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Binuclear manganese carbonyl thiocarbonyls: metal–metal multiple bonds *versus* four-electron donor thiocarbonyl groups†

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Density functional theory (DFT) studies on $Mn_2(CS)_2(CO)_8$ using the B3LYP and BP86 methods show that no less than eight different unbridged structures are of significantly lower energies than the lowest energy doubly bridged structure. The Mn–Mn single bonds in these $Mn_2(CS)_2(CO)_8$ structures range from 2.99 ± 0.02 Å for the four structures with staggered equatorial CO/CS groups to 3.12 ± 0.04 Å for the four structures with eclipsed equatorial CO/CS groups. The six lowest energy $Mn_2(CS)_2(CO)_7$ structures all have four-electron donor bridging η^2-μ-CE groups (E = S, O) and formal Mn–Mn single bonds of lengths 2.95 ± 0.01 Å, rather than only two-electron donor CO and CS groups and formal Mn=Mn double bonds. The $Mn_2(CS)_2(CO)_7$ structures with an η^2-μ-CS group are of lower energy than those with an η^2-μ-CO group. These $Mn_2(CS)_2(CO)_7$ structures are similar to the lowest energy structure for $Mn_2(CO)_9$ predicted previously as well as $(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4(\eta^2\text{-}\mu\text{-}CO)$, which has been synthesized and structurally characterized by X-ray diffraction. The lowest energy $Mn_2(CS)_2(CO)_6$ structures are predicted have a single four-electron donor bridging η^2-μ-CS group and a formal Mn=Mn double bond. However, at only slightly higher energies, $Mn_2(CS)_2(CO)_6$ structures are found with two η^2-μ-CS groups and a formal Mn–Mn single bond. A formal Mn≡Mn triple bond of length 2.36 ± 0.03 Å is found in an even higher energy unbridged $Mn_2(CS)_2(CO)_6$ structure, similar to the lowest energy $Mn_2(CO)_8$ structure found in a previous theoretical study. The lowest energy structures for $Mn_2(CS)_2(CO)_5$ have two η^2-μ-CS groups and a formal Mn=Mn double bond of length 2.57 ± 0.03 Å.

1. Introduction

Manganese carbonyl chemistry is of interest since the first example of a stable compound containing a four-electron donor bridging carbonyl group was the manganese carbonyl derivative $(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4(\eta^2\text{-}\mu\text{-}CO)$ (Fig. 1), synthesized in 1975 by heating $Mn_2(CO)_{10}$ with two molar equivalents of the small bite chelating diphosphine $Ph_2PCH_2PPh_2$ in boiling decane.[1] Determination of the structure of this manganese complex by X-ray diffraction[2] indicated a very unusual bridging CO group with an abnormally short Mn–O distance of 2.29 Å. This suggests some direct manganese–oxygen bonding as well as the usual manganese–carbon bonding to both manganese atoms that is expected for a bridging carbonyl group. The Mn–Mn distance of 2.934 Å in this diphosphine complex is very similar to the unbridged Mn–Mn single bond distance of 2.895 Å in the parent $Mn_2(CO)_{10}$, determined by X-ray diffraction (Fig. 1).[3] This suggests a metal–metal single bond in $(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4(\eta^2\text{-}\mu\text{-}CO)$. Therefore, its anomalous bridging CO group needs to be a formal four-electron donor to provide each manganese atom with the favored 18-electron configuration. Such donation of four electrons can occur through one σ-bond from the carbonyl carbon and one π-bond from the C≡O bond of the anomalous carbonyl group. The π-donation lowers the effective carbon–oxygen bond order, consistent with the very low bridging infrared ν(CO) frequency of 1645 cm^{-1} found experimentally for $(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4(\eta^2\text{-}\mu\text{-}CO)$.

The above $(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4(\eta^2\text{-}\mu\text{-}CO)$ complex may be regarded as a substitution product of $Mn_2(CO)_9$ in which four of the carbonyl groups are replaced by two bidentate phosphine ligands. The parent $Mn_2(CO)_9$ is not stable under ambient conditions but has been observed as a photolysis product of $Mn_2(CO)_{10}$ in frozen alkane matrices at 100 K.[4] An $Mn_2(CO)_8(\eta^2\text{-}\mu\text{-}CO)$ structure for $Mn_2(CO)_9$ is suggested by the very low ν(CO) frequency of 1760 cm^{-1} found experimentally in these matrices (Fig. 1). In addition,

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† Electronic supplementary information (ESI) available: Tables S1–S4: theoretical harmonic vibrational frequencies for $Mn_2(CS)_2(CO)_8$ (9 structures), $Mn_2(CS)_2(CO)_7$ (7 structures), $Mn_2(CS)_2(CO)_6$ (7 structures) and $Mn_2(CS)_2(CO)_5$ (5 structures) using the BP86 method; Tables S5–S31: theoretical Cartesian coordinates for $Mn_2(CS)_2(CO)_8$ (8 structures), $Mn_2(CS)_2(CO)_7$ (7 structures), $Mn_2(CS)_2(CO)_6$ (7 structures) and $Mn_2(CS)_2(CO)_5$ (5 structures) using the B3LYP method; complete Gaussian 03 reference (ref. 40). See DOI: 10.1039/b9nj00340a

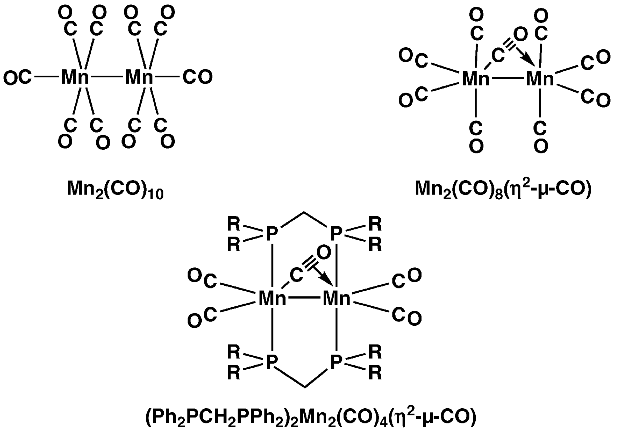

$Mn_2(CO)_{10}$
$Mn_2(CO)_8(\eta^2\text{-}\mu\text{-}CO)$
$(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4(\eta^2\text{-}\mu\text{-}CO)$

Fig. 1 Structures of some manganese carbonyl derivatives.

density functional theory (DFT) studies[5] on $Mn_2(CO)_9$ indicate the lowest energy structure to be $Mn_2(CO)_8(\eta^2\text{-}\mu\text{-}CO)$ containing a four-electron donor bridging carbonyl group with a predicted ν(CO) frequency of 1767 cm^{-1} (BP86), very close to the experimental value.

Despite the occurrence of an unusual four-electron donor $\eta^2\text{-}\mu$-CO group in $Mn_2(CO)_9$, the limited experimental[6] and more extensive theoretical work[5] on the more highly unsaturated binuclear manganese carbonyls $Mn_2(CO)_8$ and $Mn_2(CO)_7$ do not find four-electron donor $\eta^2\text{-}\mu$-CO groups in their lowest energy structures. Thus, the lowest energy structure for $Mn_2(CO)_8$ is predicted by DFT to have only terminal carbonyl groups and a very short $Mn{\equiv}Mn$ distance of $\sim$2.3 Å, suggesting the formal triple bond required to give both manganese atoms the favored 18-electron configuration.

Recent DFT studies[7] of $Fe_2(CS)_2(CO)_n$ predicted the thiocarbonyl group to behave quite differently from the carbonyl group in binuclear derivatives, particularly when the thiocarbonyl group bridges two metal atoms in the unsaturated derivatives $Fe_2(CS)_2(CO)_n$ (n = 6, 5, 4). More specifically, four-electron donor thiocarbonyl groups bonded as $\eta^2\text{-}\mu$-CS groups through both the sulfur and carbon atoms are frequently preferred energetically over metal–metal multiple bonding. These results suggest that the preferred structures for similar unsaturated binuclear manganese carbonyl thiocarbonyls $Mn_2(CS)_2(CO)_n$ (n = 7, 6, 5) might contain four-electron donor $\eta^2\text{-}\mu$-CS groups rather than multiple manganese–manganese bonds. In addition, the relative energies of unbridged $(OC)_4(SC)Mn\text{–}Mn(CS)(CO)_4$ and bridged $Mn_2(CO)_8(\mu\text{-}CS)_2$ structures for the saturated $Mn_2(CS)_2(CO)_8$ are of interest because of the greater tendency of thiocarbonyl groups to form two-electron bridging groups *versus* carbonyl groups.

