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# Synthesis of thio and mixed donor atom macrocycles containing coordinated diyne units

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The acid-catalysed reaction of the diyne complex $[\{Co_2(CO)_6\}_2(\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-}HOCH_2C_2C_2CH_2OH)]$ with a range of dithiols leads in each case to the formation of at least two cyclic products, a monomeric product $[\{Co_2(CO)_6\}_2(\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-}SCH_2C_2C{\equiv}CCH_2SR)]$ and a dimeric product $[\{Co_2(CO)_6\}_2(\mu\text{:}\eta^2\text{:}\mu\text{:}\eta^2\text{-}SCH_2C_2C_2CH_2SR)]_2$, [R = $(CH_2)_n$ ($n$ = 3–6)]. This method may also be applied to dithiols that contain additional donor atoms such as S or O to give crown type macrocycles. The crystal structures of several of the above new complexes are reported.

## Introduction

The synthesis and properties of thio-macrocycles has attracted a good deal of attention.[1–3] These compounds may be suitable for a diverse range of applications, from molecular sensors to bio-inorganic hosts.[4–10] This field has now been extended to include the synthesis of macrocycles that contain mixed-donor functionalities.[11–14] Macrocycles of this type, especially those containing both hard and soft donor atoms, are of immense interest since they can potentially bind two metals of differing character and oxidation state within the same cavity.[15] With the development of this relatively young field in mind we have devised a simple methodology for the synthesis of macrocycles that contain other donor functionalities in addition to sulfur atoms.[16] This method, which builds on the work of Went and Gruselle, is based on the acid-catalysed Nicholas reaction of bis-propargyl alcohols with dithio-ethers and dithiols and leads to the formation of macrocycles containing diyne, sulfur and oxygen donor atoms.[17,18]

## Results and discussion

### Reaction with dithiols

Reaction of $[\{Co_2(CO)_6\}_2(\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-}HOCH_2C_2C_2CH_2OH)]$ **1** with one equivalent of a range of dithiols, $HS(CH_2)_nSH$ ($n$ = 3–6), in the presence of $HBF_4{\cdot}OEt_2$ affords, after separation by column chromatography, the brown monomeric complexes $[\{Co_2(CO)_6\}_2\{\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-}SCH_2C_2C_2CH_2S(CH_2)_{n-1}CH_2\}]$ **2** ($n$ = 3); **3** ($n$ = 4); **4** ($n$ = 5); **5** ($n$ = 6), and the dark brown dimeric complexes $[\{Co_2(CO)_6\}_2\{\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-}SCH_2C_2C_2CH_2S(CH_2)_n\}]_2$ **6** ($n$ = 3); **7** ($n$ = 4); **8** ($n$ = 5); **9** ($n$ = 6), in virtually quantitative combined yield (Fig. 1).

The ratio of the monomeric product to the dimeric product is dependent on the length of the aliphatic chain of the dithiol, with monomer formation being slightly favoured by longer aliphatic chains. In the case of shorter linkers ($n$ = 3, 4) there is a marked preference for the dimer, this being present in a 2 : 1 ratio.

Presumably this product distribution stems from the fact that in the case of short linkers, the transition state required to effect monomeric ring closure is disfavoured due to its being strained, as is the monomeric product itself. Unfortunately, it was not possible to crystallise any monomeric compounds; this would have allowed comparison of the $C{\equiv}C\text{–}CH_2$ bend-back angles in the monomers with those in the dimers. This bend-back angle is a useful indicator of the amount of strain present in diyne containing macrocycles.[19]

The high degree of symmetry present in compounds **2**–**9** as well as the quadrupole broadening due to the $^{59}Co$ mean that the IR and NMR data for each monomer and its respective dimer are virtually indistinguishable, although naturally the two species are readily distinguishable by their mass spectra.

In order to identify unambiguously the new complexes the structure of one such complex, **7**, was determined by a single crystal X-ray diffraction study. Selected structural parameters are listed in Table 1 and the molecular structure is presented in Fig. 2.

The structure confirms that the molecule is comprised of four $Co_2(CO)_6$ units bridged by a 1,5,12,17-tetrathiacyclotetracosa-7-9-18-20-yne. Within the $Co_2C_2$ tetrahedral cores there are no unusual structural features, with all bond lengths and angles falling in the expected ranges.[20] The four sulfur atoms lie in a plane such that their lone pairs lie in the expected exo configuration.[21] An approximation of the cavity size can be made by studying the non-bonding sulfur–sulfur separations [S(1)–S(2) 5.074, S(1)–S(1A) 10.157, S(1A)–S(2) 7.099 Å]; these may be compared to the non-bonding S–S separation of 5.536 Å for a similar alkyne-containing thio-macrocycle reported by Went.[17]

In order to further these investigations it was decided to explore the effect of changing the linker group of the dithiol to a more rigid aryl system. Accordingly, the reaction of **1** with $1,3\text{-}C_6H_4(SH)_2$ was studied and this yielded, after separation by preparative TLC, monomeric $[\{Co_2(CO)_6\}_2(\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-}SCH_2C_2C_2CH_2S\text{-}1,3\text{-}C_6H_4)]$ **10** in 80% yield and dimeric $[\{Co_2(CO)_6\}_2(\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-}SCH_2C_2C_2CH_2S\text{-}1,3\text{-}C_6H_4)]_2$ **11** in 15% yield. The analogous reaction with $1,2\text{-}C_6H_4(SH)_2$ yields brown, monomeric $[\{Co_2(CO)_6\}_2(\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-}SCH_2C_2C_2CH_2S\text{-}1,2\text{-}C_6H_4)]$ **12** as the sole isolable product in 86% yield (Fig. 3).

Presumably the rigidity of these benzenedithiols holds the intermediate, which stems from addition of one thiol unit to the propargylium ion, in such a geometry that monomeric ring closure may proceed rapidly, explaining the high yields of the monomers.

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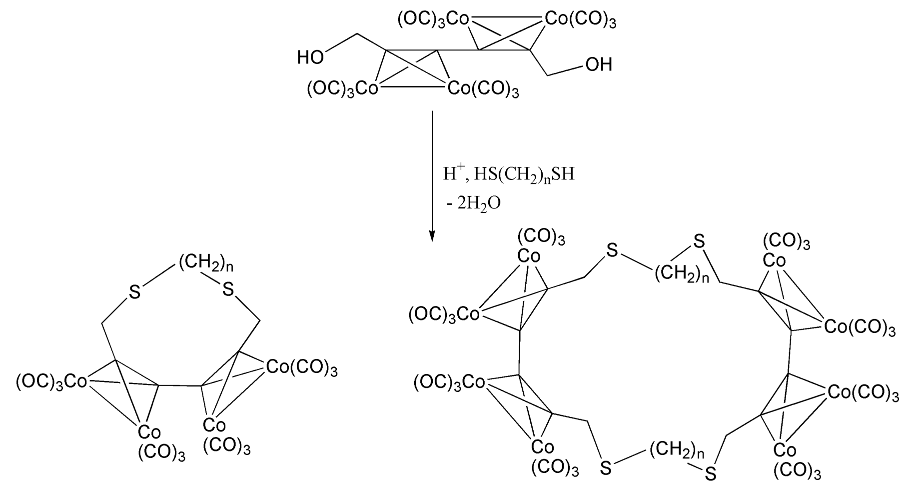
**Table 1** Selected bond lengths (Å) and angles (°) for **7**

