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Single-Crystal X-Ray Analysis of Compounds with a Covalent Metal–Metal Bond. 5. Characterization of Halogeno-Bridged Structures of Three Dimers of Halogenobis(pentacarbonylmanganio)indium(III), $[(Mn(CO)_5)_2In(\mu\text{-}X)]_2$ (X = Cl, Br, I)

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The oxidative insertion of In^IX into the Mn–Mn bond of $Mn_2(CO)_{10}$ in the presence of xylene led to clusters of the type $[(Mn(CO)_5)_2In(\mu\text{-}X)]_2$ (X = Cl, Br, I). All three clusters were characterized by osmometric, thermogravimetric, mass spectroscopic, ir, and Raman spectroscopic measurements. X-ray structural analysis shows that the three clusters are isomorphous and have similar molecular structures. The central molecular fragment of each cluster contains a planar centrosymmetric four-membered In_2X_2 ring. Each In atom is bonded to two μ-X atoms and to two Mn atoms in a distorted tetrahedral arrangement. The plane defined by the four Mn atoms is perpendicular to that defined by the In_2X_2 atoms. The Mn–In–Mn angles of the three clusters have the following values: X = Cl, 123.59 (3)°; X = Br, 124.97 (3)°; X = I, 126.37 (4)°. The shortest intramolecular nonbonding O···O contact lengths correspond to equatorial CO ligands of the two pairs of $Mn(CO)_5$ ligands above or below the In_2X_2 plane (X = Cl, 2.877 (8) Å; X = Br, 2.896 (8) Å; X = I, 2.963 (9) Å) and signify a dependence of the O···O repulsion interaction on the atomic size of the μ-X atoms. A consequence of the repulsive effect connected with the nonbonded interaction of the equatorial CO groups of the different Mn atoms is their staggered arrangement. The In_2X_2 rings have obtuse In–(μ-X)–In (X = Cl, 100.02 (5)°; X = Br, 97.42 (2)°; X = I, 94.35 (2)°) and acute (μ-X)–In–(μ-X) angles (X = Cl, 79.98 (5)°; X = Br, 82.58 (2)°; X = I, 85.65 (2)°) and the order of the nonbonded lengths In---In and X---X is In---In > X---X. These structural features of the In_2X_2 rings are reversed with respect to corresponding features of the In_2I_2 ring of the compound $[I_2In(\mu\text{-}I)]_2$ (acute In–(μ-I)–In angle, obtuse (μ-I)–In–(μ-I) angle, and the order of the length In---In < X---X), in which no comparable repulsion exists between the terminal ligands. The average In–X distances in the clusters examined are for X = Cl, 2.618 (2) Å, for X = Br, 2.757 (1) Å, and for X = I, 2.951 (1) Å. The average value of the In–Mn distance in the clusters is for X = Cl, 2.665 (1) Å, for X = Br, 2.664 (1) Å, and for X = I, 2.672 (1) Å.

Introduction

Known clusters formulated as $XIn[Mn(CO)_5]_2$ (X = Cl, Br) were isolated by the reaction of In^IBr with $Mn_2(CO)_{10}$ at 180 °C (insertion method)[1] and that of InX_3 (X = Cl, Br) with $NaMn(CO)_5$ (alkali salt method).[2] The reaction products are usually crystalline powders.[1,2] Mays[2] presumed the molecular formula $[(Mn(CO)_5)_2In(\mu\text{-}X)]_2$ (X = Cl, Br) for these solids. The present report describes the preparation of such clusters in crystalline forms (including the previously unknown one with X = I) by application of an insertion method at a reaction temperature of 125 °C. The results of the structure determination of the clusters $[(Mn(CO)_5)_2In(\mu\text{-}X)]_2$ (X = Cl, Br, I) by x-ray analysis and other characterizations of the clusters are given. The results of x-ray examinations with special regard to $[(Mn(CO)_5)_2In(\mu\text{-}I)]_2$ will be compared with the known structural features of $[I_2In(\mu\text{-}I)]_2$,[3] to get an impression about the influence of a bulky ligand like $Mn(CO)_5$ instead of I as the terminal ligand on the geometrical parameters of an In_2I_2 ring. This is a work to analyze those factors which determine the geometry of

Table I. Ir Spectroscopic Results of the Clusters $[(Mn(CO)_5)_2In(\mu\text{-}X)]_2$ [X = Cl (1), Br (2), I (3)] in the Range 2000–450 cm^{-1}

Sample	Medium	Freq, cm^{-1}					
1	Nujol solid	2102 w	2074 m	2002 vs	1974 vs	1930 sh	ν(CO)
2		2098 w	2072 m	1998 vs	1975 vs	1928 sh	
3		2096 w	2072 m	1998 vs	1975 vs	1925 sh	
1	$CHCl_3$ soln	2100 w	2070 m	1998 vs			ν(CO)
2		2099 w	2055 m	2006 vs			
3		2095 w	2048 m	2008 vs			
1	Nujol solid	673 m	655 vs	645 vs			δ(Mn-CO)
2		671 m	655 vs	645 vs			
3		669 m	653 vs	645 vs			
1	$CHCl_3$ soln	669 vs	666 s	655 m	626 w		δ(Mn-CO)
2		669 vs	667 s	656 m	639 w		
3		669 vs	667 s	655 m	640 w		
1	Nujol solid	486 w	471 w				ν(Mn-CO)
2		486 w	471 w				
3		482 w	471 w				
1	$CHCl_3$ soln	485 w					ν(Mn-CO)
2		478 w					
3		475 w					

four-membered M_2X_2 rings of compounds of the type $[L_2M(\mu\text{-}X)]_2$ (L = univalent ligand; M = Al, Ga, In, Tl in a tetrahedral environment; X = Cl, Br, I).[4-7] Another purpose of the structural analysis of these clusters is connected with the estimation of the In–Mn bond distance at an In atom with coordination number 4.[8]

Experimental Section

Preparation of $[(Mn(CO)_5)_2In(\mu\text{-}X)]_2$ [X = Cl (1), X = Br (2), X = I (3)]. **X = Cl (1).** Indium(I) chloride[9] (0.45 g, 3 mmol) and dimanganese decacarbonyl[10] (1.17 g, 3 mmol) in 3–4 ml of nitrogen-saturated xylene were heated at 125 °C for 72 h in a glass bomb tube (length 150 mm, diameter 20 mm). The resulting yellow precipitate was separated by filtration. For the separation of unreacted dimanganese decacarbonyl the precipitate was washed with petroleum ether (bp 40–60 °C). From the dried residue, yellow rhombic crystals of $[(Mn(CO)_5)_2In(\mu\text{-}Cl)]_2$ (1.46 g, 90%) were separated by hand. Anal. Calcd for $Cl_2C_{20}In_2Mn_4O_{20}$: Cl, 6.56; C, 22.23; In, 21.25; Mn, 20.34. Found: Cl, 6.96; C, 22.24; In, 20.81; Mn, 20.00.

X = Br (2). Following the procedure for product **1** dark yellow, rhombic crystals of $[(Mn(CO)_5)_2In(\mu\text{-}Br)]_2$ (1.58 g, 90%) were isolated from the reaction between indium(I) bromide (0.58 g, 3 mmol) and dimanganese decacarbonyl (1.17 g, 3 mmol). Anal. Calcd for $Br_2C_{20}In_2Mn_4O_{20}$: Br, 13.67; C, 20.54; In, 19.64; Mn, 18.79. Found: Br, 14.28; C, 21.01; In, 18.83; Mn, 19.70.

X = I (3). Orange colored rhombic crystals of $[(Mn(CO)_5)_2In(\mu\text{-}I)]_2$ (0.38 g, 20%) were obtained from the reaction between indium(I) iodide[9] (0.73 g, 3 mmol) and dimanganese decacarbonyl (1.17 g, 3 mmol). Anal. Calcd for $I_2C_{20}In_2Mn_4O_{20}$: C, 19.01. Found: C, 18.60.

Properties. Thermogravimetric measurements (Mettler thermoanalyzer, TA 1) of **1–3** were made under nitrogen atomosphere. The substances show in different temperature ranges (°C) (**1**, 216–252, 252–306; **2**, 217–254, 254–302; **3**, 152–272, 272–308) a two-step elimination of 10 carbonyl ligands.

