Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.079$
$S = 1.079$
5243 reflections
262 parameters
H atoms constrained (see below)
$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 0.4283P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.58$ e Å^{-3}
$\Delta\rho_{\min} = -2.04$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Pb1—O1	2.455 (3)	Pb1—N1	2.641 (4)
Pb1—O3	2.559 (3)	Pb1—N2	2.505 (4)
Pb1—O5	2.454 (3)		
O5—Pb1—O1	73.06 (11)	C1—O1—Pb1	118.4 (3)
O5—Pb1—N2	66.35 (12)	C3—O3—Pb1	116.7 (3)
O1—Pb1—N2	83.84 (12)	C5—O5—Pb1	116.7 (3)
O5—Pb1—O3	106.49 (12)	C8—N1—Pb1	106.8 (2)
O1—Pb1—O3	145.63 (13)	C2—N1—Pb1	105.1 (2)
N2—Pb1—O3	65.84 (12)	C9—N1—Pb1	112.8 (3)
O5—Pb1—N1	121.86 (12)	C6—N2—Pb1	109.1 (3)
O1—Pb1—N1	64.57 (11)	C4—N2—Pb1	106.8 (3)
N2—Pb1—N1	71.10 (12)	C7—N2—Pb1	110.8 (3)
O3—Pb1—N1	89.47 (13)		

All methylene H atoms were fixed and refined using the *HFIX* and *AFIX* facilities in *SHELXL*93 (Sheldrick, 1993). A riding model was used to refine the H atoms and the isotropic displacement parameters were fixed at $1.2U_{eq}$(C). The protons for two of the water molecules were found in the difference map and coordinates, occupancy and isotropic displacement parameters (0.08 Å^2) were fixed. Protons on the other water molecules were not included. All peaks with residual densities greater than 1 e Å^{-3} were within 1 Å of the Pb position.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *SHELXTL/PC* (Siemens, 1990). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1076). Services for accessing these data are described at the back of the journal.

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Bis(pyridinium) Pentachloro(pyridine-*N*)-molybdate(III)

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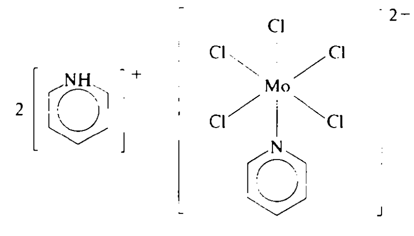
Abstract

The title complex, $(C_5H_6N)_2[MoCl_5(C_5H_5N)]$, belongs to a group of halo(pyridine)molybdenum(III) octahedral complexes. The pyridinium cations and pentachloro(pyridine-*N*)molybdate(III) anions are held together by N—H···Cl hydrogen bonds which affect the distances within the $[MoCl_5(py)]^{2-}$ anion. The anion displays a previously unobserved orientation of the coordinated pyridine, which lies in almost the same plane as two *trans*-positioned equatorial chlorines.

Comment

We report here the structure of $(pyH)_2[MoCl_5(py)]$, (I), as part of our research on halo(pyridine)molybdenum(III) coordination compounds with the formula $[MoX_{6-n}(py)_n]^{n-3}$, where n = 1, 2, 3, 4 (X = Cl$^-$, Br$^-$; py = pyridine, C_5H_5N). $(pyH)_2[MoX_5(py)]$ is the first product of the stepwise substitution of halides in

$[MoX_6]^{3-}$ with pyridine. The $[MoX_5(py)]^{2-}$ compounds display high reactivity towards pyridine; the products of further substitution are *cis*-$[MoX_4(py)_2]^-$, *trans*-$[MoX_4(py)_2]^-$ and *mer*-$[MoX_3(py)_3]$, depending on the reaction conditions. Whereas different compounds containing $[MX_5(py)]^{2-}$ (M = trivalent transition metal cation) are described in the literature, *e.g.* $K_2[IrCl_5(py)]$ (Delepine, 1923), $(pyH)_2[RhBr_5(py)]$ (Poulenc, 1935), $[(C_4H_9)_4N]_2[ReCl_5(py)]$ and $[(C_4H_9)_4N]_2[ReBr_5(py)]$ (Arp & Preetz, 1996), the first two structurally characterized examples were $[(CH_3)_4N]_2[MoCl_5(py)]$ and $[(CH_3)_2NH_2]_2[MoCl_5(py)]$ (Brenčič *et al.*, 1995).



