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The electronic structure of large organometallic clusters

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Abstract

Recent progress in the study of the physical properties of organometallic cluster molecules is surveyed. Magnetic susceptibility, EPR, electrical conductivity and UV-visible spectroscopic measurements have shown the development of “metametallic” properties in high-nuclearity clusters, which illustrate the electronic structure and bonding in these compounds.

Introduction

In more than thirty years since the discovery of an unsupported metal–metal bond in a metal carbonyl [1], very many cluster compounds have been synthesised, and structurally characterised by X-ray crystallography [2,3]. Structural parallels with fragments of metallic lattices are well-recognised [2]. Other clusters show non-lattice geometries (e.g. pentagonal shapes and rafts) which are known from electron microscopy to be adopted by small metallic crystallites [4,5,6].

Despite much interest in the structures and bonding of organometallic clusters, only within the last ten years has interest developed in their physical properties [7], and the way in which “metallic” behaviour might begin to evolve in molecular clusters of large enough size. The electronic properties of metal crystallites with a few tens or hundreds of atoms are known to be in turn modified from those of bulk metals [8], so that the transition between molecular and metallic bonding influences the activity of heterogeneous catalysts by affecting chemisorption behaviour. It is also relevant to the development of novel microelectronic materials and the control of colloid nucleation. Carbonyl clusters form an extensive series of molecules suitable for study. Also of especial interest are large organometallic clusters not yet characterised by crystallographic methods, such as $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$ with three concentric shells of 1, 12 and 42 metal atoms [9], and the palladium complex of idealised formulation $\text{Pd}_{561}(\text{phen})_{36}\text{O}_{200}$, which is believed to contain six shells of metal atoms [10] ideally numbering 1, 12, 42, 92, 162 and 252.

Magnetic properties: susceptibility studies

The geometries of organometallic clusters are understood in terms of theories which count electrons in closed shells of skeletal electron pairs [11–14]. Low-nuclearity carbonyl clusters are consequently diamagnetic, with a temperature-independent paramagnetic (TIP) susceptibility component arising from interaction between ground and excited states in the magnetic field [15]. For $\text{Os}_3(\text{CO})_{12}$ (Fig. 1), the HOMO – LUMO gap is about 3.0 eV (24000 cm^{-1}), comparable to that in low-spin octahedral complexes of the Co^{3+} ion. In larger clusters, the TIP component increases because of the reduced frontier orbital separation [15]. When this separation is small enough, a change to a high-spin electronic configuration, stabilised by electronic exchange energy, leads to overall Curie paramagnetism despite the even-electron count [19,20,21]. This parallels the low-spin to high-spin transition of octahedral ML_6 complexes, but with important differences: instead of the unpaired electrons being essentially localised in the d atomic orbitals of a single central metal atom, the molecular orbitals containing the spin density are delocalised around the cluster, and are made up of atomic orbitals of unknown hybridisation. Spin-only values of magnetic moments are not therefore to be expected.

This type of paramagnetism was first discovered experimentally for $\text{H}_2\text{Os}_{10}\text{C}(\text{CO})_{24}$ [22], and has subsequently been found to be general for osmium carbonyl clusters containing ten or more metal atoms [21,23]. Molecular orbital computations [24] suggest HOMO – LUMO gaps in these compounds to be well under 1 eV. Even-electron carbonyl clusters containing nine or more atoms of nickel [20,25], six of platinum [20,25,26] and as few as four of ruthenium [27] have also been found to be Curie paramagnetic. Their magnetic moments are all low, of the order of 1.0 Bohr Magneton per cluster, except for the nickel compounds which have larger moments [25]. Nickel is a ferromagnetic metal, so indications of bulk behaviour are already being seen at these nuclearities, as suggested computationally for ligand-free metal particles [28].

