

In an attempt to pinpoint the source of the oxide in the hexameric structures, we repeated the preparation of **2** in a vial connected through a heated capillary to a Hiden Analytical Quadrupole mass spectrometer (Warrington, England). After the addition of THF, the reaction mixture was heated and the volatile products blown into the mass spectrometer were subjected to selective ion mass (SIM) analysis. This confirmed the presence of ethylene (parent peak at 28 amu; daughter fragments at 27, 26, and 25 amu). Ethylene is commonly extruded during THF-cleavage processes,^[10] so the origin of the O²⁻ ions in **2** is almost certainly from THF. Fragmentation of THF is a complex matter, the outcome of which can differ depending on many variables such as the metal and the nature of the organyl assailant. Hard organolithium bases are known to deprotonate THF at the α -position, before undergoing a $[\pi 4s + \pi 2s]$ cycloreversion to afford enolate "CH₂=CH-O⁻" and ethylene.^[11] There are also precedents for THF fragmentation leading to M-O-M bridges in organolanthanide chemistry,^[12] and to O²⁻ in other metal^[13] and metalloid^[14] systems. Here the heterobimetallic nature of the inverse crown ether system exacerbates the complexity of the THF fragmentation process, a sign of which is that the filtrates left following the isolation of **2** and **3** darken and degrade to viscous oils in a matter of days. However the salient point is that both new compounds can be prepared reproducibly in a pure crystalline form, and isolated for future synthetic exploration, before the onset of this degradation.

Experimental Section

2 and **3**: In a typical preparation, BuNa, Bu₂Mg, and the relevant amine (5:5:15 mmol) were mixed together in a hydrocarbon solution under a protective argon atmosphere. Dry, distilled THF (5 mL, 62 mmol) was then added and the solution warmed for 30 min. Cooling the solution on the bench (for **2**) or in the refrigerator at -26 °C (for **3**) afforded colorless crystals of **2** or **3**. Yields of first batches isolated were typically 18 or 11 %, respectively. No further solids could be isolated due to degradation of the filtrate solutions. M.p. 330 °C (decomp) and 258 °C (decomp), respectively. Satisfactory analyses (C, H, N) were obtained for both compounds. ¹H NMR (400.13 MHz, [D₆]DMSO, 300 K): **2**: δ = 3.60 (m, 4H; CH₂O-THF), 1.76 (m, 4H; CH₂-THF), 1.57 (m, 2H; γ -CH₂), 1.23 (m, 4H; β -CH₂), 1.02 ppm (s, 12H; CH₃); ¹H NMR (400.13 MHz, [D₈]toluene, 300 K) **3**: δ = 3.35 (m, 4H; CH₂O-THF), 3.26 (septet, 2H; CH), 1.33 (m, 4H; CH₂-THF), 1.20 ppm (d, 12H; CH₃).

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[3] Crystal data for **3**: C₆₀H₁₃₂Mg₆N₆Na₆O₁₂; a colorless needle of approximate dimensions 0.55 × 0.10 × 0.10 mm gave a trigonal space group $R\bar{3}h$, $a = b = 23.8599(6)$, $c = 12.1274(4)$ Å, $V = 5979.1(3)$ Å³, $T = 123$ K, $Z = 3$, $\rho_{\text{calcd}} = 1.178$ Mg m⁻³, $2\theta_{\text{max}} = 52^\circ$, $\text{MoK}\alpha$, $\lambda = 0.71073$ Å. The structure was solved, and refined on F^2 , using programs of the Shelx family to convergence at $R1 = 0.0419$ (for 2019 reflections with $I > 2\sigma(I)$), $wR2 = 0.1177$, and $S = 1.022$ for 140 parameters and 2602 unique reflections. Highest residual electron density 0.437 e Å⁻³. Hydrogen atoms were placed in calculated positions and in a riding mode. Compound **2** was found to be isostructural with **3** but contained highly disordered groups at the THF positions which adversely affected the quality of the solution. CCDC-1790244 (**2**) and CCDC-1790245 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the

Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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A Unique Bismuth–Iron Chain Polymer Containing the $\cdots$ -Bi-Fe- $\cdots$ Link: Formation and Structure of $[n\text{BuBiFe}(\text{CO})_4]_\infty^{**}$

