Studies in Eight-co-ordination. Part IV.[1] Single-crystal Electronic Spectrum and Magnetic Anisotropy of Tetraphenylarsonium Tetrakis(trifluoroacetato)cobaltate(II)

By **C. David Garner** * and **Frank E. Mabbs**, Chemistry Department, University of Manchester, Manchester M13 9PL

The single-crystal polarised spin-allowed *d–d* spectra and magnetic anisotropy of $[Ph_4As]_2[Co(O_2C{\cdot}CF_3)_4]$ are reported and interpreted by use of a point-charge crystal-field model. The spectral and magnetic properties are generally consistent with the elongated tetrahedral environment provided by the four carboxylato-oxygen atoms at 200(3) pm from the metal. However, the sense of the polarisation of the '$^4A_2 \rightarrow {}^4T_1(F)$' transition suggests that the crystal-field at the cobalt(II) includes a small contribution from the four carboxylato-oxygens 311(3) pm away. Spectral data for certain spin-forbidden transitions are also reported.

TETRAPHENYLARSONIUM TETRAKIS(TRIFLUOROACETATO)-COBALTATE(II), $[Ph_4As]_2[Co(O_2C{\cdot}CF_3)_4]$, was first prepared by Bergman and Cotton[2] who determined its crystal structure, and reported its bulk magnetic and solution electronic spectral characteristics. The co-ordination of the cobalt(II) was described as intermediate between four-co-ordinate tetrahedral, and eight-co-ordinate trigonal dodecahedral (Figure 1). Four carboxylato-oxygen atoms at distance 200(3) pm from the Co^{II} define an elongated tetrahedron with O_A–Co–O_A 97(2)°, and the other four oxygen atoms, 311(3) pm from the Co^{II}, define a severely flattened tetrahedron with O_B–Co–O_B 163(2)°. The *d–d* electronic spectrum of the complex in acetonitrile exhibits absorption maxima at 7 100 (f 4.3×10^{-4}) and 17 400 cm^{-1} (f 2.62×10^{-3}), and the variation of mean magnetic moment with temperature obeys the Curie–Weiss law, with μ 4.55(5) B.M. and $\theta = 10°$.[2] These properties lead to values of the ligand-field parameters in good accord with those of typical tetrahedral cobalt(II) complexes.

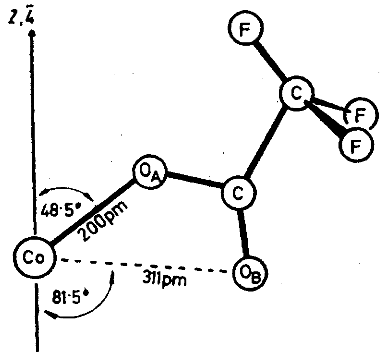

FIGURE 1 Structure of the $[Co(O_2C{\cdot}CF_3)_4]^{2-}$ ion (ref. 2)

Earlier studies of the detailed spectroscopic and magnetic properties of $CaCu(MeCO_2)_4{\cdot}6H_2O$ (ref. 3) and $[Cu(6\text{-aminohexanoic acid})_4][ClO_4]_2$ (ref. 1) showed that oxygen atoms of carboxylato-groups up to 287 pm from the metal atom could make a significant contribution to the crystal-field experienced by the metal. As a continuation of these studies we here report the polarised electronic spectra and magnetic anisotropy of single crystals of $[Ph_4As]_2[Co(O_2C{\cdot}CF_3)_4]$, and their interpretation by use of a point-charge crystal-field model.

EXPERIMENTAL AND RESULTS

Preparation.—$[Ph_4As]_2[Co(O_2C{\cdot}CF_3]_4)$ was prepared as described previously.[2] Large single crystals were obtained by setting aside an acetonitrile–toluene solution in an open flask in a P_4O_{10}-dried glove box for several weeks.

