Metal clusters: a personal perspective *

John Evans

Department of Chemistry, University of Southampton SO17 1BJ, UK

Metal cluster chemistry spans synthetic molecular chemistry, the solid state, vapour phase species and nanoparticles. The following articles show constructive overlap between these areas that provide new opportunities for research targets.

Why a Personal Perspective?

Faraday Discussions have been an established feature of the Royal Society of Chemistry for decades, affording that community a meeting format which allows all attendees to be acquainted with the papers presented and to report results, comments and criticisms in open debate. These can be very stimulating to both participants and observers. This issue of *Dalton Transactions* reports the first Dalton Division meeting of this type.

Four topics were chosen for the meeting with a Keynote lecture devoted to each. These are presented as the four Perspective articles following this overview. The topics and presenters were:

Molecular clusters – Mike Mingos
Gas-phase clusters – Martin Jarrold
Solid-state clusters – John Corbett
Colloids and catalysts – Gunter Schmid.

The bulk of the meeting consisted of short (7 minute) presentations based on the 23 full *Dalton Transactions* papers and an accompanying discussion, with about two-thirds of the time devoted to the discussion element. This aspect of Faraday Discussions is reported within the volume of the Discussions of the Faraday Society in a quasi-verbatim fashion. Rather than follow this approach, which essentially involves a second round of publication steps (submission of questions, eliciting replies and checking of proofs), the alternative adopted in this volume is that a personal view of the presentations and discussion should be given. The aim is that this should not extend the publication time beyond the normal *Dalton Transactions* range. The task of providing an overview that would represent all of the views expressed is scarcely possible, so this is strictly a personal view of the proceedings. It was though enlightened by the most open and challenging discussion of any Dalton meeting at which I have been present. My aim is to consider all of the four topics in turn and present aspects which seem to be pivotal with regard to research direction. These may be from individual insights, reports of new techniques or be a result of viewing a problem with the perspective borrowed from another field.

Molecular Clusters

Cluster complexes are one of the mainstream topics of *Dalton Transactions* and so it is not surprising that the majority of papers covered the main aspects of this research field: synthesis, structure and dynamics. As was pointed out by Brian Johnson, the reactivity of cluster complexes is still studied far less, with mechanistic papers rare shafts of light illuminating synthetic strategies and exploiting the potential for novel ligand sites and reactivities.

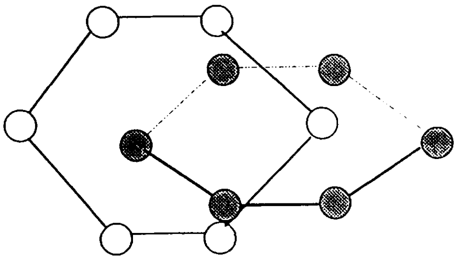

Fig. 1 Two interconnecting gold hexagons in $[\{Au_6(CCBu^t)_6\}_2]$

Synthesis and structure

Mike Mingos provided a systematic account of the flexibility of gold–gold interactions allowing a wide variety of intermolecular connectivities.[1] In particular, the contrast was made between (*a*) weaker Au···Au electronic interactions and (*b*) cluster bonding with accountable topologies dividing between spherical ($12n_s + 18$) and toroidal ($12n_s + 16$), with specific electron counting patterns (n_s = number of surface cluster atoms). The weaker interactions between $5d^{10}$ gold(I) centres (3.0–3.2 Å) are sufficiently strong (10–30 kJ mol^{-1}) to cause extended arrays in the solid state. The simplest of these was between $[Au(NH_3)_2]^+$ complexes with an Au–Au distance of 3.414 Å. A particularly elegant cluster formed by these interactions was the catenane linkages in $[\{Au_6(CCBu^t)_6\}_2]$ (Fig. 1).[1]

The theme of linking or fusing clusters *via* heavy metals was echoed in the presentation by Lutz Gade.[2] Two Os_9 units had been previously linked by mercury atoms in, for example, $[Os_{18}Hg_xC_2(CO)_{42}]^{2-}$ (x = 2 or 3). Reduction and subsequent chromatography led to the extrusion of mercury to form $[Os_{18}HgHC_2(CO)_{42}]^{3-}$. However, attempts to remove the final mercury atom to fuse the two Os_9 units had not been successful.

