Synthesis and Co-ordination Chemistry of Dicobaltcomplexed Thiacycloalkynes[†]

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The reactions of bis(2-mercaptoethyl) sulfide or bis(2-mercaptoethyl) ether with $[Co_2(\mu-HOCH_2C=$ $CCH_2OH)(CO)_6$ in the presence of HBF₄-OEt₂ afford $[Co_2\{\mu-C_2(CH_2SCH_2CH_2)_2X\}(CO)_6]$ (X = S or O) respectively together with dimeric products. The structure of the monomer $[Co_2(\mu-C_2(CH_2SCH_2CH_2)_2S]$ (CO)₆] has been established by X-ray crystallography and comprises a hexacarbonyldicobalt unit transversely bridged via the alkyne functionality of 1,4,7-trithiacycloundec-9-yne which has an exodentate conformation. Proton NMR studies of the bis(2-mercaptoethyl) sulfide derivatives reveal that the SCH₂CH₂S linkages are predominantly anti in solution. The monomers undergo carbonyl substitution by bis(diphenylphosphino)methane (dppm) to afford $[Co_2{\mu-C_2(CH_2SCH_2CH_2)_2X}(\mu-dppm)(CO)_4]$ (X = S or O) which react with $[Mo(CO)_3(\eta - C_6H_3Me_3 - 1,3,5)]$ to afford products in which the macrocycles face cap $Mo(CO)_3$ fragments. Reaction of $[Co_2\{\mu - C_2(CH_2SCH_2CH_2)_2S\}(CO)_6]$ with AgBF₄ and PPh₃ yields [Co₂{µ-C₂(CH₂SCH₂CH₂)₂S}(CO)₆{Ag(PPh₃)}]BF₄ for which an X-ray crystallographic study revealed that the Ag(PPh₃)⁺ fragment is co-ordinated by all three sulfur atoms of the ring which adopts an endodentate conformation. Reaction of $[Co_2{\mu-C_2(CH_2SCH_2CH_2)_2S(CO)_6}]$ with $[Cu(MeCN)_4]PF_6$ affords $[Co_2{\mu-C_2(CH_2SCH_2CH_2)_2S}(CO)_{6}(Cu(MeCN))]PF_{6}$ containing a labile acetonitrile ligand which undergoes substitution by phosphines. The dimeric compound $[(OC)_{6}Co_{2}{\mu}-(CCH_{2}SCH_{2}-$ CH₂SCH₂CH₂SCH₂C)₂Co₂(CO)₆] produces a 1:1 adduct when treated with AgBF₄. X-Ray crystallography reveals that the silver ion is co-ordinated by four of the six available thioether groups.

Polythioether macrocycles have been extensively studied in recent years due to their ability to co-ordinate transition metals and coinage metals in unusual oxidation states and geometries.¹ Applications of these versatile ligands are being found in nuclear medicine,² organometallic chemistry,³ and sensors for thiophilic metals such as silver.⁴ We have recently reported a synthetic route to hexacarbonyldicobalt complexed thiacycloalkynes via the acid-catalysed reaction of dithiols with $[Co_2(\mu-HOCR^1R^2C \equiv CCR^1R^2OH)(CO)_6] (R^1 = R^2 = H \text{ or}$ Me; $R^1 = H$, $R^2 = Me$).⁵ In this paper we describe the application of this methodology to the synthesis of hexacarbonyldicobalt cyclic polythioether and mixed ether-thioether systems containing three or six heteroatoms and a preliminary investigation of their co-ordination chemistry. Motivation for this study came from the previous observation that the structure of $[(Ph_3P)(OC)_5Co_2{\mu-(C_2CH_2OSiPh_2 OCH_2_2$ $Co_2(CO)_5(PPh_3)$ could be related to 7,7,16,16tetraphenyldibenzo[e,l][1,3,8,10,2,9]tetraoxadisilacyclotetradecine, highlighting the similarity in geometries of benzene-1,2-dimethanol and the co-ordinated but-2-yne-1,4-diol.⁶ Therefore the monomeric product of the acid-catalysed reaction of [Co₂(µ-HOCH₂C=CCH₂OH)(CO)₆] with bis(2-mercaptoethyl) sulfide, $[Co_2{\mu-C_2(CH_2SCH_2CH_2)_2S}(CO)_6]$,⁷ may reasonably be expected to have a similar geometry and display similar co-ordination chemistry to 2,5,8-trithia[9]-o-benzenophane (ttob). The co-ordination chemistry of 1,4,7-trithiacyclononane and related cyclic polythioethers¹ suggests that the best ligating properties are obtained when the sulfur donor atoms are preorganised in an endodentate conformation. Although the conformation of free ttob is exodentate,^{8,9} there is considerable strain in the SCH₂CH₂SCH₂CH₂S bracket and

the ligand easily converts into an endodentate conformation, as demonstrated by the structures of $[Mo(CO)_3(ttob)]$,⁹ [Cu-(PMePh₂)(ttob)]ClO₄,¹⁰ [Ag(PPh₃)(ttob)]ClO₄,¹⁰ [PdCl₂-(ttob)]¹¹ and [Ag(ttob)₂]X (X = ClO₄, BPh₄ or CF₃SO₃).¹² It has been observed that incorporation of metallocene redoxactive centres into various macrocyclic host structural frameworks is of potential use in the design of sensory devices¹³ and the use of dicobalt alkynes in sensor applications is currently being investigated.¹⁴ Parts of this work have appeared in preliminary communications.^{7,15}

Results and Discussion

Reaction of [Co₂(µ-HOCH₂C≡CCH₂OH)(CO)₆] with bis(2mercaptoethyl) sulfide in the presence of HBF₄·OEt₂ affords the cyclic compounds la and lb as well as a small amount of uncvclised $[Co_2{\mu-(HOCH_2C=CCH_2SCH_2CH_2SCH_2CH_2-}$ SH)(CO)₆]. The products were separated by column chromatography and the molecular weights of the monomer and dimer confirmed by mass spectroscopy (see Experimental section). Compounds 2a and 2b were similarly prepared by reaction of [Co2(µ-HOCH2C=CCH2OH)(CO)6] with bis(2mercaptoethyl) ether. Analytical and IR data for the new compounds are given in Table 1, NMR data in Table 2. Single crystals of la suitable for X-ray diffraction were obtained by cooling a saturated light petroleum solution of the compound to ca. 260 K. Selected structural parameters are listed in Table 3 and the molecular structure is shown in Fig. 1.

The complex has crystallographically imposed two-fold symmetry. The central sulfur atom, S(2), and the midpoint of the Co-Co(A) vector lie on the two-fold axis and atoms with a suffix A are generated by symmetry. The molecular structure comprises of a hexacarbonyldicobalt unit transversely bridged by 1,4,7-trithiacycloundec-9-yne. All the bond lengths and angles about the pseudo-tetrahedral Co_2C_2 core are within the

[†] Supplementary data available: see Instructions for Authors, J. Chem. Soc., Dalton Trans., 1993, Issue 1, pp. xxiii-xxviii.