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The construction of supramolecules or extended frameworks based on coordination and organometallic complexes is one of the major areas of current research in inorganic and organometallic chemistry.^[1] Nevertheless, this approach has received little attention in the field of organobismuth–transition-metal complexes;^[2] such complexes are of great importance mainly due to their potential applications as catalysts in olefin oxidation and ammoxidation^[3] and as precursors to a variety of electronic materials.^[4] Bismuth has been shown to form the polymer $[\text{Et}_2\text{Bi}(\text{OAr})]_\infty$ in which the alkoxide ligand bridges the Et₂Bi groups giving a helical chain with no direct Bi–Bi interaction.^[5] For the Bi-Fe-CO system, the polymer $[\{\text{PhCH}_2\text{NMe}_3\}\{(\mu\text{-H})\text{Fe}_2(\text{CO})_6\text{Bi}_2(\mu\text{-Cl})_2\}]_\infty$ was

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shown to possess “Bi₂Fe₄” tetrahedral units connected by a chloride ligand, leading to an infinite chain but without a continuous $\cdots\text{Bi-Fe}\cdots$ interaction.^[6] To date, there are no polymeric complexes that contain an infinite $\cdots\text{Bi-Fe}\cdots$ contact of any type. We report herein the unprecedented bismuth–iron chain polymer, $[\text{nBuBiFe}(\text{CO})_4]_\infty$ (**1**), which contains the unique zigzag $\cdots\text{Bi-Fe}\cdots$ chain.

In the preparation of the ring complex $[\{\text{nBuBiFe}(\text{CO})_4\}_2]$ (**2**) from the reaction of $[\text{Et}_4\text{N}]_3[\text{Bi}(\text{Fe}(\text{CO})_4)_4]$ with *n*BuBr in MeCN followed by acidification,^[7] we found that ultrasonication of **2** led to the formation of the polymeric product $[\text{nBuBiFe}(\text{CO})_4]_\infty$ (**1**). An X-ray structure analysis of crystals of **1** revealed an unusual mixed-metal chain polymer which is composed of the *n*BuBiFe(CO)₄ groups with a novel $\cdots\text{Bi-Fe}\cdots$ chain (Figure 1).^[8] To the best of our knowledge, **1** is the first infinite heteroleptic Bi–Fe-bonded chain to be structurally characterized.

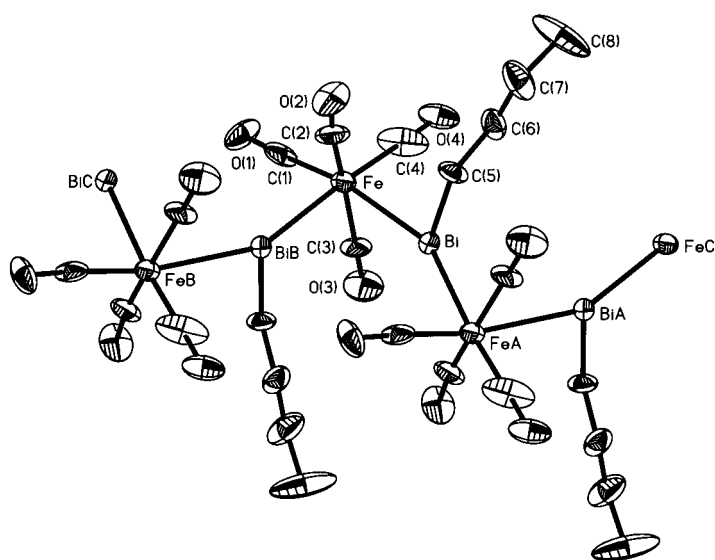


Figure 1. Structure of a segment of the polymer **1** (ORTEP diagram). Selected bond lengths [Å] and angles [°]: Bi–Fe 2.849(5), BiB–Fe 2.771(5), Bi–C(5) 2.20(3), Fe–C(1) 1.80(5), Fe–C(2) 1.74(5), Fe–C(3) 1.81(3), Fe–C(4) 1.80(5), C(5)–C(6) 1.523(19), C(6)–C(7) 1.52(2), C(7)–C(8) 1.51(2), Fe–Bi–FeA 156.46(15), Bi–Fe–BiB 81.47(12), Fe–Bi–C(5) 100.0(9), FeA–Bi–C(5) 93.6(9), Bi–Fe–C(1) 169.5(11), Bi–Fe–C(2) 86.3(15), Bi–Fe–C(3) 79.2(15), Bi–Fe–C(4) 92(2), C(1)–Fe–C(4) 97(3), BiB–Fe–C(1) 88.9(15), BiB–Fe–C(2) 79.0(18), BiB–Fe–C(3) 87.6(11), BiB–Fe–C(4) 174(2).