The magnetic properties of these large molecular clusters are termed “metametallic” [19,20] to emphasise their distinction from diamagnetic low-nuclearity clus-

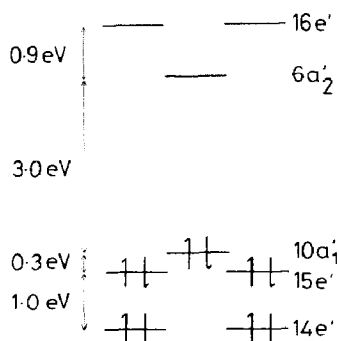


Fig. 1. Frontier orbital structure of $\text{Os}_3(\text{CO})_{12}$. Constructed from results of X_α calculations [16], with energy spacings adjusted to give better agreement with experimental measurements of electronic spectra [17], photoelectron spectra [18] and magnetic susceptibility [15]. Lowest energy allowed transitions in point group D_{3h} are: spectroscopic, $10a'_1 \rightarrow 16e'$ and $15e' \rightarrow 6a'_2$; magnetic, $10a'_1 \rightarrow 6a'_2$ (HOMO – LUMO). ($1 \text{ eV} = 8066 \text{ cm}^{-1}$)

ters and from bulk metals, which ideally show a Pauli (temperature-independent) overall paramagnetic susceptibility. Pauli paramagnetism requires an electronic band structure with energy spacings less than the thermal energy kT ; clearly not the case in these molecules, and unlikely to be attained for clusters with fewer than several hundred metal atoms.

Magnetic properties: EPR studies

The magnetic properties of paramagnetic even-electron organometallic clusters have been further characterised by EPR spectroscopy, principally of polycrystalline solid samples between -100°C and liquid helium temperatures.

For osmium carbonyls, a full variable-temperature EPR study of $\text{H}_2\text{Os}_{10}\text{C}(\text{CO})_{24}$ has been published [19], and spectral parameters of many other clusters of nuclearity up to 40 have been reported [21,23]. The general features may be summarised as follows [29]:

- the symmetry of the EPR lineshape reflects the cluster symmetry;
- significant deviations of g -value from free-spin emphasise the importance of spin-orbit coupling in this $5d$ metal;
- a lineshape distortion observed in some clusters with interstitial hydride ligands is thought to be caused by hydride mobility perturbing the dielectric properties of the solid;
- linewidths and saturation behaviour give electronic relaxation times, typically 10^{-9} seconds for T_2 (spin–spin) and 10^{-3} seconds for T_1 (spin–lattice). Electronic relaxation is slower than in bulk osmium, where additionally T_1 and T_2 are equal, emphasising the intermediate nature of the electronic structures of the osmium carbonyl clusters.

We have recently extended these EPR studies to rhodium carbonyl clusters [30]. The EPR spectrum of the even-electron $[\text{Rh}_{17}\text{S}_2(\text{CO})_{32}]^{3-}$ (Fig. 2) shows a smaller g -shift than the osmium clusters, consistent with the weaker spin-orbit coupling in

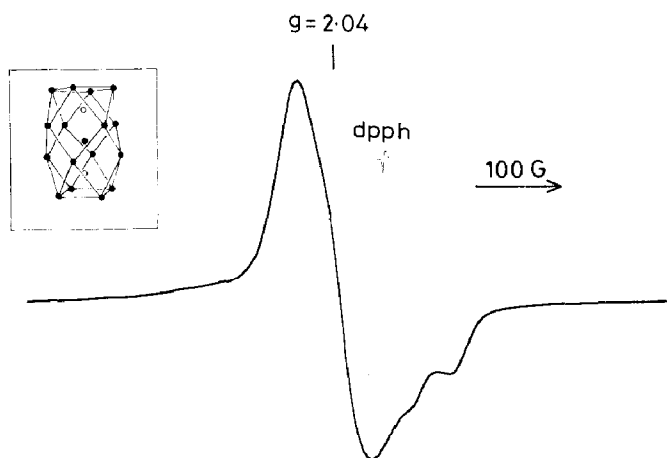


Fig. 2. EPR spectrum (JEOL PE-1-X, X-band, 9.23 GHz) of polycrystalline $[\text{Rh}_{17}\text{S}_2(\text{CO})_{32}]^{3-}$ $[\text{N}(\text{PPh}_3)_2]_3^+$ at 10 K. Microwave power 10 mW, modulation 20 G; $g = 2.04$, ΔH_{pp} 83 G. Inset: cluster structure of $[\text{Rh}_{17}\text{S}_2(\text{CO})_{32}]^{3-}$. ● rhodium; ○ sulphur.

