Magnetic Exchange and Zero-field Splitting in the d^3 $[Os^VCl_6]^-$ Ion *

Philip A. Reynolds,[a] **Christopher D. Delfs,**[a] **Brian N. Figgis,**[a] **Mark J. Henderson,**[a] **Boujemaa Moubaraki**[b] **and Keith S. Murray**[b]
[a] *Department of Chemistry, University of Western Australia, Nedlands, Western Australia 6009, Australia*
[b] *Department of Chemistry, Monash University, Clayton, Victoria 3168, Australia*

The principal magnetic susceptibilities, and magnetisations, of $[PPh_4][Os^VCl_6]$ are reported for temperatures between 4.5 and 300 K at 1.0 T, and between 2.5 and 20 K at 0.25 to 5.0 T respectively. The data are interpreted in terms of zero-field splitting of the ground $^4A_{2g}$ term [$D = -16.5(1.5)$ cm^{-1}], large because of the high spin-orbit coupling constant for the Os^{5+} ion, with smaller Ising antiferromagnetic exchange [$J = -8(2)$ cm^{-1}], probably of one-dimensional nature, given the constraints of the crystal structure. This appears to be the first observation of one-dimensional magnetic exchange in a heavy transition-metal complex. A DV-Xα calculation on the $[OsCl_6]^-$ ion in its experimental tetragonal geometry is included, which estimates, *inter alia*, the overall d-orbital splitting, 10*Dq*, the low-symmetry energy splitting of the t_{2g} orbitals, and the orbital angular momentum reduction factor, *k*. Crystal-field calculations, using similar values of these parameters, together with reasonable values for spin-orbit coupling and Racah parameters, agree with the magnetic behaviour and optical spectrum. In particular the large negative, zero-field splitting parameter, *D*, is reproduced.

The magnetic behaviour of second- and third-transition series complexes is far less well known than is that of the first series.[1] For example, it appears that no cases of linear-chain or planar magnetic exchange are known for materials in 4d or 5d systems.[2] Apart from this intrinsic interest, the larger spin–orbit coupling effects and greater covalence in such compounds may produce interesting magnetic behaviour. In the future we hope to investigate the magnetisation density in them by polarised neutron diffraction (PND), and in order to prepare for such an experiment we here examine in detail the single-crystal magnetic susceptibilities and magnetisations and other relevant properties of an example. We find evidence for substantial zero-field splitting of the $^4A_{2g}$ ground term and low-dimensional magnetic exchange.

The salt $[PPh_4][Os^VCl_6]$[3,4] is unusual amongst heavy-transition metal complexes in giving a high-spin ground state; $S = \frac{3}{2}$. In addition, it has a simple uniaxial crystal structure.[5] Both those features are attractive for PND studies. In this paper we present the single-crystal magnetic susceptibility and magnetisation behaviour for the compound between 4.5 and 200 K, and oriented polycrystalline data over the same field and temperature range. Previous magnetic studies for it were restricted to the measurement of the room-temperature magnetic moment.[3]

We show that $[PPh_4][OsCl_6]$ is probably a one-dimensional Ising-coupled system with substantial zero-field splitting (ZFS). This appears to be the first observation of lower-dimensional magnetism in a heavy-transition metal complex.

Experimental

The complex $[PPh_4][OsCl_6]$ was prepared by two different methods.[3,4] The oxidation of $[OsCl_6]^{2-}$ with PbO_2 gave the larger, better formed crystals of rod-like to platy habit with *c* long, of which the largest was almost 1 mg in mass.

Magnetic measurements between 4.5 and 300 K with fields up to 5 T were performed with a SQUID magnetometer (Quantum Dynamics Inc., CA). No attempt was made to perform random-orientation powder measurements, particularly because, for d^3 $^4A_{2g}$ ions, these are known to contain little information about ZFS. A 0.59(5) mg single crystal of the complex was glued onto a quartz fibre and measurements made with the applied magnetic field parallel to *c*. The same crystal was then reglued and measured again with the field perpendicular to *c*. Also, 38.95(5) mg of rod-like micro-crystals were placed in a gelatin capsule. This was tapped to attempt to induce ordering of *c* along the main axis. The magnetically anisotropic crystals may have been further oriented by the initial conditions of the largest magnetic field (5 T) and the lowest temperature (4.5 K) which were used for the susceptibility measurement. Subsequent repeat measurements showed the sample to be orientationally stable.

The data were corrected for the diamagnetism of the glue or the gelatin capsule, sample diamagnetism[6,7] (-322×10^6 cm^3 mol^{-1}), and temperature independent paramagnetism (54×10^{-6} cm^3 mol^{-1}), to give the paramagnetic components of the molar magnetic susceptibility, measured at 1 T, or magnetisation, as appropriate.

