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A low-valence cobalt cluster formed via capture of sulphur atom from ethanedithiol – synthesis and crystal structure of $[Co_7(\mu_4\text{-}S)_3(\mu_3\text{-}S)_3(PPh_3)_6Br] \cdot CH_3OH$

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Abstract

The low-valence cobalt cluster $[Co_7(\mu_4\text{-}S)_3(\mu_3\text{-}S)_3(PPh_3)_6Br]$ (**1**) was isolated from the reaction of $Co(PPh_3)_3Br$ with Na_2edt in ethylene chloride. The skeleton $[Co_7S_6]^+$ of **1** can be represented as a monocapped-prismane formed by the addition of the capping atom cobalt to the prismane $[Co_6S_6]$ as shown by X-ray single-crystal structure analysis. In this reaction the S^{2-} ion is derived from the edt^{2-} ion through cleavage of the C–S bond, and incorporated into the building process.

In addition to a number of transition metal–sulphur cluster compounds [1,2] some cobalt–sulphur clusters with phosphine ligands have been synthesized and characterized in our laboratory as part of a systematic investigation of their chemical properties and stereochemistry [3–6]. By employing low valent Co^+ as the starting material under definite reaction conditions, a series of polynuclear clusters has been obtained [4a,c]. Recently, we reported the crystal structure of $[Co_7S_6(PPh_3)_4X_3]$ (X = Cl or Br) (**2**) with a $[Co_7S_6]^{3+}$ core [4a]. We now present a new Co_7 cluster containing a $[Co_7S_6]^+$ core with the cobalt atoms at a lower oxidation level. Our findings may provide an example of desulphurization through disruption of the C–S bond of ethanedithiol, and may be useful for further study of the mechanism of formation of this type of reaction. Here we describe the synthesis and structural characterization of the compound $[Co_7(\mu_4\text{-}S)_3(\mu_3\text{-}S)_3(PPh_3)_6Br] \cdot CH_3OH$ (**1**). Na_2edt (H_2edt = 1,2-ethanedithiol) in methanol was added to a stirred suspension $Co(PPh_3)_3Br$ of ethylene chloride at room temperature. The mixture was then stirred for 20 h, resulting in a dark brown solution. After filtration and concentration, the solution gave black crystals of the title compound on standing at 4°C for several days. Recrystallization from a mixture of ethylene chloride–methanol yielded crystals suitable for X-ray crystallographic analysis. The solid-state IR spectrum (KBr pellets) showed bands at 750, 700, 545, 520 cm^{-1} characteristic of metal-coordinated triphenylphosphine groups. The ^1H NMR spectrum of **1** ($CDCl_3$) showed multiplet signals due to PPh_3 at 7.50 and 7.25 ppm.

An X-ray diffraction study of a single crystal established the molecular structure of compound **1** as shown in Fig. 1 (see also Crystal data). The inner Co_7 core consists of seven faces: three 4Co and four 3Co faces, in which each of the 4Co faces is quadruply bridged by one sulphur atom μ_4-S(4,5,6), and each of the 3Co faces, except the bottom face as shown in Fig. 1, is triply bridged by one sulphur atom μ_3-S(1,2,3). The structure of the $[Co_7S_6]^+$ core, which can be considered as a monocapped-prismane formed by the addition of the capping atom cobalt to the prismane $[Co_6S_6]$, consists of an apical atom Co(7), two layers of cobalt atoms, 3Co(1,2,3) and 3Co(4,5,6), and two layers of sulphur atoms, 3S(1,2,3), 3S(4,5,6). In the $Co_7S_6P_6Br$ framework which possesses a pseudo-three-fold axis through the Co(7)–Br bond, the apical Co(7) atom is terminally coordinated by one bromine atom while each of the Co(1,2,3) and Co(4,5,6) atoms is coordinated by one triphenylphosphine ligand. There are

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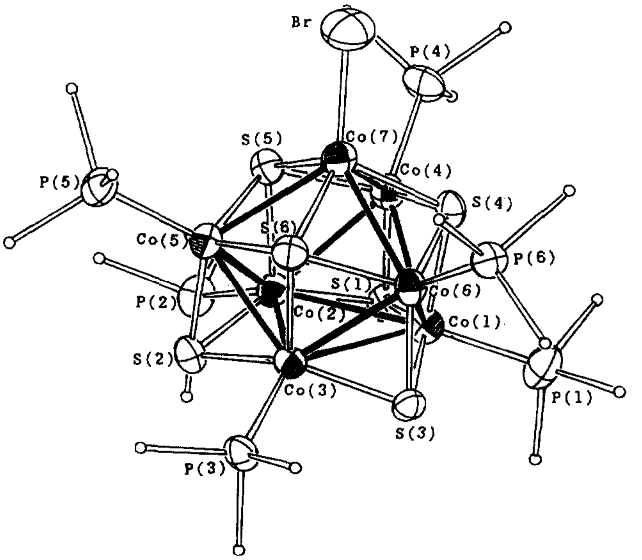

