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A hexacarbonyldicobalt(0) complex of a 'magazine-rack' molecule, $[(\eta^2\text{-}C_{32}H_{20})Co_2(CO)_6]\cdot CH_2Cl_2$

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Key indicators

Single-crystal X-ray study
T = 113 K
Mean σ(C–C) = 0.002 Å
R factor = 0.026
wR factor = 0.089
Data-to-parameter ratio = 16.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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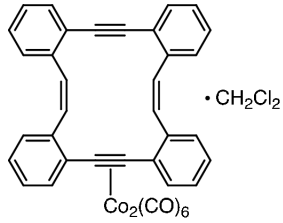
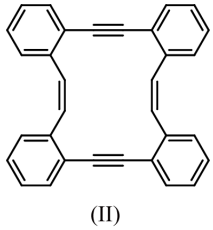
The title compound, μ-pentacyclo[26.4.0.0^{9,14}.0^{17,22}.0^{25,30}]-dotriaconta-1,3,5,9,11,13,15,17,19,21,25,27,29,31-tetradecaene-7,24-diyne-bis(tricarbonylcobalt) dichloromethane solvate, $[Co_2(\eta^2\text{-}C_{32}H_{20})(CO)_6]\cdot CH_2Cl_2$, has been prepared by treatment of a dehydrobenzoannulene with octacarbonyldicobalt. This cobalt complex is chiral in the solid state and exhibits alternate arrays of *P*- and *M*-conformations.

Comment

Various types of dehydroannulenes (Diederich, 1995; Tobe *et al.*, 1996) and their benzannelated analogs (Iyoda *et al.*, 2001; Palmer *et al.*, 2001) have been synthesized thus far. Much of the interest can be attributed to the recognition that such categories of compounds can potentially serve as versatile precursors for carbon-rich molecular (Tobe *et al.*, 1998, 2001) and polymeric systems (Dosa *et al.*, 1999). For example, it has been reported that heating of a dehydrobenzoannulene at 518 K leads to the formation of a 'graphitic onion' (Boese *et al.*, 1997). Furthermore, it has been reported that powdered cobalt metal accelerates the growth of single-wall carbon nanotubes from vaporized carbon in an arc generator (Bethune *et al.*, 1993). From these experimental results we expected that cobalt-coordinating dehydrobenzoannulenes might be promising precursors for carbon nanotubes, because they are easy to handle due to their stability in air, and might be transformed to carbon nanotubes at a lower temperature than those hitherto reported. Thus, as part of our project to explore π-conjugated cyclophane derivatives having unique structural and electronic features (Orita *et al.*, 2002; An *et al.*, 2002), we tackled the preparation of cobalt-coordinating π-conjugated cyclophanes. We envisioned that the title compound, (I), could be obtained by the reaction of $Co_2(CO)_8$ with a 'magazine-rack' type molecule, such as a cyclophane having alternating phenylene–ethynylene, as well as phenylene–ethenylene arrays, (II) (Orita *et al.*, 2002).



(I)



(II)

As shown in Fig. 1, the dicobalt complex, (I), has a linear uncoordinated acetylene moiety and a bent acetylene coordinated to the $Co_2(CO)_6$ moiety. Although, in the crystal of (II),