Mass spectroscopic measurements (Varian CH 5) were carried out at 70 eV with vaporization of **1–3** at 200–250 °C. The spectra contain no molecular ion peak of **1–3**. Ions below that peak but with a higher molecular weight than that of the monomeric ion $XIn[Mn(CO)_5]_2^+$ (X = Cl, Br, I) had a relative abundance of about 1% with respect to In = 100%. The relative abundances of some other ions (%) are given in parentheses as follows: $InMn_2(CO)_{10}^+$ (**1**, 5; **2**, 1; **3**, 2); $XIn[Mn(CO)_5]_2^+$ (**1–3**, 1); $XInMn_2^+$ (**1**, 11; **2**, 9; **3**, 10); $XInMn(CO)_5^+$ (**1**, 22; **2**, 34; **3**, 35); XIn^+ (**1**, 46; **2**, 53; **3**, 99). The main fragmentations are of the type

$$XInMn_2(CO)_5^+ \xrightarrow{-nCO} XInMn_2(CO)_{5-n}^+ \quad (n = 0\text{-}5)$$

$$XInMn(CO)_5^+ \xrightarrow{-nCO} XInMn(CO)_{5-n}^+ \quad (n = 0\text{-}5)$$

$$Mn(CO)_5^+ \xrightarrow{-nCO} Mn(CO)_{5-n}^+ \quad (n = 0\text{-}5)$$

Osmometric measurements (osmometer, Fa. Knauer) of **1–3** were made in two selected aprotic solvents of different donor ability.[14]

Table II. Ir and Raman Spectroscopic Results of the Clusters $[(Mn(CO)_5)_2In(\mu\text{-}X)]_2$ [X = Cl (1), Br (2), I (3)] in the Range below 450 cm^{-1}

Assignment[a]	Symmetry	Method	Freq, cm^{-1} 1	2	3
ν_s(In-Mn)	A_g	Ra[b]	169 s	169 s	165 s
ν_{as}'(In-Mn)	B_{2g}	Ra[b]	185 m	186 m	184 m
ν_s'(In-Mn)	B_{3u}	Ir[c]	166 m	166 m	163 m
ν_{as}(In-Mn)	B_{1u}	Ir[c]	186 s	188 s	185 s
ν(In-X-In)	B_{1u} or B_{3u}	Ir[c]	193 vs	137 vs	118 vs
ν(ring)[d]		Ra[b]	126 m	108 m	103 m
e		Ra[b]	91 s	88 s	78 s
e		Ra[b]	59 m	59 m	58 m

[a] The metal-halogen skeletons of the samples **1–3** possess D_{2h} symmetry. Therefore two ir and two Raman ν(In-Mn) modes and two ir- and three Raman-active ν(ring) modes are possible.[13] [b] Raman spectroscopy. Pattern by crystal powder techniques and use of a rotating cell. [c] Ir spectroscopy (Perkin-Elmer 180 and FIS 3). Polyethylene techniques. [d] Tentative. [e] No assignment. Modes in the region of metal-metal deformation could not be separated.

Table III. Crystallographic Data for the Clusters $[(Mn(CO)_5)_2In(\mu\text{-}X)]_2$ (X = Cl (1), X = Br (2), X = I (3))

	1	2	3
Mol wt	1080.5	1169.4	1263.4
a, Å	10.622 (3)	10.634 (4)	10.649 (2)
b, Å	10.393 (3)	10.396 (8)	10.457 (2)
c, Å	8.722 (3)	8.823 (1)	9.073 (1)
α, deg	87.56 (2)	87.79 (2)	87.67 (1)
β, deg	95.59 (2)	95.33 (1)	95.07 (1)
γ, deg	124.58 (2)	124.32 (1)	123.79 (1)
Vol of molecule (=vol of cell), $Å^3$	788.89	801.98	836.36
Formula unit/cell	1	1	1
Density (obsd),[a] g cm^{-3}	1.97	2.31	2.31
Density (calcd), g cm^{-3}	2.27	2.42	2.51
Abs coeff for Mo Kα, cm^{-1}	33.1	57.27	48.35
F(000)	512	544	584
No. of reflections	4038	3707	3597
Dimensions of the crystals, mm			
[100]	0.257	0.311	0.206
[010]	0.216	0.250	0.183
[001]	0.429	0.240	0.280
Measurement range, deg	$2 \leq \vartheta \leq 30$	$2 \leq \vartheta \leq 30$	$2 \leq \vartheta \leq 28.1$
R values, %	5.6	3.9	4.4

[a] Pycnometer method.

Results in chloroform solution: calcd for **1**, 1080.5; found, 1098; calcd for **2**, 1169.4; found, 998; calcd for **3** 1263.4; found, 1000. Results in acetonitrile (stronger donor): calcd for $ClIn[Mn(CO)_5]_2$, 540.3;

Table IV. Positional Coordinates with Standard Deviations and Anisotropic Temperature Factors β_{ik}

