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Synthesis and crystal structure of the novel trimanganese tetrathiolate incomplete cubane: $[Mo(\eta^5\text{-}C_5H_5)_2(H)CO][Mn_3(CO)_9(\mu\text{-}SC_6H_5)_4]$

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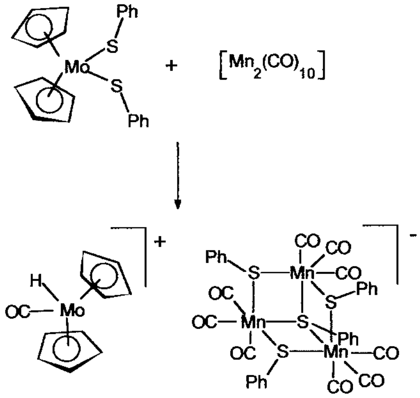
Abstract

An unexpected trimanganese(I) tetrathiolate-bridged complex, $[Mn_3(CO)_9(\mu\text{-}SC_6H_5)_4]^-$, with an incomplete cubane structure, was obtained by thermal reaction of $[Mn_2(CO)_{10}]$ with $[Mo(\eta^5\text{-}C_5H_5)_2(SC_6H_5)_2]$. The structure, established by single-crystal X-ray diffraction studies, shows the cation, $[Mo(\eta^5\text{-}C_5H_5)_2(H)CO]^+$, directed towards the vacant site of the cubane structure. Possible routes by which the anion and the cation could be formed are discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Trinuclear; Manganese incomplete cubane; Thiolate-bridged; Molybdenum biscyclopentadienyl; Carbonyl; Hydride

1. Introduction

Bent metallocene derivatives of general formula $[M(\eta^5\text{-}C_5H_5)_2(SR)_2]$ [M = Mo(IV), W(IV), Ti(IV)] proved to be adequate chelating ligands for the synthesis of heterobimetallic complexes, coordinating other metal centres through thiolate bridges [1].



Scheme 1.

However, our previous studies on the reactivity of these metallaligands showed that they can also behave as non-innocent ligands and be involved in redox processes, leading to unusual and unpredictable structures. For instance, upon reaction of $[MoCp_2(SPh)_2]$ with dirhenium decacarbonyl in refluxing xylene, we obtained the dimolybdenum(III) cation $[Mo_2(\mu\text{-}\eta^5\text{:}\eta^5\text{-}C_{10}H_8)(\mu\text{-}SPh)Cp_2]^+$ with the two Mo(III)Cp units linked by direct metal–metal bond and also by a bridging fulvalene and a bridging thiolate [2]. The counterion was the dirhenium(I) anion $[Re_2(CO)_6(\mu\text{-}SPh)_3]^-$, which had already been prepared as NEt_4 salt by Treichel and Tegen [3].

We also prepared the ditungsten(III) fulvalene analogue. However, an attempt to improve its yield with a longer reaction time led us to another product, the tetranuclear Re(I) cubane-type complex $[\{Re(CO)_3\}_4(\mu\text{-}SPh)_4]$, whose structure was confirmed by X-ray diffraction studies [4] and is similar to a published one [5]. There was substantial decomposition in the reaction and the fate of any W-containing product is unknown.

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In an attempt to extend this type of chemistry to other metal systems and in continuation of our interest in developing molybdenocene thiolate chemistry, we carried out the study of the reactivity of [$MoCp_2(SPh)_2$] with [$Mn_2(CO)_{10}$] and in this paper we report the formation of a very different product when dimanganese decacarbonyl was used instead of the rhenium analogue.

2. Results and discussion

2.1. Synthesis and characterization of [$Mo(Cp)_2(H)CO$][$Mn_3(CO)_9(\mu$-$SPh)_4$]

Reaction of equimolar amounts of [$Mo(Cp)_2(SPh)_2$] and [$Mn_2(CO)_{10}$] in xylene at 120°C for 1 h led to the formation of the new yellow–orange compound [$Mo(Cp)_2(H)CO$][$Mn_3(CO)_9(\mu$-$SPh)_4$] (**1**) in about 30% yield (Scheme 1).

