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The synthesis and structural analysis of the bis-$Co_2(CO)_6$ adduct of the cyclic tetrayne $C_{20}H_8$

Richard D. Adams *, Uwe H.F. Bunz, Wei Fu, Lamvien Nguyen

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208, USA

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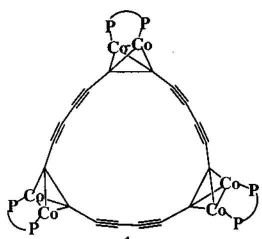
Abstract

The reaction of the cyclic tetrayne **2** with $Co_2(CO)_8$ at 25°C has yielded the double addition product, $C_{20}H_8[Co_2(CO)_6]_2$, **3** in a 39% yield. Compound **3** was characterized by a single crystal X-ray diffraction analysis. The two $Co_2(CO)_6$ groupings have been added to two alkyne groups on opposite sides of the tetrayne ring in order to minimize steric interactions. The molecule is centrosymmetrical and the central C_{12} ring is planar. The two Co–Co bonds are oriented perpendicular to the plane of the C_{12} ring.

Keywords: Cobalt; Cyclic tetrayne; Crystal structure

1. Introduction

The synthesis of cyclic polyynes [1] and their transition metal complexes [2,3] has been the focus of considerable research interest. Addition of metal atoms to the alkyne groups can increase the stability of unusual ring systems. One of the most remarkable examples of this is illustrated by the synthesis and structural characterization of the cyclic polyyne of the tris(dicobalt) complex of C_{18}, $C_{18}[Co_2(CO)_4dppm]_3$, **1** [3].



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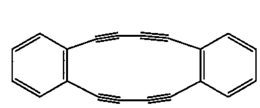

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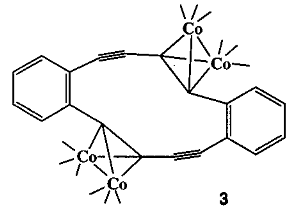
We have recently been investigating the reactivity of the cyclic tetrayne $C_{20}H_8$, **2** [4]. This compound was first synthesized in 1957 [5]. It is known to decompose slowly in solution at room temperature (r.t.) and violently in the solid state if subjected to shock [4]. In order to stabilize **2** we have investigated its reaction with $Co_2(CO)_8$. This has yielded the double addition product $C_{20}H_8[\mu\text{-}Co_2(CO)_6]_2$, **3**. Details of the synthesis and structural characterization of **3** are reported here.

2. Results and discussion

The reaction of the tetrayne **2** with $Co_2(CO)_8$ at 25°C provided the double addition product **3** in a 39% yield. Compound **3** was characterized by a combination of IR, ^{1}H-NMR and single crystal X-ray diffraction analyses. An ORTEP drawing of the molecular structure of **3** is shown in Fig. 1. Final atomic positional parameters are listed in Table 1.



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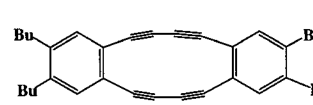

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* Corresponding author.

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Selected interatomic distances and angles are listed in Tables 2 and 3, respectively. The compound crystallizes in the centrosymmetrical space group $P\bar{1}$ with one formula equivalent in the unit cell, thus the molecule lies on a crystallographic center of symmetry. The structure shows that the $Co_2(CO)_6$ groups have been added to opposite sides of the molecule **2**, and are positioned as far as possible from each other in order minimize their steric interactions. The lengths of the Co–Co bond, 2.4720(6) Å, and the coordinated C–C triple bond C(1)–C(2), 1.356(4) Å are typical of those observed for bridging alkyne ligands in $Co_2(CO)_6$(μ-RC_2R) complexes [6]. The length of the uncoordinated triple bond C(3)–C(4) is also typical of such bonds, 1.206(4) Å and is very similar to those observed for **4**, the uncomplexed tetrabutyl derivative of **3**, 1.204 and 1.196 Å which has recently been structurally characterized [7]. Whereas the alkyne carbon atoms in **4** are slightly nonlinear, the C–C–C angles range from 165.0 to 167.4°, the alkyne carbon atoms in **3** are much closer to linear, C(2)–C(3)–C(4) = 177.3(3)° and C(3)–C(4)–C(5) = 177.4(3)°. The C_{12} ring in **3** is planar within experimental error and the Co–Co vectors lie perpendicular to the plane of this ring. Unlike **2**, compound **3** is stable in the open air in solutions at r.t. for periods of several days.

