Synthesis and Molecular Structure of the Mixed Polymeric Cobalt Compound $[Co_3(SCH_2CH_2S)_3(PEt_3)_3]_2[Co_2Cl_4(\mu\text{-}O_2SEt_2)_2]$†

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The mixed polymeric cobalt compound $[Co_3(SCH_2CH_2S)_3(PEt_3)_3]_2[Co_2Cl_4(\mu\text{-}O_2SEt_2)_2]$ **1** containing two trimers and one dimer was isolated from the reaction of $[CoCl(PEt_3)_3]$ with disodium ethane-1,2-dithiolate in 1,2-dichloroethane. It is monoclinic and crystallizes in space group $P2_1/n$, with a = 12.481(7), b = 15.70(2), c = 25.84(2) Å, β = 97.85(5)° and Z = 2 from 2436 reflections with $I > 3.50\sigma(I)$, final R = 0.062. X-Ray diffraction established that the two cobalt atoms in the dimer are linked *via* the oxygen atoms of the diethyl sulfone forming the eight-membered $Co_2O_4S_2$ ring with a crystallographic inversion centre through the whole dimer. The observed cleavage of the dithiolate C–S bond together with the formation of the bridging diethyl sulfone are discussed. In the trimer of **1**, the Co_3 isosceles triangle is capped by two bidentate $SCH_2CH_2S^{2-}$ ligands on either side of the plane with the sulfur atoms bridging the two long Co–Co bonds, while the short Co–Co bond is bridged by the third $SCH_2CH_2S^{2-}$ ligand. Considering the framework of the $Co_3P_3(SCH_2CH_2S)_3$ unit only, there is a pseudo mirror-image plane passing through the Co_3P_3 plane which bisects the C(31)–C(32) bond. The ^1H NMR spectrum of compound **1** demonstrates the retention of the solid-state structure of the trinuclear species in chloroform solution.

Organophosphine and thiolate compounds are stereochemical building blocks and important constituents in cluster molecules. In the last few years there has been growing interest in transition-metal complexes with thiolate and phosphine ligands owing to their various structural features, electronic properties and potential relevance to catalysis.[1] Relatively few cobalt complexes containing both dithiolate and monodentate phosphine ligands, however, have been investigated.[2,3] Recently we have shown that the reactions of the low oxidation state cobalt complex $[CoX(PR_3)_3]$ (R = Ph or Et, X = Cl or Br) with thiolates or dithiolates yielded a series of phosphine polycobalt compounds with thiolate and/or sulfur ligands.[4–8] By employing $Na_2(edt)$ (edt^{2-} = ethane-1,2-dithiolate) under appropriate reaction conditions we were able to isolate the complexes $[Co_4Cl(\mu_3\text{-}S)(edt)_3(PPh_3)_3]$[5] and $[Co_7Br(\mu_4\text{-}S)_3(\mu_3\text{-}S)_3(PPh_3)_6]$.[6] In addition to their different skeleton types, the two compounds are noteworthy for their synthesis. Of particular interest are those reactions in which the sulfur atoms dissociate partially or completely through the cleavage of the C–S bond of the starting organosulfur reagents and are incorporated into the final products. The new ligand $SCH_2CH_2SCH_2CH_2S^{2-}$ ($tpdt^{2-}$ = 3-thiapentane-1,5-dithiolate), produced *via* the cleavage of the C–S bond in edt, was observed in [NbS(edt)(tpdt)] and $[Ni(tpdt)(PBu_3)]$,[9] the tpdt group of which could be considered as the intermediate in the desulfurization process of the edt reagent, but as yet this type of product has not been isolated from our reaction system. As part of a study aimed at understanding the mechanisms of desulfurization occurring in this system, we have been exploring the reactivity and co-ordination chemistry of edt under various reaction conditions, and obtained a new mixed polymeric cobalt compound $[Co_3(edt)_3(PEt_3)_3]_2[Co_2Cl_4(\mu\text{-}O_2SEt_2)_2]$ **1**, which contains two trimeric and one, unexpected, dimeric cobalt cores in one molecule. The diethyl sulfone in the dimer of **1** may be related to the above mentioned tpdt ligand. Herein we report our initial results on the synthesis and characterization of compound **1** which provides a further example of the cleavage of the C–S bond in ethanedithiol.

