Paramagnetic Ellipsoids and π Bonding in Dithiocyanatotetrapyridinecobalt(II) and -iron(II)

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Average and principal susceptibilities of [$Co(py)_4(NCS)_2$] and [$Fe(py)_4(NCS)_2$] in the temperature range 80—300 K are reported. They have been fitted to the low-symmetry model described in the preceding paper, virtually perfect agreement being obtained between all three observed and calculated crystal susceptibilities for each molecule. The magnetic properties depend predominantly on π bonding, parameter values of which compare well between the two complexes and with otherwise established chemical-bonding concepts. In particular, pyridine is involved in a definite, but small, π-donating role to the metal atoms. The orientations of the molecular magnetic ellipsoids bear no simple relation to the approximate structural symmetry in these molecules.

TYPICALLY, the first step in the treatment of magnetic-anisotropy measurements on transition-metal complex ions is transformation of the experimental crystal susceptibilities into their molecular equivalents. This requires knowledge of the orientation of the principal molecular susceptibilities in the crystal frame, normally deriving from consideration of the local molecular symmetry or from some intuitively reasonable approximation to it. Several ways of manipulating the experimental data which minimize the consequences of inevitable experimental error have been described:[1] they should yield approximately equal results, however, given self-consistent data. The crystal paramagnetic susceptibilities of *trans*-[$Fe(py)_4(NCS)_2$], reported below, were treated in these various ways but yielded widely inconsistent results from the different sets of equations relating to the same physical theory. The assumption made was that the molecule could be approximated as a tetragonally distorted octahedron with a cylindrically symmetric susceptibility ellipsoid whose principal axis lay parallel to the SCN–Fe–NCS molecular direction. Not only were inconsistences found with respect to algebraic procedure, but also the resulting molecular susceptibilities appeared rhombic and, depending on the choice of ' in-plane ' directions (which should have been relatively unimportant), negative susceptibilities occasionally resulted. Similar behaviour has been noted elsewhere.[1]

The assumption of tetragonal symmetry for the molecular susceptibilities is clearly invalid, although it should be noted that it was not obviously untenable in the beginning. The geometry of the metal and ligand donor atoms above seems reasonably well described as that of a tetragonally distorted octahedron. Table 1 and Figure 1 summarize the relevant crystallographic data [2] on the co-ordination geometry of [$Fe(py)_4(NCS)_2$]. It is the orientation of the four pyridine groups around the metal atom which most markedly destroys the unique role of the SCN–Fe–NCS axis. The molecules are centrosymmetric so that the py groups do not pack in the familiar ' propeller ' arrangement. On the other hand, the orientation of these groups cannot affect the metal *via* σ bonding but only π bonding and the latter is commonly supposed to be very small for this ligand.

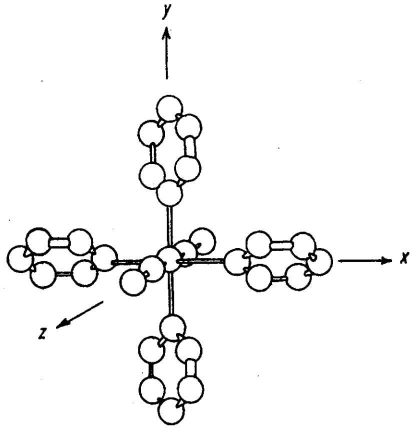

FIGURE 1 The centrosymmetric co-ordination geometry of [$M^{II}(py)_4(NCS)_2$] (M = Fe or Co)

TABLE 1

Crystallographic summary for [$Fe(py)_4(NCS)_2$]

Monoclinic *C*2/*c*

$Z = 4$

$a = 12.25, b = 13.18, c = 16.46$ Å, $\beta = 117.9°$

M–*N*CS	2.09 Å
M–*N*C_5H_5	2.24 Å
SC*N*–M–*N*C_5H_5	89.8°
C_5H_5*N*–M–*N*C_5H_5	89.4°
M–N–CS	155.3°

Anyway, the ' reasonable ' assumption of a tetragonal ligand field was soon shown to be unacceptable so that no further progress could be made without explicit recognition of the full geometry and low molecular symmetry, C_i in [$Fe(py)_4(NCS)_2$]. The theoretical model and procedures described in the preceding paper [3] were developed to handle cases such as this. One aim of this study, therefore, is to test the efficiency of that model in reproducing the details of the observed crystal susceptibilities in this compound.

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[1] M. Gerloch and P. N. Quested, *J. Chem. Soc.* (*A*), 1971, 2308.

[2] I. Søtofte and S. E. Rasmussen, *Acta Chem. Scand.*, 1967, **21**, 2028.

[3] M. Gerloch and R. F. McMeeking, preceding paper.

Two other important aims emerge simultaneously. Previous experience with molecules possessing axially symmetric magnetic properties, for example trigonally distorted octahedral iron(II)[4] or cobalt(II)[5] complexes, has revealed particular difficulties in yielding even approximately unique sets of fitting parameters, areas or volumes in multiparameter space typically defining satisfactory conditions for fit. Such a situation for fairly symmetrical molecules might deteriorate beyond utility for molecules of little or no symmetry. This was a matter of great concern to us, unnecessarily as it turned out. Finally, we are interested to find values of the angular-overlap parameters which not only fit the experimental magnetism but which also appear to be in accord with chemical-bonding ideas, so that some measure of transferability of such parameters to other molecules may confidently be made.

We report work on the isomorphous compounds $[Fe(py)_4(NCS)_2]$ and $[Co(py)_4(NCS)_2]$, thus permitting the further comparison between systems involving quite distinct orbital bases.

