Organometallic Chemistry under Hydro(solvo)thermal conditions: Synthesis and X-ray structure of $(Ph_4P)_2[Mn_3(CO)_9(S_2)_2(SH)]$, $(Ph_4P)[Mn_2(CO)_6(SH)_3]$, and $(Ph_4P)_2[Mn_4(CO)_{13}(Te_2)_3]$[**]

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Hydrothermal, or more generally, hydro(solvo)thermal syntheses may be defined as chemical reactions carried out in superheated water or organic solvents at sub-, near, or supercritical conditions.[1–3] The rapid transport ability of the solvent under such conditions often leads directly to crystal growth of the product similar to the formation of many mineral crystals in nature.[4] Thus far, the hydro(solvo)thermal synthesis has found numerous applications in solid-state chemistry and materials science.[5–6] Use of a similar concept to carry out organometallic reactions in sealed ampoules or autoclaves at elevated pressures and temperatures has opened up a new avenue for organometallic cluster chemistry.[7–8] In this report, we describe three novel cluster compounds **1**–**3**, obtained from

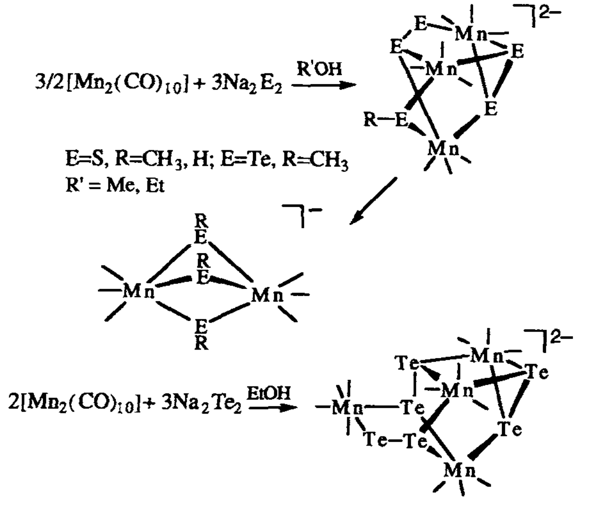
$(Ph_4P)_2[Mn_3(CO)_9(S_2)_2(SH)]$ **1**

$(Ph_4P)[Mn_2(CO)_6(SH)_3]$ **2**

$(Ph_4P)_2[Mn_4(CO)_{13}(Te_2)_3]$ **3**

ethanothermal synthesis. The formation of these compounds provides insight into the reaction pathways dictated by the solvent under the solvothermal conditions.

The reaction of $[Mn_2(CO)_{10}]$ with Na_2S_2 and ethanol in the molar ratio 1:4:80 in a sealed tube at 85 °C for 1.5 h gave **1**. When the same reaction was carried out for 80 hours, **2** was obtained. Compound **3** was synthesized analogously from the reaction of $[Mn_2(CO)_{10}]$ with Na_2Te_2 and ethanol in the molar ratio 1:2:50 (Scheme 1). The structures of **1**, **2**, and **3** were determined by single-crystal X-ray analyses.[9] The $[Mn_3(CO)_9(S_2)_2(SH)]^{2-}$ anion in **1** contains a triangle of Mn atoms bridged by two disulfide S_2^{2-} and a hydrosulfide HS^- ligand (Figure 1). The two disulfide ligands adopt different coordination modes: one is μ_3-η^1,η^1,η^1-bridging and the other μ_3-η^1,η^1,η^2-bridging. The hydrosulfide acts as a μ_2-ligand. The H atom on the monosulfide could not be located from the difference Fourier electron density map of the X-ray diffraction data. Its presence is implied by other experimental evidence (vide infra). The cluster possesses idealized C_s molecular symmetry with the mirror plane through O8/C8/Mn3/S5/S4/S1/H1. Each Mn atom is coordinated to three S atoms and three *cis* CO groups in an approximately octahedral environment. The observed Mn–Mn distances [3.523(1)–4.048(1) Å] preclude any metal–metal bonding. All Mn atoms are assigned a formal oxidation state of +I. The average Mn–S bond length of 2.372(7) Å is comparable to those of 2.34–2.38 Å found in $[Mn_4(S_2)_2(CO)_{15}]$.[10] The S–S distances of 2.076(2) and 2.055(3) Å can be considered normal single bonds.[11]



Scheme 1. Synthesis of the cluster anions **1**–**3**.

