Crystal structures of (μ₂-η²,η²-4-hydroxybut-2-yn-1-yl 2-bromo-2-methylpropanoate-κ⁴C₂,₃:C⁴C₂,₃)-bis[tricarbonylcobalt(II)](Co—Co) and [μ₂-η²,η²-but-2-yn-1,4-diyl bis(2-bromo-2-methylpropanoate)-κ⁴C₂,₃:C⁴C₂,₃]bis[tricarbonylcobalt(II)](Co—Co)

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The title compounds, [Co₂(C₆H₁₁BrO₃)(CO)₆], (1), and [Co₂(C₁₂H₁₆Br₂O₄)(CO)₆], (2), result from the replacement of two carbonyl ligands from dicobalt octacarbonyl by the alkynes 4-hydroxybut-2-ynyl 2-bromo-2-methylpropanoate and but-2-yn-1,4-diyl bis(2-bromo-2-methylpropanoate), respectively. Both molecules have classic tetrahedral C₂Co₂ cluster cores with the CoII atoms in a highly distorted octahedral coordination geometry. The alkyne ligands both adopt a cis-bent conformation on coordination. In the crystal structure of (1), classical O—H···C(C) and non-classical C—H···O contacts form inversion dimers. These combine with weak O···C(C) and Br···O contacts to stack the molecules into interconnected columns along the b-axis direction. C—H···Br contacts stabilize the packing for (2), and a weak Br···O contact is also observed. Interconnected columns of molecules again form along the b-axis direction.

1. Chemical context

In 1954 alkynes were found to act as ligands and displace two carbonyl groups from dicobalt octacarbonyl to form alkyne-hexacarbonyl-dicobalt complexes (Sternberg et al., 1954). The novelty of these compounds, together with their close isolobal relationship to other members of the ‘tetrahedrane series’ (Hoffmann, 1982), spawned enormous interest in both the hexacarbonyls and their substituted derivatives. Applications include use in organic synthesis (Melikyan et al., 2012), as biological probes (Salmain & Jaouen, 1993) and in the stabilization of high-performance energetic materials (Windler et al., 2012). Their diverse redox properties (Robinson & Simpson, 1989) have also been exploited in the development of molecular wires (McAdam et al., 1996; Hore et al., 2000; Xie et al., 2012) where alkyne-hexacarbonyl-dicobalt cores are separated by electronically conducting spacers or connecting groups. Our recent interest in incorporating redox-active organometallic species into polymer materials (Dana et al., 2007; McAdam et al., 2008) prompted us to investigate the synthesis of alkyne-hexacarbonyl-dicobalt complexes with potential ATRP initiator functionality by the incorporation of one or more known initiator substrates, such as 2-halo-2-methyl propanoyl esters (Wang & Matyjaszewski, 1995; Laurent & Grayson, 2006), into the alkyne system. The structures of two such molecules with 2-bromo-2-methylpropanoate substituents are reported here.
2. Structural commentary

The molecular structures of (1) and (2) are illustrated in Figs. 1 and 2. Both compounds are classic alkyne dicobalt cluster systems incorporating the triple bonds of 4-hydroxybut-2-ynyl 2-bromo-2-methylpropanoate for (1) and but-2-yne-1,4-diyl bis(2-bromo-2-methylpropanoate) for (2) into the tetrahedral C₂Co₂ core of the alkyne dicobalt cluster unit. The coordination geometry around each cobalt atom is distorted octahedral. Each cobalt atom carries one pseudo-axial and two pseudo-equatorial carbonyl substituents. The C2 and C3 atoms of the alkyne ligand for (1) and the corresponding C1 and C2 atoms for (2) are also pseudo-equatorial, with the bonds to the second Co atoms completing the highly distorted coordination spheres in pseudo-axial sites.

This combination of coordination spheres results in classical ‘sawhorse’ structures (Arewgoda et al., 1983) for each molecule. The CH₂OH and 2-bromo-2-ethylpropanoate substituents for (1) and the two 2-bromo-2-ethylpropanoate groups for (2), adopt a cis-bent configuration similar to the excited state of an alkyne system (Dickson & Fraser, 1974). Furthermore, the C11—Co1—Co2—C21 and C1—C2—C3—C4 planes for (1) and C15—Co1—Co2—C18 and C3—C2—C1—C8 planes for (2) are close to orthogonal with interplanar angles of 89.65 (7)° and 85.91 (7)°, respectively. The Co1—Co2 bond lengths are 2.4723 (7) Å for (1) and 2.4759 (10) Å for (2) with corresponding C2—C3 and C1—C2 distances of 1.344 (5) and 1.343 (3) Å (Tables 1 and 2). These are not unusual in comparison to those found for the 480 C₂Co₂ alkyne dicobalt clusters with 6 CO ligands found in the Cambridge Structural Database (Allen, 2002). For these, the mean Co—Co and C—C distances are found to be 2.47 (1) and 1.337 (15) Å, respectively. The eight Co—C alkyne distances average 1.958 (7) Å, again comparable to the mean value of 1.965 (5) Å found previously.

The C=O groups of the 2-bromo-2-methylpropanoate units point away from the cluster cores in both molecules. The two carbonyl groups in (2) each lie on the same side of the molecule, with the 2-bromo-2-methylpropanoate units arranged symmetrically with respect to the central C₂Co₂ unit.

Bond lengths (Allen et al., 1987) and angles in the –OC(O)–C(CH₃)₂Br chains are not unusual and are similar in both molecules.

3. Supramolecular features

In the crystal structure of (1), classical O1—H1···O3 hydrogen bonds (Table 3) are augmented by two C—H···O contacts that link adjacent molecules into inversion dimers generating R₂(10), R₂(18) and R₂(20) rings (Bernstein et al., 1995). Two additional inversion dimers also result from weaker C1—H1A···O1 and C8—H8A···O12 hydrogen bonds.
These contacts, together with weak O2⋯O21, [2.965 (4) Å; symmetry operation 1 + x, y, z] and Br1⋯O1 [3.307 (3) Å; symmetry operation −x, 1 − y, 2 − z] contacts stack the molecules into interconnected columns along the b-axis direction (Fig. 4).

