = -\frac{\alpha_3}{\gamma_3} \text{ for } K_{\parallel} > K_{\perp} \qquad (8)$$

$$\tan\phi = \frac{\gamma_3}{\alpha_3} \text{ for } K_{\perp} > K_{\parallel} \qquad (9)$$

[Co(pc)] (isomorphous with the metal-free and nickel(II) derivatives[13]) the calculated value of ϕ is $-18.3°$ whereas for [Cu(pc)] it is 71.1°, both being in good agreement with the anisotropy work. The $[Cu(pd)_2]$ data are less satisfactory because the calculated value of ϕ at 300 K (using Dahl's structural parameters[15]) is only 33°, although at lower temperatures this agrees with the measured value.

(ii) *Orientation of the Molecular Planes in the Monoclinic System.*—Again, with the assumption of axial symmetry in the susceptibility tensor, the orientation of the molecular planes can be calculated from the magnetic-anisotropy data using the relations (10) and (11) where

$$\cos 2\beta_3 = -\frac{(\chi_1 - \chi_3)}{(K_{\parallel} - K_{\perp})} \text{ for } K_{\parallel} > K_{\perp} \qquad (10)$$

$$\cos 2\beta_3 = \frac{(\chi_2 - \chi_3)}{(K_{\perp} - K_{\parallel})} \text{ for } K_{\perp} > K_{\parallel} \qquad (11)$$

β_3 is the angle between the symmetry axis of the molecule and the *b* crystallographic axis. For both the phthalocyanines $\beta_3 \simeq 50°$, which agrees with all the other measured phthalocyanines except [Fe(pc)] where the angle is *ca.* 42°. In $[Cu(pd)_2]$ the calculated value of β_3 is *ca.* 44°, in good agreement with experiment but again there is considerable temperature variation in this quantity which was also noticed by Biswas and Sengupta.[23] This is most unusual and at present we can offer no satisfactory explanation.

(d) *E.s.r. Measurements on* $[Co(pdt)_2]$.—E.s.r. measurements were made at 140 K on powdered samples of $[Co(pdt)_2]$ doped into the diamagnetic isomorphous $[Ni(pdt)_2]$.[14] Eight well resolved lines, equally spaced around a *g* value of 3.28, appeared on the low-field side of the spectrum. Under higher resolution a further seven lines, each with slight asymmetrical splitting, appeared at higher fields (Figure 5). The sets of eight and seven lines are assigned to the interaction of the unpaired electron with the Co($I = \frac{7}{2}$) nucleus. Remembering the experimental e.s.r. work on $[Co(mnt)_2]^{2-}$ and the location of the molecular axes and the assignment of the magnetic moments above, the *g* and $|A|$ values are summarised in Table 6(*a*) and are compared with the results of previous e.s.r. studies on α-[Co(pc)],[27] $[Co(mnt)_2]^{2-}$,[3] and *trans*-bis(diethylphenylphosphine)-mesitylcobalt(II),[28] $[Co(C_6H_3Me_3\text{-}2,4,6)(PEt_2Ph)_2]$. A similar comparison of the magnetic moments is made in Table 6(*b*). The striking similarity between the magnetic properties of $[Co(pdt)_2]$ and $[Co(mnt)_2]^{2-}$ emerges from Table 6 with the large in-plane anisotropy of $[Co(pdt)_2]$ being in sharp contrast to the in-plane isotropy of [Co(pc)].

(e) *Quantitative Analysis.*—(i) [Co(pc)] *and* $[Co(pdt)_2]$.—The ground state of planar cobalt(II) compounds with approximately D_4 symmetry has been studied theoretically by Griffith[4] and, more recently, by Murray and Sheahan.[29] The procedure adopted by Griffith in interpreting the e.s.r. data of [Co(pc)] was to consider all the possible ground states and determine the one which agreed best with the experimental data. A similar procedure is followed below.

