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## Structure of 1-(4-Pyridyl)pyridinium trans-Tetrachlorodi(pyridine)molybdate(III)\*

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**Abstract.**  $C_{10}H_9N_2^+[MoCl_4(C_5H_5N)_2]^-$ ,  $C_{10}H_9N_2^+ = pyp^+$ ,  $C_5H_5N = py$ ,  $M_r = 553.15$ , triclinic,  $PI$ ,  $a = 7.669$  (1),  $b = 8.949$  (1),  $c = 16.455$  (2) Å,  $\alpha = 86.77$  (1),  $\beta = 83.20$  (1),  $\gamma = 84.30$  (1)°,  $V = 1114.7$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.63$  (2),  $D_x = 1.648$  Mg m<sup>-3</sup>,  $Mo K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 1.08$  mm<sup>-1</sup>,  $F(000) = 554$ ,  $T = 293$  K,  $R = 0.037$  for 2893 reflections. The unit cell contains two independent *trans*-[ $MoCl_4py_2$ ]<sup>-</sup> octahedral anions situated on centers of symmetry and two symmetry-related *pyp*<sup>+</sup> cations. Average Mo–Cl and Mo–N(pyridine) bond lengths are 2.442 and 2.195 Å. The two rings of the cation are linked by a C–N bond of length 1.446 (9) Å.

**Introduction.** Mo<sup>III</sup> coordination compounds of the type  $M^I MoX_4L_2$  are still rare. The crystal structures of two members of this family,  $(PPh_4)MoCl_4(THF)_2$  (Hill, Leigh, Hutchinson & Zubieta, 1985) and  $(PPh_4)MoCl_4(bipy)$ , *bipy* = bipyridine (Richards, Shortman, Povey & Smith, 1987), were published recently. The only structural information about the *pyp*<sup>+</sup> cation comes from the crystal structure of *pypH*MoCl<sub>5</sub>·H<sub>2</sub>O (Brenčič, Čeh & Leban, 1988) where 1-(4-pyridyl)pyridinium (*pyp*<sup>+</sup>) is protonated. One of the reasons for this structural work was therefore to compare the

dimensions of the unprotonated *pyp*<sup>+</sup> cation with those in protonated *pypH*<sup>2+</sup>.

**Experimental.** Yellow plates were obtained from a solution of *pyH*[ $MoCl_4py_2$ ] (Brenčič, Čeh & Leban, 1986) in conc. ammonia solution to which excess *pypHCl*<sub>2</sub> dissolved in water was added. The low solubility of (*pyp*) $MoCl_4py_2$  required low concentrations of the reactants. The crystal density was determined by flotation in a mixture of organic solvents.

Crystal approximated by square plate, dimensions 0.32 × 0.16 × 0.4 mm. The unit-cell dimensions were calculated from 75 reflections ( $17 < 2\theta < 27^\circ$ ) measured on the diffractometer at 293 (1) K. The data were collected at the same temperature with an Enraf–Nonius CAD-4 diffractometer; graphite-monochromatized *Mo Kα* radiation,  $\omega$ – $2\theta$  scans,  $\theta_{min} = 1^\circ$ ,  $\theta_{max} = 28^\circ$ ,  $\theta$  scan width =  $(0.8 + 0.3 \tan \theta)^\circ$ , a horizontal counter aperture =  $(2.4 + 0.9 \tan \theta)$  mm, variable scan rate, maximum scan time = 45 s. 5077 independent reflections ( $-9 < h < 10$ ,  $-11 < k < 11$ ,  $0 < l < 21$ ) were measured, 2893 with  $I > 2\sigma(I)$  were used for the solution and refinement of the structure. Three standard reflections  $\bar{2}32$ ,  $20\bar{6}$ ,  $\bar{2}1\bar{6}$  showed no decay during data collection and no reorientation of the crystal was necessary.

Structure factors on a relative scale were calculated by applying Lorentz, polarization and absorption corrections (transmission factors were in the range

\* For a preliminary account see Brenčič, Čeh, Golič & Leban (1988).

