Single-crystal Low-temperature Magnetisation Studies of $Cs_2K[Mn(CN)_6]$†

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The magnetisation in single monoclinic crystals of $Cs_2K[Mn(CN)_6]$ has been measured from 2 to 300 K and from 0.5 to 5 T along the [100], [010], [001] and [011] crystal directions. The data, with no symmetry approximations, can be fitted by the same general ligand-field model that was used for $Cs_2K[Fe(CN)_6]$. Hardly significant changes in the already small ligand-field parameters and appropriate changes in the metal parameters were required. Such approximate transferability of a ligand-field model, between $3d^4$ and $3d^5$ low-spin systems which have very different magnetic behaviour, encourages belief in the utility and reality of ligand-field modelling.

In the past, ligand-field modelling of magnetic, spectroscopic and other experiments on transition-metal complexes has often contained ambiguities. Limited data have been fitted to oversimplified models. This is unfortunate because, particularly in low-symmetry situations, sufficient experimental information can be obtained to overdetermine all the parameters of at least a basic such model. To do that requires an appropriate mix of single-crystal experiments using some combination of magnetic susceptibility and magnetisation, ESR, polarised neutron diffraction, far infrared absorption, Raman scattering, Mössbauer spectroscopy and other relevant techniques. In such situations a ligand-field model provides a useful summary of a great deal of disparate data. The parameters of such a model can, in principle, be calculated *ab initio*,[1] although this is not yet available in practice. Such reliable ligand-field models, with no symmetry assumptions, are now available for a few cases in which the metal occupies a site of only inversion symmetry.[2-4]

A highly desirable feature for a ligand-field model is that it should hold for differing metal ions in isomorphous crystals, to give similar values of its parameters in each case. This should be so in spite of the often very different physical properties resulting arising from the different transition metals at the central site.

A ligand-field model for $Cs_2K[Fe(CN)_6]$ has been developed using extensive single-crystal magnetisation and polarised neutron diffraction results.[2,5-7] Ideally, the same ligand-field model should apply to $Cs_2K[Mn(CN)_6]$, and employ rather similar values for its parameters, even though changing the central ion from low-spin $3d^5$ Fe^{III} to low-spin $3d^4$ Mn^{III} is known to produce grossly different magnetic behaviour. In this paper we make a detailed investigation of the magnetic properties of $Cs_2K[Mn(CN)_6]$ and examine whether they can be fitted by the same ligand-field model as used for $Cs_2K[Fe(CN)_6]$ and if so, with what parameters.

Previous magnetic work on the hexacyanomanganate(III) ion has been restricted to $K_3[Mn(CN)_6]$. Powder magnetic susceptibility data were satisfactorily fitted over temperature ranges from 4.2 to 300 K using theory which is based on spin–orbit coupling[8,9] splitting of the $^3T_{1g}$ ground term, and with the addition of a splitting of that term by a ligand-field component of axial symmetry.[10-12] Single-crystal magnetic susceptibility data from 80 to 300 K and optical data have been fitted by a ligand-field model.[12,13] Ligand-field theory appears to work well in this case. The lack of very low temperature (< 80 K) data, crystal polytypism, and a phase change, complicate interpretation of the anisotropic magnetic data[13,14] for this complex.

Our data for $Cs_2K[Mn(CN)_6]$ are for single crystals, extend down to 2 K, there is no polytypism, nor is there a phase change between 2 and 300 K.

Experimental

Large single crystals of $Cs_2K[Mn(CN)_6]$ were available from the batch prepared for charge-density studies.[15] They are monoclinic, space group $P2_1/n$,[15] $a = 1198.1(3)$, $b = 819.1(2)$, $c = 768.7(5)$ pm, $\beta = 90.22(4)°$, $T = 295$ K. The cell contains two hexacyanomanganate(III) anions, related by a two-fold screw axis. Each anion is very close to octahedral in stereochemistry, although the crystallographic site symmetry is only that of inversion. The next nearest neighbour caesium and potassium ions depart substantially from cubic symmetry around the Mn centre. The structure[15] differs from that of $Cs_2K[Fe(CN)_6]$[16] only in minor details.