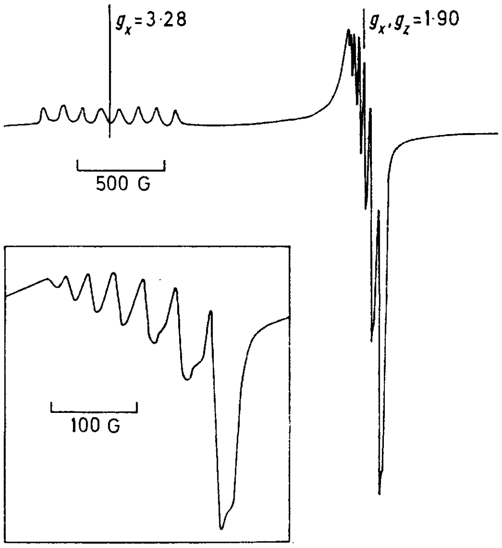

FIGURE 5 E.s.r. spectrum of $[Co(pdt)_2]$ diluted in $[Ni(pdt)_2]$ at 140 K. The inset shows the expanded region at *ca.* 1.90

Average susceptibility measurements establish that both [Co(pc)] and $[Co(pdt)_2]$ are low spin corresponding to one hole in the diamagnetic d^8 electronic configuration. The hole is assumed to lie in one of the d_{xz}, d_{yz}, d_{xy}, or d_{z^2} orbitals and we must decide which one. Taking [Co(pc)] first, Griffith has shown that if the hole lies in d_{xz} or d_{yz} then $K_{\parallel} > K_{\perp}$. Alternatively, if the hole lies in d_{xy} it can be shown easily that (*i*) both $K_{\parallel}$ and $K_{\perp}$ will have considerable temperature-independent high-frequency contributions so that $\mu_{\parallel}$ and $\mu_{\perp}$ will vary considerably with temperature, and (*ii*) $\mu_{\parallel}$ will be much larger than the experimental value for any reasonable values of the energy separations of the ground and excited states. If the hole lies in the d_{z^2} orbital then an extension of Griffith's treatment gives, to first order, equations (12) and (13) where ζ is the one-electron

$$K_{\parallel} = N\beta^2/kT \qquad (12)$$

$$K_{\perp} = \frac{N\beta^2}{4kT}\left\{2 + \frac{6\zeta}{\Delta E}\right\}^2 + \frac{3N\beta^2}{\Delta E - (\zeta/2)} + \frac{3N\beta^2}{\Delta E + (\zeta/2)} \qquad (13)$$

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[26] A. K. Gregson, unpublished work.

[27] J. M. Assour and W. K. Kahn, *J. Amer. Chem. Soc.*, 1965, **87**, 207.

[28] R. B. Bentley, F. E. Mabbs, W. R. Smail, M. Gerloch, and J. Lewis, *Chem. Comm.*, 1969, 119; *J. Chem. Soc.* (*A*), 1970, 3003.

[29] K. S. Murray and R. M. Sheahan, *J.C.S. Chem. Comm.*, 1975, 475.

spin–orbit coupling parameter and ΔE is the energy separation between d_{z^2} and the excited d_{xz}, d_{yz} state. Inspection of equations (12) and (13) shows clearly (*i*) $K_\perp > K_\parallel$ and (*ii*) while $\mu_\parallel$ is expected to remain independent of temperature $\mu_\perp$ should decrease with decreasing temperature. This is exactly what is observed experimentally. The curves in Figure 6 have been drawn assuming $\Delta E = 2\,400$ cm^{-1} and $\zeta = 400$ cm^{-1}. The agreement is very satisfactory and the ground state agrees with Griffith's interpretation of the e.s.r. data.

TABLE 6

Data for [Co(pdt)$_2$] and other planar cobalt(II) compounds

(*a*) E.s.r.

	[Co(pdt)$_2$] (present work)	α-[Co(pc)] (ref. 27)	β-[Co(pc)] (ref. 27)	[Co(mnt)$_2$]$^{2-}$ (ref. 3)	[Co(C$_6$H$_3$Me$_3$-2,4,6)(PEt$_2$Ph)$_2$] (ref. 28)	[Co(salen)] (ref. 32) *
g_x	3.28	2.42	2.92	2.789	3.72	3.18
g_y	1.904	2.42	2.89	2.025	1.96	2.05
g_z	1.899	2.01	1.91	1.977	1.74	1.92
10^4A_x/cm^{-1}	105	66	270	50	390	129
10^4A_y/cm^{-1}	*ca.* 35	66	260	28	50	90
10^4A_z/cm^{-1}	*ca.* 35	116	160	23	40	?

