DALTON

Face *versus* vertex co-ordination of tridentate crown thioethers to trinuclear cobalt clusters

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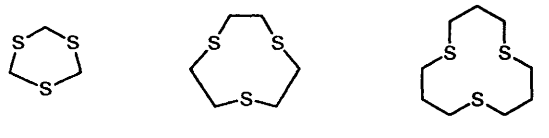
The co-ordination of the six-membered crown thioethers 1,3,5-trithiane, 2-methyl-, 2,4-dimethyl-, 2,4,6-trimethyl-, 2-benzyl- and 2,4,6-tribenzyl-1,3,5-trithiane and the nine-membered crown thioether 1,4,7-trithiacyclononane to the cobalt skeleton of various Co_3C clusters was studied. With trithiane and its derivatives complexes of the type $[Co_3(CO)_6(\mu_3\text{-}CR)(\mu_3\text{-}SCHR^1SCHR^2SCHR^3)]$ (R = Cl, Me or Ph; R^1–R^3 = H, Me or CH_2Ph) were obtained, whereas the nine-membered crown thioether gave compounds of the type $[Co_3(CO)_5(\mu\text{-}CO)(\mu_3\text{-}CR)\{(SCH_2CH_2)_3\}]$. The molecular and crystal structures of several representatives have been investigated by single-crystal X-ray diffraction. It has been shown that the trithiane ligand invariably occupies the axial co-ordination sites on the three cobalt atoms, while the trithiacyclononane chelates on one cobalt atom. The intermolecular networks of hydrogen-bonding interactions of the C–H • • • O type between the thioether hydrogens and the CO ligands have been investigated and compared with those present in other crystalline clusters carrying thioether ligands.

The co-ordination properties of crown thioethers are at present extensively studied, and they have been shown to co-ordinate more strongly to metals than do simple thioethers.[1] Crown thioethers containing three sulfur atoms are potentially tridentate ligands, particularly interesting in cluster chemistry. The six-membered crown thioether 1,3,5-trithiacyclohexane was found to co-ordinate by its three sulfur atoms to a triangular face of a metal cluster. Reaction with $[M_4(CO)_{12}]$ (M = Ir or Rh) gives $[Ir_4(CO)_9\{\mu_3\text{-}S_3(CH_2)_3\}]$ (M = Ir[2] or Rh[3]) and with $[Ru_3(CO)_{12}]$ the cluster $[Ru_3(CO)_6(\mu\text{-}CO)_3\{\mu_3\text{-}S_3(CH_2)_3\}]$ is obtained.[4,5] By contrast, the nine-membered ring 1,4,7-trithiacyclononane does not co-ordinate to a triangular face of a metal cluster. Reaction with $[Ru_6(CO)_{17}(\mu_6\text{-}C)]$ yields $[Ru_6(CO)_{14}(\mu_6\text{-}C)\{S_3(CH_2CH_2)_3\}]$ where the ligand is bound to one ruthenium atom only and, under harsher conditions, $[Ru_6(CO)_{14}(\mu_5\text{-}C)\{\mu_4\text{-}S_3(CH_2CH_2)_2\}]$ where a C_2H_4 unit of the crown thioether has been lost.[6] With $[Ru_3(CO)_{12}]$ the crown thioether also undergoes fragmentation with loss of a C_2H_4 unit to give $[Ru_3(CO)_9\{\mu\text{-}S_3(CH_2CH_2)_2\}]$ in which two ruthenium atoms are co-ordinated.[4] The twelve-membered ring 1,5,9-trithiacyclododecane co-ordinates always to one or two metal atoms of a metal cluster: with $[Os_3(CO)_{12}]$ the reaction gives $[Os_3(CO)_{11}\{S_3(CH_2CH_2CH_2)_3\text{-}S\}]$ and $[Os_4(CO)_{13}\{\mu\text{-}S_3\text{-}(CH_2CH_2CH_2)_3\text{-}S\}]$.[7] The reaction with $[Ru_3(CO)_{12}]$ gives $[Ru_6(CO)_{16}\{\mu\text{-}S_3(CH_2CH_2CH_2)_3\}]$, and a tetra- and a penta-nuclear side-product the structure and the co-ordination mode of which are not known.[7] From the reaction with $[Ru_5(CO)_{15}(\mu_5\text{-}C)]$ the clusters $[Ru_5(CO)_{13}(\mu_5\text{-}C)\{\mu\text{-}S_3\text{-}(CH_2CH_2CH_2)_3\text{-}S\}]$ and $[Ru_5(CO)_{11}(\mu_5\text{-}C)\{\mu\text{-}S_3(CH_2CH_2\text{-}CH_2)_3\text{-}S\}]$ have been isolated and characterized.[8]

Recently, the intermolecular interactions in crystals of organometallic molecules and clusters have begun to be investigated.[9] These studies have provided insight into the factors that govern crystal construction and cohesion with respect to those of organic systems. It has been shown that organometallic crystals constituted of neutral molecules can be treated as molecular crystals held together essentially by interactions of the van der Waals type[10] and by hydrogen bonds.[11] It has also been found that a relevant contribution to cohesion in crystals of cluster molecules arises most because of the presence of hydrogen bonding of the C–H • • • O type involving a CO ligand, almost ubiquitous in transition-metal cluster species.[12] It was indeed by studying the crystal structures of the two isomers of $[Ir_4(CO)_9(\mu_3\text{-}S_3C_3H_6)]$[13] that short intermolecular interactions between the H atoms of 1,3,5-trithiacyclohexane and the CO ligands were first detected. These early findings prompted us to carry out a systematic investigation by means of the structural data accumulated in the Cambridge Structural Database[14] and the discovery of such interactions in a number of crystals constituted of neutral and charged species.[15]



In this paper we report the co-ordination chemistry of 1,3,5-trithiacyclohexane and its derivatives as well as of 1,4,7-trithiacyclononane with trinuclear cobalt clusters containing a μ_3-CR capping ligand. The μ_3 *versus* single-metal co-ordination behaviour of these crown thioethers has been studied, as well as the influence of the substituents on the molecular and the crystal structure. Beside reporting on the synthesis and the solid-state molecular structure determination, this paper discusses the results of a comparison of several closely related crystal structures. The crystalline species described herein are all formed by molecules which differ little in terms of molecular shape and size and geometry so as to constitute a sample with significant statistical value.

Results and Discussion

The trinuclear clusters $[Co_3(CO)_9(\mu_3\text{-}CR)]$ (R = Cl, Me or Ph) react with the crown thioethers 1,3,5-trithiane, 2-methyl-, 2,4-dimethyl-, 2,4,6-trimethyl-, 2-benzyl- and 2,4,6-tribenzyl-1,3,5-trithiane under thermal conditions to give the trisubstitution products $[Co_3(CO)_6(\mu_3\text{-}CR)\{\mu_3\text{-}(SCHR^1SCHR^2\text{-}SCHR^3)\}]$ **1**–**17** (Scheme 1). The reaction takes place invariably in non-co-ordinating hydrocarbon solvents, as well as in ether solvents, but requires a temperature of 70 °C.

The nine-membered crown thioether 1,4,7-trithiacyclononane reacts under the same conditions with the clusters $[Co_3(CO)_9(\mu_3\text{-}CR)]$(R = Me or Ph) to form complexes of the type $[Co_3(CO)_5(\mu\text{-}CO)\ (\mu_3\text{-}CR)\{(SCH_2CH_2)_3\}]$ **18** and **19** (Scheme 2). Complexes **1–19** are intensely coloured, air-stable and are soluble in polar solvents. Crystals have been obtained from dichloromethane–hexane or –heptane mixtures.