Several different heteroatoms were reported to support or link cluster units, including (semi)interstitial boron,[3] nitrogen[4] and phosphorus.[5] Although synthetic strategies can be successful, often the instability of particular intermediates is lower than expected {*e.g.* the predicted square-pyramidal anions $[RhRu_4(nbd)(CO)_{12}(\mu_5\text{-}B)]^-$ (nbd = norbornadiene)[3]} or the closure of linked clusters into a fused unit does not proceed.[5] In the last case suggestions to use labile phosphine substituents such as $SiMe_3$ emerged. The pseudo-hydrogen group $[Au(PPh_3)]^+$ was successfully used to trap heterometallic clusters,[3] and extend cluster nuclearity.[6] The interstitial nitride in $[Fe_4N(CO)_{12}]^-$ allowed additional Fe atoms to be incorporated into the complex in two different ways.[4] Reaction with $[Fe_2(CO)_8]^{2-}$ afforded the octahedral ion $[Fe_6N(CO)_{15}]^{3-}$, whilst substitution with diferrocenylphenylphosphine provided two communicating redox centres (the ferrocenyl and Fe_4N units). An interesting variant on this theme was the linking of Ir_4 clusters by phosphaferrocenyls.[7]

---

* Based on the presentations given at Dalton Discussion No. 1, 3rd–5th January 1996, University of Southampton, UK.

Two Ir_4 clusters could be attached to the $P_3C_2Bu^t{}_2$ ligand, which could then undergo a γ-C–H oxidative addition of one of the methyl groups with one cluster. These clusters may also have a rich electrochemistry and John Nixon had targets of incorporating cationic phosphametallocenes into these linked arrays, which presumably may attain dendritic character.

Group 16 bridged clusters were also a subject of considerable interest. Structurally one of the simplest, but very difficult to characterise, was the green triniobium cluster formed from the hydrolysis of $[NbCl_3(dme)]$ (dme = dimethoxvethane).[8] Spectroscopic evidence indicated this anion to be $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3(OH_2)_9]^{4+}$, although uncertainty was evident about the degree of protonation in the aqueous solution. Interestingly, reaction with $K[HB(pz)_3]$ was reported to form $\mu_3\text{-}BO_4{}^{5-}$ with normal $HB(pz)_3{}^-$ ligands substituting the aqua groups. Larger clusters were systematically synthesised by stoichiometric hydrolysis of metal oxoalkoxides, *e.g.* $WO(OMe)_4$, or homoleptic alkoxides, *e.g.* $Nb(OMe)_5$ in non-aqueous solvents.[9] This resulted in elegant syntheses of hexametalates, *e.g.* $[TiW_5O_{19}]^{4-}$, with the ability to label with ^{17}O for NMR purposes. Some alkoxide ligands could be retained, as in $[(MeO)TiW_5O_{18}]^{3-}$, and be used as a functional group to link two octahedral clusters by an oxo bridge $\{$in $[(Nb_5WO_{18})_2(\mu\text{-}O)]^{4-}\}$. The stability of the alkoxide units varied so that only some combinations would give linked clusters at room temperature. At elevated temperature (100 °C) controlled hydrolysis of $Ti(OBu^t)_4$ in Bu^tOH–toluene was found to afford a new cluster type for Group 4 elements.[10] This resulted in a 'superkeggin' structure in $[Ti_{18}O_{28}H][OBu^t]_{17}$. Within the cluster there are 12 octahedrally coordinated Ti centres, five with distorted trigonal-bipyramidal geometry and a central tetrahedral unit. The solution of this particular structure on twinned crystals was a *tour de force*, and was only achieved using a charged-coupled device area detector and specially developed software for deconvoluting the diffraction patterns of the Siamese twin crystals. The nuclearity of alkoxide-bearing clusters was strongly governed by the bulk of the alkyl group. The synthesis was thought to proceed *via* an intermediate complex $[Ti_3O][OBu^t]_{10}$, the structure of which is likely to be similar to that of $[Ti_3O][OMe][OPr^i]_9$; the face-bridging methoxyl group is in a very sterically demanding position forming a close-packed-like array of methyl groups on one face of the molecule.

The largest chalcogenide metal clusters reported used the silyl telluroether reagent $TeBu^n(SiMe_3)$.[11] The nature of the products from the reaction with CuCl was very dependent upon the phosphine and solvent [tetrahydrofuran or 2,5,8-trioxanonane (diglyme)]. For example, with PEt_3 in thf, the complex $[Cu_{23}Te_{13}(PEt_3)_{12}]$ was isolated in 90% yield, whereas using PPh_3 in diglyme allowed isolation of $[Cu_{58}Te_{32}(PPh_3)_{16}]$. In discussion, it transpired that the redissolution of these compounds and reaction with a different phosphine could change the nuclearity of the clusters, suggesting a degree of lability in solution. The structures themselves were not fragments of bulk copper tellurides. They were best described as involving Te_n polyhedra (Fig. 2) with copper atoms on the faces of these polyhedra. These two examples contrast the hexagonal close-packed-like layered structure within the core of $[Cu_{18}(\mu_3\text{-}TeBu^n)_6Te_6(PPr^n{}_3)_8]$ and the centred icosahedron in $[Cu_{23}Te_{13}(PEt_3)_{12}]$. The bonding in these clusters is too complex to describe as being held only by strong Cu–Te interactions. There are also weak Cu···Te links and a variety of Cu–Cu distances (*e.g.* 2.38, 2.55 and 2.72 Å).