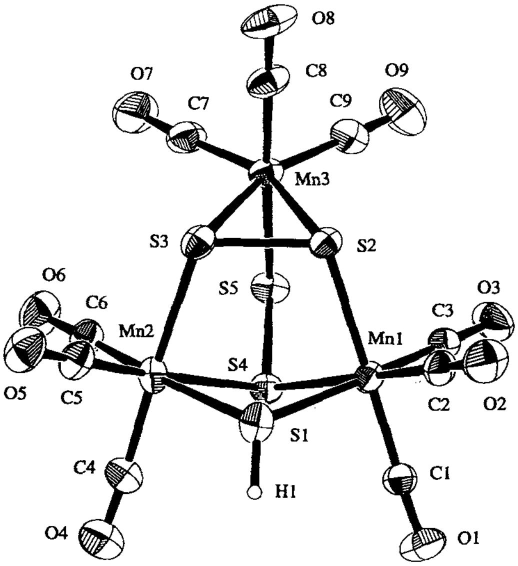


Figure 1. ORTEP representation of the structure of $[Mn_3(CO)_9(S_2)_2(SH)]^{2-}$. Selected bond lengths [Å] and bond angles [°]: Mn1–S1 2.408(2), Mn1–S1 2.402(2), Mn1–S2 2.372(2), Mn1–S4 2.349(2), S2–S3 2.076(2), S4–S5 2.055(3) Å; S1-Mn1-S2 88.10(7), S1-Mn1-S2 79.68(6), Mn1-S4-Mn2 96.82(6).

The $[Mn_2(CO)_6(SH)_3]^{2-}$ anion in **2** (Figure 2) is formed by two Mn^I centers bridged by three μ_2-HS^- ligands. The octahedral coordination of each of the Mn atoms is completed by three *cis* CO groups. Atom S1 is situated on the crystallographic twofold axis, which causes positional disorder of the attached H atom. Thanks to the high quality X-ray data collected at low temperature with the SMART diffractometer, both H1 and H2 atoms were located from the difference Fourier electron density map. The S–H bond lengths and bond angles were refined satisfactorily. Furthermore, three weak peaks at 2527, 2495, and 2478 cm^{-1} found in the FT-IR spectrum are attributable to the bridging ν(S–H) vibrations.[12] The molecule approaches D_{3h} symmetry if the H atoms are omitted. The Mn–Mn distance of

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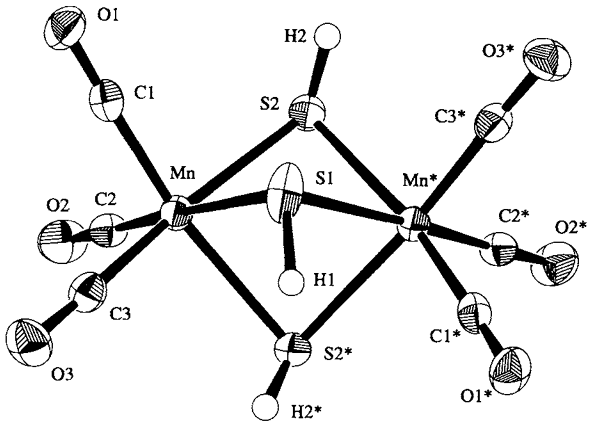

Figure 2. ORTEP representation of the structure of $[Mn_2(CO)_6(SH)_3]^-$. Selected bond lengths [Å] and bond angles [°]: Mn–S1 2.3978(9), Mn–S1 2.4091(7) or 2.4176(7), S1–H1 1.38(5), S2–H2 1.15(5) Å; S1-Mn-S2 81.51(2) or 81.33(2), S2-Mn-S2 82.47(3), Mn-S1-H1 111(2) or 99(2), Mn-S2-H2 117(2) or 99(2).