Spectroscopic characterisation

The infrared data (ν_{CO} values) of complexes **1–19** are given in Table 1; **1–17** show basically the same carbonyl stretching pattern, comprising three characteristic absorptions in the region of terminal carbonyl ligands, and there is no indication of bridging carbonyl ligands. Complexes **18** and **19** also show three absorptions in this region, plus a weak band corresponding to a bridging carbonyl ligand.

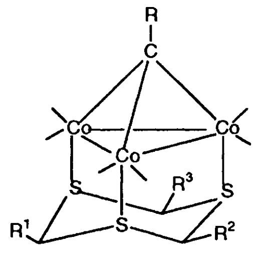
The ^1H NMR spectra of compounds **1–17** show the expected signals of the substituents R, R^1, R^2 and R^3 (Table 1). As shown previously in the case of the ruthenium cluster $[Ru_3(CO)_9\{\mu_3\text{-}S_3(CH_2)_3\}]$,[5] the co-ordination of 1,3,5-trithiane to the trinuclear metal framework results in a differentiation of the two hydrogen atoms at each of the three methylene groups. Whereas in the free crown trithioether molecule all the hydrogen atoms are equivalent, in the co-ordinated 1,3,5-trithiane three hydrogens are found to be equatorial and three axial.[4] The same differentiation between axial and equatorial hydrogen atoms is observed for the tricobalt clusters **1–3**. It gives rise to two doublets of equal intensity, the high-field doublet being assigned to the equatorial hydrides because of the deshielding influence of the cobalt atoms. The spectra of the substituted 1,3,5-trithiane derivatives **4–17** show that the substituents R^1–R^3 always occupy equatorial positions, since only the resonances of the axial hydrogen atoms are observed. For **18** and **19** the ^1H NMR spectra at ambient temperature show a multiplet for the CH_2 groups, but, at low temperature, the hydrogen atoms are different and give rise to four doublets with coupling constants in agreement with those of the clusters $[Ru_3(CO)_9\{\mu\text{-}S_3(CH_2CH_2)_2\}]$[4] and $[Ru_6(CO)_{14}(\mu_6\text{-}C)\{\mu_3\text{-}S_3(CH_2CH_2)_3\}]$.[6]

Molecular structures

An X-ray determination was carried out for the following compounds: $[Co_3(CO)_6(\mu_3\text{-}CCl)(\mu_3\text{-}S_3C_3H_6)]$ **1**, $[Co_3(CO)_6(\mu_3\text{-}CPh)(\mu_3\text{-}S_3C_3H_6)]$ **3**, $[Co_3(CO)_6(\mu_3\text{-}CPh)(\mu_3\text{-}S_3C_4H_8)]$ **6**, $[Co_3(CO)_6(\mu_3\text{-}CMe)(\mu_3\text{-}S_3C_5H_{10})]$ **8**, $[Co_3(CO)_6(\mu_3\text{-}CMe)(\mu_3\text{-}S_3C_6H_{12})]$ **11**, $[Co_3(CO)_6(\mu_3\text{-}CMe)(\mu_3\text{-}S_3C_{24}H_{24})]$ **16** and $[Co_3(CO)_5(\mu\text{-}CO)(\mu_3\text{-}CMe)\{(SCH_2CH_2)_3\}]$ **18** (Figs. 1–7). In all the structures the pyramidal Co_3C skeleton of the parent clusters is preserved with the same distances and angles, within experimental error.[16] The trithiane ligand bridges the cobalt atoms by its sulfur atoms, co-ordinated to the axial sites,

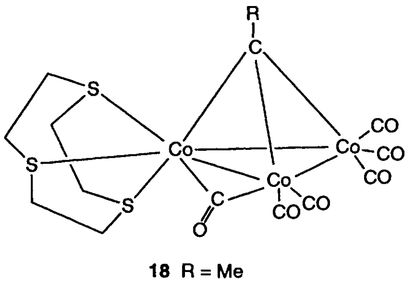
$$[Co_3(CO)_9(\mu_3\text{-}CR)] + SCHR^1SCHR^2SCHR^3 \xrightarrow{70\ ^\circ C} [Co_3(CO)_6(\mu_3\text{-}CR)\{\mu_3\text{-}(SCHR^1SCHR^2SCHR^3)\}] + 3\ CO$$

	R	R¹	R²	R³
1	Cl	H	H	H
2	Me	H	H	H
3	Ph	H	H	H
4	Cl	Me	H	H
5	Me	Me	H	H
6	Ph	Me	H	H
7	Cl	Me	Me	H
8	Me	Me	Me	H
9	Ph	Me	Me	H
10	Cl	Me	Me	Me
11	Me	Me	Me	Me
12	Cl	CH₂Ph	H	H
13	Me	CH₂Ph	H	H
14	Ph	CH₂Ph	H	H
15	Cl	CH₂Ph	CH₂Ph	CH₂Ph
16	Me	CH₂Ph	CH₂Ph	CH₂Ph
17	Ph	CH₂Ph	CH₂Ph	CH₂Ph



Scheme 1

$$[Co_3(CO)_9(\mu_3\text{-}CR)] + S_3C_6H_{12} \xrightarrow{70\ ^\circ C} [Co_3(CO)_5(\mu\text{-}CO)(\mu_3\text{-}CR)\{\mu\text{-}(SCH_2CH_2)_3\}] + 3\ CO$$



18 R = Me
19 R = Ph

Scheme 2

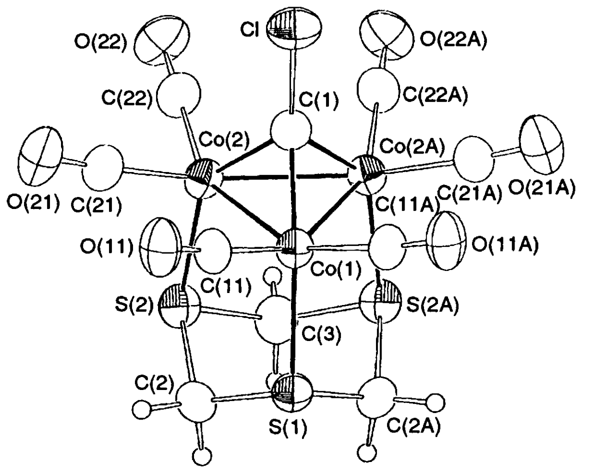


Fig. 1 Molecular structure of $[Co_3(CO)_6(\mu_3\text{-}CCl)(\mu_3\text{-}S_3C_3H_6)]$ **1**

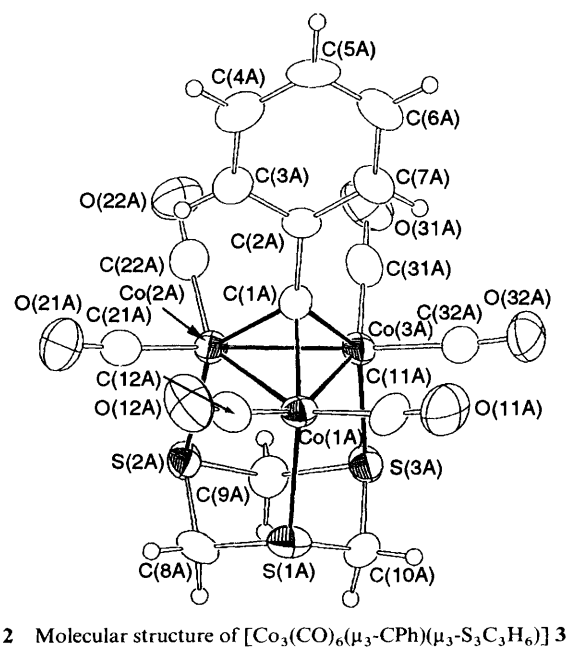


Fig. 2 Molecular structure of $[Co_3(CO)_6(\mu_3\text{-}CPh)(\mu_3\text{-}S_3C_3H_6)]$ **3**

