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Notes

A Trinuclear EMAC-Type Molecular Wire with Redox-Active Ferrocenylacetylide “Alligator Clips” Attached

John F. Berry, F. Albert Cotton,* and Carlos A. Murillo*

Laboratory for Molecular Structure and Bonding, Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

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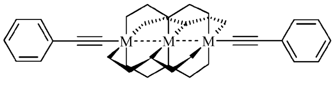
Summary: Reaction of lithium ferrocenylacetylide (LiFcA) with [Co$_3$(dpa)$_4$(NCCH$_3$)$_2$](PF$_6$)$_2$ *(dpa = 2,2′-dipyridylamide) in acetonitrile solution yields the bis-ferrocenylacetylide EMAC (extended metal atom chain)* Co$_3$(dpa)$_4$(FcA)$_2$ *in good yield and excellent purity. The crystal structure features a distinctly unsymmetrical tricobalt chain with a Co−Co bond distance of 2.3091(8) Å and a longer Co···Co separation of 2.5208(9) Å. Cyclic and differential pulse voltammetry show that the two* Fe$^{2+/3+}$ *oxidations occur nearly simultaneously, with a* $\Delta E_{1/2}$ *of 71 mV.*

Introduction

The study of potential molecular wires continues to be of considerable interest, involving many different types of molecules,[1] some of which have been put to use in various applications.[2] An issue of great importance concerning species that could potentially behave as molecular wires is the ability of these wires to transport electrons and the efficiency of the electron transfer through the wire. Thus, it is important to develop methods to test electronic communication from one end of a wire to the other.[3]

Our study of molecular wires has focused on miniaturization of a macroscopic wire to the smallest possible degree: an aligned linear array of metal atoms.[4] The ligand di-2,2′-pyridylamide, dpa, has played a major role in this chemistry because of its ability to stabilize linear chains of three divalent metal atoms in complexes of the type M$_3$(dpa)$_4$Cl$_2$ (M = Cr,[5] Co,[6] Ni,[7] Cu,[8] Ru,[9] and Rh[9]). This chemistry has also been extended by us[4,10] and others[11] to extended metal atom chains (EMACs) of four, five, seven, and nine metal atoms. The trimetal systems are the simplest, and their electronic structures are by far the best understood.[12] Thus, if it is possible to test electronic communication through the three metal atoms in these complexes, the information should be applicable to some extent to longer chains. Recently, we synthesized and studied species of type **I**, having acetylide ions in the axial positions of the molecules.[13] Here, we report the first species of type **II**, containing redox-active metal atoms connected to either end of the trimetal chain through acetylide bridges.



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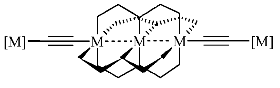

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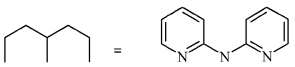

Alkynyl linkers were chosen since many species have been synthesized containing metals linked by alkynyl

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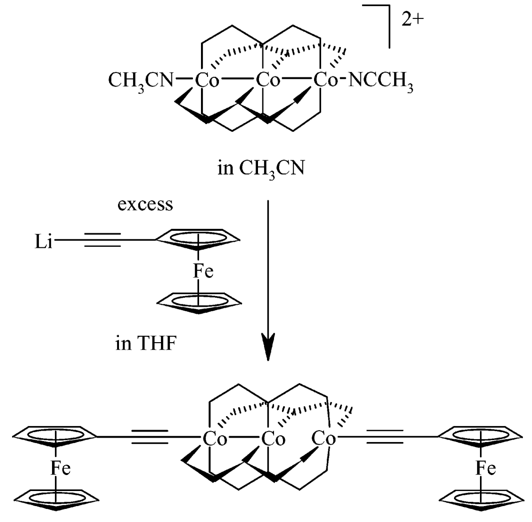
bridges, and these bridges have been shown to facilitate electron transfer from one metal to the other.[14] In this work, the easily prepared ferrocenyl acetylene (HFcA)[15] was chosen since it provides additional redox-active centers and there are many systems in which two or more FcA units are connected through organic moieties[16] or metals[17] that provide useful comparisons. In several cases, electronic communication has been observed,[18] in one case through a Pt−Pt bonded unit,[19] and also through Ru_2^{6+} units.[20]