EXPERIMENTAL

The compounds $[Co(py)_4(NCS)_2]$ and $[Fe(py)_4(NCS)_2]$ were prepared[2,6] by dissolution of the metal nitrates in aqueous pyridine, followed by addition of stoicheiometric amounts of ammonium thiocyanate causing rapid precipitation of the products. The red (cobalt) and bright yellow (iron) powders were filtered off, washed with ethanol–pyridine (9 : 1), and recrystallized from dry chloroform. Red and yellow-green elongated tablets of the cobalt and iron complexes, respectively, separated out from the chloroform solutions over a period of weeks. Decomposition of the unprotected crystals occurs on exposure to the atmosphere, most particularly so for the iron compound, but the crystals may be preserved indefinitely in stoppered bottles under a py atmosphere. After rapid weighing, crystals were given several coats of Shellac which allowed *X*-ray and anisotropy measurements to be made before serious surface decomposition occurred. Satisfactory C, H, and N analysis were obtained.

Powder susceptibilities were measured by the Gouy technique, tubes being packed under a py atmosphere and subsequently stoppered. The effective moments observed at room temperature compare favourably with values reported previously.[2] Interpolated moments in the temperature range 80—300 K are listed in Tables 2 and 3.

The crystal habit of $[M^{II}(py)_4(NCS)_2]$ (M = Fe, Co, or Ni), established by oscillation and Weissenberg *X*-ray photography, is shown in Figure 2. The crystals are monoclinic, space group *C*2/*c*, with four molecules per unit cell.

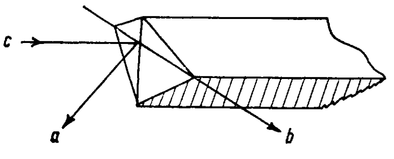

FIGURE 2 The crystal habit of $[M^{II}(py)_4(NCS)_2]$ (M = Fe or Co)

Magnetic anisotropies of several crystals weighing *ca.* 5 mg were measured by the Krishnan critical torque method, as described elsewhere.[1] Values of $\Delta\chi_b = \chi_2 - \chi_1$ were obtained with crystals mounted parallel to the torsion fibre, while measurements of $\Delta\chi_1$ and $\Delta\chi_2$ in the temperature range 80—300 K were preceded by determinations of the orientations of χ_1 and χ_2 in the crystal *ac* plane. Figure 3 shows the variations of in-plane crystal anisotropies with respect to crystal orientation using the single-axis goniometer device (' wheel ') described previously.[1] The angle ϕ subtended by the crystal *a* axis was 57° for the cobalt compound and 7° for the iron. The experimental anisotropies vanished on cyclical addition, as required, within a $\pm 3\%$ experimental error: in the case of the iron compound this is particularly satisfactory in view of the considerable experimental problems experienced with these unstable crystals. Cyclic addition to zero was also noted throughout the 80—300 K range, indicating no change in ϕ values within experimental error. Values of the principal crystal susceptibilities, derived as described elsewhere,[1] are listed with anisotropies in Tables 2 and 3. The diamagnetic anisotropy of $[M(py)_4(NCS)_2]$, estimated from the ring systems in the appropriate orientations in the crystal, are of *ca.* 10^{-4} c.g.s. units and were neglected.

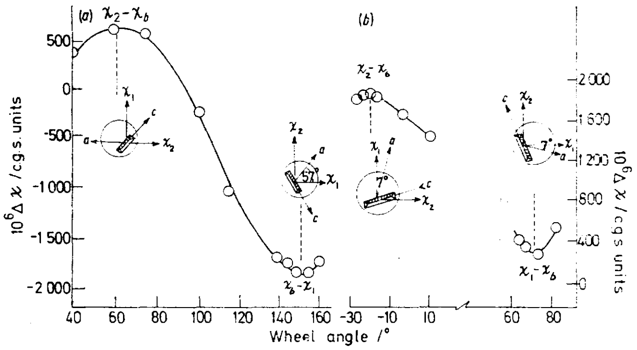

FIGURE 3 Angular variation of magnetic anisotropy in crystal *ac* planes: (*a*) $[Co(py)_4(NCS)_2]$; (*b*) $[Fe(py)_4(NCS)_2]$. Insets show crystal and axis orientation with the magnetic field horizontal, in or perpendicular to the plane of the paper

Single-crystal electronic-absorption spectra were recorded on a Cary 14 spectrophotometer in the range 6 000—25 000 cm^{-1}. The spectrum of $[Co(py)_4(NCS)_2]$ comprised one band at 9 000 cm^{-1} and a broader composite band centred at *ca.* 20 000 cm^{-1}. Polarized-light and low-temperature (*ca.* 10 K) studies failed to resolve these bands further. Similar behaviour was observed for $[Fe(py)_4(NCS)_2]$, the spectrum consisting of a single broad transition centred at *ca.* 11 100 cm^{-1}.

Fitting Procedure for $[Co(py)_4(NCS)_2]$.—The process of fitting the observed spectral and magnetic data for $[Co(py)_4(NCS)_2]$ by variation of the parameters of the model described in the previous paper[3] is now discussed. The chosen basis spans the complete spin-quartet levels, ^4P and ^4F, of the d^7 ion. Possible parameters to be varied are as follows. Interelectron-repulsion effects for the quartet levels only require one parameter and so F_2 and F_4 values were manipulated to vary the Racah *B* parameter; the spin–orbit

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[4] M. Gerloch, J. Lewis, G. G. Phillips, and P. N. Quested, *J. Chem. Soc.* (*A*), 1970, 1941.

[5] M. Gerloch and P. N. Quested, *J. Chem. Soc.* (*A*), 1971, 3729.

