Refinement of the crystal structure of *p*-nitroaniline hydrochloride, $(NO_2C_6H_4NH_3)Cl$

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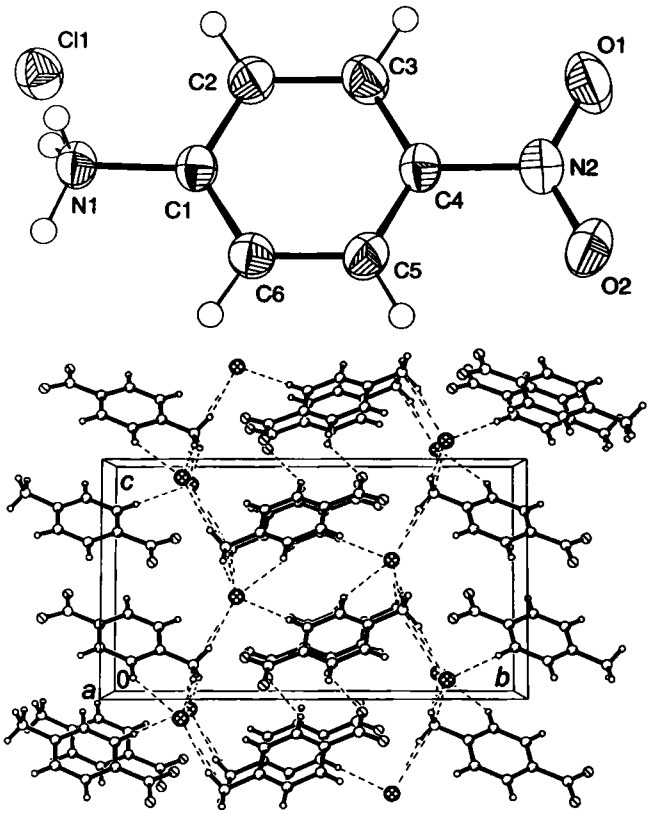

Abstract

$C_6H_7ClN_2O_2$, monoclinic, $P12_1/n1$ (no. 14), $a = 4.9807(6)$ Å, $b = 16.344(2)$ Å, $c = 9.342(1)$ Å, $\beta = 93.87(1)°$, $V = 758.7$ Å^3, $Z = 4$, $R_{gt}(F) = 0.028$, $wR_{ref}(F^2) = 0.079$, $T = 293$ K.

Source of material

The title compound was acquired as an unexpected by-product in the synthesis of the target compound $(4\text{-}NO_2C_6H_4NH_3)_2MnCl_4$ which was carried out analogously with the preparation of $(4\text{-}BrC_6H_4NH_3)_2PbCl_4$ [1]. 4-Nitrophenylamine (2.722 g, 19.7 mmol) was dissolved in concentrated hydrochloric acid (20 mmol, 37 %) with stirring under nitrogen at 70 °C. To this solution was added gradually a solution of manganese(II) chloride tetrahydrate (1.982 g, 10 mmol) in concentrated aqueous hydrochloric acid (20 ml, 37 %) with stirring under nitrogen. The resulting solution was allowed to stand at 70 °C for two hours and then slowly cooled to 40 °C at a cooling rate of 5 K/h without stirring. After twelve hours at 40 °C, long pale yellow prismatic crystals of the title compound were harvested (yield 0.263 g).

