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Two phenanthroline hydrochlorides

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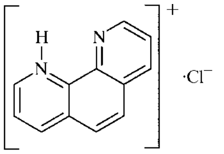
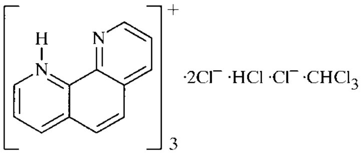
The crystal and molecular structures of two phenanthroline hydrochlorides have been determined at 173 K. 1,10-Phenanthrolin-1-ium chloride, $C_{12}H_9N_2^+\cdot Cl^-$, crystallizes in two stacks of exactly planar molecules. Both stacks are approximately parallel to the $(\bar{2}02)$ plane and the planes composing the different stacks enclose an angle of 13.29 (3)°. Tris(1,10-phenanthrolin-1-ium) dichloride (hydrogen chloride) chloride chloroform solvate, $3C_{12}H_9N_2^+\cdot 2Cl^-\cdot HCl\cdot Cl^-\cdot CHCl_3$, displays an interesting network of Cl^- mediated hydrogen bonds between the two different phenanthrolinium moieties and between a phenanthrolinium and the chloroform solvate. In addition, a hydrogen bond between the HCl and the third Cl^- ion is formed. The C—N—C angle at the protonated N atoms is, in all phenanthrolinium units of both structures, significantly larger than the C—N—C angle at the non-protonated N atom.

Comment

As a Lewis acid, trichloromethylsilane forms a complex with the Lewis bases 3,4-dimethylpyridine (Hensen & Dräbing, 1990) and 3,5-dimethylpyridine (Hensen & Dräbing, 1989; Burger *et al.*, 1992). According to the result of Kummer & Seshadri (1977), who prepared bis-phenanthroline complexes of diiodosilanes with different substituents, we tried to synthesize a complex of $MeSiCl_3$ with the Lewis base 1,10-phenanthroline. The two structures obtained, however, are products of hydrolyses of a mixture of methyltrichlorosilane and 1,10-phenanthroline.



(I)



(II)

1,10-Phenanthrolin-1-ium chloride, (I) (Fig. 1), is the first structure of the pure 1:1 compound between 1,10-phenanthroline and HCl. It consists of a protonated phenanthroline molecule and a chloride ion. Bond lengths and angles are in the usual ranges, compared with similar structures retrieved from the Cambridge Structural Database (Version 5.16, October 1998; Allen & Kennard, 1993). The finding of Hensen *et al.* (1998) that the C—N—C angle at the protonated N atom is significantly larger [C14—N1—C2 123.1 (4)°] than at the non-protonated N atom [C11—N12—C13 116.1 (3)°] is confirmed with this structure. The phenanthroline moiety is essentially planar and the chloride ion which is hydrogen bonded to N1 deviates by only 0.400 (4) Å from this plane. Three further short Cl· · ·H contacts to aromatic H atoms are found, so that the Cl^- ion is approximately tetrahedrally coordinated. The phenanthroline moieties crystallize in stacks of exactly coplanar molecules, but two differently oriented stacks can be identified (Fig. 2). Although the layers in both stacks are formed approximately parallel to the $(\bar{2}02)$ plane, these two layers are tilted at an angle of 13.29 (3)° with respect to each other.

The crystal structure of tris(1,10-phenanthrolin-1-ium) dichloride (hydrogen chloride) chloride chloroform solvate, (II) (Fig. 3), consists of three discrete protonated phenanthroline molecules, three chloride ions, an HCl molecule and a chloroform solvate. Bond lengths and angles of the phenanthrolinium units are in the usual ranges, compared with similar structures retrieved from the Cambridge Structural Database

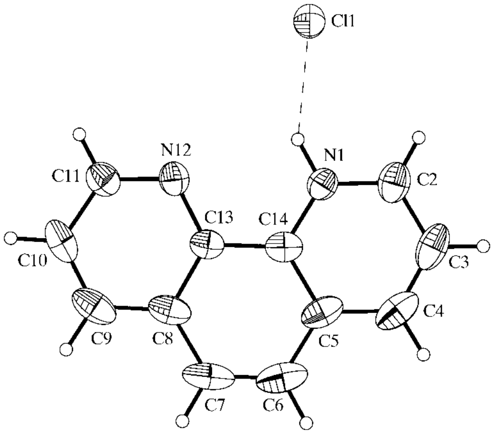


Figure 1
Perspective view of (I) with the atom numbering; displacement ellipsoids are at the 50% probability level.

