π-Bonding and Tetragonality in Dichloro- and Dibromo-tetrapyridinecobalt(II) and Diacetylacetonatodipyridinecobalt(II)†

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Average and principal magnetic susceptibilities of $[Co(py)_4Cl_2]$, $[Co(py)_4Br_2]$, and $[Co(acetylacetone)_2(py)_2]$ in the temperature range 80—300 K are reported. Interpretation within the low-symmetry angular overlap model, described recently, are characterized by fits describing an approximately linear relationship between the π-bonding parameters. The indeterminacy of absolute e_π parameter values is a consequence of the high symmetry in these molecules, actual or effective. The relative contributions of π-bonding between different ligands and with respect to different directions all appear compatible with otherwise established chemical criteria.

WE have recently reported[1] studies of the magnetic anisotropies of *trans*-$[M(py)_4(NCS)_2]$ ($M = Co^{II}$ or Ni^{II}) in which experimental data were fitted to an angular overlap based model in which no restriction to axial or higher symmetry is required. These complexes were considered at the outset of the work to be less than ideal in that the anisotropy associated with the thiocyanate groups introduced an extra parameter whose magnitude might not be checked easily against expectation. The general orientations of the magnetic ellipsoids in those molecules derived partly from this anisotropic π-bonding, removing as it does the molecular two-fold symmetry otherwise established by the pyridine ligands. It therefore seemed worthwhile to make similar studies on corresponding molecules not complicated by this feature. Of particular interest is the question of whether higher molecular symmetry helps or hinders the definition of angular overlap parameters. The present study concerns the magnetic properties of $[Co(py)_4Cl_2]$ and $[Co(py)_4Br_2]$. The role of molecular tetragonality emerges as an important feature in this work and our inclusion of a similar study of $[Co(acetylacetone)_2(py)_2]$ bears on the subject of approximations to such high molecular symmetry.

EXPERIMENTAL

The chlorine and bromine complexes were prepared by dissolving the cobalt halides in a mixture of acetone and an excess of pyridine to yield dark blue solutions. Water was removed from the solutions using 2,2-dimethoxypropane. When set aside the solutions yielded rose and rose-violet crystals of $[Co(py)_4Cl_2]$ and $[Co(py)_4Br_2]$, respectively. The complex $[Co(acetylacetone)_2(py)_2]$ was prepared similarly, but using stoicheiometric amounts of pyridine, since a mixture of adducts with the general formula $[Co_x(acetylacetone)_y(py)_z]$ are known[2] to form with an excess of pyridine. The solution yielded orange crystals of $[Co(acetylacetone)_2(py)_2]$. Satisfactory C, N, and H analyses were obtained for all three complexes.

The complex $[Co(py)_4Cl_2]$ crystallizes in the tetragonal crystal class.[3] Rose-coloured needles were obtained, elongated parallel to the unique c axis, as checked by X-ray oscillation photography. The crystal magnetic anisotropy $\Delta\chi = \chi_\perp - \chi_\parallel$ was measured in the temperature range 300—80 K by Krishnan's critical torque technique for crystals mounted perpendicular to the needle axis. Powder susceptibilities were measured by the Gouy method in the same temperature range. The results are listed in interpolated form in Table 1.

TABLE 1

Interpolated susceptibilities ($\times 10^{-6}$ c.g.s.u.) for $[Co(py)_4Cl_2]$

T/K	$\bar{\chi}$	$\chi_\perp - \chi_\parallel$	$\chi_\perp$	$\chi_\parallel$
290	10 810	2 360	11 600	9 240
280	11 170	2 500	12 000	9 500
270	11 530	2 660	12 420	9 760
260	11 900	2 850	12 850	10 000
250	12 310	3 050	13 320	10 290
240	12 790	3 250	13 870	10 620
230	13 270	3 490	14 430	10 940
220	13 810	3 730	15 050	11 320
210	14 420	3 970	15 740	11 770
200	15 080	4 240	16 490	12 250
190	15 730	4 550	17 250	12 700
180	16 580	4 900	18 210	13 310
170	17 240	5 290	19 000	13 710
160	18 200	5 700	20 100	14 400
150	18 780	6 160	20 830	14 670
140	20 300	6 800	22 570	15 770
130	21 440	7 550	23 960	16 410
120	22 890	8 500	25 720	17 220
110	24 570	9 600	27 770	18 170
100	26 550	10 400	30 020	19 620
90	28 950	12 500	33 120	20 620

