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NOTES

The Bonding Capabilities of Transition Metal Clusters

3. Two-Dimensional Supported Clusters

The structure and chemical reactivity of ultradispersed supported transition metal clusters are of obvious importance to designers of catalytic systems. Thus the recently published electron microscopy studies by the group at Exxon are of considerable interest (*1–3*). They found that Rh when ultradispersed upon silica or alumina tended to form two-dimensional clusters or rafts, which consist of layers of atoms one atom thick (*1*). Pt on TiO_2 after high-temperature H_2 reduction forms two-dimensional pillbox structures which are small clusters no more than a few layers thick (*2*). Ru–Cu bimetallic systems may be similar (*3*). Chemisorption studies indicate that for some of these two-dimensional clusters very high CO/M ratios can be achieved. A ratio of 1.73 was reached for a series of the rhodium-on-alumina experiments. The Pt pillbox clusters, on the other hand, had a low bonding capability.

Small aggregates of metal cannot be regarded as merely pieces of the bulk metal, but should instead be considered as molecular entities. They should have definite structures and form compounds with definite stoichiometries as would any small aggregate of atoms. Discrete organometallic compounds are known which contain such small clusters of transition metal atoms surrounded by suitable ligands such as carbon monoxide. For example, Rh cluster compounds such as $Rh_6(CO)_{16}$, $[Rh_{15}(CO)_{27}]^{3-}$, and $[Rh_{14}(CO)_{25}]^{4-}$ have been prepared (*4*). The largest known cluster compoud to date is a truly massive 38-Pt-atom cluster synthesized by Chini (*5*).

Recently we have published details of a molecular orbital procedure which allows us to accurately estimate the bonding capabilities of individual atoms of a cluster of metal atoms and thus to determine the stoichiometries of ligand bonding (*6, 7*). Using our method nearly all of the known organometallic cluster compounds can be accounted for. Each atom of the cluster can be assigned a characteristic number of valence molecular orbitals (CVMOs) which is dependent upon the site geometry. The CVMOs can contain metal electrons or can be used as ligand acceptor orbitals. The number of CVMOs located on an atom at a given site of a three-dimensional cluster is inversely dependent upon the number of nearest neighbors.

When metal atoms aggregate the valence atom orbitals of the atoms evolve into the band structure of the bulk metal. An atom has nine atomic orbitals, which leads to the well-known 18-electron rule of organometallic chemistry. A bulk metal has only about 5.3 occupied orbitals per metal atom as determined from magnetic data and confirmed by band structure calculations. An atom of a cluster has a number of CVMOs intermediate between the 9 orbitals of an atom and the 5.3 orbitals per atom of the bulk. The precise number depends upon the site geometry. The octahedron, **1**, has 6 A sites each with 7.17 CVMOs or a total of 43 for the entire cluster. The presence of 43 CVMOs means that a M_6 octahedral cluster compound would need 86 cluster valence electrons (CVEs). An example would be $Rh_6(CO)_{16}$ with 54 rhodium *d* electrons and 32 electrons from the donor orbitals of the 16 CO

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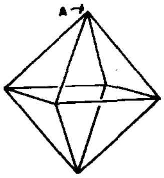

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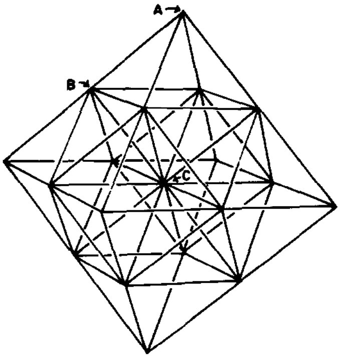

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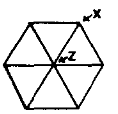
ligands for a total of 86. The next larger octahedron, 2, has 19 metal atoms, but not all are equivalent. there are 6 A atoms with 7.17 CVMOs, 12 B atoms with 6.29, and the lone interior atom C which has only 5.7 (Table 1). In general as the number of nearest neighbors goes up the number of CVMOs goes down.

