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3,12-Diaza-6,9-diazoniadispiro[5.2.5.2]hexadecane dichloride from X-ray powder data

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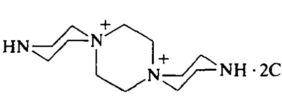
Abstract

The crystal structure of the title compound, $C_{12}H_{26}N_4^{2+}\cdot 2Cl^-$, was determined from X-ray laboratory powder data. All three rings adopt a chair conformation. Hydrogen bonds involving NH groups are absent from this structure.

Comment

The title compound, (I), is an important precursor of some anticancer agents, *e.g.* prospidine (Mikhalev *et al.*, 1972), acting as dihydrofolate reductase inhibitors (Makarov, 1996). Recently, derivatives of (I) were also found to exhibit antiviral properties (Makarov *et al.*, 1999). The title compound is hygroscopic and forms several phases with different water content. The present powder diffraction study was carried out in order to determine the structure of anhydrous 3,12-diaza-6,9-diazoniadispiro[5.2.5.2]hexadecane dichloride, since we failed to obtain single crystals.



(I)

As in the structure of 3,12-bis(2-hydroxy-3-chloropropyl)-3,6,9,12-tetraazoniadispiro[5.2.5.2]hexadecane tetrachloride (Karapetyan *et al.*, 1981), the cation of (I) occupies a special position at the inversion centre, and therefore has a *transoid* conformation relative to the central piperazinium ring. The bond lengths and angles are within the normally expected ranges. All three rings adopt chair conformations, with torsion angles within the range 52–61° (Table 2).

The crystal packing in (I) is illustrated in Fig. 1. The chloride anion makes nine Cl···H contacts shorter than 3.0 Å, the shortest being Cl···H72 (2.57 Å). The imino H atom was placed in the axial position because such an

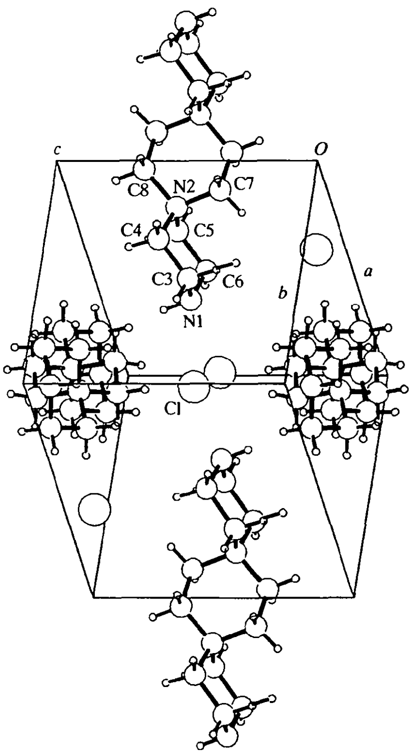


Fig. 1. Packing diagram of (I), showing the atom-numbering scheme.

orientation gives slightly better residuals, but the choice between axial and equatorial positions does not affect the conclusion that the NH group does not form hydrogen bonds, either as an H-atom donor or as an H-atom acceptor. The closest Cl···Cl contact is 5.477 (3) Å. The crystal structure contains a void centered at (0.02, 0.51, 0.21) with a radius of 1.0 Å. Nonetheless, this void is empty; no peaks in the difference Fourier map were located in this area and when an O atom was placed in this position, its occupancy factor was refined to zero. These two features, namely the absence of hydrogen bonds involving the imino group and the loose crystal packing, appear to be responsible for the instability of the title compound in air. The diffraction profile and the difference between the measured and calculated profiles after the final bond-restrained Rietveld refinement are shown in Fig. 2.

