Bis(tetrabutylammonium) tetrachlorido-manganate(II) dichloromethane disolvate

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The title compound, $(C_{16}H_{36}N)_2[MnCl_4]\cdot2CH_2Cl_2$, is an ionic organic–inorganic hybride compound consisting of a tetrabutylammonium cation and a tetra-chloridomanganate(II) anion in a 2:1 stoichiometric ratio. The cation contains a central nitrogen atom bonded to four *n*-butyl groups in a tetrahedral arrangement, while the anion contains a central Mn^{II} atom tetrahedrally coordinated by four chlorido ligands. It co-crystallized with two equivalents of dichloromethane solvent, CH_2Cl_2, to give the following empirical formula: $[(C_4H_9)_4N]_2[MnCl_4]\cdot(CH_2Cl_2)_2$. The crystal structure is mainly stabilized by Coulombic interactions.

3D view

Chemical scheme
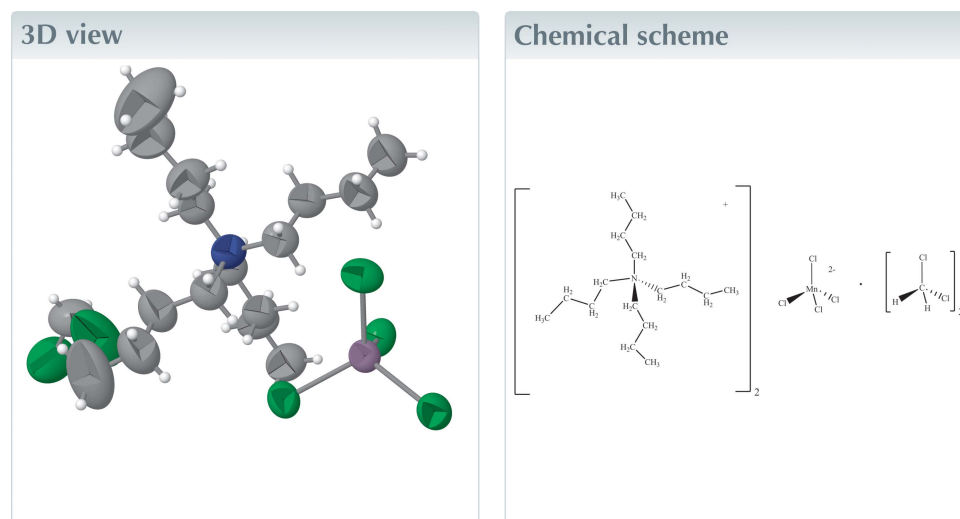
Structure description

During our efforts to prepare novel manganese-containing coordination complexes, we synthesized the previously reported non-solvated compound bis(tetrabutylammonium) tetrachloridomanganate(II). In conducting our experiments, we inadvertently obtained the disolvated title compound and determined its crystal structure. After reviewing the literature, we realised that no crystallographic data had yet been reported on either the non-solvated or solvated forms of this substance. The only crystallographic data related to this system was the powder X-ray diffraction data for the non-solvated form at 900 K after it had already undergone thermal decomposition (Styczeń *et al.*, 2009). Herein we present the results of the single-crystal structure analysis of the title compound.

The structural formula shows a ratio of 2:1 for the tetrabutylammonium cation and the tetrachloridomanganate(II) anion, combined with two solvent molecules of dichloromethane (Fig. 1). The above three molecular entities have internal symmetries allowing them to occupy different special positions in the lattice with point group symmetries $\overline{4}$.. (multiplicity 4, Wyckoff letter *a*) for the anion, and .2. (8 *d*) both for the cation and the solvent molecule. The root-mean-square deviations from ideal T_d symmetry for the
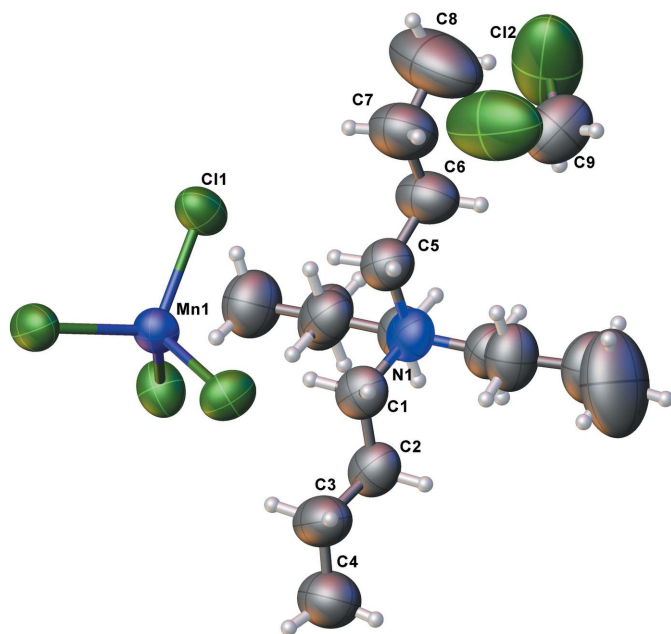
Figure 1
Molecular structures of the entities present in the title compound, with displacement ellipsoids drawn at the 50% probability level.