rhodium. One aim of this work was to find from hyperfine coupling to ^{103}Rh nuclei whether the spin density is delocalised around the cluster or localised on individual metal atoms. Although the temperature independence of the linewidth below 75 K shows that it is broadened by hyperfine coupling, the pattern could not be resolved. A similar situation was encountered in the EPR spectrum ($g = 2.09$) of a radical, believed to be $[\text{Rh}_6(\text{CO})_{16}]^+$, which was generated by the chemical oxidation of $\text{Rh}_6(\text{CO})_{16}$ in sulphuric acid [30]. Thus the degree of delocalisation of the frontier molecular orbitals around the metal clusters is not yet known.

EPR of the palladium cluster $\text{Pd}_{561}(\text{phen})_{36}\text{O}_{200}$ shows spectral features quite similar to those of $[\text{Rh}_{17}\text{S}_2(\text{CO})_{32}]^{3-}$; an asymmetric lineshape with g -values 2.010 and 2.035, and a temperature-independent linewidth [31].

It is not yet certain whether $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$, which has an odd number of electrons, shows an EPR spectrum. We have to date been able to observe only a signal exactly at the free-spin position ($g = 2.00$), which is of unclear status [32].

Electronic band structure and electron mobility

The high electrical conductivity of metals arises from the mobility of electrons with delocalised wavefunctions. We may ask to what extent electrons in large organometallic clusters are delocalised and mobile.

The macroscopic electrical conductivity of a solid made up of molecular clusters depends on the movement of electrons from cluster to cluster through the crystal. The cluster compounds $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$ and $\text{Pd}_{561}(\text{phen})_{36}\text{O}_{200}$ in polycrystalline form both show electrical conductivity with temperature-dependence consistent with a mechanism of electron-hopping between clusters [20,33,34]. This is exactly as found for granular metal semiconductors. We are also studying thin films of $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$; surprisingly, no photoconductivity in the range 400–850 nm could be detected at room temperature above the dark current [35]. The cluster absorbs light throughout this wavelength range (see below), so promotion of its electrons to excited states does not significantly increase their hopping probability.

What experimental methods can be used to determine the mobility of electrons within individual cluster molecules?

EPR gives some suggestion of high electron mobility in carbonyl clusters. The spectral parameters and electronic relaxation times resemble in some ways those found in conduction electron spin resonance of metals in colloidal (but not bulk) form [19]. The temperature-dependence of the ^{31}P NMR relaxation time T_1 in $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$ suggests interaction of the phosphine ligands with delocalised electron states in the cluster [36].

A more direct measure of electronic character comes from the molecular response to electromagnetic radiation. It is well-known in colloid science that delocalised, freely mobile conduction electrons confined within a metal particle have a characteristic frequency for collective oscillations. This “plasma resonance” is seen as an absorption band in the UV-visible spectrum of metal colloids [37,38]. Metals with s -band electronic structures show sharp, well-defined plasma resonance absorptions; for silver and gold, these correspond respectively to wavelengths of 390 and 520 nm. These absorptions weaken as the particle size is reduced, but can be observed for gold colloids of diameter as small as 10 \AA [38].

The question arose whether the recently characterised large organometallic clusters of silver and gold might show plasma resonance absorptions in their electronic spectra.