Results and Discussion

Synthesis.—The univalent cobalt reagent $[CoCl(PEt_3)_3]$ was selected as the starting material due to its chemical activity, although most cobalt–sulfide cluster compounds have been prepared using higher oxidation state Co^{2+} salts. Attempts to prepare cobalt–thiol species using $[CoX(PR_3)_{4-n}]$ (R = Ph or Et; n = 1, X = Cl or Br; n = 2, X = $\eta^5\text{-}C_5H_5$) as the low-valent reagent, in its reaction with a sodium dithiolate or thiolate in organic solvents, have led to a series of P–Co–S(R) compounds including di-, tri-, tetra-, hexa- and hepta-nuclear complexes with various cobalt oxidation states. Besides their interesting stereochemistry, these compounds are of interest for their synthetic processes, in which sulfide ligands were indirectly produced. The hexacobalt–sulfide cluster compounds $[Co_6(\mu_3\text{-}S)_8(PR_3)_6]$ (R = Ph or Et)[7] could easily be obtained from SCH_2CHMeS^{2-} (pdt^{2-} = propane-1,2-dithiolate) or other relatively more stable thiolates, such as $1,2\text{-}S_2C_6H_4^{2-}$ (bdt^{2-}) and SPh. Complexes $[Co_7Br(\mu_4\text{-}S)_3(\mu_3\text{-}S)_3(PPh_3)_6]$, $[Co_4(\eta^5\text{-}C_5H_5)_4(\mu_4\text{-}S)_2]$ and $[Co_7X_3(\mu_4\text{-}S)_3(\mu_3\text{-}S)_3(PPh_3)_4]$ (X = Br or Cl) were formed *via* the 'capture' of the sulfur atom by cobalt from the thiolates edt^{2-}, pdt^{2-} and SEt^-, respectively.[4,6] The latter two complexes could also be prepared directly with S^{2-}.[8] The above reactions show that under appropriate conditions, *e.g.* with rather long reaction times, the sulfur atoms dissociate completely from the thiolate or dithiolate and are incorporated into the cluster with none of the parent thiolate co-ordinated. It is likely that in this system, Co^I

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: $\mu_B = 9.27 \times 10^{-24}$ J T^{-1}.

