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Crystal Structure of Lignocaine Hydrochloride-Manganese Chloride Complex

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The crystal and molecular structure of lignocaine hydrochloride-manganese chloride complex, $MnCl_4C_{28}H_{44}O_2N_4$, is reported. The sample crystallizes in the space group P $2_1/c$ with a = 9.210(2) Å, b = 19.489(4) Å, c = 19.646(4) Å, β = 95.64(3)°, V = 3509.26(1) Å^3, Z = 4. The structure was solved by SHELXS-86 using 2619 reflections with $I > 3\sigma(I)$ and refined to an R value of 0.067. The complex has a stoichiometry of 1:2. The ligands and the metal group are not stacked independently.

Keywords: charge-transfer complexes, crystal structure, lignocaine, manganese chloride

INTRODUCTION

Structural work on metal complexes of lignocaine hydrochloride is interesting owing to the medical importance of lignocaine as a local anesthetic. As part of our study, the structural details of the complex of lignocaine hydrochloride with manganese chloride is reported in this paper.

EXPERIMENTAL

Single crystals suitable for x-ray diffraction work were obtained by the method of slow evaporation of a mixture of ethanol and water in which the material was dissolved. The crystals, stable at room temperature, were pale green in color. The cell parameters were determined and refined on a Siemens diffractometer using MoKα radiation. 20 reflections in the 2θ range 35° to 45° were used for refining the cell parameters. The crystal data are given in Table I.

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TABLE I

Crystal data

Empirical formula	$MnCl_4C_{28}H_{44}O_2N_4$
Formula weight	665.44
Crystal color	Pale green
Crystal dimension	0.3 x 0.3 x 0.8 mm
Space Group	P $2_1/c$ (#14)
Unit Cell dimensions	a = 9.210(2) Å
	b = 19.489(4) Å
	c = 19.646(4) Å
	β = 95.64(3)°
Volume of the unit cell	3509.26(1) $Å^3$
Z	4
Measured and Calculated densities	1.360 $Mg.m^{-3}$, 1.259 $Mg.m^{-3}$
Radiation and wavelength	MoKα, 0.71069 Å
Linear absorption coefficient (MoKα)	0.70 mm^{-1}
F(000)	1396.00
Temperature of measurement	293K
Source of material	Synthesized with commercially available ligand.

STRUCTURE SOLUTION AND REFINEMENT

The single crystal intensity data were collected within the 2θ maximum of 45° on a Siemens diffractometer using ω-2θ mode of scanning. The maximum(unsigned) values of the h, k and l are 9, 21 and 21. The radiation used for data collection was MoKα. Of the 5088 number of reflections measured 4579 were unique. Lorentz and polarization corrections were applied. 2619 reflections had an intensity $I > 3\sigma(I)$ and

$$R(\text{int}) = 0.0321. \qquad R(\text{sigma}) = 0.0441$$

TABLE II

Fractional atomic coordinates of the nonhydrogens. Quantities in the parentheses are respective e.s.d's.