Table 1 Infrared and ^1H NMR data for compounds **1–19**

Compound	$\tilde{\nu}_{CO}{}^a/cm^{-1}$	δ (*J*/Hz)
1 $[Co_3(CO)_6(\mu_3\text{-}CCl)(\mu_3\text{-}S_3C_3H_6)]^b$	2045m, 2006vs, 1972w	5.10 (d, 3 H, CH_2, $^2J_{HH}$ = 13.7) 2.99 (d, 3 H, CH_2, $^2J_{HH}$ = 13.9)
2 $[Co_3(CO)_6(\mu_3\text{-}CMe)(\mu_3\text{-}S_3C_3H_6)]^b$	2033m, 1992vs, 1956w	5.08 (d, 3 H, CH_2, $^2J_{HH}$ = 13.5) 3.12 (s, 3 H, CH_3) 2.95 (d, 3 H, CH_2, $^2J_{HH}$ = 13.2)
3 $[Co_3(CO)_6(\mu_3\text{-}CPh)(\mu_3\text{-}S_3C_3H_6)]^b$	2034m, 1996vs, 1960w	7.20–7.17 (m, 5 H, Ph) 5.14 (d, 3 H, CH_2) 3.05 (d, 3 H, CH_2)
4 $[Co_3(CO)_6(\mu_3\text{-}CCl)(\mu_3\text{-}S_3C_4H_8)]^c$	2044m, 2006vs, 1973w	5.62 (s, 1 H, CH) 5.53 (d, 2 H, CH_2, $^2J_{HH}$ = 13.9) 3.72 (d, 2 H, CH_2, $^2J_{HH}$ = 14.4) 1.21 (d, 3 H, CH_3, $^3J_{HH}$ = 7.0)
5 $[Co_3(CO)_6(\mu_3\text{-}CMe)(\mu_3\text{-}S_3C_4H_8)]^c$	2032m, 1991vs, 1955w	5.60 (m, 1 H, CH) 5.49, (d, 2 H, CH_2, $^2J_{HH}$ = 12.8) 3.58 (d, 2 H, CH_2, $^2J_{HH}$ = 13.6) 3.05 (s, 3 H, CH_3) 1.17 (d, 3 H, CH_3, $^3J_{HH}$ = 5.5)
6 $[Co_3(CO)_6(\mu_3\text{-}CPh)(\mu_3\text{-}S_3C_4H_8)]^c$	2033m, 1995vs, 1960w	7.30–7.16 (m, 5 H, Ph) 5.57 (s, 1 H, CH) 5.56 (d, 2 H, CH_2, $^2J_{HH}$ = 13.6) 3.73 (d, 2 H, CH_2, $^2J_{HH}$ = 15.6) 1.25 (d, 3 H, CH_3, $^3J_{HH}$ = 7.0)
7 $[Co_3(CO)_6(\mu_3\text{-}CCl)(\mu_3\text{-}S_3C_5H_{10})]^c$	2043m, 2005vs, 1971w	5.37 (m, 2 H, CH) 5.36 (d, 1 H, CH_2, $^2J_{HH}$ = 12.8) 3.84 (d, 1 H, CH_2, $^2J_{HH}$ = 14.2) 1.26 (d, 6 H, CH_3, $^3J_{HH}$ = 6.3)
8 $[Co_3(CO)_6(\mu_3\text{-}CMe)(\mu_3\text{-}S_3C_5H_{10})]^c$	2032m, 1991vs, 1954w	5.43 (q, 2 H, CH, $^3J_{HH}$ = 7.0) 5.42 (d, 1 H, CH_2, $^2J_{HH}$ = 14.3) 3.73 (d, 1 H, CH_2, $^2J_{HH}$ = 14.3) 3.05 (s, 3 H, CH_3) 1.22 (d, 6 H, CH_3, $^3J_{HH}$ = 7.0)
9 $[Co_3(CO)_6(\mu_3\text{-}CPh)(\mu_3\text{-}S_3C_5H_{10})]^c$	2032m, 1994vs, 1959w	7.30–7.17 (m, 5 H, Ph) 5.52 (q, 2 H, CH, $^3J_{HH}$ = 6.9) 5.49 (d, 1 H, CH_2, $^2J_{HH}$ = 14.2) 3.87 (d, 1 H, CH_2, $^2J_{HH}$ = 14.2) 1.30 (d, 6 H, CH_3, $^3J_{HH}$ = 6.9)
10 $[Co_3(CO)_6(\mu_3\text{-}CCl)(\mu_3\text{-}S_3C_6H_{12})]^c$	2042m, 2004vs, 1971w	5.42 (q, 3 H, CH, $^3J_{HH}$ = 6.7) 1.31 (d, 9 H, CH_3, $^3J_{HH}$ = 6.7)
11 $[Co_3(CO)_6(\mu_3\text{-}CMe)(\mu_3\text{-}S_3C_6H_{12})]^c$	2030m, 1990vs, 1959w	4.77 (q, 3 H, CH_3, $^3J_{HH}$ = 6.9) 3.06 (s, 3 H, CH_3) 1.45 (d, 9 H, CH_3, $^3J_{HH}$ = 6.9)
12 $[Co_3(CO)_6(\mu_3\text{-}CCl)(\mu_3\text{-}S_3C_{10}H_{12})]^c$	2040m, 2001vs, 1967w	7.33–7.22 (m, 5 H, Ph) 5.78 (m, 1 H, CH) 5.51 (d, 2 H, CH_2, $^2J_{HH}$ = 14.4) 3.71 (d, 2 H, CH_2, $^2J_{HH}$ = 14.3) 2.76 (d, 2 H, CH_2, $^3J_{HH}$ = 7.6)
13 $[Co_3(CO)_6(\mu_3\text{-}CMe)(\mu_3\text{-}S_3C_{10}H_{12})]^c$	2032m, 1992vs, 1956w	7.35–7.28 (m, 5 H, Ph) 5.74 (t, 1 H, CH, $^3J_{HH}$ = 8.0) 5.47 (d, 2 H, CH_2, $^2J_{HH}$ = 13.9) 3.57 (d, 2 H, CH_2, $^2J_{HH}$ = 14.3) 3.09 (s, 3 H, CH_3) 2.72 (d, 2 H, CH_2, $^3J_{HH}$ = 7.7)
14 $[Co_3(CO)_6(\mu_3\text{-}CPh)(\mu_3\text{-}S_3C_{10}H_{12})]^c$	2033m, 1995vs, 1961w	7.40–7.15 (m, 10 H, Ph) 5.84 (t, 1 H, CH, $^3J_{HH}$ = 7.7) 5.56 (d, 2 H, CH_2, $^2J_{HH}$ = 14.5) 3.71 (d, 2 H, CH_2, $^2J_{HH}$ = 14.3) 2.81 (d, 2 H, CH_2, $^3J_{HH}$ = 7.7)
15 $[Co_3(CO)_6(\mu_3\text{-}CCl)(\mu_3\text{-}S_3C_{24}H_{24})]^c$	2042m, 2004vs, 1971w	7.30–7.22 (m, 15 H, Ph) 5.73 (t, 3 H, CH, $^3J_{HH}$ = 7.5) 2.82 (d, 6 H, CH_2, $^3J_{HH}$ = 7.3)
16 $[Co_3(CO)_6(\mu_3\text{-}CMe)(\mu_3\text{-}S_3C_{24}H_{24})]^c$	2030m, 1991vs, 1954w	7.32–7.21 (m, 15 H, Ph) 5.64 (t, 3 H, CH, $^3J_{HH}$ = 7.5) 3.18 (s, 3 H, CH_3) 2.78 (d, 6 H, CH_2, $^3J_{HH}$ = 7.5)
17 $[Co_3(CO)_6(\mu_3\text{-}CPh)(\mu_3\text{-}S_3C_{24}H_{24})]^c$	2031m, 1994vs, 1959w	7.46–7.16 (m, 20 H, Ph) 5.77 (t, 3 H, CH, $^3J_{HH}$ = 7.6) 2.87 (d, 6 H, CH_2, $^3J_{HH}$ = 7.3)
18 $[Co_3(CO)_5(\mu\text{-}CO)(\mu_3\text{-}CMe)\{S_3(CH_2CH_2)_3\}]^c$	2030s, 1983vs, 1958s, 1804w	3.60 (s, 3 H, CH_3) 3.12–2.74 (m, 12 H, CH_2)
19 $[Co_3(CO)_5(\mu\text{-}CO)(\mu_3\text{-}CPh)\{S_3(CH_2CH_2)_3\}]^{c,d}$	2034s, 1987vs, 1964s, 1805w	7.66 (s, 2 H, Ph) 7.31 (s, 3 H, Ph) 4.28 (s, 2 H, CH_2) 3.54 (d, 3 H, CH_2, $^2J_{HH}$ = 11.2) 3.24 (d, 2 H, CH_2, $^2J_{HH}$ = 11.0) 2.91 (d, 3 H, CH_2, $^3J_{HH}$ = 4.1) 2.70 (d, 2 H, CH_2, $^3J_{HH}$ = 5.6)