| | | | | | |
|---|---|---|---|---|---|
| Co(1)–Co(3) | 2.4766(5) | Co(2)–Co(4) | 2.469(1) | C(25)–C(26) | 1.518(7) |
| Co(1)–C(23) | 1.951(5) | Co(4)–C(20) | 1.954(5) | C(26)–C(27) | 1.521(7) |
| Co(1)–C(22) | 1.981(4) | Co(4)–C(21) | 1.977(5) | C(29)–C(20a) | 1.482(7) |
| Co(3)–C(23) | 1.948(5) | C(20)–C(21) | 1.353(7) | S(1)–C(29) | 1.806(5) |
| Co(3)–C(22) | 1.963(5) | C(20)–C(29a) | 1.482(7) | S(1)–C(28) | 1.825(6) |
| Co(2)–C(20) | 1.946(5) | C(22)–C(23) | 1.354(7) | S(2)–C(25) | 1.802(6) |
| Co(2)–C(21) | 1.973(5) | C(23)–C(24) | 1.494(7) | S(2)–C(24) | 1.818(5) |
| C(22)–Co(1)–Co(3) | 50.92(14) | Co(2)–C(21)–Co(4) | 77.35(2) | C(27)–C(28)–S(1) | 114.9(4) |
| C(29)–S(1)–C(28) | 99.7(2) | C(23)–C(22)–C(21) | 141.8(5) | C(20)–Co(2)–C(21) | 40.4(2) |
| C(23)–Co(3)–C(22) | 40.50(19) | C(21)–C(22)–Co(3) | 136.8(4) | C(20)–Co(2)–Co(4) | 50.88(1) |
| C(23)–Co(3)–Co(1) | 50.74(14) | C(21)–C(22)–Co(1) | 133.7(4) | C(21)–Co(2)–Co(4) | 51.41(1) |
| C(22)–Co(3)–Co(1) | 51.55(13) | C(22)–C(23)–C(24) | 139.5(5) | C(25)–S(2)–C(24) | 100.7(3) |
| C(29a)–C(20)–Co(4) | 135.5(4) | C(24)–C(23)–Co(3) | 136.6(4) | C(12)–Co(4)–C(21) | 143.9(2) |
| C(20)–C(21)–Co(2) | 68.7(3) | C(24)–C(23)–Co(1) | 133.2(3) | C(20)–Co(4)–C(21) | 40.3(2) |
| C(22)–C(21)–Co(2) | 136.2(4) | C(23)–C(24)–S(2) | 112.2(4) | C(20)–Co(4)–Co(2) | 50.58(2) |
| C(21)–Co(4)–Co(2) | 51.24(14) | C(20)–C(21)–C(22) | 141.1(4) | C(23)–C(22)–Co(1) | 68.7(3) |
| C(21)–C(20)–C(29a) | 136.6(4) | C(20)–C(21)–Co(4) | 68.9(3) | Co(3)–C(22)–Co(1) | 77.53(2) |
| C(21)–C(20)–Co(2) | 70.9(3) | C(22)–C(21)–Co(4) | 135.2(4) | C(22)–C(23)–Co(3) | 70.3(3) |
| C(29a)–C(20)–Co(2) | 136.7(4) | C(23)–C(22)–Co(3) | 69.2(3) | C(22)–C(23)–Co(1) | 71.1(3) |
| Co(3)–C(23)–Co(1) | 78.60(18) | C(26)–C(25)–S(2) | 114.3(4) | C(20a)–C(29)–S(1) | 112.0(3) |



**2** n = 3
**3** n = 4
**4** n = 5
**5** n = 6

**6** n = 3
**7** n = 4
**8** n = 5
**9** n = 6

**Fig. 1** Reaction of [{$Co_2(CO)_6$}$_2$(μ-η$^2$:μ-η$^2$-$HOCH_2C_2C_2CH_2OH$)] with aliphatic dithiols.

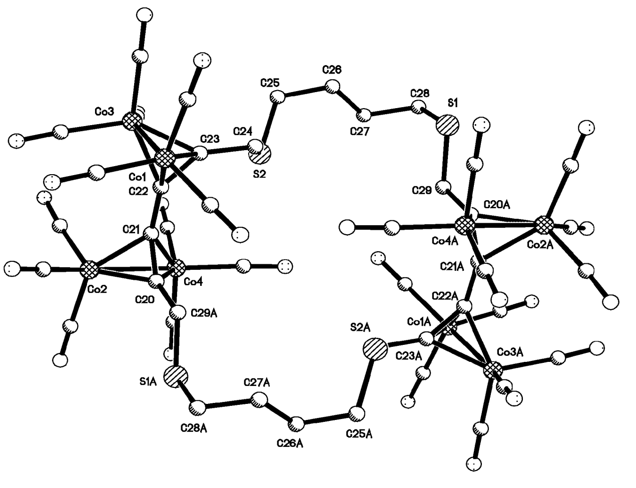


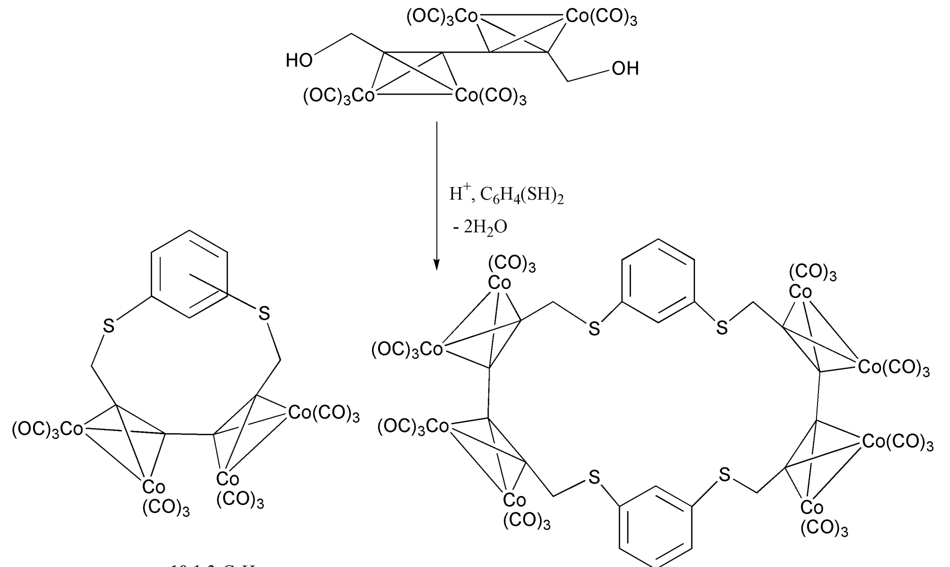
**Fig. 2** Molecular structure of [{$Co_2(CO)_6$}$_2$\{μ-η$^2$:μ-η$^2$-$SCH_2C_2C_2CH_2S(CH_2)_4$\}]$_2$ **7**.

The structures of **10** to **12** have been unambiguously confirmed by a single crystal X-ray diffraction study (Figs. 4 and 5). Relevant bond lengths and angles are given in Tables 2 to 4.

Complex **10** crystallises with two discrete independent molecules within its asymmetric unit. The bond lengths and angles of these two molecules are, for the most part, identical within experimental error. The only significant difference in bond lengths between the two molecules is the Co–Co bond lengths [Co(1)–Co(2) 2.4742(5), Co(1′)–Co(2′) 2.4571(6); Co(3)–Co(4) 2.4521(6), Co(3′)–Co(4′) 2.4560(5) Å]. The alkynic C–C separations [C(14)–C(15) 1.352(4), C(16)–C(17) 1.351(4), C(14′)–C(15′) 1.356(4), C(16′)–C(17′) 1.349(4) Å] are closely comparable and all within the expected range of 1.33–1.36 Å. The S(1)–C(19)–C(20)–C(21)–S(2) moiety, as might be expected, lies virtually within a plane (mean deviation 0.023 Å) which lies at 61.1° to the C(18)–C(17)–C(16)–C(15)–C(14)–C(13) plane.

The molecular structure of **12** is also somewhat unusual in that S(1) is slightly distorted from its preferred geometry. Thus the C(19)–C(24)–S(1)–C(13) torsion angle is 136.3°, representing a significant deviation from the preferred *gauche* arrangement of C–C–S–C bonds. The geometry around S(2) is also somewhat distorted, with torsion angles of 93.3 and −99.6° for C(17)–C(18)–S(2)–C(19) and C(24)–C(19)–S(2)–C(18) respectively. Obviously this geometry is enforced by the rigid 1,2-$C_6H_4$ linker. Other bond lengths and angles are in the expected ranges.

