

[IrAg(η^4 -C₈H₁₂)(μ -O₂CCF₃)₂]_n: A Polymeric Complex Containing an Infinite Chain of Alternating Iridium and Silver Atoms[†]

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Introduction

Linear metal chain complexes have been the subject of considerable research interest, and examples of both oligomeric and polymeric systems are known.¹ Of these, an interesting subclass consists of polynuclear metal complexes containing donor \rightarrow acceptor bonds between d⁸ and d¹⁰ transition metal atoms; complexes containing chains of three alternating d⁸ and d¹⁰ metal atoms have been synthesized.² We report herein the synthesis and structure of the first such system containing an infinite chain of alternating d⁸ and d¹⁰ metal atoms.

Experimental Section

All experiments were performed under an atmosphere of dry nitrogen; solvents were dried and deoxygenated prior to use using standard protocol. Elemental analysis was determined by Schwarzkopf Microanalytical Laboratory, Woodside, NY. ¹⁰⁹Ag NMR is referenced to external 5 M AgNO₃ in H₂O; ¹⁹F NMR is referenced to external CFC₁₃.

Preparation of [IrAg(COD)(μ -O₂CCF₃)₂]_n (COD = η^4 -1,5-Cyclooctadiene). [Ir(COD)Cl]₂ (500 mg, 0.744 mmol) was dissolved in 20 mL of toluene to give a red solution. To this was added solid silver trifluoroacetate (658 mg, 2.98 mmol) in small portions. A bright orange solution plus white precipitate formed rapidly. The reaction mixture was stirred for 16 h at room temperature. It was then filtered to afford a very light gray solid (identified by X-ray powder diffraction to be silver chloride contaminated with a small amount of metallic silver) and a light orange filtrate. The filtrate was concentrated *in vacuo* to afford a yellow-orange powder. This was recrystallized from toluene layered with petroleum ether at -40 °C to afford [IrAg(COD)(μ -O₂CCF₃)₂]_n as a yellow-orange microcrystalline solid (467 mg, 50%). The same compound can be prepared by addition of 2 equiv silver trifluoroacetate to a toluene solution of previously isolated [Ir(COD)(μ -O₂CCF₃)₂]₂.³ Anal. Calcd for IrAgC₁₂H₁₂O₄F₆: C, 22.72; H, 1.91; F, 17.97. Found: C, 22.92; H, 1.88; F, 17.60. ¹H NMR (toluene-*d*₈, 25 °C): δ 3.75 (s, 4H, olefin), 1.61 (m, 4H, CHH), 1.10 (m, 4H, CHH). ¹³C{¹H} NMR (toluene-*d*₈, 25 °C): δ 163.7 (q, *J*_{CF} = 39 Hz, O₂CCF₃), 118.2 (q, *J*_{CF} = 288 Hz, O₂CCF₃), 64.4 (olefin), 31.7 (CH₂). ¹⁹F NMR (toluene-*d*₈, 25 °C): δ -72.4. ¹⁰⁹Ag NMR (toluene-*d*₈, 25 °C): δ 227.7.

Crystallographic Study. A summary of the crystal data is given in Table 1, and selected bond lengths and distances are given in Table

Table 1. Crystal Data for [IrAg(COD)(μ -O₂CCF₃)₂]_n

formula	IrAgC ₁₂ H ₁₂ O ₄ F ₆	radiation	MoK α
fw	632.29	scan width, deg in ω	1.20–2.20
cryst system	monoclinic	scan speed, deg/min	1.50–5.00
space group	C2/c	no. of data collcd	5974
a, Å	17.076 (1)	2 θ range, deg	4.5–50.2
b, Å	10.383 (1)	no. of unique reflns, with <i>I</i> \geq 3.0 σ (<i>I</i>)	2082
c, Å	18.708 (2)	final <i>R</i> ^a	0.039
β , deg	105.905 (5)	final <i>R</i> _w ^b	0.036
T, °C	-100	error of fit	1.01
V, Å ³	3189.9	max Δ / σ	0.03
D _c , g/cm ³	2.641	largest residual density, e/Å ³	1.24, near C(22), F(21), F(23)

^a *R* = $\sum(|F_o| - |F_c|)/\sum(|F_o|)$. ^b *R*_w = $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, *w* = 1/[$\sigma^2(F_o)$].