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
				$[Mn(CO)_5]_4In_2(\mu\text{-}Cl)_2$					
In	0.000 53 (4)	−0.149 19 (4)	0.153 28 (4)	0.007 28 (5)	0.009 45 (6)	0.006 89 (5)	0.005 38 (4)	0.001 54 (4)	0.002 63 (4)
Cl	−0.044 16 (17)	−0.124 70 (16)	−0.144 91 (14)	0.011 60 (19)	0.009 41 (17)	0.005 78 (14)	0.006 48 (15)	0.000 67 (13)	0.000 93 (12)
Mn01	0.239 14 (9)	−0.163 88 (9)	0.239 29 (9)	0.007 72 (10)	0.008 68 (11)	0.005 40 (9)	0.005 75 (9)	0.000 79 (7)	0.001 22 (8)
Mn02	−0.279 59 (9)	−0.349 87 (9)	0.245 85 (9)	0.006 99 (10)	0.007 65 (10)	0.006 16 (10)	0.004 33 (8)	0.001 77 (7)	0.002 41 (8)
C01	0.397 03 (77)	−0.180 49 (84)	0.306 20 (73)	0.011 47 (84)	0.016 1 (10)	0.009 01 (76)	0.009 84 (82)	0.001 63 (65)	0.001 89 (71)
O01	0.495 02 (74)	−0.187 95 (88)	0.353 35 (74)	0.020 8 (11)	0.035 3 (15)	0.018 5 (10)	0.023 6 (12)	−0.001 53 (83)	0.001 25 (98)
C02	0.179 35 (76)	−0.183 50 (71)	0.436 52 (68)	0.012 23 (86)	0.010 51 (79)	0.008 18 (71)	0.007 23 (72)	0.001 30 (63)	0.001 28 (60)
O02	0.141 01 (78)	−0.198 57 (70)	0.556 21 (57)	0.026 6 (12)	0.021 06 (97)	0.008 82 (64)	0.014 56 (93)	0.006 34 (70)	0.002 83 (63)
C03	0.359 23 (74)	0.050 35 (71)	0.267 33 (67)	0.011 60 (84)	0.010 32 (82)	0.007 80 (70)	0.006 42 (72)	0.001 16 (61)	0.001 20 (60)
O03	0.439 20 (76)	0.180 09 (62)	0.290 42 (65)	0.020 9 (10)	0.012 31 (77)	0.014 54 (84)	0.006 07 (74)	0.000 65 (75)	−0.000 49 (63)
C04	0.278 51 (71)	−0.145 62 (69)	0.034 52 (67)	0.011 31 (79)	0.010 91 (77)	0.008 50 (72)	0.007 15 (68)	0.002 04 (61)	0.001 09 (59)
O04	0.306 53 (73)	−0.137 41 (71)	−0.089 98 (59)	0.021 1 (10)	0.021 8 (10)	0.010 03 (66)	0.011 12 (88)	0.006 20 (69)	0.001 76 (66)
C05	0.099 85 (72)	−0.376 45 (71)	0.204 42 (66)	0.012 14 (82)	0.011 06 (82)	0.007 99 (70)	0.007 86 (72)	0.002 28 (61)	0.001 17 (60)
O05	0.014 11 (69)	−0.506 07 (59)	0.186 21 (68)	0.018 35 (91)	0.011 73 (73)	0.017 16 (88)	0.006 84 (69)	0.001 51 (73)	−0.001 11 (64)
C06	−0.478 19 (69)	−0.477 88 (69)	0.297 90 (68)	0.008 82 (72)	0.009 65 (75)	0.008 54 (72)	0.004 52 (63)	0.001 63 (58)	0.002 61 (59)
O06	−0.599 57 (56)	−0.551 18 (64)	0.331 62 (65)	0.009 43 (64)	0.017 34 (85)	0.016 57 (84)	0.004 66 (62)	0.004 36 (60)	0.004 77 (69)
C07	−0.214 95 (76)	−0.449 92 (76)	0.375 73 (72)	0.011 63 (85)	0.012 09 (87)	0.009 48 (76)	0.007 60 (75)	0.003 54 (66)	0.003 90 (66)
O07	−0.176 85 (75)	−0.512 32 (70)	0.457 21 (69)	0.022 5 (11)	0.021 5 (10)	0.019 3 (10)	0.017 29 (93)	0.005 49 (82)	0.009 61 (83)
C08	−0.293 20 (73)	−0.467 89 (74)	0.084 29 (74)	0.009 70 (78)	0.010 84 (82)	0.010 05 (80)	0.005 14 (68)	0.001 06 (63)	0.000 63 (66)
O08	−0.298 51 (68)	−0.541 29 (66)	−0.012 56 (63)	0.018 48 (92)	0.017 76 (88)	0.014 00 (79)	0.009 70 (77)	0.000 72 (69)	−0.005 02 (68)
C09	−0.328 59 (69)	−0.238 78 (73)	0.114 06 (70)	0.008 72 (73)	0.011 36 (82)	0.009 03 (73)	0.005 33 (67)	0.002 18 (59)	0.003 29 (64)
O09	−0.363 07 (65)	−0.172 16 (68)	0.036 30 (64)	0.016 50 (85)	0.020 35 (94)	0.015 44 (83)	0.011 97 (79)	0.002 12 (67)	0.009 49 (71)
C10	−0.212 90 (65)	−0.200 86 (67)	0.397 35 (68)	0.008 63 (69)	0.010 15 (76)	0.009 27 (73)	0.005 80 (63)	0.002 03 (57)	0.002 45 (61)
O10	−0.174 11 (62)	−0.109 29 (60)	0.490 85 (60)	0.016 47 (80)	0.015 99 (80)	0.011 90 (68)	0.009 69 (69)	−0.000 47 (60)	−0.002 43 (60)
				$[Mn(CO)_5]_4In_2(\mu\text{-}Br)_2$					
In	−0.000 06 (4)	−0.153 61 (4)	0.156 77 (4)	0.006 86 (5)	0.008 77 (5)	0.007 38 (5)	0.004 83 (4)	0.001 49 (3)	0.002 65 (4)
Br	−0.045 88 (6)	−0.134 97 (6)	−0.154 20 (6)	0.010 70 (8)	0.008 71 (7)	0.006 36 (6)	0.005 58 (6)	0.000 63 (5)	0.000 97 (5)
Mn01	0.240 08 (9)	−0.165 02 (9)	0.240 61 (9)	0.007 47 (10)	0.008 44 (11)	0.005 88 (9)	0.005 49 (9)	0.000 82 (8)	0.001 36 (8)
Mn02	−0.280 05 (9)	−0.350 65 (9)	0.246 86 (9)	0.006 53 (10)	0.007 12 (10)	0.006 60 (10)	0.003 77 (8)	0.001 70 (8)	0.002 41 (8)
C01	0.398 38 (75)	−0.179 96 (82)	0.307 45 (73)	0.011 81 (91)	0.016 2 (11)	0.010 42 (85)	0.009 87 (88)	0.001 08 (71)	0.002 23 (77)
O01	0.497 84 (68)	−0.184 65 (82)	0.353 61 (68)	0.019 21 (97)	0.034 7 (14)	0.020 1 (10)	0.022 0 (11)	−0.001 23 (78)	0.001 62 (95)
C02	0.179 93 (72)	−0.184 69 (69)	0.435 59 (66)	0.012 06 (85)	0.010 19 (81)	0.008 57 (75)	0.007 05 (73)	0.001 36 (64)	0.001 29 (61)
O02	0.142 80 (73)	−0.199 91 (67)	0.554 49 (55)	0.028 8 (12)	0.022 2 (10)	0.010 06 (67)	0.017 34 (99)	0.006 98 (74)	0.003 90 (67)
C03	0.355 99 (71)	0.048 93 (72)	0.268 39 (66)	0.011 22 (85)	0.010 88 (88)	0.008 39 (73)	0.006 71 (75)	0.001 01 (63)	0.000 82 (63)
O03	0.432 72 (66)	0.178 24 (57)	0.287 61 (61)	0.019 16 (91)	0.010 83 (72)	0.016 48 (85)	0.005 31 (68)	0.000 64 (71)	−0.000 68 (61)
C04	0.280 95 (69)	−0.144 97 (69)	0.037 83 (66)	0.010 52 (80)	0.010 97 (82)	0 008 61 (75)	0.006 79 (71)	0.001 96 (61)	0.000 80 (62)
O04	0.309 17 (65)	−0.136 16 (66)	0.084 43 (54)	0.020 55 (95)	0.022 16 (98)	0.010 60 (68)	0.013 07 (85)	0.005 84 (65)	0.003 39 (66)
C05	0.101 88 (71)	0.376 27 (73)	0.205 58 (66)	0.011 44 (84)	0.011 28 (88)	0.008 81 (75)	0.007 71 (76)	0.001 73 (63)	0.000 89 (64)
O05	0.017 39 (63)	−0.506 06 (55)	0.185 57 (63)	0.018 33 (89)	0.011 13 (73)	0.018 92 (91)	0.006 50 (69)	0.002 59 (72)	−0.000 12 (65)
C06	−0.476 61 (67)	−0.475 71 (67)	0.299 12 (67)	0.009 27 (76)	0.009 52 (79)	0.009 25 (75)	0.004 59 (66)	0.002 17 (62)	0.002 91 (62)
O06	−0.598 40 (52)	−0.548 90 (60)	0.334 27 (60)	0.009 41 (63)	0.016 97 (82)	0.017 36 (83)	0.004 46 (61)	0.005 49 (57)	0.003 77 (67)
C07	−0.215 05 (75)	−0.449 45 (73)	0.375 36 (72)	0.012 14 (88)	0.011 27 (87)	0.011 07 (85)	0.007 26 (77)	0.004 18 (70)	0.004 96 (70)
O07	−0.177 05 (69)	−0.511 80 (67)	0.456 19 (62)	0.023 4 (11)	0.023 8 (11)	0.019 21 (95)	0.019 20 (96)	0.004 86 (78)	0.010 33 (82)
C08	−0.295 12 (70)	−0.469 16 (71)	0.087 91 (73)	0.009 49 (78)	0.009 91 (82)	0.010 70 (83)	0.004 39 (68)	0.001 69 (65)	0.001 06 (67)
O08	−0.302 58 (65)	−0.544 57 (62)	−0.007 56 (60)	0.019 45 (93)	0.016 94 (86)	0.014 03 (76)	0.009 78 (77)	0.001 49 (67)	−0.004 23 (67)
C09	−0.327 81 (63)	−0.240 55 (67)	0.116 48 (66)	0.007 82 (69)	0.009 62 (77)	0.008 95 (72)	0.004 19 (63)	0.002 02 (57)	0.002 75 (60)
O09	−0.362 66 (59)	−0.173 94 (61)	0.038 00 (59)	0.015 88 (80)	0.018 54 (88)	0.016 30 (81)	0.010 71 (73)	0.001 50 (64)	0.008 55 (69)
C10	−0.213 55 (62)	−0.199 98 (68)	0.393 91 (64)	0.007 61 (67)	0.010 61 (80)	0.008 19 (70)	0.005 62 (63)	0.001 51 (55)	0.002 58 (61)
O10	−0.174 74 (57)	−0.107 68 (57)	0.486 07 (53)	0.016 50 (79)	0.015 31 (77)	0.010 74 (63)	0.008 83 (68)	−0.000 52 (56)	−0.002 01 (57)