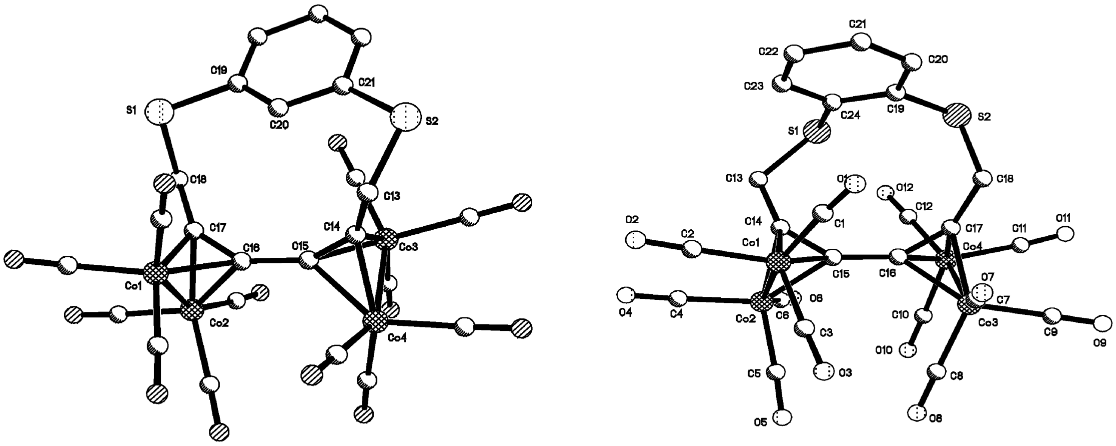
The molecular structure of **11** contains a crystallographic centre of symmetry which lies at the midpoint of the C(24)–C(13a) and C(13)–C(24a) alkynic bonds. The geometry of the pseudo-tetrahedral $Co_2C_2$ cores are unexceptional. Interestingly, S(2) and S(2A) both adopt an endodentate configuration,



**10** 1,3-$C_6H_4$
**12** 1,2-$C_6H_4$

**11**

**Fig. 3** Reaction of $[\{Co_2(CO)_6\}_2(\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-}HOCH_2C_2C_2CH_2OH)]$ with aromatic dithiols.



**10**

**12**

**Fig. 4** Molecular structure of $[\{Co_2(CO)_6\}_2(\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-}SCH_2C_2C_2CH_2SC_6H_4)]$ **10** and **12**.

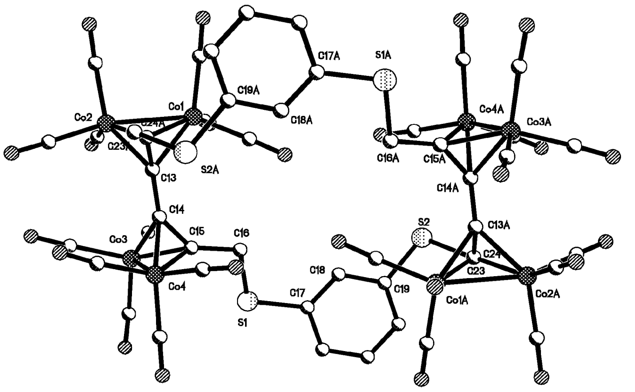


**Fig. 5** Molecular structure of $[\{Co_2(CO)_6\}_2(\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-}SCH_2C_2C_2CH_2S\text{-}1,3\text{-}C_6H_4)]_2$ **11**.

rather than the normal exodentate configuration. It is assumed that this configuration is forced upon them by the geometry of the rigid 1,3-$C_6H_4$ linker. The four sulfur atoms lie within a plane.

## Reaction with dithio(mercapto)ethers

In order to introduce added donor functionality it was decided to react **1** with dithio-ethers and -(mercapto)ethers. Thus reaction of **1** with $S(C_2H_4SH)_2$ under standard acid-catalysed conditions yields the monomer **13** and the expected dimer **14**. The structure of **13** is somewhat surprising; one of the sulfur atoms has adopted an endo configuration and is coordinated to a cobalt centre (Fig. 6). No such coordination is observed in the dimer **14**, which essentially has a structure with a configuration identical to that of complexes **6** to **9**. Reaction of **1** with $O(C_2H_4SH)_2$ under standard conditions leads to the formation of monomeric **15** and dimeric **16**, which were readily separated by column chromatography. In the case of **15** the oxygen atom, although endodentate (as is the norm with macrocylic ethers), does not coordinate to a cobalt atom. This is perhaps unsurprising given the low oxidation state of the Co centre making it more susceptible to coordination by the softer sulfur donor.[22]

The product distribution for the above reactions is heavily weighted towards formation of the monomers. It is presumed that after the first addition of dithiol an interaction between the (mercapto)ether donor atom and a cobalt centre holds the complex in such a geometry as to favour monomeric ring closure. In fact, as already noted, the (mercapto)ether S atom in complex **13** is actually coordinated to a cobalt atom in the final product. Although the oxygen donor atom is not coordinated in **15** it is still reasonable to suppose that an O–Co interaction may occur in an intermediate and that this favours monomer formation. Indeed, such an O–Co interaction has been previously

**Table 2** Selected bond lengths (Å) and angles (°) for **10**

| | | | | | |
|---|---|---|---|---|---|
| Co(1)–C(17) | 1.956(3) | Co(4)–C(14) | 1.970(3) | C(16)–C(17) | 1.351(4) |
| Co(1)–C(16) | 1.979(3) | Co(4)–C(15) | 2.002(3) | C(17)–C(18) | 1.497(4) |
| Co(1)–Co(2) | 2.4742(5) | S(1)–C(19) | 1.760(3) | C(19)–C(20) | 1.386(4) |
| Co(2)–C(17) | 1.943(3) | S(1)–C(18) | 1.804(3) | C(19)–C(24) | 1.395(4) |
| Co(2)–C(16) | 1.987(3) | S(2)–C(21) | 1.753(4) | C(20)–C(21) | 1.390(4) |
| Co(3)–C(14) | 1.960(3) | S(2)–C(13) | 1.815(3) | C(21)–C(22) | 1.399(5) |
| Co(3)–C(15) | 1.981(2) | C(14)–C(15) | 1.352(4) | C(22)–C(23) | 1.374(5) |
| Co(3)–Co(4) | 2.4521(6) | C(15)–C(16) | 1.429(4) | C(23)–C(24) | 1.380(5) |
| C(1)–Co(1)–C(17) | 100.40(12) | C(4)–Co(2)–C(17) | 101.00(1) | C(16)–C(15)–Co(4) | 134.7(2) |
| C(2)–Co(1)–C(17) | 101.98(13) | C(6)–Co(2)–C(16) | 100.48(1) | C(14)–C(15)–C(16) | 143.7(3) |
| C(3)–Co(1)–C(17) | 143.88(11) | C(5)–Co(2)–C(16) | 106.64(1) | C(19)–S(1)–C(18) | 103.2(1) |
| C(1)–Co(1)–C(16) | 100.77(12) | C(4)–Co(2)–C(16) | 139.82(1) | C(21)–S(2)–C(13) | 104.3(2) |
| C(2)–Co(1)–C(16) | 139.84(13) | C(17)–Co(2)–C(16) | 40.20(1) | C(14)–C(13)–S(2) | 115.6(2) |
| C(3)–Co(1)–C(16) | 106.03(12) | C(17)–C(16)–C(15) | 145.9(3) | C(15)–C(14)–C(13) | 141.7(3) |
| C(17)–Co(1)–C(16) | 40.15(11) | C(17)–C(16)–Co(2) | 68.2(2) | C(15)–C(14)–Co(3) | 70.8(2) |
| C(17)–Co(1)–Co(2) | 50.38(8) | C(15)–C(16)–Co(2) | 135.3(2) | C(13)–C(14)–Co(3) | 137.1(2) |
| C(16)–Co(1)–Co(2) | 51.54(8) | C(16)–C(17)–C(18) | 147.9(3) | C(15)–C(14)–Co(4) | 71.4(2) |
| C(6)–Co(2)–C(17) | 101.88(12) | C(16)–C(17)–Co(2) | 71.7(2) | C(13)–C(14)–Co(4) | 130.7(2) |
| C(5)–Co(2)–C(17) | 143.59(13) | C(18)–C(17)–Co(2) | 132.6(2) | Co(3)–C(14)–Co(4) | 77.2(1) |
| C(16)–C(17)–Co(1) | 70.8(2) | C(20)–C(21)–S(2) | 123.4(3) | C(20)–C(19)–S(1) | 123.4(2) |
| C(18)–C(17)–Co(1) | 127.6(2) | C(22)–C(21)–S(2) | 117.3(3) | C(24)–C(19)–S(1) | 116.4(3) |