Although it has been shown that $Co_2(CO)_6$ groups can even be placed on adjacent C–C triple bonds in *linear* di- and tetraynes [8], we have not yet been able to add more than two $Co_2(CO)_6$ groupings to **2**.

3. Experimental

3.1. General data

Reagent grade solvents were freshly distilled and stored over 4 Å molecular sieves. The reaction was performed under a nitrogen atmosphere. IR spectra were recorded on a Nicolet 5DXBO FTIR spectrophotometer. ^{1}H-NMR spectra were recorded on Varian Mercury spectrometers at 400 MHz. The compound $Co_2(CO)_8$ was purchased from Strem Chemicals, and was used without further purification. The tetrayne **2** was prepared according to the published procedures [7]. Product separation was performed by TLC in air on Analtech 0.25 mm silica gel 60 Å F_{254} glass plates. The elemental analysis was performed by Oneida Research Services, Whitesboro, NY.

3.2. Synthesis of $C_{20}H_8[\mu\text{-}Co_2(CO)_6]_2$, **3**

A 38.6 mg amount (0.113 mmol) of $Co_2(CO)_8$ was dissolved in 50 ml of hexane in a 100 ml three neck round bottom flask. A 5.0 ml solution of **2** in CH_2Cl_2 (ca. 11.3 M, 0.0565 mmol) was then added to the $Co_2(CO)_8$ solution. The reaction mixture was stirred for 30 min at 25°C, and then the solvent was removed in vacuo. The residue was then redissolved in CH_2Cl_2 and

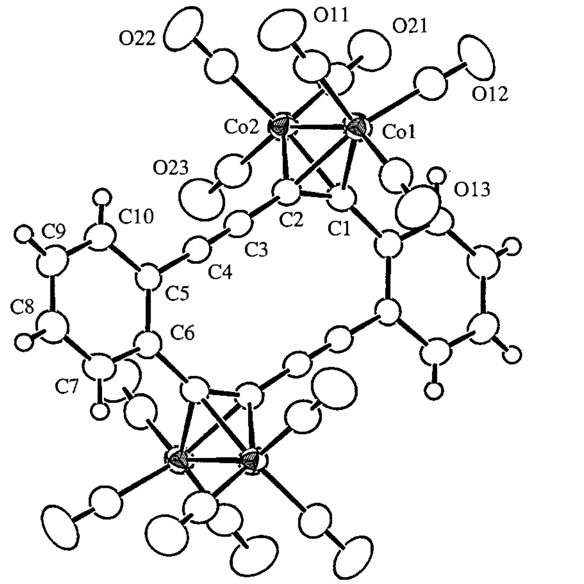

Fig. 1. An ORTEP diagram of $C_{20}H_8[\mu\text{-}Co_2(CO)_6]_2$, **3** showing 40% probability thermal ellipsoids.

Table 1
Positional and thermal parameters (B_{eq}) for $C_{20}H_8[Co_2(CO)_6]_2$, **3**