anion, S_4 symmetry for the cation and C_{2v} symmetry for the solvent molecule amount to 0.0123, 0.0501 and 0 Å, respectively, as calculated with *PLATON* (Spek, 2020), based on the *SYMMOL* program by Pilati & Forni (1998, 2000). The tetrabutylammonium cation, $(C_4H_9)_4N^+$, consists of a central nitrogen atom tetrahedrally surrounded by ordered butyl groups, with N—C bond lengths ranging from 1.505 (12) Å to 1.511 (11) Å and C—N—C bond angles in the range of 105.8 (5)–111.7 (11)°. The complex anion $MnCl_4^{2-}$ is consistent with the structure previously published for the tetramethylammonium salt (Rodríguez-Lazcano *et al.*, 2009) – the central Mn^{II} atom is bound with four chloride ligands tetrahedrally arranged. The Cl—Mn—Cl bond angles are
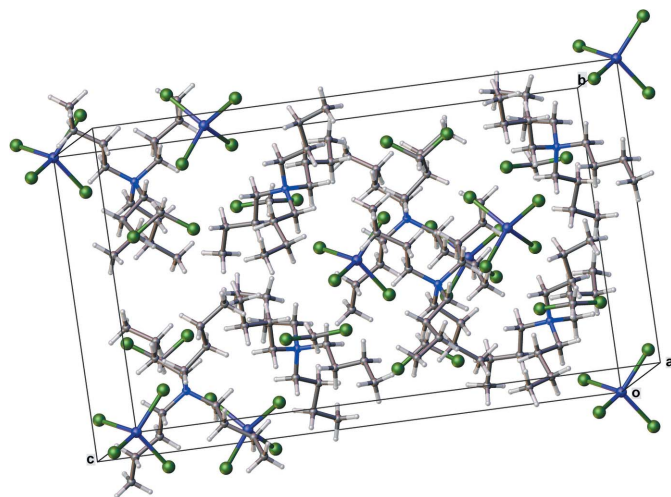
Table 1
Experimental details.

Crystal data	
Chemical formula	$(C_{16}H_{36}N)_2[MnCl_4]\cdot2CH_2Cl_2$
M_r	851.50
Crystal system, space group	Tetragonal, $I\bar{4}2d$
Temperature (K)	173
a, c (Å)	14.0775 (3), 24.3492 (8)
V (Å^3)	4825.4 (3)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	6.46
Crystal size (mm)	$0.38 \times 0.28 \times 0.13$
Data collection	
Diffractometer	ROD, Synergy Custom system, HyPix-Arc 150
Absorption correction	Analytical (*CrysAlis PRO*; Rigaku OD, 2021)
T_{min}, T_{max}	0.060, 0.359
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9265, 2334, 1567
R_{int}	0.038
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.624
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.075, 0.222, 1.06
No. of reflections	2334
No. of parameters	108
No. of restraints	47
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.35, −0.32
Absolute structure	Flack x determined using 458 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	−0.018 (8)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2021), *OLEX2.solve* (Bourhis *et al.*, 2015), *SHELXL2018/3* (Sheldrick, 2015), and *OLEX2* (Dolomanov *et al.*, 2009).

108.80 (12)-109.81 (12)°. The Mn—Cl bond lengths are all 2.364 (2) Å.

The crystal structure (Fig. 2) is stabilized primarily by Coulombic forces in the absence of classical hydrogen-bonding interactions.