Hydrogen bonding also figures prominently in the structure of (2), although in this molecule no classical hydrogen bonds are possible. Bifurcated C3⋯H3⋯O2 and C8⋯H8⋯O2 contacts (Table 4) produce \( R_1(7) \) rings while inversion-related C8⋯H8⋯O4 hydrogen bonds form \( R_2^2(10) \) rings (Fig. 5). The other significant contacts involve C⋯H⋯Br hydrogen bonds. C12⋯H12⋯Br1 contacts link molecules into \( C_2^2(14) \) chains approximately parallel to [110] while C6⋯H6⋯Br2 contacts, bolstered by short O1⋯Br2 contacts [3.296 (2) Å, symmetry operation \( x, −1 + y, z \)], form \( C_2^2(12) \) chains parallel to [010] (Fig. 6). The net result of these contacts is a series of interconnected columns of molecules stacked along the b-axis direction (Fig. 7).

### Table 3

| D—H ⋅⋅⋅A | D—H | H ⋅⋅⋅A | D ⋅⋅⋅A | D—H ⋅⋅⋅A |
|-----------|------|--------|--------|----------|
| O1⋯H1⋯O3 | 0.84 | 2.16   | 2.946  | 156      |
| C4⋯H4B⋯O3b | 0.99 | 2.60   | 3.360  | 134      |
| C7⋯H7A⋯O1i | 0.98 | 2.71   | 3.637  | 157      |
| C1⋯H1A⋯O1vi | 0.99 | 2.55   | 3.307  | 133      |
| C8⋯H8A⋯O12vi | 0.98 | 2.71   | 3.485  | 136      |

Symmetry codes: (i) \( −x, −y + 1, −z + 2 \); (ii) \( −x, −y + 2, −z + 2 \); (iii) \( −x + 1, −y + 1, −z + 1 \).

### Table 4

| D—H ⋅⋅⋅A | D—H | H ⋅⋅⋅A | D ⋅⋅⋅A | D—H ⋅⋅⋅A |
|-----------|------|--------|--------|----------|
| C12⋯H12C⋯Br1i | 0.98 | 2.99   | 3.961  | 170      |
| C6⋯H6A⋯Br2ii | 0.98 | 3.01   | 3.788  | 137      |
| C8⋯H8B⋯O4iv | 0.99 | 2.45   | 3.411  | 165      |
| C3⋯H3B⋯O2vii | 0.99 | 2.58   | 3.341  | 133      |
| C8⋯H8A⋯O2vii | 0.99 | 2.64   | 3.454  | 139      |

Symmetry codes: (i) \( x, y, z \); (ii) \( x, y + 1, z \); (iii) \( −x + 1, −y, −z + 1 \); (iv) \( −x + 1, −y + 1, −z + 1 \).

(3.296 (2) Å, symmetry operation \( x, −1 + y, z \), form \( C_2^2(12) \) chains parallel to [010] (Fig. 6). The net result of these contacts is a series of interconnected columns of molecules stacked along the b-axis direction (Fig. 7).
4. Database survey

The first structure, of dicobalt hexacarbonyl diphenylacetyl-
ene, was reported using film data (Sly, 1959). The current database
(Version 5.35, November 2013 with 1 update) details 480 hexacarbonyl structures. However, this number rises to 730 if the search is extended to cover dicobalt alkyne compounds in which one or more carbonyl group has been substituted, mainly by phosphine ligands. Interestingly there are no current examples of similar 4-hydroxybut-2-ynyl substituent, mainly by phosphine ligands. Interestingly there are no current examples of similar 4-hydroxybut-2-ynyl dicobalt; Soleilhavoup et al., 2002 among this plethora of structures, underlining the novelty of the compounds reported here.

5. Synthesis and crystallization

In typical preparations, 1:1 molar quantities of 4-hydroxybut-2-ynyl 2-bromo-2-methylpropanoate for (1) or a 2:1 molar ratio of but-2-ynyl-1,4-diyli bis(2-bromo-2-methylpropanoate) for (2) with Co2(CO)8 were allowed to react at room temperature for 1 h in CH2Cl2 under nitrogen. The reaction mixtures were filtered through silica gel to remove any insoluble impurities and the filtrates taken to dryness in vacuo. The complexes were then purified by recrystallization from hexane at 273 K. Yields were in the range 70–80%. Complexation was confirmed by the absence of a band at 1860 cm−1 in the infrared spectrum, attributable to the μ2 (bridging) carbonyl groups of the dicobalt octacarbonyl starting material. In addition, a hypsochromic shift of approximately 30 cm−1 of the remaining carbonyl stretching frequencies is seen, due to the decrease in electron density at the metal atoms upon coordination of these alkynes. Characteristic IR spectra were recorded for both products as follows: IR (ν, cm−1): (1): 3300 (broad, OH), ν(C≡O) 2099, 2062, 2032, ν(C≡O) 1735; (2): ν(C≡O) 2096, 2058, 2031, ν(C≡O) 1734.

6. Refinement

All H atoms bound to carbon were refined using a riding model with d(C–H) = 0.99 Å, Uiso = 1.2Ueq (C) for CH2, 0.98 Å, Uiso = 1.5Ueq (C) for CH3 atoms. In the final refinement, two reflections from the data for (2) with Fo << Fc were omitted from the refinement.