Single-crystal Polarised Electronic Spectra.—These were recorded from 4 to 28 kK at room temperature on a Cary 14 spectrophotometer equipped with Nicol prisms. Suitably thinned crystals of $[Ph_4As]_2[Co(O_2C{\cdot}CF_3)_4]$ were mounted on glass microscope slides to allow the incident beam to be polarised parallel or perpendicular to the crystallographic $c(\bar{4})$ axis. The spectrum in unpolarised light was also recorded. Results are summarised in Table 1 and Figure 2. Electronic spectra were also recorded at liquid-nitrogen and -helium temperatures, but no significant differences were observed and no better resolution achieved for the

TABLE 1

Room temperature single-crystal polarised electronic spectral data (kK) for $[Ph_4As]_2[Co(O_2C{\cdot}CF_3]_4)$

Assignment (T_d symmetry)	Polarisation		Assignment (D_{2d} symmetry)
	(B_2)[a]	(E)[b]	
$^4A_2 \rightarrow {}^4T_1$ (F)		7.0sh	
	7.8sh	7.6	$^4B_1 \rightarrow {}^4E$
	8.7	8.6sh	$^4B_1 \rightarrow {}^4A_2$
$^4A_2 \rightarrow {}^4T_1$ (P)	17.0	16.4	$^4B_1 \rightarrow {}^4A_2$
	18.7sh	17.6	$^4B_1 \rightarrow {}^4E$
		18.9	

sh = shoulder. [a] Parallel to c axis (z polarisation). [b] Perpendicular to c axis (xy polarisation).

---

[1] Part III, C. D. Garner, P. Lambert, F. E. Mabbs, and J. K. Porter, *J.C.S. Dalton*, 1972, **320**.

[2] J. G. Bergman, jun., and F. A. Cotton, *Inorg. Chem.*, **1966**, **5**, 1420.

[3] F. E. Mabbs and W. R. Smail, *J. Chem. Soc.* (*A*), **1970**, **1716**.

spin-allowed bands. Figure 3 summarises the spin-forbidden transitions between 21 and 28 kK † recorded at 77 K.

Magnetic Susceptibility Measurements.—The mean magnetic susceptibilities and the magnetic anisotropies were measured by the Gouy and Krishnan 'critical torque' methods, respectively, over the temperature range 80—300 K on apparatus described previously.[4] The fibre for the critical torque method was calibrated in the usual manner.[1] Results are given in Table 2 and Figure 4. The average magnetic susceptibility was measured to an accuracy of 1% at room temperature and relative values over the temperature range to 0.5%. The mean results obtained agree well with those reported earlier.[2] The magnetic anisotropy was measured on two different crystals; mean values are given in Table 2. The individual values were within 2% of the mean at all temperatures.

