C2—S3—C4—C5	−162.9 (2)	C8—O9—C10—C11	−167.0 (2)
S3—C4—C5—C6	71.8 (3)	O9—C10—C11—C12	64.0 (3)
C8—O7—C6—C5	−163.7 (2)	C10—C11—C12—S1	71.8 (2)
C4—C5—C6—O7	67.3 (3)	C2—S1—C12—C11	−161.9 (2)

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: local program. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PC-ORTEP* (Schmid & Brueggemann, 1990). Software used to prepare material for publication: *SHELXL*93.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: CF1105). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 818-820

N-Methylmorpholinium Chloride

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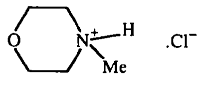
(*Received 22 November 1995; accepted 11 February 1997*)

Abstract

The hydrochloride salt of *N*-methylmorpholine, $C_5H_{12}NO^+.Cl^-$, was isolated from water as deliquescent crystals. There are hydrogen bonds between the halide ions and the morpholinium protons. Differences in the lattice dimensions of the hydrochloride and the hydrobromide are commensurate with the radii of the halide ions.

Comment

As a result of our interest in low-dimensional magnetic lattices, we have been studying complexes of the family $(LH)_2MX_4$, where M is a 2+ first-row transition metal ion, X = Cl, Br and L is an organic base. These compounds are known to pack in the crystal lattice such that low-dimensional magnetic lattices, arising from van der Waals interactions between the MX_4 ions, are frequently obtained (for example, Place & Willett, 1987*a*,*b*). The nature of these contacts is determined by L. To determine whether *N*-methylmorpholine might be suitable for the preparation of these types of complexes, we determined the structure of its hydrochloride salt, (I).



(I)

N-Methylmorpholinium chloride crystallized from water as large blocks in space group $P2_1/m$, the same as the related compounds *N*-methylmorpholine *N*-oxide (Maia, Peguy & Perez, 1981) and *N*,*N*-dimethylmorpholinium iodide (Sishen & Geller, 1987). The molecular structure is shown in Fig. 1.

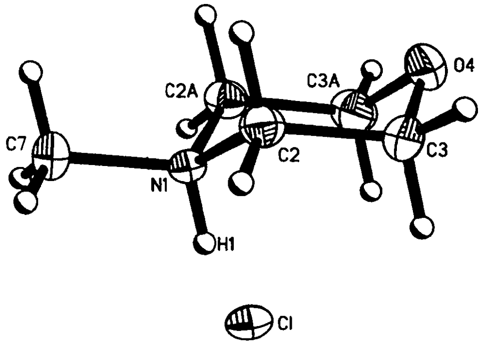


Fig. 1. The molecular structure of *N*-methylmorpholinium chloride showing 50% probability ellipsoids.

The position of the N—H proton was allowed to refine with fixed displacement parameters. The structure shows moderately strong hydrogen bonding between the halide ion and the morpholinium N—H proton. The associated distances and angles are: Cl···H—N 3.04 (1) Å and 178.4 (2)°. The packing diagram (Fig. 2) shows that the N—H···Cl hydrogen bonds are aligned roughly parallel to the c axis.

Unit-cell parameters and a partial data set were also collected for the corresponding bromide salt which were

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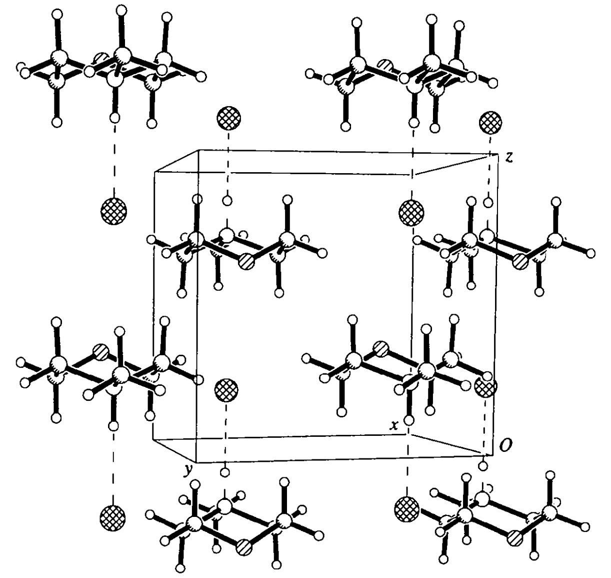