Introduction of the thiocarbonyl ligand into transition metal complexes is often difficult, owing to the instability of carbon monosulfide at temperatures above −100 °C.[8,9] Thus, reagents such as carbon disulfide (S=C=S) and thiophosgene ($S{=}CCl_2$) generally need to be used as sources of the thiocarbonyl ligand. This makes it particularly difficult to synthesize metal thiocarbonyls with several thiocarbonyl ligands. In the case of manganese, the complex $Mn_2(CS)(CO)_9$, containing only carbonyl and thiocarbonyl ligands, has been synthesized in low yield and in an impure condition by the reaction of $KMn(CO)_5$ with thiophosgene.[10] A manganese complex with a higher CS/Mn ratio, namely $Mn(CS)(CO)_4Br$, has been isolated from the bromination of $Mn_2(CS)(CO)_9/Mn_2(CO)_{10}$ mixtures generated from the $KMn(CO)_5/S{=}CCl_2$ reaction. Examples of more complicated manganese complexes containing a bridging thiocarbonyl group include $Cp(CO)Fe(\mu\text{-}CO)(\mu\text{-}CS)Mn(CO)_4$ and $Cp(R_3P)M(\mu\text{-}CO)(\mu\text{-}CS)\text{-}Mn(CO)Cp$ (Cp = $\eta^5\text{-}C_5H_5$; M = Co, Rh).[11,12]

This paper reports theoretical studies of the binuclear manganese carbonyl thiocarbonyls $Mn_2(CS)_2(CO)_n$ (n = 8, 7, 6, 5). These include the saturated derivative $Mn_2(CS)_2(CO)_8$, as well as unsaturated derivatives where n = 7, 6, and 5, requiring manganese–manganese double, triple, and quadruple bonds, respectively, to give both manganese atoms the favored 18-electron configurations if all carbonyl and thiocarbonyl groups are two-electron donors. Compounds with a 1 : 1 CS : Mn ratio were chosen for this study in order to allow for possible structures with two bridging thiocarbonyl groups. The parent saturated derivative $Mn_2(CS)_2(CO)_8$ is currently unknown but is potentially accessible from the reduction of $Mn(CS)(CO)_4Br$ with a suitable reducing agent.

2. Theoretical methods

Electron correlation effects were considered using density functional theory (DFT) methods, which have evolved as a practical and effective computational tool, especially for organometallic compounds.[13–27] Two DFT methods were used in this study. The first functional is the popular B3LYP method, which is the hybrid HF/DFT method combining the three-parameter Becke exchange functional (B3) with the Lee–Yang–Parr (LYP) generalized gradient correlation functional.[28,29] The other DFT method used in the present paper is BP86, which links Becke's 1988 exchange functional (B) with Perdew's 1986 gradient corrected correlation functional method (P86).[30,31] It has been noted elsewhere that the BP86 method may be somewhat more reliable than B3LYP for the types of organometallic systems considered in this paper.[32–34]

Our DZP basis sets used for carbon, oxygen, and sulfur add one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C) = 0.75$, $\alpha_d(O) = 0.85$, and $\alpha_d(S) = 0.70$ to the standard Huzinaga–Dunning–Hay contracted DZ sets.[35–37] The C and O basis sets are thus designated (9s5p1d/4s2p1d) and the S basis set is similarly described as (12s8p1d/6s4p1d). For Mn, in our loosely contracted DZP basis set, the Wachters primitive set[38] was used, augmented by two sets of p functions and one set of d functions, contracted following Hood *et al.*,[39] and designated as (14s11p6d/10s8p3d). For $Mn_2(CS)_2(CO)_8$, $Mn_2(CS)_2(CO)_7$, $Mn_2(CS)_2(CO)_6$ and $Mn_2(CS)_2(CO)_5$, there are 414, 384, 354 and 324 contracted Gaussian functions, respectively, with the chosen basis sets.

The geometries of all structures were fully optimized using the B3LYP/DZP and BP86/DZP methods. Vibrational frequencies were determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates. The corresponding infrared intensities were also evaluated analytically. All of the computations were carried out with the Gaussian 03 program,[40] exercising the fine grid option (75 radial shells, 302 angular points) for evaluating integrals numerically,[41] while the tight (10^{-8} Hartree) designation is the default for the self-consistent field (SCF) convergence.

In the search for minima using all currently implemented DFT methods, low magnitude imaginary vibrational frequencies are suspect because of significant limitations in the numerical integration procedures used in the DFT computations. Some such low magnitude imaginary frequencies arise from numerical errors, and some of them are genuine imaginary frequencies, indicating a transition state or saddle point. In order to resolve this problem, the structures with small imaginary frequencies were further optimized until no significant imaginary frequencies remain. Furthermore, these genuine minimum structures are compared with the precursor structures having small imaginary frequencies. If the two structures are very close in geometry and energy, the imaginary frequencies are considered to be artificial. Otherwise, they are regarded as significant so only the final optimized structures are reported herein.

The optimized structures are listed in Fig. 2–5 and Tables 1–8. A given $Mn_2(CS)_2(CO)_a$ structure is designated as **a-b**, where **a** is the number of CO groups, and **b** orders the structures according to their relative energies. Thus the lowest energy singlet structure of $Mn_2(CS)_2(CO)_8$ is designated **8-1**. In the text, energies and bond distances are listed as 0.7(1.0) kcal mol^{-1} corresponding to the results from the B3LYP (BP86) methods. The relative energies (ΔE) listed in the tables include the zero point energy corrections.

3. Results

3.1 The coordinately saturated $Mn_2(CS)_2(CO)_8$ structures isoelectronic with $Mn_2(CO)_{10}$

Nine structures were fully optimized for $Mn_2(CS)_2(CO)_8$ within 25 kcal mol^{-1} (Fig. 2 and Table 1). The eight lowest energy structures for $Mn_2(CS)_2(CO)_8$ have two octahedrally coordinated manganese atoms connected only by a direct Mn–Mn interaction without any bridging CO or CS groups.

The global minimum of $Mn_2(CS)_2(CO)_8$, namely the D_{4d} symmetry structure **8-1**, can be derived from $Mn_2(CO)_{10}$ by replacement of the two axial carbonyls with two thiocarbonyl groups. The Mn–Mn distance in **8-1** was predicted to be 3.003(2.955) Å, which is essentially the same as the previously predicted Mn–Mn distance of 3.007(2.954) Å for the lowest energy structure[5] of $Mn_2(CO)_{10}$. For comparison, the Mn–Mn distance in $Mn_2(CO)_{10}$ was determined to be 2.98 Å by gas-phase electron diffraction,[42] but only 2.895 Å by the most recent X-ray crystallography study.[3] The Mn–C(S) bond length in **8-1** was predicted to be 1.787(1.784) Å. Structure **8-2**, with an axial and an equatorial CS group, lies 0.6(0.9) kcal mol^{-1} above the global minimum of **8-1**. The Mn–Mn distance was predicted to be 3.016(2.965) Å, which is ~0.01 Å longer than that of **8-1**. The next two $Mn_2(CS)_2(CO)_8$ structures in terms of energy, namely **8-3** and **8-4** lying 1.5 ± 0.2 (2.1 ± 0.1) kcal mol^{-1} above **8-1**, have an equatorial CS group on each manganese atom in *transoid* (**8-3**) or *cisoid* (**8-4**) relative positions. The Mn–Mn distances of 3.00 ± 0.03 Å in **8-3** and **8-4** are within 0.03 Å of that for the global minimum of **8-1**. The equatorial Mn–C(S) distances of ~1.83 Å were predicted to be ~0.05 Å longer than the axial Mn–C(S) distances in **8-1**, in accord with a stronger *trans* effect of a carbonyl group relative to an Mn–Mn bond. The four $Mn_2(CS)_2(CO)_8$ structures **8-1** to **8-4** were found to be genuine minima, with all real vibrational frequencies.

The four eclipsed structures of $Mn_2(CS)_2(CO)_8$ (**8-5** to **8-8**) were all predicted to have small imaginary vibrational frequencies corresponding to internal rotation around the Mn–Mn bond. Following the associated normal modes leads to the three corresponding staggered structures. Their Mn–Mn distances, generally ~3.1 ± 0.05 Å, are slightly longer than that for **8-1**, suggesting more steric hindrance between the eclipsed equatorial CO and/or CS groups in **8-5** to **8-8**, relative to the staggered CO and CS groups in **8-1** to **8-4**. The Mn–Mn single bonds in these structures, coupled with only two-electron donor CO and CS groups, gives both manganese atoms the favored 18-electron configuration. The closeness of the energies of the corresponding staggered and eclipsed structures (within ~4 kcal mol^{-1}) suggests that $Mn_2(CS)_2(CO)_8$ is a fluxional molecule.

