Dalton Communications

Synthesis and Characterization of $[Li(OEt_2)_3]$-$[Co_2(SC_6H_2Pr^i{}_3\text{-}2,4,6)_5]$: a Compound with a Face-sharing Ditetrahedral Structure

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The reaction of $Li(SC_6H_2Pr^i{}_3\text{-}2,4,6)$ with $CoCl_2$ in diethyl ether solution affords $[Li(OEt_2)_3][Co_2(SC_6H_2Pr^i{}_3\text{-}2,4,6)_5]$ which features an anion that has a unique face-sharing structure composed of two CoS_4 tetrahedra.

The chemistry of transition-metal thiolates continues to attract widespread attention owing to its significance for a variety of fields.[1,2] Much of the work has a basis in efforts to synthesize synthetic analogues for the active sites of various metalloproteins such as alcohol dehydrogenase, ferredoxins, nitrogenases or blue copper proteins.[3,4] In a broader context they display a large variety of stoichiometries and structures that have few parallels in other species. Here we report a further new structural type for a transition-metal thiolate. This structure involves the anion $[Co_2(SC_6H_2Pr^i{}_3\text{-}2,4,6)_5]^-$ which features two geometrically distorted CoS_4 tetrahedra linked through a common face. This species forms part of the small but growing number of homoleptic cobalt(II) thiolate compounds with low aggregation numbers. These include the recently reported neutral dimer $[\{Co(SC_6H_2Bu^t{}_3\text{-}2,4,6)_2\}_2]$,[5] the mononuclear ion $[Co(SPh)_4]^{2-}$,[6] the acetonitrile adduct $[Co(SC_{10}H_{13})_3(MeCN)]^-$,[7] and the ditetrahedral, edge-sharing dimer $[Co_2(SEt)_6]^{2-}$ which exists in *syn* and *anti* configurations.[8] A number of higher nuclearity cobalt thiolate clusters have also been reported including the adamantane-like species $[Co_4(SPh)_{10}]^{2-}$,[8] the cluster $[Co_8S_6(SPh)_8]^{4-}$ {which may be reduced to $[Co_8S_6(SPh)_8]^{5-}$}[9] and the trinuclear cobalt cluster $[Co_3(\mu_3\text{-}S)\{o\text{-}(SCH_2)_2C_6H_2\}_2]^{2-}$ which was reported simultaneously by two different groups.[10,11]

The compound $[Li(OEt_2)_3][Co_2(SC_6H_2Pr^i{}_3\text{-}2,4,6)_5]$ **1*** was synthesized by the reaction of $CoCl_2$ with $Li(SC_6H_2Pr^i{}_3\text{-}2,4,6)$ in diethyl ether solution.† The product was isolated after extraction with hexane as red-brown cuboidal crystals. It was characterized structurally by X-ray crystallography,‡ ¹H NMR and UV/VIS spectroscopy and by magnetic measurements. The compound crystallizes as well separated non-interacting anions and cations. In the cation, which is illustrated in Fig. 1, each lithium ion is surrounded in a distorted trigonal-planar fashion by three ether-oxygen atoms, with angles that range from 114(2) to 127(2)°. The lithium–oxygen distances average 1.91(3) Å. A $[Li(OEt_2)_3]^+$ cation was previously reported[14] in the species $[Li(OEt_2)_3][(mes)_2BNB(mes)_2]$ (mes = $C_6H_2Me_3\text{-}2,4,6$) and it has very similar structural parameters to those in **1**. The $[Co_2(SC_6H_2Pr^i{}_3\text{-}2,4,6)_5]^-$ monoanion, the framework of which is shown in Fig. 2, has no crystallographically imposed symmetry. Two cobalt ions are bridged by three thiolato ligands, and the cobalt–cobalt distance is 2.511(4) Å. In addition, a terminal thiolato ligand is bound to each cobalt. This affords a ligand array that provides a rather distorted tetrahedral environment at the metals such that the two CoS_4 tetrahedra share a face. There is also some justification for

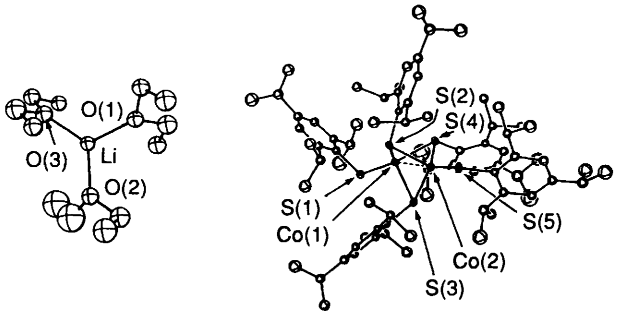

Fig. 1 Computer generated plot of $[Li(OEt_2)_3][Co_2(SC_6H_2Pr^i{}_3\text{-}2,4,6)_5]$. Hydrogen atoms have been omitted for clarity

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* This work forms part of the Ph.D. Dissertation of K. Ruhlandt-Senge, Marburg, 1991.