Results and Discussion

We recently reported an efficient method to make M−C bonds to acetylides in $M_3(dpa)_4^{2+}$ complexes (M = Cr, Co, Ni).[13] Using a similar synthetic strategy, $Co_3(dpa)_4(FcA)_2$ (**1**) was synthesized as shown in Scheme 1.

Scheme 1



1

Table 1. Selected Interatomic Distances (Å) and Angles (deg) for $Co_3(dpa)_4(FcA)_2 \cdot 0.5CH_3CN$

Co1−Co2	2.3091(8)	Co1−C	1.990(4)
Co2⋯Co3	2.5208(9)	Co3−C	2.042(5)
Co1−N	1.967[3]	C≡C	1.187[6]
Co2−N	1.918[3]	Fe−C	2.037[8]
Co3−N	2.133[3]	Fe1⋯Fe2	16.549(8)
Co1−Co2−Co3	177.06(3)	C3−Co3−Co2	176.9(1)
C1−Co1−Co2	179.2(1)	C4−C3−Co3	171.0(4)
C2−C1−Co1	176.6(4)	N−Co3−C3	99.9(2)
N−Co1−C1	94.3(2)		

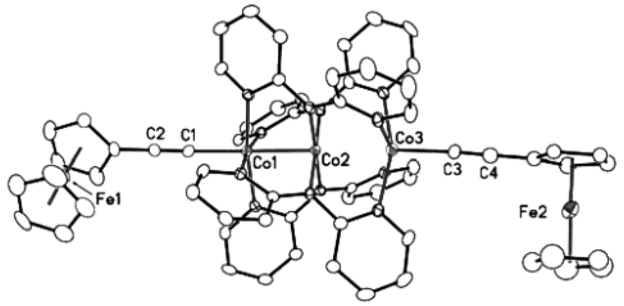


Figure 1. Thermal ellipsoid plot of **1** with ellipsoids drawn at the 30% probability level. Hydrogen atoms and disordered groups are removed for clarity.

The crystal structure of **1** (shown in Figure 1) features a distinctly unsymmetrical tricobalt chain similar to $Co_3(dpa)_4(CCPh)_2$[13] and $Co_3(dpa)_4Cl_2$[6] with a Co−Co bond distance of 2.3091(8) Å and a longer Co⋯Co separation of 2.5208(9) Å. This is consistent with a diamagnetic singly bonded Co_2^{4+} unit formed by Co1 and Co2 and an isolated Co^{2+} center, Co3. The longer Co−N and Co−C distances for Co3 (see Table 1) are also in accord with this formulation along with the fact that the C−Co−N angles for Co3 are more obtuse than they are for Co1. The Fe−C distances (av 2.037[8] Å) and C≡C distances (av of 1.187[6] Å) are essentially unchanged from those in the free HFcA ligand,[21] although in **1** one of the FcA ligands is disordered over two positions.

To see if the unsymmetrical structure of **1** persists in solution, the ^1H NMR spectrum was obtained, despite

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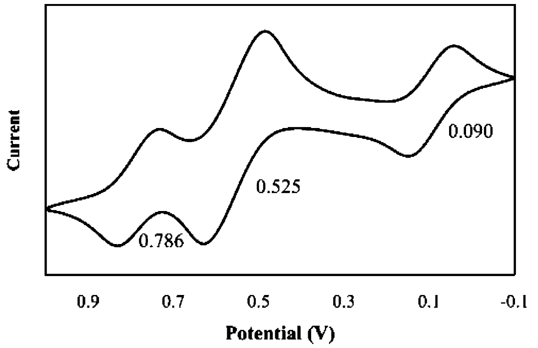

