

Paramagnetism in High-nuclearity Osmium Clusters

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The even-electron cluster $\text{H}_2\text{Os}_{10}\text{C}(\text{CO})_{24}$ exhibits intrinsic paramagnetism at temperatures below 70 K; such behaviour is characteristic of a particulate metal in the quantum-size effect regime.

There is considerable interest in the physical and chemical properties of small metallic particles with diameters less than 100 Å, not only because of their high catalytic activity¹ but also from their position as intermediaries between the atomic and metallic regimes.² Unfortunately, the detailed characterisation of finely-dispersed metallic crystallites, with unavoidable particle-size distributions within a sample, is a major experimental problem. In contrast, transition-metal cluster compounds are well characterised, molecular materials. Obtainable in exceptionally high purity, they represent metal particles of uniform size and well-established geometries. Carbonyl clusters have been viewed as models for metal crystallites,³ but almost exclusively with regard to their close-packed geometries. Discussion of bonding has successfully concentrated on the number of skeleton electron pairs required to bind the metal cluster units,⁴ implicitly assuming that the electrons are paired in closed shells to yield diamagnetic ground states. This picture is accurate for small clusters, as shown by p.e.s. studies⁵ of $\text{Os}_3(\text{CO})_{12}$ and $\text{Os}_6(\text{CO})_{18}$, but inappropriate for a large cluster where the electronic energy levels must ultimately form quasi-continuous bands, giving rise to characteristic physical properties and incipient paramagnetism.

We report the discovery of low-temperature paramagnetism in the even-electron cluster $\text{H}_2\text{Os}_{10}\text{C}(\text{CO})_{24}$,⁶ providing direct verification that this molecule, corresponding to an osmium particle of approximate overall diameter 10 Å, has magnetic properties similar to those of particulate metals, and displaying quantum-size effects.^{7,8}

Magnetic susceptibility measurements in the temperature range 4.2–300 K, and the magnetic field range 2–12 kG, were carried out using a high-sensitivity Faraday apparatus.⁹ The temperature dependence of the molar susceptibilities for $\text{Os}_3(\text{CO})_{12}$, $\text{Os}_6(\text{CO})_{18}$, and $\text{H}_2\text{Os}_{10}\text{C}(\text{CO})_{24}$ are shown in Figure 1. In the high-temperature limit, the magnitudes of the diamagnetic susceptibilities increase in the order $\text{Os}_3 < \text{Os}_6 < \text{Os}_{10}$, as expected for an increasing contribution from the number of electrons present. The two low-nuclearity clusters are diamagnetic over the entire temperature range. In contrast, the decanuclear cluster exhibits paramagnetism below ca. 70 K, conforming almost exactly with the simple Curie

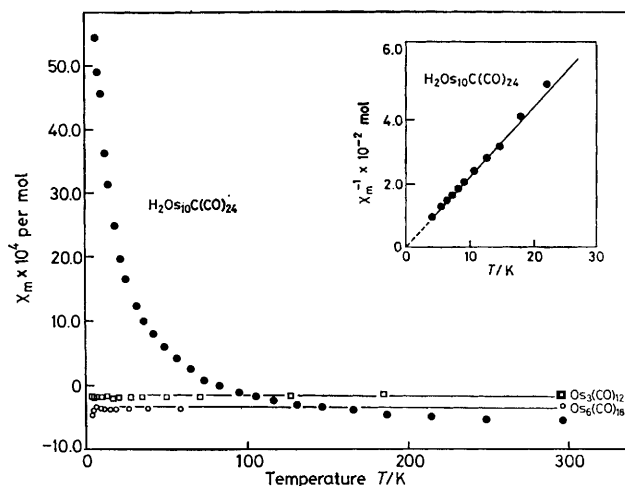


Figure 1. The molar susceptibilities (11.8 kG) of the osmium clusters $\text{Os}_3(\text{CO})_{12}$, $\text{Os}_6(\text{CO})_{18}$, and $\text{H}_2\text{Os}_{10}\text{C}(\text{CO})_{24}$. The susceptibilities have been corrected for the diamagnetism of the sample container. The insert shows a plot of the temperature dependence of the inverse susceptibility for temperatures below 25 K.

Law $\chi_M = C_M/T$ (see insert, Figure 1) with $C_M = 4.77 \times 10^{-2}$ emu K mol⁻¹, giving a nominal magnetic moment of 0.62 Bohr magnetons per cluster molecule. Magnetic impurity levels for these three osmium clusters, determined both by atomic emission spectroscopy and energy-dispersive analytical electron microscopy (e.d.a.x.), were typically less than 10 p.p.m. for Fe, Co, and Cu, so that the observed paramagnetism in $\text{H}_2\text{Os}_{10}\text{C}(\text{CO})_{24}$ far exceeds any contribution from transition-metal impurities in the sample. Indeed, the absence of any paramagnetic behaviour in the $\text{Os}_3(\text{CO})_{12}$ and $\text{Os}_6(\text{CO})_{18}$ samples illustrates the extremely high purity possible in such materials. The magnetic susceptibility of the decanuclear cluster shows no field dependence between 2 and 12 kG over

† $4\pi \chi_M$ (c.g.s. e.m.u.) = χ_M (S.I.)

the temperature range 4.2 to 300 K, again demonstrating that the observed effects do not arise from ferromagnetic impurities.

The paramagnetic behaviour of $\text{H}_2\text{Os}_{10}\text{C}(\text{CO})_{24}$ contrasts with that of bulk metals, which exhibit a small Pauli (temperature-independent) paramagnetic susceptibility, indicative of itinerant electrons in metallic conduction bands.¹⁰ A transition from Pauli- to Curie-type behaviour as the particle size decreases has indeed been predicted,⁷ and observed recently in small particles of both odd- and even-electron metals, such as lithium¹¹ and platinum.¹² In bulk metals the electronic energy levels form a continuum, but in particulate metals the energy differences between successive levels are no longer small compared with other important energies, such as the thermal energy and the electronic Zeeman energy. In this regime the paramagnetism, amongst other properties, displays quantum-size effects.^{7,8} In terms of magnetic properties, $\text{H}_2\text{Os}_{10}\text{C}(\text{CO})_{24}$ clearly behaves as a small metallic particle.

Further evidence that the magnetic behaviour of high nuclearity cluster carbonyls may be similar to that of particulate metals comes from our e.p.r. studies of $\text{H}_2\text{Os}_{10}\text{C}(\text{CO})_{24}$ and $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$.¹³ The spectra are broad (typically ca. 50 Gauss half-width at 38 K), Lorentzian lines with g -values close to free-spin. The resonances broaden as the temperature is raised, and disappear above ca. 100 K, which is consistent with our susceptibility data. This e.p.r. behaviour is directly analogous to conduction-electron spin resonance, observable in bulk for light metals,¹⁴ and in small particles of heavy metals with both odd (*e.g.* silver¹⁵) and even (*e.g.* platinum¹⁶) numbers of electrons.

Some indication of incipient metallization in large clusters also arises from recent work¹⁷ on the Herzfeld treatment of the metal-non-metal transition. Crystals of high-nuclearity cluster carbonyls contain metal atom concentrations approaching those at which, in the absence of ligands, metallization of the bulk sample might be expected. Our experimental results

clearly show that the trend towards metallic behaviour is well advanced for molecular clusters of ten osmium atoms.

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