In	−0.000 66 (5)	−0.158 70 (5)	0.161 22 (4)	0.007 56 (5)	0.008 98 (6)	0.007 58 (5)	0.005 27 (5)	0.001 78 (4)	0.002 37 (4)
I	−0.047 84 (5)	−0.148 06 (4)	−0.163 20 (4)	0.010 95 (6)	0.008 71 (6)	0.006 36 (5)	0.005 83 (5)	0.000 90 (4)	0.000 66 (4)
Mn01	0.242 46 (11)	−0.165 26 (11)	0.242 50 (10)	0.008 60 (12)	0.009 71 (13)	0.006 63 (10)	0.006 69 (11)	0.001 35 (9)	0.001 52 (9)
Mn02	−0.279 86 (10)	−0.351 30 (10)	0.249 71 (10)	0.007 45 (11)	0.007 65 (11)	0.007 04 (11)	0.004 28 (10)	0.002 10 (8)	0.002 38 (9)
C01	0.400 72 (96)	−0.178 2 (10)	0.310 59 (89)	0.013 4 (11)	0.018 6 (14)	0.011 7 (10)	0.012 2 (11)	0.000 99 (83)	0.001 32 (91)
O01	0.500 53 (90)	−0.183 3 (11)	0.355 73 (87)	0.021 1 (13)	0.038 6 (19)	0.020 4 (12)	0.024 5 (14)	−0.001 68 (96)	0.000 6 (12)
C02	0.181 91 (94)	−0.186 28 (88)	0.430 10 (78)	0.016 2 (12)	0.013 3 (11)	0.009 34 (88)	0.010 82 (98)	0.002 90 (80)	0.001 82 (75)
O02	0.144 87 (99)	−0.201 06 (87)	0.548 03 (69)	0.032 8 (17)	0.024 2 (13)	0.011 61 (84)	0.019 7 (13)	0.008 37 (95)	0.004 05 (82)
C03	0.353 37 (81)	0.045 98 (86)	0.266 10 (74)	0.011 01 (94)	0.013 0 (11)	0.008 16 (79)	0.007 40 (86)	0.000 75 (66)	0.000 87 (70)
O03	0.425 88 (81)	0.175 54 (67)	0.282 44 (75)	0.018 6 (11)	0.011 30 (84)	0.017 20 (98)	0.005 92 (77)	−0.000 71 (80)	−0.000 79 (69)
C04	0.286 40 (81)	−0.144 27 (84)	0.046 17 (76)	0.010 96 (93)	0.013 0 (10)	0.009 49 (86)	0.008 10 (83)	0.002 82 (70)	0.001 63 (72)
O04	0.315 36 (79)	−0.134 94 (83)	−0.073 52 (65)	0.020 1 (11)	0.023 2 (12)	0.011 19 (77)	0.013 87 (98)	0.005 79 (73)	0.003 23 (73)
C05	0.106 84 (89)	−0.373 88 (86)	0.207 39 (81)	0.014 0 (11)	0.012 0 (10)	0.010 74 (90)	0.009 12 (92)	0.003 09 (78)	0.001 94 (75)
O05	0.023 43 (79)	−0.501 35 (64)	0.186 24 (80)	0.021 3 (12)	0.010 74 (85)	0.022 9 (12)	0.008 27 (86)	0.004 00 (97)	−0.000 27 (78)
C06	−0.473 76 (81)	−0.472 40 (79)	0.303 93 (81)	0.009 53 (87)	0.009 53 (88)	0.010 45 (86)	0.004 09 (73)	0.002 14 (70)	0.001 53 (69)
O06	−0.594 07 (65)	−0.543 05 (73)	0.341 00 (73)	0.009 94 (74)	0.017 13 (96)	0.017 57 (96)	0.003 06 (71)	0.005 80 (66)	0.001 87 (76)
C07	−0.212 34 (93)	−0.446 68 (89)	0.375 76 (86)	0.014 1 (11)	0.012 9 (11)	0.011 60 (96)	0.009 10 (94)	0.004 64 (82)	0.005 39 (81)
O07	−0.174 45 (92)	−0.508 58 (86)	0.454 75 (79)	0.026 5 (14)	0.024 5 (13)	0.019 7 (11)	0.019 8 (12)	0.004 24 (99)	0.010 71 (99)
C08	−0.296 75 (83)	−0.472 05 (82)	0.097 08 (84)	0.010 23 (92)	0.009 99 (91)	0.011 61 (95)	0.004 76 (77)	0.002 53 (73)	0.001 02 (74)
O08	−0.306 67 (82)	−0.546 89 (73)	0.003 00 (72)	0.021 2 (12)	0.015 61 (94)	0.015 18 (91)	0.008 51 (87)	0.002 72 (81)	−0.004 35 (75)
C09	−0.328 39 (73)	−0.242 79 (75)	0.120 45 (70)	0.008 55 (79)	0.009 89 (84)	0.007 91 (74)	0.004 77 (69)	0.001 66 (59)	0.001 76 (62)
O09	−0.363 04 (70)	−0.177 71 (71)	0.042 09 (67)	0.015 08 (87)	0.017 41 (94)	0.014 97 (85)	0.009 84 (78)	0.000 25 (68)	0.006 38 (72)
C10	−0.214 36 (72)	−0.201 50 (75)	0.391 69 (70)	0.008 40 (78)	0.010 14 (86)	0.007 84 (74)	0.005 42 (69)	0.001 71 (59)	0.002 52 (64)
O10	−0.177 55 (67)	−0.109 34 (67)	0.479 37 (58)	0.016 50 (90)	0.016 28 (89)	0.010 20 (68)	0.009 78 (77)	0.000 81 (62)	−0.000 74 (63)

found, 556; calcd for $BrIn[Mn(CO)_5]_2$, 584.7; found, 524; calcd for $IIn[Mn(CO)_5]_2$, 631.7; found, 604.

Spectra. Ir (Perkin-Elmer 180, FIS 3) and Raman (Coderg PHO, krypton laser, 6471 Å) spectroscopic data are given in Tables I and II. The vibrational assignments for the $Mn_2In_2(\mu\text{-}X)_2$ skeletons (X = Cl, Br, I) are made on the basis of a comparison with corresponding vibrations known from similar compounds.[11,12]

X-Ray Crystallography. Approximate cell parameters of **1**–**3** were determined by Weissenberg and Buerger precession methods and were refined with data from a Hilger and Watts automatic single-crystal diffractometer (λ(Mo Kα) 0.709 26 Å, graphite crystal monochromator). The accurate parameters for the triclinic crystal system of **1**–**3** along with other crystal data are presented in Table III.

The measurements of the intensities of the reflections were carried out with the same diffractometer. The measurement time for each reflection was 84 s. For the measurements crystals were selected with the following values (mm) along [100], [010], and [001]: **1**, 0.26 × 0.22 × 0.43; **2**, 0.31 × 0.25 × 0.24; **3**, 0.21 × 0.18 × 0.28. Independent reflections (4038 of **1**, 3707 of **2** in the range $2° \leq \vartheta \leq 30°$, and 3597 of **3** in the range $2° \leq \vartheta \leq 28.1°$) were collected. Those independent reflections had a line profile ($I \geq 3\sigma$) which is significantly higher than the background. During the data reduction Lorentz–polarization factors were applied; error limits were calculated according to the formula

$$\sigma(I) = [S + (T_p/2T_B)^2 B + (0.03(S - B))^2]^{1/2}$$

(S is the intensity of the reflection including the intensity of the background, T_p is the measuring time for the stepwise collection of intensity S of one reflection, T_B is the measuring time for one measurement of the background, and B is the total intensity of the background.)

The positional coordinates of two In atoms and two Cl or two Br atoms and four Mn atoms were determined from a three-dimensional Patterson map of **1** and **2**. A Fourier synthesis revealed the remaining atoms of **1** and **2**. The three compounds are isomorphous. Therefore it was possible to solve the structure of **3** with the positional coordinates of **1** or **2**. All structures were solved for the space group $P\bar{1}$ (No. 2).

