References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A. & Polidori, G. (1994). *J. Appl. Cryst.* **27**, 435.

Enraf–Nonius (1988). *CAD-4 VAX/PC Fortran System. Operator's Guide to the Enraf–Nonius CAD-4 Diffractometer Hardware, its Software and the Operating System.* Enraf–Nonius, Delft, The Netherlands.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Lockhart, T. P., Calabrese, J. C. & Davidson, F. (1987). *Organometallics*, **6**, 2479–2483.

Ng, S. W. (1996). *Main Group Met. Chem.* **19**, 113–120.

Ng, S. W., Chen, W., Kumar Das, V. G. & Mak, T. C. W. (1987). *J. Organomet. Chem.* **334**, 295–305.

Ng, S. W. & Kumar Das, V. G. (1995). *Main Group Met. Chem.* **18**, 309–314.

Ng, S. W., Kumar Das, V. G., Gielen, M. & Tiekink, E. R. T. (1992). *Appl. Organomet. Chem.* **6**, 19–25.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1990). *SHELXTL/PC Users Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Spek, A. L. (1994). *PLUTON. Molecular Graphics Program.* University of Utrecht, The Netherlands.

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Solvate-Dependent Polymorphism: Crystallization of $[\{Mn(CO)_3\}_2\{\mu\text{-}(\eta^5\text{-}C_6H_6\text{-}\eta^5\text{-}C_6H_6)\}]$ from CH_2Cl_2 as a Mono-Solvate in the Rare Tetragonal Space Group $P4_2/mbc$

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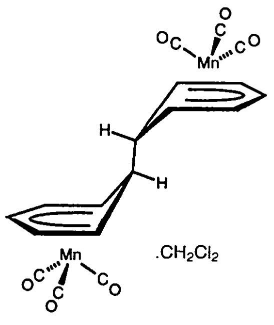
Abstract

Recrystallization from methylene chloride gives a tetragonal pseudo-polymorph of (μ-η^5:η^5-bicyclohexadienyl)bis(tricarbonylmanganese), $[Mn_2(C_{12}H_{12})(CO)_6].CH_2Cl_2$, in the rare space group $P4_2/mbc$. Molecules in these crystals and in the monoclinic unsolvated form are virtually superimposable, and it is the inclusion of the methylene chloride solvate molecule which allows for crystallization in $P4_2/mbc$. The Mn dimers are packed in layers with fourfold symmetry, with disordered methylene chloride molecules filling interstices between the layers.

Comment

There is considerable current interest in the controlled engineering of crystals using the forces commonly found in the crystalline environment which determine crystal-packing arrangements (Desiraju, 1989). Insight into such forces can be obtained from studies of systems in which changes in crystallization conditions such as temperature, solvent, counterion and concentration, cause a given compound to crystallize in two or more different polymorphs or pseudo-polymorphs (Dunitz & Bernstein, 1995; Gavezzotti, 1994), but the factors controlling the choice of form adopted by a particular compound under such varying conditions are still not properly understood. We now report an example of a molecular system in which a change of the recrystallization medium from toluene to dichloromethane results in formation of a solvate, (1), which allows the solvent molecule to occupy a niche in the lattice resulting in high packing symmetry of the molecular unit in the unusual $P4_2/mbc$ space group; only 13 other molecular and coordination compounds have been reported to crystallize in this space group to date (April 1996 version of the Cambridge Structural Database; Allen & Kennard, 1993).



(1)

The molecular unit of (1) is a dimer, $[\{Mn(CO)_3\}_2\{\mu\text{-}(\eta^5\text{-}C_6H_6\text{-}\eta^5\text{-}C_6H_6)\}]$, comprising two tricarbonylmanganese fragments connected by a bicyclohexadienyl ligand in which two benzene-derived six-membered rings are connected by a C—C single bond. This molecule can be prepared by reductive dimerization of the η^6-benzene complex $[Mn(\eta^6\text{-}C_6H_6)(CO)_3]^+$ with a single equivalent of the naphthalenide anion; the cation undergoes two-electron reduction to form the η^4-benzene complex $[Mn(\eta^4\text{-}C_6H_6)(CO)_3]^-$, and if the reductant is added slowly, the cation adds to the anion as it is formed to give (1). Unsolvated (1) crystallizes from toluene in the monoclinic space group $C2/c$, with $Z = 4$ and the dimer on a crystallographic twofold axis; we have reported previously the molecular structure of such a crystal (Lee *et al.*, 1996).

