Analytical Electron Microscopy of $[Ni_{38}Pt_6(CO)_{48}H]^{5-}$

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Approximately uniform size particles, corresponding to the dimension of the metallic skeleton of $[Ni_{38}Pt_6(CO)_{48}H]^{5-}$, have been observed in the electron microscope at low beam intensities and electron energy loss spectroscopy (e.e.l.s.) is consistent with analytical data expected for this anion; at higher electron beam intensities particle agglomeration occurs together with formation of graphitic carbon and a face-centred cubic Ni/Pt alloy.

The recent isolation and complete *X*-ray structural characterisation of large metal carbonyl clusters ($[Ni_{38}Pt_6(CO)_{48}H]^{5-}$,[1] $[HNi_{38}(CO)_{42}(C)_6]^{5-}$,[2] $[Ni_{35}(CO)_{39}(C)_4]^{6-}$,[3] and $[HNi_{34}(CO)_{38}(C)_4]^{5-}$,[3]) show that the radii of the metal skeletons approach the dimensions of the metallic crystallites which are currently of considerable interest because of their catalytic ability and other unusual physical properties.[4—6] Apart from *X*-ray analysis and recent solid state n.m.r. spectroscopic and magnetic susceptibility measurements,[7,8] much other work needs to be undertaken in order to understand the solid state properties and bonding of these large metal carbonyl clusters and their interaction with solid supports. As part of a new programme of work in this area, we now report on an analytical electron microscopic (a.e.m.) study of $(NMe_3CH_2Ph)_5[Ni_{38}Pt_6(CO)_{48}H]$, (**1**), deposited on carbon, including electron energy loss spectroscopy (e.e.l.s.) and energy dispersive analysis of *X*-rays (e.d.a.).

At low electron beam intensities, the electron micrograph of (**1**), deposited as an acetonitrile solution (*ca.* 10^{-6} M) on a carbon grid under the rigorous exclusion of oxygen, shows apparently uniform size spots (*ca.* 11 Å, Figure 1a) corresponding to the radius of the metallic skeleton (10.9 Å) in (**1**)

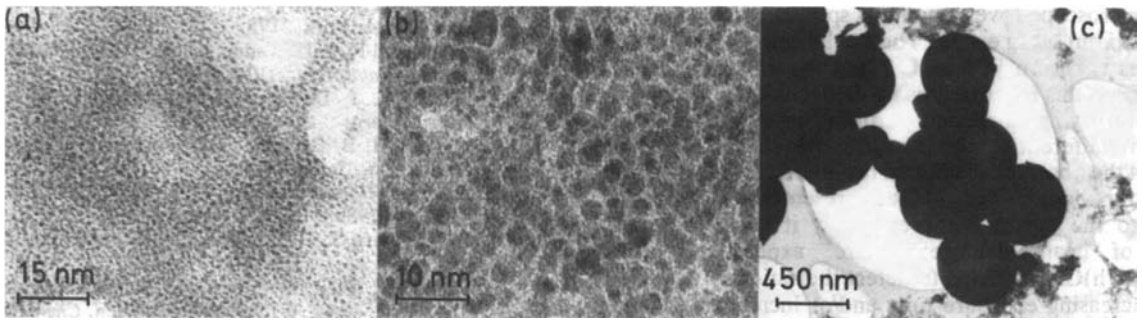
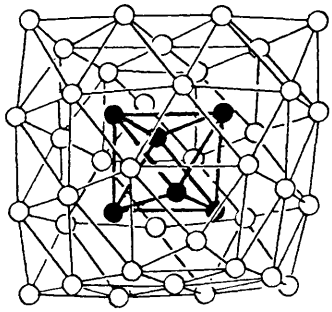


Figure 1. Electron micrograph of $(NMe_3CH_2Ph)_5[Ni_{38}Pt_6(CO)_{48}H]$ deposited on a carbon support as a solution in MeCN. (a) Initially, *ca.* 11 Å; (b) after agglomeration, but without significant beam damage, *ca.* 40 Å; (c) *ca.* 10^4 Å hollow spheres.

Table 1. Analytical results required and found for $(NMe_3CH_2Ph)_5[Ni_{38}Pt_6(CO)_{48}H]$ deposited on a carbon support from e.e.l.s.

