Organometallics **1993**, *12*, 1009–1011

5-Substituted 1,3,4-Oxathiazol-2-ones as a Sulfur Source for a Sulfido Cluster: Synthesis and Molecular Structure of the 48-Electron Equilateral Triangular Cluster Anion $[Mn_3(\mu_3\text{-}S)_2(CO)_9]^-$

Zhi-Gang Fang, T. S. Andy Hor,* K. F. Mok, and Siu-Choon Ng*

Department of Chemistry, Faculty of Science, National University of Singapore,
Kent Ridge, Singapore 0511

Ling-Kang Liu* and Yuh-Sheng Wen

Institute of Chemistry, Academia Sinica, Taipei 11529, Taiwan, ROC

Received November 4, 1992

Summary: $[Mn_3(CO)_9(\mu_3\text{-}S)_2]^-$ has been isolated from the reaction between $[Mn(CO)_5]^-$ and 5-substituted 1,3,4-oxathiazol-2-one (RCNSCO(O); R = phenyl, methyl, 3,5-dinitrophenyl) in THF. X-ray analysis revealed a D_{3h} equilateral triangular cluster with three $Mn(CO)_3$ units (Mn–Mn = 2.7680(16)–2.7918(13) Å) apically bicapped by two μ_3-S ligands. The use of 1,3,4-oxathiazol-2-ones as a sulfur precursor allows facile nucleophilic attack from the carbonylmetalate and subsequent elimination of RCN and CO_2.

Substrates commonly used for entry into sulfide clusters include S_8,[1] S_x^{2-},[2] H_2S,[3] RSH,[4] CS_2,[5] $(CH_2CH_2)S$,[6] and other sulfur-containing metalloligands.[7] These substrates generally suffer from the disadvantages of being nonselective or/and having a lack of electrophilicity, especially toward low-valent carbonylmetalates. Reported here is the use of 5-substituted 1,3,4-oxathiazol-2-one, RCNSCO(O), which offers an electrophilic site for low-temperature attack by a metal carbonyl anion and as a result leads to the facile elimination of RCN and CO_2. 1,3,4-Oxathiazol-2-ones are established precursors for the in situ generation of the unstable nitrile sulfide RCNS for various organic syntheses.[8] Its reactivity toward organometallics is largely unexplored except for a few coordinatively unsaturated fragments.[9]

1,3,4-Oxathiazol-2-ones can be conveniently prepared by treating a carboxamide, $RCONH_2$, with (chlorocarbonyl)sulfenyl chloride, ClCOSCl.[10] Addition of $[Mn(CO)_5]^-$ to a THF solution of RCNSCO(O) (R = C_6H_5, CH_3, 3,5-$C_6H_3(NO_2)_2$) at 0 °C immediately gave rise to a brown solution with rapid liberation of CO_2 ($BaCl_2$ test) and free nitrile (PhCN, *m/z* 103.04).[11] X-ray analysis of the principal product,[12] which is crystallized as the $[PPh_3Me]^+$ salt, revealed a cluster formulated as *triangulo*-$[Mn_3(\mu_3\text{-}S)_2(CO)_9]^-$. This, to our knowledge, is the first X-ray crystallographically established manganese (mono)-sulfido cluster. The structure consists of three M–M-bonded $\{Mn(CO)_3\}$ moieties linked axially by two triply bridging sulfides on either side of the molecular plane.

---

[1] Johnson, B. F. G.; Lewis, J.; Lodge, P. G.; Raithby, P. R.; Henrick, K.; McPartlin, M. *J. Chem. Soc., Chem. Commun.* **1979**, 719.

[2] (a) Müller, A.; Diemann, E. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987; Vol. 2, Chapter 16.1, p 515. (b) Ugo, R.; Monica, G. L.; Cenini, S.; Segre, A.; Conti, F. *J. Chem. Soc. A* **1971**, 522.

[3] (a) Adams, R. D.; Horváth, I. T.; Yang, L. W. *Organometallics* **1983**, *2*, 1257. (b) Deeming, A. J.; Underhill, M. *J. Organomet. Chem.* **1972**, *42*, C60.

[4] Adams, R. D.; Horváth, I. T. *Inorg. Synth.* **1989**, *26*, 303.