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Crystal structures of \( (\mu_2-\eta^2,\eta^2-4\text{-hydroxybut-2-yn-1-yl} \ 2\text{-bromo-2-methylpropanoate-}\kappa^4C^2,C^3:C^2,C^3)\)bis[tricarbonylcobalt(II)](Co—Co) and \( (\mu_2-\eta^2,\eta^2\text{-but-2-yn-1,4-diyl} \ 2\text{-bromo-2-methylpropanoate-}\kappa^4C^2,C^3:C^2,C^3)\)bis[tricarbonylcobalt(II)](Co—Co)

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Computing details

For both compounds, data collection: APEX2 (Bruker, 2011); cell refinement: APEX2 and SAINT (Bruker, 2011); data reduction: SAINT (Bruker, 2011); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL2013 (Sheldrick, 2008) and TITAN2000 (Hunter & Simpson, 1999); molecular graphics: Mercury (Macrae et al., 2008); software used to prepare material for publication: SHELXL2013 (Sheldrick, 2008), enCIFer (Allen et al., 2004), PLATON (Spek, 2009) and publCIF (Westrip, 2010).

Crystal data

\[ [\text{Co}_2(\text{C}_8\text{H}_{11}\text{BrO}_3)(\text{CO})_6] \]

\[ M_r = 521.00 \]

Triclinic, \( P\bar{1} \)

\( a = 7.3887 \) (8) Å

\( b = 11.1147 \) (12) Å

\( c = 11.7274 \) (13) Å

\( \alpha = 78.583 \) (6)°

\( \beta = 85.239 \) (6)°

\( \gamma = 76.342 \) (6)°

\( V = 916.67 \) (18) Å³

\( Z = 2 \)

\( F(000) = 512 \)

\( D_x = 1.888 \) Mg m⁻³

Mo Kα radiation, \( \lambda = 0.71073 \) Å

Cell parameters from 3089 reflections

\( \theta = 4.7–51.2^\circ \)

\( \mu = 4.03 \) mm⁻¹

\( T = 91 \) K

Irregular fragment, orange-red

0.39 × 0.16 × 0.04 mm

Data collection

Bruker APEXII CCD area-detector diffractometer

11686 measured reflections

3713 independent reflections

2966 reflections with \( I > 2\sigma(I) \)

\( \bar{R}_{	ext{free}} = 0.055 \)

\( \theta_{\text{max}} = 26.5^\circ, \theta_{\text{min}} = 3.3^\circ \)

\( h = -8 \rightarrow 9 \)

\( k = -13 \rightarrow 13 \)

\( l = -14 \rightarrow 14 \)

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Refinement

Refinement on \( F^2 \)
Least-squares matrix: full
\( R[F^2 > 2\sigma(F^2)] = 0.038 \)
\( wR(F^2) = 0.097 \)
\( S = 1.03 \)
3713 reflections
238 parameters
0 restraints

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
\( w = 1/[\sigma(Fo^2) + (0.0486P)^2] \)
where \( P = (Fo^2 + 2Fc^2)/3 \)

\( (\Delta/\sigma)_{\text{max}} = 0.001 \)
\( \Delta \rho_{\text{max}} = 0.83 \text{ e Å}^{-3} \)
\( \Delta \rho_{\text{min}} = -0.73 \text{ e Å}^{-3} \)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\( \text{Å}^2 \))

|    | x      | y      | z      | \( U_{eq} \) |
|----|--------|--------|--------|-------------|
| O1 | -0.0205 (4) | 0.8525 (2) | 1.0602 (2) | 0.0210 (6) |
| H1 | -0.0387 | 0.7844 | 1.1000 | 0.032 (8) |
| C1 | -0.1326 (5) | 0.8873 (4) | 0.9601 (3) | 0.0159 (8) |
| H1A | -0.1616 | 0.9800 | 0.9357 | 0.019 (9) |
| H1B | -0.2517 | 0.8605 | 0.9803 | 0.019 (9) |
| C2 | -0.0346 (4) | 0.8277 (3) | 0.8618 (3) | 0.0137 (7) |
| C3 | 0.0896 (4) | 0.7232 (3) | 0.8429 (3) | 0.0135 (7) |
| C4 | 0.1996 (5) | 0.6065 (3) | 0.9107 (3) | 0.0131 (7) |
| H4A | 0.2813 | 0.6282 | 0.9626 | 0.016 (9) |
| H4B | 0.1144 | 0.5594 | 0.9600 | 0.016 (9) |
| C5 | 0.3132 (3) | 0.5272 (2) | 0.8345 (2) | 0.0160 (5) |
| C6 | 0.2596 (5) | 0.4240 (3) | 0.8234 (3) | 0.0147 (8) |
| O3 | 0.1198 (4) | 0.3939 (2) | 0.8680 (2) | 0.0220 (6) |
| C7 | 0.3981 (5) | 0.3471 (3) | 0.7453 (3) | 0.0185 (8) |
| C8 | 0.3045 (6) | 0.2640 (4) | 0.6933 (3) | 0.0254 (9) |
| H7A | 0.2510 | 0.2089 | 0.7560 | 0.038 (9) |
| H7B | 0.3967 | 0.2127 | 0.6472 | 0.038 (9) |
| H7C | 0.2052 | 0.3169 | 0.6431 | 0.038 (9) |
| C9 | 0.5019 (6) | 0.4259 (4) | 0.6532 (3) | 0.0274 (9) |
| H8A | 0.4520 | 0.3703 | 0.6903 | 0.041 (10) |
| H8B | 0.5676 | 0.4733 | 0.6910 | 0.041 (10) |
| H8C | 0.4126 | 0.4847 | 0.5995 | 0.041 (10) |
| Br1 | 0.58507 (6) | 0.23943 (4) | 0.85597 (4) | 0.02956 (14) |
| Co1 | 0.14649 (6) | 0.86999 (5) | 0.73644 (4) | 0.01350 (13) |
| C11 | 0.3041 (5) | 0.9142 (3) | 0.8218 (3) | 0.0153 (8) |
| O11 | 0.4032 (3) | 0.9404 (3) | 0.8748 (2) | 0.0216 (6) |
| C12 | 0.3119 (5) | 0.7980 (4) | 0.6321 (3) | 0.0188 (8) |
| O12 | 0.4169 (4) | 0.7477 (3) | 0.5703 (2) | 0.0299 (7) |
| C13 | 0.0360 (5) | 1.0278 (4) | 0.6608 (3) | 0.0235 (9) |
| O13 | -0.0335 (4) | 1.1244 (3) | 0.6144 (3) | 0.0358 (8) |
### Geometric parameters (Å, °)