Spectroscopy and dynamics

The characterisation of interstitial elements by NMR spectroscopy has grown in recent years and in line with this, data for borides,[3] nitrides[4] and hydrides[12] were presented at the meeting. Solid-state and solution NMR data on transition-metal hydrides were reported,[12] which could link the low frequency shifts to anisotropic sites within distorted octahedra; this is analogous to the cause of the shifts of terminal and bridging hydrides attached to transition metals with partially filled d shells. A particularly striking observation was the shift difference between phases for $[Co_6H(CO)_{15}]^-$ (*viz.* +23.2 in solution and +1 in the solid state). While, in principle, this could be due to a difference in the site anisotropy between the phases, this was in marked contrast to other examples. The suggestion offered was the original proposal by Chini for high frequency proton resonances as resulting from a migration to carbonyl oxygens, essentially hydrogen bonded within the oxygen polyhedron. There was some debate about the basis of boride, carbide and nitride chemical shifts. Catherine Housecroft had observed the reliable chemical shift contribution of each connected ruthenium atom [but little effect from the $5d^{10}$ gold(I)] and Lutz Gade noted a high frequency shift caused by compression of the metal cage around a carbide, but a global rationalisation of these particular chemical shifts remains as elusive for these sites as for many others.

The non-rigidity of cluster complexes, both in terms of metal–ligand relative motions and fluxional cages was of considerable interest. Solid-state relaxation time measurements (T_1 and T_2) at high field were reported for the hydride resonances of $[Ru_2Rh_2H_2(CO)_{12}]$. These indicated only localised librations of the hydrogens which undergo labile intersite transfer in solution.[12] To obtain this result, the hydride resonance had to be resolved from that of occluded solvent; this cast doubt on previous results, obtained with much lower chemical shift dispersion, which suggested intersite fluxionality of the hydrides of $[Ru_4H_4(CO)_{12}]$ in the solid state.

The fluxionality of $[Fe_3(CO)_{12}]$ has been one of the most discussed exchange mechanisms in the last 25 years. Evidence for dynamic disorder in the solid state was reported for $[Fe_2Os(CO)_{12}]$ $\{$and also recently for $[Fe_2Ru(CO)_{12}]\}$.[13] At low temperatures the structure consisted of ordered arrays of the molecular cluster with the heavier metal in the all-terminal site (Fig. 3). As the temperature was raised, the proportion of a second orientation with the metal triangle rotated by 180° increased, presumably due to the increased entropic stabilisation of disordered solids. Carbon-13 NMR exchange spectroscopy experiments with two different mixing times indicated two

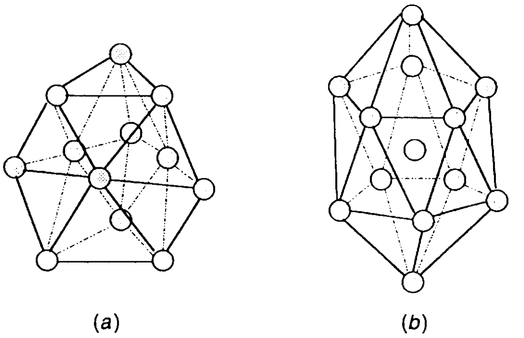
(*a*) (*b*)

Fig. 2 Tellurium core polyhedra in (*a*) $[Cu_{18}(\mu_3\text{-}TeBu^n)_6Te_6(PPr^n{}_3)_8]$ and (*b*) $[Cu_{23}Te_{13}(PEt_3)_{12}]$

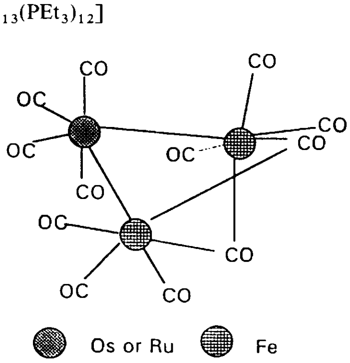

Fig. 3 Molecular structure of $[Fe_2M(CO)_{12}]$, M = Ru or Os

different dynamic processes at ambient temperatures, assigned as rotations of the metal triangle in 60° steps and a localised rotation/twist of the $Os(CO)_4$ unit. These must occur *via* relative orientations which are not observed by X-ray diffraction, either through a high degree of disorder of those orientations or, more likely, due to a low occupancy in the crystals. Brian Heaton noted that the thermal ellipsoids of the metal atoms did not demonstrate a soft potential along the proposed in-plane rotation vectors. However, it was recognised that for a disordered, heavy atom structure, these can be artefactual.