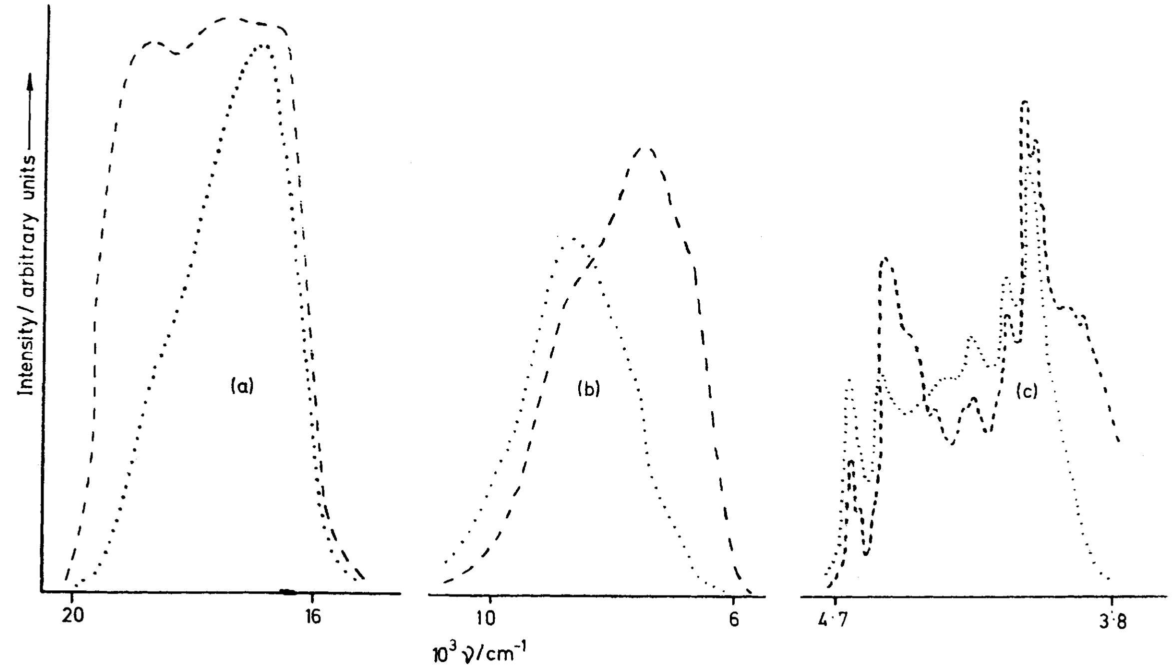

FIGURE 2 Room-temperature electronic spectra of $[Ph_4As]_2[Co(O_2C{\cdot}CF_3)_4]$ (dotted line z-, dashed line xy-polarisation)

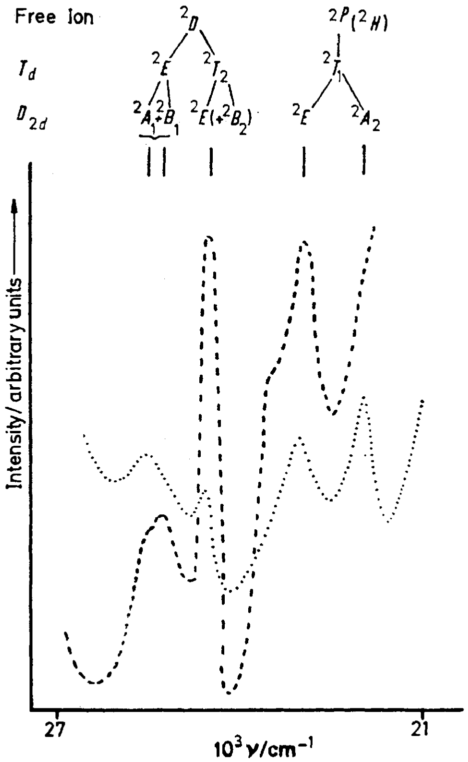

FIGURE 3 Spin-forbidden transitions recorded for $[Ph_4As]_2$-$[Co(O_2C{\cdot}CF_3)_4]$ at 77 K (dotted line z-, dashed line xy-polarisation)

Crystal-field Calculation.—The expression for the potential due to four point-charges arranged with D_{2d} symmetry about the metal has been given.[5,6] The sum of two such expressions gives the total crystal-field potential exerted at the metal by eight ligand atoms, considered to act as point negative charges, arranged with D_{2d} symmetry about the metal.[1] The effect of such potentials on the free-ion wavefunctions of cobalt(II) is shown diagramatically in Figure 5, where the loss of degeneracy is considered first for the special case of T_d symmetry and second for the more general D_{2d} situation. The matrix elements between the ^4F and ^4P eigenfunctions may be evaluated [7] in terms of the parameters B, the Racah interelectronic repulsion parameters, the crystal-field parameters Dq [$ze^2\bar{r}^4/6R^5$, R being the metal–ligand distance(s)] and Cp ($2ze^2\bar{r}^2/7R^3$), and θ, the angle(s) subtended by the metal–ligand distance(s) and the S_4 axis (Figure 1). These matrix elements for four point-charges are the same as those listed [5] for nickel(II) with the signs of both Dq and Cp reversed. The eigen-values and -functions resulting from

---

† 1 kK = 1 000 cm^{-1}.