Table 2. Selected Bond Distances (Å) and Angles (deg) for [IrAg(COD)(μ -O₂CCF₃)₂]_n

Distances			
Ir(1)–Ag(1)	2.9097(5)	Ir(1)–C(2)	2.126(9)
Ir(1)–Ag(2)	2.9078(5)	Ir(1)–C(5)	2.097(10)
Ir(1)–O(1)	2.106(7)	Ir(1)–C(6)	2.131(10)
Ir(1)–O(11)	2.084(6)	Ag(1)–O(2)	2.225(6)
Ir(1)–C(1)	2.127(9)	Ag(2)–O(21)	2.194(7)
Angles			
Ir(1)–Ag(2)–Ir(1)b	180	O(21)–Ag(2)–O(21)b	180
Ir(1)–Ag(1)–Ir(1)a	160.14(5)	O(2)–Ag(1)–O(2)a	176.2(5)
Ir(1)–Ag(1)–O(2)a	80.1(2)	Ir(1)–O(1)–C(21)b	125.6(7)
Ir(1)–Ag(1)–O(2)	100.5(2)	Ir(1)–O(11)–C(11)	126.5(6)
Ir(1)–Ag(2)–O(21)b	81.0(2)	Ag(2)–O(21)–C(21)	121.0(7)
Ir(1)–Ag(2)–O(21)	99.0(2)	Ag(1)–O(2)–C(11)a	121.6(6)
O(1)–Ir(1)–O(11)	90.1(3)		
Ag(1)–Ir(1)–O(1)	68.9(2)		
Ag(2)–Ir(1)–O(11)	68.9(2)		
Ag(1)–Ir(1)–Ag(2)	137.80(3)		

2. X-ray quality crystals were obtained by recrystallization from toluene/petroleum ether at -40 °C. An orange, parallelepiped shaped crystal (~0.10 × 0.08 × 0.10 mm) was used for data collection on a Rigaku RU300 R-AXIS image plate area detector diffractometer. The structure was solved by automated Patterson analysis (PHASE) and refined by full-matrix least-squares analysis. The data were corrected for absorption by numerical integration (transmission range 0.37–0.53). The asymmetric unit consists of one iridium cyclooctadiene fragment bound to two half-weighted silver atoms, one on a center of symmetry and the other on a 2-fold axis. The hydrogen atoms were included as fixed atoms in idealized positions (C–H = 0.95 Å). All non-hydrogen atoms were refined anisotropically. Scattering factors were taken from ref 9, including anomalous terms for iridium and silver atoms.

Results and Discussion

As previously reported, reaction between [Ir(COD)Cl]₂ (COD = η^4 -1,5-cyclooctadiene) and 2 equiv of silver trifluoroacetate in toluene gives silver chloride and [Ir(COD)(μ -O₂CCF₃)₂]₂.³ We found that addition of 2 equiv more of silver trifluoroacetate to a deep-red solution of [Ir(COD)(O₂CCF₃)₂]₂ in toluene resulted in an instantaneous color change to yellow-orange. Recrystallization of the crude product from toluene/petroleum ether afforded a bright orange, crystalline material, elemental analysis of which was consistent with the empirical formula IrAg(COD)(μ -O₂CCF₃)₂. In addition to being soluble in aromatic solvents, IrAg(COD)(μ -O₂CCF₃)₂ was found to be soluble in THF, but only sparingly soluble in methylene chloride and insoluble in alkanes.

The solid state structure of IrAg(COD)(μ -O₂CCF₃)₂ was determined crystallographically; we were surprised to discover an unprecedented infinite chain structure for this complex, with trifluoroacetate ligands bridging between alternating Ir(I) and Ag(I) atoms.⁴ An ORTEP view perpendicular to an –Ir–Ag–Ir– chain is shown in Figure 1, and an ORTEP view of the

[†] Contribution No. 6734.

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- (2) Examples of trimetallic chains include: (a) Albinati, A.; Chaloupka, S.; Demartin, F.; Koetzle, T. F.; Rüegger, H.; Venanzi, L. M.; Wolfer, M. K. *J. Am. Chem. Soc.* **1993**, *115*, 169. (b) Balch, A. L.; Catalano, V. J.; Noll, B. C.; Olmstead, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 7558. (c) Balch, A. L.; Fung, E. Y.; Olmstead, M. M. *Inorg. Chem.* **1990**, *29*, 3203. (d) Balch, A. L.; Catalano, V. J.; Olmstead, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 2010. (e) Einstein, F. W. B.; Jones, R. H.; Zhang, X.; Sutton, D. *Can. J. Chem.* **1989**, *67*, 1832. (f) Sykes, A. G.; Mann, K. R. *Inorg. Chem.* **1990**, *29*, 4449. (g) Sykes, A.; Mann, K. R. *J. Am. Chem. Soc.* **1988**, *110*, 8252. (h) Balch, A. L.; Nagle, J. K.; Oram, D. E.; Reedy, P. E., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 454. (i) Braunstein, P.; Carneiro, T. M. G.; Matt, D.; Tirpicchio, A.; Camellini, M. T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 748. (j) Connelly, N. G.; Lucy, A. R.; Payne, J. D.; Gates, A. M. R.; Geiger, W. E. *J. Chem. Soc., Dalton Trans.* **1983**, 1879.
- (3) Bianchi, F.; Gallazzi, M. C.; Porri, L.; Diversi, P. *J. Organomet. Chem.* **1980**, *202*, 99.