Table 1 Positional parameters for compound **1** with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Co(1)	0.8742(2)	0.1520(2)	0.7869(1)
Co(2)	1.0672(2)	0.0937(2)	0.7979(1)
Co(3)	1.0179(2)	0.1971(2)	0.8624(1)
Co(4)	0.4377(2)	0.0573(2)	0.0785(1)
Cl(1)	0.4698(6)	−0.0002(5)	0.1584(2)
Cl(2)	0.3481(6)	0.1806(5)	0.0808(3)
S(4)	0.3763(5)	−0.0914(4)	−0.0053(2)
S(11)	0.8496(4)	0.1500(3)	0.8697(2)
S(12)	0.9142(4)	0.0165(3)	0.7880(2)
S(21)	0.9786(4)	0.1522(3)	0.7247(2)
S(22)	0.9144(4)	0.2846(3)	0.8069(2)
S(31)	1.0989(4)	0.0733(3)	0.8832(2)
S(32)	1.1631(4)	0.2094(3)	0.8223(2)
P(1)	0.7118(4)	0.1585(4)	0.7427(2)
P(2)	1.1737(5)	0.0074(4)	0.7606(3)
P(3)	1.0452(5)	0.2794(4)	0.9322(2)
O(1)	0.352(1)	−0.019(1)	0.0297(6)
O(2)	0.578(1)	0.068(1)	0.0546(5)
C(11)	0.846(2)	0.038(1)	0.8873(8)
C(12)	0.873(2)	−0.026(1)	0.849(1)
C(13)	0.606(2)	0.195(2)	0.7789(7)
C(14)	0.623(2)	0.286(2)	0.800(1)
C(15)	0.657(2)	0.059(1)	0.717(1)
C(16)	0.711(2)	0.017(2)	0.678(1)
C(17)	0.706(2)	0.225(1)	0.6859(7)
C(18)	0.599(2)	0.230(2)	0.650(1)
C(21)	1.012(2)	0.263(1)	0.7131(7)
C(22)	0.983(2)	0.324(1)	0.7547(9)
C(23)	1.103(2)	−0.037(1)	0.7002(8)
C(24)	1.157(2)	−0.105(2)	0.674(1)
C(25)	1.226(2)	−0.085(1)	0.799(1)
C(26)	1.142(2)	−0.141(2)	0.816(1)
C(27)	1.295(2)	0.051(2)	0.738(1)
C(28)	1.274(2)	0.123(2)	0.699(1)
C(31)	1.243(2)	0.096(2)	0.900(1)
C(32)	1.272(2)	0.172(2)	0.872(1)
C(33)	0.920(2)	0.322(2)	0.951(1)
C(34)	0.934(2)	0.381(2)	0.999(1)
C(35)	1.126(2)	0.376(2)	0.928(1)
C(36)	1.076(3)	0.442(2)	0.890(1)
C(37)	1.115(2)	0.231(2)	0.991(1)
C(38)	1.061(2)	0.155(2)	1.010(1)
C(41)	0.254(2)	−0.144(2)	−0.025(1)
C(42)	0.269(4)	−0.225(2)	−0.056(1)
C(43)	0.467(2)	−0.163(2)	0.031(1)
C(44)	0.425(3)	−0.202(2)	0.073(1)

could be responsible for activating the thiolate and promoting the release of S by reductively cleaving the C–S bond. Recent investigations on the relationships between the products and reaction conditions have shown that the length of reaction time appears to be particularly significant. By shortening the reaction time (3–4 h) only some of the dithiolate undergoes desulfurization, and compound **1** and $[Co_4Cl(\mu_3\text{-}S)(edt)_3(PPh_3)_3]$ were obtained.[5] Like the edt in the latter compound, which plays a dual role providing both the bridging chelate and the capping sulfur atom,[5] the edt in compound **1** functions not only as a bridging bidentate ligand but also as a donor of the bridging diethyl sulfone *via* intramolecular C–S bond cleavage. On further reduction of the reaction time, as in the formation of $[Co_3(bdt)_3(PPh_3)_3][CoBr_3(dmf)]$ **2** (dmf = *N*,*N*-dimethylformamide) the dithiolate only co-ordinates to the metal atoms and no C–S cleavage is observed.[4]

Based on literature precedents and the products obtained from this reaction system,[5–7] a reasonable mechanism for the production of the dimeric moiety $[Co_2Cl_4(\mu\text{-}O_2SEt_2)_2]$ of compound **1** can be postulated. The $tpdt^{2-}$ ligand formed *via* the cleavage of the edt^{2-} C–S bond is known,[9] and the addition of dioxygen to sulfur by oxygenation of thiolates has also been reported.[10] Thus, it seems possible that in this system the dimeric product could be generated by first abstracting one sulfur atom from two edt^{2-} ions giving a $tpdt^{2-}$ group, then loss of two sulfur atoms from $tpdt^{2-}$ and oxygenation would form diethyl sulfone. Eventually the linking of two $CoCl_2$ units through the oxygen atoms of diethyl sulfone would afford the observed dimeric product. Besides providing a novel convenient synthetic entry into other cobalt–thiolate derivatives, the disruption of the C–S bond found in this reaction system may be related to the important primary step in hydrodesulfurization catalytic procedures.[11] Although the cleavage of the C–S bond is documented in the mononuclear complexes $[ReS(edt)_2]^-$ and $[NbS(edt)(tpdt)]^-$,[9] this is the first compound containing cobalt in a mixed polymer, of which the bridging diethyl sulfone was indirectly produced by the cleavage of the dithiolate C–S bond. This work is still in progress and the formation mechanism needs to be studied further.