The complex $[Co(py)_4Br_2]$ belongs to the orthorhombic crystal class.[4] Rose-violet hexagonal plates and blocks formed which on exposure to air deteriorated rapidly with loss of pyridine and the formation of a light blue powder. Gouy tubes were packed under a pyridine atmosphere and stoppered. For anisotropy work several coatings of shellac were found sufficient to prevent crystal decomposition. Difficulties associated with electrostatic adhesion of the crystals to the walls of the cryostat, however, necessitated the use both of fairly small crystals (*ca.* 1 mg) and low magnetic fields with a consequent reduction in accuracy. Anisotropies were measured with crystals mounted parallel to b and c axes only. The anisotropy in the bc plane was too small to measure under the conditions just mentioned: however, the small magnitude of $\Delta\chi_a$ is confirmed by the very close similarity in the magnitudes of $\Delta\chi_b$ and $\Delta\chi_c$. Results for powder susceptibilities and crystal anisotropies in the temperature range 300—80 K are collected in Table 2.

The complex $[Co(acetylacetone)_2(py)_2]$ crystallizes in both orthorhombic and monoclinic forms.[2,5] In the orthorhombic form, the *trans*-pyridine groups are staggered.

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† No reprints available.

[1] M. Gerloch, R. F. McMeeking, and A. M. White, *J.C.S. Dalton*, 1975, 2452.

[2] R. C. Elder, *Inorg. Chem.*, 1968, **7**, 1117.

[3] M. A. Porai-Koshits, *Trudy Inst., Krist. Akad. Nauk, S.S.S.R.*, 1955, 19.

[4] *Structure Reports*, 1958, **22**, 782.

[5] J. T. Haskagen and J. P. Fadcher, jun., *J. Amer. Chem. Soc.*, 1965, **87**, 2821.

The monoclinic form is isomorphous with [Ni(acetylacetone)$_2$(py)$_2$] in which the *trans*-pyridines are eclipsed. The isomorphism of the compound prepared here with the nickel compound was established by both *X*-ray powder photography and by oscillation and Weissenberg photography of single crystals. The habit adopted by the monoclinic cobalt crystal is shown in Figure 1.

TABLE 2

Interpolated susceptibilities (× 10^{-6} c.g.s.u.) for [Co(py)$_4$Br$_2$]

T/K	$\bar{\chi}$	$\chi_a-\chi_c$	$\chi_a-\chi_b$	χ_a	χ_b	χ_c
290	10 730	900	900	11 330	10 430	10 430
280	11 040	960	960	11 680	10 720	10 720
270	11 360	1 030	1 030	12 050	11 020	11 020
260	11 730	1 100	1 100	12 460	11 360	11 370
250	12 210	1 170	1 180	12 990	11 810	11 820
240	12 650	1 260	1 280	13 500	12 220	12 230
230	13 180	1 360	1 370	14 090	12 720	12 730
220	13 630	1 460	1 480	14 610	13 130	13 180
210	14 140	1 580	1 590	15 200	13 610	13 620
200	14 770	1 700	1 700	15 910	14 200	14 200
190	15 330	1 860	1 830	16 560	14 730	14 700
180	15 900	2 020	1 980	17 230	15 260	15 210
170	16 650	2 180	2 160	18 100	15 940	15 910
160	17 290	2 360	2 370	18 870	16 490	16 510
150	18 110	2 570	2 580	19 830	17 250	17 260
140	18 920	2 800	2 810	20 790	17 980	17 960
130	20 000	3 070	3 100	22 060	18 960	18 990
120	21 210	3 410	3 420	23 490	20 060	20 080
110	22 840	3 790	3 780	25 360	21 590	21 570
100	24 920	4 220	4 150	27 710	23 160	23 490
90	26 870	4 710	4 630	29 980	25 350	25 280

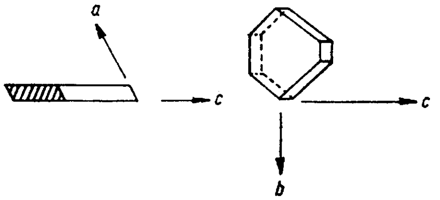

FIGURE 1 Crystal habit for the monoclinic modification of [Co(acetylacetone)$_2$(py)$_2$]

Crystal magnetic anisotropies from 300 to 80 K were determined in the *ac* plane using crystals with *b* mounted parallel to the torsion fibre using the Krishnan technique. The orientations of the principal crystal susceptibilities χ_1 and χ_2 in the *ac* plane were determined using the 'wheel' technique described earlier and the results in Figure 2 define ϕ as $-13°$. Subsequent crystal anisotropy measurements with χ_1 and χ_2 parallel to the torsion fibre were made from 300 to 80 K. Throughout this temperature range the cyclic sum of the three anisotropies $\Delta\chi_1$, $\Delta\chi_2$, and $\Delta\chi_3$ vanishes within experimental error, indicating little variation in ϕ with temperature. Powder susceptibilities were measured at similar temperatures by the Gouy method and interpolated results from all magnetic measurements are collected in Table 3.

