# Magnetic Properties of Hexakis(pyridine *N*-oxide)cobalt(II) Perchlorate

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The magnetic properties of the title compound have been measured down to 2 K using the Faraday and critical-torque techniques. Agreement has been obtained with literature values at room temperature, but not with a previous study between 1.5 and 20 K using an inductance method. The reason for the discrepancy is not clear. The angular-overlap ligand-field model (a.o.m.) has been used to interpret the results, and the inclusion of the doublet states in the basis set has a marked effect on the nature of the fit obtained. Using the restricted quartet basis set, it is necessary to have the orbital-reduction factor $k = 1.10$, but a value of $k = 1.00$ gives the best fit when the complete basis set is used. If $\zeta$ is assumed to have the free-ion value (525 $cm^{-1}$) and the co-ordinated oxygen is assumed to be $sp^2$-hybridized, then the a.o.m. parameters are found to be approximately $e_\sigma = 4\,300$ $cm^{-1}$ and $2e_{\pi x} = e_{\pi y} = 1\,330$ $cm^{-1}$. These values agree reasonably well with those obtained for the isomorphous nickel complex. The inclusion of the doublet states in $d^3$ and $d^7$ systems is important in trigonal compounds where the ground state is of $^4A$ symmetry.

THE bivalent metal pyridine *N*-oxide complexes $[M(pyo)_6]X_2$ (pyo = pyridine *N*-oxide; M = Hg, Zn, Co, Cu, Fe, Mn, or Ni; X = $ClO_4$ or $BF_4$) form an isomorphous series [1] in which the metal ion is in a site of exact $S_6$ symmetry and the molecular three-fold axis lies along the crystallographic *c* axis. Magnetic-susceptibility measurements on the nickel complexes [2-5] are consistent with a large trigonal field which is surprising since the co-ordinated oxygen atoms are at almost exactly octahedral positions.[1] On the basis of a point-charge crystal-field model [2] the trigonal field is caused by a crystallographically undetected elongation of the octahedron and, although the distortion required is only *ca.* 1°, an interpretation based on the angular-overlap model [6-9] (a.o.m.) seems more realistic from a chemical point of view. If one assumes that the trigonal field is produced only by an anisotropy in the $\pi$ bonding between the metal ion and the oxygen atom of the ligand and that the oxygen is $sp^2$-hybridized, then it is possible [4] to obtain values for the three a.o.m. parameters $e_\sigma$, $e_{\pi x}$, and $e_{\pi y}$ which are a measure of the $\sigma$-bonding contribution and $\pi$-bonding contributions in the M–O–N plane and perpendicular to this plane respectively. For a pseudo-octahedral nickel complex the interpretation of the magnetic susceptibility is simplified by the orbital non-degeneracy of the ground state, and a more stringent test of the a.o.m. is the interpretation of the magnetism of the isomorphous cobalt complex where the trigonal field decreases the orbital degeneracy of the ground state and hence has a marked effect on the average magnetic moment as well as the magnetic anisotropy. A recent paper [10] reports the principal magnetic susceptibilities of $[Co(pyo)_6][ClO_4]_2$ between 1.5 and 20 K at zero applied magnetic field. In this paper we extend the measurements to room temperature and in magnetic fields up to 5 T. Our low-temperature results differ markedly from the literature values and the reason for this discrepancy is not known.

## EXPERIMENTAL

The complex $[Co(pyo)_6][ClO_4]_2$ was prepared as for the nickel complex [2] and red rhombohedral crystals (*ca.* 10 mg) were grown from methanol. The *c* axes were located by *X*-rays and the cell constants were in agreement with the literature values.[11] The average susceptibility and magnetic anisotropy were measured by the Faraday and Krishnan critical-torque methods using equipment described previously.[12] When an attempt was made to measure the average magnetic susceptibility at 4.17 K in a magnetic field of 5 T the crystallites tended to align due to the large magnetic anisotropy and hence the magnetization results at low temperatures were determined on a mull of the complex in petroleum jelly. The absolute values of the magnetic susceptibility were obtained by scaling the results to agree with those determined at higher temperatures and lower fields (1 T). The magnetic anisotropy at low temperatures was measured in a magnetic field of 0.08 T and hence should be unaffected by magnetic saturation. At >4.6 K the average magnetic moment at zero field (obtained by extrapolation) was within 0.03 B.M.* of the value at 1 T and the discrepancy decreased rapidly with increasing temperature. The principal magnetic susceptibilities derived from $\Delta\chi$ and $\bar{\chi}$ should therefore agree with the values reported in the literature and measured at zero applied field. Our values are very different, however, and hence $\chi_\perp$ was measured directly on the Faraday balance and the values were in reasonable agreement with those obtained from $\Delta\chi$ and $\bar{\chi}$. Although the measurements of the magnetic anisotropy should not be affected by magnetic saturation, they could be affected at the lowest temperatures by the onset of magnetic ordering. The direct determination of $\chi_\perp$ could also be slightly in error, particularly at higher

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* Throughout this paper: 1 B.M. ≈ $9.27 \times 10^{-24}$ A $m^2$.

