研究简报

2-巯甲基噻吩与$[Mn_2(CO)_{10}]$原子簇化合物反应生成$[MnS(CO)_3]_4$及结构表征

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Synthesis and Molecular Structure of $[MnS(CO)_3]_4$ Derived from the Reaction of $[Mn_2(CO)_{10}]$ and 2-(Methylthio)thiophene

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The compound $[Mn_2(CO)_{10}]$ reacts with 2-(Methylthio)thiophene ($C_5H_6S_2$) while refluxing in xylene to afford a methylthio-tetramanganese product $[MnS(CO)_3]_4$, in which $C_5H_6S_2$ is cleaved with loss of thiophene. The crystal structure of $[MnS(CO)_3]_4$ has been studied by direct method. Based on the 21 685 unique reflections collected using Mo$K\alpha$ of X-ray radiation and a CCD-based detector, it is refined to an agreement index (R_1) of 0.079 0. The cell is triclinic with dimensions: a=1.719 49 nm, b=1.959 2 nm, c=2.632 6 nm and α=79.733°, β=71.407°, γ=89.387°. There are 12 unit cells of $[MnS(CO)_3]_4$ in the cell, with space group $P\bar{1}$.

Keywords: **2-(Methylthio)thiophene** **C-S bond-cleavage** **crystal-structure** **cluster**

0 Introduction

The CH_3S-substituted thiophene, 2-$MeSC_4H_3S$, could potentially coordinate through either or both of the sulfur atoms, through the π-system of the ring or, if C-H cleavage occurs, through a metal-carbon σ-bond[1]. Previously thienylphosphines were only known to coordinate through the phosphrous atom[2], but C-H activation at the thiophene ring dominates the chemistry in these clusters[3]. The 2-substituted thiophene ligand system was to allow preliminary coordination through the exocyclic heteroatom. Subsequent reaction would bring the thiophene ring into play, the use of RS-substituted cyclic compounds to induce metallation in organic rings has been employed in several cases[4]. So it was anticipated that C-H cleavage in the ring or-

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tho to the MeS group would occur. Flowed by a detail work on 2-methylthiophene reaction with triosmium-clusters $[Os_3(\mu\text{-H})(\mu\text{-MeSC}_4H_2S)(CO)_{10}]$ was published[1]. The result suggested that five different ligand sets derived from this substituted thiophene were found within various triosmium products derived from both C-H and C-S bond cleavages.

This paper on the reaction of 2-(Methylthio)thiophene with $[Mn_2(CO)_{10}]$ reports on an extension of work on 2-(Methylthio)thiophene with $[Os_3(\mu\text{-H})(\mu\text{-MeSC}_4H_2S)(CO)_{10}]$.

1 Experimental

The cluster $[Mn_2(CO)_{10}]$ and 2-methylthiothiophene were used as obtained from Aldrich.

1.1 Preparation of $[MnS(CO)_3]_4$ Single Crystal

A solution of $[Mn_2(CO)_{10}]$ (0.121 4 g, 0.031 mmol) and 2-methylthiothiophene (0.061 0 g) in xylene (50 cm^3) under nitrogen and the solution was refluxed while the course of the reaction was monitored by IR spectroscopy to establish when the reaction was complete (30 h). Low pressure removal of volatiles and TLC of the residue yielded $[MnS(CO)_3]_4$ as orange crystals (0.046 9 g, 54%) from *n*-hexane/dichloromethane. Found: C, 25.77; H, 1.56. Anal. Calc. for $C_{16}H_{12}Mn_4O_{12}S_4$: C, 25.80; H, 1.61. Crystals suitable for single-crystal structure determination were obtained from *n*-hexane/dichloromethane solvents.

1.2 IR Spectroscopic Data

IR spectra: ν(CO)/cm^{-1} (starting material in xylene), 2 044s, 2 010vs, 1 980m; ν(CO)/cm^{-1} ($[Mn_2(CO)_{10}]$ in DCM): 2 200vs, 1 944m.

1.3 Crystal Structure Determinations for Compound $[Mn_2(CO)_{10}]$

All measurements were carried out at 150(2) K on a Bruker SMART APEX diffractometer, using graphite-monochromated Mo*K*α radiation (λ =0.071 073 nm). Crystal data, intensity data collection parameters and final refinement results are summarized in Table 1. Data were corrected for Lorentz and polarization effects and for absorption based on ψ-scans.