(*b*) Single-crystal magnetic-moment data (B.M.)

	[Co(pdt)$_2$] (present work)		[Co(pc)] (present work)		[Co(C$_6$H$_3$Me$_3$-2,4,6)(PEt$_2$Ph)$_2$] (ref. 28)	
	300	100 K	300	100 K	300	100 K
μ_x	2.93	2.79	2.89	2.71	3.55	3.43
μ_y	1.89	2.00	2.89	2.71	1.84	1.46
μ_z	1.77	1.48	1.82	1.75	1.62	1.36

* salen = *NN'*-Ethylenebis(salicylaldiminato).

A more rigorous analysis of the experimental data using the matrices of Murray and Sheahan,[29] which include most of the states belonging to the d^7 electronic configuration, gives nearly identical results. The ground state is deduced to be $^2A_1$ (*i.e.* the hole in d_{z^2}) and components of the first excited $^2T_{2g}$ state (in O_h symmetry and corresponding to the excited d_{xz}, d_{yz} state) are between 2 250 and 2 500 cm^{-1} away (ζ 500 cm^{-1}) depending on the particular fit, in excellent agreement with the above perturbation treatment. One further point of interest is the position of the first excited spin-quartet state, it being predicted to lie only *ca.* 1 000 cm^{-1} above the ground state.

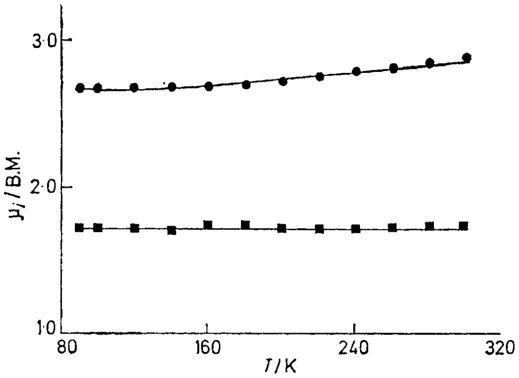

FIGURE 6 Temperature dependence of the principal magnetic moments of [Co(pc)]: (●) and (■) represent the experimental data for $\mu_\perp$ and $\mu_\parallel$, and the solid curves are theoretical plots of equations (12) and (13) using $\Delta E = 2$ 400 cm^{-1} and $\zeta = 400$ cm^{-1}

The interpretation of the magnetic properties of [Co(pdt)$_2$] is more difficult but nonetheless probably more interesting. We begin with the e.s.r. data and use the expressions for the g and A values deduced by Maki *et al.*[3] Abbreviating the orbital basis set as ε, μ, y, x, 0 (representing d_{xy}, $d_{x^2-y^2}$, d_{yz}, d_{xz}, and d_{z^2} respectively, axes defined as in Figure 2) and working in the complementary d^3 scheme (holes rather than electrons) we assume, as in [Co(pc)] above, that the strongly antibonding ε is doubly occupied and then consider the four possible ground-state configurations based on $|\varepsilon^2\rangle$.

Both the $|\varepsilon^2x\rangle$ and $|\varepsilon^2\mu\rangle$ configurations can be easily eliminated. Using the expressions for the g and A values,[3] no acceptable fit is possible. No combination of parameters is able to predict correctly the g values for $|\varepsilon^2x\rangle$, while in the $|\varepsilon^2\mu\rangle$ case both combinations of sign in A_x and A_z predict A_z to be over 100% too large or a P value ($P = g_e\beta_e g_n\beta_n\langle r^{-3}\rangle_d$ where $\langle r^{-3}\rangle_d$ is the mean inverse cube of the unpaired electron nuclear distance) an order of magnitude smaller than the free-ion value.