[4] P. Coggon, A. T. McPhail, F. E. Mabbs, and V. N. McLachlan, *J. Chem. Soc.* (*A*), 1971, 1014.

[5] M. Gerloch and R. C. Slade, *J. Chem. Soc.* (*A*), 1969, 1012.

[6] C. D. Garner and F. E. Mabbs, *J. Chem. Soc.* (*A*), 1970, 1711.

the perturbation of the free-ion terms by the crystal-field have been calculated for various values of these parameters by diagonalising the energy matrix. These and subsequent calculations were carried out by use of an Atlas computer at the University of Manchester.

TABLE 2

Magnetic susceptibilities of $[Ph_4As]_2[Co(O_2C{\cdot}CF_3)_4]$

Mean magnetic susceptibility		Magnetic anisotropy	
T/K	$10^6\bar{\chi}$ c.g.s. units	T/K	$10^6\Delta(\chi_\parallel - \chi_\perp)$ c.g.s. units
301.2	8 556	294.5	1 692
297.4	8 627	218.2	2 526
291.0	8 743	195.8	3 054
280.6	9 080	185.0	3 521
267.4	9 459	168.0	3 994
248.5	10 090	150.0	4 877
227.0	10 875	139.0	5 784
203.0	12 045	130.5	6 268
184.3	13 285	118.5	7 305
171.2	14 245	109.0	8 788
150.6	16 115	100.0	9 879
128.3	18 735		
104.7	22 925		
84.0	27 815		

	C.g.s. units				B.M.		
T/K	$10^6\bar{\chi}$	$10^6\Delta\chi$	$10^6\chi_\parallel$	$10^6\chi_\perp$	$\bar{\mu}$	$\mu_\parallel$	$\mu_\perp$
300	8 610	1 655	9 714	8 059	4.54	4.83	4.40
280	9 099	1 805	10 303	8 498	4.51	4.80	4.36
260	9 671	1 990	10 997	9 007	4.48	4.78	4.33
240	10 350	2 200	11 816	9 616	4.46	4.76	4.30
220	11 200	2 480	12 846	10 366	4.44	4.75	4.27
200	12 250	2 930	14 204	11 274	4.43	4.77	4.24
180	13 600	3 500	15 934	12 434	4.42	4.79	4.23
160	15 280	4 365	18 190	13 825	4.42	4.82	4.21
140	17 180	5 505	20 850	15 345	4.38	4.83	4.15
120	19 950	7 340	24 844	17 504	4.38	4.88	4.10
100	23 710	9 900	30 310	20 410	4.35	4.92	4.04

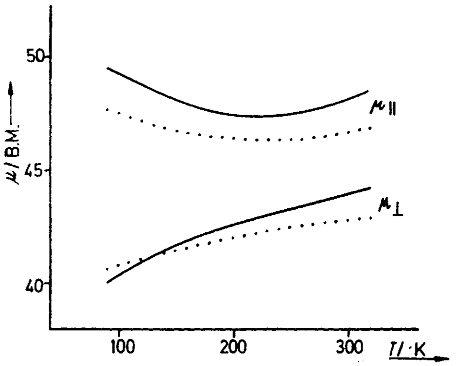

FIGURE 4 Experimental (full line) temperature-dependence of the principal magnetic moments of $[Ph_4As]_2[Co(O_2C{\cdot}CF_3)_4]$ and values (dotted line) calculated for $Dq = -1\,050$, $Cp = -3\,000$, $B = 800$, $\lambda = -172$ cm^{-1} $k_z = 1.0$ and $k_x = 0.8$