A soft potential surface has also been noted for hexanuclear clusters with the cores $[Ru_4MM']$ ($M = M' =$ Cu, Ag or Au) varying between capped trigonal-bipyramidal and capped square-pyramidal geometries.[6] In the particular examples presented, with the two Group 11 metals linked by the flexible bidentate ligand $Fe(C_5H_4PPh_2)_2$ the barrier to site exchange of the non-rigid cores ($M = M' =$ Cu or Ag) was in the region of 40 kJ mol^{-1}. A general point was noted that core rearrangements can be at least as rapid as hydride migration processes.

Gas-phase Clusters

The current state-of-the-art of the structural chemistry of mass selected cluster cations was illustrated by Martin Jarrold for $[C_n]^+$, $[MC_n]^+$ and $[M_2C_n]^+$ species.[14] The introduction of a gas-filled drift tube between the source and detection mass spectrometers allows isomeric cations to be resolved on the basis of their orientationally averaged collision cross-sections. Thus compact ions, such as fullerenes have higher velocities than ring structures. By varying the accelerating voltage on the ions the effective temperature of the clusters can be modified to probe kinetic *versus* thermodynamic isomeric preferences. For many carbon cluster cations fullerenes, graphitic sheets, polycyclic and monocyclic structures could be identified; annealing fullerene-sized clusters, such as $C_{60}{}^+$ caused the polycyclic rings to isomerise to fullerenes *and* monocyclic rings (of 25 Å diameter for $C_{60}{}^+$), and also to fragment partially by loss of C_2 units to lose their high internal energy. The incorporation of metal atoms added the complexity of establishing the metal sites, and observing the effect on the isomer stability. Palladium, as an example of a late transition element modified the distribution so that in $PdC_{50}{}^+$ there was no evidence of any fullerenes, only a broad distribution of ring types. At higher ionic energies this ion fragmented into Pd and $C_{50}{}^+$, which was mainly fullerene. More electropositive metals like Nb and La provided more robust clusters. There were significant differences between these two metals. For example, for larger clusters (> 36 carbon atoms) lanthanum was endohedral, $La@C_n{}^+$. For Nb, however, such structures were only evident for *even* carbon number clusters; for *odd* C_n, the metal atom is exohedral, probably capped at a defect site in the polyhedron. With two La atoms, both metal atoms appear to reside inside for $n > 63$ and n is *even*. For $La_2C_n{}^+$, where n is *odd*, one metal atom was located inside the cage and the second incorporated into the cage.

An alternative method of proposing structure by utilising density functional calculations was applied to copper sulfide anions, $[Cu_xS_y]^-$, formed from laser ablation of either metal sulfides or elemental mixtures.[15] Gas-phase ions up to $[Cu_{45}S_{23}]^-$ were observed. Varying reactivities could be observed with collision gases. For example, $[Cu_{10}S_6]^-$ [Fig. 4(*b*)][15] was extremely unreactive, whilst $[Cu_6S_4]^-$ [Fig. 4(*a*)] formed adducts with RSH (R = H, Pr^n or Ph). The suggestion was made by John Errington to test gas-phase reactions with phosphines in an attempt to link the chemistry with that of Dieter Fenske's group.[11] Laser ablation of $[Ru_6C(CO)_{17}]$ generated ions in the mass spectrum with $m/z > 20\,000$.[16] These appeared to be cluster aggregates of the cluster core with a residue of carbonyl ligands; for example the highest mass ion observed could correspond to $[(Ru_6C)_{29}(CO)_{83}]^+$. This cluster aggregation was reduced by partial ligand substitution by arene ligands, as in $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Me)]$, and eliminated for charged clusters. It is clear that there is substantial chemistry occurring either within the nanosecond duration of the laser-induced plume, or in the rather longer duration of its dispersal. Brian Johnson saw this as a new synthetic opportunity, but Keith Fisher offered a warning that the apparent ion distribution could be a function of the detector.