Table 1. Positional, isotropic and equivalent isotropic thermal ( $\times 10^3$ ) parameters with e.s.d.'s in parentheses

$U_{eq} = \frac{1}{3}(\text{trace of orthogonalized } U_{ij} \text{ matrix}).$

	x	y	z	U and $U_{eq}(\text{\AA}^2)^*$
Mo(1)	0	0	0	24.5
Mo(2)	0.5	0	0.5	35.0
Cl(1)	-0.2079 (2)	0.0474 (1)	0.1222 (1)	36.6
Cl(12)	-0.1869 (2)	0.1677 (1)	-0.0823 (1)	36.1
Cl(21)	0.6714 (2)	0.2087 (2)	0.4490 (1)	53.1
Cl(22)	0.7151 (2)	-0.1758 (2)	0.4242 (1)	51.1
N(11)	0.1395 (6)	0.1881 (5)	0.0292 (3)	29.9 (0.9)
C(12)	0.0491 (7)	0.3168 (6)	0.0556 (3)	32.6 (1.1)
C(13)	0.1323 (8)	0.4363 (6)	0.0769 (3)	40.1 (1.3)
C(14)	0.3138 (8)	0.4256 (6)	0.0716 (4)	40.9 (1.3)
C(15)	0.4074 (8)	0.2952 (6)	0.0449 (3)	41.3 (1.3)
C(16)	0.3164 (7)	0.1792 (6)	0.0237 (3)	35.2 (1.2)
N(21)	0.3543 (6)	0.0335 (5)	0.3917 (3)	37.0 (1.1)
C(22)	0.4412 (8)	0.0523 (7)	0.3152 (4)	41.9 (1.3)
C(23)	0.3548 (8)	0.0679 (7)	0.2462 (4)	48.2 (1.5)
C(24)	0.1755 (8)	0.0653 (7)	0.2539 (4)	47.5 (1.5)
C(25)	0.0868 (8)	0.0461 (7)	0.3307 (4)	46.0 (1.4)
C(26)	0.1779 (8)	0.0314 (6)	0.3983 (4)	43.1 (1.4)
N(31)	-0.3872 (8)	0.5504 (6)	0.1717 (4)	61.9 (1.5)
C(32)	-0.3175 (8)	0.6787 (8)	0.1820 (4)	51.7 (1.6)
C(33)	-0.1816 (8)	0.6848 (7)	0.2277 (4)	43.4 (1.4)
C(34)	-0.1133 (8)	0.5545 (6)	0.2648 (4)	40.5 (1.3)
C(35)	-0.1828 (9)	0.4209 (8)	0.2555 (4)	52.7 (1.6)
C(36)	-0.3198 (9)	0.4258 (8)	0.2091 (4)	62.0 (1.9)
N(41)	0.0361 (7)	0.5546 (6)	0.3108 (3)	44.5 (1.2)
C(42)	0.1645 (9)	0.6457 (8)	0.2864 (4)	53.2 (1.6)
C(43)	0.3066 (10)	0.6460 (9)	0.3287 (5)	66.6 (2.0)
C(44)	0.3230 (11)	0.5486 (9)	0.3951 (5)	76.1 (2.3)
C(45)	0.1933 (11)	0.4555 (9)	0.4182 (5)	76.6 (2.3)
C(46)	0.0477 (10)	0.4599 (8)	0.3772 (4)	60.8 (1.8)

\* Isotropic temperature factors are of the form  $\exp[-8\pi^2 U \times (\sin\theta/\lambda)^2]$ .