[6] G. B. Kauffman, R. A. Albers, and F. L. Harlan, *Inorg. Synth.*, 1970, **12**, 251.

coupling coefficient ζ is taken as isotropic, as is *k* the orbital-reduction factor in the magnetic-moment operator, discussed in the preceding paper. In addition we must consider up to three *e* parameters for each ligand not related to another by a centre of inversion. The number of ligand-field parameters may be reduced by making two simple assumptions; first, that the two crystallographically independent pairs of ligands are chemically equivalent in all respects except their orientations, and secondly that π bonding between metal and py is inoperative in the plane of the ligand. This leaves e_σ, $e_{\pi x}$, and $e_{\pi y}$ parameters for the thiocyanate ligands and e_σ and $e_{\pi x}$ (say) for the pyridines, a total of five ligand-field variables for a molecule presumed to have no more symmetry than it actually possesses, namely a centre of inversion. However, the complete model involves eight parameters, rendering automatic variation of all degrees of freedom impractical. We therefore sought ways of reducing the effective parameter space.

From the spectrum of [Co(py)$_4$(NCS)$_2$] and its marked insensitivity to polarization studies, even at fairly low temperatures, we deduce that the chromophore behaves essentially like that of a simple octahedral d^7 complex. Theoretically, we accept that e_π parameters are considerably smaller than e_σ on essentially three grounds. An earlier description [7] of the angular-overlap model (a.o.m.) in terms of a quasi-Wolfsberg–Helmholz model defined the *e*

TABLE 2

Interpolated average magnetic moments, principal susceptibilities, and anisotropies for [Co(py)$_4$(NCS)$_2$]

T/K	$10^6\chi$/c.g.s. units						$\bar{\mu}_{\text{eff.}}$/B.M.
	χ_1	χ_2	χ_3	$\chi_2 - \chi_3$	$\chi_2 - \chi_1$	$\chi_3 - \chi_1$	
300	9 712	12 072	11 517	600	2 360	1 850	5.16
290	10 047	12 577	12 027	620	2 530	2 050	5.17
280	10 364	13 114	12 522	635	2 750	2 200	5.18
270	10 778	13 768	13 135	655	2 990	2 380	5.21
260	11 021	14 231	13 569	693	3 210	2 580	5.19
250	11 410	14 901	14 198	705	3 500	2 800	5.19
240	11 803	15 613	14 853	730	3 810	3 020	5.20
230	12 102	16 222	15 416	762	4 120	3 270	5.18
220	12 554	17 044	16 182	795	4 490	3 560	5.18
210	12 903	17 793	16 884	828	4 890	3 900	5.16
200	13 416	18 736	17 768	865	5 320	4 250	5.16
190	13 847	19 727	18 657	910	5 880	4 650	5.14
180	14 421	20 891	19 737	958	6 470	5 120	5.14
170	14 987	22 067	20 847	1 010	7 080	5 650	5.12
160	15 555	23 345	22 030	1 080	7 790	6 240	5.10
150	16 266	24 856	23 438	1 165	8 590	6 920	5.08
140	16 998	26 518	25 004	1 258	9 520	7 750	5.06
130	17 741	28 271	26 647	1 368	10 530	8 650	5.02
120	18 794	30 594	28 822	1 493	11 800	9 750	5.00
110	19 772	33 072	31 156	1 632	13 300	11 100	4.96
100	20 586	35 886	33 709	1 804	15 300	12 750	4.90
90	21 502	39 002	36 606	1 992	17 500	14 700	4.83
80	21 863	42 063	39 845	2 215	20 200	17 980	4.70

TABLE 3

Interpolated average magnetic moments, principal susceptibilities, and anisotropies for [Fe(py)$_4$(NCS)$_2$]

T/K	$10^6\chi$/c.g.s. units						$\bar{\mu}_{\text{eff.}}$/B.M.
	χ_1	χ_2	χ_3	$\chi_2 - \chi_3$	$\chi_2 - \chi_1$	$\chi_1 - \chi_3$	
300	12 337	13 837	12 077	1 830	1 500	190	5.53
290	12 700	14 380	12 460	1 960	1 680	200	5.53
280	13 065	14 945	12 850	2 100	1 880	210	5.52
270	13 535	15 640	13 365	2 220	2 105	224	5.53
260	13 969	16 289	13 813	2 400	2 320	232	5.53
250	14 396	16 956	14 249	2 600	2 560	253	5.51
240	14 933	17 738	14 759	2 880	2 805	273	5.51
230	15 530	18 640	15 359	3 170	3 110	282	5.51
220	16 171	19 621	15 989	3 505	3 450	309	5.51
210	16 834	20 614	16 612	3 895	3 780	330	5.50
200	17 625	21 765	17 370	4 300	4 140	351	5.50
190	18 456	23 051	18 193	4 750	4 595	372	5.50
180	19 424	24 434	19 113	5 240	5 010	391	5.50
170	20 412	25 992	20 076	5 840	5 580	412	5.49
160	21 271	27 561	20 948	6 500	6 290	435	5.45
150	22 571	29 741	22 237	7 580	7 170	458	5.46
140	23 894	32 114	23 552	8 420	8 220	485	5.45
130	25 408	34 958	25 075	9 700	9 550	515	5.44
120	27 441	38 541	27 018	11 400	11 100	545	5.45
110	29 714	42 814	29 171	13 610	13 100	575	5.46
100	32 458	47 958	31 964	15 880	15 500	607	5.47
90	36 140	53 940	35 620	18 200	17 800	640	5.49

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[7] See M. Gerloch and R. C. Slade, 'Ligand Field Parameters,' Cambridge University Press, 1973, and refs. therein.