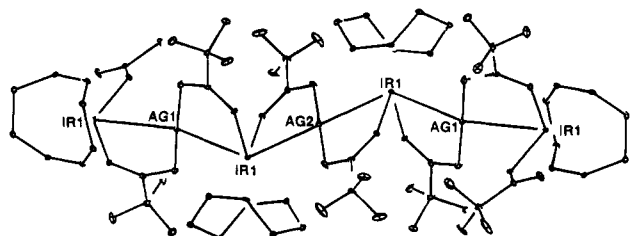


Figure 1. $[\text{IrAg}(\eta^4\text{-C}_8\text{H}_{12})(\mu\text{-O}_2\text{CCF}_3)_2]_n$ viewed approximately perpendicular to an Ir–Ag–Ir chain. Hydrogen atoms are omitted for clarity.

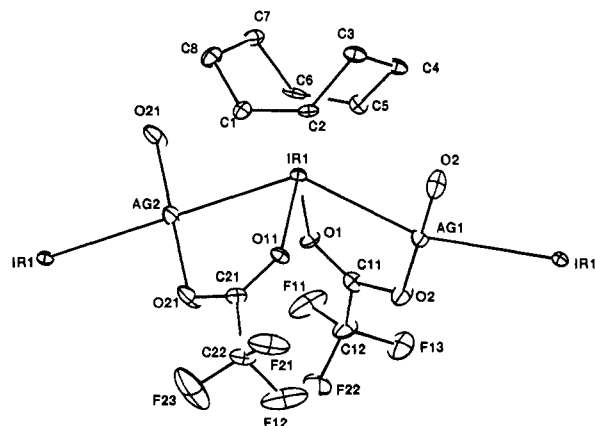


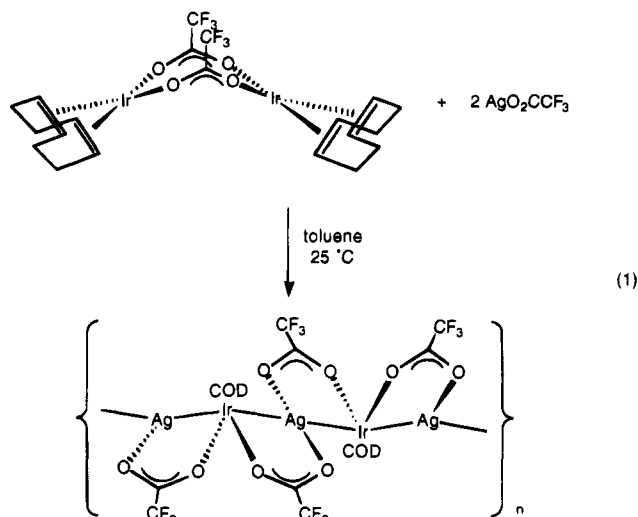
Figure 2. View of the repeating unit in $[\text{IrAg}(\eta^4\text{-C}_8\text{H}_{12})(\mu\text{-O}_2\text{CCF}_3)_2]_n$. Hydrogen atoms are omitted for clarity.

repeating unit is shown in Figure 2. Discounting interactions between iridium and silver, the geometry about iridium is square planar as expected for Ir(I). The bridging trifluoroacetate ligands, however, bring two crystallographically distinct silver atoms to within bonding distance of the iridium on either side of the square plane. The silver atoms also have approximately square planar geometries, with iridium atoms occupying *trans* positions. The net result is an infinite chain. The chains lie along a diagonal to the *a* and *c* axes of the unit cell and are surrounded by six adjacent chains in a distorted hexagonal array. The interchain separations are between 8.5 and 10 Å.