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.'s in parentheses

Mo(1)—Cl(11)	2.443 (2)	Mo(2)—Cl(21)	2.443 (2)
Mo(1)—Cl(12)	2.438 (2)	Mo(2)—Cl(22)	2.443 (2)
Mo(1)—N(11)	2.186 (5)	Mo(2)—N(21)	2.204 (5)
N(11)—C(12)	1.350 (7)	N(21)—C(22)	1.362 (8)
C(12)—C(13)	1.380 (8)	C(22)—C(23)	1.374 (9)
C(13)—C(14)	1.378 (9)	C(23)—C(24)	1.368 (9)
C(14)—C(15)	1.374 (8)	C(24)—C(25)	1.373 (9)
C(15)—C(16)	1.389 (8)	C(25)—C(26)	1.376 (9)
C(16)—N(11)	1.344 (7)	C(26)—N(21)	1.346 (8)
N(31)—C(32)	1.34 (1)	N(41)—C(42)	1.35 (1)
C(32)—C(33)	1.36 (1)	C(42)—C(43)	1.36 (1)
C(33)—C(34)	1.37 (1)	C(43)—C(44)	1.37 (1)
C(34)—C(35)	1.38 (1)	C(44)—C(45)	1.37 (1)
C(35)—C(36)	1.37 (1)	C(45)—C(46)	1.37 (1)
C(36)—N(31)	1.33 (1)	C(46)—N(41)	1.35 (1)
C(34)—N(41)	1.446 (9)		
Cl(11)—Mo(1)—Cl(12)	90.45 (5)	Cl(21)—Mo(2)—Cl(22)	90.36 (6)
N(11)—Mo(1)—Cl(11)	88.7 (1)	N(21)—Mo(2)—Cl(21)	90.5 (1)
N(11)—Mo(1)—Cl(12)	90.8 (1)	N(21)—Mo(2)—Cl(22)	89.1 (1)
N(11)—C(12)—C(13)	122.2 (5)	N(21)—C(22)—C(23)	122.2 (6)
C(12)—C(13)—C(14)	119.6 (5)	C(22)—C(23)—C(24)	119.4 (6)
C(13)—C(14)—C(15)	118.7 (6)	C(23)—C(24)—C(25)	118.8 (6)
C(14)—C(15)—C(16)	119.0 (6)	C(24)—C(25)—C(26)	120.0 (6)
C(15)—C(16)—N(11)	122.7 (5)	C(25)—C(26)—N(21)	121.8 (6)
C(16)—N(11)—C(12)	117.6 (5)	C(26)—N(21)—C(22)	117.7 (5)
N(31)—C(32)—C(33)	122.7 (6)	N(41)—C(42)—C(43)	120.9 (6)
C(32)—C(33)—C(34)	118.7 (6)	C(42)—C(43)—C(44)	119.5 (7)
C(33)—C(34)—C(35)	119.9 (6)	C(43)—C(44)—C(45)	118.7 (8)
C(34)—C(35)—C(36)	117.3 (6)	C(44)—C(45)—C(46)	121.3 (7)
C(35)—C(36)—N(31)	124.0 (7)	C(45)—C(46)—N(41)	118.9 (7)
C(36)—N(31)—C(32)	117.4 (7)	C(46)—N(41)—C(42)	120.5 (6)
C(33)—C(34)—N(41)	120.6 (5)	C(34)—N(41)—C(42)	120.3 (5)
C(35)—C(34)—N(41)	119.5 (5)	C(34)—N(41)—C(46)	119.6 (6)

0.852–0.952). From a Patterson synthesis two Mo atoms were found on special positions. Fourier syntheses combined with least-squares refinement gave the positions of the rest of the non-H atoms. Allowance was made for H-atom scattering using calculated H-atom positions and an assumed  $U_{iso} = 0.05 \text{\AA}^2$ . Anisotropic refinement on  $F$  for Mo, Cl atoms and isotropic refinement for other non-H atoms ended with  $R = 0.037$  and  $wR = 0.041$ . Weighting function of the form  $w = 0.37/[\sigma^2(F) + 0.0020F^2]$  from the *SHELX76* (Sheldrick, 1976) package of programs, was applied. The maximum shift-to-e.s.d. ratio in the last cycle was 0.11. Final difference Fourier synthesis has a ripple located at  $x = 0, y = 0, z = 0.5$  with maximum  $\Delta\rho = 2 \text{ e \AA}^{-3}$ ,  $2 \text{ \AA}$  from one of the C atoms of the coordinated pyridine. Minimum  $\Delta\rho = -0.3 \text{ e \AA}^{-3}$ .

All calculations were carried out on a CDC Cyber-172 computer with *SHELX76*. Atomic scattering factors for neutral atoms from Cromer & Mann (1968) and anomalous-dispersion corrections of Cromer (1965) were applied. Scattering factors for H atoms were from Stewart, Davidson & Simpson (1965). The positional and equivalent thermal parameters are listed in Table 1\* and bond distances and angles in Table 2. An *ac* projection of the structure showing the numbering scheme is depicted in Fig. 1.

**Discussion.** The unit cell contains two independent anions and two symmetry-related cations. Anions and

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51782 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

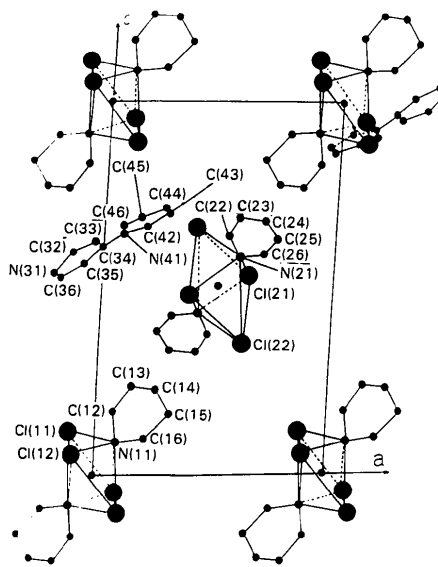


Fig. 1. *ac* projection of the structure and the numbering scheme. H atoms have been omitted for clarity.

cations are distributed in alternating layers along the *b* axis, approximately *b*/2 apart.