Atom	x	y	z	U (Å)²
MN1	0.0820(2)	0.9764(1)	0.2946(1)	0.077 (1)
CL1	-0.1441(3)	1.0219(2)	0.2458(1)	0.074 (2)
CL2	0.2366(3)	0.9652(2)	0.2067(2)	0.092 (2)
CL3	0.0291(5)	0.8744(2)	0.3492(2)	0.214 (5)
CL4	0.1691(5)	1.0564(2)	0.3783(2)	0.164 (4)
C1	0.613 (2)	1.2879(9)	0.354 (1)	0.12 (2)
C2	0.725 (2)	1.2730(8)	0.4076(9)	0.14 (1)
C3	0.771 (2)	1.2024(7)	0.4210(7)	0.10 (1)
C4	0.696 (1)	1.1530(6)	0.3779(6)	0.072 (8)
C5	0.582 (1)	1.1688(7)	0.3256(7)	0.065 (8)
C6	0.545 (2)	1.2370(9)	0.3162(9)	0.10 (1)
C7	0.505 (1)	1.1129(8)	0.2822(7)	0.075 (9)
C8	0.889 (2)	1.1806(8)	0.4754(7)	0.13 (1)
N1	0.7398(9)	1.0814(4)	0.3857(4)	0.067 (6)
C9	0.681 (1)	1.0402(5)	0.4300(5)	0.054 (6)
O1	0.5861(8)	1.0575(3)	0.4665(4)	0.092 (6)
C10	0.747 (1)	0.9677(5)	0.4340(5)	0.066 (7)
N2	0.6258(9)	0.9178(4)	0.4469(4)	0.068 (6)
C11	0.700 (1)	0.8488(5)	0.4678(6)	0.095 (9)
C12	0.586 (2)	0.7957(6)	0.4880(7)	0.12 (1)
C13	0.504 (1)	0.9127(6)	0.3863(6)	0.072 (8)
C14	0.564 (2)	0.8831(8)	0.3209(6)	0.13 (1)
C15	0.294 (4)	0.074 (1)	-0.091 (1)	0.5176(0)
C16	0.154 (4)	0.0767(9)	-0.075 (1)	0.5642(0)
C17	0.099 (3)	0.0900(8)	-0.011 (1)	0.2831(0)
C18	0.229 (2)	0.0950(6)	0.0400(7)	0.2281(0)
C19	0.380 (3)	0.0908(8)	0.034 (1)	0.2695(0)
C20	0.419 (3)	0.0794(9)	-0.038 (1)	0.3620(0)
C21	0.495 (2)	0.097 (1)	0.0939(9)	0.12 (1)
C22	-0.051 (2)	0.090 (1)	0.004 (1)	0.19 (2)
N3	0.189 (1)	0.1029(6)	0.1104(6)	0.13 (1)
C23	0.145 (1)	0.1635(8)	0.1330(7)	0.063 (9)
O2	0.139 (1)	0.2177(4)	0.1012(5)	0.129 (8)
C24	0.103 (2)	0.1635(8)	0.2082(7)	0.09 (1)
N4	0.022 (2)	0.2288(8)	0.2200(7)	0.12 (1)
C25	-0.116 (4)	0.232 (1)	0.242 (2)	0.38 (4)
C26	-0.203 (2)	0.207 (1)	0.165 (1)	0.15 (2)
C27	0.131 (2)	0.277 (1)	0.292 (1)	0.19 (2)
C28	0.135 (3)	0.248 (1)	0.352 (1)	0.21 (2)

where

$$R(\text{int}) = \sum |F^2 - \langle F^2 \rangle| \Big/ \sum F^2$$

$$R(\text{sigma}) = \sum \sigma(F^2) \Big/ \sum F^2$$

The Wilson plot[1] gave the values of U as 0.063 Å^2 where U is the mean-square

TABLE III

$u(i, j)$ or U values *100 of the nonhydrogens. Quantities in the parentheses are respective e.s.d's.