In this complex the parallel and perpendicular susceptibilities, $\chi_{\parallel}$ and $\chi_{\perp}$, are very different both in magnitude and in variation with temperature and magnetic field. Apart from the physical significance of this which we discuss below, it allowed us to improve the accuracy of the data by refining the mass of the single crystal and the degree of orientation in the microcrystalline sample by use of equation (1), where χ_{mc} is the magnetic

$$\chi_{mc} = f[a\chi_{\parallel} + (1 - a)\chi_{\perp}] \qquad (1)$$

susceptibility of the microcrystalline sample, *a* is the parameter describing the orientation ($\frac{1}{3}$ for random powder) and *f* is a correction factor which essentially uses the mass of microcrystals to correct the single-crystal mass. We obtain $a = 0.67(3)$ and a corrected crystal weight of 0.65(1) mg, giving an error of about 1% in the susceptibilities. The SQUID data on a

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* *Supplementary data available* (No. SUP 56886, 5 pp.): experimental magnetic susceptibilities and magnetic moments. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

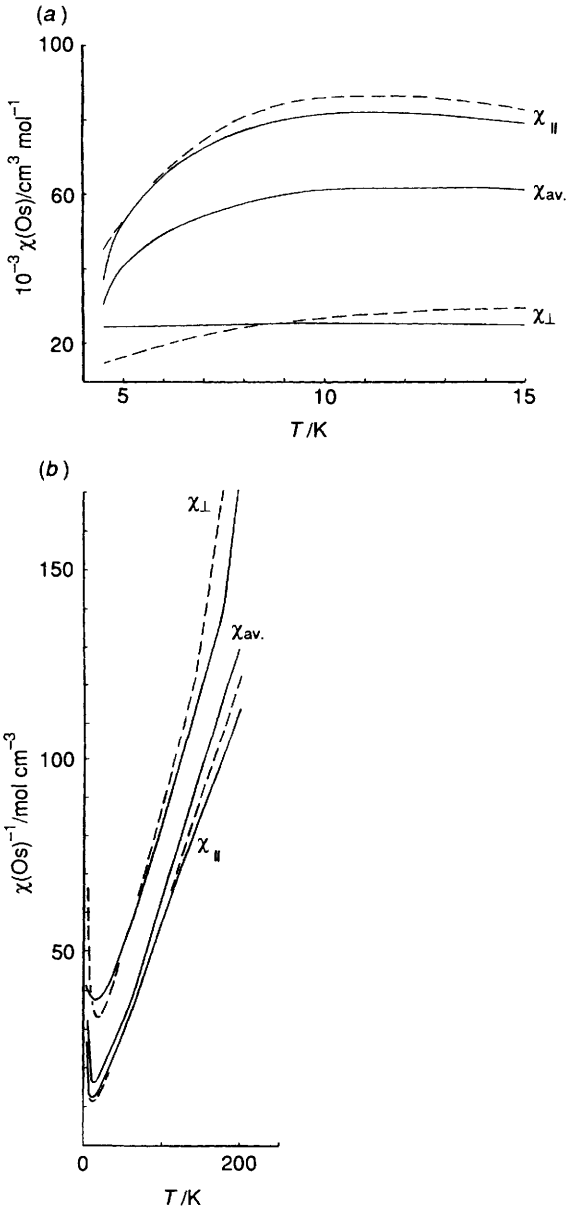

Fig. 1 (*a*) Magnetic susceptibility *versus* temperature (< 15 K) for $[PPh_4][OsCl_6]$. Solid curves are the experimental results: the scatter of points is within the linewidth. The broken lines are the results calculated from the model. (*b*) Inverse of the magnetic susceptibility *versus* temperature for $[PPh_4][OsCl_6]$. Other details are as for part (*a*)

given sample are highly reproducible when the experiment is repeated, so the errors reported were increased by 1% of the magnetisation as an assessment of systematic effects. The value of *a* shows that there is a very substantial preference for the *c* axis to lie along the applied field direction.

The susceptibilities for the single-crystal and oriented-microcrystal measurements are shown in Fig. 1 and listed in Table 1 (see SUP 56886). Fig. 2 shows and Table 2 (SUP 56886) lists the magnetisation measurements made at lower temperatures. ESR experiments on the salt gave no detectable absorption between 100 and 300 K.

Results and Discussion

To account for the magnetic results we need to consider the magnetic exchange, the ZFS effects, and constraints imposed by the crystal structure.