Magnetic measurements were performed with a Quantum Design SQUID magnetometer (Quantum Design, San Diego, USA). Temperatures were varied from 2 to 300 K and magnetic fields from 0.5 to 5 T. The crystals had morphology {100}, {011}. After alignment by optical goniometry to an accuracy better than 2°, they were glued into niches in 3 mm diameter Perspex rods. The magnetisation was measured first for the magnetic field parallel to the [100] and [011] directions, then subsequently with the field parallel to [010] and [001]. The data were corrected for the diamagnetism of the glue, of the niche in the rod, and for the molecular diamagnetism (-175×10^{-6} cm^3 mol^{-1}), to give the paramagnetic components of the molar magnetisation, M_{Mn}. The magnetic susceptibility was derived from the measurements at 1.0 T. The magnetic moment was calculated as $\mu_{eff} = 2.828(M_{Mn}T/H)^{\frac{1}{2}}$. A selection of the magnetic moment and magnetisation data is listed in Tables 1 and 2 and shown in Fig. 1. Full lists of data are deposited as SUP 56994. We estimate the errors in the magnetic moment as *ca.* 1% of their value. Relative errors, within a crystal setting, are less. For all the data, at a given temperature, the

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† *Supplementary data available* (No. SUP 56994, 9 pp.): magnetic data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: $\mu_B \approx 9.274\,02 \times 10^{-24}$ J T^{-1}.

Table 1 Experimental and calculated effective magnetic moments (μ_B) for $Cs_2K[Mn(CN)_6]$ at selected temperatures, with magnetic field *H* parallel to various crystal directions

	H‖[100]		*H*‖[011]			*H*‖[010]		*H*‖[001]	
T/K	Obs.	Calc.	Obs.	Calc.	*T*/K	Obs.	Calc.	Obs.	Calc.
2.00	0.589	0.597	—	0.612					
2.50	0.659	0.667	—	0.684	3.50	0.683	0.673	0.956	0.927
5.01	0.806	0.805	1.150	1.110	5.01	0.937	0.944	0.982	0.969
8.01	1.019	1.018	1.454	1.403	8.01	1.189	1.193	1.248	1.225
19.66	1.592	1.595	2.271	2.196	16.20	1.694	1.697	1.769	1.742
29.31	1.937	1.946	2.739	2.663	28.35	2.231	2.271	2.322	2.294
43.79	2.327	2.351	3.196	3.138	40.27	2.605	2.619	2.700	2.682
72.75	2.768	2.839	3.553	3.542	70.60	3.099	3.135	3.167	3.195
125.86	3.044	3.194	3.610	3.637	124.92	3.341	3.390	3.361	3.432
170.26	3.112	3.289	3.560	3.591	167.19	3.384	3.424	3.383	3.456
223.65	3.147	3.320	3.494	3.520	221.50	3.393	3.411	3.375	3.436
300.00	3.160	3.311	3.452	3.435	300.00	3.371	3.367	3.361	3.388

Table 2 Illustrative experimental and calculated magnetisations for $Cs_2K[Mn(CN)_6]$. The units are μ_B atom^{-1}, which may be converted to cm^3 G mol^{-1} by multiplication with the factor 5582.9

	T = 3.51 K				*T* = 10.01 K			
	H‖[010]		*H*‖[001]		*H*‖[010]		*H*‖[001]	
H/T	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
1.0	0.030	0.029	0.058	0.055	0.030	0.029	0.060	0.055
2.0	0.059	0.058	0.118	0.111	0.059	0.058	0.119	0.111
3.0	0.089	0.087	0.177	0.167	0.088	0.087	0.178	0.167
4.0	0.119	0.116	0.236	0.223	0.117	0.116	0.236	0.223
5.0	0.149	0.145	0.294	0.278	0.146	0.145	0.294	0.278