[1] A. D. van Ingen Schenau, G. C. Verschoor, and C. Romers, *Acta Cryst.*, 1974, **B30**, 1686.

[2] D. J. Mackey and S. V. Evans, *J.C.S. Dalton*, 1976, 2004.

[3] D. J. Mackey, *J.C.S. Dalton*, 1977, 40.

[4] D. J. Mackey and R. F. McMeeking, *J.C.S. Dalton*, 1977, 2186.

[5] R. L. Carlin, C. J. O'Connor, and S. N. Bhatia, *J. Amer. Chem. Soc.*, 1976, **98**, 3523.

[6] C. E. Schäffer, *Structure and Bonding*, 1968, **5**, 68.

[7] C. E. Schäffer, *Pure Appl. Chem.*, 1970, **24**, 361.

[8] C. E. Schäffer, *Structure and Bonding*, 1973, **14**, 69.

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

[10] R. L. Carlin, C. J. O'Connor, and S. N. Bhatia, *J. Amer. Chem. Soc.*, 1976, **98**, 685.

[11] T. J. Bergendahl and J. S. Wood, *Inorg. Chem.*, 1975, **14**, 338.

[12] D. J. Mackey, S. V. Evans, and R. L. Martin, *J.C.S. Dalton*, 1976, 1515.

temperatures, since it is difficult to correct for the diamagnetic contribution of the suspension as part of it extends into the region at the end of the superconducting coils where the field gradient could be very large. We were unable to measure $\chi_{\parallel}$ directly since the torque on the crystal was very large at low temperatures and the crystal was dragged to the side of the variable-temperature insert.

The magnetic anisotropy of a second crystal was also measured between 77 and 300 K and the results on the two crystals were in good agreement. The two sets of measurements using the Faraday balance ($\bar{\chi}$ and $\chi_{\perp}$) were made *ca.* 1 year apart and the calibration of the instrument was rechecked during this interval. The temperature calibration cannot be in error since the Faraday and anisotropy balances were calibrated using different GaAs diodes and measurements on the Faraday balance were further checked against literature values of the low-temperature magnetic susceptibility of $Cu[SO_4]\cdot5H_2O$. The discrepancy between our measurements and the literature results on $[Co(pyo)_6][ClO_4]_2$ at <20 K is quite surprising since there is good agreement between our values [2,3] of the low-temperature magnetic susceptibility of $[Ni(pyo)_6]X_2$ ($X = BF_4$ or $ClO_4$) and the results reported [5] by the same workers for $[Ni(pyo)_6][ClO_4]_2$. Our room temperature value of $\bar{\mu}$ for $[Co(pyo)_6][ClO_4]_2$ (4.72 B.M.) is in reasonable agreement with the literature values of 4.69 (ref. 13) and 4.84 B.M.[14]

The average magnetic susceptibility was corrected for a diamagnetic contribution using Pascal's constants and the anisotropy was corrected for a diamagnetic contribution of $(\chi_{\parallel} - \chi_{\perp}) = 111 \times 10^{-6}$ cm³ mol⁻¹ as measured for the isomorphous zinc complex. The zinc complex has been found to have a paramagnetic impurity (probably $Fe^{II}$) but the anisotropy correction is thought to be correct to within $\pm20 \times 10^{-6}$ cm³ mol⁻¹. Both these corrections are small at room temperature and negligible at low temperatures. The calculations were performed using a program described previously.[4,9] All the magnetic moments were calculated * using the equation $\mu = 2.828(\chi T)^{\frac{1}{2}}$.

## RESULTS AND DISCUSSION

For a compound in which the metal ion and the six ligating atoms have exact $O_h$ symmetry, the a.o.m. parameters are related to $Dq$ by expression (1).[4] This

$$10\,Dq = 3e_{\sigma} - 2(e_{\pi x} + e_{\pi y}) \qquad (1)$$

equation was only approximately valid for $[Ni(pyo)_6][BF_4]_2$ since there was a very slight distortion of the $NiO_6$ core along the molecular three-fold axis. In $[Co(pyo)_6][ClO_4]_2$ the oxygen atoms are at exact octahedral positions [11] and hence equation (1) holds exactly. In this case the trigonal component of the ligand field and the magnetic anisotropy are determined by the anisotropy in the $\pi$ bonding between the cobalt ion and the oxygen atoms. The trigonal field is defined by $\Delta e_{\pi} = e_{\pi x} - e_{\pi y}$ and is totally independent of the individual values of $e_{\sigma}$, $e_{\pi x}$, and $e_{\pi y}$.