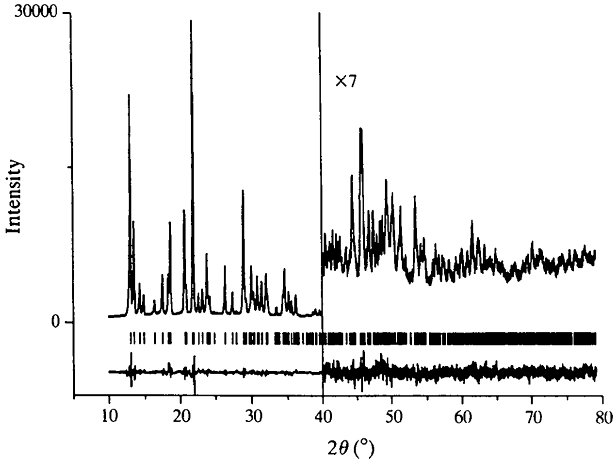


Fig. 2. The Rietveld plot for (I), showing the observed and difference profiles. The reflection positions are shown above the difference profile.

Experimental

The title compound was prepared using the well established procedure described by Mikhalev *et al.* (1972) and Makarov *et al.* (1994).

Crystal data

$C_{12}H_{26}N_4^{2+}\cdot 2Cl^-$
$M_r = 297.27$
Monoclinic
$P2_1/n$
$a = 9.684\ (3)$ Å
$b = 9.479\ (3)$ Å
$c = 8.156\ (3)$ Å
$\beta = 95.33\ (2)°$
$V = 745.8\ (4)$ Å^3
$Z = 2$
$D_x = 1.324$ Mg m^{-3}
D_m not measured

Cu $K\alpha_1$ radiation
$\lambda = 1.54059$ Å
$\mu = 3.826$ mm^{-1}
$T = 295\ (2)$ K
Specimen shape: flat sheet
7.0 × 7.0 × 1.5 mm
Particle morphology: lump-like
Colourless

Data collection

Enraf–Nonius Guinier Johannson camera FR552 powder diffractometer University of Amsterdam
Specimen mounting: pressed as a thin layer in the specimen holder of the camera
Specimen mounted in transmission mode

$T = 295\ (2)$ K
Absorption correction: none
439 independent reflections
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 7$
$l = -6 \rightarrow 6$
$2\theta_{\min} = 4.02$, $2\theta_{\max} = 79.14°$
Increment in $2\theta = 0.01°$

Refinement

Refinement on $I_{\rm net}$
$R_p = 0.045$
$R_{wp} = 0.065$
$R_{\rm exp} = 0.028$
$S = 2.3$
$2\theta_{\min} = 10$, $2\theta_{\max} = 79.14°$
Increment in $2\theta = 0.01°$
Excluded region(s): 4.02–9.99
Profile function: split-type pseudo-Voigt
117 parameters
H atoms: see below

Weighting scheme based on measured s.u.'s
$(\Delta/\sigma)_{\max} = 0.05$
$\Delta\rho_{\max} = 0.6$ e Å^{-3}
$\Delta\rho_{\min} = -0.6$ e Å^{-3}
Extinction correction: none
Preferred orientation correction: March–Dollase (Dollase, 1986)
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

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

	x	y	z	$U_{\rm eq}$
Cl	0.6895 (2)	0.2849 (2)	0.5266 (2)	0.040 (1)
N1	0.3078 (6)	0.3243 (6)	0.5330 (8)	0.049 (2)
N2	0.0825 (6)	0.1286 (6)	0.5502 (7)	0.041 (2)
C3	0.1637 (9)	0.3710 (7)	0.495 (1)	0.056 (3)
C4	0.0695 (9)	0.284 (1)	0.595 (1)	0.094 (4)
C5	0.2317 (9)	0.0886 (7)	0.5899 (9)	0.040 (3)
C6	0.3290 (9)	0.1760 (9)	0.493 (1)	0.076 (4)
C7	0.0249 (7)	0.1044 (9)	0.370 (1)	0.065 (3)
C8	−0.0101 (8)	0.0492 (9)	0.6586 (9)	0.049 (3)

Table 2. *Selected torsion angles (°)*

C6—N1—C3—C4	60.6 (9)	N2—C5—C6—N1	58.5 (9)
C5—N2—C4—C3	59.8 (8)	C8—N2—C7—C8$^{\rm i}$	−52.8 (9)
N1—C3—C4—N2	−60.2 (9)	C7—N2—C8—C7$^{\rm i}$	57.8 (9)
C4—N2—C5—C6	−60.1 (8)	N2—C8—C7$^{\rm i}$—N2$^{\rm i}$	−57.5 (9)
C3—N1—C6—C5	−58.1 (9)		

Symmetry code: (i) $-x, -y, 1 - z$.