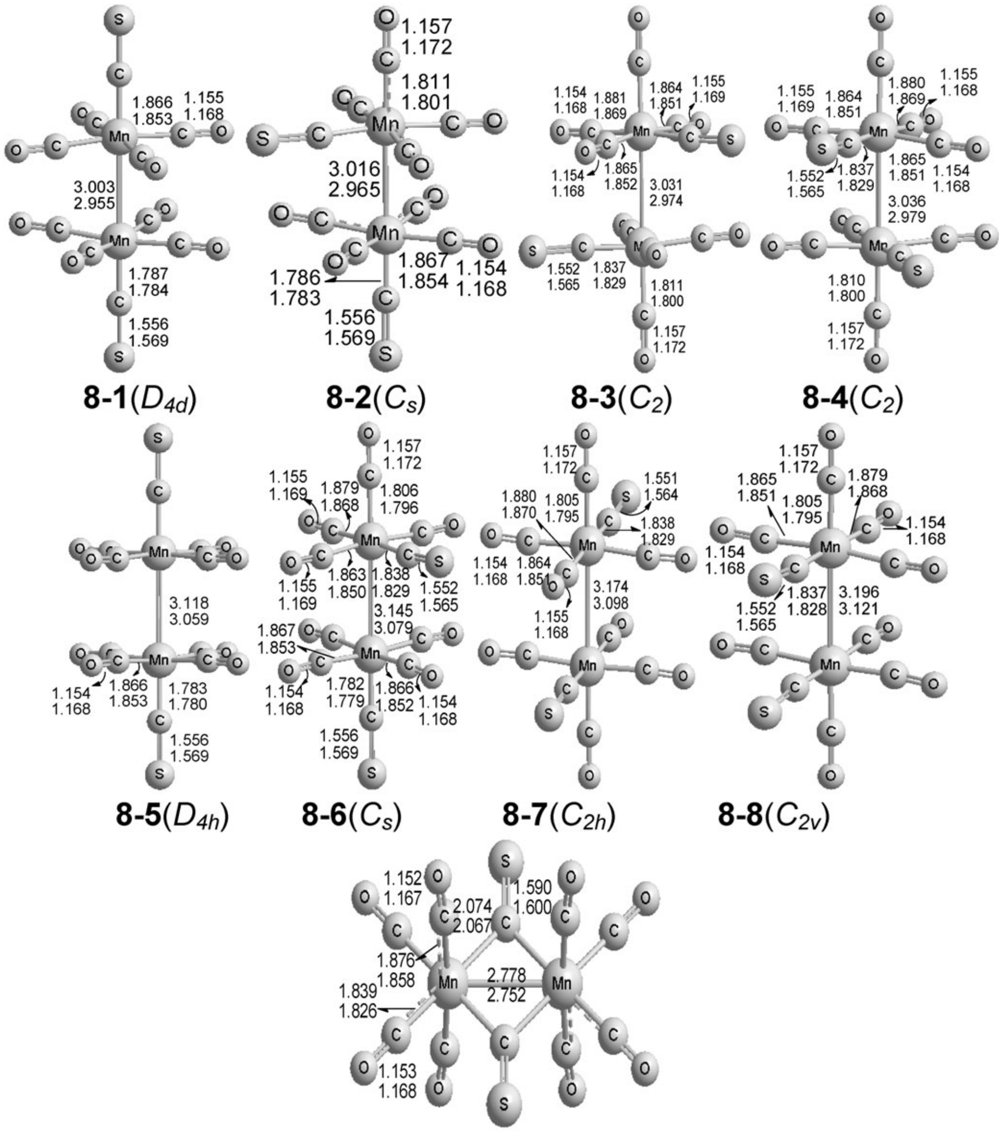
The doubly CS-bridged D_{2h} structure **8-9** for $Mn_2(CS)_2(CO)_8$ lying 13.7(10.9) kcal mol^{-1} in energy above the global minimum of **8-1** was found to be a genuine minimum without any imaginary vibrational frequencies. The predicted doubly bridged Mn–Mn single bond distance in **8-9** of 2.778(2.752) Å is ~0.2 Å shorter than the unbridged Mn–Mn single bond distances in **8-1** to **8-8**, in accordance with the expected bond-shortening effect of the two bridging groups.[7] The computed Mn–C(S) and C–S distances of the bridging CS group in **8-9** were 2.074(2.067) and 1.590(1.600) Å, respectively. Attempts to optimize the doubly bridged $Mn_2(CS)_2(CO)_8$ structures with one or two bridging CO groups led instead to one of the nine structures in Fig. 2.

The terminal CS groups in the $Mn_2(CS)_2(CO)_8$ structures **8-1** to **8-8** were predicted to exhibit ν(CS) frequencies in the range 1320–1280 cm^{-1}, similar to the terminal ν(CS) frequencies previously predicted for $Fe(CS)(CO)_n$ and $Fe_2(CS)_2(CO)_n$ derivatives.[7] The bridging CS groups in the D_{2h} structure **8-9** were predicted to exhibit significantly lower ν(CS) frequencies at 1165 and 1125 cm^{-1} (Table 2).

3.2 Coordinately unsaturated $Mn_2(CS)_2(CO)_n$ (n = 7, 6, 5) derivatives

3.2.1 $Mn_2(CS)_2(CO)_7$. A total of seven structures were found for $Mn_2(CS)_2(CO)_7$ within 25 kcal mol^{-1} of the global minimum of **7-1** (Fig. 3, and Table 3 and Table 4). All of these structures are genuine minima with no imaginary vibrational frequencies.

The four lowest energy structures of $Mn_2(CS)_2(CO)_7$ (**7-1** to **7-4** in Fig. 3) all have one four-electron donor bridging CS group, as indicated by short Mn–S distances of ~2.48 Å and ν(CS) frequencies of 1175 ± 5 cm^{-1} (Table 4). These four $Mn_2(CS)_2(CO)_7$ structures differ only in the location of the second CS group, which is a terminal CS group, predicted to



8-1(D_{4d}) **8-2**(C_s) **8-3**(C_2) **8-4**(C_2)

8-5(D_{4h}) **8-6**(C_s) **8-7**(C_{2h}) **8-8**(C_{2v})

8-9(D_{2h})

Fig. 2 The nine optimized structures of $Mn_2(CS)_2(CO)_8$. The upper distances were obtained by the B3LYP method and the lower distances by the BP86 method.

Table 1 The total energies (E, in Hartree), zero-point energy corrections (ZPE, in Hartree), relative energies (ΔE, in kcal mol^{-1}), and the number of imaginary frequencies (N_{imag}) for the optimized $Mn_2(CS)_2(CO)_8$ structures

		8-1 (D_{4d})	**8-2** (C_s)	**8-3** (C_2)	**8-4** (C_2)	**8-5** (D_{4h})	**8-6** (C_s)	**8-7** (C_{2h})	**8-8** (C_{2v})	**8-9** (D_{2h})
B3LYP	$-E$	4081.55562	4081.55456	4081.55341	4081.55296	4081.55040	4081.54857	4081.54673	4081.54627	4081.53354
	ZPE	0.08118	0.08109	0.08112	0.08113	0.08147	0.08108	0.08135	0.08137	0.08092
	ΔE	0.0	0.6	1.3	1.6	3.5	4.4	5.7	6.0	13.7
	N_{imag}	0	0	0	0	13i	20i	21i	18i	0
BP86	$-E$	4082.08379	4082.05771	4082.08055	4082.08026	4082.07856	4082.07636	4082.07427	4082.07385	4082.06621
	ZPE	0.07941	0.07927	0.07931	0.07932	0.07973	0.07958	0.07956	0.07960	0.07917
	ΔE	0.0	0.9	2.0	2.2	3.5	4.8	6.1	6.4	10.9
	N_{imag}	0	0	0	0	4i	20i	21i	16i	0

exhibit a ν(CS) frequency at 1305 ± 8 cm^{-1}. The Mn–Mn distances of ~2.98 Å (B3LYP) or ~2.92 Å (BP86) in each of these four structures correspond to the formal single bonds needed to give both manganese atoms the favored 18-electron configuration. The two lowest energy $Mn_2(CS)_2(CO)_7$ structures, namely the C_s structures **7-1** and **7-2**, have essentially the same energies despite the different location of the terminal CS group. Furthermore, the $Mn_2(CS)_2(CO)_7$ structure **7-3** lies only 0.6 kcal mol^{-1} above **7-1**/**7-2**. Even the highest energy of these four structures (**7-4**) was predicted to lie only