The values of $Dq$ (890 cm⁻¹) and $B$ (780 cm⁻¹) were taken from the literature [15] and the value of $Dq$ was kept constant while the trigonal field was varied by using expressions (2) and (3); hence the ligand field is deter-

$$10\,Dq = 3e_{\sigma} = 8\,900\ \text{cm}^{-1} \qquad (2)$$

$$e_{\pi x} = -e_{\pi y} = \tfrac{1}{2}\Delta e_{\pi} \qquad (3)$$

mined by only one unknown parameter ($\Delta e_{\pi}$). Since the complete $d^7$ manifold requires the diagonalization of a 120 × 120 matrix, the magnetic properties of $Co^{2+}$ are usually interpreted using the restricted $^4F$ and $^4P$ basis set. This involves the diagonalization of a 40 × 40 matrix and this basis set was used in our initial investigation of the magnetic properties of $[Co(pyo)_6][ClO_4]_2$. Since no doublet states are included, the Racah parameter $C$ is not required and the magnetism is a function of the three unknown parameters, $\Delta e_{\pi}$, $\zeta$, and the orbital-reduction factor $k$. The value of $\zeta$ would be expected to be no greater than the free-ion value which is reported as 515 (ref. 16), and 528 cm⁻¹.[17]

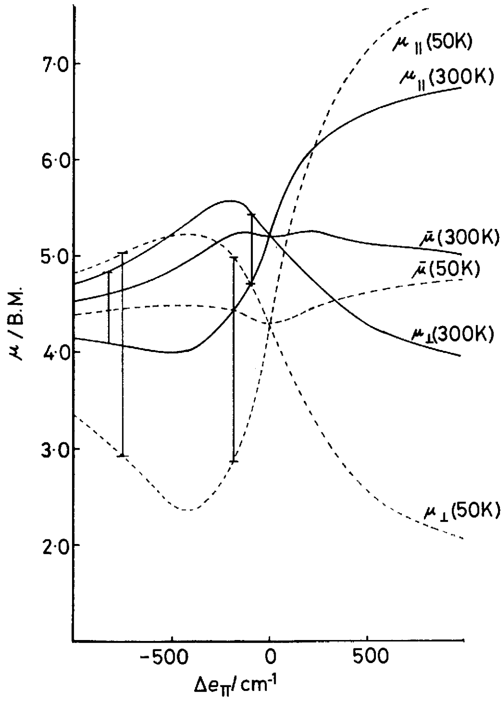

FIGURE 1 Variations of magnetic moment with $\Delta e_{\pi}$. The curves are calculated for $Dq = 890$ cm⁻¹, $B = 780$ cm⁻¹, $\zeta = 500$ cm⁻¹, and $k = 1.0$ using the restricted $^4F + {}^4P$ basis set. The vertical lines show the experimental values of the magnetic anisotropy

In Figure 1 we have plotted the average and principal magnetic moments as a function of the trigonal field at two temperatures and it is seen that the sign of the experimentally observed anisotropy ($\chi_{\perp} > \chi_{\parallel}$) can only

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* To convert into S.I. units, $\chi$ should be multiplied by $4\pi \times 10^{-6}$ and the magnetic moment is then given by the expression $\mu = 797.74(\chi T)^{\frac{1}{2}}$.

[13] J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley, and S. Y. Tyree, *J. Amer. Chem. Soc.*, 1961, **83**, 3770.

[14] R. Whyman, W. E. Hatfield, and J. S. Paschal, *Inorg. Chim. Acta*, 1967, **1**, 113.

[15] J. Reedijk, *Rec. Trav. Chim.*, 1969, **88**, 499.

[16] B. N. Figgis, ' Introduction to Ligand Fields,' Interscience, New York, 1968, p. 60.