† Under anaerobic and anhydrous conditions $CoCl_2$ (0.28 g, 2.16 mmol) and $HSC_6H_2Pr^i{}_2\text{-}2,4,6$ (1.28 g, 5.4 mmol)[12] were suspended in diethyl ether (50 cm³) and cooled in an ice-bath. A hexane solution of LiBu (3.375 cm³, 1.6 mol dm⁻³ solution, 5.4 mmol) was added dropwise *via* syringe. The mixture turned reddish brown immediately and was stirred for 6 h at ambient temperature. The volatile materials were removed under reduced pressure and the residue was taken up in warm *n*-hexane (30 cm³). Filtration and cooling to −40 °C gave the product as red-brown crystals of **1** in 32% yield (1.1 g). UV/VIS: λ_{max} = 335 nm. ¹H NMR: δ 1.12 (br d, *o*-CH_3), 1.22 (d, *p*-CH_3), 1.26 (d, *o*-CH_3), 1.34 (m, Et_2O), 2.72 (*p*-CH), 2.80 (*o*-CH), 3.82 (Et_2O) and 6.99 (*m*-CH).

‡ Crystal data at 130 K with Mo-Kα radiation (λ = 0.710 69 Å, graphite-monochromated), Siemens R3m/V with locally modified Enraf-Nonius low-temperature appratus. Crystal data: $C_{87}H_{145}Co_2LiO_3S_5$, M = 1524.2, monoclinic, space group $P2_1/n$, a = 17.394(21), b = 26.381(14), c = 20.165(16) Å, β = 90.48(2)°, U = 9248(13) Å³, Z = 4, 4229 unique observed $[I > 3\sigma(I)]$ data (total number of data 13667). Red brown cuboid: 0.4 × 0.4 × 0.3 mm. The structure was solved by a Patterson synthesis and refined by full-matrix least-squares refinement. An absorption correction utilizing $F_o - F_c$ differences was applied using the program XABS.[13] Only the cobalt and the sulfur atoms were refined anisotropically. Hydrogen atoms were included in the refinement at calculated positions using a riding model with C–H 0.96 Å and fixed U_H = 0.08 Å; $F(000)$ = 3312, μ = 0.513 mm⁻¹, $w^{-1} = \sigma^2(F) + 0.0026F^2$, 428 parameters, R = 0.078, $R'\{=[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ = 0.082. Atomic coordinates, 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.*, 1993, Issue 1, pp. xxiii–xxviii.