Noteworthy in **1** is the zigzag $\cdots\text{Bi-Fe-Bi-Fe}\cdots$ chain with alternating short (2.771(5) Å) and long (2.849(5) Å) Bi–Fe distances and alternating Bi–Fe–Bi and Fe–Bi–Fe angles of 81.47(12)° and 156.46(15)°, respectively. Notably, the neighboring *n*Bu groups are oriented in the *trans* position and the Fe(CO)₄ groups sit in the staggered-like position along the chain. The C–C distance between two “parallel” *n*Bu groups (C(8)–C(8)C) is around 1.96 Å, which is within their van der Waals contact (i.e., 3.4 Å)^[9] indicative of the weak interaction. This intramolecular interaction of the alkyl groups may partly account for the formation of **1**.

Whereas the ring complex **2** is considered as the dimeric product of the monomer $[\text{nBuBiFe}(\text{CO})_4]$ derived from the ionic complex $[\text{nBuBi}(\text{Fe}(\text{CO})_4)_3]^{2-}$,^[7] the polymer **1** can be

viewed as the polymeric product that results from the cleavage (probably by radical processes) of Bi–Fe bonds in **2** upon ultrasonication. The formation of **1** from **2** is reversible. The polymer **1** can be obtained from a solution of **2**, and **1** dissolves in most organic solvents to form the dimeric product **2** in almost quantitative yield. No analogous polymers like **1** were observed when analogous reactions were carried out for Bi compounds with shorter alkyl groups (R = Me, Et). Hence, the freedom of the alkyl groups and the effective crystal packing play an important role in the formation of **1**.

The coordination geometry at the bismuth center in **1** can be described as a pyramidal structure with an uncoordinated lone pair of electrons, which is seen in many other bismuth-containing complexes such as $[\text{R}_2\text{Bi}_2\text{Fe}_2(\text{CO})_8]$,^[7] $[\text{Et}_4\text{N}][\text{Bi-Fe}_3(\text{CO})_{10}]$,^[10] and $[\text{Et}_4\text{N}]_2[\text{Bi}_2\text{Fe}_4(\text{CO})_{13}]$.^[11] However, it is noteworthy that the Fe–Bi–Fe angle (156.46(15)°) is unusually large and the sum of the angles at the bismuth center is about 350°, not far off being planar. These two features are quite different to those of the above-mentioned complexes and the related complex $[\text{EtBi}(\text{Mo}(\text{CO})_3\text{Cp})_2]$.^[12] In the absence of multiple bonding between the Bi and Fe centers in **1**, the lone pair of electrons on the bismuth center may be in an essentially unhybridized p orbital and thus capable of interacting with the *cis*-carbonyl ligands, which might account for the *trans* orientation of the *n*Bu groups and the alternating Bi–Fe bond lengths (2.771(5) versus 2.849(5) Å). In addition, the iron atom is pseudooctahedrally coordinated to two bismuth atoms and four carbonyl groups; the Bi–Fe–Bi angle (81.47(12)°) is smaller than most angles about the iron atom due to the demands of the orientation of the chain and the *n*Bu groups. The Bi–C distance of 2.20(3) Å is similar to those in $[\text{Me}_2\text{Bi}_2\text{Fe}_2(\text{CO})_8]$ (2.28(1) Å)^[13] and $[\text{iBu}_2\text{Bi}_2\text{Fe}_2(\text{CO})_8]$ (2.29(1) Å).^[14] The C–C distances in **1** are in the range of 1.51(2)–1.52(2) Å, which are comparable to those in the related complex $[(\text{iBu})_2\text{Bi}_2\text{Fe}_2(\text{CO})_8]$.^[14] These features reflect the small distortion of the alkyl groups in polymer **1**. Work is in progress to determine the generality of the structure of **1** and to investigate its applications.

Experimental Section

All reactions were performed under an atmosphere of pure nitrogen using standard Schlenk techniques.