The relatively low yield of **1** can be explained by some accompanying decomposition, produced by the relatively high temperature of the reaction, which could initiate some redox processes. However, at lower temperatures (several hours in refluxing toluene, ~ 110°C), no reaction occurred and at a higher temperature (refluxing xylene, ~ 140°C) only decomposition products were obtained.

The compound is moderately air stable as solid but air sensitive in solution. Under inert atmosphere, it is stable in xylene but decomposes after 2–3 days in dichloromethane.

^{1}H-NMR spectroscopy confirmed the presence of the hydride at high field (δ −8.45), the two equivalent Cp rings (δ 5.28) and the four phenylthiolate groups (δ 7.32–7.01).

The IR spectrum of the compound (KBr pellet) showed a strong band at 2020 cm^{-1} and two very strong and broad absorptions at 2000 and 1930 cm^{-1}, assignable to the carbonyl stretching vibrations [ν_{CO} of [$Mn_2(CO)_{10}$] (cm^{-1}): 2044 (m), 2013 (s), 1983 (m)].

The unambiguous structural assignment is based on a single-crystal X-ray diffraction analysis.

A survey of polynuclear manganese-carbonyl complexes with bridging thiolates reveals that most attention has been accorded to dimers and tetramers [6,7]. Typical stoichiometries for such complexes are [$Mn_2(\mu$-$SR)_3(CO)_6$]$^-$, [$Mn_2(\mu$-$SR)_2(CO)_8$] and [$Mn_4(\mu$-$SR)_4(CO)_{12}$], this last one having a cubane-type structure, determined by X-ray diffraction for R = furfuryl [8]. These complexes can be prepared under mild conditions by several routes, which include reactions between [$MnX(CO)_5$] (X = halogen or hydride) and thiols, organodisulfides, organotin thiolates or silyl thiolates. Thiolate-bridged manganese cubanes have also been prepared by reaction of equimolar amounts of tricarbonylpentadienyl manganese and thiol in cyclohexane, at 25°C. Cubanes can also form, as by-products, during the preparation of dimers [6,7]. However, to our knowledge, there is no reference to any trinuclear tetrathiolate-bridged manganese-carbonyl compound.

The trinuclear manganese-carbonyl complex [$Mn_3(CO)_9(S_2)_2(SH)$]$^{2-}$ has been obtained by hydro(-solvo)thermal synthesis [9]. The X-ray structure shows a triangle of Mn atoms bridged by two disulfide ligands adopting different coordination modes and by a μ^2-SH. In the same conditions but with a longer reaction time, the dimer [$Mn_2(\mu$-$SH)_3(CO)_6$]$^-$ forms.

Reaction of the OR$^-$ bridged trimer [$Mn_3(\mu$-$OEt)_3(CO)_9$] (prepared by reaction of [$MnBr(CO)_5$] with ethanol in the presence of NEt_3 or by reaction between [Me_3SnOEt] and [$MnBr(CO)_5$]) with PhOH, boron trihalides or with HCl and HBr gives trinuclear products with the same overall structure as the parent one. Nevertheless, with PhSH, the cubane [$Mn_4(\mu$-$SPh)_4(CO)_{12}$] forms [10], and not the trinuclear analogue with thiolate bridges.

Although we have not yet carried out any experimental studies to clarify the mechanism of formation of compound **1**, some published results on the reactivity of [$MCp_2(SR)_2$] and on the chemistry of [$Mn_2(CO)_{10}$], led us to propose a possible explanation for its formation. The fact that no trinuclear manganese-carbonyl-thiolate compound has, so far, been reported in the literature (only dimers and tetramers, as mentioned above) and that the trinuclear Mn(I) incomplete cubane [$Mn_3(CO)_9(\mu$-$SPh)_4$]$^-$ (the anion of **1**) has been obtained in reaction conditions apparently favourable to a tetramer formation (excess [$Mn_2(CO)_{10}$], high temperature), supports the possibility of a trinuclear manganese-carbonyl compound being involved in this reaction.