				Analysis (%)		
Compound	Colour	Yield (%)	${ ilde{\mathbf{v}}_{\parallel}}(extsf{CO})/ extsf{cm}^{-1}$	C	Н	
1a	Red	59	2093m, 2056vs, 2031s, 2026m, 2013w ^b	33.6 (34.3)	2.6 (2.5)	
1b	Red	20	2093m, 2056vs, 2032s, 2026m, 2014w ^b	33.7 (34.3)	2.6 (2.5)	
2a	Red	38	2092m, 2055s, 2031s, 2009(sh), 1981vw ^b	34.9 (35.5)	2.6 (2.6)	
2b	Red	29	2092m, 2056s, 2031s, 2026(sh), 2009(sh), 1981vw ^b	35.4 (35.5)	2.8 (2.6)	
3-CH ₂ Cl ₂	Pink	57	2023m, 1993s, 1965m, 1947(sh) ^c	50.8 (50.5)	4.0 (4.0)	
4	Red	72	2019m, 1986s, 1958m ^d	55.2 (55.4)	4.2 (4.3)	
5	Orange	76	2098m, 2060vs, 2028s ^c	41.4 (40.6)	3.0 (2.9)	
6	Orange	72	2098m, 2061vs, 2038s ^c	25.3 (26.0)	1.8 (2.0)	
7	Red-brown	60	2097m, 2057vs, 2027s ^c	38.1 (40.0)	2.9 (2.8)	
8	Red	42	2100m, 2062vs, 2040s, 2034(sh) ^c	36.8 (36.2)	2.7 (2.5)	
9	Red	95	2026m, 1997s, 1970m, 1936s, 1832m, 1819(sh) ^c	48.0 (48.1)	3.4 (3.4)	
10	Dark red	34	2024m, 1996s, 1969m, 1931s, 1810s ^c	48.3 (48.9)	4.1 (3.5)	
11	Red	76	2097m, 2059s, 2031s ^e	28.4 (28.6)	2.1 (2.0)	

^a Calculated values are given in parentheses. ^b In light petroleum. ^c In dichloromethane. ^d In benzene. ^e In acetonitrile.



Fig. 1 The molecular structure of compound 1a showing the atom labelling system



ranges normally expected for this type of structure.6,16,17 Dimensions within the ring compare well to those found previously for other macrocyclic thioethers. Sulfur-carbon distances range from 1.803(5) to 1.821(4) Å while the nonbonded distances $S(1) \cdots S(1A)$ and $S(1) \cdots S(2)$ are 5.536 and 4.442 Å, respectively. The ideal sulfur-sulfur 'bite' of the SCH₂CH₂SCH₂CH₂S bracket has been calculated⁹ to be 6.74 Å and may account for angle C(5)-C(4)-C(4A) [149.1(2)°]

being higher than in $[Co_2(\mu-HOCH_2C=CCH_2OH)(CO)_6]$ [143.9(3)°] despite the formation of a cyclic system. In contrast the eight-membered ring system $[Co_2(\mu-CCH_2SCH_2CH_2 SCH_2C)(\mu$ -dppm)(CO)₄] (dppm = Ph₂PCH₂PPh₂) has corresponding angles of 138.2(7) and 139.3(6)^{o.5} The conformations of crown thioethers are usually described in terms of torsional angles, particularly those associated with the $SCH_2CH_2SCH_2CH_2S$ brackets which are formed due to a propensity of S-C bonds to favour gauche placement and C-C bonds to favour *anti* placement when part of a SCH_2 - $CH_2SCH_2CH_2S$ chain. The S(1)-C(6)-C(7)-S(2) torsional angle is -169.1° while the C-S-C-C torsional angles average 63.4° in accord with this general behaviour and the analogous angles found in ttob. The structure of 1a differs from that of ttob significantly in the relationship of the dicobalt fragment to the ring compared to the relationship of the o-benzene fragment to the ring in ttob. The dicobalt unit, although twisted with respect to the plane of the ring, is symmetrically disposed about each side of the ring while the o-benzene fragment lies on one side of the ring in ttob. The dihedral angle between the plane defined by the aromatic ring carbon atoms and the plane defined by the three sulfur atoms in ttob is 96.1°. This difference is also reflected in the torsional angle S(1)-C(5)-C(4)-C(4A) (-72.1°) , which is significantly different from the corresponding angles in ttob $(-138.7 \text{ and } 128.4^\circ)$.

Information concerning the conformations of compounds 1a and 1b in solution was obtained for the ¹H NMR spectra. The results indicate that the molecules are fluxional, with only one apparent AA'BB' pattern for the SCH₂CH₂SCH₂CH₂S moiety. Although the spectra were broadened by the cobalt quadrupole a simulation of 1a was obtained using LAOCOON PC¹⁸ with δ 3.07 and 2.90, J 9.1, J' 6.1 and J_{gem} –13.0 Hz, while sufficient resolution was obtained with 1b recorded in C₆D₆ to perform an iterative fit to obtain δ 2.61(2) and 2.54(2), J 10.47(3), J5.50(3) and $J_{gem} - 12.5(14)$ Hz. The observed and calculated spectra for 1b are shown in Fig. 2. The vicinal coupling constants indicate an equilibrium containing predominantly anti-SCCS fragments in both 1a and 1b.8 For 2a and 2b ¹H NMR spectra of sufficient resolution for detailed analysis were not obtained. The ¹³C NMR spectra for compounds 1 and 2 were as expected (Table 2) with only small chemical shift differences between the monomers and the dimers.

Surprisingly, reaction of $HS(CH_2CH_2S)_3H$ with $[Co_2(\mu HOCH_2C=CCH_2OH)(CO)_6$ in the presence of HBF_4 ·OEt₂ afforded compounds 1a and 1b with only a small amount of the expected $[Co_2{\mu-CCH_2(SCH_2CH_2)_3SCH_2C}(CO)_6]$. A possible explanation is that having formed one thioether linkage the second cation to be generated via protonation and loss of H₂O is stabilised by co-ordination of a thioether in the chain rather than the remaining thiol group. Such co-ordination