The electron-deficient silver atoms interact weakly with the filled $5d_{z^2}$ orbital on iridium. The Ir–Ag distances [2.9097 (5) and 2.9078 (5) Å] are approximately 0.3 Å longer than the sum of the covalent radii for these two atoms.⁵ In other crystallographically characterized complexes, distances between Ir(I) and Ag(I) vary from 2.64 to 2.87 Å;⁴ the Ir–Ag distances in $[\text{IrAg}(\text{COD})(\mu\text{-O}_2\text{CCF}_3)_2]_n$ are clearly at the high end of this range, and the bonds are probably weak. If one looks more generally at crystallographically characterized complexes containing bonds between Ir(I) and d^{10} metal atoms, the assignment of a weak bonding interaction between Ir and Ag atoms in $[\text{IrAg}(\text{COD})(\mu\text{-O}_2\text{CCF}_3)_2]_n$ still appears quite reasonable. For example, the Ir–Au distances in $[\text{AuIr}(\text{CO})\text{Cl}(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)_2][\text{PF}_6]$ and $[\text{AuIr}_2(\text{CO})_2\text{Cl}_2(\mu\text{-Ph}_2\text{PCH}_2\text{AsPhCH}_2\text{PPh}_2)_2][\text{Cl}]$ are actually longer [2.986(1) and 3.059(1), 3.012(1) Å, respectively],^{2h,6} although Ag and Au have almost identical single-bond metallic radii (1.339 vs 1.336 Å).⁵ The fact that every metal atom in the chain interacts with two neighboring metal atoms is probably partly responsible for the relatively long metal–metal bonds in $[\text{IrAg}(\text{COD})(\mu\text{-O}_2\text{CCF}_3)_2]_n$ as compared

to complexes containing only di- or trimetallic chains. Also, it is clear from Figure 2 that the silver atoms are not aligned for maximum overlap with the Ir $5d_{z^2}$ orbital, which also undoubtedly leads to relatively long Ir–Ag bonds.

The reaction of $[\text{Ir}(\text{COD})(\mu\text{-O}_2\text{CCF}_3)_2]_2$ with AgO_2CCF_3 to give $[\text{IrAg}(\text{COD})(\mu\text{-O}_2\text{CCF}_3)_2]_n$ may be followed by NMR in toluene- d_8 . Six resonances are observed for the COD ligand in the room temperature ^1H NMR of $[\text{Ir}(\text{COD})(\mu\text{-O}_2\text{CCF}_3)_2]_2$,³ indicative of the “hinged” structure shown in eq 1.⁷ Addition



of two equivalents AgO_2CCF_3 results in complete conversion to $[\text{IrAg}(\text{COD})(\mu\text{-O}_2\text{CCF}_3)_2]_n$ (eq 1), for which only three COD ligand resonances are observed in the ^1H NMR and only two COD ligand resonances in the ^{13}C NMR (at room temperature). Addition of more AgO_2CCF_3 does not lead to any change in the NMR spectra. The chemical shift of the Ag atom in the ^{109}Ag NMR of $[\text{IrAg}(\text{COD})(\mu\text{-O}_2\text{CCF}_3)_2]_n$ is 227.7 ppm, which is significantly upfield of its position in AgO_2CCF_3 (365.9 ppm) and indicates formation of an adduct. These results are at least consistent with the solid state structure for $[\text{IrAg}(\text{COD})(\mu\text{-O}_2\text{CCF}_3)_2]_n$ being maintained in solution, perhaps as oligomers over a range of molecular weights.

Preliminary evidence suggests that reaction between $[\text{Ir}(\text{COE})_2(\mu\text{-O}_2\text{CCF}_3)_2]$ (COE = cyclooctene)³ and 2 equiv of silver trifluoroacetate also leads to formation of an iridium–silver complex. However, unlike the analogous cyclooctadiene complexes, this compound is unstable and has not been fully characterized.⁸

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Supplementary Material Available: Text giving complete crystal and refinement data and tables of atomic coordinates, isotropic and anisotropic thermal parameters, interatomic distances, intramolecular angles, intramolecular nonbonding distances, and intermolecular distances (4 pages). Ordering information is given on any current masthead page.

- (4) Examples of crystallographically characterized complexes containing Ir–Ag bonds include references 2e–g and i and: (a) Albinati, A.; Anklin, C.; Janser, P.; Lehner, H.; Matt, D.; Pregosin, P. S.; Venanzi, L. M. *Inorg. Chem.* **1989**, *28*, 1105. (b) Liston, D. J.; Reed, C. A.; Eigenbrot, C. W.; Scheidt, W. R. *Inorg. Chem.* **1987**, *26*, 2739. (c) Kuyper, J.; Vrieze, K.; Olie, K. *Cryst. Struct. Commun.* **1976**, *5*, 179. (5) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Chapter 7.

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