In a hypothetical, although speculative pathway, a possible intermediate could be, for instance, the complex [$Mn_3(CO)_{14}$]$^-$, which is among the few trimetallic manganese-carbonyl anions that have been prepared and structurally characterized by single-crystal X-ray diffraction studies [6,11,12]. It has been obtained by different routes, including reaction of the reduced species [$Mn(CO)_5$]$^-$ with the parent [$Mn_2(CO)_{10}$] and its X-ray structure has been determined as an [$AsPh_4$]$^+$ salt [12b].

The formation of [$Mn(CO)_5$]$^-$ by reduction of the dimer ($E = -0.69$ V versus SSCE [13]), to give the postulated trinuclear intermediate [Mn_3CO_{14}]$^-$ by the route mentioned above, can potentially be accomplished in presence of [$Mo^{IV}Cp_2(SPh)_2$], according to the results of the oxidative electrochemistry of [$MCp_2(X)_2$], examined by cyclic voltammetry by Kotz and coworkers [14]. The oxidation of [$Mo^{IV}Cp_2(SPh)_2$] to [$Mo^VCp_2(SPh)_2$]$^+$ ($E_{1/2} = 0.31$ V versus SSCE) fol-

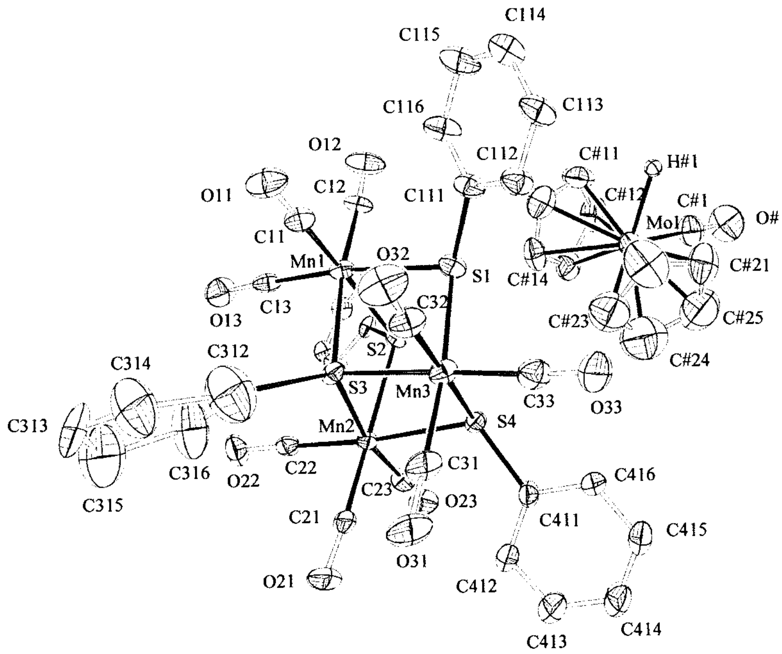

Fig. 1. ORTEP drawing of the molecular structure of $[Mo(Cp)_2(CO)(H)][Mn_3(CO)_9(\mu\text{-}SPh)_4]$.

lowed by reductive elimination of SPh has also been confirmed by chemical reaction of $[MoCp_2(SR)_2]$ with ferrocenium, and is the basis for the synthesis of cationic compounds of general formula $[Mo^{IV}Cp_2(SR)L]^+$, L being a two-electron donor ligand [15]. In this way, PhSSPh would be produced in a so-called oxidatively induced reductive elimination process.

Oxidative addition of two molecules of PhSSPh to $[Mn_3CO_{14}]^-$ (the intermediate postulated), with the necessary structural rearrangements, would not be incompatible with some of the proposed mechanisms of ligand substitution in metal carbonyl dimers [16], to give the incomplete cubane $[Mn_3(CO)_9(\mu\text{-}SC_6H_5)_4]^-$, the anion of **1**.

Coordination of a carbonyl group to the unstable molybdenocene or related species generated in the medium followed by protonation of the Mo centre by residual water (the solvent has not been previously dried) would give the cation of **1**, $[MoCp_2(H)CO]^+$.