Table 1 Analytical^a and physical data

Table 2 Hydrogen-1 and carbon-13 NMR data^a

Compound	¹ H(δ)	$^{13}C(\delta)^{b}$
19	416(s 4H CCH ₂) 309-285(m 8H CH ₂ CH ₂)	1991 (CO) 939 (C ₂) 35.0, 30.4, 28.5 (CH ₂)
14 1h	4.09 (s, 8 H CCH ₂), $3.01-2.85$ (m, 16 H CH ₂ CH ₂)	$199.2 (CO), 94.0 (C_2), 36.9, 33.6, 32.4 (CH_2)$
29	$44(s, 4H, CCH_2), 40[t, 4H, OCH_2, J(HH), 5], 29[t, 4H]$	199.8 (CO) 96.0 (C ₂) 72.3 (OCH ₂) 37.4, 33.3 (CH ₂)
	SCH ₂ , <i>J</i> (HH) 5]	())))))))))))))))))))))))))))))))))))))
2h	42(s 8 H CCH _a) 38[t 8 H OCH _a J(HH) 6] 2.9[t 8 H	199.5 (CO), 95.3 (C ₂), 71.5 (OCH ₂), 37.3, 32.9 (CH ₂)
	SCH ₂ , <i>J</i> (HH) 6]	
3	7.4-7.2 (m. 20 H. Ph), 4.15 (s. 4 H. CCH ₂), 3.50 [t. 2 H. PCH ₂ ,	205.6 (CO), 137–128 (Ph), 95.3 (C ₂), 42.5 [t, PCH ₂ , J(PC)
C	J(PH) 101, 3.14–2.88 (m, 8 H, CH ₂ CH ₂) ^c	201. 36.3. 32.6. 29.9 (CH ₂) ^c
4	7.5-7.1 (m, 20 H, Ph), 4.3 [t, 4 H, CCH ₂ , J(PH) 3], 4.1-3.8	205.0 (CO), 137–128 (Ph), 95.6 (C ₂), 71.7 (OCH ₂), 42.0 [t,
	(m, 4 H, OCH ₂), 3.4 [t, 2 H, PCH ₂ , J(PH) 10], 3.0–2.7	PCH ₂ , J(PC) 19], 38.0, 33.2 (CH ₂)
	$(m, 4 H, SCH_2)$	
5	7.5–7.3 (m, 15 H, Ph), 4.55 (s, 4 H, CCH ₂), 3.3–3.1 (m, 8 H,	200.0 (CO), 135–130 (Ph), 90.4 (C ₂), 37.1, 34.2, 31.2 (CH ₂) ^d
	CH ₂ CH ₂) ^c	
6	4.57, 4.37 [AB, 4 H, CCH ₂ , J(AB) 15], 3.3–2.9 (m, 8 H,	198.6, 197.7 (CO), 118.3 (CN), 87.1 (C ₂), 37.7, 36.7, 33.1 (CH ₂)
	CH_2CH_2 , 2.20 (s, 3 H, CH_3)	
7	7.6–7.2 (m, 15 H, Ph), 4.63, 4.56 [AB, 4 H, CCH ₂ , J(AB) 16],	199.0, 198.2 (CO), 134–129 (Ph), 86.4 (C ₂), 38.7, 37.0, 33.6
	$3.4-2.8 (m, 8 H, CH_2CH_2)$	$(CH_2)^c$
8	7.6–7.1 (m, 20 H, Ph), 4.47 (s, 8 H, CCH ₂), 3.2–2.9 (m, 16 H,	199.8 (CO), 134-130 (Ph), 103.5 [d, PC=CP, J(PC) 41], 89.1
	$CH_2CH_2)^d$	(C ₂), 38.0, 36.8, 33.7 (CH ₂)
9	7.44–7.27 (m, 20 H, Ph), 4.53 [d, 2 H, CCH ₂ , J(HH) 15], 4.33	221.9 [Mo(CO)], 219.9 [Mo(CO) ₂], 205.0, 204.3 [Co(CO) ₂],
	[d of t, 2 H, CCH ₂ , J(HH) 15, J(PH) 4], 3.46 [t, 2 H, PCH ₂ ,	137–128 (Ph), 88.1 (C ₂), 44.1 (CH ₂), 41.3 [t, PCH ₂ P, J(PC)
	$J(PH)$ 10], 3.01–2.68 (m, 8 H, $CH_2CH_2)^c$	20], 35.2, 33.5 $(CH_2)^d$
10	7.3–7.1 (m, 20 H, Ph), 4.6–2.8 (m, 14 H, CH ₂) ^c	227.0 [Mo(CO)], 220.3 [Mo(CO) ₂], 204.9, 204.6 [Co(CO) ₂],
		138–129 (Ph), 87.9 (C ₂), 71.0 (OCH ₂), 40.8 [t, PCH ₂ P, J(PC)
		20], 42.8, 33.5 (CH ₂) ^c
11	4.20 (s, 8 H, CCH ₂), 3.06 (s, 16 H, CH ₂ CH ₂) ^d	200.2 (CO), 92.5 (C ₂), 37.8, 33.9, 33.2 (CH ₂) ^d
" Chemical shift	fts (δ) in ppm, coupling constants in Hz. Measured in CDCl ₃ unless of	therwise stated. ^b Hydrogen-1 decoupled. ^c Measured in CD ₂ Cl ₂ .

^{*a*} Chemical shifts (δ) in ppm, coupling constants in Hz. Measured in CDCl₃ unless otherwise stated. ^{*b*} Hydrogen-1 decoupled. ^{*c*} Measured in CD₂Cl₂. ^{*d*} Measured in CD₃CN.

Table 3 Selected internuclear distances (Å), angles (°) and torsional angles (°) for complex 1a

Co-C(1)	1.817(6)	C(1)-O(1)	1.123(8)	CoC(2)	1.824(6)	S(2)-C(7A)	1.821(4)
Co-C(3)	1.806(6)	C(3)-O(3)	1.128(8)	Co-C(4)	1.962(4)	C(2)-O(2)	1.117(9)
Co-Co(A)	2.498(2)	C(4)- $Co(A)$	1.964(4)	Co-C(4A)	1.964(4)	C(4)C(5)	1.485(6)
S(1)-C(5)	1.815(4)	C(6)-C(7)	1.509(6)	S(1)-C(6)	1.803(5)	C(4)-C(4A)	1.346(8)
S(2)-C(7)	1.820(4)						
C(1)-Co-C(2)	106.2(3)	C(3)-Co-Co(A)	145.8(2)	S(1)-C(5)-C(4)	115.6(3)	C(4)CoC(4A)	40.1(2)
C(2)-Co-C(3)	100.5(3)	C(7)-S(2)-C(7A)	101.1(3)	S(2)-C(7)-C(6)	115.1(3)	C(5)-S(1)-C(6)	101.0(2)
C(2)-Co-C(4)	106.3(2)	C(5)-C(4)-C(4A)	149.1(2)	C(3)-Co-C(4A)	100.5(2)	S(1)-C(6)-C(7)	112.7(3)
C	C(6)-S(1)-C(5)-C(4)	69.6	C(7A)-S(2)-C(7)	-C(6) 54.3	C(5A)-C(4	A)-C(4)-C(5) 7.9	
C	C(4A) - C(4) - C(5) - S(1)) -72.1	S(1)-C(6)-C(7)-S	S(2) -169.1	C(5)-S(1)-	C(6)–C(7) 72.4	

has been observed by treating the proparglic cationic complex $[Co_2(\mu-HC\equiv CCH_2)(CO)_6]BF_4$ with SR^1R^2 ($R^1 = R^2 = Me$, Et or Pr^i ; $R^1 = Me$, $R^2 = Et$) to form $[Co_2(\mu-HC\equiv CCH_2SR^1-R^2)(CO)_6]BF_4$.¹⁹ Hydrolysis could lead to loss of the fragment $CH_2CH_2SH^+$ and result in the formation of 1a.²⁰ We have already shown that under acid conditions monomers and dimers of this type can interconvert and hence 1b could be obtained.⁵

The bis(diphenylphosphino)methane derivatives 3 and 4 were prepared by substitution of 1a and 2a respectively. Compound 3 consistently gave low carbon and hydrogen analyses (Table 1) suggesting the presence of 1 mol equivalent of dichloromethane in the solid. This was also observed in the ¹H NMR spectra. The molecular weight of 3 was confirmed by FAB mass spectroscopy (see Experimental section). The NMR spectra of 3 and 4 are similar to previously prepared compounds⁵ and were not sufficiently well resolved to establish the ring conformations.

Reaction of an acetonitrile solution of compound 1a with equimolar quantities of $AgBF_4$ and PPh_3 affords 5. Formation of a cationic complex is reflected in the IR spectrum by a small shift of the cobalt carbonyl absorptions to higher wavenumber (*ca.* 4 cm⁻¹). The NMR spectra of 5 show that the compound is fluxional at room temperature and will be discussed in detail after the results of an X-ray crystallographc study which established the solid-state structure. Selected structural

parameters are listed in Table 4 and the molecular structure is shown in Fig. 3. The $Ag(PPh_3)^+$ fragment is co-ordinated by all three sulfur atoms of the ring, which now adopts an endodentate conformation. Torsional angles about the C-C bonds are 61.4 and 63.0°. The structure can be compared with that of $[Ag(PPh_3)(ttob)]^+$ with distortions caused by the steric bulk of the dicobalt unit, and the wider angles at the acetylenic carbons $[C(2)-C(1)-C(8) \quad 147.6(6) \text{ and } C(1)-C(8)-C(7) \quad 147.8(5)^{\circ}]$ compared with those in the benzenophane (ca. 123°).¹⁰ The Ag-S distances are 2.579(2) and 2.595(2) Å for S(1) and S(3) and 2.688(2) Å for the central S(2) atom. These distances are respectively 0.014, 0.041 and 0.088 Å longer than the corresponding distances in [Ag(PPh₃)(ttob)]⁺. The S-Ag-S angles for the five-membered chelate rings are 82.1(1) and 83.7 (1)°, and the S-Ag-S angle for the seven-membered chelate ring is 104.8(1)°. The silver-phosphorus distance [2.416(2) Å] is longer than the corresponding distance in [Ag(PPh₃)(ttob)]⁺ [2.382(1) Å].