Fig. 2. Packing diagram of *N*-methylmorpholinium chloride viewed along the *a* axis.

sufficient to allow comparison. As can be seen in Fig. 2, the predominant separation between hydrogen-bonded *N*-methylmorpholinium halide pairs within the crystal is based upon contacts between the halide ions and the morpholinium rings in both the *b* and *c* axes. The closest packing contacts along the *a* axis result from interactions between *N*-methylmorpholinium ions only. As a result, the unit cell of the hydrobromide has longer *b* and *c* axes than the hydrochloride, while the *a* axis remains essentially unchanged [*a*-axis length 7.313 (3) Å for Cl and 7.288 (1) Å for Br]. The expansions of the *b* and *c* axes of 0.22 and 0.28 Å, respectively [*b*-axis length 7.122 (2) for Cl and 7.339 (1) for Br; *c*-axis length 7.072 (2) Å for Cl and 7.349 (1) for Br] are in good agreement with the corresponding increase in atomic radius from chloride (1.81 Å) to bromide (1.95 Å) (Pauling, 1948).

The *N*-methylmorpholinium cation shows internal C_s symmetry, with the N1, O4 and C7 atoms lying on the crystallographic mirror (y = 0.25). All bond lengths and angles are in reasonable agreement with those reported for the *N*-methylmorpholinium ion as its bis-TCNQ salt (Visser, de Boer & Vos, 1990). Refinement for the C7 methyl group of the chloride salt was performed with the H atoms in fixed positions, but allowing rotation about the C7—N1 bond. This resulted in one H atom lying near, but not on, the mirror. As such, the C7 H atoms are slightly disordered.

The stacking of the rings, one above the next, into pseudo-chains running parallel to the *c* axis, may make them suitable for use in isolating metal ions in low-dimensional magnetic lattices. The synthesis and structure determination of a series of bis(*N*-methylmorpholinium) tetrahalometalates is in progress.

Experimental

Crystals of (I) were grown from aqueous solutions containing equimolar amounts of *N*-methylmorpholine and the corresponding acid. Once the solutions had evaporated to the point of being viscous, they were placed in a desiccator to induce crystal growth. Crystals were then removed from the mother liquor, their surface liquid removed and were quickly mounted in a cold nitrogen stream to prevent their destruction. Once removed from the mother liquor, the deliquescent crystals dissolve completely in air in a matter of minutes. They are stable for at least 24 h at 158 K under nitrogen (and presumably at room temperature under nitrogen, although we have not tested this).

Crystal data

$C_5H_{12}NO^+.Cl^-$
M_r = 137.61
Monoclinic
$P2_1/m$
a = 7.313 (3) Å
b = 7.122 (2) Å
c = 7.0719 (15) Å
β = 94.00 (3)°
V = 367.4 (2) Å^3
Z = 2
D_x = 1.244 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 13 reflections
θ = 4.84–12.52°
μ = 0.433 mm^{-1}
T = 158 (2) K
Block
1.0 × 0.4 × 0.4 mm
Colorless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: ψ scan (*SHELXTL*; Sheldrick, 1985)
$T_{\min}$ = 0.76, $T_{\max}$ = 0.84
1510 measured reflections
1144 independent reflections
1003 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.0745
$\theta_{\max}$ = 29.99°
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 0$
$l = -9 \rightarrow 2$
3 standard reflections every 397 reflections intensity decay: 1.01%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0293
$wR(F^2)$ = 0.0823
S = 1.059
1144 reflections
46 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0532P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.413
$\Delta\rho_{\max}$ = 0.439 e Å^{-3}
$\Delta\rho_{\min}$ = −0.578 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

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

	x	y	z	$U_{\rm eq}$
Cl	0.15531 (5)	1/4	0.81180 (5)	0.02243 (13)
N1	0.1382 (2)	1/4	1.2405 (2)	0.0171 (2)
C2	0.23655 (14)	0.0783 (2)	1.31399 (15)	0.0226 (2)
C3	0.4357 (2)	0.0870 (2)	1.2653 (2)	0.0320 (3)
O4	0.5244 (2)	1/4	1.3444 (2)	0.0331 (3)
C7	−0.0579 (2)	1/4	1.2870 (2)	0.0233 (3)