parameters as in (1) where $S_{\mathrm{ML}}{}^{t}$ is the diatomic overlap integral for the M–L interaction of bonding mode t (= σ, π,

$$e_\sigma = K(S_{\mathrm{ML}}{}^{\sigma})^2,\ e_\pi = K(S_{\mathrm{ML}}{}^{\pi})^2 \qquad (1)$$

etc.) and K is defined in (2) where H_{L} and H_{M} are approximated, by (say) valence-state ionization potentials of the

$$K \sim H_{\mathrm{L}}{}^2/(H_{\mathrm{M}} - H_{\mathrm{L}}) \qquad (2)$$

ligand and metal, respectively. Taking the simplest assumption of ligand p_σ and p_π orbitals of identical energy prior to bonding, the relative geometric arrangement of these orbitals with respect to the metal leads [7] to $e_\pi/e_\sigma = 0.25$. Secondly, we note that py ligands are commonly supposed to π bond only weakly, if at all, in transition-metal complexes, reducing this ratio much further. Although this assumption is in no way incorporated into our basic model, it serves as a useful starting point to be checked later. Finally, the similar positions of py and thiocyanate in the spectrochemical series suggests that the π-bonding ability of thiocyanate is somewhat similar to that of py if we may suppose them to have similar σ-bonding abilities. We emphasize that these order-of-magnitude assumptions are made only to provide a starting point and that they are checked in some detail later.

In view of these theoretical and spectral observations, we chose initially a two-parameter model for the ligand field involving common e_σ and e_π parameters. In Figure 4 eigenvalues are shown for the ${}^4P + {}^4F$ manifolds based on the known crystallographic geometry of the molecule and as functions of e_σ and e_π/e_σ. Spin–orbit coupling was neglected and B was taken as 0.8 B_0, the free-ion value of the Racah parameter, typical of octahedral Co$^{\mathrm{II}}$ complexes. Also shown in Figure 4 are average powder magnetic moments $\bar{\mu}$ calculated under the same conditions and with $k = 1.0$ and $\zeta = 400$ cm^{-1}. From this semiquantitative treatment we note that tolerable fits to the spectrum and average monents suggest e_σ values of 3 700 ± 500 cm^{-1} with e_π/e_σ lying between 0.01 and 0.1. Until the final checking calculations, we fix e_σ(py) = e_σ(NCS) = 3 700 cm^{-1} and $B = 0.8\ B_0$ and, as ultimately demonstrated, the observations which follow are markedly insensitive to ±500 cm^{-1} variations in e_σ or ±200 cm^{-1} in B.

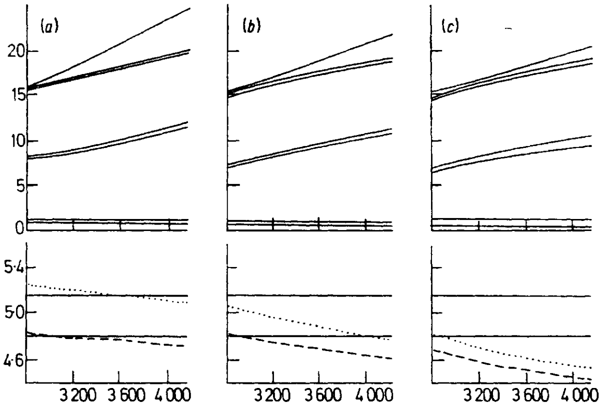

FIGURE 4 Eigenvalues for components of spin quartets as functions of an average e value and e_π/e = 0.01 (*a*), 0.1 (*b*), and 0.2 (*c*) ($\zeta = 0$, $B = 0.8\,B_0$.) and average magnetic moments calculated for $B = 0.8\ B_0$, $\zeta = 400$ cm^{-1}, and $k = 1.0$ at 90 (— — —) and 290 K (· · · ·) compared with the observed values (——)

π-Bonding Anisotropy and Fitting to Complete Susceptibility Data.—Orientations for the π bonding with py and thiocyanate ligands are defined in Figure 5. These directions were communicated to the program as follows. The σ vector was always taken from the metal to the donor atom and defined simply by the co-ordinates of these atoms from the original crystallographic report. A plane containing the σ vector was then defined by giving co-ordinates of two other atoms, N and C for the NCS group in Figure 5(*a*) and C^1 and C^2 (or C^1 and N, say) for the py in 5(*b*). Direction cosines of the normals to this plane were computed, followed by generation of the mutual normal to this and the σ axis, lying in the chosen plane.

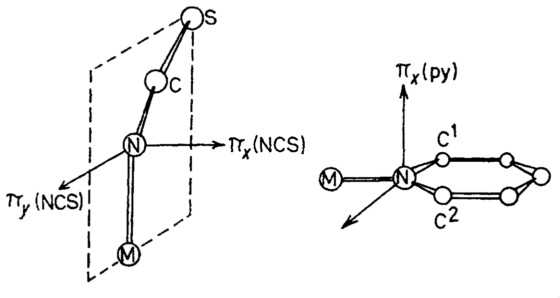

FIGURE 5 π-Bonding directions chosen for NCS$^-$ and pyridine ligands

Estimates of the e_π parameters in the nickel analogue of the present system suggest values between 100 and 600 cm^{-1}. In order to limit computation time to manageable proportions, we therefore investigated fits for all three e_π parameters varying between +800 and −800 cm^{-1}, first in large intervals of 200 cm^{-1} and finally in steps of 50 cm^{-1}. The spin–orbit parameter ζ was taken initially as 400 cm^{-1} and the orbital-reduction factor k as unity. In this way the problem was limited to three-parameter space, involving $e_{\pi x}$(NCS), $e_{\pi y}$(NCS), and e_π(py). The quality of fit was gauged by comparing each calculated principal crystal susceptibility with the observed quantity at a series of temperatures T (typically five) spanning the experimental range. Defining δ as in (3), we compute $F = S/\sum_T \delta_T{}^2$ as an

$$\delta = \frac{|\text{experimental quantity} - \text{corresponding calculated quantity}|}{|\text{experimental quantity}|} \qquad (3)$$

empirically convenient figure of merit, where S is a scaling factor. A total figure of merit for simultaneous comparison of all three principal crystal susceptibilities was computed as a function of the a.o.m. parameters: a large value of F corresponds to a good fit. Contouring in multiparameter space has the advantage of revealing the sensitivity of the fits to the various parameters and whether such fits are unique or not.