(I)

The ionic structure of $(pyH)_2[MoCl_5(py)]$ consists of planar pyridinium cations and octahedral $[MoCl_5(py)]^{2-}$ anions. The compound with the atom-numbering scheme is illustrated in Fig. 1. The anions are located on the crystallographic mirror plane which passes through atoms Mo, Cl2, Cl3, Cl4, N1 and C13, and which bisects the anions. The plane of the coordinated pyridine is perpendicular to the above-mentioned symmetry plane, *i.e.* it lies almost above two equatorial chlorines, Cl1 and its symmetry equivalent. The pyridine is slightly rotated around the Mo—N axis and an angle of 5.1 (3)° is formed between the pyridine plane and the octahedral plane defined by atoms Cl1, Cl4, N1 and Mo. The consequence of this is a short distance of 2.441 Å between the pyridine α-H and Cl1 atoms. The orientation of coordinated pyridine is significantly different from that in other $[MX_5(py)]$ compounds. In $[(CH_3)_4N]_2[MoCl_5(py)]$ and $[(CH_3)_2NH_2]_2[MoCl_5(py)]$, whose crystal structures are similar, the pyridine plane bisects the edge of a square defined by four chlorines (Brenčič *et al.*, 1995). Such an orientation is favourable since it produces minimal steric effects between the equatorial chlorines and pyridine α-H atoms: the distances between them vary from 2.753 to 3.079 Å. A similar orientation was also observed in $[(C_2H_5)_4N][PtCl_5(py)]$ (refcode JOKVIO in the Cambridge Structural Database, October 1995 release; Allen & Kennard, 1993) and $(PPh_4)[ZrCl_5(py)]$ (Ph = C_6H_5) (Chen & Cotton, 1996), which both contain a four-valent transition metal. In the latter, where the equatorial chlorines are tilted towards the pyridine, the orientation was explained in terms of hydrogen bonds between the pyridine H atoms and the equatorial chlorines. It is noteworthy that such an orientation, *i.e.* with the pyridine plane lying between the equatorial halides, was also observed in all *trans*-$[MoX_4(py)_2]^-$ compounds, where the two *trans*-positioned pyridines can either lie in the same plane {eclipsed conformation, as in *trans*-$NH_4[MoCl_4(py)_2].H_2O$ (Brenčič & Čeh, 1989)} or with the planes perpendicular to each other {staggered conformation, *e.g.* *trans*-$pyH[MoBr_4(py)_2]$ (Brenčič *et al.*, 1993)}. As a result, the Mo—N bond distance in $(pyH)_2[MoCl_5(py)]$ has been increased to 2.232 (8) Å, while the corresponding bond lengths in $[(CH_3)_4N]_2[MoCl_5(py)]$ and $[(CH_3)_2NH_2]_2[MoCl_5(py)]$ are 2.196 (4) and 2.206 (1) Å, respectively (Brenčič *et al.*, 1995). Although the nitrogen ligand in the *trans* position to the chlorine could theoretically experience the *trans* effect, it is unlikely that the lengthening of the Mo—N bond in the title compound is due to the *trans* effect.

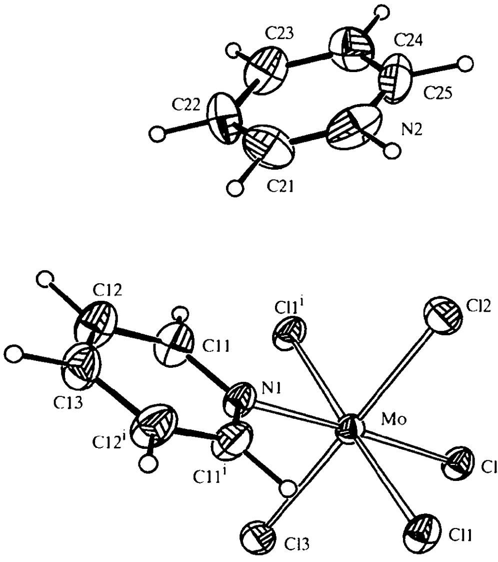


Fig. 1. *ORTEP*II (Johnson, 1976) view of the title compound with the atomic numbering scheme [symmetry code: (i) $x, \frac{3}{2}-y, z$]. Displacement ellipsoids are plotted at the 30% probability level. H atoms are of arbitrary size.

Of the five Mo—Cl bonds, one, the Mo—Cl4 bond, with a length of 2.486 (3) Å, is longer than the others, whose lengths vary from 2.430 (3) to 2.451 (2) Å. It is the longest among Mo—Cl bonds, which vary from 2.407 (2) Å in *trans*-$[MoCl_2(py)_4]Br_3$ (Rotar *et al.*, 1996) to 2.445 (1) Å in *trans*-$NH_4[MoCl_4(py)_2].H_2O$ (Brenčič & Čeh, 1989). Its lengthening may be associated with weak hydrogen bonding occurring between the N atom of the pyridinium cation and the Cl on the anion, since N2···Cl4^{ii} = 3.240 (8) Å [symmetry code: (ii) $x, y, z-1$]. This distance is slightly shorter than 3.30 Å, which is the sum of the van der Waals radii of chlorine and nitrogen (Douglas *et al.*, 1994). Other short distances between cations and anions are: N2···Cl1^{ii} = 3.328 (8) and N2···Cl2 = 3.316 (7) Å. Selected bond distances and angles are given in Table 2.

Experimental

The reaction mixture containing 5.5 mmol (3.00 g) $(pyH)_3[MoCl_6]$, 5 ml of pyridine and 54 ml of acetonitrile was stirred for 3 h at ambient temperature. Afterwards the orange precipitate, $(pyH)_2[MoCl_5(py)]$, was filtered off. The yield was 30%. The resulting filtrate was left at 281 K and red crystals were obtained after one day. Analysis calculated (measured) in %: C 35.15 (34.90), H 3.34 (3.35), N 8.20 (8.04).