During the exposures, the specimen was spun in its plane to improve particle statistics. From the Guinier photographs, a monoclinic unit cell could be derived, but these photographs showed a number of extra lines which could not be indexed with this unit cell. Since evacuation of the camera resulted in weakening of these lines, we attributed them to the hydrates of the title compound. Therefore, in order to obtain the pure anhydrous form, the specimen was heated to 313 K for 1 h. After this treatment, the extra lines disappeared, thus confirming the assumption that the material was contaminated with a hydrate. Guinier photographs of the purified specimen were made again *in vacuo*. The monoclinic cell dimensions of the title compound were determined with *ITO* (Visser, 1969) and refined with *LSPAID* (Visser, 1986) to $M_{20} = 49$ and $F_{30} = 60$ (0.010, 48) using the first 31 peak positions. The space group $P2_1/n$ was chosen on the basis of systematic extinction rules. Intensities for the structure determination and refinement were collected from the Guinier photographs in 0.01° steps using a Johannson LS18 line scanner. The structure was solved by two different methods, namely a grid search procedure (Chernyshev & Schenk, 1998) and the Patterson method used in *DIRDIF*96 (Beurskens *et al.*, 1996), on the basis of 439 intensities derived from the powder pattern with *MRIA* (Zlokazov & Chernyshev, 1992). The diffraction profile and the difference between the measured and calculated profiles after the final bond-restrained Rietveld refinement are shown in Fig. 2. All non-H atoms were refined isotropically. H atoms were placed in geometrically calculated positions and allowed to refine using bond restraints, with a common isotropic displacement parameter $U_{\rm iso}$ fixed to 0.05 Å^2. March–Dollase texture formalism (Dollase, 1986) with various directions of preferred orientation had been applied; however, the specimen turned out to be texture-free. The observed anisotropy of diffraction-line broadening was approximated by a quartic form in *hkl* (Popa, 1998).

Data collection: Johannson LS18 line-scanner data collection program. Cell refinement: *LSPAID*. Data reduction: *Profit for Windows* (Philips, 1996). Program(s) used to solve structure: *MRIA* and *DIRDIF*96. Program(s) used to refine structure: *MRIA*. Molecular graphics: *PLUTON* (Spek, 1992). Software used to prepare material for publication: *MRIA*, *SHELXL*93 (Sheldrick, 1993) and *PARST* (Nardelli, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1236). Services for accessing these data are described at the back of the journal.

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6-(2-Nitroprop-2-yl)quinoline-5-carbonitrile

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Abstract

The title compound, $C_{13}H_{11}N_3O_2$, was unexpectedly formed as a minor product from the reaction of 6-nitroquinoline with 2-nitropropane and potassium cyanide, and was selected for crystal structure determination in order to clarify its molecular structure unambiguously. The bonding pattern of the heterocyclic ring agrees with that found in other quinoline derivatives. The nitro group of the 2-nitropropyl substituent is oriented *cis* with respect to the aromatic ring. The principal packing interaction seems to be π–π stacking of the heterocyclic rings.

Comment

As part of our on-going studies on quinoline derivatives, we attempted to prepare, by treatment of 6-nitroquinoline with 2-nitropropane and potassium cyanide, the corresponding pyrrolo-quinoline derivative, (1). However, analytical data from the reaction mixture indicated, besides (1) as the main product, the presence of another compound whose structure could not be resolved unequivocally from spectroscopic methods (Macháček & Halama, 1999). This minor product is the title compound, (2), and in order to identify the structure of (2), and hence to help in clarifying the reaction mechanism, its crystal structure was determined by X-ray diffraction. Another reason for the interest in (2)