Fitting Procedure for [Co(py)$_4$Cl$_2$].—As in the earlier paper,[1] susceptibilities are calculated using the general model described earlier [6] within a basis of the free-ion spin-quartet terms, $^4P + {}^4F$. We may anticipate some difficulty applying the model to the present system in that the molecules possess exact C_4 symmetry and are characterized by only two different principal susceptibilities, $\chi_\parallel$ and $\chi_\perp$. On the other hand, this decrease in experimental information is offset to some extent by the isotropic bonding nature of the *trans*-axial halide ligands: thus we take $e_{\pi x}$(Cl) = $e_{\pi y}$(Cl), leaving a parameter set B, ξ, e_σ(Cl), e_σ(py), e_π(Cl), e_π(py), k with definitions as set out previously.[1]

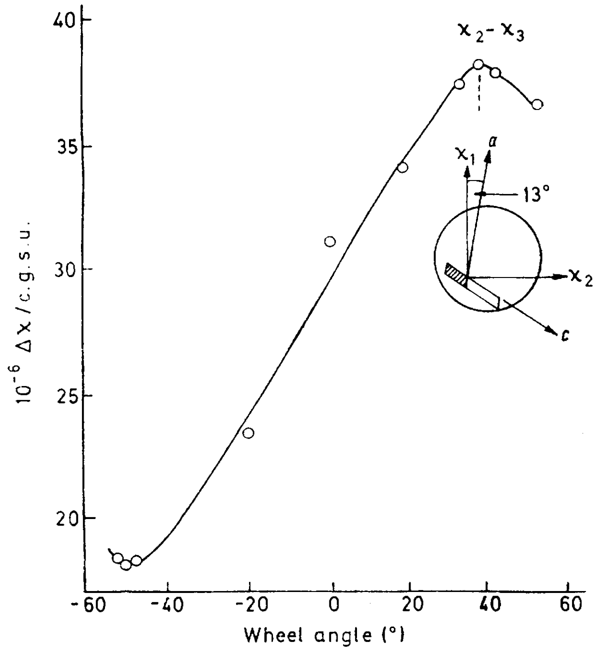

FIGURE 2 [Co(acetylacetone)$_2$(py)$_2$]: angular variation of magnetic anisotropy in crystal *ac* plane; inset shows axis orientation with magnetic field horizontal in plane of paper

TABLE 3

Interpolated susceptibilities (× 10^{-6} c.g.s.u.) for [Co(acetylacetone)$_2$(py)$_2$]

T/K	$\bar{\chi}$	$\chi_2-\chi_3$	$\chi_2-\chi_1$	$\chi_1-\chi_3$	χ_1	χ_2	χ_3
300	9 760	3 700	1 900	1 750	9 710	11 610	7 960
290	10 070	3 800	2 000	1 800	10 000	12 000	8 200
280	10 350	4 000	2 120	1 850	10 260	12 380	8 410
270	10 700	4 220	2 270	1 900	10 580	12 850	8 680
260	11 160	4 500	2 430	1 950	11 000	13 430	9 050
250	11 610	4 720	2 650	2 000	11 390	14 040	9 390
240	12 120	5 000	2 870	2 080	11 860	14 740	9 780
230	12 730	5 320	3 100	2 200	12 430	15 530	10 230
220	13 230	5 700	3 350	2 400	12 910	16 260	10 510
210	13 770	6 100	3 600	2 600	13 440	17 040	10 840
200	14 420	6 550	3 900	2 790	14 050	17 950	11 260
190	15 100	7 000	4 290	2 900	14 640	18 930	11 740
180	15 870	7 500	4 650	3 090	15 340	20 020	12 250
170	16 720	8 200	5 100	3 300	16 120	21 220	12 820
160	17 610	8 850	5 580	3 600	16 950	22 530	13 350
150	18 510	9 700	6 100	3 900	17 780	23 880	13 880
140	19 640	10 620	6 780	4 200	18 780	25 560	14 580
130	20 870	11 800	7 550	4 650	19 910	27 460	15 260
120	22 320	13 200	8 420	5 180	21 240	29 660	16 060
110	24 180	14 900	9 600	5 800	22 910	32 510	17 110
100	26 260	16 900	11 000	6 600	24 790	35 790	18 190
90	28 510	19 400	12 850	7 400	27 030	39 880	19 630
80	31 060	22 700	15 000	8 150	28 780	43 780	20 630

