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Novel metal thiolates: $[Mn_2(SC_6H_3\{SiMe_3\}_2)_4(C_4H_8O)]$, a binuclear manganese thiolate complex with tetrahedral and trigonal-planar metal coordination*

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Abstract

Reaction of $[Mn(N\{SiMe_3\}_2)_2(C_4H_8O)]$ with two equivalents of HSC_6H_3-2,6-$(SiMe_3)_2$ in n-pentane leads to the formation of $[Mn_2(SC_6H_3\{SiMe_3\}_2)_4(C_4H_8O)]$ which was isolated as the mono-pentane solvate. According to the results of an X-ray structure determination, this binuclear complex contains both trigonally and tetrahedrally coordinated manganese sites simultaneously and thus is a rare example of complexes which are built up by metal ions in the same oxidation state but with different coordination numbers.

Key words: Kinetics and mechanism; Crystal structures; Manganese complexes; Metal thiolates

Tetrahedral MS_4 units are typical features of homoleptic thiolate complexes of the divalent 3d metals Mn, Fe, Co and Zn if the ligands are sterically innocent and monofunctional. Besides simple tetrahedral compounds of general formula $[M(SR)_4]^{2-}$, other complexes of higher nuclearity with MS_4 tetrahedra connected via common sulfur atoms also exist. Striking examples are adamantane-like complexes of general formula $[M_4(SR)_{10}]^{2-}$ as well as binuclear species of general type $[M_2(SR)_6]^{2-}$ which are built up by MS_4 tetrahedra sharing vertices and edges, respectively [1]. If two MS_4 tetrahedra share a common face, binuclear complexes of general formula $[M_2(SR)_5]^-$ result. The first examples of complex anions exhibiting this extremely rare structural feature have been reported very recently [2].

Increasing the sterical requirements of the ligands, however, favours the formation of complexes with smaller coordination numbers. This tendency is demonstrated by complexes of general formula $[M_2(SC_6H_2\{2,4,6\text{-}^tBu\}_3)_4]$ (M = Mn, Fe, Co [3]; Zn [4]; Cd [5]) which do not contain tetrahedral MS_4, but trigonal-planar MS_3 coordination sites with a common edge. However, thiolates containing both three- and four-coordinated metal atoms are very rare. To our knowledge, $[Hg_5(SCH_2CH_2S)_4(SEt)_4]^{2-}$ [6] is, at present, the only example.

In this paper we report the synthesis and structure of the first binuclear thiolate complex wherein the metal atoms possess the same oxidation state but different coordination numbers. A structurally related complex with phosphide instead of thiolate ligands has already been reported [7].

The reaction of $[Mn(N\{SiMe_3\}_2)_2(C_4H_8O)]$ with two equivalents of HSR (R = C_6H_3-2,6-$\{SiMe_3\}_2$) in n-pentane results in the formation of the novel thiolate complex $[Mn_2(SC_6H_3\{SiMe_3\}_2)_4(C_4H_8O)]$ (**1**), which crystallizes as the mono-pentane solvate of formula $[Mn_2(SC_6H_3\{SiMe_3\}_2)_4(C_4H_8O)]\cdot C_5H_{12}$ (**2**)[†].

According to the results of the X-ray structure determination, each manganese atom is surrounded by three sulfur atoms (Fig. 1)[††]. Two of the four thiolate groups act as bridging ligands. The resulting central four-membered $Mn_2(\mu\text{-}S)_2$ heterocycle is not completely planar but slightly folded along its S…S diagonal. The dihedral angle between adjacent MnS_2 triangles is calculated to be 9.8°. The remarkably large distance of

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[*] Dedicated to Professor Helmut Werner on the occasion of his 60th birthday.

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[†] *Experimental.* All operations were carried out in a glove box under N_2 atmosphere. A solution of 908 mg (2.03 mmol) of $[Mn(N\{SiMe_3\}_2)_2(C_4H_8O)]$ [8] in 10 ml of n-pentane was added dropwise within a few minutes to a solution of 920 mg (4.07 mmol) of HSC_6H_3-2,6-$\{SiMe_3\}_2$ [9] in 20 ml of n-pentane. The reaction mixture was heated and the solvent was evaporated until crystallization occurred. The solution was allowed to cool down to room temperature. After 24 h yellow crystals had separated; yield 450 mg (0.36 mmol, 36%).