Crystal data

$(C_5H_6N)_2[MoCl_5(C_5H_5N)]$
$M_r = 512.51$
Orthorhombic
Pnma
$a = 18.317 (13)$ Å
$b = 14.590 (7)$ Å
$c = 7.431 (3)$ Å
$V = 1985.8 (18)$ Å^3
$Z = 4$
$D_x = 1.714$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6.41–22.45°$
$\mu = 1.336$ mm^{-1}
$T = 293$ K
Prismatic
0.30 × 0.25 × 0.18 mm
Red

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scan
Absorption correction: Gaussian (*Xtal*3.4 *ABSORB*; Hall *et al.*, 1995)
$T_{\min} = 0.727$, $T_{\max} = 0.792$
3459 measured reflections
1622 independent reflections

844 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.036$
$\theta_{\max} = 24.00°$
$h = -20 \rightarrow 0$
$k = -16 \rightarrow 15$
$l = -8 \rightarrow 0$
3 standard reflections every 100 reflections intensity decay: 4.20%

Refinement

Refinement on F
$R = 0.039$
$wR = 0.033$
$S = 1.459$
1205 reflections
118 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o)]$

$(\Delta/\sigma)_{\max} = 0.0002$
$\Delta\rho_{\max} = 1.101$ e Å^{-3}
$\Delta\rho_{\min} = -1.289$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

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

	x	y	z	$U_{\rm eq}$
Mo	0.59927 (6)	3/4	0.63168 (12)	0.0367 (5)
Cl1	0.60162 (11)	0.58205 (10)	0.6314 (2)	0.0515 (11)
Cl2	0.67003 (15)	3/4	0.3551 (3)	0.0573 (18)
Cl3	0.52491 (15)	3/4	0.9057 (3)	0.0515 (18)
Cl4	0.71157 (15)	3/4	0.8196 (3)	0.0468 (17)
N1	0.4955 (4)	3/4	0.4741 (10)	0.042 (6)
C11	0.4626 (4)	0.8278 (5)	0.4274 (10)	0.060 (5)
C12	0.3966 (5)	0.8301 (5)	0.3364 (10)	0.067 (5)
C13	0.3621 (6)	3/4	0.2923 (15)	0.065 (9)
N2	0.6528 (6)	0.5805 (5)	0.0611 (10)	0.082 (7)
C21	0.5897 (6)	0.5506 (7)	0.1230 (12)	0.082 (8)
C22	0.5810 (5)	0.4616 (7)	0.1620 (12)	0.075 (7)
C23	0.6381 (6)	0.4037 (5)	0.1379 (13)	0.078 (7)
C24	0.7041 (6)	0.4357 (7)	0.0717 (12)	0.078 (7)
C25	0.7100 (6)	0.5259 (8)	0.0356 (12)	0.080 (8)

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

Mo—Cl1	2.451 (2)	Mo—Cl4	2.486 (3)
Mo—Cl2	2.430 (3)	Mo—N1	2.232 (8)
Mo—Cl3	2.450 (3)		
Cl1—Mo—Cl2	89.42 (5)	Cl2—Mo—Cl4	91.94 (10)
Cl1—Mo—Cl3	90.60 (5)	Cl2—Mo—N1	90.6 (2)
Cl1—Mo—Cl4	89.20 (5)	Cl3—Mo—Cl4	89.60 (10)
Cl1—Mo—N1	90.83 (5)	Cl3—Mo—N1	87.9 (2)
Cl2—Mo—Cl3	178.46 (11)	Cl4—Mo—N1	177.5 (2)

Due to time constraints, no data were collected beyond $\theta = 24°$. It was possible to infer two space groups, *Pnma* and *Pna*2_1, from the systematically-absent reflections: the *Pnma* space group was deduced from the intensity statistics. An absorption correction was applied. Two peaks (1.101 and 1.013 e Å^{-3}) and a hole (−1.289 e Å^{-3}) with values exceeding 1.0 e Å^{-3} were found in the difference Fourier map. All of them are located in the Cl2—Cl3—Cl4 plane of the $[MoCl_5(py)]^{2-}$ anion. The larger peak is closest to N1 [1.165 (9) Å], the second peak lies at a distance of 1.455 (3) Å from Cl4, while the hole is located near Mo [0.621 (1) Å], where larger truncation errors and ripples are expected.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *Xtal*3.4 *DIFDAT ABSORB SORTRF ADDREF* (Hall *et al.*, 1995). Program(s) used to solve structure: *Xtal*3.4 *FOURR*. Program(s) used to refine structure: *Xtal*3.4 *CRYLSQ*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *Xtal*3.4 *BONDLA CIFIO*.

The data were collected at the Department of Crystallography, University of Pittsburgh, USA, during the Fifth Summer School of Crystallography. We would like to thank Professor Bryan Craven and Dr Brian Skelton for all their help.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1339). Services for accessing these data are described at the back of the journal.

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