Synthesis and crystallization

A similar protocol was followed as previously reported in the literature (Styczeń *et al.*, 2009). Pink $MnCl_4\cdot4H_2O$ (5.05 mmol, 1.00 g) was dissolved in warm absolute ethanol (10–15 ml). Separately, two equivalents of white $(C_4H_9)_4NCl\cdot H_2O$ (10.1 mmol, 2.81 g) were also dissolved in warm absolute ethanol (10–15 ml). The two ethanol solutions were then mixed, and the solution turned a light-green color. The ethanol was removed under reduced pressure with heating to produce a pale-green solid. The solid was recrystallized from dichloromethane/ether to give pale-green crystals. After drying the crystals under reduced pressure at 311 K, they were massed (3.07 g, 89.2% yield). They were analyzed by IR and elemental analysis. IR (cm^{-1}): 2962*m*, 2943*m*, 2875*m*, 1484*s*, 1468*m*, 1378*m*, 1151*w*, 1025*w*, 881*m*, 749*m*, 732*m*. Analysis calculated for $(C_{16}H_{36}N)_2MnCl_4$: C, 56.38; H, 10.65, N, 4.11. Found: C, 56.47; H, 11.47, N, 4.04. X-ray quality crystals were

Figure 2
Packing diagram of the crystal structure, which is stabilized primarily by Coulombic forces.

obtained from a mixture of dichloromethane/ether during a reaction involving the non-solvated form of the title compound as the starting material.

Refinement

Crystal data, data collection and structure refinement details for the reported structure is summarized in Table 1. The crystal diffracted poorly at high resolution. The average intensity drops below the 3σ level at 0.9933 Å. Consequently, the reliability factors are comparatively high. As a result of the special symmetry of the dichloromethane solvent molecule, the two H atoms (H9*A* and H9*B*) were refined with half-occupancy.

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full crystallographic data

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Crystal data

$(C_{16}H_{36}N)_2[MnCl_4]\cdot 2CH_2Cl_2$	$D_x = 1.172$ Mg m^{-3}
$M_r = 851.50$	Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Tetragonal, $I\bar{4}2d$	Cell parameters from 3369 reflections
$a = 14.0775 (3)$ Å	$\theta = 3.6$–$60.8°$
$c = 24.3492 (8)$ Å	$\mu = 6.46$ mm^{-1}
$V = 4825.4 (3)$ Å^3	$T = 173$ K
$Z = 4$	Plate, clear yellow
$F(000) = 1820$	$0.38 \times 0.28 \times 0.13$ mm