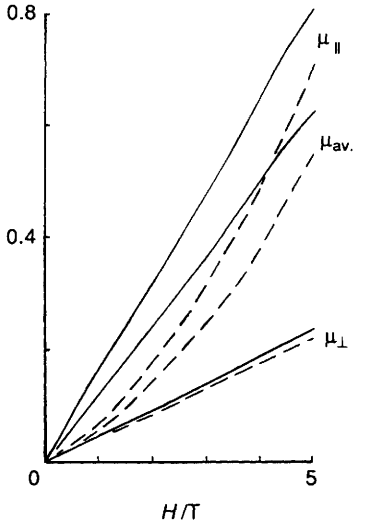

Fig. 2 Magnetic moment *versus* magnetic field for $[PPh_4][OsCl_6]$ at 4.5 (——) and 12 K (– – – –); the scatter of experimental points is within the linewidth

Crystal Structure and Magnetic Model.—The complex $[PPh_4][OsCl_6]$ crystallises in the tetragonal space group *P*4/*n* with Os ··· Os distances of 771 pm along [001] and 912 pm along [110]. The first separation involves a linear Os–Cl ··· Cl–Os contact, the second indirect non-linear contacts through the cation. We thus expect the magnetic exchange through the Cl ··· Cl path to be much the stronger. It seems likely that the magnetic exchange is one-dimensional in nature, with the interaction along [001]. The tetragonal site symmetry at the osmium centre requires only a single parameter, *D*, to describe the ZFS effects.

Dimensionality of the Magnetic Exchange.—The susceptibility of the oriented microcrystalline sample shows a maximum at 11.8(1) K, but there is no sharp feature which demonstrates magnetic order. However, the rate of change with temperature is large and increasing as the temperature is decreased to the lowest measurement temperature of 4.5 K, and we can estimate that there may be ordering at 4.3 K. Such a large difference between the ordering and χ_{max} temperatures is characteristic of low dimensionality in the exchange process. In view of the crystal structure, one-dimensional exchange provides the preferred model, as two-dimensional or dimer processes which could also cause the difference seem to be ruled out.

Magnetic Susceptibility.—We now consider the related questions of the choice of the magnetic exchange model and relative sizes of ZFS and magnetic-exchange parameters. From the simplest considerations we expect that if the exchange is dominant then Heisenberg-like behaviour will ensue for d^3 $^4A_{2g}$ ions but if the ZFS is dominant then, depending on its sign, there should result either Ising spin-$\frac{1}{2}$ or XY spin-$\frac{1}{2}$ behaviour; *viz.* spin vector confined to one direction or to a plane.[8] Although the real spin of the system is $S = \frac{3}{2}$, because of the ZFS, it is possible to employ these models using an effective spin of $S' = \frac{1}{2}$ with a corresponding multiplication of the real *g* value by 3.0 to give an effective *g*′. We actually observe a large anisotropy in susceptibility, which indicates that a model of Heisenberg exchange and small ZFS is inappropriate.

In this $^4A_{2g}$ ion the *g* tensor is not expected to be highly anisotropic and so, in view of the experimental results, Ising-like exchange with small ZFS is unlikely. An attempt to fit the data using a spin-$\frac{1}{2}$ Ising model yields some agreement when the direction of the spin is in the *ab* plane with spin perpendicular to the chain axis, as is often the case.[1] However, at low temperatures there is qualitative disagreement as the observed value of $\chi_{\parallel} - \chi_{\perp}$ is decreasing rapidly, but the calculated difference is increasing rapidly. We conclude that the exchange cannot be dominant over the ZFS.

If the ZFS parameter, D, is negative, so that the ground state is composed of $M_s = \pm\frac{3}{2}$, then the situation of an effective spin-$\frac{1}{2}$ Ising model obtains, as in the classic cases of the Co^{2+} ion in tetrahedral stereochemistry.[9] For D positive the XY exchange model is appropriate, but we do not discuss this further since it does not lead to a model in agreement with the data. Although expressions for the susceptibilities of a spin-$\frac{1}{2}$ Ising chain[10] and of the $^4A_{2g}$ term with ZFS[10] are each readily available, the combination does not seem to be. We assume, as theory for this Ising model requires, that the spin direction is parallel or antiparallel to [001]. We note that we have here the less common case in which the spin direction is along the chain length. We have used the Ansatz that the susceptibility is given by that of the $^4A_{2g}$ term including ZFS, modulated by a factor predicted from the Ising model of the magnetic exchange with parameter J, $F(J)$, *viz.* equation (2) in which $\chi_{\parallel}$ is defined by equation (3). The perpendicular susceptibility $\chi_{\perp}$ is defined by equation (4) and the relevant spin Hamiltonian $\mathscr{H}$ is defined by equation (5) where i is the chain position. We fitted these two