Figure 6(*a*) shows a region of the three-e_π-parameter space in which regions of fit are plotted for [Co(py)$_4$(NCS)$_2$]. Within the limits set above, no acceptable fits to the magnetic data were found other than those shown. In the monoclinic system, appropriate here, further experimental data are furnished by ϕ, the angle subtended by χ_1, and the

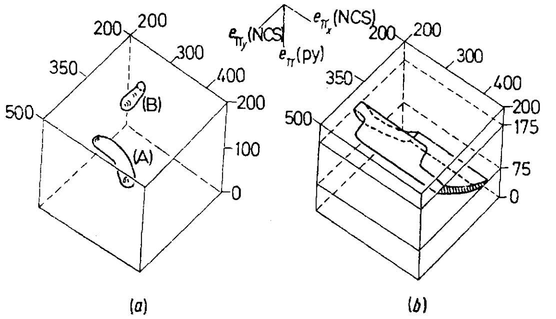

FIGURE 6 Regions of π-parameter space giving good fit (*a*) to all three principal crystal susceptibilities simultaneously and (*b*) within 10° to ϕ for $[Co(py)_4(NCS)_2]$

crystal *a* axis. Comparison of this observable between calculation and experiment is shown in Figure 6(*b*) in which a region of good fit ($|\phi_{calc.} - \phi_{obs.}| \leqslant 10°$) is shown. It is worth pointing out that ϕ is a fairly sensitive measure of the differences between susceptibilities so that agreement with experiment is likely to be less good than for the principal susceptibilities themselves. The region in Figure 6 was sampled at 50 cm^{-1} intervals in all three π parameters: the regions in 6(*a*) vary gradually with respect to $e_{\pi x}$(py), a 50 cm^{-1} change in which shifts the fitting maxima by one lattice position. All fits in region (A) of Figure 6(*a*) are characterized by a common ϕ value of 84°: those in region (B) similarly share a common ϕ value, of 30°. The region of fit to ϕ within $\pm 10°$ shown in Figure 6(*b*) falls almost exactly between the two regions of 6(*a*). Detailed investigation of the space between the regions (A) and (B) confirms that the lack of fit there is real and quite dramatic. Regions (A) and (B) therefore represent separate and distinct sections of parameter space for fitting the magnetic data of $[Co(py)_4(NCS)_2]$, although in each case the observed and calculated ϕ values differ by *ca.* 25°. It is worth noting that anywhere outside the three regions depicted in Figure 6(*a*) and 6(*b*) the calculated ϕ values are in very much worse agreement with the experimental quantity.

The effects of varying the spin–orbit coupling coefficient were studied by recalculating moments for e_π parameters in and near the regions of fit shown in Figure 6. Values for ζ between 500 and 200 cm^{-1} were considered. The positions and orientations of the best-fit regions (A) and (B) and the ϕ region in the e_π-parameter space were insensitive to variation in ζ. The quality of fit in these regions varied somewhat, with ζ giving best results for ζ *ca.* 400 cm^{-1}. Similar calculations to examine the orbital-reduction factor *k* were made. The quality of fitting here was very sensitive, no acceptable level of agreement between calculation and experiment being observed for $k < 0.9$. Finer variation of *k* by 0.02 steps between 0.9 and 1.0 revealed no significant change in the fitting regions with respect to e_π parameters, closest fitting occurring for $k = 1.0$.

Finally, the insensitivity of the average moments to e_σ parameters, noted earlier, was tested with respect to the fitting of all three principal susceptibilities. Taking e_π parameters corresponding to the best fits in Figure 6(*a*), nets were plotted corresponding to variation of fit with respect to variation of independent e_σ parameters in the range 3 400—4 000 cm^{-1} and for *B* values in the range 300—700 cm^{-1}. No distinct maxima were apparent, though higher *B* values were favoured slightly. The marked insensitivity of the detailed magnetic properties of this Co^{II} compound are not too surprising if we consider the electronic structure of the ground state from the viewpoint of the ' strong-field limit '.

For the d^3 hole-equivalent of Co^{II} ions in octahedral fields we consider ground-state $e_g{}^2t_{2g}$ determinants. At this level of approximation, the hole in the t_{2g} set is expected to be sensitive to π-bonding anisotropy but not to σ bonding as this would make similar contributions to the e_g subsets of all three $^4T_{1g}$ determinants. Obviously, neglect of lower than cubic symmetry and spin–orbit coupling invalidate this argument in all but first order, but for approximately octahedral complexes, as here, we expect that anisotropy in e_σ-bonding parameters affects the ground-state properties at essentially second-order level. This is confirmed in the present study.