| Bond          | Length (Å) | Angle (°) |
|---------------|------------|-----------|
| O1—C1         | 1.430 (4)  |           |
| O1—H1         | 0.840      |           |
| C1—C2         | 1.493 (5)  | 120.8     |
| C1—H1A        | 0.990      |           |
| C1—H1B        | 0.990      |           |
| C2—C3         | 1.344 (5)  | 109.5     |
| Co1—Co2       | 2.4723 (7) |           |
| Co1—C11       | 1.805 (4)  |           |
| Co1—C12       | 1.819 (4)  |           |

### Atomic displacement parameters (Å²)

| Atom | U₁₁   | U₂₂   | U₃₃   | U₁₂   | U₁₃   | U₂₃   |
|------|-------|-------|-------|-------|-------|-------|
| O1   | 0.0248 (14) | 0.0207 (15) | 0.0180 (14) | -0.0051 (12) | -0.0019 (11) | -0.0039 (11) |
| C1   | 0.0151 (17)  | 0.0157 (19)  | 0.0168 (19)  | -0.0025 (15)  | 0.0022 (14)  | -0.0049 (15)  |
| C2   | 0.0112 (17)  | 0.0148 (19)  | 0.0147 (18)  | -0.0052 (14)  | 0.0024 (13)  | -0.0003 (15)  |
| C3   | 0.0014 (16)  | 0.0169 (19)  | 0.0132 (18)  | -0.0063 (14)  | 0.0017 (13)  | -0.0020 (15)  |
| C4   | 0.0151 (17)  | 0.0108 (18)  | 0.0135 (18)  | -0.0024 (14)  | 0.0019 (14)  | -0.0040 (14)  |
| O2   | 0.0163 (12)  | 0.0133 (13)  | 0.0174 (13)  | -0.0020 (10)  | 0.0043 (10)  | -0.0041 (11)  |
| C5   | 0.0173 (18)  | 0.0119 (18)  | 0.0126 (18)  | -0.0001 (14)  | -0.0014 (14) | -0.0002 (14)  |
| O3   | 0.0244 (14)  | 0.0199 (15)  | 0.0229 (15)  | -0.0087 (12)  | 0.0082 (11)  | -0.0059 (12)  |
| C6   | 0.0210 (19)  | 0.0128 (19)  | 0.0185 (19)  | 0.0021 (15)   | -0.0010 (15) | -0.0025 (16)  |
| C7   | 0.030 (2)    | 0.025 (2)    | 0.023 (2)    | -0.0080 (18)  | 0.0048 (17)  | -0.0107 (18)  |
| C8   | 0.036 (2)    | 0.023 (2)    | 0.020 (2)    | -0.0042 (18)  | 0.0098 (18)  | -0.0042 (18)  |
| Br1  | 0.0302 (2)   | 0.0259 (2)   | 0.0255 (2)   | 0.00937 (17)  | -0.00436 (17) | -0.00550 (18) |
| Co1  | 0.0140 (2)   | 0.0128 (3)   | 0.0133 (3)   | -0.00413 (19) | 0.00139 (18) | -0.0009 (2)   |
| O11  | 0.0146 (17)  | 0.0111 (18)  | 0.0171 (19)  | 0.0004 (14)   | 0.0047 (15)  | -0.0014 (15)  |
| O11  | 0.0190 (13)  | 0.0231 (15)  | 0.0241 (15)  | -0.0054 (11)  | -0.0014 (11) | -0.0065 (12)  |
| C12  | 0.023 (2)    | 0.019 (2)    | 0.0168 (19)  | -0.0116 (16)  | 0.0023 (16)  | -0.0030 (16)  |
| O12  | 0.0360 (17)  | 0.0303 (17)  | 0.0251 (16)  | -0.0105 (14)  | 0.0129 (13)  | -0.0111 (14)  |
| C13  | 0.024 (2)    | 0.027 (2)    | 0.024 (2)    | -0.0126 (18)  | -0.0019 (17) | -0.0033 (18)  |
| O13  | 0.0362 (17)  | 0.0196 (17)  | 0.046 (2)    | -0.0045 (14)  | -0.0146 (15) | 0.0100 (15)   |
| Co2  | 0.0140 (2)   | 0.0139 (3)   | 0.0161 (3)   | -0.00375 (19) | -0.00161 (19) | -0.0012 (2)   |
| C21  | 0.0197 (19)  | 0.023 (2)    | 0.021 (2)    | -0.0035 (17)  | -0.0066 (16) | -0.0010 (17)  |
| O21  | 0.0254 (15)  | 0.0375 (19)  | 0.0351 (18)  | -0.0164 (14)  | -0.0022 (13) | 0.0050 (15)   |
| C22  | 0.0204 (19)  | 0.020 (2)    | 0.025 (2)    | -0.0062 (16)  | -0.0066 (16) | -0.0017 (18)  |
| O22  | 0.0389 (18)  | 0.0333 (18)  | 0.0346 (18)  | -0.0058 (14)  | -0.0004 (14) | -0.0193 (15)  |
| C23  | 0.0174 (19)  | 0.025 (2)    | 0.025 (2)    | -0.0101 (17)  | 0.0015 (16)  | -0.0041 (18)  |
| O23  | 0.0240 (15)  | 0.0204 (16)  | 0.0382 (18)  | -0.0019 (13)  | -0.0105 (13) | 0.0068 (13)   |

