Synthesis of $[AuFe_2(CO)_8]^{3-}$ and $[Au_4Fe_4(CO)_{16}]^{4-}$: X-Ray Structure of the $[Au_4Fe_4(CO)_{16}]^{4-}$ Cluster Anion in its $[NEt_4]^+$ salt

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The new $[AuFe_2(CO)_8]^{3-}$ and $[Au_4Fe_4(CO)_{16}]^{4-}$ cluster anions are isolated from the reaction in THF of $[Fe(CO)_4]^{2-}$ with $[AuBr_2]^-$ salts in molar ratios of 2 : 1 and 1 : 1 respectively; as shown by an X-ray investigation on $[NEt_4]_4[Au_4Fe_4(CO)_{16}]$ the $[Au_4Fe_4(CO)_{16}]^{4-}$ cluster anion exists in two structural modifications consisting of a square and a rectangle of gold atoms, respectively, bridged by $Fe(CO)_4$ groups on the edges.

Although several Au–Fe bimetallic derivatives are known,[1,2] the only Au–Fe cluster containing gold exclusively bonded to metals is $[AuFe_4(CO)_{16}]^{n-}$ (n = 1,2,3). The monoanion was shown by an X-ray study to consist of two $[Fe_2(CO)_8]^{2-}$ moieties linked to a central gold(III) atom adopting a square-planar coordination.[3] The existence of a wide number of Cu and Ag clusters stabilized by $Fe(CO)_4$ ligands[4,5] prompted a systematic investigation of the reaction of $[Fe(CO)_4]^{2-}$ with gold(I) compounds. Our preliminary experiments with salts or complexes such as AuCl,[6] Au(CO)Cl[7] and $Au(SEt_2)Cl$[8] gave very poor results due to the ready disproportionation of the above to Au^{III} and metallic gold. On the contrary, the use of $[AuBr_2]^-$ salts[9] led to the isolation and characterization of the new $[AuFe_2(CO)_8]^{3-}$ and $[Au_4Fe_4(CO)_{16}]^{4-}$ cluster anions, establishing the first synthetic route to gold analogues of silver in this chemistry.

The colourless $[AuFe_2(CO)_8]^{3-}$ [ν_{CO} in MeCN at 1881 (m) and 1809 (s) cm^{-1}] anion was obtained in a mixture, on adopting $[Fe(CO)_4]^{2-}$: $[AuBr_2]^-$ molar ratio of *ca.* 2 : 1, as a result of reaction (1).

$$2\,[Fe(CO)_4]^{2-} + [AuBr_2]^- \rightarrow [AuFe_2(CO)_8]^{3-} + 2\,Br^- \quad (1)$$

The sodium salt of $[AuFe_2(CO)_8]^{3-}$ was separated from the filtered THF solution by the addition of 15-crown-5. The compound displays an analytical Au : Fe ratio in keeping with the given formula and shows an IR pattern superimposable with those of the related $[M\{Fe(CO)_4\}_2]^{n-}$ (M = Zn, Cd, Hg: n = 2;[10] M = Cu, Ag: n = 3)[5] and $[M\{Fe(CO)_4\}_3]^{n-}$ (M = In, n = 3;[11] M = Sn, Pb: n = 2)[12] derivatives.

The yellow–orange $[Au_4Fe_4(CO)_{16}]^{4-}$ tetraanion was obtained *via* the reaction in THF of $[Fe(CO)_4]^{2-}$ and $[AuBr_2]^-$ in equimolar amounts. The reaction proceeds *via* equations (1) and (2). The resulting reaction mixture was filtered and the solution

$$2\,[AuFe_2(CO)_8]^{3-} + 2\,[AuBr_2]^- \rightarrow [Au_4Fe_4(CO)_{16}]^{4-} + Br^- \quad (2)$$

was precipitated by addition of tetraethylammonium bromide. $[NEt_4]_4[Au_4Fe_4(CO)_{16}]$ was separated in 40–60% yields by extraction of the resulting solid material with acetonitrile, and crystallized by layering diisopropyl ether. In acetonitrile solution it showed IR carbonyl absorptions [ν_{CO} at 1933 (s) and 1867 (s) cm^{-1}] close to those of the $[Ag_4Fe_4(CO)_{16}]^{4-}$ congener.[5]