Table 2 The ν(CO) and ν(CS) vibrational frequencies and corresponding infrared intensities (in parentheses) predicted for $Mn_2(CS)_2(CO)_8$ using the BP86 method[a]

	ν(CO)/cm^{-1}	ν(CS)/cm^{-1}
8-1 (D_{4d})	2073(0), 2013(175), 2003(0), 2003(0), 2001(2113), 2001(2113), 1970(0), 1970(0)	1317(0), 1308(1758)
8-2 (C_s)	2069(225), 2020(765), 2006(49), 2001(1152), 2001(2023), 1985(453), 1977(110), 1969(18)	1313(752), 1300(684)
8-3 (C_2)	2064(106), 2024(1393), 2004(799), 2003(1451), 1990(222), 1985(156), 1980(825), 1971(85)	1302(165), 1301(1057)
8-4 (C_2)	2067(455), 2023(1245), 2003(778), 2001(1621), 1989(599), 1988(36), 1975(411), 1972(88)	1316(859), 1289(228)
8-5 (D_{4h})	2074(0), 2016(0), 2014(286), 2004(2085), 2004(2085), 1993(0), 1970(0), 1970(0)	1319(0), 1310(1753)
8-6 (C_s)	2069(228), 2021(771), 2012(553), 2004(2069), 1997(848), 1985(301), 1976(66), 1969(11)	1315(736), 1302(706)
8-7 (C_{2h})	2064(0), 2023(1698), 2003(2075), 1998(0), 1995(664), 1986(0), 1980(604), 1969(0)	1304(0), 1304(1251)
8-8 (C_{2v})	2069(440), 2022(1505), 2011(748), 2004(2074), 1989(43), 1986(290), 1976(287), 1970(0)	1320(923), 1280(75)
8-9 (D_{2h})	2075(0), 2044(1422), 2010(0), 2004(2108), 2004(1105), 2001(455), 1999(0), 1975(0)	**1165(0), 1125(852)**

[a] **Boldface** means bridging CO or CS groups.

~2.0 kcal mol^{-1} above the global minima of **7-1**/**7-2** by either method. The small energy difference between these four $Mn_2(CS)_2(CO)_7$ structures again suggests a highly fluxional system. These Mn–Mn distances were reported to be about 2.980(2.920) Å, consistent with the singly bridged Mn–Mn single bond.

The next two $Mn_2(CS)_2(CO)_7$ structures, **7-5** and **7-6**, were predicted to lie 15.8 ± 0.3 kcal mol^{-1} above **7-1** or **7-2**. The Mn–O distances in these two structures were predicted to be ~2.24 Å with either method, indicating a four-electron donor η^2-μ-CO group. This η^2-μ-CO group exhibits an unusually low ν(CO) frequency at 1770 ± 4 cm^{-1}. The Mn–Mn distances in **7-5** and **7-6** were predicted to be ~2.98(2.94) Å, again consistent with the formal single bond needed to give both manganese atoms the favored 18-electron configuration.

A C_s unbridged structure **7-7** was also predicted for $Mn_2(CS)_2(CO)_7$, but at the relatively high energy of 22.2(24.1) kcal mol^{-1} above **7-1** or **7-2**. The predicted Mn=Mn distance in **7-7** of 2.797(2.708) Å, is ~0.2 Å shorter than the formal Mn–Mn single bonds in the unbridged $Mn_2(CS)_2(CO)_8$ structures (Fig. 2), as well as those in the $Mn_2(CS)_2(CO)_7$ structures **7-1** to **7-6** with four-electron donor bridging CS or CO groups. This is consistent with the formal Mn=Mn double bond in **7-7**, needed to give each manganese atom the favored 18-electron configuration in the presence of only two-electron donor CO and CS groups.

3.2.2 $Mn_2(CS)_2(CO)_6$.

A total of seven structures were optimized for $Mn_2(CS)_2(CO)_6$ (Fig. 4, and Table 5 and Table 6). The global minimum of $Mn_2(CS)_2(CO)_6$, namely **6-1**, as well as **6-3** at only 2.6 kcal mol^{-1} (B3LYP) or 3.4 kcal mol^{-1} (BP86) above **6-1**, has an η^2-μ-CS group, as indicated by the Mn–S distances of ~2.33 Å and ν(CS) frequencies of 1145 ± 5 cm^{-1}. These structures are derived from the $Mn_2(CS)_2(CO)_7$ structures **7-1** and **7-3**, respectively, by loss of a CO group from the "left" manganese atom (Fig. 4). The Mn–Mn distances in **6-1** and **6-3** were predicted to be ~2.89(2.82) Å, indicating Mn–Mn single bonds, thereby giving the "left" manganese atoms a 16-electron configuration and the "right" manganese atoms the favored 18-electron configuration.

The $Mn_2(CS)_2(CO)_6$ structure **6-6** at ~14.1 ± 0.5 kcal mol^{-1} above the global minimum of **6-1** (Fig. 4) is closely related to the lowest energy $Mn_2(CS)_2(CO)_6$ structures **7-1** and **7-2** by having a single four-electron donor bridging η^2-μ-CS group, as indicated by a short Mn–S distance of 2.51 Å and a predicted ν(CS) frequency of 1171 cm^{-1}. However, the Mn–S distance in **6-5** is ~0.2 Å longer than that in **6-1** and **6-3**, suggesting a weaker interaction. This may relate to the shorter (by 0.1 Å) Mn=Mn bond distance of 2.766(2.705) Å in **6-5** relative to those in **6-1** and **6-3**. This indicates a stronger manganese–manganese interaction corresponding to the formal double bond required to give both manganese atoms the 18-electron configuration.

Three $Mn_2(CS)_2(CO)_6$ structures containing two four-electron donor bridging η^2-μ-CS groups are found, namely **6-2**, **6-4** and **6-5** (Fig. 4). Structure **6-2** with two S atoms directly interacting with the "right" manganese atom is calculated to lie 1.7(0.0) kcal mol^{-1} above **6-1**. The two η^2-μ-CS groups in **6-2** are characterized by Mn–S distances of 2.51 ± 0.01 Å, and ν(CS) frequencies of 1201 and 1146 cm^{-1}. In the $Mn_2(CS)_2(CO)_6$ structure **6-4**, the Mn–S bonds involve different manganese atoms, whereas in structure **6-5**, the Mn–S bonds both involve the same manganese atom. Structure **6-4** is predicted to be a genuine minimum without any imaginary vibrational frequencies and to lie 6.4(4.5) kcal mol^{-1} in energy above **6-1**. The two η^2-μ-CS groups in **6-4** are characterized by Mn–S distances of 2.55 ± 0.1 Å, and ν(CS) frequencies of 1181 and 1157 cm^{-1}. The $Mn_2(CS)_2(CO)_6$ structure **6-5** is predicted to lie 12.8(12.0) kcal mol^{-1} above **6-1**, and also has no imaginary vibrational frequencies. The two η^2-μ-CS groups in **6-5** are characterized by Mn–S distances of 2.48 ± 0.02 Å, and ν(CS) frequencies of 1176 and 1125 cm^{-1}. The Mn–Mn distances in structures **6-2**, **6-4** and **6-5** are predicted to fall in the range 2.74 ± 0.05 Å corresponding to the formal single bonds, which are shorter than usual because of the two η^2-μ-CS bridges.

The unbridged structure **6-7** at 24.8 ± 0.1 kcal mol^{-1} above the global minimum of **6-1** is the sole $Mn_2(CS)_2(CO)_6$ structure with only two-electron donor CS and CO groups (Fig. 4). The very short Mn≡Mn distance of 2.389(2.340) Å in **6-7** corresponds to the formal triple bond needed to give both manganese atoms the favored 18-electron configuration.

3.2.3 $Mn_2(CS)_2(CO)_5$.

A total of five optimized structures with all real harmonic vibrational frequencies were found for $Mn_2(CS)_2(CO)_5$ within 25 kcal mol^{-1} of each other (Fig. 5, and Table 7 and Table 8). In general these structures are derived from various $Mn_2(CS)_2(CO)_6$ structures by the loss of a carbonyl group.