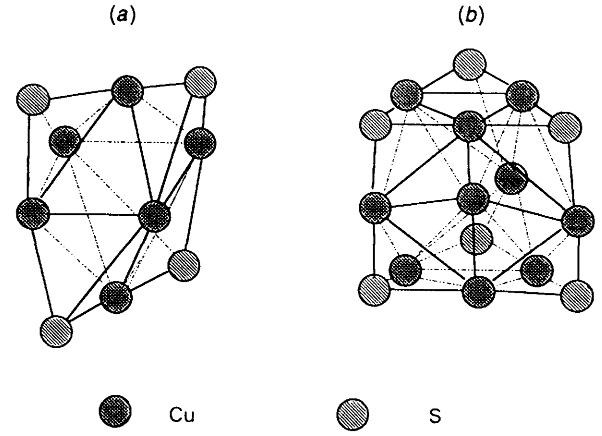

Fig. 4 Proposed structures for (*a*) $[Cu_6S_4]^-$ and (*b*) $[Cu_{10}S_6]^-$

Characterisation of clusters generated by the thermal vaporisation and matrix isolation (in adamantane or argon) of Group 1 and Group 11 metals by ESR spectroscopy has proven to be very powerful.[17] The M_3 clusters have Jahn–Teller distortions and Li_3 was found to be fluxional even at 4 K. Interaction of water with the trisodium cluster in $Na_3(H_2O)$ was also reported; the superhyperfine coupling to the protons is small and is probably more consistent with oxygen rather than hydrogen co-ordination to one of the sodiums. Co-ordination of water or ethene to trimers of either Group favoured distortion to an acute triangle, rather than the obtuse or dynamic Jahn–Teller distortions of the ligand-free clusters.

David Wales presented an overview of the empirical potential calculations of bare transition-metal clusters.[18] These were necessary because *ab initio* calculation surveys of structures are not possible for other than small clusters at present. Since there are vast numbers of local minima in structural optimisations wide ranging surveys are necessary. There is concern about the validity of these potentials, and their limitations, for example in not producing Jahn–Teller distortions; hence their value is especially important for larger clusters. Obtaining experimental evidence to calibrate these calculations was difficult, but surface studies of vapour deposited clusters were beginning to provide these. An interesting general conclusion was that skeletal electron counting rules are likely only to apply to ligated clusters; for free electron systems, 'magic number' stability is likely to be geometrically based, with structures like the Mackay icosahedron (*e.g.* M_{55}) seeding and dominating a growth mechanism. Much discussion centred around the importance of structure. Pseudo-potential calculations simulate temperatures of *ca.* 10 K, but Brian Johnson proposed that these clusters would be liquid drops at room temperature and so structure might be unimportant. David Wales replied that there were some deep minima in structures as well as many local minima. Surface melting might be somewhat above room temperature. In this debate, it is interesting that the picture of liquid water is emerging as being substantially like that of ice over a localised region and short time-scale. Liquid metals also are locally close packed. So understanding the structure of clusters (as one example of a solid structure) seems to this author to be a base point before any molecular-level understanding is possible. From that point the dynamics of any concerted fluxionality or even of melting can begin to be explained.

Solid-state Clusters

This seems an appropriate point in the discussion to turn to solid-state clusters and relate something of the geometrical beauties described by John Corbett.[19] Two aspects were covered: early transition-metal and rare-earth compounds and also Zintl-like phases. Many of the first of these contained linked or fused $[M_6(\mu_6\text{-}M')X_{12}]$ units. One remarkable structure in cubic $[Zr_6(Co)Cl_{12}]Cl_{6/2}$ contains two interpenetrating three-dimensional arrays on octahedral clusters linked by terminal chlorines to the six adjacent clusters (Fig. 5); this seems to be the ultimate catenane!

Perhaps more remarkable though are the structures of the Group 1–Group 3 alloys. This may be an inappropriate term since the reduction of Group 3 metals to negative oxidation states tilts the bonding from metallic to covalent. For example, in $Rb_3Na_{26}In_{28}$ there are linked In_{12} icosahedra and drums (hexagonal antiprisms). As remarked by Ken Wade, this complex linking of polyhedra is reminiscent of elemental boron. Other structures could be described as sheathed clusters. For example, in $Na_3K_8Tl_{13}$, the core-centred icosahedron Tl_{13} is sheathed by 32 cations (one per face and vertex of the Platonic solid). The *coup de grace* was certainly $Na_{172}In_{199}Ni_{12}$, which in the endohedral nomenclature contains the shell structures $Ni@In_{10}@Na_{37}@In_{70}$, with the In_{70} cage possessing the C_{70} fullerene geometry. John Corbett made the interesting observation that many intermetallic phase diagrams have been constructed solely from thermochemical data, with no phase confirmation by X-ray diffraction. They had found that many of the reported stoichiometries had been incorrect, thus opening up the likely existence of many more novel structures of varying dimensionality.