$$\chi = \chi(^4\mathrm{A}_{2g})\cdot F(J) \qquad (2)$$

$$\chi_{\parallel} = [Ng_{\parallel}{}^2\mu_B{}^2/4kT][1 + 9\exp(-2D/kT)] \\ [1 + \exp(-2D/kT)]^{-1}\cdot\exp(J/kT) \qquad (3)$$

$$\chi_{\perp} = \{[Ng_{\perp}{}^2\mu_B{}^2/kT][1 + \exp(-2D/kT)]^{-1} + \\ 3Ng_{\perp}{}^2\mu_B{}^2 \tanh(D/kT)/4D\}\cdot\{(kT/J)\tanh(J/2kT) + \\ [\mathrm{sech}^2(J/2kT]/2\} \qquad (4)$$

$$\mathscr{H} = -2J\Sigma S_{z,i}S_{z,i+1} + g_{\parallel}\mu_B H_z S_{z,i} + \\ g_{\perp}\mu_B(H_x S_{x,i} + H_y S_{y,i}) + D(S_z{}^2 - 1.25) \qquad (5)$$

susceptibility equations to the data, and obtained $\chi_{\parallel} = 1.85(2)$, $\chi_{\perp} = 1.64(2)$, $D = -16.5(1.5)$ cm^{-1} and $J = -8(2)$ cm^{-1} with a goodness-of-fit parameter, χ, of 8.7. This fit is given in Table 1 (SUP 56886). If we restrict the data to those above 30 K we obtain respectively the values 1.86(2), 1.72(2), −43(3) and −10(2) with $\chi = 1.6$.

We conclude that there is a large ZFS, defined by $D = -16.5(1.5)$ cm^{-1}, together with smaller antiferromagnetic-exchange effects described by an Ising spin-$\frac{1}{2}$ model with $J = -8(2)$ cm^{-1}. The exchange is sufficiently large that deficiencies in the model may well produce systematic errors in these parameters, but the overall description is not in question.

Magnetisation Measurements.—The magnetisation as a function of the applied magnetic field has been examined for a range of one-dimensional exchange models.[11] The antiferromagnetic Ising spin-$\frac{1}{2}$ model with the field parallel to the spin direction is the only case studied where, as temperature is lowered, the parallel magnetisation-*versus*-field curve departs from a straight line and becomes noticeably curved *upwards* ($d^2\mu/dH^2$ positive) for medium field strengths. In other cases, and for the free ion, the curvature of magnetisation-*versus*-field is downwards. Unfortunately, the calculation for the perpendicular direction is not available, so we cannot fit those experimental magnetisation data. However we do observe the qualitative behaviour that the parallel data are rectilinear at higher temperatures but becomes markedly upwardly curving at low temperatures, while the perpendicular data remain linear. This supports the use of Ising models, but because of the incompleteness of the theory, we cannot analyse the data further.

Table 1 Crystal-field calculations for the Os^{5+} ion to fit the $[OsCl_6]^-$ spectrum. Energies are in cm^{-1}

Assignment[a]	Experimental[14]	Approximate model[14]	Full cubic model	Tetragonal
$b\Gamma_8(^2T_{1g})$	5 800	5 801	6 254	5 952 6 270
$c\Gamma_8(^2E_g)$	7 553	7 426	7 426	7 439 7 446
$a\Gamma_6(^2T_{1g})$	7 818	7 568	7 871	7 904
$\Gamma_8(^2T_{2g})$	10 862	11 711	12 340	12 335
$d\Gamma_8(^2T_{2g})$	13 153 14 198	13 878	13 867	13 971 14 330
$e\Gamma_8(^4T_{2g})$	28 818	28 500	28 294 28 713 29 190 29 839	28 023– 29 717
$b\Gamma_6(^4T_{1g})$	32 787	32 417	31 926 33 006 33 601 34 306	31 577– 34 300

[a] These assignments have been labelled with O_h term symbols in brackets. The original assignment[14] took place with the inclusion of spin-orbit coupling and used the Double Group O_h*.

Theoretical Calculation

The conclusions reached above, given the crystal structures and experience of the first-transition series compounds, are not unexpected, except perhaps for the large size of the ZFS in a molecular geometry so close to O_h in symmetry. To check that such a large value can arise from the relatively small tetragonal distortion of the molecular geometry of the anion we performed an *ab initio* DV-Xα calculation on the $[OsCl_6]^-$ ion to estimate reasonable values of the main ligand-field parameters and the Stevens orbital reduction factor, using a program described in ref. 13.[12] We then performed a ligand-field calculation including spin-orbit coupling, to fit the available spectroscopic data and compare with the magnetic data.