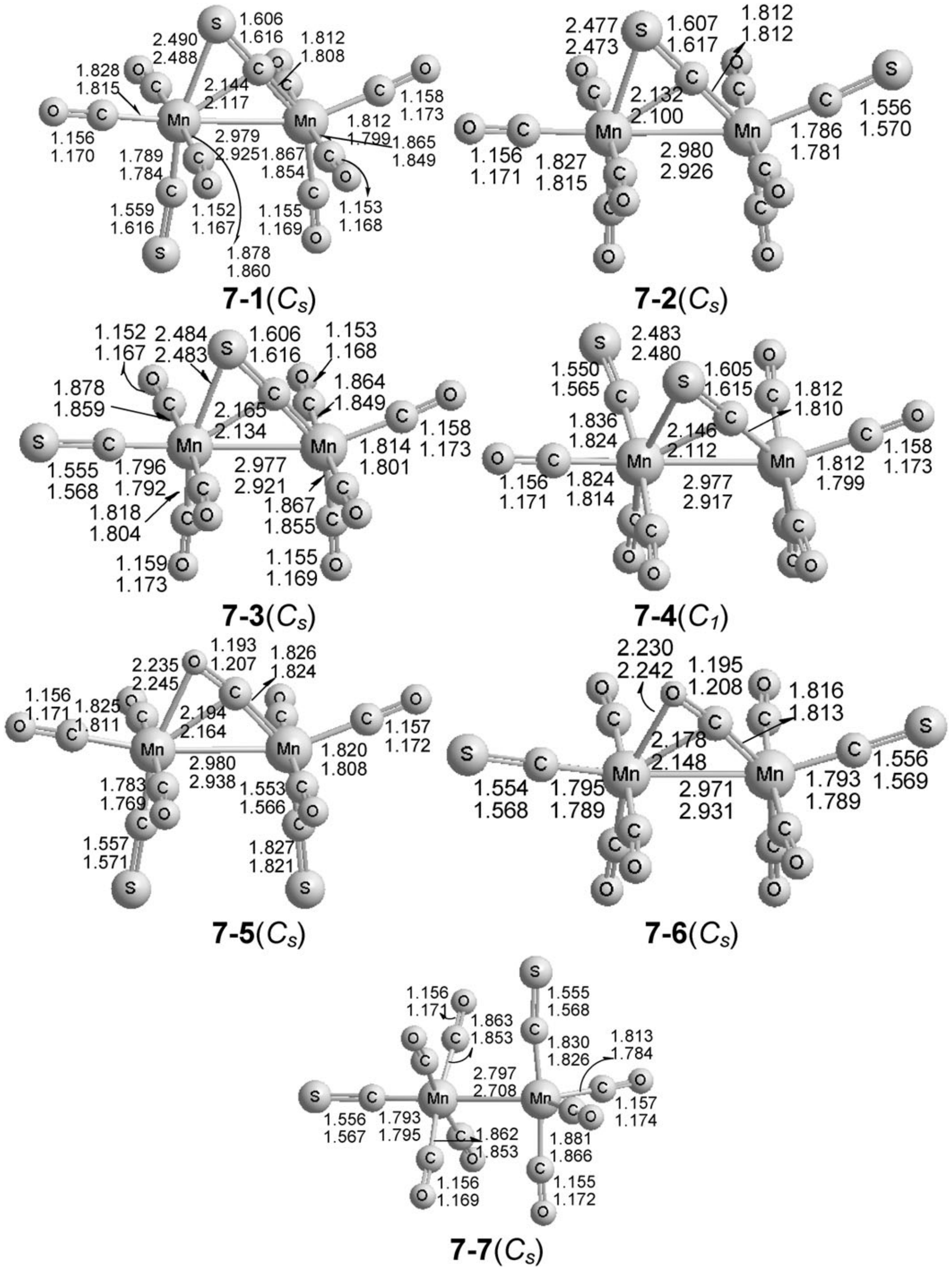


Fig. 3 The seven optimized structures of $Mn_2(CS)_2(CO)_7$. The upper distances were obtained by the B3LYP method and the lower distances by the BP86 method.

Table 3 The total energies (E, in Hartree), zero-point energy corrections (ZPE, in Hartree), relative energies (ΔE, in kcal mol^{-1}), and number of imaginary frequencies (N_{imag}) for the optimized $Mn_2(CS)_2(CO)_7$ structures

		7-1 (C_s)	**7-2** (C_s)	**7-3** (C_s)	**7-4** (C_1)	**7-5** (C_s)	**7-6** (C_s)	**7-7** (C_s)
B3LYP	$-E$	3968.20211	3968.20207	3968.20117	3968.19874	3968.17717	3968.17607	3968.16591
	ZPE	0.07298	0.07293	0.07296	0.07295	0.07281	0.07272	0.07214
	ΔE	0.0	0.0	0.6	2.1	15.5	16.2	22.2
	N_{imag}	0	0	0	0	0	0	0
BP86	$-E$	3968.72488	3968.72492	3968.72385	3968.72197	3968.69985	3968.69898	3968.68563
	ZPE	0.07144	0.07144	0.07147	0.07144	0.07124	0.07119	0.07061
	ΔE	0.0	0.0	0.7	1.8	15.6	16.1	24.1
	N_{imag}	0	0	0	0	0	0	0

Table 4 The ν(CO) and ν(CS) vibrational frequencies and corresponding infrared intensities (in parentheses) predicted for $Mn_2(CS)_2(CO)_7$ using the BP86 method[a]

	ν(CO)/cm^{-1}	ν(CS)/cm^{-1}
7-1 (C_s)	2065(68), 2029(1133), 2001(2109), 1998(109), 1990(531), 1976(782), 1972(20)	1300(515), ***1176(320)***
7-2 (C_s)	2066(348), 2027(644), 2004(741), 2002(2003), 1989(499), 1971(143), 1963(163)	1313(759), ***1171(394)***
7-3 (C_s)	2067(420), 2026(493), 2002(597), 2001(2130), 1981(859), 1973(18), 1966(10)	1311(802), ***1180(355)***
7-4 (C_1)	2062(415), 2021(1515), 2002(694), 1994(1116), 1983(407), 1978(546), 1964(103)	1297(595), ***1178(334)***
7-5 (C_s)	2059(160), 2025(1001), 2001(2117), 1991(209), 1983(776), 1971(24), ***1774(311)***	1322(873), 1286(105)
7-6 (C_s)	2060(182), 2020(181), 2001(2138), 2000(841), 1973(30), 1970(76), ***1766(386)***	1315(138), 1305(1531)
7-7 (C_s)	2050(374), 2005(937), 1997(181), 1982(1136), 1981(1556), 1962(176), 1957(25)	1309(875), 1278(591)

[a] **Boldface** means bridging CO or CS groups; ***italic bold*** implies four-electron donor CO or CS bridges.

The two lowest energy $Mn_2(CS)_2(CO)_5$ structures, namely **5-1** and **5-2** (Fig. 5), both have two four-electron donor bridging η^2-μ-CS groups. In the global minimum **5-1**, the Mn–S bonds to these η^2-μ-CS groups involve different manganese atoms and are of different lengths, namely 2.416(2.408) Å for the shorter Mn–S bond to the "right" manganese atom in Fig. 5, and 2.574(2.561) Å for the longer Mn–S bond to the "left" manganese atom in Fig. 5. Structure **5-2** for $Mn_2(CS)_2(CO)_5$ lies at 3.9(5.9) kcal mol^{-1} in energy above **5-1**. In **5-2**, the Mn–S bonds are equivalent, of length 2.413(2.388) Å to the same manganese atom, namely the "right" manganese atom in Fig. 5. The Mn=Mn bonds of 2.580(2.551) Å for **5-1** and 2.625(2.602) Å are consistent with the formal double bonds required to give both manganese atoms the favored 18-electron configuration in an $Mn_2(CS)_2(CO)_5$ structure with two four-electron donor bridging CS groups.

The next $Mn_2(CS)_2(CO)_5$ structure **5-3** (Fig. 5) lies 8.2(11.9) kcal mol^{-1} above the global minimum of **5-1**. Unlike the other four $Mn_2(CS)_2(CO)_5$ structures, the structure **5-3** has only one bridging group, namely a four-electron donor η^2-μ-CS group with an Mn–S distance of 2.310(2.301) Å and a ν(CS) frequency of 1103 cm^{-1} (Table 8). The Mn–Mn distance of 2.722(2.648) Å is probably best interpreted as a formal single bond, thereby giving both manganese atoms 16-electron configurations.