[a] In CH_2Cl_2. [b] In $CDCl_3$. [c] In $(CD_3)_2CO$. [d] At −50 °C.

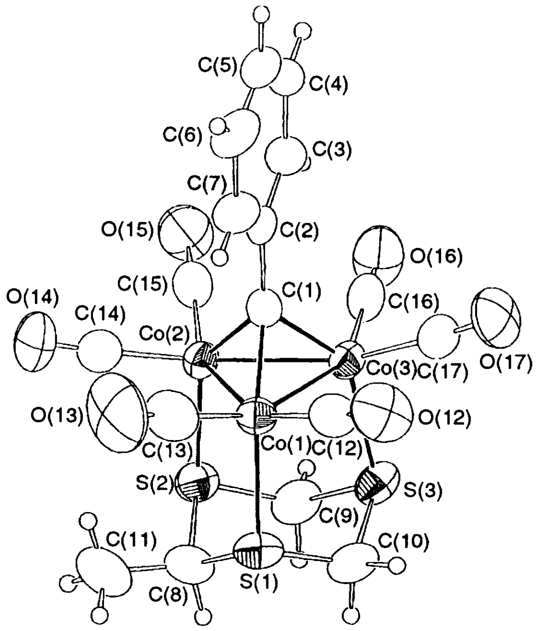


Fig. 3 Molecular structure of $[Co_3(CO)_6(\mu_3\text{-}CPh)(\mu_3\text{-}S_3C_4H_8)]$ **6**

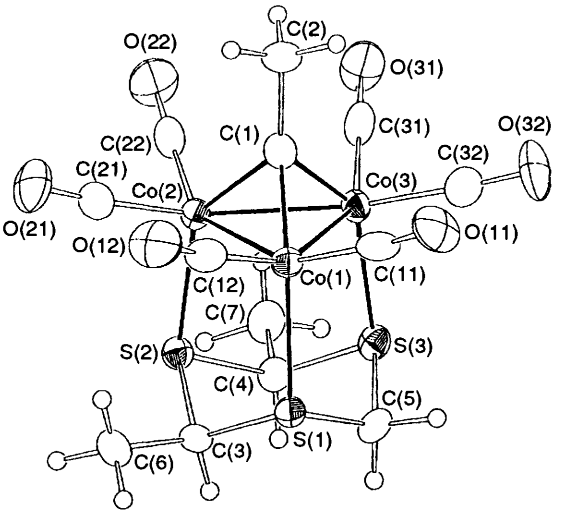


Fig. 4 Molecular structure of $[Co_3(CO)_6(\mu_3\text{-}CMe)(\mu_3\text{-}S_3C_5H_{10})]$ **8**

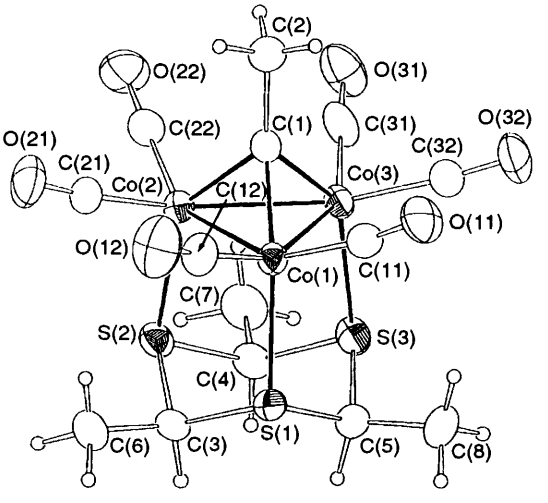


Fig. 5 Molecular structure of $[Co_3(CO)_6(\mu_3\text{-}CMe)(\mu_3\text{-}S_3C_6H_{12})]$ **11**

thus acting as a six-electron donor. It retains its chair conformation on co-ordination with the R^1–R^3 substituents in equatorial positions. The increasing volume of R^1–R^3 has no influence on the chair conformation. The ring plane S(1)–S(3) is approximately parallel to the plane of the three cobalt atoms with a dihedral angle varying from 0.73 to 0.12°, decreasing in magnitude as the size of the trithiane substituents increases (Table 2). The average Co–S distance is almost constant, within the range of 2.267–2.273 Å, for the six structures studied (Table 2). Concerning the structure of compound **18**, the three sulfur atoms of the ligand are co-ordinated to one cobalt atom, Co(1). The bridging carbonyl is asymmetrically bonded [Co(1)–C(14) 2.018(4) and Co(3)–C(14) 1.831(4) Å] because of the co-ordination of the ligand on Co(1) and is situated below the plane of the metal atoms with respect to the apical carbon. The plane formed by the three sulfur atoms is almost perpendicular to that of the cobalt atoms [dihedral angle 85.36(3)°]. One can also notice that the Co–S distances are significantly different [Co(1)–S(1) 2.2444(12), Co(1)–S(2) 2.2543(11) and Co(1)–S(3) 2.3031(12) Å] and the smallest Co–Co distance is not Co(1)–Co(3) 2.5021(8) Å which is spanned by the bridging carbonyl but Co(2)–Co(3) 2.4738(8) Å.

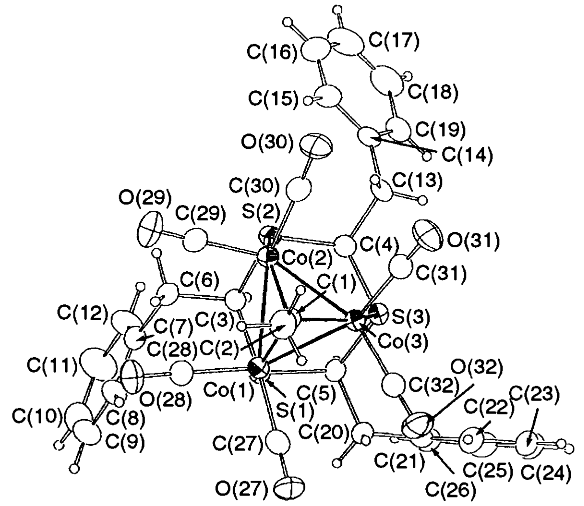


Fig. 6 Molecular structure of $[Co_3(CO)_6(\mu_3\text{-}CMe)(\mu_3\text{-}S_3C_{24}H_{24})]$ **16**