**Table 3** Selected bond lengths (Å) and angles (°) for **11**

| | | | | | |
|---|---|---|---|---|---|
| Co(1)–C(24a) | 1.949(4) | Co(3)–C(15) | 1.947(4) | S(1)–C(17) | 1.777(3) |
| Co(1)–C(13) | 1.982(4) | Co(3)–C(14) | 1.984(4) | S(1)–C(16) | 1.804(4) |
| Co(1)–Co(2) | 2.4730(7) | Co(3)–Co(4) | 2.4795(9) | S(2)–C(19) | 1.779(4) |
| Co(2)–C(24a) | 1.957(4) | Co(4)–C(15) | 1.941(4) | S(2)–C(23) | 1.822(4) |
| Co(2)–C(13) | 1.976(3) | Co(4)–C(14) | 1.965(4) | C(13)–C(24a) | 1.334(5) |
| C(23)–C(24) | 1.486(6) | C(24)–Co(1a) | 1.949(4) | C(13)–C(14) | 1.432(5) |
| C(24)–C(13a) | 1.334(5) | C(24)–Co(2a) | 1.957(4) | C(14)–C(15) | 1.359(5) |
| C(24a)–Co(1)–C(13) | 39.7(2) | C(17)–S(1)–C(16) | 103.2(2) | C(15)–C(14)–Co(4) | 68.7(2) |
| C(24a)–Co(1)–Co(2) | 50.9(1) | C(19)–S(2)–C(23) | 103.7(2) | C(13)–C(14)–Co(4) | 135.9(3) |
| C(13)–Co(1)–Co(2) | 51.23(9) | C(24a)–C(13)–C(14) | 143.3(4) | C(15)–C(14)–Co(3) | 68.3(2) |
| C(24a)–Co(2)–C(13) | 39.6(2) | C(24a)–C(13)–Co(2) | 69.4(2) | C(13)–C(14)–Co(3) | 133.2(3) |
| C(24a)–Co(2)–Co(1) | 50.6(1) | C(14)–C(13)–Co(2) | 136.4(3) | Co(4)–C(14)–Co(3) | 77.8(1) |
| C(13)–Co(2)–Co(1) | 51.4(1) | C(24a)–C(13)–Co(1) | 68.9(2) | C(14)–C(15)–C(16) | 139.9(4) |
| C(15)–Co(3)–C(14) | 40.4(1) | C(14)–C(13)–Co(1) | 132.5(3) | C(14)–C(15)–Co(4) | 70.6(2) |
| C(15)–Co(3)–Co(4) | 50.3(1) | Co(2)–C(13)–Co(1) | 77.3(3) | C(16)–C(15)–Co(4) | 135.5(3) |
| C(14)–Co(3)–Co(4) | 50.8(1) | C(15)–C(14)–C(13) | 143.7(3) | C(14)–C(15)–Co(3) | 71.2(2) |
| C(16)–C(15)–Co(3) | 133.2(3) | C(13a)–C(24)–C(23) | 140.4(4) | C(13a)–C(24)–Co(2a) | 70.9(2) |
| Co(4)–C(15)–Co(3) | 79.2(1) | C(13a)–C(24)–Co(1a) | 71.5(2) | C(23)–C(24)–Co(2a) | 128.4(2) |
| C(15)–C(16)–S(1) | 108.6(3) | C(23)–C(24)–Co(1a) | 139.3(3) | Co(1a)–C(24)–Co(2a) | 78.5(2) |

**Table 4** Selected bond lengths (Å) and angles (°) for **12**

| | | | | | |
|---|---|---|---|---|---|
| Co(1)–C(15) | 1.967(2) | Co(3)–C(16) | 1.979(2) | S(2)–C(18) | 1.826(3) |
| Co(1)–C(14) | 1.975(2) | Co(4)–C(17) | 1.943(2) | C(13)–C(14) | 1.477(3) |
| Co(1)–Co(2) | 2.4621(4) | Co(4)–C(16) | 1.975(2) | C(14)–C(15) | 1.354(3) |
| Co(2)–C(14) | 1.959(2) | S(1)–C(24) | 1.773(2) | C(15)–C(16) | 1.432(3) |
| Co(2)–C(15) | 1.991(2) | S(1)–C(13) | 1.813(2) | C(16)–C(17) | 1.349(3) |
| Co(3)–C(17) | 1.967(2) | S(2)–C(19) | 1.781(3) | C(17)–C(18) | 1.492(3) |
| C(15)–Co(1)–C(14) | 40.17(9) | C(16)–Co(3)–Co(4) | 51.43(6) | Co(2)–C(14)–Co(1) | 77.50(8) |
| C(15)–Co(1)–Co(2) | 51.98(6) | C(17)–Co(4)–C(16) | 40.26(9) | C(14)–C(15)–C(16) | 143.5(2) |
| C(14)–Co(1)–Co(2) | 50.95(6) | C(17)–Co(4)–Co(3) | 51.44(7) | C(14)–C(15)–Co(1) | 70.2(1) |
| C(14)–Co(2)–C(15) | 40.08(9) | C(16)–Co(4)–Co(3) | 51.59(7) | C(16)–C(15)–Co(1) | 131.0(2) |
| C(14)–Co(2)–Co(1) | 51.55(6) | C(24)–S(1)–C(13) | 102.4(1) | C(14)–C(15)–Co(2) | 68.7(1) |
| C(15)–Co(2)–Co(1) | 51.09(6) | C(19)–S(2)–C(18) | 101.0(1) | C(16)–C(15)–Co(2) | 137.5(2) |
| C(17)–Co(3)–C(16) | 39.96(9) | C(14)–C(13)–S(1) | 113.6(2) | Co(1)–C(15)–Co(2) | 76.93(8) |
| C(17)–Co(3)–Co(4) | 50.57(6) | C(15)–C(14)–C(13) | 142.5(2) | C(17)–C(16)–C(15) | 144.8(2) |
| C(18)–C(17)–Co(4) | 135.8(2) | C(15)–C(14)–Co(2) | 71.3(1) | C(17)–C(16)–Co(4) | 68.6(1) |
| C(16)–C(17)–Co(3) | 70.5(1) | C(13)–C(14)–Co(2) | 130.2(2) | C(15)–C(16)–Co(4) | 133.1(2) |
| C(18)–C(17)–Co(3) | 127.1(2) | C(15)–C(14)–Co(1) | 69.6(3) | C(17)–C(16)–Co(3) | 69.5(1) |
| Co(4)–C(17)–Co(3) | 77.99(9) | C(13)–C(14)–Co(1) | 137.7(2) | C(15)–C(16)–Co(3) | 134.7(2) |
| C(17)–C(18)–S(2) | 116.0(2) | Co(2)–C(14)–Co(1) | 77.50(8) | Co(4)–C(16)–Co(3) | 77.98(8) |
| C(20)–C(19)–C(24) | 119.4(2) | C(24)–C(19)–S(2) | 121.5(2) | C(16)–C(17)–C(18) | 146.1(2) |
| C(20)–C(19)–S(2) | 119.1(2) | C(19)–C(24)–S(1) | 119.5(2) | C(16)–C(17)–Co(4) | 71.1(1) |

proposed to explain why the addition of arylmethoxides to dicobalt-stabilised propargylium ions occurs preferentially at the more crowded *ortho* site rather than at the *para* position.[23]

The structures of **13** to **15** have been reported in an earlier communication.[9] The molecular structure of **16** is shown in Fig. 7, with relevant bond length and angles being presented in Table 5. The core of the 1,7,14,21-tetrathio-4,17-dioxacycloicosahexa-9,10,22,23-tetrayne is shown in Fig. 8.