Figure 2. Cyclic voltammogram of **1** taken in THF solution with 1 M NBu_4PF_6 electrolyte using Pt disk (working), Pt wire (aux.), and Ag/AgCl (reference) electrodes. The numbers next to each wave are the corresponding $E_{1/2}$ values.

the paramagnetism of the compound. The spectrum consists of only four resonances, at 51.3, 39.0 (d), 16.0 (d), and 12.0 ppm, which correspond to the pyridyl hydrogen atoms[22] and is thus consistent with equal Co1−Co2 and Co2−Co3 distances and idealized D_4 symmetry for the $Co_3(dpa)_4^{2+}$ core. Also consistent with this are the four resonances at 0.75 (2H), 0.96 (2H), 3.0 (10H), and 3.1 (4H) ppm from the hydrogen atoms of the Cp rings. The resonances at 0.75 and 0.96 ppm, which are due to the substituted Cp ring, appear at different frequencies because of the proximity of these hydrogen atoms to the helically chiral $Co_3(dpa)_4^{2+}$ unit. Though this spectrum is consistent with a symmetrical molecular structure, one cannot rule out the possibility of an unsymmetrical molecule (as found in the crystal) in which the central Co atom moves from side to side faster than the time scale of the NMR experiment. The analogous phenylacetylide complex which is also unsymmetrical in the crystal also shows a symmetrical NMR spectrum in solution,[13] as does $Co_3(dpa)_4Cl_2$,[22] which forms both symmetrical and unsymmetrical molecules in the solid state.[6b] The electronic spectrum shows absorptions at 1233, 584, 480, and 440 nm, similar to those in $Co_3(dpa)_4Cl_2$.[6]

The cyclic voltammogram for **1**, shown in Figure 2, has three reversible oxidation waves at 0.090, 0.525, and 0.786 V, with the center one corresponding to a current twice as large as each of the outer ones. Since it appears unlikely that an FcA oxidation could occur at a potential of only 0.090 V, this wave may safely be assigned to a one-electron oxidation of the $Co_3(dpa)_4^{2+}$ unit. This is in reasonable accord with the observed first oxidation of $Co_3(dpa)_4(CCPh)_2$,[13] at 0.121 V. While further assignments are a little less certain, we propose the following scheme:

$$Fe^{2+}{-}Co_3^{6+}{-}Fe^{2+} \xrightarrow[-e^-]{0.090\ V} Fe^{2+}{-}Co_3^{7+}{-}Fe^{2+}$$

$$Fe^{2+}{-}Co_3^{7+}{-}Fe^{2+} \xrightarrow[-2e^-]{0.525\ V} Fe^{3+}{-}Co_3^{7+}{-}Fe^{3+}$$

$$Fe^{3+}{-}Co_3^{7+}{-}Fe^{3+} \xrightarrow[-e^-]{0.786\ V} Fe^{3+}{-}Co_3^{8+}{-}Fe^{3+}$$

This assumes that the two FcA oxidation waves are unresolved. A value of 0.525 V seems reasonable, compared to that of ca. 0.45 V for ferrocene itself, since they are attached to the one-electron-oxidized central tricobalt unit. The higher voltage for the Co_3^{7+} to Co_3^{8+} oxidation (0.786 V) compared to the corresponding process in $Co_3(dpa)_4(CCPh)_2$ (0.725 V) seems reasonable because of the positive charges already present on the FcA units. Moreover, in the differential pulse voltammogram of **1**, the peak at 0.525 V is broadened, as expected for a two-electron process, and a value for $\Delta E_{1/2}$ (i.e., the difference in oxidation potentials of the two terminal iron atoms) can be calculated from the width of this peak by the method of Richardson and Taube.[23] The value of $\Delta E_{1/2}$ is thus 71 mV, corresponding to a comproportionation constant $K_c = 16$ for the following process:

$$\begin{array}{c} Fe^{2+}{-}Co_3^{7+}{-}Fe^{2+} + Fe^{3+}{-}Co_3^{7+}{-}Fe^{3+} \\ \Big\updownarrow K_c \\ 2\ Fe^{2+}{-}Co_3^{7+}{-}Fe^{3+} \end{array}$$