Atom	u11(U)	u22	u33	u12	u13	u23
MN1	7.70(1)	5.56(1)	4.84(9)	0.22(8)	0.98(8)	0.25(1)
CL1	7.40(2)	12.41(3)	6.16(2)	-0.88(2)	0.50(2)	1.94(2)
CL2	9.24(2)	9.22(2)	7.29(2)	1.21(2)	2.50(2)	2.73(2)
CL3	21.39(5)	6.79(2)	14.04(3)	3.37(2)	8.75(3)	1.55(3)
CL4	16.40(4)	12.11(3)	7.74(2)	-3.90(2)	-1.72(2)	-0.76(3)
C1	12.2 (2)	9.7 (1)	17.2 (2)	4.2 (1)	5.5 (1)	1.2 (1)
C2	13.5 (1)	6.6 (1)	15.0 (2)	-1.9 (1)	5.0 (1)	-2.3 (1)
C3	10.2 (1)	6.62(9)	10.4 (1)	-1.19(8)	3.77(9)	-1.26(8)
C4	7.25(8)	6.28(8)	6.69(8)	1.39(6)	3.57(6)	0.34(7)
C5	6.46(8)	8.8 (1)	9.8 (1)	4.07(8)	3.28(8)	2.13(8)
C6	9.6 (1)	10.4 (1)	13.3 (1)	5.1 (1)	3.6 (1)	2.1 (1)
C7	7.50(9)	12.5 (1)	10.4 (1)	-1.06(9)	-2.71(8)	-0.83(9)
C8	12.6 (1)	12.8 (1)	9.2 (1)	-2.1 (1)	-3.5 (1)	-0.2 (1)
N1	6.72(6)	5.41(5)	5.59(5)	0.92(4)	1.89(4)	0.03(5)
C9	5.42(6)	5.62(7)	3.73(5)	-0.19(5)	-0.11(5)	-0.63(5)
O1	9.19(6)	5.51(4)	8.39(5)	0.63(4)	4.95(5)	0.64(4)
C10	6.62(7)	4.08(6)	8.11(8)	0.64(5)	1.98(6)	0.08(6)
N2	6.85(6)	4.26(5)	6.08(5)	-0.63(4)	1.50(5)	0.10(4)
C11	9.53(9)	4.24(6)	7.58(8)	0.33(6)	1.13(7)	1.88(6)
C12	12.3 (1)	4.94(7)	12.3 (1)	1.32(7)	4.85(9)	0.07(7)
C13	7.25(8)	7.37(8)	8.22(9)	-0.82(7)	-0.32(7)	0.84(7)
C14	13.2 (1)	13.5 (1)	5.98(8)	-3.27(8)	-1.75(8)	1.0 (1)
C15	51.76(0)	9.09(0)	9.25(0)	-0.13(0)	1.20(0)	-4.29(0)
C16	56.42(0)	5.79(0)	11.46(0)	1.23(0)	-10.22(0)	-1.56(0)
C17	28.31(0)	5.84(0)	14.24(0)	0.58(0)	-13.39(0)	-4.41(0)
C18	22.81(0)	3.89(0)	7.87(0)	1.10(0)	-3.09(0)	-2.38(0)
C19	26.95(0)	9.69(0)	11.72(0)	-1.64(0)	5.40(0)	-4.65(0)
C20	36.20(0)	10.08(0)	12.23(0)	-1.38(0)	0.67(0)	-7.11(0)
C21	12.4 (1)	22.3 (2)	12.6 (1)	-7.6 (1)	-0.4 (1)	-2.6 (1)
C22	18.9 (2)	12.6 (2)	29.9 (3)	1.3 (2)	-15.6 (2)	-1.1 (2)
N3	13.0 (1)	6.27(7)	10.30(9)	2.80(6)	-2.91(7)	-0.86(7)
C23	6.33(9)	9.8 (1)	10.8 (1)	4.7 (1)	-1.62(8)	-1.80(8)
O2	12.94(8)	7.31(6)	10.82(7)	3.42(5)	2.96(6)	-0.23(6)
C24	9.0 (1)	13.2 (1)	10.6 (1)	6.3 (1)	3.28(8)	2.85(9)
N4	12.4 (1)	19.3 (2)	13.8 (1)	9.6 (1)	6.7 (1)	8.7 (1)
C25	38.2 (4)	12.7 (2)	44.8 (5)	1.9 (2)	36.4 (4)	-3.2 (2)
C26	14.7 (2)	22.7 (2)	13.4 (2)	-1.2 (2)	-1.4 (1)	-12.9 (2)
C27	18.5 (2)	19.9 (2)	11.8 (2)	-4.5 (2)	-4.4 (2)	4.1 (2)
C28	21.00(2)	20.5 (2)	17.6 (2)	4.8 (2)	-3.9 (2)	-1.5 (2)

amplitude of atomic vibration. Structure was solved using SHELXS-86.[2] Least-squares refinement using SHELX76[3] converged the residuals to 0.07. The hydrogen atoms were generated and placed at a distance of 1.08 Å from the parent atom. The isotropic temperature factors of the hydrogen atoms were set to 1.2 times of the equivalent isotropic temperature factor of the parent atom. They were not

TABLE IV

Bond lengths (Å) and bond angles (°) of the non-hydrogens. Quantities in the parentheses are respective e.s.d's.