The room-temperature ¹H NMR spectrum of compound 5 contains a single resonance due to the methylene protons adjacent to the alkyne carbons at δ 4.55, compared to δ 4.16 for 1a, and broad unresolved multiplets for the backbone methylenes and the aromatic protons. Low-temperature ¹H NMR spectra are in accord with the solid-state structure; the methylene protons adjacent to the alkyne carbons appear as an AB pattern (δ 4.63, 4.56, $J_{AB} = 16$ Hz) at 212 K, indicating that



Fig. 2 The AA'BB' ¹H NMR spectrum of the $SCH_2CH_2SCH_2CH_2S$ section of compound **1b**: (*a*) observed and (*b*) simulated with LAOCOON PC



at room temperature a fluxional process equivalences both sides of the macrocyclic ring. This is not observed in $[Ag(PPh_3)(ttob)]^+$ where the chemical shift difference between the benzylic protons is larger.¹⁰ Fluxionality in compound **5** could be achieved by the $Ag(PPh_3)^+$ pivoting about the unique sulfur and hence migrating between the two faces or by intermolecular exchange of $Ag(PPh_3)^+$ fragments.

Reaction of equimolar quantities of compounds 1a and $[Cu(MeCN)_4]PF_6$ at room temperature affords 6 containing a co-ordinated $Cu(MeCN)^+$ fragment. The NMR spectra of 6 reveal that it is static on the NMR time-scale at room temperature. The acetylenic methylenes appear as an AB



Fig. 3 The molecular structure of compound 5 showing the atom labelling system

pattern and two resonances are observed in the ¹³C-{¹H} NMR spectrum for the carbonyl ligands. The acetonitrile ligand is very labile and the highest-mass fragment observed in the FAB mass spectrum corresponds to $[M - PF_6 - MeCN]^+$. The analysis for nitrogen was consistently low, also suggesting ready loss of the acetonitrile.

Reaction of compound 6 with triphenylphosphine results in substitution of the acetonitrile with triphenylphosphine to produce 7 in a similar manner to the reactions of [Cu(MeCN)-(ttob)]⁺.¹⁰ Reaction of 6 with 1,2-bis(diphenylphosphino)ethane (dppe) abstracts the copper ion to afford [Cu(dppe)₂]⁺ and **1a** is released. This contrasts with the observation that 2,5,8,17,20,23-hexathia[9](1,2)[9](4,5)cyclophane (L) reacts with [Cu(MeCN)₄]PF₆ and dppe to afford [Cu₂L(μ -dppe)]-[PF₆]₂ in which the dppe bridges between the two copper atoms.²¹ Reaction of 6 with bis(diphenylphosphino)acetylene (dppa) which is incapable of chelation affords [Co₂{ μ -C₂(CH₂SCH₂CH₂)₂S}(CO)₆[CPF₆]₂ **8** in which the two copper centres are linked by dppa.

Attempts to prepare molybdenum tricarbonyl derivatives of 1a were hampered by its thermal instability, which rapidly decomposes above 60 °C. Compounds 3 and 4 in which the metal-metal bond is supported by a dppm ligand are more stable and were treated with $[Mo(CO)_3(\eta-C_6H_3Me_3-1,3,5)]$ in refluxing tetrahydrofuran to afford 9 and 10 which are not stable to chromatography on Florisil and were purified by filtration and crystallisation. The NMR spectra of 9 revealed that the mesitylene had been displaced by the three thioether functionalities of the macrocyclic ring. In the ¹H NMR spectrum the methylenic hydrogens appear as a doublet and a doublet of triplets, indicating that the Mo(CO)₃ fragment is coordinated to one face of the ring and is static on the NMR timescale. The small triplet coupling of 4 Hz is ascribed to long-range phosphorus coupling. The ¹³C-{¹H} NMR spectrum contains resonances due to the molybdenum carbonyl ligands at δ 221.9 and 219.9 in the ratio 1:2 and two broader peaks assigned to the cobalt carbonyls. Only one alkyne carbon resonance is observed indicating that alkyne rocking about the cobalt-cobalt vector is fast on the NMR time-scale at room temperature.⁵ Compound 10 is analogous to 9, but considerably less stable.

Table 4 Selected internuclear distances (Å), angles (°) and torsional angles (°) for complex 5

Ag-S(1)	2.579(2)	Ag-S(2)	2.688(2)	Ag-S(3)	2.595(2)	Ag–P	2.416(2)
Co(1)-Co(2)	2.466(2)	$C_{0}(1)-C(1)$	1.968(4)	Co(1)-C(8)	1.949(5)	Co(1)-C(41)	1.766(7)
Co(1) - C(42)	1.817(6)	Co(1)-C(43)	1.821(7)	Co(2)-C(1)	1.970(5)	Co(2)C(8)	1.958(5)
Co(2) - C(44)	1.816(7)	Co(2)-C(45)	1.794(5)	Co(2)-C(46)	1.826(7)	S(1)-C(2)	1.822(7)
S(1)-C(3)	1.826(5)	S(2)-C(4)	1.820(6)	S(2)-C(5)	1.819(7)	S(3)-C(6)	1.837(8)
S(3)-C(7)	1.836(6)	C(1)-C(2)	1.492(7)	C(1)-C(8)	1.328(7)	C(3)-C(4)	1.506(10)
C(5)-C(6)	1.499(7)	C(7)-C(8)	1.482(8)	C(41)-O(41)	1.127(10)	C(42)-O(42)	1.132(8)
C(43)-O(43)	1.132(10)	C(44)-O(44)	1.132(9)	C(45)-O(45)	1.130(6)	C(46)-O(46)	1.114(9)
S(1)-	-Ag-S(2)	82.1(1)	S(1)-Ag- $S(3)$	104.8(1)	S(2)-Ag-S(3)	83.7(1)	
S(1)-	-Ag-P	126.8(1)	S(2)-Ag-P	118.9(1)	S(3)-Ag-P	124.5(1)	
Ag-	S(1) - C(2)	113.8(1)	Ag - S(1) - C(3)	99.7(2)	C(2)-S(1)-C(3)) 100.0(3)	
Ag-	S(2) - C(4)	100.3(2)	Ag-S(2)-C(5)	100.1(2)	C(4)-S(2)-C(5	b) 102.5(3)	
Ag-	S(3)-C(6)	97.7(2)	Ag-S(3)-C(7)	114.7(2)	C(6)-S(3)-C(7	⁽⁾ 100.2(3)	
Ag-1	P-C(11)	118.6(2)	Ag-P-C(21)	114.7(1)	C(11)-P-C(21) 103.8(2)	
Ag-	P-C(31)	109.7(1)	C(11)-P-C(31)	103.6(2)	C(21)-P-C(31) 105.0(3)	
Co(1	1)-C(1)-Co(2)	77.5(2)	Co(1)-C(1)-C(2)	131.8(3)	Co(2)-C(1)-C	(2) 132.0(3)	
Co(1	I)C(1)C(8)	69.4(3)	Co(2)-C(1)-C(8)	69.8(3)	C(2)-C(1)-C(8	B) 147.6(6)	
S (1)-	-C(2)-C(1)	117.0(4)	S(1)-C(3)-C(4)	111.7(4)	S(2)-C(4)-C(3	6) 116.3(3)	
S(2)-	-C(5)-C(6)	115.9(4)	S(3)C(6)C(5)	116.0(5)	S(3)-C(7)-C(8	b) 113.4(4)	
Co(1	1)-C(8)-Co(2)	78.3(2)	Co(1)-C(8)-C(1)	71.0(3)	Co(2)-C(8)-C	(1) 70.7(3)	
Co(1	1)-C(8)-C(7)	133.5(3)	Co(2)-C(8)-C(7)	127.6(3)	C(1)-C(8)-C(3	7) 147.8(5)	
C(1)	-C(2)-S(1)-C(3)	62.7	C(8)-C(1)-C(2)-S(1) -3.8	C(4)-C(3)-S(1)-C(2) - 171.4	
C(5)	-S(2)-C(4)-C(3)	70.8	S(2)-C(4)-C(3)-S(1)	1) 63.0	C(6)-C(5)-S(2	-C(4) - 133.8	
C(5)	-C(6)-S(3)-C(7)	64.7	S(3)-C(6)-C(5)-S(2	2) 61.4	C(8)-C(7)-S(3	-148.4	
C(7)	-C(8)-C(1)-C(2)	7.5	S(3)-C(7)-C(8)-C(1) 63.3			