The 5.7 CVMOs of the central atom C correspond to the 5.3 occupied orbitals of the energy band of a metal (*7*). The discrepancy of 0.4 orbital is due to the *p*-orbital contribution which is not found in most band structure calculations, but which is important for cluster compounds. If a cluster is to be stabilized as a molecular entity, then the CVMOs of each metal atom must be satisfied either by containment of metal electrons or as acceptor orbitals for ligand binding. It is difficult to stabilize the interior atoms, C, of a three-dimensional cluster because they are not on the surface and normal ligand bonding is not possible. Due to this problem most known large-cluster compounds of metals like Rh contain heteroatoms within the cluster. Examples include the hydride $[Rh_{13}(CO)_{24}H_3]^{2-}$ (*8*), the carbide $[Rh_{15}(CO)_{27}C_2]^-$ (*9*), and the sulfide $[Rh_{17}(CO)_{32}S_2]^{3-}$ (*10*). Each of these clusters has a heteroatom occupying either an octahedral or a square antiprismal hole which supplies electrons to interior metal atoms.

In our previous work we have examined three-dimensional clusters since they form the cores of the known stoichiometric cluster compounds. In the work to be described here we have investigated two-dimensional clusters and will offer our explanation for the existence of such entities as supported aggregates.

Using the same methods and parameters used previously (*6, 7*) we have performed extended Hückel calculations on close-packed two-dimensional Rh clusters of up to 19 atoms. For each cluster the geometry was idealized with Rh–Rh distances of 2.69 Å corresponding to the distance in Rh metal. Molecular orbitals are calculated for each cluster and the CVMOs identified as those orbitals with energies at or below the *p* level of a free Rh atom. The analyses of the individual site bonding capacities are made using the calculated atomic coefficients of each CVMO. The results are presented in Table 1. Our calculations are for Rh but the results may be used equally well for neighboring elements of the periodic table once an allowance is made for differences in the electron count.



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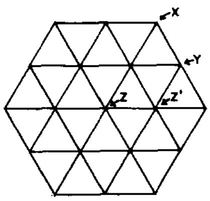

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TABLE 1

Analysis of Site Bonding Capabilities[a]

	Cluster	N	Site	N_s	N_{nn}	CVMO	s	p	d
1.	Octahedron	6	A	6	4	7.17	0.71	1.56	4.90
2.	Octahedron	19	A	6	4	7.13	0.71	1.52	4.90
			B	12	6	6.29	0.55	0.89	4.86
			C	1	12	5.71	0.44	0.54	4.74
3.	Hexagon	7	X	6	3	6.99	0.73	1.35	4.92
			Z	1	6	6.05	0.54	0.66	4.85
4.	Hexagon	19	X	6	3	6.92	0.71	1.29	4.91
			Y	6	4	6.45	0.62	0.93	4.90
			Z	1	6	5.93	0.50	0.58	4.85
			Z′	6	6	5.98	0.52	0.59	4.86

[a] N is the number of atoms; N_s is the number of such sites; N_{nn} is the number of nearest neighbors of an atom at the site; CVMO is the number of CVMOs at the site; s, p, and d are the relative contributions from the s, p, and d orbitals.

We chose to model two-dimensional clusters by considering various hexagonal Rh clusters. The smallest such cluster is the Rh_7 cluster, **3**, while the next largest is the Rh_{19} species, **4**. Table 1 shows a detailed analysis of site bonding capabilities of the individual atoms within each cluster.