The spin–orbit coupling interactions within the ^4F and ^4P terms have been calculated by use of the relationship (1).[7] The orbital-reduction parameter k is included to

$$\lambda L{\cdot}S = k_z\lambda\hat{L}_z\hat{S}_z + (k_x\lambda/2){\cdot}[\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+] \qquad (1)$$

allow for the effects of covalency and the choice of an incomplete basis set for the metal orbitals.[8] For simplicity λ was considered to have the free-ion value of -172 cm^{-1}. The magnetic properties associated with the ground state derived from the perturbation calculation were computed using the magnetic moment operators (2) and (3), all

$$\mu_z = (k_z\hat{L}_z + 2\hat{S}_z)\beta H \qquad (2)$$

$$\mu_x = (k_x\hat{L}_x + 2\hat{S}_x)\beta H \qquad (3)$$

second-order Zeeman terms within the chosen basis set being included. The computations for z and x (y) directions were independent and in these k_z and k_x took the same values as in the spin–orbit coupling perturbation.

DISCUSSION

The energy-level diagrams for a cobalt(II) ion in T_d symmetry and in D_{2d} symmetry, which is closely related to the tetrahedral one, are shown in Figure 5. The anisotropies observed in the electronic spectra and the principal magnetic moments indicate that the cobalt(II) in $[Ph_4As]_2[Co(O_2C{\cdot}CF_3)_4]$ is in an environment of symmetry lower than T_d. The nature of the polarisations of the electronic absorptions is consistent with the D_{2d} symmetry of the CoO_8 chromophore identified by X-ray crystallography.[2] The selection rules (Table 3) indicate that the $^4T_1(F)$ state is split as $^4E(7.6) <$ $^4A_2(8.7)$ and the $^4T_1(P)$ state is split as $^4A_2(17.0) <$ $^4E(17.6$—$18.9)$, although the breadth of this last level does not follow from these simple considerations. Attempts to obtain better resolution of these bands by cooling to liquid helium temperatures were unsuccessful.

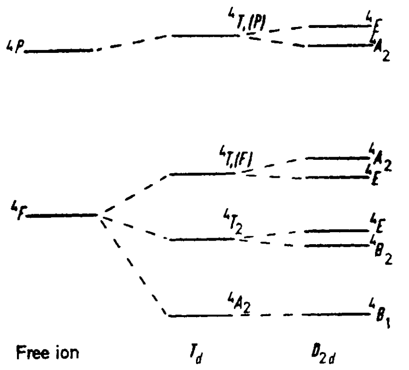

FIGURE 5 Energy levels for cobalt(II) in T_d and D_{2d} symmetries

TABLE 3

Selection rules for spin-allowed d–d transitions in cobalt(II) complexes of T_d and D_{2d} symmetry, for an electric-dipole mechanism, neglecting vibronic and spin–orbit coupling

Symmetry	Ground state	Excited state	Polarisation of electric vector	
			∥ to z	⊥ to z
T_d	$^4A_2$	$^4T_2$	F	
		$^4T_1$	A	
D_{2d}	$^4B_1$	$^4B_2$	F	F
		^4E	F	A
		$^4A_2$	A	F

F = Forbidden, A = allowed.

The sense of the anisotropy in the principal magnetic moments $\mu_\parallel > \mu_\perp$ is that expected from an elongated tetrahedral geometry about cobalt(II). This was

---

[7] B. N. Figgis 'Introduction to Ligand Fields,' Interscience, New York, 1966.

[8] M. Gerloch and J. R. Miller, *Progr. Inorg. Chem.*, 1968, **10**, 1.

initially predicted [9] by use of a simple ligand-field model for $[CoCl_4]^{2-}$ and leads to the expectation that the D_{2d} field removes the degeneracy of the $^4T_2$ level as $^4B_2 < {}^4E$. The temperature dependences of the principal magnetic moments, in particular that of $\mu_{\parallel}$, which has a minimum value at intermediate temperatures, are consistent with the absence of magnetic exchange between the Co^{II} centres, in contrast to the situation observed for Cs_3CoCl_5.[9]