BF₄

11

The dimeric compound 1b has six thioether functionalities and was treated with $AgBF_4$ to establish whether a soft metal ion could be encapsulated. Analytical data and FAB mass spectroscopy established that the product 11 was a 1:1 adduct. Compound 11 has poor solubility in most solvents and only a relatively weak ${}^{13}C{}^{1}H$ NMR spectrum could be obtained in acetonitrile. The NMR spectra indicated that 11 was either very symmetrical or fluxional. Variable-temperature studies were made impractical by the low solubility, but fortunately it was possible to obtain single crystals for X-ray crystallography. Selected structural parameters are listed in Table 5 and the molecular structure is shown in Fig. 4. The silver ion is coordinated by four of the thioether groups leaving two uncomplexed. The effect of complexation on the macrocycle conformation is demonstrated by the anti arrangements of S(1)-C(53)-C(54)-S(2) and S(5)-C(63)-C(64)-S(6) compared to the gauche arrangements of S(2)-C(55)-C(56)-S(3) and S(4)-C(61)-C(62)-S(5). The silver ion is in a severely distorted tetrahedral co-ordination sphere and is displaced towards the centre of the macrocycle. Hence the distances Ag-S(3) [2.635(3) Å] and Ag-S(4) [2.634(3) Å] are considerably longer than Ag-S(2) [2.493(3) Å] and Ag-S(5) [2.493(3) Å] and the angle S(2)-Ag-S(5) [144.2(1)°] is large. The S-Ag-S angles for the five-membered chelate rings [86.4(1) and 85.5(1)°] and for the seven-membered chelate ring [101.8(1)^o] are consistent with other silver thiamacrocycle structures.¹² At the uncomplexed end of the macrocycle the alkyne angles C(52)-C(51)-C(66) [149.1(11)°] and C(65)-C(66)-C(51) [145.8(11)°] are similar to that in 1a [149.1(2)°], while the analogous angles at the complexed end are considerably reduced [142.0(10) and 141.7(10)°]. A possible explanation of the appearance of only one acetylenic resonance, one carbonyl resonance and three methylenic resonances in the ¹³C-{¹H} NMR spectrum of 11 is that the silver ion migrates between the two ends of the macrocycle.

In conclusion it has been shown that, despite their endodentate conformations and increased steric bulk compared to simpler thiamacrocycles, dicobalt-complexed thiacycloalkynes can act as ligands for silver(I), copper(I) and molybdenum(0) centres. The use of such compounds in sensors is currently being explored.¹⁴

Experimental

The general experimental procedures have been described previously.²² The compounds $[Co_2(\mu-HOCH_2C=CCH_2OH)-(CO)_6]^{23}$ and $[Cu(MeCN)_4]PF_6^{24}$ were prepared by literature methods. Analytical and other data for the new compounds are given in Tables 1 and 2.

Reaction of $[Co_2(\mu-HOCH_2C=CCH_2OH)(CO)_6]$ with Bis(2mercaptoethyl) Sulfide.—To a solution of $[Co_2(\mu-HOCH_2-CH_2)]$

Table 5 Selected internuclear distances (Å), angles (°) and torsional angles (°) for compex 11

Ag-S(2)	2.493(3)	Ag-S(3)	2.635(3)	Ag-S(4)	2.634(3)	AgS(5)	2.493(3)
Co(1)-Co(2)	2.465(2)	Co(1)-C(51)	1.973(11)	Co(1)-C(66)	1.964(10)	Co(2)-C(51)	1.961(10)
Co(2)-C(66)	1.960(11)	Co(3)-Co(4)	2.469(2)	Co(3)-C(58)	1.967(11)	Co(3)-C(59)	1.950(10)
Co(4)-C(58)	1.940(10)	Co(4)C(59)	1.999(11)	C(51)-C(52)	1.492(16)	C(51)-C(66)	1.318(15)
C(52) - S(1)	1.824(11)	S(1)-C(53)	1.771(12)	C(53)-C(54)	1.535(17)	C(54)-S(2)	1.833(11)
S(2) - C(55)	1.804(13)	C(55)-C(56)	1.502(15)	C(56)-S(3)	1.814(12)	S(3)-C(57)	1.823(11)
C(57)-C(58)	1.481(15)	C(58)-C(59)	1.361(16)	C(59)-C(60)	1.473(16)	C(60) - S(4)	1.841(11)
S(4)-C(61)	1.828(13)	C(61)-C(62)	1.485(15)	C(62) - S(5)	1.823(13)	S(5)-C(63)	1.830(11)
C(63)-C(64)	1.534(16)	C(64)–S(6)	1.821(11)	S(6)-C(65)	1.814(12)	C(65)-C(66)	1.499(17)
S(2)–Ag–	S(3)	86.4(1)	S(2)-Ag-S(4)	119.2(1)	S(3)-Ag-S(4) 101	.8(1)
S(2)-Ag-	S(5)	144.2(1)	S(3)-Ag-S(5)	115.3(1)	S(4) - Ag - S(5)) 85.	.5(1)
Co(1)-C(51)-Co(2)	77.6(4)	Co(1) - C(51) - C(52)	131.7(7)	Co(2)-C(51)	-C(52) 130.	.1(8)
Co(1)-C(51)-C(66)	70.1(7)	Co(2)-C(51)-C(66)	70.3(6)	C(52)-C(51)	-C(66) 149.	.1(11)
C(51)-C(52)–S(1)	114.6(8)	C(52)-S(1)-C(53)	103.8(5)	S(1)-C(53)-	C(54) 110	.7(8)
C(53)-C(54)–S(2)	110.3(8)	Ag-S(2)-C(54)	115.2(4)	Ag-S(2)-C(55) 101.	.5(4)
C(54)-S(2	2)-C(55)	100.3(6)	S(2)-C(55)-C(56)	116.9(8)	C(55)-C(56)	-Ś(3) 116.	.3(9)
Ag-S(3)-	C(56)	94.4(4)	Ag-S(3)-C(57)	102.1(4)	C(56)-S(3)-	C(\$7) 99.	.9(5)
S(3)-C(57	7)-C(58)	110.6(7)	Co(3)-C(58)-Co(4)	78.4(4)	Co(3)-C(58)	-C(57) 130	.0(7)
Co(4)-C(58)–C(57)	137.2(8)	Co(3)-C(58)-C(59)	69.0(6)	Co(4)-C(58)	-C(59) 72	.1(6)
C(57)-C(58)–C(59)	142.0(10)	Co(3)-C(59)-Co(4)	77.4(4)	Co(3)-C(59)	-C(58) 70.	.3(6)
Co(4)-C(59)–C(58)	67.5(6)	Co(3)-C(59)-C(60)	139.0(8)	Co(4)-C(59)	-C(60) 131	.2(7)
C(58)C(59)–C(60)	141.7(10)	C(59)-C(60)-S(4)	107.6(7)	Ag-S(4)-C(6	50) 103.	.3(4)
Ag-S(4)-	C(61)	94.8(4)	C(60)-S(4)-C(61)	100.2(5)	S(4)-C(61)-	C(62) 116	9(9)
C(61)–C(62)–S(5)	116.3(8)	Ag-S(5)-C(62)	103.0(4)	Ag-S(5)-C(6	53) 115.	.1(3)
C(62)-S(5	5)-C(63)	101.2(6)	S(5)C(63)C(64)	107.5(8)	C(63)-C(64)	-S(6) 110.	4(8)
C(64)-S(6	6)C(65)	103.9(5)	S(6)-C(65)-C(66)	113.9(8)	Co(1)-C(66)	-Co(2) 77.	.8(4)
Co(1)-C(66)–C(51)	70.8(6)	Co(2)-C(66)-C(51)	70.4(7)	Co(1)-C(66)	-C(65) 132.	1(8)
Co(2)C(66)–C(65)	132.1(7)	C(51)-C(66)-C(65)	145.8(11)			
C(66)-C(51)-C	(52) - S(1)	77.8	C(53)-S(1)-C(52)-C(5	1) -90.9	C(54)C(5	3)–S(1)–C(52)	-94.8
S(1)-C(53)-C(53)	i4)–S(2)	-161.2	C(55)-S(2)-C(54)-C(52)	3) -179.6	C(54)–S(2))-C(55)-C(56)	88.9
S(2)-C(55)-C(55)	6)–S(3)	59.6	C(55)-C(56)-S(3)-C(5	7) 54.0	C(58)-C(5	7)-S(3)-C(56)	- 176.1
C(59)-C(58)-C	(57)–S(3)	53.4 (C(60)-C(59)-C(58)-C(57) -18.3	S(4)C(60))C(59)C(58)	59.4
C(61)-S(4)-C(6)	0)C(59)	-177.8	C(60)-S(4)-C(61)-C(62)	2) 54.4	S(4)-C(61))-C(62)-S(5)	56.6
C(61)-C(62)-S((5)-C(63)	93.6	C(64)-C(63)-S(5)-C(63)	2) -177.1	S(5)-C(63))C(64)S(6)	-158.2
C(63)-C(64)-S((6)–C(65)	-94.0	C(66)-C(65)-S(6)-C(64)	4) -93.9	C(65)-C(6	6)-C(51)-C(52)	0.5
S(6)-C(65)-C(6	6)-C(51)	67.5					