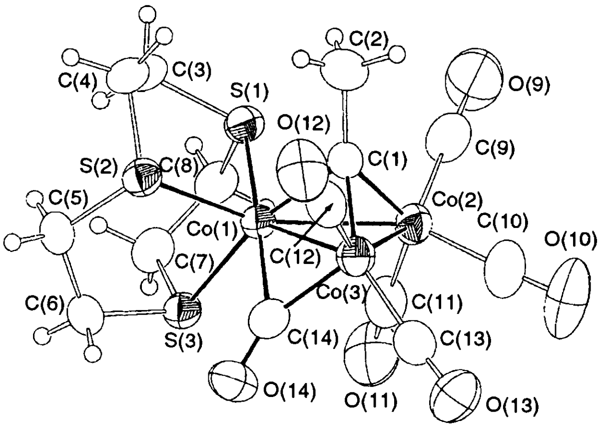


Fig. 7 Molecular structure of $[Co_3(CO)_5(\mu\text{-}CO)(\mu_3\text{-}CMe)\{(SCH_2CH_2)_3\}]$ **18**

It is known that, upon co-ordination, thioethers, as well as phosphines, increase the electron density of the metal skeleton, which would usually favour the formation of carbonyl bridges.[17] Triaxial co-ordination, however, shows surprising results: carbonyl substitution by the tridentate phosphine $HC(PPh_2)_3$ in $[Ru_3(CO)_{12}]$ gives rise to the formation of carbonyl bridges when the phosphorus ligand is triaxially co-ordinated, whereas equatorial substitution does not.[18] By contrast, in $[Ir_4(CO)_{12}]$, triaxial carbonyl substitution by $HC(PPh_2)_3$ does not give rise to carbonyl bridges, whereas equatorial substitution does.[9] However, carbonyl bridges were not observed in any of the clusters **1**–**17**. The average S–Co–(CO) angle varies from 100.8 to 104.1°. Owing to the axial co-ordination of the ligand, the

Table 2 Variation of intramolecular structure data in clusters **1**, **3**, **6**, **8**, **11** and **16**

Compound	Interplanar angle (deviation)/°	Average Co–S/Å	Average S–Co–(CO)/°	Average C–C–S/°
1	0.28 (0.07)	2.272	102.34	—
3	0.18 (0.13)	2.271	103.18	—
6	0.73 (0.07)	2.269	100.82	110.0
8	0.33 (0.06)	2.267	103.7	109.4
11	0.20 (0.05)	2.273	104.1	109.7
16	0.12 (0.05)	2.273	103.8	109.7

Table 3 Hydrogen-bonding interactions in crystalline clusters **1**, **3**, **6**, **8**, **11**, **16** and **18**

Compound	Donor–H ⋯ Acceptor	D ⋯ A/Å	H ⋯ A/Å	D–H ⋯ A/°
1	C(2)–H(2A) ⋯ O(11)	3.253	2.377	137.1
	C(2)–H(2A) ⋯ O(21)	3.282	2.412	136.6
	C(3)–H(3B) ⋯ O(22)	3.250	2.401	134.4
	C(2)–H(2B) ⋯ Cl(2)	3.795	2.902	140.0
3	C(5)–H(5A) ⋯ O(31A)	3.348	2.698	118.3
	C(6)–H(6A) ⋯ O(15B)	3.368	2.675	121.5
	C(3B)–H(3B) ⋯ O(11B)	3.497	2.741	126.9
	C(4B)–H(4B) ⋯ O(32A)	3.336	2.455	137.9
	C(5B)–H(5B) ⋯ O(32A)	3.480	2.775	122.8
	C(9)–H(9A1) ⋯ O(12A)	3.489	2.734	126.7
	C(8B)–H(8B2) ⋯ O(12A)	3.499	2.498	153.7
	C(9B)–H(9B1) ⋯ O(14B)	3.451	2.496	146.8
6	C(3)–H(3) ⋯ O(17)	3.665	2.800	137.1
	C(5)–H(5) ⋯ O(17)	3.513	2.595	142.4
	C(6)–H(6) ⋯ O(13)	3.293	2.730	112.2
	C(8)–H(8) ⋯ O(12)	3.296	2.454	133.9
	C(9)–H(9A) ⋯ O(17)	3.369	2.710	119.0
	C(10)–H(10A) ⋯ O(14)	3.549	2.681	137.1
	C(9)–H(9B) ⋯ O(16)	3.258	2.329	143.2
8	C(3)–H(3) ⋯ O(31)	3.355	2.688	119.5
	C(4)–H(4) ⋯ O(21)	3.560	2.707	135.7
	C(5)–H(5A) ⋯ O(32)	3.379	2.410	148.5
	C(2)–H(2C) ⋯ O(11)	3.617	2.550	169.5
	C(5)–H(5B) ⋯ O(12)	3.432	2.380	164.3
	C(6)–H(6B) ⋯ O(11)	3.458	2.773	121.2
	C(6)–H(6C) ⋯ O(22)	3.386	2.551	133.5
11	C(3)–H(3) ⋯ O(11)	3.473	2.591	138.3
	C(4)–H(4) ⋯ O(11)	3.424	2.538	138.6
	C(4)–H(4) ⋯ O(21)	3.724	2.749	150.0
	C(5)–H(5) ⋯ O(21)	3.453	2.424	158.9
	C(7)–H(7A) ⋯ O(22)	3.369	2.621	125.8
	C(6)–H(6C) ⋯ O(11)	3.629	2.665	148.4
	C(6)–H(6B) ⋯ O(12)	3.293	2.758	110.3
16	C(1S)–H(1S1) ⋯ S(3)	3.883	2.873	155.7
	C(8)–H(8) ⋯ O(30)	3.323	2.618	122.2
	C(11)–H(11) ⋯ Cl(1S)	3.727	2.700	158.8
	C(23)–H(23) ⋯ O(28)	3.460	2.826	117.6
	C(24)–H(24) ⋯ O(30)	3.712	2.703	155.3
	C(1S)–H(1S2) ⋯ O(28)	3.490	2.575	141.9
18	C(2)–H(2A) ⋯ O(11)	3.775	2.765	155.6
	C(4)–H(4A) ⋯ O(12)	3.616	2.631	151.3
	C(6)–H(6B) ⋯ O(12)	3.454	2.605	135.0
	C(7)–H(7A) ⋯ O(9)	3.216	2.493	123.3
	C(8)–H(8A) ⋯ O(10)	3.646	2.746	140.7
	C(3)–H(3B) ⋯ O(10)	3.293	2.750	110.8
	C(4)–H(4B) ⋯ O(14)	3.324	2.500	132.3
	C(6)–H(6B) ⋯ O(14)	3.490	2.735	126.7
	C(8)–H(8B) ⋯ O(9)	3.216	2.488	123.8

position of the carbonyl bands is not influenced by the ligand substituents R^1–R^3. In the case of tricobalt clusters, the co-ordination at a single metal gives rise to the formation of a bridging carbonyl; this is not observed with the cluster $[Ru_6(CO)_{14}(\mu_6\text{-}C)(S_3C_6H_{12})]$.[6]

Crystal structures

The crystal structures of compounds **1**, **3**, **6**, **8**, **11**, **16** and **18** have been compared in terms of packing arrangement and hydrogen-bonding interactions of the C–H ⋯ O type. As mentioned above this structural sample offers a good opportunity to investigate further the involvement of the thioether hydrogens in hydrogen bonding. In $[Ru_3(CO)_9(\mu_3\text{-}S_3C_3H_6)]$ the thioether H atoms have been found to form such bonds in the range 2.26–2.55 Å, the shortest interactions being established by the bridging ligands. Similarly in $[Ir_4(\mu_3\text{-}CO)_3(CO)_6(\mu_3\text{-}S_3C_3H_6)]$ and in $[Ir_4(CO)_9(\mu_3\text{-}S_3C_3H_6)]$ the thioether hydrogens form links in the ranges 2.23–2.48 and 2.26–2.45 Å, respectively. The hydrogen-bonding parameters for species **1**, **3**, **6**, **8**, **11**, **16** and **18** are reported in Table 3.