The remaining two $Mn_2(CS)_2(CO)_5$ structures lie >20 kcal mol^{-1} above the global minimum **5-1**. Structures **5-4** and **5-5** are closely related to **5-2** and **5-1**, respectively, except one of the bridging groups is a four-electron donor carbonyl group rather than a thiocarbonyl group. In **5-4**, the Mn–O distance to the η^2-μ-CO group is 2.218(2.190) Å and the corresponding ν(CO) frequency is very low at 1717 cm^{-1} (Table 8). In **5-5**, at 21.0(20.8) kcal mol^{-1} above **5-1**, the Mn–O distance to this η^2-μ-CO group is 2.428(2.478) Å, and this group exhibits a low ν(CO) frequency at 1782 cm^{-1} (Table 8). The Mn=Mn distances in these structures, namely 2.630 Å(2.605) for **5-4** and 2.601(2.569) Å for **5-5**, are very similar to those in the doubly CS-bridged structures **5-1** and **5-2**, and can correspond to the formal double bonds required to give each manganese atom the favored 18-electron configuration.

3.3 Dissociation energies

Table 9 reports the bond dissociation energies (BDEs) in terms of the single carbonyl dissociation steps:

$$Mn_2(CS)_2(CO)_n \rightarrow Mn_2(CS)_2(CO)_{n-1} + CO \ (n = 8, 7, 6) \quad (1)$$

These BDEs are seen to be lower than those for the simple homoleptic metal carbonyls by comparison with the experimental carbonyl dissociation energies for $Cr(CO)_6$ and $Fe(CO)_5$ of 37 and 41 kcal mol^{-1}, respectively.[43] Furthermore, the BDEs for loss of CO from the binuclear $Mn_2(CS)_2(CO)_n$ derivatives (n = 8, 7, 6) gradually increase with decreasing numbers of carbonyl groups. The smallest predicted BDE for $Mn_2(CS)_2(CO)_n$ (n = 8, 7, 6) is 15.6(19.9) kcal mol^{-1} for $Mn_2(CS)_2(CO)_8$. A driving force for this relatively low BDE may be the favorable energy of forming a four-electron donor bridging η^2-μ-CS group.

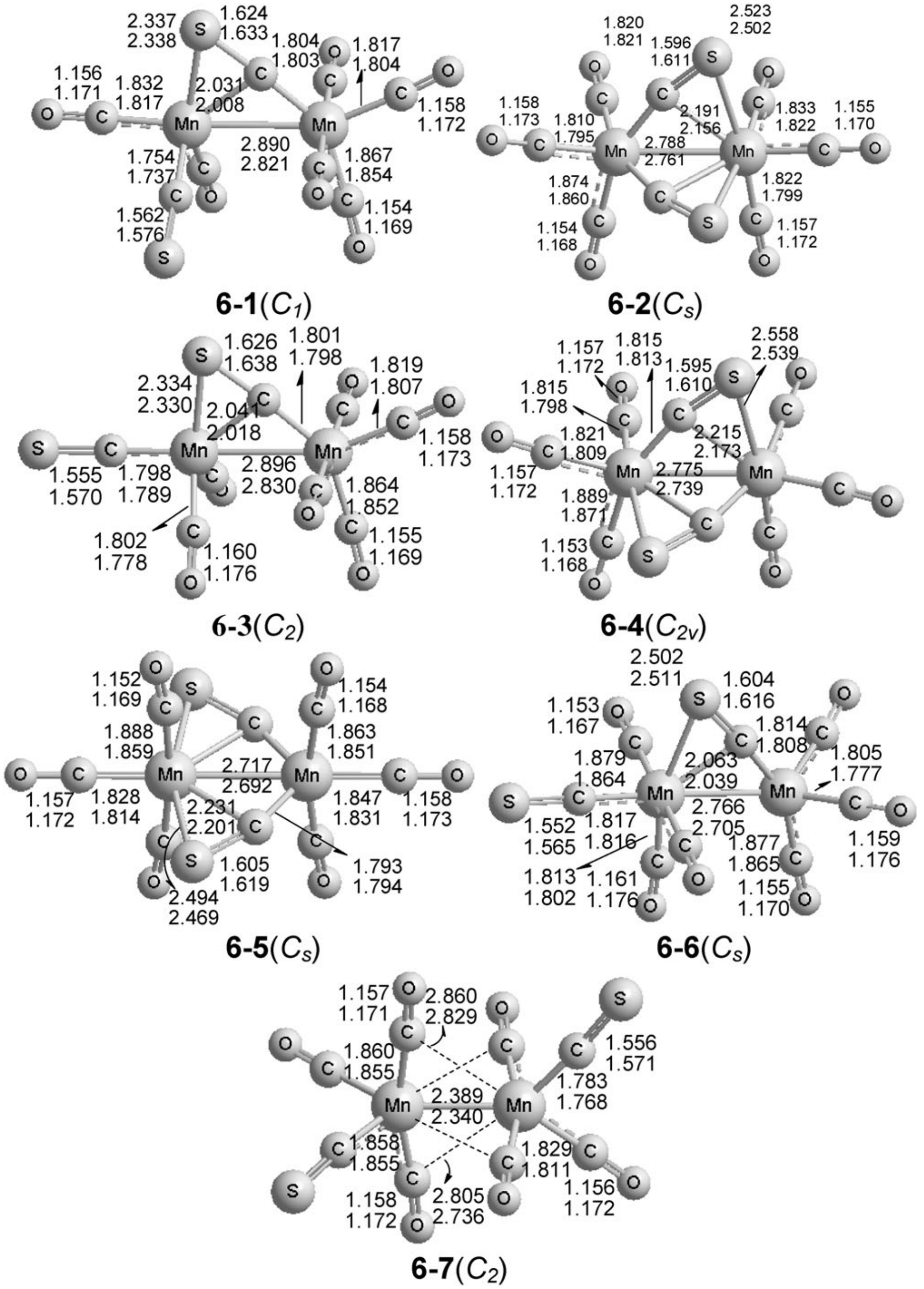
4. Discussion

4.1 Comparison of $Mn_2(CS)_2(CO)_n$ and $Mn_2(CO)_{n+2}$ structures

Previous studies[5] have shown that for $Mn_2(CO)_{10}$, the known D_{4d} staggered unbridged global minimum structure, as well as the closely related D_{4h} eclipsed structure, lie far below the doubly bridged structure of $Mn_2(CO)_8(\mu\text{-}CO)_2$ in terms of relative energy. Thus, the energy difference between the $Mn_2(CO)_{10}$ global minimum and the lowest energy doubly bridged structure $Mn_2(CO)_8(\mu\text{-}CO)_2$ was found to be 21.0 (B3LYP) or 14.8 kcal mol^{-1} (BP86).[5] A similar situation was found for the thiocarbonyls $Mn_2(CS)_2(CO)_8$, although the energy differences are somewhat smaller. Thus, the doubly bridged structure $Mn_2(CO)_8(\mu\text{-}CS)_2$ (**8-9** in Fig. 2) lies 13.7 (B3LYP) or 10.9 kcal mol^{-1} (BP86) above the $Mn_2(CS)_2(CO)_8$ global minimum of **8-1**. The latter, like the global minimum of $Mn_2(CO)_{10}$, also has a staggered arrangement of the equatorial groups. The strong preference for unbridged structures of both $Mn_2(CO)_{10}$ and $Mn_2(CS)_2(CO)_8$ over doubly bridged structures relates to the fact that the unbridged structures have the favorable octahedral six-coordination of the manganese atoms, whereas the doubly bridged structures have seven-coordinate manganese atoms.

A general feature of the structures of the binuclear unsaturated $Mn_2(CS)_2(CO)_n$ (n = 7, 6, 5) derivatives is the absence of two-electron donor bridging CS and/or CO groups in the lowest energy predicted structures. However, four-electron donor bridging η^2-μ-CS and η^2-μ-CO groups were found in most of the low energy structures. Generally, the structures with such η^2-μ-CS groups have lower energies than similar structures with η^2-μ-CO groups.

The lowest energy structure predicted for $Mn_2(CO)_9$ is an $Mn_2(CO)_8(\eta^2\text{-}\mu\text{-}CO)$ structure with a four-electron donor bridging



6-1(C_1) **6-2**(C_s) **6-3**(C_2) **6-4**(C_{2v}) **6-5**(C_s) **6-6**(C_s) **6-7**(C_2)

Fig. 4 The seven optimized structures of $Mn_2(CS)_2(CO)_6$. The upper distances were obtained by the B3LYP method and the lower distances by the BP86 method.