Fitting of the principal susceptibilities of [Co(py)$_4$Cl$_2$] begins in the same way chosen [1] for [Co(py)$_4$(NCS)$_2$] and its iron(II) analogue. The situation is, perhaps, a little less clear in that, unlike the thiocyanate molecule, the present system involves different donor atoms rendering the assumption of approximately isotropic σ-bonding less

[6] M. Gerloch and R. F. McMeeking, *J.C.S. Dalton*, 1975, 2443.

tenable. Further, π-bonding with the halogens in this molecule may be more significant than with thiocyanate. In all present multiparameter models simultaneous variation of all parameters is not practicable. We find in these tetragonal cobalt(II) systems a useful *modus operandi* in a preliminary consideration of the π-bonding rather than of the σ as in the previous paper.

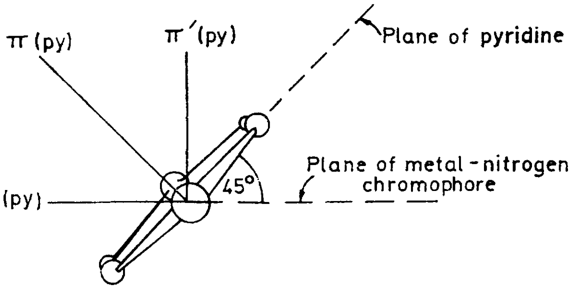

FIGURE 3 Resolution of pyridine π-bonding

As before, we consider pyridine to π-bond only in a plane perpendicular to the ring plane. It proves convenient, however, to resolve this bonding into two orthogonal directions, parallel and perpendicular to the Cl–Co–Cl axis, as shown in Figure 3. The components e_π'(py) of $e_{\pi x}$(py) are equal in the two directions because of the special orientation of the pyridine rings with respect to the plane containing the four nitrogens and the cobalt atom. So far as definition by ligand-field parameters is concerned, the molecular symmetry may be classified as D_{4h}. Note that $e_\pi'(\text{py}) = \frac{1}{2}e_{\pi x}(\text{py})$.

The splitting of the free-ion terms ^4P and ^4F by the tetragonal field is represented in Figure 4. The magnetic properties of a d^7 ion in such a crystal field is dominated by the populated levels $^4A_{2g}$ and ^4E_g. The energy separation between the orbital singlet and orbital doublet terms is a factor of particular importance, representing the Δ factor of the earlier model used for an axially distorted octahedron by Figgis.[7] Now the energy of the $^4A_{2g}$ term may be expressed in terms of the appropriate strong-field determinantal matrix element:

$$E(^4A_{2g}) = \langle|z^2,x^2-y^2,xy|V_{D_{4h}}|z^2,x^2-y^2,xy\rangle$$
$$= E(z^2) + E(x^2-y^2) + E(xy) \qquad (1)$$

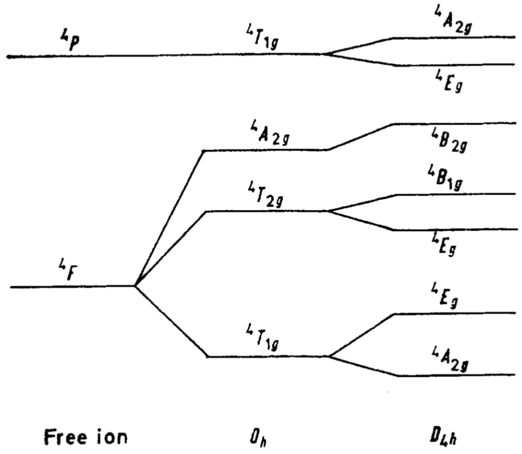

FIGURE 4 Spin-quartet terms arising in d^7 free ion, in O_h and in D_{4h} crystal symmetries

Similarly, for the ^4E_g term:

$$E(^4E_g) = a^2E(yz) + b^2E(xz) + (a^2+b^2)E(z)^2 +$$
$$(a^2+b^2)E(x^2-y^2) \qquad (2)$$

where $a^2 + b^2 = 1$ and, in D_{4h} symmetry, $E(yz) = E(xz)$. Hence

$$E(^4A_{2g}) - E(^4E_g) = 2e_\pi(\text{Cl}) + 2e_\pi'(\text{py}) - 4e_\pi'(\text{py})$$
$$= 2[e_\pi(\text{Cl}) - e_\pi'(\text{py})]$$
$$= 2\Delta\pi, \text{ say} \qquad (3)$$

Thus, at this level of approximation and ignoring spin-orbit coupling, we have the result that susceptibilities are affected strongly by the *difference* in axial and equatorial π-bonding (Δπ) rather than by their absolute values. We must not expect, therefore, to find a unique fit with respect to the π-bonding parameters but rather one that fits approximately to a linear relation between them.