Calculated principal crystal susceptibilities between 80 and 300 K for the optimum fit in region (A) of Figure 6(*a*) are shown in Figure 7 in comparison with the experimental results. The optimum fit for region (B) corresponds to the π parameters e_π (py) = 125, $e_{\pi x}$(NCS) = 200, and $e_{\pi y}$(NCS) = 200 cm^{-1}. In both cases agreement between theory and experiment is good. The less satisfactory agreement for ϕ values is a little disappointing although, as pointed out earlier, the strong dependence of calculated ϕ values on susceptibility differences suggests that we must expect this. The detailed crystallographic data used in fitting this compound were those reported for $[Fe(py)_4(NCS)_2]$ with which the cobalt compound is stated to be isomorphous. However, minor geometric differences between the molecules may exist, not only with respect to bond lengths which are implicit in the *e*-parameter values chosen, but also with regard to ligand orientations. Accordingly, we recalculated a selection of the results above corresponding to rotations of the ligands about the appropriate Co–N axes. Independent and simultaneous disorientations in the range ±5° were considered with respect to the reported [2] structure of $[Fe(py)_4(NCS)_2]$. However, for these small variations, which seem reasonable limits within the ' isostructural ' description of these molecules, very little difference was observed in any of the fits described above. The quality of fit varied slightly but not significantly and the optimal e_π parameters remained unchanged. The ϕ values could not be improved by more than 3°. We did not consider it

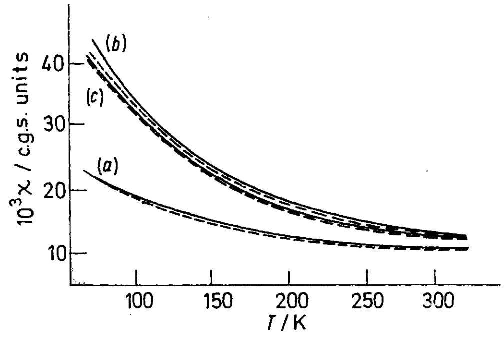

FIGURE 7 Agreement between observed (——) and calculated (— — —) crystal susceptibilities when ζ = 400 cm^{-1}, k = 1.0, e_π(py) = 100 cm^{-1}, $e_{\pi x}$(NCS) = 250 cm^{-1}, and $e_{\pi y}$(NCS) = 350 cm^{-1}: (*a*) χ_1, (*b*) χ_2, and (*c*) χ_3

worthwhile to repeat these calculations for small disorientations of the molecules as a whole, although this could provide the easiest way of improving the ϕ value.

Fitting Procedure for [Fe(py)$_4$(NCS)$_2$].—The single broad spectral band at 11 100 cm^{-1} again suggests octahedral symmetry as a suitable starting point for the analysis of the iron compound. Within the complete ^5D manifold, appropriate here, the interelectronic-repulsion operator is irrelevant and, in the limit of O_h symmetry and vanishing spin–orbit coupling, the splitting of $^5D \rightarrow {}^5E_g + {}^5T_{2g}$ is given by $10Dq$ as defined in (4). Thus for $e_\pi = 0$ an average

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

e_σ value in the compound is 3 700 cm^{-1} and for e_π/e_σ 0.1, e_σ *ca.* 4 270 cm^{-1}, *etc.* Average magnetic moments, $\bar{\mu}$, as functions of an average e_σ and e_π/e_σ are shown in Figure 8 for $\zeta = 400$ cm^{-1} and $k = 1.0$. We note, as confirmed by similar calculations at 80 K, that simultaneous fitting of the spectrum and average moment requires only small contribution from π bonding, with $e_\pi/e_\sigma \leqslant 0.1$ and e_σ in the range 3 000—4 000 cm^{-1}.

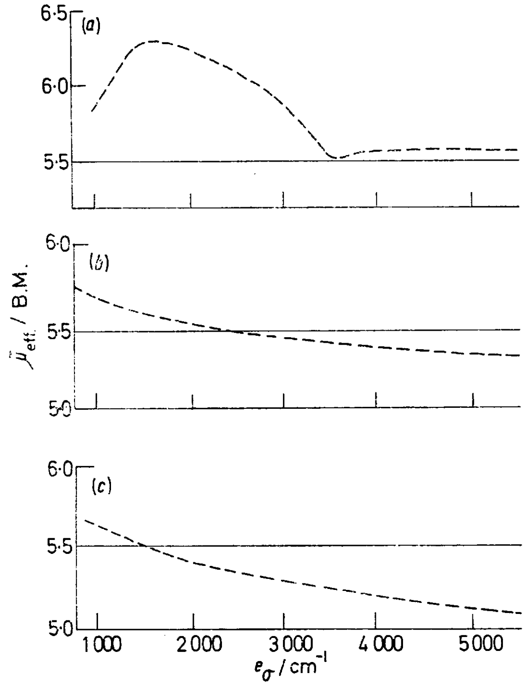

FIGURE 8 Average magnetic moments for [Fe(py)$_4$(NCS)$_2$] as functions of average e_σ and $e_\pi/e_\sigma = 0.01$ (*a*), 0.1 (*b*), and 0.25 (*c*) ($\zeta = 400$ cm^{-1}, $k = 1.0$); (——), observed values

As with the cobalt d^7 system, a description of the d^6 four-hole system for the ground state of the iron compound in terms of the strong-field $e_g{}^2t_{2g}{}^2$ configurations leads to the expectation that detailed magnetic properties should be dominated by π rather than σ bonding. This was confirmed in the e_σ range 3 000—4 000 cm^{-1} in that fits to all three principal susceptibilities, for arbitrary values of e_π, altered insignificantly for e_σ(NCS) and e_σ(py) varying independently in that range. This relative unimportance of σ-bonding parameters for the fitting of ground-state magnetic properties is obviously an important simplifying feature of the multiparameter model. It would not have emerged readily from the more conventional crystal-field models in which parameters are not so directly correlated with chemical bonding. The rule is not general, of course, depending as it does on holes in filled and half-filled t_{2g} sub-shells in the presence of filled or exactly half-filled e_g sub-shells in the case of molecules with near octahedral symmetry. However, the approach used above should be useful for all configurations with molecular geometries close to several types of more symmetrical idealized systems.