The scale factor and the atomic coordinates were refined first isotropically and then anisotropically with the program ORFLS. The refinement of all atomic parameters were terminated when the calculated shifts with the program were lower than the errors of the refined parameters. During the refinement

$$D = \sum_{hkl} w(hkl)(|F_o| - |F_c|)^2$$

was minimized, where

$$w(hkl) = 4F_o(hkl)Lp^2/\sigma^2[I(hkl)]$$

(Lp is the Lorentz–polarization factor.) For the calculations of the structural parameters, the scattering factors of Cromer and Waber[15] were used. The refinements with all of the measured reflections ended in the case of the compounds **1**–**3** with the following nonweighted R values: **1**, 0.056; **2**, 0.039; **3**, 0.044.

All calculations for structure analysis were carried out with the IBM 370/158 computer at the University of Dortmund. For data reduction the program DATAPH of Neukäter and Biedl,[16] for refinement a modified version of the program ORFLS (full-coefficient matrix) of Busing, Martin and Levy,[17] for calculations of distances and angles and for calculations of planes the programs of Pippy and Ahmed[18] were used. The mapping of the structure of **1** was done with the program of Johnson[19] on a PDP 10 computer of the Max Planck Institut für Kohlenforschung, Mülheim/Ruhr.

Results

Clusters of the type $[(Mn(CO)_5)_2In(\mu\text{-}X)]_2$ (X = Cl (**1**), Br (**2**), I (**3**)) have the structure shown in Figure 1 (X = Cl). Their atomic position parameters and the anisotropic thermal parameters are listed in Table IV. Table V gives the intramolecular bond distances and some selected nonbonded lengths, and Table VI, the bond angles. The shortest nonbonding O···O contact lengths between CO groups are presented in Tables VII and VIII. Data related to planes with the corresponding equations of some mean planes (equations have the form $AX + BY + CZ = D$) fitted by a nonweighted least-squares procedure as well as the dihedral angles between

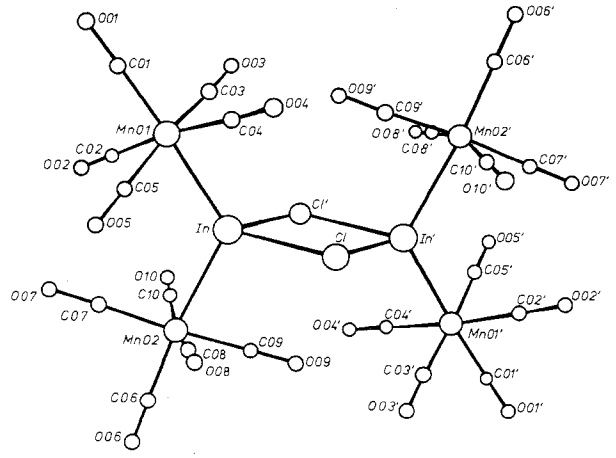

Figure 1. Molecular structure of the cluster $[(Mn(CO)_5)_2In(\mu\text{-}X)]_2$ (X = Cl, Br, I).

Table V. Intramolecular Bonded (–) and Selected Non-Bonded (· · ·) Atomic Distances (Å) of the Clusters **1–3** with Standard Deviations

	1	2	3
In-X	2.626 (1)	2.760 (1)	2.950 (1)
In-X'	2.610 (2)	2.754 (1)	2.952 (1)
Av In-X	2.618 (2)	2.757 (1)	2.951 (1)
In· · ·In'	4.012 (1)	4.143 (1)	4.329 (1)
X· · ·X'	3.365 (2)	3.639 (1)	4.012 (1)
In-Mn01	2.659 (1)	2.658 (1)	2.666 (1)
In-Mn02	2.671 (1)	2.670 (1)	2.678 (1)
Av In-Mn	2.665 (1)	2.664 (1)	2.672 (1)
Mn01-C01	1.820 (9)	1.819 (9)	1.817 (12)
Mn01-C02	1.855 (7)	1.855 (6)	1.835 (8)
Mn01-C03	1.845 (6)	1.850 (6)	1.847 (8)
Mn01-C04	1.851 (6)	1.857 (6)	1.855 (7)
Mn01-C05	1.850 (6)	1.846 (6)	1.849 (8)
Mn02-C06	1.837 (8)	1.828 (7)	1.825 (9)
Mn02-C07	1.842 (8)	1.839 (8)	1.838 (9)
Mn02-C08	1.849 (7)	1.838 (7)	1.841 (8)
Mn02-C09	1.838 (7)	1.827 (7)	1.835 (7)
Mn02-C10	1.842 (6)	1.837 (6)	1.841 (7)
Av Mn-C	1.843 (7)	1.840 (7)	1.838 (8)
C01-O01	1.124 (13)	1.124 (12)	1.133 (16)
C02-O02	1.130 (9)	1.129 (8)	1.148 (11)
C03-O03	1.127 (8)	1.121 (8)	1.134 (10)
C04-O04	1.141 (8)	1.133 (8)	1.141 (10)
C05-O05	1.126 (8)	1.132 (8)	1.130 (9)
C06-O06	1.126 (10)	1.139 (10)	1.142 (12)
C07-O07	1.137 (11)	1.139 (10)	1.139 (13)
C08-O08	1.138 (9)	1.140 (9)	1.139 (11)
C09-O09	1.128 (10)	1.141 (9)	1.139 (10)
C10-O10	1.138 (8)	1.142 (8)	1.141 (9)
Av C-O	1.132 (9)	1.134 (9)	1.139 (11)

different planes are given in Table IX.

The packing of the molecules **1–3** is presented by a stereoscopic drawing of **1** (Figure 2).

Discussion

General description. The crystals of the three clusters of the type $[(Mn(CO)_5)_2In(\mu\text{-}X)]_2$ (X = Cl, Br, I) are isomorphous. Their molecular structure is shown in Figure 1 for X = Cl. The molecule has a center of symmetry, which relates atoms with primed and unprimed labels. The four-membered In_2X_2 rings are therefore previously planar. The dihedral angles of some planes are given in Table IX. The values 90.8° (X = Cl), 91.0° (X = Br), and 91.1° (X = I) were found between the In_2X_2 plane and the plane with the atoms Mn01–Mn02–Mn01'–Mn02'. These corresponding dihedral angles of the cluster agree with D_{2h} symmetry of the metal–halogen skeleton of the three clusters. The dihedral angles