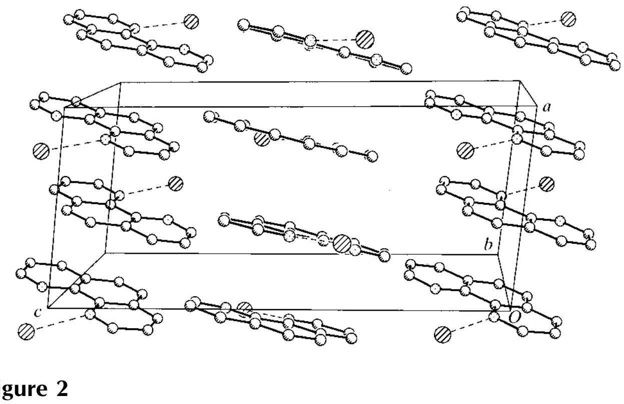


Figure 2
Packing diagram of (I); H atoms omitted.

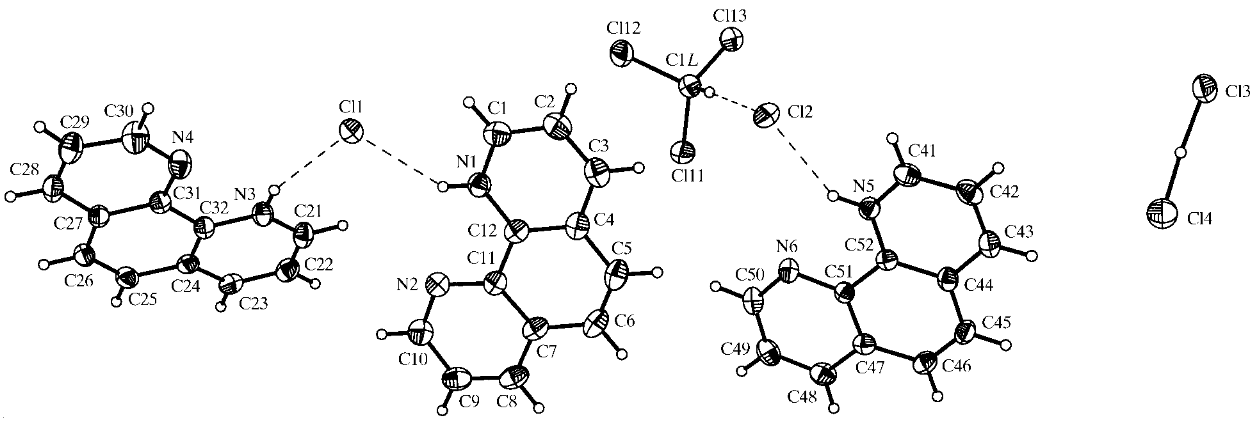


Figure 3
Perspective view of (II) with the atom numbering; displacement ellipsoids are at the 50% probability level.

(Version 5.16, October 1998; Allen & Kennard, 1993), and the C—N—C angles show the values in the same range as already found for (I). In contrast to other structures [$C_{12}H_9N_2^+ \cdot NO_3^- \cdot C_{12}H_8N_2 \cdot H_2O$ (Thevenet & Rodier, 1981), $C_{24}H_{17}N_4^+ \cdot ClO_4^-$ (Maresca *et al.*, 1989), $C_{12}H_9N_2^+ \cdot C_5H_{10}I_2NS_2Te^- \cdot C_{12}H_8N_2$ and $C_{12}H_9N_2^+ \cdot C_5H_{10}Br_2NS_2Te^- \cdot C_{12}H_8N_2$ (Krishnakumar *et al.*, 1996), and $C_{12}H_9N_2^+ \cdot Cl^- \cdot 2C_{12}H_8N_2$ (Hensen *et al.*, 1998)], the protonated phenanthrolines do not form a hydrogen bond to a second phenanthroline. Two phenanthrolinium molecules form a hydrogen bond to the same Cl^- ion, namely Cl1. The third phenanthrolinium and the chloroform are both connected *via* hydrogen bonds to Cl2, whereas the third Cl^- ion, Cl3, forms a hydrogen bond to the HCl molecule. It might be surprising that the Cl^- is protonated and not an additional N atom of the phenanthrolines, because Cl^- ($pK_a = -6$) is a weaker base than phenanthroline ($pK_a = 4.48$). However, a comparable structural motif was found 30 times in the Cambridge Structural Database (Version 5.16, October 1998; Allen & Kennard, 1993) with the following mean geometric parameters: Cl—H 1.3 (2), H···Cl 2.1 (2), Cl···Cl 3.3 (2) Å, Cl—H···Cl 166 (16)°. Compared with the mean values extracted from the database, the distances between the two Cl atoms and the hydrogen bridging them are more equal in (II), but since the determination of H atoms by means of X-ray structure analysis is a difficult chapter, we do not want to overemphasize this point. Furthermore, the Cl···Cl distance in (II) is slightly shorter than the mean distance in the database structures, but this might be partially due to the fact that (II) was measured at low temperature. The geometric parameters of all these hydrogen bonds are summarized in Table 4. The sum of the bond angles at all protonated N atoms in both structures is exactly 360°. Furthermore, the crystal packing is stabilized by several short Cl···H—C contacts. The phenanthrolinium molecules of (II) also form stacks. One is built up by exactly coplanar layers of the phenanthrolinium which is hydrogen bonded to the chloroform solvate. The other one is formed by intermittant layers [tilted at 5.1 (1)° to each other] of the remaining two phenanthroline units. Furthermore, there is a short Cl···Cl distance, Cl13···Cl2(x, $1 + y$, z) 3.300 (1) Å.

