

TaS₂.^[6] Only assumptions can be made about the arrangement of the intercalated molecules in the phases with the smaller interlayer spacing. An undistorted all-*gauche* structure of the C₄F₉ chains is unlikely, because of the size of the fluorine atoms. If, as is assumed, the chains have a twisted *anti* conformation, they must be more strongly tilted at an angle of 40° to the plane of the layers (see Fig. 2b). However, a distorted all-*gauche* conformation or a conformation with *anti* and *gauche* sequences cannot be ruled out. Only one phase was observed for stage 2 as well as stage 1 in the case of the homologous perfluorohexanesulfonic acids. These compounds are not so well ordered; the *d*_i spacings of ca. 2900 pm and 2620 pm, however, are consistent with the *anti* conformation, analogous to those in Figure 2a.

Experimental

Ca. 4–5 mg of Madagascar graphite (>99.5% C, flakes of ca. 2 mm diameter) was packed in a platinum gauze pouch and anodically oxidized in perfluorobutanesulfonic acid (liberated from C₄F₉SO₃K [7] with 100% H₂SO₄). Platinum was used as counter electrode; a relatively large piece of graphite foil (Sigraflex) was used as reference electrode. Upon galvanostatic oxidation well-structured potential/charge curves were obtained only at a very small current density, e.g. 10 µA with 5 mg of graphite, i.e. less than 500 µA per cm² of the prism faces of the graphite flakes. In the potentiodynamic reaction, the current/voltage curves were well-resolved only at a sweep rate below 5–10 µV/s. The use of highly oriented pyrographite (HOPG) gave similar, but not quite so well-structured curves. After a charge transfer corresponding to the selected points of the curves, the oxidation was interrupted and the graphite salt transferred to X-ray capillaries under the acid for taking Debye-Scherrer photographs. For determining the fluorine, the flakes were freed from adhering perfluorobutanesulfonic acid by rinsing with syrupy phosphoric acid and combusted with Na₂O₂/NaOH in a Parr bomb; the fluoride that was formed was determined with an ion-selective electrode by the standard-addition method.

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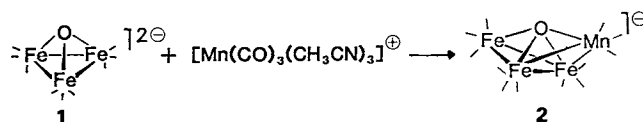
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Synthesis and Structure of [(PPh₃)₂N][Fe₃Mn(CO)₁₂(μ₄-O)]: A Butterfly Oxo Cluster**

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There has been considerable recent interest in the synthesis of clusters that contain substituent-free main-group elements to provide a conceptual bridge between organometallic chemistry and the areas of inorganic solid-state chemistry and surface chemistry.^[1] Among the first-row elements, carbido and nitrido carbonyl clusters are now known which have coordination environments about the main-group atoms ranging from those presumed for sur-

faces to those observed in solid-state compounds.^[2] The synthesis and chemistry of clusters comprised of metal atoms in low oxidation states that contain an oxo ligand is much less well developed. There are only a few examples of clusters containing the μ₃-oxo ligand,^[3] a coordination mode common for oxygen atoms bound to surfaces.^[4] Additionally, to the best of our knowledge, there are no oxo carbonyl clusters belonging to the interesting class of μ₄-L butterfly clusters, which have been intensely studied recently for L=C and N;^[5] nor are there any other higher-nuclearity oxo clusters in which the oxo ligand is bound to more than three metal atoms. We report here on the synthesis and characterization of PPN[Fe₃Mn(CO)₁₂(μ₄-O)] **2** (PPN=[(PPh₃)₂N]⁺), a mixed-metal cluster which represents the first butterfly oxo compound and is a step toward building higher-nuclearity oxo clusters.



Treatment of the orange-red PPN salt of [Fe₃(CO)₉(μ₃-O)]²⁻ **1**^[3] with one equivalent of [Mn(CO)₃(CH₃CN)₃][PF₆]^[6] in acetone followed by crystallization from Et₂O/pentane gives the dark brown butterfly oxo cluster PPN[Fe₃Mn(CO)₁₂(μ₄-O)] **2** in 75% yield.^[7] The structure of **2** is shown in Figure 1 (see also Table 1).^[8] The

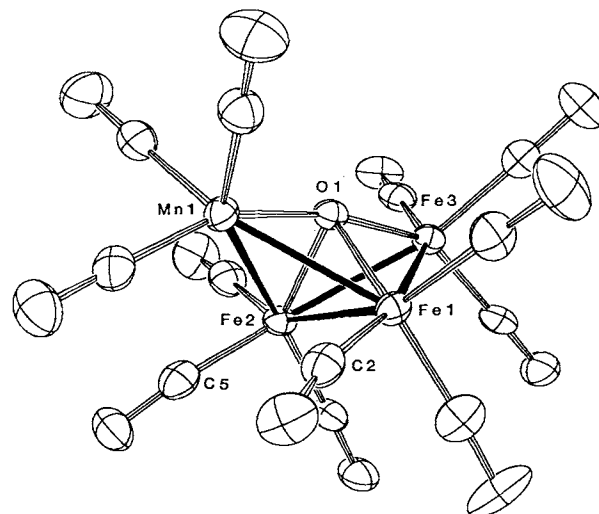


Fig. 1. Crystal structure of **2**. Thermal ellipsoid plot at 40% probability [8].

count of 62 cluster valence electrons, consistent with molecular orbital descriptions of the butterfly carbides,^[9] is achieved by counting the oxo ligand as a six electron donor. All oxygen-metal distances are short (average: 1.89(2) Å). The Mn atom occupies a wingtip position in the butterfly arrangement, in contrast to the analogous carbido cluster, [Fe₃Mn(CO)₁₃(μ₄-C)]⁺, where the Mn atom occupies a hinge site.^[5b] The average Fe-Mn distance (2.61(2) Å) is considerably longer than the average Fe-Fe distance (2.51(1) Å). Two Fe-bound CO ligands form semi-bridges to the Mn atom (Mn1-C2=2.675(5), Mn1-C5=2.736(5) Å), consistent with the preference of manganese for a higher coordination number.



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