The formation of sulfur macrocycles containing dialkyne units

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Treatment of the dialkyne complex $[\{Co_2(CO)_6\}_2\{\mu\text{-}\eta^2\!:\!\mu\text{-}\eta^2\text{-}HOCH_2C \equiv CC \equiv CCH_2OH\}]$ with $HBF_4 \cdot OEt_2$ at -78 °C and the subsequent addition of $[HS(CH_2)_2]_2X$ (X = S or O) affords the novel macrocyclic complexes $[\{Co_2(CO)_5\}\{Co_2\text{-}(CO)_6\}\{(\mu\text{-}\eta^2\text{-}C \equiv CCH_2SCH_2CH_2)_2S\}]$ **1a**, $[\{Co_2(CO)_6\}_2\{(\mu\text{-}\eta^2\text{-}C \equiv CCH_2SCH_2CH_2)_2O\ \}]$ **2a** and $[\{Co_2(CO)_6\}_2\{(\mu\text{-}\eta^2\text{-}C \equiv CCH_2SCH_2CH_2)_2X\}]_2$ [X = S **1b** or O **2b**].

Crown thioethers and related sulfur macrocycles have been the subject of numerous studies owing to their ability to bind metal ions more strongly than mono- or bi-dentate thioethers.[1] Structural studies on uncoordinated sulfur macrocycles have shown that the sulfur atoms tend to adopt an exodentate conformation in which all the sulfur lone pairs are orientated out of the macrocyclic cavity.[2] Therefore these macrocycles must undergo substantial conformational change in order to coordinate to an added metal ion. Several sulfur macrocycles undergo this type of conformational change on reaction with added metal ions such as Pd(II),[3] Hg(II),[4] Ni(II)[5] or Ag(I)[6,7] to give cyclic systems in which at least two of the sulfur atoms have co-ordinated to the metal and are in an endodentate configuration.

We now report the synthesis of several new sulfur macrocycles† (Fig. 1) and, in particular, of the novel complex $[\{Co_2(CO)_5\}\{Co_2(CO)_6\}\{(\mu\text{-}\eta^2\text{-}C \equiv CCH_2SCH_2CH_2)_2S\}]$ **1a** which contains a dialkyne unit and three sulfur donor atoms of which only one is endodentate and coordinated to a metal.

The X-ray crystal structure‡ of **1a** (Fig. 2) confirms that a 13-membered macrocyclic ring has formed. Two of the sulfur atoms are exodentate to the ring but the central sulfur atom is endodentate and coordinated axially to one of cobalt atoms already present in the molecule rather than to an added metal ion. This mode of coordination of a sulfur macrocycle containing three sulfur atoms is unprecedented. In contrast
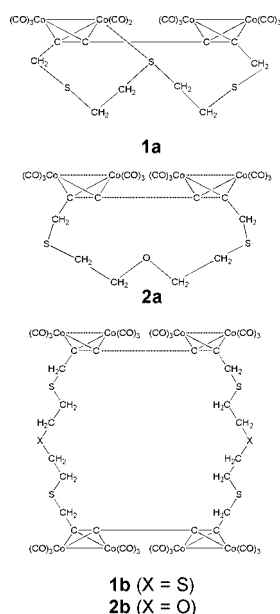
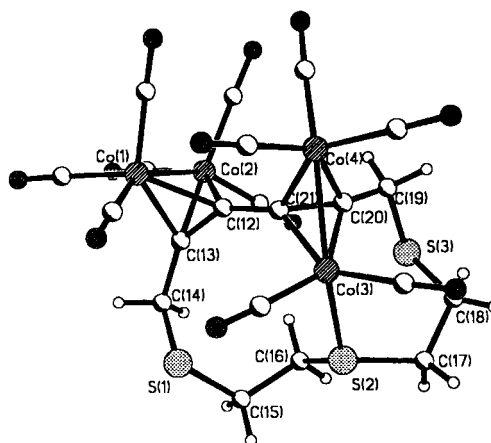complex **1b** (Fig. 3),‡ the dimer of **1a**, contains no Co–S interactions.

