Synthesis, Characterization and Electrochemical Behaviour of the $[Fe_4Au(CO)_{16}]^{n-}$ (n = 1,2,3) Clusters. X-Ray Structure of $[NMe_3CH_2Ph]_2[Fe_4Au(CO)_{16}]Cl$

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The new green $[Fe_4Au(CO)_{16}]^-$ cluster anion, isolated from the reaction of $[Fe_3(CO)_{11}]^{2-}$ with $[AuCl_4]^-$ salts, displays a bow-tie metal structure similar to that of the $[Fe_4M(CO)_{16}]^{2-}$ (M = Pd, Pt) dianions; its chemical and electrochemical reduction sequentially affords the corresponding $[Fe_4Au(CO)_{16}]^{2-}$ and $[Fe_4Au(CO)_{16}]^{3-}$ anions, the former of which may be considered as a formal d^9 gold(II) complex of the $[Fe_2(CO)_8]^{2-}$ ligand.

Several Cu–Fe and Ag–Fe bimetallic clusters are known, in which $Fe(CO)_4$ moieties formally behaving as two- or four-electron donors are present, *e.g.* $[Cu_3Fe_3(CO)_{12}]^{3-}$,[1] $[Ag_4Fe_4(CO)_{16}]^{4-}$,[2] $[M_5Fe_4(CO)_{16}]^{3-}$ (M = Cu, Ag),[1,2] $[Cu_6Fe_4(CO)_{16}]^{2-}$,[3] $[Ag_6Fe_3(CO)_9\{CH(PPh_2)_3\}]^4$ and $[Ag_{13}Fe_8(CO)_{32}]^{4-}$.[5] Although several Au–Fe bimetallic derivatives have already been reported,[6–8] Au–Fe clusters containing gold exclusively coordinated by metals and related to the above Cu–Fe and Ag–Fe compounds are not known.[8] We report here our first results in this area, which consist of the synthesis of the series of new Au–Fe mixed clusters of general formula $[Fe_4Au(CO)_{16}]^{n-}$ (n = 1, 2, 3), the X-ray structural analysis of $[NMe_3CH_2Ph]_2[Fe_4Au(CO)_{16}][Cl]$, and a comparison of their spectroscopic and electrochemical behaviour with those of the $[Fe_4M(CO)_{16}]^{2-}$ (M = Pd, Pt)[9] and the $[Fe_4M'(CO)_{16}]^{2-}$ (M' = Cd, Hg) derivatives.[10]

The deep green $[Fe_4Au(CO)_{16}]^-$ monoanion [ν_{CO}/cm^{-1} in tetrahydrofuran (thf) 2015 s, 1990m and 1957mw has been obtained in variable yields by reaction of any of the miscellaneous iron carbonyl anions {*e.g.* $[Fe(CO)_4]^{2-}$, $[Fe_2(CO)_8]^{2-}$ and $[Fe_3(CO)_{11}]^{2-}$} with either $[AuCl_4]^-$ or $Au(SEt_2)Cl$ in thf. Although each of the above possible combinations of reagents eventually affords a mixture of $[Fe_4Au(CO)_{16}]^-$, a yet uncharacterized Au–Fe carbonyl cluster and some gold metal, the highest yields (*ca.* 80%) in the former were obtained by using $[Fe_3(CO)_{11}]^{2-}$ and $[AuCl_4]^-$. The $[Fe_4Au(CO)_{16}]^-$ monoanion has been separated from the reaction mixture by extraction into $CHCl_3$ and crystallized from thf by layering with n-hexane.