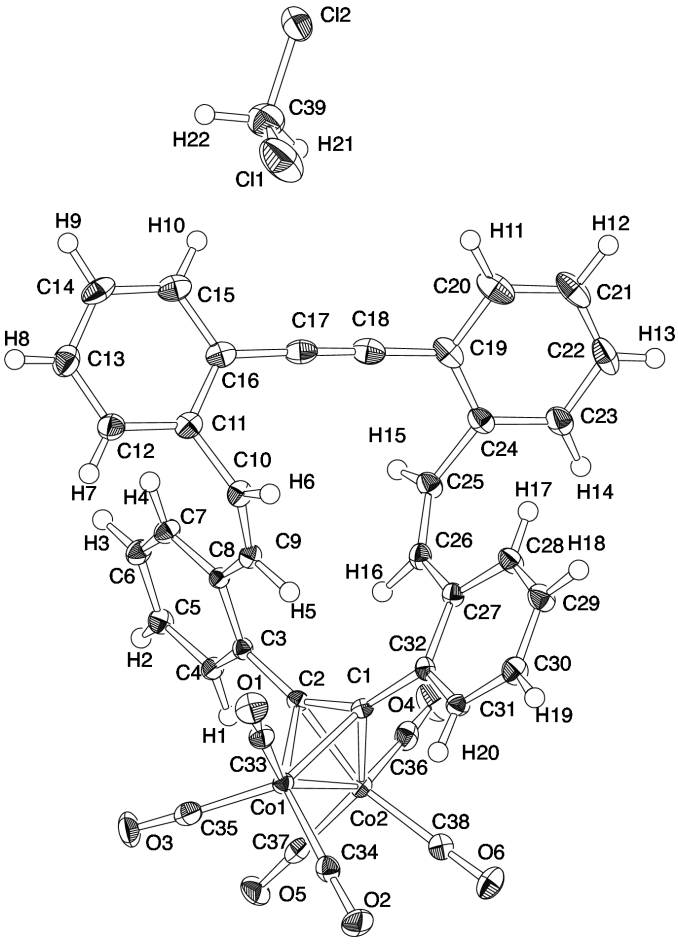


Figure 1
The molecular structure of the title complex. Displacement ellipsoids are drawn at the 50% probability level.

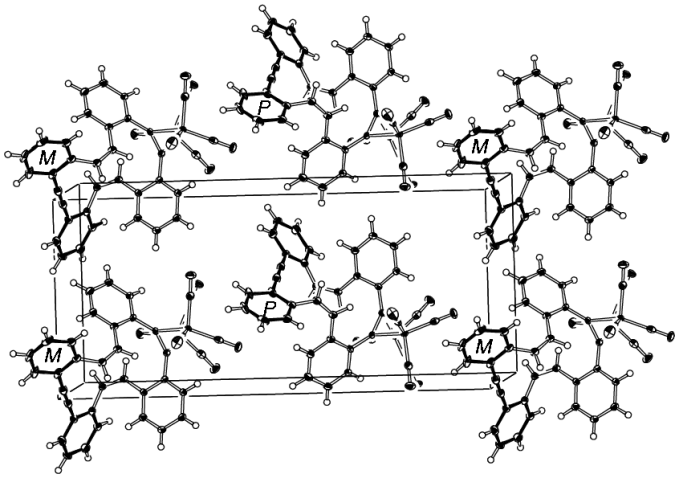


Figure 2
View of the packing of the title complex in the crystal. Displacement ellipsoids are drawn at the 50% probability level. The dichloromethane molecules have been omitted for clarity.

two phenylenes are connected by acetylene with a dihedral angle of 23.0°, in the cobalt complex, (I), the corresponding dihedral angle between the C11—C16 and C19—C24 planes was found to be 30.8 (1)°. It has been reported that, in the solid state, the π-conjugated cyclophane (II) adopts a concave structure like a magazine-rack, with alternate arrays of the *P*- and *M*-conformations. Upon formation of complex (I), this concave feature was lost, but (I) is still chiral and retains alternate arrays of the *P*- and *M*-conformers with respect to the uncoordinated diphenylacetylene moiety in the crystal; this is illustrated in Fig. 2.

Experimental

Preparation of (I): to a flame-dried flask were added (II) (100.1 mg, 0.5 mmol), $Co_2(CO)_8$ (512.9 mg, 0.5 mmol) and CH_2Cl_2 (10 ml). The mixture was stirred for 12 h at room temperature in the dark. After evaporation, hexane was added to the residual black solids and the mixture filtered through a thin layer of silica gel. After evaporation of the resulting filtrate, dark-purple crystals were obtained in 50–60% yield.