Mn1 - Cl1	2.376(3)	C11 - C12	1.56 (2)
Mn1 - Cl2	2.355(3)	C13 - C14	1.56 (2)
Mn1 - Cl3	2.332(4)	C15 - C16	1.36 (4)
Mn1 - Cl4	2.349(4)	C15 - C20	1.48 (3)
C1 - C2	1.43 (2)	C16 - C17	1.43 (3)
C1 - C6	1.35 (2)	C17 - C18	1.49 (2)
C2 - C3	1.46 (2)	C17 - C22	1.44 (3)
C3 - C4	1.42 (2)	C18 - C19	1.42 (2)
C3 - C8	1.51 (2)	C18 - N3	1.47 (2)
C4 - C5	1.43 (2)	C19 - C20	1.50 (2)
C4 - N1	1.46 (1)	C19 - C21	1.52 (2)
C5 - C6	1.38 (2)	N3 - C23	1.34 (2)
C5 - C7	1.52 (2)	C23 - O2	1.23 (1)
N1 - C9	1.34 (1)	C23 - C24	1.56 (2)
C9 - O1	1.23 (1)	C24 - N4	1.50 (2)
C9 - C10	1.54 (1)	N4 - C25	1.38 (2)
C10 - N2	1.52 (1)	N4 - C27	1.90 (2)
N2 - C11	1.54 (1)	C25 - C26	1.71 (1)
N2 - C13	1.56 (1)	C27 - C28	1.31 (3)

Cl1 - Mn1 - Cl2	107.94(2)	C10 - N2 - C13	113.47(1)
Cl1 - Mn1 - Cl3	106.81(1)	C11 - N2 - C13	114.50(1)
Cl1 - Mn1 - Cl4	105.05(2)	N2 - C11 - C12	110.66(1)
Cl2 - Mn1 - Cl3	115.26(1)	N2 - C13 - C14	111.64(2)
Cl2 - Mn1 - Cl4	112.69(1)	C16 - C15 - C20	121.89(2)
Cl3 - Mn1 - Cl4	108.43(1)	C15 - C16 - C17	129.17(2)
C2 - C1 - C6	120.96(2)	C16 - C17 - C18	106.23(2)
C1 - C2 - C3	120.1 (9)	C16 - C17 - C22	127.70(2)
C2 - C3 - C4	114.56(2)	C18 - C17 - C22	125.68(2)
C2 - C3 - C8	124.9 (8)	C17 - C18 - C19	131.97(2)
C4 - C3 - C8	120.54(2)	C17 - C18 - N3	112.42(2)
C3 - C4 - C5	124.43(2)	C19 - C18 - N3	115.56(3)
C3 - C4 - N1	118.10(2)	C18 - C19 - C20	114.81(3)
C5 - C4 - N1	117.4 (6)	C18 - C19 - C21	122.88(2)
C4 - C5 - C6	117.2 (6)	C20 - C19 - C21	122.31(2)
C4 - C5 - C7	121.28(2)	C15 - C20 - C19	115.69(2)
C6 - C5 - C7	121.48(2)	C18 - N3 - C23	121.07(8)
C1 - C6 - C5	122.63(2)	N3 - C23 - O2	126.17(1)
C4 - N1 - C9	121.10(1)	N3 - C23 - C24	115.08(9)
N1 - C9 - O1	124.73(2)	O2 - C23 - C24	118.71(7)
N1 - C9 - C10	113.66(5)	C23 - C24 - N4	108.44(1)
O1 - C9 - C10	121.6 (7)	C24 - N4 - C25	124.63(7)
C9 - C10 - N2	107.46(1)	N4 - C25 - C26	94.93(2)
C10 - N2 - C11	106.62(2)	C25 - N4 - C27	100.82(3)

refined. The details of the final least-squares refinement are as follows: Function minimized: $\Sigma\, w(|F_0| - |F_c|)^2$; unit weights; highest $|\Delta|/\sigma = 0.003$; Goodness of fit (GooF) = 2.7667; $R_f = 0.0668$, $R_w = 0.0668$; maximum and minimum peaks in the final difference map 0.50, -0.29 Å^{-3}, respectively where