The crystal structure of $[NMe_3CH_2Ph]_2[Fe_4Au(CO)_{16}][Cl]$ has been determined by X-ray crystallography.† An ORTEP[13] drawing of the $[Fe_4Au(CO)_{16}]^-$ monoanion is shown in Fig. 1, together with the most significant bond parameters. The Au atom sits on a centre of symmetry but the idealized molecular symmetry is D_{2h}. The $[Fe_4Au(CO)_{16}]^-$ anion can be described in terms of two $[Fe_2(CO)_8]^{2-}$ anions linked to a central gold(III) atom adopting a square-planar coordination. The CO ligands are terminally bonded; eight equatorial groups lie in the bow-tie plane and the remaining eight are in axial positions. The axial carbonyl groups are tilted towards the central gold (average Au···C contact 2.9 Å). The coordination geometry of the Fe atoms is distorted octahedral and the Fe–Fe distance, 2.771(2) Å, is comparable with that found in the $[Fe_2(CO)_8]^{2-}$ dianion {2.844(1), 2.787(2) and 2.792(1) Å as its $[NEt_4]^+$,[14] $[N(PPh_3)_2]^+$,[15] and $[PPh_4]^+$[16] salts, respectively}. The structure of $[Fe_4Au(CO)_{16}]^-$ is closely related to that of $[Fe_4M(CO)_{16}]^{2-}$ (M = Pd, Pt),[9] which may be likewise considered as d^8 M^{II} complexes of the bidentate $[Fe_2(CO)_8]^{2-}$ ligand. The major difference is in the axial carbonyl groups; in contrast with the present complex, in these complexes only one axial carbonyl of each $Fe(CO)_4$ moiety is bent towards the

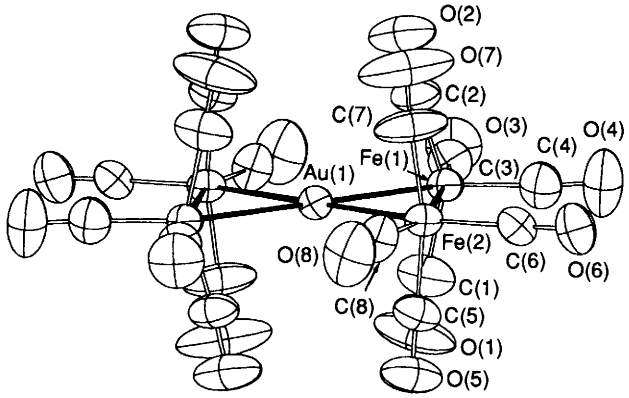

Fig. 1 ORTEP[13] drawing of the $[Fe_4Au(CO)_{16}]^-$ anion with thermal ellipsoids drawn at the 30% probability level. The Au atom is located on an inversion centre. Selected bond distances (Å) and angles (°): Fe(1)–Au(1) 2.583(1), Fe(2)–Au(1) 2.607(1), Fe(1)–Fe(2) 2.771(2), Fe(1)–C(1) 1.79(1), C(1)–O(1) 1.13(1), Fe(1)–C(2) 1.77(1), C(2)–O(2) 1.14(1), Fe(1)–C(3) 1.77(1), C(3)–O(3) 1.14(1), Fe(1)–C(4) 1.77(1), C(4)–O(4) 1.15(1), Fe(2)–C(5) 1.79(1), C(5)–O(5) 1.14(1), Fe(2)–C(6) 1.79(1), C(6)–O(6) 1.13(1), Fe(2)–C(7) 1.79(1), C(7)–O(7) 1.11(1), Fe(2)–C(8) 1.76(1), C(8)–O(8) 1.15(1), Au(1)···C(1) 2.84, Au(1)···C(2) 2.79, Au(1)···C(5) 2.97, Au(1)···C(7) 3.00 Å, C(2)–Fe(1)–C(1) 151.3(6), C(7)–Fe(2)–C(5) 166.5(6)°.