3.154(1) Å suggests no metal–metal bonding interactions. The average Mn–S bond distance of 2.408(6) Å is slightly longer than that in **1**.

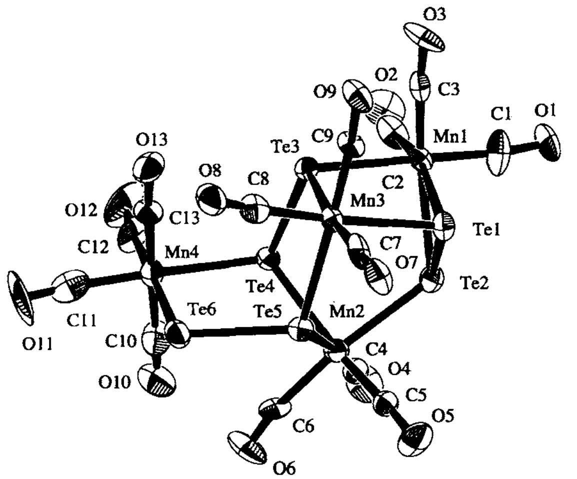

Figure 3. ORTEP representation of the structure of $[Mn_4(CO)_{13}(Te_2)_3]^{2-}$. Selected bond lengths [Å] and bond angles [°]: Te1–Mn1 2.684(4), Te3–Mn1 2.643(4), Te5–Mn2 2.662(4), Te6–Mn(4) 2.717(5), Te1–Te2 2.723(3), Te3–Te4 2.777(2); Te1-Mn1-Te2 61.1(1), Te1-Mn1-Te3 84.1(1), Te2-Mn2-Te4 89.3(1), Te2-Mn2-Te5 98.5(1), Mn1-Te1-Mn3 94.3(1), Mn2-Te4-Mn(4) 112.9(1).

Figure 3 is the ORTEP representation of the $[Mn_4(CO)_{13}(Te_2)_3]^{2-}$ anion in **3**. It consists of an $Mn(CO)_4$ and three $Mn(CO)_3$ fragments bridged in an unusual fashion by three ditelluride Te_2^{2-} ligands. First, three $Mn(CO)_3$ fragments and three ditelluride Te_2^{2-} ligands define a $[Mn_3(CO)_9(Te_2)_3]^{2-}$ cluster core, reminiscent of the $[Mn_3(CO)_9(S_2)_2(SH)]^{2-}$. The minor change in bonding mode of a Te_2^{2-} unit in **3** stems from the need to accommodate another Mn center: atom Te4 is detached from Mn3 so that Te4 and Te6 can form new bonds with the $Mn(CO)_4$ fragment while Te3 is connected to Mn3 instead. Two of the ditelluride Te_2^{2-} ligands in **3** are bound to three, and the third Te_2^{2-} ligand to four Mn centers. Their coordination modes can be designated as $\mu_3,\eta^1,\eta^1,\eta^2$-bridging for $\{Te1-Te2\}^{2-}$, $\mu_4,\eta^1,\eta^1,\eta^1,\eta^1$-bridging for $\{Te3-Te4\}^{2-}$, and $\mu_3,\eta^1,\eta^1,\eta^1$-bridging for $\{Te5-Te6\}^{2-}$. All the Mn atoms can be assigned the formal oxidation state +I and are in approximately octahedral environments with either *cis* C_{3v} or C_{2v} local symmetry. The Mn ··· Mn distances range from 3.91 to 5.41 Å, thus excluding any possibility of metal–metal bonding. The average Mn–Te bond lengths of 2.665(7) Å is comparable to those of 2.676(1) and 2.671(1) Å found in *cis*-$\{[Na([18]crown-6)]\cdot 2THF\}[Mn(CO)_4(TePh)_2]$.[13] The Te–Te bond lengths are, on average, 2.75(2) Å and can be considered normal single bonds.[14]