With the $|\varepsilon^2y\rangle$ configuration, terms in C_i^2 (coefficients in the expressions for g and A) must be retained for g_y and g_z to be less than 2.0023. With A_y and A_z differing in sign it is possible to obtain $P = 0.0195$ and K (Fermi-contact interaction term) = 0.125, only if the first coefficient $C_1 = 0.105$. This compares favourably with the free-ion values of P and K, 0.022 and 0.3 respectively.[30] However, this value of C_1 leads to unacceptable (*i.e.* positive) values for either C_2, C_3, or C_4 in predicting g_y and g_z to be less than 2.0023.

On the other hand, the $|\varepsilon^20\rangle$ configuration appears to account quite well for the spin-Hamiltonian parameters. The two C_i coefficients calculated from g_x and g_y predict g_z to be 1.864, in good agreement with the experimental value of 1.889. Again, with A_x and A_y differing in sign, it is possible to calculate P and K to be 0.0167 and 0.137 respectively, suitably reduced from the free-ion

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[30] A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc.*, 1951, **A206**, 173.

values quoted above. These values of P and K predict A_z to be 49×10^{-4} cm^{-1}, in quite good agreement with 35×10^{-4} cm^{-1}, the experimental value.

The magnetic moments, based on the $|\varepsilon^2 0\rangle$ ground state, can now be calculated using the energy-level scheme outlined in Figure 7. With this ground state, only the configurations $|\varepsilon^2 y\rangle$ and $|\varepsilon^2 x\rangle$ mix *via* spin–orbit coupling, the various matrices required for the calculation of the magnetic properties being listed in ref. 25. The crystal-field matrix elements are diagonal and can be parameterized as Δ_{xz} and Δ_{yz} corresponding to the $d_{xz} \rightarrow d_{z^2}$ and $d_{yz} \rightarrow d_{z^2}$ one-electron transition energies. McGarvey [31] pointed out that in D_{2h} or lower symmetry $|\mu\rangle$ and $|0\rangle$ can mix so $|0\rangle$, modified by $|0\rangle = a|0\rangle + b|\mu\rangle$ where $a^2 + b^2 = 1$, has been used. Possible matrix elements between the $|\varepsilon^2 0\rangle$ ground state and the excited state $|\varepsilon^2 \mu\rangle$ are in b^2 and so are neglected. Analysis of the magnetic moments using the program VVLECK [25] leads to $\zeta/\Delta_{yz} = 0.21$ and $\zeta/\Delta_{xz} = 0.04$, and assuming $\zeta = 400$ cm^{-1} (reduced by 25% from its free-ion value) $\Delta_{yz} = 1\,900$ cm^{-1} and $\Delta_{xz} = 10\,000$ cm^{-1} with $b = 0.0$. A slightly better fit is obtained if b is allowed to increase to 0.10, Δ_{yz} and Δ_{xz} now being 2 200 and 10 000 cm^{-1}, respectively. These two energies may be associated with the two low-lying absorption bands in the electronic spectrum of the compound. The calculated g values (from the eigenvectors of the magnetic matrices) are also nearly identical to those calculated using the formulae given by Maki *et al.*[3] and, of course, with the experimental values.

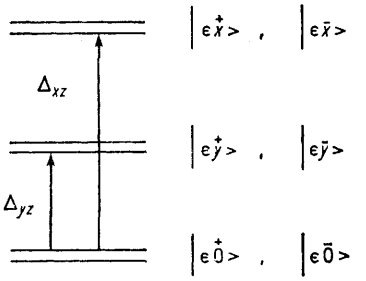

FIGURE 7 Proposed simplified energy-level scheme for [Co(pdt)$_2$]

The more complete analysis of the magnetic data using the matrices of Murray and Sheahan [29] is not very informative, mainly because of the experimental scatter in μ_y and μ_z. However, two points are to be noted. First, there appear to be several states lying in the same region as predicted above, namely at *ca.* 2 000 and 10 000 cm^{-1}, and secondly there is again a component of an excited spin-quartet state at *ca.* 1 000 cm^{-1} above the ground state, thus emphasizing the possible importance of low-lying spin-quartet states above the ground doublet state of planar cobalt(II) compounds.