Table 2 Selected bond distances (Å) and angles (°) for compound **1**

Co(1)–Co(2)	2.556(4)	Co(2)–S(32)	2.218(6)
Co(1)–Co(3)	2.562(4)	Co(4)–O(1)	1.95(1)
Co(2)–Co(3)	2.462(4)	Co(4)–O(2)	1.94(1)
Co(1)–S(11)	2.202(6)	Co(4)–Cl(1)	2.241(7)
Co(1)–S(12)	2.184(7)	Co(4)–Cl(2)	2.240(8)
Co(1)–S(21)	2.205(5)	S(11)–C(11)	1.82(2)
Co(1)–S(22)	2.187(7)	S(12)–C(12)	1.85(2)
Co(2)–S(12)	2.248(6)	S(4)–O(1)	1.51(2)
Co(2)–S(21)	2.253(6)	S(4)–C(41)	1.75(2)
Co(2)–S(31)	2.208(6)	S(4)–C(43)	1.77(3)
Co(2)–Co(1)–S(12)	55.9(2)	Co(1)–Co(3)–S(22)	53.5(2)
Co(2)–Co(1)–S(21)	55.9(2)	Co(2)–Co(3)–S(31)	56.0(2)
Co(3)–Co(1)–S(12)	97.1(2)	Co(2)–Co(3)–S(32)	56.3(2)
Co(3)–Co(1)–S(21)	97.6(2)	S(11)–Co(3)–S(31)	95.2(2)
S(12)–Co(1)–S(22)	151.6(2)	S(31)–Co(3)–S(32)	79.4(2)
S(11)–Co(1)–S(21)	152.1(2)	O(1)–Co(4)–O(2)	106.7(6)
Co(2)–Co(1)–P(1)	150.1(2)	Cl(1)–Co(4)–O(1)	111.1(5)
Co(3)–Co(1)–P(1)	152.4(2)	Cl(1)–Co(4)–O(2)	105.8(5)
S(11)–Co(1)–P(1)	105.4(2)	Cl(2)–Co(4)–O(1)	108.6(5)
S(12)–Co(1)–P(1)	104.2(2)	Cl(2)–Co(4)–O(2)	114.1(5)
S(21)–Co(1)–P(1)	102.6(2)	O(1)–S(4)–O(2)	117(1)
S(22)–Co(1)–P(1)	104.2(2)	O(1)–S(4)–C(43)	109(1)

Structure.—A single crystal of compound **1** has been characterized by X-ray diffraction. Final positional parameters and selected bond distances and angles are listed in Tables 1 and 2, respectively. The molecular structure consists of three well separated discrete units, two similar trimers $[Co_3(edt)_3(PEt_3)_3]$ and one dimer $[Co_2Cl_4(\mu\text{-}O_2SEt_2)_2]$. The two cobalt atoms in the dimer (interatomic distance 4.88 Å) are linked *via* the oxygen atoms of two diethyl sulfone ligands forming a $Co_2O_4S_2$ eight-membered ring with a crystallographic inversion centre. Moreover, each Co is further co-ordinated to two terminal chloride ligands and therefore is surrounded by two oxygen and two chlorine atoms as shown in Fig. 1. The Co atoms of the dimer are at the centre of a distorted tetrahedron, with bond angles varying between 105.8(5) [Cl(1)–Co(4)–O(2)] and 114.1(5)° [O(2)–Co(4)–Cl(2)] and with mean bond lengths Co(4)–O 1.94 and Co(4)–Cl 2.240 Å. The Co(4)–O distance (1.94 Å) is somewhat shorter than those in $[Co_4Na_3(\mu_3\text{-}O)_2(SC_5H_4NO)_8(dmf)_4]^+$ (2.01 and 2.12 Å)[12] and $[CoBr_3(dmf)]^-$ of **2** (2.07 Å).[4]