Table VI. Bond Angles (deg) of the Clusters **1–3** with Standard Deviations

	1	2	3
In-X-In'	100.02 (5)	97.42 (2)	94.35 (2)
X-In-X'	79.98 (5)	82.58 (2)	85.65 (2)
Mn01-In-Mn02	123.59 (3)	124.97 (3)	126.37 (4)
X-In-Mn01			
X-In-Mn01	114.53 (4)	113.33 (3)	111.96 (3)
X'-In-Mn01	118.33 (4)	117.27 (3)	115.68 (3)
Average	116.43 (4)	115.30 (3)	113.82 (3)
X-In-Mn02			
X-In-Mn02	105.10 (4)	104.66 (3)	104.41 (3)
X'-In-Mn02	106.43 (4)	105.51 (3)	104.86 (3)
Average	105.77 (4)	105.09 (3)	104.64 (3)
In-Mn-C_{ax}			
In-Mn01-C01	177.04 (25)	176.58 (25)	175.50 (31)
In-Mn02-C06	174.56 (22)	175.08 (22)	175.61 (26)
Average	175.80 (24)	175.83 (23)	175.56 (29)
In-Mn-C_{eq}			
In-Mn01-C02	84.81 (22)	84.61 (22)	84.53 (28)
In-Mn01-C03	88.83 (22)	88.42 (22)	88.46 (26)
In-Mn01-C04	88.63 (22)	88.83 (21)	89.69 (26)
In-Mn01-C05	84.44 (22)	83.64 (22)	82.59 (27)
In-Mn02-C07	92.74 (24)	91.90 (23)	90.80 (29)
In-Mn02-C08	81.78 (23)	82.15 (22)	82.99 (26)
In-Mn02-C09	82.93 (22)	83.33 (21)	83.79 (23)
In-Mn02-C10	83.54 (21)	83.15 (20)	83.15 (23)
Average	85.96 (22)	85.75 (22)	85.75 (26)
Mn-C_{ax}-O_{ax}			
Mn01-C01-O01	177.05 (76)	177.00 (74)	178.16 (94)
Mn02-C06-O06	177.23 (64)	177.41 (62)	177.15 (75)
Average	177.14 (70)	177.21 (68)	177.66 (85)
Mn-C_{eq}-O_{eq}			
Mn01-C02-O02	178.64 (69)	178.43 (66)	178.83 (84)
Mn01-C03-O03	175.47 (68)	176.32 (66)	177.51 (77)
Mn01-C04-O04	176.79 (66)	176.83 (64)	177.38 (77)
Mn01-C05-O05	178.55 (66)	179.32 (65)	179.68 (80)
Mn02-C07-O07	178.95 (71)	178.82 (69)	178.15 (86)
Mn02-C08-O08	177.89 (68)	177.83 (66)	179.66 (78)
Mn02-C09-O09	177.44 (67)	177.29 (61)	177.74 (70)
Mn02-C10-O10	178.85 (62)	178.81 (60)	178.16 (68)
Average	177.82 (67)	177.96 (65)	178.39 (78)
C_{ax}-Mn-C_{eq}			
C01-Mn01-C02	92.66 (33)	92.40 (33)	91.40 (42)
C06-Mn02-C07	92.69 (32)	92.98 (31)	93.41 (38)
C01-Mn01-C03	92.66 (33)	93.16 (33)	93.42 (40)
C01-Mn01-C04	93.87 (33)	94.15 (32)	94.37 (40)
C01-Mn01-C05	94.06 (33)	94.76 (33)	95.57 (41)
C06-Mn02-C08	98.60 (31)	98.49 (31)	98.32 (37)
C06-Mn02-C09	91.64 (31)	91.78 (30)	91.99 (35)
C06-Mn02-C10	96.28 (30)	96.29 (29)	95.64 (34)
Average	94.06 (32)	94.25 (32)	94.27 (38)
C_{eq}-Mn-C_{eq}			
C02-Mn01-C03	88.84 (32)	88.56 (31)	89.33 (38)
C03-Mn01-C04	91.71 (31)	91.43 (31)	90.73 (36)
C04-Mn01-C05	88.17 (31)	88.59 (31)	88.37 (37)
C05-Mn01-C02	90.51 (31)	90.52 (31)	90.66 (39)
C07-Mn02-C08	88.55 (33)	88.97 (32)	89.06 (39)
C08-Mn02-C09	91.45 (32)	90.94 (30)	90.86 (35)
C09-Mn02-C10	89.51 (30)	89.01 (29)	89.46 (33)
C10-Mn02-C07	89.37 (31)	89.84 (31)	89.30 (37)
Average	89.76 (31)	89.73 (31)	89.72 (37)

Table VII. Intramolecular Nonbonded O· · ·O Lengths (Å) of the Clusters **1–3** with Standard Deviations

	1	2	3
O03-O09' or O03'-O09	2.877 (8)	2.896 (8)	2.963 (9)
O04-O09' or O04'-O09	2.968 (9)	2.979 (8)	3.038 (10)
O02-O07 or O02'-O07'	3.155 (10)	3.173 (9)	3.189 (12)
O05-O07 or O05'-O07'	3.237 (10)	3.278 (10)	3.331 (12)

of each cluster between the Mn01–Mn02–Mn01'–Mn02' plane and the plane with axial C atoms C01–C06–C01'–C06' (X = Cl, 0.42°; X = Br, 0.25°; X = I, 0.18°) as well as with the

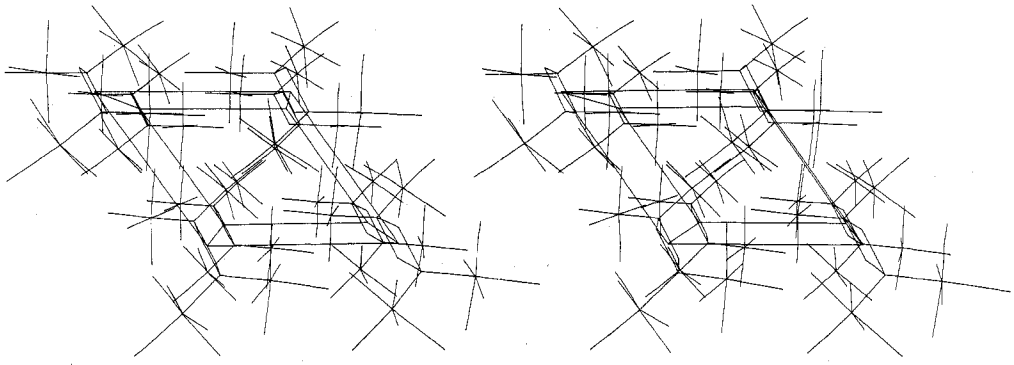

Figure 2. Stereoscopic view of the packing of the molecules $[(Mn(CO)_5)_2In(\mu\text{-}Cl)]_2$ in the crystal.

Table VIII. Intermolecular Nonbonded O···O Lengths (Å) of the Clusters **1-3** with Standard Deviations

	1	2	3
O03–O06 or O03′–O06	3.085 (9)	3.082 (9)	3.135 (10)
O08–O09′ or O08′–O09	3.097 (10)	3.073 (9)	3.067 (11)
O02–O10′ or O02′–O10	3.028 (9)	3.030 (9)	3.068 (11)
O10–O10′	3.041 (10)	3.062 (9)	3.142 (10)

plane with the atoms O01–O06–O01′–O06′ (X = Cl, 0.29°; X = Br, 0.44°; X = I, 0.77°) show that these atoms are fairly close to being in one plane.

The equatorial CO groups of a $Mn(CO)_5$ ligand are orientated in such a way that the CO groups of neighboring ligands are staggered and the steric hinderance is minimized (Figure 1). In comparison with other clusters[19,20] with $Mn(CO)_5$ ligands, some of the observed intra- and intermolecular nonbonding O···O contact lengths (Table VII and XIII) are rather short. For each cluster the shortest intramolecular O···O contact lengths (Table VII) between the equatorial CO groups of the atoms Mn01 and Mn02′ (or Mn01′ and Mn02) are as follows: for O03–O09′ or O03′–O09, X = Cl, 2.877 (8) Å; X = Br, 2.896 (8) Å; X = I, 2.963 (9) Å; for O04–O09′ or O04′–O09, X = Cl, 2.968 (9) Å; X = Br, 2.979 (8) Å; X = I, 3.038 (10) Å. The other intramolecular O···O contact lengths between the equatorial CO groups attached to Mn01 and Mn02 (or Mn01′ and Mn02′) are not below 3 Å; for O02–O07 or O02′–O07′, X = Cl, 3.155 (10) Å; X = Br, 3.173 (9) Å; X = I, 3.189 (12) Å; for O05–O07 or O05′–O07′, X = Cl, 3.237 (10) Å; X = Br, 3.278 (10) Å; X = I, 3.331 (12) Å; these values are in a range close to the shortest intermolecular nonbonding O···O contact lengths (Table VIII) of O03–O06 or O03′–O06′ (X = Cl, 3.085 (9) Å; X = Br, 3.082 (9) Å; X = I, 3.135 (10) Å). The influence of the nonbonding interaction between the CO groups is taken into account in the discussion of the molecular fragments of these clusters.

The Indium Coordination Polyhedron. This polyhedron is a distorted tetrahedron formed by ligand atoms around each In atom in the clusters of the type $[(Mn(CO)_5)_2In(\mu\text{-}X)]_2$ (X = Cl, Br, I). Compared to the ideal tetrahedral angle the Mn–In–Mn angles [X = Cl, 123.59 (3)°; X = Br, 124.97 (3)°; X = I, 126.37 (4)°] are enlarged and the X–In–X′ angles [X′ = X: X = Cl, 79.98 (5)°; X = Br, 82.58 (2)°; X = I, 85.65 (2)°] are reduced. Considering the corresponding angles of $[I_2In(\mu\text{-}I)]_2$[3] (I–In–I = 125.1°; (μ-I)–In–(μ-I) = 93.7°) the first terminal angle at In is in good agreement with the found Mn–In–Mn angles but the angle with the bridging atoms has changed from an obtuse (μ-I)–In–(μ-I) angle of 93.7° to an acute (μ-I)–In–(μ-I) angle of 85.65 (2)° in the cluster $[(Mn(CO)_5)_2In(\mu\text{-}I)]_2$.