Alkali-metal clusters are also formed from the vapour deposition of the metals into the faujasite zeolites M-Y.[20] Effectively the metals are dissolved in the zeolites forming cluster crystals templated by the zeolites cavities. The well known Na_4^{3+} ion was found to reside in the smaller sodalite cavities, rather than the supercage. This exhibits a sharp ESR spectrum with sodium hyperfine interactions. Over 64 sodium atoms can be deposited per unit cell, and as the addition increases the coupling is lost, probably due to electron interactions between the clusters. Deposition of potassium into K-Y leads to both K_4^{3+} clusters in the sodalite cage and the diamagnetic K_{12}^{4+} within the supercage. The metal–metal distances are thought to be dominated by the preferred M–O distances. The excess of electron density remains associated with the cationic network, rather than the aluminosilicate framework.

Colloids and Catalysts

Aqueous sols of transition metals have been stabilised by sulfonated triphenylphosphine and other ligands.[21] The ligands may form a double-layer protecting the colloid from aggregation. Gunter Schmid's group have developed procedures which provide a very narrow size distribution (monodispersed in colloidal parlance) in which the mean number of metal atoms appears to be close to the geometric 'magic numbers', such as the Mackay icosahedron sequence (see above). For example, the shorthand 'Au_{55}' label is ascribed to materials containing particles with a metal core of 1.4 nm diameter and a ligand shell giving a total external diameter of 2.1 nm. Other preparations give larger clusters, such as the 'Pt_{309}' material (protected by phenanthroline or sulfonated phenanthroline) which shows nine lattice fringes in the transmission electron microscopy (TEM) image, and a diameter of 2.2 nm (consistent with *ca.* 300 Pt atoms). As the particle size decreases the 'free' electron wavelength becomes restricted and significant deviations from the properties of bulk metal occur, for example in their specific heat. Scanning tunnelling microscopy (STM) at liquid helium temperatures suggests the formation of discrete energy levels. Gold-197 (formed by neutron bombardment of the Pt atoms) Mössbauer spectra of 'Pt_{309}' show three identifiable sites: core (indistinguishable from gold metal), phenanthroline co-ordinated (edge sites) and peroxo co-ordinated (face sites); ^{195}Pt NMR shows a Knight shift for the core atoms only. These materials have interesting electronic and chemical properties. The ligand sheath is found to affect the selectivity of, for example, alkyne hydrogenation. A particularly interesting result was that the coating of palladium by gold still maintained activity. The electronic absorption spectrum suggested that the excited state exhibits Au→Pd electron transfer (rather than the reverse expected for the ground state). This has become the basis of a photovoltaic effect with these clusters attached to *n*Si. Using bifunctional and spacer ligands, networks of clusters could be formed on surfaces, and clusters have been intercalated into porous alumina with the aim of forming bundles of cluster wires. Matrix assisted laser desorption ionisation (MALDI) mass spectrometry of '$Pd_{561}(phen)_{60}(O_2CMe)_{180}$' (phen = 1,10-phenanthroline) contained a broad spread of anions with *m*/*z ca.* 62 500, corresponding approximately to this formulation.[22] Fragmentation patterns roughly correspond to the stripping of shells from this five-shell polyhedron; it was acknowledged that this seemed an unlikely ionisation process, illustrating again the complex chemistry within laser desorption processes.

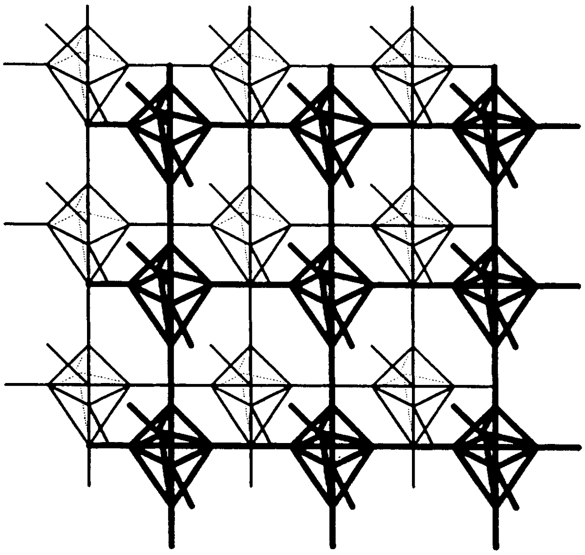

Fig. 5 Two-dimensional slice of the interlocking three-dimensional networks in $[Zr_6(Co)Cl_{12}]Cl_{6/2}$

Groups 10 and 11 nanoparticles were also reported from metal vapour deposition into ketones containing polymeric stabilisation agents.[22] The MALDI spectrum of one of the gold preparations in butan-2-one showed a peak ion distribution around 4860 (perhaps corresponding to $[Au_{21}L_{10}]^+$), and other ions with *m*/*z* over 9000. Again, very small, ordered particles could be observed by TEM (down to 1 nm). These were images supported on silica microspheres and also on the cubic microcrystals of the (100) faces on an MgO smoke; the gold particles had an epitaxial relationship with the MgO. Surprisingly, the sols were stable only *above* a critical concentration (0.01%), otherwise they could be stable for many months. Mike Mingos was interested in the potential of these sols for complex formation however most attempts had either caused dissolution or flocculation.