Experimental

Preparation of (I): methyltrichlorosilane (1 mmol) and 1,10-phenanthroline (2 mmol) were mixed. The mixture was heated above the melting point of phenanthroline (390 K). During cooling to 298 K a white solid precipitated. The clear solution was removed by a syringe. The solid was dried *in vacuo* (2–3 mbar for 8 h; 1 mbar = 100 Pa), the powder was transferred into a glove box under nitrogen. Crystals of (I) were obtained by sublimation at (2–3 mbar) and 315 K.

Preparation of (II): methyltrichlorosilane (1 mmol) was dissolved in 20 ml $CHCl_3$. During continuous stirring, a solution of 1,10-phenanthroline (2 mmol) in chloroform was added. The solvent was slowly removed *in vacuo* (2–3 mbar) at 300 K. Crystals were obtained after a few days.

Compound (I)

Crystal data

$C_{12}H_9N^+ \cdot Cl^-$
$M_r = 216.66$
Monoclinic, $P2_1/c$
$a = 6.877$ (1) Å
$b = 9.787$ (1) Å
$c = 15.547$ (2) Å
$\beta = 96.91$ (2)°
$V = 1038.8$ (2) Å^3
$Z = 4$
$D_x = 1.385$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1982 reflections
$\theta = 1$–25°
$\mu = 0.331$ mm^{-1}
$T = 173$ K
Plate, colourless
0.25 × 0.20 × 0.10 mm

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.922$, $T_{\max} = 0.968$
7686 measured reflections
1884 independent reflections
1093 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.083$
$\theta_{\max} = 26.03$°
$h = -8 \rightarrow 8$
$k = -10 \rightarrow 11$
$l = -18 \rightarrow 18$
53 standard reflections
frequency: 720 min
intensity decay: none

Table 1
Selected geometric parameters (Å, °) for (I).

N1—C2	1.331 (5)	C11—N12	1.321 (5)
N1—C14	1.373 (5)	N12—C13	1.362 (5)
C2—N1—C14	123.1 (4)	C11—N12—C13	116.1 (3)

Acta Cryst. (2000). C**56**, 208–210 Karl Hensen *et al.* • $3C_{12}H_9N_2^+ \cdot 2Cl^- \cdot HCl \cdot Cl^- \cdot CHCl_3$ and $C_{12}H_9N^+ \cdot Cl^-$ **209**

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

$D—\text{H}\cdots A$	$D—\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D—\text{H}\cdots A$
N1—H1···Cl1	0.95 (4)	2.16 (4)	2.986 (4)	145 (4)
C2—H2···Cl1^{i}	0.95	2.79	3.462 (4)	128.4
C4—H4···Cl1^{ii}	0.95	2.57	3.424 (4)	150.1
C9—H9···Cl1^{iii}	0.95	2.70	3.527 (4)	146.4

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $x, 1 + y, z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.150$
$S = 1.050$
1884 reflections
140 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0535P)^2 + 0.6383P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.56$ e Å^{-3}
$\Delta\rho_{\min} = -0.31$ e Å^{-3}

Compound (II)