These magnetic and predicted optical properties are very similar to those reported by Busetto *et al.*[32] for several quadridentate Schiff-base complexes of Co^{II}. The ordering of the one-electron energy levels and the interpretation of the various parameters [Table 6(a)] is very similar to the procedures and results outlined above and lends support to our basic contention of a ground state with the electron hole in the d_{z^2} orbital and quite a marked rhombic character in the plane of the molecule.

Other things being equal, the mixing of $d_{x^2-y^2}$ into the ground state introduces anisotropy into the plane of the molecule which in the present example is obviously very important. With no mixing the total anisotropy must arise from the splitting (abnormally large here) of the normally degenerate d_{xz}, d_{yz} pairs of orbitals. It seems likely that small admixtures of $d_{x^2-y^2}$ into the ground-state configuration $|\varepsilon^2 0\rangle$ are present, but still the ligand field must depend on the electron density about the metal ion rather than on the geometrical disposition of the ligand atom. Admixtures of this kind have little effect on the alternative ground-state configurations where the total anisotropy must arise entirely from the energy difference between d_{xz} and d_{yz}, thus offering further evidence for a d_{z^2} ground state. Because increasing Δ_{yz} and decreasing Δ_{xz} (chemically desirable, Figure 7) and the introduction of mixing have the opposite effect, it is difficult to obtain a unique fitting to the moments and g values although the set shown in Figure 4 is quite satisfactory. It must be emphasized that the parameter values (Δ_{yz}, Δ_{xz}, a, and b) obtained above are probably not unique and their interpretation, especially within the framework of the very simple energy-level diagram of Figure 7, can be at best only a guide to the real situation.

Calculated magnetic moments based on the $|\varepsilon^2 y\rangle$ ground state found by Maki *et al.*[3] for [Co(mnt)$_2$]$^{2-}$ can be made to agree with the experimental magnetic moments of [Co(pdt)$_2$] but the deduced coefficients C_i do not predict the correct g values; the more direct e.s.r. evidence also does not favour this ground-state configuration. It is concluded therefore that the available experimental data can be better rationalized by using the configuration . . . [d_{z^2}].[1]

Apart from [Co(pc)] above, other low-spin d^7 complexes have been shown to have similar ground-state electronic configurations. The g values and nitrogen hyperfine interaction of [Fe(CN)$_5$(NO)]$^{3-}$ have been interpreted along these lines.[33] Single-crystal magnetic measurements on [Co(C$_6$H$_3$Me$_3$-2,4,6)(PEt$_2$Ph)$_2$] [28] and e.s.r. data of several cobalt(II) Schiff-base complexes [32] have also shown that the unpaired electron is in the d_{z^2} orbital. This is entirely consistent with Griffith's suggestion [4] that the d_{z^2} orbital should lie between the d_{xy} and d_{xz}, d_{yz} orbitals if there is no out-of-plane interaction or otherwise lie above. Extensive out-of-plane bonding from ligand to metal (π_V[L]$\rightarrow p_z$[M]) and from metal to ligand (d_π[M]$\rightarrow d_\pi$[L]) ensures that d_{z^2} is quite high in energy. The large in-plane anisotropy observed in [Co(pdt)$_2$] and in some of the other planar cobalt(II)

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[31] R. B. McGarvey, ref. 1, vol. 3, p. 160.

[32] C. Busetto, F. Cariati, A. Fusi, M. Gullotti, F. Morazzoni, A. Pasini, R. Ugo, and V. Valenti, *J.C.S. Dalton*, 1973, 754.

[33] J. B. Raynor, *Nature*, 1964, **201**, 1216.

compounds then appears to arise from the proximity of the d_{z^2} and d_{yz} levels relative to the d_{xz} level. The in-plane isotropy of [Co(pc)] follows naturally from the near degeneracy of the d_{xz} and d_{yz} orbitals. This is well illustrated by the calculated single-electron excitation energies. In both [Co(pdt)$_2$] and [Co(pc)] $d_{z^2} \rightarrow d_{yz}$ is *ca.* 2 000 cm^{-1}, whereas $d_{z^2} \rightarrow d_{xz}$ is 10 000 cm^{-1} in [Co(pdt)$_2$] but still *ca.* 2 000 cm^{-1} in [Co(pc)]. A final remark concerning the series of cobalt(II) compounds studied by Bentley *et al.*[28] is in order. They found that, as the ligand field became stronger and less symmetrical, the anisotropy increased, due in part to a greater d_{xz}, d_{yz} splitting and also to increased mixing between d_{z^2} and $d_{x^2-y^2}$.