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

N1—C2	1.4931 (13)	C2—C3	1.521 (2)
N1—C7	1.493 (2)	C3—O4	1.425 (2)
C2^i—N1—C2	109.93 (12)	O4—C3—C2	111.19 (10)
C2—N1—C7	111.71 (7)	C3—O4—C3^i	109.08 (13)
N1—C2—C3	109.48 (10)		

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

Due to the instability of the crystals in air at room temperature, crystals were examined for quality after mounting in the cold stream of the diffractometer. A large (1.0 mm) crystal was used after the first several proved unsuitable. The crystal was optically centered with great care and an empirical absorption correction (*via* ψ scans) was used to account for intensity errors that may have resulted from small sections of the crystal not being fully bathed in the uniform X-ray beam. A partial data set for the corresponding bromide salt was also collected (the crystal was lost prior to completion). Solution and refinement of the truncated data gave results that were sufficiently conclusive to show that the compounds are isostructural. The lattice parameters of the hydrobromide [$a = 7.228\,(1)$, $b = 7.339\,(1)$, $c = 7.349\,(1)$ Å, $\beta = 92.92\,(1)°$] were determined from 35 reflections in the range $9.49 < \theta < 25.02°$. $(\Delta/\sigma)_{max}$ may be regarded as being on the high side, but this is attributed to disorder in the C7 H atoms [$(\Delta/\sigma)_{mean} = 0.01$].

Data collection: *XSCANS* (Siemens, 1992). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Sheldrick, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

Financial support from the New Zealand Lottery Scientific Research Committee for the purchase of a diffractometer is gratefully acknowledged, as well as the Chemistry Department at the University of Canterbury for providing facilities during the author's sabbatical stay. The author is also indebted to the referees and editor for many helpful suggestions.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: TA1080). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 820–823

1-Methylbenzothiazolinospiro-2,3′-(2-methyl[3*H*]phenanthr[9,10-*b*][1,4]oxazine) and 1-Methylbenzothiazolinospiro-2,3′-(2′-methyl[3*H*]naphth[2,1-*b*][1,4]oxazine)†

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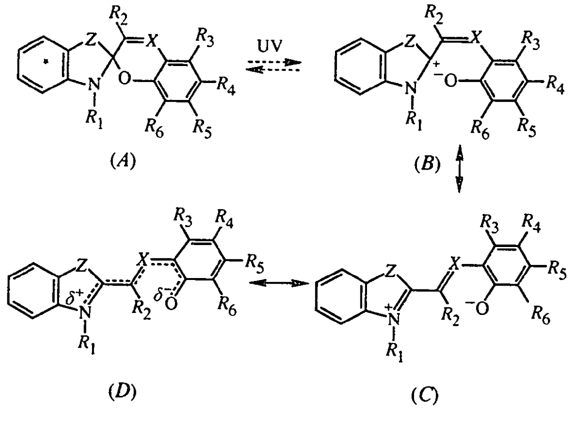
(*Received 27 August 1996; accepted 2 January 1997*)

Abstract

The single-crystal X-ray structures of two thiazolinospiro derivatives, $C_{24}H_{18}N_2OS$ and $C_{20}H_{16}N_2OS$, suggest that their lack of photochromic behavior is due to electron-pair delocalization which reduces potential stabilization of a cationic intermediate.

Comment

Photochromic materials have been known since the 1950s (Hirshberg, 1950, 1956). Current interest stems from their potential application as optical information storage media based on the photochromic reaction.



Many spirooxazine compounds, (*A*), undergo this reversible change of color under the influence of UV radiation in solution. NMR evidence (Samat, Kister, Garnier, Metzger & Guglielmetti, 1975) supports the

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† Alternative names: 3-methyl-2,3-dihydro-1,3-benzothiazolespiro-2,2′-(3-methyl-2*H*-phenanthr[9,10-*b*][1,4]oxazine) and 3-methyl-2,3-dihydro-1,3-benzothiazolespiro-2,2′-(3-methyl-2*H*-naphth[2,1-*b*][1,4]-oxazine).

Acta Crystallographica Section C
ISSN 0108-2701