The Rh_7 cluster has a total of 48 CVMOs, meaning that for stability as a molecular entity there must be 96 cluster valence electrons. The Rh_7 has only 63 Rh d electrons so 33 electrons must be supplied by ligands such as CO or oxygen atoms of the support. An example of a hypothetical species meeting this criteria would be the anion $[Rh_7(CO)_{16}]^-$. The free valencies may also be expressed in terms of theoretical ligands per Rh ratios (L/Rh) which would in this case be equal to 2.36 (Table 2). The 48 CVMOs are not distributed equally over the various atom sites. The corner atoms, X, each have 6.98 CVMOs while the central atom, Z, has only 6.05 with the difference due mainly to the p-orbital contribution.

A similar analysis of the Rh_{19} cluster gives similar results. Each of the central Z atoms contribute about 5.95 CVMOs to the cluster with 6.91 from each corner atom, X. The edge atoms, Y, are intermediate with 6.45 CVMOs. Thus the same trend is observed as we saw in the three-dimensional clusters; as the number of nearest neighbors increases the number of CVMOs at a site decreases.

The surprising aspect of these results is that the number of CVMOs of a central atom, Z, of a two-dimensional cluster with 6 nearest neighbors is 5.95 which is only slightly greater than the 5.7 CVMOs located on the central C atom of the octahedral cluster which has all 12 of the nearest neighbors of a close-packed lattice. This means that the energy band structure is almost as fully developed in the two-dimensional case as it would be for a three-dimensional cluster. This occurs only for an atom which is surrounded in two dimensions. A three-dimensional edge atom B of the Rh_{19} octahedron also has 6 nearest neighbors but makes a higher (6.29) CVMO contribution to the cluster.

The theoretical L/Rh ratio for a Rh_{19} cluster is 1.96, which is smaller than the 2.36 value found for Rh_7. These ratios serve as a general indicator of bonding capacity.

Using the site analysis data of Table 1 the total number of CVMOs can be calculated for larger hexagons which are too large to be treated explicitly on our computer. The next larger hexagonal cluster would contain 37 Rh atoms, including 19 interior atoms (Z), 12 edge atoms (Y), and 6 corner atoms (X). Summing the Rh_{19} results for each of these sites, the total number of CVMOs for the entire cluster can be estimated and a theoretical L/Rh ratio can be determined. The results are shown in Table 2 for clusters as large as Rh_{331}. Also shown is the maximum dimension of each hexagonal cluster. Similar methods were used to determine L/Rh ratios for a series of octahedral clusters as well, Table 3, using our previously published site analyses (*7*).

Rh Rafts

The existence of alumina-supported Rh rafts was established by Yates *et al.* (*1*) who used a combination of electron microscopy and chemisorption to characterize them fully. Their samples contained a range of cluster sizes with maximum dimensions of about 40 Å. The highest observed CO/Rh ratios were equal to 1.7 for samples of 1% Rh on alumina H_2 reduced at 200°C. The average raft size in these clusters was equal to 15.1 Å. This observed ratio is in reasonable agreement with the calculated L/Rh ratios for clusters of this size range (Table 2).

The question remains as to why the two-dimensional clusters form in the first place. To answer this question one needs to compare the bonding capacities of two-dimensional clusters with those of three-dimensional clusters of similar sizes. The L/Rh ratios of the Rh_{331} hexagon and the Rh_{344} octahedron are similar. This means that for molecular stability the two clusters would need to bind to a similar number of ligating atoms, which would most likely be the oxygen atoms of the oxide support. The key difference is in the relative numbers of surface atoms.

TABLE 2

Theoretical Bonding Capacities of Hexagonal Clusters Expressed as Ligands per Rhodium Ratios

Cluster	L/Rh[a]	Dimension[b] (Å)
Rh_1	4.50	2.7
Rh_7	2.36	8.1
Rh_{19}	1.92	13.4
Rh_{37}	1.76	18.8
Rh_{61}	1.68	24.2
Rh_{91}	1.63	29.6
Rh_{127}	1.60	35.0
Rh_{169}	1.58	40.4
Rh_{217}	1.56	45.7
Rh_{271}	1.54	51.1
Rh_{331}	1.53	56.5

[a] The ratio L/Rh is the number of two-electron-donor ligands per Rh atom needed for molecular stability.