	C/N	C/O	C/Ni	O/Ni
Found	∞	0.96 (±0.13)	1.36 (± 0.26)	1.40 (±0.12)
$[Ni_{38}Pt_6(CO)_{48}H]^{5-}$	∞	1.00	1.26	1.26
$(NMe_3CH_2Ph)_5[Ni_{38}Pt_6(CO)_{48}H]$	19.6	2.04	2.58	1.26



● = Pt

Figure 2. Metallic skeleton in $[Ni_{38}Pt_6(CO)_{48}H]^{5-}$.

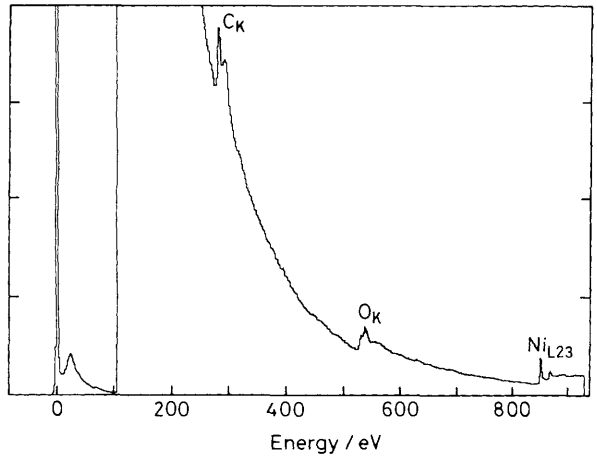


Figure 3. E.e.l.s. of $(NMe_3CH_2Ph)_5[Ni_{38}Pt_6(CO)_{48}H]$ deposited on a carbon support.

(see Figure 2).[1] As the electron beam intensity increases, agglomeration first occurs to give approximately uniform size particles (*ca.* 40 Å, Figure 1b) before beam damage is suffered with the formation of a nickel/platinum alloy and graphitic carbon (see later). Both agglomeration and beam damage are found to be dependent on electron beam intensity and total dose.

Elemental analysis on the 11 Å particles observed in the electron microscope (over a nominal spot size of 200 nm) has been carried out using e.e.l.s. The e.e.l.s. spectrum of the 11 Å particles is shown in Figure 3 and the analytical results obtained from this spectrum, using the technique of core-loss analysis employing calculated partial (ionisation) cross sections of the different elements,[9] are shown in Table 1 which shows that the observed elemental ratios are very close to that expected for the anion of (**1**). It is presently not clear what happens to the cation but presumably it is not observed because of beam damage; control experiments using $(NMe_3CH_2Ph)Cl$ also failed to detect the cation.

With increasing exposure time and/or increasing electron beam intensity, electron micrographs show a skin of graphitic carbon (from e.e.l.s.) to form around the metal particles which are a Ni/Pt alloy; this has been shown to have a face-centred cubic structure from electron diffraction (the lattice parameter, a_0, is 3.58 ± 0.2 Å) but the exact composition seems to depend both on the electron beam intensity and dosage in a manner which is not yet clear.

It should also be mentioned that large (*ca.* 10^4 Å), hollow spheres of (**1**) have often been observed in the above work. The spheres are clearly hollow because they are electron transparent and, by altering the objective lens current, it is possible to focus on the top and bottom surfaces; solid features of this size and composition would be electron dense at 120 kV. Examination of the spheres by e.d.a. shows them to consist of discrete cluster units of approximate composition Ni : Pt 3 : 1 which are held together in some presently undefined way. Beam damage causes surface striations, resulting in formation of a web-like sphere, which then becomes fluid-like and collapses to a solid particle of the Ni/Pt alloy described above. There has been a recent report of an electron microscopic study[10] of the presumed Au_{55} cluster $Au_{55}(PPh_3)_{12}Cl_6$.[11] In this case the ligands could not be detected in the electron microscope and are presumably lost on electron impact but the remaining gold particles show a similar dynamic behaviour to that described above.

These first results using a.e.m. to study large metal carbonyl clusters provide very encouraging data and this method of analysis of clusters promises to become as useful as a.e.m. is proving to be in the structural characterisation of catalyst particles and new inorganic materials.[12]

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