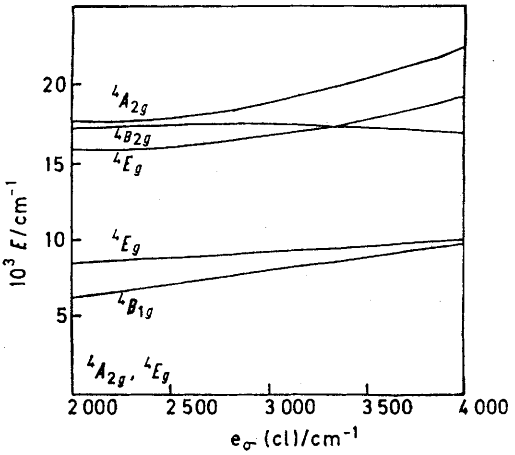

FIGURE 5 Eigenvalues of spin-quartet terms in D_{4h} symmetry as functions of e_σ (Cl): e_σ (py) = 3 700 cm^{-1}, e_π (py) = 100 cm^{-1}, e_π (Cl) = 300 cm^{-1}, $B = 0.8\, B_0$, $\zeta = 0$

In order to test this and to begin to establish numerical values, however, it is still necessary to determine approximate values for the σ-bonding parameters even though, in common with $[\text{Co(py)}_4(\text{NCS})_2]$, susceptibilities should be relatively insensitive to them. The electronic spectra of $[\text{Co(py)}_4\text{Cl}_2]$ have been reported[8] to comprise bands at 8 700, 16 130, and 19 220 cm^{-1}, assigned respectively to transition from the ground states to ^4E_g, $^4B_{1g}$; to $^4E_g(^4P)$; and to $^4A_{2g}(^4P)$, $^4B_{2g}$. Let us take e_σ and e_π values for pyridine from the earlier study[1] of $[\text{Co(py)}_4(\text{NCS})_2]$ of 3 700 and 100 cm^{-1}, together with a guessed value of e_π(Cl) at 300 cm^{-1} (but see later): then the dependence of spin-quartet eigenvalues on e_σ(Cl) in the range 2 000 to 4 000 cm^{-1} is as shown in Figure 5. A value of 3 000 to 3 500 cm^{-1} for e_σ(Cl) appears to fit the spectrum satisfactorily, a figure close enough for the present purpose of determining the e_π parameters. Later checks confirmed the insensitivity of principal susceptibilities to variations of ±500 cm^{-1} in the e_σ values, as was observed for the cobalt and iron thiocyanate complexes.

With these values of e_σ for pyridine and chlorine, together

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[7] B. N. Figgis, M. Gerloch, J. Lewis, F. E. Mabbs, and G. A. Webb, *J. Chem. Soc.* (*A*), 1968, 2086.

[8] A. B. P. Lever, *Co-ordination Chem. Rev.*, 1968, **3**, 119.

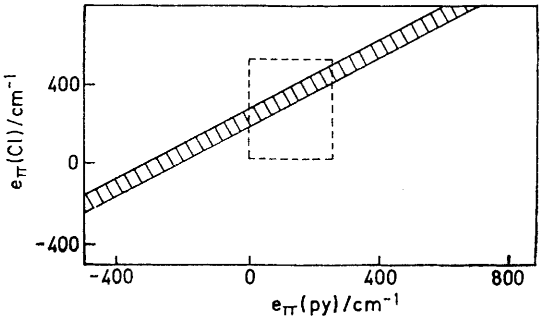

FIGURE 6 [Co(py)$_4$Cl$_2$]: linear relationship between e_π (Cl) and e_π (py) for regions of acceptable fit (in hatched area). e_σ (py) = 3 700 cm^{-1}, e_σ (Cl) = 3 000 cm^{-1}, ζ = 400 cm^{-1}, k = 1.0, B = 0.8 B_0