Structures were determined by direct methods. All non-H atoms were refined anisotropically and H-atoms on the -SCH_3 were included in the model in

Table 1 Crystal Data and Structure Refinement for $[Mn_4(SMe)_4(CO)_{12}]$

chemical formula	$C_{16}H_{12}Mn_4O_{12}S_4$
formula weight	744.26
temperature / K	150(2)
radiation	MoKα
wavelength / nm	0.071 073
srystal system	triclinic
space group	$P\bar{1}$
a / nm	1.719 49(18)
b / nm	1.959 2(2)
c / nm	2.632 6(3)
α / (°)	79.733(2)
β / (°)	71.407(2)
γ / (°)	89.387(2)
cell volume / nm^3	8.261 0(15)
Z	12
calculated density / ($g\cdot cm^{-3}$)	1.795
F(000)	4 416
crystal colour size / mm	dark, 0.20 × 0.19 × 0.08
data collection method	bruker SMART APEX diffractometer ω rotation with narrow frames
θ range for data collection / (°)	1.06 to 28.36
index ranges	*h* −22 to 22, *k* −25 to 26, *l* −33 to 33
completeness to θ=26.00°	99.3%
reflection collected	74 156
independent reflections	38 281 (R_{int}=0.732)
reflection with $F^2 > 2\sigma$	21 685
absorption correction	semi-empirical from equivalents
min. and max. transmission	0.673 2 and 0.855 5
structure solution	direct methods
refinement method	full-matrix-block least-squares on F^2
weighting parameters *a*, *b*	0.059 9, 2.992 6
data / restraints / parameter	382 81 / 0 / 1 969
final *R* indices [$F^2 > 2\sigma$]	R_1=0.079 0, wR_2=0.154 5
R indices (all data)	R_1=0.146 0, wR_2=0.180 7
goodness-of-fit on F^2	1.010
largest and mean shift/su	0.046 and 0.005
largest diff. peak and hole / ($e\cdot nm^{-3}$)	1 065 and −762

Table 2　Selected Bond Lengths (nm) and Angles (°) for [$Mn_4(SMe)_4(CO)_{12}$]

Mn(21)-S(21)	0.235 6(2)	Mn(21)-S(23)	0.236 8(2)	Mn(21)-S(24)	0.237 5(2)
Mn(21)-C(211)	0.179 0(9)	Mn(21)-C(212)	0.181 0(8)	Mn(21)-C(213)	0.179 9(9)
C(211)-O(211)	0.116 0(10)	C(212)-O(212)	0.115 5(9)	C(213)-O(213)	0.116 3(10)
S(21)-C(321)	0.179 7(7)	S(22)-C(322)	0.182 2(7)	S(23)-C(323)	0.180 8(7)
S(24)-C(324)	0.182 5(7)				
S(21)-Mn(21)-S(23)	77.80(7)	S(21)-Mn(21)-S(24)	77.50(7)	S(23)-Mn(21)-S(24)	77.89(7)
S(23)-Mn(21)-C(213)	95.3(3)	S(24)-Mn(21)-C(213)	96.1(3)	S(23)-Mn(21)-C(211)	77.80(7)
C(211)-Mn(21)-C(212)	92.7(4)	C(211)-Mn(21)-C(213)	90.9(4)	Mn(23)-S(21)-Mn(24)	101.13(8)
Mn(21)-S(21)-Mn(24)	101.14(8)	Mn(21)-S(21)-Mn(23)	101.67(8)	Mn(21)-S(21)-C(321)	117.7(3)

idealized positions riding on the carbon atoms with C-H distances fixed at 0.096 nm. The selected bond lengths and angles are listed in Table 2. All calculations were carried out using or SHELXL93[5].

2　Results and Discussion

2.1　Description of the [$MnS(CO)_3]_4$ Structure

As shown in Fig.1, in the product [$MnS(CO)_3]_4$, four Mn and four S atoms formed a cube complex. Each Mn and S atom occupied the eight peaks and alternately linked together. The four -CH_3 linked with each S atom and the dozen -CO divided into three components linked with four Mn atoms. The bond lengths of Mn(21)-S(21), Mn(21)-S(23) and Mn(21)-S(24) are 0.235 6(2) nm, 0.236 8(2) nm and 0.237 5(2) nm, respectively; Mn(21)-C(211), Mn(21)-C(212) and Mn(21)-C(213) are 0.179 0(9) nm, 0.181 0(8) nm and 0.179 9(9) nm; C(211)-O(211), C(212)-O(212) and C(213)-O(213) are 0.116 0(10) nm, 0.115 5(9) nm and 0.116 3(10) nm. The bond angles of S(21)-Mn(21)-S(23), S(21)-Mn(21)-S(24) and S(23)-Mn(21)-S(24) are 77.80(7)°, 77.50(7)° and 77.89(7)°.

