The Properties of Spontaneously Magnetic Osmium Clusters probed by E.S.R. Spectroscopy

Simon R. Drake,[a] Peter P. Edwards,[a] Brian F. G. Johnson,[a] Jack Lewis,[a] David Obertelli,[b] and Nicholas C. Pyper[a]

[a] *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.*

[b] *The Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, U.K.*

E.s.r. measurements show that spontaneously paramagnetic clusters composed of between 10 and 40 osmium atoms all have magnetic properties reminiscent of molecules, rather than the bulk metal.

The discovery[1—7] of spontaneous paramagnetism in a variety of transition metal cluster compounds is intriguing for two reasons. First, it raises the question of the theoretical origin[8] of such magnetic behaviour in systems which, containing an even number of electrons, would be expected to be diamagnetic. Secondly, it is also of interest in the context of the insulator–metal transition.[7,9] Such a change in the electronic structure must occur as the number of constituent atoms in the cluster is progressively increased from numbers characteristic of molecular species to the nearly infinite number present in the bulk metal.

Here we report e.s.r. measurements which are used to extract both electron spin–spin (T_{2e}) and spin–lattice (T_{1e}) relaxation times from e.s.r. spectra for a range of spontaneously paramagnetic osmium clusters. The results are used to locate these species within the overall conceptual framework which we have recently devised[8] for understanding cluster electronic structures over the entire range of metal nuclearity.

Osmium clusters having nuclearities of 3—8 show no e.s.r. signal.[8] This would be expected for systems designated as belonging to Class I in our scheme,[8] in which the occupied molecular orbitals all contain two electrons in accord with the Aufbau principle to yield a non-magnetic species. The osmium clusters of higher nuclearity ($m > 10$, m = no. of metal nuclei) showed strong e.s.r. signals from which the T_{1e} and T_{2e} relaxation times were extracted by the microwave power saturation method.[10] The ground states of these molecules are paramagnetic because, for these large clusters, the HOMO/LUMO gap has become sufficiently small that it is energetically favourable to promote one electron out of the HOMO into the LUMO.[8] This process reduces the electron–electron repulsion since the HOMO and LUMO occupy spatially non-identical regions. The ground state will therefore contain

Table 1. Electron g-value and spin–lattice (T_{1e}) and spin–spin (T_{2e}) relaxation times for osmium carbonyl clusters (**1**)—(**3**).

Cluster	T/K	g	$10^4 \times T_{1e}$/s[a]	$10^{10} \times T_{2e}$/s[a]
(**1**)	4	2.083[b]	22 (±6)	1.90 (±0.3)
	84	2.083	4.9	2.0
	141	2.083	0.12	2.0
(**2**)	5.5	2.18	4.8	3.3
	80	2.18	1.8	3.2
	140	2.18	0.13	3.1
(**3**)	4.2	2.09	3.8	41
	85	2.09	2.3	39
	140	2.09	1.8	42

[a] Typical fractional error estimates given in first entry. [b] g Value for anisotropic spectra quoted as $g_{av.} = 1/3(g_{para} + 2\,g_{perp})$, where g_{para}, g_{perp} are parallel and perpendicular g values, respectively.

unpaired electrons, belonging to Class II in our scheme,[8] if this reduction in the repulsion energy exceeds the increase in the effective one-electron energy arising from the promotion. The latter will approximate the lowest electronic excitation energy of the first positive ion of the cluster.[8]

Table 1 summarises both the T_{1e} and T_{2e} data and observed g-factors at several temperatures for three of these spontaneously magnetic molecules, $[Os_{10}C(CO)_{24}(AuPMe_2Ph)_2]$ (**1**), $[H_2Os_{20}Hg(C)_2(CO)_{48}]$ (**2**), and $[N(PPh_3)_2]_2[Os_{40}Hg_3(C)_4(CO)_{96}]$ (**3**). The data are typical of the results obtained for a total of six magnetic osmium clusters studied.[8] In all of these systems T_{1e} was not only much longer than T_{2e}, but also decreased with increasing temperature.

Since an osmium nucleus has no spin, electron spin relaxation *via* interaction with nuclear spins cannot be responsible for the observed electron relaxation. The intermolecular exchange of electrons between one cluster and another can, in principle, provide a mechanism for spin–lattice relaxation.[11] However, the relaxation rates originating from this mechanism are temperature independent, in contrast to the marked temperature dependence of T_{1e} observed experimentally (Table 1). There is also no evidence that spin exchange contributes significantly to the spin–lattice relaxation even at the lowest temperature.

The magnitudes of spin–orbit interactions are greater than those of electron spin–spin interactions by a factor of the order of Z^2 (where Z is the nuclear charge). Neither of these interactions can, by itself, provide a mechanism for spin–lattice relaxation unless there is some process which causes the interaction to become time dependent.[12] The high nuclear charge of osmium ($Z = 76$) suggests strongly that spin–lattice relaxation arising from spin–spin interactions will be negligible compared with that arising from the modulation of the spin–orbit interaction by lattice vibrations (phonons). Since the deviation (Δg) of the electron g-value from free spin also arises from spin–orbit coupling,[11,12] one would expect T_{1e}^{-1} (the electron spin–lattice relaxation rate) to correlate with the magnitude of Δg if phonon modulation of the spin–orbit coupling was the dominant source of the spin–lattice relaxation.[13] It is well established that this is indeed the case for molecular radicals having substantial g-shifts.[14] The relaxation rates of the osmium clusters (Table 1) are qualitatively similar to those observed for molecular radicals having comparable g-shifts. This provides strong evidence both that the relaxation arises from the spin–orbit phonon mechanism and that the osmium clusters have the properties of molecules despite the substantial number of metal atoms contained in them.

Bulk osmium metal, like the metals of groups 1 and 2, differs from these spontaneously paramagnetic clusters in one fundamental regard; at absolute zero these metals would have closed shell electronic ground states designated as belonging to Class IV in our scheme.[8] In this class, both the HOMO and the LUMO are delocalised over the entire metal as Bloch states.[15] Hence the electronic repulsion would not be reduced by promoting an electron from the HOMO to the LUMO. Thus the driving force for the emergence of spontaneous paramagnetism is absent in the Class IV bulk metal. The e.s.r. spectrum of a bulk metal arises solely from the Pauli paramagnetism which is necessarily induced when the sample is placed in the external magnetic field required for the execution of the e.s.r. experiment.[16]

The spin relaxation properties of bulk metals can be expected to differ significantly from those of the osmium clusters because the phonon energy spectrum in a bulk metal would be quite unlike that of an isolated cluster molecule. Indeed it is known that $T_{1e} = T_{2e}$ for bulk metals,[16] in contrast to the results (Table 1) on our clusters. Furthermore, it has also been predicted that T_{1e} in bulk osmium metal would be substantially different from those of our clusters.[1,2] Evidence that this is indeed the case comes from the T_{1e} value of 10^{-12} s measured in a conduction electron paramagnetic resonance experiment at 4.2 K.[17]

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