Data collection

ROD, Synergy Custom system, HyPix-Arc 150 diffractometer	$T_{min} = 0.060$, $T_{max} = 0.359$
Radiation source: Rotating-anode X-ray tube, Rigaku (Cu) X-ray Source	9265 measured reflections
	2334 independent reflections
	1567 reflections with $I > 2\sigma(I)$
Mirror monochromator	$R_{int} = 0.038$
Detector resolution: 10.0000 pixels mm^{-1}	$\theta_{max} = 74.1°$, $\theta_{min} = 3.6°$
ω scans	$h = -17 \rightarrow 16$
Absorption correction: analytical	$k = -16 \rightarrow 17$
(*CrysAlisPro*; Rigaku OD, 2021)	$l = -27 \rightarrow 29$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.075$	$w = 1/[\sigma^2(F_o^2) + (0.1133P)^2 + 4.1001P]$
$wR(F^2) = 0.222$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
2334 reflections	$\Delta\rho_{max} = 0.35$ e Å^{-3}
108 parameters	$\Delta\rho_{min} = -0.32$ e Å^{-3}
47 restraints	Absolute structure: Flack x determined using
Primary atom site location: iterative	458 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Hydrogen site location: mixed	Absolute structure parameter: $-0.018 (8)$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{iso}*/U_{eq}$
Mn1	0.500000	0.000000	0.750000	0.0722 (7)
Cl1	0.37996 (17)	−0.06513 (19)	0.69347 (9)	0.0925 (8)
Cl2	0.2523 (6)	0.1511 (5)	0.4325 (2)	0.248 (4)
C9	0.250000	0.2191 (18)	0.375000	0.152 (9)
H9	0.204 (11)	0.254 (12)	0.382 (8)	0.182*
N1	0.3681 (8)	0.250000	0.625000	0.090 (3)
C1	0.4291 (7)	0.2541 (7)	0.6760 (3)	0.094 (3)
H1A	0.466853	0.194827	0.677948	0.112*
H1B	0.386692	0.255178	0.708408	0.112*
C2	0.4966 (8)	0.3374 (6)	0.6802 (3)	0.100 (3)
H2A	0.540087	0.337104	0.648222	0.120*
H2B	0.459916	0.397367	0.679322	0.120*
C3	0.5535 (9)	0.3328 (8)	0.7322 (5)	0.125 (4)
H3A	0.587481	0.271263	0.733181	0.150*
H3B	0.509107	0.334000	0.763696	0.150*
C4	0.6252 (10)	0.4116 (9)	0.7396 (6)	0.142 (5)
H4A	0.664940	0.416247	0.706657	0.213*
H4B	0.665249	0.397709	0.771501	0.213*
H4C	0.591855	0.471854	0.745395	0.213*
C5	0.3081 (8)	0.1621 (7)	0.6308 (4)	0.101 (3)
H5A	0.270075	0.167990	0.664871	0.121*
H5B	0.350980	0.106950	0.635531	0.121*
C6	0.2413 (9)	0.1411 (9)	0.5839 (5)	0.127 (4)
H6A	0.278449	0.128709	0.550114	0.152*
H6B	0.200173	0.196905	0.577132	0.152*
C7	0.1799 (11)	0.0552 (10)	0.5969 (6)	0.155 (5)
H7A	0.221001	0.001495	0.608109	0.186*
H7B	0.137194	0.070402	0.627982	0.186*
C8	0.1215 (16)	0.026 (2)	0.5479 (8)	0.260 (13)
H8A	0.162622	0.022088	0.515483	0.390*
H8B	0.071993	0.074082	0.541378	0.390*
H8C	0.091990	−0.035380	0.554830	0.390*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0805 (10)	0.0805 (10)	0.0555 (13)	0.000	0.000	0.000
Cl1	0.0873 (14)	0.1130 (18)	0.0771 (12)	0.0069 (13)	−0.0096 (11)	−0.0207 (12)
Cl2	0.359 (8)	0.258 (7)	0.127 (3)	−0.111 (7)	−0.053 (5)	0.044 (4)
C9	0.17 (2)	0.137 (19)	0.145 (18)	0.000	0.050 (17)	0.000
N1	0.115 (8)	0.085 (7)	0.070 (6)	0.000	0.000	0.020 (5)
C1	0.122 (7)	0.096 (6)	0.063 (5)	−0.006 (6)	0.003 (5)	0.014 (4)
C2	0.130 (7)	0.093 (6)	0.077 (5)	0.000 (7)	0.003 (6)	0.009 (5)
C3	0.152 (10)	0.106 (8)	0.117 (9)	−0.022 (8)	−0.028 (8)	0.008 (6)
C4	0.146 (10)	0.140 (11)	0.139 (11)	−0.018 (9)	−0.018 (9)	0.005 (9)

C5	0.117 (8)	0.098 (7)	0.088 (6)	−0.007 (6)	0.000 (6)	0.008 (5)
C6	0.141 (10)	0.131 (10)	0.109 (8)	−0.030 (9)	−0.017 (8)	0.008 (7)
C7	0.166 (13)	0.163 (12)	0.136 (11)	−0.029 (11)	−0.028 (10)	−0.005 (10)
C8	0.22 (2)	0.32 (3)	0.24 (2)	−0.11 (2)	−0.07 (2)	0.06 (2)

Geometric parameters (Å, º)

Mn1—Cl1^i	2.364 (2)	C3—H3B	0.9900
Mn1—Cl1^{ii}	2.364 (2)	C3—C4	1.510 (10)
Mn1—Cl1^{iii}	2.364 (2)	C4—H4A	0.9800
Mn1—Cl1	2.364 (2)	C4—H4B	0.9800
Cl2—C9	1.695 (15)	C4—H4C	0.9800
C9—H9	0.83 (15)	C5—H5A	0.9900
C9—H9^{iv}	0.83 (15)	C5—H5B	0.9900
N1—C1^v	1.511 (11)	C5—C6	1.510 (10)
N1—C1	1.511 (11)	C6—H6A	0.9900
N1—C5	1.505 (12)	C6—H6B	0.9900
N1—C5^v	1.505 (12)	C6—C7	1.519 (11)
C1—H1A	0.9900	C7—H7A	0.9900
C1—H1B	0.9900	C7—H7B	0.9900
C1—C2	1.513 (9)	C7—C8	1.505 (11)
C2—H2A	0.9900	C8—H8A	0.9800
C2—H2B	0.9900	C8—H8B	0.9800
C2—C3	1.500 (9)	C8—H8C	0.9800
C3—H3A	0.9900		