The DV-Xα calculations were performed both with O_h symmetry for the $[OsCl_6]^-$ ion and also with the tetragonal, non-centrosymmetric, molecular geometry found in the crystal structure of $[PPh_4][OsCl_6]$.[5] The calculations used frozen cores for the Os and Cl atoms, 5d, 6s and 6p active functions on Os and 3s, 3p and 3d functions on Cl, with 7000 integration points and multipoles of order three in the expansion of the molecular potential in each case.[13] The DV-Xα calculation of the $[OsCl_6]^-$ ion is non-relativistic, and so must be regarded with some reservation, but it does show that of the order of 40% of the spin is delocalised onto the chlorine atoms. It gives $10Dq = 24\,400$ cm^{-1} and a separation of the components of the Os t_{2g} orbitals of about 300 cm^{-1}. These results correspond to a very covalent system, and suggest a value for k of *ca.* 0.6. Preetz and Bruns[14] and Magnusson[3] estimate from optical spectra values of k ranging from 0.46 to 0.62, in reasonable agreement with this calculation.

The relevant ligand-field parameters have been estimated by Preetz and Bruns[14] by comparison of an approximate crystal-field treatment with the optical spectrum of $[NEt_4][OsCl_6]$. We reproduce their experimental and theoretical results in the first two columns of Table 1. The spectrum of the present tetraphenylphosphonium salt[3] is virtually the same as for the tetraethylammonium salt, and the parameters should be very similar. In the third column we have used their parameters in a complete full d-manifold crystal-field calculation for the Os^{5+} ion. Because the fit obtained from the original parameters was then poorer, we changed the C/B Racah parameter ratio from 4.0 to 4.75 and made small adjustments to other parameters. We also included a lowering in symmetry to tetragonal *via* a $3d_{xy}/3d_{xz,yz}$ orbital splitting of 500 cm^{-1}. Then, as seen in the fourth column, a good fit was restored ($10Dq = 28\,500$, $\xi = 2700$, $B = 280\ \text{cm}^{-1}$).

The way in which the magnetic susceptibility is reproduced by the ligand-field model can be summarised by considering the ZFS parameter and the effective g values deduced for use in connection with equations (3) and (4). We find that a splitting of 500 cm^{-1} for the t_{2g} orbitals of O_h symmetry, so that the $5d_{xz}$ and $5d_{yz}$ orbital energies lie higher relative to $5d_{xy}$ in the experimental tetragonal geometry, also reproduces the experimental ZFS parameter of $D = -16.5\ \text{cm}^{-1}$ if we use a value of k of 0.5. To obtain a similar ZFS by splitting of e_g orbitals requires a 5000 cm^{-1} separation between the $5d_{z^2}$ and $5d_{x^2-y^2}$ energies. Of course, the ZFS observed must have contributions from both such d-orbital splittings but given the closeness of the geometry to octahedral, the t_{2g} splitting mechanism must be dominant. From the crystal-field parameters we can calculate the magnetic susceptibilities at higher temperatures. We find that they correspond to effective values of $g_{\parallel} = 1.65$ and $g_{\perp} = 1.58$. These are lower than the experimentally determined values of 1.85 and 1.64 respectively, but in the correct order. They also show the large reduction from 2.00 arising from the large spin–orbit coupling. It is interesting to see that the ESR g values obtained by calculating the Zeeman splitting at each level are different again. For the ground state $M_s = \pm\frac{3}{2}$ we obtain $g_{\parallel} = 1.67$ and $g_{\perp} = 0.03$. For the higher lying $M_s = \pm\frac{1}{2}$ state the results are $g_{\parallel} = 1.60$ and $g_{\perp} = 1.70$. This difference is due to the large and different orbital moment contributions in each level. It is also an indication of the limits of the spin-Hamiltonian formalism.

We conclude that a modest 500 cm^{-1} splitting of the 5d t_{2g} levels is sufficient to give the large ZFS observed, because of the very large spin–orbit coupling constant for the Os^{5+} ion, and that the magnetic susceptibility and the optical spectrum are both reasonably consistent with the same ligand-field model. The 500 cm^{-1} splitting is in fair agreement with the DV-Xα calculation based upon the experimental geometry which gives a value of 300 cm^{-1}. This is as good as can be expected in view of the limitations of such a calculation and of the ligand-field treatment of the Os^{5+} ion.

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