Fig. 4 The molecular structure of compound 11 showing the atom labelling system

C=CCH₂OH)(CO)₆] (11.16 g, 30.0 mmol) in CH₂Cl₂ (200 cm³) was added bis(2-mercaptoethyl) sulfide (4.62 g, 30.0 mmol) and four drops of HBF₄·OEt₂. The resulting mixture was stirred for 24 h, after which time an excess of NaHCO₃ (*ca.* 1 g) was added and the solvent reduced to *ca.* 50 cm³ *in vacuo*. The solution was dried over sodium sulfate and filtered through a short plug of Celite (1.5 × 3 cm). The solvent was removed *in vacuo* and the residue chromatographed on a Florisil column (10 × 2.0 cm) eluting with light petroleum (b.p. 40–60 °C)–CH₂Cl₂ (4:1) to produce a red band. Removal of the solvent *in vacuo* afforded compound 1a (8.64 g, 17.63 mmol). Mass spectrum (FAB): *m/z* 491, [*M* +H]⁺; 434, 406, 378, 350 and 322 [*M* – *n*CO]⁺ (*n* = 2–6). Elution of the column with light petroleum-CH₂Cl₂ (1:1) produced a second red band which after removal of the solvent afforded 1b (2.99 g, 3.05 mmol). Mass spectrum (FAB):

m/z 812, 728, 700, 672 and 644, $[M - nCO]^+$ (n = 6, 9-12). Finally elution with a 9:1 solvent mixture produced a third red band of $[Co_2(\mu$ -HOCH₂C=CCH₂SCH₂CH₂SCH₂CH₂SCH₂CH₂SH)-(CO)₆] (1.30 g, 2.56 mmol).

Reaction of $[Co_2(\mu-HOCH_2C=CCH_2OH)(CO)_6]$ with Bis(2mercaptoethyl) Ether.—To a solution of $[Co_2(\mu-HOCH_2-C=CCH_2OH)(CO)_6]$ (0.8 g, 2.20 mmol) in CH_2Cl_2 (60 cm³) was added bis(2-mercaptoethyl) ether (0.30 g, 2.20 mmol) and four drops of HBF₄·OEt₂. The resulting mixture was stirred for 30 h, after which time an excess of NaHCO₃ (*ca.* 0.25 g) was added and the solvent removed *in vacuo*. The residue was extracted with light petroleum (5 × 10 cm³) and filtered through a short plug of magnesium sulfate (1.5 × 3 cm). The solvent was removed *in vacuo* and the residue chromato-

Table 6 Atomic coordinates $(\times 10^4)$ for compound **1a**, with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	У	Ζ
Со	434(1)	1709(1)	1119(1)
S(1)	-2053(1)	3389(1)	2712(2)
S(2)	0	5298(1)	2500
C(1)	1583(5)	1224(3)	1572(9)
O(1)	2314(4)	963(3)	1894(8)
C(2)	- 376(5)	1048(3)	77(9)
O(2)	- 893(5)	653(3)	- 545(8)
C(3)	825(4)	2257(3)	-646(7)
O(3)	1039(3)	2640(3)	-1695(5)
C(4)	-442(3)	2455(2)	2105(5)
C(5)	-1260(3)	2873(2)	1301(5)
C(6)	-1214(3)	4101(2)	3392(5)
C(7)	-1010(3)	4663(2)	2047(5)

graphed on a Florisil column (10×1.5 cm). Elution with light petroleum-CH₂Cl₂ (3:2) produced a red band which after removal of the solvent *in vacuo* afforded compound **2a** (0.40 g, 0.84 mmol). Mass spectrum (electron impact, EI): m/z 474, 446, 418, 390, 362, 334 and 306, $[M - nCO]^+$ (n = 0-6). Further elution of the column with CH₂Cl₂-tetrahydrofuran (thf) (98:2) yielded a second red band which upon removal of the solvent afforded **2b** (0.30 g, 0.32 mmol).

Carbonyl-substitution Reactions.—Complex 1a (0.24 g, 0.49 mmol) and dppm (0.19 g, 0.49 mmol) were dissolved in benzene (15 cm³), the resulting solution refluxed for 20 min and then the solvent was removed *in vacuo*. The residue was dissolved in CH₂Cl₂ and filtered through a plug of Florisil (5 × 1.5 cm) before crystallisation by addition of light petroleum to afford compound 3 (0.23 g, 0.28 mmol). Mass spectrum (FAB): m/z 819 $[M + H]^+$. Complex 4 was prepared in a similar manner.

Preparation of $[Co_2\{\mu-C_2(CH_2SCH_2CH_2)_2S\}(CO)_6$ [Ag-(PPh₃)]BF₄ 5.—To a solution of $[Co_2\{\mu-C_2(CH_2SCH_2-CH_2)_2S\}(CO)_6]$ (3.23 g, 6.6 mmol) in MeCN (200 cm³) was added dropwise a solution of AgBF₄ (1.27 g, 6.6 mmol) and PPh₃ (1.72 g, 6.6 mmol) in MeCN (50 cm³) over a period of 10 min and allowed to stir for 24 h. After reduction of the solvent volume to *ca*. 50 cm³ under reduced pressure the solution was filtered through a Celite pad (5 × 1.5 cm) and then the solvent removed *in vacuo*. The residue was recrystallised from CH₂Cl₂ by addition of Et₂O to afford compound **5** (4.74 g, 5.0 mmol). Mass spectrum (FAB): m/z 859, 775, 719 and 691, $[M - BF_4 - nCO]^+$ (n = 0, 3, 5 or 6).

Preparation of $[Co_2{\mu-C_2(CH_2SCH_2CH_2)_2S}(CO)_6-{Cu(MeCN)}]PF_6 6.$ —To a solution of $[Co_2{\mu-C_2(CH_2SCH_2-CH_2)_2S}(CO)_6]$ **1a** (3.23 g, 6.6 mmol) in MeCN (200 cm³) was added dropwise a solution of $[Cu(MeCN)_4]PF_6$ (2.46 g, 6.6 mmol) in MeCN (50 cm³) over a period of 15 min and allowed to stir for 24 h. After reduction of the solvent volume to *ca*. 40 cm³ under reduced pressure the solution was filtered through a Celite pad (5 × 1.5 cm) and then further reduced to *ca*. 5 cm³. Addition of Et₂O (80 cm³) afforded a crystalline product after 2 h at 263 K which was washed with Et₂O (10 cm³) to afford compound **6** (3.51 g, 4.8 mmol). Mass spectrum (FAB): m/z 553, 525, 497, 469, 441, 413 and 385, $[M - MeCN - nCO]^+$ (n = 0–6).