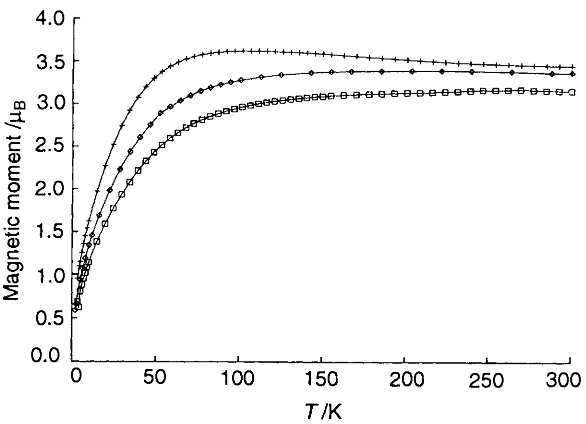

Fig. 1 Experimental magnetic moment *versus* temperature for single crystals of $Cs_2K[Mn(CN)_6]$; +, *H*‖[001]; ◆, *H*‖[100]; □, *H*‖[010]

magnetisation is very closely proportional to the applied magnetic field, so we give only the [010] and [001] data at a pair of temperatures, to illustrate this fact.

Ligand-field Theory

Ligand-field theory was first applied to metal ions located on sites of high crystallographic symmetry, *viz.* cubic and uniaxial. In these situations we can use parameters, such as *Dq*, *Ds* and *Dt*, whose conceptual origin lies in the electrostatic crystal field.[17] These parameters determine the value of those elements of the general fourteen-parameter crystal-field matrix which are not by symmetry zero. Each of the matrix elements may depend on a combination of the parameters.

When we descend to lower symmetry, use of this method becomes cumbersome as more and more parameters are needed, whose values seem arbitrary, and which may affect any of the crystal-field matrix elements. The initial attempts to impose non-crystallographic symmetry by appealing to observed structure and chemical intuition often fail. Later attempts to construct a low-symmetry field as a sum of fixed metal–ligand properties, the angular overlap model (AOM), proves more successful.[1] This still involves assumptions, which must be tested against experiment, for example, as to cylindrical symmetry of π interactions. This enables the construction of a set of AOM parameters which both summarise much data and predict new data on new complexes. Nevertheless, for an individual crystal the AOM ligand-field matrix, because of symmetry assumptions and the assumed connection between ligand field and ligand orientation around the metal, may contain hidden constraints.

An alternate way of generalising ligand-field theory to low-symmetry sites has been demonstrated by Doerfler on the ammonium iron(II) Tutton salt.[3] For those systems with no orbital moment associated with e_g orbitals, we make assumptions about the lowest states, in the hypothetical absence of spin-orbit coupling. Thus, in roughly octahedral symmetry the magnetic properties of the three lowest states are described by molecular orbitals with arbitrary combinations of the three t_{2g} d orbitals. Given molecular orbital and state orthonormality, we thus require three coefficients mixing the t_{2g} orbitals to describe the wavefunctions of the three states. Further, two energies, describing the state separations, are also required. While there may be spin in molecular orbitals containing the e_g d orbitals there is assumed to be no mixing of t_{2g} into these and *vice versa*. We may relate the $3 + 2 = 5$ parameters required with the five independent elements within the t_{2g} manifold in the crystal-field matrix. In terms of the full 5×5 symmetric traceless crystal-field matrix, we make elements connecting t_{2g} to e_g orbitals zero, and the energy of the orbitals e_g infinite, to give a t_{2g} orbital basis. We thus have a general crystal field, within the assumption that e_g and t_{2g} d orbitals are mutually exclusive sets. This is a simple approximation which, since only five parameters are involved, can be tested on single-crystal data. This has been done with some success previously.[2-4,7]

Practical calculations, using the BFDN program suite,[4] require calculation of the crystal-field matrix, using two energy parameters and a rhombic crystal-field component oriented at arbitrary angles to the ligand axes. This is equivalent to rotating the axes so that the three lowest states are diagonal in $x'y'$, $x'z'$ and $y'z'$, by three Euler angles; thus describing the t_{2g} mixing coefficients in the ligand original xyz coordinate system. The spin–orbit coupling then further mixes these three lower states to produce the final ground, and first few excited, states. To obtain the crystal properties we must then sum over the ions in the crystal unit cell. In this case our assumption of a rhombic field component with axes abc^*, as for $Cs_2K[Fe(CN)_6]$,[2,7] makes the two formally magnetically inequivalent ions equivalent.

We use this general t_{2g}, five crystal-field parameter, model in our calculations below.