The trimer $[Co_3(edt)_3(PEt_3)_3]$ in complex **1** is formed from an isosceles triangle of cobalt atoms with each cobalt bearing one triethylphosphine ligand. Considering the framework of the $Co_3P_3(edt)_3$ unit only, there is a pseudo mirror-image plane passing through the Co_3P_3 plane and bisecting the C(31)–C(32) bond. There are two co-ordination modes of the bidentate edt^{2-} ligand which either caps the three metal atoms of the

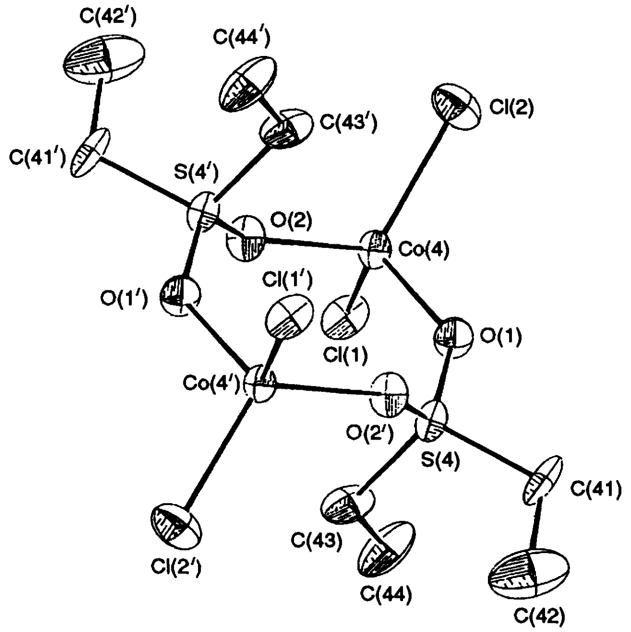

Fig. 1 A perspective view of $[Co_2Cl_4(\mu\text{-}O_2SEt_2)_2]$

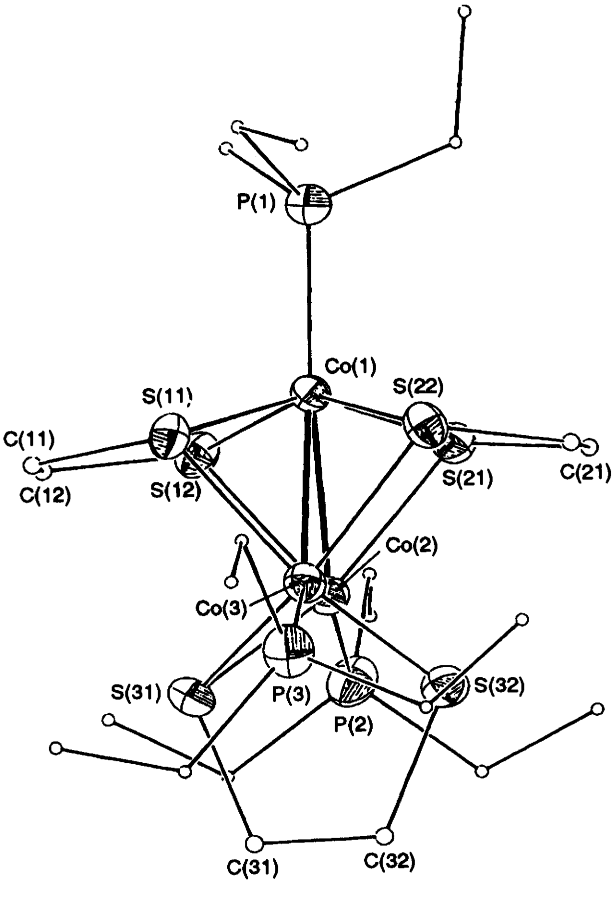

Fig. 2 A perspective view of $[Co_3(edt)_3(PEt_3)_3]$

triangular plane or bridges two of the metal atoms. The two long Co(1)–Co(2) (2.556 Å) and Co(1)–Co(3) (2.562 Å) bonds are both bridged on two sides by a bidentate edt^{2-} ligand with the mirror plane crossed by the two ligands, while the short Co(2)–Co(3) bond (2.462 Å), at the bottom of the isosceles triangle, is bridged by the third edt^{2-} ligand as shown in Fig. 2. The trimer is similar in structure to the related trinuclear cobalt complexes $[Co_3(bdt)_3(PPh_3)_3]^+$ **2**[4] and neutral $[Co_3(bdt)_3(PBu^n_3)_3]$ **3**[2] with bridging benzene-1,2-dithiolate ligands (bdt^{2-}). Some bond distances and angles for the trinuclear portions of complexes **1**–**3** are listed in Table 3 for comparison. The Co(2)–Co(3) bond in **1** is slightly shorter than the corresponding one in complex **2** (2.482 Å) and slightly longer than that in **3** (2.451 Å). The average Co–Co distance (2.527 Å) in **1** is between those of complexes **3** (2.517 Å) and **2** (2.539 Å) and similar to that of $[Co_3(CO)_6(PPh_3)S(S_2COMe)]$ (2.52 Å),[13] but shorter than that of $[Co_3(\eta^5\text{-}C_5H_5)_3(\mu_4\text{-}S)_2]$ (2.687 Å).