Table 5 The total energies (E, in Hartree), zero-point energy corrections (ZPE, in Hartree), relative energies (ΔE, in kcal mol^{-1}), and number of imaginary frequencies (N_{imag}) for the optimized $Mn_2(CS)_2(CO)_6$ structures

		6-1 (C_1)	**6-2** (C_s)	**6-3** (C_2)	**6-4** (C_{2v})	**6-5** (C_s)	**6-6** (C_s)	**6-7** (C_2)
B3LYP	$-E$	3854.83600	3854.83331	3854.83202	3854.82603	3854.81588	3854.81495	3854.79760
	ZPE	0.06441	0.06419	0.06426	0.06414	0.06419	0.06377	0.06311
	ΔE	0.0	1.8	2.6	6.4	12.8	13.6	24.9
	N_{imag}	0	0	1 (7i)	0	0	1 (11i)	0
BP86	$-E$	3855.35255	3855.35257	3855.34728	3855.34558	3855.33368	3855.32982	3855.31451
	ZPE	0.06315	0.06308	0.06300	0.06288	0.06297	0.06256	0.06166
	ΔE	0.0	0.0	3.4	4.5	12.0	14.6	24.8
	N_{imag}	0	0	1 (12i)	0	0	0	0

Table 6 The ν(CO) and ν(CS) vibrational frequencies and corresponding infrared intensities (in parentheses) predicted for $Mn_2(CS)_2(CO)_5$ using the BP86 method[a]

	ν(CO)/cm^{-1}	ν(CS)/cm^{-1}
6-1 (C_1)	2060(419), 2007(709), 1997(1297), 1993(890), 1981(787), 1951(179)	1305(515), ***1150(316)***
6-2 (C_s)	2047(496), 2010(1894), 1998(847), 1984(708), 1972(366), 1965(261)	***1201(360)***, ***1146(174)***
6-3 (C_s)	2060(643), 2001(463), 1997(1518), 1985(1081), 1971(67), 1947(294)	1301(754), ***1140(344)***
6-4 (C_2)	2045(505), 2008(1760), 1990(1145), 1980(818), 1975(37), 1970(289)	***1181(408)***, ***1157(194)***
6-5 (C_{2v})	2055(13), 2021(1092), 1996(1812), 1983(112), 1972(1145), 1958(384)	***1176(303)***, ***1125(349)***
6-6 (C_s)	2046(212), 2008(1077), 1990(1451), 1975(1077), 1954(431), 1950(12)	1306(923), ***1171(309)***
6-7 (C_2)	2035(161), 1995(1322), 1981(874), 1975(235), 1962(922), 1960(559)	1305(329), 1301(953)

[a] **Boldface** means bridging CO or CS groups; ***italic bold*** implies four-electron CS bridges.

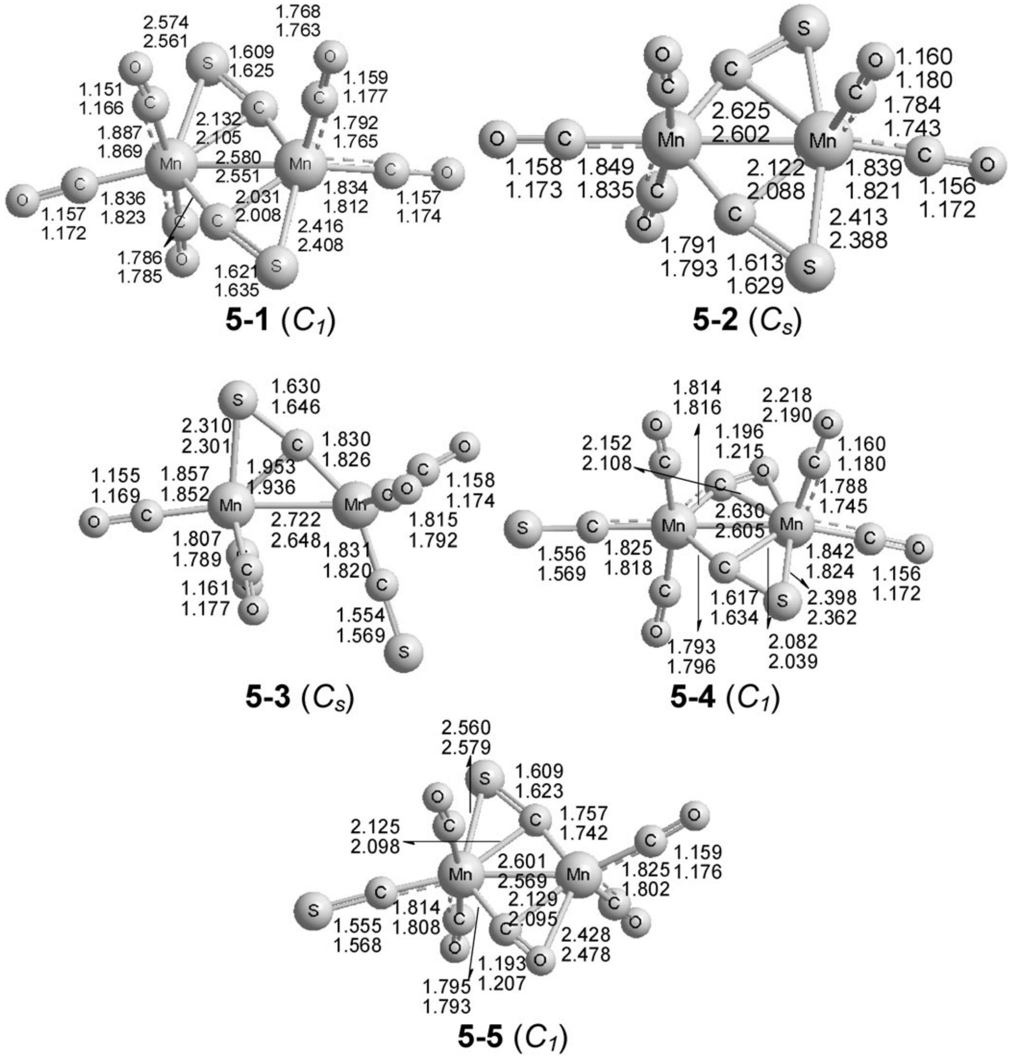

5-1 (C_1)
5-2 (C_s)
5-3 (C_s)
5-4 (C_1)
5-5 (C_1)

Fig. 5 The five optimized structures of $Mn_2(CS)_2(CO)_5$. The upper distances were obtained by the B3LYP method and the lower distances by the BP86 method.

CO group and a formal Mn–Mn single bond.[5] Such a structure is closely related to the stable small bite chelating ditertiary phosphine complex $(Ph_2PCH_2PPh_2)_2Mn_2(CO)_4(\eta^2\text{-}\mu\text{-}CO)$, which has been synthesized[1] and structurally characterized by X-ray crystallography.[2]

The four lowest energy structures for $Mn_2(CS)_2(CO)_7$ (**7-1** to **7-4** in Fig. 3) all have a single four-electron donor η^2-μ-CS group, and differ only in the position of the terminal CS group relative to the central $Mn_2(\eta^2\text{-}\mu\text{-}CS)$ system. Their relative energies fall within the narrow range of ~2 kcal mol^{-1}. The next two structures for $Mn_2(CS)_2(CO)_7$ (**7-5** and **7-6** in Fig. 3) both have a single four-electron donor η^2-μ-CO group and lie in the narrow energy range of 16 ± 1 kcal mol^{-1} above the $Mn_2(CS)_2(CO)_7$ global minimum of **7-1**. All six of these $Mn_2(CS)_2(CO)_7$ structures can be considered as analogues of the lowest energy $Mn_2(CO)_9$ structure with a four-electron

Table 7 The total energies (E, in Hartree), zero-point energy corrections (ZPE, in Hartree), relative energies (ΔE, in kcal mol^{-1}), and number of imaginary frequencies (N_{imag}) for the optimized $Mn_2(CS)_2(CO)_5$ structures

		5-1 (C_1)	**5-2** (C_s)	**5-3** (C_1)	**5-4** (C_1)	**5-5** (C_1)
B3LYP	$-E$	3741.46025	3741.45400	3741.44664	3741.42751	3741.42609
	ZPE	0.05589	0.05579	0.05527	0.05548	0.05525
	ΔE	0.0	3.9	8.2	20.3	21.0
	N_{imag}	0	0	0	0	0
BP86	$-E$	3741.97305	3741.96007	3741.93872	3741.93980	3741.93184
	ZPE	0.05496	0.05475	0.05425	0.05439	0.05424
	ΔE	0.0	5.9	11.9	23.7	20.8
	N_{imag}	0	0	0	0	0