(ii) [Cu(pc)] *and* [Cu(pd)$_2$]. The ground state of Cu^{II} in [Cu(pc)] and [Cu(pd)$_2$] is $^2B_{2g}$ (hole in d_{xy}, axes as defined in Figure 2). The sign of the molecular magnetic anisotropy in both these compounds ($K_{\parallel} > K_{\perp}$) is inconsistent with a $^2A_{2g}$ ground state (hole in d_{z^2}). For the $^2B_{2g}$ ground state the magnetic susceptibilities are given by equations (14)—(16) where $\Delta E_{\parallel}$ and $\Delta E_{\perp}$ are

$$K_{\parallel} = \frac{N\beta^2 g_{\parallel}^2}{4kT} + \frac{8N\beta^2\kappa^2}{\Delta E_{\parallel}} \qquad (14)$$

$$K_{\perp} = \frac{N\beta^2 g_{\perp}^2}{4kT} + \frac{2N\beta^2\kappa^2}{\Delta E_{\perp}} \qquad (15)$$

$$g_{\parallel} = 2 + \frac{8\kappa\zeta}{\Delta E_{\parallel}};\; g_{\perp} = 2 + \frac{2\kappa\zeta}{\Delta E_{\perp}} \qquad (16)$$

the $^2B_{2g} \rightarrow {}^2B_{1g}$ and $^2B_{2g} \rightarrow {}^2E_g$ positive-hole transitions, respectively; ζ is the one-electron spin–orbit coupling parameter and κ is the orbital-reduction parameter, assumed isotropic in the present work. We now attempt to apply the magnetic-anisotropy technique to the question of the electronic structure of these two compounds. In the case of [Cu(pc)] and [Cu(pd)$_2$] the ground state is now well established from e.s.r. and other studies, although the relative ordering and positions of the excited states is still uncertain.

For [Cu(pc)] no information regarding the *d–d* transitions is available from the optical spectrum because of the intense low-energy charge-transfer bands. E.s.r. data are available and have been used to determine the position and relative ordering of the ^2E_g and $^2B_{1g}$ states, but with conflicting conclusions. For instance, Harrison and Assour[34] place the $^2B_{1g}$ level above ^2E_g whereas earlier calculations of Kivelson and Nieman[35] place ^2E_g above $^2B_{1g}$. In a preliminary communication[12] we have shown that a measurement of the molecular paramagnetic anisotropy and using equations (14)—(16) enables the correct position and relative ordering of these two excited states to be decided and our results agreed very well with the assignments of Harrison and Assour ($\Delta E_{\parallel} = 27\,000$ cm^{-1} and $\Delta E_{\perp} = 17\,000$ cm^{-1}). The value for $\Delta E_{\parallel}$ is unusually large and, although consistent with the e.s.r. data, possibly reflects limitations in the model (extensive π bonding, *etc.*) rather than a true indication of a *d–d* electronic transition. Unfortunately, the anisotropy measurements, like the e.s.r. data, provide no information on the position of the $^2A_{2g}$ state.