A purely statistical value of K_c would be 4. The Fe to Fe separation in the $[Co_3(dpa)_4(FcA)_2]^+$ ion is presumably about the same as it is in the neutral compound **1**, namely, 16.6 Å. We may compare this with the situation in the compound $(DAniF)_3Mo_2(O_2C(HC{=}CH)_4CO_2)Mo_2(DAniF)_3$, where DAniF is the di-*p*-anisylformamidinate ion and the linker is the texate dianion, which has a conjugated system of four *trans* double bonds. In this compound the two redox centers are separated by 16.2 Å and $\Delta E_{1/2}$ is 65 mV. It may thus be concluded that the communication in **1**, though small, is comparable to that provided by the texate dianion.

Attempts to isolate or spectroscopically observe compounds containing $\mathbf{1}^{n+}$ ions were unsuccessful. Chemical or electrochemical oxidation procedures led only to decomposition.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of dry nitrogen gas using standard Schlenk techniques. Toluene, THF, and hexanes were purified by means of a Glass Contour solvent system. Other solvents were distilled in a nitrogen atmosphere over appropriate drying agents prior to use. $Co_3(dpa)_4(NCMe)_2(PF_6)_2$[24] and HFcA[15] were prepared according to previously reported methods. IR spectra were taken on a Perkin-Elmer 16PC FTIR spectrometer using KBr pellets. Cyclic voltammograms were taken on a CH Instruments electrochemical analyzer using 1 M NBu_4PF_6 solutions 0.05 mM in **1** in THF. The electrodes were Pt disk (working), Pt wire (auxiliary), and Ag/AgCl (reference). ^1H NMR spectra were obtained on a VXR-300 NMR spectrometer. Mass spectrometry data (electrospray ionization) were recorded at the Laboratory for Biological Mass Spectrometry at Texas A&M University, using an MDS Series Qstar Pulsar with a spray voltage of 5 keV. UV−visible−near-IR spectra were obtained on a Cary 17 spectrophotometer.

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[21] HFcA crystal data: triclinic, $P\bar{1}$, $a = 9.4665(5)$ Å, $b = 11.7709(7)$ Å, $c = 13.7417(8)$ Å, $\alpha = 74.483(1)°$, $\beta = 79.592(1)°$, $\gamma = 70.922(1)°$, $d = 1.509$ g cm^{-3}, $\mu = 1.572$ mm^{-1}, R1 ($I > 2\sigma(I)$): 0.0235, wR2 ($I > 2\sigma(I)$): 0.0622, R1 (all data): 0.0268, wR2 (all data): 0.0648.

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Elemental analysis was carried out by Canadian Microanalytical Services in British Columbia, Canada, on a sample from which the interstitial solvents have been removed by vacuum.