Fig. 2 Molecular structure of **1a**. Selected bond lengths (Å) and angles (°): Co(3)–S(2) 2.2702(8), S(2)–C(16) 1.820(3), S(2)–C(17) 1.824(3), C(16)–C(15) 1.531(4), S(1)–C(15) 1.812(3), C(17)–C(18) 1.526(4), S(3)–C(18) 1.815(3), C(12)–C(13) 1.351(4), C(21)–C(20) 1.354(3), S(2)–Co(3)–Co(4) 154.30(2), C(15)–C(16)-S(2) 110.3(2), C(17)–C(18)-S(3) 115.4(2), C(16)–C(15)–S(1) 114.0(2), C(18)–C(17)-S(2) 117.7(2), C(20)–C(19)-S(3) 113.5(2).
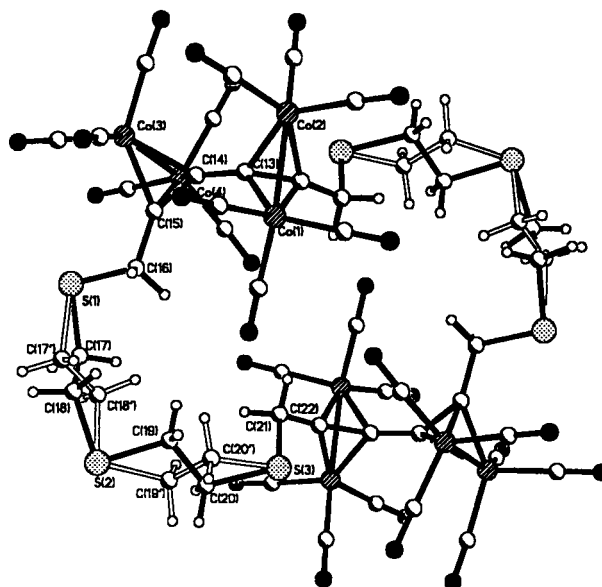

Fig. 3 Molecular structure of **1b** showing the two orientations of the disorder within the ring system. Selected bond lengths (Å) and angles (°): S(1)–C(17) 1.793(6), S(1)–C(17') 1.976(14), S(2)–C(19) 1.823(9), S(2)–C(19') 1.846(9), S(2)–C(18) 1.817(6), S(2)–C(18') 1.831(13), S(3)–C(20) 1.847(9), S(3)–C(20') 1.807(9), C(17)–C(18) 1.518(9), C(17')–C(18') 1.48(2), C(19)–C(20) 1.523(10), C(19')–C(20') 1.490(12), C(22)–C(13) 1.356(5), C(14)–C(15) 1.359(5), C(16)–S(1)–C(17) 100.0(3), C(16)-S(1)–C(17') 95.5 (5), C(17)–C(18)-S(2) 115.1(4), C(17')–C(18')–S(2) 104.9(10), C(18)–S(2)–C(19) 90.1(3), C(18')–S(2)–C(19') 96.2(5), S(2)–C(19)–C(20) 107.3(6), S(2)–C(19')–C(20') 112.0(6), C(19)–C(20)–S(3) 111.4(6), C(19')–C(20')–S(3) 110.8(6), C(20)–S(3)–C(21) 99.7(3), C(20')–S(3)–C(21) 101.9(3). (Primed atoms refer to the second orientation of the disordered ring system).
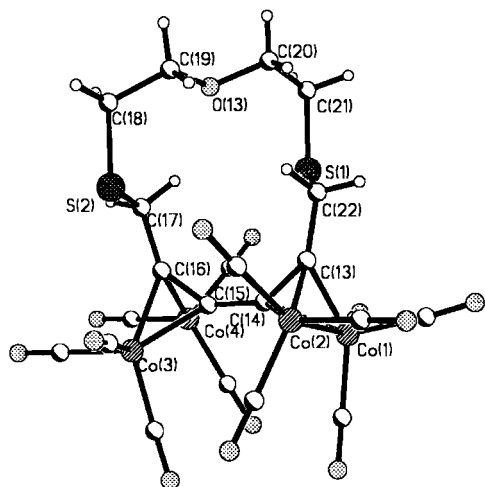

Fig. 1 The new sulfur macrocycles containing dialkyne units.