Crystal data

$3C_{12}H_9N_2^+\cdot 2Cl^-\cdot HCl\cdot Cl^-\cdot CHCl_3$
$M_r = 805.81$
Monoclinic, $P2_1/c$
$a = 26.017$ (3) Å
$b = 7.2220$ (10) Å
$c = 19.461$ (2) Å
$\beta = 90.770$ (10)°
$V = 3656.3$ (8) Å^3
$Z = 4$
$D_x = 1.464$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 1$–25°
$\mu = 0.581$ mm^{-1}
$T = 173$ (2) K
Plate, colourless
0.46 × 0.34 × 0.18 mm

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.776$, $T_{\max} = 0.903$
52608 measured reflections
7983 independent reflections
5433 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.058$
$\theta_{\max} = 27.90°$
$h = -32 \rightarrow 32$
$k = -9 \rightarrow 9$
$l = -25 \rightarrow 24$
426 standard reflections frequency: 1200 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.090$
$S = 1.054$
7983 reflections
467 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0279P)^2 + 2.6109P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

N1—C1	1.336 (3)	C30—N4	1.332 (3)
N1—C12	1.369 (3)	N4—C31	1.368 (3)
C10—N2	1.339 (3)	N5—C41	1.335 (3)
N2—C11	1.369 (3)	N5—C52	1.370 (3)
N3—C21	1.338 (3)	C50—N6	1.334 (3)
N3—C32	1.370 (3)	N6—C51	1.365 (3)
C1—N1—C12	123.2 (2)	C30—N4—C31	116.0 (2)
C10—N2—C11	116.3 (2)	C41—N5—C52	123.3 (2)
C21—N3—C32	123.1 (2)	C50—N6—C51	116.38 (19)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

$D—\text{H}\cdots A$	$D—\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D—\text{H}\cdots A$
C1—H1*A*···Cl1	0.95	2.89	3.380 (3)	113.1
C21—H21···Cl1	0.95	2.95	3.371 (3)	108.2
C46—H46···Cl2^{i}	0.95	3.01	3.818 (2)	144.3
C48—H48···Cl2^{i}	0.95	2.89	3.733 (3)	148.8
C23—H23···Cl3^{ii}	0.95	2.73	3.607 (3)	153.8
C25—H25···Cl3^{ii}	0.95	2.83	3.676 (3)	149.2
C29—H29···Cl3^{iii}	0.95	3.04	3.716 (3)	129.1
C49—H49···Cl3^{iv}	0.95	2.80	3.633 (3)	146.3
C2—H2···Cl4^{v}	0.95	2.79	3.534 (3)	135.5
C6—H6···Cl4^{vi}	0.95	3.03	3.787 (3)	137.8
C45—H45···Cl11^{iv}	0.95	3.08	3.947 (2)	152.4
C26—H26···Cl11^{vii}	0.95	2.96	3.886 (2)	166.2
C25—H25···Cl12^{vii}	0.95	2.95	3.655 (2)	132.3
C42—H42···Cl12^{viii}	0.95	3.10	3.959 (2)	151.8
C45—H45···Cl13^{iv}	0.95	2.89	3.723 (2)	147.3
C48—H48···Cl13^{ix}	0.95	3.06	3.824 (2)	138.2
N1—H1···Cl1	0.84 (3)	2.42 (3)	3.128 (2)	143 (2)
N3—H3···Cl1	0.86 (2)	2.29 (3)	3.038 (2)	146 (2)
C1*L*—H1*L*···Cl2	1.00	2.35	3.349 (3)	173.1
N5—H5···Cl2	0.85 (2)	2.33 (2)	3.079 (2)	146 (2)
Cl4—H4···Cl3	1.49 (3)	1.67 (3)	3.1485 (11)	176 (2)

Symmetry codes: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $x - 1, y, z$; (iii) $x - 1, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $2 - x, 1 - y, 1 - z$; (v) $2 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (vi) $2 - x, -y, 1 - z$; (vii) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (viii) $2 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (ix) $x, \frac{3}{2} - y, z - \frac{1}{2}$.

All H atoms were located by difference Fourier synthesis and the H atoms bonded to carbon were refined with fixed individual displacement parameters [$U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$] using a riding model with C—H(aromatic) = 0.95 or C—H(tertiary) = 1.00 Å, respectively. H atoms bonded to N and Cl were refined freely.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1328). Services for accessing these data are described at the back of the journal.

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