Reaction of $[Co_2\{\mu-C_2(CH_2SCH_2CH_2)_2S\}(CO)_6\{Cu(Me-CN)\}]PF_6$ with Phosphines.—To a solution of $[Co_2\{\mu-C_2(CH_2SCH_2CH_2)_2S\}(CO)_6\{Cu(MeCN)\}]PF_6$ 6 (0.10 g, 0.14 mmol) in MeCN (40 cm³) was added dropwise a solution of PPh₃ (0.035 g, 1.4 mmol) in MeCN (10 cm³). The resulting mixture was stirred for 2 h and then the solvent was removed *in vacuo*. The red-brown product was washed with Et₂O (3 × 20 cm³) and dried under vacuum to afford $[Co_2\{\mu-C_2(CH_2)CH_2(CH_2)C$

SCH₂CH₂)₂S}(CO)₆{Cu(PPh₃)}]PF₆ 7 (0.081 g, 0.08 mmol). Mass spectrum (FAB): m/z 815, 787, 759, 731, 703, 675 and 647, $[M - PF_6 - nCO]^+$ (n = 0-6). ³¹P-{¹H} NMR (CD₂Cl₂): δ 3.98. Compound 8 was prepared in a similar manner. Mass spectrum (FAB): m/z 1647, $[M - PF_6]^+$.

Reactions with $[Mo(CO)_3(\eta-C_6H_3Me_{3}-1,3,5)]$.—A solution of compound **3** (0.13 g, 0.16 mmol) and $[Mo(CO)_3(\eta-C_6H_3-Me_{3}-1,3,5)]$ (0.05 g, 0.17 mmol) in thf (20 cm³) was refluxed for 30 min. The solvent was removed *in vacuo* and the residue dissolved in CH₂Cl₂ (20 cm³) before filtering through a plug of Celite (5 × 1.5 cm). Reduction of the solvent volume *in vacuo* and addition of light petroleum afforded compound **9** (0.15 g, 0.015 mmol).

To a solution of complex 4 (0.95 g, 1.27 mmol) in thf (40 cm³) was added [Mo(CO)₃(η -C₆H₃Me₃-1,3,5)] (0.38 g, 1.27 mmol) and the resulting solution refluxed for 0.75 h, after which time the solution was cooled to room temperature and the solvent removed *in vacuo*. The resulting dark red residue was dissolved in CH₂Cl₂-light petroleum (1:1) then filtered through a plug of Celite (7 × 1.5 cm). The solvent was again removed *in vacuo* and then the residue recrystallised four times from CH₂Cl₂ (2.5 cm³) by addition of light petroleum (80 cm³) to afford compound **10** as a dark red precipitate (0.40 g, 0.43 mmol).

Reaction of Compound 1b with AgBF₄.—To solution of compound 1b (0.14 g, 0.14 mmol) in MeCN (20 cm³) was added AgBF₄ (0.028 g, 0.14 mmol). The mixture was stirred for 3 h at room temperature and then the solvent reduced *in vacuo* to *ca*. 2 cm³. Diethyl ether was added to precipitate the product, which was recrystallised by slow diffusion of Et₂O into a CH₂Cl₂ solution to afford red crystals of compound 11 (0.13 g, 0.11 mmol). Mass spectrum (FAB): m/z 1089, $[M - BF_4]^+$

Crystal Structure Determinations.—Crystals of compound 1a were obtained from light petroleum as deep red prisms with dimensions ca. $0.62 \times 0.60 \times 0.45$ mm. Data were collected using a Nicolet P3 diffractometer (295 K, Mo–K α X-radiation, graphite monochromator, $\overline{\lambda} = 0.710$ 73 Å). Of the 1997 data collected (Wyckoff ω scans, $2\theta \leq 50^{\circ}$), 1192 unique data had $F \geq 5\sigma(F)$, and only these were used for the structure solution and refinement. The data were corrected for Lorentz, polarisation and X-ray absorption effects, the latter by a method based upon azimuthal scan data.²⁵

Crystal data for 1a: $C_{14}H_{12}Co_2O_6S_3$, M = 490.3, orthorhombic, space group *Pbcn*, a = 13.458(4), b = 18.195(5), c = 7.996(2) Å, U = 1958.1(9) Å³, Z = 4, $D_c = 1.66$ g cm⁻³, F(000) = 984, μ (Mo-K α) = 20.2 cm⁻¹.

The structure was solved by conventional heavy-atom methods and successive Fourier difference syntheses were used to locate all non-hydrogen atoms. The complex has crystallographically imposed two-fold symmetry. The central sulfur atom, S(2), and the midpoint of the Co-Co(A) vector lie on the two-fold axis and atoms with a suffix 'A' are generated by symmetry. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions (C-H 0.96 Å) with fixed isotropic thermal parameters (U = 0.08 Å²). Refinement by full-matrix least squares led to R = 0.038 (R' = 0.042) and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.005|F|^2]$ gave a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks > 0.4 or < -0.4 e Å⁻³. Atomic coordinates are listed in Table 6.

Crystals of compound 5 were obtained by solvent diffusion from CH₂Cl₂-light petroleum as deep red prisms with crystal dimensions *ca.* $0.62 \times 0.50 \times 0.45$ mm. Data were collected using a Siemens R3m/V diffractometer (295 K, Mo-K α Xradiation, graphite monochromator, $\lambda = 0.710$ 73 Å). Of the 6825 data collected (Wyckoff ω scans, $2\theta \leq 50^{\circ}$), 5131 unique data had $F \geq 5\sigma(F)$, and only these were used for the structure solution and refinement. The data were corrected as above.

Atom	x	у	Z	Atom	x	у	z
Ag	4957(1)	1371(1)	3024(1)	C(46)	8032(5)	4474(5)	674(4)
Co(1)	5032(1)	3188(1)	875(1)	O(46)	8531(5)	4266(5)	52(4)
Co(2)	7239(1)	4767(1)	1708(1)	C(11)	1530(4)	-738(4)	1972(3)
S(1)	5675(1)	3627(1)	3976(1)	C(12)	237(5)	-1022(5)	2094(4)
S(2)	7300(1)	1802(1)	4135(1)	C(13)	-839(5)	- 1560(6)	1285(5)
S(3)	6222(1)	1037(1)	1630(1)	C(14)	- 586(6)	-1838(6)	348(5)
P	2971(1)	-89(1)	2997(1)	C(15)	653(6)	-1553(7)	226(4)
C(1)	5985(4)	3924(4)	2263(3)	C(16)	1725(5)	-1002(5)	1051(4)
C(2)	5530(5)	4342(4)	3193(3)	C(21)	3219(4)	-1363(4)	3060(3)
C(3)	7481(5)	4033(5)	4279(4)	C(22)	4405(5)	-1193(4)	3631(4)
C(4)	7887(6)	3399(5)	4812(4)	C(23)	4632(6)	-2124(5)	3692(4)
C(5)	8283(5)	1585(5)	3217(5)	C(24)	3696(6)	-3249(5)	3168(4)
C(6)	7531(6)	705(5)	2186(5)	C(25)	2530(5)	-3431(4)	2597(4)
C(7)	7237(5)	2387(4)	1586(4)	C(26)	2295(5)	-2486(4)	2543(4)
C(8)	6544(4)	3224(4)	1699(3)	C(31)	2338(4)	559(4)	4067(3)
C(41)	3739(6)	1991(6)	852(6)	C(32)	2130(5)	1595(4)	4240(4)
O(41)	2926(5)	1230(6)	852(7)	C(33)	1636(6)	2118(5)	5032(4)
C(42)	5272(6)	2479(5)	- 354(4)	C(34)	1423(6)	1655(5)	5703(4)
O(42)	5437(6)	2005(5)	-1108(3)	C(35)	1648(6)	647(5)	5541(4)
C(43)	4087(5)	4084(5)	779(4)	C(36)	2095(5)	87(4)	4720(3)
O(43)	3527(5)	4654(4)	706(3)	В	1280(7)	3414(6)	2745(6)
C(44)	6765(5)	6004(5)	1813(4)	F(1)	481(6)	3906(5)	2886(10)
O(44)	6462(5)	6770(4)	1873(4)	F(2)	1968(13)	3681(7)	3573(5)
C(45)	8696(5)	5503(4)	2703(4)	F(3)	2189(7)	3818(6)	2329(7)
O(45)	9593(4)	5968(4)	3346(3)	F(4)	653(5)	2239(4)	2258(3)