[5] (a) Broadhurst, P. V.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Organomet. Chem.* **1980**, *194*, C35. (b) Adams, R. D.; Golembeski, N. M.; Selegue, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 546.

[6] (a) Adams, R. D.; Babin, J. E.; Tasi, M. *Inorg. Chem.* **1986**, *25*, 4514. (b) Darensbourg, D. J.; Sanchez, K. M.; Delord, T.; Zalewski, D. J. *Inorg. Chem.* **1988**, *27*, 821.

[7] (a) Vahrenkamp, H. *Adv. Organomet. Chem.* **1983**, *22*, 169. (b) Briant, C. E.; Hor, T. S. A.; Howells, N. D.; Mingos, D. M. P. *J. Chem. Soc., Chem. Commun.* **1983**, 1118. (c) Briant, C. E.; Hor, T. S. A.; Howells, N. D.; Mingos, D. M. P. *J. Organomet. Chem.* **1983**, *256*, C15. (d) Gilmour, D. I.; Luke, M. A.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1987**, 2, 335. (e) Adams, R. D.; Babin, J. E.; Tasi, M. *Inorg. Chem.* **1986**, *25*, 4460.

[8] Paton, R. M. *Chem. Soc. Rev.* **1989**, *18*, 33 and references therein.

[9] Beck, W.; Leidl, E.; Keubler, M.; Nagel, U. *Chem. Ber.* **1980**, *113*, 1790.

[10] (a) Muhlbauer, E.; Weiss, W. British Patent 1,079,348, Aug 16, 1967. (b) Howe, R. K.; Franz, J. E. *J. Org. Chem.* **1974**, *39*, 962. (c) Paton, R. M.; Ross, J. F.; Crosby, J. *J. Chem. Soc., Chem. Commun.* **1979**, 1146.

[11] $Mn_2(CO)_{10}$ (0.195 g, 0.5 mmol) was dissolved in THF (10 mL) under an argon atmosphere, and the solution was cooled to 0 °C. Sodium amalgam (3%) (2.13 g) was added, and the mixture was stirred at 0 °C for 1 h followed by another 1 h at room temperature (25 °C). The almost colorless solution thus obtained was cooled to 0 °C before being filtered into a Schlenk tube containing a THF solution (10 mL) of 5-phenyl-1,3,4-oxathiazol-2-one (0.180 g, 1.0 mmol) at 0 °C. The solution turned brown immediately. Stirring was continued for 3 h at 0 °C before the mixture was warmed slowly to room temperature. Further stirring overnight gave a dark brown solution, which was evaporated to dryness and the residue washed with hexane (2 × 10 mL) before being extracted into MeOH (10 mL). A filtered MeOH solution (5 mL) of $[PPh_3Me]^+Br^-$ (1.0 g) was added, and the mixture was stirred for 30 min and evaporated to dryness under vacuum. The dark brown residue was extracted into THF (2 × 10 mL), and the solution was filtered to remove the excess $[PPh_3Me]^+$ and Na^+ salts and evaporated to dryness in vacuo. The residue was dissolved in 2-propanol (10 mL), to which was added hexane (15 mL). Upon slow cooling at −10 °C, dark brown crystals of $[Ph_3PMe][Mn_3(\mu_3\text{-}S)_2(CO)_9]$ (0.110 g, 44% based on $Mn_2(CO)_{10}$) of analytical quality were deposited and collected by filtration; mp 84–86 °C dec. Anal. Calcd for $C_{28}H_{18}Mn_3O_9PS_2$: C, 44.3; H, 2.4; P, 4.1; Mn, 21.8. Found: C, 44.1; H, 2.4; P, 4.0; Mn, 21.7. IR (ν(CO)): in $CHCl_3$, 1981 (s), 1938 (m), 1916 (sh) cm^{-1}; in CH_3OH, 1982 (s), 1941 (m), 1918 (w) cm^{-1}. The preparation can also be carried out by using methyl- or (3,5-dinitrophenyl)oxathiazolone as the substrate. Single crystals suitable for X-ray diffraction study were grown by slow diffusion of hexane into a sample solution in 2-propanol at −10 °C.