### Supporting information

Co2 −0.11056 (6) 0.76340 (5) 0.73243 (4) 0.01475 (14)
C21 −0.2640 (5) 0.6741 (4) 0.8176 (3) 0.0216 (9)
O21 −0.3575 (4) 0.6190 (3) 0.8772 (3) 0.0327 (7)
C22 −0.0153 (5) 0.6651 (4) 0.6246 (3) 0.0216 (9)
O22 0.0493 (4) 0.6009 (3) 0.5607 (3) 0.0342 (7)
C23 −0.2750 (5) 0.8974 (4) 0.6540 (3) 0.0216 (8)
O23 −0.3745 (4) 0.9823 (3) 0.6055 (2) 0.0293 (7)
| Distance (Å) | Standard Deviation (Å) |
|-------------|------------------------|
| C2—Co2      | 1.972 (3)              |
| C3—C4       | 1.476 (5)              |
| C3—Co1      | 1.956 (4)              |
| C3—Co2      | 1.960 (3)              |
| C4—O2       | 1.455 (4)              |
| C4—H4A      | 0.9900                 |
| C4—H4B      | 0.9900                 |
| O2—C5       | 1.331 (4)              |
| C5—O3       | 1.207 (4)              |
| C5—C6       | 1.535 (5)              |
| C6—C7       | 1.516 (5)              |
| C6—C8       | 1.526 (5)              |
| C6—Br1      | 1.981 (3)              |
| C1—O1—H1    | 109.5                  |
| O1—C1—C2    | 111.1 (3)              |
| O1—C1—H1A   | 109.4                  |
| C2—C1—H1A   | 109.4                  |
| O1—C1—H1B   | 109.4                  |
| C2—C1—H1B   | 109.4                  |
| H1A—C1—H1B  | 108.0                  |
| C3—C2—C1    | 140.2 (3)              |
| C3—C2—Co1   | 69.5 (2)               |
| C1—C2—Co1   | 135.5 (3)              |
| C3—C2—Co2   | 69.5 (2)               |
| C1—C2—Co2   | 135.7 (2)              |
| Co1—C2—Co2  | 77.75 (13)             |
| C2—C3—C4    | 138.8 (3)              |
| C2—C3—Co1   | 70.4 (2)               |
| C4—C3—Co1   | 135.6 (2)              |
| C2—C3—Co2   | 70.5 (2)               |
| C4—C3—Co2   | 135.3 (3)              |
| Co1—C3—Co2  | 78.29 (13)             |
| O2—C4—C3    | 111.1 (3)              |
| O2—C4—H4A   | 109.4                  |
| C3—C4—H4A   | 109.4                  |
| O2—C4—H4B   | 109.4                  |
| H4A—C4—H4B  | 108.0                  |
| C5—O2—C4    | 117.6 (3)              |
| C5—O2—O21ii | 142.6 (2)              |
| C4—O2—O21ii | 89.70 (19)             |
| O3—C5—O2    | 124.9 (3)              |
| O3—C5—C6    | 123.7 (3)              |
| O2—C5—C6    | 111.4 (3)              |
| C7—C6—C8    | 112.2 (3)              |
| C7—C6—C5    | 110.8 (3)              |
| C8—C6—C5    | 114.1 (3)              |
### Crystal data

[C\(_{2}(C_{12}H_{16}Br_{2}O_{4})(CO)_{6}\)]

\( M_r = 669.99 \)

Triclinic, \( P\bar{1} \)

\( a = 9.392 (5) \) Å

\( b = 10.710 (5) \) Å

\( c = 13.269 (5) \) Å

\( \alpha = 71.314 (5) ^\circ \)

\( \beta = 71.973 (5) ^\circ \)

\( \gamma = 84.630 (5) ^\circ \)

\( V = 1202.3 (10) \) Å\(^3\)

\( Z = 2 \)

\( F(000) = 656 \)

\( D_r = 1.851 \) Mg m\(^{-3}\)

Mo K\(\alpha\) radiation, \( \lambda = 0.71069 \) Å

Cell parameters from 5837 reflections

\( \theta = 2.3–30.9 ^\circ \)

\( \mu = 4.75 \) mm\(^{-1}\)

\( T = 91 \) K

Rod, dark red

\( 0.25 \times 0.11 \times 0.06 \) mm

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### Hydrogen-bond geometry (Å, °)

| D—H···A   | D—H  | H···A | D···A  | D—H···A |
|-----------|-------|-------|--------|---------|
| O1—H1···O3\(iii\) | 0.84  | 2.16  | 2.946 (4) | 156     |
| C4—H4B···O3\(iii\) | 0.99  | 2.60  | 3.360 (4) | 134     |
| C7—H7A···O1\(iii\) | 0.98  | 2.71  | 3.637 (5) | 157     |
| C1—H14···O1\(iv\) | 0.99  | 2.55  | 3.307 (5) | 133     |
| C8—H8\&···O12\(v\) | 0.98  | 2.71  | 3.485 (5) | 136     |

Symmetry codes: (iii) \( x, y+1, z \); (iv) \( x, y+2, z \); (v) \( x+1, y, z+1 \).