[17] A. Abragam and B. Bleaney, ' Electron Paramagnetic Resonance of Transition Ions,' Clarendon, Oxford, 1970, p. 378.

be reproduced if $\Delta e_\pi$ is negative. It can also be seen that the magnetic anisotropy at 300 and 50 K goes through a maximum value at approximately $\Delta e_\pi = -400$ cm$^{-1}$. Similar curves are obtained for any reasonable values of $k$ and $\zeta$ and the experimental magnetic anisotropy corresponds to $\Delta e_\pi$ values of *ca.* $-800$ or $-200$ cm$^{-1}$. This ambiguity is readily resolved since both the absolute values and temperature dependences of the average magnetic moment are very different in the two cases and it was not possible to obtain a fit for $\Delta e_\pi$ *ca.* $-200$ cm$^{-1}$. Decreasing $k$ decreased both $\mu_\parallel$ and $\mu_\perp$, while decreasing $\zeta$ had the effect of decreasing $\mu_\perp$ and increasing $\mu_\parallel$ (*i.e.* decreasing the anisotropy). It is worth noting that the average magnetic moment at room temperature can vary by 0.7 B.M. depending on the value of the trigonal field, in contrast to the average magnetic moments of ions having orbitally non-degenerate ground states where variations of up to 0.02 B.M. are more common.[11,18]

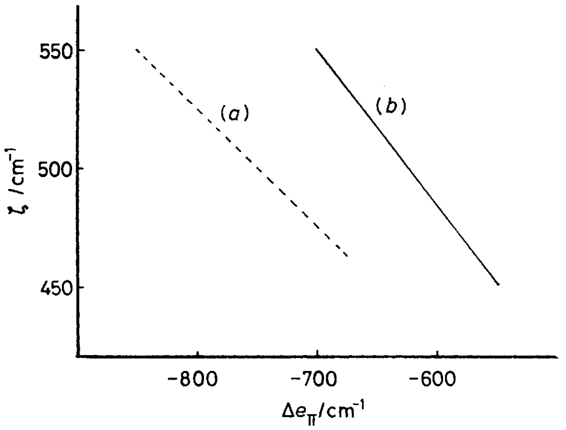

FIGURE 2 Values of $\zeta$ and $\Delta e_\pi$ needed for the best fit to the magnetic moments of $[Co(pyo)_6][ClO_4]_2$ using $Dq = 890$ cm$^{-1}$, $B = 780$ cm$^{-1}$, and $k = 1.0$: (*a*) $^4F$ and $^4P$ basis set; (*b*) complete basis set with $C = 3\,033$ cm$^{-1}$

In order to obtain an estimate of the discrepancy between the calculated and observed values, the least-squares standard deviation was evaluated for both principal magnetic moments at ten temperatures between 30 and 300 K. The values at <30 K were not used since the experimental results could be affected by the combined effects of magnetic saturation and magnetic exchange since the complex is known [10] to be antiferromagnetic with $T_N$ *ca.* 0.42 K. No unique fit was found, but for $k = 1$ the best fit for both $\mu_\parallel$ and $\mu_\perp$ was obtained for the values of $\zeta$ and $\Delta e_\pi$ shown in Figure 2(*a*). The standard deviation was *ca.* 0.10 B.M. for both $\mu_\parallel$ and $\mu_\perp$. The sign of the trigonal field is such that the orbital singlet ($^4A_{1g}$) component of the $^4T_{1g}$ ($O_h$) term lies lower in energy. Second-order spin–orbit mixing with other states at higher energy then splits this $^4A_{1g}$ level into two Kramers doublets and it is this splitting which dominates the magnetic anisotropy. Thus for all the values of $\zeta$ and $\Delta e_\pi$ shown in Figure 2(*a*) the zero-field splitting ($\Delta$) of the $^4A_{1g}$ level was found to be 53 cm$^{-1}$. Although it is possible to obtain a fit when $\zeta$ is greater than the free-ion value, the fit becomes very poor for $\zeta < 475$ cm$^{-1}$.

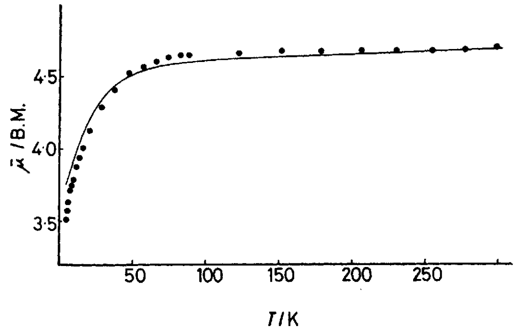

FIGURE 3 Calculated average magnetic moment of $[Co(pyo)_6][ClO_4]_2$. The curve is virtually identical for parameter sets 2 and 9 from the Table. (●), Experimental values

The fit obtained is not particularly good and, since the calculated values of $\mu_\parallel$ and $\mu_\perp$ were low on average, the fit could only be improved by taking $k > 1$. The best fit was obtained for $k = 1.10$, and for $\Delta e_\pi$ and $\zeta$ values of $-800$ and 525 cm$^{-1}$ respectively the standard deviation of the fit was reduced to 0.06 B.M. The calculated and experimental values of $\bar{\mu}$ and $\Delta\chi$ are compared in Figures 3—5. Values of $k$ greater than unity have been postulated before,[19] but one obvious reason for the anomalous value of $k$ was that an incomplete basis set had been used and it was decided to do some calculations using the complete $d^7$ manifold.