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Discussion

The title compound crystallizes with one 4-nitroanilinium and one chloride ion in the asymmetric unit (figure, top). Both the 4-nitroanilinium and the chloride ion are located on general positions. The 4-nitroanilinium layers in the crystal structure encapsulate the chloride ions (figure, bottom). The phenyl ring and the N1 and N2 atoms are practically planar, N1 and N2 atoms show the largest deviations from the plane of –0.0345 Å and –0.0315 Å, respectively. Planes defined by N2–C1–C2–C3–C4–C5–C6–N1 in each 4-nitroanilinium monolayer are parallel to each other. The planes of the neighboring monolayers make a dihedral angle of 20.7°. The bond lengths and angles are within expected ranges. Their uncertainties are decreased by a factor of almost three compared with those achieved in the first structure determination [2]. N–H···Cl bonds as well as C–H···Cl and C–H···O bonds are found in the crystal structure, which have a great effect in maintaining its stability. The N–H distances, H···Cl distances and N–H···Cl angles, are for N1–H1A···Cl1(½+*x*,½–*y*,–½+*z*): 0.94(2) Å, 2.29(3) Å, 166.7(19)°; for N1–H1B···Cl1: 0.88(2) Å, 2.35(2) Å, 162.5(19)°; for N1–H1C···Cl1(–½+*x*,½–*y*,–½+*z*): 0.87(3) Å, 2.32(3) Å, 156(2)°. Compared with the former bonds, the latter bonds [C3–H3···O1(–*x*,–*y*,1–*z*), C5–H5···Cl1(1½–*x*,–½+*y*,½–*z*), C6–H6···Cl1(½+*x*,½–*y*,–½+*z*)] have two characteristics: the H···Cl distances are longer and C–H···Cl (or O) angles deviate stronger from 160°. These details indicate that the C–H···Cl or C–H···O bonds are weaker than N–H···Cl hydrogen bonds.

Table 1. Data collection and handling.

Crystal:	pale yellow prism, size 0.22 × 0.31 × 0.39 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	4.51 cm^{-1}
Diffractometer, scan mode:	Bruker P4, ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2162, 1491
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1210
$N(param)_{refined}$:	129
Programs:	SHELXTL [3], WinGX [4]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1A)	4*e*	0.180(5)	0.289(1)	0.572(3)	0.058(6)
H(1B)	4*e*	0.044(4)	0.255(2)	0.699(2)	0.057(6)
H(1C)	4*e*	–0.106(5)	0.282(1)	0.571(3)	0.058(7)
H(2)	4*e*	–0.291(4)	0.338(1)	0.819(2)	0.042(5)
H(3)	4*e*	–0.380(5)	0.467(1)	0.911(2)	0.059(6)
H(5)	4*e*	0.202(4)	0.559(1)	0.674(2)	0.047(5)
H(6)	4*e*	0.275(4)	0.430(1)	0.582(2)	0.055(6)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4*e*	−0.0055(3)	0.3734(1)	0.6918(2)	0.0325(8)	0.0263(8)	0.0303(8)	0.0020(7)	0.0008(6)	0.0002(6)
C(2)	4*e*	−0.1985(4)	0.3823(1)	0.7899(2)	0.042(1)	0.0286(9)	0.043(1)	−0.0024(8)	0.0124(8)	0.0036(7)
C(3)	4*e*	−0.2441(4)	0.4590(1)	0.8457(2)	0.042(1)	0.0351(9)	0.0393(9)	0.0028(8)	0.0138(8)	0.0000(7)
C(4)	4*e*	−0.0946(3)	0.5241(1)	0.8014(2)	0.0359(9)	0.0262(8)	0.0329(8)	0.0039(7)	0.0003(7)	−0.0015(7)
C(5)	4*e*	0.0998(4)	0.5157(1)	0.7053(2)	0.042(1)	0.0284(9)	0.042(1)	−0.0048(8)	0.0093(8)	−0.0004(7)
C(6)	4*e*	0.1434(4)	0.4386(1)	0.6487(2)	0.0388(9)	0.0328(9)	0.0397(9)	−0.0022(7)	0.0134(8)	−0.0013(7)
N(1)	4*e*	0.0321(3)	0.29219(9)	0.6303(2)	0.0378(9)	0.0261(7)	0.0379(8)	0.0005(6)	0.0061(7)	−0.0019(6)
N(2)	4*e*	−0.1468(3)	0.60624(9)	0.8581(2)	0.0463(9)	0.0325(8)	0.0374(8)	0.0044(7)	0.0026(7)	−0.0037(6)
O(1)	4*e*	−0.3387(3)	0.61485(8)	0.9320(2)	0.0653(9)	0.0395(8)	0.0609(9)	0.0092(7)	0.0261(7)	−0.0058(6)
O(2)	4*e*	0.0003(3)	0.66209(8)	0.8276(2)	0.067(1)	0.0339(7)	0.073(1)	−0.0122(7)	0.0192(8)	−0.0134(7)
Cl(1)	4*e*	0.48420(9)	0.68867(3)	0.57885(4)	0.0436(3)	0.0359(3)	0.0348(2)	−0.0034(2)	0.0075(2)	−0.0015(2)

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