The complex $[MoCp_2(H)CO]^+$ has also been obtained by Caulton [17] in different conditions, with $[MoCp(CO)_3]^-$ as counterion.

2.2. X-ray structure of $[Mo(Cp)_2(CO)(H)][Mn_3(CO)_9(\mu\text{-}SPh)_4]$

The X-ray study showed that the structure is formed by complex cations $[Mo(Cp)_2(CO)(H)]^+$ and complex anions $[Mn_3(CO)_9(\mu\text{-}SPh)_4]^-$, the cation being directed towards the empty corner of the incomplete cubane structure of the anion, as shown in Fig. 1.

The relative representation of the two fragments (Fig. 2) shows that the cubane has a face parallel to the *ac* plane (B face), with the diagonals of this face parallel to *c* and *a* crystallographic directions. The cationic fragment has the MCp_2 bisecting plane parallel to the *bc* crystallographic plane (A face)

Selected bond lengths an bond angles are given in Tables 1 and 2.

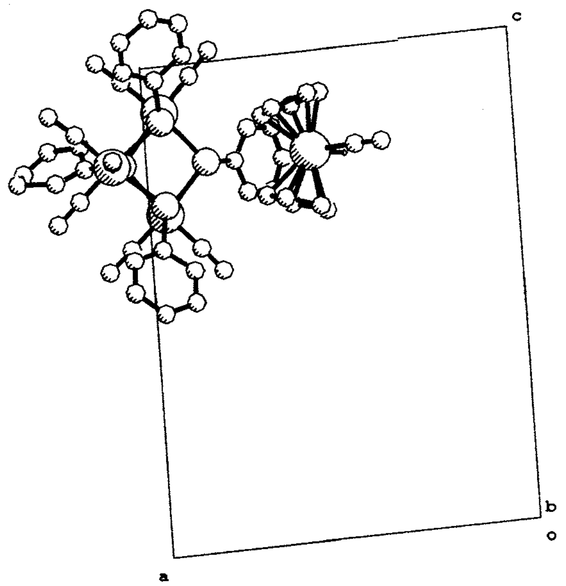

Fig. 2. Molecular structure of **1** viewed along *b* (crystallographic axis are also drawn in the picture).

Table 1
Selected bond lengths (Å) and bond angles (°) for the cation, $[MoCp_2(H)CO]^+$

Mo–Cp(1)	1.88	Cp(1)–Mo–Cp(2)	144.7
Mo–Cp(2)	1.94	H(1)–Mo–C(1)	81.0(9)
Mo–H(1)	1.89	O(1)–C(1)–Mo	179(3)
Mo–C(1)	1.92(3)		
C–O	1.21(3)		
C–C (range)	1.28(3)–1.40(4)		

2.2.1. *Molecular structure of* $[Mn_3(CO)_9(\mu\text{-}SPh)_4]^-$

The molecular structure shows an anionic fragment with a cubane-type structure where three corners are occupied by Mn metallic centres coordinated to three carbonyl groups in a distorted octahedral structure with the CO groups almost linear (179° ≥ Mn–C–O ≥ 175°); four corners are occupied by phenylthiolate (SPh) bridging ligands and, surprisingly, the eighth corner is vacant.

The sulfur S(3) of the thiolate group bridging the three Mn atoms has a distorted tetrahedral geometry, the Mn–S(3) bond distances (2.359(5)–2.375(5) Å) being very close to the ones found in $[Mn_4(CO)_{12}(\mu\text{-}SR)_4]$, (R = furfuryl, Mn–S average 2.366(4) Å) [9]. The other three sulfur atoms are bridging only two metal centres but present similar Mn–S–Mn angles and slightly longer Mn–S distances than the μ^3-SPh, suggesting a similar geometry, with the lone pair of these S atoms occupying the fourth position of the corresponding 'tetrahedrals', apparently being closer to an sp^3 than to an sp^2 hybridization.