Atom	*x*	*y*	*z*	B_{eq}
Co(1)	0.15554(4)	0.18488(4)	−0.11598(5)	2.975(9)
Co(2)	0.31068(4)	0.37472(4)	0.10199(5)	3.03(1)
O(11)	0.0940(3)	0.3414(3)	−0.4061(3)	6.71(8)
O(12)	−0.0757(3)	0.2287(3)	−0.0201(3)	6.19(8)
O(13)	0.1197(3)	−0.1295(3)	−0.2843(3)	6.54(8)
O(21)	0.1346(3)	0.5037(3)	0.2702(4)	6.69(8)
O(22)	0.3015(3)	0.5962(3)	−0.1141(4)	6.52(8)
O(23)	0.5725(3)	0.4480(3)	0.3772(3)	6.43(7)
C(1)	0.3041(3)	0.1570(3)	0.0980(3)	2.82(6)
C(2)	0.3535(3)	0.1834(3)	−0.0129(3)	2.74(6)
C(3)	0.4453(3)	0.1430(3)	−0.0854(3)	2.72(6)
C(4)	0.5203(3)	0.1079(3)	−0.1545(3)	2.62(5)
C(5)	0.6044(3)	0.0679(3)	−0.2431(3)	2.44(5)
C(6)	0.6873(3)	−0.0607(3)	−0.2195(3)	2.68(6)
C(7)	0.7635(3)	−0.0946(4)	−0.3146(4)	3.50(7)
C(8)	0.7611(3)	−0.0051(4)	−0.4268(4)	3.86(8)
C(9)	0.6810(3)	0.1213(4)	−0.4489(4)	3.71(7)
C(10)	0.6037(3)	0.1572(3)	−0.3590(4)	3.21(6)
C(11)	0.1144(3)	0.2810(4)	−0.2967(4)	4.12(8)
C(12)	0.0106(3)	0.2113(4)	−0.0623(4)	3.90(7)
C(13)	0.1310(3)	−0.0082(4)	−0.2188(4)	4.13(8)
C(21)	0.2027(4)	0.4563(4)	0.2063(4)	4.38(8)
C(22)	0.3054(3)	0.5130(4)	−0.0299(4)	4.11(8)
C(23)	0.4712(4)	0.4202(4)	0.2706(4)	4.20(8)
H(1)	0.555(3)	0.230(3)	−0.369(3)	2.4(6)
H(2)	0.677(3)	0.180(3)	−0.519(4)	3.6(7)
H(3)	0.808(3)	−0.032(4)	−0.487(4)	4.5(7)
H(4)	0.816(3)	−0.179(3)	−0.300(3)	3.3(6)

Table 2
Selected interatomic bond distances for $C_{20}H_8[Co_2(CO)_6]_2$, **3**[a,b]

Atom	Distance	Atom	Distance
Co(1)–Co(2)	2.4720(6)	C(1)–C(2)	1.356(4)
Co(1)–C(1)	1.977(3)	C(1)–C(6)	1.464(4)
Co(1)–C(2)	1.974(3)	C(2)–C(3)	1.395(4)
Co(1)–C(11)	1.833(3)	C(3)–C(4)	1.206(4)
Co(1)–C(12)	1.818(3)	C(4)–C(5)	1.426(4)
Co(1)–C(13)	1.802(4)	C(5)–C(6)	1.414(4)
Co(2)–C(1)	1.958(3)	C(5)–C(10)	1.405(4)
Co(2)–C(2)	1.978(3)	C(6)–C(7)	1.395(4)
Co(2)–C(21)	1.824(3)	C(7)–C(8)	1.373(4)
Co(2)–C(22)	1.830(3)	C(8)–C(9)	1.380(4)
Co(2)–C(23)	1.797(4)	C(9)–C(10)	1.369(4)
O–C(av)	1.132(4)		

[a] Distances are in angstroms (Å).
[b] Estimated standard deviations in the least significant figure are given in parentheses.

transferred to TLC plates and eluted using hexane solvent. Two bands were eluted. The first band (yellow) was unreacted **2**. The second band (red) yielded 8.7 mg of the product $C_{20}H_8[Co_2(CO)_6]_2$, **3**, in a 39% yield (based on Co). The product is stable to air in solution for periods of several days. Analytical and spectral data for **3**: IR (νCO (cm^{-1}, in hexane) 2097 (w), 2090 (s), 2066 (vs), 2059 (m), 2040 (s), 2029 (vs); ^{1}H-NMR (δ, in acetone-d$_6$): 7.72 (d, 2H, $J=8.0$ Hz), 7.52 (dt, 4H, $J=8.0$, $J=1.4$), 7.43 (dd, 2H, $J=8.0$, $J=1.4$). Anal. Calc. (found) for **3**: C, 46.86 (46.81); H, 0.98 (1.04).

4. Crystallographic analysis

Dark red crystals of **3** suitable for diffraction analysis were grown by slow evaporation of the solvent at 25°C from solutions in a CH_2Cl_2/hexane solvent mixture.