The computer program PLATON [19a] was used to analyse the geometrical features of the hydrogen-bonding patterns, while SCHAKAL 93 [19b] was used for the graphical representation of these patterns. The H-atom coordinates were normalized to give C–H distances (1.08 Å) corresponding to typical neutron-diffraction values. We have adopted a threshold value of 2.8 Å for listing the C–H••• O interactions[19c] although only the shortest and (presumably) the strongest interactions will be described in detail in the discussion of the individual crystal structures.

[Co$_3$(CO)$_6$(μ$_3$-CCl)(μ$_3$-S$_3$C$_3$H$_6$)] 1. The six oxygen atoms belonging to the CO ligands all participate in short C–H ••• O interactions with the radial H atoms of the CH$_2$ groups. Each H atom interacts with two oxygens [H(2A) ••• O(11) 2.377, H(2A) ••• O(21) 2.412, H(3B) ••• O(22) 2.401 Å], and the bifurcated pattern is doubled by an inversion centre relating the neutral molecules and the three surrounding ones, as shown in Fig. 8. The crystal contains disordered CH$_2$Cl$_2$ solvent molecules which could be detected because of the presence of spurious peaks in the Fourier map. Fig. 9 shows that indeed there is an empty 'channel' extending along the *c*-axis in the crystal packing, in which the disordered solvent molecule could be nicely accommodated.

[Co$_3$(CO)$_6$(μ$_3$-CPh)(μ$_3$-S$_3$C$_3$H$_6$)] 3. Cluster **3** differs from **1** by the presence of a phenyl group formally replacing the Cl atom on the top of the cobalt triangle. Short C–H ••• O interactions are observed between phenyl H atoms and CO ligands [H(4B) ••• O(32A) 2.455, H(8B2) ••• O(12A) 2.498 Å], linking the two independent molecules (A and B in Fig. 10) in the crystal. A third short interaction [H(9B1) ••• O(14B) 2.496 Å], present twice because of an inversion centre, links two molecules of type B.

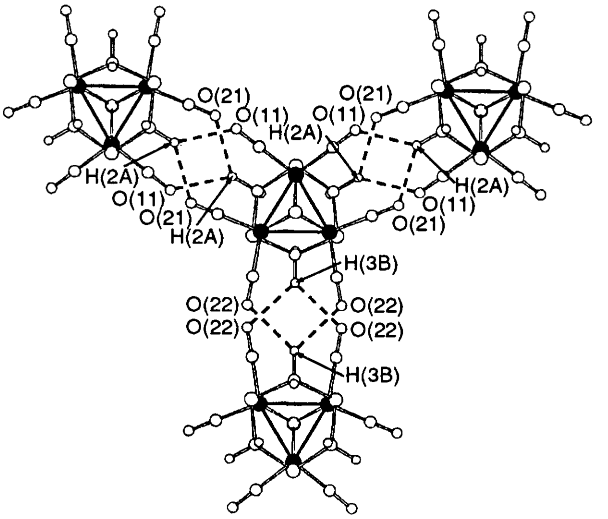


Fig. 8 Bifurcated hydrogen bonds in crystalline cluster **1**

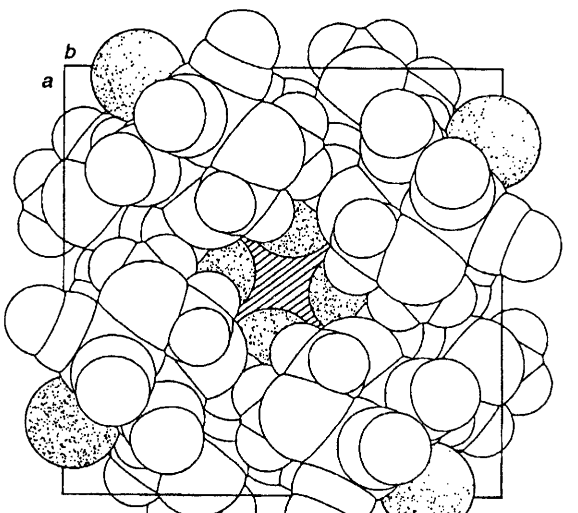


Fig. 9 Packing projection along the *c* axis of crystalline cluster **1**, showing one of the channels (diagonal lines) probably occupied by the disordered solvent molecules. Shaded spheres represent Cl atoms

[Co$_3$(CO)$_6$(μ$_3$-CPh)(μ$_3$-S$_3$C$_4$H$_8$)] 6. A methyl group formally replaces one radial H(CH$_2$) atom in molecule **3**. A very short CH ••• O interaction is observed between a CO ligand and a radial H(CH$_2$) atom [H(9B) ••• O(16) 2.329 Å]. Again, this interaction is present twice due to the presence of an inversion centre, resulting in the formation of a 'dimer' as shown in Fig. 11.

[Co$_3$(CO)$_6$(μ$_3$-CMe)(μ$_3$-S$_3$C$_5$H$_{10}$)] 8. Short hydrogen-bond interactions involving the two H atoms belonging to the unique CH$_2$ moiety [H(5A) ••• O(32) 2.410, H(5B) ••• O(12) 2.380 Å], and larger distances connecting H (methyl) atoms with the carbonyl ligands, are reported in Table 3.

[Co$_3$(CO)$_6$(μ$_3$-CMe)(μ$_3$-S$_3$C$_6$H$_{12}$)] 11. When the radial H(CH$_2$) atoms are replaced by methyl groups the shortest (< 2.6 Å) CH ••• O interactions are observed between the axial H(CH$_2$) atoms and two CO ligands belonging to two neighbouring molecules in the crystal [H(3) ••• O(11) 2.591, H(4) ••• O(11) 2.538, H(5) ••• O(21) 2.424 Å], as shown in Fig. 12 [the long contact O(21) ••• H(4) 2.749 Å is also drawn in this figure, to indicate the presence of bifurcated interactions for both O atoms]. The methyl hydrogens are involved in systematically longer contacts.

[Co$_3$(CO)$_6$(μ$_3$-CMe)(μ$_3$-S$_3$C$_{24}$H$_{24}$)] 16. The crystal structure of cluster **16** is particularly relevant because it affords an indirect proof of the importance of the C–H ••• O interactions involving the thioether H atoms. Owing to the presence of the bulky benzyl groups distributed in a helicoidal fashion under

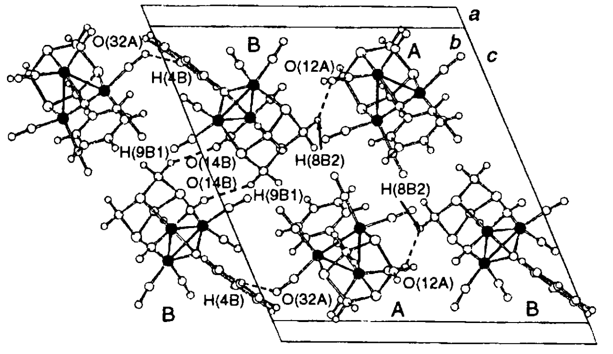


Fig. 10 Hydrogen-bonding interactions linking the two independent molecules A and B in crystalline cluster **3**

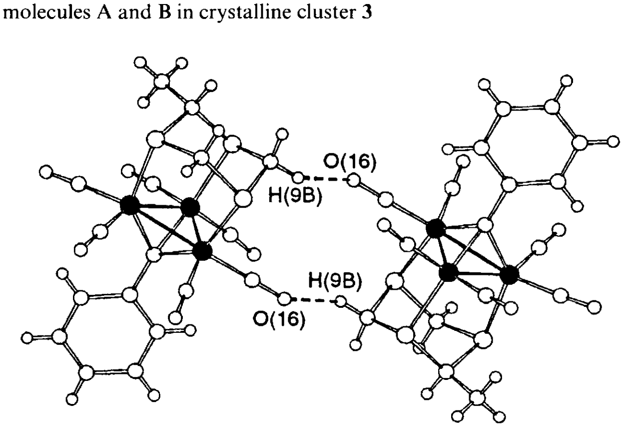


Fig. 11 'Dimer' formation *via* short hydrogen bonds in crystalline cluster **6**