Table 8 The ν(CO) and ν(CS) vibrational frequencies and corresponding infrared intensities (in parentheses) predicted for $Mn_2(CS)_2(CO)_5$ using the BP86 method[a]

	ν(CO)/cm^{-1}	ν(CS)/cm^{-1}
5-1 (C_1)	2047(219), 1992(1120), 1991(970), 1980(1440), 1954(410)	***1168(376)***, ***1124(125)***
5-2 (C_s)	2045(317), 1997(917), 1993(1448), 1973(961), 1943(409)	***1158(296)***, ***1098(268)***
5-3 (C_1)	2016(175), 1994(1962), 1964(882), 1959(485), 1939(364)	1281(430), ***1103(417)***
5-4 (C_1)	2038(72), 1997(1259), 1993(1281), 1942(453), ***1717(297)***	1300(796), ***1121(410)***
5-5 (C_1)	2037(21), 1992(1363), 1984(1314), 1945(536), ***1782(384)***	1303(892), ***1182(285)***

[a] **Boldface** means bridging CO or CS groups; ***italic bold*** implies four-electron CS bridges.

Table 9 Bond dissociation energies (kcal mol^{-1}) for successive removal of carbonyl groups from $Mn_2(CS)_2(CO)_n$

	B3LYP	BP86
$Mn_2(CS)_2(CO)_8 \rightarrow Mn_2(CS)_2(CO)_7 + CO$	15.6	19.9
$Mn_2(CS)_2(CO)_7 \rightarrow Mn_2(CS)_2(CO)_6 + CO$	23.5	28.3
$Mn_2(CS)_2(CO)_6 \rightarrow Mn_2(CS)_2(CO)_5 + CO$	29.6	32.2

donor η^2-μ-CO group. The predicted formal Mn–Mn single bond distance in this $Mn_2(CO)_9$ [$Mn_2(CO)_8$(η^2-μ-CO)] structure of 2.94 ± 0.03 Å is very close to the predicted Mn–Mn distances of 2.95 ± 0.03 Å in all six of the $Mn_2(CS)_2(CO)_5$(η^2-μ-CO)$_2$ and $Mn_2(CO)_7$(η^2-μ-CS)$_2$ structures for $Mn_2(CS)_2(CO)_7$ (**7-1** to **7-6** in Fig. 3).

The next higher energy structure for $Mn_2(CO)_9$ is an unbridged structure lying 5.8(7.2) kcal mol^{-1} above the global minimum.[5] An analogous $Mn_2(CS)_2(CO)_7$ structure **7-7** (Fig. 3) was found, but at the much higher relative energy of 22.2(24.1) kcal mol^{-1} above **7-1**. The Mn═Mn formal double bond distance of 2.75 ± 0.05 Å predicted for the $Mn_2(CS)_2(CO)_7$ structure **7-7** is very close to the 2.74 ± 0.04 Å Mn═Mn distance predicted for the lowest energy unbridged $Mn_2(CO)_9$ structure.

In an earlier study[5] of the more highly unsaturated $Mn_2(CO)_8$ derivatives, no structures were found containing four-electron donor bridging η^2-μ-CO groups. By contrast, the six lowest energy structures for $Mn_2(CS)_2(CO)_6$, namely **6-1** to **6-6** in Fig. 4, all contain at least one four-electron donor η^2-μ-CE groups (E = S, O), and thus have no counterparts in the corresponding $Mn_2(CO)_8$ structures. However, the relatively high energy unbridged $Mn_2(CS)_2(CO)_6$ structure **6-7** (Fig. 4) is very similar to the interesting global minimum structure found for $Mn_2(CO)_8$, which consists of two $Mn(CO)_4$ units linked by a very short Mn≡Mn formal triple bond. The predicted Mn≡Mn formal triple bond distance of 2.33 ± 0.03 Å in this $Mn_2(CO)_8$ structure is very similar to the predicted Mn≡Mn distance of 2.36 ± 0.03 Å in the $Mn_2(CS)_2(CO)_6$ structure **6-7**.

Re-examination of the $Mn_2(CO)_7$ structures[5] indicates that one of the structures (**7-3** in ref. 5) contains two four-electron bridging η^2-μ-CO groups, as indicated by the unusually low ν(CO) frequencies of 1747 and 1718 cm^{-1}. Structures **5-2** and **5-5** for $Mn_2(CS)_2(CO)_5$ (Fig. 5) are closely related to this $Mn_2(CO)_7$ structure, but with one (**5-4**) or two (**5-2**) η^2-μ-CS groups in place of one or two of the η^2-μ-CO groups in the $Mn_2(CO)_7$ structure. The formal Mn═Mn double bond length in this $Mn_2(CO)_7$ structure of 2.59 ± 0.02 Å is very similar to those of 2.59 ± 0.03 Å in the $Mn_2(CS)_2(CO)_5$ structures **5-2** and **5-4**. None of the other $Mn_2(CS)_2(CO)_5$ structures in Fig. 5 has any counterpart in the $Mn_2(CO)_7$ structures found in the previous work.[5]

4.2 Manganese–manganese bond lengths

An earlier study on iron carbonyl thiocarbonyls[7] related the lengths of Fe–Fe bonds to the number of bridging groups as well as the formal bond order. The Fe–Fe bond lengths were found to decrease, not only with increasing formal bond order, but also with increasing numbers of bridging groups. Similar observations can be made for the Mn–Mn distances in the binuclear $Mn_2(CS)_2(CO)_n$ derivatives discussed in this paper. Thus, for the structures with doubly bridged Mn–Mn single bonds, namely the high energy $Mn_2(CS)_2(CO)_8$ structure **8-9** (Fig. 2) and the $Mn_2(CS)_2(CO)_6$ structures **6-2**, **6-4** and **6-5** (Fig. 4), the bond lengths fall in the range from 2.70 Å for **6-4** to 2.78 Å for **6-6**. The Mn–Mn bonds in the singly bridged $Mn_2(CS)_2(CO)_7$ structures **7-1** to **7-6** (Fig. 3) are significantly longer, in the narrow range of 2.95 ± 0.01 Å. The unbridged Mn–Mn bonds in the seven lowest energy $Mn_2(CS)_2(CO)_8$ structures **8-1** to **8-8** are longer still, falling in the wider range of 2.98 Å for **8-1** to 3.16 Å for **8-8**. Among these eight $Mn_2(CS)_2(CO)_8$ structures, the three lowest energy structures with staggered arrangements of the equatorial CO and CS groups, namely **8-1** to **8-4** (Fig. 2), have shorter Mn–Mn distances in the narrow range of 2.98–3.01 Å. However, the next four $Mn_2(CS)_2(CO)_8$ structures with eclipsed arrangements of the equatorial CO and CS groups, namely **8-5**, to **8-8** (Fig. 2), have slightly longer Mn–Mn distances in the range of 3.08–3.20 Å.

Similar relationships between the number of bridging groups and the Mn=Mn bond distances were also observed for the $Mn_2(CS)_2(CO)_n$ derivatives with formal double bonds. Thus, the three doubly bridged $Mn_2(CS)_2(CO)_5$ structures **5-1**, **5-2** and **5-4** (Fig. 5) have Mn=Mn bond lengths in the range of 2.55–2.61 Å, which is significantly shorter than the 2.70–2.78 Å range for the doubly bridged Mn–Mn single bonds noted above. The singly bridged $Mn_2(CS)_2(CO)_6$ structures **6-1**, **6-2** and **6-5** exhibit longer Mn=Mn distances in the range of 2.73 Å for **6-5** to 2.86 Å for **6-1** and **6-2**. In this case, however, the unbridged $Mn_2(CS)_2(CO)_7$ structure **7-7** has an Mn=Mn double bond length of 2.75 Å, at the lower end of the range of the Mn=Mn double bond lengths in the singly bridged structures.

The only $Mn_2(CS)_2(CO)_n$ structure with a formal Mn≡Mn triple bond found in this research is the unbridged $Mn_2(CS)_2(CO)_6$ structure **6-7** (Fig. 4). This structure has an Mn≡Mn distance of 2.36 Å, which is ~0.2 Å shorter than the shortest Mn=Mn formal double bond reported here.

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