Attempts to use IR and ^1H NMR spectroscopy to confirm the presence of the SH^- ligand in **1** have thus far been unsuccessful. The $\nu(S-H)$ vibrational modes may be too weak to be detected.[12] On the other hand, a trace amount of acid or base in solution has been known to cause exchange broadening and collapse of the SH^- proton NMR signal in other metal hydrosulfide complexes.[15] The hydrosulfide ligand in **1** is formulated as a result of the following observations: 1) If the monosulfide ligand were not protonated, mixed valence would have to be invoked for the Mn centers in **1**. However, magnetic susceptibility measurements showed that the compound is diamagnetic, which is supportive of an assignment of the precise formal oxidation state +I to the Mn atoms; 2) the control reactions carried out in superheated MeOH gave **4** and **5**, the methylated analogues of **1** and **2**, as confirmed by single crystal X-ray analyses.[16] The cluster ions $[Mn_3(CO)_9(E_2)_2(ER)]^{2-}$ (E = S, R = CH_3, H; E = Te, R = CH_3)[17] are formed by attack of the solvent (MeOH or EtOH) on the coordinated monochalcogenide ligands because of the nucleophilicity or Lewis basicity of such atoms.[7] However, tellurium is unable to follow the same course of reaction if protonation is required. This is consistent with the lower Lewis basicity of telluride relative to sulfide. Instead, the monotelluride ligand is replaced by a ditelluride ligand, and the structure expands to include an extra $Mn(CO)_4$ fragment. Therefore, we speculate that **1** and **3** are probably formed by the same pathway, but the ultimate structure is controlled by the need to satisfy the electronic requirements of the monochalcogenide ligand. This leads to either methylation, protonation, or replacement of the monochalcogenide with a dichalcogenide in this position.

$(Ph_4P)_2[Mn_3(CO)_9(S_2)_2(SCH_3)]$ **4**

$(Ph_4P)[Mn_2(CO)_6(SCH_3)_3]$ **5**

Pure **1** failed to react with EtOH to give **2**. The formation of the latter may have involved, besides EtOH, some unidentified intermediate species generated in situ. We have also been unable to prepare **1**, **2**, or **3** from the refluxing ethanol solution. Kolis and co-workers have shown that the solution reaction between $[M_2(CO)_{10}]$ (M = Mn or Re) and K_2E_x (E = S, Se; x = 2–4) in DMF gives the E_4^{2-}-containing dimers $(Ph_4P)_2[M_2(E_4)_2(CO)_6]$.[18] Heating of the latter in DMF leads to the formation of homoleptic $(Ph_4P)_2[M(E_4)_2]$.[18] All this underscores the intrinsic difference of the chemistry under hydro(solvo)thermal conditions and that at ambient temperatures and pressures.

Experimental Section

Na_2S_2 and Na_2Te_2 were prepared by treating a stoichiometric amount of sulfur (or tellurium) with sodium metal in liquid ammonia. Other reagents were used as obtained. All the manipulations were carried out under a dry nitrogen atmosphere in a Labconco glovebox.

1: A sample of $[Mn_2(CO)_{10}]$ (40 mg, 0.1 mmol), Na_2S_2 (44 mg, 0.4 mmol), and Ph_4PBr (252 mg, 0.6 mmol) was ground and mixed thoroughly in a mortar with a pestle. The reagents were loaded into a thick-walled Pyrex tube (~25 cm long). After addition of EtOH (0.4 mL), the tube was frozen with liquid N_2, evacuated, and sealed with a flame. The tube was heated at 85 °C for 1.5 h to afford orange single crystals of $(Ph_4P)_2[Mn_3(CO)_9(S_2)_2(SH)]$. Analytically pure crystals can be isolated in 34% yield by washing with ethanol and diethyl ether. Mid-IR spectrum in the CO region: $\tilde{\nu}$ = 1999(sh), 1972(s), 1955(s), 1900(sh), 1878(s), and 1859(sh) cm^{-1}.