The molecular structure of $[NEt_4]_4[Au_4Fe_4(CO)_{16}]$ has been determined by X-ray crystallography.† The unit cell contains two anions placed around non-equivalent inversion centres, therefore there are two independent anions each conforming to a precise C_i symmetry. Both anions contain a planar arrangement of metal atoms consisting of an inner rectangle of Au atoms and four edge-bridging C_{2v}-$Fe(CO)_4$ groups. The ide-

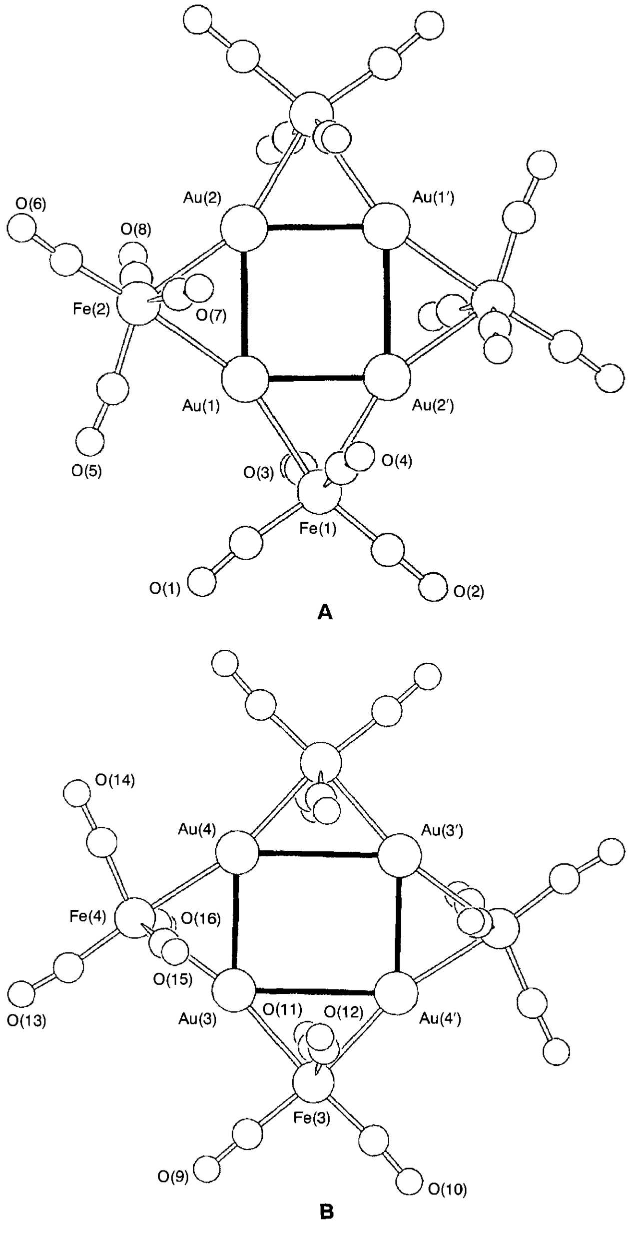

Fig. 1 Perspective drawing of the D_{4h} **A** and D_{2h} **B** deformation isomers of the $[Au_4Fe_4(CO)_{16}]^{4-}$ tetraanion. Both anions sit around inversion centres. Selected bond distances (Å) and angles (°) for **A**: Au(1)–Au(2) 2.973(2), Au(2)–Au(1′) 2.831(2), Au(1)–Fe(1) 2.640(5), Au(1)–Fe(2) 2.612(5), Au(2)–Fe(2) 2.593(5), Au(2′)–Fe(1) 2.612(5), Fe–C_{ax} 1.76 (av), C–O_{ax} 1.15 (av), Fe–C_{eq} 1.75 (av), C–O_{eq} 1.15 (av), Au(1)···C(5) 2.61(4), Au(1)···C(3) 2.85(3), Au(2)···C(8) 2.60(4), Au(2)···C(7) 2.72(4), Au(1)–Fe(1)–Au(2′) 65.2(1), Au(1)–Fe(2)–Au(2) 69.6(1), C(4)–Fe(1)–C(3) 151(2), C(7)–Fe(2)–C(8) 145(2); for **B**: Au(3)–Au(4) 2.932(2), Au(3)···Au(4″) 3.400(2), Au(3)–Fe(3) 2.545(5), Au(3)–Fe(4) 2.589(5), Au(4)–Fe(4) 2.566(5), Au(4)–Fe(3″) 2.566(5), Fe–C_{ax} 1.76 (av), C–O_{ax} 1.15, Fe–C_{ax} 1.76 (av), C–O_{ax} 1.15 (av), Fe–C_{eq} 1.76 (av), C–O_{eq} 1.15 (av), Au(3)···C(15) 2.41(3), Au(3)···C(11) 2.57(4), Au(3)···C(16) 2.69(4), Au(3)···C(12) 2.78(4), Au(4)···C(11″) 2.64(4), Au(4)···C(16) 2.82(3), Au(4)···C(14) 2.84(4), Au(3)–Fe(4)–Au(4) 69.3(1), Au(3)–Fe(3)–Au(4″) 83.4(2), C(12)–Fe(3)–C(11) 131(2), C(15)–Fe(4)–C(16) 137(2).