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(2) \( [\mu_2-\eta^2,\eta^2-\text{But-2-yne-1,4-diyl\ bis(2-bromo-2-methylpropanoate)}-\kappa^4C_2,C:C^2,C^2] \)bis[tricarbonylcobalt(II)](Co—Co)

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### Crystal data

\[ \text{Co}_2(\text{C}_6\text{H}_4\text{Br}_2\text{O}_4)(\text{CO})_6] \]

\( M_r = 669.99 \)

Triclinic, \( P\bar{1} \)

\( a = 9.392 (5) \) Å

\( b = 10.710 (5) \) Å

\( c = 13.269 (5) \) Å

\( \alpha = 71.314 (5) ^\circ \)

\( \beta = 71.973 (5) ^\circ \)

\( \gamma = 84.630 (5) ^\circ \)

\( V = 1202.3 (10) \) Å\(^3\)

\( Z = 2 \)

\( F(000) = 656 \)

\( D_r = 1.851 \) Mg m\(^{-3}\)

Mo K\(\alpha\) radiation, \( \lambda = 0.71069 \) Å

Cell parameters from 5837 reflections

\( \theta = 2.3–30.9 ^\circ \)

\( \mu = 4.75 \) mm\(^{-1}\)

\( T = 91 \) K

Rod, dark red

\( 0.25 \times 0.11 \times 0.06 \) mm

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Acta Cryst. (2014). E70, 9-13
Data collection
Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2011)
T\text{min} = 0.611, T\text{max} = 1.000
21546 measured reflections

Refinement
Refinement on F^2
Least-squares matrix: full
R[F^2 > 2σ(F^2)] = 0.031
wR(F^2) = 0.069
S = 0.95
8127 reflections
293 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

Special details
Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

| x     | y     | z     | U_{iso}*/U_{eq} |
|-------|-------|-------|-----------------|
| Br1   | 0.75011 (2) | 0.49577 (2) | 0.81786 (2) | 0.02064 (5) |
| C7    | 0.6143 (2) | 0.74032 (18) | 0.72699 (17) | 0.0192 (4) |
| H7A   | 0.5332 | 0.7891 | 0.6996 | 0.029* |
| H7B   | 0.7079 | 0.7554 | 0.6657 | 0.029* |
| H7C   | 0.6260 | 0.7708 | 0.7862 | 0.029* |
| C6    | 0.4399 (2) | 0.56200 (19) | 0.87435 (16) | 0.0167 (4) |
| H6A   | 0.3511 | 0.6010 | 0.8526 | 0.025* |
| H6B   | 0.4533 | 0.5981 | 0.9300 | 0.025* |
| H6C   | 0.4270 | 0.4662 | 0.9061 | 0.025* |
| C5    | 0.5769 (2) | 0.59405 (18) | 0.77269 (16) | 0.0140 (4) |
| C4    | 0.5703 (2) | 0.54055 (17) | 0.68077 (16) | 0.0134 (4) |
| O2    | 0.63231 (16) | 0.58983 (13) | 0.58281 (11) | 0.0182 (3) |
| O1    | 0.48633 (15) | 0.43066 (12) | 0.72283 (11) | 0.0140 (3) |
| C3    | 0.4766 (2) | 0.36816 (18) | 0.64290 (15) | 0.0143 (4) |
| H3A   | 0.5769 | 0.3390 | 0.6063 | 0.017* |
| H3B   | 0.4373 | 0.4311 | 0.5848 | 0.017* |
| C2    | 0.3747 (2) | 0.25397 (17) | 0.70430 (15) | 0.0126 (4) |
| C1    | 0.3246 (2) | 0.15033 (18) | 0.68869 (15) | 0.0123 (4) |
| C8    | 0.3382 (2) | 0.09321 (18) | 0.59884 (16) | 0.0147 (4) |
| H8A   | 0.3121 | 0.1598 | 0.5358 | 0.018* |
| H8B   | 0.4424 | 0.0644 | 0.5715 | 0.018* |
| O3    | 0.23609 (15) | −0.01940 (12) | 0.64364 (11) | 0.0149 (3) |
### Atomic displacement parameters (Å$^2$)