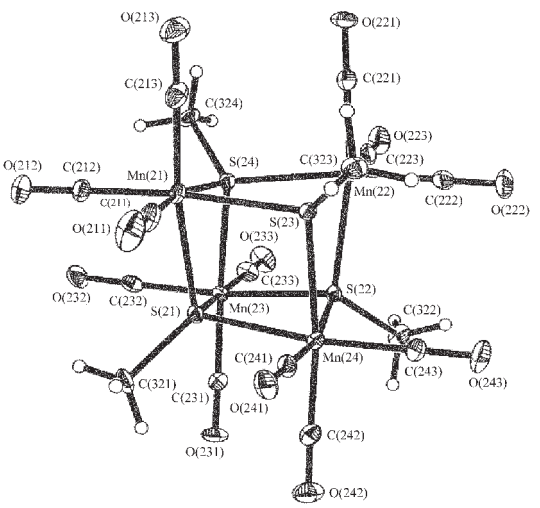
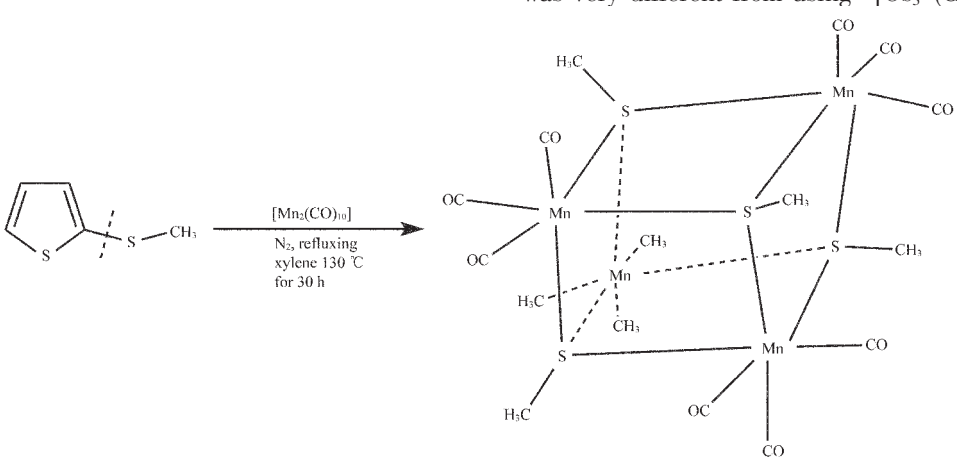


Fig.1　Crystal structure of [$Mn_4(SMe)_4(CO)_{12}$]

2.2　Description of the Reaction

The structure of [$MnS(CO)_3]_4$ suggested that the reaction of 2-(Methylthio) thiophene with [$Mn_2(CO)_{10}$] was very different from using [$Os_3(CO)_{10}(MeCN)_2$][1].



Scheme 1　Formation of [$Mn_4(SMe)_4(CO)_{12}$] by cleavage of C-S bond

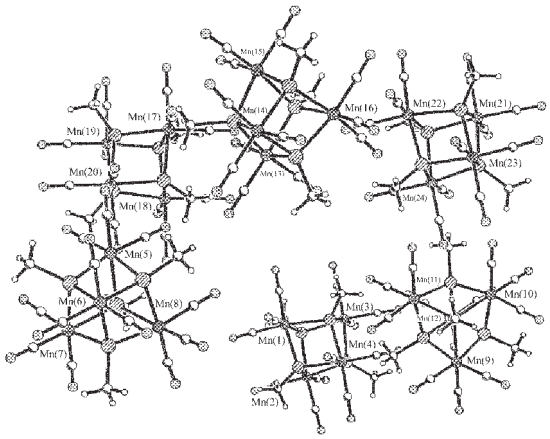


Fig.2 Crystal packing of $[Mn_4(SMe)_4(CO)_{12}]$

Obviously, the reaction included a C-S cleavage process. However we don't know if the thiophene ring is still kept or not. The reaction could be shown in Scheme 1.

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References

[1] Arce A. J., Deeming A. J., De Sanctis Y., Speel D. M., Trapani A. Di. *J. Organo-metallic Chemistry*, **1999**,**580**,370.

[2] Rasanen T. M., Jaake-lainen S., Pakkanen T. A. *J. Organometallic Chemistry*, **1998**,**553**,453.

[3] Deeming A. J., Jayasuriya S. N., Arce A. J., De Sanctis Y. *Organometallics*, **1996**,**15**,786.

[4] Deeming A. J., Arce A. J., De Sanctis Y. *Angew. Chem. Int. Ed. Eng.*, **1994**,**33**,1381.

[5] Sheldrick G. M. *SHELXTL* 93, *Programme for Refinement of Crystal Structure*, University of Gottingen, **1993**.