The inclusion of all the doublet levels had a marked effect on the calculated magnetic moments and, although the previous interdependence of the parameters $\Delta e_\pi$ and $\zeta$ remained, it was found that a smaller value of the trigonal field was needed for a given value of $\zeta$ [see Figure 2(*b*)]. Moreover, the best fit was obtained for $k = 1.00$, and using values of $\zeta$ and $\Delta e_\pi$ from Figure 2(*b*) the calculated magnetic properties were virtually identical to those shown in Figures 3—5 using the restricted $^4F$

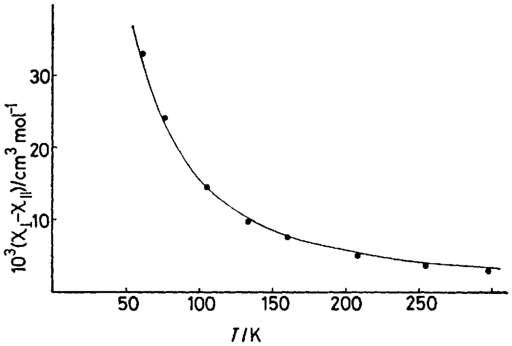

FIGURE 4 Calculated magnetic anisotropy of $[Co(pyo)_6][ClO_4]_2$. The same comments apply as for Figure 3

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[18] D. J. Mackey, *Mol. Phys.*, 1977, **33**, 849.

[19] J. J. Salzmann and H. H. Schmidtke, *Inorg. Chim. Acta*, 1969, **3**, 207.

and $^4P$ basis set. In agreement with the earlier observation that the magnetic anisotropy was dominated by the zero-field splitting, the value of $\Delta$ obtained from diagonalization of the complete basis set was found to be 51 cm$^{-1}$, similar to the value of 53 cm$^{-1}$ obtained from calculations involving only the quartet levels.

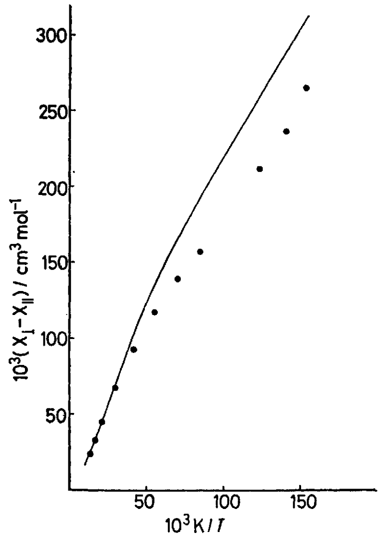

Figure 5 Calculated magnetic anisotropy of $[Co(pyo)_6][ClO_4]_2$ at low temperatures. The same comments apply as for Figure 3

The values of $Dq$ and $B$ in the literature were obtained from solution spectra and it is possible that they could differ in the solid state. In addition, the value of the Racah parameter $C$ is unknown since no spin-forbidden bands were observed; hence these three parameters were varied to determine what effect they had on the magnetism. The results are shown in the Table together with a number of calculations for various combinations of $\Delta e_\pi$ and $\zeta$ obtained from Figure 2(*b*) and two calculations using the restricted $^4F + {}^4P$ basis set. It is apparent that the magnetic properties are not very dependent on $Dq$, $B$, or $C$ although the fit is improved slightly when $Dq$ is reduced to 840 cm$^{-1}$. Hence the actual energies of the higher-lying levels, including the doublet states, are not very important although it is essential that the complete basis set is used.