| Atom | $U^{11}$  | $U^{22}$  | $U^{33}$  | $U^{23}$  | $U^{12}$  | $U^{13}$  |
|------|-----------|-----------|-----------|-----------|-----------|-----------|
| Br1  | 0.01709 (11) | 0.02490 (11) | 0.02151 (11) | -0.00005 (8) | -0.00881 (8) | -0.00622 (8) |
| C7   | 0.0267 (12) | 0.0152 (9) | 0.0180 (10) | -0.0055 (8) | -0.0077 (8) | -0.0054 (8) |
| C6   | 0.0178 (10) | 0.0187 (9) | 0.0128 (9) | -0.0030 (8) | -0.0027 (7) | -0.0047 (7) |
| C5   | 0.0169 (10) | 0.0136 (8) | 0.0136 (9) | -0.0020 (7) | -0.0076 (7) | -0.0034 (7) |
| C4   | 0.0150 (10) | 0.0116 (8) | 0.0143 (9) | -0.0023 (7) | -0.0058 (7) | -0.0031 (7) |
| O2   | 0.0226 (8) | 0.0179 (7) | 0.0127 (7) | -0.0087 (6) | -0.0023 (6) | -0.0031 (5) |
| O1   | 0.0181 (7) | 0.0130 (6) | 0.0118 (6) | -0.0078 (5) | -0.0031 (5) | -0.0041 (5) |
| C3   | 0.0191 (10) | 0.0138 (8) | 0.0114 (9) | -0.0060 (7) | -0.0036 (7) | -0.0051 (7) |
| C2   | 0.0122 (9) | 0.0124 (8) | 0.0128 (9) | -0.0011 (7) | -0.0033 (7) | -0.0035 (7) |
| C1   | 0.0105 (9) | 0.0135 (8) | 0.0124 (9) | -0.0008 (7) | -0.0026 (7) | -0.0038 (7) |
| C8   | 0.0146 (10) | 0.0147 (8) | 0.0136 (9) | -0.0066 (7) | -0.0006 (7) | -0.0043 (7) |
| O3   | 0.0168 (7) | 0.0145 (6) | 0.0134 (7) | -0.0068 (5) | -0.0011 (5) | -0.0056 (5) |
| C9   | 0.0129 (9) | 0.0141 (8) | 0.0190 (10) | 0.0017 (7) | -0.0070 (7) | -0.0077 (7) |
| O4   | 0.0279 (9) | 0.0270 (8) | 0.0163 (7) | -0.0110 (7) | -0.0035 (6) | -0.0086 (6) |
| C10  | 0.0140 (10) | 0.0123 (8) | 0.0207 (10) | 0.0002 (7) | -0.0067 (8) | -0.0059 (7) |
| C11  | 0.0216 (12) | 0.0227 (10) | 0.0312 (12) | -0.0052 (9) | -0.0156 (9) | -0.0059 (9) |
| C12  | 0.0267 (13) | 0.0314 (12) | 0.0347 (13) | -0.0165 (10) | 0.0075 (10) | -0.0190 (11) |
| Br2  | 0.03671 (15) | 0.01571 (10) | 0.05628 (17) | 0.00796 (9) | -0.03120 (13) | -0.01135 (10) |
Co1 0.01475 (14) 0.01102 (12) 0.01208 (12) −0.00128 (10) −0.00391 (10) −0.00241 (9)
C13 0.0217 (11) 0.0184 (10) 0.0198 (10) 0.0038 (8) −0.0049 (8) −0.0061 (8)
O13 0.0383 (10) 0.0140 (7) 0.0350 (9) −0.0047 (7) −0.0020 (8) −0.0037 (7)
C14 0.0262 (12) 0.0153 (9) 0.0186 (10) −0.0013 (8) −0.0096 (9) −0.0005 (8)
O14 0.0538 (12) 0.0281 (8) 0.0198 (8) 0.0015 (8) −0.0169 (8) −0.0103 (7)
C15 0.0238 (12) 0.0183 (9) 0.0152 (9) 0.0005 (8) −0.0089 (8) −0.0019 (8)
O15 0.0179 (9) 0.0433 (10) 0.0290 (9) 0.0048 (7) −0.0082 (7) −0.0100 (7)
Co2 0.01267 (13) 0.01312 (12) 0.01367 (13) −0.00069 (10) −0.00305 (10) −0.00523 (10)
C16 0.0151 (10) 0.0245 (10) 0.0152 (9) 0.0001 (8) −0.0015 (8) −0.0102 (8)
O16 0.0219 (9) 0.0329 (9) 0.0241 (8) −0.0118 (7) 0.0022 (7) −0.0117 (7)
C17 0.0194 (11) 0.0220 (10) 0.0252 (11) 0.0015 (8) −0.0068 (9) −0.0108 (9)
O17 0.0380 (11) 0.0400 (10) 0.0421 (11) 0.0063 (8) −0.0098 (8) −0.0299 (9)
C18 0.0180 (11) 0.0202 (10) 0.0251 (11) 0.0012 (8) −0.0053 (9) −0.0114 (8)
O18 0.0359 (10) 0.0342 (9) 0.0285 (9) 0.0105 (7) −0.0173 (8) −0.0102 (7)

Geometric parameters (Å, º)