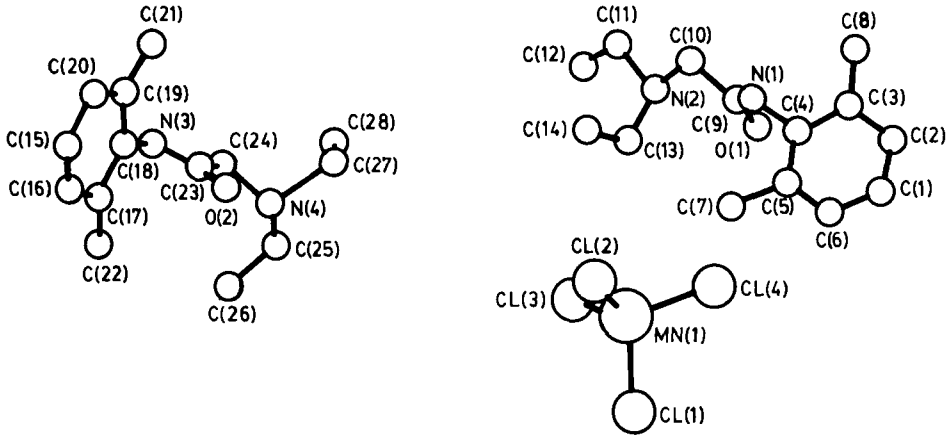

FIGURE 1 Projection of the molecule on the test plane.

$$R_f = \frac{\sum ||F_0| - |F_c||}{\sum |F_0|},$$

$$R_w = \left[\frac{\sum w(|F_0| - |F_c|)^2}{\sum wF_0^2}\right]^{1/2}$$

and

$$\text{GooF} = \frac{\sqrt{\left[\sum (w(F_0 - F_c)^2)\right.}}{(\text{no. of observations} - \text{no. of parameters})}$$

RESULTS AND DISCUSSION

The final positional coordinates of all the atoms, thermal parameters, bond distances and angles are given in Tables II–IV, respectively. The bond distances and angles are in agreement with the standard values. The N4—C27 bond distance is slightly larger than the standard value. Repeated trials with least-squares calculations and difference maps revealed the atoms at the same positions. Refinement of the positional occupancy factors did not also improve the situation. One might hence conclude that this non-standard length is related to the large flexibility of the ethyl chain attached to the N4 atom.

The stoichiometry of the complex is 1:2. The projection of the molecule on the best plane is shown in Figure 1. The thermal parameters of the atoms of one of the phenyl group C15 to C20 is quite high. This may be due to the distortion of the phenyl ring plane introduced by the methyl side groups. The metal-chlorine tetrahedron is distorted. This sort of a distortion of the coordination polyhedron

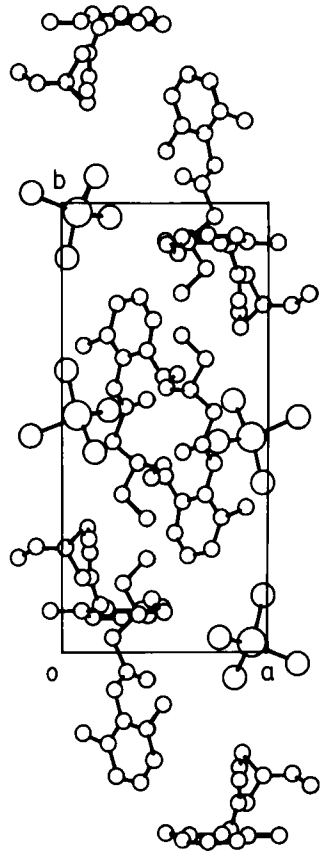

FIGURE 2 Packing of the molecules down "c."

is quite common to manganese complexes.[4-13] The metal atom to chlorine atom distances is comparable to the values quoted elsewhere.[14-17]

The packing of the molecules viewed down c axis is shown in Figure 2. The ligands and metal group are not stacked independently unlike in the case of lignocaine hydrochloride platinum complex[14] and lignocaine tetrachloroferrate complex.[15] The packing is similar to the complex of lignocaine tetrachlorocuprate[16] and lignocaine tetrachlorocobaltate.[17] As found in the complex of platinum chloride with lignocaine hydrochloride, the molecules exist independently.[14,18]

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