Regarding the organic core, internal hydrogen bonding seems to play some part in defining the geometry of the ring.

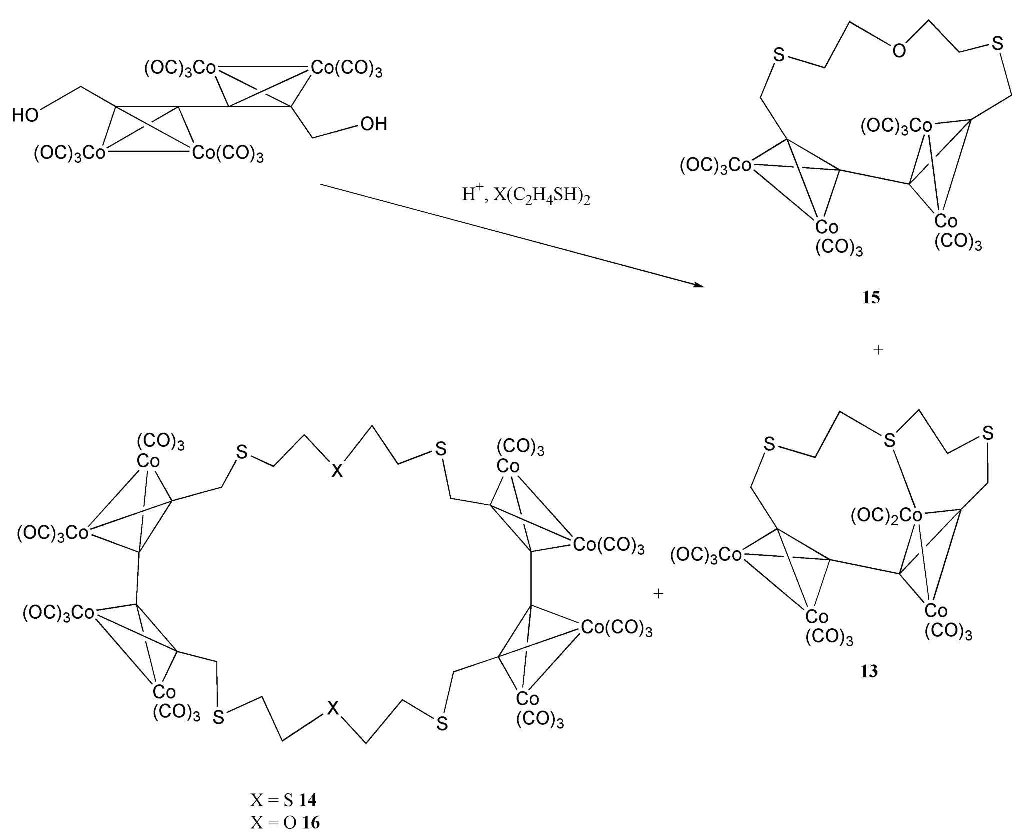


**Fig. 6** Reaction of **1** with dimercaptoethers.

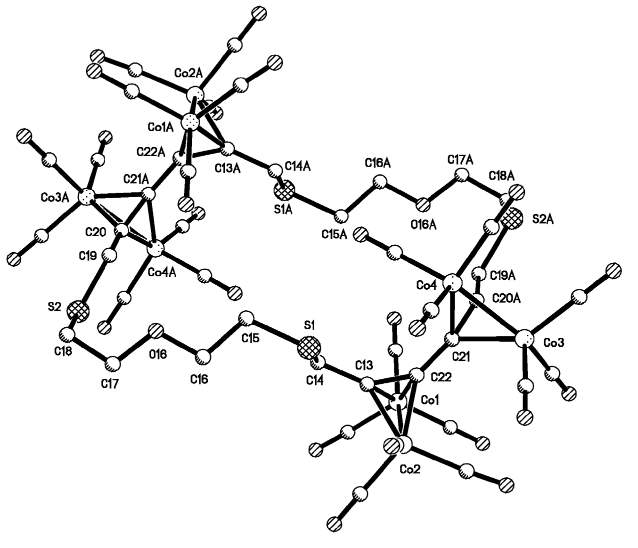


**Fig. 7** Molecular structure of $[\{Co_2(CO)_6\}_2\{\mu\text{-}\eta^2\text{:}\mu\text{-}\eta^2\text{-}SCH_2C_2C_2\text{-}CH_2S(CH_2)_2O(CH_2)_2\}]_2$ **16**.

The H(19b) ··· O(16) and H(19d) ··· O(16A) separations are 2.397 Å, and can be compared to the analogous separation of 2.5 Å in 18-crown-6,[24] and the separation of *ca.* 2.46 Å in a bis-dicobalt complexed 1,16,11,16-tetraoxacycloicosa-8,18-diyne.[25] The donor atoms sit above and below a plane; thus S(1A) and S(2A) lie *ca.* 0.25 Å above the plane, whilst S(1) and S(2) lie 0.25 Å below the plane with O(16) and O(16A) lying 0.379 Å above and below the plane respectively. Sulfur–carbon bonds prefer a *gauche* conformation, whereas oxygen–carbon bonds prefer an *anti* conformation.[21] This is reflected by the torsion angles of the S–C–C–O, C–S–C–C, and C–O–C–C bonds. Thus the S(1)–C(15)–C(16)–O(16) angle is −178.2° whereas the S(2)–C(18)–C(17)–O(16) angle is 63.8°, indicating that the latter lies *gauche*, and the former *anti*, as has been previously observed for an $18S_4O_2$ macrocylce.[26] The determining factor appears to be the conformation of the C–C–O–C bonds which all lie *anti*, whereas half the C–S–C–C bonds are the preferred *gauche* and half the *anti* conformation.

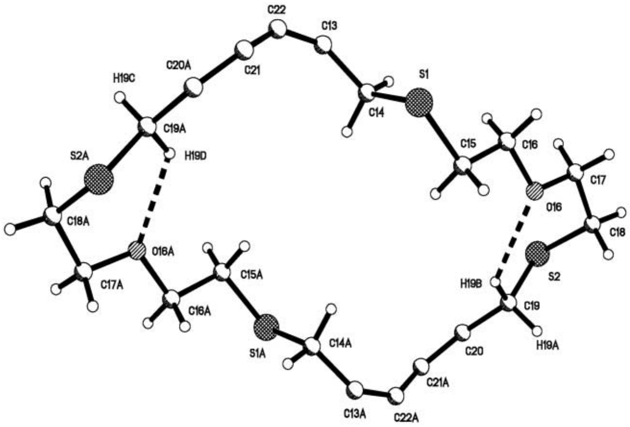


**Fig. 8** Organic core of **16**.

A comparison of pertinent bond lengths and angles for the crystallographically characterised complexes is given in Table 6. It is interesting to note that the monomeric complexes **10** and **12** contain significantly larger alkyne bend back angles (mean 144.5°) compared to those of the dimeric complexes **7**, **11** and **16** (mean 139.1°). Furthermore, the mean Co–Co bond length in the monomeric complexes is 0.01 Å shorter than that of the dimeric complexes, although interestingly there is no significant difference in the mean alkynic C–C bond lengths. These differences are attributed to the smaller bite of the monomeric spacer group which necessarily causes distortion in the diyne unit.