[12] X-ray diffraction data were collected using a Nonius diffractometer, with graphite-monochromatized Mo Kα radiation (λ = 0.7093 Å). Data for $[PPh_3Me][Mn_3(\mu_3\text{-}S)_2](CO)_9$, $C_{28}H_{18}Mn_3O_9PS_2$: MW = 758.34, triclinic; space group $P1$; a = 14.160(5) Å, b = 10.277(4) Å, c = 11.002(3) Å, α = 95.67(4)°, β = 87.21(4)°, γ = 100.39(3)°; V = 1566.3(9) Å^3; Z = 2; d_{calcd} = 1.608 g cm^{-3}; μ = 1.37 mm^{-1}; no. of reflections 3455 ($2\theta < 49.8°$, $I > 2\sigma(I)$ (unique reflections 5484)); $R(\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ = 0.034; $R_w(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$ = 0.037; goodness of fit $([\Sigma w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2})$ 1.38; maximum residue electron density 0.300 e/Å^3, deepest hole −0.270 e/Å^3. The structure was solved by the heavy-atom method and refined by a block-diagonal least-squares method. A more detailed summary of data collection and structure refinement (Table S1) is given in the supplementary material.

0276-7333/93/2312-1009$04.00/0

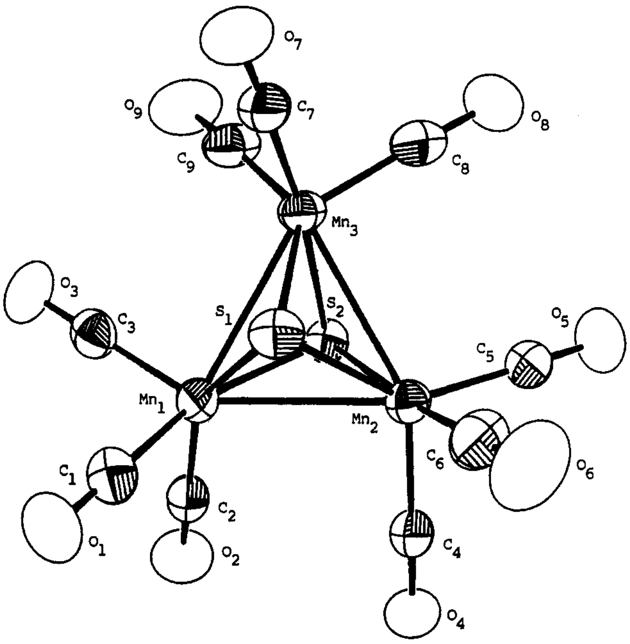
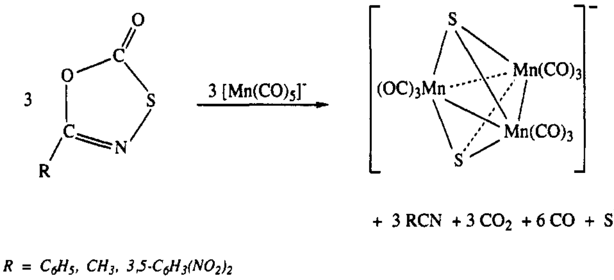


Figure 1. ORTEP drawing of $[Mn_3(\mu_3\text{-}S)_2(CO)_9]^-$. Selected bond distances (Å): Mn(1)–Mn(2) = 2.7840(15), Mn(1)–Mn(3) = 2.7680(16), Mn(2)–Mn(3) = 2.7918(13), Mn(1)–S(1) = 2.2365(14), Mn(2)–S(1) = 2.2210(16), Mn(3)–S(1) = 2.2259(16), Mn(1)–S(2) = 2.2633(16), Mn(2)–S(2) = 2.2671(16), Mn(3)–S(2) = 2.2594(15), Mn(1)–C(1) = 1.803(5), Mn(1)–C(2) = 1.802(5), Mn(1)–C(3) = 1.780(5), Mn(2)–C(4) = 1.775(5), Mn(2)–C(5) = 1.815(6), Mn(2)–C(6) = 1.802(6), Mn(3)–C(7) = 1.796(5), Mn(3)–C(8) = 1.785(6), Mn(3)–C(9) = 1.788(6). Selected bond angles (deg): Mn(2)–Mn(1)–Mn(3) = 60.42(4), Mn(1)–Mn(2)–Mn(3) = 59.57(4), Mn(1)–Mn(3)–Mn(2) = 60.01(4), S(1)–Mn(1)–S(2) = 88.52(6), S(1)–Mn(2)–S(2) = 88.80(6), S(1)–Mn(3)–S(2) = 88.88(6), mean Mn–S(1)–Mn = 77.21(6), mean Mn–S(2)–Mn = 75.78(5).