Table 4 Experimental data, method of synthesis and elemental analysis for compounds **1**–**19**

Compound	Method (t/h)	Ligand[a]	Mass/mg (yield, %)	Formula	Analysis (%)[b] C	H
1	A (5)	**I**	66 (59)	$C_{10}H_6ClCo_3O_6S_3$	22.60 (22.65)	1.25 (1.15)
2	B (5)	**I**	72 (64)	$C_{11}H_9Co_3O_6S_3$	25.90 (25.90)	1.80 (1.80)
3	C (4)	**I**	35 (32)	$C_{16}H_{11}Co_3O_6S_3$	33.65 (33.60)	2.00 (1.95)
4	C (2)	**II**	42 (37)	$C_{11}H_8ClCo_3O_6S_3$	24.55 (24.25)	1.95 (1.50)
5	C (7)	**II**	36 (31)	$C_{12}H_{11}Co_3O_6S_3$	27.65 (27.50)	2.30 (2.10)
6	C (3)	**II**	32 (29)	$C_{17}H_{13}Co_3O_6S_3$	34.85 (34.85)	2.30 (2.25)
7	B (3)	**III**	65 (56)	$C_{12}H_{10}ClCo_3O_6S_3$	23.10 (25.80)	2.05 (1.80)
8	C (6)	**III**	35 (30)	$C_{13}H_{13}Co_3O_6S_3$	29.20 (29.00)	2.35 (2.45)
9	C (3)	**III**	81 (70)	$C_{18}H_{15}Co_3O_6S_3$	36.05 (36.00)	2.40 (2.50)
10	B (5)	**IV**	75 (62)	$C_{13}H_{12}ClCo_3O_6S_3$	27.55 (27.25)	2.05 (2.10)
11	C (6)	**IV**	35 (30)	$C_{14}H_{15}Co_3O_6S_3$	30.40 (30.45)	2.65 (2.75)
12	A (4)	**V**	60 (46)	$C_{17}H_{12}ClCo_3O_6S_3$	32.75 (32.90)	1.95 (1.95)
13	B (5)	**V**	79 (60)	$C_{18}H_{15}Co_3O_6S_3$	36.10 (36.00)	2.70 (2.50)
14	C (4)	**V**	39 (31)	$C_{23}H_{17}Co_3O_6S_3$	41.45 (41.70)	2.15 (2.60)
15	A (4.5)	**VI**	54 (43)	$C_{31}H_{24}ClCo_3O_6S_3$	46.50 (46.50)	2.90 (3.00)
16	C (6)	**VI**	82 (48)	$C_{32}H_{27}Co_3O_6S_3$	48.60 (49.25)	3.40 (3.50)
17	C (5.5)	**VI**	80 (50)	$C_{37}H_{29}Co_3O_6S_3$	52.75 (52.75)	3.35 (3.45)
18	B (3.5)	**VII**	65 (62)	$C_{14}H_{15}Co_3O_6S_3$	30.60 (30.45)	2.45 (2.75)
19	B (3.5)	**VII**	58 (50)	$C_{19}H_{17}Co_3O_6S_3\cdot 0.25CH_2Cl_2$	36.40 (36.40)	2.75 (2.75)

[a] **I** = 1,3,5-Trithiane; **II** = 2-methyl-1,3,5-trithiane; **III** = 2,4-dimethyl-1,3,5-trithiane; **IV** = 2,4,6-trimethyl-1,3,5-trithiane; **V** = 2-benzyl-1,3,5-trithiane; **VI** = 2,4,6-tribenzyl-1,3,5-trithiane; **VII** = 1,4,7-trithiacyclononane. [b] Calculated values in parentheses.

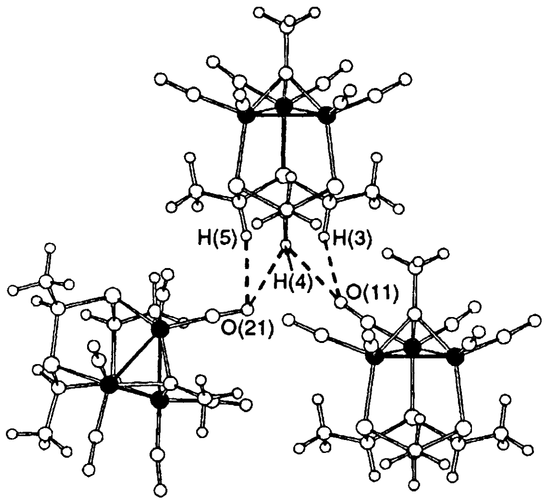


Fig. 12 Bifurcated hydrogen-bonding interactions in crystalline cluster **11**

the cluster base, the volume occupation is optimized by tightly interlocking the benzyl groups belonging to two molecules (related by a centre of inversion) as shown in Fig. 13. In doing so, however, the H atoms of the 'good donor' CH units of the thioether are completely encapsulated within the benzyl sheath and are not available for close contacts with the neighbouring acceptor carbonyl oxygens. This results in a general lengthening of the intermolecular H···O distances (see Table 3). The crystal structure of **16** represents a different compromise between close packing and the maximization of the CH···O interactions. The latter interactions are sacrificed to achieve a more efficient interlocking of the bulky groups. The solvent molecule (CH_2Cl_2), on the contrary, participates in the hydrogen-bonding pattern *via* one Cl atom [C(11)–H(11)···Cl(1) 2.700 Å] and two H atoms [C(1S)–H(1S1)···S(3) 2.873, C(1S)–H(1S2)···O(28) 2.575 Å].

[$Co_3(CO)_5(\mu$-$CO)(\mu_3$-$CMe)\{S_3(CH_2CH_2)_3\}$] 18. The shortest hydrogen-bonding interactions in crystalline cluster **18** are bifurcated interactions between a terminal CO ligand and two adjacent CH_2 groups on a neighbouring molecule [H(7A)···O(9) 2.493, H(8B)···O(9) 2.488 Å]. The bridging CO ligand is involved in one short [H(4B)···O(14) 2.500 Å] and two long (> 2.7 Å) interactions, contrary to what is usually observed with bridging carbonyl ligands, more basic with respect to the terminal co-ordination.[15d] The different behaviour in **18** is probably due to the partial screening exerted by the trithiacyclononane on the C(14)–O(14) ligand.

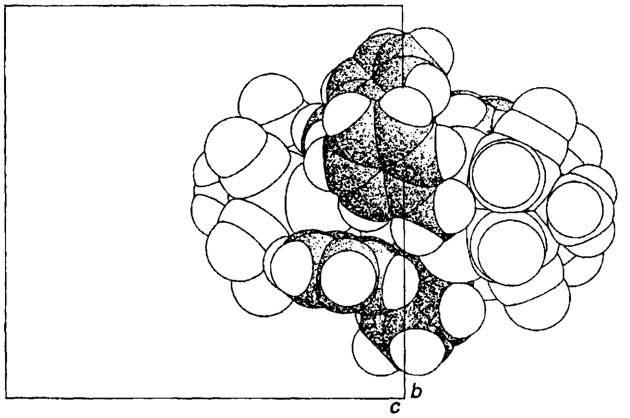


Fig. 13 Tight interlocking of the benzyl groups belonging to two molecules related by an inversion centre in crystalline cluster **16**. Shaded parts represent the carbon atoms of the benzyl groups