Table 3
Selected interatomic bond angles for $C_{20}H_8[Co_2(CO)_6]_2$, **3**[a,b]

Atom	Angle	Atom	Angle
Co(2)–Co(1)–C(1)	50.72(8)	Co(1)–C(2)–C(1)	70.1(2)
Co(2)–Co(1)–C(2)	51.34(7)	Co(1)–C(2)–C(3)	130.1(2)
C(1)–Co(1)–C(2)	40.1(1)	Co(2)–C(2)–C(1)	69.0(2)
Co(1)–Co(2)–C(1)	51.44(8)	Co(2)–C(2)–C(3)	134.0(2)
Co(1)–Co(2)–C(2)	51.20(8)	C(1)–C(2)–C(3)	147.4(3)
C(1)–Co(2)–C(2)	40.3(1)	C(2)–C(3)–C(4)	177.3(3)
Co(1)–C(1)–Co(2)	77.8(1)	C(3)–C(4)–C(5)	177.4(3)
Co(1)–C(1)–C(2)	69.8(2)	C(4)–C(5)–C(6)	121.8(2)
Co(1)–C(1)–C(6)	130.3(2)	C(4)–C(5)–C(10)	119.4(2)
Co(2)–C(1)–C(2)	70.6(2)	C(1)–C(6)–C(5)	122.0(2)
Co(2)–C(1)–C(6)	135.0(2)	C(1)–C(6)–C(7)	119.7(2)
C(2)–C(1)–C(6)	145.1(2)	Co–C–O(av)	178.0(3)
Co(1)–C(2)–Co(2)	77.5(1)		

[a] Angles are in degrees (°).
[b] Estimated standard deviations in the least significant figure are given in parentheses.

Table 4
Crystallographic data for compound **3**

Formula	$Co_4C_{32}O_{12}H_8$
Formula weight	820.14
Crystal system	Triclinic
Lattice parameters	
a (Å)	10.903(2)
b (Å)	8.994(1)
c (Å)	8.873(2)
α (°)	99.72(2)
β (°)	113.90(2)
γ (°)	86.43(2)
V (Å^3)	784.1(8)
Space group	$P\bar{1}$ (#2)
Z	1
$D_{calc.}$ (g cm^{-3})	1.74
μ(Mo–K$_\alpha$) (cm^{-1})	21.44
Temperature (°C)	20
$2\theta_{max}$ (°)	50
No. Obs. ($I>3\sigma$)	2333
No. variables	234
Goodness-of-fit	2.01
Max. shift in final cycle	0.01
Residuals: R; R_w[a]	0.029; 0.036
Abs. Cor.	Difabs
Transmission coeff. max/min	1.00/0.62
Largest peak in final diff. map (e Å^{-3})	0.39

[a] $R=\Sigma_{hkl}(||F_{obs}|-|F_{calc}||)/\Sigma_{hkl}|F_{obs}|$; $R_w=[\Sigma_{hkl}w(|F_{obs}|-|F_{calc}|^2)/\Sigma_{hkl}wF^2_{obs}]^{1/2}$, $w=1/\sigma^2(F_{obs})$; GOF $=[\Sigma_{hkl}(w(|F_{obs}|-|F_{calc}|))^2/(n_{data}-n_{vari})]^{1/2}$.

The crystal used for the diffraction measurements was mounted in thin-walled glass capillary. The diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated Mo–K$_\alpha$ radiation at 20°C. The crystallographic unit cell was determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table 4. All data processing was performed on a Silicon-Graphics INDIGO[2] Workstation by using the TEXSAN structure solving program library obtained from the Molecular Structure Corporation, The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures [9a]. Anomalous dispersion corrections were applied to all non-hydrogen atoms [9b]. Lorentz/polarization (Lp) corrections were applied to the data. Full matrix least-squares refinements minimized the function: $\Sigma_{hlk}w(|F_o|-|F_c|)^2$, where $w=1/\sigma^2(F)$, $\sigma(F)=\sigma(F_o^2)/2F_o$ and $\sigma(F_o^2)=[\sigma(l_{raw})^2+0.02\,l_{net})^2]^{1/2}/\text{Lp}$.

Compound **3** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by successful solution and refinement of the structure. The structure was solved by a combination of direct methods (SIR92) and difference Fourier syntheses. All nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located and refined with isotropic thermal parameters.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 102549 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk, or www: http://www.ccdc.cam.ac.uk.

Acknowledgements

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