Although [Cu(pd)$_2$] has been subjected to several single-crystal optical spectral studies, no unambiguous assignments of the *d–d* transitions have been made. Ferguson[21] was first to measure the single-crystal polarized spectra of [Cu(pd)$_2$] but the interpretation was marred by errors in the original crystal-structure determination. Piper and Belford,[36] with the advantage of accurate crystallographic data, attempted to reinterpret Ferguson's crystal spectra but they noted that a unique assignment was not possible because of the unfavourable molecular stacking in the crystal. However, some tentative assignments were made. The band at 15 600 cm^{-1} was assigned to $d_{xy} \rightarrow d_{x^2-y^2}$ ($\Delta E_{\parallel}$) while bands at 14 500 and 18 000 cm^{-1} could both be assigned to $d_{xy} \rightarrow d_{xz}, d_{yz}$ ($\Delta E_{\perp}$). Dijkgraaf[24] remeasured the crystal spectra and also assigned the band at 15 600 cm^{-1} to $d_{xy} \rightarrow d_{x^2-y^2}$ ($\Delta E_{\parallel}$) but suggested that the band at 14 500 cm^{-1} originated from a Davydov-type splitting, although this has been subsequently discounted.[37] More recently, Hathaway *et al.*[38] tentatively assigned the spectrum of [Cu(3-Me-pd)$_2$] with $\Delta E_{\parallel} = 15\,500$ cm^{-1}, $\Delta E_{\perp} = 14\,000$—15 800 cm^{-1}, and the highest-energy band at 19 200 cm^{-1} to $d_{xy} \rightarrow d_{z^2}$.

It is rather difficult to decide uniquely from the magnetic-anisotropy data the position or even the relative ordering of the excited ^2E_g and $^2B_{1g}$ states in [Cu(pd)$_2$]. The various interpretations of the electronic spectrum outlined above agree in that the band at 15 600 cm^{-1} is due to the $^2B_{2g} \rightarrow {}^2B_{1g}$ transition ($\Delta E_{\parallel}$). The assignment of the $^2B_{2g} \rightarrow {}^2E_g$ transition ($\Delta E_{\perp}$) remains equivocal and both the observed bands at 14 500 and 18 000 cm^{-1} have been assigned to it. A consideration of equations (14)—(16) shows that small changes in $\Delta E_{\perp}$ (*i.e.* of the order of 4 000—5 000 cm^{-1}) will have little effect on $K_{\perp}$ and, in fact, the calculated differences are of the same order as the differences introduced by experimental errors in K_i and g_i. In [Cu(pc)] the molecular magnetic anisotropy was very sensitive to the ΔE values because the two alternative assignments involved large variations in both $\Delta E_{\parallel}$ and $\Delta E_{\perp}$ and so allowed a unique description of the excited states.[12] In [Cu(pd)$_2$] it does seem clear though that when the experimental *g* values ($g_{\parallel}$ 2.27 and $g_{\perp}$ 2.05)[16] are inserted into equations (14)—(16) the high-frequency perpendicular susceptibility has to be as small as possible, which indicates $\Delta E_{\perp} = 18\,000$ cm^{-1}. With this assignment and an isotropic orbital-reduction parameter of $\kappa^2 = 0.80$, the theoretical values of K_i (Table 4) are in satisfactory agreement with those determined experimentally. The alternative assignment ($\Delta E_{\perp}$ 14 500

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[34] S. E. Harrison and J. M. Assour, *J. Chem. Phys.*, 1964, **40**, 365.

[35] D. Kivelson and R. Nieman, *J. Chem. Phys.*, 1961, **35**, 149.

[36] T. S. Piper, and R. L. Belford, *Mol. Phys.*, 1962, **5**, 169; see also J. Ferguson, R. L. Belford, and T. S. Piper, *J. Chem. Phys.*, 1962, **37**, 1569.

[37] R. L. Belford and J. W. Carmichael, *J. Chem. Phys.*, 1967, **46**, 4515.

[38] B. J. Hathaway, D. E. Billing, and R. J. Dudley, *J. Chem. Soc. (A)*, 1970, 1420.

cm^{-1}) cannot be eliminated completely as changes in the orbital-reduction parameter can absorb differences between the two assignments, although angular-overlap calculations by Hitchman[39] suggest that the former assignment ($\Delta E_{\perp}$ 18 000 cm^{-1}) is the correct one.

We thank Dr. G. A. Heath for much help and advice in the preparation of [Co(pdt)$_2$], Mr. R. M. Sheahan for some calculations on the d^7 system, and Drs. P. E. Fielding and A. G. McKay for the phthalocyanine crystals.

[5/2331 *Received, 28th November, 1975*]

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[39] M. A. Hitchman, personal communication.