Conclusion

The co-ordination reactions studied, by varying the steric requirements of the crown thioethers, allow several conclusions to be drawn. First, only the six-membered crown thioethers are able to co-ordinate by their three sulfur atoms to a triangular face of a Co_3C cluster in a μ_3 fashion. Secondly, in this case neither the substituents on the crown thioether nor on the methylidyne carbon of the cluster cause considerable changes in the molecular structure: both the chair conformation of the trithiane ligand and the terminal co-ordination mode of the six carbonyls of the cobalt framework are retained. Furthermore, we have been able to show that the hydrogen atoms of the thioether ligands are, in general, sufficiently polar to form preferential intermolecular interactions with the carbonyl

Table 5 Crystallographic and selected experimental data for complexes **1**, **3**, **6**, **8**, **11**, **16** and **18**

	1	**3**	**6**	**8**	**11**	**16**	**18**
Formula	$C_{11}H_8Cl_3Co_3O_6S_3$	$C_{16}H_{11}Co_3O_6S_3$	$C_{17}H_{13}Co_3O_6S_3$	$C_{13}H_{13}Co_3O_6S_3$	$C_{14}H_{15}Co_3O_6S_3$	$C_{33}H_{29}Cl_2Co_3O_6S_3$	$C_{14}H_{15}Co_3O_6S_3$
M	615.49	572.22	586.24	538.20	552.23	865.43	552.23
Crystal shape	Cubic blocks	Thin plates	Flat needles	Rectangular rods	Rods	Blocks	Rods
Crystal colour	Dark red	Dark red	Dark violet	Dark violet	Dark violet	Deep red	Dark red
Crystal system	Tetragonal	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$I4/m$	$P\bar{1}$	$P2_1/c$	$P2/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a/Å	16.580(1)	8.411(2)	14.828(2)	13.608(2)	15.119(1)	12.526(2)	16.130(1)
b/Å	16.580(1)	15.756(4)	8.821(2)	8.750(2)	9.010(1)	16.780(1)	7.600(1)
c/Å	13.350(2)	16.933(5)	16.528(5)	15.815(2)	15.477(1)	17.029(1)	17.218(1)
α/°		111.57(2)					
β/°		100.85(1)	104.07(2)	91.04(1)	108.86(1)	93.87(1)	115.08(1)
γ/°		97.86(1)					
U/Å^3	3669.9(6)	1996.8(9)	2097.0(8)	1882.8(6)	1995.1(3)	3571.1(6)	1911.7(3)
Z	8	4	4	4	4	4	4
D_c/g cm^{-3}	2.228	1.903	1.857	1.899	1.838	1.745	1.919
Crystal size/mm	0.34 × 0.34 × 0.34	0.87 × 0.36 × 0.04	0.76 × 0.57 × 0.11	0.46 × 0.19 × 0.15	0.72 × 0.46 × 0.19	0.57 × 0.46 × 0.27	0.91 × 0.30 × 0.30
Reflections	20	25	25	26	26	24	22
θ Range for cell/°	14–22	14–20	14–19.5	14–18.5	14–19.5	13–19	13–20
μ(Mo-Kα)/mm^{-1}	3.485	2.807	2.675	2.870	2.805	1.745	2.928
T/K	193(2)	293(2)	293(2)	193(2)	293(2)	293(2)	293(2)
Maximum, minimum transmission			0.173, 0.073	1.000, 0.730	0.1911, 0.0987	0.2654, 0.1873	0.1522, 0.1061
No. reflections measured	3344	6994	6119	6632	7024	6264	4379
No. reflections observed	2459	4817	3298	2398	2708	3730	2784
No. reflections used	3080	6257	5328	3221	3324	5542	3971
θ Range/°	2–32.5	2–25	2–30	2–25	2–25	2–25	2–28
hkl Ranges	0–25, 0–25, 0–20	−9 to 9, −18 to 17, 0–20	−20 to 20, −12 to 0, −23 to 0	−16 to 16, 0–10, −18 to 18	−17 to 17, 0–10, −18 to 18	−14 to 14, 0–19, −20 to 0	−18 to 20, 0–9, −22 to 0
Final R_1, wR_2[a]	0.0725, 0.2159	0.0661, 0.1546	0.0471, 0.0969	0.0322, 0.0591	0.0270, 0.0554	0.0498, 0.1119	0.0736, 0.0748
(all data)	0.0991, 0.2486	0.1067, 0.1896	0.1064, 0.1180	0.0527, 0.0641	0.0430, 0.0610	0.0975, 0.1310	0.0736, 0.0855
No. refined parameters	122	505	262	278	295	425	236
Goodness of fit, S[b]	1.102	1.065	0.907	0.904	0.967	0.962	0.917
Maximum Δ/σ	0.067	−0.003	0.001	−0.002	−0.003	0.002	0.000
Maximum, minimum electron density/e Å^{-3}	3.870, −2.117	0.903, −1.037	0.883, −0.434	0.387, −0.381	0.303, −0.221	0.331, −0.719	0.435, −0.367

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(wF_o^4)\}^{\frac{1}{2}}$. [b] $S = [\Sigma w(F_o^2 - F_c^2)^2]/(n - p)^{\frac{1}{2}}$, n = number of reflections, p = parameters used. $w = 1/[\sigma^2(F_o^2) + (0.0402P)^2 + 8.2700P]$ where $P = (F_o^2 + 2F_c^2)/3$.

oxygens. The distances for some of these C–H···O interactions are towards the lower limit of the range observed for these links and are strictly comparable to those usually established by H atoms bound to sp^2 carbons (such as in cyclopentadienyl ligands, for instance) rather than for those formed by CH$_3$ groups or other sp^3-carbon atoms. In the absence of serious steric problems these interactions (which are abundant because of the large number of donor and acceptor groups available in these complexes) play a far from negligible role in the stabilization of the crystal structures.

Experimental

General comments

All manipulations, except the chromatographic separations, were carried out under nitrogen and with deoxygenated solvents. The clusters [Co$_3$(CO)$_9$(CR)] (R = Cl, Me or Ph) were prepared by literature methods,[20] substitution of trithiane was done following the procedure of Edema *et al.*[21] 1,3,5-Trithiane and 1,4,7-trithiacyclononane were commercially available (Aldrich). All compounds were synthesized with one of the three methods described below and complementary information is given in Table 4.

Syntheses

Method A. A mixture of the cobalt cluster (100 mg) and the crown thioether (1 equivalent) was refluxed in tetrahydrofuran (thf) (20 cm^3). After cooling, the solvent was evaporated under vacuum and the residue washed twice with hexane (5 cm^3), to remove unreacted starting materials. The desired compound was extracted twice with dichloromethane (5 cm^3) and the solution filtered. Slow diffusion of hexane (25 cm^3) into the dichloromethane solution allowed crystallization.

Method B. A mixture of the cobalt cluster (100 mg) and the crown thioether (1 equivalent) was refluxed in heptane (20 cm^3). The red-brown precipitate was filtered off from the hot solution and dissolved in dichloromethane (8 cm^3). Diffusion of heptane (10 cm^3) into this solution allowed crystallization.

Method C. A mixture of the cobalt cluster (100 mg) and the ligand (1 equivalent) was refluxed in thf (25 cm^3). The solvent was evaporated in vacuum and the residue chromatographed on silica plates. Elution with dichloromethane–hexane (3:2) gave three fractions: the first one gave unreacted parent cluster, the second was not identified and the third, extracted with dichloromethane, gave the desired product. Slow evaporation of a mixture of dichloromethane–hexane resulted in the formation of crystals.

Crystallography

Data for the crystal structure analyses were collected on a Stoe-Siemans AED2 four-circle diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) and with the ω–θ scan mode. The structures were solved by SHELXS 86[22] and refined with SHELXL 93.[23] Hydrogen atoms were included in calculated positions and treated as riding atoms. No absorption correction was applied for complexes **1** and **3**; for **6**, **8**, **11**, **16** and **18** the DIFABS program was used.[19a] Refinement was on F^2. Experimental details are given in Table 5.

Complete atomic co-ordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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