The Mn–In–Mn angle in the three clusters is remarkably unchanged compared with the corresponding angles in similar clusters $[Br_2InCo_2(CO)_8]^-$ (Co–In–Co = 124.3°)[21] and $X_2Sn[Mn(CO)_5]_2$ (X = Cl, Mn–Sn–Mn = 126.25°; X = Br, Mn–Sn–Mn = 125.88°).[22] Therefore only a small change of the M′–M–M′ angles (M′ = Mn, Co; M = In, Sn) exists in

Table IX. Equation of Plane for the Clusters **1-3** and Corresponding Dihedral Angles[a]

	Plane no.	Through the Atoms	Equation of plane
1	1	In, Cl, In′, Cl′	$0.8964X + 0.4351Y - 0.0843Z = 0$
1	2	Mn01, Mn02, Mn01′, Mn02′	$0.2120X - 0.6156Y - 0.7590Z = 0$
1	3	C01, C06, C01′, C06′	$0.2132X - 0.6098Y - 0.7633Z = 0$
1	4	O01, O06, O01′, O06′	$0.2170X - 0.6152Y - 0.7580Z = 0$
2	1	In, Br, In′, Br′	$0.8974X + 0.4341Y - 0.0792Z = 0$
2	2	Mn01, Mn02, Mn01′, Mn02′	$0.2124X - 0.6187Y - 0.7564Z = 0$
2	3	C01, C06, C01′, C06′	$0.2139X - 0.6154Y - 0.7587Z = 0$
2	4	O01, O06, O01′, O06′	$0.2179X - 0.6219Y - 0.7521Z = 0$
3	1	In, I, In′, I′	$0.9002X + 0.4290Y - 0.0752Z = 0$
3	2	Mn01, Mn02, Mn01′, Mn02′	$0.2161X - 0.6295Y - 0.7464Z = 0$
3	3	C01, C06, C01′, C06′	$0.2182X - 0.6308Y - 0.7446Z = 0$
3	4	O01, O06, O01′, O06′	$0.2194X - 0.6389Y - 0.7373Z = 0$

		Angle, deg		
Plane no.	Plane no.	1	2	3
1	2	90.789	91.035	91.115
1	3	90.566	90.870	91.047
1	4	90.530	90.853	91.218
2	3	0.415	0.245	0.178
2	4	0.293	0.441	0.774
3	4	0.484	0.580	0.633

[a] Distances of the given atoms from the planes 0.0 Å; $\chi^2 = 0.0$.

Table X. Comparison of the Structural Parameters in X-Bridged Compounds with Tetrahedral Coordinated M Atoms (M = Al, Ga, In; X = Cl, Br, I)

Compd	M-X, Å	M···M, Å	X···X, Å	M-X-M, deg	X-M-X, deg	L-M-L,[a] deg	Ref
$[(CH_3)_2Al(\mu\text{-}Cl)]_2$	2.303	3.274	3.241	89.4	90.6	126.9	26
$[(CH_3)AlCl(\mu\text{-}Cl)]_2$	2.26	3.21	3.15	91	89	124.5	27
$[Br_2Al(\mu\text{-}Br)]_2$	2.38	3.14	3.59	82	98		28
$[Cl_2Ga(\mu\text{-}Cl)]_2$	2.29	3.12	3.35	86	94	123	29
$[I_2In(\mu\text{-}I)]_2$	2.84	3.88	4.14	86	94	125.1	3
$[(Mn(CO)_5)_2In(\mu\text{-}Cl)]_2$	2.618	4.012	3.365	100.02	79.98	123.59	*b*
$[(Mn(CO)_5)_2In(\mu\text{-}Br)]_2$	2.757	4.143	3.639	97.42	82.58	124.97	*b*
$[(Mn(CO)_5)_2In(\mu\text{-}I)]_2$	2.951	4.329	4.012	94.35	85.65	126.37	*b*

[a] L = terminal ligand. [b] This work.

the present case of two transition metal carbonyl ligands and two X ligand atoms attached to different main group metals M with an isoelectronic valence shell, and this seems to be nearly independent of the different ligand functions of the X atoms with respect to the main group metal M. The In-Mn01 distances are 2.659 (1), 2.658 (1), and 2.666 (1) Å; the In-Mn02 distances are 2.671 (1), 2.670 (1), and 2.678 (1) Å for the clusters with X = Cl, Br, and I, respectively. The In-Mn02 distances are 0.012 (1) Å longer than the In-Mn01 distances. The average values of the In-Mn bond distances in these clusters (X = Cl, 2.665 (1) Å; X = Br, 2.664 (1) Å; X = I, 2.672 (1) Å) show only small differences. These In-Mn distances (In atom coordination number 4) are longer than the corresponding In-$Mn(CO)_5$ distance of 2.596 (1) Å in the cluster $Mn_2(CO)_8[\mu\text{-}InMn(CO)_5]_2$[8] (In atom, coordination number 3) with change of the formal valence-shell occupation at In from $5s^25p^4$ to $5s^25p^6$. Previous In-$Mn(CO)_5$ bond distances were found in the range of 2.678 (X = I) to 2.596 Å ($Mn_2(CO)_8[\mu\text{-}InMn(CO)_5]_2$). They are about 2.61 Å, which is the sum of covalent single-bond radii of In (1.44 Å) and Mn (1.17 Å) supposed by Pauling. Therefore the observed In-Mn distances indicate σ bonds; a corresponding explanation was given for the In-Co bonds in the clusters $[N(C_2H_5)_4][Br_2InCo_2(CO)_8]$,[21] $In_3Br_3Co_4(CO)_{15}$,[23] and $In[Co(CO)_4]_3$.[24]

The Four-Membered In_2X_2 Rings. The centrosymmetric In_2X_2 rings form the central molecular fragment in the clusters of the type $[(Mn(CO)_5)_2In(\mu\text{-}X)]_2$ (X = Cl, Br, I). Regarding the values of the angles, In-X-In′ [X = Cl, 100.02 (5)°; X = Br, 97.42 (2)°; X = I, 94.35 (2)°] is enlarged above 90° whereas X-In-X′ [X = Cl, 79.98 (5)°; X = Br, 82.58 (2)°; X = I, 85.65 (2)°] is smaller than 90°. Contrary to that the M-X-M angle is obtuse in most other known similar compounds of M = Al, Ga, and In of the type $[L_2M(\mu\text{-}X)]_2$ (L = ligand, X = Cl, Br, I; Table X), which have two halogeno bridges with a tetrahedral coordinated M atom and no transition metal carbonyl as ligand L. If L becomes a steric expansive ligand as $Mn(CO)_5$ instead of I, the extent of the variation of the In_2I_2 ring angles from $[I_2In(\mu\text{-}I)]_2$ [In-(μ-I)-In = 86.3° and (μ-I)-In-(μ-I) = 93.7°] to $[(Mn(CO)_5)_2In(\mu\text{-}I)]_2$ [In-(μ-I)-In = 94.35° and (μ-I)-In-(μ-I) = 85.65°] is very large [ΔIn-(μ-I)-In = Δ(μ-I)-In-(μ-I) = 8.05°]. The L-In-L angles (L = I or $Mn(CO)_5$) reflect a nearly complete insensitivity with this variation of L (ΔL-In-L = 1.27°). Such unchanged L-In-L angles can be considered as a typical property with respect to the small change of known L-M-L angles in compounds of the type $[L_2M(\mu\text{-}X)]_2$ (Table X). Therefore the observed behavior of the L-In-L angles supports the assumption that, in general, little variation is to be expected with different ligand types L.