TABLE

Calculated properties of $[Co(pyo)_6][ClO_4]_2$

| Set | $k$ | $\zeta$ (cm$^{-1}$) | $\Delta e_\pi$ (cm$^{-1}$) | $Dq$ (cm$^{-1}$) | $B$ (cm$^{-1}$) | $C$ (cm$^{-1}$) | Basis set [a] | $\sigma_\parallel$ [b] (B.M.) | $\sigma_\perp$ [b] (B.M.) | $g_\parallel$(G) [c] | $g_\perp$(G) [c] | $g_\parallel$(E) [c] | $\Delta$ (cm$^{-1}$) | $\frac{g_\parallel(E)}{g_\parallel(G)}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.00 | 550 | −700 | 890 | 780 | 3 030 | F | 0.06 | 0.05 | 2.232 | 4.864 | 6.427 | 51 | 2.88 |
| 2 | 1.00 | 525 | −665 | 890 | 780 | 3 030 | F | 0.06 | 0.05 | 2.224 | 4.863 | 6.400 | 51 | 2.88 |
| 3 | 1.00 | 500 | −630 | 890 | 780 | 3 030 | F | 0.07 | 0.05 | 2.216 | 4,861 | 6.373 | 51 | 2.88 |
| 4 | 1.00 | 450 | −550 | 890 | 780 | 3 030 | F | 0.09 | 0.05 | 2.202 | 4.867 | 6.311 | 51 | 2.87 |
| 5 | 1.00 | 525 | −665 | 840 | 780 | 3 030 | F | 0.05 | 0.05 | 2.235 | 4.879 | 6.431 | 52 | 2.88 |
| 6 | 1.00 | 525 | −665 | 890 | 820 | 3 030 | F | 0.07 | 0.05 | 2.225 | 4.870 | 6.400 | 52 | 2.88 |
| 7 | 1.00 | 525 | −665 | 890 | 780 | 2 800 | F | 0.06 | 0.06 | 2.227 | 4.859 | 6.402 | 48 | 2.88 |
| 8 | 1.00 | 525 | −665 | 890 | 780 | — | Q | 0.28 | 0.05 | 2.201 | 4.881 | 6.376 | 69 | 2.90 |
| 9 | 1.10 | 525 | −800 | 890 | 780 | — | Q | 0.07 | 0.05 | 2.204 | 4.869 | 6.479 | 53 | 2.94 |

[a] The symbols F and Q refer to the full basis set and the $^4F + {}^4P$ basis set respectively. [b] Least-squares standard deviation of the fit to ten experimental values between 30 and 300 K. [c] The symbols G and E refer to the ground state and first excited state respectively. $g_\perp(E) = 0$ by symmetry.

The effect of including the doublet levels is shown more clearly in Figure 6 where we compare the interpolated values of $\mu_\parallel$, $\mu_\perp$, and $\bar{\mu}$ with magnetic moments calculated using identical values of the various parameters within the two basis sets. The difference between the two calculations can be explained by referring to the Table where it is seen that the inclusion of the doublet levels has only a slight effect on the $g$ values but the zero-field splitting is decreased by *ca.* 25%. Since the upper level has a much larger value of $g_\parallel$, the lowering of this level produces a fairly large increase in $\mu_\parallel$ due to its greater population. The effect on $\mu_\perp$ is less pronounced since there are no matrix elements of $\mu_\perp$ within the upper level and this operator only affects the perpendicular magnetic moment in second order. At temperatures significantly greater than $\Delta/k$ the zero-field splitting has a negligible [20] effect on $\bar{\mu}$ and hence the calculated high-temperature average magnetic moments are unaffected by the inclusion of the doublet levels.

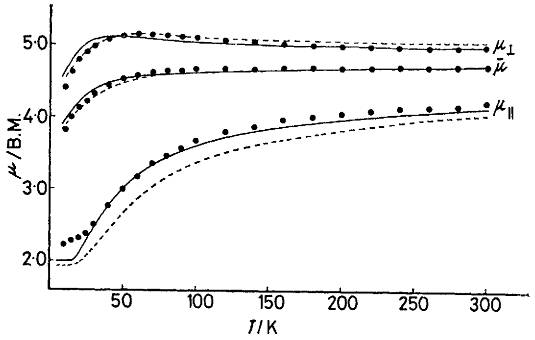

FIGURE 6 Calculated magnetic moments for parameter sets 2 (——) and 8 (– – – –) of the Table. The interpolated experimental values are shown for comparison

In the Table we have also included the calculated $g$ values for the two lowest Kramers doublets. The $^4A_{1g}$ state from which they arise can be characterized by fictitious spin-projection quantum numbers having half-integral values ranging from $^+\frac{3}{2}$ to $^-\frac{3}{2}$. An axial crystal field splits this state into two doublets characterized by $M_s = \pm\frac{3}{2}$ and $M_s = \pm\frac{1}{2}$ and the magnitude of the

[20] J. S. Griffith, 'The Theory of Transition Metal Ions,' Cambridge University Press, 1964, p. 265.