Fig. 4 Molecular structure of **2a**. Selected bond lengths (Å) and angles (°): O(13)–C(19) 1.420(4), O(13)–C(20) 1.419(4), C(20)–C(21) 1.508(5), C(19)–C(18) 1.516(4), S(1)–C(21) 1.809(3), S(2)–C(18) 1.815(3), S(1)–C(22) 1.813(3), S(2)–C(17) 1.824(3), C(16)–C(15) 1.345(4), C(14)–C(13) 1.343(4), C(18)–C(19)–O(13) 108.6(3), C(21)–C(20)–O(13) 109.0 (3), C(19)–C(18)–S(2) 115.0(2), C(20)–C(21)-S(1) 115.3(2), C(13)–C(22)–S(1) 108.7(2).

All the carbon–sulfur bond lengths in **1a** and **1b** fall within the expected range for macrocylic thioethers, ranging from 1.793(6) to 1.846(9), as do all the carbon–carbon single bond lengths which range from 1.48(2) to 1.531(4).[1] The carbon–carbon triple bond lengths range from 1.351(4) to 1.359(5), typical of coordinated alkynes.[6,8] The cobalt–sulfur bond distance of 2.2702(8) in **1a** is also typical of other reported values.[9]

The novel macrocycle **1a** and its dimer **1b** are synthesized† by the reaction of [{Co$_2$(CO)$_6$}$_2$[μ-η^2:μ-η^2-HOCH$_2$C≡CC≡C-CH$_2$OH}] with 1 equiv. of [HS(CH$_2$)$_2$]$_2$S in the presence of catalytic amounts of HBF$_4$·OEt$_2$ at −78 °C and separated by chromatography in an analogous manner to that reported by Went and coworkers for the related mono-alkyne complexes.[6] Substitution of [HS(CH$_2$)$_2$]$_2$S by [HS(CH$_2$)$_2$]$_2$O affords the related macrocyclic compounds **2a**, **2b** in which the central sulfur atom in **1a**, **1b** is replaced by an oxygen atom. The combined yields of the monomer (**a**) and the dimer (**b**) are in excess of 90% in each case.

The X-ray crystal structure‡ of **2a**, (Fig. 4), again confirms the presence of a 13- membered macrocyclic ring as in **1a**.

The central oxygen atom of the ring, although it is endodentate as is typical of crown ethers, does not coordinate to a cobalt centre in contrast to the central sulfur atom in **1a** and, as a consequence, there is no loss of a carbonyl group from either of the Co$_2$(CO)$_6$ units in **2a** both of which remain intact. The two sulfur atoms in **2a** adopt the same geometry as the corresponding sulfur atoms in **1a** and are exodentate. All carbon–sulfur bonds in **2a** fall within the expected range of values, as do the carbon–carbon single bonds of the crown thioether.[1]

An inspection of the crystal structures reveals that in each case the CH$_2$ protons are in different environments; this results in complicated ^{1}H NMR spectra in the SCH$_2$ and OCH$_2$ regions comprising of overlapping multiplets. The ^{13}C NMR spectra exhibit only one resonance due to a CO group, as is common for alkyne-bridged dicobalt complexes; localized site exchange[10] or a trigonal twist[11] has been proposed previously to explain this fluxionality.

In linear diyne complexes containing two coordinated dicobalt hexacarbonyl fragments these fragments are co-ordinated *trans* to each other such that the two Co-Co vectors are almost parallel.[12] The steric demands of the cyclic diynes in **1a**, **1b** and **2a** do not allow this relative orientation and the two fragments are twisted to varying degrees such that the two Co–Co vectors approach an orthogonal configuration.

The influence of the nature of the linking groups and of the donor atoms on the geometry of these macrocyclic dialkyne complexes is under further study.

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