Clusters with $\{M_3S_2\}$ as the molecular core are well-cited because of their characteristic bonding and electronic properties and their role in cluster synthesis.[13] Among the better known examples are $M_3S_2(CO)_9$ (M = Fe,[14] Ru,[1,6a,15] Os[16]) (50 e), $[Co_3S_2Cp_3]^n$ (n = 0, +1) (50/49 e),[17] and $Ni_3S_2Cp_3$ (53 e).[18] The title 48-electron cluster is considered electron-precise for metal triangles in which all the metal electrons are bonding in nature. Surprisingly perhaps, we are unable to identify other 48-electron $\{M_3S_2\}$ carbonyl clusters with an equilateral metal triangle in the literature. The closest relative is found in the isoelectronic $[Co_3S_2(MeCp)_3]^{2+}$, which has been recently described.[19] A structural feature is the near-idealized D_{3h} trigonal-bipyramidal frame with three Mn–Mn bonds of very similar lengths (2.7680(15)–2.7918(13) Å) and the near-perfect internal ∠Mn–Mn–Mn (59.57(4)–60.42(4)°). The Mn–Mn bond length is shorter than those in $Mn_2(CO)_{10}$ (2.977(11) Å)[20] and the 48-electron hydrido-bridged cluster $Mn_3(\mu\text{-}H)_3(CO)_{12}$ (mean 3.111(2) Å)[21] but is unexceptional compared to other Mn(I)–Mn(I)-bonded complexes (mean 2.766 Å).[22] The Mn–S lengths (mean 2.2455(15) Å) are slightly shorter than those in the disulfido polynuclear aggregate complex $Mn_4(S_2)_2(CO)_{15}$ (2.34–2.38 Å)[23] but is comparable to that in $(CO)_6Fe_2(\mu\text{-}CO)_2(\mu_3\text{-}S)Mn(MeCp)$ (48 e) (2.206(2) Å).[24] The high symmetry of the bicapped metal plane and the strong M–M interaction is also reflected in the S(1)–Mn–S(2) angles, which are essentially constant and close to 90°.

The present ring-opening reaction can be depicted by the equation



The exact mechanism of the cluster formation is presently unclear, although the first step is almost certainly nucleophilic attack by the metal anion on the carboxyl carbon, which leads to the rupture of the C–S bond. Such electrophilicity of the oxathiazolones has been reported in some of their organic reactions with Grignard reagents and other substrates.[8,25] Free nitrile sulfide (alkyl thiocyanate), though known to desulfurate easily,[26] is unlikely to be the active substrate, as its extrusion from the five-membered heterocycles usually requires forcing conditions such as photolysis or thermal trapping with a dipolarophile.[27] The present reaction is also in contrast with the oxidative additions of oxathiazolones to Pd(0) and Pt(0) phosphine complexes, which give N-thiohydroximato (RC(O)NS) complexes through CO extrusion from the heterocycle.[9]

The ready synthesis of the heterocycle, its good shelf life and yet high reactivity towards the carbonylmetalates, its selective release of a monosulfur atom, and the facile elimination of inert nitrile and CO_2 make it an attractive reagent for sulfido-cluster synthesis. So far, we have not

---

[13] (a) Zanello, P. *Coord. Chem. Rev.* **1988**, *83*, 199. (b) Adams, R. D. *Polyhedron* **1985**, *4*, 2003. (c) Lockemeyer, J. R.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 5733. (d) Adams, R. D.; Horváth, I. T. *J. Am. Chem. Soc.* **1984**, *106*, 1869. (e) Chesky, P. T.; Hall, M. B. *Inorg. Chem.* **1983**, *22*, 2998. (f) Griewe, G. L.; Hall, M. B. *Inorg. Chem.* **1988**, *27*, 2250.