The first candidate was $\text{Ag}_{20}\text{Au}_{18}(\text{PPh}_3)_{12}\text{Cl}_{14}$, which in solution shows a strong absorption at 495 nm, the same wavelength as the plasma resonance absorption in mixed AgAu colloids. Teo proposed [39] this band to be a molecular plasma resonance. We have cast doubt on this assignment, and suggested a weak absorption at 510 nm in the spectrum of $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$ as a more likely possibility [40]. In turn, Kreibig has demonstrated that this absorption probably arises from aggregates of cluster molecules in solution, and that any plasma resonance absorption in individual $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$ molecules is too weak to be observed above the spectral background [41].

We are currently studying the electronic absorption spectrum of $\text{Pd}_{561}(\text{phen})_{36}\text{O}_{200}$. Unfortunately the different electronic structure of palladium causes the plasma resonance absorption in Pd colloids to occur at about 230 nm, a region of the spectrum obscured in organometallic clusters by electronic transitions within the π -systems of the ligands.

At present therefore, no electronic plasma resonance absorption has definitely been observed in an organometallic cluster molecule.

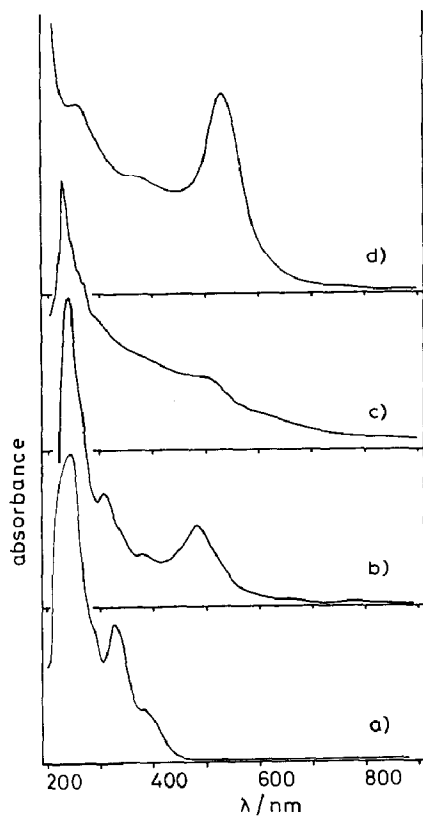


Fig. 3. UV-visible spectra (Shimadzu UV 240). (a) $\text{Os}_3(\text{CO})_{12}$ in CH_2Cl_2 solution; (b) $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}[\text{N}(\text{PPh}_3)_2]_2^+$ in CH_2Cl_2 solution; (c) $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$ in CH_2Cl_2 solution; (d) Au colloid, 150–200 Å diameter, in aqueous solution.

A more positive conclusion concerns the buildup of electronic structure away from the well-separated energy levels of low-nuclearity clusters towards the continuous band structure of metals (Fig. 3) [40]. The UV-visible absorption bands of small clusters such as $\text{Os}_3(\text{CO})_{12}$ are essentially one-electron transitions [17]. At nuclearity 10, the bands may represent envelopes of individual absorptions [42], but are still discrete and well-defined. In contrast, the UV-visible spectrum of $\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6$ much more closely resembles that of colloidal gold. It is dominated by a single, broad absorption from 250 nm to beyond 800 nm, which represents transitions from the closely spaced electronic levels of the developing $5d$ "band" into the $6s,6p$ "band" of the cluster [40]. In colloidal gold (150 Å diameter), this interband transition is fully developed, with additional features corresponding to fine structure in the $5d$ band's density of states (Fig. 3).

Thus the distribution of electronic energy levels in an organometallic cluster acquires some features of bulk-like character at quite low nuclearities. On the other hand, other aspects of electronic structure such as cluster ionisation potential [18] may develop much more slowly. For example, ^{195}Pt NMR chemical shifts of large platinum carbonyl clusters are much more typical of molecular complexes than of metallic platinum [43].

Conclusion

Studies of organometallic clusters by a range of physical methods have revealed some unusual "metametallic" properties. These illustrate the development of electronic structure in clusters away from that of small molecules, at least some way towards that of metal colloids and bulk metals. Implications for the chemical reactivity of metal clusters and the heterogeneous catalytic activity of metallic crystallites have yet to be fully explored.

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