Table 2
Selected bond lengths (Å) and bond angles (°) for the anion $[Mn_3(CO)_9(\mu\text{-}SC_6H_5)_4]^-$

Mn(1)–C(12)	1.77(2)	Mn(1)–S(3)	2.359(5)
Mn(1)–C(13)	1.75(2)	Mn(1)–S(2)	2.412(5)
Mn(1)–C(11)	1.76(2)	Mn(1)–S(1)	2.428(6)
Mn(2)–C(22)	1.75(2)	Mn(2)–S(3)	2.366(5)
Mn(2)–C(21)	1.79(2)	Mn(2)–S(2)	2.410(4)
Mn(2)–C(23)	1.81(2)	Mn(2)–S(4)	2.408(5)
Mn(3)–C(33)	1.74(2)	Mn(3)–S(3)	2.375(5)
Mn(3)–C(32)	1.79(2)	Mn(3)–S(4)	2.408(5)
Mn(3)–C(31)	1.81(2)	Mn(3)–S(1)	2.430(6)
Mn–C (range)	1.74(2)–1.81(2)	C–O (range)	1.13(2)–1.18(3)
C–C (Ph rings)	1.18(4)–1.53(4)	S–C (range)	1.79(2)–1.81(2)
C(13)–Mn(1)–S(1)	172.9(6)	C(13)–Mn(1)–S(2)	90.3(6)
C(11)–Mn(1)–S(1)	90.6(6)	C(11)–Mn(1)–S(2)	172.4(6)
C(12)–Mn(1)–S(1)	95.8(7)	C(12)–Mn(1)–S(2)	93.2(6)
C(33)–Mn(3)–S(1)	99.8(7)	C(21)–Mn(2)–S(2)	172.8(6)
C(32)–Mn(3)–S(1)	92.4(7)	C(23)–Mn(2)–S(2)	94.2(6)
C(31)–Mn(3)–S(1)	170.0(7)	C(22)–Mn(2)–S(2)	96.0(5)
C(12)–Mn(1)–S(3)	172.1(7)	C(33)–Mn(3)–S(4)	94.6(8)
C(13)–Mn(1)–S(3)	94.7(5)	C(32)–Mn(3)–S(4)	174.8(7)
C(11)–Mn(1)–S(3)	92.4(6)	C(31)–Mn(3)–S(4)	90.0(7)
C(22)–Mn(2)–S(3)	95.4(6)	C(22)–Mn(2)–S(4)	173.5(6)
C(21)–Mn(2)–S(3)	93.1(5)	C(21)–Mn(2)–S(4)	96.1(6)
C(23)–Mn(2)–S(3)	170.1(6)	C(23)–Mn(2)–S(4)	91.8(6)
C(32)–Mn(3)–S(3)	96.6(7)		
C(31)–Mn(3)–S(3)	92.2(7)		
C(33)–Mn(3)–S(3)	173.4(8)		
S–Mn–S (range)	78.7(2)–85.3(2)	C–S–Mn (range)	111.2(5)–119.4(8)
C–Mn–C (range)	87.4(7)–93.7(8)	Mn–S–Mn (range)	97.0(2)–102.8(2)

The Mn–Mn distances (3.61–3.66 Å) are longer than the ones found in clusters were direct Mn–Mn interaction occurs (< 3 Å) [12,18], confirming the lack of direct interaction among manganese atoms.

2.2.2. *Molecular structure of* $[Mo(Cp)_2(H)CO]^+$

In the direction of the vacant corner, a cationic biscyclopentadienylmolybdenum fragment $[Mo(\eta^5\text{-}C_5H_5)_2(H)CO]^+$ was located. The hydrogen atom of the cationic fragment was located in a difference Fourier map at 1.89 Å from the molybdenum atom and the H–Mo–C angle was found to be 81.0(9)°. The bond distances Mo–CO (1.92(3) Å) and C–O (1.21(3) Å) on the current structure, are slightly different from those observed in the same species with another counter-ion (1.991(5) and 1.140(7) Å, respectively) [17]. However, in the last case, some interaction between cations (H-bonding) occurs.

3. Experimental

3.1. *General procedures*

All manipulations and reactions were performed under dinitrogen or argon atmosphere using standard Schlenk-tube techniques. The NMR spectra were recorded on a Varian 300 spectrometer using $SiMe_4$ as internal reference for ^{1}H-NMR. Deuterated solvents were dried over molecular sieves and degassed by the freeze–thaw method at least three times prior to use.

