Synthesis and Crystal Structure of a Square Planar Tetra-cobalt Complex with Two Quadruply-bridging Sulphur Atoms $[(\eta^5\text{-Cp})_4Co_4(\mu_4\text{-S})_2]$

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The cluster compound $[(\eta^5\text{-Cp})_4Co_4(\mu_4\text{-S})_2]$ was isolated from the reaction between $[(\eta^5\text{-Cp})Co(PR_3)_2]$ and Li_2S at 60 °C; the tetramer is capped by two quadruply-bridging sulphur atoms above and below the Co_4 square plane to form a distorted octahedral core Co_4S_2 as shown by X-ray single crystal structural analysis.

Transition metal–sulphur clusters with cyclopentadienyl ligands have attracted the attention of numerous investigators in the past few years because of their variations of structure types, unusual stereochemistry and physicochemical properties.[1–4] A number of polynuclear cyclopentadienyl cobalt–sulphur complexes have been prepared and well characterized.[5–7] Dahl and co-workers reported the crystal structures of $[Co_4(\eta^5\text{-Cp})_4(\mu_3\text{-S})_2(\mu_3\text{-S}_2)_2]$ and $[Co_4(\eta^5\text{-Cp})_4(\mu_3\text{-S})_4]$ (n = 0, +1) both of which contain a distorted tetrahedral array of cobalt atoms with triply-bridging sulphur atoms without direct metal–metal interaction.[7] Herein we describe a square planar tetra-cobalt complex with two quadruply bridged sulphur atoms, $[Co_4(\eta^5\text{-Cp})_4(\mu_4\text{-S})_2]$.

The compound $[Co(\eta^5\text{-Cp})(PPh_3)_2]$ in toluene was added to a stirred solution of Li_2S in ethanol under a nitrogen atmosphere and the mixture was stirred at 60 °C for 4 hours. Air was then introduced to the mixture and the brown product precipitated. After filtration, the crude product was purified by recrystallization from warm *N,N*-dimethylformamide (DMF) in 61% yield. Single crystals suitable for X-ray crystallographic analysis were obtained by recrystallization from toluene–DMF. The title compound is air-stable and soluble in DMF or Me_2SO, but insoluble in less polar organic solvents. Substitution of Li_2S with elemental sulphur under the same reaction conditions also leads to the product. The IR spectrum shows characteristic bands ascribable to the cobalt–cyclopentadienyl group at 1435, 1110, 990, 860, 750, 720 cm^{-1} [7,8] and one Co–S stretching absorption at 520 cm^{-1}. The formal oxidation state of cobalt atom is 2+ and each cobalt atom should be a paramagnetic centre. The ^{1}H NMR spectrum showed a broad peak at high field (δ 1.3) for Cp compared to a narrow peak at δ 5.3 for the diamagnetic cyclopentadienyl ligand confirming the paramagnetic character of the title compound.[9]

An X-ray diffraction study of a single crystal established the molecular structure of the title compound as shown in Fig. 1.†

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† *Crystal data* for: $C_{20}H_{20}Co_4S_2$, M = 560, monoclinic, $P2_1/n$, a = 9.701(3), b = 7.671(3), c = 13.147(5) Å, β = 106.65(4); T = 23 °C, V = 937.33 Å^3, Z = 2; D_c = 1.985 g cm^{-3}, μ(Mo-Kα) = 36.93 cm^{-1}. Crystal dimensions 0.4 × 0.4 × 0.15 mm. Determination of cell constants and data collection were carried out at room temperature with Mo-Kα radiation on a RIGAKU AFC5R four-circle diffractometer in the range of $2' < 2\theta < 52.4$. A total of 2137 reflections were measured and 1555 reflections with $I > 3\sigma(I)$ were used in structure solution and refinement. Intensity data used in the structure determination and refinement were corrected for Lorentz-polarization factors, linear decay, and DIFABS. The structure was solved by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. The final conventional factors are R = 0.038 and R_w = 0.041. All calculations were carried out on a VAX 11/785 computer with the SDP program package. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