Recrystallization of (1) from methylene chloride gives a methylene chloride-solvated pseudo-polymorph of (1) in the tetragonal space group $P4_2/mbc$ (No. 135). A

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molecule of the dimer (Fig. 1) resides on a 2/*m* site of symmetry at $(0,0,\frac{1}{2})$, with a twofold axis bisecting the C(3)—C(3*A*) bond perpendicularly. A mirror plane, perpendicular to the twofold axis, contains the Mn, C(3), C(6), C(2) and O(2) atoms. The solvate contains a single molecule of methylene chloride per dimer unit, which resides on a 222 site at $(0,0,\frac{1}{4})$. This solvent molecule exhibits disorder which has been modeled with two orientations such that the Cl atoms are fully occupied and shared by both orientations.

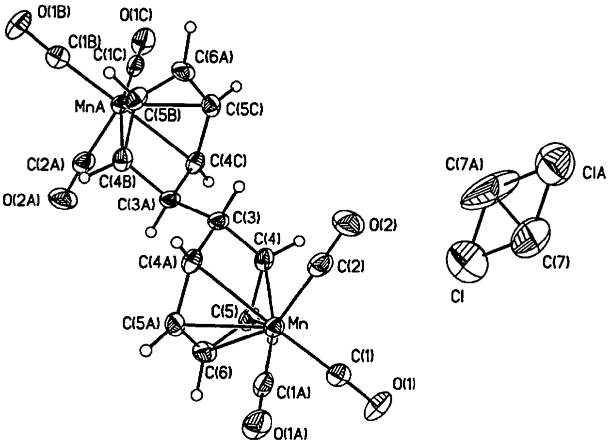

Fig. 1. The molecular structure of (1) with displacement ellipsoids shown at the 50% probability level.

The dimers in the two forms are virtually superimposable, with no significant differences in molecular geometry, and it is the inclusion of the methylene chloride solvent which allows for crystallization in $P4_2/mbc$. In the solvate, the molecular units are packed in layers with fourfold symmetry (Fig. 2) and the ability of the molecules to pack efficiently in such layers is a necessary condition for adoption of the observed space group. The role of the methylene chloride is to fill interstices between the layers (Fig. 3); each Cl atom of the methylene chloride fits into notches between two pairs of carbonyl ligands with close contacts to both the C and O atoms of each carbonyl ligand [Cl···C 3.67 (1) and 3.53 (1) Å, and Cl···O 3.62 (1) and 3.37 (1) Å; *cf.* 3.45 and 3.27 Å for the sum of van der Waals radii of Cl and C, and Cl and O, respectively (Bondi, 1964)]. The 275 Å^3 increase in the unit-cell volume from 1708 Å^3 in the unsolvated structure to 1983 Å^3 in the solvated structure is in reasonable agreement with the volume required to accommodate all atoms of the four dichloromethane molecules in the unit cell (assuming 10 Å^3 per atom) and in excellent agreement with the volume required if the disordered methylene chlorides are each treated as eight-atom molecules.

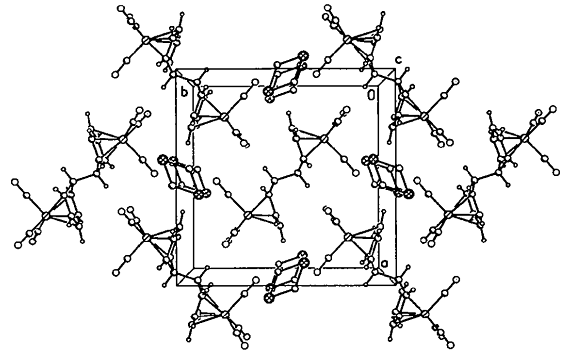

Fig. 2. The fourfold packing of the complex molecules within a layer.