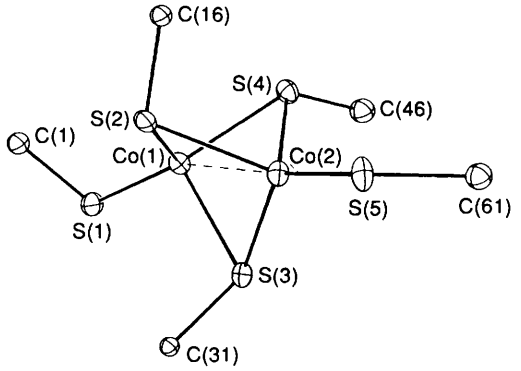

Fig. 2 Computer generated plot of the core of the $[Co_2(SC_6H_2Pr^i{}_3\text{-}2,4,6)_5]^-$ anion. Hydrogen atoms have beem omitted for clarity. Important bond distances (Å) and angles (°) are as follows: Co(1) ··· Co(2) 2.511(4), Co(1)–S(1) 2.191(5), Co(1)–S(2) 2.309(5), Co(1)–S(3) 2.314(5), Co(1)–S(4) 2.348(5), Co(2)–S(2) 2.322(5), Co(2)–S(5) 2.216(5), Co(2)–S(3) 2.371(5), Co(2)–S(4) 2.336(5), O(1)–Li–O(2) 114(2), O(1)–Li–O(3) 118(2), O(2)–Li–O(3) 127(2), Co(2)–Co(1)–S(1) 152.1(2), Co(2)–Co(1)–S(2) 58.8(1), S(1)–Co(1)–S(2) 115.6(2), Co(2)–Co(1)–S(3) 57.4(1), S(2)–Co(1)–S(3) 99.5(2), Co(2)–Co(1)–S(4) 57.4(1), S(1)–Co(1)–S(4) 148.6(2), S(2)–Co(1)–S(4) 88.4(2), S(3)–Co(1)–S(4) 94.5(2), S(2)–Co(2)–S(3) 97.5(2), S(2)–Co(2)–S(4) 87.2(2), S(3)–Co(2)–S(4) 94.6(2), S(3)–Co(2)–S(5) 128.9(2), S(2)–Co(2)–S(5) 112.8(2), S(3)–Co(2)–S(5) 128.9(2), S(4)–Co(2)–S(5) 125.6(2), Co(1)–S(2)–Co(2) 64.9(1), Co(1) –S(3)–Co(2) 65.6(1), Co(2)–S(4)–Co(1) 64.8(1), S(4)–Co(2)–S(5) 125.6(2), Co(1)–Co(2)–S(3) 57.1(1), Co(1)–Co(2)–S(4) 57.8(1)

viewing the structure as a face-sharing tetrahedron and trigonal bipyramid (which has an apex missing) owing to the extremely wide S(1)–Co(1)–S(4) angle of 148.6(2)°. The Co–S distances for the bridging thiolato groups are in the range 2.309(5)–2.371(5) Å, the Co–S–Co angles, 64.8(1), 64.9(1) and 65.6(1)° are remarkably acute. The cobalt–sulfur distances for the terminal ligands are 2.191(5) and 2.215(5) Å.

The $[Co_2(SC_6H_2Pr^i{}_3\text{-}2,4,6)_5]^-$ anion is apparently the first example of a molecular species with two tetrahedra sharing a common face.* It should be noted, however, that the coordination spheres at cobalt are severely distorted with angles in the range 88.4(2)° [S(2)–Co(1)–S(4)] to 148.6(2)° [S(1)–Co(1)–S(4)] for Co(1) and 87.2(2)° [S(2)–Co(2)–S(4)] to 128.9(2)° [S(3)–Co(2)–S(5)] for Co(2). The bridging Co–S bond length, 2.34(2) Å (av.), is in good agreement with those observed in $[Co_2(SEt)_6]^{2-}$ [2.363 Å (av.)].[8] The Co–S bond length for the terminal groups 2.20(1) Å (av.) is in the lower end of the range for terminal Co–S distances.[7,8,10,11] The narrow Co–S–Co angles of the bridging thiolato ligands, which range from 64.8(1) to 65.6(1)°, may be contrasted with those in the edge-sharing structure of $[Co_2(SEt)_6]^{2-}$ which has Co–S–Co angles near 80°.[8] The Co ··· Co distance in **1**, 2.511(4) Å, is shorter than those reported in $[Co_3(\mu_3\text{-}S)\{o\text{-}(SCH_2)_2C_6H_2\}_3]^{2-}$ (2.715–2.825 Å),[10,11,12] $[Co_2(SEt)_6]^{2-}$ [8] [3.020(3)–3.045(2) Å] or in $[\{Co(\mu\text{-}SC_6H_2Pr^i{}_3\text{-}2,4,6)\{N(SiMe_3)_2\}_2]$ (2.712 Å).[15] It is slightly longer than those in $[Co_2(\eta^5\text{-}C_5H_5)(C_{10}Cl_4S_4)]$[16] which has Co ··· Co distances of 2.415 and 2.434 Å. The UV/VIS λ_{max} value of 335 nm for **1** is in good agreement with the S ⟶ Co core charge-transfer band (λ_{max} 343 nm) found for $[Co_8S_6(SPh)_8]^{4-}$.[9] The ^1H NMR spectrum of **1** affords two sets of $2,4,6\text{-}Pr^i{}_3C_6H_2$ peaks in a 3 : 2 ratio at normal chemical shifts, indicating that **1** is diamagnetic at room temperature. Magnetic studies of solid samples of **1** at ambient temperature confirmed its diamagnetic character. This suggests a strong antiferromagnetic interaction between the cobalt centres. The synthesis of the iron analogue of **1** is in progress and will be published together with more detailed investigation of **1**.

Acknowledgements

We thank the National Science Foundation for financial support.

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Received 5th *November* 1991; *Communication* 2/05900B

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* *Note added at proof.* After the submission of this communication we became aware of the face-sharing species $[NEt_4][CO_2(SEt)_5]$[17] which was published while our work was being reviewed.