splitting will depend on the amount of orbital angular momentum mixed into the state by spin–orbit coupling. Since the $^4A_{1g}$ state originated from a $^4T_{1g}(O_h)$ state which had been split by *ca.* 1 500 cm$^{-1}$ by the trigonal field, it contains a significant orbital contribution and thus the splitting of 51 cm$^{-1}$ is relatively large. From the Table it can be seen that the $M_s = \pm\frac{1}{2}$ doublet lies lower in energy and the deviation of $g_{\parallel}$(G) from 2.00 is due to the admixed orbital angular momentum. For the first excited state characterized by $M_s = \pm\frac{3}{2}$ the magnetic-moment operator has no matrix elements in the perpendicular direction and $g_{\perp}$(E) is zero by symmetry. If the two Kramers doublets could really be labelled in terms of the projections of a fictitious spin operator, then the higher-energy Kramers doublet would be split by an amount exactly three times that of the lower doublet in a magnetic field applied parallel to the three-fold axis, *i.e.* $g_{\parallel}$(E)/$g_{\parallel}$(G) should be exactly 3.0 and not *ca.* 2.88 as shown in the Table. Hence the low-temperature magnetic properties cannot be truly represented within the spin-Hamiltonian formalism appropriate to a quartet state since the trigonal field required to split the state by 51 cm$^{-1}$ is so large that the wavefunctions of the $^4A_{1g}$ state are considerably changed. When the splitting is much smaller, as found in the $^4A_{2g}(O_h)$ ground state of Mn$^{4+}$ in $[\mathrm{NH_4}]_6[\mathrm{MnMo_9O_{32}}]\cdot 8\mathrm{H_2O}$ where $\Delta = 1.72$ cm$^{-1}$, the spin-Hamiltonian and crystal-field calculations are identical and it is then obviously advantageous to calculate the magnetic properties within the spin-Hamiltonian formalism.[18]

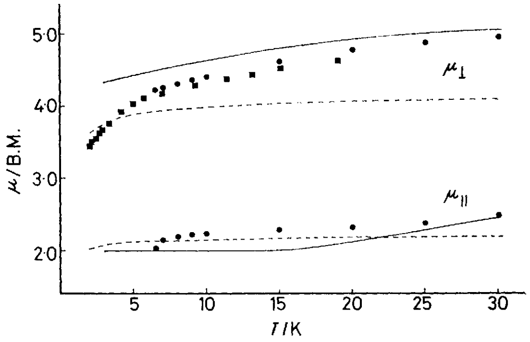

FIGURE 7 Calculated magnetic moments for parameter set 2 of the Table (——). The experimental values were obtained from the average susceptibility and the magnetic anisotropy (●) or by direct measurement on a single crystal (■). (– – – –), Best fit to the experimental values of ref. 10

*Low-temperature Results.*—The experimental values obtained at <30 K present a dilemma since they do not agree with the literature values nor do they agree well with the principal magnetic moments calculated using the parameters obtained from fitting the magnetism between 30 and 300 K (Figure 7). Although the discrepancy between our results and the literature values could be due to an impurity in $[\mathrm{Co(pyo)_6}][\mathrm{ClO_4}]_2$ this is considered unlikely. In order to explain the difference any impurity would have to have both a large average magnetic moment and a large magnetic anisotropy at low temperature and the only obvious candidate is the iron(II) ion. We have measured the average magnetic moment of $[\mathrm{Fe(pyo)_6}][\mathrm{ClO_4}]_2$ down to 2 K and the value is significantly higher than that of the cobalt complex. Moreover, it has been reported [21] that the ground state of this complex is a doublet having $g_{\parallel}$ *ca.* 9 and $g_{\perp}$ *ca.* 0 with no other states within 100 cm$^{-1}$. Hence, at low temperatures, $\mu_{\parallel} \gg \mu_{\perp}$ and it is not possible to explain the differences between our results and the literature values in terms of an impurity having a larger average magnetic susceptibility and a very large magnetic anisotropy of the opposite sign to that observed for the cobalt complex.

At <30 K the experimental values of $\mu_{\perp}$ become increasingly lower than the calculated values and this is probably due to the effects of magnetic exchange. The same explanation probably accounts for the discrepancy between the calculated and observed magnetic anisotropy at <20 K (see Figure 5). The behaviour at low temperatures is quite similar to that observed in the isomorphous nickel complex,[2] and cannot be explained in terms of a temperature-dependent trigonal field since it is not possible to simultaneously decrease both the average magnetic susceptibility and the magnetic anisotropy by such a mechanism. At temperatures low enough to depopulate the first excited state the value of $\mu_{\parallel}$ should be independent of temperature since there are no matrix elements of $\hat{\mu}_{\parallel}$ between the ground state and the $M_s = \pm\frac{3}{2}$ state and hence the second-order Zeeman contribution should be much smaller than the first-order contribution. Experimentally, $\mu_{\parallel}$ is found to be almost constant below *ca.* 25 K apart from a slight decrease at <7 K which could be due to exchange effects. In agreement with the known antiferromagnetic interactions in $[\mathrm{Co(pyo)_6}][\mathrm{ClO_4}]_2$, the field dependence of the perpendicular magnetic moment at low temperatures is not a simple function of $H/T$ as expected for an isolated Kramers doublet (Figure 8).