1: *n*BuBr (3 mL, 27.94 mmol) was added dropwise to a sample of $[\text{Et}_4\text{N}]_3[\text{Bi}(\text{Fe}(\text{CO})_4)_4]$ (2.54 g, 2.00 mmol) in MeCN (40 mL). The mixed solution was heated at 40–42 °C for 24 h, and the resulting solution was filtered and dried under vacuum to give a residue to which HOAc (10 mL) was added. The mixture was stirred at room temperature for 20 h, and the HOAc was removed under vacuum. The residue was extracted with hexane (40 mL) several times and the hexane extract was showed to contain the dimeric complex **2** (0.30 g).^[7] The hexane solution containing **2** was concentrated, and subsequently ultrasonicated in a water bath with an ultrasonicator (50 Hz, 4 amp, 110 V) for 20 min. The resultant solution was cooled in a freezer to give crystals of $[\text{nBuBiFe}(\text{CO})_4]_\infty$ (**1**). Yield: 0.28 g. IR (nujol): $\tilde{\nu}_{\text{CO}}$ = 2034 (s), 1998 (w), 1983 cm^{−1} (s, br); m.p. 71 °C; elemental analysis (%) calcd for $[\text{nBuBiFe}(\text{CO})_4]_\infty$: C 22.14, H 2.09; found: C 22.12; H 2.10. Polymer **1** decomposed quickly into the dimeric species in most organic solvents.

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- [8] **1**: $C_8H_6BiFeO_4$, $M_r = 433.98$, monoclinic, space group $C2$, $a = 17.347(6)$, $b = 7.152(2)$, $c = 9.523(5)$ Å, $\beta = 92.96(4)^\circ$, $V = 1179.9(8)$ Å³, $Z = 4$, $\rho_{\text{calc}} = 2.443$ g cm⁻³, $\mu = 16.109$ mm⁻¹, $\lambda = 0.70930$ Å, transmission range 0.54–1.00, crystal dimensions about $0.40 \times 0.50 \times 0.60$ mm³. A total of 1134 unique reflections were collected on a Nonius (CAD-4) diffractometer at 298 K in the 2θ range 2.0–50°. Full-matrix least-squares refinement on F^2 converged to $R = 0.0628$ (all data), 0.0542 ($I > 2\sigma(I)$); $wR = 0.1763$ (all data), 0.1635 ($I > 2\sigma(I)$). All calculations were performed by using SHELXTL packages. CCDC-177971 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
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[{Fe(OMe)₂[O₂CC(OH)Ph₂]}₁₂]: Synthesis and Characterization of a New Member in the Family of Molecular Ferric Wheels with the Carboxylatobis(alkoxo) Bridging Unit**

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High-nuclearity transition-metal clusters continue to attract a great deal of interest, partly because of their fascinating physical properties and partly for the architectural beauty of their structures. An interesting subarea of 3d metal cluster chemistry is the small but growing family of molecules that have circular structures. Large cyclic polymetallic clusters are valued for their ability to mimic the properties of linear coordination polymers.^[1] For example, theories developed for analyzing magnetically coupled ring systems have been extensively applied to calculate the thermodynamic properties of 1D materials.^[2] Furthermore, the chemistry of circular molecular clusters is also associated with supramolecular chemistry. Anion and cation recognition provide the possibility of controlling the size of clusters. A representative example of this approach is the ability to address the synthesis of molecular rings by exploiting host–guest interactions with alkali-metal cations, because alkali-metal cations are hosted by rings of different size. Thus, hexairon(III)^[3–5] and hexamanganese(III)^[6] complexes with cyclic M₆O₁₂ cores can easily accommodate Li⁺ and Na⁺ ions, both in the solid state and in solution, whereas Cs⁺ ions require larger rings, such as M₈O₁₆.^[5]

Metal rings have excited mankind since mythological times.^[7] The largest cyclic structure containing exclusively paramagnetic 3d metals is the Ni₂₄^{II} wheel reported by Winpenny and co-workers,^[8] which is approximately an order of magnitude smaller than the giant wheels constructed from molybdate fragments by the Müller group;^[9] a Ni₁₂^{II} wheel is also known.^[10] Large, cyclic, polymetallic arrangements of other 3d metals, either unsupported or supported (by ions or molecules as guests), have been found for chromium(III),^[11] manganese(II),^[12] iron(II),^[13] iron(III),^[12, 14] cobalt(II),^[15] and copper(II).^[16]

Restricting further discussion to the so-called ferric wheels with nuclearities equal to or higher than ten, the structurally characterized complexes that contain O-donor groups as bridging ligands are [{Fe(OMe)₂(O₂CCH₂Cl)}₁₀]^[14a] [{Fe(OMe)₂(O₂CMe)}₁₀]^[14b] [{Fe(OMe)₂L}₁₀]^[14c] where L[–] is

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