Deposition of metal vapours and a cluster beam source onto highly oriented pyrolytic graphite (HOPG) was monitored by scanning electron microscopy (SEM) and STM.[23] This shows the preferences for clusters to aggregate on deep steps. Implantation of small clusters with an energy of 200 eV afforded a broad particle size distribution, showing both the source clusters and also larger aggregates. However, at higher impact energies (400 eV) the incidence size was maintained, probably due to their trapping as relatively deep implants. The SEM images of very small Ag particles (down to 12 atoms) showed commensurate growth on the graphite planes and also electronic screening of the particle by the semiconductor substrate. In an exchange between Richard Palmer and Peter Edwards, it was noted that the drop in ionisation energy from that of atomic silver might be needed to allow this electron transfer; this reduction from Ag_7 and higher mass clusters was confirmed by Bryn Mile.

Metal particles could also be formed by hydrogen reduction of occluded cobalt(II) nitrate into the zeolite Na–X.[24] These attained a particle size of 150–250 Å, shown by TEM to be both within the bulk of the zeolite microcrystals and also on their surfaces. These particles are much too large to be contained with a single supercage. Interestingly, hydrogenation of vapour-deposited $[Pd(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)]$ also resulted in particles larger than the supercage.[25] In this case most particles were of about 25 Å diameter. The Pd content indicated that these particles would be about 100 Å apart. Carbon monoxide adsorption occurred on both the Na^+ and Pd particles (terminal and bridging sites). While the three-dimensional template of an aluminosilicate lattice might seem to be an attractive template for cluster growth (as observed for Group 1 metals[20]) transition metals show both the ability to migrate and aggregate (either gathering at defect regions or causing them).

Protected colloids have been shown to provide catalysts (for the synthesis of crown ethers)[26] and also as the basis of a highly sensitive analytical technique.[27] The colloidal rhodium catalyst (for aromatic hydrogenation)[26] was protected by tertiary amines. The structure of the protecting layer was probed by ^{13}C NMR spectroscopy, TEM and diffusion coefficient measurements. The NMR spectra showed similar behaviour for different chain lengths of amine. The external radius estimates from the diffusion coefficient measurements were considerably smaller than the sum of the metal particle size and the amine chain length, suggesting the alkyl chains may be prone to the surface for the first few carbon atoms. It is noteworthy that the NMR spectra of the amines show a dynamic equilibrium between the dissolved and adsorbed amines; this may be significant for the catalytic properties.

Surface-enhanced Raman and surface-enhanced resonance-Raman spectroscopy are two related techniques. The laser frequency can be matched to a surface plasmon to provide enhanced Raman activity of adsorbed molecules (or those within 20 Å of the surface); this activity is further enhanced when the excitation frequency matches that of a chromophore within the adsorbate. Reliable preparations of silver colloids and aggregation with poly-L-lysine and ascorbic acid have been developed to probe the applicability of these methods in analysis.[21] Surface-enhanced resonance-Raman spectroscopy was found to be prodigiously sensitive for dyes such as rhodamine 6G. Reliable quantitative signal intensity of molecular vibrations could be observed down to 6×10^{-18} mol dm^{-3}; it was expected that instrumental improvement could give single molecule counting. The techniques can also be applied to the study of adsorbate structures. The Group 11 metals provide the highest sensitivity due to the overlap of laser sources with their plasmon frequencies, but the technique could be extended to the study of chromophoric adsorbates on other metals albeit with a loss of sensitivity.

Conclusion

The separate themes of the meeting certainly showed significant overlaps not only in general thinking but in providing visions for future developments. As examples one can cite:

- size selection of vapour-phase clusters for materials synthesis
- ligand and ionic linking of clusters to form arrays of superclusters or nanoparticles
- surface etching to provide templates for cluster synthesis
- use of laser ablation vaporisation for synthesis
- use of π-acid ligands in collision experiments on vapour-phase clusters.

Characterisation of all these clusters is difficult, but the advances in mass spectrometry, drift tube design, solid-state NMR spectroscopy, X-ray diffraction, force microscopy and computational methods provide great opportunities. As ever, a combination of technical skill and clarity of vision is needed to exploit these to most benefit. This meeting suggested to me that these are not commodities in short supply.