Table 7 Atomic coordinates $(\times 10^4)$ for compound 5, with e.s.d.s in parentheses

Table 8 Atomic coordinates ($\times 10^4$) for compound 11, with e.s.d.s in parentheses

Atom	x	у	Ζ	Atom	x	у	Ζ
Aσ	6.052(1)	2.004(1)	2.980(1)	O(43)	10.887(13)	961(3)	4 385(7)
Co(1)	4 285(2)	4 133(1)	2.662(1)	C(51)	6 231(14)	3 786(3)	2 731(7)
$C_0(2)$	7 345(2)	4 166(1)	3 532(1)	C(52)	6 906(15)	3 587(3)	2,007(7)
Co(3)	4 786(2)	620(1)	2 406(1)	S(1)	5 184(5)	3 376(1)	1 172(2)
Co(4)	7 834(2)	603(1)	3 301(1)	C(53)	4 980(16)	2 948(3)	1 626(8)
can	2 361(19)	3 880(4)	2 163(9)	C(54)	6 130(15)	2.679(3)	1227(7)
0(11)	1123(12)	3 720(3)	1 857(9)	S(2)	5 380(4)	2226(1)	1.387(2)
$\tilde{C}(12)$	4 562(17)	4 394(4)	1 674(9)	C(55)	6 944(15)	1 978(3)	874(8)
0(12)	4 835(15)	4 531(3)	1 050(7)	C(56)	8 655(16)	1 873(3)	1 480(8)
C(13)	3202(18)	4 426(4)	3 375(9)	S(3)	8 464(4)	1 599(1)	2 449(2)
O(13)	2 541(13)	4 609(3)	3 793(7)	C(57)	7 119(14)	1 238(3)	1 876(7)
C(21)	8 324(17)	4 431(4)	2 746(8)	C(58)	6 660(14)	982(3)	2 545(7)
O(21)	8 928(13)	4 586(3)	2 237(7)	C(59)	5 921(14)	963(3)	3 301(7)
C(22)	9 365(18)	3 963(4)	4 122(9)	C(60)	5 472(15)	1 184(3)	4 036(7)
O(22)	10 655(12)	3 837(3)	4 478(7)	S(4)	3 932(4)	1 531(1)	3 509(2)
C(23)	6 902(16)	4 459(3)	4 430(8)	C(61)	3 634(16)	1 778(3)	4 519(8)
O(23)	6 522(14)	4 632(3)	4 969(7)	C(62)	5 269(15)	1 906(3)	5 126(7)
C(31)	5 199(16)	369(3)	1 436(8)	S(5)	6 731(4)	2 188(1)	4 605(2)
O(31)	5 571(13)	229(3)	822(7)	C(63)	5 934(15)	2 629(3)	4 840(7)
C(32)	3 672(18)	294(4)	3 044(9)	C(64)	6 988(15)	2 900(3)	4 392(7)
O(32)	3 056(14)	114(3)	3 470(7)	S(6)	6 939(4)	3 332(1)	4 927(2)
C(33)	2 847(17)	864(3)	1 881(8)	C(65)	5 087(16)	3 557(3)	4 222(8)
O(33)	1 649(12)	1 016(3)	1 530(7)	C(66)	5 608(14)	3 783(3)	3 493(7)
C(41)	7 507(16)	268(3)	4 119(8)	B`́	6 013(13)	2 288(3)	8 035(6)
O(41)	7 197(16)	64(3)	4 614(6)	F(1)	4 564(18)	2 089(5)	7 767(13)
C(42)	8 952(16)	361(3)	2 499(8)	F(2)	7 368(18)	2 081(4)	8 416(9)
O(42)	9 544(13)	221(3)	1 974(7)	F(3)	5 687(21)	2 528(3)	8 642(9)
C(43)	9 708(17)	820(3)	3 955(8)	F(4)	6 435(25)	2 455(5)	7 316(9)
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Crystal data for 5. $C_{32}H_{27}AgBCo_2F_4O_6PS_3$, M = 947.2, triclinic, space group *PI*, a = 10.820(5), b = 13.293(7), c = 15.273(9) Å, $\alpha = 113.49(4)$, $\beta = 95.17(4)$, $\gamma = 107.24(4)^\circ$, U = 1869(2) Å³, Z = 2, $D_c = 1.68$ g cm⁻³, F(000) = 944, μ (Mo-K α) = 16.7 cm⁻¹.

The structure was solved and refined as above, leading to R = 0.039 (R' = 0.045), and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0007|F|^2]$ gave a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks >0.87 or < -0.75 e Å⁻³. Atomic coordinates are listed in Table 7.

Crystals of compound 11 were grown from CH₂Cl₂-OEt₂ as

thin red needles and that used was cut from a needle and had dimensions ca. $0.60 \times 0.20 \times 0.10$ mm. Data were collected using a Siemens R3m/v diffractometer (291 K, Mo-Ka Xradiation, graphite monochromator, $\bar{\lambda} = 0.710$ 73 Å). Of the 6159 data collected (Wyckoff ω scans, $2\theta \leq 45^{\circ}$), 3614 unique data had $F \ge 4\sigma(F)$, and only these were used for the structure

solution and refinement. The data were corrected as above. Crystal data for 11. $C_{28}H_{24}AgBCo_4F_4O_{12}S_6$, M = 1175.2, monoclinic, space group $P2_1/n$, a = 7.666(3), b = 37.736(12), c = 14.997(5) Å, $\beta = 100.78(3)^\circ$, U = 4262(2) Å³, Z = 4, $D_c = 1.83$ g cm⁻³, F(000) = 2320, μ (Mo-K α) = 23.4 cm⁻¹. The structure was solved by conventional heavy-atom

methods and successive Fourier difference syntheses were used to locate all non-hydrogen atoms. The crystal diffracted comparatively poorly, and the relatively long b axis led to difficulty in adequately resolving some of the most intense lowangle reflections. Owing to the limited data, carbon atoms were refined with isotropic thermal parameters. Hydrogen atoms were included in calculated positions with fixed isotropic thermal parameters. The asymmetric unit contains a disordered BF₄⁻ counter ion which was refined as an idealised rigid group with correspondingly large anisotopic thermal parameters for the constituent atoms. Attempts to model the positions of the disordered fluorine atoms in more detail were less satisfactory and led to unstable refinements. Final R = 0.057 (R' = 0.057) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + \sigma^2(F)]$ $0.001|F|^2$]. The final electron-density difference synthesis showed no peaks > 1.14 or < -0.59 e Å⁻³, the former being in the vicinity of the BF_4^- anion. Given these problems the final level of refinement achieved was surprisingly good. Atomic coordinates are listed in Table 8.

All calculations were performed on a Digital MicroVax II computer with the SHELXTL PLUS system of programs.²⁵ Scattering factors with corrections for anomalous dispersion were taken from ref. 26.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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