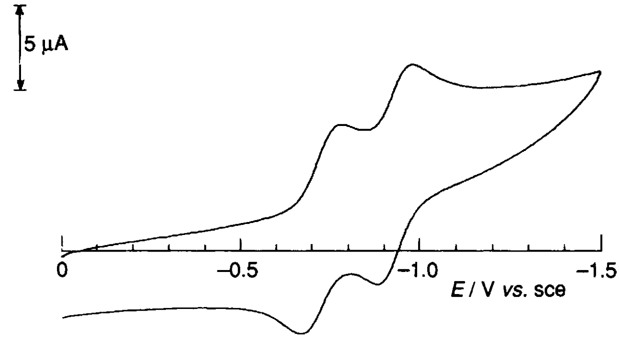

Fig. 2 Cyclic voltammogram recorded at a platinum electrode for an acetonitrile solution containing $[NEt_4][Fe_4Au(CO)_{16}]$ (5.0×10^{-4} mol dm^{-3}) and $[NEt_4]ClO_4$ (0.1 mol dm^{-3}). Scan rate 0.2 V s^{-1}.

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† *Crystal data* for $C_{36}H_{32}AuClFe_4N_2O_{16}$: M_r = 1204.456, orthorhombic, space group $Pccn$ (No. 56), a = 23.618(4), b = 16.600(3), c = 11.594(3) Å, V = 4545.5 Å^3, Z = 4, D_c = 1.76 g cm^{-3}, $F(000)$ = 2360, μ(Mo-Kα) = 47.27 cm^{-1}. No. of data measured 7320 (+h, +k, ±l), no. of unique observed reflections with $F_o > 4\sigma(F_o)$ 4321, no. of parameters 270. Diffraction data collected on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo-Kα radiation (ω-scan) at room temperature between $2 < \theta < 27°$. Intensity data were corrected for linear isotropic decay, Lorentz and polarization effects. The structure was solved by direct methods (SHELXS 86)[11] and Fourier syntheses and refined by full-matrix least-squares calculations (SHELX 76).[12] All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed in calculated positions (C–H = 1.08 Å). Final agreement indices: R = 0.047, R_w = 0.052. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

central atom (Pd–C$_{av}$ = 2.37, Pt–C$_{av}$ = 2.28 Å),[9] so as to give rise to a superimposed tetrahedral coordination of carbon atoms. The significance of bent carbonyl groups is controversial.[1,17,18] The differences in bending of the axial carbonyls in the above compounds clearly point out the relative significance of repulsive inter-ligand electronic effects within each Fe(CO)$_4$ moiety *vs.* attractive M–CO electronic effects on substitution of Pd or Pt with Au.

Consideration of $[Fe_4Au(CO)_{16}]^-$ as a formal d^8 gold(III) complex of the $[Fe_2(CO)_8]^{2-}$ bidentate 4-electron ligand suggests the possible presence of a low-lying gold orbital. In fact, the $[Fe_4Au(CO)_{16}]^-$ monoanion can be reduced with sodium naphthalenide in thf to the corresponding di- and tri-anion and, as illustrated in Fig. 2, in acetonitrile solution it shows the reversible one-electron reduction steps in eqn. (1).

$$[Fe_4Au(CO)_{16}]^- \underset{-e}{\overset{\substack{E^{\circ\prime} = -0.73\,V \\ +e}}{\rightleftarrows}} [Fe_4Au(CO)_{16}{}^{2-} \underset{-e}{\overset{\substack{E^{\circ\prime} = -0.93\,V \\ +e}}{\rightleftarrows}} [Fe_4Au(CO)_{16}]^{3-} \quad (1)$$

Both the $[Fe_4Au(CO)_{16}]^{2-}$ [ν_{CO}/cm^{-1} (thf) 1984s, 1945ms, 1770mw and 1741mw] and the $[Fe_4Au(CO)_{16}]^{3-}$ [ν_{CO}/cm^{-1} (thf) 1979m, 1931s and 1766m] anions are fairly stable in the absence of protic solvents and under strictly anaerobic conditions. The liquid nitrogen X-band EPR spectrum of the paramagnetic $[Fe_4Au(CO)_{16}]^{2-}$ dianion, electrogenerated in acetonitrile solution at −20 °C (E_w = −0.8 V), displays a complex absorption pattern. The second derivative lineshape is well resolved and allows the detection of the characteristic four-line pattern of an Au centre (I_{Au} = 3/2) in a rhombic structure ($g_l = 2.046 \pm 0.005$, $g_m = 1.980 \pm 0.005$, $g_h = 1.959 \pm 0.005$; $a_l = 27.0 \pm 0.5$ G, $a_m = 16.5 \pm 0.5$ G, $a_h = 16.5 \pm 0.5$ G; 1 G = 10^{-4} T) overlapping a less intense signal ($g_{\parallel} = 2.008 \pm 0.005$, $g_{\perp} = 1.980 \pm 0.005$) of axial symmetry. A full rationalization of such a spectrum is not straightforward; however, the measured a_{Au} values are intermediate between those of previously reported dithiocarbamate, dithiolate and methylthioaniline Au^{II} complexes, respectively.[19,20] On increasing the temperature above the liquid phase transition value, only a broad unresolved signal is obtained.