[b] The maximum diagonal dimension.

TABLE 3

Theoretical Bonding Capacities of Octahedral Clusters Expressed as Ligands per Rhodium Ratios

Cluster	L/Rh[a]	L/Rh_s[b]	Dimension[c] (Å)
Rh_1	4.50	4.50	2.7
Rh_6	2.67	2.67	6.5
Rh_{19}	2.03	2.14	10.3
Rh_{44}	1.77	2.05	14.1
Rh_{85}	1.62	2.09	17.9
Rh_{146}	1.53	2.19	21.7
Rh_{231}	1.51	2.38	25.5
Rh_{334}	1.48	2.58	29.3

[a] The ratio L/Rh is the number of two-electron-donor ligands per Rh atom needed for molecular stability.

[b] The ratio L/Rh_s is the number of ligands per surface Rh atom.

[c] The maximum diagonal dimension.

The larger an octahedral cluster becomes, the smaller the percentage of surface atoms. Ratios of needed ligands per surface atom, L/Rh_S, are also shown in Table 3. These ratios are of necessity larger than the L/Rh ratios and are much larger than the corresponding hexagonal values. Steric requirements will prevent the actual attainment of ratios higher than about 2.0 for the larger clusters. This means that the free valencies of these clusters cannot be met and that the cluster will lack molecular stability. The difficulty lies in the need to satisfy the valencies of the interior atoms which cannot bind to external ligands. Two-dimensional clusters are, on the other hand, all surface. Each atom is exposed on both sides of the cluster and the desired L/Rh ratios may easily be met.

Since three-dimensional Rh clusters of modest size cannot be stabilized as molecules, they will deform and rearrange to form two-dimensional clusters. If a three-dimensional cluster is of sufficient size, it will lose its molecular properties and will not be subject to these distortions. At this point it is not possible to say how large a cluster must be for that to happen, but it is likely to be several hundred atoms.

In summary Rh rafts are found because they can be stabilized as molecules by the available ligating atoms of the support, while three-dimensional clusters cannot.

Heteroatoms

There is one mechanism for the supported three-dimensional clusters to gain the stability they otherwise lack. This is by the introduction of heteroatoms. A heteroatom such as a carbon or oxygen atom introduced into the octahedral holes of a cluster of metal atoms does not appreciably change the orbital structure, but does supply the electrons needed to stabilize the interior atoms. As previously noted (*7*) most large Rh organometallic cluster compounds contain such heteroatoms.

The presence or absence of heteroatoms may thus have a direct effect upon the structure of supported metal aggregates. It is possible that such heteroatoms may come from the support or from the solvent or substrate. The manner of catalyst preparation may thus have a role. In a dirty preparation with heteroatoms available three-dimensional clusters should predominate, while in a more carefully controlled clean experiment two-dimensional clusters may form. Experiments to test this hypothesis would be useful.

Pt on TiO_2

Baker *et al.* (*2*) have studied Pt on TiO_2. Under high-temperature H_2 reduction the Pt forms flat two-dimensional pillbox structures. Upon oxidation they grow in thickness and lose their two-dimensional character. Upon rereduction the pillbox structures return. It was hypothesized that these changes in structure were due to a change in the TiO_2 support, but we wish to suggest the possibility that the loss of two dimensionality may be due instead to the introduction of oxygen heteroatoms into the clusters during the oxidation process. Upon rereduction the oxygen interstitials would be removed and a reformation to the pillbox structures would take place. The crystalline TiO_2 support used in these experiments may differ from other supports such as silica or alumina, for which no pillbox structures were observed (*2*), by being cleaner and relatively free of loose heteroatoms.

These admittedly speculative analyses may or may not be correct in detail, but we are confident that our main hypothesis is correct. Small metal clusters are molecular entities which should exhibit definite structures and definable stoichiometries as would any small aggregate of atoms.

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