Discussion and Ligand-field Calculations

The broad features observed in earlier magnetic susceptibility studies on the hexacyanomanganate(III) ion are also seen here. For each direction of the magnetic field the effective magnetic moment rises slightly at first as the temperature decreases from 300 K, but reaches a maximum at *ca.* 150 K. Then there is a steep decline to the lowest temperatures (Fig. 1).

The corresponding magnetisation rises slowly as the temperature is decreased, becoming almost constant below about 20 K. It remains linearly dependent on the applied magnetic field even at the lowest temperatures, so that the magnetic susceptibility is independent of the field strength. These effects are well understood.[9-12] Splitting of the cubic $^3T_{1g}$ term by spin–orbit coupling to give a ground state with $J = 0$, with excited states with $J = 1$ and $J = 2$ lying higher, leads to just such qualitative effects.

The interesting features for the present purposes are the anisotropy effects. The moment along [010] is less than that along [100], which is in turn less than that along [001]. The corresponding magnetisations differ by up to a factor of two at similar experimental conditions. The temperature at which the effective magnetic moment peaks also varies. It is 270 K for $\boldsymbol{H}\|[010]$, 221 K for $\boldsymbol{H}\|[100]$ and 107 K for $\boldsymbol{H}\|[001]$.

We now examine whether the ligand-field model used to explain the magnetic properties of $Cs_2K[Fe(CN)_6]$ is successful also in this case. Again we use the coordinate system x along a, y along b, and z along c^*, as was found experimentally for $Cs_2K[Fe(CN)_6]$,[2] and consider only the t_{2g} orbitals. Restriction to the t_{2g} basis leaves four parameters to be fixed. They are the spin–orbit coupling constant, ζ, the Stevens reduction factor, k,[18] presumably reflecting covalence and other factors,[1,19] and the energies of $3d_{xz}$ and $3d_{yz}$ orbitals relative to the $3d_{xy}$ orbital. The factor k can be fixed at 0.7 on the basis of the amount of π delocalisation from the 3d t_{2g} orbitals shown by a charge-density study on the same compound, and by a modest level *ab initio* molecular orbital calculation using the local density approximation,[15] if we assume it reflects only covalence in this case. A change in k of 0.1 degrades the fit, but by only a small amount.

The magnetic data fit well to the model when we use the set of parameters $\zeta = 240(20)$, $E(3d_{xz}) = -100(10)$ and $E(3d_{yz}) = -60(10)$ cm^{-1}. The value in parentheses is an estimate of the standard deviation. The results are shown in Tables 1 and 2. The parameter errors quoted were not derived by least-squares analysis, but give an estimate as to when the fit is significantly degraded. Such a good fit to the data here with only three variables is good evidence for the validity of the modelling. In addition, the fitted spin–orbit coupling constant is 0.70 of the free-ion value. This reduction matches the estimate of the Stevens reduction factor well, as might be expected if the orbital angular momentum is changed in the same way as in the determination of the g values.

The model predicts nine low-energy states derived from spin–orbit and low-symmetry splitting of the $^3T_{1g}$ state at energies 0, 101, 123, 149, 339, 342, 380, 394 and 399 cm^{-1}.

Conclusion

A general t_{2g} basis ligand-field model, assuming only inversion symmetry on the Mn site, provides a good fit to the magnetic data. Both the effective spin–orbit coupling constant and the Stevens orbital reduction factor are reduced from free-ion values by a factor of 0.7 indicating, as expected, substantial covalence. The fitted ligand-field energies of $-100(10)$ and $-60(10)$ cm^{-1} compare quite well with those for $Cs_2K[Fe(CN)_6]$ *viz.* $-60(10)$ and $-60(10)$ cm^{-1}. Although -100 and -60 cm^{-1} are almost 100% different, we should remember that low-symmetry ligand-field energy splittings can extend to a few thousand wavenumbers in extreme cases. In this context the 40 cm^{-1} difference is not significant. It appears that these ligand-field energies are approximately transferable between the two sets of $(CN)_6$ octahedra, and do reflect bonding information.

Concerning further experiments, conventional EPR is neither observed nor expected, given the even value of S, but it may be possible to observe some of the eight lowest excited states by means of electronic Raman spectroscopy. This latter possibility will be investigated later.

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