[14] In the trinuclear unit of **1** the average Co(1)–S distance (2.195 Å) between Co(1) and the edt [S(11–22)] ligands is relatively short compared with the average distance (2.216 Å) of Co(2,3)–S between Co(2,3) and edt [S(31,32)], and with that (2.255 Å) between Co(2,3) and edt [S(11–22)]. All the above mentioned Co–S distances in the trimer of complex **1** are shorter than the corresponding ones in the bdt-containing complexes **2** and **3** as shown in Table 3. Therefore, the mean Co–S distance of 2.222 Å in **1** is the shortest in comparison to those in **2** (2.248 Å) and **3** (2.271 Å). The average Co–P bond distance (2.202 Å) in **1** is similar to that (2.203 Å) in **3**, both being shorter than that in complex **2** (2.223 Å) due to the difference between alkyl (**1** and **3**) and aryl groups (**2**) on the phosphine. The P(1)–Co(1)–S angles in edt^{2-}-containing **1** (102.6–105.4°) are somewhat different to the corresponding ones (97.25–111.49°) in bdt^{2-}-containing **2**. The co-ordination sphere of each cobalt atom in the trimer of **1** is a distorted square pyramid with the four sulfur atoms of edt^{2-} lying at the corners of the square and one phosphorus atom of the phosphine ligand in the apical position.

Table 3 Comparison of average atomic distances (Å) and bond angles (°) for the trinuclear species in **1**, **2** and **3**

	1	**2**	**3**
Co–Co	2.527	2.539	2.517
Co(2)–Co(3)	2.462	2.482	2.451
Co(1)–Co(2,3)	2.559	2.568	2.550
Co–S	2.222	2.248	2.271
Co(1)–S	2.195	2.211	2.220
Co(2,3)–S(11–22)	2.255	2.279	2.316
Co(2,3)–S(31,32)	2.216	2.254	2.277
Co–P	2.202	2.223	2.203
Co(2)–Co(1)–Co(3)	57.5(1)	57.811(7)	57.44(3)
Co(1)–Co(2)–Co(3)	61.1(1)	60.73(2)	61.10(3)
Co(1)–Co(3)–Co(2)	61.4(1)	61.46(2)	61.45(3)
Co(1)–S–Co(2,3)	70.2	69.2	68.4
Co(2)–S–Co(3)	67.5	66.82	65.12