π *Bonding in* [Fe(py)$_4$(NCS)$_2$].—With e_σ values fixed at 3 700 cm^{-1}, investigation of the dependence of the magnetic susceptibilities on π bonding was pursued in a similar manner to that for the cobalt compound. This began with a wide range of e_π values, sampled at fairly coarse intervals of 200 cm^{-1}, for $\zeta = 400$ cm^{-1}. The π-bonding directions were defined in the same way as for [Co(py)$_4$(NCS)$_2$]. Figure 9 shows two distinct regions of fit, (C) and (D). Region (D) was discarded because it corresponds to an unacceptable value for ϕ of $-70°$ compared with the experimental value of $+7°$. Further, the fits in this region involve negative e_π parameters for both thiocyanate and py ligands, implying π-accepting roles for both ligands: a change in the bonding role of thiocyanate, in particular, on replacing Co$^{\text{II}}$ by Fe$^{\text{II}}$ seems unlikely. In contrast, region (C) in Figure 9 is favoured because the best fit to principal crystal susceptibilities occurs with $e_{\pi x}$(NCS) = 400, $e_{\pi y}$(NCS) = 600, and e_π(py) = 200 cm^{-1} when the calculated ϕ value of 2° agrees remarkably well with the observed value of 7°. The e_π values quoted thus far correspond to sampling with a preliminary coarse grid of 200 cm^{-1} units.

The region spanned by e_π(NCS) values between 0 and 600 cm^{-1} was investigated in detail using 25 cm^{-1} increments with e_π(py) in 50 cm^{-1} steps, sufficient to define the region (C). Repeating the process for a selection of ζ values showed that while the quality of fit depended on ζ somewhat, the position of the optimal-fitting region (C) did not. Figure 10 shows the effect of variation of spin–orbit coupling on the best fit, defined with respect to principal susceptibilities and ϕ values simultaneously at 290 and 90 K. The best agreement was found for ζ in the range 300—350 cm^{-1}. As for the cobalt compound, the region

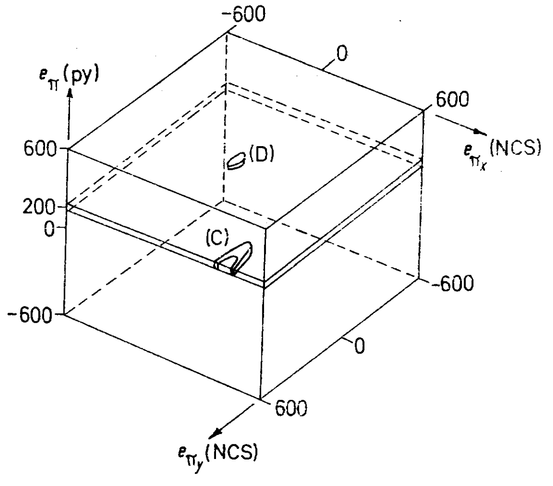

FIGURE 9 Regions of π-parameter space giving good fit to all three crystal susceptibilities of [Fe(py)$_4$(NCS)$_2$] simultaneously

of best fit depended little on k, but, unlike the situation for $[Co(py)_4(NCS)_2]$, fits for the orbital-relation factor $k = 0.9$ were only slightly worse than for $k = 1.0$. The quality of fit deteriorated rapidly for $k < 0.9$.

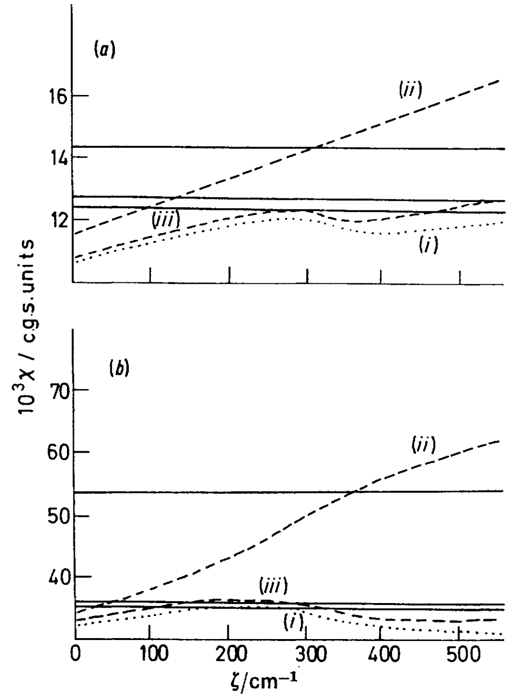

FIGURE 10 Variation of calculated (— — —) crystal susceptibilities $[Fe(py)_4(NCS)_2]$ as functions of ζ for σ- and π-bonding parameters corresponding to optimal fit in region (C) of Figure 9 at 290 (*a*) and 90 K (*b*): (*i*) χ_1, (*ii*) χ_2, and (*iii*) χ_3; (——), observed values

After these investigations of the sensitivity of the π-bonding parameters to ζ and k, the overall best fit (Figure 11) occurred for $e_{\pi x}$(NCS) = 350, $e_{\pi y}$(NCS) = 450, and e_π(py) = 100 cm^{-1}, under which conditions the calculated ϕ value of 5° agreed almost perfectly with that observed.

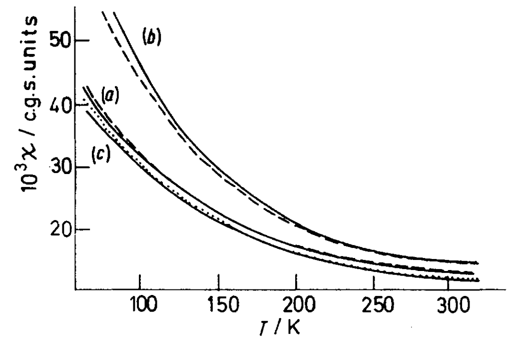

FIGURE 11 Agreement between observed (——) and calculated (— — —) crystal susceptibilities when ζ = 350 cm^{-1}, k = 1.0, e_π(py) = 100 cm^{-1}, $e_{\pi x}$(NCS) = 350 cm^{-1}, and $e_{\pi y}$(NCS) = 450 cm^{-1}: (*a*) χ_1, (*b*) χ_2, and (*c*) χ_3

Outside the region of good fit (C) in Figure 9 the calculated ϕ value deteriorated dramatically to −60°.