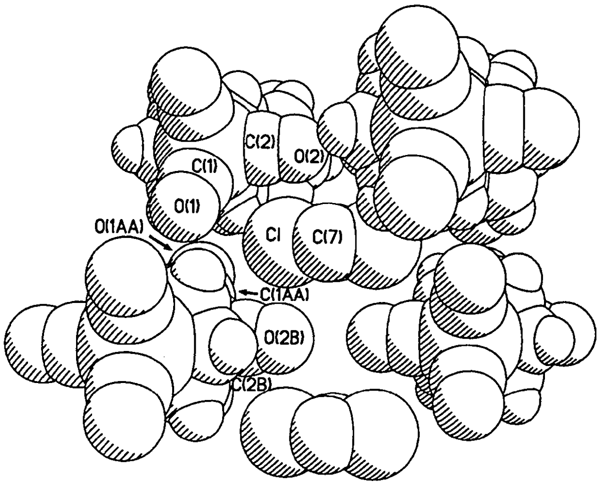

Fig. 3. The interaction of methylene chloride solvate molecules with $[\{Mn(CO)_3\}_2\{\mu\text{-}(\eta^5\text{-}C_6H_6\text{-}\eta^5\text{-}C_6H_6)\}]$ layers.

Experimental

Reactions and manipulations were carried out under a nitrogen atmosphere by means of standard Schlenk and cannula techniques. Samples of $[\{Mn(CO)_3\}_2\{\mu\text{-}(\eta^5\text{-}C_6H_6\text{-}\eta^5\text{-}C_6H_6)\}]$ were prepared from $[Mn(\eta^6\text{-}C_6H_6)(CO)_3]^+$ as reported previously (Lee *et al.*, 1996) and crystals of the solvate were prepared by slowly cooling a saturated solution of (1) in methylene chloride to 195 K and maintaining that temperature for several days.

Crystal data

$[Mn_2(C_{12}H_{12})(CO)_6].CH_2Cl_2$
$M_r = 519.08$
Tetragonal
$P4_2/mbc$
$a = 12.529\,(4)$ Å
$c = 12.635\,(8)$ Å
$V = 1983.4\,(15)$ Å^3
$Z = 4$
$D_x = 1.738$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10\text{–}15°$
$\mu = 1.53$ mm^{-1}
$T = 233\,(2)$ K
Block
0.34 × 0.15 × 0.15 mm
Orange

Data collection

Siemens *P*3 diffractometer
ω scans
Absorption correction: empirical *via* ψ scans (*SHELXTL*5.2; Siemens, 1994)
$T_{\min} = 0.64$, $T_{\max} = 0.79$
845 measured reflections
836 independent reflections
577 observed reflections [$I > 2\sigma(I)$]
$\theta_{\max} = 24.09°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 14$
3 standard reflections monitored every 197 reflections intensity decay: <1%

Refinement

Refinement on F^2
$R(F) = 0.052$
$wR(F^2) = 0.155$
$S = 1.062$
835 reflections
78 parameters
H-atom parameters not refined and solvent H atoms not included
$w = 1/[\sigma^2(F_o^2) + (0.0637P)^2 + 7.9153P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 0.63$ e Å^{-3}
$\Delta\rho_{\min} = -0.63$ e Å^{-3}
Extinction correction: *SHELXTL*5.2
Extinction coefficient: 0.0027 (8)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Mn	0.1950 (1)	0.1914 (1)	1/2	0.0280 (5)
O(1)	0.3310 (4)	0.2953 (4)	0.3404 (4)	0.0525 (14)
C(1)	0.2765 (4)	0.2550 (5)	0.4009 (5)	0.0353 (14)
O(2)	0.0195 (6)	0.3468 (6)	1/2	0.060 (2)
C(2)	0.0892 (8)	0.2896 (7)	1/2	0.041 (2)
C(3)	0.0195 (6)	0.0591 (6)	1/2	0.030 (2)
C(4)	0.0886 (5)	0.0862 (4)	0.4068 (4)	0.0316 (12)
C(5)	0.1937 (5)	0.0511 (4)	0.4045 (5)	0.0333 (14)
C(6)	0.2470 (7)	0.0309 (6)	1/2	0.038 (2)
Cl	0.0845 (3)	0.4155 (3)	1/4	0.1087 (14)
C(7)†	0.0405 (15)	0.5405 (15)	1/4	0.182 (22)