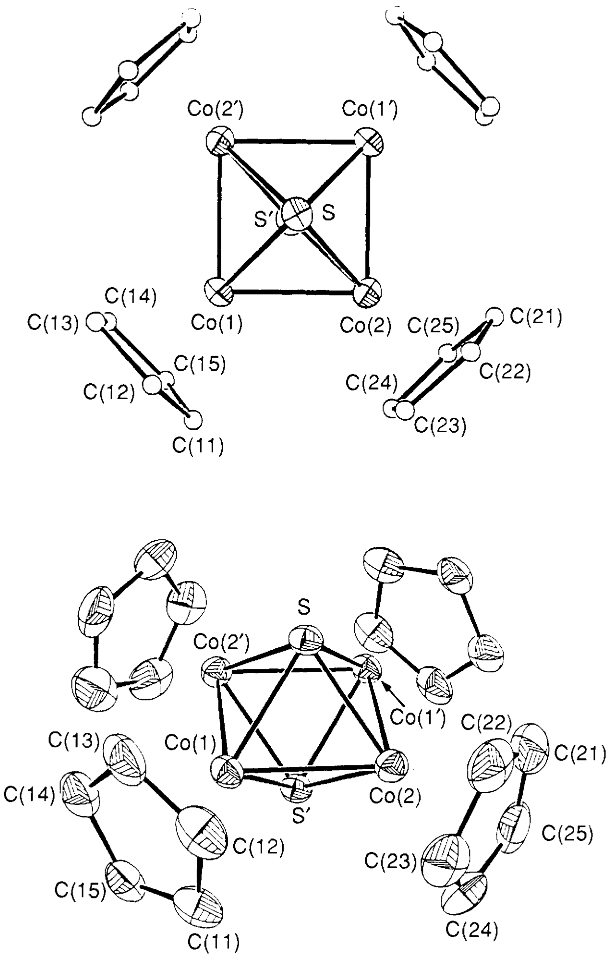

Fig. 1 Top and 'side' views of $[(\eta^5\text{-Cp})_4Co_4(\mu_4\text{-}S)_2]$. Selected atomic distances (Å) and bond angles (°) are: Co(1)–Co(2) 2.4383(9), Co–S 2.225(1)–2.233(1), Co–C(Cp) 2.072(5)–2.128(5), C–C 1.395(8)–1.447(7); Co–Co–Co 89.97(3)–90.03(3), Co(1)–S–Co(2) 66.27(4), Co(1)–S–Co(1') 101.33(4), C–C–C (within a Cp) 106.7(5)–109.2(5).

The four cobalt atoms are at the four corners of a square plane which is capped by two quadruply-bridging sulphur atoms above and below to give a distorted octahedral Co_4S_2 core. Each of the four cyclopentadienyl ligands chelates to one cobalt atom with five equal Co–C distances (2.105 ± 0.018 Å).‡ The line passing through two diagonal cobalt atoms intersects at the centroids of and is perpendicular to the two opposite cyclopentadienyl rings. One C atom of each Cp ring is essentially in the plane containing Co_4. Therefore, the entire molecule conforms closely to a distorted octahedral C_{4h} symmetry with the rotation axis passing through the two quadruply-bridging sulphur atoms and the centre of the tetra-cobalt square plane. The Co–Co distance of 2.438(1) Å is shorter than those of the isoelectronic tetranuclear compounds but with rectangular Co_4 planes, $[Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}S)_2]$ (2.48 and 2.60 Å)[10] and $[Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PPh)_2]$ (2.519 and 2.697 Å);[11] with tetrahedral Co_4, $[Co_4Cp_4(\mu_3\text{-}S)_4]$ (3.295 Å) and $[Co_4Cp_4(\mu_3\text{-}S)_2(\mu_3\text{-}S_2)_2]$ (3.27 and 3.70 Å);[7] or of the trinuclear compounds, $[Co_3Cp_3(\mu_3\text{-}S)_2]^+$ (2.56 Å) and $[Co_3Cp_3(\mu_3\text{-}S)_2]$ (2.687 Å).[1] From the 18-electron rule and the 64e count in the title compound, one would expect four Co–Co metal bonds which could account for the short Co–Co distance and stabilize the cluster compound. By the same token, this distance is longer than those in the more electron-deficient compounds such as $[Co_4Cp_4(\mu_3\text{-}CO)_2]$ (60e, 2.406 Å)[12] or $[Co_3(C_5Me_5)_3(\mu_3\text{-}CMe)]$ (2.369 Å).[13]

The average of Co–S bond length (2.229 Å) is slightly shorter than that in $[Co_3(\eta^5\text{-}Cp)_3(\mu_3\text{-}S)_2]$ or $[Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}S)_2]$ (2.26 Å). The atomic distances for Co(1)–S and Co(2)–S are 2.228(1) and 2.233(1) Å, respectively, while those for Co(1)–S' and Co(2)–S' are 2.231(1) and 2.225(1) Å, respectively. The observed variation in Co–S distances is due to the steric interactions of a slightly distorted Co_4S_2 octahedron.

The four independent Co–C(Cp) distances range from 2.072(5) to 2.128(5) Å, with a mean value of 2.105 Å, which is similar to those found in other cyclopentadienyl cobalt clusters.[5–7,9] The bond angles of Co(1')–S–Co(1) (101.36°) and Co(1)–S–Co(2) (66.27°) are appreciably smaller than the corresponding ones in $[Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}S)_2]$.

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‡ Average value with standard deviation.