with a nominal value for ζ of 400 cm^{-1}, the dependence of simultaneously acceptable fits to experimental values of $\chi_{\parallel}$ and $\chi_{\perp}$ were calculated as functions of the π-bonding with both ligands. Fitting spaces were constructed as described in the previous paper.[1] The prediction of a linear relation between e_π(Cl) and e_π(py) for good fit over wide ranges of both parameters is confirmed in Figure 6. No satisfactory agreement with experiment was found outside the hatched area. Apart from investigations of the influence of variations in ζ and k, this figure summarizes all that may be determined about π-bonding from the present susceptibility data. However, if the model we have used throughout this and earlier papers is to have any chemical utility, we must surely expect a degree of transferability of parameters from one system to another. The molecules [Co(py)$_4$(NCS)$_2$] and [Co(py)$_4$Cl$_2$] are closely related. In both cases the four pyridine ligands all lie in the equatorial plane and we may assume that they share common π-bonding parameters, at least approximately. The different orientations of the pyridine groups in the two molecules should have little bearing on this, a major purpose of the model being to factor out such purely geometrical features. A section of Figure 6 has been marked out, corresponding to the assumption that e_π(py) in [Co(py)$_4$Cl$_2$] takes a value close to +100 cm^{-1}, as in the thiocyanate compound.[1] We now examine this region in more detail. We note that the e_π(Cl) value of *ca.* 300 cm^{-1} following from this assumption corresponds with the 'guessed' value used in the earlier estimation of suitable σ-bonding parameters. In truth the actual exploration progressed *via* a circular path.

The functional dependence of the orbital reduction factor k is shown in Figure 7, from which we note that broader areas of fit correspond to k in the range 0.8—0.9. However, lower values also appear possible and we can merely note the contrast with the behaviour in the thiocyanate molecule where k values very close to unity are preferred. Similar tolerance in ζ values has been noted also, lower values yielding broader regions of fit in e_π space for lower k values. In that it might be appropriate to replace the orbital angular momentum operator l in the spin–orbit coupling operator by kl, this correlation between the influence of k and parameters is unexceptional. While little information about k and ζ values is to be had from the present study, it is worth noting that the region of fit with respect to the e_π parameters is scarcely affected by their variation.

Comparison with [Co(py)$_4$Br$_2$].—The complex [Co(py)$_4$Br$_2$] belongs to the orthorhombic crystal class although its magnetic behaviour is pseudo-tetragonal: $\chi_a > \chi_b \approx \chi_c$. The molecular geometries of the bromo- and chloro-complexes are similar, the equatorial pyridine groups adopting a 'propeller' conformation inclined at 45° to the Co–N plane. The procedure for fitting the susceptibilities was much the same as for the chloro-compound, similar arguments being made to restrict the effective parameterization to e_π(Br) and e_π(py). Acceptable fits to all three principal susceptibilities again lie close to a linear relationship between axial and equatorial e_π parameters, but in this case are bounded, in one direction at least, occurring for positive e_π parameter values only. As indicated earlier the dependence of the susceptibilities upon $\Delta\pi$ is not complete, spin–orbit coupling serving to blur the simple relationship previously established. Figure 8 shows the relationship between the π-bonding parameters near the region e_π(py) $\sim$ 100 cm^{-1}. Best fits occur for k values in the region 0.8—0.9, but neither k nor ζ can be sensitively established. Once again, the relationship between e_π(axial) and e_π(equatorial) appears insensitive to either k or ζ values. With e_σ(py) $\sim$ 4 000 cm^{-1}, e_π(py) $\sim$ 200 cm^{-1}, e_π(Br) $\sim$ 600 cm^{-1}, eigenvalues of the complete spin-quartet manifold are plotted with respect to e_σ(Br) in Figure 9. Observed transitions, with their reported assignments,[9] are indicated in the Figure, suggesting e_σ(Br) $\sim$ 3 000—3 500 cm^{-1}.

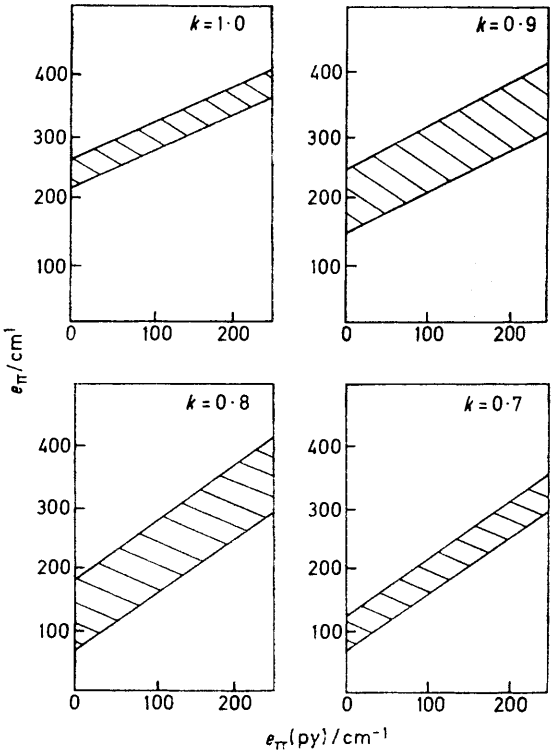

FIGURE 7 [Co(py)$_4$Cl$_2$]: dependence of fits in π parameter space on k

Taking approximately equal values for e_σ(Cl) and e_σ(Br) in the chloro- and bromo-molecules at *ca.* 3 000 cm^{-1} and e_π parameters of 250 and 600 cm^{-1} for the respective