DISCUSSION

In terms of the general aims set for this work, we find first that the low-symmetry model described in the previous paper permits excellent fits to all three principal crystal susceptibilities in both $[Co(py)_4(NCS)_2]$ and $[Fe(py)_4(NCS)_2]$. Secondly, it transpires that while some parameter values have been established only approximately those which are of principal concern to the ground-state magnetic properties are fixed fairly sharply. It is particularly interesting and important that the division into poorly and well established parameters in the angular-overlap scheme follows a natural ' bonding ' division into σ and π bonding. Thus, once the complexities of ζ, k, and B parameters were empirically removed, or at least diminished, the present study devolved into an investigation of π bonding. Two equally satisfactory fits were found for the cobalt complex, one for the iron, as summarized in Table 4. We note several points with these results. First, the sensitivity of fit for e_π(py) is *ca.* ±50 cm^{-1}. The present study shows unambiguously that some π bonding to pyridine is necessary to account for the magnetic properties, but only a little. Negative or zero e_π values for py give wholly unacceptable comparison with experiment. The small extent of ligand π donation appears to agree qualitatively with a.o.m. spectral studies on $[Ni(py)_4(NCS)_2]$ and, more importantly, with general chemical evidence with respect to py as a ligand.[8,9] It is particularly encouraging to see that a ligand-field model for magnetism as general as that used here is capable of fitting experimental data accurately with parameters which correlate well with otherwise established chemical concepts. The general agreement between e_π(py) values for the cobalt and iron compounds reinforces these points. The somewhat greater e_π values for the thiocyanate ligand also seem sensible, particularly when we note the agreement between the two complexes with respect to the relative magnitudes of $e_{\pi x}$ and $e_{\pi y}$: the electronic-basis sets used for these two systems are quite different, of course.

TABLE 4

Summary of e_π parameters (cm^{-1})

	Fit	$e_{\pi x}$(NCS)	$e_{\pi y}$(NCS)	e_π(py)
$[Co(py)_4(NCS)_2]$	(A)	250	350	100
	(B)	200	200	125
$[Fe(py)_4(NCS)_2]$	(C)	350	450	100

The relative magnitudes of e parameters for the Co^{II} and Fe^{II} compounds must be viewed empirically. Thus we expect the energy of the metal orbitals for d^6 to lie at higher energy than those of d^7 involving the higher nuclear charge. Equation (2) therefore suggests larger e parameters in the iron than in the cobalt compound.

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[8] M. A. Hitchman, *Inorg. Chem.*, 1972, **11**, 2387.

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

On the other hand, the greater effective nuclear charge on the cobalt ion will contract the *d* orbitals more and reduce the magnitude of the appropriate overlap integrals. No doubt a compromise is reached between the two opposing effects.

Comparison of observed and calculated susceptibilities has taken place at the crystal rather than the molecular level for reasons discussed in the preceding paper. It is still of interest, however, to consider the calculated molecular magnetic ellipsoids in view of the initial difficulties experienced with the interpretation of the crystal susceptibilities under the assumption of tetragonal symmetry, outlined in the introduction. The molecular properties are, of course, those first calculated, crystal susceptibilities following from a simple tensorial transformation and summation. The directions of the calculated principal molecular susceptibilities with respect to the molecules are listed in Table 5, corresponding to the fits (A)—(C) in Table 4. The reference molecular axes, labelled in Figure 1, have the following direction cosines with respect to the crystal axes:

TABLE 5

Orientations of molecular magnetic ellipsoids in $[Co(py)_4(NCS)_2]$ and $[Fe(py)_4(NCS)_2]$ at 290 K

		Orientation/°		
		X	Y	Z
(*a*) Fit (A), $[Co(py)_4(NCS)_2]$, $\phi = 84°$				
K_1	14 505	77.7	97.5	14.5
K_2	9 190	112.5	25.8	78.1
K_3	10 677	26.0	65.5	98.3
(*b*) Fit (B), $[Co(py)_4(NCS)_2]$, $\phi = 29°$				
K_1	8 854	127.1	47.2	65.3
K_2	12 499	73.8	47.9	133.4
K_3	12 930	41.7	72.8	53.5
(*c*) Fit (C), $[Fe(py)_4(NCS)_2]$, $\phi = 5°$				
K_1	10 799	74.9	108.1	23.9
K_2	13 168	138.7	58.0	66.8
K_3	15 332	52.6	38.0	84.6

	a	b	c'
X	0.5067	0.7665	−0.3947
Y	−0.0980	−0.4037	−0.9097
Z	−0.8565	0.4996	−0.1295

It should be clear that no simple relation between the obvious structural (σ-bonding directions) and magnetic axes is apparent. Nor is there any simple relation between the orientations of the molecular magnetic ellipsoids in the iron and cobalt molecules: that there need be none follows in these very low-symmetry molecules from the different *d* configuration involved.

All this serves to emphasize strongly that paramagnetic properties reflect electronic arrangements in only a few levels of the complete manifold. Thus, while *approximately* higher symmetry resulting from appropriate geometrical structural features must be incorporated into the electronic structure *as a whole*, such approximations need not extend uniformly throughout the electronic manifold and be reflected in diverse properties which depend more on some levels than on others. In systems lacking sufficient exact symmetry to predetermine the orientation of the magnetic ellipsoid we must expect that approximate structural and chemical symmetry will provide a completely unreliable guide. We therefore consider that the use of a model such as that described in the previous paper and exploited in this is now mandatory in magnetic studies on low-symmetry molecules.

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