## Representative decomplexation

In order to demonstrate that the hexacarbonyldicobalt protecting group may readily be removed complex **4** was chosen to investigate a representative decomplexation. Thus stirring an acetone solution of **4** with an excess of ammonium ceric nitrate led to a rapid effervescence and a colour change from brown to

**Table 5** Selected bond lengths (Å) and angles (°) for **16**

| | | | | | |
|---|---|---|---|---|---|
| Co(1)–C(13) | 1.950(3) | Co(4)–C(21) | 1.972(3) | O(16)–C(16) | 1.414(3) |
| Co(1)–C(22) | 1.998(3) | S(1)–C(15) | 1.805(3) | O(16)–C(17) | 1.421(3) |
| Co(1)–Co(2) | 2.4648(5) | S(1)–C(14) | 1.828(3) | C(17)–C(18) | 1.511(4) |
| Co(2)–C(13) | 1.952(3) | S(2)–C(18) | 1.810(3) | C(21)–C(20a) | 1.351(3) |
| Co(2)–C(22) | 1.961(2) | S(2)–C(19) | 1.811(3) | C(21)–C(22) | 1.427(4) |
| Co(3)–C(20a) | 1.952(3) | C(10)–O(10) | 1.132(3) | C(19)–C(20) | 1.487(4) |
| Co(3)–C(21) | 1.974(2) | C(13)–C(22) | 1.350(4) | C(20)–C(21a) | 1.351(3) |
| Co(3)–Co(4) | 2.4796(5) | C(13)–C(14) | 1.477(4) | C(20)–Co(4a) | 1.944(3) |
| Co(4)–C(20a) | 1.944(3) | C(15)–C(16) | 1.514(4) | C(20)–Co(3a) | 1.952(2) |
| | | | | | |
| C(1)–Co(1)–C(13) | 104.2(1) | C(5)–Co(2)–C(13) | 139.4(1) | C(16)–O(16)–C(17) | 111.9(2) |
| C(3)–Co(1)–C(13) | 144.0(1) | C(6)–Co(2)–C(22) | 101.8(1) | O(16)–C(16)–C(15) | 108.0(2) |
| C(2)–Co(1)–C(13) | 98.1(11) | C(4)–Co(2)–C(22) | 142.9(1) | O(16)–C(17)–C(18) | 108.3(2) |
| C(1)–Co(1)–C(22) | 100.6(1) | C(5)–Co(2)–C(22) | 101.1(1) | C(17)–C(18)–S(2) | 113.5(2) |
| C(3)–Co(1)–C(22) | 108.8(1) | C(15)–S(1)–C(14) | 99.5(1) | C(20a)–C(21)–C(22) | 141.1(2) |
| C(2)–Co(1)–C(22) | 137.0(1) | C(18)–S(2)–C(19) | 99.5(1) | C(20a)–C(21)–Co(4) | 68.7(2) |
| C(13)–Co(1)–C(22) | 40.0(1) | C(22)–C(13)–C(14) | 141.5(3) | C(22)–C(21)–Co(4) | 135.1(2) |
| C(1)–Co(1)–Co(2) | 150.6(1) | C(22)–C(13)–Co(1) | 71.9(2) | C(20a)–C(21)–Co(3) | 69.0(2) |
| C(3)–Co(1)–Co(2) | 97.9(1) | C(14)–C(13)–Co(1) | 131.2(2) | C(22)–C(21)–Co(3) | 136.0(2) |
| C(2)–Co(1)–Co(2) | 99.6(1) | C(22)–C(13)–Co(2) | 70.2(1) | Co(4)–C(21)–Co(3) | 77.9(1) |
| C(13)–Co(1)–Co(2) | 50.9(8) | C(14)–C(13)–Co(2) | 136.3(2) | C(13)–C(22)–C(21) | 142.4(3) |
| C(22)–Co(1)–Co(2) | 50.84(7) | Co(1)–C(13)–Co(2) | 78.3(1) | C(13)–C(22)–Co(2) | 69.5(2) |
| C(6)–Co(2)–C(13) | 100.6(1) | C(13)–C(14)–S(1) | 110.5(2) | C(21)–C(22)–Co(2) | 136.0(2) |
| C(4)–Co(2)–C(13) | 105.8(1) | C(16)–C(15)–S(1) | 111.9(2) | C(13)–C(22)–Co(1) | 68.1(2) |
| C(21)–C(22)–Co(1) | 134.5(2) | Co(2)–C(22)–Co(1) | 77.00(9) | C(20)–C(19)–S(2) | 111.2(2) |
| C(21a)–C(20)–C(19) | 138.6(3) | C(21a)–C(20)–Co(4a) | 71.0(2) | C(19)–C(20)–Co(4a) | 133.5(2) |
| C(21a)–C(20)–Co(3a) | 70.8(2) | C(19)–C(20)–Co(3a) | 136.6(2) | Co(4a)–C(20)–Co(3a) | 79.1(1) |

**Table 6** Comparison of pertinent bond lengths (Å) and angles (°)

| | 7 | 10 | 11 | 12 | 16 |
|---|---|---|---|---|---|
| Mean Co–Co | 2.473 | 2.463 | 2.476 | 2.462 | 2.472 |
| Mean Co–C | 1.961 | 1.968 | 1.961 | 1.970 | 1.963 |
| Mean C≡C | 1.353 | 1.351 | 1.346 | 1.351 | 1.350 |
| $C_2$–$C_2$ | 1.428 | 1.429 | 1.432 | 1.432 | 1.427 |
| | | | | | |
| Mean S–C–C≡ | 112.1 | 115.8 | 112.4 | 114.8 | 110.9 |
| Mean C–C≡C | 138.05 | 144.8 | 140.15 | 144.3 | 140.05 |

orange. Removal of the solvent, followed by hydrolysis and extraction with dichloromethane led to the isolation of an off-white solid identified as the free macrocycle 1,7dithiacyclotrideca-9,11-diyne **17**.

## Conclusion

Dimeric products containing two diyne units are favoured if a dithiol, $SH(CH_2)_nSH$, with a short aliphatic linker group is used, whereas longer aliphatic linkers give a more mixed product distribution containing a higher proportion of monomeric products. If a rigid linker group such as 1,2- or 1,3-$C_6H_4S_2$ is used then monomer formation is favoured almost exclusively.

We have demonstrated that the new complexes may be readily deprotected by treatment with ammonium ceric nitrate. Ongoing investigations by our group are aimed at studying the coordination chemistry of both the cobalt-protected and the free macrocycles.

## Experimental

### General procedures

Unless otherwise stated all experiments were carried out under an atmosphere of dry, oxygen-free nitrogen, using conventional Schlenk line techniques, and solvents freshly distilled from the appropriate drying agent. NMR spectra were recorded in $CDCl_3$ using a Bruker DRX 400 spectrometer, with TMS as an external standard for $^1H$ and $^{13}C$ spectra. Infrared spectra were, unless otherwise stated, recorded in dichloromethane solution in 0.5 mm NaCl solution cells, using a Perkin-Elmer 1710 Fourier Transform spectrometer. FAB mass spectra were obtained using a Kratos MS 890 instrument, using 3-nitrobenzyl alcohol as a matrix. Preparative TLC was carried out on 1 mm silica plates prepared at the University of Cambridge. Column chromatography was performed on Kieselgel 60 (70–230 mesh ASTM). Unless otherwise stated, all reagents were obtained from commercial suppliers and used without further purification. $[\{Co_2(CO)_6\}_2(\mu\text{-}\eta^2{:}\mu\text{-}\eta^2\text{-}HOCH_2C_2C_2CH_2OH)]$ was prepared by the literature method.[27,28]

### Crystal structure determinations

X-Ray diffraction data were collected using a Nonius-Kappa CCD diffractometer, equipped with an Oxford Cryosystems cryostream. Data reduction and cell refinement were performed with the programs DENZO[29] and COLLECT[30] and multi-scan absorption corrections were applied to all intensity data with the program SORTAV.[31] Structures were solved and refined with the programs SHELXS97 and SHELXL97[32] respectively. Crystal data collection and refinement details are summarised in Table 7.

CCDC reference numbers 172436–172440.

See http://www.rsc.org/suppdata/dt/b1/b109341j/ for crystallographic data in CIF or other electronic format.