alized molecular symmetry is D_{4h} for molecule **A** (Fig. 1) [if the distortions of the $Fe(CO)_4$ groups are ignored and the Au_4 unit is described as a square] and D_{2h} for molecule **B** in which the Au_4 unit is definitely elongated. The two anions can be considered as deformation isomers and a major difference is found in the edges of the Au_4 rectangles [2.831–2.973 in **A** and 2.932–3.400(2) Å in **B**; the latter $Au\cdots Au$ contact is 0.52 Å longer than the Au–Au bond distance (2.88 Å) in gold metal and suggests the absence of any significant bonding interaction]. The same kind of deviation from an idealized M_4 square has been found in the silver analogue $[Ag_4Fe_4(CO)_{16}]^{4-}$.[5] It can be attributed to the extreme softness of the M–M contacts and reflects the strength and symmetry of the cation–anion interactions. It is worth noting that the loosening of the Au–Au contacts in **B** with respect to **A** is compensated by some tightening of the Au–Fe bonds (average 2.567 and 2.611 Å, respectively). The average Fe–Au bond distance found in **B** is shorter than the formal Au^{III}–Fe distance (2.595 Å) found in $[AuFe_4(CO)_{16}]^-$.[3] This is in keeping with the results of MO calculations carried out on related Cu–Fe[13] and Ag–Fe[5] derivatives, which indicated an overwhelming significance of the M–Fe over the M–M interactions. The more elongated structural modification of $[Au_4Fe_4(CO)_{16}]^{4-}$ may be seen as a snapshot of the deformation which has been suggested as necessary for the transformation of $[Ag_4\{\mu_2\text{-}Fe(CO)_4\}_4]^{4-}$ in a 4-electron 8-crown-2 pseudo-ligand which coordinates an Ag^+ ion and gives rise to $[Ag_5\{\mu_2\text{-}Fe(CO)_4\}_2\{\mu_3\text{-}Fe(CO)_4\}_2]^{3-}$.[5]

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Footnote

† *Crystal data* for $C_{48}H_{80}Au_4Fe_4N_4O_{16}$: M = 1980.4, triclinic, space group $P\bar{1}$ (No. 2), a = 12.570(6), b = 21.815(6), c = 11.847(7) Å, α = 90.77(4), β = 107.90(4), γ = 85.98(3)°, U = 3084(1) Å^3, Z = 2, D_c = 2.133 Mg m^{-3}, $F(000)$ = 1888, λ = 0.71073 Å, T = 298 K, μ(Mo-Kα) = 10.453 mm^{-1}. Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Mo-Kα radiation, ω scan mode, 4927 independent reflections ($\pm h$, $\pm k$, $+l$) were collected to $2\theta_{max}$ = 40° and corrected for the effects of decay and absorption. Automatic direct methods (SHELXS 86)[14] identified the positions of the metal atoms and iterative cycles of least-squares refinement (on F^2) and difference Fourier synthesis located the remaining non-hydrogen atoms. The metal atoms were refined anisotropically and the hydrogen atoms were placed in calculated positions (C–H = 0.96 Å). Refinement on F^2 (SHELXL 93)[15] against 3388 data led to final convergence with R_1 = 0.088, wR_2 = 0.21, and S = 1.051 [$F_o > 4\sigma F_o$] for 345 refined parameters.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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