Acknowledgements

I wish to thank the staff of the Royal Society of Chemistry both in Burlington House and the Dalton office for their time and effort towards this volume. I am also grateful to the Scientific Committee (Peter Edwards, Brian Johnson, Mike Mingos, Paul Raithby and Tony Stace) and Local Committee (Judith Corker, Gill Reid, Bill Levason and Mark Weller) most especially for carrying out a significant part of their excellent advice at very short notice.

References

1 D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1996, 561.

2 L. H. Gade, B. F. G. Johnson, J. Lewis, M. McPartlin and I. J. Scowen, *J. Chem. Soc., Dalton Trans.*, 1996, 597.

3 A. D. Hattersley, C. E. Housecroft and A. L. Rheingold, *J. Chem. Soc., Dalton Trans.*, 1996, 603.

4 R. Della Pergola, C. Bandini, F Demartin, E. Diana, L. Garlaschelli, P. L. Stanghellini and P. Zanello, *J. Chem. Soc., Dalton Trans.*, 1996, 747.

5 B. F. G. Johnson, J. Lewis, E. Nordlander and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1996, 755.

6 I. D. Salter, V. Sik, S. A. Williams and T. Adatia, *J. Chem. Soc., Dalton Trans.*, 1996, 643.

7 M. H. A. Benvenutti, P. B. Hitchcock, J. F. Nixon and M. D. Vargas, *J. Chem. Soc., Dalton Trans.*, 1996, 739.

8 S. Minhas and D. T. Richens, *J. Chem. Soc., Dalton Trans.*, 1996, 703.

9 W. Clegg, M. R. J. Elsegood, R. J. Errington and J. Havelock, *J. Chem. Soc., Dalton Trans.*, 1996, 681.

10 C. F. Campana, Y. Chen, V. W. Day, W. G. Klemperer and R. A. Sparks, *J. Chem. Soc., Dalton Trans.*, 1996, 691.

11 J. F. Corrigan, S. Balter and D. Fenske, *J. Chem. Soc., Dalton Trans.*, 1996, 729.

12 T. Eguchi, B. T. Heaton, R. Harding, K. Miyagi, G. Longoni, J. Nähring, N. Nakamura, H. Nakayama, T. A. Pakkanen, J. Pursiainen and A. K. Smith, *J. Chem. Soc., Dalton Trans.*, 1996, 625.

13 L. J. Farrugia, A. M. Senior, D. Braga, F. Grepioni, A. G. Orpen and J. G. Crossley, *J. Chem. Soc., Dalton Trans.*, 1996, 631.

14 K. B. Shelimov, D. E. Clemmer and M. F. Jarrold, *J. Chem. Soc., Dalton Trans.*, 1996, 567.

15 K. Fisher, I. Dance, G. Willett and M.-N. Yi, *J. Chem. Soc., Dalton Trans.*, 1996, 709.

16 M. J. Dale, P. J. Dyson, B. F. G. Johnson, P. R. R. Langridge-Smith and H. T. Yates, *J. Chem. Soc., Dalton Trans.*, 1996, 771.

17 B. Mile, P. D. Stillman, A. R. Yacob and J. A. Howard, *J. Chem. Soc., Dalton Trans.*, 1996, 653.

18 D. J. Wales, L. J. Munro and J. P. K. Doye, *J. Chem. Soc., Dalton Trans.*, 1996, 611.

19 J. D. Corbett, *J. Chem. Soc., Dalton Trans.*, 1996, 575.

20 L. J. Woodall, P. A. Anderson, A. R. Armstrong and P. P. Edwards, *J. Chem. Soc., Dalton Trans.*, 1996, 719.

21 G. Schmid, V. Maihack, F. Lantermann and S. Peschel, *J. Chem. Soc., Dalton Trans.*, 1996, 589.

22 R. W. Devenish, T. Goulding, B. T. Heaton and R. Whyman, *J. Chem. Soc., Dalton Trans.*, 1996, 673.

23 G. M. Francis, I. M. Goldby, L. Kuipers, B. von Issendorff and R. E. Palmer, *J. Chem. Soc., Dalton Trans.*, 1996, 665.

24 I. Hussain, I. Gameson, P. A. Anderson, P. P. Edwards and A. Dyer, *J. Chem. Soc., Dalton Trans.*, 1996, 775.

25 L. Sordelli, G. Martra, R. Psaro, C. Dossi and S. Coluccia, *J. Chem. Soc., Dalton Trans.*, 1996, 765.

26 T. Yonezawa, T. Tominaga and D. Richard, *J. Chem. Soc., Dalton Trans.*, 1996, 783.

27 C. Rodger, W. E. Smith, G. Dent and M. Edmondson,. *J. Chem. Soo., Dalton Trans.*, 1996, 791.