These spectral and magnetic data can be satisfactorily reproduced by the point-charge crystal-field model, using the values for the parameters $Dq = -1\,050$, $Cp = -3\,000$, $B = 800$, $\lambda = -172$ cm^{-1}, $k_z = 1.0$, $k_x = 0.8$. The '$^4A_2 \rightarrow {}^4T_1(F)$,' and '$^4A_2 \rightarrow {}^4T_1(P)$' spectral transitions are thus calculated to occur in the ranges 7.5—8.4 and 17.6—18.4 kK, respectively (*cf.* data of Table 1 and Figure 2, a and b) and the calculated temperature variations of $\mu_{\parallel}$ and $\mu_{\perp}$ compare favourably with the experimental data (Figure 3). The *d–d* transition energies define the values of Dq and B reasonably accurately and, assuming λ -172 cm^{-1}, the magnitudes and the temperature dependence of the principal magnetic moments determine values for k_z and k_x. The appropriate value for Cp is not so readily fixed; the chosen value gives what is generally considered [10] to be a sensible $Cp : Dq$ ratio; however, no other significance is attached to this quantity. This model calculates that the '$^4A_2 \rightarrow {}^4T_2$' transition should occur in the range 4.4—4.9 kK. The electronic spectrum in this region (Figure 2c) is, however, dominated by overtones of the vibrational modes of the trifluoroacetato and/or tetraphenylarsonium groups which will obscure what is expected [11] to be only a very weak electronic absorption. The zero-field splitting(s) $M_J = |\tfrac{3}{2}| < M_J = |\tfrac{1}{2}|$ is calculated as 21 cm^{-1}; the sense of this splitting and such a large value of δ probably account for the failure to obtain an e.s.r. spectrum of this system, even at temperatures down to 140 K.

The inclusion of spin–orbit coupling in the crystal-field model complicates the interpretation of the sense of the splittings of the tetrahedral T_1 and T_2 levels in D_{2d} symmetry, since it effectively mixes the simple D_{2d} wavefunctions. A calculation performed with the same values of Dq, Cp, and B but without the spin–orbit coupling does, however, produce the splitting sequences $^4T_1(P)$; $^4E > {}^4A_2$, $^4T_1(F)$; $^4A_2 > {}^4E$, in agreement with the polarised spectral data, and $^4T_2$; $^4E > {}^4B_2$, consistent with a general interpretation of the sense of the magnetic anisotropy. An inspection of the corresponding eigenfunctions obtained with the inclusion of spin–orbit coupling revealed that, although the various symmetry species are 'scrambled' to some extent, the general sense of these splittings is still maintained. It is of interest that, although the majority of the experimental data could be reproduced satisfactorily by use of a point-charge crystal-field approach for the $Co(O_A)_4$ chromophore alone, the sense of the splitting of the $^4T_1(F)$ level ($^4A_2 > {}^4E$) could not then be obtained. Therefore it seems that the point-charge model for the $Co(O_A)_4$ chromophore alone is lacking in this important respect. Although this deficiency may result from certain limitations of the model, it does seem to be significant that the inclusion of point-charge effects from the more distant oxygen atoms (O_B) corrects this deficiency.

Spin-forbidden transitions were observed in the range 21—28 kK and these are presented in Figure 3 together with a tentative assignment based on the expected levels [7] and the sense of the polarisation observed.

We thank the S.R.C. for financial support.

[5/1087 *Received, 5th June,* 1975]

[9] B. N. Figgis, M. Gerloch, and R. Mason, *Proc. Roy. Soc.*, 1964, **A279**, 210.

[10] C. J. Ballhausen and M. Ancon, *Mat. Fys. Medd. Dansk Vid. Selsk.*, 1958, **31**, 3.

[11] I. H. Hillier, J. A. Kendrick, F. E. Mabbs, and C. D. Garner, *J. Amer. Chem. Soc.*, to be published.