The change of the (μ-I)-In-(μ-I) and In-(μ-I)-In angles is not primarily due to different electronic bond factors of the terminal ligands attached to the In atoms but to some other effect, which leads to an explanation of the obtained direction of their change. The strikingly close approach of equatorial CO groups to different Mn atoms in their energetically favored staggered position and the large variations of the C(equatorial)-Mn-In angles (see later; Table VI) indicate that the effect is due to repulsions. If the repulsion is indicated by intramolecular nonbonding O···O contact lengths between these CO groups (Table VII), it is much stronger for the CO groups (no. 03-09′ or 03′-09; 04-09′ or 04′-09) above and below the In_2I_2 plane than between the CO groups (no. 02-07 or 02′-07′; 05-07 or 05′-07′) on the left and the right sides of the cluster (Figure 1). Because of the already mentioned rigidity of the Mn-In-Mn angles the shortest present O···O contacts above and below the In_2I_2 plane cannot be enlarged by a scissorlike movement of the Mn atoms (no. 01-02 or 01′-02′) to diminish the O···O repulsion. Therefore the equatorial CO groups above and below the In_2I_2 plane try to reduce the repulsions shown by the present O···O contact lengths by influencing the structural parameters of the In_2I_2 ring. A reduction of the repulsions implies an enlargement of the In-(μ-I)-In angle and a reduction of the (μ-I)-In-(μ-I) angle against the corresponding structural parameters in the In_2I_2 ring of $[I_2In(\mu\text{-}I)]_2$, which exhibits no comparable compulsion by I as terminal ligand. Furthermore an enlargement of the In-(μ-I) bond distance cannot be excluded. So the observed change of the In_2I_2 ring angles of the cluster follows a reduction of the repulsion between the equatorial CO ligands above and below the In_2I_2 plane. Therefore the repulsion between these CO groups is the main factor influencing the structural parameters of the In_2I_2 ring and gives the explanation of the observed direction of the change in the In_2I_2 ring angles from $[I_2In(\mu\text{-}I)]_2$ to $[(Mn(CO)_5)_2In(\mu\text{-}I)]_2$.

The same comparison is not possible for the In_2X_2 rings of the compounds $[X_2In(\mu\text{-}X)]_2$ (X = Cl, Br) because their x-ray structure analyses are not yet available.

If the In_2X_2 ring angles of the three clusters are compared with one another, they should show an increase of the In-(μ-X)-In and a decrease of the (μ-X)-In-(μ-X) angle with the decreasing atomic size of X. Such a reduction of the atomic size of X causes a stronger repulsion between the equatorial CO groups (no. 03-09′ or 03′-09; 04-09′ or 04′-09) above and below the In_2X_2 ring. To reduce this repulsion the In_2X_2 ring angles change in the observed manner.

The In-X and In-X′ distances of each of the three examined In_2X_2 rings differ only a little in the case of X = Cl or Br and they are not significantly different for X = I (Table V). The In-X distances agree with the concept of a symmetrical halogeno bridging bond MX_2M, which is described by a MO treatment elsewhere.[6] The following average In-X distances correspond to the clusters: In-Cl = 2.618 (2) Å, In-Br = 2.757 (1) Å, and In-I = 2.951 (1) Å. The In-I distance has a larger value than the corresponding value of In-I = 2.84 Å in $[I_2In(\mu\text{-}I)]_2$.[3] The reason for the enlargement of the In-I distance (ΔIn-I = 0.111 Å) may be the order of decrease in electronegativity of the terminal ligands $\varkappa_I > \varkappa_{Mn}$ and the described repulsion effect (see later). If the already mentioned average In-X distances (InX_{obsd}) of the clusters are compared with the sum of the covalent single-bond radii of In and X of Pauling (InX_{calcd}: InCl = 2.43 Å, InBr = 2.58 Å, InI = 2.77

Å), an enlargement ($InX_{obsd} - InX_{calcd} = \Delta InX$ ($\Delta InCl$ = 0.188 Å, $\Delta InBr$ = 0.177 Å, ΔInI = 0.181 Å)) of the InX_{osbd} distances against the corresponding InX_{calcd} distances from the single-bond radii is evident. The enlargement has the order $\Delta InCl > \Delta InBr < \Delta InI$. If the series of ΔInX values would follow the order of the electronegativity differences ($\varkappa_X - \varkappa_{In} = \Delta\varkappa_{InX}$) $\Delta\varkappa_{InCl} > \Delta\varkappa_{InBr} > \Delta\varkappa_{InI}$,[25] then the expected order ought to be $\Delta InCl < \Delta InBr < \Delta InI$; a greater value $\Delta\varkappa_{InX}$ would cause a smaller enlargement ΔInX. This is observed only in the series $\Delta InBr < \Delta InI$, whereas the actually observed order in the case of the series $\Delta InCl > \Delta InBr$ does not agree with this model. Therefore it is at least for the chlorine-bridged cluster reasonable to take into account a weakening of the In–Cl–In bridging bond caused by an intramolecular repulsion effect between the terminal ligands.

The nonbonding structural parameters of the In_2X_2 rings (In···In, X···X) show with respect to the increasing atomic size of the μ-X atom in the three clusters an increase of the In···In and X···X lengths (Tables V and X). The nonbonding lengths In···In′ = 4.329 Å and I···I′ = 4.012 Å of $[(Mn(CO)_5)_2In(\mu\text{-}I)]_2$ support also the described repulsion effect, because each length between these atoms is significantly longer (ΔIn···In = 0.449 Å) or shorter (ΔI···I = 0.128 Å) in comparison with those parameters known from $[I_2In(\mu\text{-}I)]_2$,[3] which does not exhibit such a strong repulsion of its terminal I ligands. Furthermore the described accommodation of the I···I and In···In nonbonding lengths under the mentioned repulsion indicates that the deciding factors influencing the structural parameters of such In_2X_2 rings in the clusters of the type $[(Mn(CO)_5)_2In(\mu\text{-}X)]_2$ (X = Cl, Br, I) are not to be seen in the repulsion between the highly electronegative μ-X atoms.

The examination of In_2X_2 rings will be continued with the x-ray analyses of the clusters $[(Re(CO)_5)_2In(\mu\text{-}X)]_2$ (X = Cl, Br, I).

The Manganese Polyhedron. The coordination polyhedron around each Mn atom in the three clusters is a distorted octahedron (Figure 1). As mentioned above the shortest intramolecular nonbonding O···O contact lengths are in general relatively shorter than the known corresponding contact lengths from other clusters with $Mn(CO)_5$ ligands.[20,27] The observed C(equatorial)–Mn–In angles (Table VI) show the largest variation for the smallest bridging atom Cl, with the values 81.78 and 92.74°, and the difference between such extreme values decreases (X = Cl, 10.96°; Br, 9.75°; I, 7.81°) with an increase of the atomic size of the μ-X atom for the corresponding angles of the clusters. Besides packing forces, mainly the intramolecular repulsion between the equatorial CO ligands of different Mn atoms in the neighborhood seems to be responsible for the large change in these angles. The average value of this angle of each cluster (umbrella effect) is nearly equal: 85.96 (22)° (X = Cl), 85.75 (22)° (X = Br), and 85.75 (26)° (X = I). Furthermore these values show only a little difference against the value of the corresponding angle in the clusters $Mn_2(CO)_8[\mu\text{-}InMn(CO)_5]_2$[8] (85.4°) and $X_2Sn[Mn(CO)_5]_2$[22] (X = Cl = Br, 86.9°).

The average Mn–C distances are 1.843 (7) Å (X = Cl), 1.840 (7) Å (X = Br), and 1.838 (8) Å (X = I). The magnitude of these Mn–C distances as well as the average C–O bond distance of the three clusters (Table V, C–O = 1.135 (10) Å) agrees with those of corresponding bond distances known from the $Mn(CO)_5$ ligands in other compounds.[8,20,22]

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Registry No. **1**, 36501-37-8; **2**, 36491-06-2; **3**, 60224-28-4; dimanganese decacarbonyl, 10170-69-1; indium(I) chloride, 13465-10-6; indium(I) bromide, 14280-53-6; indium(I) iodide, 13966-94-4.

Supplementary Material Available: Listings of structure factor amplitudes (54 pages). Ordering information is given on any current masthead page.

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