[††] *Crystal data.* Siemens P4RA four circle diffractometer, rotating anode generator, Mo Kα radiation ($\lambda = 0.71073$ Å), graphite monochromator, scintillation counter, $T = 150$ K, empirical absorption corrections; SHELXTL-PLUS programs, direct methods, full-matrix least-squares refinements; $C_{57}H_{104}Mn_2OS_4Si_8$, formula weight 1268.24, orthorhombic, space group $P2_12_12_1$, $a = 15.958(2)$, $b = 17.088(3)$, $c = 26.536(5)$ Å, $V = 7235$ Å^3, $Z = 4$, $D_x = 1.164$ g cm^{-3}, μ(Mo Kα) = 0.63 mm^{-1}, transmission range 0.843–0.759, crystal dimensions c. 0.45 × 0.41 × 0.33 mm, ω-scan, $2\theta_{max} = 54°$, 8616 unique reflections, R (R_w) = 0.0409 (0.0368) for 6789 observed reflections with $I > 2\sigma(I)$, 653 variables, non-hydrogen atoms anisotropic, H atoms at idealized positions, one common isotropic temperature factor for H within each residue, one extinction parameter, one scaling factor.

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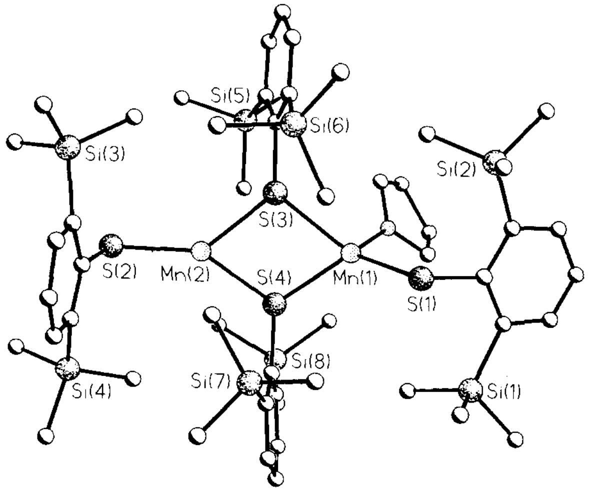

Fig. 1. $[Mn_2(SC_6H_3\{SiMe_3\}_2)_4(C_4H_8O)]$: molecular structure and atomic labels in crystals of **2**. Important distances (Å) and angles (°): Mn(1)...Mn(2) 3.777(1), Mn(1)–S(1) 2.359(1), Mn(1)–S(3) 2.492(1), Mn(1)–S(4) 2.500(1), Mn(1)–O 2.113(3), Mn(2)–S(2) 2.343(1), Mn(2)–S(3) 2.419(1), Mn(2)–S(4) 2.445(1); S(1)–Mn(1)–S(3) 123.1(1), S(1)–Mn(1)–S(4) 128.1(1), S(1)–Mn(1)–O 106.9(1), S(3)–Mn(1)–S(4) 78.2(1), S(3)–Mn(1)–O 110.7(1), S(4)–Mn(1)–O 107.0(1), S(2)–Mn(2)–S(3) 139.3(1), S(2)–Mn(2)–S(4) 135.4(1), S(3)–Mn(2)–S(4) 80.7(1).

3.777(1) Å between the manganese atoms is the result of a comparably short S...S distance being 3.148(1) Å in length. Other consequences of the short S...S separation are unusual M–S–M bridging angles of 99.6(1) and 100.5(1)°, respectively; compared with corresponding angles observed in tetrahedrally coordinated binuclear metal sites, these values are substantially large [1, 2].

While Mn(2) does not bind to additional ligands, the coordination sphere of Mn(1) is completed by a terminally bonded thf molecule. We are therefore faced with a binuclear molecule which contains both a trigonally (mean valence angle 118.5°) and a tetrahedrally coordinated manganese atom (mean valence angle 109.0°).

This unusually mixed coordination state is clearly reflected by two sets of Mn–(μ-S) distances. The bonds of Mn(1) are *c.* 0.065 Å longer on average than the corresponding ones of Mn(2). This observation is in accordance with the expectation that a reduction of the coordination number is correlated with a shortening of the remaining bonds. A similarly pronounced influence of the coordination number is also observed with respect to the terminal Mn–S bonds. In this case, the Mn–S distance decreases by 0.016 Å to 2.343 Å on going from Mn(1) (*CN* 4) to Mn(2) (*CN* 3). The metric data of the trigonal-planar fragment of **1** are in good agreement with those of the compound $[Mn_2(SC_6H_2\{2,4,6\text{-}^tBu\}_3)_4]$ [3], whereas the tetrahedral fragment shows distinct similarities to the mononuclear compound $[Mn(SR)_2(thf)_2]$ ($R = C_6H_2\text{-}2,4,6\text{-}\{CF_3\}_3$) [10].

A comparison of the overall structure of **1** with that of $[Mn_2(SC_6H_2\{2,4,6\text{-}^tBu\}_3)_4]$ [3] suggests that it should be possible to remove the coordinated thf molecule. The resulting homoleptic complex with two chemically identical manganese sites should undergo reversible and selective functionalization reactions induced by suitable donor molecules. This expected behaviour is currently under investigation.

Supplementary material

Further details of the crystal structure investigation (tables of atomic coordinates, bond lengths and angles, thermal parameters and structure factors) may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftliche-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, Germany on quoting the depository number CSD-58124, the names of the authors and the journal citation.

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