[14] (a) Rives, A. B.; You, X.-Z.; Fenske, R. F. *Inorg. Chem.* **1982**, *21*, 2286. (b) Wei, C. H.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 493. (c) Adams, R. D.; Babin, J. E. *Inorg. Chem.* **1986**, *25*, 3418.

[15] Adams, R. D.; Babin, J. E. *Inorg. Chem.* **1986**, *25*, 4010.

[16] (a) Adams, R. D.; Horváth, I. T.; Segmüller, B. E.; Yang, L. W. *Organometallics* **1983**, *2*, 144. (b) Adams, R. D.; Horváth, I. T.; Segmüller, B. E.; Yang, L. W. *Organometallics* **1983**, *2*, 1301.

[17] (a) Sorai, M., Kosaki, A.; Suga, H.; Seki, S.; Yoshida, T.; Otsuka, S. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2364. (b) Frisch, P. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1972**, *94*, 5082. (c) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456. (d) Madach, T.; Vahrenkamp, H. *Chem. Ber.* **1981**, *114*, 505.

[18] Vahrenkamp, H.; Uchtman, V. A.; Dahl, L. F. *J. Am. Chem. Soc.* **1968**, *90*, 3272.

[19] Pulliam, C. R.; Thoden, J. B.; Stacy, A. M.; Spencer, B.; Englert, M. H.; Dahl, L. F. *J. Am. Chem. Soc.* **1991**, *113*, 7398.

[20] Almenningen, A.; Jacobson, G. G.; Seip, H. M. *Acta Chem. Scand.* **1969**, *23*, 865.

[21] Kirtley, S. W.; Olsen, J. P.; Bau, R. *J. Am. Chem. Soc.* **1973**, *95*, 4532.

[22] Holloway, C. E.; Melnik, M. *J. Organomet. Chem.* **1990**, *396*, 129.

[23] (a) Küllmer, V.; Röttinger, E.; Vahrenkamp, H. *J. Chem. Soc., Chem. Commun.* **1977**, 782. (b) Küllmer, V.; Röttinger, E.; Vahrenkamp, H. *Z. Naturforsch., B* **1979**, *34*, 224.

[24] Winter, A.; Zsolnai, L.; Huttner, G. *J. Organomet. Chem.* **1984**, *269*, C29.

[25] (a) Westphal, G.; Weise, A.; Otto, A. *Z. Chem.* **1977**, *17*, 295. (b) Rajca, A.; Grobelny, D.; Witek, S.; Zbirovsky, M. *Synthesis* **1983**, 1032.

[26] Wentrup, C.; Kambouris, P. *Chem. Rev.* **1991**, *91*, 363 and references therein.

[27] (a) Franz, J. E.; Howe, R. K.; Pearl, H. K. *J. Org. Chem.* **1976**, *41*, 620. (b) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565.

succeeded in preparing the title cluster from other common sulfur sources. The possibility for the involvement of a thiocyanate (or isothiocyanate[28]) complex as an intermediate is being looked into. The cluster shows no reactivity toward electrophiles such as CH_3I and $TlNO_3$.

Acknowledgment. This work would not have been possible without financial support from the Academia Sinica and the National University of Singapore (NUS) in the form of a grant (RP 850030). Z.-G.F. is grateful to the NUS for a scholarship award. We are appreciative of the technical support from our department at the NUS.

Supplementary Material Available: Complete tables of crystal data and refinement details, atomic positional and thermal parameters, bond lengths and angles, torsional angles, and anisotropic thermal parameters and a figure giving an additional view of $[PPh_3Me][Mn_3(\mu_3\text{-}S)_2(CO)_9]$ (7 pages). Ordering information is given on any current masthead page.

OM9207018

---

[28] (a) Cullen, E. P.; Fortune, J.; Manning, A. R.; McArdle, P.; Cunningham, D.; Stephens, F. S. *Organometallics* **1990**, *9*, 1443. (b) Lee, G. R.; Cooper, N. J. *Organometallics* **1989**, *8*, 1538. (c) Demartin, F.; Cenini, S.; Pizzotti, M.; Porta, F. *J. Chem. Soc., Dalton Trans.* **1987**, 605.