Cl1^i—Mn1—Cl1^{ii}	109.81 (6)	H3A—C3—H3B	107.5
Cl1^{ii}—Mn1—Cl1	108.80 (12)	C4—C3—H3A	108.5
Cl1^i—Mn1—Cl1^{iii}	108.80 (12)	C4—C3—H3B	108.5
Cl1^{iii}—Mn1—Cl1	109.81 (6)	C3—C4—H4A	109.5
Cl1^i—Mn1—Cl1	109.81 (6)	C3—C4—H4B	109.5
Cl1^{ii}—Mn1—Cl1^{iii}	109.81 (6)	C3—C4—H4C	109.5
Cl2—C9—Cl2^{iv}	111.3 (14)	H4A—C4—H4B	109.5
Cl2^{iv}—C9—H9	120 (10)	H4A—C4—H4C	109.5
Cl2—C9—H9	100 (10)	H4B—C4—H4C	109.5
Cl2^{iv}—C9—H9^{iv}	100 (10)	N1—C5—H5A	108.3
Cl2—C9—H9^{iv}	120 (10)	N1—C5—H5B	108.3
H9—C9—H9^{iv}	107 (10)	N1—C5—C6	116.1 (8)
C1—N1—C1^v	110.7 (10)	H5A—C5—H5B	107.4
C5^v—N1—C1^v	105.8 (5)	C6—C5—H5A	108.3
C5—N1—C1	105.8 (5)	C6—C5—H5B	108.3
C5—N1—C1^v	111.4 (6)	C5—C6—H6A	109.5
C5^v—N1—C1	111.4 (6)	C5—C6—H6B	109.5
C5—N1—C5^v	111.7 (11)	C5—C6—C7	110.6 (9)
N1—C1—H1A	108.2	H6A—C6—H6B	108.1
N1—C1—H1B	108.2	C7—C6—H6A	109.5
N1—C1—C2	116.2 (7)	C7—C6—H6B	109.5
H1A—C1—H1B	107.4	C6—C7—H7A	109.4

C2—C1—H1A	108.2	C6—C7—H7B	109.4
C2—C1—H1B	108.2	H7A—C7—H7B	108.0
C1—C2—H2A	109.4	C8—C7—C6	111.0 (12)
C1—C2—H2B	109.4	C8—C7—H7A	109.4
H2A—C2—H2B	108.0	C8—C7—H7B	109.4
C3—C2—C1	111.0 (7)	C7—C8—H8A	109.5
C3—C2—H2A	109.4	C7—C8—H8B	109.5
C3—C2—H2B	109.4	C7—C8—H8C	109.5
C2—C3—H3A	108.5	H8A—C8—H8B	109.5
C2—C3—H3B	108.5	H8A—C8—H8C	109.5
C2—C3—C4	115.2 (9)	H8B—C8—H8C	109.5
N1—C1—C2—C3	−179.5 (10)	C1—C2—C3—C4	178.4 (11)
N1—C5—C6—C7	−175.7 (11)	C5^v—N1—C1—C2	−58.2 (12)
C1^v—N1—C1—C2	59.3 (7)	C5—N1—C1—C2	−179.8 (9)
C1^v—N1—C5—C6	−58.6 (12)	C5^v—N1—C5—C6	59.6 (8)
C1—N1—C5—C6	−179.0 (10)	C5—C6—C7—C8	−173.2 (16)

Symmetry codes: (i) $y+1/2$, $-x+1/2$, $-z+3/2$; (ii) $-x+1$, $-y$, z; (iii) $-y+1/2$, $x-1/2$, $-z+3/2$; (iv) $-x+1/2$, y, $-z+3/4$; (v) x, $-y+1/2$, $-z+5/4$.