The monocation $[Co_3(bdt)_3(PPh_3)_3]^+$ **2** with benzenedithiolate ligands could be compared with neutral $[Co_3(bdt)_3(PBu^n_3)_3]$ **3**, the latter of which shows two reversible redox couples in its cyclic voltammogram corresponding to one-electron redox reactions.[2] The electrochemical behaviour of compound **1** is much similar to neutral **3**, also having two redox couples: a reversible reduction at −1.36 V ($E_{\frac{1}{2}} = -1.28$ V, $i_{pa}/i_{pc} \approx 1$) and a reversible oxidation at 0.65 V ($E_{\frac{1}{2}} = +0.59$ V, $i_{pa}/i_{pc} \approx 1$) in MeCN solution in the region −1.60 to +1.00 V at ambient temperature. The similar cyclic voltammograms imply that the trinuclear units in **1** are neutral and the above redox couples may correspond to the one-electron redox reactions shown in equation (1). The solution conductivity of compound

$$[Co_3(edt)_3(PEt_3)_3]^+ \underset{-e}{\overset{+e}{\rightleftharpoons}} [Co_3(edt)_3(PEt_3)_3] \underset{-e}{\overset{+e}{\rightleftharpoons}} [Co_3(edt)_3(PEt_3)_3]^- \qquad (1)$$

1 ($\Lambda = 118$ S cm^2 mol^{-1}) in MeCN at ambient temperature is low for a 1:1 salt which may also indicate that $[Co_3(edt)_3(PEt_3)_3]_2[Co_2Cl_4(\mu\text{-}O_2SEt_2)_2]$ **1** is in the neutral form and contains co-crystallized neutral species.

Like the trinuclear complexes in **2** and **3**, the trimer of **1** in solution retains its solid-state structure. The ^1H NMR of complex **1** in $CDCl_3$ at ambient temperature shows resonances at δ 2.42 and 2.30 (2:1) attributable to the two sets of co-ordinated edt^{2-} groups, and the multiplet peaks at δ 1.96, 1.02 and 1.98, 1.19 with an intensity ratio of 2:1 are due to the two sets of triethylphosphine ligands. The remaining set of two signals at δ 2.21 and 1.27, also multiplet peaks, is assigned to diethyl sulfone in the dimer of **1**. The infrared spectrum (KBr pellet) of **1** exhibited strong characteristic bands for bridging diethyl sulfone at 1350, 1260 and 1030 cm^{-1}, as compared with that of the free ligand (1320, 1290 and 1130 cm^{-1}). The red shift of 100 cm^{-1} for the S–O absorption in **1** is probably due to the ligation of diethyl sulfone to cobalt through the oxygen atoms, so that the S–O bond is weakened.

Compound **2**, containing tri- and mono-nuclear units, can be considered as possessing two effective magnetic centres. One contains two Co^{2+} and one Co^{3+} in the isosceles triangle having low-spin ($S = \frac{1}{2}$) and intermediate-spin ($S = 1$) states respectively, while the other contains only Co^{2+} in a high-spin ($S = \frac{3}{2}$) state. The observed magnetic moment of **2** at room temperature (4.57 μ_B) is somewhat smaller than the calculated value (5.39 μ_B), indicating antiferromagnetic coupling amongst the Co atoms in the triangular cation with short Co–Co distances. Compound **1** with two trimers and one dimer has a magnetic moment (μ_{eff}) of 3.80 μ_B at room temperature, from which it is deduced that all cobalt ions are in a low-spin state and antiferromagnetic interaction amongst the three cobalt atoms in the trimer is predicted.

Experimental

Operations unless specified otherwise were performed under a pure dinitrogen atmosphere, using conventional Schlenk techniques. Solvents were dried over molecular sieves and degassed with pure nitrogen before use. Disodium ethane-1,2-dithiolate was prepared from sodium and H_2edt in EtOH and the resulting white solid was collected by filtration, washed with diethyl ether, and dried *in vacuo*.[15] The compound $[CoCl(PEt_3)_3]$ was prepared according to a modified published procedure.[16] The reagents ethane-1,2-dithiol, triethylphosphine and cobalt(II) chloride were purchased from Aldrich. Elemental analyses were performed at this Institute.