Synthesis of $Co_3(dpa)_4(FcA)_2$, 1. HFcA (269 mg, 1.28 mmol) was dissolved in 5 mL of THF and treated with 0.8 mL of a 1.6 M solution of methyllithium in Et_2O at 0 °C. The resulting orange solution was allowed to warm to room temperature over the course of 0.5 h. This solution was then added to a solution of $[Co_3(dpa)_4(NCCH_3)_2](PF_6)_2$ (525 mg, 0.427 mmol) in 25 mL of acetonitrile, whereupon a lustrous brown microcrystalline precipitate was observed. The mixture was stirred for 0.5 h, and the solids were collected by filtration, washed with 2 × 15 mL of Et_2O, and extracted with 2 × 12 mL of toluene containing a small amount of CH_3CN. The combined extracts were layered with hexanes, and large crystals formed after a few days. Yield: 373 mg, 68%. IR (KBr, cm^{-1}): 3446 m, br, 3067 w, 2963 w, 2081 w (C/C), 1591 s, 1545 m, 1468 vs, 1424 vs, 1368 s, 1311 m, 1261 m, 1220 m, 1152 s, 1103 s, 1014 m, 918 w, 881 w, 807 m, 761 m, 737 m, 619 w, 524 w, 469 m, 429 w. UV−vis−NIR (THF solution, λ, nm (ϵ, M^{-1} cm^{-1})): 1233 (100), 584 (2000), 480 (sh, 7000), 440 (sh, 20 000), 328 (80 000), 295 (sh, 60 000), 229 (90 000). ^1H NMR (C_6D_6, δ, ppm): 51.250 s (pyridyl CH), 39.048 d ($J = 7$ Hz, pyridyl CH), 15.982 d ($J = 6$ Hz, pyridyl CH), 12.036 s (pyridyl CH), 3.087 s (4 H, C≡CCp CH), 2.999 s (10 H, Cp), 0.956 s (2 H, C/CCp CH), 0.747 s (2 H, C≡CCp CH). ESI+ mass spectrum (m/z): 1275 M^+, 1066 $(M - FcA)^+$. Anal. Calcd for $Co_3C_{64}H_{50}N_{12}Fe_2$: C 60.26, H 3.95, N 13.18. Found: C 60.18, H 4.08, N 13.23.

X-ray Crystallography. A suitable crystal was mounted on the end of a quartz fiber by a small amount of grease and transferred to the goniometer of a Bruker SMART 1000 CCD area detector system, where it was cooled to −60 °C for the duration of the experiment. Crystals of **1**·$0.5CH_3CN$ are twinned in such a way that two domains are related to each other by a 180° rotation about a line parallel to the *a* axis. This sort of twinning has been observed before in complexes of dpa,[12d] and the X-ray data for both twin components in SHELX HKLF5 format were used for successful refinement. Initial unit cell parameters were obtained from GEMINI[25] software and refined using SMART software.[26] Data integration, correction for Lorentz and polarization effects, and final cell refinement were performed by SAINTPLUS.[27] The data were further corrected for absorption by TWINABS.[28] The initial structure solution was obtained via the direct methods routine in SHELXTL.[29] Subsequent refinement cycles (based on F^2) and Fourier synthesis revealed the positions of all the non-hydrogen atoms. These atoms (with the exception of disordered groups) were refined using anisotropic displacement tensors. All hydrogen atoms were added in calculated positions for the final refinement cycle. Crystal data and convergence statistics are given in Table 2.

Table 2. Crystal Data for $Co_3(dpa)_4(FcA)_2 \cdot 0.5CH_3CN$

formula	$C_{65}H_{51.5}Co_3Fe_2N_{12.5}$
fw	1293.06
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	17.514(3)
b, Å	15.102(3)
c, Å	21.434(4)
β, deg	99.355(4)
V, Å^3	5594(2)
Z	4
d(calc), g cm^{-3}	1.539
R1,[a] wR2[b] ($I > 2\sigma I$)	0.0443, 0.1119
R1,[a] wR2[b] (all data)	0.0663, 0.1228

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/3[w(F_o^2)^2]]^{1/2}$, $w = 1/F^2(F_o^2) + (aP)^2 + bP$, where $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$.

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Note Added in Proof. Electrochemical studies of tricobalt EMAC complexes with various metals attached through axial cyanide linkages have been recently reported. As in **1**, the two appended metal atoms are oxidized at nearly the same potential. See: Sheng, T.; Appelt, R.; Comte, V.; Vahrenkamp, H. *Eur. J. Inorg. Chem.* **2003**, 3731.

Supporting Information Available: Crystallographic data for **1**·$0.5CH_3CN$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049979D

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