The reduction of $[Fe_4Au(CO)_{16}]^-$ causes a notable change in the IR carbonyl absorption pattern, as shown by the presence of an intense absorption in the bridging carbonyl region. In particular the IR spectrum of $[Fe_4Au(CO)_{16}]^{2-}$ is different from that of $[Fe_4M(CO)_{16}]^{2-}$ (M = Pd, Pt), but superimposable on that of $[Fe_4M'(CO)_{16}]^{2-}$ (M′ = Cd, Hg),‡ which probably show a twist towards tetrahedral coordinations of two $[Fe_2(CO)_6(\mu\text{-}CO)_2]^{2-}$ moieties around the central d^{10} ion, as occurs in the known $[Fe_6M'(CO)_{20}(\mu\text{-}CO)_2]^{2-}$,[21] and $[Fe_4M''(CO)_{16}]^{n-}$ (M″ = Sn, Pb; n = 0, 2).[22] Both the change in the carbonyl stereochemistry and, possibly, the alleged twist from square-planar towards tetrahedral coordination of the gold atom are likely responsible for the electrochemical quasi-reversibility of the 1−/2− and 2−/3− electron transfers indicated by the peak-to-peak separations of 116 and 105 mV, respectively, measured at 0.2 V s^{-1}. Under the same experimental conditions, the one-electron oxidation of ferrocene ($E^{\circ\prime}$ = +0.38 V, *vs.* standard calomel electrode, sce) displays a peak-to-peak separation of 70 mV. In spite of such a slowing down of the electron transfer rates, the actual geometrical reorganizations accompanying the two sequential electron additions do not cause framework destruction.

In contrast, both the $[Fe_4M(CO)_{16}]^{2-}$ (M = Pd, Pt) complexes undergo more severe, framework-destroying, rearrangements since their access to the 1− and 3− overall charges is irreversible (2−/3−), or coupled with chemical complications (1−/2−).[23] Accordingly, their chemical reduction with sodium naphthalenide in thf give rise to a mixture of the parent $[Fe_3(CO)_{11}]^{2-}$ and yet unknown products.

It appears reasonable to conclude that the reported structural differences between the $[Fe_4Au(CO)_{16}]^-$ and $[Fe_4M(CO)_{16}]^{2-}$ (M = Pd, Pt) derivatives (bent carbonyl groups) are electronically significant and signal a difference in their chemical and electrochemical behaviour.

Further work is in progress in attempts to isolate and structurally characterize the reduction products of both $[Fe_4Au(CO)_{16}]^-$ and $[Fe_4M(CO)_{16}]^{2-}$ (M = Pd, Pt).

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‡ The $[Fe_4M'(CO)_{16}]^{2-}$ (M′ = Cd, Hg) dianions have been isolated as $[NMe_4]^+$ and $[PPh_4]^+$ salts by reaction of $[Fe_2(CO)_8]^{2-}$ and M′Cl$_2$ in thf in a 2 : 1 molar ratio and by layering of toluene (M′ = Cd, ν_{CO}/cm^{-1} 2008w, 1984s, 1927s and 1752m; M′ = Hg, ν_{CO}/cm^{-1} 2020mw, 1985s, 1930s and 1740m).[10]