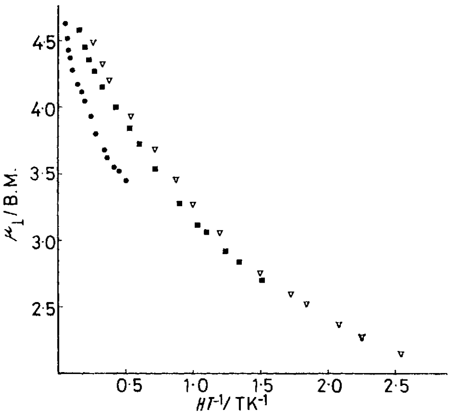

FIGURE 8 Experimental values of $\mu_{\perp}$ at low temperatures in fields of 1 (●), 3 (■), and 5 T (▽)

The e.s.r. spectrum of cobalt doped into the iso-

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[21] J. R. Sams and T. B. Tsin, *Chem. Phys.*, 1976, **15**, 209.

morphous zinc complex has been recorded[10] at 4.2 K and the $g$ values of the ground-state Kramers doublet ($g_{\parallel}$ 2.26 ± 0.01, $g_{\perp}$ 4.77 ± 0.01) are in reasonable agreement with the calculated values from our high-temperature fit (see Table).

*Conclusions.*—Although the oxygen atoms are at exactly octahedral positions in $[Co(pyo)_6][ClO_4]_2$, the magnetic anisotropy is very large and can be satisfactorily interpreted in terms of the angular-overlap model by an anisotropy in the $\pi$ bonding between the cobalt ion and the oxygen atoms. Although no unique fit was obtained, $\Delta e_{\pi}$ was found to be in the range $-550$ to $-700$ cm$^{-1}$. Since the value of $k$ was found to be unity it is reasonable to expect that $\zeta$ should be close to the free-ion value, and if this is taken as 525 cm$^{-1}$ then from Figure 2(*b*) $\Delta e_{\pi}$ is found to be $-665$ cm$^{-1}$. The Co–O–N angle in $[Co(pyo)_6][ClO_4]_2$ is 119°,[14] and if the oxygen atom is assumed to be $sp^2$-hybridized then it is easy to show that $e_{\pi x} = \frac{1}{2}e_{\pi y}$. Combining this with the value of $\Delta e_{\pi}$ and using equation (1), we find that $e_{\sigma}$ *ca.* 4 300 cm$^{-1}$ and $2e_{\pi x} = e_{\pi y} \simeq 1\,330$ cm$^{-1}$. These values agree reasonably well with those obtained[4] for the isomorphous nickel complex (4 390, 830, and 1 660 cm$^{-1}$ respectively) when it was also assumed that $k = 1$ and $\zeta$ had the free-ion value.

It is important to note that very different values of these a.o.m. parameters would have been obtained if the calculations had only been performed on the restricted $^4F + {}^4P$ basis set and we would also have required a value of $k$ greater than unity. Both the calculated zero-field splitting of the $^4A_{1g}$ state and the magnetic anisotropy are very dependent on the inclusion of the doublet levels and the situation is similar to that found[18] for the manganese(IV) ion in $[NH_4]_6[MnMo_9O_{32}]\cdot 8H_2O$. In the latter compound the zero-field splitting of the $^4A_{2g}$ ground state and the magnetic anisotropy were much smaller than observed in $[Co(pyo)_6][ClO_4]_2$, but the relative effect of including the doublet levels was even more pronounced and both properties increased approximately three-fold when the doublet levels were included. For both $d^3$ and $d^7$ configurations in trigonal fields it is necessary to diagonalize the complete basis set in order to obtain meaningful values of the magnetic anisotropy and zero-field splittings, although average magnetic moments and $g$ values are fairly insensitive to the choice of basis set.

The $^4T_{1g}(O_h)$ state is split by the trigonal field and spin–orbit coupling into six Kramers doublets at energies of *ca.* 0, 51, 1 300, 1 500, 1 700, and 1 900 cm$^{-1}$, the exact values of the higher levels varying by *ca.* ±100 cm$^{-1}$ depending on the values of $\zeta$ and $\Delta e_{\pi}$ used [see Figure 2(*b*)]. An attempt was made to locate the first excited state using a laser Raman spectrometer and, although a transition was observed at *ca.* 50 cm$^{-1}$, the spectrum was identical to that of the zinc complex and it seems that any transition in this region is being obscured by lattice phonons or local modes.

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