2: This compound was prepared analogously except that the sealed tube was heated at 85 °C for 80 hours. Orange-yellow, cube-shaped single crystals were isolated in 70% yield. Mid-IR spectrum in the CO region: $\tilde{\nu}$ = 1994(s), 1910(sh), 1898(s), 1884(s), and 1863(sh) cm^{-1}.

3: The sealed Pyrex tube containing $[Mn_2(CO)_{10}]$ (80 mg, 0.2 mmol), Na_2Te_2 (120 mg, 0.4 mmol), Ph_4PBr (252 mg, 0.6 mmol), and 0.4 mL EtOH was heated at 85 °C for 14 hours. After washing with ethanol and diethyl ether, black single crystals of **3** were separated by hand in about 55% yield. Mid-IR spectrum in the CO region: $\tilde{\nu}$ = 2030(s, sharp), 1962(vs, broad), 1929(s, shoulder), 1883(s, multiple) cm^{-1}. Semi-quantitative elemental analysis by SEM-EDAX: P/Mn/Te = 1/2.07/3.11.

Satisfactory C and H analyses were obtained for **1** and **2**. The phase identity and homogeneity of the three compounds was confirmed by comparing their experimental X-ray powder diffraction patterns of bulk material with those of calculated from the single crystal X-ray data.

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[16] **4**: triclinic, space group $P\bar{1}$ (no. 2), $a = 20.70(1)$, $b = 23.40(1)$, $c = 12.837(5)$ Å, $\alpha = 91.86(4)$, $\beta = 90.50(4)$, $\gamma = 69.84(4)°$, $V = 5835(9)$ Å^3, $Z = 2$; **4**: triclinic, space group $P\bar{1}$ (no. 2), $a = 10.162(6)$, $b = 11.667(7)$, $c = 16.665(9)$ Å, $\alpha = 107.15(5)$, $\beta = 92.75(5)$, $\gamma = 113.44(4)°$, $V = 1701(4)$ Å^3, $Z = 2$.

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A Five-Atom Molecule which Enantiomerizes in a Single Step via Chiral Transition States **

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Dedicate to Professor Kurt Mislow

Racemizations of chiral molecules do not necessarily involve achiral transition states or intermediates. A rubber glove, turned inside out by stripping it from the right hand, will then fit the left without going through a symmetric representation. Mislow demonstrated in 1955[1] an enantiomerization involving only chiral intermediates along the whole path (termed a "chiral path") in dissymmetric biphenyl derivatives.[2, 3]

Other enantiomerizations along chiral paths, involving one or more reaction steps, are known. The stereomutation of phosphoranes substituted with five different groups by the Berry pseudorotation mechanism,[4] which proceeds through five steps (that is, four intermediate configurations and five transition states), the enantiomerization of triarylamines ("molecular propellers") by a sequence of three two-ring flips,[5, 6] correlated rotation of "gear" systems such as appropriately substituted bis-(9-tripticyl)-methane,[7] as well as the internal rotation of Mislow's biphenyl,[1, 2] are examples with complicated, many atom molecules. A recently synthesized chiral knot from single-stranded DNA may enantiomerize without even being able to assume any achiral conformation.[8] The racemizations of a number of *o,o'*-bridged biphenyls are more recent single-step examples.[9]

The simplest possible asymmetric enantiomerization of a real molecule would require only five atoms as well as a single reaction step, that is, without an intervening minimum.[10] The goal of this research was to locate a chemically feasible possibility with a chiral path of minimum energy and a low barrier. The demonstration of such an example computationally did not prove to be easy.

As the stereomutation of methane has been computed to occur via a nonplanar transition state (a $CH_2 \cdot H_2$ complex),[11] the hypothetical chiral isotopomer CHDTMu (Mu = muonium, a hydrogen-like particle) might enantiomerize by an asymmetric path. This barrier for CH_4, although below the H_2 elimination threshold, was computed to be very high (107 ± 2 kcal mol^{-1} and 5 ± 1 kcal mol^{-1} at 0 K) above the CH dissociation energy.[11] We have not been able to find any chiral five-atom methane-based molecule (for example CHFClBr, recently dis-

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