Fig. 1. A perspective view of $[Co_7(\mu_4\text{-}S)_3(\mu_3\text{-}S)_3(PPh_3)_6Br]$. Selected atomic distances (Å) and bond angles (°) are as follows: Co(1)–Co(2) 2.892(3), Co(1)–Co(3) 2.919(4), Co(2)–Co(3) 2.921(3), Co(1)–Co(6) 2.578(4), Co(2)–Co(4) 2.576(3), Co(2)–Co(5) 2.595(4), Co(4)–Co(7) 2.705(3), Co(5)–Co(7) 2.680(3), Co(6)–Co(7) 2.698(4), Co(2)–S(1) 2.176(5), Co(3)–S(3) 2.182(5), Co(7)–S(4) 2.222(5), Co(7)–S(6) 2.205(5), Co(1)–P(1) 2.234(5), Co(7)–Br 2.369(3); Co(1)–Co(2)–Co(3) 60.29(7), Co(3)–Co(6)–Co(7) 85.67(9), Co(4)–Co(7)–Co(5) 90.81(9), S(4)–Co(4)–S(5) 104.0(2), S(6)–Co(7)–Br 120.4(2).

three types of Co–Co bond: the short bonds (2.585 Å) of Co(1,2,3)–Co(4,5,6) between the two cobalt layers, the medium bonds (2.694 Å) of Co(4,5,6)–Co(7) between the upper layer and the apical cobalt atom, and the long bonds (2.911 Å) within the lower 3Co(1,2,3) layer. The Co ⋯ Co distance (3.83 Å) being non-bonding in the upper 3Co(4,5,6) layer is comparatively much longer than that in the bottom layer (2.911 Å).

The skeleton $[Co_7S_6]^+$ of compound **1** is similar to the core $[Co_7S_6]^{3+}$ in $[Co_7S_6(PPh_3)_4X_3]$ (X = Br or Cl) (**2**) [5], but different from the core $[Co_7S_6]^{2+}$ in $[Co_7S_6(PPh_3)_5Cl_2]$ (**3**), which possesses practically no symmetry element [2b]. The cluster core of **2** can be generated from that in Fig. 1 by replacing three P(4,5,6) with three X, and the apical bromine atom with phosphorus. The average Co–Co distances of 2.694 Å and 2.911 Å for the Co(7)–Co(4,5,6) and lower 3Co(1,2,3) layer respectively in **1** are longer than those of compound **2** (2.607 Å and 2.883 Å) and compound **3** (2.631 Å and 2.885 Å). The Co(7)–(μ_4-S) distance (2.214 Å) and Co–(μ_3-S) distances (2.181 Å) found here are comparable with the corresponding distances 2.16 Å and 2.13 Å respectively in **2**. Unlike compounds **2** and **3**, in which the CoS_3E (E = P or Cl, Br) units are nearly tetrahedral, the coordination spheres of Co(7) and Co(4,5,6) in **1** are irregular with bond angles ranging from 101.9° to 120.4°.

Compound **1** has cobalt atoms with a nominal mean oxidation state of 1.85^+. In addition to the interesting structural characteristics, cluster **1** is significant for its synthetic route. $CoBr(PPh_3)_3$ was found in this system to react with dithiolate, yielding an unexpected polynuclear Co–S compound. In the light of these results, it is likely that in the presence of Co^+ and PPh_3, the S^{2-} ion dissociates from the edt^{2-} ion by cleavage of the C–S bond, followed by congregation with coordination-unsaturated Co–PPh_3 fragments to form the cluster. This type of reaction bears an apparent similarity to the preparation of $[ReS(edt)_2]^-$, $[NbS(edt)(SC_2H_4SC_2H_4S)]^-$ and $[Ni(SC_2H_4SC_2H_4S)PPh_3]$ in which disruption of the C–S bond is thought to take place [5,7]. All of these compounds are mono-nuclear dithiolato complexes with or without terminal sulphur atoms, and were obtained using the same initial reactant Na_2edt ($NaSCH_2CH_2SNa$). Substitution of Na_2pdt (H_2pdt = 1,2-propanedithiol) for Na_2edt also leads to the polynuclear clusters $[Co_6S_8(PPh_3)_6 \cdot L$ (L = solvents) [4c]. No cleavage of the C–S bond was observed when the high oxidation state cobalt compound $CoCl_2(PPh_3)_2$ was used as the starting material with edt^{2-} or pdt^{2-} under similar conditions. Although disruption of the C–S bond is documented [5,7], this is the first example of polynuclear cluster formation with bridged S^{2-} groups obtained by sulphur atom capture from dithiolate reactants. Further study of the formation mechanism of these clusters via such reactions is under way.

Crystal data. For $C_{109}H_{94}Co_7BrOP_6S_6$, $M = 2290.63$, monoclinic, space group $P2_1/c$, $a = 22.213(10)$, $b = 24.974(10)$, $c = 20.231(7)$ Å, $\beta = 98.57(4)°$, $V = 11097.0$ Å^3, $Z = 4$, $D_c = 1.371$ g cm^{-3}, $F(000) = 4664$, $\mu = 16.1$ cm^{-1}. Crystal dimensions 0.4 × 0.5 × 0.3 mm. Determination of cell constants and data collection were carried out at room temperature with Mo Kα radiation on a Rigaku AFC 5R four-circle diffractometer in the range $1° < \theta < 25°$. A total of 20572 refections was collected and 5449 reflections with $I > 3.0\sigma(I)$ were used for structure determination and refinement. The coordinates of all metal atoms were determined by direct methods and the remaining non-hydrogen atoms were located from successive difference Fourier syntheses. The structure was refined by a full-matrix least-squares technique with anisotropic temperature factors for all cobalt, sulphur and phosphorus atoms and isotropic temperature factors for the remaining non-hydrogen atoms. The final R and R_w are both 0.077. All calculations were carried out on a VAX/785 computer using an SDP program package.

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