Preparation of $[Co_3(edt)_3(PEt_3)_3]_2[Co_2Cl_4(\mu\text{-}O_2SEt_2)_2]$ **1**.—Disodium ethane-1,2-dithiolate (0.52 g, 3.8 mmol) in MeOH (10 cm^3) was added to a slurry of $[CoCl(PEt_3)_3]$ (1.35 g, 3 mmol) in $ClCH_2CH_2Cl$ (100 cm^3). The solution immediately turned dark brown and was stirred for 4 h at room temperature. After filtration, the solution was condensed to give an oil which was treated with dmf (20 cm^3). Diethyl ether (10 cm^3) was added, and the solution was exposed to air, then kept at −4 °C for several days. The brown crystalline product (0.36 g, 45%) was collected, washed with diethyl ether, and dried *in vacuo*. IR (KBr): 2955, 1350, 1260, 1030, 755, 710, 422, 296 cm^{-1} (Found: C, 31.2; H, 6.8; P, 9.2; S, 21.4. $C_{56}H_{134}Cl_4Co_8O_4P_6S_{14}$ requires C, 31.7; H, 6.4; P, 8.8; S, 21.2%).

Spectroscopic Measurements.—Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer, ^1H NMR spectra on a Varian FT-80A spectrometer with $CDCl_3$ as solvent and $SiMe_4$ as internal standard, downfield shifts being regarded as positive. Cyclic voltammetry was performed with a model CV-1B electrochemical apparatus equipped with an X-Y recorder in a three electrode cell with Pt working and auxiliary electrodes and a saturated calomel reference electrode. The supporting electrolyte was NBu_4ClO_4 and the scan rate was 150 mV s^{-1}. Magnetic susceptibilities (χ_g) were measured using a powdered sample at room temperature on a home-made Gouy–Faraday magnetic balance using the Faraday method.[17] Effective magnetic moments (μ_{eff}) were calculated using the diamagnetic molar correction (χ_{diam}) of the ligands: $\mu_{eff} = 2.84 [(\chi_M - \chi_{diam})T]^{\frac{1}{2}} \mu_B$.

Table 4 Crystallographic data for compound **1**

Formula	$C_{56}H_{134}Cl_4Co_8P_6S_{14}$
M	2119.63
Crystal system	Monoclinic
Space group	$P2_1/n$ (no. 14)
a/Å	12.481(7)
b/Å	15.70(2)
c/Å	25.84(2)
β/°	97.85(5)
U/Å^3	5016
Z	2
T/K	296
λ/Å	0.710 69
D_c/g cm^{-3}	1.40
μ(Mo-Kα)/cm^{-1}	18.05
F(000)	2200
Crystal size/mm	0.40 × 0.30 × 0.20
Scan method	θ–2θ
2θ range/°	2–50
Index range/°	6–12
No. of observed data [$I > 3.50\sigma(I)$]	2436
R^a	0.062
R'^b	0.072

^{a} $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. ^{b} $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

Crystal Structure Determination.—A brown single crystal of complex **1** suitable for X-ray diffraction was sealed in a capillary tube under nitrogen and data were collected at ambient temperature on a Rigaku AFC5R diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). The crystallographic and data collection and refinement parameters are summarized in Table 4. Cell constants were obtained by least-squares refinement using 25 high-angle reflections. Intensity data were corrected for Lorentz-polarization and empirical absorption. Calculations were performed on a VAX 11/785 computer with the SDP program package.[18] The structure was solved by direct methods and then by differential Fourier syntheses. All non-hydrogen atoms were refined by a full-matrix least-squares technique with anisotropic thermal parameters. Hydrogen atoms were added to the structure factor calculations in idealized positions but their coordinates and thermal parameters were not refined.

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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