| Bond/Distance | Length  | Angle  |
|---------------|---------|--------|
| Br1—C5        | 1.998 (2)| O3—C9  | 1.338 (2) |
| C7—C5        | 1.519 (3)| C9—O4  | 1.202 (2) |
| C7—H7A       | 0.9800  | C9—C10 | 1.528 (3) |
| C7—H7B       | 0.9800  | C10—C11| 1.513 (3) |
| C7—H7C       | 0.9800  | C10—C12| 1.513 (3) |
| C6—C5        | 1.518 (3)| C10—Br2| 1.983 (2) |
| C6—H6A       | 0.9800  | C11—H11A| 0.9800 |
| C6—H6B       | 0.9800  | C11—H11B| 0.9800 |
| C6—H6C       | 0.9800  | C11—H11C| 0.9800 |
| C5—C4        | 1.524 (3)| C12—H12A| 0.9800 |
| C4—O2        | 1.207 (2)| C12—H12B| 0.9800 |
| C4—O1        | 1.341 (2)| C12—H12C| 0.9800 |
| O1—C3        | 1.452 (2)| Co1—C15 | 1.803 (2) |
| C3—O1        | 1.474 (3)| Co1—C14 | 1.819 (2) |
| C3—H3A       | 0.9900  | Co1—C13 | 1.826 (2) |
| C3—H3B       | 0.9900  | C13—O13 | 1.135 (2) |
| C1—C2        | 1.343 (3)| C14—O14 | 1.136 (3) |
| Co1—Co2      | 2.4759 (10)| C15—O15 | 1.128 (3) |
| C1—Co1       | 1.960 (2)| Co2—C18 | 1.805 (2) |
| C1—Co2       | 1.949 (2)| Co2—C16 | 1.820 (2) |
| C2—Co1       | 1.9508 (19)| Co2—C17 | 1.835 (2) |
| C2—Co2       | 1.948 (2)| C16—O16 | 1.136 (2) |
| C1—C8        | 1.473 (3)| C17—O17 | 1.130 (3) |
| C8—O3        | 1.460 (2)| C18—O18 | 1.137 (3) |
| C8—H8A       | 0.9900  | O1—Br2i | 3.2960 (18) |
| C8—H8B       | 0.9900  |        |        |
| C5—C7—H7A    | 109.5   | C11—C10—C9| 110.93 (16)|
| C5—C7—H7B    | 109.5   | C12—C10—C9| 114.10 (17)|
| H7A—C7—H7B   | 109.5   | C11—C10—Br2| 106.58 (14)|
| C5—C7—H7C    | 109.5   | C12—C10—Br2| 107.91 (15)|
| Bond/Distance | Angle | Angle | Angle |
|---------------|-------|-------|-------|
| C9—C10—Br2   | 102.33(13) | 109.5 | 109.5 |
| C10—C11—H11A | 109.5 | 109.5 | 109.5 |
| C10—C11—H11B | 109.5 | 109.5 | 109.5 |
| C10—C11—H11C | 109.5 | 109.5 | 109.5 |
| H11A—C11—H11B | 109.5 | 109.5 | 109.5 |
| H11B—C11—H11C | 109.5 | 109.5 | 109.5 |
| C10—C12—H12A | 109.5 | 109.5 | 109.5 |
| H12A—C12—H12B | 109.5 | 109.5 | 109.5 |
| H12B—C12—H12C | 109.5 | 109.5 | 109.5 |
| C14—C15—Co1 | 97.61(10) | 97.61(10) | 97.61(10) |
| C14—C15—Co2 | 103.39(10) | 103.39(10) | 103.39(10) |
| C14—C15—Co3 | 106.12(9) | 106.12(9) | 106.12(9) |
| C14—C15—Co4 | 96.50(8) | 96.50(8) | 96.50(8) |
| C14—C15—Co5 | 102.92(9) | 102.92(9) | 102.92(9) |
| C14—C15—Co6 | 100.56(9) | 100.56(9) | 100.56(9) |
| C14—C15—Co7 | 102.92(9) | 102.92(9) | 102.92(9) |
| C14—C15—Co8 | 100.56(9) | 100.56(9) | 100.56(9) |
| C14—C15—Co9 | 102.92(9) | 102.92(9) | 102.92(9) |
| C14—C15—Co10 | 100.56(9) | 100.56(9) | 100.56(9) |
| C14—C15—Co11 | 102.92(9) | 102.92(9) | 102.92(9) |
| C14—C15—Co12 | 100.56(9) | 100.56(9) | 100.56(9) |
| C14—C15—Co13 | 102.92(9) | 102.92(9) | 102.92(9) |
| C14—C15—Co14 | 100.56(9) | 100.56(9) | 100.56(9) |
| C14—C15—Co15 | 102.92(9) | 102.92(9) | 102.92(9) |
| C14—C15—Co16 | 100.56(9) | 100.56(9) | 100.56(9) |
| C14—C15—Co17 | 102.92(9) | 102.92(9) | 102.92(9) |
| C14—C15—Co18 | 100.56(9) | 100.56(9) | 100.56(9) |
| C14—C15—Co19 | 102.92(9) | 102.92(9) | 102.92(9) |
| C14—C15—Co20 | 100.56(9) | 100.56(9) | 100.56(9) |
| C14—C15—Co21 | 102.92(9) | 102.92(9) | 102.92(9) |
| C14—C15—Co22 | 100.56(9) | 100.56(9) | 100.56(9) |
| C14—C15—Co23 | 102.92(9) | 102.92(9) | 102.92(9) |
| C14—C15—Co24 | 100.56(9) | 100.56(9) | 100.56(9) |
| C14—C15—Co25 | 102.92(9) | 102.92(9) | 102.92(9) |
| C14—C15—Co26 | 100.56(9) | 100.56(9) | 100.56(9) |
| C14—C15—Co27 | 102.92(9) | 102.92(9) | 102.92(9) |
| C14—C15—Co28 | 100.56(9) | 100.56(9) | 100.56(9) |
| C14—C15—Co29 | 102.92(9) | 102.92(9) | 102.92(9) |
| C14—C15—Co30 | 100.56(9) | 100.56(9) | 100.56(9) |
| C14—C15—Co31 | 102.92(9) | 102.92(9) | 102.92(9) |
| C14—C15—Co32 | 100.56(9) | 100.56(9) | 100.56(9) |
| C14—C15—Co33 | 102.92(9) | 102.92(9) | 102.92(9) |
| C14—C15—Co34 | 100.56(9) | 100.56(9) | 100.56(9) |
| C14—C15—Co35 | 102.92(9) | 102.92(9) | 102.92(9) |
| C14—C15—Co36 | 100.56(9) | 100.56(9) | 100.56(9) |

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C11—C10—C12  113.98 (19)  O18—C18—Co2  177.7 (2)
C6—C5—C4—O2  151.45 (19)  Co1—C2—C1—C8  −139.0 (3)
C7—C5—C4—O2  23.2 (3)  C3—C2—C1—Co2  −139.2 (3)
Br1—C5—C4—O2  −92.5 (2)  Co1—C2—C1—Co2  84.98 (6)
C6—C5—C4—O1  −28.7 (2)  C3—C2—C1—Co1  135.8 (3)
C7—C5—C4—O1  −156.98 (16)  Co2—C2—C1—Co1  −84.98 (6)
Br1—C5—C4—O1  87.39 (16)  C2—C1—C8—O3  −174.7 (2)
O2—C4—O1—C3  2.0 (3)  Co2—C1—C8—O3  −60.5 (2)
C5—C4—O1—C3  −177.82 (15)  C1—C8—O3—C9  172.04 (16)
O2—C4—O1—Br2i  −83.95 (19)  Co1—C1—C8—O3  −84.98 (6)
C5—C4—O1—Br2i  96.19 (14)  O3—C9—C10—Br2  86.7 (2)
O2—C4—O1—C3  −177.82 (15)  C8—O3—C10—Br2  −94.18 (16)
Symmetry code: (i) x, y+1, z.

Hydrogen-bond geometry (Å, °)

| D—H···A     | D—H | H···A | D···A  | D—H···A |
|-------------|------|-------|--------|---------|
| C12—H12C···Br1ii | 0.98 | 2.99 | 3.961 (3) | 170 |
| C6—H6.4···Br2i  | 0.98 | 3.01 | 3.788 (2) | 137 |
| C8—H8B···O4iii | 0.99 | 2.45 | 3.411 (3) | 165 |
| C3—H3B···O2iv  | 0.99 | 2.58 | 3.341 (3) | 133 |
| C8—H8A···O2iv  | 0.99 | 2.64 | 3.454 (3) | 139 |

Symmetry codes: (i) x, y+1, z; (ii) x-1, y-1, z; (iii) -x+1, -y, -z+1; (iv) -x+1, -y+1, -z+1.