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[9] D. A. Rowley and R. S. Drago, *Inorg. Chem.*, 1967, **6**, 1092.

halogens, the latter figures deriving from the assumption of approximately equal pyridine π-bonding in all three complexes $[Co(py)_4X_2]$ (X = NCS, Cl, or Br), we may deduce $10Dq$ values from the relation

$$10Dq = 3e_\sigma - 4e_\pi \qquad (4)$$

finding $10Dq(Cl) \sim 7\,800$ cm^{-1}, $10Dq(Br) \sim 6\,600$ cm^{-1}. These values are clearly approximate, not only for the reasons already stated, but also because of the averaging process implied in the use of (4) to define an 'axial' Dq value in a molecule of less than octahedral symmetry. However, the values serve as a guide. The processes by which they were obtained have been clearly stated and chosen without prejudice: the result we obtain seems sensible in terms of the spectrochemical series. The relative magnitudes of the σ-bonding in the chloro- and bromo-complexes are not satisfactorily defined by the susceptibility work, but it does seem clear that the contributions to the π-antibonding energies of the metal d orbitals from the bromine ligands is two to three times more than from the chlorines.

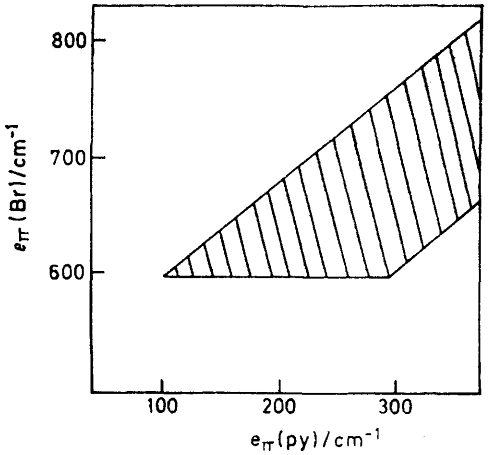

FIGURE 8 $[Co(py)_4Br_2]$: fitting region for all three crystal susceptibilities as function of π-parameters

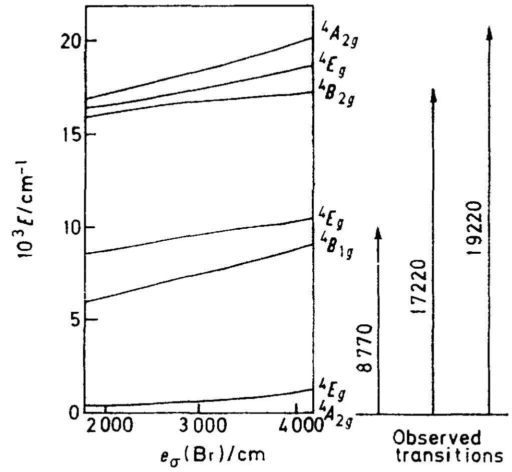

FIGURE 9 Eigenvalues of spin-quartet terms in D_{4h} symmetry as functions of e_σ (Br): e_σ (py) = 3 700 cm^{-1}, e_π (py) = 100 cm^{-1}, e_π (Br) = 600 cm^{-1}, $B = 0.8\,B_0$, $\zeta = 0$. Observed transitions and reported assignments are also shown

Approximate Tetragonality in $[Co(acetylacetone)_2(py)_2]$.—The molecules just discussed involved four pyridine ligands in the equatorial plane of a distorted octahedron. In $[Co(acetylacetone)_2(py)_2]$, two pyridine groups occupy the axial sites instead. The molecular geometry of $[Ni(acetylacetone)_2(py)_2]$ with which the present modification of the cobalt complex is isomorphous is shown in Figure 10. The equatorial sites are now occupied by two coplanar acetylacetone chelate ligands, the donor atoms of which conform closely to a square. π-Bonding orbitals on the donor oxygen atoms may be defined along the directions shown and it is worth pointing out that, under the assumption of these atoms occupying the corners of a square, the crystal field in this plane is isotropic. That is, in this approximation, no electronic property of the metal d orbital recognizes the chelating nature of the acetylacetone ligands. Thus it appears that the major lowering of the molecular symmetry from tetragonal is the π-bonding of the axial pyridine groups. This effect would be removed also if these groups were staggered as reported for the orthorhombic modification. At this stage, therefore, and depending upon the π-bonding contribution of the axial pyridines, the overall symmetry in $[Co(acetylacetone)_2(py)_2]$ appears to be both actually and effectively rhombic and we might anticipate fitting of magnetic susceptibilities to resemble the case of $[Co(py)_4(NCS)_2]$.