† Site occupancy = 0.50.

Table 2. *Selected geometric parameters* (Å, °)

Mn—C(1)	1.802 (6)	O(2)—C(2)	1.131 (11)
Mn—C(2)	1.808 (10)	C(3)—C(4)	1.501 (7)
Mn—C(6)	2.114 (8)	C(3)—C(3^{i})	1.559 (15)
Mn—C(5)	2.132 (6)	C(4)—C(5)	1.389 (8)
Mn—C(4)	2.214 (5)	C(5)—C(6)	1.402 (7)
O(1)—C(1)	1.143 (7)	Cl—C(7)	1.661 (12)
C(1)—Mn—C(1^{ii})	88.1 (4)	C(4^{ii})—C(3)—C(4)	103.4 (6)
C(1)—Mn—C(2)	96.6 (3)	C(4)—C(3)—C(3^{i})	113.4 (5)
C(1)—Mn—C(6)	104.2 (3)	C(5)—C(4)—C(3)	119.4 (5)
C(2)—Mn—C(6)	150.8 (4)	C(4)—C(5)—C(6)	119.4 (6)
O(1)—C(1)—Mn	177.7 (5)	C(5)—C(6)—C(5^{ii})	118.7 (8)
O(2)—C(2)—Mn	176.5 (8)		

Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $x, y, 1 - z$.

Data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991). Cell refinement: *P3/P4-PC Diffractometer Program*. Data reduction: *SHELXTL*5.2 (Siemens, 1994). Program(s) used to solve structure: *SHELXTL*5.2. Program(s) used to refine structure: *SHELXTL*5.2. Molecular graphics: *SHELXTL*-5.2. Software used to prepare material for publication: *SHELXTL*5.2.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1272). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Desiraju, G. R. (1989). In *Crystal Engineering*: *The Design of Organic Solids*. Elsevier: New York.
Dunitz, J. D. & Bernstein, J. (1995). *Acc. Chem. Res.* **28**, 193–200.
Gavezzotti, A. (1994). *Acc. Chem. Res.* **27**, 309–314.
Lee, S., Lovelace, S. R., Arford, D. J., Geib, S. J., Weber, S. G. & Cooper, N. J. (1996). *J. Am. Chem. Soc.* **118**, 4190–4191.
Siemens (1991). *P3/P4-PC Diffractometer Program.* Version 4.27. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1994) *SHELXTL*5.2. *Software for Single Crystal Structure Determination.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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Aqua[2,6-diacetylpyridinedi(benzoic acid hydrazone)]nitratocobalt(II) Nitrate at 173 K

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Abstract

The structure of aqua(nitrato-*O*){pyridine-2,6-diylbis[*N*-(1-ethylideneamino)benzamide]-O^1,N^2,N^1,N^5,O^2}-cobalt(II) nitrate, $[Co(NO_3)(C_{23}H_{21}N_5O_2)(H_2O)]NO_3$, was redetermined at 173 K. There are only small differences between the bond distances in the cation at 173 K relative to the room-temperature determination reported previously. The average difference is 0.006 Å for all 45 bond distances and only 0.004 Å for 27 bonds if the two phenyl rings and two nitrate ions, which have large thermal motions, are excluded. The Co^{II} atom is in the center of a pentagonal bipyramid consisting of the pentadentate ligand, with a water molecule and monodentate nitrate ligand in the axial positions.