$[Mo(\eta^5\text{-}C_5H_5)_2(SPh)_2]$ was prepared by reported methods [19]. Commercial $[Mn_2(CO)_{10}]$, purchased from Aldrich and *p*-xylene purchased from Merck, were used without further purification.

3.2. *Preparation of* $[Mo(Cp)_2CO(H)][Mn_3(CO)_9\text{-}(\mu\text{-}SPh)_4]$

A xylene suspension of $[MoCp_2(SPh)_2]$ (450 mg, 1 mmol) and $[Mn_2(CO)_{10}]$ (390 mg, 1 mmol) was heated with constant stirring for 1 h at 120°C. The resulting yellow–brownish solution was separated from an oily residue by filtration and evaporated to dryness under vacuo, giving a yellow–orange product in 32% yield (180 mg).

A few orange crystals, suitable for X-ray diffraction studies were obtained by slow diffusion of diethyl ether in a xylene solution of the compound.

IR [KBr], ν_{CO} (cm^{-1}): 2020 (strong), 2000 and 1930 (strong, broad).

^{1}H-NMR [CDCl$_3$]: δ 7.32 (m), 7.14 (m) and 7.01 (m) (μ-SC$_6$*H*$_5$, 20 H); 5.28 (s, η^5-C$_5$*H*$_5$, 10 H); −8.45 (s, Mo−*H*).

3.3. Crystal data

The complex [MoCp$_2$CO(H)][Mn$_3$(CO)$_9$(μ-SPh)$_4$]·0.5[(CH$_3$CH$_2$)O] ($C_{46}H_{36}O_{10.5}Mn_3MoS_4$), $M = 1140.7$, crystallizes in the monoclinic space group $P2_1/n$ with $a = 13.371(4)$, $b = 19.931(2)$, $c = 17.861(4)$ Å; $\beta = 92.48(1)°$; $V = 4756$ Å^3; $Z = 4$, $D_{calc} = 1.59$ g cm^{-3}; $\mu(\text{Mo}-K_\alpha) = 12.7$ cm^{-1} and $F(000) = 2288$. The unit cell and orientation matrix were obtained by least-squares refinement of 25 centred reflexions. A total of 6051 reflections $1.5 < \theta < 22$ were collected by the $\omega-2\theta$ scan mode, in an Enraf-Nonius TURBO CAD4 diffractometer equipped with a rotating anode, using graphite-monochromated radiation. Three standard reflexions were monitored during data collection but no decay or instrumental instability was detected (the loss of intensity is less than 0.1% h^{-1}). Using the CAD4 software, data were corrected for Lorentz and polarization effects and empirically for absorption (minimum transmission factor 92.1% average transmission factor 97.2%). A total of 5828 unique reflexions with $F \geq 0$ ($R_{int} = 0.04$) were used in structure solution and refinement of 561 parameters. The position of the Mo atom was obtained by a tridimensional Patterson synthesis. All the other non-hydrogen atoms were located in subsequent difference Fourier maps and refined with anisotropic thermal motion parameters. The hydrogen atoms were inserted in calculated positions and refined isotopically with fixed distances (1.08 Å) to the parent carbon atom, Final refinement[3] converged at $R_1 = 0.095$. The largest peak in the final difference Fourier synthesis was 0.87 e Å^{-3}. Lists of observed and calculated structure factors, tables of anisotropic thermal parameters, hydrogen atomic coordinate, bond lengths and angles and inter and intra molecular contact distances are available as supplementary material. The structure solution and refinement were done with SHELX-76 [20] and the illustrations were drawn with ORTEP-II [21]. The atomic scattering factors and anomalous scattering terms were taken from *International Tables* [22].

4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 147444 for **1** ($C_{46}H_{31}Mn_3MoO_{10.5}S_4$), [Mo(Cp)$_2$(H)CO][Mn$_3(CO)_9$(μ-SPh)$_4$]·0.5Et$_2$O. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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