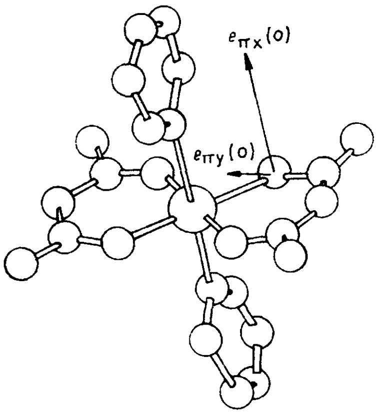

FIGURE 10 Molecular co-ordination geometry of $[Co(acetylacetone)_2(py)_2]$ and definition of π-bonding directions for the acetylacetone ligands

For the purpose of testing this prediction, nominal e_σ values of 3 500 cm^{-1} were assumed and the simultaneous fitting of all three principal crystal susceptibilities was studied as a function of the three π-bonding parameters e_π(py), $e_{\pi x}$(acac), $e_{\pi y}$(acac). For a given value of e_π(py), satisfactory fits were found with respect to a linear relationship between the two π-bonding parameters for acetylacetone rather like the situation for the tetragonal chloro- and bromo-complexes and unlike that for the thiocyanate molecules. The linear relationship varied little with the value chosen for e_π(py), fits being disposed about a two-dimensional sheet in the π-parameter space shown in Figure 11. The sheet is bounded in the e_π(py) co-ordinate in that no fits outside the range for e_π(py) of -200 to $+400$ cm^{-1} were possible. These limiting values concur with the previous finding of a small π-bonding participation by pyridine ligands. Modification of (3) to allow anisotropic in-plane π-bonding leads to the expression

$$`E(^4A_{2g}) - E(^4E_g)' = E(xy) - E(yz) = 4e_{\pi y}(\text{acac}) - 2e_{\pi x}(\text{acac}) - 2e_{\pi}'(\text{py}) \quad (5)$$

so that for a constant, and particularly small, value of e_π(py), the linear fitting region with respect to the π-bonding parameters of acetylacetone can be rationalized. The relevance of this relationship does, however, depend upon the degree of tetragonality shown in the molecule as a whole and so to some extent the occurrence of the linear fit in Figure 11 implies that, despite the eclipsed conformation of the axial pyridines, the overall electronic symmetry in the ground states closely approximates a tetragonal description. This may result from the nominally reversed sense of tetragonality of the acetylacetone molecule compared with the $[Co(py)_4X_2]$ systems, so relegating the anisotropic π-bonding of the pyridine ligands here to a second-order role.

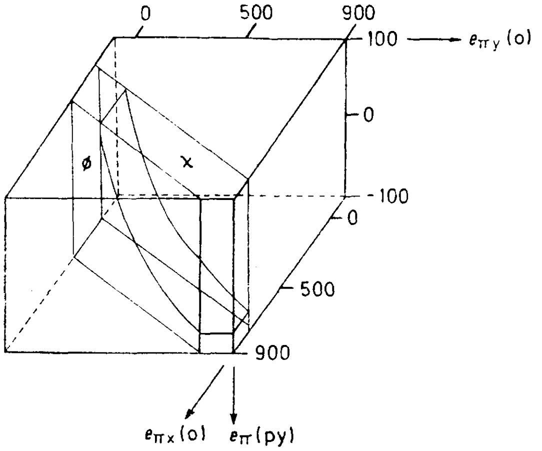

FIGURE 11 $[Co(acetylacetone)_2(py)_2]$: fitting region in π-parameter space (see text)

Finally, we have superimposed on the fits in Figure 11, the region which gives satisfactory agreement between calculated and observed ϕ values. This restricts possible e_π values further and at least gives the qualitative prediction that $e_{\pi x}(\text{acac}) > e_{\pi y}(\text{acac})$. This result is again readily acceptable in terms of the π_x-bonding being associated with the π-bond delocalized over the O–C–C–C–O skeleton of the acetylacetone ligand.

Overall we conclude that the angular overlap model furnishes a very useful parameterization scheme for the analysis of magnetic susceptibilities, its particular advantage being the apparent and correlatable relationship with established chemical-bonding concepts. Based admittedly on a small number of cases studied so far, we also have the provocative generalization that the quality and uniqueness of fits to magnetic susceptibilities appear to be optimized in the lower symmetry systems—a situation not expected at the outset of this programme to investigate the feasibility of interpreting the magnetic properties of unsymmetrical molecules.

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