Crystal data

$[Co_2(C_{32}H_{20})(CO)_6]\cdot CH_2Cl_2$
M_r = 775.37
Monoclinic, $P2_1/c$
a = 13.0348 (3) Å
b = 10.9999 (3) Å
c = 23.8599 (5) Å
β = 94.584 (1)°
V = 3410.1 (1) Å^3
Z = 4
D_x = 1.510 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9554 reflections
θ = 2.9–27.5°
μ = 1.18 mm^{-1}
T = 113.1 K
Plate, dark purple
0.30 × 0.15 × 0.10 mm

Data collection

Rigaku R-AXIS-IV diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.719, T_{max} = 0.889
18 119 measured reflections
7873 independent reflections
6460 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.019
θ_{max} = 27.5°
$h = -16 \rightarrow 16$
$k = -14 \rightarrow 14$
$l = -21 \rightarrow 30$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.089
S = 0.90
7523 reflections
464 parameters
All H-atom parameters refined
$w = 1/[0.002F_o^2 + \sigma^2(F_o)]/(4F_o^2)$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.72 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co2—Co1	2.4524 (3)	C2—C3	1.4707 (19)
Co1—C2	1.9731 (13)	C16—C17	1.440 (2)
Co1—C1	1.9798 (14)	C17—C18	1.201 (2)
C2—C1	1.346 (2)		
C1—C2—C3	147.39 (14)	C2—C3—C4	118.80 (13)
C16—C17—C18	178.10 (17)		
C3—C2—C1—C32	−2.8 (6)		

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Rigaku, 1999); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 for Windows (Farrugia, 1998); software used to prepare material for publication: *CrystalStructure* (Molecular Structure Corporation & Rigaku, 2001).

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References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

An, D. L., Nakano, T., Orita, A. & Otera, J. (2002). *Angew. Chem. Int. Ed.* **41**, 171.

Bethune, D. S., Kiang, C. H., de Vries, M. S., Gorman, G., Savoy, R., Vazquez, J. & Beyers, R. (1993). *Nature (London)*, **363**, 605–607.

Boese, R., Matzger, A. J. & Vollhardt, K. P. C. (1997). *J. Am. Chem. Soc.* **119**, 2052–2053.

Diederich, F. (1995). *Modern Acetylene Chemistry*, edited by P. J. Stang and F. Diederich. VCH: Weinheim.

Dosa, P. I., Erben, C., Iyer, V. S., Vollhardt, K. P. C. & Wasser, I. M. (1999). *J. Am. Chem. Soc.* **121**, 10430–10431.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565–565.

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.

Iyoda, M., Horino, T., Takahashi, F., Hasegawa, M., Yoshida, M. & Kuwatani, Y. (2001). *Tetrahedron Lett.* **42**, 6883–6886.

Molecular Structure Corporation & Rigaku (2001). *CrystalStructure*. Version 2.00. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA, and Rigaku, 3-9-12 Akishima, Tokyo 196-8666, Japan.

Orita, A., Jiang, L., Tsuruta, M. & Otera, J. (2002). *Chem. Lett.* pp. 136–137.

Palmer, G. J., Parkin, S. R. & Anthony, J. E. (2001). *Angew. Chem. Int. Ed.* **40**, 2509–2512.

Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.

Rigaku (1999). *TEXSAN*. Version 1.10. Rigaku Corporation, Tokyo, Japan.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Tobe, Y., Matsumoto, H., Naemura, K., Achiba, Y. & Wakabayashi, T. (1996). *Angew. Chem. Int. Ed. Engl.* **35**, 1800–1802.

Tobe, Y., Nakagawa, N., Kishi, J., Sonoda, M., Naemura, K., Wakabayashi, T., Shida, T. & Achiba, Y. (2001). *Tetrahedron*, **57**, 3629–3636.

Tobe, Y., Nakagawa, N., Naemura, K., Wakabayashi, T., Shida, T. & Achiba, Y. (1998). *J. Am. Chem. Soc.* **120**, 4544–4545.