### Reaction of 1 with dithiols

**General method.** To a solution of **1** (0.5 g, 0.75 mmol) in dichloromethane (50 ml) was added 5–6 drops of 54 wt% $HBF_4{\cdot}Et_2O$ at −78 °C. The appropriate dithiol (0.8 mmol, 1.1 equiv.) was added to the resultant mixture and the solution allowed to warm to room temperature. After 2 hours an excess of $NaHCO_3$ was added, followed by $MgSO_4$. The mixture was filtered through a silica plug, the solvent removed *in vacuo* and the residue applied to the base of TLC plates and eluted with hexane–dichloromethane (3 : 1) in all cases.

**With $HS(CH_2)_3SH$.** Elution afforded green crystalline **2** (0.11 g, 20%) and dark brown crystalline **6** (0.48 g, 43%).

*Data for* **2**. IR ($\nu$CO/cm$^{-1}$): 2090.8(m), 2080.1(m), 2059.2(s), 2026.9(m); $^1H$ NMR: $\delta$ 4.15 (s, 4H, $CCH_2$), 2.97 [t, 4H, $SCH_2$, $J$(HH) 6 Hz], 2.02 (q, 2H, $CH_2$); $^{13}C$ NMR: $\delta$ 199.3 (CO), 95.6, 84.2 ($C_2$), 36.6 ($CCH_2$), 33.4 ($SCH_2$), 29.6 ($CH_2$); FAB MS: $m/z$ 754 $M^+$; $M^+ - n$CO ($n$ = 0–12); Analysis for $C_{21}H_{10}O_{12}S_2Co_4$: C 33.50(33.45), H 1.41(1.34)%.

**Table 7** X-Ray crystallographic data for the new complexes[a]

| Complex | **7** | **10** | **11** | **12** | **16** |
|---|---|---|---|---|---|
| Empirical formula | $C_{44}H_{24}Co_8O_{24}S_4$ | $C_{24}H_8Co_4O_{12}S_2$ | $C_{48}H_{16}Co_8O_{24}S_4$ | $C_{24}H_8Co_4O_{12}S_2$ | $C_{44}H_{24}Co_8O_{26}S_4$ |
| Weight | 1536.31 | 788.14 | 1576.29 | 788.14 | 1568.31 |
| Crystal system | Triclinic | Triclinic | Triclinic | Monoclinic | Triclinic |
| Crystal size | 0.18 × 0.18 × 0.10 | 0.23 × 0.18 × 0.18 | 0.14 × 0.07 × 0.07 | 0.46 × 0.42 × 0.10 | 0.18 × 0.18 × 0.05 |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $C_2/c$ | $P\bar{1}$ |
| $a$/Å | 9.4440(10) | 13.1458(2) | 9.0208(11) | 32.9896(9) | 9.5307(3) |
| $b$/Å | 10.9660(7) | 16.0321(4) | 10.5638(13) | 11.5540(3) | 10.9647(3) |
| $c$/Å | 14.3500(9) | 16.5151(4) | 15.0520(13) | 16.1586(3) | 15.2452(5) |
| $\alpha$/° | 105.700(3 | 61.743(2) | 97.803(6) | 90 | 107.324 |
| $\beta$/° | 90.290(4) | 68.506(2) | 96.594(7) | 113.071(14) | 93.669(2) |
| $\gamma$/° | 101.800(4) | 88.404(2) | 91.095(5) | 90 | 104.731(2) |
| $V$/Å$^3$ | 1397.57(19) | 2807.26(11) | 1410.8(3) | 5666.4(2) | 1454.80(8) |
| $Z$ | 1 | 4 | 1 | 8 | 1 |
| $D_c$/Mg m$^{-3}$ | 1.825 | 1.865 | 1.855 | 1.848 | 1.790 |
| Absorption coefficient/mm$^{-1}$ | 2.541 | 2.533 | 2.520 | 2.510 | 2.445 |
| $F$(000) | 760 | 1552 | 776 | 3104 | 776 |
| $\theta$ range/° | 2.95 to 25.11 | 1.47 to 27.46 | 1.38 to 27.51 | 3.53 to 27.49 | 1.41 to 25.05 |
| Index ranges | $0 \le h \le 11$ | $0 \le h \le 17$ | $0 \le h \le 11$ | $-42 \le h \le 41$ | $-11 \le h \le 11$ |
|  | $-13 \le k \le 12$ | $-20 \le k \le 20$ | $-13 \le k \le 13$ | $-14 \le k \le 14$ | $-12 \le k \le 13$ |
|  | $-17 \le l \le 17$ | $-19 \le l \le 21$ | $-19 \le l \le 19$ | $-19 \le l \le 20$ | $-18 \le l \le 17$ |
| Reflections measured | 9804 | 33397 | 13816 | 26919 | 8804 |
| Independent reflections | 4943 | 12637 | 6351 | 6457 | 5116 |
| $R_{int}$ | 0.0450 | 0.0856 | 0.0805 | 0.0622 | 0.0478 |
| Goodness of fit on $F^2$ | 1.067 | 1.011 | 0.989 | 1.027 | 1.040 |
| Final $R$ indices $R1$ | 0.0390 | 0.0398 | 0.0496 | 0.0353 | 0.0322 |
| $wR2$ | 0.0842 | 0.0835 | 0.0767 | 0.0820 | 0.0748 |
| $R$ indices (all data) $R1$ | 0.0791 | 0.0718 | 0.1130 | 0.0511 | 0.0481 |
| $wR2$ | 0.1214 | 0.1194 | 0.1725 | 0.0884 | 0.1004 |
| Largest diff. peak and hole/e Å$^{-3}$ | 0.678 and −0.708 | 0.598 and −0.679 | 0.509 and −0.801 | 0.567 and −0.728 | 0.506 and −0.445 |

[a] Data in common: temperature of collection 180(2) K, wavelength 0.71069 Å.

*Data for **6**.* IR ($\nu$CO/cm$^{-1}$): 2097.9(m), 2982.2(m), 2059.3(s), 2027.1(s); $^1$H NMR: $\delta$ 4.07 (s, 8H, CCH$_2$), 2.84 [t, 8H, SCH$_2$, $J$(HH) 7], 2.00 [m, 4H, CH$_2$ $J$(HH) 7 Hz]; $^{13}$C NMR: $\delta$ 199.3 (CO), 94.5, 84.2 ($C\equiv C$), 37.2 ($\equiv CCH_2$), 31.9 (SCH$_2$), 29.7 (CH$_2$); FAB MS: $m/z$ 1508 M$^+$, M$^+$ − $n$CO ($n$ = 0–24); Analysis for $C_{42}H_{20}O_{24}S_4Co_8$: C 33.65(33.45), H 1.47(1.34)%.

**With HS(CH$_2$)$_4$SH.** Elution afforded brown crystalline **3** (0.11 g, 20%) and brown crystalline **7** (0.61 g, 54%).

*Data for **3**.* IR ($\nu$CO/cm$^{-1}$): 2100.2(m), 2080.8(s), 2059.7(vs), 2025.4(s); $^1$H NMR: $\delta$ 4.15 (s, 4H, CCH$_2$), 2.83 (br, s, 4H, SCH$_2$), 1.95–1.70 (m, 4H, CH$_2$); $^{13}$C NMR: $\delta$ 198.8 (CO), 37.4($\equiv CCH_2$), 33.6 (SCH$_2$), 29.7(CH$_2$); FAB MS: $m/z$ 768 M$^+$, M$^+$ − $n$CO ($n$ = 1–12); Analysis for $C_{22}H_{12}O_2S_2Co_4$: C 34.62(34.40), H 1.77(1.57)%.