Anions are located on inversion centers. Planes of the pyridine ligands form 86.7 and 87.7° angles with the basal planes, cut the Cl(11)—Cl(12) vector in half and the Cl(21)—Cl(22) vector in the proportion 0.48:0.52. Mo—Cl bond lengths range from 2.438 (2) to 2.443 (2) Å. Comparable values were found in the crystal structures of (PPh<sub>4</sub>)MoCl<sub>4</sub>(THF)<sub>2</sub> (Hill, Leigh, Hutchinson & Zubieta, 1985) and (PPh<sub>4</sub>)MoCl<sub>4</sub>(bipy) (Richards, Shortman, Povey & Smith, 1987). Mo—N(pyridine) distances of 2.186 (5) and 2.204 (5) Å fall in the range of Mo<sup>III</sup>—N(pyridine) bonds in MoCl<sub>3</sub>py<sub>3</sub> (Brenčič, 1974). Pyridine rings are planar to within 0.02 Å. Average C—C and C—N bonds are 1.38 and 1.35 Å. All *cis* octahedral angles are close to 90°.

All atoms of the cation, pyp<sup>+</sup>, are in general positions. The atoms N(31), C(34), N(41) and C(44) are approximately collinear. The two pyridine rings of the cation are bonded through a C(34)—N(41) bond of 1.446 (9) Å. The same bond in pypH<sup>2+</sup> from the crystal structure of pypHMoCl<sub>4</sub>·H<sub>2</sub>O (Brenčič, Čeh & Leban, 1988) is significantly shorter, 1.36 (2) Å, reflecting the variability of C—N single bonds. The angle between the pyridine rings is 35°. The corresponding angle in pypH<sup>2+</sup> is 38°. Average ring C—C,

C—N bonds in the cation are 1.37 and 1.34 Å. The shorter C—N values helped in the identification of the correct positions of the N atoms.

The closest contact between anion and cation is 3.29 (2) Å: C(14)(anion)···N(31) (1+x, y, z) (cation).

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## Röntgenstrukturanalyse von Diaquadinitratodioxouran(VI)– 1,4,7,10,13-Pentaoxacyclopentadecan

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(Eingegangen am 23. April 1988; angenommen am 1. August 1988)

**Abstract.** [U(NO<sub>3</sub>)<sub>2</sub>O<sub>2</sub>(C<sub>10</sub>H<sub>20</sub>O<sub>5</sub>)(H<sub>2</sub>O)<sub>2</sub>], *M<sub>r</sub>* = 668.21, triclinic, *P*1̄, *a* = 8.389 (4), *b* = 8.971 (4), *c* = 16.735 (6) Å, *α* = 115.20 (3), *β* = 91.99 (3), *γ* = 110.05 (3)°, *V* = 1046.1 Å<sup>3</sup>, *D<sub>x</sub>* = 2.064 Mg m<sup>-3</sup>, λ(Mo Kα) = 0.71069 Å, *μ* = 7.42 mm<sup>-1</sup>, *T* = 295 K, *R* = 6.0% (*wR* = 6.3%) for 3929 observed reflections. Two bidentate nitrate and two water ligands are arranged around the central U atom in a vertical plane to the uranyl group. Hydrogen bonds are formed between the 15-crown-5 macrocyclic molecules and the water ligands of the metal complex.

0108-2701/89/081146-04\$03.00

**Einleitung.** Komplexe mit U<sup>IV</sup> bzw. der Uranylgruppe als Koordinationszentrum und Kronenethern als potentiellen Liganden lassen sich prinzipiell in zwei Kategorien einteilen, die sich in der Art der Wechselwirkung zwischen dem Zentralatom und dem Kronenetherliganden unterscheiden (elBasyouny, 1983). Unter günstigen Bedingungen kann es zur Einlagerung des Urankations in die Höhle des makrocyclischen Liganden kommen, so daß direkte Wechselwirkungen zwischen dem zentralen Kation und den Ethersauerstoffatomen resultieren. Beispielhaft für diesen Verbin-

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