*Data for **7**.* IR ($\nu$CO/cm$^{-1}$): 2100.1(m), 2081.8(s), 2058.0(vs), 2025.9(s); $^1$H NMR: $\delta$ 3.98 (s, 8H, CCH$_2$), 2.68 [t, 8H, SCH$_2$, $J$(HH) 6 Hz], 1.80–1.60 (m, 8H, CH$_2$); $^{13}$C NMR: $\delta$ 198.8 (CO), 37.4 ($\equiv CCH_2$), 33.6 (SCH$_2$), 29.7 (CH$_2$); FAB MS: $m/z$ 1536 M$^+$, M$^+$ − $n$CO ($n$ = 1–24); Analysis for $C_{44}Co_8H_{24}O_{24}S_4$: C 34.12(34.40), H 1.62(1.57)%.

**Reaction with HS(CH$_2$)$_5$SH.** Elution gave dark brown crystalline **4** (0.18 g, 31%) and dark brown crystalline **8** (0.43 g, 38%).

*Data for **4**.* IR ($\nu$CO/cm$^{-1}$): 2101.3(s), 2082.3(s), 2059.8(vs), 2030.2(vs); $^1$H NMR: $\delta$ 4.23 (s, 4H, CCH$_2$), 2.78–2.65 (m, 4H, SCH$_2$), 1.79–1.65 (m, 6H, CH$_2$); $^{13}$C NMR: $\delta$ 199.6 (CO), 96.2, 84.7 ($C\equiv C$), 36.7 ($\equiv CCH_2$), 32.9 (SCH$_2$), 28.3, 26.0(CH$_2$); FAB MS: $m/z$ 782 M$^+$, M$^+$ − $n$CO ($n$ = 1–12); Analysis for $C_{23}H_{14}O_{12}S_2Co_4$: C 35.78(35.32), H 1.96(1.80)%.

*Data for **8**.* IR ($\nu$CO/cm$^{-1}$): 2101.1(m), 2082.5(s), 2059.8(vs), 2028.4(s); $^1$H NMR: $\delta$ 4.09 (s, 8H, CCH$_2$), 2.71 [t, 8H, SCH$_2$, $J$(HH) 6 Hz], 1.84–1.68 (m, 12H, CH$_2$); $^{13}$C NMR: $\delta$ 199.1 (CO), 94.2, 82.3 ($C\equiv C$), 37.5 ($\equiv CCH_2$), 33.8 (SCH$_2$), 29.5, 28.11 (CH$_2$); FAB MS: $m/z$ 1564 M$^+$, M$^+$ − $n$CO ($n$ = 1–24); Analysis for $C_{46}H_{28}O_{24}S_4Co_8$: C 35.62(35.35), H 1.86(1.80)%.

**Reaction with HS(CH$_2$)$_6$SH.** Elution afforded dark brown crystalline **5** (0.21 g, 36%) and dark brown crystalline **9** (0.43 g, 37%).

*Data for **5**.* IR ($\nu$CO/cm$^{-1}$): 2101.6(s), 2082.4(s), 2059.3(vs), 2029.8(vs); $^1$H NMR: $\delta$ 4.29 (s, 4H, CCH$_2$), 2.80 [t, 4H, SCH$_2$, $J$(HH) 6 Hz], 1.88–1.54 (m, 8H, CH$_2$); $^{13}$C NMR: $\delta$ 199.3 (CO), 100.8, 94.4 ($C\equiv C$), 38.04 ($\equiv CCH_2$), 32.3, 32.0 (SCH$_2$), 29.1, 25.2, 23.0 (CH$_2$); FAB MS: $m/z$ 796 M$^+$, M$^+$ − $n$CO ($n$ = 1–12); analytical for $C_{24}H_{16}O_{12}S_2Co_4$: C 36.19(36.20), H 2.05(2.03).

*Data for **9**.* IR ($\nu$CO/cm$^{-1}$): 2101.0(m), 2082.1(s), 2059.0(vs), 2028.5(s); $^1$H NMR: $\delta$ 4.05 (s, 8H, CCH$_2$), 2.72 [t, 8H, SCH$_2$, $J$(HH) 7 Hz], 2.16–1.45 (m, 16H, CH$_2$); $^{13}$C NMR: $\delta$ 198.7 (CO), 101.4, 89.3 ($C\equiv C$), 37.03 ($\equiv CCH_2$), 33.5, 31.3 (SCH$_2$), 29.2, 27.9, 26.6, 22.4 (CH$_2$); FAB MS: $m/z$ 1592 M$^+$, M$^+$ − $n$CO ($n$ = 2–24); Analysis for $C_{48}H_{32}O_{24}S_4Co_8$: C 36.14(36.20), H 2.11(2.03)%.

**Reaction with 1,3-C$_6$H$_4$(SH)$_2$.** Elution afforded green–brown crystalline **10** (0.42 g, 73%) and brown crystalline **11** (0.22 g, 19%).

*Data for **10**.* IR ($\nu$CO/cm$^{-1}$): 2101.1(m), 2082.1(s), 2058.1(vs), 2028.3(s), 2014.8(sh); $^1$H NMR: $\delta$ 7.17–7.06 (m, 4H, Ph), 4.08 (s, 4H, CCH$_2$); $^{13}$C NMR: $\delta$ 198.5 (CO), 138.1–123.1 (Ph), 103.6, 92.9 ($C\equiv C$), 37.9 ($\equiv CCH_2$); FAB MS: $m/z$ 788 M$^+$, M$^+$ − $n$CO ($n$ = 1–12); Analysis for $C_{24}H_8O_{12}S_2Co_4$: C 39.55(39.81), H 1.07(1.11)%.

*Data for **11**.* IR ($\nu$CO/cm$^{-1}$): 2096.7(m), 2082.8(m), 2062.2(vs), 2036.2(s); $^1$H NMR: $\delta$ 7.90–7.37 (m, 8H, Ph), 4.12 (s, 8H, CCH$_2$); $^{13}$C NMR: $\delta$ 197.6 (CO), 138.8–123.4 (Ph), 93.4 (C$_2$), 31.9 (CCH$_2$); FAB MS: $m/z$ 1576 M$^+$, M$^+$ − $n$CO ($n$ = 5–24); Analysis for $C_{48}H_{16}O_{24}S_4Co_8$: C 39.52(39.81), H 1.12(1.11)%.

**Reaction with 1,2-C$_6$H$_4$(SH)$_2$.** Elution gave brown crystalline **12** (0.56 g, 86%).

IR ($\nu$CO/cm$^{-1}$): 2098(m), 2083(m), 2061(vs), 2036(s); $^1$H NMR: $\delta$ 7.77–7.01 (m, 4H, Ph), 4.56 (s, 4H, CH$_2$); $^{13}$C NMR: $\delta$ 198.76 (s, CO), 139.73, 135.01, 129.47 (s, aromatic), 98.92, 93.35 (s, $C\equiv C$), 43.04 (s, $\equiv CCCH_2$); FAB MS: $m/z$ 788 M$^+$, M$^+$ − $n$CO ($n$ = 1–12); Analysis for $C_{24}H_8O_{12}S_2Co_4$: C 39.68(39.81), H 1.07(1.11)%.

### Deprotection of 4

To a stirred acetone solution of **4** (300 mg, 0.2 mmol) was added ammonium ceric nitrate (1.2 g, excess) in small portions in the open air. The resulting solution was stirred for 2 h during which time the colour changed from brown to orange, the solvent was removed *in vacuo*, and the residue redissolved in 50 ml $H_2O$. Extraction with dichloromethane (3 × 30 ml), followed by drying over $MgSO_4$ and evaporation of the organic extracts led to the isoltion of **17** as an off-white solid.

$^1H$ NMR: $\delta$ 3.34 (s, 4H, $CCH_2$), 2.88 (m, 4H, $SCH_2$), 2.65 (m, 4H, $SCH_2C\mathit{H}_2$), 2.40 (m, $CH_2CH_2\mathit{C}H_2$); $^{13}C$ NMR: $\delta$ 74.75 (C≡C), 74.13 (C≡C), 30.66 ($\equiv C\mathit{C}H_2$), 25.47 ($S\mathit{C}H_2CH_2$), 22.66 ($CH_2\mathit{C}H_2CH_2$), 20.16 ($CH_2CH_2\mathit{C}H_2$); FAB MS: *m*/*z* 210.1 ($M^+$).

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